Utilization of the $[CpMo(CO)_2(\eta^3\text{-}2\text{-}CH_2COC_3H_4)]^-$ Enolate for Stereoselective Synthesis of (1*R* *,3*S* *)-4-Pentene-1,3-diols

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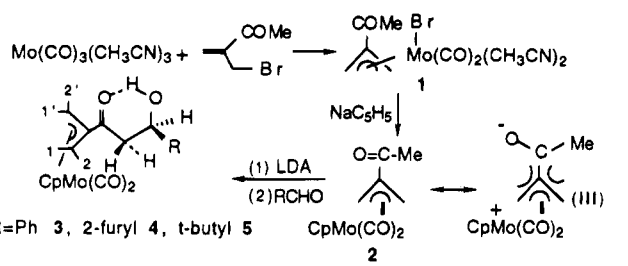
The enolate anion of $[CpMo(CO)_2(\eta^3\text{-}2\text{-}CH_3COC_3H_4)]$ (**2**), readily generated by lithium diisopropylamide in cold THF (−78 °C), underwent alkylation with aldehydes to give the aldol products **3**–**5** in good yields. X-ray diffraction measurement of **3** shows strong intramolecular hydrogen bonding within the ketone and alcohol groups. The Me_4NBH_4 reduction of **3**–**5** via proton-chelation control in benzene/CH_3OH proceeded with fair diastereoselectivities in favor of the *syn*-1,3-diol. Addition of PhSNa to the NO^+ cation of the π-allyl *syn*-1,3-diols **6**–**8** gave (1*R* *,3*S* *)-1-R-4-((phenylthio)methyl)-4-pentene-1,3-diols (R = phenyl (**9**), furyl (**10**), *tert*-butyl (**11**)).

Introduction

The aldol reaction is an important process for forming carbon–carbon bonds in organic synthesis.[1,2] Although transition-metal enolates are known for virtually every triad of transition metals,[3] few are useful for organic synthesis. The best recognized transition-metal enolates belong to the $CpFe(CO)PPh_3(COCHRLi)$ (R = H, alkyl) system, examined thoroughly by Liebeskind[4] and Davies.[5] These reports[4,5] reveal that the iron enolate is effective in directing chiral transfer to the newly generated carbon center in reactions such as alkylation, aldol condensation, imine addition, and epoxide opening. Molybdenum π-allyl compounds $CpMo(CO)_2(\pi\text{-allyl})$ have proven to be useful in organic synthesis.[6,7] The enolates of these complexes are known for both cyclic[8,9] and acyclic[10] systems. A stereocontrolled aldol reaction of the former is generally more difficult than of the latter because of the former's conformational inflexibility. We

Chart 1

Scheme 1



previously reported[10] diastereoselective aldol reactions of the enolate anion of **I**, and its subsequent application for stereoselective synthesis of 1,3-diols, 1,3,5-triols, highly substituted tetrahydrofurans, *cis*-1,3-dienes, and *cis*-1,3,5-trienes. In this paper, we report the enolate reaction of type **II**, in which the enolate is linked to the central carbon of the allyl group. Applications of this enolate for stereoselective synthesis of acyclic 1,3-diols are described. The stereochemical course of the reaction is quite distinct from that of enolate (**I**).

Results and Discussion

As shown in Scheme 1, treatment of $Mo(CO)_3(CH_3CN)_3$ with 3-(bromomethyl)-3-buten-2-one[11] in a mixed THF/CH_3CN solvent at 40 °C for 4 h produced the orange solid **1** (90%), slightly soluble in common organic solvents. Further treatment of **1** with NaCp in THF at 23 °C for 2 h led to displacement of two carbonyl and bromide ligands by the cyclopentadienyl group[12] to yield the key compound **2** in 60% yield after workup. At −60 °C, the ^1H NMR spectrum showed the presence of *exo*/

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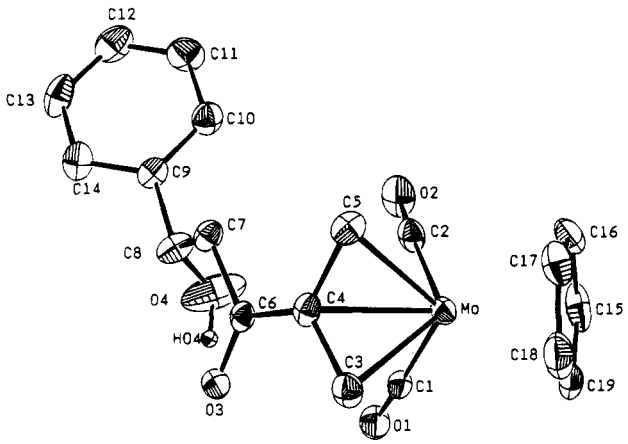

Figure 1. Molecular structure of **3**.

