Organometallics 1984, *3*, 927–932

Asymmetric Syntheses of (−)-Cycloocten-3-ol and (−)-3-Deuteriocyclooctene via Nucleophilic Attack on (η^3-Cyclooctenyl)molybdenum Complexes

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Received December 28, 1983

Nucleophilic attack on the exo isomer of (neomenthylcyclopentadienyl)carbonylnitrosyl(η^3-cyclooctenyl)molybdenum(II) cations provides a facile route to optically pure allylically substituted cyclic olefins. A given configuration at the metal center controls the configuration at the allylic center owing to preferential attack cis to the nitrosyl ligand in the exo isomer. The pure (*R*)-[NMCpMo(NO)(CO)(η^3-C_8H_{13})]$^+$ cation was obtained from (*S*)-NMCpMo(NO)(Br)(η^3-C_8H_{13}), which was readily separated from the diastereomeric mixture of the bromide complex. Thus, reaction of deuteride and water with the (+)-(*R*)-[NMCpMo(NO)(CO)(η^3-C_8H_{13})]$^+$ cation provided (−)-(*R*)-3-deuteriocyclooctene and (−)-(*R*)-cycloocten-3-ol upon liberation of the olefin from the complex. The crystal and molecular structure of (*S*)-NMCpMo(NO)(Br)(η^3-C_8H_{13}) was determined by X-ray crystallographic analysis. This compound, $MoBrONC_{23}H_{36}$, crystallizes in the triclinic space group *P*1 with one molecule in the unit cell of dimensions a = 6.697 (1) Å, b = 9.710 (2) Å, c = 9.908 (2) Å, α = 108.74 (2)°, β = 104.46 (2)°, and γ = 95.10 (1)°. For 1674 reflections [$F^2 \geq 3\sigma(F^2)$] and 241 parameters the structure refined to R_1 = 0.032 and R_2 = 0.033.

The use of metal complexes to enhance asymmetric induction in nucleophilic additions to allylic systems has been under investigation for a number of years;[1-3] however, only recently has significant progress been made in the development of systems with very high optical yields.[3,4] We have attempted to develop an approach in which the nature of the asymmetric induction can be controlled by the unsymmetrical electronic nature of molybdenum complexes containing nitrosyl and carbonyl ligands. This contrasts with the approach pursued by Trost[1] and Bosnich[3] using palladium catalysts which allow rationalization of optical yields in terms of steric interactions.[3] In an earlier paper,[4] we reported that cationic NMCpMo(NO)(CO)(allyl) complexes provide a well-defined system which provides a high degree of asymmetric induction. We now wish to report the use of this system to produce optically active cyclocten-3-ol and 3-deuteriocyclooctene in high enantiomeric excess. These syntheses provide not only the first examples of the preparations of these optically active compounds but also insight into the nature of the chiral induction and alternative procedures for the use of these molybdenum complexes in asymmetric synthesis.

Experimental Section

General Synthetic Procedures. All operations involving the handling of organometallic complexes in solution were carried out under an atmosphere of nitrogen by using standard inert-atmosphere techniques. All solvents were dried before use. THF was distilled from sodium benzophenone ketyl under nitrogen before use. Dichloromethane and CH_3CN were distilled from CaH_2 under nitrogen before use.

Neomenthylcyclopentadiene was prepared according the method of Cesarotti, Kagan, et al.,[5] with the exception that the reflux period with NaCp was increased to 10 h.

NMR spectra were obtained with Bruker spectrometers operating at 270 and 500 MHz. The chemical shifts are reported as parts per million downfield from Me_4Si. Optical rotations were measured with a Perkin-Elmer 241 polarimeter with a thermostated cell. Sample concentrations were measured by weighing the complex on a microbalance (±1 μg), weighing the solvent, and converting to grams per 100 cubic centimeters by using the density of the solvent.

Preparation of NMCpMo(CO)$_2$(η^3-C_8H_{13}). This complex was synthesized following Hayter's procedure for an analogous allyl.[6,7] The allyl bromide needed for this synthesis was conveniently obtained by treatment of cyclooctene with *N*-bromosuccinimide.[8,9]

A 200-mL, three-neck, round-bottom flask equipped with a magnetic stirrer, reflux condenser, thermometer, and nitrogen inlet was charged with 10.0 g (37.9 mmol) of $Mo(CO)_6$ (sublimed) and 100 mL of CH_3CN. The resulting suspension was first heated gently to boiling and then heated to *vigorous* reflux. After 5 h at reflux, the reaction mixture (a yellow solution) was treated with a solution of 7.1 g (37.9 mmol) of 3-bromocyclooctene in 10 mL of THF. A bright orange solid precipitated after a period of 0.5 h. The reaction mixture was cooled to 0 °C, and the supernatant was decanted. The crystals were washed with two 10-mL portions of CH_3CN. The residual solvent was removed by vacuum at room temperature to yield 14.4 g (90%) of [$(CH_3CN)_2MoBr(CO)_2$(η^3-C_8H_{13})] as bright yellow crystals.

In the final step of the synthesis, lithium neomenthylcyclopentadienide was added to the acetonitrile adduct giving the desired allyl product in 80% yield. The LiNMCp was prepared from a solution of 2.11 g (10.0 mmol) of freshly prepared neomenthylcyclopentadienide[5] in 10 mL of THF by the addition of 6.9 mL of 1.6 M *n*-BuLi in hexane. The resulting suspension was added via syringe to a suspension of [$(CH_3CN)_2MoBr(CO)_2$(η^3-C_8H_{13})] in 25 mL of THF contained in a 100-mL, round-bottom flask equipped with a magnetic stirrer and a no-air stopper. The yellow starting material dissolved over 15 min to form an orange solution. After the solution was stirred for 6 h at 25 °C, removal of the solvent on a rotary flash evaporator left an orange-red crystalline residue.

