extracted three times with a total of 4 mL of *n*-hexane. The combined extracts were filtered and evaporated to dryness. The residue was dried in vacuo to give 770 mg (88%) as a brownish oil. The ^{1}H NMR spectrum revealed a mixture of three isomers in the ratio **16**:**17**:**18** = 70:10:20: ^{1}H NMR (C_6D_6), **16**, δ 5.69-5.55 (m, 2 H, H5 and H6), 3.99 (d, 1 H, $H9_{cis}$), 3.81 (d, 1 H, $H9_{trans}$), 3.21 (s, 3 H, $-OCH_3$), 2.96 (m, 1 H, H7), 2.25 (m, 1 H, H4'), 2.01 (m, 1 H, H4), 1.23 (d, 3 H, 7-CH_3), 1.20 (br, -OH, partially coincide with 7-CH_3), 1.02 (d, 3 H, 3-CH_3), 0.93 (s, 9 H, H1), coupling constants (Hz), ^2J = 2.1 ($H9_{cis}$, $H9_{trans}$), ^3J = 7.0 (H7, 7-CH_3), ^4J = 0.8 (H4 or H4', 3-CH_3); **17**, δ 3.20 (s, $-OCH_3$), 1.25 (d, 7-CH_3, ^3J(H7, 7-CH_3) = 7.0 Hz); **18**, δ 4.01 (d, $H9_{cis}$), 3.87 (d, $H9_{trans}$), 3.09 (s, $-OCH_3$), 1.71-1.54 (m, H4 and H5, assignment not certain), 1.30 (br, -OH), 1.04 (d, 3-CH_3), 0.94 (s, H1), coupling constants (Hz), ^2J = 1.9 ($H9_{cis}$, $H9_{trans}$), ^4J = 0.8 (H4 or H4', 3-CH_3), the remaining signals of **17** and **18** were not localized; ^{13}C NMR (C_6D_6), **16**, δ 167.6 (C8), 136.8 (C5, 154), 126.4 (C6, 159), 79.5 (C9, 157), 75.5 (C3), 54.5 ($-OCH_3$, 143), 42.6 (C7, 127), 40.0 (C4, 125), 37.9 (C2), 25.7 (C1, 129), 22.0 (3-CH_3, 125), 19.0 (7-CH_3, 127); **17** and **18**, δ 166.6 (C8), 137.0, 136.9 (C5), 126.6 (C6), 79.9 (C9, 157), the remaining signals of **17** and **18** were not localized; IR (NaCl), mixture of isomers, 3499, 1653, 1605, 976 cm^{-1}; MS (EI) 226 ($M^{\bullet+}$, 0.1) 101 (100); exact mass (CI) calcd for $C_{14}H_{26}O_2$ 227.2011 ($M + H^+$), found 227.2014.

(2*R,6*S**)-*trans*-6-Hydroxy-2,6,7,7-tetramethyl-3-octenoic Acid, 19 and (2*R**,6*R**)-20.** To a solution of 1.19 g (1.36 mmol) of **6a**/**7a** in 40 mL of THF were added 187 mg (1.96 mmol) of pyridine *N*-oxide in 6.8 mL of THF and 75 μL (4.16 mmol) of water. The mixture was stirred for 2 h. The solvent was removed in vacuo. To the orange, viscous residue was added 20 mL of diethyl ether and 20 mL of water. The mixture was acidified with 2 M hydrochloric acid (pH 3). The organic phase was separated, and the water phase was extracted three times with 30-mL portions of diethyl ether. The combined organic phases were washed once with brine, filtered through alumina (neutral, activity grade III), and extracted three times with 30-mL portions of 2/3 saturated sodium carbonate solution. The combined extracts were washed once with diethyl ether and acidified with 5 M hydrochloric acid to pH 3. The cloudy water phase was extracted five times with 30-mL portions of diethyl ether. The combined organic phases were washed with half concentrated brine, dried over sodium sulfate, filtered, and evaporated to dryness. The residue was redissolved in a small amount of acetone to remove grease. The acetone solution was evaporated in vacuo to give 70 mg (20%) of **19**/**20** as a yellowish oil: ^{1}H NMR (C_6D_6), **19**, δ 6.8 (br, 2 H, -OH and $-CO_2H$), 5.78-5.42 (m, 2 H, H3 and H4), 3.07 (quintet, 1 H, H2), 2.24 (br dd, 1 H, H5'), 1.93 (dd, 1 H, H5), 1.18 (d, 3 H, 2-CH_3), 1.00 (s, 3 H, 6-CH_3), 0.89 (s, 9 H, H8), coupling constants (Hz), ^2J = 13.9 (H5, H5'), ^3J = 7.0 (H2, H3), 7.0 (H2, 2-CH_3), 7.3 (H4, H5), 6.0 (H4, H5'); **20**, δ 3.06 (quintet, H2), 0.90 (s, H8), the remaining signals of **20** were not localized; ^{13}C NMR (C_6D_6), **19**, δ 180.7 (C1), 132.3 (C4, 158), 129.1 (C3, 150), 76.5 (C6), 43.0 (C2, 131), 39.7 (C5, 127), 37.9 (C7), 25.5 (C8, 125), 21.6 (6-CH_3, 125), 17.2 (2-CH_3, 129); **20**, δ 180.6 (C1), 132.5 (C4), 43.2 (C2), 39.6 (C5), 17.3 (2-CH_3), the remaining signals of **20** were not localized; IR (NaCl), mixture of isomers, 3428, 3301, 1711, 974 cm^{-1}; MS (EI), 101 (100).

