Synthesis and Structure of (η^5-cyclohexadienyl)Mn(CO)$_3$ and Cationic (η^6-arene)Mn(CO)$_3$ Complexes Comprising a Double Bond Conjugated to the π System

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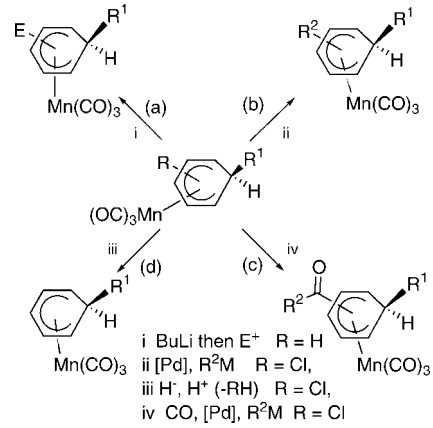
Addition of a Grignard reagent to keto-substituted (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes leads to the corresponding alcohols in very good yields. After acidic treatment, dehydration occurs, which gives rise to the formation of unprecedented (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes substituted by a double bond conjugated to the π system as the major compounds, along with uncoordinated trienones due to the rearrangement of the intermediate carbocation. The structure of one of these η^5 complexes has been determined by X-ray crystallography as well as one of the corresponding cationic (η^6-arene)Mn(CO)$_3$ complexes formed upon hydride abstraction.

Introduction

Cationic (η^6-arene)tricarbonylmanganese complexes constitute an important class of organometallic compounds[1] due to the very electrophilic character of the arene ring coordinated to the Mn(CO)$_3$ entity, leading to useful synthons in organometallic and organic syntheses.[2] *Ipso* chloride substitutions in cationic (η^6-chloroarene)Mn(CO)$_3$ allow clean nucleophile introductions, restricted to amino, oxo, and thio nucleophiles.[1] However the main reactions described are addition reactions affording stable neutral (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes.[1,3] The η^5 complexes have recently received much attention thanks to the discovery of two new methodologies for their functionalization, which broaden the scope of their applications. Indeed, it has been reported first that very efficient lithiation/electrophilic quench gives rise to the formation of the corresponding diversely substituted η^5 complexes[4] (Scheme 1, step a; in this scheme are reported the more recent developments of η^5 complex chemistry that do not affect their hapticity). Second, when they bear a halogen substituent on the π system, they are easily transformed, by palladium-catalyzed cross-coupling reactions, into the corresponding compounds due to the *ipso* substitution of the halogen[5] (Scheme 1, step b) or into the keto derivatives if the coupling is achieved under carbonylative conditions (Scheme 1, step c).[6] Very recently, these η^5 keto complexes have been shown to undergo hydride reduction into the corresponding alcohol derivatives, with an unexpected addition of the nucleophile to an internal carbon atom of the π system.[7] Finally, when the η^5 complexes are substituted by a good leaving

Scheme 1



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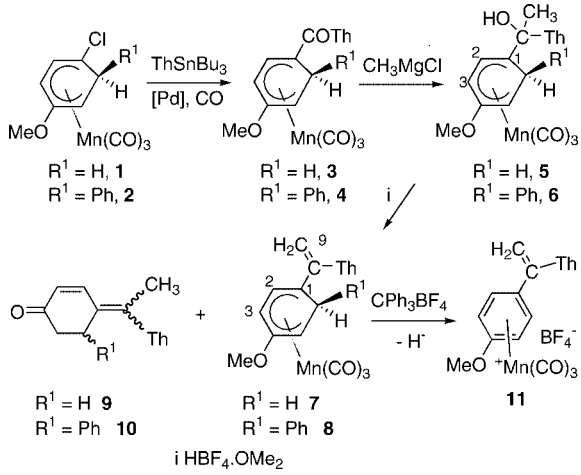
Scheme 2



group R, such a methoxy, a chloride, or an amino group, they can eliminate RX after an acidic treatment[8] via *cine*[9] and *tele*[10] nucleophilic substitutions (Scheme 1, step d).