Table 1. Selected Bond Distances and Angles for 3

Mo–C1	1.958(7)	C4–C6	1.483(9)
Mo–C2	1.961(7)	C6–C7	1.522(9)
Mo–C3	2.302(6)	C6–O3	1.218(8)
Mo–C4	2.270(6)	C7–C8	1.482(10)
Mo–C5	2.286(7)	C8–C9	1.518(10)
C1–O1	1.157(8)	C8–O4	1.283(10)
C2–O2	1.147(8)	O3–HO4	2.030(5)
C3–C4	1.416(9)	O4–HO4	0.949(7)
C4–C5	1.399(10)		
C1–Mo–C2	78.4(3)	Mo–C4–C6	114.3(4)
C1–Mo–C3	82.0(3)	C3–C4–C5	114.7(6)
C1–Mo–C4	86.98(24)	C3–C4–C6	118.8(6)
C1–Mo–C5	119.36(25)	C5–C4–C6	125.6(6)
C2–Mo–C3	125.7(3)	Mo–C5–C4	71.5(4)
C2–Mo–C4	92.51(24)	C4–C6–C7	118.2(6)
C2–Mo–C5	84.9(3)	C4–C6–O3	122.3(6)
C3–Mo–C4	36.08(23)	C7–C6–O3	119.4(6)
C3–Mo–C5	62.2(3)	C6–C7–C8	114.9(6)
C4–Mo–C5	35.76(24)	C7–C8–C9	112.8(6)
Mo–C1–O1	177.5(6)	C7–C8–O4	117.8(7)
Mo–C2–O2	176.3(6)	C9–C8–O4	111.4(6)
Mo–C3–C4	70.7(3)	C6–O3–HO4	92.2(4)
Mo–C4–C3	73.2(4)	C8–O4–HO4	95.5(7)
Mo–C4–C5	72.7(4)	O3–HO4–O4	140.7(4)

endo conformers[13] (*endo*/*exo* = 9/1) distinguishable by the chemical shifts of the H^1 and H^2 protons. The *syn*-H^1 proton of the exo isomer generally has smaller chemical shifts than that of the endo isomer due to the greater shielding of the cyclopentadienyl group.[13] We assigned the major species with H^1 and H^2 signals at δ 1.76 and 3.12 ppm, respectively, to the endo conformer, whereas the minor species with H^1 and H^2 signals at δ 1.08 and 3.28 ppm, respectively, corresponds to the exo conformer. The enolate anion of **2** was readily generated with lithium diisopropylamide at −78 °C, which reacted smoothly with aldehydes to give β-hydroxyl ketone compounds **3**–**5** in 78–83% yield. Proton NMR signals of **3**–**5** were broad at 23 °C but showed two sets of well-defined spectra at −50 °C. We assign them to endo and exo isomers, as chemical shifts of their allylic *syn* and *anti* protons are near those of *exo*/*endo* conformers of **2**. For all cases, the *endo* isomer was the dominant species in solution (>90%).

Figure 1 shows the molecular structure of **3**, and the selected bond distances and angles are given in Table 1. The molecule has an *endo* conformation, i.e., the mouth of the allyl group faces the cyclopentadienyl

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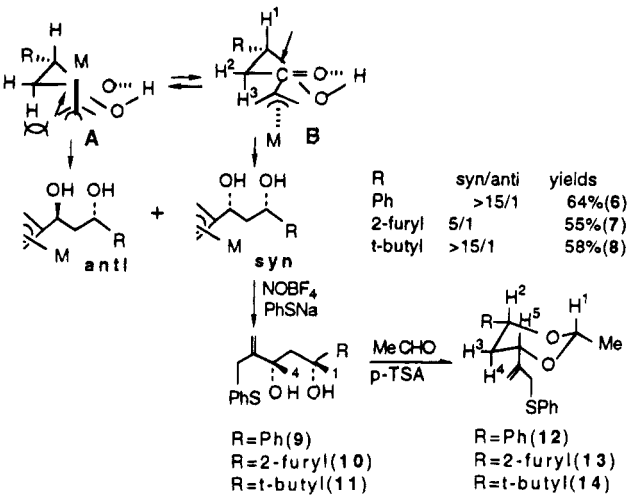
Scheme 2



[a] M = $CpMo(CO)_2$.

group. The Mo–C(3) (2.302(6) Å), Mo–C(4) (2.270(6) Å), and Mo–C(5) (2.286(7) Å) lengths represent normal Mo–allyl bond distances. The C(4)–C(6) (1.483(9) Å) and C(6)–O(3) (1.218(8) Å) bond lengths are between those of the corresponding single and double bonds, respectively. Atoms C(3), C(4), C(5), C(6), C(7), and O(3) are coplanar within 0.066 Å. This information suggests the resonance form **III**, as depicted in Scheme 1. The ν(C(6)–O(3)) stretching frequencies of **3**–**5** were observed in the 1665–1645 cm^{-1} region, further supporting this structure. This structure will produce a highly negative charge at the O(3) atom, in favor of linking the O(4)–H group as an intramolecular hydrogen bond. The latter was indicated by the close O(3)···O(4) (2.830(8) Å) length (ORTEP labeling) and was further confirmed according to the Fourier difference map, which reveals that the O(3)–HO(4) group locks the O(4), C(6), C(7), and C(8) atoms into a twisted-chair conformation as represented by **A**, given in Scheme 2. The chairlike structure is evident from the Newman projection that shows a staggered conformation along the C(7)–C(8) bond. In the ^1H NMR spectra of **3**–**5**, the proton coupling parameters J_{13} = 9–10 Hz and J_{12} = 0–3 Hz are characteristic of axial–axial and axial–equatorial proton interactions consistent with the X-ray conformation. The hydroxyl proton of **3**–**5** has a chemical shift at δ 3.5–4.1 ppm ($CDCl_3$, −30 to −60 °C) as a sharp singlet which broadens in the presence of excess CH_3OH (10 equiv).

Stereoselective hydride reduction of β-hydroxyl ketones utilizing metal-chelation control has been well studied.[14,15] Both *syn*- and *anti*-diols can be selectively generated, depending on both the types of the chelation and the reducing reagents. Utilizing an intramolecular hydrogen bond to achieve *syn* reduction of β-hydroxy

(14) For anti-selective reduction of β-hydroxyl ketones, see: (a) Evans, D. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1990**, *112*, 9712. (b) Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560. (c) Anwar, S.; Davis, A. P. *Tetrahedron* **1988**, *44*, 3761.

