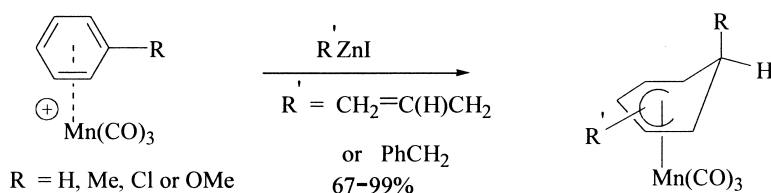


Alkylation of (η -Arene)Mn(CO)⁺ Cations with Organozinc Reagents

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Notes

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

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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

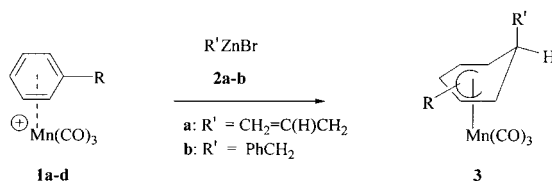
Nucleophilic additions to arenes coordinated to a transition metal have attracted considerable interest in organic synthesis.¹ Transition metals, such as chromium, manganese, iron, or ruthenium, have been used to activate arenes toward nucleophilic substitution and addition reactions. A wide range of nucleophiles add to (η^6 -arene) $Mn(CO)_3^+$ complexes: lithium² 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.

(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.

Scheme 1



a: R = H
 b: R = CH₃
 c: R = Cl
 d: R = OMe

a: R = H, R' = CH₂=C(H)CH₂, 93%
 b: R = CH₃, R' = CH₂=C(H)CH₂, *m*, 88%
 c: R = Cl, R' = CH₂=C(H)CH₂, *o/m* = 1/2, 99%
 d: R = OCH₃, R' = CH₂=C(H)CH₂, *m*, 54%
 e: R = H, R' = PhCH₂, 96%
 f: R = CH₃, R' = PhCH₂, *m*, 92%
 g: R = Cl, R' = PhCH₂, *o/m* = 1/2, 96%
 h: R = OCH₃, R' = PhCH₂, *o/m* = 1/7, 67%

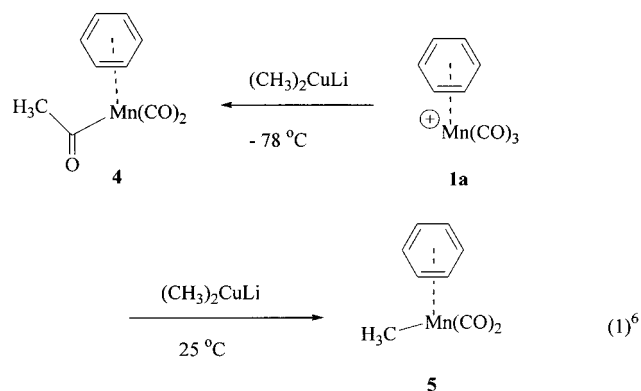
Results and Discussion

Cations **1a–d** were prepared by heating $Mn(CO)_5Br$ 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 $-10^\circ C$ 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 ¹H 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 known³ 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 CH₃ (to give **3b** and **3f**, respectively), similar to that reported for Grignard³ and lithium reagents.⁵ The zinc reagents added both ortho and meta to the chloro substituent in [(C₆H₅Cl) $Mn(CO)_3$]⁺ (**1c**) to afford **3c** and **3g**, respectively. The addition of allylic zinc reagent (**2a**) to [(C₆H₅OMe) $Mn(CO)_3$]⁺ (**1d**) occurred exclusively meta to the OMe to

(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.

