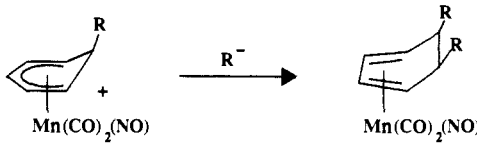
Mechanism of Stereospecific Endo Addition of Hydride to Cyclohexadienylmanganese and -rhenium Complexes

R. D. Pike, W. J. Ryan, N. S. Lennhoff, J. Van Epp, and D. A. Sweigart*

Contribution from the Department of Chemistry, Brown University, Providence, Rhode Island 02912. *Received November 9, 1989*

Abstract: The addition of hydride donors ($NaBH_4$, $LiBEt_3H$, etc.) to the ring in (cyclohexadienyl)$M(CO)(NO)(L)^+$ (M = Mn, Re; L = CO, PMe_3) gives the cyclohexadiene complexes with the added hydride situated stereospecifically endo to the metal. IR and NMR show that (6-*exo*-$PhC_6Me_5H)Re(CO)_2NO^+$ (**1**) reacts with Bu_4NBH_4 in CH_3CN at −35 °C to form a neutral formyl intermediate that more slowly converts to the cyclohexadiene complex. The manganese analogue reacts more rapidly with hydride donors than does **1** and does not show spectral evidence for a formyl intermediate; nevertheless, it is probable that a reactive formyl species is formed initially, followed by hydride migration to the cyclohexadienyl ring. With (6-*exo*-$PhC_6H_6)Mn(NO)(L\text{-}L)^+$ (**6**, L-L = dppe; **7**, L-L = dppen), which do not contain a carbonyl ligand, hydride donors react by exo attack at the C-2 carbon to give the novel σ,π-allyl complexes (6-*exo*-Ph,1-σ-3-5-η-$C_6H_7)Mn(NO)(L\text{-}L)$; the structure of the σ,π-allyl product with L-L = dppen was verified by X-ray diffraction. The conclusion is reached that endo addition to a coordinated cyclohexadienyl ring requires a carbonyl ligand. For hydride additions to coordinated cyclic π-hydrocarbons in general, it is likely that the ability to form a formyl intermediate is a necessary but not sufficient condition to guarantee that the hydride will be situated endo in the final product. Indirect evidence, based on recent observations that certain organolithium reagents react with (cyclohexadienyl)$Mn(CO)(NO)L^+$ via initial carbonyl attack, suggests that the formyl intermediate converts to a metal carbonyl hydride prior to the hydride migration to the dienyl ring to give the ultimate *endo*-diene product.

The addition of nucleophiles to coordinated π-hydrocarbons, as typified by reaction 1, is one of the fundamental reactions of organometallic chemistry. The exploitation of reactions of this

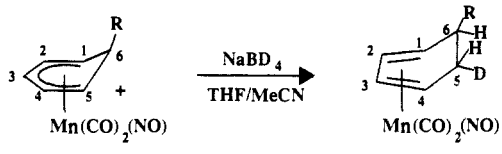


(1)

type for synthetic purposes has benefited from studies of the associated thermodynamic, mechanistic, regiochemical, and stereochemical factors. For example, extensive kinetic studies of phosphorus and nitrogen donor addition to coordinated cyclic and acyclic π-hydrocarbons show that the relative electrophilic reactivities of the organometallic complexes are *independent* of the nucleophile.[1-7] This remarkable result means that it is possible to predict the extent to which various organometallic fragments will activate a π-hydrocarbon upon coordination.

Reaction 1 illustrates the common regiochemical result that nucleophiles add at the terminus of the π-system. Attack at an internal position is, however, known to occur in some cases (vide infra). Reaction 1 also typifies the stereochemistry generally, namely, that the product has the nucleophile situated on the side of the π-system opposite the metal and its other ligands. Most likely, this exo stereochemistry results from direct bimolecular attack on the exo face of the π-hydrocarbon. When the nucleophile attacks initially at the metal or a CO ligand, subsequent migration of the nucleophile to the π-hydrocarbon would be expected to give an endo product. There are a few reports of endo addition, but the role of intermediates is not clear. Thus, simply heating (cyclohexadienyl)$Os(CO)_3^+$ in methanol products the *endo*-methoxycyclohexadiene complex, $(C_6H_7OMe)Os(CO)_3$.[8] In contrast, the addition of NaOMe to $(C_6H_7)Os(CO)_3^+$ in methanol gives the carbomethoxy intermediate $(C_6H_7)Os(CO)_2CO_2Me$, which upon heating rearranges to the *exo*-OMe product. With $(C_6H_7)Fe(CO)_3^+$, the *endo*-methoxycyclohexadiene complex is formed in methanol, but only after complete initial reaction to give the *exo*-OMe analogue. In another study, it is claimed[9] that certain tertiary phosphines add in an endo manner to (cycloheptadienyl)$Fe(CO)_3^+$ in acetonitrile via an intermediate suggested to contain a Fe–PR_3 link; with most phosphines and in other solvents the addition is stereospecifically exo.

In this paper we are concerned with the stereochemical course of hydride addition to coordinated π-hydrocarbons. Hydride donors ($LiAlH_4$, $NaBH_4$, $LiBR_3H$, etc.) have been shown[10,11] to add stereospecifically exo to a variety of complexes: $(C_6H_6)Mn(CO)_3^+$, $(C_6H_7)Mn(CO)_3$, $(C_7H_8)Mn(CO)_3^+$, $(C_6Me_6)Re(CO)_3^+$, $(C_6H_nMe_{6-n})Cr(CO)_2NO^+$, $(C_7H_7)Cr(CO)_3^+$, $(C_6H_7)Fe(CO)_3^+$, $(C_4H_4)Fe(CO)(L)NO^+$, and $(C_6H_6)FeCp^+$. There are several reports of hydride addition yielding a mixture of exo and endo products.[12,13] These include reactions of (tropylium)$Mo(CO)_3^+$ and (1,5-dimethyl-3-methoxycyclohexadienyl)$Fe(CO)_3^+$. With the latter complex it is possible that the endo product arises from exo attack to an internal position (C-2) in the π-system, followed by hydride migration via the metal to C-1. Stereospecific endo addition of hydride is extremely rare. The first example, reported by us in 1982, was $NaBD_4$ addition to (6-*exo*-phenylcyclohexadienyl)$Mn(CO)_2NO^+$ in THF/MeCN as shown in eq 2.[14] Since then, we have found[1,15-19] that hydride



(2)

(1) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.
(2) Honig, E. D.; Meng, Q.-J.; Robinson, W. T.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1985**, *4*, 871.
(3) Alavosus, T. J.; Sweigart, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 985.
(4) Camaioni, C. A.; Sweigart, D. A. *J. Organomet. Chem.* **1985**, *282*, 107.
(5) Chung, Y. K.; Sweigart, D. A. *J. Organomet. Chem.* **1986**, *308*, 223.
(6) Honig, E. D.; Sweigart, D. A. *J. Organomet. Chem.* **1986**, *308*, 229.
(7) Hanna, T.; Lennhoff, N. S.; Sweigart, D. A. *J. Organomet. Chem.* **1989**, *377*, 133.
(8) Bryan, E. G.; Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Schiavon, G. M. *J. Organomet. Chem.* **1977**, *129*, C19. Burrows, A. L.; Hine, K.; Johnson, B. F. G.; Lewis, J.; Parker, D. G.; Poe, A.; Vichi, E. J. S. *J. Chem. Soc., Dalton Trans.* **1980**, 1135.
(9) Brown, D. A.; Glass, W. K.; Hussein, F. M. *J. Organomet. Chem.* **1981**, *218*, C15. Brown, D. A.; Chawla, S. K.; Glass, W. K.; Hussein, F. M. *Inorg. Chem.* **1982**, *21*, 2726. Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K.; Sayal, P. K. *Organometallics* **1984**, *3*, 1137.
(10) Bird, P. H.; Churchill, M. R. *J. Chem. Soc., Chem. Commun.* **1967**, 777. Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem. Soc. A* **1968**, 332. Birch, A. J.; Chamberlain, K. B.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1900. Connelly, N. G.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2334. Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638.
(11) Honig, E. D.; Sweigart, D. A. Unpublished results.
(12) Faller, J. W. *Inorg. Chem.* **1980**, *19*, 2857.
(13) Birch, A. J.; Ratnayake Bandara, B. M.; Chamberlain, K.; Chauncy, B.; Dahler, P.; Day, A. I.; Jenkins, I. D.; Kelly, L. F.; Khor, T.-C.; Kretschmer, G.; Liepa, A. J.; Narula, A. S.; Raverty, W. D.; Rizzardo, E.; Sell, C.; Stephenson, G. R.; Thompson, D. J.; Williamson, D. H. *Tetrahedron* **1981**, *37*, 289. Birch, A. J.; Stephenson, G. R. *J. Organomet. Chem.* **1981**, *218*, 91.