Acknowledgment. Financial support from the Fonds der Chemischen Industrie, the Volkswagen-Stiftung, and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged. F.S. thanks the Volkswagen-Stiftung and the Verband der Chemischen Industrie for a Kekulé-Stipendium.

Registry No. **3a**, 124535-63-3; **3b**, 129174-02-3; **3c**, 129261-21-8; **3d**, 129261-83-2; **4a**, 129150-46-5; **5a**, 129261-20-7; **5b**, 129150-45-4; **6a**, 129214-75-1; **6a**-d_3, 129213-54-3; *cis*-**6c**, 129150-56-7; *trans*-**6c**, 129261-82-1; *cis*-**6d**, 129261-22-9; *trans*-**6d**, 129150-55-6; **7a**, 129150-47-6; **7a**-d_3, 129150-53-4; **8**, 129150-49-8; **9**, 129150-50-1; **10**, 129150-51-2; **11**, 129213-52-1; **12**, 129150-52-3; **13**, 129213-53-2; **15**, 129150-54-5; **16**, 129150-39-6; **17**, 129150-40-9; **18**, 129150-41-0; **19**, 129150-42-1; **20**, 129150-43-2.

Supplementary Material Available: Tables of bond distances and angles for **6a** and **9** (16 pages); listings of observed and calculated structure factors for **6a** and **9** (63 pages). Ordering information is given on any current masthead page.

Regio- and Stereocontrolled Functionalization of Acyclic Molybdenum-η^3-Allyl Complexes

Wen-Jung Vong,[†] Shie-Ming Peng,[‡] Shie-Hsiung Lin,[†] Wen-Jye Lin,[†] and Rai-Shung Liu*,[†]

Contribution from the Departments of Chemistry, National Tsing Hua University, Hsinchu 30043, and National Taiwan University, Taipei 10764, Taiwan, Republic of China.
Received June 1, 1990

Abstract: Chemical transformation of the ester $CpMo(CO)_2$(*syn*-η^3-1-C_3H_4COOMe) to its η^3-allyl alcohol, acid, acid chloride, and amide has been achieved. Treatment of $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4CHR(OH)$) (R = H (**2f**), CH_3 (**2g**)) with $(CF_3SO_2)_2O$ in ether at -78 °C stereoselectively generates, the air-stable *s-trans*-η^4-diene cations, which have been characterized by appropriate physical methods. The ionization process proceeds via an intramolecular S_N2 mode. The *s-trans*-η^4-*cis*-pentadiene cation reacts with water, alcohol, thiol, and amine to give η^3-allyl derivatives, which retain the same configuration as that of **2g**. The enolate $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4COCH_2Li$) condenses with aldehyde at -78 °C to yield the aldol products $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4COCH_2CHR(OH)$) (R = Ph (**6a**), CH_3 (**6b**), $(CH_3)_2CH$ (**6c**)) with good diastereoselectivity. The major diastereomer has been isolated and characterized by X-ray diffraction. Further reduction of this diastereomer with $NaBH_4$ produces the corresponding 1,3-diol as a single diastereomer. Utilization of **2g** and **6e** in synthesis of acyclic 1,3-diol and 1,3,5-triol has been achieved, with excellent stereoselectivity; a mechanism is been proposed.

Introduction

The chemical transformation of an organic functional group adjacent to an organometallic unit has been an area of considerable interest.[1-3] In the course of functionalization, the organometallic unit commonly serves as a chiral auxiliary; thus, a highly diastereoselective and stereospecific reaction pattern is followed. The complexes of the type $CpMo(CO)_2(\eta^3$-allyl) represent one case in which the organic moiety has exhibited interesting chemical

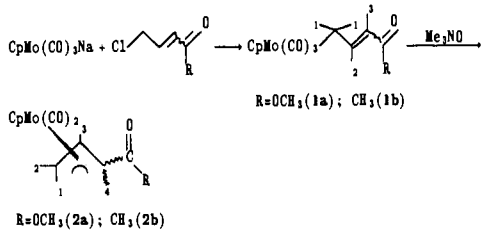
[†] National Tsing Hua University.
[‡] National Taiwan University.

(1) (a) Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379. (b) Semmelhack, M. F. *J. Organomet. Chem. Libr.* **1976**, *1*, 361. (c) Pearson, A. T. *Acc. Chem. Res.* **1980**, *13*, 463. (d) Pearson, A. J. *Pure Appl. Chem.* **1983**, *55*, 1767.

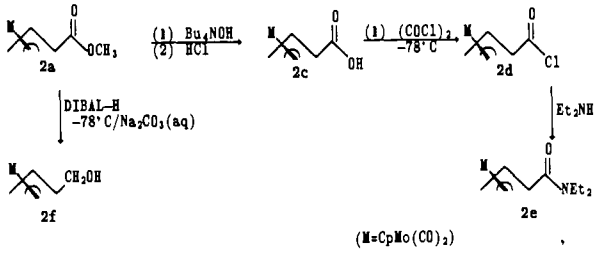
(2) Walls, M. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 59, p 1019.

0002-7863/91/1513-573$02.50/0

Scheme I



Scheme II



reactivity. Nevertheless, as noted in earlier papers, the scope of studies has been limited mainly to the cyclic allyl complexes, particularly in the $CpMo(CO)_2(\eta^3$-cyclohexenyl) and $CpMo(CO)_2(\eta^4$-hexadiene) systems by the nucleophilic addition and hydride abstraction relationship.[4,5] Faller et al. have recently reported[6] that $CpMo(NO)(Cl)$(*syn*-crotyl) condenses with aldehyde to yield a homoallyl alcohol. Stereocontrolled functionalization of the precursor $CpMo(CO)_2(\eta^3$-allyl) in the acyclic system[7] appears to be a valuable route once the chemistry has been expanded. In this paper, we report the stereochemical course in functionalization of $CpMo(CO)_2(\eta^3$-4-oxoallyl). Herein we report the effectiveness of the $CpMo(CO)_2$(*syn*-η^3-C_3H_4R) unit in asymmetric carbon induction.