The crude orange-red product was dissolved in a mixture of pentane and CH_2Cl_2 (1:1), and chromatographed over a 2.5 × 12 cm column of alumina (Fisher Adsorption Grade). Removal of solvent from the eluent gave 3.62 g (75%) of a yellow crystalline

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product. Recrystallization from pentane gave the product as yellow needles: mp 89 °C; ^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz) δ 5.327, 5.135, 5.080, 4.984 (q, 4 H, CpH of NMCp, J = 2 Hz), 4.089 (t, 1 H, H_1, J = 8.27 Hz), 3.688 (m, 2 H, H_2), 2.793 (m, 1 H, H of NMCp), 2.325 (m, 2 H, H_{31}), 2.202 (m, 2 H, H_{32}), 2.070, 1.822 (m, 2 H, H of NMCp), 0.928, 0.898, 0.705 (d, 9 H, 3Me of NMCp, J = 6 Hz). Carbonyl bands were observed in cyclohexane solution in the IR spectrum at 1935 and 1886 cm^{-1}. Anal. Calcd for $C_{25}H_{36}MoO_2$: C, 64.64; H, 7.81. Found: C, 64.56; H, 7.86. The solution of the product gave $[\alpha]_D$ +44° (c 0.197, pentane, 25 °C).

Mixture of (+)- and (−)-[NMCpMo(NO)(CO)(η^3-C_8H_{13})]-BF_4. A 100-mL, three-neck, round-bottom flask equipped with a magnetic stirrer and nitrogen inlet was charged with 1.00 g (2.15 mmol) of [NMCpMo$(CO)_2$(η^3-C_8H_{13})] and 10 mL of CH_3CN; to this solution at 0 °C was added 0.258 g (2.15 mmol) of $NOBF_4$. The resulting yellow-orange suspension was stirred for 5 min at 0 °C. The oily yellow product (1.218 g, 99%) was collected by the removal of the solvent. Its ^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz) showed two sets of resonances in a 3:2 ratio: major, δ 6.429, 5.867, 5.773 (q, 4 H, CpH of NMCp, J = 2 Hz), 6.219 (qd, 1 H, H_1, J = 8.2, 1.7 Hz), 5.958 (m, 1 H, H_3), 4.929 (t, 1 H, H_2), 0.977, 0.963, 0.769 (d, 9 H, 3 Me of NMCp, J = 6 Hz); minor, δ 6.214, 6.036, 5.925, 5.790 (q, 4 H, CpH of NMCp, J = 2 Hz), 6.088 (qd, 1 H, H_1, J = 8.2, 1.7 Hz), 5.998 (m, 1 H, H_3), 4.970 (t, 1 H, H_2, J = 8.6 Hz), 0.968, 0.945, 0.781 (d, 9 H, 3Me of NMCp, J = 6 Hz). Carbonyl and nitrosyl bands were observed in $CDCl_3$ solution in the IR at 2037 and 1698 cm^{-1}.

Mixture of (+)- and (−)-NMCpMo(NO)(Br)(η^3-C_8H_{13}). A 100-mL, three-neck, round-bottom flask equipped with a magnetic stirrer and nitrogen inlet was charged with 1.218 g (2.15 mmol) of the mixture of [NMCpMo(NO)(CO)(η^3-C_8H_{13})]BF_4 and 30 mL of acetone. To this solution at 25 °C was added 0.442 g (4.30 mmol) of NaBr. The reaction mixture was stirred for 2 h, and the solvent was then removed under vacuum.

The crude product was dissolved in a mixture of pentane and CH_2Cl_2 (1:1) and separated from a white residue by filtration. This solution was chromatographed on a silica gel column. A yellow band was collected, and the solvent was evaporated to yield an orange product. ^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz) of two isomers in a 3:2 ratio: major, δ 6.215 (qd, 1 H, H_1, J = 8.8, 1.5 Hz), 5.921, 5.602, 5.552, 5.463 (q, 4 H, CpH of NMCp), 5.179 (t, 1 H, H_2, J = 8.8Hz), 4.060 (dtd, 1 H, H_3, J = 8.4, 8.3, 1.7 Hz), 0.970, 0.915, 0.783 (d, 9 H, 3Me of NMCp, J = 6 Hz); minor, δ 6.046 (qd, 1 H, H_1, J = 8.8, 1.5 Hz), 5.835, 5.641, 5.552, 5.552 (q, 4 H, CpH of NMCp), 5.127 (t, 1 H, H_2, J = 8.8 Hz), 3.971 (dtd, 1 H, H_3, J = 8.4, 8.3, 1.7 Hz), 0.966, 0.871, 0.755 (d, 9 H, 3Me of NMCp, J = 6 Hz). IR (cyclohexane, NO): 1647 cm^{-1}.

Isolation of Pure (−)$_D$-NMCpMo(η^3-C_8H_{13})(NO)(Br). Two grams of the mixture of (+)- and (−)-NMCpMo(C_8H_{13})(NO)(Br) (3.86 mmol) was dissolved in 15 mL of acetone, and 5 mL of pentane was added to the solution. The solution was cooled to −15 °C for 2 days, and yellow-orange crystals were collected. The NMR of these crystals showed there was no trace of a second isomer and that only one set of resonances were present: ^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz) δ 6.215 (qd, 1 H, H_1, J = 8.8, 1.5 Hz), 5.921, 5.602, 5.552, 5.463 (q, 4 H, CpH of NMCp, J = 2 Hz), 5.179 (t, 1 H, H_2, J = 8.7 Hz), 4.060 (dtd, 1 H, H_3, J = 10.1, 8.2, 1.5 Hz), 0.970, 0.915, 0.787 (d, 9 H, 3Me of NMCp, J = 6 Hz). These yellow-orange crystals melted at 153–155 °C dec. A nitrosyl band was observed in cyclohexane solution in the IR spectrum at 1647 cm^{-1}. The solution of the product gave $[\alpha]_D$ − 586° (c 0.063, $CDCl_3$, 25 °C). Anal. Calcd for $BrC_{23}H_{36}MoNO$: C, 53.29; H, 7.00. Found: C, 53.32; H, 7.02.