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ketones has been reported for a δ-hydroxy β-keto ester.[16] We are interested in the possibility that an intramolecular hydrogen bond of **3**–**5** may act as a strong bridge to induce stereoselectivity. The reduction of the β-hydroxyl ketones **3**–**5** with Me_4NBH_4 (ca. 10 equiv) in cold benzene/CH_3OH (volume ratio 1/1, 0 °C, 12 h) proceeded relatively smoothly (yields >85%), and the *syn/anti* ratios of the products **6**–**8** are provided in Scheme 1. For all cases, only one rotamer was found for **6**–**8**, and the absence of the exo isomer may be due to its steric interaction between the Cp and $CH(OH)CH_2CH(OH)R$ groups. The *syn/anti* ratio was 5/1 for **7** (R = furyl), but only the *syn*-diol isomer was detected in NMR spectra of **6** (R = phenyl) and **8** (R = *tert*-butyl). Further recrystallization of the *syn*–*anti* mixture of **7** from a saturated hexane/ether solution provided pure *syn*-1,3-diols (>75%). Confirmation of the *syn* stereochemistry of **6**–**8** relies on NOE difference spectra of their acetal derivatives **12**–**14** (*vide supra*). We believe that the stereochemical course of the 1,3-diol induction may not be identical to those of metal-chelated β-hydroxy ketones because the $CpMo(CO)_2(\pi$-allyl) fragment[10] is a more strongly stereodirecting template than the ring conformation. As shown in Scheme 2, structure **B** is the conformation according to the X-ray structure, which has an equatorial R substituent to minimize steric hindrance. The conformation **A**, however, likely exists in solution because it is easily derived from **B** by rotation of the allyl–ketone bond. This rotational energy barrier is expected to be very small because the ^1H NMR spectra of the related compound **2** ($CDCl_3$, −60 °C) showed chemical equivalence for the two ends of allylic *syn* and *anti* protons. For both **A** and **B**, hydride preferentially approaches the ketone group opposite to the π-allyl fragment; therefore, **A** and **B** preferably generate the *anti*- and *syn*-diols, respectively, as depicted in Scheme 2. Nevertheless, hydride addition to the ketone group of **B** is sterically more favorable than for **A** because the axial H^3 proton of the latter imposes additional steric hindrance for equatorial hydride attack. This mechanism is consistent with our results that *syn*-diols are the major products. The *syn* selectivity is more favorable for a bulky R substituent than for a small R group, assuming that R occupies the equatorial position of **B**. For small R groups, an additional chairlike structure with an axial R substituent may contribute to the reaction in favor of *anti* selectivity.

Demetalation of these *syn*-diol compounds is essential if their organic applications are to be substantiated. Employing Faller's method,[15] we treated **6**–**8** with $NOBF_4$ (1 mol equiv) to generate an electrophilic cation[17] which then reacted with PhSNa to give, after Ce(IV) oxidation, (1*R* *,3*S* *)-1-R-4-((phenylthio)methyl)-4-pentene-1,3-diol (R = Ph (**9**), 2-furyl (**10**), *tert*-butyl (**11**)) in 68–71% yield. We further treated these *syn*-diols with acetaldehyde in the presence of *p*-toluenesulfonic acid catalyst to give acetals **12**–**14** each as a single diastereomer. Irradiation of the H^1 proton (δ 4.93 ppm) of **12** gave rise to an intensity increase of H^2 (δ 4.62 ppm) and H^5 (δ 4.51 ppm) proton signals by 3.1% and 4.5%, respectively, confirming an acetal structure with equatorial phenyl and vinyl substituents. The coupling parameters J_{24}, J_{45} = 9–11 Hz and J_{23}, J_{35} = 2–3 Hz, are consistent with those expected for axial–axial and axial–equatorial proton coupling, respectively. The stereochemistry of **12**–**14** confirms the *syn*-diol configuration of **6**–**8**.

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Experimental Section

All operations were carried out under argon in a Schlenk apparatus or in a glovebox. The solvents diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over calcium hydride and distilled before use. 3-(Bromomethyl)-3-buten-2-one was prepared according to the procedure in the literature.[11]

All ^1H NMR (400 and 300 MHz) and ^{13}C NMR (100 and 75 MHz) spectra were obtained on either a Bruker AM-400 or a Varian Gemini 300 spectrometer; chemical shifts are reported relative to $SiMe_4$ standard. Elemental analyses were preformed at National Cheng Kung University, Tainan, Republic of China. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. High-resolution mass spectra were recorded on a JEOL HX 110 spectrometer.

Synthesis of Bis(acetonitrile)bromodicarbonyl(η³-(1,2,3)-2-acetylallyl)molybdenum (1). $Mo(CO)_6$ (13.5 g, 51.1 mmol) in CH_3CN (54 mL) was heated under reflux for 8 h. To the resulting yellow solution was added a THF solution (13 mL) of 3-(bromomethyl)-3-buten-2-one (10 g, 61.35 mmol) at 40 °C, and the solution was kept at this temperature for 4 h. The solution was concentrated to half its volume, and the resulting precipitate was collected by filtration and washed with CH_3CN (2 × 10 mL) to give **1** as an orange solid (22.1 g, 46 mmol, 90%) slightly soluble in common solvents. IR (Nujol, cm^{-1}): ν(CO) 1958 (s), 1879 (s), and 1604 (m). ^1H NMR (CD_3CN, 300 MHz): δ 1.28 (2H, s, H^1), 2.31, 2.37 (s, s, 6H + 3H, $2CH_3CN + CH_3CO$), 3.51 (2H, s, H^2). Anal. Calcd for $C_{11}H_{13}MoO_3BrN_2$: C, 33.27; H, 3.30; N, 7.05. Found: C, 33.41; H, 3.50; N, 7.22.