Results and Discussion

The well-known nucleophilic anion metal salt $CpMo(CO)_3Na$ can normally be alkylated by using alkyl halides leading to complexes $CpMo(CO)_3R$. As expected, the treatment of this anion with methyl 4-chloro-2-butenoate and 5-chloro-3-penten-2-one produced the η^1-complexes **1a** and **1b** as depicted in Scheme I. The two complexes were stable enough for isolation in ca. 45–55% yield and could be fully characterized. ^1H and ^{13}C NMR data support an η^1-configuration. Both *Z* and *E* isomers were detected for **1a** and **1b** with a *Z*/*E* ratio ca. 52:48 and 19:81, respectively. The *E* isomer has the characteristic coupling constant J_{23} = 15.0–16.0 Hz whereas the *Z* isomer has J_{23} = 10.5–11.0 Hz.

When excess Me_3NO was present, compounds **1a** and **1b** each lost one CO molecule to give $CoMo(CO)_2(\eta^3$-1-$C_3H_4COR)$) (R = OCH_3 (**2a**), CH_3 (**2b**)). Each exists in syn and anti diastereoisomers with the syn/anti ratios of 1:1 and 6.2:1 for **2a** and **2b**, respectively; the syn and anti isomers of **2a** and **2b** are separable on a silica column. All the syn and anti isomers of **2a** and **2b** show the presence of exo and endo conformers.[8] For **2a** and **2b**, the exchange of exo and endo isomers operates at ambient temperatures whereas the syn and anti isomers do not interconvert even at elevated temperatures. From a variable-temperature ^1H NMR spectrum for the exo and endo exchange, ΔG^* is calculated to be 15.2 and 14.8 kcal mol^{-1} for the syn isomers of **2a** and **2b**, respectively.

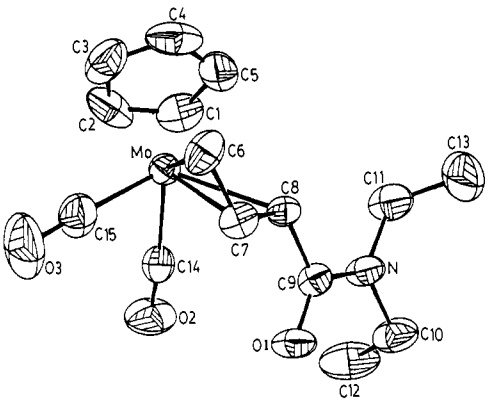
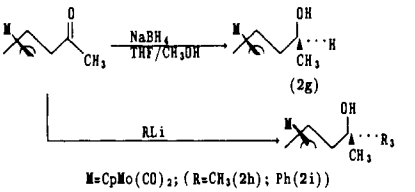


Figure 1. ORTEP drawing of **2e**.

Table I. Selected Bond Distances and Angles of **2e**

	Bond Distances, Å		
Mo–C(6)	2.323 (6)	C(8)–C(9)	1.484 (8)
Mo–C(7)	2.302 (5)	C(9)–N	1.350 (8)
Mo–C(8)	2.313 (6)	C(9)–O(1)	1.231 (8)
Mo–C(14)	1.949 (7)	C(10)–N	1.471 (8)
Mo–C(15)	1.947 (7)	C(11)–N	1.457 (9)
C(6)–C(7)	1.383 (8)	C(14)–O(2)	1.153 (8)
C(7)–C(8)	1.384 (10)	C(15)–O(3)	1.141 (9)
	Bond Angles, deg		
C(6)–Mo–C(7)	34.80 (20)	C(6)–C(7)–C(8)	117.8 (6)
C(6)–Mo–C(8)	61.46 (22)	Mo–C(8)–C(7)	72.1 (4)
C(6)–Mo–C(14)	123.10 (25)	Mo–C(8)–C(9)	122.7 (4)
C(6)–Mo–C(15)	81.8 (3)	C(7)–C(8)–C(9)	117.7 (5)
C(7)–Mo–C(8)	34.9 (3)	C(8)–C(9)–N	118.9 (5)
C(7)–Mo–C(14)	91.48 (23)	C(8)–C(9)–O(1)	121.1 (6)
C(7)–Mo–C(15)	87.1 (3)	N–C(9)–O(1)	120.0 (5)
C(8)–Mo–C(14)	83.41 (23)	Mo–C(14)–O(2)	175.3 (6)
C(8)–Mo–C(15)	118.00 (25)	Mo–C(15)–O(3)	117.4 (7)
C(14)–Mo–C(15)	77.2 (3)	C(9)–N–C(10)	118.3 (5)
Mo–C(6)–C(7)	71.7 (3)	C(9)–N–C(11)	125.7 (5)
Mo–C(7)–C(6)	73.5 (3)	C(10)–N–C(11)	115.9 (5)
Mo–C(7)–C(8)	73.0 (3)		