0002-7863/90/1512-4798$02.50/0

addition to this class of electrophiles is stereospecifically (and kinetically) endo in a general sense. For example, the stereochemistry is endo regardless of the hydride source, the nature of the R group, or the presence of substituents on the dienyl C-1 to C-5 carbons. Similarly, the ring may be cycloheptadienyl, one of the CO ligands may be substituted by a tertiary phosphine, or the metal can be replaced by rhenium and hydride addition is still endo. The only other reported example of stereospecific endo hydride addition to a coordinated ring deals with [(thiabenzene 1-oxide)$Cr(CO)_2NO]PF_6$, which reacts to give a σ,π-allyl product.[20]

The endo stereochemistry observed in these reactions suggests an initial interaction with the metal to form a M–H or M–CHO species, followed by hydride migration to give the diene (or σ,π-allyl) product. The nitrosyl ligand could act as an electron sink if a metal hydride is formed initially. However, a nitrosyl group is not sufficient to guarantee endo addition (vide supra). There are a number of reactions known in which the hydride ligand in a metal hydride (reactant or intermediate) migrates to an endo position in a cyclic π-hydrocarbon.[21] (Apparently, (arene)$Mn(CO)_2H$ is an exception.[22]) A study of $LiAlD_4$ addition to $CpFe(dppe)CO^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) showed[23] that at low temperature the metal formyl forms, which upon warming converts to CpFe(dppe)(CO)D; thermal migration of the deuteride from this complex gave the *endo*-D diene, $(C_5H_5D)Fe(dppe)CO$. In contrast, addition of $LiAlD_4$ to $CpFe(dppe)CO^+$ at high temperature gave the *exo*-D diene, suggesting that direct attack on the ring can compete with attack on a CO. It is also possible that the initial interaction with hydride sources is single-electron transfer to generate a 19- or 17-electron species, depending on the bonding mode of the nitrosyl. However, single-electron transfer does not necessarily lead to an endo product, as shown with hydride addition to (arene)$FeCp^+$ complexes, which are known to involve initial electron transfer[24] but give exo products.[11]

In this paper we present results of synthetic, low-temperature IR, low-temperature NMR, electrochemical, and X-ray studies designed to probe the mechanism of hydride addition to the ring in (cyclohexadienyl)$Re(CO)_2NO^+$ and (cyclohexadienyl)$Mn(L)(L')NO^+$ cations (L = L' = CO; L = CO, L' = PMe_3; L = L' = $^1/_2$dppe; L = L' = $^1/_2$dppen) (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene). When at least one CO ligand is present, the addition to give the diene is endo; a formyl intermediate was detected with rhenium as the metal. With (6-*exo*-phenylcyclohexadienyl)$Mn(NO)dppen^+$, which contains no CO ligand, hydride attacks in an exo manner to give a σ,π-allyl product.

Experimental Section

General Procedures. All solvents were purified by standard methods, and all synthetic procedures were carried out under an atmosphere of nitrogen or argon. IR spectra were recorded on a Mattson Alpha Centauri FTIR, and ^1H NMR spectra were obtained on a Bruker WM250 or AM400 instrument. The syntheses of all new cyclohexadienyl complexes are described below; others were prepared as previously reported.[16,18]

[(6-*exo*-PhC_6H_6)Mn(CO)(NO)PMe_3]PF_6. PMe_3 (7.25 mL of 1.00 M THF solution) was added via syringe and with stirring to a room-temperature solution of $[(C_6H_6)Mn(CO)_3]PF_6$[16,25] (2.62 g, 7.24 mmol) in 150 mL of CH_3CN. IR spectra showed, as expected,[25] the immediate formation of (6-*exo*-$PMe_3C_6H_6)Mn(CO)_3^+$ (ν_{CO} 2028, 1951 cm^{-1}). The mixture was stirred for 5 h under a 52-W incandescent lamp, resulting in complete conversion to $[(C_6H_6)Mn(CO)_2PMe_3]PF_6$. The reaction mixture was concentrated to 30 mL and filtered and the product precipitated with diethyl ether. Residual PMe_3 was removed by overnight Soxhlet extraction with ether. The yellow crystalline product was obtained in 75% yield: 2.22 g, 5.41 mmol; IR (CH_2Cl_2) 2004, 1960 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 6.04 (d, J = 1.6 Hz, C_6H_6), 1.65 (d, J = 10.4 Hz, PMe_3).

Over the course of 2 h, PhMgBr (7.0 mL of 3.0 M ether solution) was added via syringe to a cooled (0 °C) solution of $[(C_6H_6)Mn(CO)_2PMe_3]PF_6$ (1.27 g, 3.09 mmol) in 120 mL of CH_2Cl_2. At this point IR spectra showed that the reaction was complete. Water (1 mL) was added and the solvent removed. To the yellow residue was added water (10 mL) and the slurry extracted with three 25-mL portions of ether. The ether was dried for 2 h over $MgSO_4$, filtered, and evaporated to yield a yellow-brown oil that was chromatographed on neutral alumina with ether. Solvent removal left 0.929 g of bright yellow crystals (2.72 mmol, 88%) of (6-*exo*-$PhC_6H_6)Mn(CO)_2PMe_3$: IR (C_5H_{12}) 1941, 1881 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.1 (m, Ph), 5.46 (tt, J = 6.4, 1.5 Hz, H^3), 4.58 (q, J = 5.2 Hz, $H^{2,4}$), 3.73 (t, J = 6.0 Hz, H^6), 3.09 (td, J = 6.0, 1.1 Hz, $H^{1,5}$), 1.29 (d, J = 8.5 Hz, PMe_3). Anal. Calcd for $C_{17}H_{20}O_2PMn$: C, 59.6; H, 5.90. Found: C, 59.9; H, 5.96.