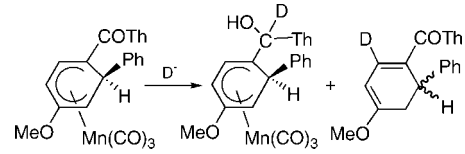
Here we report a preliminary study on the reactivity of (η^5-ketocyclohexadienyl) $Mn(CO)_3$ complexes toward a Grignard reagent and the behavior of the newly formed alcohol derivatives in acidic medium.

Results and Discussion

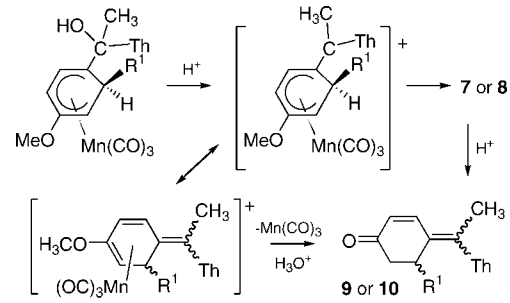
The complexes **3** and **4** used as starting materials in this study were readily obtained by Stille reaction of complexes **1** and **2** with $ThSnBu_3$ (Th = 2-thienyl) and Pd_2dba_3 and $AsPh_3$ as the catalytic system, after carbonylative conditions, Scheme 2.[6] The latter were obtained by nucleophilic addition of phenyl magnesium chloride or lithium aluminum hydride onto the [(η^6-*para*-chloroanisole)$Mn(CO)_3$]$^+BF_4^-$ complex.[8] When complexes **3** and **4** reacted with methyl magnesium chloride, the two alcohols **5** and **6** corresponding to the regioselective addition of the Grignard reagent to the keto function were formed in 72 and 86% yield, respectively, Scheme 2. For each alcohol, two diastereoisomers, due to the planar chirality of the complexes, were formed with no diastereoselectivity for alcohol **5** and with 40% de for **6** according to crude mixture ^{1}H NMR spectra. The two sets of diastereoisomers were carefully purified by silica gel chromatography, and their ^{1}H NMR spectra showed for the H2, H3, and H5 proton signals, chemical shifts specific for 1,5-disubstituted η^5 systems.

Thus, the π system remains intact with no incorporation of the nucleophile at an internal position of the cyclohexadienyl ring, unlike the deuteride addition, which occurs not only to the ketone carbonyl group but also to the C2 carbon atom to form a deuterated cyclohexadiene (Scheme 3).[7] The observed diastereoselectivity stresses out the importance of the nature of the substituent on the sp^3 carbon atom. It likely originates in the relative size of the $Mn(CO)_3$ tripod, which hinders one face of the cyclohexadienyl ring and of the axial sp^3 carbon atom substituent. If one assumes that the keto group adopts the same conformation in **3** and **4**,[11] the nucleophile could add either *syn* or *anti* to the metal entity when no sterically demanding group is present at the C6 carbon atom such as in **3**, whereas the phenyl group at C6 in the ketone **4** would favor the addition *syn* to the $Mn(CO)_3$ tripod, which could explain the observed limited de.

Scheme 3



Scheme 4



Complexes **5** and **6** reacted with $HBF_4 \cdot OMe_2$ to afford complexes **7** and **8** in 45 and 71% yield, respectively, together with trienones **9** and **10** in 40 and 25% yield, respectively. The formation of the different products could be explained with the following mechanism (Scheme 4). In the presence of an acid, a cationic intermediate could be formed after abstraction of the hydroxy group, leading, on one side, to the double-bond formation of complexes **7** or **8** and, on the other one, to organic compounds **9** or **10** after decoordination and hydrolysis of the trienol ether.[12] Exposing isolated samples of **7** and **8** to the acidic reaction conditions used for their preparation gave the dienones **9** and **10**, in agreement with another possible pathway for the formation of these dienones.

Taking advantage of the rearomatization procedure by *exo*-hydride abstraction already successfully exploited in our group,[5b,c,6] we submitted complex **7** to the action of CPh_3BF_4 and isolated the cationic (η^6-arene)$Mn(CO)_3$ complex **11** in 30% yield (Scheme 2). The ^{1}H NMR spectrum exhibits two doublets at 6.55 and 7.30 ppm for the H2, H3, H5, and H6 protons, in good agreement with the presence of a *para*-disubstituted arene ring. The olefinic H9 proton signals show two singlets at 5.86 and 5.83 ppm, at higher frequencies than the corresponding ones of complex **7** (two singlets at 5.33 and 5.28 ppm), stressing the strong electron-withdrawing effect of the arene ring coordinated to the $Mn(CO)_3$ entity.

