# Stereospecific Endo Hydride Addition to Cyclohexadienylmanganese Complexes

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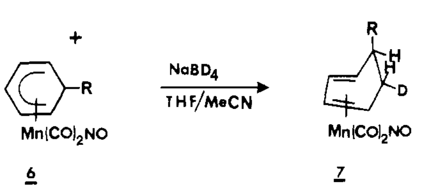
*Summary:* $^1$H NMR and X-ray structural studies show that borohydride addition to dicarbonylnitrosylcyclohexadienylmanganese cations to give cyclohexadiene complexes occurs in a stereospecific endo fashion. This is the first example of stereospecific endo hydride addition to a coordinated cyclic $\pi$-hydrocarbon.

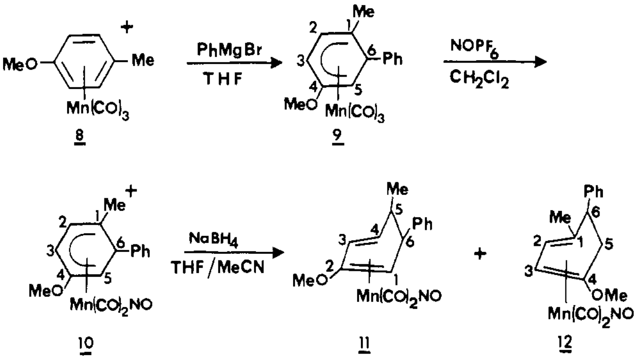
The addition of nucleophiles to coordinated cyclic $\pi$-hydrocarbons is a fundamental organometallic reaction that finds mechanistic, synthetic, and catalytic applications. Virtually all carbon, nitrogen, phosphorus, oxygen, and sulfur donor nucleophiles add stereospecifically exo to the coordinated ring. Lewis et al.[2] have shown that methoxide can add to cyclohexadienyltricarbonyliron to give the endo cyclohexadiene, but even in this case the *kinetic* product is the exo isomer.

Hydride donors (LiAlH$_4$, NaBH$_4$, LiBR$_3$H, etc.) also usually add to coordinated rings in a stereospecific exo manner. For example, exo hydride addition has been verified for (C$_6$H$_6$)Mn(CO)$_3^+$ (1),[3] (C$_6$H$_7$)Mn(CO)$_3$ (2),[3] (C$_6$Me$_6$)Re(CO)$_3^+$ (3),[4] (C$_6$H$_7$)Fe(CO)$_3^+$ (4),[5] and (C$_6$H$_6$)Cr(CO)$_2$NO$^+$ (5).[6] There are, however, several reports[7-10] of hydride addition yielding a mixture of exo and endo products with the amount of endo being at most 50%; due to the reaction conditions used, some of these results may reflect thermodynamic exo/endo equilibration. We recently reported[11] hydride addition to **6** (R = Ph, Me) according to eq 1 and provided NMR evidence that this high yield (>90%) reaction represented the first example of stereospecific endo addition to a coordinated ring. Furthermore, the products obtained were kinetic ones since at equilibrium the exo:endo distribution of deuteride in **7** would be close to 1:1. We have designed a reaction scheme to rigorously test these novel conclusions, and this is reported herein.



(1)

Scheme I



Complexes **8** and **9** (see Scheme I) were prepared in yields of 68% and 100%, respectively, by methods previously described.[12,13] Reaction of **9** with NOPF$_6$ produced **10** quantitatively as the PF$_6^-$ salt.[14] To **10** in THF/MeCN (2:1) at −5 °C under nitrogen excess NaBH$_4$ was added, and the mixture was stirred for 30 min and then allowed to warm to room temperature. Solvent evaporation followed by extraction with pentane gave an isolated yield of 89% of a 1.5:1 mixture of **11** and **12**. Separation was effected by TLC on alumina with hexane. Complex **11** is very stable, but **12** slowly decomposes in solution.[15,16]

NMR decoupling experiments showed that 5-H and 6-H in **11** are coupled by $J$ = 11 Hz, which strongly implies that 5-H is endo, as shown.[11] The reason for doing the chemistry illustrated in Scheme I was to conclusively prove the endo addition by obtaining the X-ray structure of **11**. Slow cooling of a pentane solution of **11** gave suitable crystals for X-ray diffraction.[17] Figure 1 shows the structure, and Table I gives some pertinent bond lengths and angles. The crystal structure of **11** consists of well-separated monomeric units and confirms that hydride addition to **10** occurs

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[13] Compound **9**: IR (hexane) $\nu_{CO}$ 2015, 1942, 1935 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 250 MHz) $\delta$ 1.62 (s, Me), 3.32 (m, 6-H), 3.47 (s, OMe), 3.88 (d, 5-H), 4.67 (d, 2-H), 5.55 (m, 3-H).