To (6-*exo*-$PhC_6H_6)Mn(CO)_2PMe_3$ (0.713 g, 2.09 mmol) in 40 mL of CH_2Cl_2 at room temperature was added $NOPF_6$ (0.364 g, 2.08 mmol) with stirring. The solution turned red and effervesced. After 30 min the product was precipitated with ether and purified by dissolving in CH_3CN, filtering, and reprecipitating with ether to give 0.696 g (68%) of the yellow-orange [(6-*exo*-$PhC_6H_6)Mn(CO)(NO)PMe_3]PF_6$: IR ($CH_2Cl_2$) 2032, 1784 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.27, 6.98 (q, d, J = 7.6 Hz, Ph), 6.58 (t, J = 5.3 Hz, H^3), 5.71 (q, J = 6.5 Hz, H^2), 5.46 (t, J = 6.4 Hz, H^4), 5.19 (t, J = 6.3 Hz, H^5), 3.75 (m, $H^{1,6}$), 1.63 (d, J = 11.2 Hz, PMe_3). Anal. Calcd for $C_{16}H_{20}O_2NP_2F_6Mn$: C, 39.3; H, 4.13; N, 2.86. Found: C, 38.3; H, 4.10; N, 2.68. (It may be noted that the PBu_3 analogue can be synthesized with a greater yield (85%).[16]) Hydride reagents, e.g., $NaBH_4$, readily convert [(6-*exo*-$PhC_6H_6)Mn(CO)(NO)PMe_3]PF_6$ to the cyclohexadiene complex, (6-*exo*-$PhC_6H_7)Mn(CO)(NO)PMe_3$, in good yields; synthetic and characterization details are presented elsewhere.[19]

[(6-*exo*-PhC_6H_6)Mn(NO)dppe]PF_6. [(6-*exo*-$PhC_6H_6)Mn(CO)_2NO]PF_6$ (1.21 g, 2.75 mmol) and dppe (Strem, 1.20 g, 3.01 mmol) were suspended in 150 mL of CH_2Cl_2. The evolution of CO and a color change from yellow to red began immediately; the mixture was refluxed for 4 h, after which the solution was homogeneous and the color a deep red-brown. The solution was concentrated to 25 mL and the product precipitated with diethyl ether. Purification was effected by overnight Soxhlet extraction with toluene. Air-stable red-orange crystals of [(6-*exo*-$PhC_6H_6)Mn(NO)dppe]PF_6$ (1.68 g, 78%) were obtained by slow precipitation from acetonitrile with ether: IR (CH_2Cl_2) 1754 cm^{-1}; ^1H NMR[26] (CD_2Cl_2) δ 7.5 (m, Ph^{dppe}), 7.07 (m, $Ph^{6\text{-exo}}$), 6.65 (t, J = 3.5 Hz, H^3), 6.51 (d, J = 4.2 Hz, $Ph^{6\text{-exo}}$), 5.22 (t, J = 3.7 Hz, $H^{2,4}$), 3.47 (m, CH_2CH_2), 3.05 (br, $H^{1,5}$), 1.94 (t, J = 3.3 Hz, H^6). Anal. Calcd for $C_{38}H_{35}NOP_3F_6Mn$: C, 58.2; H, 4.51; N, 1.79. Found: C, 58.3; H, 4.63; N, 1.67.

[(6-*exo*-PhC_6H_6)Mn(NO)dppen]PF_6. [6-*exo*-$PhC_6H_6)Mn(CO)_2NO]PF_6$ (0.775 g, 1.76 mmol) and dppen (Pressure; 0.703 g, 1.78 mmol) were suspended in 50 mL of CH_2Cl_2. Evolution of CO occurred, and the color changed from yellow to red as the mixture was refluxed for 1 h. The solution was concentrated to 10 mL and treated as above with the dppe analogue to yield air-stable orange crystals: 0.731 g, 53%; IR (CH_2Cl_2) 1763 cm^{-1}; ^1H NMR[26] (CD_2Cl_2) δ 8.46 (d, J = 57 Hz; dd, J = 45, 12 Hz, CHCH), 7.3 (m, Ph^{dppen}), 7.07 (m, $Ph^{6\text{-exo}}$), 6.81 (t, J = 5.7 Hz, H^3), 6.48 (d, J = 4.2 Hz, $Ph^{6\text{-exo}}$), 5.19 (br, $H^{2,4}$), 3.25 (br, $H^{1,5}$), 1.90 (t, J = 5.9 Hz, H^6). Anal. Calcd for $C_{38}H_{33}NOP_3F_6Mn$: C, 58.4;

(14) Chung, Y. K.; Choi, H. S.; Sweigart, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* **1982**, *104*, 4245.
(15) Chung, Y. K.; Honig, E. D.; Robinson, W. T.; Sweigart, D. A.; Connelly, N. G.; Ittel, S. D. *Organometallics* **1983**, *2*, 1479.
(16) Chung, Y. K.; Sweigart, D. A.; Connelly, N. G.; Sheridan, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 2388.
(17) Honig, E. D.; Sweigart, D. A. *J. Chem. Soc., Chem. Commun.* **1986**, 691.
(18) Pike, R. D.; Alavosus, T. J.; Camaioni-Neto, C. A.; Williams, J. C.; Sweigart, D. A. *Organometallics* **1989**, *8*, 2631.
(19) Pike, R. D.; Ryan, W. J.; Carpenter, G. B.; Sweigart, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 8535.
(20) Weber, L.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 498.
(21) Roth, W. R.; Grimme, W. *Tetrahedron Lett.* **1966**, 2347. Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1980**, *102*, 3490. Karel, K. J.; Brookhart, M.; Aumann, R. *J. Am. Chem. Soc.* **1981**, *103*, 2695. Bunting, H. E.; Green, M. L. H.; Newman, P. A. *J. Chem. Soc., Dalton Trans.* **1988**, 557. Baudry, D.; Boydell, P.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1986**, 531.
(22) Rush, P. K.; Noh, S. K.; Brookhart, M. *Organometallics* **1986**, *5*, 1745. Wilmoth, M. A.; Bernhardt, R. J.; Eyman, D. P.; Huffman, J. C. *Organometallics* **1986**, *5*, 2559.
(23) Davies, S. G.; Hibberd, J.; Simpson, S. J.; Thomas, S. E.; Watts, O. *J. Chem. Soc., Dalton Trans.* **1984**, 701.
(24) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.
(25) Kane-Maguire, L. A. P.; Sweigart, D. A. *Inorg. Chem.* **1979**, *18*, 700.
(26) It was determined that, in these and similar complexes, rotation of the cyclohexadienyl ring (at room temperature) is comparable to the NMR time scale, which led to some partially decoalesced signals; a full study of the fluxional properties is in progress: Alavosus, T. J.; Bushweller, C. H.; Lennhoff, N. S.; Pike, R. D.; Sweigart, D. A. Research in progress.

H, 4.26; N, 1.79. Found: C, 58.5; H, 4.46; N, 1.73.

Hydride Addition Reactions. To [(6-*exo*-PhC_6H_5)Mn(NO)dppe]PF_6 (44.2 mg, 0.0565 mmol) suspended in 15 mL of THF at 0 °C was added $LiBEt_3H$ (0.060 mL of 1.0 M THF solution) via syringe and with stirring. The orange suspension became homogeneous and red within a few minutes. After 10 min the solvent was evaporated, and the red-brown residue was taken up into ether and filtered through a plug of deactivated neutral alumina. Solvent evaporation left (6-*exo*-Ph,1-σ,3-5-η-C_6H_7)-Mn(NO)dppen as an air-sensitive red-brown solid: 34.0 mg, 94%; IR (ether) 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5 (m, Ph^{dppe}), 6.92 (t, J = 7.2 Hz, $Ph^{6\text{-exo}}$), 6.71 (d, J = 7.1 Hz, $Ph^{6\text{-exo}}$), 4.59 (t, J = 6.5 Hz, H^4), 4.46 (br t, H^5), 4.16 (br, t, H^3), 2.9 (m, CH_2CH_2), 2.45 (t, J = 5.2 Hz, H^6), 1.62 (d, J = 14 Hz, $H^{2\text{-exo}}$), 0.94 (m, $H^{2\text{-endo}}$), −1.33 (m, H^1). Upon standing in solution or attempting chromatography, the complex converted to an unidentified red byproduct, which may be $Mn(NO)(dppe)_2$: IR (ether) 1660 cm^{-1}; ^1H NMR (C_6D_6) δ 7.3 (m, Ph), 2.0 (m, CH_2CH_2).

