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Molecular Structure of (η^6-Fluorenyl)manganese Tricarbonyl. A Significantly Distorted η^6-Arene Complex

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The molecular structure of $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ has been determined. (The ligand $C_{13}H_9^-$ is the fluorenyl anion, coordinated through one six-membered ring.) The complex crystallizes in the space group $P2_1/c$. The unit cell parameters are $a = 9.610$ (3) Å, $b = 22.778$ (5) Å, $c = 13.396$ (2) Å, $\beta = 91.54$ (2)°, $V = 2931$ Å^3, $d_{calcd} = 1.36$ g/cm^3, $d_{obsd} = 1.38$ g/cm, and $Z = 8$. A total of 4357 unique reflections were collected at −65 °C. The structure was solved by direct methods and was refined by a blocked full-matrix refinement technique to a value of $R_1 = 0.041$. The molecular structure is described as intermediate between a η^6-zwitterionic complex (similar to $Fe(\eta\text{-}C_5H_5)(\eta^6\text{-}C_{13}H_9)$) and a η^5-cyclohexadienyl complex. Five carbons in the complexed six-membered ring are coplanar; the sixth carbon, C(10), is bent out of this plane by approximately 15°. The Mn–C(10) bond distance is 2.511 Å, in comparison to remaining metal–carbon bonding distances which fall in the range 2.11–2.29 Å. Variations in bond lengths in the fluorenyl fragment of the complex, though small, are in the direction expected for the cyclohexadienyl representation. The structural data indicate that this complex has more cyclohexadienyl character than does $Fe(\eta\text{-}C_5H_5)(\eta^6\text{-}C_{13}H_9)$, a compound whose structure had been reported earlier.

Introduction

A green crystalline compound, $Fe(\eta\text{-}C_5H_5)(\eta^6\text{-}C_{13}H_9)$ (I), was prepared in our laboratory several years ago.[1] According to a crystallographic study, the fluorenyl ($C_{13}H_9^-$) group in this compound coordinates to iron via one of the six-membered rings. Bond distance and bond angle data are generally in accord with the representation of I as a zwitterion (Figure 1A) with the positive charge localized at the metal and the negative charge residing largely at the C(9) carbon of the ligand. The basicities of the uncomplexed anionic ligand, $C_{13}H_9^-$, and the complex with respect to protonation are comparable, in agreement with this representation.

Preparation of a manganese tricarbonyl complex of the fluorenyl ligand, analogous to I, was accomplished concurrent to the above study.[2] Qualitative evidence indicated that this compound, $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ (II), had a basicity which was much diminished from the basicities of I and of the anion $C_{13}H_9^-$. This can best be explained by assuming that in II the negative charge is not localized at C(9) but is instead substantially delocalized to the metal and associated carbonyl ligands. This explanation seems sensible since the acceptor ability of carbonyl groups relative to other ligands in organometallic complexes is exceptional. The implication of such charge delocalization is, however, that the complex might be represented in valence bond terms as an (η^5-cyclohexadienyl)metal complex; see Figure 1B.

The structural differences between complexes, assuming the limiting forms illustrated in Figure 1A,B, ought to be substantial. However, it seems probable that real compounds will assume structures somewhere between these two extremes, although such structures may resemble one form more than the other. Also, the fused rings of the fluorenyl ligand system will resist distortion, and this could limit the use of structural data in assessing the bonding in these systems. Nevertheless, significant differences in structural parameters should be evident in well chosen examples. The acid–base data on I and II suggested that the structural differences in these complexes might be significant. This study, the determination of the structure of II, was undertaken to allow comparison of these compounds.

