# Hydrodemethoxylation, Hydrodechloration, Hydrodesulfurization, and Hydrodeamination of Neutral ($\eta^5$-X-substituted-cyclohexadienyl)tricarbonylmanganese Complexes (X = OMe, Cl, SPh, $NEt_2$) upon Treatment with Hydride and Then Acid: *cine* and *tele* Nucleophilic Substitutions

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*Received August 6, 1996*⊗

Treatment of ($\eta^5$-X-substituted-cyclohexadienyl)tricarbonylmanganese complexes (X = alkoxy, halogeno, dimethylamino and thio) with hydrides and a proton source gave $\eta^5$-cyclohexadienyl complexes resulting from a cleavage of the C−O, C−Cl, C−N and C−S bonds: The $\eta^3$-substituted cyclohexenyl intermediates underwent elimination of an agostic hydrogen and the alkoxy, halogeno, amino, or thio group.



## Introduction

The consequences of the electronic influence of aromatic complexation by transition-metal groups have been increasingly developed.[1] We have previously shown that ($\eta^6$-phenoxy-, alkoxy-, halogeno-, and (dimethylamino)arene)chromium tricarbonyl complexes undergo cleavage of aromatic carbon−oxygen,[2] carbon−halogen,[3a] and carbon−nitrogen[3b] bonds upon treatment with hydrides or nucleophiles and then acids: The isomeric ($\eta^5$-cyclohexadienyl)chromium tricarbonyl hydrides are in equilibrium with isomeric ($\eta^4$-cyclohexadiene)chromium tricarbonyl complexes prior to elimination of PhOH, ROH, ClH, and $NMe_2H$, respectively. We have now undertaken an analogous study with arene−manganese complexes **1.** We were encouraged by Brookhart and Lukacs's demonstration of the facile isomerization of cyclohexenyl isomers **5** involving a Mn−H−C agostic bond:[4c] Complex **5** was obtained by treating the arene manganese complex **1** with hydrides and then with water *via* complexes **3** and **4** (Scheme 1a).[4] So the goal was to know if neutral substituted $\eta^5$-cyclohexadienyl complexes **2** treated with hydrides and acids could give neutral $\eta^5$-cyclohexadienyl complexes **6** (Scheme 1b).

## Results and Discussion

To obtain complex **6**,[4c] we chose different $\eta^5$-cyclohexadienyl complexes **2a**−**d** (Scheme 1b) substituted by alkoxy, amino, thio, and halogeno groups and treated them with hydride and then a proton source. Herein, we report that *cine* and *tele* substitutions are involved when treating neutral ($\eta^5$-X-substituted-cyclohexadienyl)tricarbonylmanganese complexes **2a**−**d** (X = OR, Cl, SPh, $NR_2$) with hydride and acid, and we discuss the role of the agostic hydrogen in the final HX elimination step.

**(1) $\eta^5$-Alkoxycyclohexadienyl Complexes.** Addition of L-selectride (1.5 equiv) to the $\eta^5$-complex **2a**[5a] followed by protonation with MeOH or $CF_3CO_2H$ and heating in THF for 3 h resulted in the formation of the known ($\eta^5$-cyclohexadienyl)manganese tricarbonyl **6a** in 65% yield (Scheme 2).[5bc,6] When $CF_3CO_2D$ or MeOD was used as the proton source the mixture yielded $\eta^5$-cyclohexadienyl complexes **6a**,**b** in 51% yield (1/1). This is in agreement with a nonconcerted elimination of H (or D) and OMe. It is noteworthy that complex **6b** is deuterated at an *endo* and not at an *exo* position.[7] When we treated complex **2a** with $LiEt_3BD$ and subsequently with MeOH, we obtained a single deuterated cyclohexa-

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⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) (a) Kündig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L.L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Interscience: New York, 1988; Vol. 36, p 2. (c) Astruc, D. *Top. Curr. Chem.* **1991**, *160*, 47. (d) Semmelhack, M. F. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, U.K., 1991; p 517. (e) Davies, S. G.; Hume, W. E. *J. Chem. Soc., Chem. Commun.* **1995**, 251.

(2) (a) Rose-Munch, F.; Rose, E.; Semra, A. *J. Chem. Soc., Chem. Commun.*, **1986**, 1108. (b) Rose-Munch, F.; Djukic, J. P.; Rose, E. *Tetrahedron Lett.* **1990**, *31*, 2589. (c) Review: Rose-Munch, F.; Rose, E. *Trends in Organometallic Chemistry*; Research Trends: Trivandrum, India. 1994; Vol. 1, p 669.

(3) (a) Djukic, J. P.; Geysermans, P.; Rose-Munch, F.; Rose, E. *Tetrahedron Lett.* **1991**, *32*, 6703. (b) Djukic, J. P.; Rose-Munch, F.; Rose, E. *J. Chem. Soc. Chem. Commun.* **1991**, *22*, 1634. (c) Djukic, J. P.; Rose-Munch, F.; Rose, E.; Simon, F.; Dromzee, Y. *Organometallics* **1995** *14*, 2027.

(4) (a) Brookhart, M.; Lukacs, A. *J. Am. Chem. Soc.* **1984**, *106*, 4161. (b) In particular, the reduction of ($\eta^6$-anisole)manganese tricarbonyl hexafluorophosphate (**1a**) to (methoxycyclohexenyl)manganese tricarbonyl (**5a**) was investigated. (c) Using 1 equiv of hydride $KB(O\text{-}i\text{-}Pr)_3H$, the single 2-substituted cyclohexadienyl complex **2a** (X = OMe) is obtained. By using 3.5 equiv of hydride, the isomeric 1-methoxy anion **3f** (X = OMe; Scheme 1) and the 2-methoxycyclohexa-1,3-diene anion are observed after 12 h at reflux in THF. Subsequent protonation of this mixture resulted in isolation of the single methoxy-substituted bridged isomer **5** (X = OMe, Scheme 1). In the experimental part, they noticed that "all attempts to purify the material on alumina columns resulted in loss of methanol from the complex to yield (cyclohexadienyl)-manganese tricarbonyl".

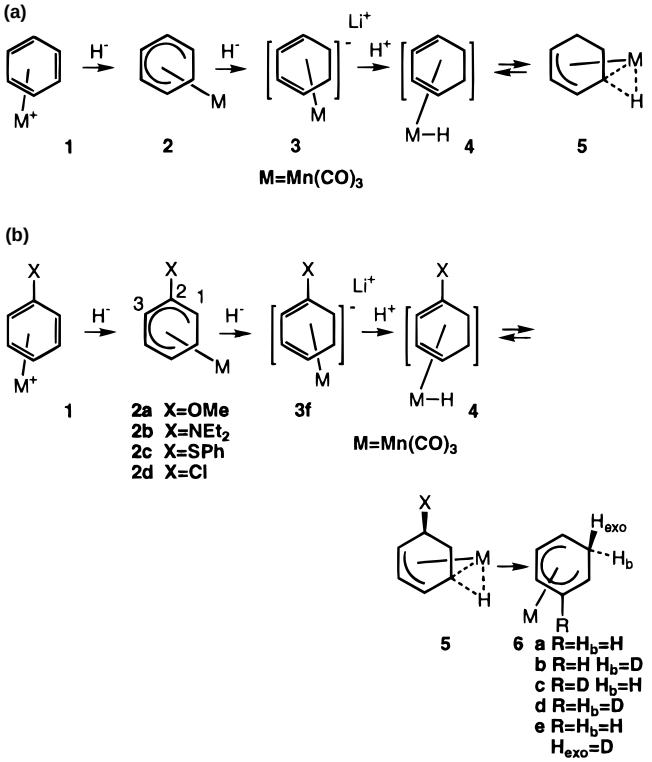
(5) (a) **2a** is obtained by treatment of (anisole)manganese tricarbonyl hexafluorophosphate (**1**) (X = OMe) with $LiAlH_4$ (0.5 equiv).[4a] (b) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807. (c) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1683.

(6) See the analogous chromium $\eta^5$-cyclohexadienyl anionic complex: Djukic, J. P.; Rose-Munch, F.; Rose, E.; Dromzee, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6434.

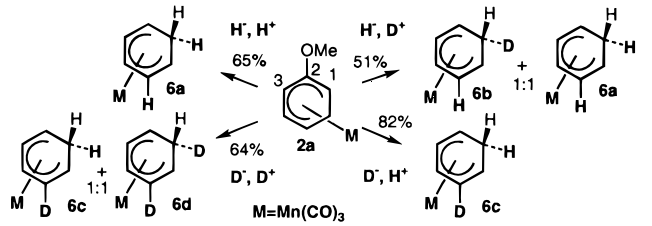
(7) The $H_{exo}$ resonance at 1.47 ppm in $C_6D_6$ is absent (see the Experimental Section).

S0276-7333(96)00621-8 CCC: $12.00 

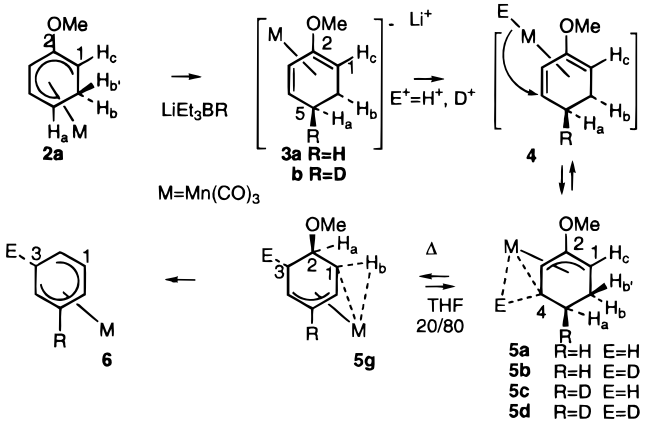
**Scheme 1**




**Scheme 2**




**Scheme 3**




dienyl complex **6c** in 82% yield. By treatment of complex **2a** with $LiEt_3BD$ and then $CF_3CO_2D$, complexes **6c**,**d** were formed in 64% yield (1/1). These results are consistent with a four-step mechanism. The hydride addition and the protonation reaction have been previously reported.[4a] It is the last step that is of particular interest to us.

**Hydride Addition.** Addition of 1 equiv of $LiEt_3BH$ (or $LiEt_3BD$) to **2a** generated a single 5-hydrogeno- (or deuterio) 2-methoxycyclohexa-1,3-diene anion **3a** (or **3b**) (Scheme 3). The $^1H$ NMR data of complex **3a** in THF-$d_8$ in a sealed tube under $N_2$ were in good agreement with a regioselective addition of the hydride (deuteride) to the C-5 carbon and not the C-1 carbon.[8−11]

**Protonation.** Addition of MeOH or $CF_3CO_2H$ to **3a** at −78 °C followed by warming to rt (room temperature) for 20 min and extraction gave the known stable 2-methoxy-substituted ($\eta^3$-cyclohexenyl)manganese tricarbonyl **(5a).**[4,12] This occurred via protonation of the anionic species **3a** followed by migration of the hydrogen to the proximal face of the cycle (Scheme 3).[13a]

**Isomerization.** Heating in THF-$d_8$ at 70 °C in a sealed NMR tube caused isomerization of the purified complex **5a**. After 30 min an equilibrium was reached between **5a** and another complex in a 80:20 ratio. $^1H$ NMR data of the mixture indicated that the new complex could be another cyclohexenyl species **5g** (E = R = H, Scheme 3) with a C-4, C-5, C-6 $\pi$-allyl moiety and a methoxy group at the C-2 position.[14,15] It was noteworthy that, in the absence of acid or base, no MeOH elimination occurred during this isomerization and that the equilibrium ratio remained at 80:20 even after 3 h of heating.

**Elimination.** To understand the formation of, for example, **6c**,**d** (50:50, Scheme 2) by treatment of **2a** with $D^-$ and $D^+$, we considered all the possible hydrogen migrations of the dideuterated complex **5d** (Scheme 3).[15] In the case of **5f1** and **5f4** (Scheme 4), 1,5-elimination could occur between the OMe and the agostic hydrogen $H_b$ of **5f1** or the agostic deuterium $\beta$ to the methoxy group of **5f4**. In the case of **5g1** and **5g2**, there is the possibility for 1,2-elimination of OMe and the agostic deuterium of **5g1** or the agostic $H_b$ hydrogen of **5g2**.