Isolation of Pure (+)$_D$-NMCpMo(η^3-C_8H_{13})(NO)(Br). The solution from which (−)$_D$-NMCpMo(η^3-C_8H_{13})(NO)(Br) had been isolated was evaporated and the residue dissolved in a minimum amount of CH_2Cl_2. Pentane was added dropwise until the solution became cloudy. The solution was stored at −15 °C to allow the product to crystallize. The yellow needles melted at 125–128 °C dec, and cyclohexane solutions showed a single NO band in the IR at 1647 cm^{-1}. The solution of the product gave $[\alpha]_D$ +334° (c 0.036, $CDCl_3$, 25 °C). Its ^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz) showed that only one set of resonances were present: δ 6.046 (qd, 1 H, H_1, J = 9.1, 1.5 Hz), 5.835, 5.641, 5.552, 5.552 (q, 4 H, Cp of NMCp, J = 2 Hz), 5.127 (t, 1 H, H_2, J = 8.7 Hz), 3.971 (dtd, 1 H, H_3, J = 10.1, 8.2, 1.5 Hz), 3.155 (m, 1 H, H of NMCp), 0.966, 0.871, 0.755 (d, 9 H, 3Me of NMCp, J = 6 Hz). Anal. Calcd for $BrC_{23}H_{36}MoNO$: C, 53.29; H, 7.00. Found: C, 53.34, H, 7.04.

Preparation of (+)$_D$-[NMCpMo(η^3-C_8H_{13})(NO)(CO)]PF_6. The bromide complex (−)$_D$-NMCpMo(η^3-C_8H_{13})(NO)(Br) (103.6 mg, 0.3 mmol) was dissolved in 30 mL of CH_2Cl_2 at 25 °C in a 40-mL centrifuge bottle. Silver hexafluorophosphate (50.6 mg, 0.2 mmol) was added to the solution. The color of the solution changed from yellow-orange into bright yellow, and a precipitate was formed. The solution was stirred in the dark for 5 min, and the precipitate was separated by centrifugation. The air-sensitive supernatant was transferred by cannula into a Fischer–Porter pressure bottle. The solution was stirred under 5-atm pressure of carbon monoxide for 30 min and was filtered through a glass fiber filter. The solvent was removed from the yellow filtrate by a rotary flash evaporator, and the the residue was recrystallized from a CH_2Cl_2–pentane mixture to give a yellow crystalline product (110 mg, 0.18 mmol, 90%): mp 64–67 °C; ^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz) δ 6.429, 5.911, 5.867, 5.773 (q, 4 H, CpH of NMCp, J = 2 Hz), 6.219 (qd, 1 H, H_1, J = 8.2, 1.7 Hz), 5.958 (m, 1 H, H_3), 4.929 (t, 1 H, H_2, J = 8.6 Hz), 0.977, 0.963, 0.769 (d, 9 H, 3Me of NMCp, J = 6 Hz); IR (cyclohexane, CO, NO) 2067, 1706 cm^{-1}; $[\alpha]_D$ +204° (c 0.117, $CDCl_3$, 25 °C). Anal. Calcd for $C_{24}F_6H_{36}MoNO_2P$: C, 47.14; H, 5.93. Found: C, 47.2; H, 6.00.

Preparation of (−)$_D$-NMCpMo(NO)(CO)(η^2-$C_8H_{13}OH$). The (+)$_D$-[NMCpMo(NO)(CO)(η^3-C_8H_{13})]PF_6 complex (0.18 mmol) was dissolved in 30 mL of THF at 25 °C, and water (5 mL, 278 mmol) was added to the solution. The solution was stirred for 15 min, and the product was extracted with ether. The organic solution was dried over Na_2SO_4, and the solvent was removed with a rotary flash evaporator. A yellow oil (69.6 mg, 0.14 mmol, 80% yield) was collected. Several attempts were made to crystallize this material; however, they were unsuccessful. Its ^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz) showed the following resonances: δ 6.076, 5.593, 5.498, 4.859 (q, 4 H, CpH of NMCp, J = 2 Hz), 3.809 (m, 1 H, H_{31}), 3.131 (t, 1 H, H_2, J = 8.2 Hz), 2.833 (td, 1 H, H_1, J = 8.2, 3.7 Hz), 2.727 (dq, 1 H, H_{81}, J = 13.0, 3.0 Hz), 2.138 (m, 1 H, H_{82}), 0.918, 0.906, 0.758 (d, 9 H, 3Me of NMCp, J = 6 Hz). Carbonyl and nitrosyl bands were observed at 1933 and 1639 cm^{-1} in the IR spectrum (cyclohexane). The solution of the product gave $[\alpha]_D$ −95.1° (c 0.740, $CDCl_3$, 25 °C). Anal. Calcd for $C_{24}H_{37}MoNO_3$; C, 59.62; H, 7.71. Found: C, 59.06; H, 7.42.

Isolation of Optically Active (−)$_D$-Cycloocten-3-ol. A $CDCl_3$ solution of (−)$_D$-NMCpMo(NO)(CO)(η^2-$C_8H_{13}OH$) (69.6 mg, 0.14 mmol) was sealed in a NMR tube *under air* for 3 days, after which the metal complex decomposed completely (monitored by ^{1}H NMR). The volume of this solution was reduced to 0.5 mL and was chromatographed on silica gel (4 cm × 2 cm) by using a fixed volume collection method. Each fraction was checked on a silica gel TLC plate (eluted with CH_2Cl_2), and fractions that contained a substance with R_f 0.22 were combined. The solvent of this solution was carefully removed with a rotary flash evaporator, and optically active 3-cyclooctenol (14.1 mg, 0.112 mmol, 80% yield) was obtained. The solution of this compound gave $[\alpha]_D$ −12.1° ($CDCl_3$, 25 °C).

