Reactivity of Keto-Substituted (η^5-Cyclohexadienyl)Mn(CO)$_3$ Complexes toward Hydrides

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Received November 8, 2005

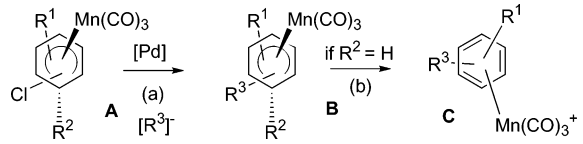
Reaction of hydrides with (η^5-ketocyclohexadienyl)Mn(CO)$_3$ complexes yielded the corresponding alcohols as major products but also cyclohexadienes due to the addition of hydride to the C_2 carbon of the C_1-C_5 π-system. This unexpected regioselectivity has been established by different labeling experiments. The structures of one of the starting keto-substituted (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes and its corresponding alcohol have been determined by X-ray crystallography.

Introduction

Transition metal complexes containing an arene ligand bonded in an η^6-manner constitute an important class of organometallic compounds and have been intensively investigated for many years.[1] Among them, cationic (arene)Mn(CO)$_3$ complexes are particularly attractive because of the greatly enhanced electrophilic character of the arene ring leading to useful synthons in synthesis,[1] to remote activation of chemical bonds,[2] and to the elaboration of supramolecular metal−organometallic coordination networks.[3]

Due to the positive charge on these complexes, a nucleophile can easily add to the arene ring, giving rise to the formation of neutral η^5-cyclohexadienyl complexes that are stable and whose electrophilic properties present the following main significant features. They include (1) nucleophilic additions at the carbon π-system[4] as well as at a carbonyl ligand[5] and (2) *cine* and *tele* substitutions of leaving groups of the cyclic dienyl ligand.[6] Recently, the first report of a novel and versatile route to functionalized η^5-complexes greatly expanded the scope of arene−manganese chemistry.[7] Indeed, arylation, carbonylation, and substitution by alkyne, alkene, and heteroatom-based nucleophiles were performed through Pd-catalyzed reactions (Scheme 1, path a). The formation of a large panel of functionalized η^5-cyclohexadienyl complexes **B**, starting from η^5-chlorocyclohexadienyl complexes **A**, opened a new area for the application of such complexes (for example: upon *exo*-hydride abstraction, unprecedented η^6-arene cations **C** could be obtained, Scheme 1, path b). Compounds **B** obtained under carbonylation conditions (R_3 = COR) were particularly of interest considering their potential in organic as well as in organometallic chemistry. It is the reason we undertook the study of the reactivity of these new (η^5-ketocyclohexadienyl)Mn(CO)$_3$ derivatives.

Scheme 1. Pd-Catalyzed Reactions Applied to (η^5-Cyclohexadienyl)Mn(CO)$_3$ Complexes



We describe herein the preliminary results concerning the reaction of hydrides with (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes **3** substituted by a carbonyl group.

Results and Discussion

The requisite starting (η^5-cyclohexadienyl)tricarbonylmanganese complexes were prepared according to the procedure we recently developed (Scheme 2).[7] The first step involved a nucleophilic addition of Grignard reagents (RMgX, R = Ph and *o*-tolyl) to the 4-chloroanisole derivative **1**, leading to the corresponding η^5-cyclohexadienyl complexes **2a**[7b] and **2c** after regioselective addition of the nucleophile, *meta* to the methoxy group, in good to excellent yields (92 and 95% yield, respectively). The second step, a Stille reaction under carbon monoxide atmosphere, with thienyl-2-tributyltin and $Pd_2(dba)_3$/$AsPh_3$ as the catalytic system, gave rise to the formation of the desired keto complexes **3a**[7b] and **3c** in good yields (71 and 77% yield, respectively) after coupling and insertion of a carbonyl group.

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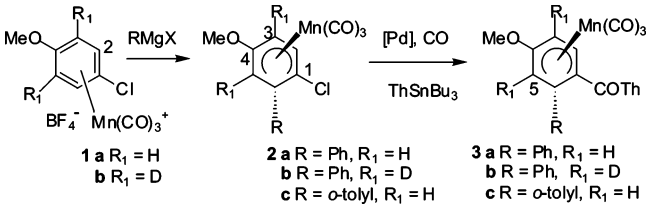
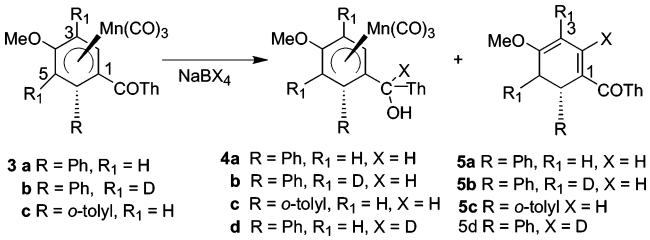
10.1021/om050956o CCC: $33.50
Publication on Web 08/12/2006

Scheme 2. Syntheses of (η^5-Ketocyclohexadienyl)Mn(CO)$_3$ Complexes



Scheme 3. Reaction of (η^5-Ketocyclohexadienyl)Mn(CO)$_3$ Complexes with Hydrides (or Deuterides)



Given that these complexes possess three electrophilic sites—the Mn(CO)$_3$ entity, the complexed arene ring, and the acyl group—we undertook the study of their reactivity toward hydrides. Thus, we reacted 4 equiv of $NaBH_4$ with **3a** and we obtained three compounds: the two first ones were identified as the expected η^5-diastereoisomeric complexes corresponding to the reduction of the keto group, **4a** (82% yield, ratio 58/42), and the third one, an unexpected minor product **5a**, that we succeeded in isolating in 13% yield, due to the addition of hydride to the π-system of the starting material. The same reaction could be run with **3c** and led to the formation of the two diastereomers **4c** (66% yield, ratio 78/22) and 1,3-cyclohexadiene **5c** in 20% yield. We cannot interpret these modest diastereoselectivities even if the tolyl group of **4c** seems to play a significant role with respect to the phenyl group of **4a** (Scheme 3). Complexes **4a** and **4c** represent, to our knowledge, the first examples of η^5 Mn complexes substituted by an alcohol group, α to the π-system, which show unexpected reactivity, which we will describe elsewhere.[8]