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(11) A preferred conformation of the keto function, "*anti*" to the sp_3 carbon atom, has been confirmed by preliminary theoretical investigations currently in progress.

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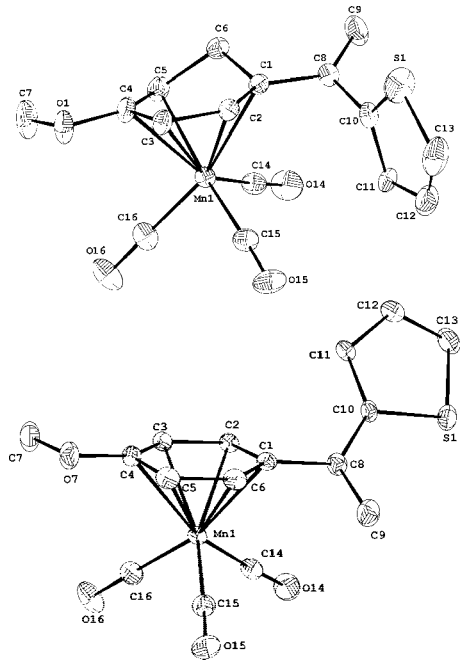

Figure 1. ORTEP representations of complexes **7** and **11** with thermal ellipsoids at the 30% probability level. Selected bond lengths for **7** (Å): C8−C9 1.344(4), C1−C8 1.484(3), C8−C10 1.497(4), C1−C2 1.415(3), C2−C3 1.431(3), C3−C4 1.427(4), C4−C5 1.409(3), C5−C6 1.518(4), C6−C1 1.528(3), Mn−C1 2.285(2), Mn−C2 2.148(2), Mn−C3 2.148(2), Mn−C4 2.215(3), Mn−C5 2.229(2). For **11**: C8−C9 1.342(3), C1−C8 1.499(3), C8−C10 1.470(3), C1−C2 1.431(3), C2−C3 1.406(3), C3−C4 1.423(3), C4−C5 1.408(3), C5−C6 1.420(3), Mn−C1 2.206(2), Mn−C2 2.1713(19), Mn−C3 2.196(2), Mn−C4 2.282(2), Mn−C5 2.212(2), Mn−C6 2.190(2).

Very few examples of η^6 Mn complexes substituted by a conjugated double bond have been described in the literature,[13–15] whereas the analogous derivatives of the isoelectronic neutral chromium complexes have been known for many years.[16] In contrast, to the best of our knowledge, no synthesis of an η^5 Mn complex with the π system conjugated to a double bond has been reported so far.

Pleasingly, we obtained monocrystals of complexes **7** and **11** suitable for radiocrystallographic analyses, and ORTEP views are presented Figure 1 as well as some selected bond lengths. The η^5 structure of complex **7**[17] is confirmed by the five coplanar carbon atoms of the π system, while the remaining sp^3 C6 carbon atom is located 40° above this plane. The C8═C9 double bond is in the [C1C8C9] plane, which makes a dihedral angle of 31° away from the metal with the five coplanar carbon atoms.

The structure of complex **11**[17] shows a staggered conformation of the $Mn(CO)_3$ tripod with respect to the carbon atoms of the arene ring. It is noteworthy that an almost *anti*-eclipsed conformation was found in the related *para*-disubstituted complex where the methylene group is replaced by an oxygen atom,[6a] stressing the importance of the electronic effect of the arene ring substituents on the $Mn(CO)_3$ tripod conformation. The value of the torsion angles C1−C100−Mn−C14, C3−C100−Mn−C16, and CC100−Mn−C15 (C100 being the center of the six-membered ring) are 37.08°, 39.43°, and 37.79°, respectively. The C8═C9 double bond, oriented toward the metal, is in the [C1C8C9] plane, which makes a dihedral angle of 40° with the arene ring plane, the thiophene plane being oriented away from the metal. Thus in the solid state, the double bond is not conjugated to the π system in the η^5 and in the η^6 complexes **7** and **11**. In both of them, the double-bond length is roughly the same: 1.344 and 1.342 Å, respectively. Furthermore, there is a distortion of the aromatic ring of complex **11**; indeed the Mn−C4 bond (2.282 Å) that is substituted by the methoxy group is longer than the five other Mn−C bonds (2.206, 2.190, 2.212, 2.196, 2.171 Å), in good agreement with what has been reported for arenetricarbonylchromium complexes[20] and the bending effect opposite the metal moiety of the OMe π donor substituent.

