Controlling the Regioselectivity of Nucleophilic Addition on Unsaturated Ligands Bound to Molybdenum. The Cationic [CpMo(NO)(CO)(cyclooctenyl)]$^+$ System

J. W. Faller,* K. H. Chao, and H. H. Murray

Department of Chemistry, Yale University, New Haven, Connecticut 06511

Received January 17, 1984

Extraordinarily high regioselectivity has been observed in nucleophilic additions to the two isomers of the [CpMo(NO)(CO)(cyclooctenyl)]$^+$ cation. The isomers of the cation differ in the orientation of the η^3-C_8H_{13} ring relative to the η^5-C_5H_5 ring and are denoted exo when the methylenes of the C_8 ring are distal to the Cp ring or endo when they are proximal to the Cp ring. In the case of deuteride addition >99% (*RR*,*SS*)-CpMo(NO)(CO)(η^3-C_8H_{13}D) is formed from the exo cation, whereas ~95% selectivity for formation of the *RS*,*SR* product was observed for the endo cation. High regioselectivity for addition to the exo isomer for nucleophiles, such as HO^-, $Me_2NCS_2^-$, and dimethylmalonate, was also observed. The regioselectivity of nucleophilic addition to the endo isomer, however, varied with the type of nucleophile and the conditions. These results have been rationalized by consideration of the interconversion rates of the cations and intermediates produced in the reaction. The formation of the nucleophile–carbon bond is directed by the NO group and occurs cis to NO in both exo and endo isomers. The stereochemistry of the product HO^- addition to the exo isomer was established as (*RR*,*SS*)-(η^5-C_5H_5)Mo(NO)(CO)(η^2-C_8H_{13}OH) by X-ray crystallographic analysis. Crystal data: triclinic $P\bar{1}$ (No. 2); a = 8.477 (1) Å, b = 9.050 (2) Å, c = 9.906 (2) Å, α = 87.11 (1)°, β = 85.60 (1)°, γ = 72.41 (1)°, V = 722.0 (3) Å^3; Z = 2. The proton α to the η^3-allyl moiety and cis to NO was shown to be the most acidic in the CpMo(NO)(CO)(cyclooctenyl) cation by proton abstraction to yield *cis*-(η^5-C_5H_5)Mo(NO)(CO)(C_8H_{12}). The stereochemistry of this cyclooctadiene complex was determined by X-ray crystallographic analysis. Crystal data: monoclinic $P2_1/n$ (No. 14); a = 8.8361 (1) Å, b = 7.308 (1) Å, c = 21.474 (2) Å, β = 98.32 (1)°, V = 1372.2 (6) Å^3; Z = 4.

The complexation of unsaturated organic substrates to a transition metal activates otherwise unreactive centers.[1] The molybdenum allyl system (η^5-C_5H_5)Mo(L)(L′)(η^3-C_3H_5) is of particular interest because of the highly regioselective additions that occur when the complexes are cationic and when different ligands subject the allyl moiety to an asymmetric electronic environment.[2-6] We have shown that analogues of [CpMo(NO)(CO)(η^3-C_3H_5)]$^+$ complexes are of great utility owing to their case of preparation and the high yields obtained in nucleophilic additions to the allyl that form neutral η^2-olefin complexes.[2-6] The reactivity of the cyclooctenylmolybdenum system was investigated in order to delineate some of the factors responsible for the selectivity. The geometric constraints imposed by the cyclooctenyl ring effectively preclude π–σ–π rearrangements and also require a single stable conformation at the metal. The more cleanly interpretable results from the cyclooctenyl compound also provide a basis for understanding analogous reactions of the parent η^3-C_3H_5 system.

Experimental Section

All reactions were carried out in oven-dried glassware under nitrogen using standard inert-atmosphere techniques. All solvents were dried before use. THF was distilled from sodium and benzophenone. Acetonitrile and dichloromethane were distilled from calcium hydride before use as reaction solvents. Crystalline cyclopentadienyllithium was purchased from Alfa Products, Danvers, Mass. All IR spectra were obtained from a Perkin-Elmer 237B grating spectrometer referenced to the 1601 cm^{-1} band of polystyrene. The silica gel used for chromatographic separations was Mallinckrodt SilicAR CC-7 Special. NMR spectra were obtained by using a Bruker HX-270 spectrometer operating at 270 MHz for protons and 41.4 MHz for ^{2}H or a Bruker WM-500 spectrometer operating at 500 MHz for proton and 76.6 MHz for ^{2}H. The preparations of the dicarbonyl and carbonyl nitrosyl derivatives that are reported here give improved yields over those published previously.[3]

Preparation of (η^5-C_5H_5)Mo(CO)$_2$(η^3-C_8H_{13}). Six grams (0.55 mol) of cyclooctene was combined with 40 mL of CCl_4, 0.25 g of benzoyl peroxide, and 9.70 g (0.55 mol) of *N*-bromosuccinimide. The solution was heated under reflux for 1 h, after which all of the white solid floated to the surface of the solution. The solution was filtered and the solvent removed with a rotary flash evaporator. The crude product was distilled under vacuum (1 mmHg), and 8.2 g (44 mmol) of 3-bromocyclooctene was collected between 52 and 53 °C in 80% yield. Molybdenum carbonyl, 11.5 g (44 mmol) was suspended in 250 mL of CH_3CN, and the solution was heated to reflux for 3 h. After the formation of the Mo(CO)$_3$-(CH_3CN)$_3$, 8.2 g (44 mmol) of 3-bromocyclooctene was added dropwise to the hot solution and the mixture was stirred for 1.5 h. A yellow precipitate began to appear after 1 h. The solvent was removed by vacuum, and 200 mL of freshly distilled THF was added. CpLi, 3 g (43.6 mmol), was suspended in 150 mL of THF, and the CpLi solution was added dropwise to the solution of (C_8H_{13})Mo(CO)$_2$(CH_3CN)$_2$Br. After the addition was complete, the progress of the reaction was monitored by TLC and the solution was stirred for 15 h. The reaction mixture was filtered, and the solvent was removed under vacuum. The residue was dissolved in the 15 mL of a solvent mixture (50% CH_2Cl_2, 50% petroleum ether), and the solution loaded onto an alumina column (5 cm × 20 cm). A wide yellow-orange band was eluted withCH_2Cl_2–petroleum ether mixture, and the solvent was removed under vacuum. The residue was extracted with petroleum ether, and the yellow extracts were combined and reduced in volume. The residue was dissolved in petroleum ether and chromatographed on a silica gel column (5 cm × 10 cm); a bright yellow band was collected. Alternatively, the compound can be

(1) Baker, R. *Chem. Rev.* **1973**, *73*, 487. Alper, H. "Transition Metals in Organic Synthesis"; Academic Press: (1976), vol 2 (1978). Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463. Trost, B. M. *Ibid.* **1980**, *13*, 385. Backvall, J. E. *Ibid.* **1983**, *16*, 335–342. Bosnich, B.; Mackenzie, P. B. *Pure Appl. Chem.* **1982**, *54*, 189–195. Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *J. Organomet. Chem.* **1983**, *2*, 400–409.

(2) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2470. Faller, J. W.; Rosan, A. M. *Ibid.* **1977**, *99*, 4858. Faller, J. W.; Rosan, A. M. *Ibid.* **1976**, *98*, 3388.

(3) Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251–275. Faller, J. W.; Shvo, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5398.

(4) Faller, J. W.; Rosan, A. M. *Ann. N.Y. Acad. Sci.* **1982**, *54*, 189–195.

(5) Faller, J. W.; Chao, K. H. *J. Am. Chem. Soc.* **1983**, *105*, 3893–3898.

(6) Faller, J. W.; "Fundamental Research in Homogeneous Catalysis"; Ishii, Y., Tsutsui, M., Eds.; Plenum Press: New York, 1978; Vol. 2.

0276-7333/84/2303-1231$01.50/0

purified by Soxhlet extraction with petroleum ether.[3] Solvent was removed under vacuum to yield 11.6 g (80%) of yellow crystals of $CpMo(CO)_2(\eta^3\text{-}C_8H_{13})$: mp 117–118 °C; IR (cyclohexane) 1954, 1878 cm^{-1}; ^1H NMR (270 MHz, 25 °C, $CDCl_3$) δ 5.23 (s, Cp), 4.15 (t, Hc, J = 8.1 Hz), 3.74 (ddd, H_1, H_3, J = 8.1, 8.2, 8.5 Hz), 2.30, 2.18, 1.46, 1.20 (m, methylene). Anal. Calcd for $C_{15}H_{18}MoO_2$: C, 55.22; H, 5.55. Found: C, 55.22%; H, 5.59.

Preparation of *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]BF_4. *Note*: Care must be taken to carry out the reactions and perform recrystallizations quickly to avoid isomerization to the exo isomer.

One gram (3.3 mmol) of $CpMo(CO)_2(\eta^3\text{-}C_8H_{13})$ was suspended in 8 mL of acetonitrile and the temperature of the solution lowered to 0 °C. Nitrosyl tetrafluoroborate, 0.36 g (3.3 mmol), was added to the solution in increments over 1 min, and the mixture was allowed to stir for an additional minute. The dark yellow solution was added dropwise to a centrifuge bottle containing 150 mL of ether producing an immediate yellow precipitate. The bright yellow solid was separated by centrifugation and decantation of the pale yellow supernatant. Drying the powder under vacuum gave *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]BF_4: 1.30 g, 96%; mp 88–90 °C dec; IR (CH_2Cl_2) 2084, 1712 cm^{-1}; ^1H NMR (270 MHz, 25 °C, acetone-d_6) δ 6.44 (s, Cp), 6.42 (dtd, H_3, J = 8.7, 9.0, 2.1 Hz), 5.96 (dtd, H_1, J = 10.2, 8.4, 2.3 Hz), 5.59 (dd, H_2, J = 8.7, 8.4 Hz), 3.05 (m, $H_{4\delta}$), 2.64 (m, $H_{8\delta}$), 2.15–1.65 (m, methylenes). The endo isomer was conveniently characterized by ^1H resonances at δ 6.44 for the Cp and δ 5.59 for the central allyl proton (H_2).

