to the placement of the tube in the NMR probe and a delay of approximately 2-3 min was incurred to tune the *sym*-tetrachloroethane line width to an acceptable level (~1.0 Hz). Acquisitions were then started immediately (that the ratio of substrates was 1.0:1.0 was double-checked by integration). The data are given in Figure 1.

Characterization of Reaction Product Bis[[2-[7-(acetylamino)-1,8-naphthyridinyl]]methyl]amine (14). The precipitate from either the catalyzed or uncatalyzed reaction was filtered off and then partitioned between aqueous $NaHCO_3$ and CH_2Cl_2. The CH_2Cl_2 layer was separated, dried (Na_2SO_4), and evaporated to give **14** as a solid: mp 238-241 °C dec; ^1H NMR (DMSO-d_6) 2.17 (6 H, s), 4.15 (4 H, s), 7.76 (2 H, d, J = 8.3 Hz), 8.32-8.39 (6 H, m), 11.04 (2 H, s) (the $(CH_2)_2NH$ proton was not visible); exact mass calcd for $C_{22}H_{20}N_7O_2$ [M + H - 2H]$^+$ 414.1679, found 414.1674.

Template 41 (Scheme V). Template **41** was insoluble in $CDCl_3$ alone. However, a soluble form was obtained by dissolving, in a 1.0:1.0 ratio, amino substrate **10** and template **41** in dichloromethane/methanol (9:1) and evaporating the solvent, with any residual traces of solvent being removed on a high-vacuum pump (complete removal of the solvent was established by ^1H NMR of the complex). The **10·41** complex thereby obtained could then be weighed accurately into an NMR tube and dissolved directly in $CDCl_3$ (0.500 mL) to give a 0.0040 M solution of template **41** and amino substrate **10**. After addition of the internal standard, the bromomethylene substrate **42** (1.0 equiv) was added just prior to placing the NMR tube in the probe, and acquisition, as with template **9**, was started immediately following tuning of the *sym*-tetrachloroethane line width. The data are given in Figure 3.

The experiment demonstrating inhibition of the **41**-catalyzed reaction between **10** and **42** was conducted as above, except that 1 equiv of **26** was added to the NMR tube (exchange is rapid) prior to the addition of **42**.

Characterization of Reaction Product *N*-[[2-[7-(Acetylamino)-1,8-naphthyridinyl]]methyl]-*N*-[[2-[7-oxo-1,8-naphthyridinyl]]methyl]amine (45). The precipitate from either the catalyzed or uncatalyzed reaction was filtered off and washed with a small amount of $CDCl_3$ to give **45**·HBr as a beige solid: mp 177-179 °C dec; ^1H NMR (DMSO-d_6) δ 2.20 (3 H, s), 4.30 (2 H, s), 4.45 (2 H, s), 6.59 (1 H, d, J = 9.3 Hz), 7.40 (1 H, d, J = 7.9 Hz), 7.56 (1 H, d, J = 8.2 Hz), 7.95 (1 H, d, J = 9.3 Hz), 8.18 (1 H, d, J = 7.9 Hz), 8.40 (1 H, d, J = 8.9 Hz), 8.44 (1 H, d, J = 8.2 Hz), 8.47 (1 H, d, J = 8.9 Hz), 10.99 (1 H, br s), 12.12 (1 H, br s); mass spectrum (FAB + NBA) 375 [**45** + H]$^+$.

Acknowledgment. We are grateful to the National Institutes of Health for a grant (GM39072) in support of this work, to Dr. A. J. Culshaw for tying some experimental loose ends, to Ms. Robin LeGallo for assistance in the preparation of intermediates, and to Dr. S. H. Bell for some preliminary experiments. We thank Professors E. R. Kantrowitz, E. J. Billo, and D. J. Sardella for assistance with kinetic analyses, binding studies, and NMR measurements, and Dr. A. Echavarren and Professor W. W. Cleland for helpful discussions. We also acknowledge with appreciation the NIH-supported mass spectrometry facility at Michigan State University (D. Gage, director) for providing high-resolution mass spectra.

Stereocontrol during the Alkylation of Enolates Attached to π-Allyl-Mo(CO)$_2$Cp Systems

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Abstract: The preparations of dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-oxocyclohexenyl)molybdenum (**4**) and dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-oxocycloheptenyl)molybdenum (**27**) are described. Deprotonation of **4** using lithium diisopropylamide at −100 °C, followed by treatment of the enolate with electrophiles (alkyl halides, benzaldehyde, Michael acceptors), leads to stereospecific alkylation at C-4 anti to the Mo(CO)$_2$Cp group. Deprotonation of the alkylation products occurs regiospecifically at C-6 and enolate alkylation gives 4-exo,6-exo-disubstituted complexes stereospecifically. The corresponding seven-membered ring complex **27** is deprotonated regiospecifically at C-4 on treatment with base, and the enolate can be alkylated stereospecifically anti to the metal. The stereochemical outcome of nucleophile addition to the ketone of the alkylation products from **4** and **27** is different and is explained on the basis of conformational arguments. The conformation of the cycloheptenyl complexes **25** and **31a** were confirmed by single-crystal X-ray structure determination. $C_{14}H_{16}O_3Mo$ (**25**) crystallizes with space-group symmetry of $P2_1/c$. The unit-cell dimensions were a 11.694 (4), b 17.775 (6), c 13.114 (4) Å, β 96.38 (3)°, V 2708.9 (15) Å^3, and Z = 8. The structure was refined to convergence with a final value of R = 4.28%, R_w = 6.38% ($F \geq 6.0\sigma$). Similarly, $C_6H_{20}O_3Mo$ (**31a**) crystallized with space-group symmetry of $P2_1/c$. The unit cell dimensions were a 9.719 (3), b 12.955 (4), c 12.120 (4) Å, β 103.48 (2)°, V 1484.1 (8) Å^3, and Z = 4. This structure was refined to final values of R = 2.77%, R_w = 5.13% ($F \geq 6.0\sigma$).

One of our major interests is the use of electrophilic transition-metal π-complexes in stereocontrolled carbon–carbon bond formation.[1] This is illustrated schematically in Figure 1, where sequential nucleophile addition/hydride-abstraction/nucleophile addition reactions are used to introduce two carbon substituents with defined relative stereochemistry onto six- and seven-membered rings with use of reactive diene-Mo(CO)$_2$Cp complexes. We have recently begun to investigate the reactions of carbanions generated on π-allyl-molybdenum complexes; our earlier studies were aimed at using cyano-stabilized carbanions to generate quaternary carbon centers.[2] During these studies it was noted that there is an apparent stabilization of carbanion by the adjacent π-allyl-Mo(CO)$_2$Cp moiety, a fairly common occurrence in organometallic chemistry.[3] In the light of these experiments, and

(1) (a) Organoiron complexes: Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060. Pearson, A. J.; Ray, T. *Tetrahedron Lett.* **1986**, *27*, 3111. Pearson, A. J.; Lai, Y. S.; Lu, W.; Pinkerton, A. A. *J. Org. Chem.* **1989**, *54*, 3882. (b) Organomolybdenum complexes: Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748. Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276.

(2) Pearson, A. J.; Khetani, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6778. See also ref 8 for acyclic systems.

(3) See, for example: Kundig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855. Williams, G. M.; Rudisill, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 3357. Brookhart, M.; Rush, P. K.; Noh, S. K. *Organometallics* **1986**, *5*, 1745. Brookhart, M.; Nohn, S. K.; Timmers, F. J. *Organometallics* **1987**, *6*, 1829. Brookhart, M.; Noh, S. K.; Timmers, F. J.; Hong, Y. H. *Organometallics* **1988**, *7*, 2458. Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: New York, 1982; Chapter 5.

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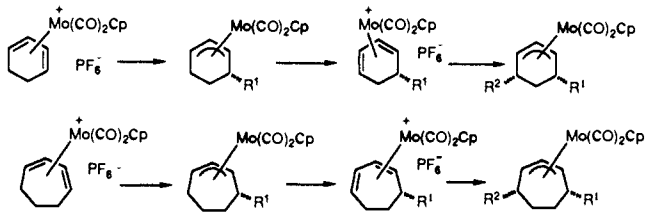
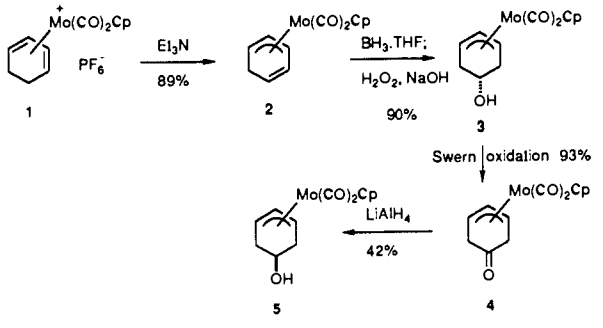


Figure 1. Stereocontrolled double functionalization via nucleophile addition to cyclodiene-Mo(CO)$_2$Cp complexes (Cp = η^5-cyclopentadienyl).

related work of Green et al.,[4] it seemed likely that enolate generation from keto-substituted complexes would be a facile process and that the metal could be used to control stereochemistry *and* regiochemistry during their formation and reactions. Multiple functionalization via enolate chemistry is not possible with the complexes reported by Green, owing to the position of the ketone carbonyl (see compound **9** later). This paper describes some experiments undertaken to address these issues using six- and seven-membered ring systems.[5]

Results

(1) Cyclohexenyl-Mo(CO)$_2$Cp Systems. Treatment of [(cyclohexadiene)Mo(CO)$_2$Cp]$^+$PF$_6^-$ (**1**) with triethylamine gave the η^3-dienyl complex **2** in 89% yield, which was readily converted to the alcohol **3** in 90% yield by hydroboration, a regio- and stereospecific reaction. The exo stereochemistry was assigned by comparison with coupling-constant data reported by Faller et al.[6] for related cyclohexenyl-Mo(CO)$_2$Cp complexes, and is confirmed by X-ray crystal structure determination on the corresponding cycloheptenyl-Mo(CO)$_2$Cp complex (later). Swern oxidation of **3** proceeded cleanly to give the ketone **4** in 75% overall yield from the diene complex **1**. Treatment of **4** with lithium aluminum hydride gave the unstable alcohol **5**, shown to be epimeric with **3** by its ^{1}H NMR spectrum.