Scheme III



Functionalization of 2a. We have examined the reactivity of the ester group of **2a**. Treatment of the syn isomer of **2a** with 1.2 molar equiv of Bu_4NOH in refluxing THF for 20 min, followed by acidification with dilute aqueous HCl solution, generated the air-stable yellow precipitate $CpMo(CO)_2$(*syn*-η^3-1-C_3H_4COOH) (**2c**). Attempts to obtain **2c** by acid-catalyzed hydrolysis were unsuccessful but resulted in formation of a blue precipitate of undetermined composition after reflux of its THF solution with 2 M HCl for 2 h. Further recrystallization from CH_3COCH_3 at −30 °C produced needlelike orange crystals with the purity warranting satisfactory elemental analysis. Treatment of **2c** with oxalyl chloride in CH_2Cl_2 at 23 °C produced an air-sensitive acid chloride **2d** in 55% yield, which was characterized by IR, mass, and NMR spectra. Its solution exhibited terminal M–CO stretching in the infrared at 1955 and 1850 cm^{-1}. The ^1H and ^{13}C NMR spectra are consistent with the given formula. The COCl carbon resonated at δ 172 ppm. Complex **2d** reacted with

(3) (a) Hegedus, L. S. *Tetrahedron* **1984**, *40*, 2415. (b) Tsuji, J. *Synthesis* **1984**, 369; *Pure Appl. Chem.* **1981**, 2371. (c) Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(4) (a) Pearson, A. J.; Khan, M. D.; Clardy, J. C.; He, C.-H. *J. Am. Chem. Soc.* **1985**, *107*, 2748. (b) Pearson, A. J.; Blystone, S. L.; Nav, H.; Pinkerton, A. A.; Rodeu, B. A.; Yoon, J. *Ibid.* **1989**, *111*, 134. (c) Pearson, A. J.; Khan, M. N. *Ibid.* **1984**, *106*, 1872. (d) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400.

(5) For a leading reference, see: Pearson, A. J. *Synlett* **1990**, 10.

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

(7) For use of organometallic complexes in directing asymmetric carbon induction of acyclic molecules, see: (a) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. (b) Broadly, K.; Davies, S. G. *Tetrahedron Lett.* **1984**, *25*, 1743. (c) Liebeskind, L. S.; Fengl, R. W.; Wolper, M. E.; Goedken, V. *Ibid.* **1985**, *26*, 3075.

(8) (a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858. (b) Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840.

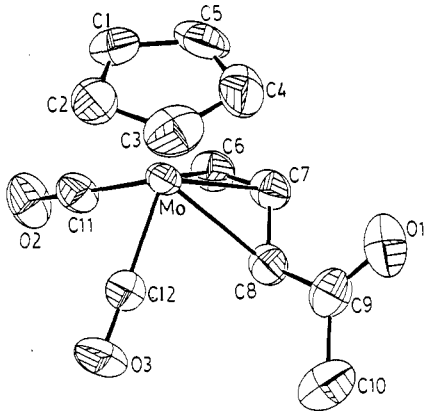


Figure 2. ORTEP drawing of **2b**.

Table II. Selected Bond Distances and Angles of **2b**

	Bond Distances, Å		
Mo–C(6)	2.357 (4)	C(7)–C(8)	1.408 (5)
Mo–C(7)	2.218 (4)	C(8)–C(9)	1.471 (6)
Mo–C(8)	2.349 (4)	C(9)–C(10)	1.502 (6)
Mo–C(11)	1.950 (4)	C(9)–O(1)	1.217 (5)
Mo–C(12)	1.957 (4)	C(11)–O(2)	1.151 (5)
C(6)–C(7)	1.388 (6)	C(12)–O(3)	1.149 (4)
	Bond Angles, deg		
C(6)–Mo–C(7)	35.16 (15)	Mo–C(7)–C(6)	77.89 (23)
C(6)–Mo–C(8)	61.70 (14)	Mo–C(7)–C(8)	77.17 (21)
C(6)–Mo–C(11)	73.47 (16)	C(6)–C(7)–C(8)	119.3 (3)
C(6)–Mo–C(12)	115.71 (15)	Mo–C(8)–C(7)	67.07 (20)
C(7)–Mo–C(8)	35.76 (14)	Mo–C(8)–C(9)	115.88 (24)
C(7)–Mo–C(11)	106.09 (16)	C(7)–C(8)–C(9)	122.5 (3)
C(7)–Mo–C(12)	109.70 (15)	C(8)–C(9)–C(10)	116.4 (4)
C(8)–Mo–C(11)	109.78 (15)	C(8)–C(9)–O(1)	122.9 (4)
C(8)–Mo–C(12)	75.41 (14)	C(10)–C(9)–O(1)	120.7 (4)
C(11)–Mo–C(12)	79.55 (16)	Mo–C(11)–O(2)	177.7 (4)
Mo–C(6)–C(7)	66.95 (21)	Mo–C(12)–O(3)	178.8 (3)

amine Et_2NH to produce the molybdenum amide $CpMo(CO)_2$-(*syn*-η^3-$C_3H_4CONEt_2$) (**2e**). Reduction of the ester **2a** with 3 molar equiv of DIBAL-H yielded $CpMo(CO)_2$(*syn*-η^3-$C_3H_4CH_2OH$) (**2f**) in 35% yield.

The molecular structure of **2e** has been elucidated by X-ray diffraction. An ORTEP drawing of the structure is given in Figure 1 and selected bond distances and angles are given in Table I. The allyl mouth has an endo orientation with respect to the Cp group. On the amide moiety, the nitrogen atom shows partial π-bonding to the C(9) atoms, as indicated by its planar geometry as well as the relatively short C(9)–N distances (1.350 (8) Å) with respect to the length of the normal CN single bond (1.47 (1) Å). The C(9)–O(1) bond (1.231 (8) Å) is slightly longer than the normal CO double bond (1.20 Å).