Synthesis of (η⁵-Cyclopentadienyl)dicarbonyl(η³(1,2,3)-2-acetylallyl)molybdenum (2). To **1** (22.14 g, 46 mmol) in THF (40 mL) was added a THF solution (10 mL) of NaCp (56 mmol), and the mixture was stirred for 2 h at 23 °C before a saturated NH_4Cl solution (20 mL) was added. The solution was concentrated to half its volume; the organic layer was extracted with diethyl ether (2 × 40 mL) and evaporated to dryness. The residues were eluted through a silica column (diethyl ether/hexane 1/1) to develop a yellow band (R_f 0.56) which provided **2** as a yellow crystalline solid (9.8 g, 32.7 mmol, 60% yield). IR (Nujol, cm^{-1}): ν(CO): 1963 (s), 1879 (s), 1656 (m). ^1H NMR (−40 °C, 400 MHz, $CDCl_3$): δ, *endo* isomer (90%), 1.76 (s, 2H, H^1), 2.10 (s, 3H, COMe), 3.12 (s, 2H, H^2), 5.25 (s, 5H, Cp); *exo* isomer (10%), 1.08 (s, 2H, H^1), 2.27 (s, 3H, COMe), 3.28 (s, 2H, H^2), 5.15 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$, 100 MHz): *endo* isomer, 24.4 (Me), 34.8 (CH^1H^2), 89.8 (Cp), 92.5 (*C*-CO), 199.3 (*C*OMe), 234.7 (W-2CO). Mass (12 eV, *m/e*): 302 (M^+), 274 (M^+ − CO), 246 (M^+ − 2CO). Anal. Calcd for $MoC_{12}H_{12}O_3$: C, 48.02; H, 4.03. Found: C, 48.42; H, 4.24.

Synthesis of (η⁵-Cyclopentadienyl)dicarbonyl[η³(1,2,3)-2-(1′-oxo-3′-hydroxy-3′-phenylylpropyl)allyll]molybdenum (3). To a THF solution of **2** (0.90 g, 3.0 mmol) was added a THF solution (5 mL) of lithium diisopropylamide [$(i\text{-}Pr)_2NH$ (1.26 mL, 9.0 mmol), BuLi (5.4 mL, 1.6 M, 8.6 mmol)] at −78 °C, and the mixture was stirred for 1 h before addition of a saturated NH_4Cl solution. The solution was concentrated to half its volume, and the organic layer was extracted with diethyl ether (2 × 20 mL), dried over $MgSO_4$, and finally evaporated to dryness. The residues were eluted through a silica column to develop a yellow band that gave **3** as a yellow

solid (0.89 g, 2.41 mmol, 81%). IR (Nujol, cm^{-1}): ν(CO) 1967 (s), 1889 (s), 1648 (m). ^1H NMR (−60 °C, 400 MHz, $CDCl_3$): δ, *endo* isomer (92%), 1.71, 1.73 (s, s, 1H, 1H, $H^1 + H^{1'}$), 2.66 (dd, 1H, J = 17.4, 9.8 Hz, CH*H'*), 2.77 (dd, 1H, J 17.4, 1.5 Hz, C*H* H'), 3.00 (d, 1H, J = 3.9 Hz, H^2), 3.10 (d, 1H, J = 3.9 Hz, $H^{2'}$), 4.10 (s, 1H, OH), 5.03 (1H, dd, J = 9.8, 1.5 Hz, C*H* Ph), 5.23 (s, 5H, Cp), 7.30−7.20 (5H, m, Ph); *exo* isomer (8%), selected peak, 0.92, 1.04 (s, s, 1H, 1H, $H^1 + H^{1'}$), 3.20 (d, 1H, J = 3.9 Hz, H^2), 3.24 (d, 1H, J = 3.9 Hz, $H^{2'}$), 5.20 (s, 5H, Cp), the rest of the peaks were masked by those of the *endo* isomer. ^{13}C NMR (−60 °C, $CDCl_3$, 400 MHz): δ 34.2, 34.4, 44.7 ($CH^1H^2 + CH^1H^{2'} + CHH'$), 70.3 (*C*Ph), 89.8 (Cp), 91.5 (*C*-CO), 125.7, 127.5, 128.5, 142.8 (Ph), 202.1 (*C*CO), 233.4, 234.9 (2 Mo-CO). Mass (12eV, *m/e*): 408 (M^+). Anal. Calcd for $C_{19}H_{18}MoO_4$: C, 56.17; H, 4.47. Found: C, 56.12; H, 4.58.