With the ketone **4** in hand we turned our attention to the chemistry of its derived enolate. Deprotonation of **4** is very facile; treatment with mild base (K_2CO_3, THF/MeOH, 16 h, room temperature) gave the rearranged ketone **6**, suggesting participation of the π-allyl-molybdenum system in enolate stabilization. When this reaction was carried out in CD_3OD solvent, the dideuterated complex **8** was obtained. Since it is known[4] that mono-deuteration of the indenyl complex **9** occurs under these conditions, to give **10**, we presume that the C-5 deuterium is introduced by a dual mechanism, both before and after rearrangement, the latter via **7**, as summarized in Scheme I. According to ^{1}H NMR spectroscopy, both deuteriums are exo to the metal, suggesting that the C-6 deuterium is introduced by direct protonation at carbon rather than via a Mo–H(D) intermediate.[7]

Scheme I. Rearrangement of Complex **4** to **6** and Deuterium Incorporation

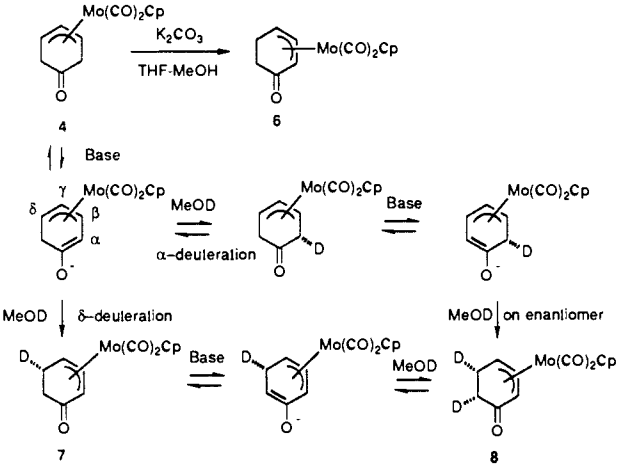
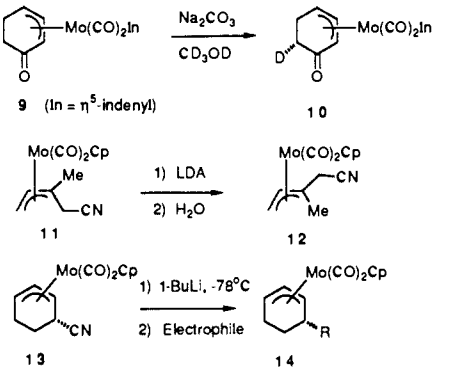


Table I. Alkylation of Enolates from (η^3-Cyclohexenyl)-Mo(CO)$_2$Cp Ketone Derivatives

complex	electrophile	product (Yield, %)
4	D_2O	**15**, R = D (55)
4	MeI	**15**, R = Me (73)
4	$BrCH_2CO_2Me$	**15**, R = CH_2CO_2Me (68)
4	PhCHO	**15**, R = CH(OH)Ph (62)[a]
4	MeCO·Cl	**15**, R = MeCO (78)
4	CH_2=$CHSO_2Ph$	**15** + **17**, R = $CH_2CH_2SO_2Ph$ (19 and 21)[b]
4	MeI	**17**, R = Me (61)[c] (77)[d]
15, R = Me	MeI	**17**, R = Me (49)
15, R = Me	CH_2=$CHSO_2Ph$	**16**, R = Me, R′ = $CH_2CH_2SO_2Ph$ (78)
15, R = Me	CH_2=$C(SO_2Ph)CO_2Me$	**16**, R = Me, R′ = $CH_2CH(SO_2Ph)CO_2Me$ (100)
15, R = Me	$BrCH_2CO_2Me$	**16**, R = Me, R′ = CH_2CO_2Me (82)

[a] This reaction could not be driven to completion; unreacted starting material was recovered. This is due to the facile reversibility of the reaction.[5] [b] Not optimized; reaction run at −30 °C. [c] Using 2.1 equiv of LDA and excess MeI. [d] Using *n*-BuLi as base.

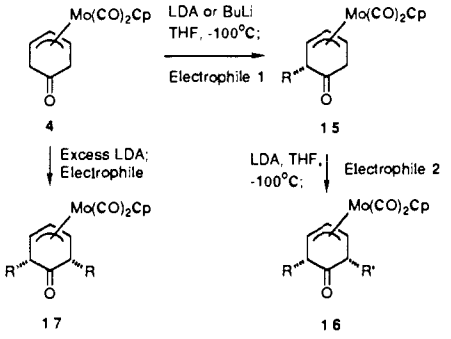
However, there is sufficient uncertainty concerning NMR assignments for complex **6** that this conclusion remains tentative. These results do indicate that there is some delocalization of negative charge through the π-allyl-Mo(CO)$_2$Cp, and this is consistent with our earlier observations[8] on the rearrangement of complex **11** to give **12** and on the decyanation of complex **13**. However, protonation of enolate intermediates at the δ-carbon appears to be irreversible, since treatment of **6** with K_2CO_3 in the presence of *d*-methanol gives only α-deuterated product.



Treatment of complex **4** in tetrahydrofuran solution with lithium diisopropylamide at low temperature gave a deep red-colored solution, indicating the formation of enolate. Quenching with D_2O

(4) Green, M.; Greenfield, S.; Grimshire, J.; Kersting, M.; Orpen, A. G.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 97.
(5) Preliminary studies: Pearson, A. J.; Perry, M. W. D. *J. Chem. Soc., Chem. Commun.* **1989**, 389. Pearson, A. J.; Mortezaei, R. *Tetrahedron Lett.* **1989**, *30*, 5049.
(6) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400.
(7) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 80–93 and Chapter 8.
(8) Pearson, A. J.; Holden, M. S.; Simpson, R. *Tetrahedron Lett.* **1986**, *27*, 4121.

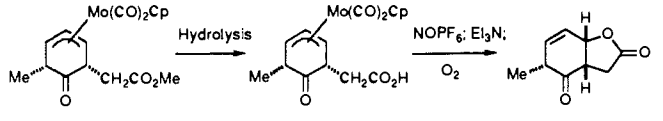
Scheme II. Stereo- and Regiocontrolled Alkylation of 5-Oxocyclohexenyl-$Mo(CO)_2Cp$ Complexes



at low temperature gave complex **15** (R = D). Alkylation of **4** was readily accomplished by treatment of the enolate with the appropriate electrophile. Best results were obtained by generating the enolate at temperatures below −100 °C. The alkylation agent must be added at $t < -100$ °C, and the reaction mixture is allowed to warm to room temperature or below very slowly. Poorer yields were obtained when these operations were conducted at −70 °C, and under these conditions appreciable decomposition of the anion to give phenol was observed. Optimized reactions are summarized in Scheme II, and Table I.

A variety of bases could be used to generate the enolate in these reactions; *n*-butyllithium and potassium *tert*-butoxide both effected deprotonation of **4**. Clean alkylation of the enolate could be accomplished in all cases. Most notably, use of 2.1 equiv of LDA, together with excess methyl iodide effected α,α'-dialkylation in good yield. No *gem*-dialkyl product was observed during this reaction or during the alkylations of **15**, indicating that only axial proton is removed, as expected[9] (see later).

Attempts to decomplex the ketone products **15–17** met with only limited success, which we assumed was due to the presence of the ketone carbonyl. For example, treatment of **17** (R = Me) with bromine or iodine[1] or with $NOPF_6$ followed by water[10] gave mixtures of cyclohexene derivatives in low yield. Similarly, the use of our lactonization procedure[1] was problematic. Hydrolysis of the methyl ester **16** (R = Me, R′ = CH_2CO_2Me) afforded the carboxylic acid **18** in 62% yield, and treatment of this with $NOPF_6$, followed by Et_3N and air oxidation, gave the lactone **19** in 17% yield (much lower than complexes which lack the ketone[1]). We were unable to improve this reaction, but these results do indicate that it is possible to achieve regioselectivity during demetalation of unsymmetrically substituted complexes.



In contrast to these results the alcohol derivative **20**, obtained by reduction of **17** (R = Me) with $LiAlH_4$, was readily demetalated. Treatment with bromine at low temperature afforded the bromocyclohexene derivative **21**, but this compound was quite unstable and was not fully characterized. Therefore, the following procedure was devised. A solution of the complex in tetrahydrofuran was treated with bromine (2 equiv) at −70 °C. When complete disappearance of starting material was evidenced by TLC, a solution of sodium thiophenoxide was added and the reaction was continued at −70 °C for 5 min. By using this method, the stable thioether **22** was produced in 87% yield. The all-equatorial substitution was shown by ^1H NMR spectroscopy, thereby confirming the stereodirecting effect of the $Mo(CO)_2Cp$ group during enolate alkylation, ketone reduction, and demetalation.

(9) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: New York, 1983.
(10) Faller, J. W.; Chao, K. H. *Organometallics* **1984**, *3*, 927. Faller, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231.

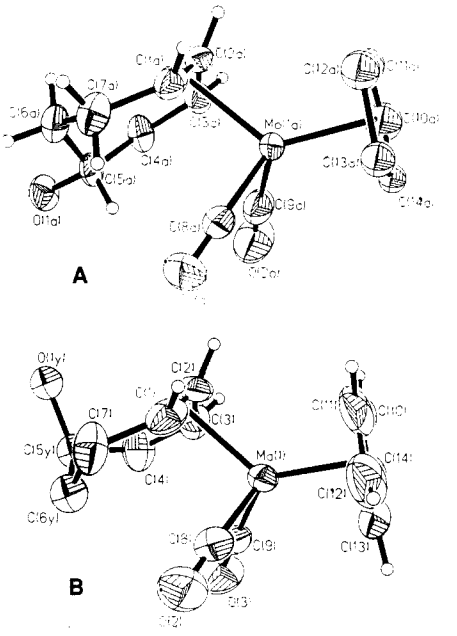


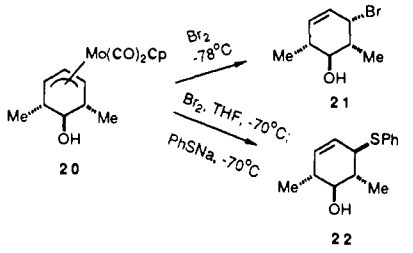
Figure 2. X-ray crystal structure of dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5-*exo*-hydroxycycloheptenyl)molybdenum (**25**) showing both half-chair conformations. Ellipsoids are drawn at 50% probability. Structure A shows the equatorial conformer (one disordered cyclopentadienyl ring is omitted for clarity). Structure B shows the axial conformer.