Transformation to the *s-trans*-Diene Cation. The syn isomer of **2b** was readily separable from the anti form on a silica column. Reduction of the syn isomer with $NaBH_4$ in CH_3OH, followed by hydrolysis, produced $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4CH(OH)$-CH_3) (**2g**) in good yield (85%). The ^1H NMR spectra of **2g** showed the presence of exo and endo conformers. This exo–endo assignment is based on both a comparison of the chemical shifts of the allylic protons and a variable-temperature ^1H NMR spectrum, which exhibits a low barrier ($\Delta G^{\ddagger}$ = 15.3 kcal mol^{-1}) to exchange of the two conformers according to a metal–allyl bond rotation mechanism. The assignment of the *RR,SS* configuration to **2g** relies on structural elucidation of **2b**. An ORTEP drawing is provided in Figure 2. The allyl and carbonyl atoms are in a sickle-shaped conformation. **2g** presumably arose from hydride addition to the carbonyl group trans to the $CpMo(CO)_2$ unit. The syn isomer of **2b** reacted with CH_3Li and PhLi to give CpMo-$(CO)_2$(*syn*-η^3-1-$C_3H_4C(OH)RCH_3$) (R = CH_3 (**2h**), Ph (**2i**)). **2h** and **2i** each exist in exo and endo conformations. As a general feature of **2f–2i**, the exo isomer exhibited H^1 and H^4 resonances at δ 0.17–0.18 and 1.8–2.0 ppm, respectively, whereas the corresponding protons of the endo isomer resonated at δ 1.7–2.0 and 2.8–3.0 ppm, respectively. The chemical shift differences of these two isomers arise from the different allyl orientation with respect to the Cp group. For **2i**, only one diastereoisomer was isolated and assigned to the *RS,SR* configuration; presumably PhLi added trans to the $CpMo(CO)_2$ unit.

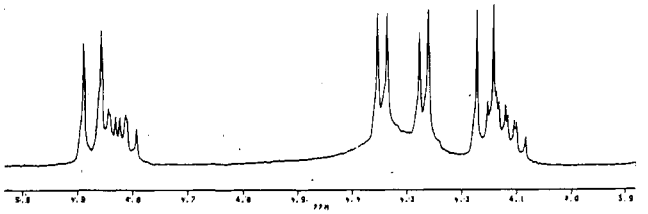
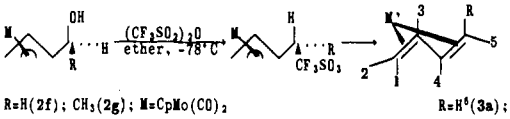


Figure 3. ^1H NMR spectrum of **3a** in the δ 4.00–5.00 ppm (acetone-d_6), which shows the six inequivalent butadiene resonances.

Table III. Product Analysis of the Reaction between **3b** and Nucleophiles

	yield, %	
Nu	product A	product B
H_2O (**2i**)	75	
CH_3OH (**4a**)	67	
C_2H_5OH (**4b**)	59	
C_2H_5SH (**4c**)	34	24
$(CH_3)_2CHNH_2$ (**4d**)	57	
$[(CH_3)_2CH]_2NH$ (**4e**)	7	42
CH_3Li (**4f**)	49	

An interesting stereochemical transformation of the η^3-allyl alcohol is the formation of the *s-trans*-η^4-diene cation.[9,10] The cations **3a** and **3b** were generated as yellow-orange precipitates



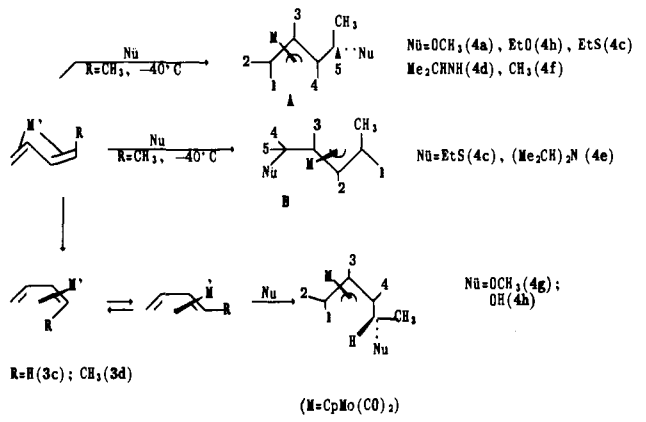
as the alcohols **2f** and **2g** were treated with 1 molar equiv of $(CF_3SO_2)_2O$ in ether at −78 °C. The *s-trans*-η^4-dienes **3a** and **3b** in solid form are stable to air and can be kept at −20 °C for several days; their elemental analyses are satisfactory. Characterization of **3a** was achieved by ^1H and ^{13}C NMR spectra in acetone-d_6 at −40 °C. In the case of **3b**, characterization by NMR spectra encountered difficulties because of its facile conversion to the more stable *s-cis*-η^4-pentadiene (**3d**) in acetone-d_6. In the ^1H NMR spectrum of **3a** (Figure 3), six inequivalent butadiene protons were observed in the δ 4.0–5.0 ppm region and, interestingly, one of the internal protons resonated the most upfield (δ 4.15 ppm). The magnitude J_{34} = 8.2 Hz is considerably larger than that of common *s-cis*-butadienes. The four butadiene carbons resonate at δ 66.1, 67.1, 84.9, and 96.2 ppm. The unsymmetric butadiene environment remains until the temperature is warmed to 0 °C, where the NMR signals turn broad and show resonances identical with those of the *s-cis*-butadiene **3c**. In the case of **3d**, two *s-cis*-diene species (*cis,trans*-pentadiene) were observed to reach a state of equilibrium at which the trans/cis ratio is ca. 15; each of the latter exists in exo and endo stereoisomers. As confirmed in an early report,[8a] these four isomers undergo exchange via a mechanism in which both metal–diene rotation and metal–diene flipping are operative.