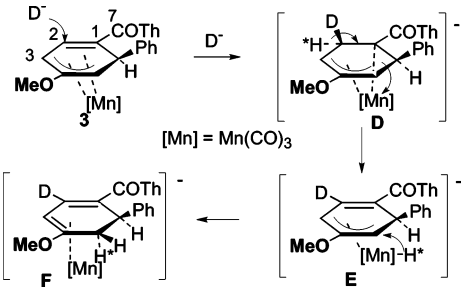
To interpret without any ambiguity the NMR data, we repeated the same reactions starting from the labeled (η^5-1-chloro-3,5-dideuterio-4-methoxy-6-phenylcyclohexadienyl)Mn(CO)$_3$ complex **2b** (R_1 = D) obtained in 83% yield from **1b**.[9] Under the same experimental conditions as the ones used for the preparation of **3a**, complex **3b** was synthesized and isolated in 68% yield. After hydride treatment, two diastereomeric alcohols **4b** were recovered in 69% yield in a 60/40 ratio as well as cyclohexadiene **5b**, which could not be obtained in a pure form. The disappearance of the ^{1}H NMR signals at 5.87 and 3.81 ppm allowed us to assign these chemical shifts to the H_3 and H_5 protons in **3a** (Table 1). Similarly, the disappearance of the signals at 5.64 and 3.38 ppm in one diastereomer of **4b** as well as those at 5.37 and 3.36 ppm in the other one was in agreement with their attributions as H_3 and H_5 protons in **4a** (Table 1). We have to point out an unexpected deshielding effect of the H_2 proton (6.36 ppm) of **3a** with respect to the H_3 proton (5.87 ppm) certainly due to the electronic effect of the keto group, whereas in complex **4a**, the H_3 proton is, as expected for an η^5-Mn complex, the most deshielded (Table 1). To shed light on the mechanism of the formation of the cyclohexadienes **5**, we used $NaBD_4$ in the reduction step starting from **3a**. As expected, we isolated two monodeuterated alcohols **4d**, allowing us to assign the 5.29 and 5.27 chemical shifts to the two diastereomeric H_7 protons in **4a** and the cyclohexadiene **5d**. To our great surprise, this cyclohexadiene **5d** was labeled by a deuterium atom at the C_2 carbon. Indeed three unambiguous proofs for attack at C_2 were obtained from the ^{1}H and ^{13}C NMR spectra: (i) the disappearance in **5d** of the signal at 7.33 ppm (d, J = 6.6 Hz) attributed to the H_2 proton in compound **5a**, (ii) the disappearance of the 6.6 Hz J value of the H_3 signal in **5a** (5.23, dd, J = 6.6 and 1.8 Hz) which becomes a doublet in **5d** (5.23, d, J = 1.8 Hz), (iii) and finally, the appearance of a triplet for the carbon C_2 bearing the deuterium atom at 138.9 ppm (J = 24 Hz) in **5d**.

Table 1. Selected ^{1}H NMR Data of Complexes 1a, 2a−c, 3a−c, and 4a−c

	H_2	H_3	H_5	H_6
1a[a]	7.51	6.65	6.65	7.51
2a[b]	5.22	5.56	3.56	4.30
2b[b]	5.22			4.30
2c[b]	5.39	5.56	3.64	4.54
3a[b]	6.36	5.87	3.81	4.80
3b[b]	6.36			4.80
3c[b]	6.59	5.90	3.89	4.83
4a[b,c]	5.05	5.64	3.38	4.23
	5.36	5.37	3.36	4.11
4b [b,c]	5.05			4.23
	5.36			4.11
4c[b]	5.19	5.59	3.47	4.47

[a] Me_2CO-d_6. [b] $CDCl_3$. [c] Two diastereomers.

Scheme 4. Suggested Mechanism for the Formation of Cyclohexadiene 5d Labeled at the C_2 Carbon



This clearly means that addition of the hydride occurred to an internal position of the π-system rather than to the expected terminal C_5 carbon.

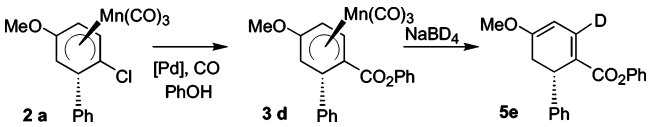
Thus the mechanism that can be suggested for the formation of the cyclohexadienes is represented Scheme 4. The η^5-system has been represented as an $\eta^2(C_1-C_2):\eta^3(C_3,C_4,C_5)$ moiety for clarity reasons and also to represent the enone $C_2=C_1-C_7(O_5)-$, which may play a role in the observed regioselectivity. *exo* 1−4 addition of deuteride to the C_2 carbon of the enone could afford $\eta^1:\eta^3$ anionic complex **D**. Insertion of the Mn moiety into the $C-H_{2endo}$ hydrogen (H*) and decoordination of the $C_1=C_2$ double bond could give the 18-electron η^3-anionic manganese hydride **E**. Reductive elimination could give the unstable η^4-anionic manganese cyclohexadiene **F**, which after workup could liberate the cyclohexadiene **5d**.

We have to point out the formation of the cyclohexadienes **5** even if the yields are not satisfying. Indeed, nucleophilic addition to (η^5-cyclohexadienyl)Mn(CO)$_3$, lacking a keto substituent, has already been reported, but in this case the neutral starting

(8) Eloi, A.; Norel, L.; Tranchier, J. P.; Rose-Munch, F.; Rose, E., in preparation.

(9) **2b** was easily obtained from the dideuterated complex of *para*-chloroanisole complex **1b** (R_1 = D) that we prepared by regioselective lithiation of **1a** with n-BuLi, followed by D_2O treatment. See: Slocum, D. W.; Dietzl, P. *Tetrahedron Lett.* **1999**, *40*, 1823, for the preparation of the monodeuterated **1b**, R = D.

Scheme 5. Synthesis of a Benzyloxycarbonyl-Substituted (η^5-Cyclohexadienyl)$Mn(CO)_3$ Complex and Reaction with Deuterides



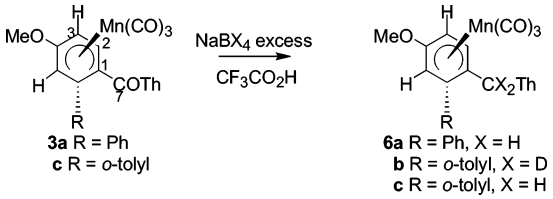
complex needs to be activated. In other words displacement of one carbonyl ligand by a three-electron nitrosyl ligand is necessary in order to increase the electrophilicity of the cationic complex, thus facilitating the reaction with the nucleophile.[10] To our knowledge, very few examples relate the nucleophilic attack on *neutral* (η^5-cyclohexadienyl)$Mn(CO)_3$. On one hand, Mc Daniel et al.[11] showed that stabilized carbanions could add to neutral η^5-complexes to give the extremely oxygen sensitive, corresponding anionic η^4-diene complexes in the presence of HMPA. After exposure to oxygen or air, these unstable intermediates gave rise to the formation of free substituted cyclohexadienes. On the other hand, Brookhart et al.[12] reported the addition of strong hydrides such as $LiEt_3BH$ or $LiAl(OR)_3H$ to neutral η^5-complexes, yielding anionic cyclohexa-1,3-dienes, which could be trapped by a proton source to afford bridged cyclohexenyl manganese complexes via Mn−H−C agostic bonds.