Table II. Selected Bond Lengths (Å) for Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5-*exo*-hydroxycycloheptenyl)-molybdenum (**25**) (Conformation A Only)

Mo(1a)–C(1a)	2.371 (7)	C(2a)–C(3a)	1.399 (11)
Mo(1a)–C(2a)	2.212 (7)	C(3a)–C(4a)	1.535 (10)
Mo(1a)–C(3a)	2.367 (7)	C(4a)–C(5a)	1.542 (9)
Mo(1a)–C(9a)	1.904 (4)	C(5a)–C(6a)	1.509 (10)
Mo(1a)–C(11a)	2.407 (18)	C(6a)–C(7a)	1.524 (11)
C(1a)–C(2a)	1.421 (11)	C(5a)–O(1a)	1.451 (8)

Table III. Selected Bond Angles for Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-*exo*-hydroxycycloheptenyl)molybdenum (**25**) (Conformation A Only)

C(1a)–Mo(1a)–C(9a)	119.5 (2)	C(4a)–C(5a)–C(6a)	113.4 (6)
C(8a)–Mo(1a)–C(9a)	81.5 (3)	C(1a)–C(7a)–C(6a)	115.7 (7)
C(9a)–Mo(1a)–C(10a)	89.6 (2)	C(5a)–C(6a)–C(7a)	114.8 (6)
C(1a)–Mo(1a)–C(10a)	139.9 (2)	O(1a)–C(5a)–C(6a)	109.5 (5)
C(1a)–C(2a)–C(3a)	123.9 (6)	O(1a)–C(5a)–C(4a)	101.3 (3)
C(2a)–C(3a)–C(4a)	127.5 (6)		



(2) Cycloheptenyl-$Mo(CO)_2Cp$ Systems. The keto derivative **27** was prepared from [cycloheptadiene-$Mo(CO)_2Cp]^+PF_6^-$ (**23**) in analogous fashion to the synthesis of **4**. All steps were high yielding, although hydroboration of **24** gave a mixture of the desired alcohol **25** and cycloheptenyl-$Mo(CO)_2Cp$ **26**. The latter compound results from hydrolysis of the organoborane intermediate, an uncommon but not unobserved occurrence. Since **25** and **26** are readily separated by chromatography and **26** can be converted to **23** by treatment with Ph_3CPF_6, the overall transformation proceeds in good yield. Since the NMR data is more

Scheme III

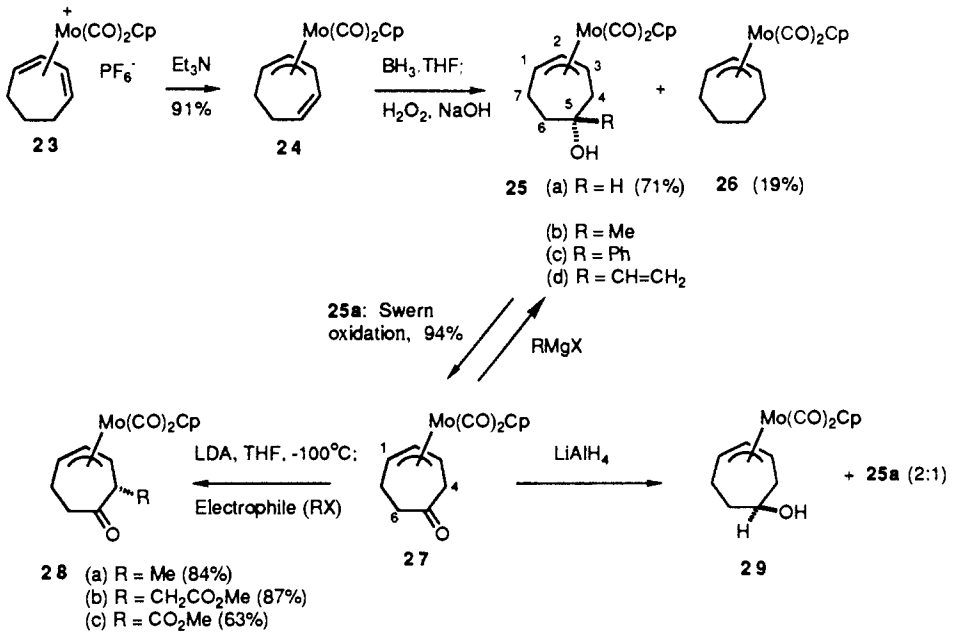


Table IV. Selected Bond Lengths (Å) for Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*exo*-hydroxy-4-*exo*-methyl-5-*endo*-methylcycloheptenyl)molybdenum (**31a**)

Mo-C(1)	2.378 (5)	C(1)-C(2)	1.405 (7)	C(6)-C(7)	1.498 (6)
Mo-C(2)	2.209 (5)	C(2)-C(3)	1.421 (6)	C(1)-C(7)	1.512 (7)
Mo-C(3)	2.365 (5)	C(3)-C(4)	1.517 (5)	C(4)-C(8)	1.526 (7)
Mo-C(10)	1.926 (5)	C(4)-C(5)	1.542 (6)	C(5)-C(9)	1.514 (6)
Mo-C(13)	2.380 (3)	C(5)-C(6)	1.526 (7)	O(1)-C(5)	1.440 (6)

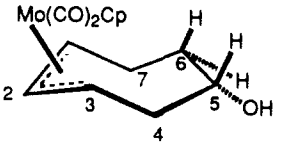


Figure 3. Chair conformation for complex **25** showing eclipsing of C-5-OH with C-6-H and other eclipsing interactions.

difficult to interpret with the seven-membered ring system, the stereochemistry of **25** was confirmed by X-ray crystallography and is shown in Figure 2. Selected bond lengths and bond angles are listed in Tables II and III. Interestingly, two half-chair conformations are observed, and presumably this relieves the eclipsing of C-H and C-OH that would occur in a chair conformation (Figure 3). This observation, which is consistent with our earlier proposal for the conformation of substituted cycloheptenyl-Mo(CO)$_2$Cp complexes based on NMR coupling constants,[1] will be discussed later.

On the basis of the supposition that the π-allyl-Mo(CO)$_2$Cp system participates in carbanion stabilization,[8] deprotonation of **27** was expected to occur regioselectively at C-4. This was indeed the case. Treatment with LDA (*or* KOBu^t), followed by electrophile, furnished exclusively the substituted complexes **28** (Scheme III). The stereochemistry was assigned by analogy with the hydroboration results and was confirmed by X-ray crystallography on a later derivative. Thus, the stereochemical outcome of additions to the C=C double bond, adjacent to the π-allyl-Mo(CO)$_2$Cp system is controlled by the sterically demanding metal moiety. This is *not* the case during nucleophile addition to **27**. Reduction with LiAlH$_4$ gave a 2:1 mixture of the secondary alcohol **29** and **25** (by ^{1}H NMR spectroscopy). Reaction of **27** with the sterically demanding reducing agent LiAlH(OBu^t)$_3$ in THF at −30 °C gave a 2:1 mixture in *favor of* **25** (97% yield). On this basis, the stereochemistry shown in structure **25** was also (tentatively) assigned to the products of reaction of **27** with Grignard reagents which are presumed to be sterically more demanding than LiAlH$_4$. We had initially anticipated that **27**

Table V. Selected Bond Angles for Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*exo*-hydroxy-4-*exo*-methyl-5-*endo*-methylcycloheptenyl)molybdenum (31a)

C(1)-Mo-C(2)	35.4 (2)	C(2)-C(3)-C(4)	127.0 (4)
C(2)-Mo-C(3)	36.0 (1)	C(3)-C(4)-C(5)	117.2 (3)
C(1)-Mo-C(3)	63.4 (2)	C(3)-C(4)-C(8)	106.3 (4)
C(1)-Mo-C(10)	71.1 (2)	C(4)-C(5)-C(6)	113.3 (4)
C(1)-Mo-C(15)	106.0 (1)	C(5)-C(6)-C(7)	116.3 (4)
C(1)-C(2)-C(3)	123.7 (4)	O(1)-C(5)-C(9)	104.4 (4)
C(2)-C(1)-C(7)	126.5 (4)	O(1)-C(5)-C(6)	109.5 (3)

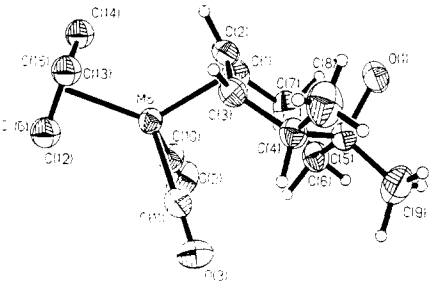
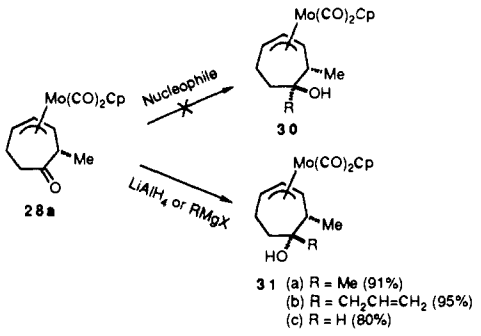


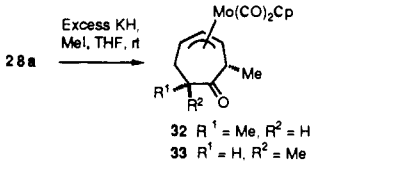
Figure 4. X-ray crystal structure of dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*exo*-hydroxy-4-*exo*-methyl-5-*endo*-methylcycloheptenyl)molybdenum (**31a**). Ellipsoids are drawn at 50% probability and one disordered cyclopentadienyl ligand is omitted for clarity.

and the alkylated compounds **28** would react stereoselectively with carbon nucleophiles anti to the molybdenum to give, e.g., **30**, and a single product was indeed observed for each reaction on **27** and **28a**. Since ^{1}H NMR was rather inconclusive with regard to stereochemistry, the tertiary alcohol obtained from reaction of **28a** with methylmagnesium bromide was submitted for X-ray crystallography. This showed that the nucleophile had added syn to the metal, giving complex **31a** (Figure 4, Tables IV and V). By analogy, we have assigned structure **31** to all products of nucleophile addition. It is noteworthy that reduction of **28a** with LiAlH$_4$ at −78 °C gives a single product **31c**, while reduction at 0 °C gives a 2:1 mixture of stereoisomers in favor of **31c**.

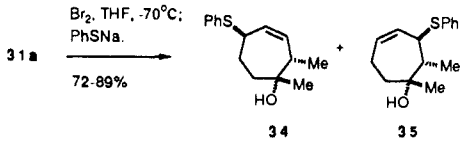
Deprotonation of **28a** was more difficult than the corresponding cyclohexenyl derivative. Treatment with LDA at low temperature, followed by D$_2$O quench gave no deuterated product, and attempted methylation also failed. Raising the temperature to 0 °C during LDA treatment did not lead to improvement. Treatment with Bu^{t}Li led to the tertiary alcohol from nucleophile addition. Alkylation of **28a** was accomplished by treatment with excess potassium hydride at room temperature in the presence



of excess methyl iodide. However, this gave an equimolar mixture of stereoisomers **32** and **33**.



Decomplexation of the alkylated complexes **28** was problematic, again due to the presence of the ketone. Treatment of the tertiary alcohol **31a** with bromine gave a mixture of allylic bromides which could not be purified chromatographically, owing to their facile rearrangement on silica gel. Attempted decomplexation using the method of Faller et al.[10] ($NOPF_6$ then H_2O) also failed. Reaction of **31a** with bromine, followed by in situ treatment with sodium thiophenoxide, gave good yields of the stable allylic thioethers **34** and **35**. The composition of the product mixture varied somewhat according to reaction temperature, presumably due to competing rearrangement of the intermediate allylic bromides. At −75 °C a 3:1 mixture in favor of **34** was obtained, while at 0 °C a 2:1 mixture was produced.