Conclusion

We have shown that (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes substituted by a keto group react with a Grignard reagent to yield the corresponding alcohols as the sole products in high yield. The low de observed in one case gives some hope to explore more deeply the diastereoselection of this reaction. The dehydration of these alcohols in acidic medium affords, as the major compounds, unprecedented η^5 complexes with the double bond conjugated to the π system, whose formation mechanism and reactivity are currently under investigation.

Experimental Section

All reactions were routinely performed under a dry nitrogen atmosphere using standard Schlenk techniques. THF was dried over sodium benzophenone ketyl and distilled. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled over KOH and stored under nitrogen over 4 Å molecular sieves. Acetone and benzaldehyde were distilled over K_2CO_3. NMR spectra were recorded on a Bruker ARX 200 MHz or AC 400 MHz spectrometer. ^1H and ^{13}C signals of NMR solvents were used as internal standard respectively at $\delta = 7.26$ ppm and $\delta = 77.36$ ppm in $CDCl_3$ and at $\delta = 2.09$ ppm and $\delta = 30.60$ ppm in acetone. Infrared spectra were measured on a Bruker Tensor 27 spectrometer. Elemental analyses were performed by the Service Central d'Analyze du CNRS. Mass spectra were performed by the Laboratory of Mass Spectroscopy, Université des Sciences et Techniques, Lille, by the Groupe de Spectrométrie de Masse (UMR 7613, UPMC), and by the Service de Spectrométrie de Masse de l'ENS (Chemistry Dept, Paris).

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(17) Crystal data of **7** and **11**. Data were recorded at room temperature on a Kappa-CCD Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and the ω-scan technique. The structure was solved by direct methods and refined with full-matrix least-squares technique on F using the Crystals[18] programs. Molecular structures were drawn with the program Cameron.[19] Complex **7**: $C_{16}H_{13}MnO_4S$, $M = 356.27$; monoclinic, $a = 6.7948(6)$ Å, $b = 19.899(3)$ Å, $c = 12.1956(15)$ Å, $U = 1613.3(3)$ Å^3, $T = 250$ K, space group $P2_1/n$, $Z = 4$, 15 998 reflections measured, 4629 unique ($R_{int} = 0.043$), which were used in all calculations. The final $wR(F^2)$ was 0.054 (all data). Complex **11**: $C_{16}H_{12}BF_4MnO_4S$, $M = 442.07$; monoclinic, $a = 16.8079(7)$ Å, $b = 7.1173(3)$ Å, $c = 29.7749(17)$ Å, $U = 3558.1(3)$ Å^3, $T = 150$ K, space group $P2_1/c$, $Z = 8$, 52 256 reflections measured, 10 041 unique ($R_{int} = 0.040$), which were used in all calculations. The final $wR(F^2)$ was 0.053 (all data).

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Preparation of Complex 5. To a solution of (η^5-ketocyclohexadienyl)Mn(CO)$_3$ (**3**) (0.250 g, 0.70 mmol) in THF (15 mL) was added MeMgCl (0.93 mL, 2.8 mmol, 3 N) at 0 °C. The yellow solution was stirred at 0 °C for 20 min. Then water (30 mL) was added and the aqueous phase was extracted with Et_2O (3 × 30 mL). The organic phase was washed with water (50 mL) and a saturated solution of NaCl (50 mL). After drying over $MgSO_4$ the solvent was removed under reduced pressure and the desired product was dried *in vacuo*. The yellow oil was purified on a silica gel chromatography column (Merck silica gel 60, 15–40 μm, petroleum ether/Et_2O). Two diastereoisomers were obtained (0.185 g, 72%).

