Resolution of CpMo(NO)X(η^3-2-methallyl) Complexes and Their Enantioselective Reactions with an Aldehyde

J. W. Faller,* Jenna Thu Nguyen, W. Ellis, and Maria R. Mazzieri

Department of Chemistry, Yale University, New Haven, Connecticut 06511-8118

Received October 15, 1992

(*R*)- and (*S*)-CpMo(NO)(η^3-methallyl)((*S*)-(+)-10-camphorsulfonate) (Cp = cyclopentadienyl) have been prepared and separated. This provides a route for resolution of the chiral molybdenum center and allows the isolation of enantiomerically pure CpMo(NO)(η^3-methallyl)X (X = Cl, Br, I) complexes. Reaction of (+)-CpMo(NO)(η^3-methallyl)Cl with benzaldehyde in the presence of methanol yields (*S*)-(−)-3-methyl-1-phenyl-3-buten-1-ol, in >98% ee. (+)-CpMo(NO)(η^3-methallyl)I (1) was found to have the *R* configuration by X-ray crystallography.

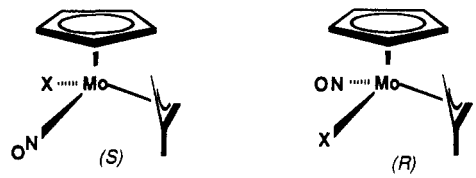
Introduction

Reactions of allylmetal compounds with prochiral aldehydes, yielding chiral homoallylic alcohols, have been widely investigated due to their application in acyclic stereoselective synthesis.[1-4] These homoallylic alcohols are often used as important building blocks in the synthesis of natural products such as polyoxo-macrolides.[1] Organometallic complexes containing allylboron, -titanium, -zirconium, -albuminum, -tin, and -chromium functionalities have been successfully utilized in this strategy.[2a] Allylborane complexes can be prepared with a wide variety of chiral auxiliaries, and these compounds have been extensively researched. Hoffmann et al. have reported the isolation of chiral alcohols with 45–77% ee from chiral allylboronates derived from camphor glycols.[2] Allylboronates derived from tartrate have been used by Roush et al. to prepare alcohols with 71–87% ee,[3] and allylboranes derived from α-pinene, utilized by Brown et al., generate alcohols with 86–96% ee.[4] According to Sato et al., some cyclopentadienyltitanium complexes can also yield homoallylic alcohols with high diastereoselectivity,[5] but some chiral analogues have met with limited success.[6] Titanium allyls with ligands derived from sugars have shown to yield homoallylic alcohols in high enantiomeric purity.[7]

We have demonstrated that the condensation of aldehydes with allylmolybdenum-containing complexes occurs with high stereoselectivity.[8] In our previous work, we have shown that the condensation of benzaldehyde with NMCpMo(NO)(η^3-methallyl)Cl (NMCp = neomenthylcyclopentadienyl) proceeds with 97% stereoselectivity.[8] These allylmolybdenum systems are air-stable and require no special precautions for manipulation at room temperature. This has a clear advantage over the allylboron systems, since some of these reagents decompose easily and the reactions must be conducted at very low temperature.[8a] We report that CpMo(NO)(η^3-methallyl)X (X = Cl, Br, I) complexes have been resolved and enantiomerically pure CpMo(NO)(η^3-methallyl)X complexes have been isolated. Reactions between these CpMo(NO)(η^3-methallyl)X complexes and benzaldehyde proceed with high enantioselectivity.

Results

The CpMo(NO)(η^3-methallyl)X complexes have a stereogenic center at the metal. Fortunately, the *R* and *S* chirality descriptors are the same for the same sense of chirality of the metal center for the cases of X = camphorsulfonate, Cl, Br, or I.



In order to resolve complexes containing this stereogenic metal center, we have previously replaced the Cp ligand by a neomenthylcyclopentadienyl group,[9,10] which yields diastereomeric complexes. These diastereomers can then be separated by fractional recrystallization to yield diastereomerically pure allylmolybdenum compounds.[9,10] We have developed an alternative approach to resolution which involves the separation of diastereomers formed by the replacement of the halide with an enantiomerically pure camphorsulfonate moiety. The diastereomeric camphorsulfonate complexes can be resolved by their solubility differences. The major advantage of this method is that the diastereomerically pure camphorsulfonate complexes can be subsequently converted back to the halide compounds, which are expected to be enantiomerically pure owing to retention of configuration at the metal center throughout the conversion.[9,10] This allows recovery of the

(1) (a) Paterson, I.; Mansuri, M. M. *Tetrahedron* **1985**, *41*, 3569. (b) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. (c) Heathcock, C. H. *Asymmetric Synth.* **1984**, *3*, 111.

(2) (a) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (b) Hoffmann, R. W.; Herold, T. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 768.