Discussion

There are marked differences in the stereodirecting power of the $Mo(CO)_2Cp$ group attached to six- or seven-membered ring π-allyl ligands, which appears to be a result of conformational effects. Previous X-ray crystallographic studies by Faller et al.,[6] Green et al.,[4] and in our laboratory[11] show that in cyclohexenyl-$Mo(CO)_2Cp$ complexes the six-membered ring adopts a chair conformation regardless of substitution pattern (Figure 5), despite the fact that the C–C bond rotations necessary for chair $\rightleftarrows$ boat interconversion are not restricted (according to Dreiding models). The seven-membered ring in cycloheptenyl-$Mo(CO)_2Cp$ appears to be conformationally more mobile. Introduction of substituents leads to C–C bond rotations that place the ring in half-chair conformations. For complex **25a** this relieves the eclipsing interactions between C–OH and C-6–H bonds, and between C-4–C-5 and C-6–C-7 bonds. For substituted complexes such as **28** and **31** this also relieves a 1,4-diaxial interaction between the C-4 substituent and the C-7 hydrogen. Such conformational preferences are clearly influential in determining the stereochemical outcome of a variety of reactions. Ketone derivatives such as **28a** appear to adopt a half-chair conformation in which the methyl group is quasi equatorial. In this conformation, nucleophilic attack occurs syn to the molybdenum because anti approach is hindered by the ring carbons (Figure 6). Furthermore, in this conformation *both* C-6–H bonds are almost orthogonal to the ketone carbonyl π-system, and deprotonation to give the enolate is expected to be slow (as observed). Surprisingly, no C-4 enolate is formed (both methylation products **32** and **33** show *two* methyl doublets in the ^1H NMR spectrum), even though the endo C-4–H bond is almost perfectly aligned with the C=O π-bond to allow deprotonation. Perhaps the stabilizing effect of the π-allyl-$Mo(CO)_2Cp$ system cannot come into play here because it requires an anti C–H bond[2] and steric hindrance dominates the picture. The C-6 enolate, once formed, is also conformationally mobile, and alkylation is not stereoselective.

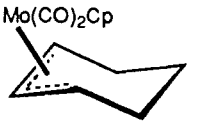


Figure 5. Chair conformation for cyclohexenyl-$Mo(CO)_2Cp$.

In summary, the use of a transition-metal moiety in stabilizing enolates and controlling stereochemistry during their reactions appears to be promising. At this stage, the six-membered ring molybdenum system is better behaved and allows stereocontrolled multiple functionalization of cyclohexenes. We are currently examining the application of this chemistry in the synthesis of defined target molecules.

Experimental Section

General procedures are the same as previously described.[1] Complete NMR assignments are made for complexes **28b**, **29d**, and **31a**, which are representative of substituted cycloheptenyl-Mo complexes. All others can be inferred from this data.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-cyclohexa-1,3-dienyl)molybdenum (2). To a stirred suspension of complex **1** (1.55 g, 3.67 mmol) in dichloromethane (15 mL) at room temperature was added triethylamine (1.5 mL, 10.65 mmol). The reaction mixture was stirred for 25 min, water (10 mL) was added, and the layers were separated. The aqueous layer was extracted with dichloromethane (7 mL), and the organic layers were combined, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (40 g silica gel, Et_2O eluent) afforded the complex **2** (0.97 g, 89%) as a yellow crystalline solid: mp 94.5–95.5 °C; R_f 0.7 (Et_2O); IR ($CHCl_3$) 1930, 1846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.11 (1 H, m, H-4), 5.25 (5 H, s), 4.61 (1 H, m, H-2), 4.13 (2 H, d, J = 1.8 Hz, H-1 and H-3), 3.98 (1 H, m, H-5), 2.59 (1 H, d, J = 22 Hz, one of H-6), 2.42 (1 H, d, J = 22 Hz, one of H-6); HRMS calcd for $C_{13}H_{12}MoO_2$ (^{96}Mo) 297.9897, found 297.9898. Anal. Calcd: C, 52.72; H, 4.08. Found: C, 52.58; H, 4.14.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5-*exo*-hydroxycyclohexenyl)molybdenum (3). To a stirred solution of complex **2** (0.97 g, 3.28 mmol) in THF (15 mL) at 0 °C was added borane–THF (Aldrich, 1.0 M, 3.5 mL, 3.5 mmol). The cooling bath was removed, and the mixture was stirred for 80 min. Water (4 mL) was added, followed by 15% aqueous NaOH (6 mL) and 30% aqueous hydrogen peroxide (6 mL). The reaction was stirred at room temperature for 40 min, ether (30 mL) was added, and the layers were separated. The aqueous layer was extracted with ether, and the organic extracts were combined, washed with water (2 × 20 mL), then brine (20 mL), dried ($MgSO_4$), and concentrated. Purification by flash chromatography (40 g silica gel, 60% EtOAc in hexanes) gave the complex **3** (0.92 g, 90%) as yellow crystals: mp 160–160.5 °C (decomposition over the range 151–159 °C); R_f 0.5 (Et_2O/EtOAc, 1:1); IR ($CHCl_3$) 3615, 3540–3160, 1935, 1855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.29 (5 H, s), 4.15 (1 H, t, J = 6.9 Hz), 3.59–363 (2 H, m), 2.64 (1 H, tt, J = 9.3, 6.6 Hz), 1.79 and 2.22 (4 H, AB_q of dd, J_{gem} = 14.1, J_{vic} = 9.3, 1.0 and 6.6, 3.4), 1.46 (1 H, exch D_2O); HRMS calcd for $C_{13}H_{14}MoO_3$ (^{98}Mo) 315.9998, found 315.9996. Anal. Calcd: C, 49.70; H, 4.49. Found: C, 49.45; H, 4.50.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5-oxocyclohexenyl)molybdenum (4). Dimethyl sulfoxide (470 μL, 6.6 mmol) in dichloromethane (2 mL) was added dropwise over 25 s to a stirred solution of oxalyl chloride (300 μL, 3.3 mmol) in dichloromethane (8 mL) maintained at −60 °C. The resulting solution was stirred for 2 min, and then a solution of complex **3** (0.926 g, 2.93 mmol) and dichloromethane (24 mL) was added over 4 min, residual traces of **3** being washed in with 2 mL of dichloromethane. The solution was stirred at −159 ± 2 °C for 15 min, and triethylamine (2.1 mL, 15 mmol) was added. After 5 min at $T <$ −55 °C the flask was removed from the cooling bath and allowed to warm to room temperature. Water (15 mL) was added, and the layers were separated. The aqueous layer was extracted with dichloromethane (15 mL), and the combined organic extracts were washed sequentially with brine (20 mL), dilute HCl (20 mL), water (20 mL), 6% aqueous po-

(11) Pearson, A. J.; Blystone, S. L.; Nar, H.; Pinkerton, A. A.; Roden, B. A.; Yoon, J. *J. Am. Chem. Soc.* **1989**, *111*, 134.