To [6-*exo*-PhC_6H_6)Mn(NO)dppen]PF_6 (42.0 mg, 0.0538 mmol) suspended in 30 mL of THF at 0 °C was added $LiBEt_3H$ (0.10 mL of 1.0 M THF solution) via syringe and with stirring. The orange suspension became homogeneous and red almost immediately. After 1 h the solvent was removed and the red-orange residue taken up into $CDCl_3$ and filtered through a plug of deactivated neutral alumina. Solvent evaporation left (6-*exo*-Ph,1-σ,3-5-η-C_6H_7)Mn(NO)dppen as an air-stable orange solid: 32.1 mg, 94%; IR (ether) 1681 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.25 (d, J = 48; d, J = 15, CHCH), 7.5 (m, Ph^{dppen}), 7.04 (t, J = 7.3 Hz, $Ph^{6\text{-exo}}$), 6.50 (d, J = 7.0 Hz, $Ph^{6\text{-exo}}$), 4.74 (t, J = 6.3 Hz, H^4), 4.69 (br t, H^5), 4.40 (br t, H^3), 2.42 (t, J = 5.2 Hz, H^6), 1.54 (d, J = 13 Hz, $H^{2\text{-exo}}$), 0.82 (dt, J = 13, 5.8 Hz, $H^{2\text{-endo}}$), −1.66 (m, H^1).

Electrochemistry. Cyclic voltammograms were recorded on ca. 5 × 10^{-4} M solutions of the organometallic species in purified dichloromethane containing 0.10 M Bu_4NPF_6. Potential scans of 200 mV/s were generated with a BAS CV27 potentiostat. The working electrode was a 3-mm-diameter glassy carbon disk, and the counterelectrode was a platinum wire. The reference consisted of a Metrohm Ag/AgCl electrode in CH_2Cl_2, which was 0.10 M in Bu_4NClO_4 and saturated with LiCl. Connection to the electrochemical cell was made via a salt bridge containing 0.10 M Bu_4NPF_6 in CH_2Cl_2. Nitrogen saturated with solvent was bubbled through the solution for 10 min and then blanketed over the solution during measurements. All peak potentials and $E_{1/2}$ values were referenced to ferrocene, which had an $E_{1/2}$ value of 0.52 V under the experimental conditions used.

X-ray Structure of (6-*exo*-Ph,1-σ,3-5-η-C_6H_7)Mn(NO)dppen. Crystals suitable for X-ray diffraction were grown by layering an ether solution of the complex with pentane in a 5-mm NMR tube at room temperature. A single crystal (0.48 × 0.36 × 0.42 mm) was glued to a glass fiber, and a Nicolet R3m diffractometer (Mo Kα radiation, 0.710 69 Å) was used to collect data by the θ–2θ technique. Three standard reflections were monitored every 100 reflections. The structure was solved by direct methods with the SHELXTL 5.1 program. The hydrogen atoms H-3, H-4(axial), H-4(equatorial), H-5, and H-7 (see Figures 4 and 5) were located in a difference Fourier map and refined isotropically with the bond length restriction r = 0.96 Å. The other hydrogen atoms were placed in theoretical positions. The difference Fourier maps indicated the presence of a highly disordered small molecule not within van der Waals contact of the manganese complex. An ^1H NMR spectrum ($CDCl_3$) of several of the crystals grown for X-ray studies showed that the complex crystallized with one molecule of diethyl ether. The disordered nature of the ether molecule is the reason for the rather large R value. Relevant crystal data are as follows: formula $C_{38}H_{34}NOP_2MnEt_2O$, space group $P2_12_12_1$ (orthorhombic), a = 9.286 (3) Å, b = 18.046 (7) Å, c = 22.812 (12) Å, V = 3822.5 Å^3, Z = 4, d_{calcd} = 1.24 g cm^{-3}. Data collected at 20 °C: μ = 4.4 cm^{-1}, 2θ limits 4.0–45.0°, 353 variables refined with 2598 unique reflections $I > 1.0\sigma(I)$ to R = 0.078 (R_w = 0.085), GOF = 1.36.

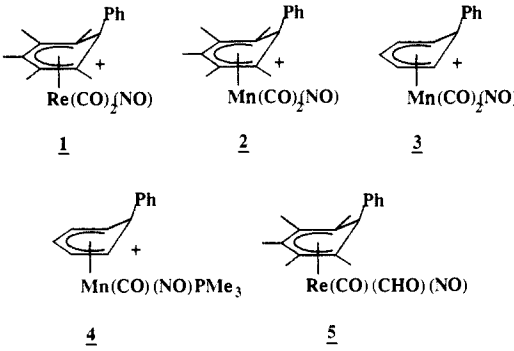
Low-Temperature IR and NMR. The LTIR apparatus was based on a design provided by Professor J. Hubbard, Utah State University. A demountable liquid IR cell containing permanently sealed CaF_2 windows was modified by adding an external frame made of Voltrex brand Teflon shrink tubing, type TTS, connected at three corners by glass elbows and by a glass T-tube at the fourth corner. Pin holes were made in the shrink tubing so that chilled nitrogen gas flowing in from the free end of the T-tube would flow out onto the salt plates in the middle of the frame. An Omega Type T thermocouple was inserted between the cell windows and the cooling frame to monitor the temperature. House nitrogen was used as the cooling gas, the flow of which was controlled by a gate valve and a Whitey valve. The gas flowed through a copper coil immersed in liquid nitrogen and then through a dewared line into the cooling frame. The gap in the FTIR sample compartment necessary to accommodate the dewared line was covered tightly with parafilm so that the spectrometer could be properly purged with nitrogen.

The LTIR spectra were recorded and stored with a routine consisting of 16 scans and a resolution of 4 cm^{-1}; this permitted new spectra to be recorded at 1-min intervals. The IR background was obtained with the cell filled with solvent and room-temperature nitrogen flowing through the cooling frame. Then a 0.3-mL solution containing 2 mg of the manganese or rhenium cyclohexadienyl complex was loaded into the LTIR cell. The bottom port of the cell was fitted with a rubber septum, the top port was closed with a Teflon plug, and both ports were then sealed with parafilm. A 1-mL solution of Bu_4NBH_4 was prepared at a concentration such that 0.05 mL was equivalent to 0.3 mL of the complex solution. The nucleophile solution was then loaded into a 1-mL syringe and a 23-cm needle attached. The needle was inserted into the LTIR cell via the septum on the bottom port, with the syringe remaining outside the IR sample compartment. After purging, the IR spectrum of the dienyl complex was recorded, and the Dewar containing the copper cooling coil was then filled with liquid nitrogen. The temperature was slowly lowered and stabilized at −35 °C (CH_3CN) or −90 °C (CH_2Cl_2) by adjusting the flow control valves. An IR spectrum of the dienyl complex was obtained at low temperature, and 0.05 mL of the nucleophile was injected into the cell. IR spectra were recorded periodically until all reactant had been converted to the cyclohexadiene product. The cell was returned slowly to room temperature and a final spectrum recorded. Slow cooling/warming of the cell is necessary to avoid thermal shock to the salt plates.

Low-temperature ^1H NMR spectra of the metal complexes were obtained with a ca. 3.5-mL solution containing 5–8 mg of the complex in a 10-mm NMR tube capped with a rubber septum. After the spectrum of the complex was recorded and without the sample being warmed, a solution containing 1 equiv of Bu_4NBH_4 in a small volume was injected via syringe to the bottom of the NMR tube and the spin rate increased to vortex and homogenize the sample. Spectra were recorded every 64 s, starting approximately 1.5 min following injection. At the end of the experiments, each solution was warmed to room temperature and a final NMR spectrum recorded.