(3) (a) Roush, W. R.; Walts, A. E.; Hoong, L. K. *J. Am. Chem. Soc.* **1985**, *107*, 8186. (b) Roush, W. R.; Halterman, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 294. (c) Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 3422. (d) Roush, W. R.; Palkowitz, A. D.; Palmer, M. A. J. *J. Org. Chem.* **1987**, *52*, 316.

(4) (a) Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092. (b) Brown, H. C.; Jadhav, P. K.; Bhat, K. S.; Perumal, P. T. *J. Org. Chem.* **1986**, *51*, 432. (c) Brown, H. C.; Bhat, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 293. (d) Brown, H. C.; Krishna, S. B.; Randad, R. S. *J. Org. Chem.* **1987**, *52*, 320.

(5) (a) Sato, F.; Iijima, S.; Sato, M. *Tetrahedron Lett.* **1981**, *22*, 243. (b) Sato, F.; Iida, K.; Iijima, S.; Moriya, H.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1140.

(6) Collins, S.; Kuntz, B. A.; Hong, Y. *J. Org. Chem.* **1989**, *54*, 4154.

(7) Riediker, M.; Duthaler, R. O. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 494.

(8) (a) Faller, J. W.; Linebarrier, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937. (b) Faller, J. W.; John, J. A.; Mazzieri, M. R. *Tetrahedron Lett.* **1989**, *30*, 1769. (c) Faller, J. W.; DiVerdi, M. J.; John, J. A. *Tetrahedron Lett.* **1991**, *32*, 1271.

(9) Faller, J. W.; Shvo, Y.; Chao, K.-H.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251.

(10) Faller, J. W.; Shvo, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5398.

0276-7333/93/2312-1434$04.00/0

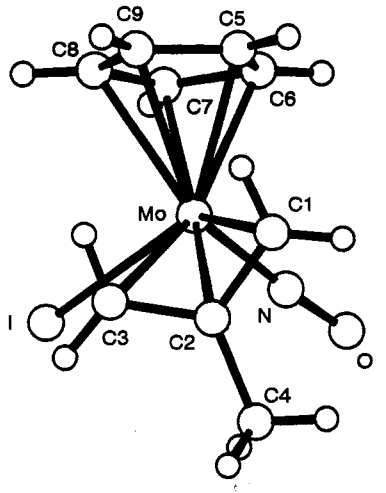


Figure 1. Molecular structure of (*R*)-(+)-CpMo(NO)(η^3-methallyl)I (1). Hydrogen atoms are shown in calculated positions.

resolving agent and provides enantiomeric molybdenum reagents. These Cp reagents avoid possible adverse diastereomeric differentiation arising from interactions with chiral groups other than those at the metal center, as might be found with the NMCp reagents. The isolation of product from the reagent is also more readily effected with the Cp reagents than with the NMCp reagents.

CpMo(NO)(η^3-methallyl)I treated with AgL^S (L^S = (1*S*)-(+)-10-camphorsulfonate) in benzene at 5–10 °C yielded an initial mixture of CpMo(NO)(η^3-methallyl)L^S from which a precipitate was obtained having a (−)-**5**:(+)-**4** ratio of 84:16. Further precipitation yielded a second crop of the camphorsulfonate complex with a (−)-**5**:(+)-**4** ratio of 20:80. Further recrystallizations afforded (+)-CpMo(NO)(η^3-methallyl)L^S in >98% de, but we were unable to isolate X-ray-quality crystals of this isomer. We were, however, able to obtain suitable crystals of the (−)-**5** isomer. These crystals did not provide a high-quality X-ray structure owing to the presence of disordered solvent molecules; however, from the X-ray crystallographic data and the known configuration of the camphorsulfonate, it was clear that (−)-CpMo(NO)(η^3-methallyl)L^S has the *S* configuration. We had previously shown that conversion to the halide complexes proceeds with retention at the metal center.[9,10] These results were reconfirmed here, because (*R*)-(+)-CpMo(NO)(η^3-methallyl)L^S yielded (+)-CpMo(NO)(η^3-methallyl)I, which was determined to have the *R* configuration by anomalous dispersion X-ray crystallography (see Figure 1).

It would follow that all of the halide exchange reactions generally occur with retention.[9,10] In this case the similarity of the CD spectra for (+)-**1**, (+)-**2**, and (+)-**3** are indicative that all have the same absolute configuration (see Figure 2). The signs of the two long-wavelength transitions also indicate the absolute configuration in the neomenthylcyclopentadienyl derivatives, for which we have also determined absolute configurations. A comparison of (+)-**1** and (−)-(neomenthylCp)Mo(NO)(I)(methallyl) is shown in Figure 3. All of these results provide further confirmation of retention in halide exchange reactions for these compounds.