(8) The same regioselectivity was observed in the case of cationic complexes: Davies, S. G.; Green, M. L. H.; Mingos, M. P. *Tetrahedron* **1978**, *34*, 3047.

(9) (a) Brookhart et al. obtained two isomers of this diene anion by using another source of hydride.[4a] (b) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1981**, *103*, 989. (c) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638.

(10) Roell, B. C., Jr.; McDaniel, K. F.; Vaughan, W. S.; Macy, T. S. *Organometallics* **1993**, *12*, 224.

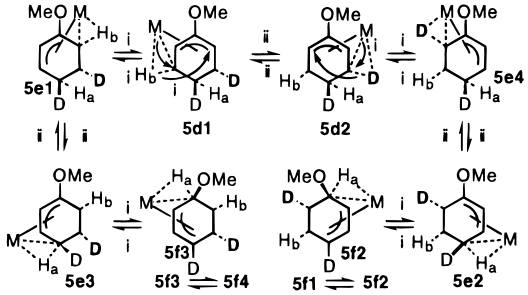
(11) (a) Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882. (b) Birch, A. J.; Jenkins, I. D. *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, p 1.

(12) 500 MHz $^1H$ NMR ($C_6D_6$) for **5a**: The signals are difficult to interpret but can be resolved by the simulation program PANIC (see Experimental Section).

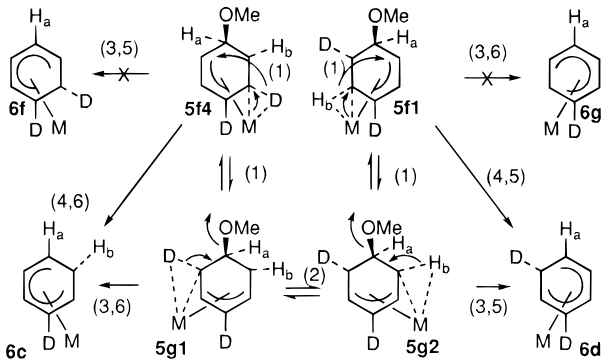
(13) (a) Brookhart, M.; Lukacs, A. *Organometallics* **1983**, *2*, 649. (b) Munro, G. A. M.; Pauson, P. L. *Z. Anorg. Allg. Chem.* **1979**, *458*, 211.

(14) We could not exclude a C-3, C-4, C-5 $\pi$-allyl complex. It appears that the C-4, C-5, C-6 $\pi$-allyl complex is preferred because the H-5 proton resonance of **5g** (E = R = H; Scheme 3) in THF-$d_8$ is a triplet ($J$ = 3.6 Hz) at 4.54 ppm and the resonances of the H-$1_{exo}$ and H-$3_{exo}$ protons are at 2.00 ppm. The other resonances could not be ascertained because they appear under the **5a** complex signals. We favor structure **5g** for multiplicities and simplicity reasons; indeed the other possible isomers are less symmetrical and should have more peaks: the H3 proton of complex **5e1** or **5e3** and the H1 proton of **5e4** or **5e2** should each appear as a doublet.

(15) Complex **5d** can be represented by $\pi$-allyl complexes **5d1** and **5d2** having respectively $H_b$ and D agostic hydrogens. Note that the four **5e** complexes and the four **5f** complexes are also in equilibrium: (i) isomerization, 1,4-hydrogen migration; (ii) $\pi$ allyl complex with the other agostic bond.

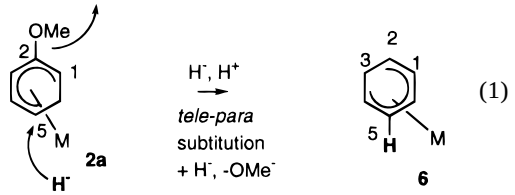


**Scheme 4. 1,2- or 1,5-Elimination of Methanol[a]**



[a] Key: (1) isomerization, 1,4-hydrogen migration; (2) $\pi$ allyl complex with the other agostic bond[15]; (3) 1,2-elimination; (4) 1,5-elimination; (5) $-MeOH_b$; (6) $-MeOD$.

Either of these eliminations explained the substitution pattern in the final product.[16] In fact, we never observed a 1,2-elimination of a methoxy group with a nonagostic hydrogen: complexes **6f**,**g**, for example, were not formed (Scheme 4). Thus in the hydrido-demethoxylation of complex **2a**, hydride addition occurred at the C-5 carbon and elimination of MeO at the C-2 carbon (eq 1). By analogy with nucleophilic aromatic substitu-



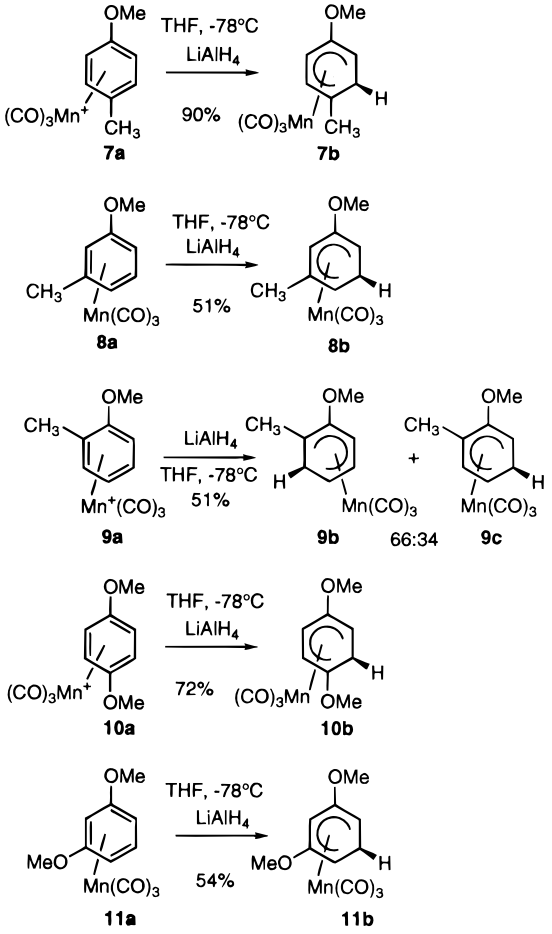
(1)

tion in the case of (arene)tricarbonylchromium complexes,[2] this hydrido−demethoxylation is a *tele-para* nucleophilic substitution (eq 1).[17]

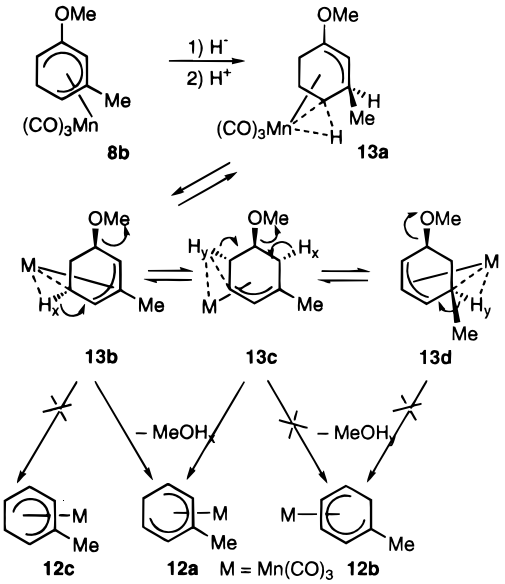
We prepared other $\eta^6$-alkoxyarene derivatives **7a** (*para*-methoxytoluene, 37% yield), **8a** (*meta*-methoxytoluene, 43% yield), **9a** (*ortho*-methoxytoluene, 61% yield), **10a** (*para*-methoxyanisole, 46% yield), and **11a** (*meta*-methoxyanisole, 95% yield) and treated them with hydride ($LiAlH_4$, THF, −78 °C). $\eta^5$-Complexes **7b** (90% yield), **8b** (50% yield), **9b**,**c** (50% yield), **10b** (72% yield), and **11b** (54% yield) were obtained (Scheme 5). In the case of *para*- and *meta*-methoxytoluene complexes **7a** and **8a** and in the case of **11a**, hydride addition occurred exclusively *meta* with respect to the methoxy group, but in the case of *ortho*-methoxytoluene complex **9a**, a 66:34 ratio of cyclohexadienyl complexes **9b**,**c** was recovered which corresponded to an addition of the hydride *ortho* and *para* to the methyl group (Scheme 5).

Addition of L-selectride (4 equiv) to the $\eta^5$-complex **8b** followed by protonation with MeOH and heating in THF resulted in the formation of ($\eta^5$-3-methylcyclohexadienyl)manganese tricarbonyl (**12a**) in 51% yield as a unique isomer (Scheme 6). We did not observe ($\eta^5$-1-methyl or 2-methylcyclohexadienyl)manganese tricarbonyl isomers **12b** or **12c** which are well described in the literature.[13] This clearly excluded the $\eta^3$-intermediates **13c**,**d** and favored the $\eta^3$-intermediate **13b** in good agreement with literature data indicating that the equilibrium is often reached in favor with the 2-substituted $\pi$-allyl system.[4] Thus complex **8b** can give the intermediate **13a** after addition of hydride and a proton source which could isomerize into **13b** (Scheme 6). Because the 1,5-elimination of $MeOH_x$ involved the metal, we represented this reaction by four arrows in Scheme 7, but for clarity reason, we used in this article

**Scheme 5**



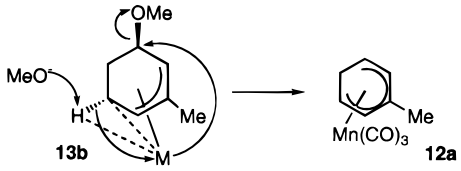
**Scheme 6**



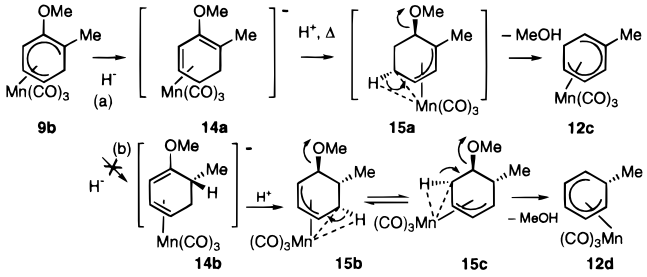
(16) Kristjansdottir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983. Our data prove that the agostic hydrogen $H_b$ is eliminated preferentially over the axial deuterium D α to the OMe group of complex **5g2**, for example.

(17) The term *tele* substitution is used to denote reactions in which the entering group takes up a position more than one atom away from the atom to which the leaving group is attached: Glossary of Terms used in Physical Organic Chemistry. Gold, V., Ed. *Pure Appl. Chem.* **1979**, *51*, 1725. *cine* substitution denotes reaction in which the entering group takes up a position *ortho* to the leaving group.

**Scheme 7**




**Scheme 8**

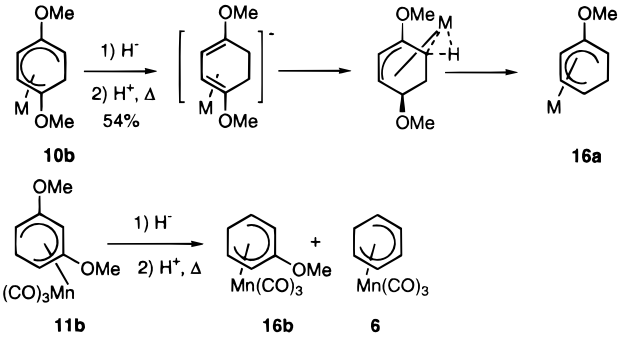



the formalism described in Scheme 6 in order to show the transformation of **13b** into **12a** for example.