Determination of the Optical Purity of Cycloocten-3-ol. A chiral shift reagent tris[3-((trifluoromethyl)hydroxymethylene)-*d*-camphorato]europium, was added in portions to a benzene-d_6 solution of optically active cycloocten-3-ol. The induced shifts were monitored by ^{1}H NMR after each addition. The addition was stopped when the H_{41} resonance moved from δ 2.0 and split into two resonances at δ 3.708 and 3.892. The ratio between these two resonances was 27:1, indicating an ee of 93%. This resonance was tentatively assigned to the proton on C(4) which was adjacent to the hydroxyl carbon (C(3)). Addition of small amount of racemic cycloocten-3-ol moved these two resonances upfield and reduced the difference between them from 0.188 to 0.165 ppm; furthermore, a different ratio of intensities was produced. These observations confirmed that the ratio we had observed was indeed the true ratio between the two enantiomers.

Since the measured specific rotation of the 93% optically pure compound was −12.1°, enantiomerically pure (−)-cycloocten-3-ol should have a specific rotation of $[\alpha]_D$ −13.0°.

Preparation of (−)$_D$-NMCpMo(NO)(CO)(η^2-$C_8H_{13}D$). The optically pure complex (+)$_D$-[NMCpMo(NO)(CO)(η^3-C_8H_{13})]PF_6 (110 mg, 0.18 mmol) was suspended in 30 mL of THF at 25 °C and was cooled to −78 °C, and $NaCNBD_3$ (11 mg, 0.18 mmol) was added to the suspension. The mixture was stirred for 30 min and the solvent removed with a rotary flash evaporator. The yellow residue was chromatographed on a silica gel column eluted with a mixture of CH_2Cl_2 and pentane (1:1). A yellow band was collected, the solvent removed, and the residue recrystallized from pentane to give a 95% yield of yellow crystals (80.3 mg) melting at 85–87 °C: IR (CO, NO, cyclohexane) 1966, 1607 cm^{-1}. A solution of this compound gave $[\alpha]_D$ −132° (c 0.096, $CDCl_3$, 25 °C). The ^1H NMR ($CDCl_3$, 25 °C, 270 MHz) showed the following resonances: δ 5.983, 5.400, 5.117, 5.033 (q, 4 H, CpH of NMCp, J = 2 Hz), 3.098 (dd, 1 H, H_2, J = 10.9, 10.1 Hz), 2.965 (td, 1 H, H_1, J = 10.7, 3.3 Hz), 2.888 (m, 1 H, H of NMCp), 2.625 (m, 1 H, H_{31}), 0.942, 0.900, 0.758 (d, 9 H, 3Me of NMCp, J = 6 Hz). Anal. Calcd for $C_{24}DH_{36}MoNO_2$: C, 61.53; H, 8.17. Found: C, 61.57; H, 8.21.

Greater than 95% selectivity for formation of the (R,R) isomer was observed as indicated by nearly complete absence of the H_8 proton resonance. Hence, this compound acts as an effective chiral shift reagent for determining the optical purity of the bound 3-deuteriocyclooctene.

Isolation of Optically Active 3-Deuteriocyclooctene. The olefin complex $(-)_D$-NMCpMo(NO)(CO)(η^2-$C_8H_{13}D$) (80 mg, 0.17-mmol) was dissolved in 1 mL of $CDCl_3$, and this solution was sealed with air at room temperature. It was allowed to stand for 48 h, until the complex decomposed completely (monitored by ^1H NMR). The reaction was essentially quantitative to yield the free olefin in solution (by NMR). After the solution was passed through a short column of silica gel, the solvent was separated by gas chromatography with 6 ft × 1/8 in. column (10% UC-W98 silicone gum, 120 °C, flow 80 cm^3/min) and the optically active 3-deuteriocyclooctene was collected with a retention time of 4 min. The solution of this product showed only NMR resonances characteristic of 3-deuteriocyclooctene and showed $[\alpha]_D$ −1.2° (c 0.037, $CDCl_3$, 25 °C). On the basis of the optical purity of the NMCpMo(NO)(CO)($C_8H_{13}D$) complex and the >95% regioselectivity of deuteride addition, it follows that the 3-deuteriocyclooctene is >90% optically pure.

Reaction of $(+)_D$-[NMCpMo(NO)(CO)(η^3-C_8H_{13})]PF_6 and NaBr. $(+)_D$-[NMCpMo(NO)(CO)(η^3-C_8H_{13})]PF_6 (55 mg, 0.09 mmol) was suspended in 10 mL of acetone at 25 °C. Sodium bromide (9.2 mg, 0.09 mmol) was added to the solution. The solution was stirred vigorously for 30 min, during which the color of the solution changed from yellow to bright orange. The solvent was removed and the residue chromatographed on a silica gel column with dichloromethane. A yellow band was collected and the solvent evaporated to yield yellow-orange crystals which melted at 153–155 °C dec; IR (cyclohexane, NO) 1647 cm^{-1}; $[\alpha]_D$ −586° (c 0.031, $CDCl_3$, 25 °C). These properties, as well as the NMR spectrum, were identical within experimental error with those of $(-)_D$-(S)-NMCpMo(NO)(Br)(η^3-C_8H_{13}), for which the X-ray crystal structure was determined.