Preparation of *exo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]BF_4. This isomer can be obtained by dissolving the endo isomer, allowing it to stand at room temperature for 3 h to isomerize, and precipitating the exo complex with ether. The most efficient procedure uses iodide catalysis and avoids some decomposition.

To one gram (25 mmol) of *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]BF_4 in 15 mL of acetone at 25 °C was added 19 mg (0.13 mmol) of NaI. After the solution was stirred to 0.5 h, the solvent was removed under vacuum. The residue was washed with ether to remove any remaining CpMo(NO)(I)(η^3-C_8H_{13}), recrystallized from acetone–ether, and dried under vacuum. The exo isomer was obtained as pale yellow microcrystals: 0.90 g, 90%; ^1H NMR (270 MHz, 25 °C, acetone-d_6) δ 6.46 (dtd, H_3, J = 9.7, 8.6, 2.2 Hz), 6.34 (s, Cp), 5.93 (dtd, H_1, J = 10.2, 8.6, 2.3 Hz), 5.02 (dd, H_2, J = 8.6, 8.6 Hz), 2.72 (m, $H_{4\delta}$), 2.61 (ddt, $H_{8\delta}$, J = 14.9, 8.4, 4.2 Hz), 2.00–1.50 (m, methylene). The exo isomer is most conveniently identified by ^1H resonances at δ 6.34 for the Cp and δ 5.02 for the central allyl proton (H_2). With the exception of the NMR spectrum the exo isomer has virtually the same physical properties as the endo isomer.

Preparation of *endo*- and *exo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]PF_6. These complexes were prepared by addition of $NOPF_6$ to $(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_8H_{13})(CO)_2$ in acetonitrile at 0 °C in a manner analogous to that used for preparation of the BF_4^- salt. The properties of the tetrafluoroborate and hexafluorophosphate salts are virtually identical. Anal. Calcd for *exo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]PF_6: C, 35.34; H, 3.83. Found: C, 35.27; H, 3.83.

Preparation of CpMo(NO)(CO)(η^2-C_8H_{13}OH). Five hundred milligrams (1.1 mmol) of *exo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]PF_6 was suspended in 20 mL of freshly distilled THF, and the solution was cooled to −78 °C. A solution containing 163 mg (1.1 mmol) of cyclohexyldiethylamine and 19 mg (1.1 mmol) of water in freshly distilled THF was added slowly to the solution, and the solution was stirred for 0.5 h. The solution was passed through an acidic alumina column (2 cm × 5 cm) three times to remove base, and then the solvent was removed. The residue was dissolved in a solvent mixture of 75% petroleum ether and 25% $CHCl_3$ and chromatographed on a silica gel column (2 cm × 15 cm). A yellow band was collected, and the solvent was removed under vacuum. The CpMo(NO)(CO)(η^2-C_8H_{13}OH) complex was obtained as yellow crystals: 254 mg, 70%; mp 110–112 °C dec; IR (cyclohexane) 1974 (CO), 1636 cm^{-1} (NO); ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 5.58 (s, Cp), 3.80 (m, $H_{3\alpha}$), 3.20 (dd, H_2, J = 9.9, 9.9 Hz), 2.91 (m, H_1), 2.74 (m, $H_{8\delta}$), 2.14 (m, $H_{8\alpha}$), 1.78 and 1.60 (m, methylenes). Under the same conditions, the endo cation gave the same product and no indication of a second isomer was observed. We attribute this to rapid base-catalyzed interconversion of the endo to the exo isomer.

Reaction between *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]PF_6 and Water. Five hundred milligrams (1.1 mmol) of *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]PF_6 was suspended in 20 mL of freshly distilled THF, and a solution of 190 mg (11 mmol) of water in THF was added slowly to the suspension at 25 °C and the solution was stirred until the reaction was complete (0.5 h, monitored by TLC). The solution was passed through a dry silica gel column (2 cm × 5 cm) to remove excess water and acid. Then the solvent was removed and the residue purified as above to yield 266 mg (71%) of the yellow product. Two isomers of the CpMo(NO)(CO)(η^2-C_8H_{13}OH) complex were obtained in a ratio of 2.72:1 with the major isomer being the same as that found in the preparations with the exo cation. The ^1H NMR (270 MHz, $CDCl_3$, 25 °C) gave two sets of resonances: major, δ 5.58 (s, Cp), 3.80 (m, H_3), 3.20 (t, H_2, J = 9.9 Hz), 2.92 (tdd, H_1, J = 10.8, 3.5 Hz); minor, δ 5.54 (s, Cp), 3.84 (m, H_3), 3.27 (t, H_2, J = 9.5 Hz), 3.22, the remaining resonances overlapped with the major isomer.

Preparation of CpMo(NO)(CO)(η^2-C_8H_{12}). Two hundred milligrams (0.43 mmol) of *exo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]PF_6 was suspended in 10 mL of freshly distilled THF, and the solution was cooled to −78 °C. A solution containing 90 mg (0.43 mmol) of cyclohexyldiethylamine in freshly distilled THF was added slowly to the solution, and the solute was stirred for 5 min. The solution was passed through an acidic alumina column to remove the amine and the ammonium salts. Then the solvent was removed. The residue was dissolved in a solvent mixture of 75% pentane and 25% CH_2Cl_2 and was chromatographed on a silica gel column (2 cm × 15 cm). A yellow band was collected, and the solvent was removed under vacuum. The CpMo(NO)(CO)(η^2-C_8H_{12}) complex was obtained as yellow crystals: 91.4 mg, 65%; mp 89–92 °C; IR (cyclohexane) 1983 (CO), 1661 (NO) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 6.02 (dq, H_3, J = 11.8, 1.8 Hz), 5.528 (s, Cp), 5.38 (dddd, H_4, J = 11.8, 6.6, 3.6, 1.8 Hz), 3.90 (dm, H_2, J = 10.3, 1.8 Hz), 3.03 (td, H_1, J = 10.3, 3.3 Hz), 2.68 (dq, $H_{8\delta}$, J = 12.5, 3.3 Hz), 2.15–1.65 (m, methylenes).

Preparation of CpMo(NO)(CO)(η^2-C_8H_{14}). To 1.37 g (3.3 mmol) of the endo-PF_6 complex in THF at −78 °C was added 0.22 g (3.3 mmol) of $NaCNBH_3$. The reaction mixture was stirred for 2 h at −78 °C and then was slowly brought up to ambient temperature. The solvent was removed and the olefin complex taken up in toluene and chromatographed on a silica column. The olefin complex separated as a yellow band and the solvent evaporated to yield a bright yellow solid: 0.98 g, 90%; mp 112–113 °C; IR (cyclohexane) 1966 (CO), 1635 (NO) cm^{-1}; ^1H NMR (270 MHz, 25 °C, $CDCl_3$) δ 5.34 (s, Cp), 3.18 and 3.00 (td, H_1, H_2, J = 10.5, 3.5 Hz), 2.62 and 2.42 (dq, $H_{3\beta}$, $H_{8\delta}$, J = 13.6, 3.3 Hz), 1.73 (m, methylenes), 1.58 (m, methylenes). Anal. Calcd for $C_{14}H_{19}MoNO_2$: C, 51.07; H, 5.81. Found: C, 50.98; H, 5.83.

Preparation of (*RR*,*SS*)-CpMo(NO)(CO)(η^2-C_8H_{13}D). This complex was prepared as the analogous hydride except that 22 mg (3.3 mmol) of $NaCNBD_3$ was used in a reaction with the exo cation. The selectivity was high as indicated by a nearly complete absence of the δ 2.42 resonance in the ^1H NMR.

Preparation of (*RS*,*SR*)-CpMo(NO)(CO)(η^2-C_8H_{13}D). This complex was prepared in the same manner as the cis isomer except that the endo cation was used. Rigorous attention to maintaining low temperature during all phases of the reaction are required to give high selectivity. Greater than 95% selectivity was observed as indicated by a nearly complete absence of the ^1H resonance at δ 2.62.

Assignment of Resonances in CpMO(NO)(CO)(η^2-C_8H_{13}D). The resonances at δ 2.42 and 2.62 can be assigned to protons adjacent to the double bond on the β-face of the ring by comparison to shifts in other derivatives. The dimethylmalonate product isomers, for example, show a resonance at δ 2.46 for this β-proton cis to the NO and δ 2.74 for the β-proton trans to the NO, whereas the protons on the α-face all resonate at fields higher than δ 1.74. For the limited group of nucleophiles studied here, it also appears that for these β-protons adjacent to the olefin, the one cis to NO resonates ~0.2–0.3 ppm to higher field than the one trans to NO.