We generated another example by performing the same reaction with an η^5-(cyclohexadienyl)tricarbonylmanganese complex **3d** substituted by an ester group, which is known to be less reactive toward $NaBH_4$, Scheme 5. Addition of $NaBD_4$ (8 equiv) to complex **3d** required more time to yield the cyclohexadiene **5e**, which was recovered in a more satisfying 36% yield besides unreacted starting material (40%). All the NMR data confirmed again that the C_2 carbon was deuterated.

The literature contains only scattered reports of nucleophilic attacks at the internal C_2 position (rather than at C_1) of dienyl systems to generate σ,η^3-enediyl species, and they involve tungsten,[13] iron,[14] and osmium[15] complexes. To our knowledge, only two series of examples of such attack at C_2 have been reported in organomanganese complex chemistry: the first one relates the reaction of certain carbon-based nucleophiles with open neutral (η^5-pentadienyl)$Mn(CO)_3$ complexes, generating (σ,η^3-pentenediyl)manganese derivatives.[16] The second one involves hydride addition to (η^5-cyclohexadienyl)$Mn(NO)(L)_2^+$ cations, giving rise to the formation of (σ,η^3-cyclohexenediyl)-manganese complexes.[17]

We took advantage of our results to try a further reduction of complexes **3a** and **3c**. An excess of $NaBH_4$ was reacted with these complexes, and after addition of acetic acid,[18] we were able to isolate complexes **6a** in 53% yield and **6c** in 65% yield, corresponding to the complete reduction of the C_7 carbon (Scheme 6).

Scheme 6. Reaction of (η^5-Ketocyclohexadienyl)$Mn(CO)_3$ Complexes with Hydrides (or Deuterides) in Excess



Thus, the keto function has been reduced into an alcohol function in the presence of $NaBH_4$, and after addition of acid, the C_7 carbocation could be formed and trapped by $NaBH_4$ in excess.[18] This mechanism was confirmed by the following experiment: using $NaBD_4$ instead of $NaBH_4$, under the same reaction conditions, complex **3c** gave rise to the formation of **6b** in 58% yield labeled by two deuterium atoms incorporated on the C_7 atom (disappearance of the NMR signals corresponding to the H_7 hydrogens of **6c** at 3.10 and 3.24 ppm).

Well-formed crystals for X-ray analysis were obtained after crystallization of complexes **3a** and **4a** (major diastereomer) from an hexane/diethyl ether mixture.[19] The two ORTEP views are presented in Figure 1 as well as some selected bond lengths.

The 1.233 Å value for the C_7O_5 bond length in **3a** is in agreement with a C═O double bond, whereas the corresponding alcohol **4a**, vide infra, presents a 1.398 Å bond length for the single C−O bond. The η^5-cyclohexadienyl moieties exhibit the classical five-coplanar-carbon geometry (C_1,C_2,C_3,C_4,C_5) with carbon C_6 lying out of this plane. The dihedral angles between the C_1,C_2,C_3,C_4,C_5 and $C_1C_6C_5$ planes reach 38° for **3a** and 32° for **4a**. The Mn−C bond lengths range from 2.119 to 2.215 Å for **3a** and from 2.135 to 2.230 Å for **4a**. The sp_3 C_6 carbon is eclipsed by one of the Mn−CO bonds, in agreement with what is usually observed in η^5 Mn complexes.[7]

Conclusion

This work describes the reactivity study of (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes substituted by a carbonyl group (ketone and ester) toward hydrides. It shows that, under the experimental conditions we used, addition of hydrides mainly occurred to the keto group, giving the corresponding alcohols, but also to the π-system of the complex, yielding decoordinated functionalized cyclohexadienes. Only the corresponding cyclohexadiene has been recovered starting from the (η^5-cyclohexadienyl)$Mn(CO)_3$ complex substituted by an ester group. Thus, the carbonyl function activated the η^5-system toward nucleophile addition and, unexpectedly, the addition of the hydride occurred to an internal position rather than to a terminal carbon. A mechanism to explain this unusual regioselectivity has been suggested by using labeling experiments. Work is in progress

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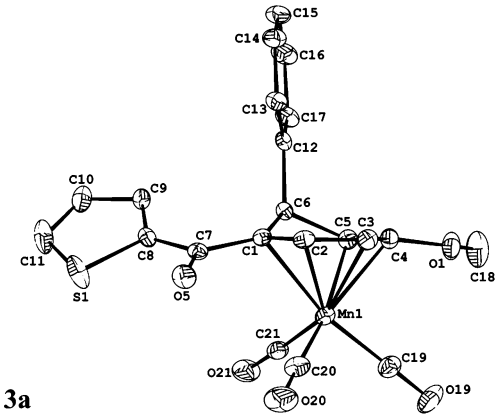
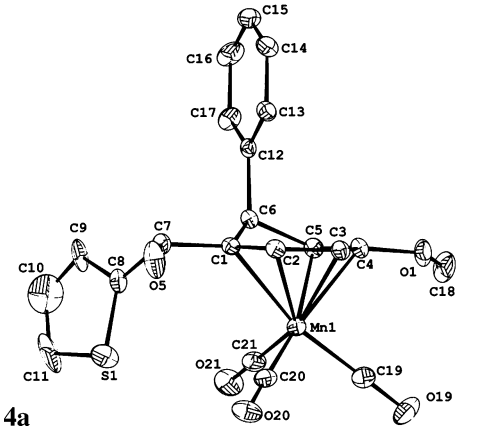
(19) Crystal data for **3a**: $C_{21}H_{15}MnO_5S$, fw = 434.34, monoclinic, *a* (Å) = 9.4929(6), *b* (Å) = 11.3400(8), *c* (Å) = 19.1506, α (deg) = 90, *β* (deg) = 100.134(4), *γ* (°) = 90, *V* (Å^3) = 2029.4(3), *Z* = 4, space group $P2_1/n$, density *ρ* (g cm^3) = 1.42, *θ* limits (deg) = 2−27.5, no. of data collected = 12 729, no. of unique data collected = 4629, no. of unique data used for refinement $2124(F_o)^2 > 3\sigma(F_o)^2$, $R(F) = 0.0392$, $R_w(F^2) = 0.0433$. Crystal data for **4a**: $C_{21}H_{16}MnO_5S$, fw = 435.35, triclinic, *a* (Å) = 9.4006(15), *b* (Å) = 10.4439(15), *c* (Å) = 11.9184(14), α (deg) = 102.274-(12), *β* (deg) = 104.203(11), *γ* (deg) = 112.428(14), *V* (Å^3) = 985.5(3), *Z* = 2, space group = $P\bar{1}$, density *ρ* (g cm^3) = 1.47, *θ* limits (deg) = 2.2−25, no. of data collected = 7835, no. of unique data collected = 3452, no. of unique data used for refinement $1920(F_o)^2 > 1.5\sigma(F_o)^2$, $R(F) = 0.0540$, $R_w(F^2) = 0.0596$.