Complex 5a: 105 mg, 40% yield. IR (neat): 2004 [Mn(CO)$_3$], 1909 [Mn(CO)$_3$], 2940 [OH]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.94 (m, 4H, H_{6exo} and H_9), 2.87 (m, 2H, H_5 and H_{6endo}), 3.45 (s, 3H, H_7), 5.29 (dd, 1H, $^3J_{2-3}$ = 6.0 Hz, $^4J_{2-6endo}$ = 1.0 Hz, H_2), 5.69 (dd, 1H, $^3J_{3-2}$ = 6.0 Hz, $^4J_{3-5}$ = 2.72 Hz, H_3), 6.85 (m, 2H, H_{Th}), 7.16 (d, 1H, ^3J = 4.4 Hz, H_{Th}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.1 (C_6), 30.6 (C_9), 36.8 (C_5), 54.5 (C_7), 65.6 (C_3), 74.2 (C_8), 76.6 (C_1), 91.5 (C_2), 123.8, 124.9, 126.7 (C_{11}, C_{12}, C_{13}), 143.4 (C_4), 149.9 (C_{10}). HRMS (ESI) *m/z*: calcd for $C_{16}H_{15}NaMnO_5S$, 396.9918; found, 396.9912 [M + Na]$^+$. Anal. Calcd for $C_{16}H_{15}MnO_5S$: C, 51.34; H, 4.04. Found: C, 51.08; H, 3.91.

Complex 5b: 80 mg, 32% yield. IR (neat): 2004 [Mn(CO)$_3$], 1909 [Mn(CO)$_3$], 2940 [OH]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.58 (s, 3H, H_9), 1.94 (d, 1H, $^3J_{6exo-6endo}$ = 12.6 Hz, H_{6exo}), 3.02 (m, 2H, H_5 and H_{6endo}), 3.45 (s, 3H, H_7), 5.06 (d, 1H, $^3J_{2-3}$ = 6.0 Hz, H_2), 5.71 (dd, 1H, $^3J_{3-2}$ = 6.0 Hz, $^4J_{3-5}$ = 2.5 Hz, H_3), 6.81–7.15 (m, 2H, H_{Th}), 7.17 (d, 1H, ^3J = 1.2 Hz, H_{Th}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6 (C_6), 29.8 (C_9), 37.2 (C_5), 54.5 (C_7), 65.4 (C_3), 74.7 (C_8), 77.6 (C_1), 91.5 (C_2), 123.2, 124.4, 126.9 (C_{11}, C_{12}, C_{13}), 143.6 (C_4), 150.1 (C_{10}). HRMS (ESI) *m/z*: calcd for $C_{16}H_{15}NaMnO_5S$, 396.9918; found, 396.9912 [M + Na]$^+$. Anal. Calcd for $C_{16}H_{15}MnO_5S$: C, 51.34; H, 4.04. Found: C, 51.01; H, 3.89.

Complex 6a: 45 mg, 30% yield. IR (neat): 2008 [Mn(CO)$_3$], 1912 [Mn(CO)$_3$], 2978 [OH]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.69 (s, 3H, H_9), 3.36 (dd, 1H, $^3J_{5-6}$ = 6.4 Hz, $^4J_{5-3}$ = 2.6 Hz, H_5), 3.40 (s, 3H, H_7), 4.4 (dd, 1H, $^3J_{6-5}$ = 6.3 Hz, $^3J_{6-2}$ = 1.1 Hz, H_6), 5.36 (dd, 1H, $^3J_{2-3}$ = 5.9 Hz, $^4J_{2-6}$ = 1.3 Hz, H_2), 5.66 (dd, 1H, $^3J_{3-2}$ = 6.0 Hz, $^4J_{3-5}$ = 2.5 Hz, H_3), 6.55–7.26 (m, 8H, H_{Ph} and H_{Th}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.8 (C_9), 44.4 (C_6), 44.7 (C_5), 54.5 (C_7), 64.8 (C_3), 74.6 (C_8), 87.3 (C_1), 91.8 (C_2), 124.5, 126.5, 127.0, 128.4 (C_{Th} and C_{Ph}), 142.0 (C_4), 146.0 (C_{10}), 146.4 (C_{14}). HRMS (MALDI-TOF) *m/z*: calcd for $C_{22}H_{17}MnO_4S$, 432.023; found, 432.003 [M − H_2O]$^+$. Anal. Calcd for $C_{22}H_{19}MnO_5S$: C, 58.66; H, 4.25. Found: C, 58.43; H, 4.04.