Treatment of benzaldehyde with (+)-CpMo(NO)(η^3-methallyl)X (X = Cl, Br, I) complexes yielded the chiral homoallylic alcohol (*S*)-(−)-3-methyl-1-phenyl-3-buten-1-ol (**6**) with an ee between 90 and >98%. The enantiomeric purity of **6** was determined by ^{1}H NMR spectroscopy (250 MHz) using a chiral shift reagent, tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III),[Eu(hfc)$_3$]. The proton α to the hydroxyl, a triplet at δ 4.81, became a broad singlet, which subsequently split into two singlets upon further additions of Eu(hfc)$_3$. A typical experiment showed singlets at δ 19.77 and 19.18 which were sufficiently separated to obtain an accurate integration. The ortho phenyl protons also separated into two doublets (δ 14.15, 13.69) that could also be used to calculate the enantiomeric purity. The results of these experiments are summarized in Table I.

The rate of the reaction is dependent on the allylmolybdenum compound. The reaction rates follow the order Cl > Br > I, with the chloride reaction (entry 6, Table I) giving the best optical yield, >98%. The slowest reaction (entry 1) gives the lowest ee, 88%. For this type of reaction, there is a correlation between the enantioselectivity and

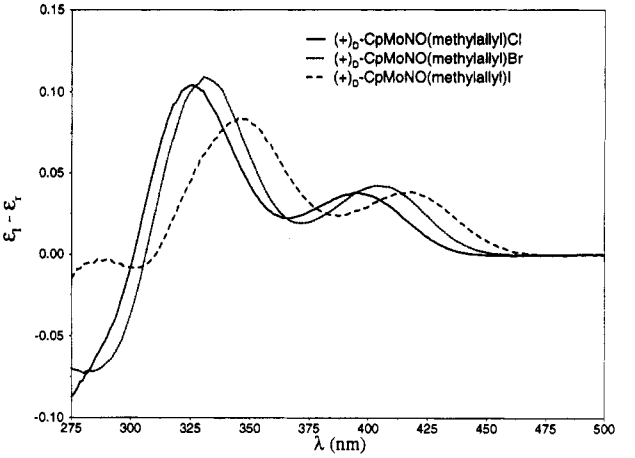


Figure 2. CD spectra of **1**, **2**, and **3** in $CHCl_3$.

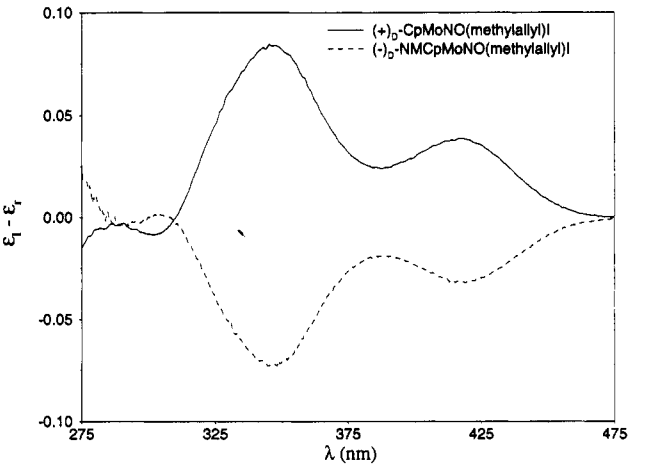
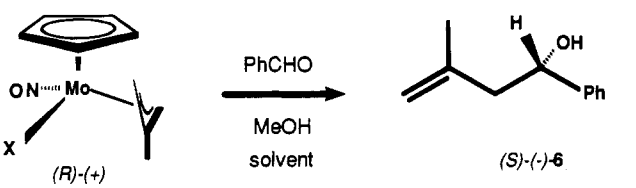


Figure 3. Comparison of the CD spectra of (*R*)-(+)-CpMo(NO)(η^3-methallyl)I and (*S*)-(−)-(NMCp)Mo(NO)(η^3-methallyl)I in $CHCl_3$.



1, X = I
2, X = Br
3, X = Cl
4, X = L^S

Table I. Effect of Reagent and Reaction Conditions on the Optical Yield of (*S*)-(-)-3-Methyl-1-phenyl-3-buten-1-ol ((-)-6)

entry no.	reagent[a]	amt of PhCHO (equiv)	concn[b] (mol/L)	solvent	time (h)	conversn, (%)	purity (% ee)
1	(+)-**1**	2	0.25	$CDCl_3$	45	91	88
2	(+)-**1**	2	0.99	$CDCl_3$	14	90	92
3	(+)-**2**	2	0.31	$CDCl_3$	24	100	90
4	(+)-**2**	10	0.37	$CDCl_3$	2	100	97
5	(+)-**2**	2	0.37	CD_2Cl_2	7	100	91
6	(+)-**3**	2	0.24	$CDCl_3$	11	100	>98
7	(+)-**4**[c]	2	0.32	$CDCl_3$	2	100	94

[a] The enantiomeric purity of the molybdenum reagents was >98%. [b] Concentration of molybdenum reagent. [c] Compound (-)-**5** gives (*R*)-(+)-3-methyl-1-phenyl-3-buten-1-ol.

the rate of the reaction[8]—the faster the reaction, the higher the ee. No significant loss of enantiomeric purity is observed with these complexes in pure solvents during the time periods used in Table I. Some racemization might occur under the reaction conditions, which might account for improved optical yield in the products with faster reaction times.