3a



4a

Figure 1. ORTEP representations of complexes **3a** and **4a**. Selected bond lengths (Å) **3a**: C_7-O_5 1.233(4), C_1-C_7 1.474(5), C_1-C_2 1.428(5), C_2-C_3 1.396(5), C_3-C_4 1.422(6), C_4-C_5 1.385(5); **4a**: C_7-O_5 1.398(7), C_1-C_7 1.514(7), C_1-C_2 1.390(7), C_2-C_3 1.402(7), C_3-C_4 1.420(8), C_4-C_5 1.390(8). The percent of probability of the thermal ellipsoids is 30%.

to broaden the nucleophile panel in order to explore new perspectives in the reactivity of such complexes and in their applications in organic as well as in organometallic synthesis.

Experimental Section

General Considerations. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere using Schlenk tube techniques. THF was dried over sodium benzophenone ketyl and distilled. Infrared spectra were measured on a Perkin-Elmer 1420 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on Bruker AC200 and AC400 spectrometers. Elemental analyses were performed by Le Service de Microanalyses de l'Université Pierre et Marie Curie. UV−vis spectra were recorded on a UVIKON 923 spectrometer and mass spectra on a MALDI-TOF spectrometer.

[(η^6-1-Chloro-4-methoxybenzene)Mn(CO)$_3$][BF$_4$] (1a) was prepared following the previously described procedure.[6]

1-Chloro-3-deutero-4-methoxybenzene.[9] *para*-Chloroanisole (5.0 mL; 40.7 mmol; 1 equiv) was placed in a 100 mL, two-neck flask with 20 mL of cyclohexane and THF (4 mL; 49.4 mmol; 1.2 equiv). n-BuLi (32 mL; 48 mmol; 1.2 equiv) was added at −78 °C. The solution was stirred at rt for 1 h. Then an excess of D_2O was added. After 20 min stirring, the yellow solution was filtered over Celite, washed with 2 × 50 mL of water, dried over $MgSO_4$, and filtered. Solvents were removed under reduced pressure to give a yellow oil (5.63 g; 39.3 mmol; 96% (lit.[9] 86%)). ^1H NMR (Me_2CO-d_6, 200 MHz): 3.83 (3H, s, OMe); 6.98 (1H, m, H_3); 7.31 (2H, m, H_2 and H_6).

1-Chloro-3,5-dideutero-4-methoxybenzene. The dideuterated derivative was obtained by the same procedure as the monodeuterated one:[9] the preceding monodeuterated complex (5.63 g; 39.2 mmol; 1 equiv) reacted with n-BuLi (32 mL; 48 mmol; 1.2 equiv) in 20 mL of cyclohexane and THF (4 mL; 49.4 mmol; 1.2 equiv). A yellow oil (5.16 g; 35.7 mmol; 91%) was obtained. ^1H NMR (Me_2CO-d_6, 200 MHz): 3.83 (3H, s, OMe); 7.33 (2H, m, H_2 and H_6).

[(η^6-1-Chloro-3,5-dideutero-4-methoxybenzene)Mn(CO)$_3$][BF$_4$] (1b). Complex **1b** was prepared by the same procedure as complex **1a**: $BF_4Mn(CO)_5$ was prepared in situ with $AgBF_4$ (1.93 g; 9.93 mmol; 1.2 equiv) and $BrMn(CO)_5$ (3.09 g; 11.2 mmol; 1.3 equiv). Then 1-chloro-3,5-dideutero-4-methoxybenzene (1 mL; 8.30 mmol; 1 equiv) was added. After precipitation, a yellow solid was filtered (1.72 g; 4.64 mmol; 56%). ^1H NMR (Me_2CO-d_6, 200 MHz): 4.21 (3H, s, OMe); 7.48 (2H, s, H_2 and H_6). ^{13}C NMR (Me_2CO-d_6, 100 MHz): 58.3 (OMe); 82.9 (t, J = 27 Hz, C_3, C_5); 103.5 (C_2, C_6); 106.2 (C_1); 147.4 (C_4); 214.4 (CO−Mn). HRMS: calcd for $C_{10}H_5D_2O_4MnCl$, 282.9539; found, 282.9536 $[M]^+$.

(η^5-1-Chloro-3,5-dideutero-4-methoxy-6-phenylcyclohexadienyl)Mn(CO)$_3$ (2b). Complex **2b** was obtained by the same procedure as complex **2a**:[7] complex **1b** (0.200 g; 0.540 mmol; 1 equiv) reacted with PhMgCl (1 mL; 2 mmol; 3.7 equiv) in 10 mL of THF to afford, after workup and purification, a yellow solid (0.162 g; 0.449 mmol; 83%). ^1H NMR ($CDCl_3$, 200 MHz): 3.48 (3H, s, OMe); 4.29 (1H, d, J = 1.5 Hz, H_6); 5.21 (1H, d, J = 1.5 Hz, H_2); 7.00 (2H, m, H_9 and H_{11}); 7.21 (3H, m, H_8, H_{10}, and H_{12}). ^{13}C NMR ($CDCl_3$, 100 MHz): 52.0 (C_6); 54.7 (OMe); 80.0 (C_1); 92.2 (C_2); 126.0 to 132.4 (C_8, C_9, C_{10}, C_{11}, and C_{12}); 141.4 (C_4); 143.6 (C_7). HRMS-CI: calcd for $C_{16}H_{11}D_2O_4MnCl$, 361.0008; found, 361.0005 $[M + 1]^+$. Anal. Calcd for $C_{16}H_{10}D_2O_4MnCl$: C, 53.33; H, 3.92. Found: C, 53.48; H, 3.67.