Complex 6b: 133 mg, 56% yield. IR (neat): 2008 [Mn(CO)$_3$], 1912 [Mn(CO)$_3$], 2978 [OH]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.54 (s, 3H, H_9), 3.33 (dd, 1H, $^3J_{5-6endo}$ = 6.3 Hz, $^4J_{5-3}$ = 2.4 Hz, H_5), 3.39 (s, 3H, H_7), 4.3 (s, 1H, $^3J_{6endo-5}$ = 6.3 Hz, H_{6endo}), 5.41 (d, 1H, $^3J_{2-3}$ = 6.1 Hz, H_2), 5.70 (dd, 1H, $^3J_{3-2}$ = 6.0 Hz, $^4J_{3-5}$ = 2.5 Hz, H_3), 6.62–7.28 (m, 8H, H_{Ph} and H_{Th}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.1 (C_9), 44.1 (C_6), 45.2 (C_5), 54.5 (C_7), 64.7 (C_3), 75.2 (C_8), 86.7 (C_1), 91.9 (C_2), 124.1, 126.7, 127.0, 128.4 (C_{Th} and C_{Ph}), 141.4 (C_4), 146.8 (C_{10}), 151.7 (C_{14}). HRMS (MALDI-TOF) *m/z*: calcd for $C_{22}H_{17}MnO_4S$, 432.023; found, 432.003 [M − H_2O]$^+$. Anal. Calcd for $C_{22}H_{19}MnO_5S$: C, 58.66; H, 4.25. Found: C, 58.39; H, 4.02.

Preparation of Complex 7 and Compound 9. To a solution of (η^5-alcohol cyclohexadienyl)Mn(CO)$_3$ (**5**) (0.121 g, 0.32 mmol) in CH_2Cl_2 (5 mL) was dropped slowly HBF_4·OMe_2 (0.185 mL, 1.79 mmol) at −35 °C. The brown solution was stirred at −35 °C for 1 h 30 min. Then water (10 mL) was added at room temperature and the aqueous phase was extracted with Et_2O (4 × 10 mL). The organic phase was washed with water (10 mL) and a saturated solution of NaCl (10 mL). After drying over $MgSO_4$ the solvent was removed under reduced pressure and the desired product was dried *in vacuo*. The yellow oil was purified on a silica gel chromatography column (Merck silica gel 60, 15–40 μm, petroleum ether/Et_2O). Two compounds (**7** and **9**) were obtained.

Complex 7: 51 mg, 45% yield. IR (neat): 2010 [Mn(CO)$_3$], 1925 [Mn(CO)$_3$]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.45 (d, 1H, $^2J_{6exo-6endo}$ = 11.1 Hz, H_{6exo}), 3.04 (m, 2H, H_5 et H_{6endo}), 3.52 (s, 3H, H_7), 4.87 (d, 1H, $^3J_{2-3}$ = 5.9 Hz, H_2), 5.33 (s, 1H, H_{9a}), 5.28 (s, 1H, H_{9b}), 5.65 (dd, 1H, $^3J_{3-2}$ = 5.9 Hz, $^4J_{3-5}$ = 2.52 Hz, H_3), 6.81 (d, 1H, ^3J = 2.2 Hz, H_{Th}), 6.83–6.79 (m, 2H, H_{Th}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.9 (C_6), 36.2 (C_5), 54.5 (C_7), 65.2 (C_3), 70.8 (C_8), 77.4 (C_1), 93.3 (C_2), 117.3 (C_9), 125.1, 125.7, 126.8 (C_{11}, C_{12}, C_{13}), 142.1 (C_4), 143.7 (C_{10}). HRMS (ESI) *m/z*: calcd for $C_{16}H_{13}MnO_4S$, 354.9837; found, 354.9831 [M − H]$^-$. Anal. Calcd for $C_{16}H_{13}MnO_4S$: C, 53.93; H, 3.68. Found: C, 54.25; H, 3.81. This compound was crystallized in a petroleum-ether/ether mixture giving yellow crystals.