Synthesis of (η^5-Cyclopentadienyl)dicarbonyl[η^3(1,2,3)-2-(1′-oxo-3′-hydroxy-3′-(2″-furyl)propyl)allyl]molybdenum (4). This compound was similarly prepared from the enolate of **2** (0.90 g, 3.0 mmol) and 2-furaldehyde (0.48 g, 5.0 mmol), and the yield of **4** (0.93 g, 2.34 mmol) was 78%. IR (Nujol, cm^{-1}): ν(CO) 1951 (s), 1893 (s), 1668 (m). ^1H NMR (−30 °C, $CDCl_3$, 400 MHz): δ, *endo* isomer (90%), 1.75, 1.77 (s, s, 1H, 1H, $H^1 + H^{1'}$), 2.87 (dd, 1H, J = 17.5, 9.3 Hz, CH*H'*), 2.97 (dd, 1H, J = 17.5, 2.8 Hz, C*H* H'), 3.06 (d, 1H, J = 3.4 Hz, H^2), 3.12 (d, 1H, J = 3.4 Hz, $H^{2'}$), 4.09 (s, 1H, OH), 5.08 (d, 1H, J = 9.3, 2.8 Hz, C*H*(OH)), 5.27 (s, 5H, Cp), 6.24 (1H, d, J = 3.2 Hz, C_3H_3O), 6.30 (dd, 1H, J = 3.2, 1.3 Hz, C_4H_3O), 7.36 (d, 1H, J = 1.3 Hz, C_4H_3O); *exo* isomer (10%) 1.04, 1.12 (s, s, 1H, 1H, $H^1 + H^{1'}$), 3.29 (br s, 2H, $H^2 + H^{2'}$), 5.22 (s, 5H, C_5H_5), 6.30 (br s, 1H, C_4H_3O), 6.37 (br s, 1H, C_4H_3O), 7.40 (s, 1H, C_4H_3O), the rest of the peaks were masked by those of the *endo* isomer. ^{13}C NMR (−30 °C, 100 MHz, $CDCl_3$): δ 34.0, 34.2, 40.7 ($CH^1H^2 + CH^1H^{2'} + CHH'$), 64.1 (CH(OH)), 89.7 (Cp), 92.4 (*C*-CO), 106.3, 110.1, 142.1, 154.4 (C_4H_3O), 201.5 (C-*C*O), 233.4, 234.4 (W-2CO). Mass (12 eV, *m/e*): 398 (M^+). Anal. Calcd for $C_{17}H_{16}MoO_5$: C, 51.53; H, 4.07. Found: C, 51.71; H, 4.14.

Synthesis of (η^5-Cyclopentadienyl)dicarbonyl[η^3(1,2,3)-2-(1′-oxo-3′-hydroxy-3′-*tert*-butylpropyl)allyl]molybdenum (5). This compound was similarly prepared from the enolate of **2** (0.90 g, 3.0 mmol) and trimethylacetaldehyde (0.43 g, 5 mmol), and the yield of **5** (0.97 g, 2.5 mmol) was 83%. IR (Nujol, cm^{-1}): ν(CO) 1951 (s), 1893 (s), 1668 (m). ^1H NMR (−60 °C, 400 MHz, $CDCl_3$): δ, *endo* isomer (88%), 0.86 (s, 9H, CMe_3), 1.75 (s, s, 1H, 1H, $H^1 + H^{1'}$), 2.39 (dd, 1H, J = 17.3, 10.6 Hz, CH*H'*), 2.63 (dd, 1H, J = 17.3, 1.4 Hz, C*H*H'), 3.08 (d, 1H, J = 3.2 Hz, H^2), 3.12 (d, 1H, J = 3.2 Hz, $H^{2'}$), 3.59 (s, 1H, OH), 3.63 (dd, 1H, J = 10.6, 1.4 Hz, C*H*(OH)), 5.26 (s, 5H, Cp); *exo* isomer (12%), 0.93 (s, 9H, CMe_3), 0.94, 1.02 (s, s, 1H, 1H, $H^1 + H^{1'}$), 2.60 (dd, 1H, J = 17.3, 10.1 Hz, CH*H'*), 2.82 (d, 1H, J = 17.3, C*H*H'), 3.30 (br s, 2H, $H^2 + H^{2'}$), 3.85 (br d, 1H, J = 10.1 Hz, C*H*Ph), 5.23 (s, 5H, Cp). ^{13}C NMR (−60 °C, 100 MHz, $CDCl_3$): δ *endo* isomer, 25.6 (Me), 34.0, 34.2, 36.8 ($CH^1H^2 + CH^1H^{2'} + CHH'$), 74.9 (CH(OH)), 89.7 (Cp), 91.4 (*C*CO), 203.1 (*C*CO), 233.6, 234.6 (2W-CO). Mass (12 eV, *m/e*): 388 (M^+). Anal. Calcd for $C_{17}H_{22}MoO_4$: C, 52.86; H, 5.74. Found: C, 52.82; H, 5.80.

Synthesis of (η^5-Cyclopentadienyl)dicarbonyl[η^3(1,2,3)-2-(1′-hydroxy-3′-hydroxy-3′-phenylpropyl)allyl]molybdenum (6). To a CH_3OH solution (5 mL) of **3** (0.20 g, 0.50 mmol) was added a benzene solution (10 mL) of Me_4NBH_4 (0.43 g, 4.90 mmol) in an ice bath; stirring was maintained for 10 h, during which period the ice bath naturally warmed to 23 °C. A saturated NH_4Cl solution (10 mL) was slowly added, and the organic layer was extracted with diethyl ether (2 × 20 mL), dried over $MgSO_4$, and evaporated in vacuo. Further elution through a silica column provided **6** as the *syn*-diol isomer (0.19 g, 0.47 mmol, 95%). IR (Nujol, cm^{-1}): ν(CO) 1946 (s), 1861 (s). ^1H NMR ($CDCl_3$, 400 MHz, −30 °C): δ 1.83 (s, 1H, H^1), 1.92 (s, 1H, $H^{1'}$), 2.06−2.13 (m, 2H, CHH'), 2.65 (br s, 1H, OH), 2.73 (s, 1H, H^2), 3.13 (br s, 1H, H^2), 3.58 (br s, 1H, OH), 3.91 (br d, J = 9.3 Hz, C*H*(OH)), 4.91 (br d, 1H, J = 9.6 Hz, C*H*Ph), 5.22 (s, 5H, Cp), 7.20−7.35 (5H, m, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz, −30 °C): δ 30.6, 34.7, 49.8 ($CH^1H^2 + CH^1H^{2'} + CHH'$), 74.9, 76.2 (2CH(OH)), 90.6 (Cp), 112.7 (*C*-CH^1H^2), 125.6, 127.5, 128.4, 143.9 (Ph), 240.2, 242.6 (2W-CO). Mass (12 eV, *m/e*): 410 (M^+). Anal. Calcd for $C_{19}H_{20}MoO_4$: C, 55.88; H, 4.90. Found: C, 55.70; H, 4.91.

