Notes

Alkylation of (η^6-Arene)Mn(CO)$_3$ Cations with Organozinc Reagents

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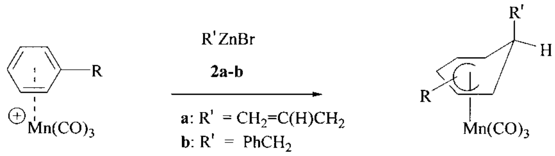
Received April 24, 2001

Summary: Additions of allylic and benzylic zinc reagents to (η^6-arene)Mn(CO)$_3$ cations proceed in an anti fashion to give the C-6 allylic- and benzylic-substituted (η^5-cyclohexadienyl)Mn(CO)$_3$ neutral complexes, respectively. The reaction of less reactive primary organozinc reagents bearing an ester or a cyano group with the cations affords the α-alkylation products. Treatment of the organozinc reagent containing an acetoxy group with (η^6-benzene)Mn(CO)$_3^+$ complex in THF results in alkylation of the cation at the C-2 position of THF.

Introduction

Nucleophilic additions to arenes coordinated to a transition metal have attracted considerable interest in organic synthesis.[1] Transition metals, such as chromium, manganese, iron, or ruthenium, have been used to activate arenes toward nucleophilic substitution and addition reactions. A wide range of nucleophiles add to (η^6-arene)Mn(CO)$_3^+$ complexes: lithium[2] and Grignard reagents,[3] as well as ketone enolates, malonates, and lithium aluminum hydride.[3] Reports on the addition of organozinc reagents to (η^6-arene)Mn(CO)$_3^+$ complexes are not available. In this contribution, we report the efficient addition of allylic and benzylic zinc reagents to (η^6-arene)Mn(CO)$_3^+$ complexes in tetrahydrofuran (THF), which proceeds in an anti fashion to afford the C-6-substituted cyclohexadienyl complexes. When the less reactive primary organozinc reagents bearing an ester or a cyano group are used, the additions occur at the α-carbon of the functionalized zinc reagents. The reaction of the zinc reagent containing an acetoxy functional group with (η^6-benzene)Mn(CO)$_3^+$ in THF results in alkylation of the cation at the C-2 position of THF to afford the C-6 exo THF-substituted (η^5-cyclohexadienyl)Mn(CO)$_3$ neutral complex.

Scheme 1



1a-d

3

a: R = H
b: R = CH$_3$
c: R = Cl
d: R = OMe

a: R = H, R' = CH$_2$=C(H)CH$_2$, 93%
b: R = CH$_3$, R' = CH$_2$=C(H)CH$_2$, *m*, 88%
c: R = Cl, R' = CH$_2$=C(H)CH$_2$, *o/m= 1/2, 99%*
d: R = OCH$_3$, R' = CH$_2$=C(H)CH$_2$, *m*, 54%
e: R = H, R' = PhCH$_2$, 96%
f: R = CH$_3$, R' = PhCH$_2$, *m*, 92%
g: R = Cl, R' = PhCH$_2$, *o/m= 1/2, 96%*
h: R = OCH$_3$, R' = PhCH$_2$, *o/m= 1/7, 67%*

Results and Discussion

Cations **1a**−**d** were prepared by heating Mn(CO)$_5$Br and the corresponding arenes in the presence of AlCl$_3$ according to a literature procedure.[4] Addition of a THF solution of allylic zinc reagent **2a** or benzylic zinc reagent **2b** (2.0 mol equiv) to a stirred suspension of cations **1a**−**d** in THF at −10 °C under nitrogen gave good yields (54−99%) of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes **3a**−**h** (Scheme 1). The trans relationship between the nucleophile and the metal moiety of complexes **3** was assigned on the basis of chemical shifts at C-6 in their ^{1}H NMR spectra. For example, the peak at δ 2.57 (1H, m) assigned as an endo proton at the C-6 carbon for complex **3a** is consistent with those of the known[3] exo C-6-substituted (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes. As can be seen in Scheme 1, zinc reagent addition to cation **1** is subject to substituent directive effects. For example, addition of allylic or benzylic zinc reagents to [(toluene)Mn(CO)$_3$]$^+$ (**1b**) favored the position meta to CH$_3$ (to give **3b** and **3f**, respectively), similar to that reported for Grignard[3] and lithium reagents.[5] The zinc reagents added both ortho and meta to the chloro substituent in [(C$_6$H$_5$Cl)Mn(CO)$_3$]$^+$ (**1c**) to afford **3c** and **3g**, respectively. The addition of allylic zinc reagent (**2a**) to [(C$_6$H$_5$OMe)Mn(CO)$_3$]$^+$ (**1d**) occurred exclusively meta to the OMe to