(η^5-1-Chloro-4-methoxy-6-*o*-tolylcyclohexadienyl)Mn(CO)$_3$ (2c). The same procedure as for complex **2a** was used: complex **1a** (0.562 g; 1.53 mmol; 1 equiv) reacted with *o*-tolylmagnesium bromide (1.9 M in Et_2O) (1.2 mL; 2.28 mmol; 1.5 equiv) in 20 mL of THF to give, after workup and purification, a yellow solid (0.540 g; 1.45 mmol; 95%). IR ($CHCl_3$): 1910, 2008 (CO(Mn)). ^1H NMR ($CDCl_3$, 200 MHz): 2.37 (3H, s, H_{13}); 3.39 (3H, s, OMe); 3.64 (1H, dd, J = 6.4 and 2.8 Hz, H_5); 4.54 (1H, dd, J = 6.4 and 1.8 Hz, H_6); 5.39 (1H, dd, J = 6 and 1.8 Hz, H_2); 5.53 (1H, dd, J = 6 and 2.8 Hz, H_3); 7.09 (4H, m, H_8, H_9, H_{10}, and H_{11}). ^{13}C NMR ($CDCl_3$, 100 MHz): 19.5 (CH_3); 46.0 (C_5); 49.0 (C_6); 54.7 (OMe); 64.2 (C_3); 79.2 (C_1); 93.3 (C_2); 126.2 to 130.8 (C_8, C_9, C_{10}, C_{11}); 133.9 to 141.2 (C_4, C_7, C_{12}); 221.6 (CO−Mn). Anal. Calcd for $C_{17}H_{14}ClMnO_4$: C, 54.84; H, 3.79. Found: C, 54.56; H, 4.09.

Complexes 3b,c were prepared following the previously described procedures.[7b]

Complex 3b: 68% yield. IR ($CHCl_3$): 1963, 2026 (CO(Mn)), 1610 (CO). ^1H NMR ($CDCl_3$, 200 MHz): 3.52 (3H, s, OMe); 4.80 (1H, d, J = 1.4 Hz, H_6); 6.36 (1H, d, J = 1.3 Hz, H_2); 6.93 to 7.53 (8H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}). ^{13}C NMR ($CDCl_3$, 100 MHz): 40.3 (C_6); 44.9 (br, C_5); 54.9 (OMe); 61.0 (C_1); 72.0 (br, C_3); 97.6 (C_2); 125.4 and 128.5 (C_{13}, C_{14}); 126.8 to 131.9 (C_9, C_{10}, C_{11}, C_{15}); 141.9 to 146.0 (C_4, C_8, C_{12}); 188.1 (C_7); 218.7 (CO−Mn). HRMS-CI: calcd for $C_{21}H_{14}D_2MnO_5S$, 437.0224; found, 437.0222 $[M + 1]^+$. Anal. Calcd for $C_{21}H_{13}D_2MnO_5S$: C, 57.80; H, 3.93. Found: C, 57.91; H, 3.70.

Complex 3c: 77% yield. IR ($CHCl_3$): 1963, 2026 (CO(Mn)); 1610 (CO). ^1H NMR ($CDCl_3$, 200 MHz): 2.42 (3H, s, CH_3); 3.43 (3H, s, OMe); 3.89 (1H, dd, J = 6.6 and 2.5 Hz, H_5); 4.83 (1H, dd, J = 6.6 and 1.5 Hz, H_6); 5.90 (1H, dd, J = 6.3 and 2.5 Hz, H_3); 6.59 (1H, dd, J = 6.3 and 1.5 Hz, H_2); 6.81 to 7.51 (7H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}). ^{13}C NMR ($CDCl_3$, 100 MHz): 19.5 (CH_3); 39.2 (C_6); 45.8 (C_5); 54.8 (OMe); 59.6 (C_1); 72.0 (C_3); 99.1 (C_2); 126.3 to 132.1 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}); 133.1 to143.4 (C_4, C_8, C_{12}, C_{17}); 188.2 (C_7); 219.7 (CO−Mn). Anal. Calcd

for $C_{22}H_{17}MnO_5S$: C, 58.93; H, 3.82. Found: C, 58.74, H, 3.69. HRMS-CI: calcd for $C_{22}H_{18}MnSO_5$, 449.0255; found, 449.0251 $[M + 1]^+$

Complex 3d: Complex **2a** (0.317 g, 0.88 mmol, 1 equiv), $AsPh_3$ (0.095 g, 0.31 equiv), and Pd_2dba_3 (0.081 g, 0.09 mmol, 0.1 equiv) were introduced into a two-neck flask. PhONa was prepared by adding NaH (0.025 g; 1.06 mmol; 1.2 equiv) to PhOH (0.074 g; 0.79 mmol; 0.9 equiv), in THF (7 mL) under N_2. THF (15 mL) was introduced into the flask. A red color appeared, and CO was bubbled through the solution for 10 min at room temperature. The solution of PhONa was then transferred into the flask. CO was bubbled into the reaction mixture for 2 h under reflux. The reaction was stirred for 2.5 h under THF reflux. After filtration on Celite, a yellow solution was recovered and washed with water. The water phase was extracted with pentane (70 mL).The combined organic phases were washed with a saturated solution of NaCl (80 mL). The solution was dried over $MgSO_4$ and evaporated under reduced pressure. A silica gel chromatography column afforded complex **3d** in 56% yield, 219 mg. IR: 2017, 1930, 1710 cm^{-1}. ^1H NMR ($CDCl_3$): 3.57 (3H, s OMe); 3.75 (1H, dd, $J = 5$ and 2 Hz, H_5); 4.54 (1H, d, $J = 6$, H_6); 5.93 (1H, dd, $J = 6$ and 2 Hz); 6.14 (1H, d, $J = 5$ Hz, H_2). 6.76−7.82 (10H, Ph). ^{13}C NMR: ($CDCl_3$): 41.0 (C_6); 45.6 (C_5); 52.9 (C_{quat}); 55.4 (OMe); 72.9 (C_3); 97.5 (C_2); 125.8−131.0 (Ph); 135.2; 144.4; 146.2; 151.2 (C_1, C_4, C_8, C_{12}); 169.4 (CO). Anal. Calcd for $C_{23}H_{17}MnO_6$: C, 62.16; H, 3.86. Found: C, 61.51; H, 3.63.