Results and Discussion

Hydride Addition to (Cyclohexadienyl)M(CO)(NO)L$^+$ Cations. As described previously,[14-16,18,19] hydride reagents ($NaBH_4$, Bu_4NBH_4, Bu_4NBH_3CN, $LiBEt_3H$, etc.) in a variety of solvents add stereospecifically endo to the dienyl ring in complexes **1–4**



1 **2** **3** **4** **5**

to give the corresponding cyclohexadiene complexes, as illustrated by eq 2. A series of IR and NMR experiments were performed in an attempt to detect any reaction intermediates, which in view of the stereochemistry are most likely to be a metal hydride or formyl. With **1** very strong evidence was obtained that hydride attack leads to a formyl complex prior to formation of the diene product. Figures 1 and 2 show IR spectra in CH_3CN of **1** with an equivalent amount of Bu_4NBH_4 added. At room temperature the ν_{CO} and ν_{NO} bands of **1** convert smoothly to those of the diene,[18] with no intermediate in evidence. However, at −35 °C there is rapid ($t_{1/2}$ < 1 min) formation of an intermediate having ν 1986, 1704, 1602 cm^{-1}, which more slowly converse to diene product ($t_{1/2} \approx$ 8 min). The intermediate is almost certainly the formyl **5**, and confirmatory evidence is provided by LTNMR data. An ^1H NMR spectrum obtained within 3 min of mixing **1** and Bu_4NBH_4 in CD_3CN at −35 °C showed the expected formyl resonance (δ 15.49). There was no resonance in the metal hydride region. The IR and NMR data for **5** are quite similar to that reported[27] for CpRe(CO)(NO)CHO (ν 1985, 1709, 1614 cm^{-1}; δ 15.77).

(27) Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589. Tam, W.; Lin, G.-Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525.

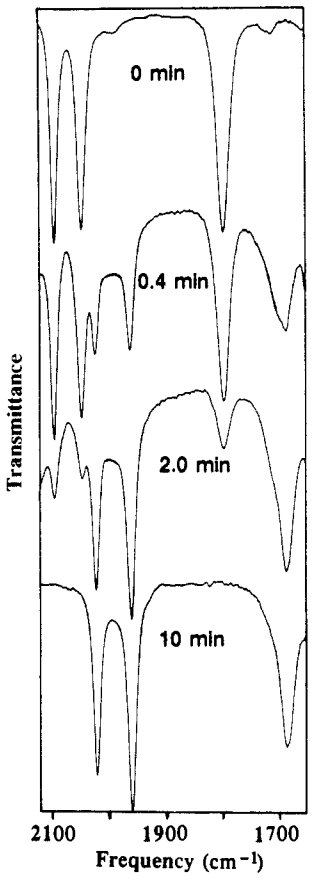


Figure 1. IR spectral changes upon the addition of Bu_4NBH_4 to [(6-*exo*-PhC_6Me_5H)$Re(CO)_2NO$]PF_6 (**1**) in acetonitrile at room temperature.

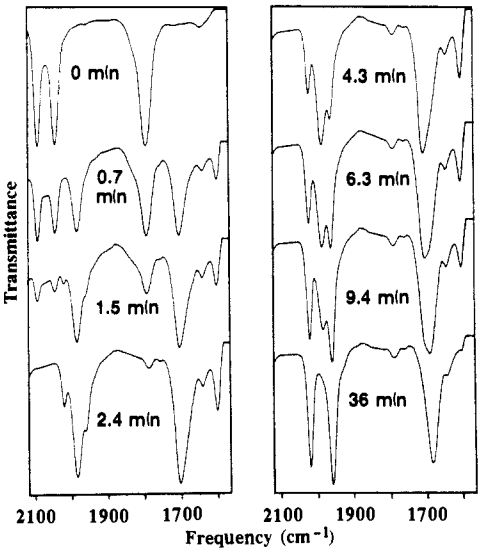


Figure 2. IR spectral changes upon the addition of Bu_4NBH_4 to [(6-*exo*-PhC_6Me_5H)$Re(CO)_2NO$]PF_6 (**1**) in acetonitrile at −35 °C.

In contrast to the behavior of **1**, complex **2** did not give spectral evidence for a formyl intermediate. Even at −90 °C in CH_2Cl_2 IR spectra show only **2** and product diene when Bu_4NBH_4 is added; similar behavior was obtained at −35 °C in CH_3CN except that the reaction time was less ($t_{1/2}$ < 1 min compared to $t_{1/2} \approx$ 4 min). An IR experiment with **3** in CH_3CN at −35 °C likewise showed only reactant and diene product bands, with $t_{1/2} \ll 1$ min. The ^1H NMR spectrum obtained within 3 min of mixing **2** and Bu_4NBH_4 in CD_2Cl_2 at −90 °C did not show evidence for any intermediate species. In order to slow the rate of diene formation and perhaps increase the chances of detecting a formyl, a CO ligand in **3** was replaced by the more electron-donating PMe_3 to give **4**. Complex **4** reacts cleanly with $NaBD_4$ and $LiBEt_3D$ to give the *endo*-diene. IR spectra in CH_3CN at −35 °C showed that **4** and Bu_4NBH_4 react quite slowly ($t_{1/2} \approx$ 130 min), but again no intermediates were seen (Figure 3).

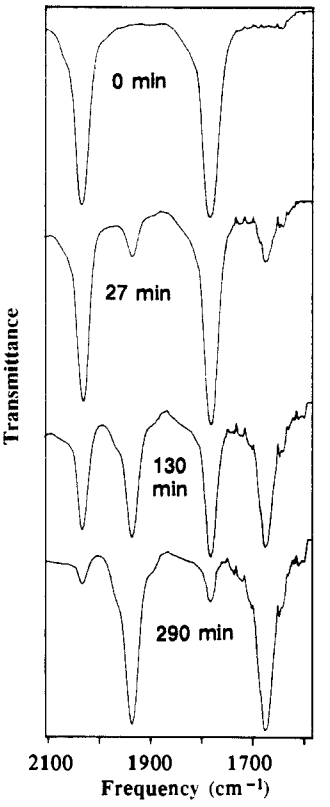


Figure 3. IR spectral changes upon the addition of Bu_4NBH_4 to [(6-*exo*-PhC_6H_6)$Mn(NO)(CO)PMe_3$]PF_6 (**4**) in acetonitrile at −35 °C.

The inability to observe a formyl species in the reaction of **2** or **3** with hydride does not necessarily mean that it does not lie on the reaction pathway and is responsible for the observed endo stereochemistry. It is possible that the formyl forms but reacts at a rate fast enough that its accumulation is prevented. In other words, the rate-limiting step may be attack by hydride on the carbonyl with the manganese complexes. It is known[27] from work with $CpM(CO)(NO)L^+$ cations (L = CO, PR_3) that CpM(CO)(NO)CHO is much more thermally stable with rhenium than with manganese. This does not mean that the equilibrium constant for formation of the formyl is greater for rhenium; rather it only means that the manganese formyl, once formed, is more reactive. This may account for the ca. 10-fold greater rate of diene formation from BH_4^- and **2** compared to **1**. Support for this possibility stems from previous observations[1] that nucleophilic attack on ligands coordinated to manganese and rhenium occurs at similar rates. The IR data summarized above indicated that the rate of formyl formation with **1** is similar to the rate of diene formation with **2**, suggesting that the rate-limiting step in the latter case may be formation of the formyl.

The room-temperature IR spectrum of **1** and Bu_4NBH_4 does not show the formyl intermediate, yet we know that the endo stereochemistry observed with the diene is not temperature-dependent. This argues for the same mechanism at different temperatures. The failure to detect the formyl with **1** at room temperature probably reflects a smaller formation constant compared to −35 °C (the formyl is likely produced exothermically).

It may be noted that theoretical work suggests[28] that hydride attack will occur on the nitrosyl in preference to a carbonyl when both options are available, although there may be subsequent rearrangement to the thermodynamically favored formyl. We found no evidence for attack on the nitrosyl and in the next section

(28) Fenske, R. F.; Millet, M. C. *Organometallics* **1986**, *5*, 1243.