As an aside to this discussion, we note that there is one other significant chemical difference between I and II. Whereas I appears to be a stable species, II is found to undergo a slow unidirectional isomerization in which the metal tricarbonyl unit migrates to the five-membered ring of the ligand. A reversible migration of the chromium tricarbonyl group between sites on the five- and six-membered rings of the ligand in the anion $[Cr(CO)_3(C_{13}H_9)]^-$ has also been reported recently.[3]

Experimental Section

Crystals of $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ suitable for X-ray diffraction studies were obtained by chilling of a hexane solution of this compound (II) to dry ice temperature. A single crystal of approximate dimensions 0.25 × 0.45 × 0.55 mm was mounted in a thin-walled glass capillary for X-ray study. Preliminary examination of the crystal on a Syntex $P\bar{1}$ diffractometer showed the crystal to be monoclinic. The observed systematic absences for $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) uniquely define the space group as $P2_1/c$. The unit cell parameters (at −65 °C λ(Mo Kα) = 0.71073 Å) are $a = 9.610$ (3) Å, $b = 22.778$ (5) Å, $c = 13.396$ (2) Å, and $\beta = 91.54$ (2)°. These parameters were determined from a least-squares refinement utilizing the setting angles of 30 accurately centered reflections (25° < 2θ < 34°) each collected at $\pm 2\theta$. The unit cell volume of 2931 Å^3 led to a calculated density of 1.36 g/cm^3 for eight formula units of $Mn(CO)_3(C_{13}H_9)\cdot 0.5C_6H_{14}$ per unit cell. Thus there are two independent molecules in the asymmetric unit. The experimental density of 1.38 g/cm^3 was measured by flotation in $H_2O/ZnBr_2$ solutions.

X-ray intensity data were collected at −65 ± 5 °C by using a Syntex $P\bar{1}$ diffractometer equipped with a graphite-monochromated Mo Kα X-radiation source. A total of 4357 unique reflections with $(\sin\theta)/\lambda \le 0.649$ Å^1 were collected by using a θ–2θ step scan technique with a scan range of 0.8° below 2θ(Mo Kα_1) to 0.8° above 2θ(MoKα_2) and a variable scan rate (2.0–24.0°/min). During the data collection four standard reflections from diverse regions of reciprocal space were monitored every 50 reflections. The intensities of the standard reflections showed no systematic variations during the time required to collect the data. The intensity data were reduced and standard deviations calculated

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[3] Ustynyuk, N. A.; Lokshin, B. V.; Oprunenko, Yu. F.; Roznyatovsky, V. A.; Luzikov, Yu. N.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1980,** *202,* 279–289.

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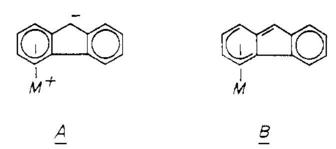

Figure 1. η^6-Zwitterionic (A) and η^5-cyclohexadienyl (B) representations for a metal complex of the fluorenyl ligand.

Table I. Atomic Positional Parameters for $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ (Non-Hydrogen Atoms)