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[1] Pape, A. R.; Kaliappan, K. P.; Kündig, E. P. *Chem. Rev.* **2000**, *100*, 2917.

[2] (a) Semmelhack, M. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 12, p 979. (b) Pauson, P. L.; Siegal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1683. (c) Rose-Munch, F.; Gagliardini, V.; Renard, C.; Rose, E. *Coord. Chem. Rev.* **1998**, *178*−*180*, 249. (d) Rose-Munch, F.; Rose, E. *Curr. Org. Chem.* **1999**, *3*, 445. (e) Djukic, J.-P.; Rose-Munch, F.; Rose, E.; Vaissermann, J. *Eur. J. Inorg. Chem.* **2000**, 1295.

[3] (a) Balssa, F.; Gagliardini, V.; Rose-Munch, F.; Rose, E. *Organometallics* **1996**, *15*, 4373. (b) Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053. (c) Pike, R. D.; Sweigart, D. A. *Synlett* **1990**, 565.

[4] Coffield, T. H.; Sandel, V.; Closson, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 5826.

[5] Semmelhack, M. F.; Clark, G. *J. Am. Chem. Soc.* **1977**, *99*, 1675.

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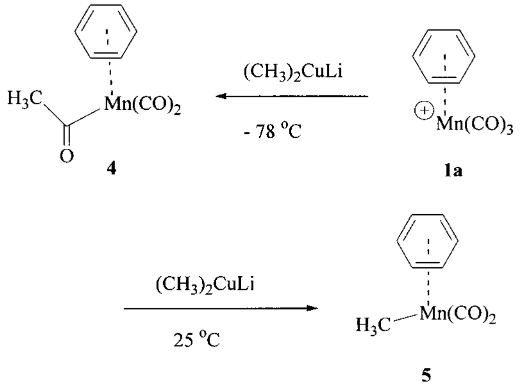
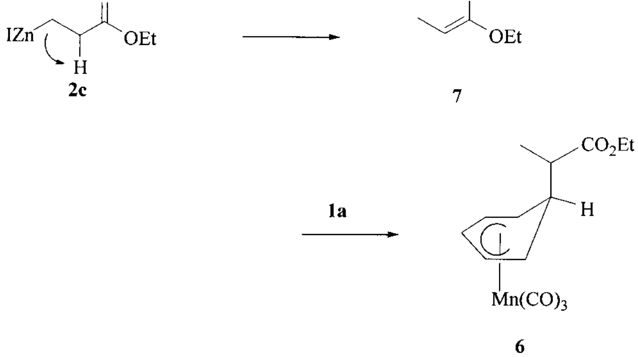
provide complex **3d**, while the addition of benzylic zinc reagent (**2b**) to cation **1d** favored the position meta to OMe (*o*/*m* = 1:7). The addition of lithium dimethylcuprate to cation **1a** is known to occur exclusively at the carbonyl ligand to afford the acyl complex **4** at −78 °C and the alkyl complex **5** at 0 °C (eq 1).[6] However, reaction of zinc−copper reagents[7] does not lead to the formation of the acyl or alkyl complexes. For example, in our preliminary results, addition of the zinc−copper reagent ($PhCH_2Cu(CN)ZnI$) to cation **1a** occurs at the arene ligand to generate complex **3e** as the only isolated product in good yields (70−80%) at both −78 and 0 °C.