tassium carbonate (10 mL), and water, then dried ($MgSO_4$), and concentrated. Purification by flash chromatography (10% EtOAc in CH_2Cl_2) gave the ketone **4** (0.856 g, 93%) as yellow crystals: mp 187–9 °C; IR ($CHCl_3$) 1952, 1874, 1711 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.23 (5 H, s), 4.21 (1 H, t, J = 7.0 Hz), 3.85 (2 H, dt, J = 7.0, 2.0 Hz), 2.96 and 2.80 (2 H, AB$_q$ of d, J = 18.3, 1.8 and 18.3, 2.4 Hz); HRMS calcd for $C_{13}H_{12}MoO_3$ (for ^{98}Mo) 313.9841, found 313.9842. Anal. Calcd: C, 50.02; H, 3.87. Found: C, 50.06; H, 3.77.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*endo*-hydroxycyclohexenyl)molybdenum (5). To a stirred solution of complex **4** (10.6 mg, 0.034 mmol) in THF (3 mL), cooled to 0 °C, was added lithium aluminum hydride (6.5 mg, 0.171 mmol). After 10 min the reaction was quenched with saturated aqueous ammonium chloride (2 mL) and extracted with ether in the usual way. Purification by preparative TLC (10% EtOAc in CH_2Cl_2) gave the complex **5** (4.5 mg, 42%) as an air-sensitive unstable yellow oil: R_f 0.5 (4:1 CH_2Cl_2/EtOAc); IR ($CHCl_3$) 3595, 3540–3280, 1941, 1856 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.27 (5 H, s), 4.36 (1 H, t, J = 6.7 Hz), 3.78 (2 H, t, J = 6.8z), 3.56 (1 H, tt, J = 8.7, 6.6 Hz), 2.65 (2 H, dt, J = 16.2, 6.8 Hz), 1.62 (2 H, dd, J = 16.2, 8.3 Hz); HRMS calcd for $C_{13}H_{14}MoO_3$ (^{98}Mo) 315.9998, found 315.9995.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*exo*-methyl-5-oxocyclohexenyl)molybdenum (15, R = Me). Lithium diisopropylamide (1.2 mmol) was prepared in THF (5 mL) at 0 °C and then cooled to −100 °C. To the stirred solution was added dropwise the ketone **4** (312 mg, 1 mmol) in THF (30 mL) over a period of 20 min. After a further 15 min at −100 °C methyl iodide (300 mg) was added, and the reaction mixture was allowed to warm to −35 to −30 °C and was stirred at this temperature for 1.5 h, after which time it was warmed slowly to −5 °C and quenched by the addition of saturated aqueous NH_4Cl (5 mL). The product was extracted with ether in the usual way and separated by flash chromatography. This gave monoalkylated product **15** (R = Me) (252.5 mg, 77%), mp 201–202 °C, dimethylated compound **17** (R = Me) (15 mg, 4.5%), and unreacted starting material (10 mg, 3%). The monomethyl derivative gave the following: R_f 0.7 (9:1, CH_2Cl_2/EtOAc); IR ($CHCl_3$) 1954, 1876, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.27 (5 H, s), 4.21 (1 H, t, J = 7.0 Hz), 3.63–3.90 (2 H, m), 3.13 (1 H, dd, J = 17.8, 3.2 Hz), 2.83 (1 H, qd, J = 7.0, 2.8 Hz), 2.75 (1 H, dd, J = 17.8, 2.1 Hz), 1.25 (3 H, d, J = 7.0 Hz). Anal. Calcd for $C_{14}H_{14}MoO_3$: C, 51.55; H, 4.33. Found: C, 51.49; H, 4.18.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-oxocyclohexenyl)molybdenum (6). To a stirred suspension of the complex **4** (105.5 mg, 0.338 mmol) in dry methanol (15 mL) were added anhydrous potassium carbonate (516 mg, 0.373 mmol) and THF (20 mL). The resulting solution was stirred at room temperature for 18 h and then concentrated, and the crude product was purified by column chromatography (7 g silica gel, 28% CH_2Cl_2 in EtOAc, followed by EtOAc) to give **6** (86.1 mg, 82%) as a yellow crystalline solid: mp 145–7 °C; R_f 0.2 (35% EtOAc in CH_2Cl_2); IR ($CHCl_3$) 1969, 1893, 1631 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.40 (5 H, s), 4.83 (1 H, td, J = 6.0, 0.9 Hz), 4.20 (1 H, ddd, J = 6.1, 1.6, 3.4 Hz), 3.87 (1 H, dd, J = 6.0, 1.6 Hz), 2.13 and 2.49 (2 H, ABq of dt and dddd, J_{gem} = 15.7, J_{vic} = 9.3, 2.4 (dt) and 8.9, 7.0, 3.4, 0.9 (dddd), H-6), 1.69 and 1.85 (2 H, ABqdd, J_{gem} = 19.5, J_{vic} = 9.3, 7.0 and 8.9, 2.4 Hz, H-5). Anal. Calcd for $C_{13}H_{12}MoO_3$: C, 50.02; H, 3.87. Found: C, 50.37; H, 4.10.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-[(methoxycarbonyl)-methylene]-5-oxocyclohexenyl]molybdenum (15, R = CH_2CO_2Me). LDA (0.19 mmol) was prepared in THF (2 mL) at 0 °C as described above and cooled to −100 °C. To this stirred solution was added dropwise a solution of **4** (56 mg, 0.18 mmol) in THF (10 mL). After 15 min methyl bromoacetate (48.5 μL, 0.51 mmol) in THF (2 mL) was added. The mixture was allowed to warm slowly to −20 °C and maintained at this temperature for 1 h, after which time ether (5 mL) and saturated aqueous NH_4Cl (3 mL) were added. The usual ether extraction/aqueous workup, followed by flash chromatography (10% EtOAc in CH_2Cl_2), afforded complex **15** (R = CH_2CO_2Me) (47 mg, 68%) as a yellow oil: R_f 0.5 (10% EtOAc in CH_2Cl_2); IR ($CHCl_3$) 1955, 1880, 1735, 1712 (sh) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.25 (5 H, s), 4.21 (1 H, t, J = 7 Hz), 3.88–3.68 (2 H, m), 3.64 (3 H, s), 3.24–3.00 (2 H, m), 2.78 (1 H, dd, J = 18.6, 2.4 Hz), 2.50 (2 H, m); HRMS calcd for $C_{16}H_{16}MoO_5$ (^{98}Mo) 386.0057, found 386.0063.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-(α-hydroxybenzyl)-5-oxocyclohexenyl]molybdenum (15, R = CHOHPh). By following the above procedure, ketone **4** (54.7 mg, 01.75 mmol) was converted to the enolate in THF (10 mL) at −100 °C. Benzaldehyde (25 μL, 0.25 mmol) was added and the temperature was raised to −42 °C. After 4 h the reaction was quenched by the addition of water (5 mL). Ether extraction in the usual way, followed by preparative TLC (20% EtOAc in CH_2Cl_2), gave recovered starting material (13.1 mg, 24%) and complex **15** (R = CHOHPh) as a 2:1 mixture of diastereomers as a yellow oil that slowly solidified: mp 125–6 °C; R_f 0.3 (10% EtOAc in CH_2Cl_2); IR ($CHCl_3$) 3600, 3550–3200, 1954, 1877, 1708 cm^{-1}; ^{1}H NMR ($CDCl_3$) (major isomer) δ 7.29–7.42 (5 H, m), 5.24 (5 H, s), 4.96 (1 H, dd, J = 4.7, 3.7 Hz, benzylic), 4.44 (1 H, t, J = 7.0 Hz), 3.88 (1 H, m), 3.48 (1 H, dt, J = 6.9, 2.2 Hz), 3.14 (1 H, m), 2.88 and 3.08 (2 H, AB$_q$d, J_{gem} = 18.2, J_{vic} = 2.0 and 2.9 Hz), 2.40 (1 H, d, J = 4.7 Hz, exch D_2O), (minor isomer) δ 7.29–7.42 (5 H, m), 5.24 (5 H, s), 4.56 (1 H, dd, J = 8.5, 2.6 Hz), 4.25 (1 H, t, J = 6.9 Hz), 3.88 (1 H, m), 3.33 (1 H, dt, J = 6.8, 2.0 Hz), 3.08–3.11 (1 H, m), 2.88 and 3.08 (2 H, AB$_q$d, J_{gem} = 18.2, J_{vic} = 2.0 and 2.9 Hz), 2.53 (1 H, d, J = 2.2 Hz, exch D_2O). Anal. Calcd for $C_{20}H_{18}MoO_4$: C, 57.42; H, 4.34. Found: C, 57.78; H, 4.64.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*exo*-acetyl-5-oxocyclohexenyl)molybdenum (15, R = $COCH_3$). The enolate of **4** (0.236 mmol) in THF (12 mL) was treated with acetyl chloride (0.25 mL, 3.5 mmol) at −75 °C for 20 min. Aqueous $NaHCO_3$ (5 mL) and ether (10 mL) were added, and the flask was removed from the cooling bath and allowed to warm to room temperature. The layers were separated, and the aqueous phase was extracted in the usual way with ether. Purification by preparative TLC (20% EtOAc in CH_2Cl_2) afforded the complex **15** (R = $COCH_3$) (65.2 mg, 78%) as a yellow solid: mp 120–122 °C; R_f 0.6 (20% EtOAc in CH_2Cl_2); IR ($CHCl_3$) 1957, 1878, 1720, 1701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.33 (5 H, s), 4.49 (1 H, t, J = 6.6 Hz), 3.87–3.94 (2 H, m), 3.81 (1 H, dt, J = 6.8, 2.6 Hz), 2.87 and 3.09 (2 H, AB$_q$d, J_{gem} = 17.6, J_{vic} = 2.8 and 3.1 Hz), 2.23 (3 H, s). Anal. Calcd for $C_{15}H_{14}MoO_4$: C, 50.86; H, 3.98. Found: C, 50.69; H, 3.87.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-[2-(phenylsulfonyl)ethyl]-5-oxocyclohexenyl]molybdenum (15, R = $CH_2CH_2SO_2Ph$). The enolate of **4** (0.174 mmol) in THF (10 mL) was treated with phenyl vinyl sulfone (61.7 mg, 0.367 mmol) at −30 °C for 3.5 h. The reaction was quenched with aqueous ammonium chloride, and the product was extracted with ether in the usual way and purified by preparative TLC (17:1, CH_2Cl_2/EtOAc). Three bands were obtained: starting material **4** (22.1 mg, 41%), complex **15** (R = $CH_2CH_2SO_2Ph$, 16.0 mg, 19%, R_f = 0.4 in 10% EtOAc/CH_2Cl_2), and complex **17** (R = $CH_2CH_2SO_2Ph$, 24.7 mg, 22%, R_f = 0.3 in 10% EtOAc/CH_2Cl_2). The following data were obtained. **15**: IR ($CHCl_3$) 1958, 1880, 1709, 1309, 1152, 1088 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.44–7.59 and 7.77–7.82 (5 H, m), 5.23 (5 H, s), 4.21 (1 H, t, J = 7.2 Hz), 3.82 (1 H, dd, J = 7.2, 2.9 Hz), 3.71 (1 H, dt, J = 7.0, 2.7 Hz), 2.65–3.16 (4 H, m), 2.53–2.62 (1 H, m), 2.04–2.17 (1 H, m), 1.74–1.93 (1 H, m). **17**: mp 186–8 °C; IR ($CHCl_3$) 1961, 1884, 1702, 1311, 1153, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.55–7.69 and 7.88–7.92 (10 H, m), 5.31 (5 H, s), 4.32 (1 H, t, J = 6.8 Hz), 3.84 (2 H, d, J = 6.8 Hz), 2.96 and 3.19 (4 H, AB$_q$dd, J_{gem} = 13.9, J_{vic} = 11.2, 5.0 and 11.3, 4.9 Hz), 2.65 (2 H, t, J = 7.6 Hz), 2.05–2.19 (2 H, m), 1.87–2.01 (2 H, m). Anal. Calcd for $C_{29}H_{28}MoS_2O_7$: C, 53.70; H, 4.35. Found: C, 53.81; H, 4.26.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4,6-*exo*-dimethyl-5-oxocyclohexenyl)molybdenum (17, R = Me). To a stirred solution of *n*-butyllithium (250 μL of 1.4 M solution, 0.35 mmol) in THF (1 mL) at −100 °C was added dropwise a solution of the ketone **4** (50 mg, 0.16 mmol) in THF (5 mL). After 20 min, methyl iodide (0.4 mL, 7 mmol) was added dropwise, the reaction mixture was allowed to warm to −20 °C and stirred for 1 h at this temperature, the cooling bath was removed, and the reaction was quenched with aqueous NH_4Cl (2 mL). Ether extraction in the usual way, followed by preparative TLC, afforded complex **17** (R = Me) (40 mg, 77%) as a yellow crystalline solid: decomposition 215 °C; R_f 0.8 (10% EtOAc/CH_2Cl_2); IR ($CHCl_3$) 1950, 1870, 1697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.22 (5 H, s), 4.17 (1 H, t, J = 7.0 Hz), 3.80 (2 H, d, J = 7.0 Hz), 2.80 (2 H, q, J = 7.3 Hz), 1.27 (6 H, d, J = 7.3 Hz); HRMS calcd for $C_{15}H_{16}MoO_3$ (^{98}Mo) 342.0159, found 342.0162. Anal. Calcd: C, 52.95; H, 4.74. Found: C, 52.97; H, 4.84.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-[2-(phenylsulfonyl)ethyl]-6-methyl-5-oxocyclohexenyl]molybdenum (16, R = Me, R′ = $CH_2CH_2SO_2Ph$). To a stirred solution of LDA (0.17 mmol) in THF (25 μL) at −100 °C was added dropwise a solution of the ketone **15** (R = Me) (25 mg, 0.08 mmol) in THF (3 mL). The mixture was stirred for 15 min at −100 °C, phenyl vinyl sulfone (41 mg, 0.24 mmol) in THF (1 mL) was added, the mixture was warmed to −20 °C, and stirring was continued at this temperature for 1 h. The reaction was quenched at −20 °C by addition of saturated aqueous NH_4Cl (1 mL), and the product was extracted with ether and purified by preparative TLC in the usual way, giving 26.6 mg (78%) of **16** (R = Me, R′ = $CH_2CH_2SO_2Ph$): mp >175 °C dec; R_f 0.32 (EtOAc/hexane, 1:1), and unreacted starting material (6.5 mg); IR ($CHCl_3$) 1950, 1870, 1700, 1445, 1305, 1150, 1085 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.82 (2 H, m), 7.60–7.44 (3 H, m), 5.23 (5 H, s), 4.17 (1 H, t, J = 7 Hz), 3.75 (2 H, m), 3.12 (1 H, m), 2.90–2.51 (3 H, m), 2.16–1.84 (2 H, m), 1.11 (3 H, d, J = 7.3 Hz); HRMS calcd for $C_{22}H_{22}MoO_5S$ (^{98}Mo) 496.0247, found 496.0252.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-[2-(methoxycarbonyl)-2-(phenylsulfonyl)ethyl]-6-methyl-5-oxocyclohexenyl]molybdenum (16, R = Me, R′ = $CH_2CH(SO_2Ph)CO_2Me$). By using the same procedure as