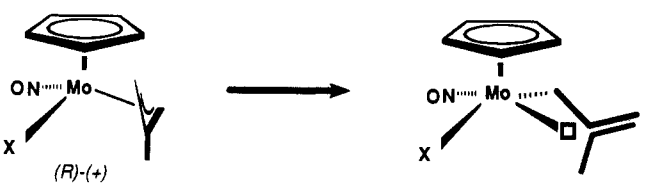
This reaction is a presumably a second-order reaction;[8] thus, the rate of the reaction would be expected to depend upon the concentration of the starting reagents. This can be seen in entry 2, where concentrations were increased by a factor of 4 by using less solvent, whereupon the rate of the reaction increased and the optical yield also improved from 88% to 92%. In entry 4, the amount of aldehyde used was increased from 2 to 10 equiv, resulting in decreased reaction time and increased optical yield. Changing the solvent from $CDCl_3$ to CD_2Cl_2 (entry 5) also greatly increased the rate of the reaction, but the ee only increased by a modest amount.

The camphorsulfonates are also reasonable reagents and are comparable to or somewhat faster than the chlorides in reactivity. We have generally included an alcohol in the solvent to provide protons and release the product alkoxide from the metal. For some aldehydes, methanol in the mixed solvent forms acetals or hemiacetals with the substrate to some extent, and this can interfere with the reaction. There is a greater tendency to form hemiacetals and acetals with **4** or **5** than with the halide complexes. This tendency can be reduced by using a bulkier alcohol, such as 2-propanol, as a reagent to release the homoallylic alkoxide from the metal. The shelf life of the unpurified camphorsulfonates is also shorter. Consequently, the halides, which are stable at room temperature indefinitely, often make them the preferred reagents. The overall stability and ease of crystallization of **2** and **3** make them particularly suitable for purification. Repeated crystallizations of **4** over long time intervals sometimes results in partial decomposition. Once **4** has been crystallized to >90% ee, conversion to **2** or **3** for final resolution by recrystallization to give products of high enantiomeric purity is also a viable alternative.

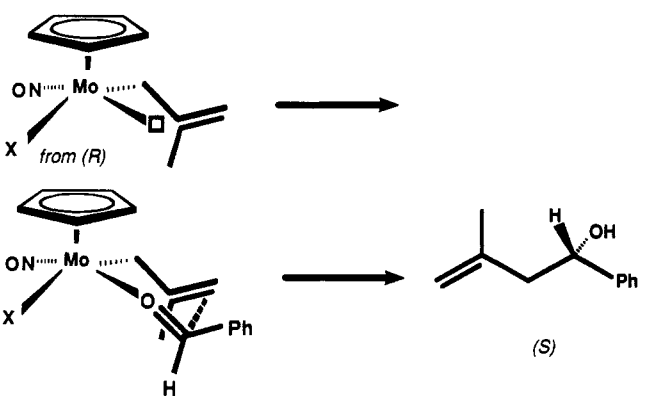
Discussion

The selectivity of the molybdenum system arises from the electronic asymmetry caused by the difference in the back-bonding between the nitrosyl and halide ligands.[8] The allyl carbon bond cis to the nitrosyl, C(1)–C(2), is longer than the bond trans to the nitrosyl, C(2)–C(3). On the basis of crystallographic data, the distortion of the π-allyl compound to σ–π bonding is indicated by the C(1)–C(2) bond length of 1.39 (1) Å compared to the C(2)–C(3) bond length of 1.37 (1) Å. The stronger bond of C(1) to Mo is indicated by the length of 2.272 (8) Å compared to the Mo–C(3) value of 2.407 (8) Å. Similar effects were noted in the neomenthylcyclopentadienyl analog of the bromide.[8b] In some previous structures of halides of this type, there appeared be an extraordinary distortion of C(1)–C(2) relative to C(2)–C(3) bond lengths. We feel that the modest difference in C–C bond lengths (of marginal significance here) is probably more correct and that large differences observed in some systems could possibly be a consequence of unresolved conformational disorder in the solid. We are currently investigating this possibility. In all systems that we have examined so far, the C–C bond cis to halide is shorter than that cis to NO, and furthermore, the Mo–C bond cis to halide is much longer than that cis to NO. Reference to Figure 1 also shows the striking effect of the electronic asymmetry of the metal center on the orientation of the allyl moiety. The terminal carbons of the allyl tend to orient parallel to the Mo–I bond. Thus, the I–Mo–C(3) plane makes a dihedral angle of only 18° with the Mo–C(1)–C(2) plane.