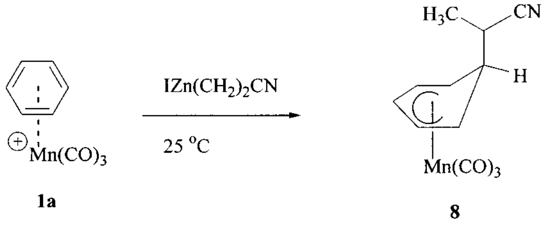


(1)[6]

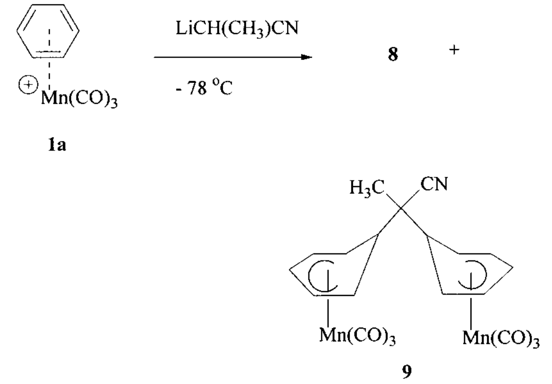
Interestingly, with the less reactive ester-functionalized zinc reagent $IZn(CH_2)_2CO_2Et$ (**2c**), the alkylation occurred at the α-carbon at 25 °C in THF to give the stabilized cyclohexadienyl complex **6** as the major product in 64% yield. The deprotonation of the α-proton may occur to give zinc-enolate **7** (Scheme 2), since it was found that the addition of **7** to cation **1a** produced complex **6** as the sole product. Similarly, treatment of the cyano-functionalized organozinc reagent $IZn(CH_2)_2CN$ (**2d**) with cation **1a** also provided the α-alkylated product **8** in 45% yield (eq 2). Rose and coworkers reported that addition of the cyano-stabilized lithium reagent 2-lithiopropionitrile to cation **1a** at −78 °C in THF produces complex **8** and the dinuclear complex **9** in a ratio of 7:1 in good yield (eq 3).[8] The formation of complex **9** was due to deprotonation of the acidic proton, α to the cyano group of complex **8**, under basic reaction conditions. Unlike the lithium reagent, the mild zinc reagent **2d** does not abstract the α-proton of complex **8** under the reaction conditions, and dinuclear species **9** is not formed.

Scheme 2





(2)



(3)[8]

Reaction of the acetoxy-functionalized zinc reagent $IZn(CH_2)_3OAc$ (**2e**) with **1a** in THF resulted in alkylation of cation **1a** at the C-2 position of THF to afford complex **10** as the only product in 68% yield. Deprotonation occurred at the C-2 position of THF (Scheme 3) to produce the zinc reagent **11**, and anti addition of **11** to cation **1a** furnished **10**. The proof of the structure of **10** was accomplished by X-ray diffraction analysis (Figure 1, Table 1).

Attempted alkylation of cation **1a** using the functionalized zinc−copper reagents derived from zinc reagents **2c**−**e** failed to give any substituted cyclohexadienyl complex under the same reaction conditions.

The reaction outlined herein demonstrates that the addition of reactive allylic and benzylic zinc reagents to (η^6-arene)$Mn(CO)_3$ cations proceeds in an anti fashion to give the C-6 allylic- and benzylic-substituted (η^5-cyclohexadienyl)$Mn(CO)_3$ neutral complexes, respectively. While reaction of the cations with less reactive ester- or cyano-functionalized organozinc reagents affords the α-alkylation products, that with an acetoxy-functionalized organozinc reagent in THF produces a THF-substituted (η^5-cyclohexadienyl)$Mn(CO)_3$ neutral complex.

Experimental Section

General Considerations. All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Tetrahydrofuran (THF) was distilled under nitrogen from a deep blue sodium benzophenone ketyl solution. Cations **1a**−**d** were prepared by heating $Mn(CO)_5Br$ and the corresponding arenes in the presence of $AlCl_3$ according to literature procedures.[4] Organozinc reagents were prepared according to literature procedures.[7] Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel

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(6) Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *1*, 1730.