Compound 9 (mixture of *E* and *Z*): 26 mg, 40% yield. IR (neat): 1680 [CO]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.27 (s, 3H, H_{8E} or H_{8Z}), 2.30 (s, 3H, H_{8E} or H_{8Z}), 2.47 (t, 1H, ^3J = 7.0 Hz, H_{6E} or H_{6Z}), 2.59 (t, 1H, ^3J = 7.0 Hz, H_{6E} or H_{6Z}), 2.85 (t, 1H, ^3J = 6.7 Hz, H_{5E} or H_{5Z}), 2.99 (t, 1H, ^3J = 6.6 Hz, H_{5E} or H_{5Z}), 5.87 (d, 1H, ^3J = 10.1 Hz, H_{3E} or H_{3Z}), 5.98 (d, 1H, ^3J = 10.1 Hz, H_{3E} or H_{3Z}), 6.87 (m, 4H, H_{Th}), 7.35 (m, 2H, H_{Th}), 7.47 (d, 1H, ^3J = 10.2 Hz, H_{2E} or H_{2Z}), 7.56 (d, 1H, ^3J = 10.2 Hz, H_{2E} or H_{2Z}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8 (C_{8E} or C_{8Z}), 22.6 (C_{8E} or C_{8Z}), 27.2 (C_{5E} or C_{5Z}), 28.9 (C_{5E} or C_{5Z}), 37.0 (C_{6E} or C_{6Z}), 37.4 (C_{6E} or C_{6Z}), 125.7–128.3 (C_{ThE}, C_{ThZ}, C_{3E}, C_{3Z}, C_{7E}, C_{7Z}), 129.7 (C_{1E} or C_{1Z}), 130.5 (C_{1E} or C_{1Z}), 134.2 (C_{9E} or C_{9Z}), 135.3 (C_{9E} or C_{9Z}),143.9 (C_{2E} or C_{2Z}), 145.9 (C_{2E} or C_{2Z}), 199.8 (C_{4E} or C_{4Z}), 200.0 (C_{4E} or C_{4Z}). HRMS (ESI) *m/z*: calcd for $C_{12}H_{12}ONaS$, 227.0501; found, 227.0507 [M + Na]$^+$. Anal. Calcd for $C_{12}H_{12}OS$: C, 70.57; H, 5.93. Found: C, 70.71; H, 6.11.

Complex 8: 109 mg, 71% yield. IR (neat): 2008 [Mn(CO)$_3$], 1914 [Mn(CO)$_3$]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.48 (s, 3H, H_7), 3.61 (dd, 1H, $^3J_{5-6endo}$ = 6.4 Hz, $^4J_{5-3}$ = 2.7 Hz, H_5), 4.50 (d, 1H, $^3J_{6endo-5}$ = 6.3 Hz, H_{6endo}), 5.20 (dd, 1H, $^3J_{2-3}$ = 6.0 Hz, $^4J_{2-6endo}$ = 1.5 Hz, H_2), 5.27 (s, 1H, H_9), 5.51 (s, 1H, $H_{9'}$), 5.58 (dd, 1H, $^3J_{3-2}$ = 6.0 Hz, $^4J_{3-5}$ = 2.5 Hz, H_3), 6.87–7.21 (m, 8H, H_{Ph} and H_{Th}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.5 (C_6), 44.2 (C_5), 54.6 (C_7), 65.5 (C_3), 74.9 (C_1), 92.3 (C_2), 117.7 (C_9), 125.2–128.6 (C_{Ph} and C_{Th}), 140.3 (C_4), 142.5 (C_{10}), 145.7 (C_{14}). HRMS (ESI) *m/z*: calcd for $C_{22}H_{18}MnO_4S$, 433.0306; found, 433.0300 [M + H]$^+$. Anal. Calcd for $C_{22}H_{18}MnO_4S$: C, 61.11; H, 3.97. Found: C, 61.37; H, 4.15.

Compound 10 (mixture of *E* and *Z*): 25 mg, 25% yield.