The low energy barrier of ~18 kcal/mol in the CpMo(NO)(η^3-allyl)X and CpMo(NO)(η^3-crotyl)X complexes for syn–anti averaging cis to NO supports a π–σ–π interconversion mechanism in which the Mo–C bond cis to NO is retained and a vacant site is produced trans to NO.[8b]



Although there is predominantly one isomer in the methallyl case, the σ intermediate is expected to be readily formed. This would produce a site trans to NO to which an aldehyde could bind. An antiperiplanar arrangement of the phenyl relative to the Cp is also expected in order to minimize steric interactions with the Cp ring.[11] The metal thus serves to orient the aldehyde as well as activate it to attack by the allyl. Since only one face of the aldehyde is accessible to the allyl, the stereochemical outcome of the reaction is predetermined.

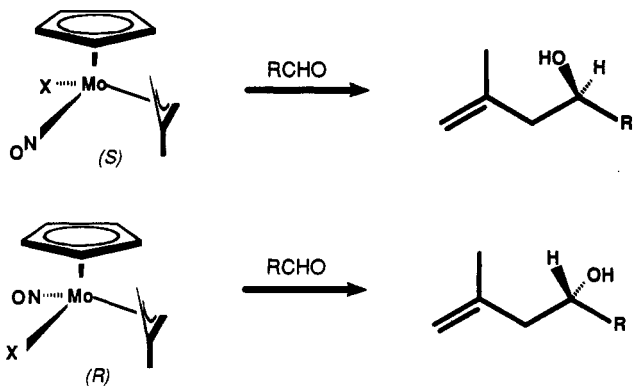


We have proposed that the transition state involves a chairlike configuration, as shown for the methallylmolybdenum complex with the *R* configuration at the metal

(11) Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579.

center.[8b] A similar transition state was suggested by Sato et al.[5b] for the allyltitanocene systems. In this case, the *R* reagent would produce attack on the *si* face of the aldehyde. This would explain the high enantiofacial selectivity in these reactions, as well as the diastereoselectivity observed with crotyl reagents.[8b]

It appears that, in these reactions, the stereochemistry of the products is controlled by the electronic asymmetry at the metal center rather than by the steric effects of the aldehyde substituents. This reagent control of stereochemistry would imply that preferences of Cram's rule[12] would be overcome. As a result, with enantiomerically pure chiral aldehydes, the formation of either Cram or anti-Cram products should be controlled by choosing either the *R* or *S* allylmolybdenum reagent. We are currently investigating this possibility and in certain cases have found that virtually complete reagent control of the stereochemistry has been observed; and we will report on these observations in the future.[14]



It appears that substituted allyls can be separated readily by using camphorsulfonates, but we have been unable to effect the resolution of the parent allyl, CpMo(NO)(η^3-allyl)X, by this method. The crotyl analogue, however, can be separated by this approach, and the reactions of some CpMo(NO)(η^3-crotyl)X complexes give very high enantioselectivity and high diastereoselectivity.[14]

Experimental Section

All manipulations were performed using standard Schlenk conditions. Deuterated solvents were purchased from CID Isotopes and were dried with 4-Å molecular sieves. CH_2Cl_2 and acetonitrile were purified by distillation from CaH_2 under nitrogen before use. THF was purified by distillation from potassium benzophenone under nitrogen before use. All other solvents were of analytical grade and were used without further purification. Adsorption alumina (100–200 mesh) was purchased from Fisher. All NMR spectra were acquired on Bruker WM 250–MHz and Yale 490-MHz spectrometers. Chemical shifts are reported in ppm downfield from TMS. IR data were obtained using a Nicolet 5-SX FT-IR spectrometer. Elemental analyses were obtained from Atlantic Microlab. Optical rotations were measured with a Perkin-Elmer 241 polarimeter using a thermostated cell. Circular dichroism data were obtained with an Aviv Model 60DS CD spectropolarimeter. Sample concentrations for rotations and CD measurements were prepared by weighing the complex on a microbalance (±1 μg) and weighing the solvent, which was converted to grams per 100 cm^3 by using the density of the solvent. CD experiments were performed using approximately 5×10^{-4} M solutions. All reactions involving silver salts were performed under conditions of minimal lighting.