Although the *s-trans*-diene cation **3b** could not be characterized by NMR spectra, the salt in ether at −40 °C displayed a remarkable reactivity toward diverse nucleophiles including H_2O, alcohol, amine, thiol, and alkyllithium. Structural analyses of the products enable one to characterize the diene configuration; a summary of the results appears in Table III. In a typical

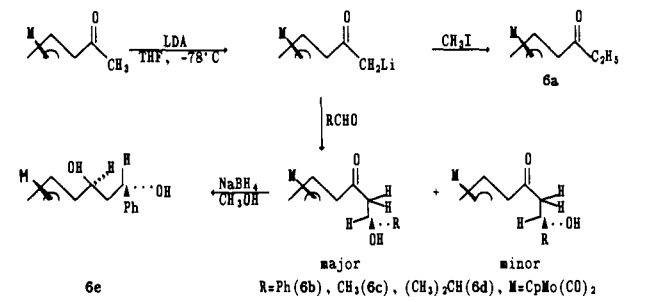
(9) Erker, G.; Wicker, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Kruger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344. (b) Nakamura, A.; Yasuda, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723.

(10) Benyunes, S. A.; Green, M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268.

Scheme IV

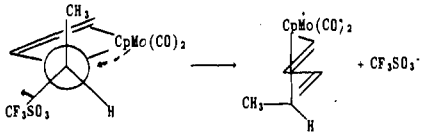


Scheme V



reaction, nucleophiles were added to **3b** in ether at −40 °C, which led to gradual disappearance of **3b**. Two classes of products A and B were obtained, which resulted from the addition at the α- and δ-carbons of the ligand. The regioselectivity depended strongly on the size of the entering group. Small nucleophiles H_2O, CH_3OH, C_2H_5OH, CH_3Li, and $(CH_3)_2CHNH_2$ yielded only type A products whereas $(Me_2CH)_2NH$ produced only the type B product. For C_2H_5SH, both A and B products were produced and readily separated on a silica column in the yields 44% and 31%, respectively. We conclude that type A complexes retain configuration identical with that of **2g** as hydrolysis of the cation regenerates **2g**. This result implies that nucleophiles added trans to the *s-trans*-diene. In type B, the anti-methyl group is indicated by not only the coupling constant J_{12} = 7.0 and J_{23} = 10.2 Hz but also the relatively upfield resonance (δ 1.00 ppm) in the exo isomer. The methylene protons H^4 and H^5 are diastereotopic and exhibit an ABX pattern. The yields of A and B provided direct evidence for generation of the *s-trans*-η^4-*cis*-pentadiene configuration of **3b**. For further comparison, we have examined the reaction of **3d** with H_2O and CH_3OH, which yielded products assigned to $CpMo(CO)_2$(*anti*-η^3-1-$C_3H_4CH(Nu)(CH_3)$) (Nu = OCH_3 (**4g**), OH (**4h**)). The products are assumed to have an anti substituent as indicated by the coupling constant J_{34} = 7.2 Hz.

The mechanism of the formation of the *s-trans*-diene **3b** derived from **2g** deserves special attention. The process precludes the formation of a free carbonium ion at the $CH(CH_3)$ carbon. According to our proposal, the Fisher projection below represents the key conformation of the intermediates in which the CF_3SO_3 anion lies trans to the $CpMo(CO)_2$ unit. Apparently the ionization process follows an intramolecular S_N2 mechanism[11] in which



(11) An intramolecular S_N2 mechanism is known for derivatives of ferrocenes, see: (a) Little, W. F.; Lynam, K. W.; Williams, R. *J. Am. Chem. Soc.* **1964**, *86*, 3055. (b) Beckwich, A. L. J.; Leydon, R. J. *J. Am. Chem. Soc.* **1964**, *86*, 953. (c) Trifan, D. S.; Nicholas, L. *J. Am. Chem. Soc.* **1957**, *79*, 2746.

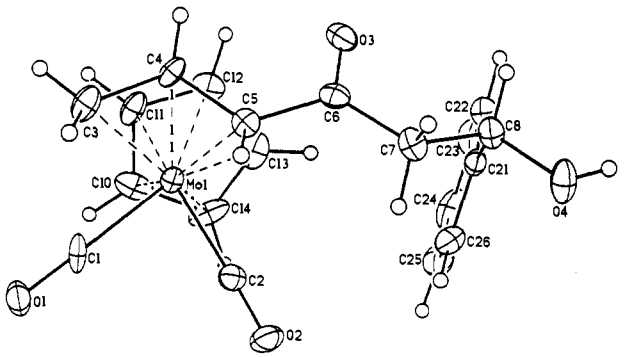
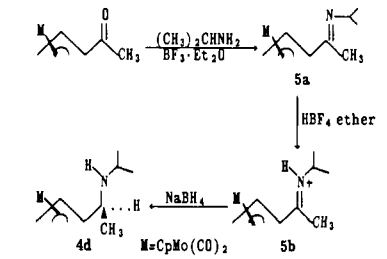


Figure 4. ORTEP drawing of **6b**.

the $CpMo(CO)_2$ unit acts as a base to displace $CF_3SO_3^-$ anion in the opposite direction. The resulting *s-trans*-η^4-*cis*-pentadiene is further stabilized by the $CpMo(CO)_2$ fragment. A similar process is known for derivatives of ferrocene[11] and (butadiene) iron tricarbonyl complexes.[12]