Table I. Atom Coordinates for Complex **9**

atom	x	y	z	atom	x	y	z	atom	x	y	z
Mn	3428 (1)	9335 (1)	1672 (1)	C22	3147 (6)	7011 (4)	3278 (3)	H9	1586	11137	2780
P1	3340 (2)	8084 (1)	1693 (1)	C23	1674 (6)	6885 (4)	3343 (3)	H10	800	11733	3641
P2	5847 (2)	9198 (1)	1658 (1)	C24	720 (6)	7100 (4)	2902 (3)	H11	2132	11611	4514
O	3216 (7)	9404 (4)	428 (2)	C25	1240 (6)	7440 (4)	2396 (3)	H12	4249	10892	4526
N	3267 (7)	9388 (3)	949 (3)	C26	2714 (6)	7566 (4)	2330 (3)	H13	5034	10295	3665
C1	5171 (8)	7734 (4)	1588 (4)	C27	7581 (6)	10121 (3)	2350 (2)	H15	1091	8492	881
C2	6227 (9)	8203 (4)	1556 (4)	C28	8322 (6)	10316 (3)	2859 (2)	H16	−158	7891	118
C3	3513 (7)	9408 (4)	2606 (3)	C29	8481 (6)	9801 (3)	3311 (2)	H17	370	6648	−111
C4	1886 (9)	9301 (5)	2677 (4)	C30	7899 (6)	9093 (3)	3253 (2)	H18	2147	6005	422
C5	1355 (9)	9544 (5)	2095 (4)	C31	7158 (6)	8898 (3)	2744 (2)	H19	3396	6607	1185
C6	1939 (9)	10181 (5)	1840 (4)	C32	6998 (6)	9412 (3)	2293 (2)	H21	4682	7438	2726
C7	3300 (8)	10456 (3)	2015 (3)	C33	8321 (5)	9445 (3)	953 (2)	H22	3803	6864	3581
C8	3887 (8)	10224 (4)	2604 (3)	C34	9108 (5)	9827 (3)	529 (2)	H23	1316	6651	3692
C9	2128 (5)	11087 (3)	3135 (2)	C35	8468 (5)	10405 (3)	217 (2)	H24	−294	7013	2947
C10	1663 (5)	11440 (3)	3646 (2)	C36	7040 (5)	10600 (3)	329 (2)	H25	584	7587	2092
C11	2452 (5)	11368 (3)	4163 (2)	C37	6253 (5)	10219 (3)	753 (2)	H27	7471	10475	2039
C12	3706 (5)	10942 (3)	4170 (2)	C38	6893 (5)	9641 (3)	1065 (2)	H28	8723	10804	2899
C13	4171 (5)	10588 (3)	3660 (2)	H1	5349	7211	1557	H29	8992	9935	3661
C14	3382 (5)	10661 (3)	3143 (2)	H2	7190	8035	1479	H30	8009	8739	3564
C15	1306 (6)	7985 (3)	787 (3)	H3	4249 (41)	9165 (26)	2832 (19)	H31	6757	8410	2705
C16	566 (6)	7629 (3	336 (3)	H4a	1418 (77)	9601 (35)	2969 (25)	H33	8761	9048	1168
C17	879 (6)	6893 (3)	200 (3)	H4e	1605 (78)	8799 (15)	2758 (30)	H34	10090	9693	452
C18	1932 (6)	6512 (3)	516 (3)	H5	403 (37)	9383 (46)	1991 (35)	H35	9009	10667	−75
C19	2672 (6)	6868 (3)	967 (3)	H6	1408	10437	1540	H36	6600	10998	114
C20	2359 (6)	7605 (3)	1103 (3)	H7	3773 (66)	10877 (23)	1845 (26)	H37	5271	10353	831
C21	3667 (6)	7351 (4)	2771 (3)	H8	4896	10329	2643				

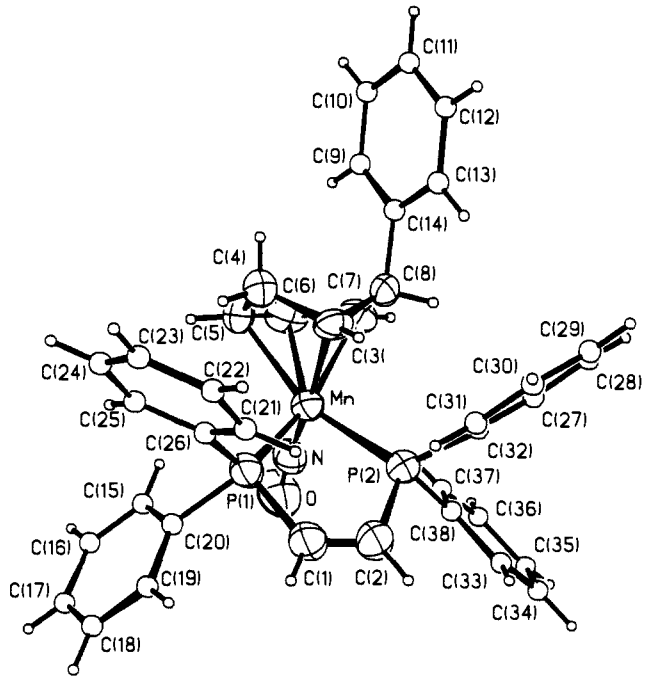
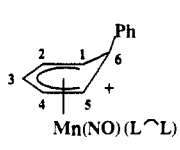
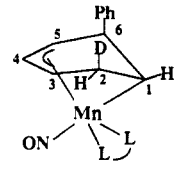


Figure 4. ORTEP drawing of (6-*exo*-Ph,1-σ,3-5-η-C_6H_7)Mn(NO)dppen (**9**) with the thermal ellipsoids at the 50% probability level.

show that the presence of a carbonyl ligand is required for the endo stereochemistry.

Hydride Addition to (Cyclohexadienyl)M(NO)(L-L)$^+$ Cations. In order to test the possible requirement that a carbonyl ligand must be present to get the endo stereochemistry in reaction 2, complexes **6** and **7** were synthesized. The reaction of $LiBEt_3D$





6: L⌒L = dppe

7: L⌒L = dppen

8: L⌒L = dppe

9: L⌒L = dppen

Table II. Selected Bond Distances (Å) and Angles (deg) for Complex **9**

Bond Distances

Mn–P1	2.260 (2)	C3–C8	1.512 (10)	P1–C26	1.823 (7)
Mn–N	1.660 (6)	C5–C6	1.398 (13)	P2–C32	1.840 (6)
Mn–C5	2.186 (8)	C7–C8	1.509 (10)	O–N	1.190 (8)
Mn–C7	2.171 (6)	Mn–P2	2.259 (2)	C3–C4	1.532 (11)
P1–C20	1.842 (6)	Mn–C3	2.136 (6)	C4–C5	1.485 (13)
P2–C2	1.845 (8)	Mn–C6	2.094 (9)	C6–C7	1.415 (11)
P2–C38	1.848 (5)	P1–C1	1.829 (8)	C8–C14	1.533 (8)
C1–C2	1.297 (11)				

Bond Angles

P1–Mn–P2	85.8 (1)	P1–Mn–N	94.3 (2)
P2–Mn–N	94.7 (2)	P1–Mn–C3	92.4 (2)
P2–Mn–C3	89.1 (2)	N–Mn–C3	172.5 (3)
P1–Mn–C5	97.5 (3)	P2–Mn–C5	154.2 (2)
N–Mn–C5	110.4 (3)	P2–Mn–C6	137.6 (2)
P1–Mn–C6	134.4 (2)	P1–Mn–C7	157.0 (2)
N–Mn–C6	94.6 (3)	N–Mn–C7	107.4 (3)
P2–Mn–C7	99.3 (2)	Mn–P1–C1	108.0 (3)
Mn–P1–C20	118.1 (2)	C1–P1–C20	101.6 (3)
Mn–P1–C26	122.8 (2)	C1–P1–C26	102.9 (3)
C20–P1–C26	100.6 (3)	Mn–P2–C2	107.3 (3)
Mn–P2–C32	123.0 (2)	C2–P2–C32	101.1 (3)
Mn–P2–C38	119.1 (2)	C2–P2–C38	103.1 (3)
C32–P2–C38	100.3 (2)	Mn–N–O	176.6 (6)
P1–C1–C2	118.9 (6)	P2–C2–C1	118.9 (7)
Mn–C3–C4	93.5 (4)	Mn–C3–C8	93.7 (4)
C4–C3–C8	110.5 (6)	C3–C4–C5	101.3 (6)
Mn–C5–C4	92.9 (5)	Mn–C5–C6	67.4 (5)
C4–C5–C6	119.1 (8)	Mn–C6–C5	74.5 (5)
Mn–C6–C7	73.6 (4)	C5–C6–C7	121.1 (7)
Mn–C7–C6	67.7 (4)	Mn–C7–C8	92.4 (4)
C6–C7–C8	118.5 (6)	C3–C8–C7	101.0 (5)
C3–C8–C14	115.3 (5)	C7–C8–C14	117.4 (5)