[14] Compound **10**: IR (CH$_3$NO$_2$) $\nu_{CO}$ 2103, 2068 cm$^{-1}$, $\nu_{NO}$ 1833 cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$) $\delta$ 1.96 (s, Me), 3.87 (s, OMe), 4.14 (d, 6-H), 4.28 (m, 5-H), 5.73 (m, 2-H), 6.65 (dd, 3-H). Anal. Calcd for C$_{16}$H$_{15}$NO$_4$MnPF$_6$: C, 39.60; H, 3.12; N, 2.89. Found: C, 39.42; H, 3.20; N, 2.69.

[15] Compound **11**: IR (hexane) $\nu_{CO}$ 2034, 1983 cm$^{-1}$, $\nu_{NO}$ 1748 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.36 (d, $J$ = 7 Hz, Me), 2.18 (m, 5-H), 2.64 (dd, $J$ = 3.5, 7 Hz, 4-H), 3.63 (t, $J$ = 2.5, 2.5 Hz, 1-H), 3.67 (s, OMe), 3.73 (dd, $J$ = 2.5, 11 Hz, 6-H), 5.43 (dd, $J$ = 2.5, 7Hz, 3-H). Coupling constant assignments: $J$(5-H, 5-Me) = 7 Hz, $J$(4-H,3-H) = 7 Hz, $J$(5-H,6-H) = 11 Hz, $J$(4-H, 5-H) = 3.5 Hz, $J$(1-H,6-H) = 2.5 Hz, $J$(1-H,3-H) = 2.5 Hz. Anal. Calcd for C$_{16}$H$_{16}$NO$_4$Mn: C, 56.32; H, 4.72; N, 4.10. Found: C, 56.50; H, 4.90; N, 4.00.

[16] Compound **12**: IR (hexane) $\nu_{CO}$ 2029, 1968 cm$^{-1}$, $\nu_{NO}$ 1739 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 1.63 (s, Me), 2.32 (dd, $J$ = 5, 16 Hz, 5-H exo), 2.88 (dd, $J$ = 11, 16 Hz, 5-H endo), 3.35 (m, 6-H), 3.53 (s, OMe), 4.93 (d, $J$ = 5 Hz, 2-H), 5.83 (d, $J$ = 5 Hz, 3-H). Compound too unstable for elemental analysis.

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Table I. Selected Bond Lengths (Å) and Angles (deg) for Complex **11**

Bond Lengths

| | | | |
|---|---|---|---|
| Mn-C1 | 1.823 (4) | C4-O4 | 1.362 (4) |
| Mn-C2 | 1.841 (4) | O4-C9 | 1.404 (4) |
| Mn-N | 1.675 (3) | C3-C4 | 1.401 (4) |
| C1-O1 | 1.151 (5) | C3-C8 | 1.510 (4) |
| C2-O2 | 1.127 (5) | C4-C5 | 1.407 (4) |
| N-O3 | 1.174 (3) | C5-C6 | 1.418 (5) |
| Mn-C3 | 2.134 (3) | C6-C7 | 1.500 (4) |
| Mn-C4 | 2.145 (3) | C7-C8 | 1.565 (5) |
| Mn-C5 | 2.079 (3) | C7-C10 | 1.525 (4) |
| Mn-C6 | 2.118 (3) | C8-C11 | 1.519 (4) |

Bond Angles

| | | | |
|---|---|---|---|
| Mn-C1-O1 | 178.0 (3) | C4-C3-C8 | 120.9 (2) |
| Mn-C2-O2 | 178.4 (3) | C3-C8-C11 | 113.8 (3) |
| Mn-N-O3 | 176.7 (3) | C6-C7-C10 | 109.2 (3) |
| C3-C4-C5 | 114.8 (3) | C7-C8-C11 | 114.3 (2) |
| C4-C5-C6 | 112.4 (3) | C8-C7-C10 | 114.7 (3) |
| C5-C6-C7 | 119.9 (3) | O4-C4-C5 | 125.9 (2) |
| C6-C7-C8 | 108.7 (2) | O4-C4-C3 | 118.9 (3) |
| C3-C8-C7 | 108.6 (2) | | |

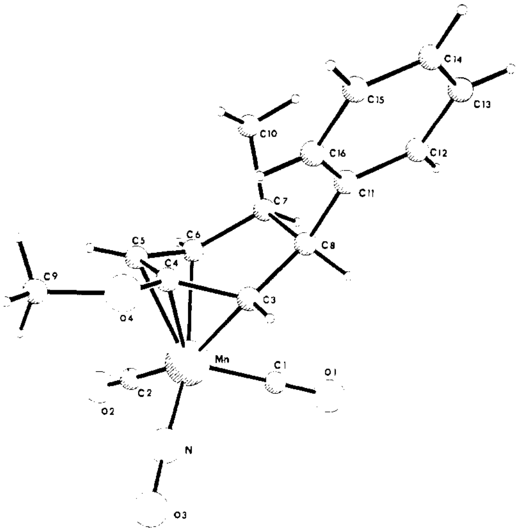

**Figure 1.** Structure and atom numbering scheme for dicarbonylnitrosyl[1-4-$\eta^4$-(2-methoxy-5-methyl-6-phenylcyclohexa-1,3-diene)]manganese, complex **11**.