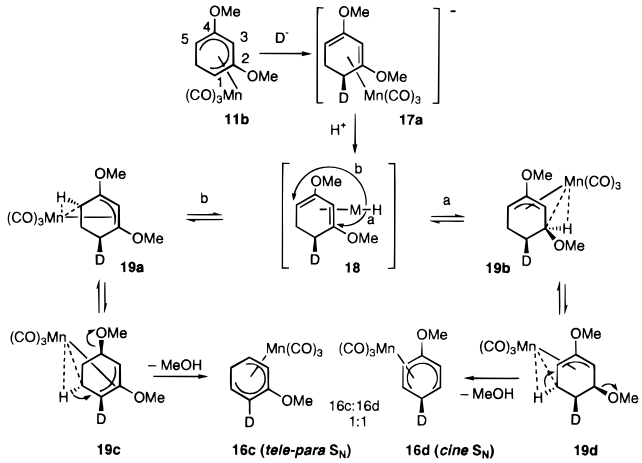
Addition of L-selectride (4 equiv) to the $\eta^5$-complex **9b** followed by protonation with MeOH (6 equiv) and heating in THF resulted in the formation of ($\eta^5$-2-methylcyclohexadienyl)manganese tricarbonyl (**12c**) in 70% yield as a unique isomer (Scheme 8, path a). Again, we did not observe during this clean reaction the formation of other isomers which permitted us to propose the following mechanism described in Scheme 8. Hydride addition took place only at the position *para* to the methoxy group and gave the anionic complex **14a**. Addition of MeOH afforded, after isomerization, the $\eta^3$-cyclohexenyl complex **15a** which can eliminate MeOH in order to liberate the isomer **12c**. This is a *tele-para* nucleophilic substitution.[17,18] Thus we can exclude the addition of the hydride on the carbon bearing the methyl group, the C1 carbon, because the formation of the well-known $\eta^5$-cyclohexadienyl complex **12d** bearing an *endo* methyl group is not detected (Scheme 8, path b).[13] Indeed, anionic complex **14b** treated by MeOH should give complex **15b**, in equilibrium with complex **15c** which could respectively undertake 1,5- and 1,2-eliminations of MeOH. It is worthy to note that the same reaction with complex **7b** using the same experimental conditions did not work at all. When complex **7b** is treated with L-selectride and then with MeOH, a color change was observed in good agreement with $\eta^4$-cyclohexadiene and $\eta^3$-cyclohexenyl complexes, but decomposition occurred and no $\eta^5$-methylcyclohexadienyl complex was recovered. For unknown reasons, the fact that the cycle was substituted by a good leaving group *para* to a methyl group inhibited the elimination step. The energetic barrier which was necessary to isomerize these $\eta^3$-disubstituted-cyclohexenyl complexes was probably too high. We observed the same phenomena in the case of complex **21c**; vide infra.

Addition of L-selectride (4 equiv) to the $\eta^5$-complex **10b** followed by protonation with MeOH (6 equiv) and heating in THF resulted in the formation of ($\eta^5$-2-methoxycyclohexadienyl)manganese tricarbonyl (**16a**) in 54% yield as a unique isomer (Scheme 9). In the case of the *meta*-disubstituted $\eta^5$-cyclohexadienyl complex **11b**, the same reaction gave the expected monomethoxy $\eta^5$-cyclohexadienyl complex **16b** (25% yield) but also the

**Scheme 9**




**Scheme 10**




unexpected unsubstituted $\eta^5$-cyclohexadienyl complex **6** (8% yield), whose formation is difficult to explain without evoking an ipso hydride addition[3c,6,19] on a carbon bearing a methoxy group.

If complex **11b** was treated with lithium triethylborodeuteride, two monodeuterated, monomethoxylated complexes **16c**,**d** were obtained as major products (Scheme 10), and the 1:1 ratio of these complexes was determined by $^1$H NMR spectroscopy. This showed that addition of deuteride occurred at the C1 carbon of the $\eta^5$-2,4-dimethoxycyclohexadienyl complex **11b**. The anionic complex **17a** treated with MeOH can give a manganese hydride intermediate **18** which could migrate either to the C2 carbon (path a) or to the C5 carbon (path b) and afforded the $\eta^3$-cyclohexenyl complexes **19a**,**b**. 1,5-Elimination of MeOH of complexes **19c**,**d** produced two complexes **16c,d**. Thus complexes **16c**,**d** were respectively obtained via *tele-para*[17,18] and *cine*[17,20] nucleophilic substitutions.

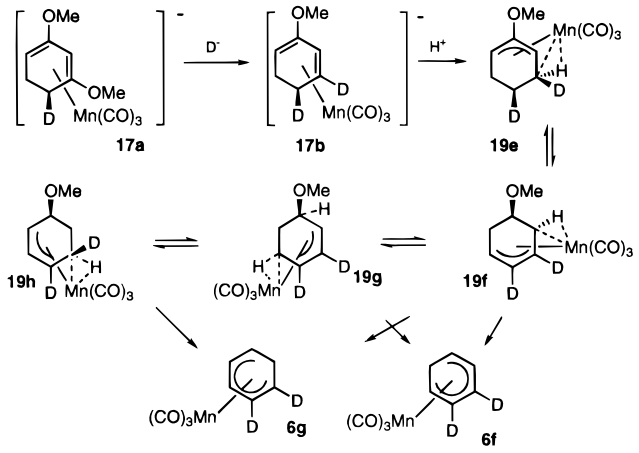
We obtained also two $\eta^5$-cyclohexadienyl complexes **6f**,**g** as minor products whose $^1$H NMR spectrum showed their substitution by two deuterium atoms and the abscence of a methoxy group. The formation of these complexes was difficult to interpret; nevertheless, we suggest as for the formation of complex **6**, Scheme 9, the very speculative *ipso* substitution of the methoxy group at the C2 carbon of complex **17a** by the deuteride which could give another anionic complex **17b** (Scheme 11). Protonation with MeOH could give the $\eta^3$-cyclo-

(18) Rose-Munch, F.; Rose, E.; Semra, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1108; **1987**, 1942.

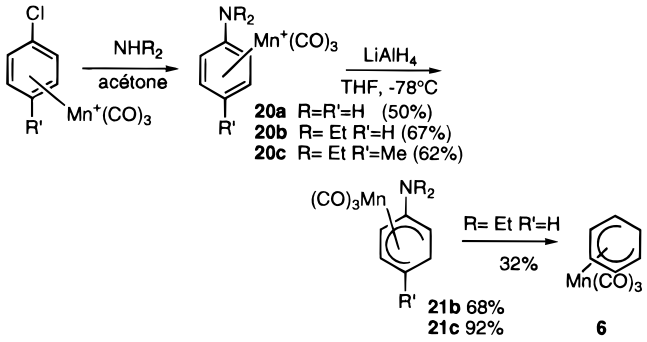
(19) (a) Nicholls, B.; Whitting, M. C. *Proc. Chem. Soc.* **1958**, 152. (b) Boutonnet, J. C.; Rose-Munch, F.; Rose, E.; Semra, A. *Bull. Soc. Chim. Fr.* **1987**, 640. (c) Rose-Munch, F.; Aniss, K.; Rose, E.; Vaisserman, J. *J. Organomet. Chem.* **1991**, *415*, 223.

(20) (a) Rose-Munch, F.; Rose, E.; Semra, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1151. (b) Rose-Munch, F.; Rose, E.; Semra, A.; Bois, C. *J. Organomet. Chem.* **1989**, *363*, 103.

**Scheme 11**




**Scheme 12**

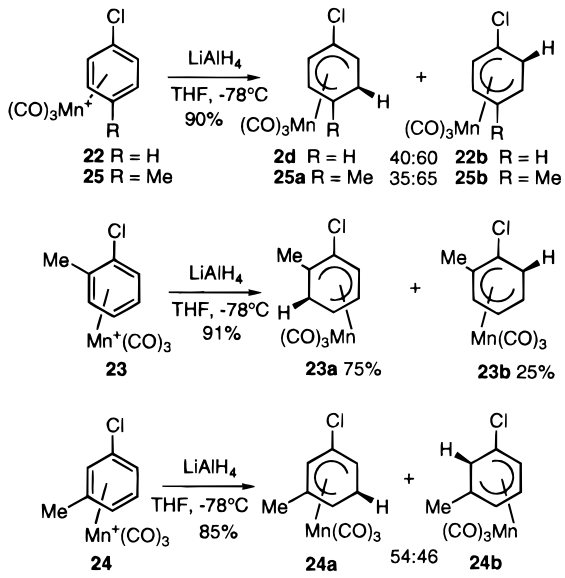



hexenyl complex **19e**. After isomerization, complexes **19f**,**g**,**h** could eliminate MeOH and yield complexes **6f**,**g**.

**(2) $\eta^5$-Aminocyclohexadienyl Complex.** The direct preparation of an ($\eta^6$-aniline)tricarbonylmanganese complex is possible if the arene is mixed with $BF_4Mn(CO)_5$, but this reaction is not reproducible and the yield is low. Therefore, we preferred to obtain the aniline derivatives using the Pauson method: *ipso* addition of $NH_3$ or an amine to the chlorobenzene derivative.[21] The complex of aniline **20a** is obtained in 50% yield by treating (chlorobenzene)tricarbonylmanganese with $NH_3$.[22] *N*,*N*-Diethylaniline[22] and *para*-methyl-*N*,*N*-diethylaniline complexes are also prepared by addition of $HNEt_2$ to the corresponding cationic chloro- and (*para*-methylchlorobenzene)tricarbonylmanganese complexes in respectively 67 and 62% yield.

Addition of $LiAlH_4$ to (*N*,*N*-diethylamino- and (*para*-methyl-*N*,*N*-diethylaminobenzene)tricarbonylmanganese (**20b**[22] and **20c**) gave exclusively the *meta*-addition products **21b**,**c** in respectively 68 and 92% yield. Addition of L-selectride to the $\eta^5$-complex **21b** followed by protonation with $CF_3CO_2H$ at −78 °C gave after warming the solution at room temperature complex **6** in 32% yield (Scheme 12). If the reaction was performed directly with complex **20b** and hydride followed by acid, the yield was even lower (9%). In the case of the *para*-disubstituted complex **21c**, no complex **6** was observed perhaps for steric or electronic reasons; isomerization was probably too slow and decomposition occurred. The same observation was made for complex **7b** (vide supra).

**Scheme 13**




**(3) $\eta^5$-Chlorocyclohexadienyl Complex.** The hexafluorophosphate of chlorobenzene (**22**), *ortho*-, *meta*-, and *para*-methylchlorobenzene (**23**−**25**), and (*ortho*-, *meta*-, and *para*-methoxychlorobenzene)tricarbonylmanganese complexes (**26**−**28**) have been prepared using Pauson's method in 33, 41, 49, 44, 64, 37, and 70% yield, respectively.[21] Addition of $LiAlH_4$ to the complexes of chlorobenzene (**22**) and *para*-methylchlorobenzene (**25**) gave in the first case a 40:60 mixture of two regioisomers **2d**[22] and **22b**[22] and a 35:65 mixture of **25a**,**b** in the second case, as mentioned by Pauson et al.[21] In the case of the *meta*-disubstituted complex **24**, a 54:46 mixture of complexes **24a**,**b** was obtained. The major isomer corresponded to an addition *meta* to the methyl and the chloro group. The addition of the hydride on the C2 carbon, between the methyl and the chloro group, was rather unexpected because this is a more crowded position. Stephenson et al. obtained also this regioselectivity by adding MeMgBr to the (2,4-dimethylanisole)tricarbonylmanganese complex.[23]

In the case of the *ortho*-disubstituted complex **23**, a 75:25 mixture of complexes **23a**,**b** was obtained. Again the regioselectivity was unexpected; the major isomer corresponded to an addition of the hydride *ortho* to the methyl group and *meta* to the chloro group (Scheme 3).