Preparation of (*RR*,*SS*)-CpMo(NO)(CO)[η^2-C_8H_{13}-(S_2CNMe_2)]. One gram (2.5 mmol) of *exo*-[CpMo(NO)(CO)(C_8H_{13})]BF_4 was suspended in 20 mL of freshly distilled THF and the temperature of the solution lowered to −78 °C. Sodium dimethyldithiocarbamate, 333 mg (2.5 mmol), was added to the solution, which was stirred for 4 h, after which the reaction was complete as indicated by TLC. The temperature of the solution

Table I. Crystallographic Data for X-ray Diffraction Studies

	$CpMo(NO)(CO)(C_8H_{12})$	$CpMo(NO)(CO)(C_8H_{13}OH)$
(A) Crystal Data		
formula	$Mo_1O_2N_1C_{14}H_{17}$	$Mo_1O_3N_1C_{14}H_{19}$
temp, ±3 °C	23	22
space group	$P2_1/n$, No. 14	$P\bar{1}$, No. 2
a, Å	8.836 (1)	8.477 (1)
b, Å	7.308 (1)	9.050 (2)
c, Å	21.474 (2)	9.906 (2)
α, deg		87.11 (1)
β, deg	98.32 (1)	85.60 (1)
γ, deg		72.41 (1)
V, Å^3	1372.2 (6)	722.0 (3)
M	327.24	345.25
ρ_{calcd}, g/cm^3	1.58 (Z = 4)	1.59 (Z = 2)
(B) Measurement of Intensity Data		
radiation	Mo Kα (0.710 73 Å)	
monochromator	graphite	
detector aperture, mm		
horizontal (A + B tan θ), A, B	3.0, 1.0	
vertical	4.0	
reflctns measd	$+h,+k,\pm l$	$+h,\pm k,\pm l$
max 2θ, deg	50	50
scan type	moving crystal–stationary counter	
ω scan width (A + 0.347 tan θ), deg, A =	0.90	0.80
background	$^1/_4$ additional at each end of scan	
ω scan rate (variable)		
max, deg/min	10.0	10.0
min, deg/min	1.4	1.2
no. of reflctns measd	2770 with absences	2511
data used [$F^2 \geq n\sigma(F^2)$]	1746 [2σ]	2093 [3σ]
(C) Treatment of Data		
abs correctn	not applied	not applied
abs coeff, cm^{-1}	9.3	8.98
p factor	0.02	0.02
final residuals R_1, R_2	0.020, 0.002	0.019, 0.022
esd of unit weight	1.31	1.26
largest shift/error value on final cycle	0.02	0.00
largest peak in final difference Fourier, e/Å^3	0.09	0.22

was raised to 25 °C and the solvent removed. The residue was dissolved in pentane and subjected to chromatography on a 2 × 10 cm silica gel column to yield a bright yellow band. Removal of the solvent gave a single pure isomer of $CpMo(NO)(CO)[\eta^2$-$C_8H_{13}(S_2CNMe_2)]$: 960 mg, 82%; mp 73–77 °C dec; IR (methylene chloride) 1960 (CO), 1630 (NO) cm^{-1}; ^{1}H NMR (270 MHz, −50 °C, $CDCl_3$) δ 5.55 (s, Cp), 4.08 (td, H_3, J = 10.3, 2.5 Hz), 3.52 and 3.42 (s, NMe), 3.14 (dd, H_2, J = 10.3, 10.1 Hz), 2.98 (td, H_1, J = 10.3, 2.0 Hz), 2.74 (dq, H_8, J = 13.1, 3.4 Hz), 2.58–1.50 (m, methylenes).

Reaction of Dithiocarbamate with *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]BF_4. One gram of the endo cation was treated as above with sodium dimethyldithiocarbamate. After chromatography a yellow solid was isolated upon removal of the solvent. NMR showed that the solid contained a mixture of two isomers in a ratio of 3:1. The minor isomer was identified as the *RR,SS* isomer by comparison with the spectrum of the pure isomer prepared above. The major isomer, however, was a new product that exhibited resonances (270 MHz, −50 °C, $CDCl_3$) for the major isomer at δ 5.52 (s, Cp), 4.03 (ddd, H_3, J = 12.1, 11.1, 3.5 Hz), 3.59, 3.46 (s, NMe), 3.05 (dd, H_2, J = 12.1, 10.1 Hz), 3.10 (t, H_1, J = 10.1 Hz), and 2.26–1.50 (m, methylenes). The principal physical differences between the two isomers is the appearance of the NMR spectrum wherein the most distinguishing features are the chemical shifts of the Cp and NMe resonances: major, δ 5.52, 3.59, 3.46; minor, δ 5.55, 3.52, 3.52. The isomer with the δ 5.52 (Cp) also decomposes more rapidly than that with the δ 5.55 (Cp).

Reaction of Sodium Dimethylmalonate with *endo*-[CpMO(NO)(CO)(η^3-C_8H_{13})]PF_6. Five hundred milligrams of the endo cation (1.1 mmol) was suspended in 20 mL of freshly distilled THF, and 170 mg (1.1 mmol) of sodium dimethylmalonate was added to the solution at 25 °C. The solution was stirred until the reaction was complete (by TLC). The solvent was removed, and residue was dissolved in a solvent mixture of 50% petroleum ether and 50% CH_2Cl_2 and chromatographed on a silica gel column (2 cm × 15 cm). A yellow band was collected, and the solvent was removed to yield 436 mg (90%) of the yellow product. Two isomers of the $CpMo(NO)(CO)[\eta^2$-3-((dicarbomethoxy)methyl)cyclooctene] were obtained with a trans:cis ratio of 2:1. The ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) gave two sets of resonances: major, δ 5.460 (s, Cp), 4.126 ($H_{malonate}$), 3.793, 3.766 (s, 2 × 3 H, Me_a, Me_b), 2.46 (m, H_{88}); minor, δ 5.516 (s, Cp), 4.230 (m, $H_{malonate}$), 3.751, 3.732 (s, 2 × 3 H, Me_a, Me_b), 2.74 (m, H_{88}). All other resonances were at higher field than δ 1.74.

Reaction of Sodium Dimethylmalonate with *exo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]PF_6. Five hundred milligrams of the exo cation were treated as above for the endo cation. The NMR of the product showed only a single isomer of the product, which corresponded to the minor isomer obtained from the endo cation, that is δ 5.516 (s, Cp), 4.230 ($H_{malonate}$), 3.751, 3.732 (s, 2 × 3 H, Me_a, Me_b), and 2.74 (m, H_{88}).

Crystallographic Analysis. Crystals suitable for diffraction analysis were obtained from dichloromethane–hexane solutions by cooling to −10 °C. The crystals were mounted in thin-walled glass capillaries. Diffraction measurements were carried out on an Enraf-Nonius CAD-4 fully automated four-cycle diffractometer. Unit cells were determined from 25 randomly selected reflections by using CAD-4 automatic search, center, index, and least-squares routines. The crystal data and the data collection parameters are listed in Table I.

All calculations were performed on Digital PDP 11/45 and 11/23 computers using the Enraf-Nonius SDP program library (version 18). Absorption corrections were not performed owing to the low absorption coefficients. Anomalous dispersion corrections[7a] were added to the neutral atom scattering factors[7b] used for all non-hydrogen atoms. Full-matrix least-squares refinements

(7) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

Table II. Positional and Thermal Parameters for CpMo(NO)(CO)($C_8H_{13}OH$)

atom	x/a	y/b	z/c	B,[a] Å²
Mo	−0.20010 (2)	−0.13531 (2)	−0.18635 (2)	2.547 (4)
O(1)	−0.0219 (2)	−0.1521 (2)	0.0661 (2)	4.06 (4)
O(2)	−0.3583 (2)	−0.3922 (2)	−0.0723 (2)	5.72 (5)
O(3)	0.2139 (2)	−0.0922 (2)	−0.2570 (2)	4.97 (4)
N	−0.0914 (2)	−0.1529 (2)	−0.0361 (2)	2.80 (4)
C	−0.2998 (3)	−0.3000 (3)	−0.1163 (3)	3.70 (6)
Cp(1)	−0.3325 (4)	0.1310 (3)	−0.1743 (3)	5.14 (7)
Cp(2)	−0.2291 (3)	0.1104 (3)	−0.2920 (3)	4.81 (7)
Cp(3)	−0.2899 (3)	0.0285 (3)	−0.3813 (3)	4.36 (6)
Cp(4)	−0.4288 (3)	−0.0021 (3)	−0.3173 (3)	4.53 (6)
Cp(5)	−0.4541 (3)	0.0600 (3)	−0.1885 (3)	4.90 (7)
C(1)	−0.0382 (3)	−0.3621 (3)	−0.2925 (2)	3.02 (5)
C(2)	0.0399 (3)	−0.2453 (2)	−0.3146 (2)	2.73 (5)
C(3)	0.1990 (3)	−0.2461 (3)	−0.2553 (2)	3.21 (5)
C(4)	0.3554 (3)	−0.3415 (3)	−0.3357 (3)	3.72 (6)
C(5)	0.3940 (3)	−0.5174 (3)	−0.3238 (3)	4.22 (6)
C(6)	0.2818 (4)	−0.5870 (3)	−0.3963 (3)	4.43 (6)
C(7)	0.1505 (4)	−0.6361 (3)	−0.3066 (3)	5.30 (7)
C(8)	0.0362 (3)	−0.5100 (3)	−0.2137 (3)	4.09 (6)
Hp(1)	−0.312 (4)	0.178 (3)	−0.106 (3)	6.9 (8)
Hp(2)	−0.144 (3)	0.143 (3)	−0.312 (3)	5.0 (6)
Hp(3)	−0.248 (3)	0.002 (3)	−0.458 (2)	4.4 (6)
Hp(4)	−0.488 (3)	−0.048 (3)	−0.347 (3)	5.5 (7)
Hp(5)	−0.536 (3)	0.061 (3)	−0.136 (3)	6.3 (8)
H(1)	−0.106 (3)	−0.369 (3)	−0.355 (2)	3.5 (5)
H(2)	0.025 (3)	−0.193 (3)	−0.401 (2)	4.1 (6)
H(3)	0.206 (2)	−0.292 (2)	−0.167 (2)	2.7 (5)
H(41)	0.444 (3)	−0.310 (3)	−0.301 (2)	3.9 (6)
H(42)	0.347 (3)	−0.312 (2)	−0.427 (2)	3.0 (5)
H(51)	0.393 (3)	−0.543 (3)	−0.232 (2)	4.3 (6)
H(52)	0.505 (3)	−0.563 (2)	−0.360 (2)	3.7 (5)
H(61)	0.347 (3)	−0.676 (3)	−0.442 (3)	4.7 (6)
H(62)	0.225 (3)	−0.511 (2)	−0.464 (2)	3.5 (5)
H(71)	0.205 (3)	−0.723 (3)	−0.253 (3)	5.7 (7)
H(72)	0.076 (3)	−0.667 (3)	−0.362 (3)	5.7 (7)
H(81)	0.094 (3)	−0.491 (3)	−0.143 (2)	3.8 (5)
H(82)	−0.053 (3)	−0.547 (3)	−0.171 (3)	4.5 (6)
H	0.152 (3)	−0.045 (3)	−0.204 (3)	5.0 (6)