atom	*x*	*y*	*z*
1Mn	0.10302 (7)	−0.10990 (4)	0.80414 (5)
1C(1)	0.0779 (5)	−0.01173 (25)	0.7839 (3)
1C(2)	−0.0455 (5)	−0.04174 (24)	0.7658 (3)
1C(3)	−0.1009 (4)	−0.08050 (25)	0.8375 (4)
1C(4)	−0.0282 (4)	−0.08816 (22)	0.9302 (3)
1C(5)	0.1839 (4)	−0.08453 (22)	1.1267 (3)
1C(6)	0.2821 (5)	−0.06909 (26)	1.2002 (3)
1C(7)	0.3775 (4)	−0.02455 (25)	1.1850 (3)
1C(8)	0.3794 (4)	0.00632 (23)	1.0963 (3)
1C(9)	0.2535 (4)	0.01823 (23)	0.9239 (3)
1C(10)	0.1412 (4)	−0.01057 (23)	0.8814 (3)
1C(11)	0.0937 (4)	−0.05654 (21)	0.9489 (3)
1C(12)	0.1857 (4)	−0.05355 (22)	1.0365 (3)
1C(13)	0.2813 (4)	−0.00793 (22)	1.0208 (3)
1C(14)	0.1244 (5)	−0.1796 (3)	0.8635 (4)
1O(1)	0.1391 (4)	−0.22383 (22)	0.9058 (3)
1C(15)	0.0676 (5)	−0.14454 (25)	0.6850 (4)
1O(2)	0.0463 (4)	−0.16572 (19)	0.60901 (25)
1C(16)	0.2860 (5)	−0.10395 (23)	0.7775 (3)
1O(3)	0.4018 (3)	−0.10002 (17)	0.76089 (24)
2Mn	0.46913 (8)	0.25145 (4)	0.94898 (5)
2C(1)	0.2882 (8)	0.2257 (3)	1.0438 (5)
2C(2)	0.4125 (10)	0.2069 (4)	1.0833 (4)
2C(3)	0.5020 (7)	0.1725 (3)	1.0293 (5)
2C(4)	0.4663 (5)	0.15710 (24)	0.9324 (4)
2C(5)	0.3246 (6)	0.13348 (28)	0.7095 (4)
2C(6)	0.2327 (11)	0.1258 (4)	0.6304 (5)
2C(7)	0.0975 (13)	0.1448 (5)	0.6311 (7)
2C(8)	0.0463 (7)	0.1723 (4)	0.7149 (7)
2C(9)	0.1138 (6)	0.2076 (3)	0.8950 (6)
2C(10)	0.2352 (5)	0.20299 (26)	0.9499 (4)
2C(11)	0.3401 (5)	0.17490 (23)	0.8896 (3)
2C(12)	0.2749 (5)	0.16199 (24)	0.7926 (4)
2C(13)	0.1352 (6)	0.1816 (3)	0.7976 (5)
2C(14)	0.5703 (6)	0.3013 (3)	1.0245 (4)
2O(1)	0.6378 (5)	0.33314 (21)	1.0725 (3)
2C(15)	0.3719 (6)	0.3098 (3)	0.8881 (4)
2O(2)	0.3071 (4)	0.34575 (22)	0.8493 (3)
2C(16)	0.6020 (6)	0.25253 (26)	0.8574 (4)
2O(3)	0.6855 (5)	0.25216 (20)	0.7979 (3)
C(1)	−0.4317 (9)	0.0053 (5)	0.5215 (6)
C(2)	−0.3221 (11)	0.0269 (4)	0.4576 (6)
C(3)	−0.1792 (10)	0.0295 (4)	0.5045 (5)

by using methods similar to those described previously.[4] The linear absorption coefficient was 8.4 cm^{-1}, and absorption corrections were applied by using an empirical psi scan method.

The structure was solved by direct methods using the MULTAN[5] package and the 410 reflections with the highest values of $|E|$. An E map based upon these reflections revealed both manganese atoms, three oxygen atoms, and 11 carbon atoms. Difference electron density maps revealed the rest of the 43 nonhydrogen atoms. The model was refined by a blocked full-matrix refinement technique using the 2377 reflections with $F_o^2 > 2\sigma(F_o^2)$. Atomic form factors were taken from Cromer and Waber[6] and that for hydrogen from Stewart, Davidson, and Simpson.[7] Isotropic refinement on the non-hydrogen atoms converged with $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.098$ and $R_2 = [\sum_w(|F_o| - |F_c|)^2/\sum_w(F_0)^2]^{1/2} = 0.127$. A difference electron density map revealed positions for most of the hydrogen atoms. The hydrogen atoms were included in the model in fixed idealized positions (d(C–H) = 0.95 Å), each with an isotropic thermal parameter one unit larger than the equivalent isotropic thermal parameter of the atom to which it is attached. All nonhydrogen atoms were assumed to vibrate anisotropically. This final model converged with $R_1 = 0.041$ and $R_2 = 0.049$. This final difference electron density map was featureless. The estimated error in an observation of unit weight was 1.39, and the