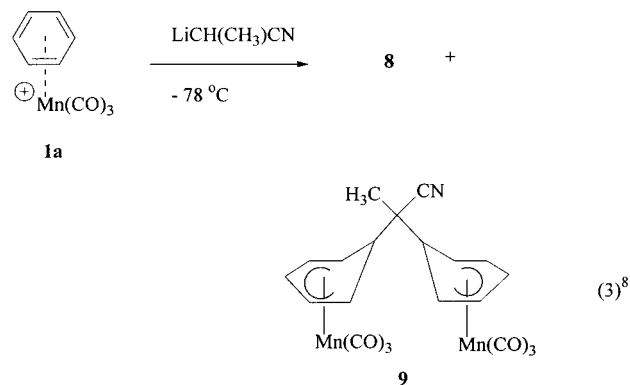
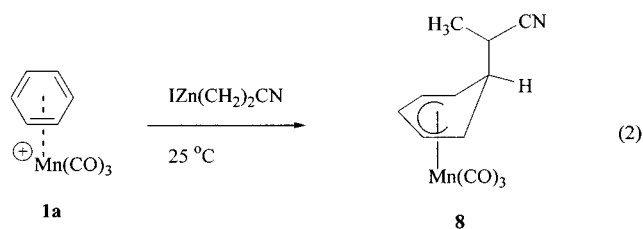
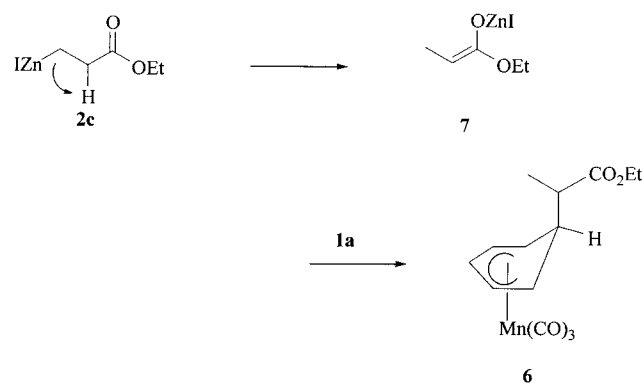
provide complex **3d**, while the addition of benzylic zinc reagent (**2b**) to cation **1d** favored the position meta to OMe (*o/m* = 1:7). The addition of lithium dimethylcuprate to cation **1a** is known to occur exclusively at the carbonyl ligand to afford the acyl complex **4** at $-78\text{ }^\circ\text{C}$ and the alkyl complex **5** at $0\text{ }^\circ\text{C}$ (eq 1).⁶ However, reaction of zinc-copper reagents⁷ does not lead to the formation of the acyl or alkyl complexes. For example, in our preliminary results, addition of the zinc-copper reagent ($\text{PhCH}_2\text{Cu}(\text{CN})\text{ZnI}$) 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 $0\text{ }^\circ\text{C}$.



Interestingly, with the less reactive ester-functionalized zinc reagent $\text{IZn}(\text{CH}_2)_2\text{CO}_2\text{Et}$ (**2c**), the alkylation occurred at the α -carbon at $25\text{ }^\circ\text{C}$ 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 $\text{IZn}(\text{CH}_2)_2\text{CN}$ (**2d**) with cation **1a** also provided the α -alkylated product **8** in 45% yield (eq 2). Rose and co-workers reported that addition of the cyano-stabilized lithium reagent 2-lithiopropionitrile to cation **1a** at $-78\text{ }^\circ\text{C}$ 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.

Reaction of the acetoxy-functionalized zinc reagent $\text{IZn}(\text{CH}_2)_3\text{OAc}$ (**2e**) with **1a** in THF resulted in alkyla-

Scheme 2



tion 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 $(\eta^6\text{-arene})\text{Mn}(\text{CO})_3$ cations proceeds in an anti fashion to give the C-6 allylic- and benzylic-substituted $(\eta^5\text{-cyclohexadienyl})\text{Mn}(\text{CO})_3$ 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 $(\eta^5\text{-cyclohexadienyl})\text{Mn}(\text{CO})_3$ 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 $\text{Mn}(\text{CO})_5\text{Br}$ 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

(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.

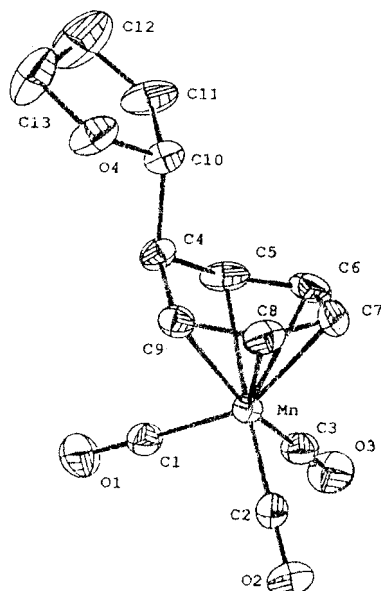
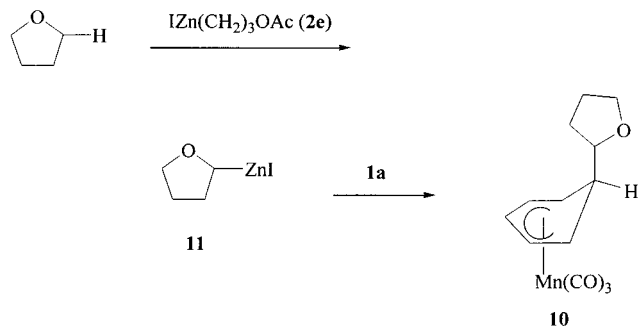


Figure 1. ORTEP drawing of complex **10** (at the 30% probability level). Hydrogens are omitted for clarity. Selected bond distances (Å): Mn–C5 = 2.197(4), Mn–C6 = 2.120(4), Mn–C7 = 2.115(4), C5–C6 = 1.396(7), C6–C7 = 1.408(8), C4–C10 = 1.537(5). Selected bond angles (deg): Mn–C5–C4 = 94.85(22), Mn–C6–C5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



(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. ¹H 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 CHCl₃ (7.26 ppm) as internal standard. ¹³C NMR spectra were recorded with JEOL-EX 400 (100.4 MHz) and Varian G-200 (50 MHz) spectrometers with CDCl₃ (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, Tai-chung, Taiwan.