[a] Isotropic thermal parameters are given for hydrogen atoms, and B_{eqv} is given for all non-hydrogen atoms. A table of anisotropic thermal parameters is available in the supplementary material.

minimized the function $\sum_{hkl} w(F_o - F_c)^2$, where the weighting factor $w = 1/(\sigma(F))^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

The unit cell for CpMo(NO)(CO)(η^2-$C_8H_{13}OH$) was triclinic, and the structure was successfully refined assuming that space group was $P\bar{1}$. The monoclinic space group $P2_1/n$ for CpMo(NO)(CO)(η^2-C_8H_{12}) was established by the systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$. The structures were solved by a combination of Patterson and difference Fourier techniques. The carbon and nitrogen atoms in the carbonyl and nitrosyl were distinguished initially by refining both as carbon atoms. The nitrogen atom showed a smaller isotropic temperature factor than the carbon in both structures: $C_8H_{13}OH$, $B_C = 3.60$ Å², $B_N = 1.57$ Å²; C_8H_{12}, $B_C = 3.52$ Å², $B_N = 2.56$ Å². The correct assignments are also based on the indications that have been found consistently in over 20 structures of this type which we have determined. These indicators are (alcohol, diene) (1) the shorter Mo–N distance (Mo–N = 1.786, 1.794 Å; Mo–C = 1.997, 1.973 Å); (2) the smaller M–N–O angle (Mo–N–O = 174.8, 172.8°; Mo–C–O = 177.9, 178.4°); and (3) the tilting of the olefinic ligand to align with the Mo–CO axis. The hydrogen atoms were located in the differnce Fourier maps after the other atoms had been refined anisotropically. Full-matrix least-squares refinement using anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged to the final residuals shown in Table I. The largest peaks in the final difference Fourier syntheses were in the vicinity of the metal atoms. Final atomic coordinates and thermal parameters are listed in Tables II and III. Bond distances and angles with esds from the inverse matrix obtained on the final cycle of least-squares refinement are listed in Tables IV–VII. The anisotropic thermal parameters and the structure factor amplitudes are provided in the supplementary material.

Table III. Positional and Thermal Parameters for CpMo(NO)(CO)(C_8H_{12})

atom	x/a	y/b	z/c	B,[a] Å
Mo	0.12130 (2)	0.21330 (3)	0.34340 (1)	2.784 (4)
O(1)	0.1983 (3)	−0.2039 (3)	0.3430 (1)	6.47 (6)
O(2)	0.4481 (2)	0.3132 (3)	0.3388 (1)	5.86 (6)
N	0.3191 (2)	0.2709 (3)	0.3448 (1)	3.43 (5)
Cp(1)	0.0063 (4)	0.2408 (5)	0.2389 (1)	5.47 (8)
Cp(2)	−0.1021 (4)	0.1564 (5)	0.2701 (2)	6.15 (9)
Cp(3)	−0.1464 (3)	0.2755 (5)	0.3144 (1)	5.49 (7)
Cp(4)	−0.0643 (3)	0.4413 (5)	0.3108 (1)	4.71 (7)
Cp(5)	0.0262 (3)	0.4178 (5)	0.2628 (1)	4.89 (7)
C(1)	0.1416 (3)	0.1181 (4)	0.4489 (1)	2.83 (5)
C(2)	0.1056 (3)	0.3041 (4)	0.4446 (1)	3.12 (5)
C(3)	0.2096 (3)	0.4588 (4)	0.4669 (1)	3.88 (6)
C(4)	0.3064 (3)	0.4777 (4)	0.5200 (1)	4.00 (7)
C(5)	0.3466 (3)	0.3570 (5)	0.5764 (1)	4.48 (7)
C(6)	0.2460 (3)	0.1924 (4)	0.5844 (1)	4.21 (7)
C(7)	0.2901 (3)	0.0198 (4)	0.5511 (1)	3.76 (6)
C(8)	0.2928 (3)	0.0463 (3)	0.4804 (1)	3.15 (6)
C	0.1708 (3)	−0.0500 (4)	0.3441 (1)	3.96 (7)
Hp(1)	0.063 (3)	0.190 (4)	0.205 (1)	5.9 (8)
Hp(2)	−0.131 (3)	0.050 (4)	0.266 (1)	6.2 (8)
Hp(3)	−0.213 (3)	0.260 (4)	0.342 (1)	5.7 (8)
Hp(4)	−0.070 (3)	0.548 (3)	0.334 (1)	4.5 (6)
Hp(5)	0.090 (3)	0.498 (4)	0.251 (1)	5.5 (7)
H(11)	0.069 (2)	0.047 (3)	0.451 (1)	2.7 (5)
H(21)	0.009 (2)	0.332 (3)	0.442 (1)	2.6 (5)
H(31)	0.208 (3)	0.564 (3)	0.441 (1)	4.4 (6)
H(41)	0.358 (3)	0.592 (3)	0.521 (1)	3.9 (6)
H(51)	0.457 (3)	0.308 (3)	0.574 (1)	4.5 (6)
H(52)	0.343 (3)	0.432 (4)	0.612 (1)	4.7 (6)
H(61)	0.136 (3)	0.227 (3)	0.572 (1)	3.5 (6)
H(62)	0.255 (3)	0.163 (3)	0.629 (1)	4.1 (6)
H(71)	0.221 (3)	−0.075 (3)	0.558 (1)	4.0 (6)
H(72)	0.390 (3)	−0.020 (3)	0.571 (1)	4.1 (6)
H(81)	0.374 (2)	0.134 (3)	0.475 (1)	2.8 (5)
H(82)	0.317 (3)	−0.076 (3)	0.462 (1)	3.6 (6)

[a] Isotropic thermal parameters are given for hydrogen atoms, and B_{eqv} is given for all non-hydrogen atoms. A table of anisotropic thermal parameters is available in the supplementary material.

Table IV. Selected Bond Lengths (Å)

	CpMo(NO)-(CO)($C_8H_{13}OH$)	CpMo(NO)-(CO)(C_8H_{12})
Mo–Cp(1)	2.336 (3)	2.334 (3)
Mo–Cp(2)	2.361 (2)	2.376 (3)
Mo–Cp(3)	2.401 (2)	2.400 (3)
Mo–Cp(4)	2.390 (2)	2.372 (3)
Mo–Cp(5)	2.337 (3)	2.349 (3)
Mo–C(1)	2.344 (2)	2.353 (3)
Mo–C(2)	2.292 (2)	2.295 (3)
Mo–N	1.786 (2)	1.794 (2)
Mo–C	1.997 (2)	1.973 (3)
C–O(2)[a]	1.145 (3)	1.152 (4)
N–O(1)[a]	1.211 (2)	1.206 (3)
Cp(1)–Cp(2)	1.389 (4)	1.391 (6)
Cp(2)–Cp(3)	1.402 (4)	1.386 (6)
Cp(3)–Cp(4)	1.390 (4)	1.420 (5)
Cp(4)–Cp(5)	1.395 (4)	1.404 (5)
Cp(5)–Cp(1)	1.388 (4)	1.394 (5)
C(1)–C(2)	1.408 (3)	1.396 (4)
C(2)–C(3)	1.509 (3)	1.492 (4)
C(3)–C(4)	1.534 (3)	1.331 (4)
C(4)–C(5)	1.525 (4)	1.498 (5)
C(5)–C(6)	1.527 (4)	1.520 (5)
C(6)–C(7)	1.527 (4)	1.528 (5)
C(7)–C(8)	1.546 (4)	1.533 (4)
C(8)–C(1)	1.502 (3)	1.502 (4)
C(3)–O(3)	1.435 (3)	

[a] In the C_8H_{12} complex C–O(1) and N–O(2) are given.

Table V. Selected Bond Angles (deg) for $CpMo(NO)(CO)(C_8H_{13}OH)$

N-Mo-C	90.75 (9)	Mo-N-O(1)	174.8 (2)	C(2)-C(1)-C(8)	122.9 (2)
N-Mo-Cp(1)	96.27 (10)	Mo-C-O(2)	177.9 (2)	C(1)-C(2)-C(3)	125.2 (2)
N-Mo-C(1)	99.28 (8)	Cp(2)-Cp(1)-Cp(5)	108.4 (3)	C(2)-C(3)-C(4)	113.5 (2)
N-Mo-C(2)	92.18 (8)	Cp(1)-Cp(2)-Cp(3)	107.6 (3)	C(2)-C(3)-O(3)	110.6 (2)
C-Mo-Cp(1)	124.82 (11)	Cp(2)-Cp(3)-Cp(4)	107.6 (3)	C(4)-C(3)-O(3)	104.8 (2)
C-Mo-C(1)	74.83 (9)	Cp(3)-Cp(4)-Cp(5)	107.9 (3)	C(3)-C(4)-C(5)	116.4 (2)
C-Mo-C(2)	109.52 (9)	Cp(1)-Cp(5)-Cp(4)	108.0 (3)	C(4)-C(5)-C(6)	116.3 (2)
C(1)-Mo-C(2)	35.34 (7)			C(5)-C(6)-C(7)	116.1 (2)
				C(6)-C(7)-C(8)	115.6 (2)
				C(1)-C(8)-C(7)	111.2 (2)