($LiBEt_3H$) or $NaBD_4$ ($NaBH_4$) with **6** and **7** occurs cleanly to give products **8** and **9**, which by ^1H NMR were determined to be of the σ,π-allyl type (see the Experimental Section). This means that the hydride added at the C-2 position of the dienyl ring. The principal finding is that the hydride (deuteride) is situated exo in **8** and **9**. This was initially ascertained by decoupling and deuteration experiments: the added hydride gave a clean doublet (absent when deuteride was used) that was coupled only to the other H-2 hydrogen (which, on the other hand, was coupled to H-1 and H-3). The neutral dppe complex **8** has only marginal stability at room temperature, but the dppen analogue **9** is stable,

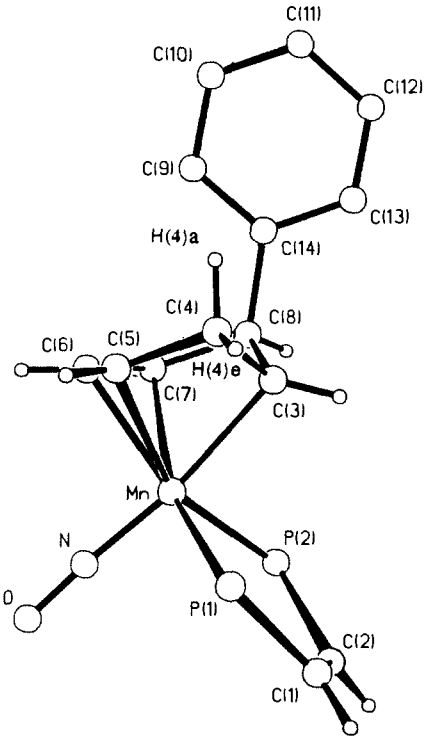
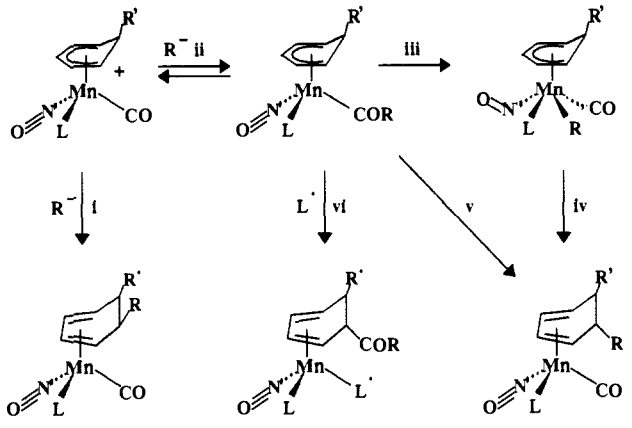


Figure 5. Abbreviated structural drawing of (6-*exo*-Ph,1-σ,3-5-η-C_6H_7)Mn(NO)dppen.

and its structure (in the protio form) was verified by X-ray diffraction. Figure 4 gives the ORTEP diagram and numbering scheme, while Figure 5 shows the pertinent structural features in a truncated but clearer manner. Atom coordinates are given in Table I, and selected bond lengths and angles are in Table II. The structural features of **9** are generally ordinary except that they constitute a rare example of a σ,π-cyclohexenyl complex (the first to our knowledge to be structurally characterized). The Mn–N–O linkage is linear (176.6 (6)°), and the nitrosyl ligand is situated under the allylic π-system. Referring to Figures 4 and 5, the dihedral angles H3–C3–C4–H4(axial) and H3–C3–C4–H4(equatorial) are 86 (5)° and 38 (6)°, respectively. These values confirm the ^{1}H NMR assignments, which were based on the assumption of little or no coupling between H-4(axial) and H-3 (or H-5). Hence, the conclusion that hydride adds exo to **6** and **7** is confirmed.

Nucleophilic addition to the internal C-2 position of a dienyl ring is well-known with seven-membered rings[29] but is very rare with six-membered ones.[30] It is known that terminal nucleophilic attack generally occurs with (diene)$Co(CO)_3^+$ complexes, whereas the (diene)$Fe(CO)_3$ analogues are much more likely to undergo internal attack. These systems have been examined theoretically,[31] and it was shown that as the electrophilic complex is made more electron-rich, a repulsive four-electron interaction between the complex and nucleophile HOMO's becomes significant and can lead to attack being favored at an internal carbon. It seems likely that such factors obtain in this study, for which there is a switch from terminal to internal hydride attack as the L and L′ ligands in (cyclohexadienyl)Mn(NO)(L)(L′)$^+$ become more electron-rich. The increased electron density as L and L′ are changed from carbonyl to phosphine ligands is semiquantitatively reflected in the reduction potentials. These were measured at room temperature in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as electrolyte. For (*exo*-PhC_6H_6)Mn(NO)(L)(L′)$^+$ the peak potentials, relative to ferrocene having $E_{1/2}$ = 0.52 V, are as follows: −0.20 V (L = L′ = CO); −0.79 V (L = CO, L′ = PMe_3); −1.17 V (L = L′ = $^1/_2$dppen); and −1.19 V (L = L′ = $^1/_2$dppe).

Scheme I



General Mechanistic Comments. Our work shows that stereospecific endo addition of hydride to (cyclohexadienyl)Mn(NO)(L)(L′)$^+$ cations requires the presence of at least one carbonyl ligand. In work with (cyclohexadienyl)$Fe(CO)_3^+$ complexes it was suggested[13] that the *endo*/*exo*-diene product mixtures sometimes obtained with hydride donors can be understood in terms of attack as a CO to give a formyl intermediate, with the stronger hydride donors giving more endo product because of the greater ease of attack at CO. The argument that the ease of attack at CO correlates with the amount of endo product suggests that those complexes having the most electrophilic CO ligands (high ν_{CO} frequencies) should be most likely to give endo products. However, this is not the case, e.g., ν_{CO} of (arene)$Mn(CO)_3^+$ is much higher than ν_{CO} of **4**, yet the former gives only exo and the latter endo hydride addition. Thus, it is possible that the ability to form a formyl intermediate is necessary but not sufficient to guarantee an endo product. It is conceivable that the endo stereochemistry involves conversion of the formyl to a metal carbonyl hydride, M(CO)(H), followed by migration of the hydride to the ring. The presence of a nitrosyl ligand allows a M(CO)(H) species to form and maintain an 18-electron count by bending of the NO ligand.

Scheme I provides a summary of reasonable pathways available for a general nucleophile (R^-). Direct attack at the ring by pathway i gives the *exo*-diene. With hydride as the nucleophile we have presented evidence that a formyl complex is formed initially via route ii. Note that initial attack at a CO does not preclude *exo*-diene product provided ii is reversible. However, with hydride the ultimate product is the *endo*-diene, which may be generated from the formyl via iii and iv or directly via v. It is conceivable that the entire formyl group could migrate to the dienyl ring in the presence of a donor L′ (e.g., THF or MeCN solvent) according to vi, but this route is not found with hydride.