Typical Procedure for the Syntheses of Complexes 4a−d: Preparation of complex 4a. Complex **3a** (0.215 g; 0.49 mmol; 1 equiv) was placed in a 100 mL Schlenck flask with 15 mL of THF. This yellow solution was cooled at 0 °C and transferred into a 50 mL two-neck flask that contained $NaBH_4$ (0.076 g; 2 mmol; 4.1 equiv). The yellow heterogeneous solution was stirred at 0 °C for 1 h, then at rt for 1 h, and refluxed for 4 h. Then 20 mL of a saturated solution of NH_4Cl was added to the orange solution, which was extracted with 50 mL of Et_2O. The organic phase was extracted with 50 mL of Et_2O and washed with 50 mL of water, 50 mL of a saturated solution of K_2CO_3, and 50 mL of a saturated solution of NaCl. After filtration over $MgSO_4$, solvents were removed under reduced pressure, and the residue was chromatographed on a silica gel chromatography column (PE) to afford two yellow solids (0.159 g; 0.36 mmol; 82%), identified as diastereomers of **4a** in a 58/42 ratio and cyclohexadiene **5a** in 13% yield.

Major diastereomer 4a: IR ($CHCl_3$): 1913, 2008 (CO(Mn)). ^1H NMR ($CDCl_3$, 200 MHz): 2.14 (1H, d, $J = 3.1$ Hz, H_8); 3.36 (1H, dd, $J = 6.2$ and 2.4 Hz, H_5); 3.40 (3H, s, OMe); 4.11 (1H, dd, $J = 6.2$ and 1 Hz, H_6); 5.27 (1H, d, $J = 3.1$ Hz, H_7); 5.36 (1H, dd, $J = 6.0$ and 1.0 Hz, H_2); 5.67 (1H, dd, $J = 6.0$ and 2.4 Hz, H_3); 6.62 to 7.35 (8H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}). ^{13}C NMR ($CDCl_3$, 100 MHz): 44.8 (C_5); 45.4 (C_6); 54.4 (OMe); 65.0 (C_3); 72.5 (C_7); 79.6 (C_1); 91.6 (C_2); 124.6 to 128.6 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}); 141.8 (C_4); 145.8 (C_8); 146.2 (C_{12}). SM (electrospray): calcd for $C_{21}H_{17}MnO_5SNa$, 459.0075; found, 459.0057. Anal. Calcd for $C_{21}H_{17}MnO_5S$: C, 57.80; H, 3.93. Found: C, 57.55; H, 3.63.

Minor diastereomer 4a: IR ($CHCl_3$): 1909, 2007 (CO(Mn)). ^1H NMR ($CDCl_3$, 200 MHz): 2.13 (1H, d, $J = 3.1$ Hz, H_8); 3.38 (1H, dd, $J = 6.2$ and 2.5 Hz, H_5); 3.45 (3H, s, OMe); 4.23 (1H, d, $J = 6.2$ Hz, H_6); 5.05 (1H, d, H_2, $J = 5.9$ Hz, H_2); 5.29 (1H, d, $J = 3.5$ Hz, H_7); 5.64 (1H, dd, $J = 5.9$ and 2.5 Hz, H_3); 6.73 to 7.11 (8H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}). ^{13}C NMR ($CDCl_3$, 400 MHz): 43.7 (C_5); 44.9 (C_6); 54.4 (OMe); 64.8 (C_3); 71.0 (C_7); 81.1 (C_1); 90.6 (C_2); 125.1 to 128.2 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}); 142.1 (C_4); 145.1 (C_8); 145.4 (C_{12}). Anal. Calcd for $C_{21}H_{17}O_5MnS$: C, 57.80; H, 3.93. Found: C, 57.45; H, 3.78. SM (electrospray): calcd for $C_{21}H_{17}O_5MnSNa$, 459.0075; found, 459.0069.

Complex 4b: yield 69%, two diastereoisomers in a 60/40 ratio.

Major diastereomer 4b: IR ($CHCl_3$): 1913, 2008 (CO(Mn)). ^1H NMR ($CDCl_3$, 200 MHz): 2.14 (1H, s, H_8); 3.40 (3H, s, OMe); 4.11 (1H, d, $J = 0.8$ Hz, H_6); 5.28 (1H, s, H_7); 5.36 (1H, d, $J = 0.8$ Hz, H_2); 6.62 to 7.35 (8H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}). ^{13}C NMR ($CDCl_3$, 100 MHz): 45.6 (C_6); 54.7 (OMe); 72.8 (C_7); 79.9 (C_1); 91.9 (C_2); 124.8 to 128.8 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}); 142.0 (C_4); 146.0 (C_8); 146.5 (C_{12}). Anal. Calcd for $C_{21}H_{15}O_5D_2SMn$: C, 57.53; H, 4.37. Found: C, 57.48; H, 4.31.

Minor diastereomer 4b: IR ($CHCl_3$): 1909, 2007 (CO(Mn)). ^1H NMR ($CDCl_3$, 200 MHz): 2.13 (1H, d, $J = 3.4$ Hz, H_8); 3.45 (3H, s, OMe); 4.23 (1H, s, H_6); 5.05 (1H, s, H_2); (1H, d, $J = 3.5$ Hz, H_7); 6.73 to 7.11 (8H, m, H_9, H_{10}, H_{11}, H_{13}, H14, H_{15}, H_{16}, H_{17}).

Complex 4c: yield 66%, two diastereoisomers in a 78/22 ratio.

Major diastereomer 4c: IR ($CHCl_3$): 1913, 2008 (CO(Mn)). ^1H NMR ($CDCl_3$, 200 MHz): 2.17 (1H, d, H_8, $J = 3.4$ Hz); 2.33 (3H, s, *o*-Me); 3.36 (3H, s, OMe); 3.44 (1H, dd, $J = 6.1$ and 2.5 Hz, H_5); 4.31 (1H, dd, $J = 6.1$ and 1.2 Hz, H_6); 5.22 (1H, d, $J = 3.4$ Hz, H_7); 5.51 (1H, dd, $J = 6.0$ and 1.2 Hz, H_2); 5.62 (1H, dd, $J = 6.0$ and 2.5 Hz, H_3); 6.81 to 7.18 (7H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}). ^{13}C NMR ($CDCl_3$, 100 MHz): 19.6 (*o*-Me); 41.3 (C_6); 44.7 (C_5); 54.7 (OMe); 65.0 (C_3); 72.9 (C_7); 79.3 (C_1); 92.9 (C_2); 124.9 to 130.8 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}); 133.3 (C_{17}); 142.0 (C_4); 143.7 (C_8); 146.1 (C_{12}). Anal. Calcd for $C_{22}H_{19}O_5$-SMn: C, 58.67; H, 4.25. Found: C, 58.42; H, 4.16.