Crystallographic Analyses. 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-circle diffractometer. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. The crystal data and the data collection parameters are listed in Table I. Data processing was 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. Neutral atom scattering factors were calculated by standard procedures.[10a] Anomalous dispersion corrections were applied to all atoms.[10b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Table I. Crystallographic Data for X-ray Diffraction Studies for (−)-NMCpMo(NO)Br(C_8H_{13})

(A) Crystal Data	
formula	$Mo_1Br_1O_1N_1C_{23}H_{36}$
temp, ±3 °C	23
space group	$P1$, No. 1
a, Å	6.697 (1)
b, Å	9.710 (2)
c, Å	9.908 (2)
α, deg	108.7[illegible] (2)
β, deg	104.46 (2)
γ, deg	95.10 (1)
V, Å^3	1162.6 (9)
M_r	518.40
ρ_{calcd}, g/cm^3	1.48
(B) Measurement of Intensity Data	
radiation	Mo Kα (0.710 73 Å)
monochromator	graphite
detector aperture, mm	
horizontal ($A + B$ tan θ), A and B	3.0 and 1.0
vertical	4.0
reflctns measd	$+h, \pm k, \pm l$
max 2θ, deg	50
scan type	moving crystal–stationary counter
ω scan width (A + 0.347 tan θ), deg, A =	0.90
background	1/4 additional at each end of scan
ω scan rate (variable)	
max, deg/min	10.0
min, deg/min	1.3
no. of reflfns measd	2025
data used [$F^2 \geq 3\sigma(F^2)$]	1674
(C) Treatment of Data	
abs correctn	not applied
abs coeff, cm^{-1}	22.6
p factor	0.02
final residuals R_1 and R_2	0.032 and 0.033
esd of unit weight	1.70
largest shift/error value on final cycle	0.04
largest peak in final difference Fourier, e/Å^3	0.44

The triclinic space group $P1$ was established by the requirement of the presence of a single enantiomer within in the unit cell. The structure was solved by a combination of Patterson and difference Fourier techniques. The correct enantiomer was chosen on the basis of the known chirality of the neomenthyl group.[9] Most hydrogen atoms could be located in the difference Fourier maps after the other atoms had been refined anisotropically. Hydrogen atoms were included in the final refinement stages at fixed idealized locations. The values of the fractional coordinates are listed in Table II. The bond lengths and angles and the esds obtained from the inverse matrix obtained on the final cycle of refinement are given in Tables III and IV. Tables of anisotropic thermal parameters, structure factor amplitudes, and the calculated positions of the hydrogen atoms are included in the supplementary material.

The compound also crystallizes in a second modification for which the monoclinic space group $P2_1$ was established by the systematic absences $0k0$, $k = 2n + 1$. The cell parameters were a = 6.584 (2) Å, b = 18.263 (4) Å, c = 9.939 (2) Å, β = 103.39 (2)°, and V = 1162.6 (9) Å^3. Anisotropic refinement of 1708 reflections as above converged to yield the final residuals R_1 = 0.034 and R_2 = 0.035. The molecular structure was essentially identical with the triclinic structure except that the isopropyl group of the neomenthyl group was disordered. All of the data for this structure are included in the supplementary material.

Results

In order to unambiguously establish the absolute configuration at the metal center of the complexes used in this study, an X-ray crystallographic study of $(-)_D$-NMCpMo(NO)(Br)(η^3-C_8H_{13}) was undertaken.[11] Refer-

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(10) "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 (–)-NMCpMo(NO)(Br)(C_8H_{13}) {*P*1}

atom	*x/a*	*y/b*	*z/c*	B_{eqv}, Å^2
Mo	0.0000	0.0000	0.0000	3.15 (1)
Br	–0.3624 (1)	–0.1814 (1)	–0.1030 (1)	5.63 (2)
O	–0.1492 (9)	0.2196 (6)	0.2201 (6)	6.3 (2)
N	–0.0864 (9)	0.1263 (7)	0.1362 (6)	4.1 (2)
Cp(1)	0.089 (1)	0.1797 (7)	–0.1002 (7)	3.5 (2)
Cp(2)	0.246 (1)	0.0882 (8)	–0.1036 (7)	3.7 (2)
Cp(3)	0.147 (1)	–0.0574 (8)	–0.2051 (8)	4.1 (2)
Cp(4)	–0.063 (1)	–0.0574 (9)	–0.2614 (7)	4.5 (2)
Cp(5)	–0.102 (1)	0.0862 (8)	–0.1937 (8)	4.0 (2)
C(1)	0.320 (1)	0.0239 (8)	0.1825 (8)	4.5 (2)
C(2)	0.220 (1)	–0.1250 (8)	0.1151 (7)	4.0 (2)
C(3)	0.041 (1)	–0.1840 (8)	0.1342 (8)	4.1 (2)
C(4)	–0.023 (1)	–0.1328 (9)	0.2747 (9)	5.2 (2)
C(5)	0.133 (2)	–0.1564 (11)	0.4076 (9)	6.9 (2)
C(6)	0.355 (2)	–0.1086 (12)	0.4286 (11)	7.2 (2)
C(7)	0.446 (2)	0.0538 (11)	0.4569 (10)	7.0 (2)
C(8)	0.339 (1)	0.1176 (9)	0.3395 (9)	5.7 (2)
Cm(1)	0.116 (1)	0.3475 (7)	–0.0279 (8)	3.6 (2)
Cm(2)	0.208 (1)	0.4271 (8)	–0.1198 (8)	4.6 (2)
Cm(3)	0.447 (1)	0.4248 (9)	–0.0870 (9)	5.3 (2)
Cm(4)	0.561 (1)	0.4937 (9)	0.0745 (10)	5.8 (2)
Cm(5)	0.477 (1)	0.4270 (8)	0.1727 (8)	4.6 (2)
Cm(6)	0.238 (1)	0.4185 (8)	0.1364 (8)	4.5 (2)
Cm(7)	0.088 (1)	0.3732 (8)	–0.2857 (8)	5.5 (2)
Cm(8)	–0.130 (2)	0.4014 (11)	–0.3110 (10)	7.5 (3)
Cm(9)	0.195 (2)	0.4478 (12)	–0.3738 (11)	7.8 (3)
Cm(10)	0.587 (2)	0.5143 (10)	0.3370 (11)	6.7 (3)