Imination and Enolate Formation. Complex **2b** was further converted to imine in the presence of $BF_3{\cdot}EtO_2$. The isopropylimine derivative (**5a**) was isolated as brick red crystals in



ca. 65% yield. Further protonation of **5a** in ether by HBF_4 ether gave the iminium salt **5b** in ca. 82% yield. Examination of ^1H and ^{13}C NMR data indicates that **5b** adopts an η^3-allyl rather than *s-trans*-diene mode because of its close resemblance to **5a** in its ^1H NMR pattern. The presence of the ν(CN) double bond is shown by its infrared absorption at 1612 (w) cm^{-1}. Complex **5b** was further reduced by $NaBH_4$ in THF and produced $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4CHCH_3NHCHMe_2$) (**4d**). The latter has also been obtained from the reaction involving Me_2CHNH_2 and *s-trans*-η^4-diene (**3b**).

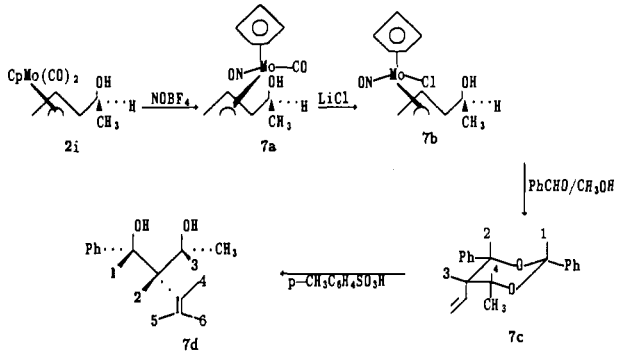
Organometallic complexes bearing enolate have been utilized effectively in synthetic chemistry; the most prominent example is the iron–acyl enolate $CpFe(CO)(PPh_3)(COCH_2Li)$.[7] The ketone methyl of the syn isomer of **2b** is acidic and readily formed the enolate upon treatment with lithium diisopropylamide at −40 °C in THF. The enolate is stable at −40 °C and was alkylated with CH_3I to give **6a**. Treatment of this enolate with aldehyde gave $CpMo(CO)_2$(*syn*-η^3-$C_3H_4COCH_2CH(OH)R$) (R = Ph (**6b**), CH_3 (**6c**), $(CH_3)_2CH$ (**6d**)) in two diastereomers; the ratios were 87:13, 78:22, and 53:47 for **6b**, **6c**, and **6d**, respectively. The two diastereomers were distinguished by the high-field proton resonances of the $CHCO$ and $CH(OH)$ hydrogens at these two asymmetric carbons but were more distinguishable in the methylene protons. As a common feature, the methylene protons of the major isomers of **6b–6d** have a greater separation of chemical shifts and a larger geminal coupling constant than those of the minor isomers. The major isomer of **6b** has been obtained in pure form by fractional crystallization from a saturated ether solution. The specific configuration of the molecule has been clarified by X-ray diffraction; an ORTEP drawing is provided in Figure 4. Similar to **2b**, the allyl and ketone carbons retain a sickle-shaped conformation. The OH group tilts away from the C(6)–O(3) group and evidently no intramolecular hydrogen bond is formed. The isolation of this diastereomer has been utilized for stereoselective synthesis of 1,3-diol after reduction with $NaBH_4$ in CH_3OH; only one diastereomer was formed in 81% yield. The

(12) Green, R. *Synthesis* **1989**, 341.

Table IV. Bond Lengths and Bond Angles of **6b**

	Bond Lengths, Å		
Mo(1)-C(1)	1.938 (7)	Mo(1)-C(2)	1.955 (12)
Mo(1)-C(3)	2.346 (11)	Mo(1)-C(4)	2.207 (9)
Mo(1)-C(5)	2.325 (8)	O(1)-C(1)	1.163 (8)
O(2)-C(2)	1.136 (15)	O(3)-C(6)	1.244 (10)
O(4)-C(8)	1.427 (11)	C(3)-C(4)	1.379 (13)
C(4)-C(5)	1.415 (14)	C(5)-C(6)	1.461 (10)
C(6)-C(7)	1.488 (13)	C(7)-C(8)	1.510 (11)
	Bond Angles, deg		
C(1)-Mo(1)-C(2)	79.2 (5)	C(1)-Mo(1)-C(3)	72.6 (4)
C(2)-Mo(1)-C(3)	112.7 (5)	C(1)-Mo(1)-C(4)	105.7 (4)
C(2)-Mo(1)-C(4)	109.1 (4)	C(3)-Mo(1)-C(4)	35.1 (3)
C(1)-Mo(1)-C(5)	112.0 (3)	C(2)-Mo(1)-C(5)	75.6 (4)
C(3)-Mo(1)-C(5)	62.5 (4)	C(4)-Mo(1)-C(5)	36.3 (4)
Mo(1)-C(1)-O(1)	179.6 (8)	Mo(1)-C(2)-O(2)	177.6 (9)
Mo(1)-C(3)-C(4)	66.9 (6)	Mo(1)-C(4)-C(3)	78.0 (6)
Mo(1)-C(4)-C(5)	76.4 (5)	C(3)-C(4)-C(5)	120.3 (8)
Mo(1)-C(5)-C(4)	67.3 (5)	Mo(1)-C(5)-C(6)	114.1 (6)
C(4)-C(5)-C(6)	121.2 (7)	O(3)-C(6)-C(5)	120.2 (8)
O(3)-C(6)-C(7)	121.1 (7)	C(5)-C(6)-C(7)	118.7 (7)
C(6)-C(7)-C(8)	115.4 (7)	O(4)-C(8)-C(7)	106.3 (6)

Scheme VI

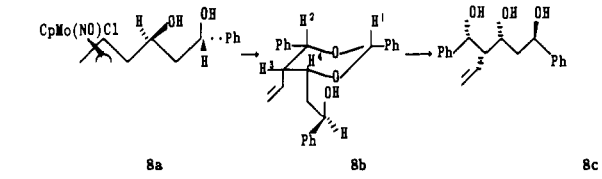


specific configuration depicted is assigned to **6e**; presumably, hydride added trans to the ketone with respect to the bulky $CpMo(CO)_2$ unit.