Table VI. Selected Bond Angles (deg) for $CpMo(NO)(CO)(C_8H_{12})$

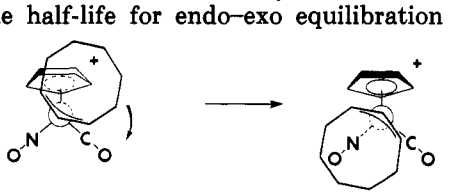
N-Mo-C	90.83 (12)	Mo-N-O(2)	172.8 (2)	C(2)-C(1)-C(8)	123.3 (3)
N-Mo-Cp(1)	106.48 (13)	Mo-C-O(1)	178.4 (3)	C(1)-C(2)-C(3)	126.4 (2)
N-Mo-C(1)	96.59 (10)	Cp(2)-Cp(1)-Cp(5)	107.0 (3)	C(2)-C(3)-C(4)	130.1 (3)
N-Mo-C(2)	96.2 (1)	Cp(1)-Cp(2)-Cp(3)	109.6 (3)	C(3)-C(4)-C(5)	132.8 (3)
C-Mo-Cp(1)	99.0 (1)	Cp(2)-Cp(3)-Cp(4)	107.5 (3)	C(4)-C(5)-C(6)	118.9 (2)
C-Mo-C(1)	73.7 (1)	Cp(3)-Cp(4)-Cp(5)	106.6 (3)	C(5)-C(6)-C(7)	114.0 (3)
C-Mo-C(2)	108.6 (1)	Cp(4)-Cp(5)-Cp(1)	109.2 (3)	C(6)-C(7)-C(8)	113.6 (2)
C(1)-Mo-Cp(1)	156.0 (1)			C(1)-C(8)-C(7)	110.5 (2)
C(2)-Mo-Cp(1)	143.9 (1)				
C(1)-Mo-C(2)	34.9 (1)				

Table VII. Selected Bond Angles (deg) for $CpMo(NO)(CO)(C_8H_{12})$

N-Mo-C	90.83 (12)	C(4)-C(5)-C(6)	118.9 (2)	C(4)-C(5)-H(51)	106 (2)
N-Mo-Cp(1)	106.48 (13)	C(5)-C(6)-C(7)	114.0 (3)	C(4)-C(5)-H(52)	107 (2)
N-Mo-C(1)	96.59 (10)	C(6)-C(7)-C(8)	113.6 (2)	C(6)-C(5)-H(51)	107 (2)
N-Mo-C(2)	96.2 (1)	C(1)-C(8)-C(7)	110.5 (2)	C(6)-C(5)-H(52)	106 (2)
C-Mo-Cp(1)	99.0 (1)	Cp(2)-Cp(1)-Hp(1)	129 (2)	H(51)-(5)-H(52)	112 (2)
C-Mo-C(1)	73.7 (1)	Cp(5)-Cp(1)-Hp(1)	124 (2)	C(5)-C(6)-H(61)	109 (2)
C-Mo-C(2)	108.6 (1)	Cp(1)-Cp(2)-Hp(2)	127 (2)	C(5)-C(6)-H(62)	109 (2)
C(1)-Mo-Cp(1)	156.0 (1)	Cp(3)-Cp(2)-Hp(2)	123 (2)	C(7)-C(6)-H(61)	113 (2)
C(2)-Mo-C(1)	143.9 (1)	Cp(2)-Cp(3)-Hp(3)	130 (2)	C(7)-C(6)-H(62)	107 (2)
C(1)-Mo-C(2)	34.9 (1)	Cp(4)-Cp(3)-Hp(3)	122 (2)	H(61)-(6)-H(62)	104 (2)
Mo-N-O(2)	172.8 (2)	Cp(3)-Cp(4)-Hp(4)	128 (2)	C(6)-C(7)-H(71)	108 (2)
Mo-C-O(1)	178.4 (3)	Cp(5)-Cp(4)-Hp(4)	125 (2)	C(6)-C(7)-H(72)	108 (2)
Cp(2)-Cp(1)-Cp(5)	107.0 (3)	Cp(1)-Cp(5)-Hp(5)	124 (2)	C(8)-C(7)-H(71)	110 (2)
Cp(1)-Cp(2)-Cp(3)	109.6 (3)	Cp(4)-Cp(5)-Hp(5)	127 (2)	C(8)-C(7)-H(72)	110 (2)
Cp(2)-Cp(3)-Cp(4)	107.5 (3)	C(2)-C(1)-H(11)	116 (2)	H(71)-(7)-H(72)	106 (2)
Cp(3)-Cp(4)-Cp(5)	106.6 (3)	C(8)-C(1)-H(11)	113 (2)	C(1)-C(8)-H(81)	110 (2)
Cp(4)-Cp(5)-Cp(1)	109.2 (3)	C(1)-C(2)-H(21)	116 (2)	C(1)-C(8)-H(82)	111 (2)
C(2)-C(1)-C(8)	123.3 (3)	C(3)-C(2)-H(21)	114 (2)	C(7)-C(8)-H(81)	109 (2)
C(1)-C(2)-C(3)	126.4 (2)	C(2)-C(3)-H(31)	118 (2)	C(7)-C(8)-H(82)	108 (2)
C(2)-C(3)-C(4)	130.1 (3)	C(4)-C(3)-H(31)	112 (2)	H(81)-(8)-H(82)	109 (2)
C(3)-C(4)-C(5)	132.8 (3)	C(3)-C(4)-H(41)	111 (2)		
		C(5)-C(4)-H(41)	116 (2)		

Results

Exo–Endo Equilibration in the $CpMo(NO)(CO)(\eta^3\text{-}C_8H_{13})$ Cation. As in other molybdenum allyl systems[2,3,6] the addition of NO^+ to the $CpMo(CO)_2(\eta^3\text{-}C_8H_{13})$ gave the endo cation as the initially formed product. This kinetically controlled isomer distribution contains effectively only the endo isomer; however, the steric interaction between the Cp ring and the methylenes of the eight-membered ring make the exo isomer more stable thermodynamically. Thus upon standing the product cation converts almost exclusively to the exo isomer (eq 1). The half-life for endo–exo equilibration for the



(1)

$CpMo(NO)(CO)(\eta^3\text{-}C_8H_{13})$ cation in acetone at 25 °C was observed to be 35 min.[3] Thus, at low temperatures one would anticipate that a fast reaction could be carried out on the pure endo isomer before any significant amount of isomerization to the exo form took place. The steric interaction of the C_8 ring with the Cp ligand forces >99% of the cation to be in the exo form when equilibrium is established.

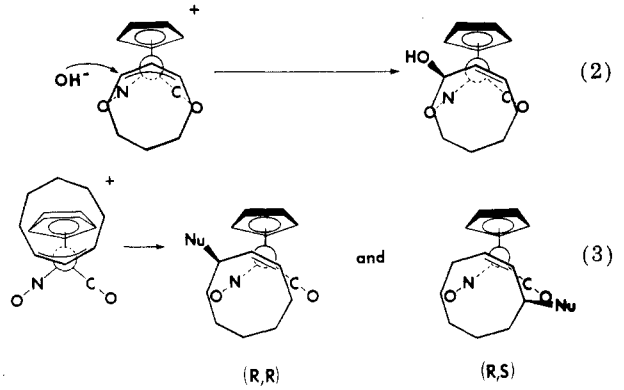
We have previously noted,[3] however, that the endo to exo interconversion could be catalyzed by I^-. Thus we have found that addition of 1% iodide is sufficient to promote complete interconversion of the endo isomer to the exo isomer in less than 1 min.[3,8] Thus, one must take care in the interpretation of stereochemical results that a reagent does not promote the endo to exo interconversion.[9]

The Regiochemistry of Nucleophilic Addition. The addition of nucleophiles to analogous acyclic allyl complexes generally yields a single isomer corresponding to addition of the allyl cis to the nitrosyl group of the exo isomer. Addition of D^-, OH^-, or $Me_2NCS_2^-$ groups to the *exo*-$[CpMo(NO)(CO)(\eta^3\text{-}C_8H_{13})]$ cation at low temperature results in regioselectivity >95% in each case. Assuming all of the these nucleophiles attack the same site under these conditions, it follows from the crystal structure of the $C_8H_{13}OH$ product (see below) that attack occurs cis to nitrosyl and on the side opposite to the metal, which we designate as the β face of the bound olefin (eq 2).

Addition to the endo isomer at room temperature, however, produces variable results in regioselectivity, which, depending upon the nucleophile and the conditions, yields ratios of diastereomers from 99:1 to 1:99 (eq 3).[10]

(8) Faller, J. W.; Rosan, A.; Katahira, D.; Murray, H. H.; Chao, K. H.; Shvo, Y. *Organometallics*, submitted for publication.

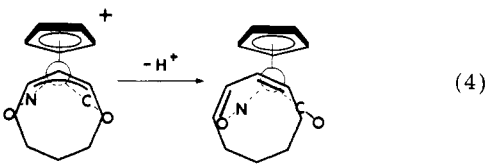
(9) The terms exo and endo used are in this paper to refer to the orientation of the allyl group relative to the cyclopentadienyl ring. Some workers use there terms to refer to the non-metal side vs. the metal side of metal π complexes. We use the descriptors β and α to distinguish non-metal side and metal side.



The barriers to rotation of the olefin in these product complexes are low, and the steric interactions of the C_8 ring with the Cp are great; hence, only the exo conformers are observed. The variation in selectivity that is observed here appears to be a consequence of the relative reactivity of the endo isomer and the rate of endo to exo interconversion under the reaction conditions.

Identification of Diastereomers. To provide an unequivocal starting point for identifying diastereomers, a single-crystal X-ray diffraction study of the product alcohol from the exo cation CpMo(NO)(CO)(η^2-$C_8H_{13}OH$) was undertaken. The ORTEP diagram shown in Figure 1 conclusively shows that (1) the OH is cis to the nitrosyl, (2) the OH is β to the Mo, and (3) the ring is in the exo conformation.

Proton Abstraction from the *exo*-[CpMo(NO)(CO)(η^3-C_8H_{13})] Cation. In order to investigate the possibility that the regiochemistry was directed by the effective charges or the relative acidities of the two termini of the allylic moiety, we determined the structure of the product resulting from removal of a proton from the cation by a base. The structure of this cyclooctadiene complex (Figure 2) suggests that the proton had been removed from the side cis to the nitrosyl (i.e., C-4, see eq 4).