Table II. Bond Distances for $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ (Å)

	molecule	
	1	2
C(1)-C(2)	1.385 (6)	1.362 (9)
C(2)-C(3)	1.420 (7)	1.382 (9)
C(3)-C(4)	1.419 (6)	1.380 (7)
C(1)-C(10)	1.427 (6)	1.441 (8)
C(10)-C(11)	1.465 (6)	1.457 (6)
C(4)-C(11)	1.392 (6)	1.388 (6)
C(9)-C(10)	1.373 (6)	1.366 (8)
C(11)-C(12)	1.451 (5)	1.457 (6)
C(9)-C(13)	1.446 (6)	1.452 (9)
C(5)-C(6)	1.390 (6)	1.372 (9)
C(6)-C(7)	1.386 (7)	1.370 (14)
C(7)-C(8)	1.380 (6)	1.387 (14)
C(5)-C(12)	1.399 (6)	1.385 (7)
C(12)-C(13)	1.407 (6)	1.418 (7)
C(8)-C(13)	1.403 (6)	1.397 (10)
Mn-C(1)	2.264 (6)	2.258 (6)
Mn-C(2)	2.161 (5)	2.148 (6)
Mn-C(3)	2.130 (4)	2.114 (6)
Mn-C(4)	2.191 (4)	2.161 (6)
Mn-C(10)	2.511 (5)	2.505 (5)
Mn-C(11)	2.293 (4)	2.271 (5)
C(14)-O(1)	1.161 (6)	1.157 (6)
C(15)-O(2)	1.140 (5)	1.145 (6)
C(16)-O(3)	1.145 (5)	1.146 (6)
Mn-C(14)	1.786 (7)	1.790 (7)
Mn-C(15)	1.804 (5)	1.806 (7)
Mn-C(16)	1.808 (5)	1.794 (6)

Table III. Selected Bond Angles for $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ (Deg)

	molecule	
	1	2
C(1)-C(2)-C(3)	121.6 (4)	121.8 (6)
C(2)-C(3)-C(4)	119.0 (4)	119.6 (6)
C(3)-C(4)-C(11)	119.1 (4)	120.5 (5)
C(4)-C(11)-C(10)	122.2 (4)	120.6 (4)
C(11)-C(10)-C(1)	114.8 (4)	114.1 (5)
C(10)-C(1)-C(2)	120.8 (4)	120.8 (6)
C(9)-C(10)-C(11)	109.9 (4)	109.2 (5)
C(10)-C(11)-C(12)	105.8 (4)	107.2 (4)
C(11)-C(12)-C(13)	107.4 (4)	106.2 (5)
C(12)-C(13)-C(9)	109.5 (4)	109.2 (5)
C(13)-C(9)-C(10)	107.4 (4)	108.3 (5)
C(5)-C(6)-C(7)	121.3 (4)	123.1 (8)
C(6)-C(7)-C(8)	121.6 (4)	120.3 (7)
C(7)-C(8)-C(13)	118.6 (3)	119.2 (8)
C(8)-C(13)-C(12)	119.5 (4)	118.3 (7)
C(13)-C(12)-C(5)	121.6 (4)	122.2 (5)
C(12)-C(5)-C(6)	117.4 (4)	116.9 (7)
Mn-C(14)-O(1)	177.3 (5)	178.8 (6)
Mn-C(15)-O(2)	178.9 (5)	178.1 (6)
Mn-C(16)-O(3)	179.8 (4)	178.5 (5)
C(14)-Mn-C(15)	91.2 (2)	93.2 (3)
C(15)-Mn-C(16)	91.1 (2)	92.9 (2)
C(16)-Mn-C(14)	93.1 (2)	89.5 (3)

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(6) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, Table 2.2B.