Table III. Selected Bond Distances (Å) for (–)-NMCpMo(NO)Br(C_8H_{13}) {*P*1}

Mo-Br	2.623 (1)	C(1)-C(2)	1.403 (9)
Mo-N	1.764 (5)	C(1)-C(8)	1.495 (10)
Mo-Cp(1)	2.368 (6)	C(2)-C(3)	1.364 (9)
Mo-Cp(2)	2.377 (6)	C(3)-C(4)	1.505 (9)
Mo-Cp(3)	2.405 (6)	C(4)-C(5)	1.558 (11)
Mo-Cp(4)	2.383 (6)	C(5)-C(6)	1.457 (17)
Mo-Cp(5)	2.309 (6)	C(6)-C(7)	1.549 (16)
		C(7)-C(8)	1.541 (11)
Mo-C(1)	2.373 (6)		
Mo-C(2)	2.307 (6)		
Mo-C(3)	2.544 (7)	Cm(1)-Cm(2)	1.566 (10)
		Cm(1)-Cm(6)	1.519 (9)
N-O	1.204 (6)	Cm(2)-Cm(3)	1.552 (10)
		Cm(2)-Cm(7)	1.528 (10)
Cp(1)-Cp(2)	1.435 (8)	Cm(3)-Cm(4)	1.485 (12)
Cp(1)-Cp(5)	1.406 (9)	Cm(4)-Cm(5)	1.516 (12)
Cp(1)-Cm(1)	1.528 (9)	Cm(5)-Cm(6)	1.536 (11)
Cp(2)-Cp(3)	1.426 (9)	Cm(5)-Cm(10)	1.521 (11)
Cp(3)-Cp(4)	1.381 (9)	Cm(7)-Cm(8)	1.480 (12)
Cp(4)-Cp(5)	1.419 (9)	Cm(7)-Cm(9)	1.558 (13)

Table IV. Selected Bond Angles (deg) for NMCpMo(NO)Br(C_8H_{13}) {*P*1}

Br-Mo-N	91.52 (17)	Mo-N-O	173.84 (47)
Br-Mo-Cp(1)	123.97 (14)	C(2)-C(1)-C(8)	123.91 (59)
Br-Mo-C(1)	134.11 (16)	C(1)-C(2)-C(3)	125.57 (62)
Br-Mo-C(2)	102.64 (18)	C(2)-C(3)-C(4)	125.40 (62)
Br-Mo-C(3)	74.19 (16)	C(3)-C(4)-C(5)	112.12 (61)
N-Mo-Cp(1)	93.13 (22)	C(4)-C(5)-C(6)	115.70 (72)
N-Mo-C(1)	90.19 (25)	C(5)-C(6)-C(7)	121.52 (82)
N-Mo-C(2)	108.37 (22)	C(6)-C(7)-C(8)	115.93 (71)
N-Mo-C(3)	94.22 (22)	C(1)-C(8)-C(7)	114.13 (64)
C(1)-Mo-C(2)	34.86 (22)		
C(1)-Mo-C(3)	59.95 (22)		
C(2)-Mo-C(3)	32.20 (22)		

ence to the known absolute configurations[9] of the chiral centers in the neomenthyl group allowed straightforward determination of the configuration of the metal center.[11] The (–)$_D$ complex was shown to have the (*S*) configuration as shown in Figure 1.

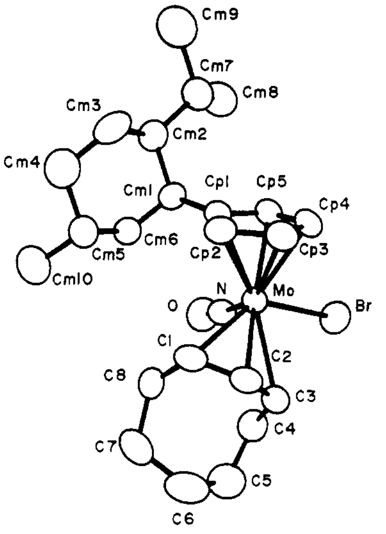

Figure 1. An ORTEP diagram showing 50% probability ellipsoids for (–)$_D$-(*S*)-*exo*-NMCpMo(NO)(Br)(η^3-C_8H_{13}) {*P*1}.

We have also shown previously[9] that the iodide (–)$_D$-*exo*-CpMo(NO)(I)(η^3-C_8H_{13}) also has the (*S*) configuration. Since there are several reversals of sign in the ORD spectra of these complexes, it is marginal to assume correlations of configuration with signs of rotation unless the complexes are very similar. Nevertheless, it is interesting to note that the halides of the same configuration have the same sign of rotation at the sodium D line.

A pure enantiomeric bromide can be converted to a pure enantiomeric carbonyl cation by abstraction of bromide by silver ion and subsequent treatment with a modest pressure of carbon monoxide (eq 1). The nature of the stereochemical consequences of this transformation can

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[11] NMCp is an abbreviation for the neomenthylcyclopentadienyl group. Exo and endo refer the orientation of the allyl group relative to the cyclopentadienyl ring. In this paper only the chirality descriptor for the CpMo(NO)(X)(allyl) portion is appended to the name for simplicity. 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.[12-14]

[12] LeComte, C.; Dusausay, Y.; Protas, J.; Tirouflet, J.; Dormond, A. *J. Organomet. Chem.* 1974, *73*, 67–76.

[13] Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* 1975, *97*, 6598.