endo. This result and the correlation of NMR coupling constants for **11** and **7** also confirm that deuteride adds stereospecifically endo to **6** as shown in eq 1.[11]

The diene portion of **11** (C3-C4-C5-C6, Figure 1) is approximately planar (maximum deviation 0.034 Å; C3-C4-C5-C6 dihedral angle = 7.1°). The carbon atoms C3-C6-C7-C8 are only roughly planar (maximum deviation 0.058 Å). The dihedral angle between these two planes is 42.5°, a typical value for cyclohexadiene complexes.[19,20] A small dihedral angle of −10.3° for H7-C7-C8-H8 agrees with the large coupling constant (11 Hz) for H7-H8. The hydrogen atoms H3, H5, and H6 are displaced slightly (0.06 Å) toward the metal, an expected result.[20] Bond lengths and angles for **11** are typical, except for the C8-C7-C10 and C7-C8-C11 angles of 114.7 (3)° and 114.3 (2)°, respectively, which are several degrees larger than expected probably due to slight steric repulsion of the exo methyl and phenyl groups.

Having established that borohydride adds stereospecifically endo to complexes **6** and **10**, it remains to unravel the reasons why dicarbonylnitrosylcyclohexadienylmanganese cations react in this unique manner. Although the answer is not yet known, several observations can be made at this time. Endo hydride addition is not due to steric congestion around the carbon being attacked since **3** undergoes exo hydride addition and **6** (R = Me, Ph) is known to add $PBu_3$ exo with little steric interaction in the diene products.[21] We also found that hydride adds endo to **6** (R = Ph) even when one of the CO ligands is replaced by the bulky $PBu_3$ ligand.[6] Brookhart et al.[10] have proposed that *apparent* endo hydride addition at a carbon bonded to a methyl in tricarbonyl(1,3,5-trimethylcyclohexadienyl)manganese may in fact occur via exo addition at an unsubstituted carbon to give a $\sigma,\pi$-allyl intermediate that undergoes endo hydride migration via the metal to give product. Such a mechanism in our reactions can be ruled out because of the results of eq 1 with borodeuteride and because the reaction conditions are too mild to allow ring isomerizations.

Endo hydride addition to **6** and **10** suggests an initial interaction at the metal or CO, followed by migration to the ring. The presence of a nitrosyl ligand may be important since it can act as an electron sink if the metal is attacked. It is also quite possible that the initial interaction of borohydride and **6** and **10** involves single electron transfer to generate a reactive radical that can be a 19- or 17-electron species depending on the nitrosyl bonding mode. However, electron transfer does not necessarily lead to an endo product since (arene)Fe(cp)$^+$ cations give exo hydride addition products[6] that are thought to be formed following initial electron transfer.[22]

Experiments designed to establish the mechanism of endo hydride addition to **6**, **10**, and related species are in progress.

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**Registry No.** **8**, 86748-09-6; **9**, 86765-93-7; **10**, 86765-95-9; **11**, 86748-10-9; **12**, 86748-11-0.

**Supplementary Material Available:** Listings of observed and calculated structure factors, anisotropic thermal parameters, hydrogen isotropic thermal parameters, atomic coordinates, interatomic distances, and bond angles (13 pages). Ordering information is given on any current masthead page.

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(17) Crystal data: $C_{16}H_{16}NO_4Mn$, orange-red color, $M_r$ 341.25, space group $P2_1/c$, $a$ = 12.086 (4) Å, $b$ = 10.599 (3) Å, $c$ = 13.114 (3) Å, $\beta$ = 108.96 (2)°, $Z$ = 4, $\rho_{calcd}$ = 1.427 g/cm$^3$; 1802 unique reflections with $F_o > \sigma(F_o)$ were measured by using Mo K$\alpha$ radiation (graphite monochromator) and a Nicolet R3 diffractometer. The structure was solved by using direct and vector methods and refined by using the blocked-cascade least-squares method as implemented by Sheldrick.[18] At convergence $R$ and $R_w$ had values of 0.037 and 0.054, respectively, and there was no residual electron density peaks as high as those assigned to the last located hydrogen atom. In the final cycles hydrogen atoms were included in calculated positions ($r_{C-H}$ = 0.96 Å) for the methyl and phenyl groups, but the positional parameters for H3, H5, H6, H7, and H8 were refined. Anisotropic thermal parameters were refined for non-hydrogen atoms. For the hydrogen atoms isotropic thermal parameters were tied to the equivalent isotropic thermal parameters of their attached carbon atoms.

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