(7) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Table IV. Least-Squares Planes for $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$[a]

atom	dist from plane, Å	atom	dist from plane, Å
Plane A1			
$0.609\,47X - 0.693\,68Y - 0.383\,86Z + 3.700\,54 = 0$[b]			
C(1)*	−0.141	C(8)*	0.053
C(2)*	0.011	C(9)*	0.055
C(3)*	0.108	C(10)*	0.030
C(4)*	0.057	C(11)*	−0.057
C(5)*	−0.075	C(12)*	−0.078
C(6)*	−0.012	C(13)*	−0.002
C(7)*	0.052	Mn	−1.730
Plane A2			
$0.0341\,20X + 0.869\,20Y - 0.357\,87Z - 0.132\,27 = 0$			
C(1)*	−0.151	C(8)*	0.082
C(2)*	0.008	C(9)*	0.049
C(3)*	0.129	C(10)*	0.011
C(4)*	0.076	C(11)*	−0.073
C(5)*	−0.088	C(12)*	−0.080
C(6)*	−0.023	C(13)*	0.013
C(7)*	0.048	Mn	−1.720
Plane B1			
$0.531\,39X - 0.756\,90Y - 0.380\,43Z + 3.55\,223 = 0$			
C(1)*	−0.009	C(11)*	0.010
C(2)*	0.008	Mn	−1.723
C(3)*	0.002	C(10)	0.203
C(4)*	−0.011	C(9)	0.351
Plane B2			
$0.450\,46X + 0.825\,87Y - 0.339\,14Z - 0.582\,16 = 0$			
C(1)*	−0.002	C(11)*	0.004
C(2)*	−0.001	Mn	−1.715
C(3)*	0.005	C(10)	0.214
C(4)*	−0.006	C(9)	0.395
Plane C1			
$0.733\,92X - 0.604\,52Y - 0.309\,72Z + 2.74\,702 = 0$			
C(1)*	0.0	C(11)*	0.0
C(10)*	0.0	Mn	−1.439
Plane C2			
$0.201\,69X + 0.876\,57Y - 0.436\,96Z + 1.11\,847 = 0$			
C(1)*	0.0	C(11)*	0.0
C(10)*	0.0	Mn	−1.427
Plane D1			
$0.650\,87X - 0.664\,15Y - 0.367\,79Z + 3.381\,66 = 0$			
C(5)*	0.002	C(12)*	−0.005
C(6)*	0.001	C(13)*	0.006
C(7)*	−0.000	Mn	−1.540
C(8)*	−0.003	C(9)	0.075
Plane D2			
$0.282\,23X + 0.882\,89Y - 0.375\,29Z + 0.067\,92 = 0$			
C(5)*	0.005	C(12)*	−0.007
C(6)*	0.003	C(13)*	0.002
C(7)*	−0.008	Mn	−1.532
C(8)*	0.006	C(9)	0.038
Plane E1			
$0.631\,51X - 0.652\,78Y - 0.418\,41Z + 4.122\,83 = 0$			
C(9)*	−0.003	C(12)*	−0.003
C(10)*	0.002	C(13)*	0.004
C(11)*	0.000	Mn	−1.694
Plane E2			
$0.290\,60X + 0.894\,30Y - 0.340\,26Z - 0.367\,54 = 0$			
C(9)*	−0.007	C(12)*	−0.005
C(10)*	0.003	C(13)*	0.007
C(11)*	0.001	Mn	−1.641
Plane F1			
$0.572\,01X - 0.731\,71Y - 0.370\,69Z + 3.505\,37 = 0$			
C(1)*	−0.077	C(10)*	0.099
C(2)*	0.008	C(11)*	−0.057
C(3)*	0.038	Mn	−1.746
C(4)*	−0.011		
Plane F2			
$0.404\,86X + 0.840\,65Y - 0.359\,73Z + 0.190\,36 = 0$			
C(1)*	−0.072	C(10)*	0.103
C(2)*	−0.000	C(11)*	−0.067
C(3)*	0.042	Mn	−1.740
C(4)*	−0.005		