Minor diastereomer 4c: IR ($CHCl_3$): 1909, 2007 (CO(Mn)). ^1H NMR ($CDCl_3$, 200 MHz): 2.16 (1H, d, $J = 3.4$ Hz, H_8); 2.34 (3H, s, *o*-Me); 3.45 (3H, s, OMe); 3.47 (1H, dd, $J = 6.4$ and 2.6 Hz, H_5); 4.47 (1H, d, $J = 6.4$ Hz, H_6); 5.19 (2H, m, H_2 and H_7); 5.59 (1H, dd, $J = 5.9$ and 2.6 Hz, H_3); 6.68 to 7.14 (7H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}). ^{13}C NMR ($CDCl_3$, 100 MHz): 19.7 (*o*-Me); 40.9 (C_6); 44.2 (C_5); 54.7 (OMe); 64.7 (C_3); 71.6 (C_7); 81.0 (C_1); 92.2 (C_2); 125.3 to 130.5 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}); 133.3 (C_{17}); 142.2 (C_4); 143.4 (C_8); 145.4 (C_{12}). Anal. Calcd for $C_{22}H_{19}O_5SMn$: C, 58.67; H, 4.25. Found: C, 58.98; H, 4.55.

Complex 4d: yield 71%, two diastereoisomers in a 55/45 ratio.

Major diastereomer 4d: IR ($CHCl_3$): 1913, 2007 (CO(Mn)). ^1H NMR ($CDCl_3$, 200 MHz): 2.14 (1H, s, H_8); 3.36 (1H, dd, $J = 6.2$ and 2.4 Hz, H_5); 3.40 (3H, s, OMe); 4.11 (1H, dd, $J = 6.2$ and 1 Hz, H_6); 5.36 (1H, dd, $J = 6$ and 1 Hz, H_2); 5.67 (1H, dd, $J = 6$ and 2.4 Hz, H_3); 6.62 to 7.35 (8H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}). ^{13}C NMR ($CDCl_3$, 100 MHz): 44.8 (C_5); 45.3 (C_6); 54.4 (OMe); 65.0 (C_3); 72.5 (br, C_7); 79.5 (C_1); 91.6 (C_2); 124.6 to 128.6 (C_9, C_{10}, C_{11}, C13, C_{14}, C_{15}, C_{16}, C_{17}); 141.8 (C_4); 145.7 (C_8); 146.1 (C_{12}). HRMS-CI: calcd for $C_{21}H_{17}DO_5SMn$, 438.0318; found, 438.0315 $[M + 1]^+$. Anal. Calcd for $C_{21}H_{16}DMnO_5S$: C, 57.66; H, 4.15. Found: C, 57.72; H, 4.01.

Minor diastereomer 4d: IR ($CHCl_3$): 1910, 2007 (CO(Mn)). ^1H NMR ($CDCl_3$, 200 MHz): 2.16 (1H, s, H_8); 3.39 (1H, dd, $J = 6.2$ and 2.5 Hz, H_5,); 3.44 (3H, s, OMe); 4.22 (1H, d, $J = 6.2$ Hz, H_6); 5.01 (1H, d, $J = 5.9$ Hz, H_2); 5.64 (1H, dd, $J = 5.9$ and 2.5 Hz, H_3); 6.73 to 7.11 (8H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}). ^{13}C NMR ($CDCl_3$, 100 MHz): 43.7 (C_5); 44.9 (C_6); 54.4 (OMe); 64.8 (C_3); 71.0 (br, C_7); 81.1 (C_1); 90.6 (C_2); 125.1 to 128.2 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}); 142.1 (C_4); 145.1 (C_8); 145.4 (C_{12}).

Cyclohexadiene 5a: IR: no CO(Mn) bonds, 1611 (CO). ^1H NMR ($CDCl_3$, 200 MHz): 2.52 (1H, dd, $J = 17.4$ and 2.5 Hz, $H_{5\ exo}$); 3.07 (1H, ddd, $J = 17.4$, 9.8, and 1.8 Hz, $H_{5\ endo}$); 3.67 (3H, s, OMe); 4.35 (1H, dd, H_6, $J = 9.8$ and 2.5 Hz); 5.23 (1H, dd, $J = 6.6$ and 1.8 Hz, H_3); 7.06 (1H, s, H_{Th}); 7.1−7.2 (5H, H_{Ph}); 7.33 (1H, d, $J = 6.6$ Hz, H_2); 7.54 (2H, H_{Th}). ^{13}C NMR ($CDCl_3$, 100 MHz): 35.6 (C_5); 37.6 (C_6); 55.5 (OMe); 93.0 (C_3); 126.2, 126.5, 127.0, 127.2, 128.4, 130.8, 131.6, 131.6 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}); 139.1 (C_2); 142.8 (C_8); 144.0 (C_{12}); 164.8 (C_4); 186.3 ($C_{C=O}$). HRMS-CI: calcd for $C_{18}H_{17}O_2S$, 297.0949; found, 297.0945

$[M + 1]^+$. Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.95; H, 5.45. Found: C, 72.61; H, 5.27.

Cyclohexadienes 5b and **5c** could not be obtained in a pure form: estimated yield 20% based on the NMR spectra of the crude mixtures.

Cyclohexadiene 5d: IR ($CHCl_3$): 1611 (CO). ^{1}H NMR ($CDCl_3$, 200 MHz): 2.52 (1H, dd, $J = 17.4$ and 2.5 Hz, $H_{5\ exo}$); 3.07 (1H, ddd, $J = 17.4$, 9.8, and 1.8 Hz, $H_{5\ endo}$); 3.67 (3H, s, OMe); 4.35 (1H, dd, $J = 9.8$ and 2.5 Hz, H_6); 5.23 (1H, d, $J = 1.8$ Hz, H_3); 7.06 (1H, s, H_{Th}); 7.1−7.2 (5H, H_{Ph}); 7.54 (2H, H_{Th}). ^{13}C NMR ($CDCl_3$, 100 MHz): 35.0 (C_5); 37.6 (C_6); 55.5 (OMe); 93.0 (C_3); 126.2, 126.5, 127.0, 128.4, 130.8, 131.6, 131.6 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}); 139.0 (C_2, t $J = 24$ Hz); 142.8 (C_8); 144.0 (C_{12}); 164.8 (C_4); 186.3 ($C_{C=O}$). Anal. Calcd for $C_{18}H_{15}DO_2S$: C, 72.70; H, 5.77. Found: C, 72.82; H, 5.59.