Table II. Crystallographic Data for (+)-CpMo(NO)(I)(2-methallyl)

$MoIONC_9H_{12}$	fw: 373.04
a = 7.232(1) Å	space group: $P2_12_12_1$ (No. 19)
b = 11.971(2) Å	T = 23 °C
c = 13.678(2) Å	ρ = 2.092 g/cm^3
V = 1184.3(6) $Å^3$	μ = 36.29 cm^{-1}
Z = 4	R = 0.028
	R_w = 0.031

Table III. Positional Parameters and *B*(eq) Values for (+)-CpMo(NO)(I)(2-methallyl)

atom	*x*	*y*	*z*	*B*(eq) ($Å^2$)
I	0.2886(1)	0.62377(4)	0.84949(4)	5.12(2)
Mo	0.2082(1)	0.84635(4)	0.80293(4)	3.32(2)
O	−0.1798(7)	0.7847(5)	0.7902(6)	6.6(3)
N	−0.025(1)	0.8066(6)	0.7903(6)	5.5(4)
C(1)	0.199(2)	0.9487(8)	0.6632(7)	6.2(4)
C(2)	0.235(1)	0.8404(8)	0.6320(5)	5.4(4)
C(3)	0.397(1)	0.7934(8)	0.6655(6)	5.8(5)
C(4)	0.100(2)	0.774(1)	0.5748(8)	13.(1)
C(5)	0.263(3)	1.0242(7)	0.8634(8)	9.4(8)
C(6)	0.135(2)	0.968(1)	0.927(1)	8.7(8)
C(7)	0.240(2)	0.883(1)	0.9673(7)	8.1(7)
C(8)	0.414(2)	0.892(1)	0.9330(9)	7.9(7)
C(9)	0.432(2)	0.974(1)	0.8704(9)	6.9(6)

The purities of **1** and **2** were verified by HPLC with a Daicel Chiralcel OD column. The conditions for **1** are 97:3 heptane/ethanol and a flow rate of 0.25 mL/min. The retention time for the (+) isomer is 140 min and the (−) isomer is 152 min. The conditions for **2** are 96:4 heptane/ethanol and a flow rate of 0.25 mL/min. The retention time for the (+) isomer is 112 min and for the (−) isomer is 122 min.

Crystallographic Studies. A large crystal of **1** measuring approximately 1.00 × 0.24 × 0.24 mm was cut to yield a crystal approximately 0.21 × 0.24 × 0.24 mm for X-ray analyses. The remaining portion was dissolved and the rotation observed to assure that a crystal of (+)-**1** had been selected. The crystal was mounted in a capillary, and data were collected on a Nonius CAD4 diffractometer using Mo Kα radiation. Systematic absences consistent with $P2_12_12_1$ and an orthorhombic cell were found. The positions of the molybdenum and iodine atoms were determined from the Patterson map, and the remaining nonhydrogen atoms were found in subsequent difference Fourier maps using the TEXSAN structure determination package. Isotropic refinement of all atoms converged to R = 0.0734 and R_w = 0.0881 for the *R* isomer. The absolute configuration was determined at this point, as the *S* isomer yielded R = 0.0759 and R_w = 0.0914. Several hydrogen atom peaks were observed in the difference Fourier map, and one was selected to determine the conformation of the methyl group. All hydrogen atoms were included in calculated positions. Anisotropic refinement and absorption corrections were carried out for both hands by following procedures outlined elsewhere.[15] For the *R* configuration the refinement converged to R = 0.0278 and R_w = 0.0309 (GOF = 1.724), whereas for the *S* configuration the refinement converged to R = 0.0316 and R_w = 0.0361 (GOF = 2.013). The results establish the absolute configuration for (+)-**1** as *R*. The results are given in full in the supplementary material but are summarized in Tables II and III.

Crystals for X-ray study were obtained from CH_2Cl_2/pentane. A crystal of (−)-**5** was mounted in a capillary, and data were collected on a Nonius CAD4 diffractometer using Mo Kα radiation. Systematic absences consistent with $P2_1$ and a monoclinic cell with a = 9.313(3) Å, b = 20.747(7) Å, c = 12.511(3) Å, β = 92.26(2) Å, and V = 2415.4(13) $Å^3$ were found. Following procedures analogous to those described above, we located two independent molecules of **5** and two disordered pentane mole-

(12) Cram, D. J.; Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828.
(13) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K.-H. *Organometallics* **1983**, *2*, 400.
(14) Faller, J. W.; Mazzieri, M. Unpublished observations.
(15) Faller, J. W.; Linebarrier, D. L. *Organometallics* **1990**, *9*, 3182–3184.

cules. Satisfactory models for the pentanes were not found, although the full anisotropic refinement for the two molecules of **5** and isotropic refinement of the pentane carbons gave R = 0.066. As the absolute stereochemistry of **5** can be determined from the known configuration of (1*S*)-10-camphorsulfonate, the structure served to show that the configuration at the metal center for (−)-**5** was *S*. The results are given in full in the supplementary material.

Silver (*S*)-(+)-10-Camphorsulfonate. A solution of (*S*)-(+)-10-camphorsulfonic acid (16.43 g, 70.73 mmol) in 80 mL of water was treated with 8.11 g (35.0 mmol) of silver oxide. The mixture was stirred for 5 min, during which all but a small black residue remained. The mixture was centrifuged and decanted. The clear supernatant was evaporated to dryness. The white solid recovered was washed with cold water and dried under vacuum. The yield was 22.96 g (96.7%).