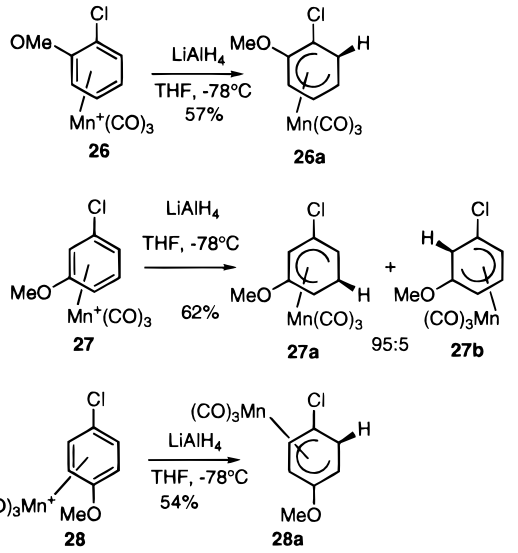
We then considered the case of arenes substituted by a methoxy and a chloro group. So, we undertook the addition of hydride to (*ortho*-, *meta*-, and *para*-chloroanisole)tricarbonylmanganese complexes **26**−**28**. Addition of hydride to the *ortho* complex (2-chloroanisole) **26** yielded complex **26a** in 57% yield. Addition occurred again on an hindered position, the C3 carbon. This position is preferred by the synergic effect of the chloro and the methoxy groups; thus, only one isomer is obtained (Scheme 14). The same reaction with the complex of 3-chloroanisole (**27**) afforded two neutral complexes **27a**,**b** (62% yield, 95:5 ratio), and with the 4-chloroanisole complex **28**, only one isomer was obtained: complex **28a**. We observed that addition of hydride occurred preferentially on a carbon bearing a hydrogen which resonated at the lowest field and (or) which was deshielded or less shielded during the

(21) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975,** 1677. See also ref 5c.

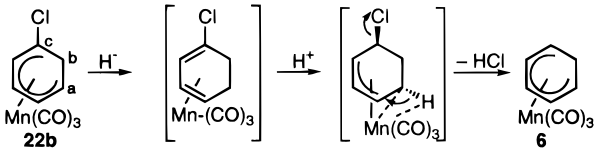
(22) Rose-Munch, F.; Balssa, F.; Gagliardini, V.; Rose, E.; Vaisserman, J. Manuscript in preparation covering the X-ray structures of **20a,b**, **2b,d**, and **22b**.

(23) Alexander, R. P.; Morley, C.; Stephenson, G. R. *J. Chem. Soc., Perkin Trans 1* **1988**, 2069.

**Scheme 14**




**Scheme 15**



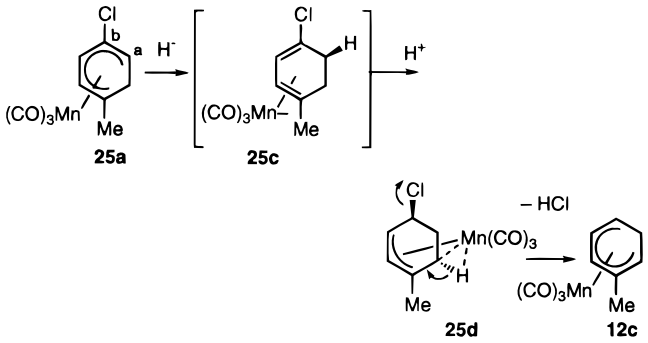

complexation of the free arene by the manganese tricarbonyl entity.

Complex **22b** treated with L-selectride and $CF_3CO_2H$ at −78 °C gave the $\eta^5$-cyclohexadienyl complex **6** in 39% yield. It was worthy to note that this reaction was possible even at −78 °C. In the case of complex **24b**, no reaction occurred; for this reason we have excluded the possibility of an ipso addition of the hydride on the carbon bearing the chloride atom. Thus the mechanism of the formation of **6** did not involve an *ipso* substitution but a $\pi$-allyl complex with an agostic hydrogen which was eliminated with the chloride atom (1,5-elimination: this is a *tele* a,c substitution; Scheme 15). The same reaction with complex **2b** gave **6** in 23% yield. If (chlorobenzene)tricarbonylmanganese complex **22** was reacted with L-selectride (3 equiv) and $CF_3CO_2H$ at −78 °C, complex **6** was directly obtained in 32% yield.

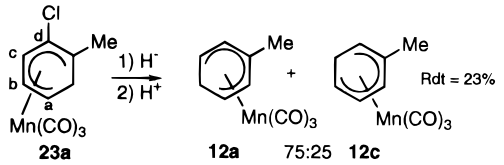
Complex **25a** treated with L-selectride and $CF_3CO_2H$ gave complex **12c** in 20% yield. The addition of hydride could occur only on the carbon adjacent to the chloride atom and not to the carbon substituted by the methyl group. The anionic complex **25c** treated with an acid gave the $\pi$-allyl complex **25d** which could eliminate HCl: this is a *cine* a,b substitution via a 1,5-elimination (Scheme 16). Similarly, complex **25b** afforded complex **12c** in 17% yield. This is a *tele* a,c substitution; hydride addition gave the same complex **25c**. In the same conditions, complex **24a** yielded only complex **12a** (18%). This result was in good agreement with the mechanism described in the case of the *meta*-disubstituted complex **8b** (Scheme 6: complexes **12b**,**c** were not formed) Complex **23a** treated in the same conditions gave two complexes **12a**,**c** in 23% yield (75:25; Scheme 17, *tele* a,d substitution). Similarly, complex **23b** afforded complexes **12a,c** in 16% yield (60/40, *tele* a,c substitution; Scheme 18).

The disubstituted ($\eta^5$-chloromethoxycyclohexadienyl)-tricarbonylmanganese complexes **26a**, **27a**, and **28a**,

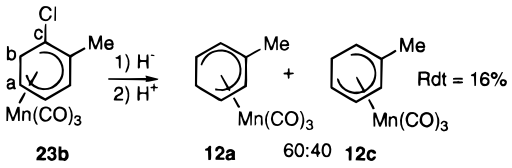
**Scheme 16**



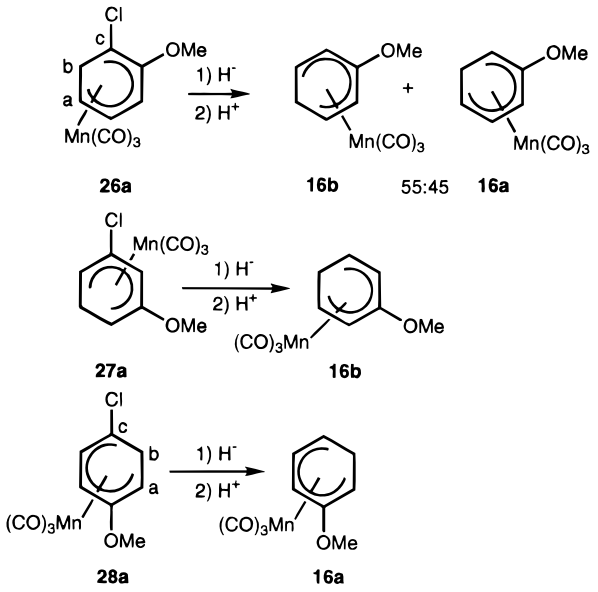

**Scheme 17**




**Scheme 18**



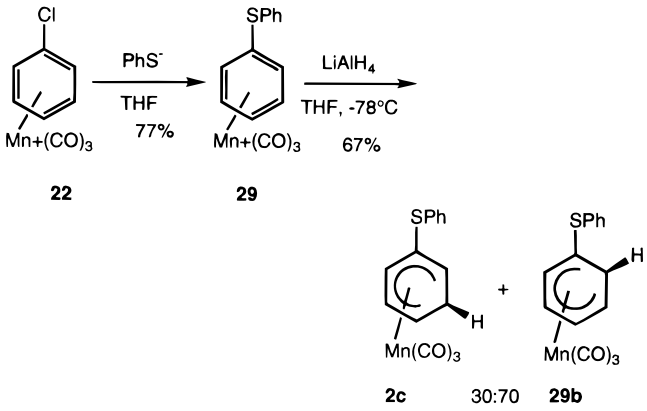

**Scheme 19**




treated with L-selectride and $CF_3CO_2H$, yielded respectively complexes **16a**,**b** (41%) in the ratio 45:55 (**16b** (19%), **16a** (41%) (Scheme 19)). In each case, the chloride atom was eliminated. This was not unexpected because this reaction occurred at very low temperature for chloro or chloro methyl derivatives but required higher temperatures (in boiling THF) in the case of methoxy or methyl methoxy derivatives. In the case of complexes **26a**, **27a**, and **28a**, the reaction required 1 or 2 min at room temperature. It was even possible in the case of these complexes to observe the yellow color of $\pi$-allyl complexes with an agostic hydrogen bond.

**(4) $\eta^5$-(Thioalkoxy)cyclohexadienyl Complex.** We did not suceed in directly preparing thioether complexes by using thioether derivatives and a manganese source because the sulfur atom coordinated directly to the

**Scheme 20**




manganese entity. The complex of diphenyl thioether (**29**) was obtained in 77% yield by treating (chlorobenzene)tricarbonylmanganese hexafluorophosphate with benzenethiolate in THF.[21] Addition of hydride gave two complexes **2c** and **29b** in 71% yield. The effect of the thiophenyl group was not sufficient to induce a good regioselectivity, and *meta* and *ortho* additions occurred in the ratio 30:70. Complex **29b** treated with L-selectride and water and then heated in refluxing THF for 20 h afforded complex **6** in 33% yield. It is worthy to note that we never succeeded in the case of ($\eta^6$-arene)-tricarbonylchromium complexes to cleave the C−S bond after addition of a hydride and an acid.[19b]

In conclusion, we herein described the first *cine* and *tele* nucleophilic substitutions of neutral ($\eta^5$-substituted-cyclohexadienyl)manganese tricarbonyl complexes. The transformations are affected by treatment with hydrides and then acids. In the case of methoxy-substituted $\eta^5$-cyclohexadienyl complexes, the driving force of the reaction appears to be elimination in the last step of OMe and of an agostic hydrogen either $\alpha$ or $\beta$ to the methoxy group of the neutral ($\eta^3$-cyclohexenyl)tricarbonylmanganese complex **5**. This gives rise to a stable ($\eta^5$-cyclohexadienyl)tricarbonylmanganese complex. In the case of other leaving groups (Cl, $NEt_2$, SPh), the reaction is too fast to allow isolation of the intermediates.



## Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. The ($\eta^6$-arene)tricarbonylmanganese complexes were generally stable in air for a long period of time in the solid state. Nevertheless, many derivatives were found to decompose fast in THF solutions on exposure to air. Consequently, all experiments involving (arene)tricarbonylmanganese complexes and their derivatives were always protected from exposure to light and oxygen. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl under dry nitrogen atmosphere and distilled just before use. Before NMR experiments were performed, NMR solvents and tubes were purged with dry nitrogen to remove oxygen. $^1$H and $^{13}$C NMR spectra were acquired on Brücker AC 200 and 400 spectrometers, and chemical shifts were reported in parts per million downfield of $Me_4Si$. $^1$H NMR spectra were referenced against the residual $^1$H impurity of the deuterated solvent ($\delta$ (ppm) 7.15 ($C_6D_6$), 3.58 and 1.73 ($C_4D_8O$)), and $^{13}$C NMR spectra were referenced against the $^{13}$C resonance of the solvent ($\delta$ 128.0 ($C_6D_6$), 25.3, 67.4 ($C_4D_8O$)). IR spectra were performed on a Perkin-Elmer 1420. Mass spectra were obtained on a Nermag R 30-40 spectrometer, with a direct insert source and using electronic impact (EI) and chemical ionization (CI) methods. Elemental analyses (reported in % mass) were performed by "Le Service de Microanalyses de l'Université P. et M. Curie" and by the "Service Central d'Analyse du CNRS" at Vernaison, France. Melting points were measured on a Reichert apparatus.

**Preparation of Tricarbonyl($\eta^6$-arene)manganese Complexes. Tricarbonyl($\eta^6$-benzene)manganese (7a).**[24,9c] Yield: 92%; lit.[9c] 77%. IR ($CH_3CN$): $\nu$(CO) 2075, 2035, 2010 cm$^{-1}$. $^1$H NMR ($(CD_3)_2CO$): $\delta$ 6.88, s. $^{13}$C NMR ($(CD_3)_2CO$): $\delta$ 216.3 (Mn(*C*O)$_3$), 102.5 (CH).