Cyclohexadiene 5e. Using the same experimental conditions as those described for **3a**, complex **3d** (0.219 g; 0.97 mmol; 1 equiv), solid $NaBD_4$ (0.083 g; 1.97 mmol; 4 equiv), and THF (20 mL) were stirred for 52 h at room temperature and under reflux for 28 h, and 4 equiv of $NaBD_4$ was added again to reach complete conversion. After the usual workup and purification with a silica gel chromatography column, **5e** was obtained as a yellow oil in 36% yield (52 mg) besides decomposition products. If the reaction time was reduced to 10 h at room temperature and 6 h under reflux, the same yield was obtained and 40% of the starting material was recovered. IR ($CHCl_3$): 1711. ^{1}H NMR ($CDCl_3$, 200 MHz): 2.53 (1H, dd, $J = 17$ and 2 Hz, H_{5exo}); 3.16 (1H,ddd $J = 17$, 10, and 2 Hz, H_{5endo}); 3.68 (3H, s OMe); 4.19 (1H, dd, $J = 2$ and 10 Hz, H_6); 5.26 (1H, d, $J = 2$ Hz, H_3); 7.36−6.78 (10H, Ph). ^{13}C NMR ($CDCl_3$), 100 MHz): 35.7 (C_5); 37.7 (C_6); 55.6 (OMe); 93.0 (C_3); 115.4−129.7 (Ph); 138.6 (t, C_2); 120.7;143.0; 151.2; 164.7 (C_1, C_4, C_8, C_{12}); 165.7 (CO). Anal. Calcd for $C_{20}H_{17}DO_3$, 307.13: C, 78.14; H, 6.23. Found: C, 78.30; H, 6.18.

Typical Procedure for the Syntheses of Complexes 6a−c: Preparation of 6a. Complex **3a** (0.129 g; 0.297 mmol; 1 equiv) was dissolved in 15 mL of THF in a 100 mL Schlenck flask. The yellow solution was cooled to 0 °C and tranferred to a 50 mL two-necked flask containing $NaBH_4$ (0.047 g; 1.24 mmol; 4.2 equiv). The yellow, heterogeneous solution was stirred at 0 °C for 1 h, then at rt for 1 h, and refluxed for 4 h. Then CF_3CO_2H (0.4 mL; 5.2 mmol; 17 equiv) was added at 0 °C to afford a yellow solution, which was extracted with 50 mL of Et_2O. The organic phase was extracted with 50 mL of Et_2O and washed with 50 mL of water, 50 mL of a saturated solution of K_2CO_3, and 50 mL of a saturated solution of NaCl. After filtration over $MgSO_4$, solvents were removed under reduced pressure, and the residue was chromatographed on silica gel (Et_2O/PE) to afford a yellow solid, **6a** (0.066 g; 0.16 mmol; 53%). IR ($CHCl_3$): 1907, 2005 (CO(Mn)). ^{1}H NMR (C_6D_6, 200 MHz): 2.74 (3H, s, OMe); 3.00 (1H, dd, $J = 6.1$ and 2.5 Hz, H_5); 3.13 (1H, d, $J = 16.5$ Hz, H_7); 3.28 (1H, d, $J = 16.5$ Hz, $H_{7'}$); 3.83 (1H, d, $J = 6.1$ Hz, H_6); 4.34 (1H, d, $J = 5.9$ Hz, H_2); 5.00 (1H, dd, $J = 5.9$ and 2.5 Hz, H_3); 6.77 to 6.99 (8H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}). ^{13}C NMR (C_6D_6, 100 MHz): 34.5 (C_7); 43.2 (C_5); 48.5 (C_6); 53.8 (OMe); 64.0 (C_3); 80.7 (C_1); 90.7 (C_2); 124.6 to 128.5 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}); 138.9 (C_4); 142.2 (C_8); 145.5 (C_{12}). Anal. Calcd for $C_{21}H_{17}MnO_4S$: C, 60.00; H, 4.08. Found: C, 59.98; H, 4.01.

Complex 6b: yield 58%. IR ($CHCl_3$): 1907, 2005 (CO). ^{1}H NMR (C_6D_6, 200 MHz): 2.08 (3H, s, *o*-Me); 2.66 (3H, s, OMe); 3.23 (1H, dd, $J = 5.9$ and 2.4 Hz, H_5); 4.17 (1H, dd, $J = 5.9$ and 1 Hz, H_6); 4.55 (1H, dd, $J = 5.8$ and 1 Hz, H_2); 4.95 (1H, dd, $J = 5.8$ and 2.4 Hz, H_3); 6.60 to 6.92 (7H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}). HRMS-CI: calcd for $C_{22}H_{18}D_2MnO_4S$, 437.0588; found, 437.0589 $[M + 1]^+$. Anal. Calcd for $C_{22}H_{17}D_2MnO_4S$: C, 60.54; H, 4.85. Found: C, 60.69; H, 4.62.

Complex 6c: yield 65%. IR ($CHCl_3$): 1907, 2005 (CO(Mn)). ^{1}H NMR (C_6D_6, 200 MHz): 2.08 (3H, s, *o*-Me); 2.67 (3H, s, OMe); 3.10 (1H, d, $J = 16.8$ Hz, H_7); 3.23 (1H, dd, $J = 6.0$ and 2.4 Hz, H_5); 3.24 (1H, d, $J = 16.8$ Hz, $H_{7'}$); 4.17 (1H, dd, $J = 6$ and 1 Hz, H_6); 4.55 (1H, dd, $J = 5.8$ and 1 Hz, H_2); 4.95 (1H, dd, $J = 5.8$ and 2.4 Hz, H_3); 6.60 to 6.92 (7H, m, H_9, H_{10}, H_{11}, H_{13}, H_{14}, H_{15}, H_{16}). ^{13}C NMR (C_6D_6, 100 MHz): 19.2 (*o*-Me); 34.6 (C_7); 43.4 (C_5); 44.4 (C_6); 53.7 (OMe); 63.8 (C_3); 79.8 (C_1); 91.8 (C_2); 124.7 to 130.0 (C_9, C_{10}, C_{11}, C_{13}, C_{14}, C_{15}, C_{16}); 133.7 (C_{17}); 138.7 (C_4); 142.1 (C_8); 142.7 (C_{12}). Anal. Calcd for $C_{22}H_{19}MnO_4S$: C, 60.82; H, 4.41. Found: C, 60.92; H, 4.13.

Acknowledgment. The financial support by CNRS is kindly acknowledged. We thank Marie Anne Letellier and Lucie Norel for partial preliminary results, Dr. Patrick Herson (Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR 7071, Université P. et M. Curie, Paris) for the X-ray studies, and Prof. C. Rolando and Dr. G. Ricart from the "Université des Sciences et Techniques" de Lille (France) for MS and HRMS analyses.

Supporting Information Available: Text giving tables of crystal data, atomic coordinates, and bond distances and angles for complexes **3a** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050956O