CpMo(NO)(η^3-methallyl)L^S. The CpMo(NO)(η^3-methallyl)I complex was prepared by published methods.[12] To a solution of CpMo(NO)(η^3-methallyl)I (4.05 g, 10.9 mmol) in benzene (90 mL) was added 3.80 g (11.2 mmol) of silver (*S*)-(+)-10-camphorsulfonate. Silver iodide precipitated immediately, but the reaction mixture was stirred for 1 h at 5–10 °C. The mixture was centrifuged, and the solution was decanted into 200 mL of cold pentane. A yellow product (A) precipitated from the pentane solution. The silver iodide precipitate was extracted twice with 30 mL of benzene. The extractions were added to 300 mL of cold pentane, and the solid recovered was combined with A. The diastereomeric ratio (−)-**5**:(+)-**4** in A was 84:16. Three more extractions were performed, using 30 mL of CH_2Cl_2 for each extraction. These were combined and were added to 300 mL of cold pentane. A second crop of product B was precipitated from the solution, and the diastereomeric ration (−)-**5**:(+)-**4** was 20:80. After resolution (see below), 1.70 g (32.8%) of the (+)-CpMo(NO)(η^3-methallyl)L^S compound with >97% de was recovered. The yield for the (−) isomer is 0.72 g (14%).

Resolution of (*R*)-(+)-CpMo(NO)(η^3-methallyl)L^S (4). In a typical experiment, an 85:15 mixture of (+)- and (−)-CpMo(NO)(η^3-methallyl)L^S was dissolved in a slight excess of CH_2Cl_2 and pentane was added until solid began to precipitate. The solution was left for 10 min, and after precipitation had ceased, the solution was decanted. The product was isolated as a yellow powdery solid. This was repeated twice, after which a >97% de mixture of the (+) isomer, **4**, was isolated. ^{1}H NMR ($CDCl_3$, 490 MHz): δ 6.01 (s, 5 H, H Cp); δ 4.64 (s, 1 H, H_a); δ 4.10 (d, J = 4.2 Hz, 1 H, H_a); δ 3.33, 2.81 (d, J = 15.8 Hz, 1 H each, $-CH_2SO_3$); δ 2.53 (dd, J = 4.2, 2.4 Hz, 1 H, $H_{s'}$); δ 2.50 (d, J = 2.4 Hz, 1 H, $H_{a'}$); δ 2.30 (s, 3 H, Me); δ 1.09, 0.82 (s, 3 H each, Me of L^S); δ 2.61–1.33 (resonances of L^S). IR (CH_2Cl_2, cm^{-1}): ν_{NO} = 1666, $\nu_{C=O}$ = 1743. Anal. Calcd for $C_{19}H_{27}O_5MoNS$: C, 47.80; H, 5.70; N, 2.93; S, 6.72. Found: C, 47.70; H, 5.69; N, 2.97; S, 6.78. $[\alpha]^{24}_D$ = +211° (c = 0.775, $CHCl_3$, 98% de).

Resolution of (*S*)-(−)-CpMo(NO)(η^3-methallyl)L^S (5). The (−) isomer can be isolated in >98% de by recrystallization of a mixture that is greater or equal to 7:1 (−)- and (+)-CpMo(NO)(η^3-methallyl)L^S with CH_2Cl_2 and hexane. ^{1}H NMR ($CDCl_3$, 490 MHz): δ 6.02 (s, 5 H, H Cp); δ 4.63 (s, 1 H, H_a); δ 4.09 (d, J = 4.2 Hz, 1 H, H_a); δ 3.34, 2.84 (d, J = 15.8 Hz, 1 H each, $-CH_2SO_3$); δ 2.52 (dd, J = 4.2, 2.4 Hz, 1 H, $H_{s'}$); δ 2.49 (d, J = 2.4 Hz, 1 H, $H_{a'}$); δ 2.30 (s, 3 H, Me); δ 1.08, 0.83 (s, 3 H each, Me of L^S); δ 2.61–1.33 (resonances of L^S). This material crystallizes with varying amounts of hexane in the lattice; hence, the rotation is not a reliable guide to purity: $[\alpha]^{24}_D$ = −150° (c = 0.913, $CHCl_3$, 98% de). Anal. Calcd for $C_{19}H_{27}O_5MoNS$ (sample crushed to a powder and kept under high vacuum for 1 day to remove solvent): C, 47.80; H, 5.70; N, 2.93; S, 6.72. Found: C, 47.93; H, 5.68; N, 2.97; S, 6.78.