(7) (a) Knochel, P.; Yeh, M. C. P.; Berk, S.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2392. (b) Yeh, M. C. P.; Sheu, B. A.; Fu, H. W.; Tau, S. I.; Chuang, L. W. *J. Am. Chem. Soc.* **1993**, *115*, 5941.

(8) Rose, E.; Corre-Susanne, C. L.; Rose-Munch, F.; Renard, C.; Gagliardini, V.; Teldji, F.; Vaissermann, J. *Eur. J. Inorg. Chem.* **1999**, 421.

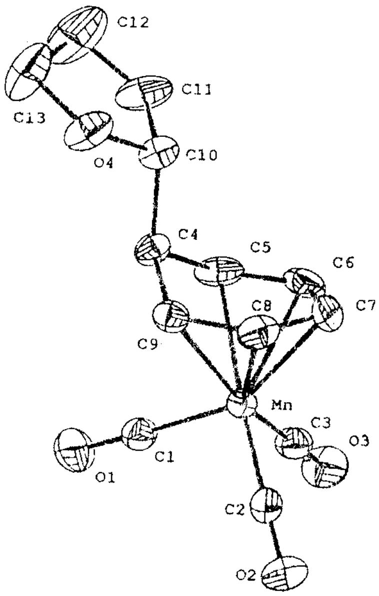

Figure 1. ORTEP drawing of complex **10** (at the 30% probability level). Hydrogens are omitted for clarity. Selected bond distances (Å): Mn−C5 = 2.197(4), Mn−C6 = 2.120(4), Mn−C7 = 2.115(4), C5−C6 = 1.396(7), C6−C7 = 1.408(8), C4−C10 = 1.537(5). Selected bond angles (deg): Mn−C5−C4 = 94.85(22), Mn−C6−C5 = 74.18(23), Mn−C7−C6 = 70.77(24), C5−C4−C10 = 112.2(3), C4−C5−C6 = 119.0(4), C10−O4−C13 = 108.5(3).

Scheme 3

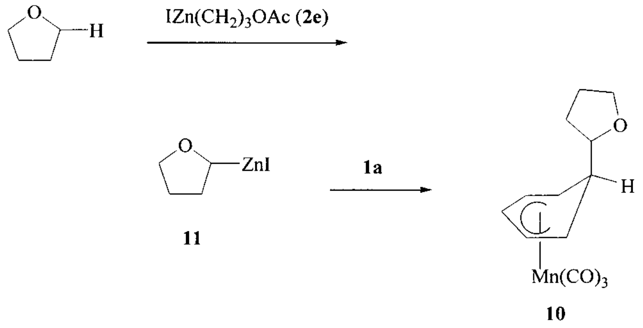

Table 1. Crystallographic Data for 10

empirical formula	$C_{13}H_{13}MnO_4$
fw	288.18
cryst syst	monoclinic
space group	*P*21/*c*
a, Å	9.930(2)
b, Å	9.846(3)
c, Å	13.158(3)
α, deg	90.0(2)
β, deg	91.95(2)
γ, deg	90.0(2)
V, Å^3	1285.7(6)
Z	4
D(calcd), g cm^{-3}	1.489
μ, cm^{-1}	1.03
diffractometer	Nonius (CAD4)
radiation *λ*, Å	0.70930
temp, °C	20
2*θ* range, deg	16.42−25.70
no. of ind reflns ($I > 2\sigma(I)$)	2007
GOF on F^2	1.7850
R_f,[a] R_w[a]	0.044, 0.032

[a] $R_f = \Sigma(F_o - F_c)/\Sigma(F_o)$ and $R_w = [\Sigma(w(F_o - F_c)^2)/\Sigma(wF_o^2)]^{1/2}$.