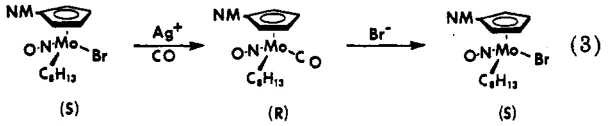
[14] Sloan, T. E. *Top. Stereochem.* 1981, *12*, 1–36.

be deduced by reconversion to the bromide by addition of NaBr (eq 2).

$$\text{(-)-NMCpMo(NO)(Br)(C}_8\text{H}_{13}) \xrightarrow{\text{CO}} \text{(+)-NMCpMo(NO)(CO)(C}_8\text{H}_{13}) \quad (1)$$

$$\text{(+)-NMCpMo(NO)(CO)(C}_8\text{H}_{13}) \xrightarrow{\text{Br}} \text{(-)-NMCpMo(NO)(Br)(C}_8\text{H}_{13}) \quad (2)$$

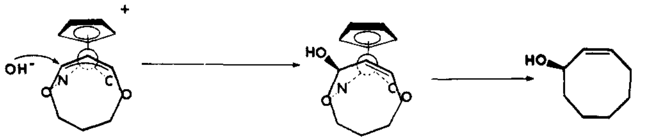
Since we have already shown[9] that carbonyl displacement by halide occurs with retention of configuration, this demands that the first step also occurs with retention (eq 3).[15]



(3)

The absence of epimerization at the CpMo(η^3-C_8H_{13})(NO)(solvent) center might at first appear unexpected; however, this "memory effect" and the ability for a solvated complex to retain its stereochemistry have been observed occasionally in other chiral cyclopentadienylmetal complexes.[16,17]

We have previously shown that reaction of water with *exo*-CpMo(NO)(CO)(η^3-C_8H_{13}) gives the alcohol resulting from addition cis to the NO.[18] It follows that the alcohol produced on the neomenthylcyclopentadienyl analogue should have the same relative configuration (eq 4).[19] Thus

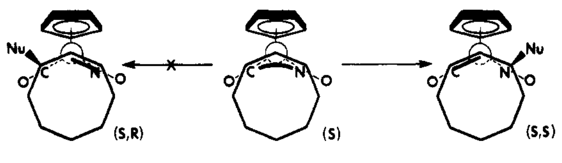


(4)

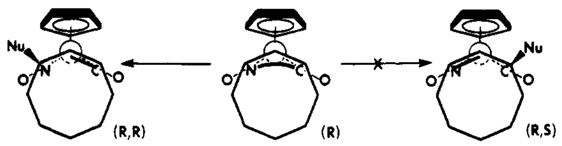
the reactions with (+)-(*R*)-NMCpMo(NO)(CO)(η^3-C_8H_{13}) should yield the (*R*) alcohol, which we have observed to have $[\alpha]_D$ −12.1° (93% ee). A related experiment starting with (+) cation and using $CNBD_3^-$ as a nucleophile produced optically active 3-deuteriocyclooctene with $[\alpha]_D$ −1.2°, presumably having the (*R*) configuration.

Discussion

Owing to the thermodynamic stability of the exo isomer of the CpMo(NO)(CO)(η^3-C_8H_{13}) cation and the powerful directing effect of the nitrosyl group, predominantly one enantiomeric product should be produced from a reaction on a given enantiomer of a an *exo*-(η^3-cyclooctenyl)molybdenum complex (eq 5 and 6).[4,18] Attachment of a neomenthyl group to the cyclopentadienyl ring of simple allylmolybdenum complexes had proven to be a valuable method of producing diastereomers of significantly different physical properties. In the case of the η^3-cyclooctenyl system, however, we were not able to separate the diastereomers that were formed. We observed two different sets of ^1H NMR shifts that arose from the (*R*) and (*S*) epimers of the NMCpMo(NO)(CO)(η^3-C_8H_{13}) cation; nevertheless, repeated attempts to separate these two diastereomers through recrystallization failed. Attempts were made to use chromatography to effect a separation; however, the complexes decomposed on the column.



(5)



(6)

We, therefore, tried to develop a facile separation procedure, which would be generally useful for this as well as other more highly substituted allyl systems. Resolutions are most conveniently achieved on a large scale by crystallizations; however, in difficult cases, column chromatography or HPLC often can provide alternatives if the compound can survive the chromatographic process. Thus, we turned our attention to the neutral NMCpMo(η^3-C_8H_{13})(NO)(halide) complexes. The halide complexes are robust air-stable compounds that can withstand chromatography. In general, it appears that the bromides are the most resistant to decomposition. We, therefore, attempted separation of the (*S*) and (*R*) diastereomers of NMCpMo(η^3-C_8H_{13})(NO)(Br), which are formed in a ratio of 65:35. Fortunately, a nearly pure sample of the (−)-(*S*)-NMCpMo(η^3-C_8H_{13})(NO)(Br) can be obtained in one crystallization from the mixture.

Treatment of the bromide with silver ion and CO gave only the exo isomer of (+)-(*R*)-NMCpMo(NO)(CO)(η^3-C_8H_{13}). For the cyclooctenyl complex, the exo isomer is thermodynamically more stable than the endo isomer and, therefore, after the conversion process only the exo isomer was present. In the initial treatment of NMCpMo(CO)$_2$(η^3-C_8H_{13}) with NO^+ to yield the cation, the endo conformer is formed initially. It was to our advantage that only one conformational isomer was present because a mixture of conformational isomers could potentially yield a diastereomeric mixture of products.[4,9,18]

The observation that the reaction between the cationic cyclooctenyl complex and water could form the alcohol showed that the cationic cyclooctenyl complex was more acidic than a water proton. However, since the cationic species is a highly stabilized carbonium ion, it is also a good leaving group. Thus, the alcohol is subject to decomposition by acid. The reaction is carried out with excess water to shift the equilibrium as well as moderate the acidity of the solution; nevertheless, the product is not stable in water for extended periods. We found that optimal yields were obtained when the progress of the reaction was monitored carefully and the product isolated promptly when it was complete.

In principle, a wide range of nucleophiles could be added to this system[4,19] to produce optically active olefins. One of the more novel, however, is the addition of deuteride, which allows the preparation of optically active hydrocarbons with chiral CHD centers. We found that keeping the reaction temperature at −78 °C was important in the

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(15) The chirality can be described adequately by assuming the Cp, NO, allyl, and X are tetrahedrally arranged about the molybdenum atom. Endo and exo isomerism are considered separately. By "having the same sense of chirality" we mean that the Cp, NO, and allyl maintain the same position relative to Mo and to each other, but X is either CO or Br. The chirality descriptors for the (+)-carbonyl cation and the (−)-bromide are opposite; however, they both have the same sense of chirality.