General Procedure for Addition of Organozinc Reagents to (η^6 -Arene)Mn(CO)₃ Cations. In a typical proce-

Table 1. Crystallographic Data for **10**

empirical formula	C ₁₃ H ₁₃ MnO ₄
fw	288.18
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	9.930(2)
<i>b</i> , Å	9.846(3)
<i>c</i> , Å	13.158(3)
α , deg	90.0(2)
β , deg	91.95(2)
γ , deg	90.0(2)
<i>V</i> , Å ³	1285.7(6)
<i>Z</i>	4
<i>D</i> (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>I</i> > 2 σ (<i>I</i>))	2007
GOF on <i>F</i> ²	1.7850
<i>R</i> _{<i>i</i>} , ^a <i>R</i> _w , ^a	0.044, 0.032

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

cedure, 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 \times 3) and brine (50 mL \times 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 (CH₂Cl₂) 3076, 2970, 2926, 2484, 2014, 1940, 1638, 1421, 1277, 994 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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 C₁₂H₁₁MnO₃ 258.0089, found 258.0099.

(6-*exo*-(Propen-3-yl)-2-methylcyclohexadienyl)tricarbonylmanganese complex (3b): 88% (0.24 g); IR (CH₂Cl₂) 3074, 2924, 2010, 1940, 1639, 1437, 1425, 1381, 1186, 997 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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 C₁₃H₁₃MnO₃ 272.0245, found 272.0239.

(6-*exo*-(Propen-3-yl)-2-chlorocyclohexadienyl)tricarbonylmanganese (meta isomer of 3c): 66% (0.19 g); IR (CH₂Cl₂) 3046, 2928, 2022, 1944, 1639, 1431, 1429, 1054 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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 C₁₂H₁₀ClMnO₃ 291.9699, found 291.9690.

(6-*exo*-(Propen-3-yl)-2-methoxycyclohexadienyl)tricarbonylmanganese complex (3d): 54% (0.16 g); IR (CH₂Cl₂) 3058, 2928, 2002, 1920, 1603, 1493, 1465, 1217 cm⁻¹; ¹H NMR

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

(400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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⁺ - CH₂=CHCH₂, 100), 204 (95), 164 (95); HRMS (EI) m/e calcd for C₁₃H₁₃MnO₄ 288.0194, found 288.0199.

**(6-*exo*-Benzylcyclohexadienyl)tricarbo-
nylmanganese complex (3e):** 96% (0.30 g); IR (CH₂Cl₂) 3078, 3030, 2958, 2862, 2014, 1939, 1601, 1493, 1077 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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 C₁₆H₁₃MnO₃ 308.0244, found 308.0238.

**(6-*exo*-Benzyl-2-methylcyclohexadienyl)tricarbo-
nylmanganese complex (3f):** 92% (0.30 g); IR (CH₂Cl₂) 3074, 2936, 2020, 1937, 1606, 1459, 1424, 1276, 1153 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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 C₁₇H₁₅MnO₃ 322.0402, found 322.0410.

**(6-*exo*-Benzyl-2-chlorocyclohexadienyl)tricarbo-
nylmanganese (meta isomer of 3g):** 64% (0.22 g); IR (CH₂-Cl₂) 3034, 2928, 2022, 1938, 1604, 1427, 1251, 1055 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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 C₁₆H₁₂ClMnO₃ 341.9855, found 341.9833.

**(6-*exo*-Benzyl-2-methoxycyclohexadienyl)tricarbo-
nylmanganese (meta isomer of 3h):** 59% (0.20 g); IR (CH₂-Cl₂) 3058, 2928, 2002, 1920, 1603, 1493, 1465, 1217 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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 C₁₄H₁₅Mn 254.0516, found 254.0508.

**(6-*exo*-(Ethyl propionate-2-yl)cyclohexadienyl)tricarbo-
nylmanganese complex (6):** 64% (0.20 g); IR (CH₂Cl₂) 3064, 2932, 2856, 2014, 1937, 1723, 1456, 1373, 1049 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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 C₁₄H₁₅MnO₅ 318.0299, found 318.0290.

**(6-*exo*-(Tetrahydrofuran-2-yl)cyclohexadienyl)tri-
carbonylmanganese complex (10):** 64% (0.20 g); mp 85–87 °C; IR (CH₂Cl₂) 3065, 2932, 2856, 2012, 1937, 1732, 1606, 1456, 1367, 1273 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100.4 MHz, CDCl₃) 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 C₁₃H₁₃MnO₄ 288.0194, found 288.0191. Crystals suitable for X-ray diffraction were grown from CH₂Cl₂.

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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>.

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