(Kieselgel 60, 230−400 mesh) using the indicated solvents.[9] All melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. ^{1}H nuclear magnetic resonance (NMR) spectra were obtained with JEOL-EX 400 (400 MHz) and Varian G-200 (200 MHz) spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CHCl_3$ (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with JEOL-EX 400 (100.4 MHz) and Varian G-200 (50 MHz) spectrometers with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge *(m/e)* with percent relative abundance. Satisfactory elemental analyses could not be obtained for all complexes, and relevant NMRs are given in the Supporting Information. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

General Procedure for Addition of Organozinc Reagents to (η^6-Arene)Mn(CO)$_3$ Cations. In a typical procedure, to a solution of cation **1a** (0.36 g, 1.0 mmol) in 10 mL of THF at −10 °C was added rapidly, neat, via syringe, allylic zinc bromide (**2a**) (2.0 mmol). The reaction was stirred at 0 °C for 3 h (25 °C for functionalized zinc reagents **2c**−**e**). The reaction mixture was quenched with 5.0 mL of saturated ammonium chloride solution via syringe needle and stirred at 25 °C for 15 min, after which time the reaction mixture was diluted with hexane (30 mL). The resultant solution was washed with water (50 mL × 3) and brine (50 mL × 3), dried over anhydrous magnesium sulfate (5.0 g), and concentrated to give the crude mixture.

(6-*exo*-(Propen-3-yl)cyclohexadienyl)tricarbonylmanganese complex (3a): yield 93% (0.24 g); IR (CH_2Cl_2) 3076, 2970, 2926, 2484, 2014, 1940, 1638, 1421, 1277, 994 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (t, J = 5.4 Hz, 1 H), 5.49 (m, 1 H), 4.96 (d, J = 10.8 Hz, 1 H), 4.92 (d, J = 16.8 Hz, 1 H), 4.81 (dd, J = 6.3, 5.4 Hz, 2 H), 3.20 (dd, J = 7.3, 6.3 Hz, 2 H), 2.57 (m, 1 H), 1.46 (t, J = 7.3 Hz, 2 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 222.94, 133.35, 116.76, 96.09, 79.67, 57.16, 46.86, 34.70; MS (20 eV) *m/e* 258 (M$^+$, 1), 216 (100), 189 (75), 174 (100); HRMS (EI) *m/e* calcd for $C_{12}H_{11}MnO_3$ 258.0089, found 258.0099.

(6-*exo*-(Propen-3-yl)-2-methylcyclohexadienyl)tricarbonylmanganese complex (3b): 88% (0.24 g); IR (CH_2Cl_2) 3074, 2924, 2010, 1940, 1639, 1437, 1425, 1381, 1186, 997 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (d, J = 5.4 Hz, 1 H), 5.49 (m, 1 H), 4.95 (d, J = 10.3 Hz, 1 H), 4.81 (d, J = 17.1 Hz, 1 H), 4.78 (t, J = 5.4 Hz, 1 H), 3.16 (t, J = 6.4 Hz, 1 H), 3.13 (d, J = 5.9 Hz, 1 H), 2.59 (m, 1 H), 1.85 (s, 3 H), 1.49 (m, 2 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 223.05, 133.42, 111.20, 94.63, 80.48, 58.38, 57.34, 46.97, 36.00, 22.50; MS (20 eV) *m/e* 272 (M$^+$, 1), 229 (100), 187 (70); HRMS (EI) *m/e* calcd for $C_{13}H_{13}MnO_3$ 272.0245, found 272.0239.

(6-*exo*-(Propen-3-yl)-2-chlorocyclohexadienyl)tricarbonylmanganese (*meta* isomer of **3c**): 66% (0.19 g); IR (CH_2Cl_2) 3046, 2928, 2022, 1944, 1639, 1431, 1429, 1054 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (d, J = 5.9 Hz, 1 H), 5.46 (m, 1 H), 4.99 (d, J = 9.8 Hz, 1 H), 4.90 (d, J = 17.1 Hz, 1 H), 4.78 (dd, J = 5.9, 6.3 Hz, 1 H), 3.51 (d, J = 5.9 Hz, 1 H), 3.14 (dd, J = 6.3, 6.8 Hz, 1 H), 2.73 (m, 1 H), 1.49 (m, 2 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 223.71, 132.60, 117.51, 92.91, 79.73, 58.26, 58.15, 53.41, 46.53, 38.21; MS (20 eV) *m/e* 292 (M$^+$, 1), 253 (33), 251 (100), 225 (5), 223 (15), 209 (28), 207 (80), 197 (13), 195 (31), 169 (13), 167 (39); HRMS (EI) *m/e* calcd for $C_{12}H_{10}ClMnO_3$ 291.9699, found 291.9690.