**Tricarbonyl($\eta^6$-anisole)manganese.**[21] Yield: 70%. $^1$H NMR ($(CD_3)_2CO$): $\delta$ 7.14 (2H, t, $J$ = 7, H-3, H-5); 6.44 (2H, d, $J$ = 7, H-2, H-6); 6.28 (1H, t, $J$ = 7, H−4); 4.17 (3H, s, OC*H*$_3$). $^{13}$C NMR ($(CD_3)_2CO$): $\delta$ 216.21 (Mn(*C*O)$_3$); 150.74 (C-1); 106.11 (C-3); 90.56 (C-4); 83.82 (C-2); 58.76 (O*C*H$_3$).

**Tricarbonyl($\eta^6$-chlorobenzene)manganese.**[21] Yield: 33%. $^1$H NMR ($(CD_3)_2CO$): $\delta$ 7.19 (2H, t, $J$ = 6.5, H-3, H-5); 7.11 (2H, d, $J$ = 6.5, H-2, H-6), 6.71 (1H, t, $J$ = 6.5, H−4). $^{13}$C NMR ($(CD_3)_2CO$): $\delta$ 214.92 (Mn(*C*O)$_3$), 121.08 (C-1), 103.41 (C-3, C-5), 99.75 (C-2, C-6), 97.38 (C-4).

**Tricarbonyl($\eta^6$-4-methylanisole)manganese (7a).** $BrMn(CO)_5$ (3.63 mmol, 1 g) was heated at 90 °C with $AlCl_3$ (7.5 mmol, 1 g) and 4-methylanisole (20 mL) in a two-neck flask for 3 h. After cooling of the reaction mixture, water (30 mL) was added. The aqueous phase was washed three time with $Et_2O$ (50 mL). Addition of aqueous $HPF_6$ (65%) to the aqueous phase yielded a precipitate **7a**, which was filtered out on a frit, washed with water, and ether. After drying of the precipitate under reduced pressure, a slightly yellow powder was obtained (538 mg, 37% yield). IR ($CH_3CN$): $\nu$(CO) 2060, 2000 cm$^{-1}$. $^1$H NMR ($(CD_3)_2CO$): $\delta$ 7.02 (2H, d, $J$ = 7.5, H-3, H-5), 6.44 (2H, d, $J$ = 7,5, H-2, H-6), 4.13 (3H, s, OC*H*$_3$), 2.47 (3H, s,C*H*$_3$). $^{13}$C NMR ($(CD_3)_2CO$): $\delta$ 216,56 (Mn(*C*O)$_3$), 108.29 (C-3, C-5), 148.47 (C-1), 108.29 (C-4), 84.04 (C-2, C-6), 58.74 (OMe). Anal. Calcd for $C_{11}H_{10}O_4MnPF_6$ ($M_r$ = 406): C, 32.53; H, 2.48. Found: C, 32.58; H, 2.42.

**Tricarbonyl($\eta^6$-3-methylanisole)manganese (8a).** Using the same procedure, a slightly yellow powder was obtained 43% yield. IR ($CH_3CN$): $\nu$(CO) 2060, 2000 cm$^{-1}$. $^1$H NMR ($(CD_3)_2CO$): $\delta$ 7.12 (1H, t, $J$ = 7, H-5), 6.41 (1H, s, H-2), 6.31 (1H, d, $J$ = 7, H-6), 6.16 (1H, d, $J$ = 7, H-4), 4.17 (3H, s, OC*H*$_3$), 2.64 (3H, s, C*H*$_3$). $^{13}$C NMR ($(CD_3)_2CO$): $\delta$ 216.72 (Mn(*C*O)$_3$), 151.04 (C-1), 124.58 (C-3), 105.66 (C-5), 90.67 (C-4), 84.87 (C-2), 81.03 (C-6), 58.57 (O*C*H$_3$), 20.50 (*C*H$_3$). Anal. Calcd for $C_{11}H_{10}O_4MnPF_6$ ($M_r$ = 406): C, 32.53; H, 2.48. Found: C, 32.38; H, 2.49.

**Tricarbonyl($\eta^6$-2-methylanisole)manganese (9a).** Using the same procedure, a slightly yellow powder was obtained 61% yield. IR ($CH_3CN$): $\nu$(CO) 2060, 2000 cm$^{-1}$. $^1$H NMR ($(CD_3)_2CO$): $\delta$ 7.10 (1H, d, $J$ = 6.5, H-3), 6.97 (1H, t, $J$ = 6.5, H-5), 6.55 (1H, d, $J$ = 6.5, H-6), 6.27 (1H, t, $J$ = 6.5, H-4), 4.23 (3H, s, OC*H*$_3$), 2.45 (3H, s, C*H*$_3$). $^{13}$C NMR ($(CD_3)_2CO$): $\delta$ 216.67 (Mn(*C*O)$_3$), 148.41 (C-1), 106.04 (C-3), 104.29 (C-2), 103.06 (C-5), 90.64 (C-4), 80.83 (C-6), 58.77 (O*C*H$_3$), 15.42 (*C*H$_3$). Anal. Calcd for $C_{11}H_{10}O_4MnPF_6$ ($M_r$ = 406): C, 32.53; H, 2.48. Found: C, 32.65; H, 2.53.

**Tricarbonyl($\eta^6$-4-methoxyanisole)manganese[13b] (10a).** 4-Methoxyanisole (20 g), $BrMn(CO)_5$ (3 g, 10.9 mmol), and $AlCl_3$ (3 g, 22.5 mmol) were combined. The solution is heated at 100 °C for 3 h. Yield: 46%. $^1$H NMR ($(CD_3)_2CO$): $\delta$ 6.68 (4H, s), 4.05 (6H, s, OC*H*$_3$). $^{13}$C NMR ($(CD_3)_2CO$): $\delta$ 216.73 (Mn(*C*O)$_3$), 140.99 (C-1, C-4), 86.02 (C-2, C-3, C-5, C-6), 58.72 (O*C*H$_3$).

**Tricarbonyl($\eta^6$-3-methoxyanisole)manganese (11a).** $AgBF_4$ (2 g, 10.2 mmol) and $BrMn(CO)_5$ (3 g, 10.9 mmol) were heated for 3 h under reflux in $CH_2Cl_2$ (30 mL), 3-methoxyanisole (2.5 mL) was added, and the solution was heated for 18 h. The reaction mixture was cooled and filtered on Celite in order to eliminate the precipitate AgBr. The solution was evaporated under reduced pressure. The oily product was dissolved in the minimum of acetone and poured into ether (300 mL) in order to precipitate the complex and dried under

(24) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807.

vacuum. A yellow powder was obtained (3.51 g, 95% yield). IR ($CH_3CN$): $\nu$(CO) 2060, 2000 $cm^{-1}$. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 7.11 (1H, *t*, $J = 7$, H-5), 6.31 (1H, t, $J = 2$, H-2), 6.09 (2H, dd, $J = 7$ and 2, H-4, H-6), 4.15 (6H, s, $OCH_3$). $^{13}C$ NMR ($(CD_3)_2CO$): $\delta$ 216.82 ($Mn(CO)_3$), 76.17 (C-4 and C-6), 151.78 (C-1 and C-3), 71.59 (C-2), 106.70 (C-5), 58.81 ($OCH_3$). Anal. Calcd for $C_{11}H_{10}O_5MnBF_4$ ($M_r = 363.94$): C, 36.30; H, 2.48. Found: C, 36.65; H, 2.23.

**Tricarbonyl($\eta^6$-*N*,*N*-diethylaniline)manganese (20b).**[21] To an acetone solution (30 mL) of (chlorobenzene)tricarbonylmanganese hexafluorophosphate (870 mg, 2 mmol)[21] was added $NHEt_2$ (420 $\mu$L, 4 mmol). The resulting mixture was stirred for 10 min and added to an $Et_2O$ solution (300 mL) of 65% $HPF_6$ (5 mL). A yellow precipitate was recovered by filtration, washed with ether and water, and dried under vacuum (576 mg, 67% yield). $C_{13}H_{16}O_3NMnPF_6$ ($M_r = 433.16$). IR ($CH_3CN$): $\nu$(CO) 2060, 2000 $cm^{-1}$. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 6.85 (t, 2H, $J = 7$, H-3, H-5), 3.69 (q, 4H, $J = 7$, H-7, H-9), 6.04 (1H, t, J = 7, H-4), 1,33 (6H, t, $J = 7$, H-8, H-10), 5.81 (2H, d, $J = 7$, H-2, H-5). $^{13}C$ NMR ($(CD_3)_2CO$): $\delta$ 218.0 Mn-($CO)_3$, 148.48 (C-1), 106.29 (C-3, C-5), 83.23 (C-4), 73.64 (C-2, C-6), 45.61 (C-7, C-9), 11.26 (C-8, C-10).

**Tricarbonyl($\eta^6$-*p*-methyl-*N*,*N*-diethylaniline)manganese (20c).** Using the same procedure with (*p*-chlorotoluene)-tricarbonylmanganese hexafluorophosphate[21] (1 g, 2.44 mmol) and 550 $\mu$L of $NHEt_2$, complex **20c** was obtained in 62% yield (673 mg). IR ($CH_3CN$): $\nu$(CO) 2040, 1990 $cm^{-1}$. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 6.84 (2H, d, $J = 8$, H-3, H-5), 5.78 (2H, d, $J = 8$, H-2, H-6), 3.66 (4H, q, $J = 7$, H-8, H-10), 2.43 (3H, s, $CH_3$), 1.31 (6H, t, $J = 7$, H-9, H-11). $^{13}C$ NMR ($(CD_3)_2CO$): $\delta$ 218.39 ($Mn(CO)_3$), 145.29 (C-1), 106.34 (C-3, C-5), 100.02 (C-4), 73.28 (C-2, C-5), 45.96 (C-10, C-8), 18.39 (C-9, C-11), 11.52 ($CH_3$). Anal. Calcd for $C_{14}H_{18}O_3NMnPF_6$ ($M_r = 447.19$): C, 37.61; H, 3.83; N, 3.13. Found: C, 37.42; H, 3.96; N, 3.06.

**Tricarbonyl($\eta^6$-2-chlorotoluene)manganese (23).** 2-Chlorotoluene (30 mL), $BrMn(CO)_5$ (2.3 g, 8.36 mmol), and $AlCl_3$ (2.3 g, 17.25 mmol) were combined. The reaction mixture heated for 3 h at 100 °C (1.38 g, 41% yield). IR ($CH_3CN$): 2080, 2040. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 7.21 (1H, dd, $J = 7$ and 1, H-6), 7.08 (1H, dd, $J = 7$ and 1, H-3), 6.92 (1H, dd, $J = 7$ and 1, H-5), 6.76 (1H, td, $J = 7$ and 1, H-4), 2.73 (3H, s, $CH_3$). $^{13}C$ NMR ($(CD_3)_2CO$): $\delta$ 215.11 ($Mn(CO)_3$), 102.94 (C-3), 101.51 (C-6), 100.42 (C-5), 99.36 (C-4), 19,00, $CH_3$). Anal. Calcd for $C_{10}H_7O_3ClMnPF_6$ ($M_r = 410.52$): C, 29.25; H, 1.71. Found: C, 29.11; H, 1.68.

**Tricarbonyl($\eta^6$-3-chlorotoluene)manganese (24).** 3-Chlorotoluene (25 mL), $BrMn(CO)_5$ (3 g, 22.5 mmol), and $AlCl_3$ (3 g, 22.5 mmol) were combined. The reaction mixture was heated for 2 h at 100 °C (2.19 g, 49% yield). IR ($CH_3CN$): 2080, 2040. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 7.16 (1H, t, $J = 7$, H-5), 6.96 (1H, s, H-2), 6.88 (1H, d, $J = 7$, H-6), 6.49 (1H, d, $J = 7$, H-4), 2.68 (3H, s, $CH_3$). $^{13}C$ NMR ($(CD_3)_2CO$): $\delta$ 215.07 (Mn-($CO)_3$), 104.19 (C-5), 99.60 (C-2), 96.74 (C-4), 96.38 (C-6), 19.87, $CH_3$). Anal. Calcd for $C_{10}H_7O_3ClMnPF_6$ ($M_r = 410.52$): C, 29.25; H, 1.71. Found: C, 29.09; H, 1.73.