10a: IR (neat): 1658 [CO]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.22 (s, 3H, H_8), 2.92 (d, 1H, $^2J_{5exo-5endo}$ = 8.1 Hz, H_{5exo}), 3.09 (dd, 1H, $^2J_{5endo-5exo}$ = 8.1 Hz, $^3J_{5endo-6endo}$ = 3.2 Hz, H_{5endo}), 4.44 (d, 1H, $^3J_{6endo-5endo}$ = 3.2 Hz, H_{6endo}), 5.92 (d, 1H, $^3J_{3-2}$ = 5.1 Hz, H_3), 7.04–7.43 (m, 8H, H_{Ph} and H_{Th}), 7.62 (d, 1H, $^3J_{2-3}$ = 5.2 Hz, H_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.8 (C_8), 43.0 (C_6), 44.3 (C_5), 89.1 (C_1), 126.6 (C_3), 126.8–127.6 (C_{Ph} and C_{Th}), 145.3 (C_2), 132.5, 137.7, 141.5, 143.4 (C_Q), 196.4 (C_4). HRMS (ESI) *m/z*: calcd for $C_{18}H_{16}ONaS$, 303.0814; found, 303.0820 [M + Na]$^+$.

10b: IR (neat): 1658 [CO] cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (s, 3H, H_8), 2.85 (d, 1H, $^2J_{5exo-5endo}$ = 8.1 Hz, H_{5exo}), 2.99 (dd, 1H, $^2J_{5endo-5exo}$ = 8.1 Hz, $^3J_{5endo-6endo}$ = 3.0 Hz, H_{5endo}), 4.62 (d, 1H, $^3J_{6endo-5endo}$ = 3.0 Hz, H_{6endo}), 5.99 (d, 1H, $^3J_{3-2}$ = 5.1 Hz, H_3), 7.04–7.43 (m, 8H, H_{Ph} and H_{Th}), 7.71 (d, 1H, $^3J_{2-3}$ = 5.1 Hz, H_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.7 (C_8), 44.3 (C_6), 45.0 (C_5), 89.1 (C_1), 126.4 (C_3), 125.5–127.5 (C_{Ph} and C_{Th}), 143.7 (C_2), 131.5, 136.0, 142.7, 143.4 (C_Q), 196.6 (C_4).

Preparation of Complex 11. To a solution of complex **7** (0.077 g, 0.21 mmol) in CH_2Cl_2 (5 mL) was added CPh_3BF_4 (0.072 g, 0.21 mmol) in 5 mL of CH_2Cl_2. The mixture was stirred at room temperature for 30 min. The η^6-cationic (arene)Mn(CO)$_3$ was

precipitated by adding 30 mL of dry Et_2O, filtered, washed with Et_2O, and dried *in vacuo*. A yellow solid was obtained (0.028 g, 0.06 mmol, 30%).

Complex 11: 30% yield. IR (neat): 2064 [$Mn(CO)_3$], 2000 [$Mn(CO)_3$]. ^{1}H NMR (200 MHz, (C_2D_6CO): δ 4.23 (s, 3H, H_7), 5.96 (s, 1H, H_{9a}), 5.94 (s, 1H, H_{9b}), 6.55 (d, 2H, ^3J = 7.6 Hz, H_3 et H_5), 7.14–7.20 (m, 2H, H_{Th}), 7.30 (d, 2H, ^3J = 7.6 Hz, H_2 et H_6), 7.63 (d, 1H, ^3J = 3.9 Hz, H_{Th}). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 59.1 (C_7), 74.2 (C_8), 79.1 (C_1), 83.0 (C_3 et C_5), 104.4 (C_2 et C_6), 121.9 (C_9), 128.1, 128.7, 130.1 (C_{11}, C_{12}, C_{13}), 140.8 (C_4), 150.4 (C_{10}). HRMS (ESI) *m/z*: calcd for $C_{16}H_{12}MnO_4S$, 354.9837; found, 354.9831 $[M - BF_4]^+$. Anal. Calcd for $C_{16}H_{12}MnO_4SBF_4$: C, 43.44; H, 2.74. Found: C, 43.21; H, 2.57. This compound was crystallized in a mixture of ether and acetone, giving yellow crystals.

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Supporting Information Available: Text giving X-ray crystallographic data for complexes **7** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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