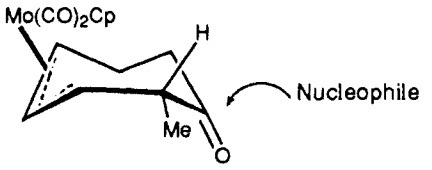


Figure 6. Half-chair conformation of (4-methylcycloheptenyl)-Mo-$(CO)_2Cp$ showing quasi-equatorial methyl and preferred endo nucleophile approach.

above, the enolate from **15** (R = Me) was treated with methyl 2-(phenylsulfonyl)propenoate[12] to give the product as a mixture of diastereomers (quantitative yield), R_f 0.37 (EtOAc/hexane, 1:1). Crystallization from EtOAc/hexane gave pure diastereomer A, mp >198 °C dec; the liquors gave diastereomer B contaminated with small amounts of A: IR ($CHCl_3$) 1950, 1870, 1732, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) (A) δ 7.83–7.77 (2 H, m), 7.77–7.50 (3 H, m), 5.28 (5 H, s), 4.25 (1 H, t, J = 7 Hz), 3.89–3.76 (3 H, m), 3.61 (3 H, s), 2.83 (1 H, q, J = 7.5 Hz), 2.69–2.45 (2. H, m), 2.37–2.11 (1 H, m), 1.20 (3 H, d, J = 7.5 Hz); (B) 7.82–7.78 (2 H, m), 7.74–7.50 (3 H, m), 5.24 (5 H, s), 4.21–4.17 (2 H, m), 3.81–3.69 (2 H, m), 3.48 (3 H, s), 2.80 (1 H, q, J = 7.5 Hz), 2.70–2.06 (3 H, m), 1.15 (3 H, d, J = 7.5 Hz). Anal. (A) Calcd for $C_{24}H_{24}MoO_7S$: C, 52.18; H, 4.38. Found: C, 52.26; H, 4.38.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-[(methoxycarbonyl)-methyl]-6-methyl-5-oxocyclohexenyl]molybdenum (16, R = Me, R′ = CH_2CO_2Me). By using the same procedure as above the enolate from **15** (R = Me) was treated with methyl bromoacetate to give complex **16** (R = Me, R′ = CH_2CO_2Me, 82% yield; using *n*-BuLi as base gave 73% yield): mp 171–173 °C; R_f 0.2 (EtOAc/hexane, 1:1); IR ($CHCl_3$) 1950, 1873, 1735, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.28 (5 H, s), 4.26 (1 H, t, J = 7.0 Hz), 3.96–3.85 (2 H, m), 3.70 (3 H, 2), 3.25–3.17 (1 H, m), 2.87 (1 H, q, J = 7.4 Hz), 2.64 (1 H, dd, J = 15, 5 Hz), 2.50 (1 H, dd, J = 15, 10 Hz), 1.28 (3 H, d, J = 7.4 Hz); HRMS calcd for $C_{17}H_{18}MoO_5$ (^{98}Mo) 400.0214, found 400.0209. Anal. Calcd: C, 51.27; H, 4.56. Found: C, 51.43, H, 4.62.

Lactonization of Carboxylic Acid 18. The acid **18** (63.0 mg, 0.16 mmol, from hydrolysis of the methyl ester using KOH, THF, MeOH, H_2O, room temperature) was stirred in acetonitrile (2 mL) at 0 °C while $NOPF_6$ (42 mg, 0.24 mmol) was added. After 30 min, triethylamine (33.4 μL, 0.24 mmol) was added, and stirring was continued for 5 min. The acetonitrile was removed in vacuo, chloroform (5 mL) was added, and the mixture was stirred under oxygen atmosphere at room temperature overnight. Filtration through Celite, followed by preparative TLC afforded the lactone **19** (4.6 mg, 17%) as a colorless oil: IR ($CHCl_3$) 1785, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.01–5.90 (2 H, m), 5.40 (1 H, m), 3.38–3.29 (2 H, m), 3.16 (1 H, m), 2.6 (1 H, dd, J = 9.6, H.2 Hz), 1.20 (3 H, d, J = 7 Hz); HRMS calcd for $C_9H_{10}O_3$ 166.0630, found 166.0628.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*endo*-hydroxy-4,6-*exo*-dimethylcyclohexenyl)molybdenum (20). A solution of the ketone **17** (R = Me, 100 mg, 0.29 mmol) in THF (7 mL) was added dropwise to a stirred suspension of lithium aluminum hydride (41 mg, 1.08 mmol) in THF (3 mL) cooled to −30 °C. After the solution was warmed to room temperature ether, followed by aqueous NH_4Cl, was added, and the organic layer was separated, washed with water, dried ($MgSO_4$), and concentrated. The product was rapidly purified by chromatography (20 mg silica gel, 50 mL 10% EtOAc in CH_2Cl_2 to give complex **20** (100 mg, 99.5%): mp 124–126 °C dec; R_f 0.5 (10% EtOAc in CH_2Cl_2); IR ($CHCl_3$) 3590, 3545, 1938, 1855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.19 (5 H, s), 4.29 (1 H, t, J = 6.6 Hz), 3.39 (2 H, d, J = 6.6 Hz), 2.35 (1 H, t, J = 8.8 Hz), 1.54 (2 H, dq, J = 8.8, 7.6 Hz), 1.49 (1 H, s, exch D_2O), 1.13 (6 H, d, J = 7.6 Hz); HRMS calcd for $C_{14}H_{18}MoO_2$ (M − CO, ^{98}Mo) 316.0367, found 316.0371.

5-Hydroxy-4,5-dimethyl-3-(phenylthio)cyclohexene (22). To a stirred solution of complex **20** (50 mg, 0.154 mmol) in THF (1 mL) at −70 °C was added dropwise a solution of bromine (15.8 μL, 0.30 mmol) in dichloromethane (500 μL). Examination of the reaction by TLC indicated total conversion of starting material after 2 h, whereupon a solution of sodium thiophenoxide (101.1 mg, 0.77 mmol) in THF (2 mL) was added dropwise. After 5 min, the reaction mixture was allowed to warm to room temperature, water (2 mL) and ether (5 mL) were added, and the organic layer was separated, washed with brine, water, then dried ($MgSO_4$), and concentrated. Purification by chromatography (5 g of silica gel, hexane followed by 10% CH_2Cl_2/hexane, followed by CH_2Cl_2) afforded the product **22** (29.5 mg, 87%) as a white crystalline solid: mp 61–63 °C; R_f 0.4 (10% EtOAc/CH_2Cl_2); IR ($CHCl_3$) 3520, 2960, 1588, 1475, 1460, 1265, 1045, 1023 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47–7.39 (2 H, m), 7.33–7.23 (3 H, m), 5.66 (1 H, dt, J = 10, 2.5 Hz), 5.40 (1 H, dt, J = 10, 1.9 Hz), 3.36 (1 H, ddt, J = 10, 3.6, 2.2 Hz), 3.06 (1 H, dd, J = 10.3, 10.2 Hz), 2.04 (1 H, exch D_2O), 1.73–1.57 (2 H, m), 1.33 (3 H, d, J = 6.5 Hz), 1.07 (3 H, d, J = 7.0 Hz); HRMS calcd for $C_{14}H_{18}OS$ 234.1078, found 234.1080.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-cycloheptadienyl)molybdenum (24). This was prepared in 94% yield by using a procedure identical with that for complex **2** (10.8 g of **23** and 10 mL of Et_3N gave 7.0 g of **24**): R_f 0.8 (Et_2O), mp 92–93 °C; IR ($CHCl_3$) 1940, 1850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.01–5.92 (1 H, m), 5.27 (5 H, s), 5.12 (1 H, dt, J = 11.1, 5.6 Hz), 4.43–4.36 (1 H, m), 4.15–4.07 (2 H, m), 2.38–2.29 (1 H, m), 2.16–1.99 (2 H, m), 1.50–1.41 (1 H, m); HRMS calcd for $C_{14}H_{14}MoO_2$ 312.0054, found 312.0069.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*exo*-hydroxycycloheptenyl)-molybdenum (25a). This was prepared by the method used for **3** (7.0 g of **24** gave 5.25 g of **25a**, 71% yield; complex **26** was also formed in 19% yield): R_f 0.4 (Et_2O); mp 114–116 °C; IR ($CHCl_3$) 3600, 3500–3300, 1935, 1850 cm^{-1}; ^1H NMR ($CDCl_3$) 5.27 (5 H, s), 4.06 (1 H, ddt, J = 8.7, 7.0, 1.6 Hz), 3.91–3.87 (1 H, m), 3.79 (1 H, t, J = 8.7, H-2), 2.92–2.87 (1 H, m), 2.58–2.44 (2 H, m), 2.37 (1 H, ddd, J = 15.7, 7.9, 4.9 Hz), 2.12 (1 H, dddd, J = 16.8, 10.2, 4.7, 1.7 Hz), 1.41–1.32 (1 H, m), 1.26–1.20 (1 H, m). Anal. Calcd for $C_{14}H_{16}MoO_3$: C, 51.23; H, 4.91. Found: C, 51.36; H, 4.82.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-oxocycloheptenyl)molybdenum (27). This was prepared by Swern oxidation of **25**, as for complex **4** (3.0 g of **25** gave 2.7 g of **27**, 80% yield): R_f 0.5 (10% EtOAc in CH_2Cl_2); mp 177–178 °C dec; IR ($CHCl_3$) 1945, 1860, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.31 (5 H, s), 4.20 (1 H, m), 3.85 (2 H, m), 3.30 (1 H, dd, J = 16.6, 5.4 Hz), 3.09 (1 H, d, J = 16.6 Hz), 2.30 (1 H, m), 2.20–2.01 (2 H, m), 1.74–1.60 (1 H, m); HRMS calcd for $C_{14}H_{14}MoO_3$ 328.0003, found 327.9995. Anal. Calcd: C, 51.55, H, 4.33. Found: C, 51.44; H, 4.13.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*endo*-hydroxycycloheptenyl)molybdenum (29). To a stirred suspension of $LiAlH_4$ (14 mg, 0.3 mmol) in THF (10 mL) at −22 °C was added the ketone **27** (30 mg, 0.1 mmol) in THF (10 mL). After 1 h at −22 °C, the reaction was quenched with saturated aqueous NH_4Cl (8 mL) and the product was extracted with ether in the usual way. NMR showed a 2:1 ratio of **29** and **25a**. Purification by preparative TLC gave **29** as an unstable yellow oil (29.6 mg, 99%): R_f (silica gel, ether); IR (CCl_4) 3600, 5520–3300, 1950, 1860 cm^{-1}; NMR ($CDCl_3$, decomposes in solution) 5.26 (5 H, s), 4.07 (1 H, m), 3.76 (2 H, m), 3.24 (1 H, td, J = 10.4, 4.7 Hz), 2.95–2.80 (1 H, m), 2.79–2.02 (2 H, m), 1.41–1.19 (2 H, m), 0.56 (1 H, dddd, J = 13.5, 12.2, 10.5, 3.9 Hz); HRMS calcd for $C_{14}H_{16}MoO_3$ 330.0154, found 330.0122.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*exo*-hydroxy-5-*endo*-methylcycloheptenyl)molybdenum (25b). A solution of complex **27** (49.5 mg, 0.15 mmol) in THF (5 mL) was added dropwise to a stirred solution of methylmagnesium bromide (1 mL of 3.0 M solution in THF at −20 °C. The temperature was raised to 0 °C, and stirring was continued for 2 h, at which time the reaction was quenched (10 mL of saturated aqueous NH_4Cl), and the product was extracted with ether in the usual way. Purification by preparative TLC (40% EtOAc in hexane) afforded complex **25b** (38 mg, 73%) as yellow crystals: R_f 0.15 (40% EtOAc in hexane); mp 134–136 °C; IR ($CHCl_3$) 3580, 1930, 1840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.27 (5 H, s), 4.19 (1 H, m), 3.86 (1 H, t, J = 8.4 Hz), 3.67 (1 H, tt, J = 8.4, 1.5 Hz), 2.6 (1 H, dd, J = 17.5, 1.5 Hz), 2.5 (1 H, m, obscured), 2.32 (1 H, dd, J = 17.5, 0.9 Hz), 2.00 (1 H, dq, J = 16.5, 3.5 Hz), 1.78 (1 H, s, br, exch D_2O), 1.29–1.17 (1 H, m), 1.04 (3 H, s), 0.55 (1 H, ddd, J = 14.3, 12.7, 4.0 Hz). Anal. Calcd for $C_{15}H_{18}MoO_3$: C, 52.64; H, 5.30. Found: C, 52.40; H, 5.22.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*exo*-hydroxy-5-*endo*-phenylcycloheptenyl)molybdenum (25c). This was prepared in 99% yield by reaction of **27** with PhMgBr, as described for **25b**: mp 153–154 °C dec; IR ($CDCl_3$) 3620, 1940, 1850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.13 (5 H, m), 5.31 (5 H, s), 4.28 (1 H, m), 3.93 (1 H, t, J = 8.6 Hz), 3.70 (1 H, m), 2.69–2.54 (3 H, m), 2.10 (1 H, dq, J = 16.4, 3.6 Hz) 2.1 (1 H, s, exch D_2O), 1.41 (1 H, dt, J = 14.5, 3.8 Hz), 1.14 (1 H, ddd, J = 14.5, 12.5, 3.8 Hz); HRMS calcd for $C_{20}H_{20}MoO_3$ 406.0472, found 406.0413.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*exo*-hydroxy-5-*endo*-vinylcycloheptenyl)molybdenum (25d). This was prepared in 68% yield by using vinylmagnesium bromide as above (49 mg of **27** and 1.5 mL of 1.0 M THF solution of Grignard reagent gave 36 mg of **25d**): R_f 0.4 (10% EtOAc in CH_2Cl_2); mp 83–85 °C; IR ($CHCl_3$) 3600, 1940, 1855 cm^{-1}; ^1H NMR ($CDCl_3$) 5.76 (1 H, dd, J = 17.3, 10.7 Hz, vinyl), 5.28 (5 H,