**Tricarbonyl($\eta^6$-4-chlorotoluene)manganese (25).**[21] 4-Chlorotoluene (25 mL), $BrMn(CO)_5$ (1.5 g, 5.45 mmol), and $AlCl_3$ (1.5 g, 11.25 mmol) were combined. The reaction mixture was heated for 3 h at 100 °C (0.98 g, 44% yield). IR (Nujol): 2080, 2030, 2000. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 7.16 (2H, d, $J = 7$, H-2, H-6), 6.94 (2H, d, $J = 7$, H-3, H-5), 2.57 (3H, s, $CH_3$). $^{13}C$ NMR ($(CD_3)_2CO$): $\delta$ 215.04 ($Mn(CO)_3$), 117.11, 117.26 (C-1, C-4), 101.21 (C-2, C-6), 19.27, $CH_3$), 102.19 (C-3, C-5). $C_{10}H_7O_3$-$ClMnPF_6$ ($M_r = 410.52$).

**Tricarbonyl($\eta^6$-2-chloroanisole)manganese (26).** See **11a** for the experimental part. 2-Chloroanisole (2.5 mL, 20.33 mmol), $AgBF_4$ (2 g, 10.2 mmol), and $BrMn(CO)_5$ (3 g, 10.9 mmol) were combined. Yield: 64% (2.385 g). IR ($CH_3CN$): $\nu$(CO) 2080, 2030 $cm^{-1}$. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 7.55 (1H, d, $J = 6.5$, H-6), 7.04 (1H, t, $J = 6.5$, H-3), 6.81 (1H, d, $J = 6.5$, H-3), 6.40 (1H, t, $J = 6.5$, H-5), 4.35 (3H, s, $OCH_3$). $^{13}C$ NMR ($(CD_3)_2CO$): $\delta$ (215.66 ($Mn(CO)_3$), 103.38 (C-1), 146.52 (C-2), 90.74 (C-4), 105.68 (C-3), 81.59 (C-6), 103.62 (C-5), 59.94 ($OCH_3$). Anal. Calcd for $C_{10}H_7O_4ClMnBF_4$ ($M_r = 368.35$): C, 32.60; H, 1.91. Found: C, 32.76; H, 1.89.

**Tricarbonyl($\eta^6$-3-chloroanisole)manganese (27).** See **11a** for the experimental part. 3-Chloroanisole (1.5 mL, 11.2 mmol), $AgBF_4$ (1.11 g, 5.72 mmol), and $BrMn(CO)_5$ (1.73 g, 6.3 mmol) were combined. Yield: 37% (0.769 g). IR ($CH_3$-CN): $\nu$(CO) 2080, 2020 $cm^{-1}$. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 7.33 (1H, t, $J = 7$, H-5), 6.89 (1H, s, H-2), 6.62 (1H, d, $J = 7$, H-6), 6.37 (1H, d, $J = 7$, H-4), 4.27 (3H, s, $OCH_3$). Anal. Calcd for $C_{10}H_7O_4ClMnBF_4$ ($M_r = 368.35$): C, 32.60; H, 1.91. Found: C, 31.91; H, 1.93.

**Tricarbonyl($\eta^6$-4-chloroanisole)manganese (28).** See **11a** for the experimental part. 4-Chloroanisole (2.5 mL, 20.3 mmol), $AgBF_4$ (1.98 g, 10.17 mmol), and $BrMn(CO)_5$ (3.075 g, 11.2 mmol) were combined. Yield: 70% (2.61 g). IR ($CH_3$-CN): $\nu$(CO) 2080, 2020 $cm^{-1}$. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 6.59 (2H, d, $J = 7$, H-5, H-3), 7.44 (2H, s, H-2, H-6), 4.17 (3H, s, $OCH_3$). Anal. Calcd for $C_{10}H_7O_4ClMnBF_4$ ($M_r = 368.35$): C, 32.60; H, 1.91. Found: C, 32.55; H, 1.89.

**Tricarbonyl($\eta^6$-diphenyl sulfide)manganese (29).**[21] This was made by using the same procedure with (chlorobenzene)-tricarbonylmanganese hexafluorophosphate[21] (397 mg, 1 mmol) and PhSNa prepared by treating thiophenol (PhSH) (2 mmol, 200 $\mu$L) and NaH (2.5 mmol, 60 mg) in THF (15 mL). After 10 min, 3 mL of aqueous $HPF_6$ (65%) was added. THF was evaporated under reduced pressure, and the yellow residue was dissolved in the minimum of acetone. This solution was slowly poured into a solution of ether (150 mL). The yellow precipitate was filtered out, dried under vacuum, and recrystallized in the minimum amount of acetone and ether (359 mg, 77% yield). IR ($CH_3CN$): $\nu$(CO) 2070, 2020 $cm^{-1}$. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 7.79 (5H, m, free arene), 7.04 (2H, t, $J = 6.5$, H-3, H-5), 6.51 (1H, t, $J = 6.5$, H-4), 6.44 (2H, d, $J = 6.5$, H-2, H-5). $^{13}C$ NMR ($(CD_3)_2CO$): $\delta$ 216.01 ($Mn(CO)_3$), 125.40 (C-1), 103.82 (C-3, C-5), 95.14 (C-4), 94.19 (C-2, C-6).

**Preparation of Tricarbonyl($\eta^5$-cyclohexadienyl)manganese Complexes. Tricarbonyl($\eta^5$-2-methoxy-1−5-cyclohexadienyl) manganese (2a).**[4a,21] To a THF solution (12 mL) of (anisole)tricarbonylmanganese hexafluorophosphate (800 mg, 2.04 mmol) at −78 °C was added a 1 M solution of $LiAlH_4$ (1 mL, 1 mmol) in THF at −78 °C under nitrogen. The resulting mixture is stirred for 1 min at room temperature and then cooled at −78 °C before slow addition of 1 mL of $H_2O$. The reaction mixture is added to a 50/50 (pentane/dilute aqueous solution of HCl) solution. The organic phase is washed with 50 mL of an aqueous solution of $KHCO_3$, water (50 mL), and brine (50 mL), dried over $MgSO_4$, and filtered through a Celite column. Pentane is removed under $N_2$ flow at 0 °C. The oily residue is purified by flash silica gel chromatography to give a yellow powder (323 mg, 1.30 mmol, 64% yield). $^1H$ NMR (200 MHz, $C_6D_6$): $\delta$ 5.24 (d, $J = 6$, 1H, $H_3$), 4.16 (t, $J = 6$ Hz, 1H, $H_4$), 2.77 (s, 3H, $OCH_3$), 2.29 (m, 1H, $H_5$, $H_{6endo}$), 1.66 (1H, d, $J = 11$ Hz, 1H $H_{6exo}$). $^{13}C$ NMR (200 MHz, $C_6D_6$): $\delta$ 224.45 (Mn−CO), 143.70 ($C_2$), 94.20 ($C_4$), 67.90 ($C_3$), 53.50 ($OCH_3$), 51.10 ($C_5$), 35.80 ($C_1$), 26.6 ($C_6$). IR ($CHCl_3$): 2005, 1915 $cm^{-1}$. Anal. Calcd for $C_{10}H_9MnO_4$: C, 48.10; H, 3.66. Found: C, 48.16; H, 3.71.

**Tricarbonyl($\eta^5$-2-(diethylamino)-1−5-cyclohexadienyl)manganese (2b).** To a THF solution (15 mL) of complex **20b** (810 mg, 1.87 mmol) at −78 °C was added a solution of $LiAlH_4$ (1 mL, 1 mmol) in THF at −78 °C. The resulting mixture was stirred for 1 min at room temperature and then cooled at −78 °C before slow addition of 1 mL of $H_2O$. The reaction mixture was added to a 50/50 (pentane/aqueous solution of HCl) solution. The organic phase was washed with 50 mL of an aqueous solution of $KHCO_3$, water, and brine, dried over $MgSO_4$, and filtered through a Celite column. Pentane was removed under $N_2$ flow at 0 °C. The oily residue is purified by flash chromatography to give a yellow powder (362.5 mg, 1.27 mmol, 68% yield). $^1H$ NMR (200 MHz, $C_6D_6$): $\delta$ 4.76 (dd, $J = 2.5$ and 6, 1H, $H_3$), 4.48 (t, $J = 6$, 1H, $H_4$), 2.50 (m, 6H, $H_5$, $H_{6endo}$, $CH_2CH_3$), 2.25 (m, 1H, $H_1$), 2.03 (d, $J = 12$, 1H, $H_6$exo), 0.78 (t, $J = 7$, 6H, $CH_2CH_3$). $^{13}C$ NMR (200 MHz,

$C_6D_6$): $\delta$ 224.3, 137.14 ($C_2$), 95.98 ($C_4$), 62.63 ($C_3$), 50.86 ($C_5$), 30.61 ($C_1$), 27.06 ($C_6$, $CH_2CH_3$), 12.50 ($CH_2CH_3$). IR ($CHCl_3$): 2000, 1910 $cm^{-1}$. Anal. Calcd for $C_{13}H_{16}O_3MnN$: C, 53.94; H, 5.57; N, 4.84. Found: C, 53.96; H, 5.58; N, 4.67.

**Tricarbonyl($\eta^5$-2-(thiophenyl)-1−5-cyclohexadienyl)-manganese (2c) and Tricarbonyl($\eta^5$-1-(thiophenyl)-1−5-cyclohexadienyl)manganese (29b).** The procedure is identical with that used for complex **2b**: 145 mg (0.3 mmol) of (diphenyl sulfide)tricarbonylchromium (**29**) and 0.15 mL (0.15 mmol) of $LiAlH_4$ were used. A yellow powder is obtained (66.3 mg, 67% yield), the flash chromatography of which gives the product **2c** (addition of $H^-$ to *meta* position/SPh) and the isomeric compound **29b** (addition of $H^-$ to *ortho* position/SPh) in a 25/75 ratio. $^1$H NMR (200 MHz, $C_6D_6$) of complex **2c**: $\delta$ 7.10 (m, 5H, arom H), 5.02 (d, $J$ = 5 Hz, 1H, $H_3$), 4.03 (t, $J$ = 5 Hz, 1H, $H_4$), 2.77 (m, 1H, $H_1$), 2.27 (m, 2H, $H_5$ and $H_6$endo), 1.60 (d, $J$ = 12 Hz, 1H, $H_6$exo). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 223, 135−128 (arom C), 116.55 ($C_2$), 95.36 ($C_4$), 80.22 ($C_3$), 51.81 ($C_5$), 50.70 ($C_1$), 26.54 ($C_6$). IR ($CHCl_3$): 2020, 1940 $cm^{-1}$. Anal. Calcd for $C_{15}H_{11}O_3MnS$: C, 55.22; H, 3.39. Found: C, 54.38; H, 3.51. $^1$H NMR (200 MHz, $C_6D_6$) of complex **29b** (yellow solid, 46.4 mg): $\delta$ 7.10 (m, 5 H, arom H), 4.85 (t, $J$ = 5 Hz, 1H, $H_3$), 4.59 (d, $J$ = 5 Hz, 1H, $H_2$), 4.02 (t, $J$ = 5, 1H, $H_4$), 2.43 (m, 2H, $H_5$ and $H_6$endo), 2.01 (d, $J$ = 11 Hz, 1H, $H_6$-exo). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 222.45, 134−127 (arom C), 100.73 ($C_2$), 96.03 ($C_4$), 78.17 ($C_3$), 61.50 ($C_1$), 51.37 ($C_5$), 30.78 ($C_6$). IR ($CHCl_3$): 2020, 1940 cm $^{-1}$. Anal. Calcd for $C_{15}H_{11}O_3MnS$: C, 55.22; H, 3.39. Found: C, 54.28; H, 3.61.