Synthesis of (η^5-Cyclopentadienyl)dicarbonyl[η^3(1,2,3)-2-(1′-hydroxy-3′-hydroxy-3′-(2″-furyl)propyl)allyl]molybdenum (7). This compound was similarly prepared from Me_4NBH_4 (0.43 g, 4.90 mmol) reduction of **4** (0.22 g, 0.55 mmol) in methanol/benzene (1/2); the product was a mixture of *syn*/*anti* diol isomers (0.22 g, 0.50 mmol, 90%, *syn*/*anti* = 5/1). Further recrystallization of the mixtures from a saturated diethyl ether/hexane solution gave the *syn*-diol isomer as a yellow viscous solid (0.14 g, 0.35 mmol, 73%). IR (Nujol): ν(CO) 1952 (s), 1865 (s). ^1H NMR ($CDCl_3$, −30 °C, 400 MHz): δ *syn* isomer, 1.81 (s, 1H, H^1), 1.93 (s, 1H, $H^{1'}$), 2.13−2.25 (m, 2H, CHH'), 2.60 (br s, 1H, OH), 2.71 (d, 1H, J = 3.0 Hz, H^2), 3.08 (d, 1H, J = 3.0 Hz, $H^{2'}$), 3.78 (br s, 1H, OH), 3.83 (dd, 1H, J = 9.2, 2.8 Hz, C*H*(OH)), 4.93 (dd, 1H, J = 9.6, 2.9 Hz, C*H*(OH)), 5.30 (s, 5H, Cp), 6.20 (d, 1H, J = 2.8 Hz, C_4H_3O), 6.28 (dd, 1H, J = 2.8, 1.7 Hz, C_4H_3O), 7.32 (d, 1H, J = 1.7 Hz, C_4H_3O); *anti* isomer, 1.84 (s, 1H, H^1), 1.95 (s, 1H, $H^{1'}$), 3.10 (d, J = 3.0 Hz, $H^{2'}$), 5.12 (dd, 1H, J = 5.6, 2.6 Hz, CH(OH)), 5.31 (s, 5H, Cp), 6.23 (d, 1H, J = 2.8 Hz, C_4H_3O), 6.30 (dd, 1H, J = 2.8, 1.7 Hz, C_4H_3O); the rest of the peaks of the *anti* isomer were masked by those of the major *syn* isomer. ^{13}C NMR ($CDCl_3$, −30 °C, 100 MHz): δ 31.1, 34.9, 46.1 ($CH^1H^2 + CH^1H^{2'} + CHH'$), 68.0, 75.4 (2CH(OH)), 90.5 (Cp), 105.8 (C-CH^1H^2), 110.2, 112.7, 142.0, 156.0 (C_4H_3O), 239.5, 242.0 (2W-CO). Mass (12 eV, *m/e*): 400 (M^+). Anal. Calcd for $C_{17}H_{18}MoO_5$: C, 51.25; H, 4.52. Found: C, 51.40; H, 4.66.

Synthesis of (η^5-Cyclopentadienyl)dicarbonyl[η^3(1,2,3)-2-(1′-hydroxy-3′-hydroxy-3′-*tert*-butylpropyl)allyl]molybdenum (8). This compound was similarly prepared from Me_4NBH_4 (0.43 g, 4.90 mmol) reduction of **5** (0.21 g, 0.54 mmol) in methanol/benzene (1/2); the product was obtained as the pure *syn*-diol isomer (0.19 g, 0.47 mmol, 87%). IR (Nujol, cm^{-1}): ν(CO) 1946 (s), 1861 (s). ^1H NMR ($CDCl_3$, −30 °C, 400 MHz): δ 0.96 (s, 9H, Me), 1.60 (ddd, 1H, J = 13.5, 10.5, 10.0 Hz, CH*H'*), 1.75 (s, 1H, H^1), 1.85 (s, 1H, $H^{1'}$), 2.03 (dt, 1H, J = 13.5, 2.5 Hz, C*H*H'), 2.72 (1H, d, J = 3.0 Hz, H^2), 2.93 (1H, d, J = 3.0 Hz, $H^{2'}$), 3.65 (1H, dd, J = 10.5, 2.5 Hz, C*H*(OH)), 3.86 (1H, dd, J = 10.0, 2.5 Hz, C*H*(OH)), 5.21 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$, −30 °C, 100 MHz): 25.3 (Me), 34.6, 38.7, 41.4 ($CH^1H^{1'} + CH^2H^{2'} + CHH'$), 76.2, 80.5 (2*C*H(OH)), 90.7 (Cp), 112.9 (C-CH^1H^2), 240.9, 242.9 (2W-CO). Mass (12eV, *m/e*): 390 (M^+). Anal. Calcd for $C_{17}H_{24}MoO_4$: C, 52.58; H, 6.23. Found: C, 52.66; H, 6.41.