(12) Methyl 2-(phenylsulfonyl)propenoate was prepared from methyl (phenylsulfonyl)acetate by the three-step sequence: (a) NaH, MeI, THF; (b) NaH, PhSeBr, THF; (c) *m*-CPBA, CH_2Cl_2 (selenoxide elimination).

s, Cp), 5.11 (1 H, dd, J = 17.3, 1.2 Hz, vinyl), 4.86 (1 H, dd, J = 10.7, 1.2 Hz, vinyl), 4.2 (1 H, m, H-1), 3.88 (1 H, t, J = 8.6 Hz, H-2), 3.68 (1 H, ddt, J = 8.6, 7.3, 1.4 Hz, H-3), 2.55 (2 H, m, H-7, H-4), 2.38 (1 H, dd, J = 17.5, 1.6 Hz, H-4'), 2.04 (1 H, dq, J = 16.3, 3.6 Hz, H-7'), 1.68 (1 H, s, exch D_2O, OH), 1.32–1.21 (1 H, m, H-6), 0.64 (1 H, ddd, J = 14.4, 12.7, 4.0 Hz, H-6'). Anal. Calcd for $C_{16}H_{18}MoO_3$: C, 54.25; H, 5.12. Found: 53.60; H, 5.28.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*exo*-methyl-5-oxocycloheptenyl)molybdenum (28a). This was prepared in an identical fashion as complex **15** (R = Me) (976 mg of **27** with 15.0 mmol of LDA and excess CH_3I gave 855 mg of **28a**; yield 84%): R_f 0.5 (40% EtOAc in hexane); mp 142–143 °C. A small amount (3% of rearranged complex) analogous to **6** was also isolated: IR ($CDCl_3$) 1940, 1855, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.32 (5 H, s), 4.2 (1 H, m), 3.81 (1 H, t, J = 8.6 Hz), 3.52 (1 H, dt, J = 8.6, 1.6 Hz), 3.0 (1 H, qd, J = 6.9, 1.6 Hz), 1.28 (3 H, d, J = 6.8 Hz), 2.40–2.25 (1 H, m), 2.18–1.95 (1 H, m), 2.0 (1 H, ddd, J = 15.7, 6.8, 3.8 Hz), 1.71–1.58 (1 H, m). Anal. Calcd for $C_{15}H_{16}MoO_3$: C, 52.95; H, 4.74. Found: C, 52.73; H, 4.49.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-[(methoxycarbonyl)-methyl]-5-oxocycloheptenyl]molybdenum (28b). This was prepared in analogous fashion to **15** (R = CH_2CO_2Me) (50 mg of **27** gave 44 mg of **28b**; yield 73%; yellow oil): R_f 0.3 (40% EtOAc in hexane); IR ($CHCl_3$) 1950, 1865, 1735, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.26 (5 H, s, Cp), 4.22 (1 H, m, H-1), 3.83 (1 H, t, J = 8.6 Hz, H-2), 3.67 (3 H, s, ester), 3.46 (1 H, dt, J = 8.6, 1.5 Hz, H-3), 3.36 (1 H, ddd, J = 8.0, 5.7, 1.4 Hz, H-4), 2.94 (1 H, dd, J = 16.4, 8.8 Hz, CH_2CO_2Me), 2.56 (1 H, dd, J = 16.4, 5.7 Hz), 2.39–2.24 (1 H, m), 2.19–1.96 (1 H, m), 1.76–1.65 (1 H, m). Anal. Calcd for $C_{17}H_{18}MoO_5$: C, 51.27; H, 4.56. Found: C, 51.01; H, 4.53.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-(methoxycarbonyl)-5-oxocycloheptenyl]molybdenum (28c). This was prepared as above by reacting the enolate of **27** with methyl cyanoformate at −78 °C (50 mg of **27** gave 36 mg of **28c**; yield 63%; yellow oil): R_f 0.2 (30% EtOAc in hexane); IR (CH_2Cl_2) 1940, 1860, 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.29 (5 H, s), 4.10 (1 H, m), 3.87 (3 H, s), 3.55 (1 H, t, J = 8.4 Hz), 3.31 (1 H, ddd, J = 17.5, 8.4, 1.5 Hz), 2.67 (1 H, d, J = 17.5 Hz), 2.37–2.00 (3 H, m), 0.99–0.84 (1 H, m). Anal. Calcd for $C_{16}H_{16}MoO_5$: C, 50.01; H, 4.2. Found: C, 49.84; H, 4.16.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*exo*-hydroxy-4-*exo*-methyl-5-*endo*-methylcycloheptenyl)molybdenum (31a). Reaction of **28a** (719 mg) with an excess of methylmagnesium bromide at 0 °C, as described for **29b** gave **31a** (727 mg, 96% yield) as yellow crystals: R_f 0.3 (40% EtOAc in hexane); mp 162–164 °C; IR ($CHCl_3$) 3580, 1940, 1850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.28 (5 H, s, Cp), 4.18 (1 H, m, H-1), 3.82 (1 H, t, J = 9.0 Hz, H-2), 3.34 (1 H, d, J = 9.0 Hz, H-3), 2.51 (1 H, ddt, J = 16.4, 12.4, 3.5 Hz, H-7), 2.21 (1 H, q, J = 7.2 Hz, H-4), 1.97 (1 H, dq, J = 16.4, 3.7 Hz, H-7'), 1.26 (3 H, d, J = 7.2 Hz, CH_3), 1.31–1.23 (1 H, m, obscured, H-6), 1.02 (3 H, s, CH_3), 0.55 (1 H, ddd, J = 14.4, 12.4, 3.6 Hz, H-6'). Anal. Calcd for $C_{16}H_{20}MoO_3$: C, 53.94; H, 5.66. Found: C, 54.19; H, 5.46.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*endo*-allyl-5-*exo*-hydroxy-4-*exo*-methylcycloheptenyl)molybdenum (31b). This was prepared as described above by using allylmagnesium bromide (50 mg of **28a** gave 53 mg of **31b**; 95% yield): R_f 0.2 (30% EtOAc in hexane), mp 82–83 °C; IR ($CHCl_3$) 3580, 1930, 1850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.72–5.54 (1 H, m), 5.27 (5 H, s), 5.05–4.94 (2 H, m), 4.24–4.17 (1 H, m), 3.83 (1 H, t, J = 8.8 Hz), 3.33 (1 H, d, J = 8.8 Hz), 2.46 (1 H, ddt, J = 16.6, 13.0, 3.8 Hz), 2.31 (1 H, q, J = 7.1 Hz), 2.21–2.06 (2 H, m), 1.98 (1 H, dq, J = 16.6, 3.6 Hz), 1.57 (1 H, s, exch D_2O), 1.33 (1 H, dt, J = 14.5, 3.8 Hz), 2.24 (3 H, d, J = 7.1 Hz), 0.46 (1 H, ddd, J = 14.5, 13.0, 3.6 Hz). Anal. Calcd for $C_{18}H_{22}MoO_3$: C, 56.55; H, 5.80. Found: C, 56.80; H, 5.84.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*exo*-hydroxy-4-*exo*-methylcycloheptenyl)molybdenum (31c). To a stirred suspension of $LiAlH_4$ (8 mg) in THF (1 mL) at −78 °C was added dropwise a solution of **28a** (49 mg, 0.15 mmol) in THF (2 mL). After 1.5 h, the reaction was quenched with aqueous NH_4Cl, warmed to room temperature, and extracted with ether in the usual way. Purification by preparative TLC afforded the crystalline complex **31c** (39 mg, 80%): R_f 0.3 (30% EtOAc, hexane); mp 113–115 °C; IR ($CHCl_3$) 3610, 1935, 1850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.24 (5 H, s), 4.13–4.04 (1 H, m), 3.74 (1 H, dt, J = 8.8, 0.9 Hz), 3.54 (1 H, d, J = 8.8 Hz), 3.19 (1 H, dd, J = 8.8, 3.4 Hz), 2.59–2.32 (2 H, m), 2.03 (1 H, dddd, J = 16.8, 6.8, 4.5, 2.3 Hz), 1.61–1.44 (2 H, m, one exch D_2O), 1.25 (3 H, d, J = 7.1 Hz), 0.72 (1 H, ddd, J = 13.9, 9.3, 4.4 Hz). Anal. Calcd for $C_{15}H_{18}MoO_3$: C, 52.64; H, 5.30. Found: C, 52.82; H, 5.29.