**Tricarbonyl($\eta^5$-1-chloro- and 2-chloro-1−5-cyclohexadienyl)manganese (22b,2d).** The method is identical with that used for complex **2b**: 1.15 g (2.9 mmol) of **1** (X = Cl) and 1.5 mL (1.5 mmol) of $LiAlH_4$ was used. After flash chromatography, two isomeric complexes are isolated: **2d** (232 mg, 0.92 mmol, 32% yield) and **22b** (352 mg, 1.39 mmol, 48% yield). $^1$H NMR (200 MHz, $C_6D_6$) of **2d:** $\delta$ 5.43 (d, $J$ = 5 Hz, 1H, $H_3$), 3.85 (t, $J$ = 5 Hz, 1H, $H_4$), 2.63 (m, 1H, $H_5$), 2.07 (m, 2H, H1 and $H_6$endo), 1.44 (d, $J$ = 14, 1H, $H_6$exo). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 222.3, 116.33 ($C_2$), 99.0 ($C_3$), 79.5 ($C_1$, $C_4$), 51.37 ($C_5$), 27.1 ($C_6$). IR ($CHCl_3$): 2020, 1940 $cm^{-1}$. Anal. Calcd for $C_9H_6ClO_3Mn$: C, 42.80; H, 2.39. Found: C, 42.67; H, 2.56. $^1$H NMR (200 MHz, $C_6D_6$) of **22b:** $\delta$ 4.71 (t, $J$ = 6 Hz, 1H, $H_3$), 4.50 (d, $J$ = 6 Hz, 1H, $H_2$), 3.82 (d, $J$ = 6 Hz, 1H, $H_4$), 2.71 (dd, $J$ = 6 and 14, $H_{6endo}$), 2.36 (t, $J$ = 6 Hz, 1H, $H_5$), 2.03, (d, $J$ = 14 Hz, $H_{exo}$). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 222.3, 97.35 ($C_2$), 96.05 ($C_4$), 79.71 ($C_3$), 74.07 ($C_1$), 53.11 ($C_5$), 35.11 ($C_6$). IR ($CHCl_3$): 2020, 1940 $cm^{-1}$. Anal. Calcd for $C_9H_6ClO_3Mn$: C, 42.80; H, 2.39. Found: C, 42.95; H, 2.45.

**Tricarbonyl($\eta^5$-1-methyl, 2-chloro and 1-chloro-2-methyl-1−5-cyclohexadienyl)manganese (23a,b).** The method is identical with that used for complex **2b**: 1 g (2.43 mmol) of **23** in 30 mL of THF, (1.2 mmol) of $LiAlH_4$ in 1.2 mL of THF, 5 min at −78 °C and then at rt. Yield: 91% (589 mg). After flash chromatography, two isomeric complexes are isolated: **23a** (440 mg, 1.65 mmol) and **23b** (20 mg, 0.06 mmol). $^1$H NMR (200 MHz, $C_6D_6$) of **23a** (yellow solid)**:** $\delta$ 5.36 (d, $J$ = 6 Hz, 1H, $H_3$), 3.86 (t, $J$ = 6 Hz, 1H, $H_4$), 2.14 (dd, $J$ = 6 and 13 Hz 1H, $H_{6endo}$), 2.01 (t, $J$ = 6 $H_5$), 0.92 (s, 3H, Me), 1.61 (d, $J$ = 13Hz, $H_{6exo}$). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 222.50, 114.50 ($C_2$), 93.50 ($C_4$), 65.80 ($C_1$), 48.70 ($C_5$), 33.10 ($C_6$), 77.8 ($C_3$), 20.70 ($CH_3$). IR ($CHCl_3$): 2010, 1940 $cm^{-1}$. Anal. Calcd for $C_{10}H_8ClMnO_3$: C, 45.06; H, 3.02. Found: C, 45.45.10; H, 2.99. $^1$H NMR (200 MHz, $C_6D_6$) of **23b** (yellow solid)**:** $\delta$ 4.74 (d, $J$ = 5 Hz, 1H, $H_3$), 3.88 (dd, $J$ = 5 and 8 Hz, 1H, $H_4$), 2.77 (dd, $J$ = 8 and 13, 1H, $H_{6endo}$), 2.73 (t, $J$ = 8 Hz 1H, $H_5$), 2.10 (d, $J$ = 13 $H_{6exo}$), 1.65 (s, $CH_3$). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 222.27, 110.33 ($C_1$), 95.20 ($C_4$), 77.70 ($C_3$), 75.40 ($C_2$), 53.20 ($C_5$), 36.70 ($C_6$), 20.04 ($CH_3$). IR ($CHCl_3$): 2010, 1940 $cm^{-1}$. Anal. Calcd for $C_{10}H_8ClMnO_3$: C, 45.06; H, 3.02. Found: C, 45.09; H, 3.11.

**Tricarbonyl($\eta^5$-2-chloro-4-methyl and 1-chloro-5-methyl-1−5-cyclohexadienyl)manganese (24a,b).** The method is identical with that used for complex **2b**: 615 mg (1.5 mmol) of **24**, 1 mL in THF (1 mmol) of $LiAlH_4$, 2 min at −78 °C. Yield: 85% (340 mg). After flash chromatography, two isomeric complexes are isolated: **24a** (182 mg, 0.38 mmol) and **24b** (158 mg, 0.59 mmol). $^1$H NMR (200 MHz, $C_6D_6$) of **24a** (yellow solid)**:** $\delta$ 5.34 (t, $J$ = 1 Hz, 1H, $H_3$), 2.65 (dd, $J$ = 1 and 6 Hz, 1H, $H_1$), 2.14 (dt, $J$ = 3 and 13 Hz 1H, $H_{6\ endo}$), 1.98 (d, $J$ = 6 $H_5$), 1.47 (d, $J$ = 13 Hz, 1H, $H_6$exo), 1.18 (s, $CH_3$). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 222.23, 115.47 ($C_2$), 109.45 ($C_4$), 81.15 ($C_3$), 52.00 ($C_1$), 51.55 ($C_5$), 29.60 ($C_6$), 21.55 ($CH_3$). IR ($CHCl_3$): 2010, 1940 $cm^{-1}$. Anal. Calcd for $C_{10}H_8ClO_3Mn$: C, 45.06; H, 3.02. Found: C, 45.15; H, 2.98. $^1$H NMR (200 MHz, $C_6D_6$) of **24b** (yellow solid)**:** $\delta$ 4.58 (t, $J$ = 5 Hz, 1H, $H_3$), 4.54 (d, $J$ = 5 Hz, 1H, $H_2$), 3.59 (d, $J$ = 5, 1H, $H_4$), 2.66 (d, $J$ = 13 Hz, 1H, $H_{6\ endo}$), 2.17 (d, $J$ = 13 $H_{6exo}$), 1.04 (s, $CH_3$). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 222.28, 95.65 ($C_2$), 94.50 ($C_4$), 73.18 ($C_1$), 72.76 ($C_3$), 71.90 ($C_5$), 40.27 ($C_6$), 23.04 ($CH_3$). IR ($CHCl_3$): 2010, 1940 $cm^{-1}$. Anal. Calcd for $C_{10}H_8ClO_3Mn$: C, 45.06; H, 3.02. Found: C, 45.72; H, 3.08.

**Tricarbonyl($\eta^5$-1-chloro-4-methyl and 2-chloro-5-methyl-1−5-cyclohexadienyl)manganese (25a,b).** The method is identical with that used for complex **2b**: 2.14 g (5.22 mmol) of **25**, 2.6 mL (1.5 mmol) of $LiAlH_4$, 5 min at −78 °C. Yield: 90% (1.25 g). After flash chromatography, two isomeric complexes are isolated: **25a** (440 mg, 1.65 mmol) and **25b** (810 mg, 3.04 mmol). $^1$H NMR (200 MHz, $C_6D_6$) of **25a:** $\delta$ 5.30 (dd, $J$ = 2 and 5 Hz, 1H, $H_3$), 3.58 (d, $J$ = 5 Hz, 1H, $H_2$), 2.61 (dd, $J$ = 2 and 5 Hz, 1H, $H_5$), 2.60 (d, $J$ = 13 Hz, $H_6$exo), 2.03 (ddd, $J$ = 2, 5, and 13 Hz, 1H, $H_6$endo). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 222.0, 115.70 ($C_4$), 98.82 ($C_2$), 7.03 ($C_3$), 71.00 ($C_1$), 49.70 ($C_5$), 32.90 ($C_6$), 22.70 ($CH_3$). $^1$H NMR (200 MHz, $C_6D_6$) of **25b:** $\delta$ 4.58 (d, $J$ = 6 Hz, 1H, $H_3$), 4.48 (dd, $J$ = 2 and 6 Hz, 1H, $H_2$), 2.73 (ddd, $J$ = 2, 6, 14 Hz, 1H, $H_{6endo}$), 2.29 (d, $J$ = 6, Hz, $H_5$), 2.07 (d, $J$ = 14 Hz, 1H, $H_{6exo}$), 1.13 (s, Me). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 223.00, 111.30 ($C_1$), 95.96 ($C_3$), 77.00 ($C_2$), 74.36 ($C_4$), 54.30 ($C_5$), 36.50 ($C_6$), 21.30 ($CH_3$).

**Tricarbonyl($\eta^5$-1-chloro, 2-methoxy 1−5-cyclohexadienyl)manganese (26a).** The method is identical with that used for complex **2b**: 620 mg (1.68 mmol) of **26** in 10 mL of THF, (0.84 mmol) of $LiAlH_4$ in 0.84 mL of THF, 5 min at −78 °C. The mixture is stirred at rt until the obtention of a limpid solution. Yield: 57% (270 mg). After flash chromatography, complex **26a** is isolated. $^1$H NMR (200 MHz, $C_6D_6$) of **26a** (yellow solid)**:** $\delta$ 4.52 (d, $J$ = 6 Hz, 1H, $H_3$), 3.79 (t, $J$ = 6 Hz, 1H, $H_4$), 3.00 (s, 3H, $CH_3$), 2.83 (dd, $J$ = 6 and 13, Hz, $H_{6endo}$), 2.40 (t, $J$ = 6 Hz, 1H, $H_5$), 2.19 (d, $J$ = 13 Hz, 1H, $H_{6exo}$). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 222.41, 139.55 ($C_1$), 92.27 ($C_4$), 62.82 ($OCH_3$), 61.89 ($C_3$), 52.26 ($C_5$), 37.45 ($C_6$). Anal. Calcd for $C_{10}H_8ClO_4Mn$: C, 42.51; H, 2.85. Found: C, 42.45; H, 2.88.

**Tricarbonyl($\eta^5$-2-chloro-4-methoxy and 1-chloro-5-methoxy-1−5-cyclohexadienyl)manganese (27a,b).** The method is identical with that used for complex **2b**: 737 mg (2 mmol) of **27** in 30 mL of THF, (1 mmol) of $LiAlH_4$ in 1 mL of THF, 5 min at −78 °C. The mixture is stirred at rt until the obtention of a limpid solution. Yield: 62% (348 mg). After flash chromatography, complexes **27a** (330 mg, 1.16 mmol) and **27b** (17 mg, 0.06 mmol) are isolated. $^1$H NMR (200 MHz, $C_6D_6$) of **27a** (yellow solid)**:** $\delta$ 5.66 (t, $J$ = 1.8 Hz, 1H, $H_3$), 2.63 (m, 4H, $H_1$ or $H_5$ and $OCH_3$), 2.15 (dt, $J$ = 6 and 12 Hz, 1H, $H_{6endo}$), 2.12 (m, $H_5$ or $H_1$), 1.50 (d, $J$ = 13 Hz, 1H, $H_{6exo}$). $^{13}$C NMR (200 MHz, $C_6D_6$): $\delta$ 221.70, 140.50 ($C_4$), 114.00 ($C_2$), 70.00 ($C_3$), 54.00, 53.10, 37.45 ($OCH_3$, $C_1$, $C_5$), 28.80 ($C_6$). Anal. Calcd for $C_{10}H_8ClO_4Mn$: C, 42.51; H, 2.85. Found: C, 42.63; H, 2.94. $^1$H NMR (200 MHz, $C_6D_6$) of **27b** (yellow solid)**:** $\delta$ 4.60 (d, $J$ = 6 Hz, 1H, $H_2$), 4.35 (t, 1H, $J$ = 6 Hz, $H_3$), 3.27 (d, $J$ = 14 Hz, 1H, $H_{6endo}$), 2.80 (d, $J$ = 6 Hz, $H_4$), 2.65 (d, $J$ = 14 Hz, 1H, $H_{6exo}$).