Discussion

A wide variety of nucleophiles can be added to the CpMo(NO)(CO)(η^3-C_8H_{13}) cation.[2] Soft nucleophiles, such as malonate or enamines, have also been added in high yield with high regioselectivity to the exo isomer at low temperatures. Variability in regioselectivity is observed with the endo isomer depending upon temperature, the nucleophile, and the conditions. This contrasts with acyclic allyls[2] that generally yield the same regioisomer regardless of conditions or type of nucleophile. This discussion will focus on allylic substitution of D^-, HO^-, and Me_2NSCS^-.[14]

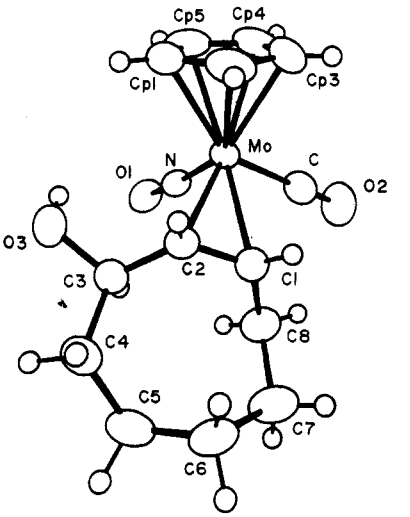


Figure 1. An ORTEP view of CpMo(NO)(CO)(η^2-$C_8H_{13}OH$) showing 50% probability ellipsoids for the non-hydrogen atoms. The thermal parameters for the hydrogen atoms are reduced to $B = 1$ Å^2 for clarity. The *R,R* configuration is shown. Since the racemate was crystallized and the space group is centrosymmetric, the *S,S* configuration is also present in the unit cell.

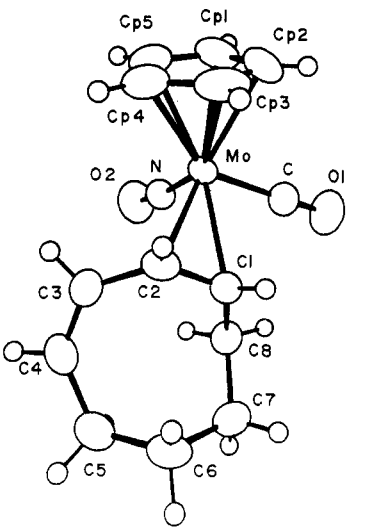


Figure 2. An ORTEP view of CpMo(NO)(CO)(η^2-C_8H_{12}) showing 50% probability ellipsoids for the non-hydrogen atoms. The thermal parameters for the hydrogen atoms are reduced to $B = 1$ Å^2 for clarity. The free C=C double bond is cis to the nitrosyl. The *R* configuration at the metal is shown.

Deuteride Addition. The addition of deuteride by reaction of cyanoborodeuteride to the cation provides an illustrative example of the effective reversal of product regiochemistry that can be obtained with this system.

Deuteride addition to the exo and endo cation gave two different isomers as indicated by regioselective ^2H incorporation into the allylic position of the η^2-olefin product. The deuterated product from the *exo*-CpMo(NO)(CO)(η^3-C_8H_{13}) cation resulted in 99% deuterium incorporation (from ^2H NMR) at the allylic position having a chemical shifft of δ 2.42. The deuterated product from the *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})] cation resulted in 97% deuterium incorporation (from ^2H NMR) at the allylic

(10) In this paper the chirality descriptor for the CpMo(NO)(CO)(olefin) is given first. The priorities are determined on the basis of assuming a polyhapto ligand is a pseudoatom of atomic number equal to that of the bound atoms.[11-13] Only the *R* configuration is shown in many of the diagrams, even though the experiments were carried out on racemic mixtures. The *R* configuration is determined by the priority order Cp > olefin > NO > CO. Although several chiral centers are present in the C_8 ring, only the descriptor is given for the carbon that has been attacked by the nucleophile (i.e. C-3). For the cases discussed here, where the priority of Nu is either greater than a carbon or is between carbon and hydrogen, the descriptor for the bound and the free olefin is the same. This is *not* true for carbon nucleophiles. The priorities for C-3 in the (*R,R*)-alcohol are O > C_{MCH} > C_{CHH} > H.

(11) LeComte, C.; Dusausay, Y.; Protas, J.; Tirouflet, J.; Dormond, A. *J. Organomet. Chem.* **1974**, *73*, 67-76.

(12) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598.

(13) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1-36.

(14) Similar patterns are found with C–C bond-forming reagents. We have avoided the inclusion of the these compouds in the discussion because of the possible confusion arising from the chirality descriptors sometimes being reversed, even though the sense of the chirality is the same.[10]

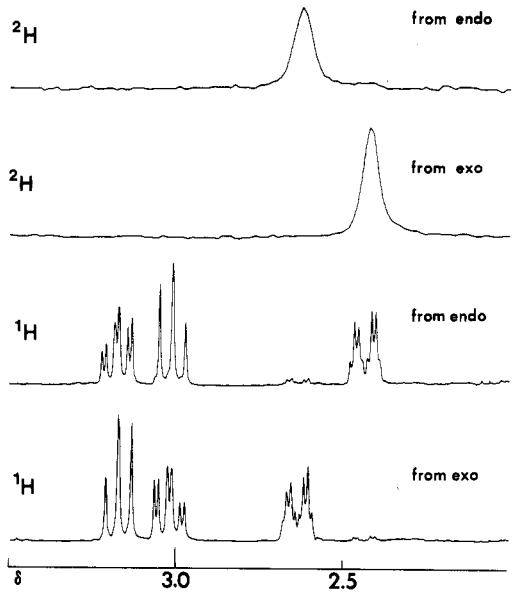


Figure 3. The $^2H\{^1H\}$ and ^1H NMR spectra of the product from deuteride addition to the *exo*- and *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})] cations.

proton having a chemical shift of δ 2.62 and 3% at δ 2.42[15] as shown in Figure 3. These results indicate that the stereochemistry of the product from the nucleophilic addition to the allyl moiety could be controlled by the conformation of the reactant cation. Furthermore, they show that the reactions with the endo cation can be as selective for addition at one carbon, as the exo cation is for addition at another.

The Pathway of Nucleophilic Addition. It appears that all additions of nucleophiles studied here occur via attack on the non-metal or β side of the olefin.[9] This contrasts to systems where prior coordination to the metal[16,17] or to a carbonyl might occur and yield an α attack.

The β-attack pathway is generally found for olefinic moieties bound to coordinatively saturated metal complexes.[1] Analogies also may be found in our investigations of [CpMo(CO)$_2$(cyclohexadiene)]$^+$ reactions,[1] Sweigart's study[18] of nucleophilic additions to [(6β-phenylcyclohexadienyl)Mn(CO)$_2$(NO)]$^+$ and Brookhart's demonstration of hydride addition to [(η^6-C_6D_6)Mn(CO)$_3$]$^+$ to yield ([6β-^{1}H]hexadeuteriocyclohexadienyl)manganese tricarbonyl.[19,20] The X-ray structure of the $C_8H_{13}OH$ derivative demonstrated that addition of hydroxide to the exo isomer occurs to give the product with the nucleophile cis to the NO on the β face of the allyl (Figure 1). Owing to the similarities in coupling constants, it follows that the two regioisomers obtained in the deuterium addition are β-deuterio adducts, which differ only by having the deuterium either cis or trans to the nitrosyl group. Furthermore, these results show that in this case *the stereochemistry of the products can be controlled entirely by the conformation of the reactant cations.* Since only the exo conformation of the olefinic product is stable, the results suggest that attack occurs cis to the nitrosyl in both the endo cation and the exo cation (Figure 4).

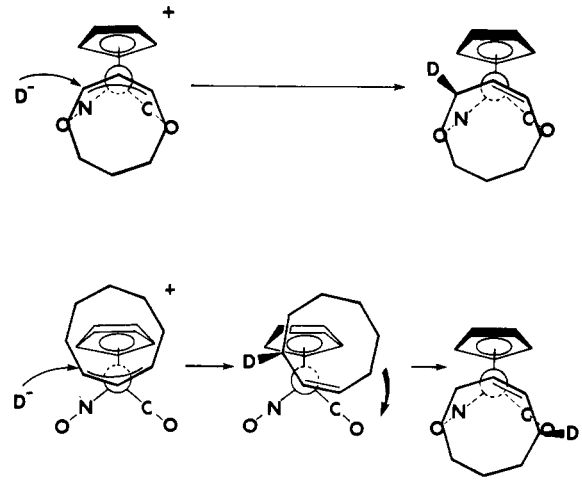


Figure 4. The consequence of β cis addition to the endo isomer of the [CpMo(NO)(CO)(η^3-C_8H_{13})] cation producing the stable conformation of the η^2-olefin complex with the nucleophile trans to the nitrosyl compared with the effective cis addition to the exo cation.

Carrying out the deuterium addition reactions at low temperature is essential for obtaining high regioselectivities, especially with the endo isomer. These deuterium addition results show that the attack can be directed with selectivities of >97% in either the exo or endo cations. Thus, the observation that reactions of the endo cation at room temperature produces a mixture of isomers suggests that the apparent lack of selectivity is the result of reaction with both endo and exo *complexes rather than an inherent lack of high regioselectivity in the endo isomer.* An important observation in this context is that no interconversion between isomers of the olefin complex was observed over a period of 12 h.

A simple rationalization of the high selectivities observed at low temperatures is that reaction of the cyclooctenyl cation occurs before any endo cation can convert to the exo cation. Although we believe this view is essentially correct, other results suggest that it may need minor modification (see below).