Generation and Methylation of Enolate from Complex 28a. To a stirred suspension of potassium hydride (35% dispersion in oil, 1.5 mmol) in THF (3 mL) and methyl iodide (2 mL) at room temperature was added the ketone **28a** (50 mg, 0.15 mmol) in one portion. Stirring was continued for 5 h, after which time excess base was destroyed by dropwise addition of aqueous NH_4Cl (10 mL), and the product was extracted with ether in the usual way to give an equimolar mixture of **32** and **33** (63% yield) which could be separated by preparative TLC (30% EtOAc in hexane) but the stereochemistry could not be rigorously assigned. One isomer gave the following: mp 108–110 °C; IR ($CHCl_3$) 1940, 1860, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.32 (5 H, s), 4.11 (1 H, m), 3.78 (1 H, t, J = 8.6 Hz), 3.50 (1 H, d, J = 8.6 Hz), 2.99 (1 H, q, J = 6.8 Hz), 2.08–1.87 (2 H, m), 1.61–1.30 (1 H, m), 1.28 (3 H, d, J = 6.8 Hz), 0.90 (3 H, d, J = 6.8 Hz). Anal. Calcd for $C_{16}H_{18}MoO_3$: C, 54.25; H, 5.42. Found: C, 53.60; H, 5.28.

Decomplexation of 31a. By following the same procedure as for decomplexation of **20** but using 1 equiv of bromine, 76.0 mg of **31a** gave 30 mg (89%) of a 3:1 mixture of regioisomeric thioethers **34** and **35** and 30 mg of recovered starting material. These were separated by preparative TLC: R_f (**34**) 0.5, (**35**) 0.4 (40% EtOAc in hexane); (**34**) IR ($CHCl_3$) 3590, 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.42–7.20 (5 H, m), 5.76–5.72 (2 H, m), 3.95 (1 H, m), 1.90–1.75 (2 H, m), 2.22–2.04 (2 H, m), 1.36 (3 H, s), 1.21 (3 H, d, J = 7.0 Hz); (**35**) IR ($CHCl_3$) 3600, 3060, 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.45–7.20 (5 H, m), 5.86 (1 H, ddd, J = 11.3, 6.4, 2.0 Hz), 5.39 (1 H, dd, J = 11.3, 5.0 Hz), 3.99–3.88 (1 H, m), 2.59 (1 H, q, br, J = 7.2 Hz), 2.16–1.92 (2 H), 1.85–1.65 (2 H), 1.43 (1 H, s, exch D_2O), 1.22 (3 H, s), 1.07 (3 H, d, J = 7.2 Hz); HRMS calcd for $C_{15}H_{20}Os$ 248.1235, found (**34**) 248.1239, (**35**) 248.1232.

X-ray Diffraction Analysis. The crystals for both $C_{14}H_{16}O_3Mo$ and $C_{16}H_{20}O_3Mo$ were sealed in glass capillary tubes under an argon atmosphere. The parameters for X-ray data collection and structural refinement are summarized in the supplementary material.[13] Atomic coordinates, isotropic, and anisotropic displacement coefficients are given in the supplementary material.

Refinement and Description of the Structures. $C_{14}H_{16}O_3Mo$ (25). Two conformers are observed in the crystalline state. They have different conformations of the cycloheptenyl ring. Figure 2 shows the thermal ellipsoid plots and atomic numbering schemes of the two conformers observed in the crystalline state. Tables II and III give selected interatomic bond lengths and angles. The complete list of lengths and angles are included in the supplementary material.

One conformer has the hydroxide ligand in an equatorial position (molecule A), while the other has the hydroxide in an axial position (molecule B). The cyclopentadienyl ring in molecule A is disordered. This disorder was modeled by locating 10 coplanar peaks of electron density equidistant from the Mo atom and fixing their occupancy factor at 0.5. Two staggered, superimposed cyclopentadienyl rings resulted. Each ring was fit as a rigid, regular pentagon; carbon–carbon bond distances were fixed at 1.420 Å. In molecule B, atoms C5, C6, and O1 are disordered. Two enantiomers of the seven-membered ring occur, where a mirror plane bisects C-5 and C-6 and intersects C-2. The disordered atoms are labeled with Y or Z (supplementary material). Each of the Y,Z atoms were refined in alternating least-squares cycles. In these refinement cycles, either the isotropic thermal parameter or the occupancy factor values were held constant while the other was free. Furthermore, the occupancy factors were constrained in two ways: (1) the values for all three atoms in one disorder model were equal, and (2) the sum of the occupancy factors for symmetry-related atoms in both models equaled one. Refinement was continued in this fashion to convergence. None of the disordered atoms were refined anisotropically. Hydrogen atoms were calculated at idealized positions only for the ordered atoms.

$C_{16}H_{20}O_3Mo$ (31b). Shown in Figure 4 are the thermal ellipsoid plot and atomic numbering scheme for the molecule. Selected interatomic bond lengths and angles are given in Tables IV and V.

The cyclopentadienyl rings were disordered and refined as previously described for molecule A of $C_{14}H_{16}O_3Mo$.

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(13) Sheldrick, G. M. *SHELXTL Plus, Release 3.4, program for crystal structure determination.* Nicolet Instrument Corporation (Siemens): Madison, WI, 1988. (Computer program.)

87-04812) and the National Institutes of Health (Grant No. S10 RR04277).

Supplementary Material Available: Tables of crystal data, data collection, data reduction, refinement details, positional and thermal parameters, and bond distances and angles for the crystal structures of $C_{14}H_{16}O_3Mo$ (**25**) and $C_{16}H_{20}O_3Mo$ (**31b**) and thermal ellipsoid plot of the *Z* enantiomer of $C_{14}H_{16}O_3Mo$ (22 pages). Ordering information is given on any current masthead page.

Mechanistic Aspects on the Formation of Chiral Allenes from Propargylic Ethers and Organocopper Reagents

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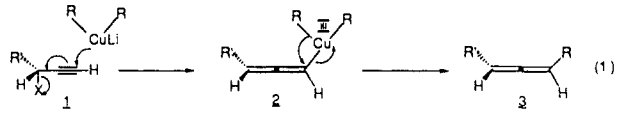
Abstract: Propargylic ethers react with organocopper reagents to afford allenes by a syn addition to the triple bond followed by a β-elimination of the resulting alkenyl copper species. With use of chiral propargylic ethers and stoichiometric organocopper reagent, it was shown that the β-elimination step is purely anti, resulting in the formation of a chiral allene with 96% optical yield. The same reaction, run with a Grignard reagent RMgX and a catalytic amount of a Cu^I salt, affords allenes through an anti or syn overall process. The crucial step is the β-elimination of the intermediate alkenyl organometallic species, which is of anti type with RMgI and of syn type with RMgCl. Propargylic acetates, which also afford allenes in this reaction, but through a Cu^{III} intermediate, are not sensitive to this "halogen effect".

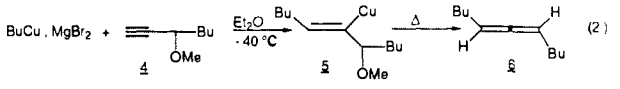
Introduction

One of the most popular methods for the synthesis of allenes is the reaction of propargylic derivatives with organocopper reagents.[1] Since the first report by Crabbé et al.,[2] many authors have used modified organocopper reagents, with stoichiometric or catalytic amounts of Cu^I salt. The propargylic substrate itself varies from ethers and epoxides to various esters of more or less reactivity. The question of the mechanism and of the stereochemistry of this substitution reaction arose quickly, and chiral propargylic esters of type **1** were used to produce chiral allenes of type **3**. It is presently believed that these reactions proceed through a Cu^{III} intermediate **2** resulting from an anti S_N2' nucleophilic attack of the Cu^I atom.[3] This intermediate collapses by reductive elimination to allene **3** with *retention* of configuration. The overall result is an ANTI process (eq 1). During our work



(1)

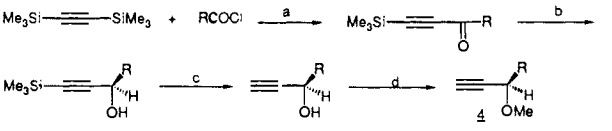
on the carbocupration of alkynes,[4] we had the opportunity to demonstrate that the formation of allene **6** from propargylic *ether* **4** follows a different path[5] (eq 2). A syn addition takes place,



(2)

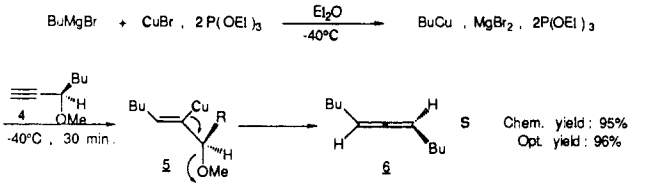
first, producing an alkenyl copper reagent **5**, which can be trapped with various electrophiles. Upon warming, **5** undergoes a β-elimination, leading to allene **6**. The nature of this β-elimination

Scheme I



a) $AlCl_3$, CH_2Cl_2 ; b) $LiAlH_4$ / Darvon alcohol ; c) KF, DMF d) NaH, MeI / THF

Scheme II



was, at that time, unknown, and the aim of this article is to report our recent results in this field.[6]

Such a study requires optically active propargylic ethers, which were prepared from the corresponding alcohols by a nonracemizing etherification procedure.[7] The needed alcohols were prepared by enantioselective reduction[8] of ynones, according to the sequence in Scheme I. Many methods exist for the enantioselective reduction of ynones, but high levels of induction are obtained only with costly reagents or/and tedious preparation of chiral auxiliaries.[9] For a mechanistic study, propargylic ethers of moderate ee are acceptable, provided they can be prepared in bulk. This is the case with the $LiAlH_4$/Darvon alcohol procedure.[8b] The enantiomeric excesses range from 37% to 58%.

(1) (a) Landor, S. R. *The Chemistry of the allenes*; Academic Press: New York, 1982. (b) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Chemistry*; Wiley: New York, 1984.
(2) Rona, P.; Crabbe, P. *J. Am. Chem. Soc.* **1968**, *90*, 4733.
(3) Dollat, J. M.; Luche, J. L.; Crabbe, P. *J. Chem. Soc., Chem. Commun.* **1977**, 761.
(4) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.
(5) Alexakis, A.; Normant, J. F.; Villieras, J. *J. Mol. Catal.* **1975/76**, *1*, 43.
(6) For a preliminary account of this work see: Marek, I.; Mangeney, P.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 5499.
(7) Barton, D.; Brown, C. A. *Synthesis* **1974**, 434.
(8) (a) Vigneron, J. P.; Bloy, V. *Tetrahedron Lett.* **1979**, *29*, 2683. (b) Brinckmeyer, R. S.; Kapoor, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 8339.
(9) Grandbois, E. R.; Howard, S. I.; Morrison, J. D. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, p 71.

0002-7863/90/1512-8042$02.50/0