Synthesis of 1-Phenyl-4-((phenylthio)methyl)-4-pentene-*syn*-1,3-diol (9). To a CH_3CN solution of **6** (0.19 g, 0.47 mmol) was added $NOBF_4$ (0.060 g, 0.50 mmol) at 0 °C, and the mixture was stirred for 20 min before addition of PhSNa (0.10 g, 0.80 mmol). After stirring for 1 h, $(NH_4)_2Ce(NO_3)_6$ (0.55 g, 1.00 mmol) was slowly added, and an aqueous saturated NaOAc solution (1 mL) was then added. After stirring for 30 min, to the mixture was added water (10 mL), and the organic layer was extracted with diethyl ether (2 × 10 mL). After removal of the solvent in vacuo, the residues were chromatographed on a preparative TLC plate to produce an organic band (R_f 0.40, diethyl ether/hexane 1/1) that afforded **9** as an oil (0.10 g, 0.33 mmol, 70%). IR (neat, cm^{-1}): ν(OH) 3450 (s); ν(C=C) 1645 (w), 1604 (w). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.84 (ddd, 1H, J = 14.5, 3.0, 2.3 Hz, CH*H'*), 1.94 (dt, 1H, J = 14.5, 9.8 Hz, C*H*H'), 3.55 (AB q, J = 14.2 Hz, S-CH_2), 4.54 (dd, 1H, J = 9.8, 2.3 Hz, C*H*(OH)), 4.88 (dd, 1H, J = 9.8, 3.0 Hz, C*H*Ph), 4.99 (s, 1H, =CH*H'*), 5.11 (s, 1H, =C*H*H'), 7.18−7.29 (10H, m, Ph). HRMS: calcd for $C_{18}H_{20}SO_2$ 300.1184, found 300.1176.

Synthesis of 1-(2′-Furyl)-4-((phenylthio)methyl)-4-pentene-*syn*-1,3-diol (10). This compound was similarly prepared from **7** (0.22 g, 0.55 mmol), $NOBF_4$ (0.070 g, 0.58 mmol),

and PhSNa (0.10 g, 0.80 mmol); the yield of **10** was 67% (0.11 g, 0.37 mmol). IR (Nujol, cm^{-1}): ν(OH) 3400 (vs); ν(C=C) 1640 (m), 1600 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 2.06–2.10 (m, 2H, CHH′), 3.55 (AB q, 2H, J = 14.3 Hz, S-CH_2), 4.48 (dd, 1H, J = 9.8, 3.6 Hz, C*H*(OH)), 4.89 (dd, 1H, dd, J = 8.3, 4.4 Hz, C*H*(OH)), 4.99 (s, 1H, =CH*H*′), 5.12 (s, 1H, =C*H*H′), 6.21 (d, 1H, J = 3.0 Hz, C_4H_3O), 6.25 (dd, 1H, J = 2.7, 1.4 Hz, C_4H_3O), 7.29 (m, 5H, Ph), 7.29 (d, 1H, J = 1.4 Hz, C_4H_3O). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 36.6 (CHH′), 40.8 (S-CH_2), 70.8, 73.6 (2*C*H(OH)), 114.3 (=CH_2), 145.9 (=C), 105.9, 110.2, 126.5, 128.7, 130.2, 135.8, 142.0, 155.9 (Ph + C_4H_3O). HRMS: calcd for $C_{16}H_{18}SO_3$ 290.0976, found 290.0968.

Synthesis of 1-*tert*-Butyl-4-((phenylthio)methyl)-4-pentene-*syn*-1,3-diol (11). This compound was similarly prepared from **8** (0.19 g, 0.47 mmol), $NOBF_4$ (0.060 g, 0.50 mmol), and PhSNa (0.10 g, 0.80 mmol), and the yield of **10** was 68% (95 mg, 0.34 mmol). IR (Nujol, cm^{-1}): ν(OH) 3423 (vs); ν(C=C) 1646 (m), 1606 (m). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.95 (s, 9H, Me), 1.62 (ddd, 1H, J = 14.8, 2.3, 1.5 Hz, CH*H*′), 1.84 (ddd, 1H, J = 14.8, 10.4, 9.9 Hz, C*H*H′), 3.55 (dd, 1H, J = 10.4, 1.5 Hz, C*H*(OH)), 3.69 (AB q, 2H, J = 14.2 Hz, S-CH_2), 4.54 (dd, 1H, J = 9.9, 2.3 Hz), 5.10 (s, 1H, =CH*H*′), 5.24 (s, 1H, =C*H*H′), 7.24–7.40 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.2 (Me), 34.9 (CHH′), 40.9 (S-CH_2), 75.0, 80.7 (2CH(OH)), 113.9, 136.1 (CH_2=C), 126.4, 128.8, 129.9, 146.5 (Ph). HRMS: calcd for $C_{16}H_{24}SO_2$ 280.1497, found 280.1500.