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(17) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151–206.

(18) Faller, J. W.; Chao, K. H.; Murray, H. H., submitted for publication in *Organometallics*.

(19) Several chiral centers are present in the coordinated cyclooctenyl moiety; however, only the configuration at the hydroxy-substituted carbon (C(3)) is given. When two descriptors are given, the first is that of the metal atom.[12,14]

regioselectivity of the deuteride addition. The reaction rate for this addition is fast. Therefore, in order to keep a high ratio of relative rates of different pathways, it appears that a low reaction temperature is advisable. The regioselectivity for the addition is >98% cis to the nitrosyl with use of this procedure.

The yields of the nucleophilic addition products are high. For practical use in organic synthesis, high yield methods for removing the resulting olefin from the metal are required. Oxidation by ceric ion is fast and effective but can sometimes lead to contamination with fragments from the neomenthyl group or oxidation of the product. We have chosen air oxidation because it is mild (albeit slow) and quantitative. Generally, removing the olefin from the metal is not a problem; but, separating the olefin from the solvent and organic decomposition products may be difficult. In practical applications, the intended use of the product might well determine the method of choice.

We have discussed some of the origins of the selectivity previously,[4,18,20] and the subject is still under investigation. The electronic asymmetry of the metal environment plays an important role. Some of the effects of the electronic asymmetry can be seen in Figure 1 and Table III. In particular one might note that the C(1)-C(3) carbons of the allyl tend to align parallel to the Mo-Br bond. This can be attributed to relative depletion of the back-bonding in the d-orbital parallel to the Mo-N-O bond relative to that parallel to the Mo-Br bond.[20] Also the Mo-C(1) bond length is considerably shorter than the Mo-C(3) length [i.e., 2.373 (6) and 2.544 (7) Å]. The ring appears to constrain the C(1)-C(2) and C(2)-C(3) lengths to comparable distances [1.403 (9) and 1.364 (9) Å] whereas the difference is significant in open-chain allyls.[21-23]

The carbonyl nitrosyl cations show a similar tendency for the allyl group to orient parallel to the Mo-C-O bond. The most important consequence of the electronic asymmetry, however, is its ability to effect reaction at the position cis to the NO in the exo isomer. This has provided an effective synthetic procedure for the preparation of chiral allylically substituted olefins in high optical purity. It appears that this approach may be particularly useful for mechanistic studies[24] when one needs a preparation of optically active hydrocarbons in which the chirality arises solely from the isotopic differences between H and D atoms.

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

Registry No. NMCpMo$(CO)_2(\eta^3\text{-}C_8H_{13})$, 89689-87-2; $[(CH_3CN)_2MoBr(CO)_2(\eta^3\text{-}C_8H_{13})]$, 81923-03-7; (+)-[NMCpMo(NO)(CO)$(\eta^3\text{-}C_8H_{13})]BF_4$, 89689-90-7; (+)-[NMCpMo(NO)(CO)$(\eta^3\text{-}C_8H_{13})]PF_6$, 89772-14-5; (−)-[NMCpMo(NO)(CO)$(\eta^3\text{-}C_8H_{13})]BF_4$, 89771-47-1; (+)-NMCpMo(NO)(Br)$(\eta^3\text{-}C_8H^{13})$, 89689-91-8; (−)-NMCpMo(NO)(Br)$(\eta^3\text{-}C_8H^{13})$, 89771-48-2; $(-)_D$-NMCpMo(NO)(CO)$(\eta^2\text{-}C_8H^{13}OH)$, 89689-92-9; $(-)_D$-NMCpMo(NO)(CO)$(\eta^2\text{-}C_8H^{13}D)$, 89689-93-0; $Mo(CO)_6$, 13939-06-5; $NOBF_4$, 14635-75-7; NaBr, 7647-15-6; 3-bromocyclooctene, 7422-06-2; (−)-cycloocten-3-ol, 62210-83-7; (−)-3-deuteriocyclooctene, 89689-94-1; silver hexafluorophosphate, 26042-63-7; neomenthylcyclopentadiene, 89689-88-3.

Supplementary Material Available: Tables of anisotropic temperature factors, calculated hydrogen atom positions, and structure factors for both crystal modifications of the bromide structure and tables of crystal data, positional parameters, bond lengths, and bond angles for the $P2_1$ modification (26 pages). Ordering information is given on any current masthead page.

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(23) The $P2_1$ crystal modification of this compound shows similar effects. The Mo-C(1) and Mo-C(3) lengths are 2.353 (7) and 2.547 (8) Å whereas the C(1)-C(2) and C(2)-C(3) lengths are 1.34 (1) and 1.34 (1) Å.

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Communications

Aryl Group Interchange between Triarylphosphines Catalyzed by Group 8 Transition Metals

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Received October 25, 1983

Summary: Group 8 transition metals catalyze intermolecular aryl scrambling of triarylphosphines. Reaction rates vary among metals and among different complexes of a metal.

Soluble transition-metal phosphine complexes are catalysts for a variety of industrial processes,[1] since they offer unique chemical properties and process advantages. Catalyst stability is an important consideration in these processes both because of the cost of the catalysts and because of the effects of changing catalyst activity on the process operation and efficiency.

Metal-catalyzed phosphine decompositions have been observed in several instances. For example, it has been known[2,5] that triphenylphosphine slowly decomposes during rhodium-catalyzed propylene hydroformylation to propyldiphenylphosphine. The direct carbon-phosphorus bond cleavage of triphenylphosphine has been observed with certain rhodium clusters,[3] as well as with mononuclear rhodium-phosphine complexes.[4]

Such phosphine decompositions both generate bypro-

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