(6-*exo*-(Propen-3-yl)-2-methoxycyclohexadienyl)tricarbonylmanganese complex (3d): 54% (0.16 g); IR (CH_2Cl_2) 3058, 2928, 2002, 1920, 1603, 1493, 1465, 1217 cm^{-1}; ^{1}H NMR

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[9] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(400 MHz, $CDCl_3$) δ 5.71 (d, J = 5.9 Hz, 1 H), 5.48 (m, 1 H), 4.96 (d, J = 9.3 Hz, 1 H), 4.87 (d, J = 17.1 Hz, 1 H), 4.83 (t, J = 5.9 Hz, 1 H), 3.46 (s, 3 H), 3.12 (m, 2 H), 2.70 (m, 1 H), 1.45 (m, 2 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 222.65, 142.58, 133.42, 116.85, 92.45, 68.02, 57.52, 54.14, 47.36, 42.46, 37.41; MS (20 eV) *m*/*e* 247 ($M^+ - CH_2{=}CHCH_2$, 100), 204 (95), 164 (95); HRMS (EI) *m*/*e* calcd for $C_{13}H_{13}MnO_4$ 288.0194, found 288.0199.

(6-*exo*-Benzylcyclohexadienyl)tricarbonylmanganese complex (3e): 96% (0.30 g); IR (CH_2Cl_2) 3078, 3030, 2958, 2862, 2014, 1939, 1601, 1493, 1077 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00−7.26 (m, 5 H), 5.83 (t, J = 5.4 Hz, 1 H), 4.86 (dd, J = 5.9, 5.4 Hz, 2 H), 3.16 (t, J = 5.9 Hz, 2 H), 2.73 (m, 1 H), 1.96 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 222.84, 137.13, 129.05, 128.24, 126.05, 96.07, 79.84, 56.99, 48.58, 36.77; MS (20 eV) *m*/*e* 308 (M^+, 1), 216 (65), 217 (100), 160 (45); HRMS (EI) *m*/*e* calcd for $C_{16}H_{13}MnO_3$ 308.0244, found 308.0238.

(6-*exo*-Benzyl-2-methylcyclohexadienyl)tricarbonylmanganese complex (3f): 92% (0.30 g); IR (CH_2Cl_2) 3074, 2936, 2020, 1937, 1606, 1459, 1424, 1276, 1153 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93−7.29 (m, 5 H), 5.66 (d, J = 5.4 Hz, 1 H), 4.81 (dd, J = 5.4, 6.6 Hz, 1 H), 3.11 (m, 2 H), 2.75 (m, 1 H), 1.95 (dd, J = 12.1, 7.3 Hz, 2 H), 1.85 (s, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 222.90, 137.25, 129.07, 128.16, 125.98, 111.19, 94.67, 80.57, 58.30, 57.19, 48.70, 38.14, 22.49; MS (20 eV) *m*/*e* 322 (M^+, 1), 238 (100), 231 (100), 204 (50); HRMS (EI) *m*/*e* calcd for $C_{17}H_{15}MnO_3$ 322.0402, found 322.0410.

(6-*exo*-Benzyl-2-chlorocyclohexadienyl)tricarbonylmanganese (*meta* isomer of **3g**): 64% (0.22 g); IR (CH_2Cl_2) 3034, 2928, 2022, 1938, 1604, 1427, 1251, 1055 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97−7.32 (m, 5 H), 6.05 (d, J = 5.2 Hz, 1 H), 4.81(dd, J = 6.7, 6.0 Hz, 1 H), 3.42 (d, J = 6.0 Hz, 1 H), 3.08 (dd, J = 6.7, 6.1 Hz, 1 H), 2.87 (m, 1 H), 2.02 (d, J = 7.1 Hz, 2 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 221.53, 136.49, 129.06, 128.36, 126.30, 115.49, 92.94, 79.81, 58.00, 48.27, 40.26; MS (20 eV) *m*/*e* 342 (M^+, 1), 260 (6), 258 (17), 253 (14), 251 (47), 197 (8), 195 (20), 92 (11), 90 (36), 55 (100); HRMS (EI) *m*/*e* calcd for $C_{16}H_{12}ClMnO_3$ 341.9855, found 341.9833.