We have recently obtained indirect evidence that the formyl intermediate converts to diene product via iii and iv and not directly via v. This stems from the observation[32] that certain organolithium reagents (LiPh, LiMe, etc.) react rapidly and cleanly with **3** and **4** at low temperature via ii to give M–COR species that, upon warming, give good yields of *free* diene possessing trans substituents R′ and COR; presumably this occurs by pathway vi. That this is not observed with hydride donors may reflect the well-known instability of metal formyls with respect to metal carbonyl hydrides—a transformation that could be facilitated by bending of the NO ligand (route iii). In any case, we suggest that it is the instability of the formyl intermediate rather than the ability to attack a CO that distinguishes hydride from many other nucleophiles.

One final observation concerning the mechanism of endo hydride addition deals with complex **4**. The chiral nature of **4** means that diastereomers can be formed[19] in the reaction with hydride.

(29) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060.
(30) Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Parker, D. G. *J. Organomet. Chem.* **1980**, *194*, C11.
(31) Sautet, P.; Eisenstein, O.; Nicholas, K. M. *Organometallics* **1987**, *6*, 1845.
(32) Pike, R. D.; Sweigart, D. A. Unpublished results.

It was found[19] that $NaBH_4$ gives a 2:1 diastereomer ratio whereas $LiBEt_3H$ gives only one diastereomer. If the proposed formyl species were a true intermediate, the stereochemical outcome of the reaction should not depend on the hydride source. However, this would not be the case if the borane product (BEt_3) or other electrophilic species (Li^+) were associated with the carbonyl oxygen and thereby able to influence the subsequent migration, whether from a M(CHO) or M(CO)(H) intermediate.

Acknowledgment. This work was supported by a grant from the National Science Foundation (no. CHE-8821588).

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **9** (4 pages); listings of observed and calculated structure factors for **9** (9 pages). Ordering information is given on any current masthead page.

Organometallic Chemistry in Supercritical Fluids: The Generation and Detection of Dinitrogen and Nonclassical Dihydrogen Complexes of Group 6, 7, and 8 Transition Metals at Room Temperature

Steven M. Howdle,* Michael A. Healy, and Martyn Poliakoff*

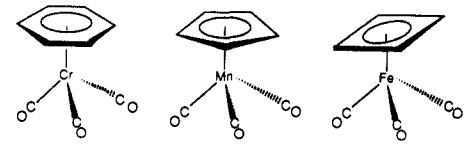
Contribution from the Department of Chemistry, University of Nottingham, Nottingham, England NG7 2RD. *Received December 18, 1989*

Abstract: The complete miscibility of N_2 and H_2 with supercritical fluids is used to stabilize unstable, and previously unknown, dinitrogen and dihydrogen complexes which would normally decay rapidly at ambient temperatures. UV photolysis of a series of $(C_nR_n)M(CO)_3$ compounds [M = Fe, Mn, Re or Cr; R = H for n = 4; R = H or Me for n = 5 or 6] dissolved in supercritical Xenon (scXe) under a high pressure of N_2 or H_2 leads to the formation of $(C_nR_n)M(CO)_2(N_2)$ and $(C_nR_n)M(CO)_2(H_2)$ complexes at room temperature. Re and Fe undergo facile substitution of more than one CO group by N_2, while Cr and Mn do not. For all elements except Re, the spectroscopic evidence suggests that the $(C_nR_n)M(CO)_2(H_2)$ complexes contain the "nonclassical" η^2-H_2 ligand. No IR bands directly associated with η^2-H_2 in these compounds have been observed, but the experiments were sufficiently sensitive to detect the ν(H-H) band of $W(CO)_5(H_2)$ under similar conditions. Most of these dihydrogen complexes decompose by reaction with CO to regenerate the $(C_nR_n)M(CO)_3$ starting material, but significant amounts of $Fe(CO)_5$ are formed in the decay of $(C_4H_4)Fe(CO)_2(H_2)$. Kinetic measurements between 11 and 80 °C show that $(C_6H_5Me)Cr(CO)_2(H_2)$ reacts with CO with an activation energy of 70 ± 5 kJ mol^{-1}, which may correspond to the Cr-(η^2-H_2) bond dissociation energy.

There is continuing interest in transition-metal complexes containing the η^2-H_2 ligand, so-called "nonclassical" dihydrogen compounds.[1] The first example was isolated[2] only in 1984, but, since then, a large number of compounds have been found to be nonclassical. Although the existence of these compounds has stimulated several theoretical studies,[3] it is still far from clear precisely which factors are the most important in determining whether a particular dihydrogen ligand is classical or nonclassical. Nevertheless, several useful analogies have emerged.

There are similarities between the bonding in dinitrogen and dihydrogen complexes, and, for a given ML_n fragment, the corresponding $ML_n(H_2)$ and $ML_n(N_2)$ complexes often have similar properties.[4] Indeed, it has been suggested[5] that, for d^6 centers at least, the wavenumber of the ν(N-N) IR band of $ML_n(N_2)$ is one indicator of classical/nonclassical behavior in the corresponding ML_nH_2 species. Equally, there are strong similarities between η^2-H_2 ligands and the "arrested" oxidative addition of $HSiR_3$ to d^6 centers.[6]

Such analogies have prompted us to search for previously unknown[7] dihydrogen complexes derived from the half-sandwich complexes, **1-3**, because these $(C_nH_n)M(CO)_2$ moieties are known



1 2 3

to undergo arrested oxidative addition[6,8] and to form relatively stable dinitrogen complexes.[9] Furthermore, if the dihydrogen

(1) For recent reviews of "nonclassical" dihydrogen complexes, see: (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (c) Ginsburg, A. G.; Bagaturyants, A. A. *Metalloorganicheskaya. Khim.* **1989**, *2*, 249.

(2) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P.; Wasserman, H. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(3) See, e.g.: (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705. (b) Rabaa, H.; Saillard, J.-Y.; Schubert, H. *J. Organomet. Chem.* **1987**, *330*, 397. (c) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (d) Burdett, J. K.; Phillips, J. R.; Poliakoff, M.; Pourian, M.; Turner, J. J.; Upmacis, R. K. *Inorg. Chem.* **1987**, *26*, 3054. (e) Kober, E. M.; Hay, P. J. *The Challenge of d and f Electrons*; Salahub, D. R., Zerner, M. C., Eds.; ACS Symposium Series 394; American Chemical Society: Washington, DC, 1989; p 92. (f) Pacchiani, *J. Am. Chem. Soc.* **1990**, *112*, 80.

(4) Crabtree, R. H. *Inorg. Chim. Acta* 1986, *125*, L7. Jackson, S. A.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J.; Burdett, J. K.; Grevels, F.-W. *J. Chem. Soc., Chem. Commun.* **1987**, 678. Joshi, A. M.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1785.

(5) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowych, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674.

(6) For a recent review of such compounds, see: Schubert, U. *Adv. Organomet. Chem.* In press.

(7) There was, before we started this work, evidence for an unstable, partly characterized compound formed on protonation of $[CpMn(CO)_2]^{2-}$ in low-temperature solutions (Leong, V. S.; Cooper, N. J. *Organometallics* **1988**, *7*, 2080). Allowing for solvent shifts in the IR, it can been seen that this compound was probably the same species as $CpMn(CO)_2(H_2)$ observed in scXe in this paper.

(8) (a) Hill, R. H.; Wrighton, M. S. *Organometallics* **1985**, *4*, 413; **1987**, *6*, 632. (b) Young, K. M.; Wrighton, M. S. *Ibid.* **1989**, *8*, 1063.

(9) (a) Sellmann, D.; Maisel, G. *Z. Naturforsch.* **1972**, *27b*, 465. (b) Sellmann, D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 919. (c) Sellmann, D. *J. Organomet. Chem.* **1972**, *36*, C27. (d) Cusanelli, A.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1719. (e) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

0002-7863/90/1512-4804$02.50/0