Dithiocarbamate Addition. The high selectivities observed with the deuteride reaction suggested a similar pattern for other nucleophiles. Thus, the single isomer arising from the reaction of dithiocarbamate with the exo cation could be anticipated. The observed regioselectivity of >99% in this reaction implied the formation of *RR,SS* isomer (i.e., the cis product) by analogy with the known structure of the alcohol. The product obtained from the addition of dithiocarbamate to the endo isomer, however, was a mixture of isomers in a ratio of 1:3. Thus, a (*RR,SS*):(*RS,SR*) or cis:trans ratio of 1:3 was obtained.[21] This

(15) The isotope effect in the addition tends to amplify the percentage hydride in the cyanoborodeuteride. As can be seen in the ^{1}H spectrum of Figure 3, there is a small percentage (~5%) of η^2-C_8H_{14} impurity in the η^2-$C_8H_{13}D$ compound.

(16) Brookhart, M.; Pinhas, A. R.; Lukacs, A.; *Organometallics* **1982**, *1*, 1730–1731.

(17) Faller, J. W. *Inorg. Chem.* **1980**, *19*, 2859.

(18) Chung, Y. K.; Choi, H. S.; Sweigart, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* **1982**, *104*, 4245–4247.

(19) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1980**, *102*, 3490.

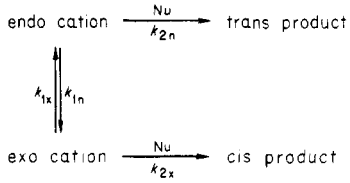
(20) The α addition of nucleophiles is very rare, and when it occurs, it can generally be attributed to prior coordination to the metal or its ligands. The only exception that might suggest some caution in our interpretation is the deuteride addition to [(6β-phenylcyclohexadienyl)-Mn(CO)$_2$(NO)]$^+$, which is claimed to occur by α attack.[9,18] We believe that β attack by hydride such as we[1] and others[19] have found in most cases is occurring in the CpMo(NO)(CO)(C_8H_{13}) system. In particular, the similarity in regioselectivity with other nucleophiles favors this interpretation. Furthermore, there are no steric constraints, such as exist in the manganese system, which might tend to disfavor β attack.

(21) Since there is effectively only one conformation of the olefinic product in the η^2-C_8H_{13}–Nu system, there is no ambiguity in referring to the *RR,SS* diastereomeric pair as the cis product or the *RS,RS* diastereomeric pair as the trans product. As cis and trans are much easier to visualize and the nomenclature does not vary with nucleophile priorities, these terms will be used frequently in this discussion. Note, however, that this nomenclature will lead to difficulties if there is not a single preferred conformation of the olefin.

Table VIII. Product Distributions in $[CpMo(NO)(CO)(\eta^3\text{-}C_8H_{13})]^+$ Reactions

expt	starting cation	reagent	temp, °C	% cis product
1	exo	$NCBD_3^-$	−78	99
2	endo	$NCBD_3^-$	−78	3
3	exo	$Me_2NCS_2^-$	−78	99
4	endo	$Me_2NCS_2^-$	−78	25
5	exo	H_2O/amine	−78	99
6	endo	H_2O/amine	−78	99
7	endo	H_2O/amine	25	99
8	exo	H_2O	25	99
9	endo	H_2O	25	73
10	exo	Na malonate	25	99
11	endo	Na malonate	25	33

Scheme I. A Simple Set of Pathways for the Reactions



result contrasts with the deuterium addition, where selectivities were high, at least at low temperature.

OH^- Addition. To obtain high product yields, this reaction must be carried out under carefully controlled conditions. The acid produced by direct reaction of water with the cation can lead to protonation of the alcohol and decomposition of the product when the solution is concentrated. The highest yields are obtained for the alcohol complexes when the reaction with water is carried out in the presence of base. As excess base promotes decomposition of the product, the reactions are best carried out a low temperature.

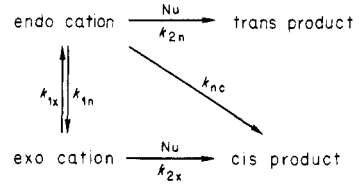
The η^2-$C_8H_{13}OH$ product is obtained as only a single isomer in the presence of base at low temperature when the starting reagent is either the endo or the exo cation. Reaction of water with the endo cation at room temperature in the absence of base, however, produces two isomers. This is a situation analogous to that found with the dithiocarbamate. Thus, in the absence of base, one obtains the cis η^2-alcohol from the exo isomer (Figure 1) and a mixture of the cis and trans η^2-alcohol from the endo isomer.

The Kinetic Factors Which Determine Regioselectivity. With the results of the D^-, HO^-, and $Me_2NCS_2^-$ additions in hand, it is now appropriate to attempt a consistent rationalization of all of these observations, which are summarized in Table VIII.

The exo cation yields a single product, i.e., the cis or *RR,SS* isomer. On basis of the deuteride results and with the assumption that the initial attack goes directly to product, one would anticipate that the endo cation would yield the trans product as shown in Figure 4. Since the half-time for interconversion of the free cation from endo to exo is very slow at low temperatures and the reaction with most reagents is relatively fast, one would not expect starting cation isomerization to be a problem. Thus, all low-temperature reactions would be expected to be regioselective, as observed with the deuteride. At higher temperatures, some cation interconversion could take place during the reaction and account for the apparent lack of selectivity in the endo cation. This suggests kinetics Scheme I as a starting point.

The product distribution would therefore be determined by the relative speed at which endo–exo took place and the reaction rate with nucleophile. Furthermore, one might expect that k_{2x} would not be equal to k_{2n}. Given that

Scheme II. Reaction Paths Allowing Direct Conversion of the Endo Cation to the Cis Product



$k_{2x}[Nu] \approx k_{2n}[Nu] \gg k_{1n} > k_{1x}$, one would expect that the product distribution would reflect the starting cation concentrations. This is generally the case for most nucleophiles reacting with $CpMo(NO)(CO)(C_8H_{13})$ cation at low temperature. The variable product distributions that were sometimes found with the endo isomer might be attributed to competitive rates for endo–exo equilibration and nucleophilic attack. At room temperature, however, the endo–exo equilibration half-time is 35 min for the pure cation in solution. In the absence of any influence from the nucleophilic reagent on the equilibration rate, one would not be able to account for the variations in cis:trans product distribution with Scheme I.

The equilibration is remarkably accelerated, however, by addition of catalytic amounts of iodide.[3,8] Thus, it is reasonable to consider reagent-promoted endo–exo equilibration. NMR experiments with only 0.5 an equiv of nucleophilic reagent/equiv cation[8] have confirmed that dithiocarbamate as well as other bases can catalyze this interconversion. Thus, in the cases of addition to the endo cation by dithiocarbamate at room temperature and H_2O/amine at low temperature, the formation of only the trans product can be attributed to acceleration of endo–exo equilibration by the reagents.

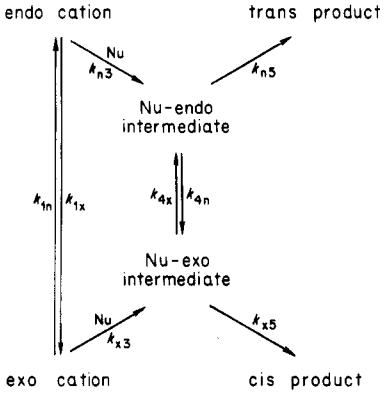
Consideration of the effects of the magnitudes of the rate constants in Scheme I would thus appear to offer an attractive rationale for the product distributions, particularly if one recognizes the possibility of reagent-promoted acceleration of starting cation isomers. This would require additional second-order terms in the rate equations for the endo–exo interconversion. Unfortunately, although this scheme appears to account for most situations, it does not stand up to a more careful kinetic analysis.

For example, NMR studies of the reaction rates of endo–exo cation mixtures[8] show that the endo:exo ratio of cations is not affected appreciably by $NCBD_3^-$ or H_2O during the reaction.[22] This implies that in some cases there is a path by which the endo cation can yield the cis product without first converting into the free exo cation. This suggests that crossover terms must be considered as shown in Scheme II.

Scheme II allows for the regioselectivity of the reactions on the endo cation to deteriorate. Thus, one might suspect that the factors controlling the regiochemistry are not as strong in the endo isomer as in the exo isomer. Alternatively, this could be formulated in terms of the activation energies for attack cis to NO vs. cis to CO differing by a greater amount in the exo vs. the endo isomer. This scheme can adequately account for most observations. Nevertheless, at the risk of becoming cumbersome, a somewhat more elaborate scheme which considers the intermediates involved in reagent-assisted endo–exo interconversion has many advantages.

(22) This result shows that the rate for disappearance of the endo cation is comparable to that of the exo cation for these reagents (i.e., $k_{2n} \approx k_{2x}$). We have shown previously,[5] however, that $k_{2x} \gg k_{2n}$ for enamine reaction with CpMo(NO)(CO)(1,3-dimethylallyl) cation. Hence, there appears to be a fairly wide variability in the relative magnitude of these parameters.

Scheme III. The Principal Paths Believed To Be Involved in Reactions with Many Nucleophiles[a]



[a] More direct paths from cations to products are not included here but may be important in some cases.