(*R*)-(+)-CpMo(NO)(η^3-methallyl)I (1). To a solution of (+)-CpMo(NO)(η^3-methallyl)L^S (0.224 g, 0.469 mmol) in $CHCl_3$ (10 mL) was added an excess of sodium iodide (5 equiv). The reaction mixture was stirred at room temperature for 30 min. The solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2. The solution was passed through an alumina plug, and the solvent was removed in vacuo. The red-orange solid was isolated, and the yield was 0.166 g (94.7%). (*R*)-(+)-CpMo(NO)(η^3-methallyl)I was recrystallized from CH_2Cl_2 and hexane. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 5.88 (s, 5 H, H Cp); δ 4.25 (s, 1 H, H_a); δ 4.13 (d, J = 4.2 Hz, 1 H, H_s); δ 2.82 (dd, J = 4.2, 2.1 Hz, 1 H, $H_{s'}$); δ 2.36 (d, J = 2.4 Hz, 1 H, $H_{a'}$); δ 2.08 (s, 3 H, CH_3). IR (CH_2Cl_2): ν_{NO} = 1656 cm^{-1}. Anal. Calcd for $C_9H_{12}O_5IMoNO$: C, 28.98; H, 3.24; N, 3.75. Found: C, 29.24; H, 3.21; N, 3.61. $[\alpha]^{24}_D$ = +472° (c = 0.158, $CHCl_3$, 99% ee).

(*R*)-(+)-CpMo(NO)(η^3-methallyl)Br (2). The preparation of the (+) bromide compound was similar to that for the (+) iodide compound, except excess sodium bromide was used. ^{1}H NMR ($CDCl_3$, 490 MHz): δ 5.87 (s, 5 H, H Cp); δ 4.52 (d, J = 4.1 Hz, 1 H, H_a); δ 3.73 (s, 1 H, H_a); δ 3.05 (dd, J = 4.1, 2.1 Hz, 1 H, $H_{s'}$); δ 2.34 (d, J = 2.1 Hz, 1 H, $H_{a'}$); δ 1.93 (s, 3 H, CH_3). IR (CH_2Cl_2): ν_{NO} = 1653 cm^{-1}. Anal. Calcd for $C_9H_{12}O_5BrMoNO$: C, 33.15; H, 3.71; N, 4.30. Found: C, 33.22; H, 3.69; N, 4.24. $[\alpha]^{24}_D$ = +387° (c = 0.603, $CHCl_3$, 99% ee).

(*R*)-(+)-CpMo(NO)(η^3-methallyl)Cl (3). The preparation of the (+) chloride compound was similar to the (+) iodide compound except excess sodium chloride was used. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 5.88 (s, 5 H, H Cp); δ 4.47 (s, 1 H, H_a); δ 3.91 (d, J = 4.2 Hz, 1 H, H_s); δ 2.67 (dd, J = 4.1, 2.2 Hz, 1 H, $H_{s'}$); δ 2.37 (d, J = 2.2 Hz, 1 H, $H_{a'}$); δ 2.15 (s, 3 H, CH_3). IR (CH_2Cl_2): δ_{NO} = 1653 cm^{-1}. Anal. Calcd for $C_9H_{12}O_5ClNO$: C, 38.39; H, 4.30; N, 4.97. Found: C, 38.35; H, 4.31; N, 4.91. $[\alpha]^{24}_D$ = +313° (c = 0.268, $CHCl_3$, 98% ee).

Reaction of (*R*)-(+)-CpMo(NO)(η^3-methallyl)Br and Benzaldehyde. All condensation experiments were performed using a general method. In a typical reaction, (*R*)-(+)-CpMo(NO)(η^3-methallyl)Br (43.5 mg, 0.133 mmol) and benzaldehyde (0.027 mL, 0.266 mmol), along with MeOH (0.009 mL, 0.222 mmol) and $CDCl_3$ (0.35 mL), were allowed to react in an NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy (250 MHz) and was considered complete upon the disappearance of the Cp resonance of the starting material. The alcohol, (*S*)-(−)-3-methyl-1-phenyl-3-buten-1-ol, was purified after isolation by preparative TLC. In the case where the reactions were only 90% completed, an internal integration standard, dichloroethane (δ 3.70), was used. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.40–7.23 (m, 5 H, H Cp); δ 4.91, 4.85 (m, 1 H, each, H_2C=CH–); δ 4.80 (t, J = 6.5 Hz, 1 H, –C*H*OH); δ 2.42 (d, J = 6.5 Hz, 2 H, $-CH_2-$); δ 2.10 (br s, 1 H, O*H*); δ 1.79 (s, 3 H, Me).

Acknowledgment. We thank the National Science Foundation for support of this research. M.R.M. was a recipient of a fellowship from the Consejo Nacional de Investagaciones Científicas y Técnicas (CONICET) of Argentina.

Supplementary Material Available: For (+)-**1**, crystallographic data for X-ray diffraction studies (Table S-1), intramolecular bond distances (Table S2), intramolecular bond angles (Table S3), and U values (Table S4), and for (−)-**5**, crystallographic data (Table S5), positional parameters and B(eq) values (Table S6), and drawings of molecules **1** and **2** (Figures S1 and S2) (10 pages). Ordering information is given on any current masthead page.

OM920639E