(6-*exo*-Benzyl-2-methoxycyclohexadienyl)tricarbonylmanganese (*meta* isomer of **3h**): 59% (0.20 g); IR (CH_2Cl_2) 3058, 2928, 2002, 1920, 1603, 1493, 1465, 1217 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97−7.28 (m, 5 H), 5.73 (d, J = 5.9 Hz, 1 H), 4.87 (dd, J = 5.9, 6.4 Hz, 1 H), 3.40 (s, 3 H), 3.08 (dd, J = 5.9, 7.3 Hz, 1 H), 2.99 (d, J = 6.3 Hz, 1 H), 2.83 (m, 1 H), 2.06 (m, 1 H), 1.92 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 222.44, 142.58, 137.14, 129.10, 128.26, 126.09, 92.55, 68.26, 57.32, 54.09, 49.09, 42.29, 39.55; MS (20 eV) *m*/*e* 254 ($M^+ - 3CO$, 100), 246 (100), 190 (80), 162 (80); HRMS (EI) *m*/*e* calcd for $C_{14}H_{15}Mn$ 254.0516, found 254.0508.

(6-*exo*-(Ethyl propionate-2-yl)cyclohexadienyl)tricarbonylmanganese complex (6): 64% (0.20 g); IR (CH_2Cl_2) 3064, 2932, 2856, 2014, 1937, 1723, 1456, 1373, 1049 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (t, J = 5.4 Hz, 1 H), 4.89 (dd, J = 6.4, 5.4 Hz, 2 H), 4.12 (q, J = 7.3 Hz, 2 H), 3.22 (dd, J = 6.4, 7.3 Hz, 2 H), 2.73 (m, 1 H), 1.64 (m, 1 H), 1.27 (t, J = 7.3 Hz, 3 H), 0.90 (d, J = 7.3 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 222.52, 173.91, 96.59, 96.29, 80.24, 60.29, 55.29, 53.57, 50.32, 37.57, 14.27, 12.28; MS (20 eV) *m*/*e* 318 (M^+, 1), 234 (75), 217 (100); HRMS (EI) *m*/*e* calcd for $C_{14}H_{15}MnO_5$ 318.0299, found 318.0290.

(6-*exo*-(Tetrahydrofuranyl-2-yl)cyclohexadienyl)tricarbonylmanganese complex (10): 64% (0.20 g); mp 85−87 °C; IR (CH_2Cl_2) 3065, 2932, 2856, 2012, 1937, 1732, 1606, 1456, 1367, 1273 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (t, J = 5.4 Hz, 1 H), 4.78 (t, J = 6.4 Hz, 2 H), 3.57−3.74 (m, 2 H), 3.30 (dd, J = 5.9, 7.3 Hz, 1 H), 2.97 (dd, J = 5.9, 7.3 Hz, 1 H), 2.83 (m, 1 H), 2.52 (m, 1 H), 1.73 (m, 3 H), 1.28 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 222.77, 97.03, 96.79, 85.12, 79.76, 67.73, 55.79, 52.02, 39.88, 27.17, 25.17; MS (20 eV) *m*/*e* 288 (M^+, 1), 217 (100), 204 (10), 199 (30), 181 (30), 161 (40); HRMS (EI) *m*/*e* calcd for $C_{13}H_{13}MnO_4$ 288.0194, found 288.0191. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2.

Acknowledgment. This work was supported by a grant from the National Science Council (NSC 89-2113-M-003-004).

Supporting Information Available: Tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for complex **10**, analytical data for complexes *o*-**3c**, *o*-**3g**, and *o*-**3h**, and additional NMR spectra for **3a**, *o*-**3c**, **3e**, *o*-**3g**, *m*-**3g**, *m*-**3h**, **6**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010338H