Angles (Deg) between Normals of Planes

planes	angle	planes	angle	planes	angle	planes	angle
B1,C1	15.1	B2,C2	15.6	B1,D1	8.7	B2,D2	10.4
C1,E1	9.0	C2,E2	7.6	B1,E1	8.6	B2,E2	10.0
D1,E1	3.2	D2,E2	2.2				

[a] The designations 1 and 2 associated with these planes refer to molecules 1 and 2, respectively. The planes are defined in an orthonormal system with axis 2 the unit vector in the *b* direction, axis 3 the unit vector in the *c** direction, and axis 1 the unit vector (axis 2 × axis 3). [b] Atoms used in calculating the least-squares plane are marked with an asterisk.

final data/parameter ratio was 6.1. A listing of the final observed and calculated structure amplitudes (×10) is available as supplementary material, as are the anisotropic thermal parameters and hydrogen atomic positional parameters. Non-hydrogen atomic coordinates are listed in Table I. Bond distances for $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ are listed in Table II, selected bond angles are given in Table III, and several least-squares planes are described in Table IV.

Results and Discussion

Single crystals of II were grown at low temperatures, and X-ray diffraction data were obtained at −65 °C. The space group was determined to be $P2_1/c$, and there are eight formula units per unit cell. Four molecules of hexane were retained in the crystal. Solution of the structure confirmed the presence of two independent molecules of II in the asymmetric unit. The structure was refined by standard techniques, the results converging to a final structure with discrepancy factors $R_1 = 4.1\%$ and $R_2 = 4.9\%$. An ORTEP drawing of molecule 1 is presented in Figure 2. Bond distances and angles for molecules 1 and 2 are listed in Tables II and III.

It may be noted that there are no substantial differences in the structural data between molecules 1 and 2. The four hexane molecules in the unit cell were located; there is no evidence for bonding interactions between these solvent molecules and the molecules of II.

The structural parameters associated with the manganese tricarbonyl fragment of II are unexceptional. Manganese–carbon distances vary from 1.78 to 1.81 Å; these are characteristic values for this type of bond. The carbon–oxygen bond distances are between 1.14 and 1.16 Å.

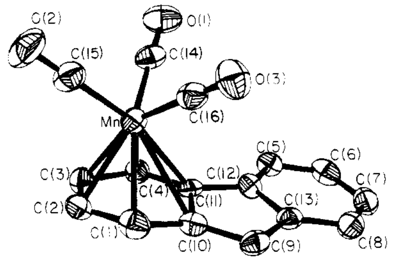

Figure 2. ORTEP drawing of $Mn(CO)_3(\eta^3\text{-}C_{13}H_9)$ (molecule 1) showing the atom numbering scheme. The atom labels in Tables I, V, and VI are prefixed with 1 or 2 to denote molecule 1 or molecule 2, respectively. The thermal ellipsoids are 50% probability envelopes.

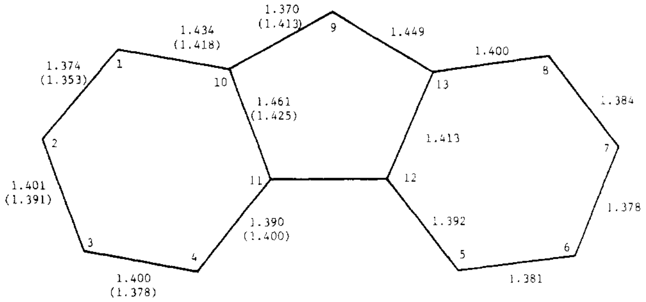

Figure 3. Comparison of averaged bond lengths in $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ with symmetry-averaged bond lengths of alkali metal–fluorenyl salts (values in parentheses).