Synthesis of (2*R* *,4*S* *,6*R* *)-2-Methyl-4-(((phenylthio)methyl)vinyl)-6-phenyl-1,3-dioxane (12). To **9** (0.10 g, 0.33 mmol) in diethyl ether (15 mL) was added *p*-toluenesulfonic acid (7 mg, 0.036 mmol) and acetaldehyde (0.38 mL, 0.67 mmol); the mixture was stirred for 3 h before addition of a saturated $NaHCO_3$ solution. The organic layer was extracted with diethyl ether, dried over $MgSO_4$, and evaporated to dryness. Elution on a preparative TLC plate (diethyl ether/hexane 1/1) produced an organic band (R_f 0.6) of **12** (66 mg, 60%). IR (neat, cm^{-1}): ν(C=C) 1634 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 1.68 (d, 3H, J = 5.0 Hz, Me), 1.80 (ddd, 1H, J = 13.2, 9.2, 9.0 Hz, H^4), 1.93 (ddd, 1H, J = 13.2, 1.8, 1.5 Hz, H^3), 3.77 (AB q, 1H, J = 14.3 Hz, S-CH_2′), 4.51 (dd, 1H, J = 9,2, 1.5 Hz, H^5), 4.62 (dd, 1H, J = 9.0, 1.8 Hz, H^2), 4.93 (q, 1H, J = 5.0 Hz, H^1), 5.24 (s, 1H, =CH*H*′), 5.35 (s, 1H, =C*H*H′), 7.58–7.16 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.2 (Me), 36.9, 37.4 (S-CH_2 + CH^3H^4), 76.3, 78.4 (CH^1 + CH^2), 99.2 (CH^2), 114.2, 136.0 (CH_2=C), 125.9, 126.3, 127.8, 128.5, 128.8, 129.9, 141.5, 143.9 (2 Ph). HRMS: calcd for $C_{20}H_{22}SO_2$ 326.1340, found 326.1335.

Synthesis of (2*R* *,4*S* *,6*R* *)-2-Methyl-4-(((phenylthio)methyl)vinyl)-6-(2′-furyl)-1,3-dioxane (13). This compound was similarly prepared from **10** (0.11 g, 0.37 mmol), *p*-toluenesulfonic acid (7 mg, 0.036 mmol), and acetaldehyde (0.38 mL, 0.67 mmol); the yield of **13** (65 mg, 0.20 mmol) was 54%. IR (neat, cm^{-1}): ν(C=C) 1638 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 1.36 (d, 3H, J = 5.2 Hz, Me), 1.89 (ddd, 1H, J = 13.6, 11.3, 10.8 Hz, H^4), 2.04 (ddd, 1H, J = 13.6, 2.6, 2.5 Hz, H^3), 3.66 (AB q, 2H, J = 14.2 Hz, S-CH_2′), 4.40 (dd, 1H. J = 10.6, 2.8 Hz, H^5), 4.76 (dd, 1H, J = 11.3, 2.5 Hz, H^2), 4.89 (q, 1H, J = 5.2 Hz, H^1), 5.08 (s, 1H, =CH*H*″), 5.18 (s, 1H, =C*H*H′), 6.30 (d, 1H, J = 2.4 Hz, C_4H_3O), 6.33 (dd, 1H, J = 2.4, 1.4 Hz, C_4H_3O), 7.17–7.32 (m, 5H, Ph), 7.38 (d, 1H, J = 1.4 Hz, C_4H_3O). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.1 (Me), 33.2, 36.9 (S-CH_2 + CH^3H^4), 71.7. 76.2 (CH^1 + CH^5), 99.2 (CH^2), 107.2, 110.2, 153.4 (C_4H_3O), 114.5, 136.2 (CH_2=C), 126.4, 128.9, 130.0, 142.5, 153.4 (Ph + C_4H_3O). HRMS: calcd for $C_{18}H_{20}SO_3$ 316.1133, found 316.1140.

Synthesis of (2*R* *,4*S* *,6*R* *)-2-Methyl-4-(((phenylthio)methyl)vinyl)-6-*tert*-butyl-1,3-dioxane (14). This compound was similarly prepared from **11** (0.95 g, 0.34 mmol), *p*-toluenesulfonic acid (7 mg, 0.036 mmol), and acetaldehyde (0.38 mL, 0.67 mmol); the yield of **14** (58 mg, 0.19 mmol) was 57%. IR (neat, cm^{-1}): ν(C=C) 1638 (m), 1600 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.89 (s, 9H, Me), 1.36 (d, 3H, J = 5.0 Hz, Me), 1.45 (ddd, J = 13.7, 11,1, 10.9 Hz, H^4), 1.57 (ddd, 1H, J = 13.7, 2.4, 2.2 Hz, H^3), 3.22 (dd, 1H, J = 11.1, 2.2 Hz, H^2), 4.23 (dd, 1H, J = 10.9, 2.4 Hz, H^5), 4.70 (q, J = 5.0 Hz, Me), 5.06 (1H, s, =CH*H*′) 5.15 (1H, s, =C*H*H′), 7.17–7.35 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): 21.1 (Me), 25.7 (Me), 29.6 (CH^3H^4), 33.8 (*C*Me_3), 36.8 (S-CH_2), 76.4, 83.9 (CH^1 + CH^5), 98.9 (CH^2), 113.8, 136.4 (CH_2=C), 126.2, 128.8, 129.8, 144.5 (Ph). HRMS: calcd for $C_{18}H_{26}SO_2$ 306.1653, found 306.1660.

X-ray Diffraction Measurement. A single crystal of **3** was sealed in a glass capillary under an inert atomsphere. Data for **3** were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation, and the structure was solved by the heavy-atom method; all data reduction and structure refinement were performed with the NRCC-SDP package. For **3,** the non-hydrogen atoms and the O(4)H hydrogen were refined with anisotropic parameters and the remaining hydrogens included in the structure factor calculation were placed in idealized positions.

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Supplementary Material Available: Tables of atomic coordinates, all bond distances and angles, and thermal parameters for **3** (5 pages). Ordering information is given on any current masthead page.

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