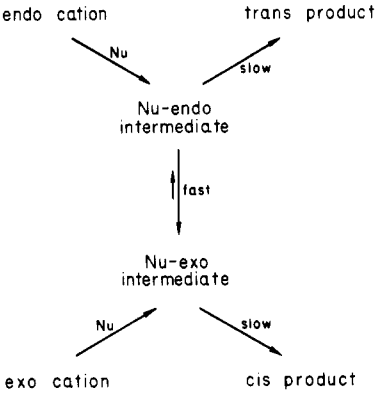
Since the selectivity is so high in some cases, we suggest that there is considerable advantage in proposing an intermediate that allows rearrangement of the ring before the formation of the transition state that leads to product. This is an alternative to assuming an increase of direct attack on the position trans to NO in the endo isomer. We have therefore developed Scheme III as a convenient set of pathways to consider for separating the kinetic features of importance in the control of the regiochemistry. This modification of the possible reaction paths yields a kinetics scheme that allows for the formation of an intermediate in which the ring can rearrange to the more stable orientation. Thus, within Scheme III it is feasible to consume endo cation and still produce the cis product.[23]

We refer to the pathway that involves rearrangement of the ring in the intermediate (i.e., conversion of the endo intermediate to the exo intermediate) as *reagent-assisted interconversion*. Although Scheme III is more cumbersome, it provides the basis for rationalization of a large body of information on acyclic allyls and multiply substituted allyls. We favor an interpretation involving *reagent-assisted interconversion* within an intermediate to trans attack in the endo isomer [i.e., a direct route from the endo cation to cis product is not accessable]. Experimentally distinguishing between these pathways, however, is difficult. Further elaboration of the pathways is underway and is treated in other papers.[8]

The important feature to be recognized is that when a starting cation is not the thermodynamically preferred isomer, the reagent may accelerate the normal interconversion rate. This is a critical aspect if one wishes to predict the regiochemistry of the reaction and the stereochemistry of the products. From the standpoint of synthetic applications, if one starts with the thermodynamically stable exo isomer, one can reliably predict that the site of attack by soft nucleophiles will be cis to the nitrosyl and yield the cis products.

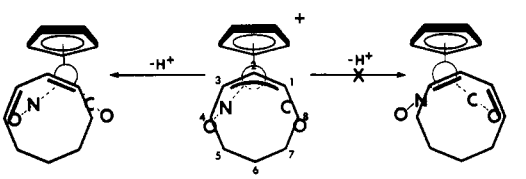
(23) If the formation of the intermediate was reversible, the effect could be observed as catalysis of the endo–exo interconversion [i.e., $k_{3n} \approx k_{3n}[Nu] \gg k_{1n}$]. This type of *reagent-promoted* interconversion is observed with dithiocarbamate and in the presence of base. It is also the basis of iodide-catalyzed endo–exo interconversion.[3,8] For example, reversible binding to a carbonyl would produce a neutral complex, in which the barrier to rearrangement would be expected to be lower. However, we expect that for most reagents which form an allyl–Nu bond, once the intermediate has formed, it does not dissociate. In this situation the product would be formed directly from the intermediate and there would be no back-reaction after the intermediate was formed. We are still developing our hypotheses regarding the nature of these intermediates. In some cases it would appear to be an ion pair in which an increase rate of rotation would occur. In others, a weak binding to a carbonyl or allyl seems appropriate.

Scheme IV. The Important Paths in Acyclic Allyl Reactions



The Origin of the High Regioselectivity. It is clear that nucleophilic attack occurs cis to nitrosyl in preference to trans to nitrosyl. Theoretical results on charge distributions and orbital overlaps between the allyl and the nucleophile predicted cis attack in the exo cation.[24] Although the site of nucleophilic attack on symmetrical systems has been studied theoretically for a number of cases,[25] the studies of the effect of electronic asymmetry have been limited.[24,26]

Although the view that charge distribution controls the selectivity is an oversimplification, the increased charge on the carbon cis to the NO was predicted for the exo cation.[24] In an effort to provide further indirect evidence for the greater positive charge cis to NO, we abstracted a proton from the cation to find which side was more acidic. The deprotonation by base is also extraordinarily regioselective and occurs cis to NO. Thus the proton is removed from C-4 not C-8 (eq 5).



(5)

This result also implies that the allyl terminus cis to NO has a greater positive charge in the exo isomer. A more complete investigation of the origins of the selectivity must include an evaluation of the transition-state energies and how they are affected by the alignment of the olefinic moiety with the Mo–C–O bond. This preference for alignment along the Mo–C–O bond is clearly evident in the ground-state structures of the olefin complexes (Figures 1 and 2), and this also plays a role in relative barrier heights for rotation of the allyls and olefins.[3,8] Suffice it to say at this point that the directing influence of the CpMo(NO)(CO) moiety is extraordinary and the electronic asymmetry induced in the system is effective in determining the regiochemistry.

Implications to Reactions of the Parent Allyl. Our original observation that addition of cyanoborodeuteride to either *endo*- or *exo*-[CpMo(NO)(CO)(η^3-C_3H_5)] cation gave predominantly (~94%) one diastereomer has been reproduced many times in this laboratory. This result contrasts sharply with the addition to the [CpMo(NO)-

(24) Schilling, B. E.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592–598.
(25) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, 3047–3077.
(26) Eisenstein, O.; Hoffmann, R.; *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320.

(CO)(η^3-C_8H_{13})] cations, for which the starting isomer can influence diastereomeric product distribution.

The same product regiochemistry observed upon the addition of D^- to the exo and endo isomer of the [CpMo(NO)(CO)(allyl)] cation can be satisfactorily explained by reference to Scheme III. In the specific case of the η^3-C_3H_5 cation, the reaction appears to yield product only after reaching equilibrium between the intermediates Nu–endo and Nu–exo. Assuming that the Nu–endo intermediate only yields cis product (from cis addition to the endo cation) and Nu–exo yields the trans product (from cis addition to the exo cation), one obtains the reaction paths in Scheme IV.

Therefore, regardless of the exo:endo starting isomer ratio, the product ratio would be influenced primarily by the equilibrium constant between the Nu–endo and Nu–exo intermediate. Hence a single ratio of the product (cis product:trans product) of 16:1 persisted for all starting conditions.

Conclusion

The most important aspect to the cyclooctenyl complex reactivity was that the addition of some nucleophiles to the η^3-cyclooctenyl complexes to give the neutral η^2-olefin products occurred faster than reagent-assisted endo–exo equilibration. Hence, unlike the allyl or crotyl analogues, the stereochemistry of the product could be governed to a large degree by the conformation of the reactant cation. This observation indicated that attack of nucleophile always occurs on the same side of the allyl moiety relative to NO in the exo and endo cation.[27]

Recognition that reagent-assisted endo–exo interconversion of CpMo(NO)(CO)(allyl) cations may occur in the presence of the nucleophilic reagent is an important feature in efforts to predict the product distributions from these reactions. Thus in acyclic systems, such as the η^3-C_3H_5 allyl cation, it appears that the reagent-assisted endo–exo equilibration was reached faster than product formation. Consequently, one often observes the same isomeric product regardless of the conformation of the starting cation in acyclic systems. Attack cis to NO in *both* endo and exo cations, when considered with the relative rates of attack on the endo and exo cation, as well as the possibility of the reagent-assisted endo–exo interconversion, provides a consistent picture, which allows the rationalization of a large body of product distribution data on substituted allyls.[2,3,5,8]

With an appreciation of these factors, one can reliably predict the site of attack by soft nucleophiles. Thus, for synthetic applications, if one starts with a thermodynamically stable exo cation, one expects nucleophilic addition cis to the nitrosyl and the formation of cis products. This approach has allowed us to develop syntheses of (–)-cycloocten-3-ol and (–)-3-deuteriocyclooctene in high optical yield.[28]

Acknowledgment. This research was supported by National Science Foundation Grant CHE82-08042. We also wish to thank the NSF for its support of the Northeast Regional NMR Facility (Grant CHE79-16210).

Registry No. (η^5-C_5H_5)Mo(CO)$_2$(η^3-C_8H_{13}), 81923-02-6; *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]BF_4, 90081-04-2; *exo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]BF_4, 81923-05-9; *endo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]PF_6, 90129-01-4; *exo*-[CpMo(NO)(CO)(η^3-C_8H_{13})]PF_6, 90081-05-3; (*RR,SS*)-CpMo(NO)(CO)(η^2-C_8H_{13}OH), 90030-06-1; (*RS,SR*)-CpMo(NO)(CO)(η^2-C_8H_{13}OH), 90081-06-4; CpMo(NO)(CO)(η^2-C_8H_{12}), 90030-07-2; CpMo(NO)(CO)(η^2-C_8H_{14}), 90030-08-3; (*RR,SS*)-CpMo(NO)(CO)(η^2-C_8H_{13}D), 90030-09-4; (*RS,SR*)-CpMo(NO)(CO)(η^2-C_8H_{13}D), 90081-07-5; (*RR,SS*)-CpMo(NO)(CO)[η^2-C_8H_{13}(S_2CNMe_2)], 90030-10-7; (*RS,SR*)-CpMo(NO)(CO)[η^2-C_8H_{13}(S_2CNMe_2)], 90081-08-6; *trans*-CpMo(NO)(CO)[B] (B = η^2-3-((dicarbomethoxy)methyl)cyclooctene), 90030-11-8; *cis*-CpMo(NO)(CO)[B] (B = η^2-3-((dicarbomethoxy)methyl)cyclooctene), 90081-09-7; Mo(CO)$_3$(CH_3CN)$_3$, 15038-48-9; (C_8H_{13})Mo(CO)$_2$(CH_3CN)$_2$Br, 81923-03-7; CpLi, 16733-97-4; $NOPF_6$, 16921-91-8; $NaCNBH_3$, 25895-60-7; $NaCNBD_3$, 25895-62-9; cyclooctene, 931-88-4; 3-bromocyclooctene, 7422-06-2; molybdenum carbonyl, 56779-83-0; nitrosyl tetrafluoroborate, 14635-75-7; sodium dimethyldithiocarbamate, 128-04-1; sodium dimethylmalonate, 18424-76-5.

Supplementary Material Available: Tables of anisotropic thermal parmeters and structure factor tables for both structures (23 pages). Ordering information is given on any current masthead page.

(27) The increase in endo–exo interconversion rate that occurs in the presence of nucleophiles was not understood in the initial studies with unsubstituted acyclic allyls. Therefore, the results in the acyclic system were originally interpreted in terms of trans attack on the endo isomer.[2]

(28) Faller, J. W.; Chao, K. H. *Organometallics*, in press.