Although the portion of this ligand encompassing the noncomplexed arene ring in the fluorenyl ligand is planar, the complexed arene ring is distinctly not planar. Atoms C(1), C(2), C(3), C(4), and C(11) of the complexed ring lie in one plane, but C(10) is bent out of that plane, away from the manganese atom (see planes B1 and B2). The dihedral angle formed between plane B (carbon atoms C(1), C(2), C(3), C(4), and C(11)) and plane C (C(1), C(10), and C(11)) is slightly greater than 15° in the two independent molecules. This value is larger than the dihedral angle of about 10° determined for the iron–fluorenyl complex (I). Distortion from planarity is typical in all cyclohexadienylmetal complexes; for example, in cyclohexadienylmanganese tricarbonyl, the related dihedral angle is 43°.[8] Similar diihedral angles have been measured for dicarbonyl-(3-[π-(2-cyclohexadienyl)]-σ-propenoyl)iron (39°),[9] $Re(CO)_3(\eta^5\text{-}C_6Me_6H)$ (50°),[10] tricarbonyl[bis(ethoxycarbonyl)methyl]cyclohexadienylmanganese (41°),[11] and the related complex bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II) (43°).[12] The out-of-plane bending in cyclohexadienylmetal complexes has been attributed, in part, to electronic factors; the methylene group bends away from the metal to avoid a secondary antibonding interaction between the metal and the endo hydrogen atom of the methylene group.[13] It seems obvious that this dihedral angle for I and II would not approach the values seen for these monocyclic cyclohexadienyl complexes; the fused rings in the fluorenyl ligand system would prohibit such large distortions from planarity.

In compound II, the average manganese–C(10) distance (in the two molecules) is 2.51 Å, substantially greater that the bond lengths between manganese and the other carbon atoms in this ring which range from about 2.11–2.29 Å. In I the iron–C(10) distance if 2.316 Å, and the other iron–carbon distances range from 2.04 to 2.15 Å.

Carbon–carbon bond distances in the fluorenyl ligand also reflect the inclination toward an η^5-cyclohexadienyl-type structure. The C(1)–C(10) and C(11)–C(10) bond lengths are both larger than other carbon–carbon bond lengths in this ring and in the noncomplexed ring. The C(10)–C(9) bond length is short while the C(9)–C(13) bond length is long, reflecting the tendency expressed in valence bond structure B (Figure 1) to achieve, respectively, double- and single-bond character for these bonds. The differences in the analogous carbon–carbon bond lengths in I are somewhat smaller. An interesting comparison can also be made between the carbon–carbon distances in II and the analogous (symmetry-averaged) distances in $K(TMED)^+C_{13}H_9^-$, a primarily ionic complex of the fluorenide ion in which the anion geometry is presumed to be little perturbed by the metal. This comparison is made in Figure 3.

As indicated in the introduction, the structural parameters for I and II were expected to be in accord with a representation of metal–ligand bonding intermediate between zwitterionic (A) and cyclohexadienyl (B). Clearly, this is seen to be so from the structural data. Chemical evidence suggested that II should have more cyclohexadienyl character than I, and, overall, this prediction appears to be verified. The most definitive evidence of an inclination toward a cyclohexadienylmetal structure in II is the distortion of C(10) away from the metal. This type of distortion had been identified in I, but it is magnified in II. In I, small bond length variations in the fluorenyl ligand supported the suggestion of some cyclohexadienyl character in the ligand; in II these variations are magnified. The variation of structure parameters in II is presumably the result of the greater extent of donation of charge from the ligand system to the metal, resulting from the higher acceptor ability of the carbonyl groups on the metal.

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Registry No. $Mn(CO)_3(C_{13}H_9)\cdot{}^1/_2C_6H_{14}$, 81725-21-5.

Supplementary Material Available: Table V, atomic positional parameters for $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ (hydrogen atoms), Table VI, anisotropic thermal parameters for $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$, and a listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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