**Tricarbonyl($\eta^5$-1-chloro-4-methoxy-1−5-cyclohexadienyl)manganese (28a).** The method is identical with that used for complex **2b**: 370 mg (1 mmol) of **28** in 10 mL of THF, (0.25 mmol) of $LiAlH_4$ in 0.25 mL of THF, 5 min at −78 °C. The mixture is stirred at rt until the obtention of a limpid solution at 0 °C for 5 min. Yield: 54% (153 mg). After flash chromatography, complex **28a** is isolated. $^1$H NMR (200 MHz, $C_6D_6$) of **28a** (yellow solid)**:** $\delta$ 4.81 (dd, $J$ = 3 and 6 Hz, 1H,

$H_3$), 4.51 (dd, $J$ = 2 and 6 Hz, 1H, $H_2$), 2.60 (s, 3H, $OCH_3$), 2.76 (ddd, $J$ = 2, 6, and 13 Hz, $H_{6endo}$), 2.35 (dd, $J$ = 3 and 6 Hz, 1H, $H_5$), 2.16 (d, $J$ = 13 Hz, 1H, $H_{6exo}$). $^{13}C$ NMR (200 MHz, $C_6D_6$): $\delta$ 222.01, 142.25 ($C_4$), 93.75 ($C_2$), 73.59 ($C_1$), 64.78 ($C_3$), 53.93 ($OCH_3$), 39.26 ($C_5$), 36.90 ($C_6$). Anal. Calcd for $C_{10}H_8ClMnO_4$: C, 42.51; H, 2.85. Found: C, 42.55; H, 2.82.

**Tricarbonyl($\eta^5$-cyclohexadienyl)manganese (6).** A typical procedure for addition of $H^-$ (or $D^-$), followed by protonation (or deuteration), to complexes **2** (X = OMe, $NEt_2$, SPh, or Cl) is described for the preparation of complex **6c:**

To a THF solution (10 mL) of complex **2a** (140 mg, 0.56 mmol) at −78 °C is added a solution of 1 M $LiEt_3BD$ in THF (1.7 mL, 1.7 mmol). The reaction mixture is then stirred for 20 min at rt. After being cooled again at −78 °C, a solution of 90 $\mu$L (2 mmol) of MeOH in THF is added. The resulting solution is refluxed for 3 h, then cooled with an ice bath, and added in a 50/50 (pentane/water) mixture. The organic phase is washed twice with water and then with brine, dried over $MgSO_4$, and filtered through a Celite column. Solvents are removed under a $N_2$ flow at 0 °C. The oily residue is purified by flash chromatography to give a yellow powder (100 mg, 0.46mmol, 82% yield). $^1H$ NMR (400 MHz, $C_6D_6$) (see the numeration described in Scheme 3): $\delta$ 5.05 (d, $J$ = 6 Hz, 1H, $H_6$), 4.04 (t, $J$ = 6 Hz, 1H, $H_1$), 2.20 (m, 2H, $H_2$ and $H_4$), 2.09 (dt, $J$ = 6 and 13 Hz, 1H, $H_3$endo), 1.47 (d, $J$ = 12.47 Hz, $H_3$-exo). $^{13}C$ NMR (400 MHz, $C_6D_6$): $\delta$ 223.63 ($Mn(CO)_3$), 97.87 ($C_1$), 97.14 ($C_4$), 79.51 ($C_6$), 48.96 ($C_2$ and $C_4$), 24.07 ($C_3$). IR ($CHCl_3$): 2005, 1935 $cm^{-1}$. Anal. Calcd for $C_9H_6DO_3Mn$: C, 49.33; H, 3.22. Found: C, 49.05; H, 3.18. MS (EI): $m/z$ 219.

**Preparation of Complexes 6a,b,e.** The method is identical with that used for **6c**: 84 mg (0.34 mL) of **2a**, 1 mL (1 mmol) of 1 M L-selectride in THF, and 85 $\mu$L (1.1 mmol) of $CF_3COOD$. After flash chromatography, a yellow powder is obtained (38.1 mg, 51% yield) which is a 50/50 mixture of complexes **6a**,**b** according to spectroscopic data . Anal. Calcd: C, 49.45; H, 3.22. Found: C, 49.23; H, 3.19. MS (EI): $m/z$ 218 (**6a**), 219 (**6b**). IR ($CHCl_3$): 2005, 1940 $cm^{-1}$. The two methylene protons of $C_6H_7Mn(CO)_3$ (**6a**) resonate at $\delta$ 2.09 (dt, br, $J$ = 13 and 6) and 1.47 ($H_{exo}$, d, $J$ = 13) in $C_6D_6$. In the case of a 50:50 mixture of **6a**,**b**, the $H_{exo}$ proton resonates at $\delta$ 1.47 as a broad singlet and the $H_{endo}$ resonates at $\delta$ 2.06 with half the intensity: $\delta$ 5.05 (t, $J$ = 6, $H_6$), 4.04 (t, $J$ = 6), 2.20 (t, $J$ = 6). The $^1H$ NMR spectrum of complex **6e** deuterated at the *exo* position, easily obtained by addition of $D^-$ to (benzene)-manganese tricarbonyl tetrafluoroborate, did not present the signal at the highest field:[5] the $H_{exo}$ resonance at 1.47 ppm in $C_6D_6$ is absent.

**Preparation of Complexes 6c,d.** The method is identical with that used for **6c**: 124 mg (0.5 mmol) of **6a**, 1.5 mL (1.5 mmol) of 1 M $LiEt_3BD$ in THF, and 125 mL (1.6 $\mu$mol) of $CF_3$-COOD. After flash chromatography, a yellow powder is obtained (70.8 mg, 64% yield) which is a 50/50 mixture of complexes **6c**,**d** according to spectroscopic data. Anal. Calcd: C, 49.22; H, 3.21. Found: C, 48.31; H, 3.30. MS (EI): $m/z$ 219 (**6c**), 220 (**6d**). IR ($CHCl_3$): 2005, 1940 $cm^{-1}$. **6d** in a mixture of **6c**,**d** (50:50): the resonance of $H_{endo}$ has half the intensity; $\delta$ 1.46 ($m_{br}$ $H6_{exo}$), 2.20 ($m$), 4.04 (t, $J$ = 6), 5.05 (d, $J$ = 6).

**Preparation of Anionic Complex 3a.** To a THF solution (2.5 mL) of complex **2a** (400 mg, 1.6 mmol) at −78 °C is added a 1 M solution in THF of L-selectride (2.4 mL, 2.4 mmol). The reaction mixture is stirred at room temperature for 15 min and cooled in liquid $N_2$, and a mixture of toluene (10 mL) and pentane (15 mL) is added to induce the formation of two liquid phases. The upper phase is removed, and additional mixture (toluene−pentane) is added to wash the lower phase. Solvents are removed under a 0.1 Torr vacuum to give an oily yellow residue. This complex is not stable for very long in a drybox, but $^1H$ and $^{13}C$ data can be obtained in a sealed NMR tube under dry $N_2$. The NMR spectrum is similar to those described by Brookhart et al. for the anionic ($\eta^4$-cyclohexadiene)manganese tricarbonyl[9a] and to those described by Birch et al. for ($\eta^4$-2-methoxycyclohexadiene)iron tricarbonyl.[11] No analysis and no mass spectrum have been attempted. $^1H$ NMR (400 MHz, THF-$d_8$): $\delta$ 4.38 (dd, $J$ = 2 and 5 Hz, 1H, $H_3$), 3.39 (s, 3H, $OCH_3$), 2.56 (dd, $J$ = 1.8 and 6.5 Hz, 1H, $H_1$), 1.68 (m, 1H, $H_4$), 1.5 (m, 4H, $H_5$ and $H_6$). $^{13}C$ NMR (THF-$d_8$): $\delta$ 233.49 (CO), 138.9 ($C_2$), 63.35 ($C_3$), 53.03 ($OCH_3$), 49.87 ($C_1$), 41.52 ($C_4$), 28.33 ($C_5$ or $C_6$), 26.91 ($C_6$ or $C_5$).

**Preparation of Complex 5a and Isomerization.** The procedure is identical with that previously described for **6c**, except the reflux. The reaction mixture is immediately extracted after MeOH addition: 250 mg (1 mmol) of **2a**, 2 mL (2 mmol) of 1 M L-selectride in THF, and 81 $\mu$L (2 mmol) of MeOH. An oily yellow residue is obtained after chromatography (170 mg, 0.68 mmol, 68% yield; lit.[4a] 79.1%). $^1H$ NMR (500 MHz, $C_6D_6$) for **5a**: the signals are difficult to interpret but can be resolved by the simulating program PANIC (parameter adjustment in NMR by iteration calculation) except the Hb′ proton. The numeration is described in Scheme 3. The R = H signal appeared at $\delta$ −0.06 in $C_6D_6$ as a doublet of triplet of triplet with 14 peaks: $J_{gem(R,Ha)}$ = −12.17, $J_{(R,Hb)}$ = 9.33, $J_{(R,Hb')}$ = 4.63. The Ha proton appeared at 0.17 ppm as a doublet of triplet of triplet with 15 peaks: $J_{gem(Ha,R)}$ = −12.17, $J_{(Ha,Hb')}$ = 6.05, $J_{(Ha,Hb)}$ = 2.02. The Hb′ and H4exo protons resonated at 0.84 ppm as a 14-peak signal, and the Hc protons, at 3.89 ppm as a 12-peak signal. Using the same program, we propose the following $J$ values: $J_{(Hb',Hc)}$ = 3.24, $J_{(Hb',Hb)}$ = −16.53, $J_{(Hb',Ha)}$ = 6.05, $J_{(Hb',R)}$ = 4.63, $J_{(Hc,Hb)}$ = 5.94. At rt the agostic signal (Hb, $H_{4endo} = E_{proton}$) resonated as a broad signal at −6; 2.99 (s, 3H, OMe). $^{13}C$ NMR ($C_6D_6$) $\delta$: 222.5, Mn*C*O; 141.6, ($C_2$); 55.2 ($C_{1,3}$); 53.2 (OMe); 17.6 ($C_5$); 16.9 ($C_{4,6}$). IR ($CHCl_3$): 2050, 2010, 1960, 1925 $cm^{-1}$.

**Isomerization.** Heating pure complex **5a** dissolved in THF-$d_8$ at 70 °C in a sealed NMR tube causes isomerization. After 30 min an equilibrium is reached between **5a** and another complex in a 80:20 ratio. $^1H$ NMR data of the mixture indicate that the new complex could be another cyclohexenyl species **5g** (E = R = H; Scheme 3) with a C-4, C-5, C-6 $\pi$-allyl moiety and a methoxy group at the C-2 position.[14,15] Treating a 20:80 mixture of **5a**,**g** with 0.2 equiv of acid should replace **5g** with **6** and leave **5a** behind as a reviewer suggested to us. But we did not attempt it because it was too difficult to know the quantity of material we exactly had in hand in the reaction mixture in the drybox. We excluded the case of elimination from the unconjugated diene complex, i.e. double bonds between C1,C6 and C3,C4, as suggested by a reviewer, because there is no reason for a conjugated diene to be deconjugated. Indeed, it should give a $\sigma$(C1), $\pi$(C3,C4) complex via an unlikely migration of the hydride E of complex **4** to the C2 carbon followed by an oxidative addition of the hydrogen Hb (carbon C6) by Mn.

**Acknowledgment.** We thank Profs. G. Dana and N. Platzer and Drs. J. P. Djukic and O. Convert for helpful discussions. This work was supported by grants from the French Ministry of University and Scientific Research to F.B. and V.G.

OM960621U