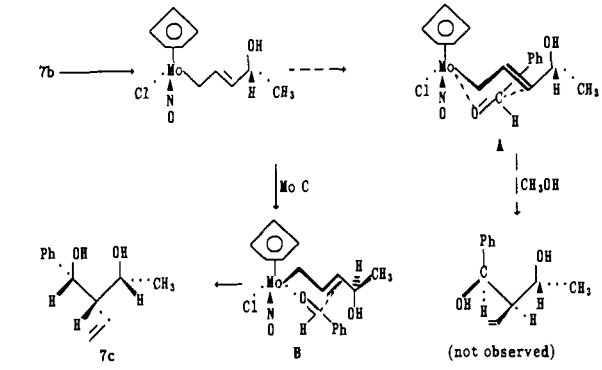
It is of great interest to compare the diastereoselectivity of the well-known enolate $CpFe(CO)(PPh_3)(COCH_2Li)$, which gives 1:1 diastereomers with lithium as the counterion.[7] In the presence of zinc chloride and diisobutylaluminum chloride, the aldol reaction of iron-acyl enolate was achieved with excellent diastereoselectivity. Nevertheless, the ketone of **6b** and **6c** can be further functionalized. In this manner, the synthetic application of the enolates in our system may be superior to those of iron-acyl analogues if the diastereoselectivity can be further improved with suitable ions.

Asymmetric 1,3-Diol Synthesis. Stereoselective synthesis of 1,3-diol has been a subject of considerable interest because it is a basic skeleton for natural products such as polyoxo ionophores, macrolides, and ansamycins.[13,14] The ultimate aim of this study is to provide an efficient asymmetric synthesis of 1,3-diol and homologues according to Scheme VI. The dicarbonyl complex **2g** was treated with $NOBF_4$ in CH_3CN at 0 °C. After purification, the NO-η^3-allyl salt (**7a**) was treated with LiCl to yield the chloride **7b**. Purification of **7b** was achieved by means of silica column chromatography. Notably, one diastereomer was observed for **7a** and **7b**, which contain three chiral centers. Stirring of **7b** with 2.5 molar equiv of benzaldehyde in CH_2Cl_2 in the presence of CH_3OH, after 2 days, led to gradual deposition of a red precipitate. The acetal **7c** was isolated in 52% yield from the CH_2Cl_2

Scheme VII



Scheme VIII



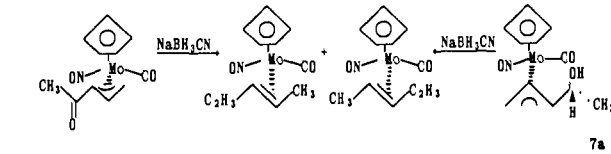
phase. The reaction proceeded in a highly stereospecific manner and no second diastereomer was detected in the ^1H NMR limit. The specific configuration of this six-member acetal has been readily elucidated by ^1H NMR spectra. The magnitudes of the coupling constants J_{23} = 2.3 and J_{34} = 2.1 Hz imply that H^2 and H^4 occupy axial positions where H^3 is situated in an equatorial position. This structural assignment is further confirmed by a NOE experiment; irradiation of the H^2 resonance gives rise to 6.2% an 3.2% increases in intensities of the H^1 and H^4 protons, respectively. Hydrolysis of **7c** with p-$CH_3C_6H_4SO_3H$ gave 1,3-diol **7d** in a single isomer (56% yield, diastereomeric purity >98%). This synthetic approach is extensive and has been further applied to 1,3,5-triol synthesis. The chloride complex **8a** was similarly prepared from **6e** in a moderate yield (48%). Treatment of **8a** with benzaldehyde/CH_3OH, after 2 days, stereospecifically produced the acetal **8b** (51%). No second acetal was observed in the ^1H NMR limit. Its structural assignment relies primarily on a 2D COSY spectrum. In a NOE experiment, the H^1 signal (δ 5.97 ppm) exerted significant Overhauser enhancement on the H^2 and H^4 signals whereas the $CH_2CH(OH)Ph$ was unaffected. Hydrolysis of **8b** with p-$CH_3C_6H_4SO_3H$ produced the sole triol (**8c**) in 43% in a single diastereomer.

It is imperative to correlate the stereochemistry of **7c** and **7d** with that of **2g**. Based on Faller's concept,[6] a plausible mechanism is proposed in Scheme VII. According to our related work,[15] for **7a**, NO^+ replaces the carbonyl trans to the $CH(OH)CH_3$ group in the exo isomer. Subsequently, chloride replaces the remaining CO ligand[16] to give the only detectable *exo*-**7b** isomer. The exo conformation is indicated by the long-range NMR coupling between the H^2 and Cp protons (J = 1.2 Hz). A 2 D NOSEY spectrum confirmed this stereochemical arrangement. In **7b** the allyl carbon trans to NO tends to dissociate[17] to leave a vacant

(13) (a) Yue, S.; Duncan, J. S.; Yamamoto, Y.; Hutchinson, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 1253. (b) Lipshutz, B. H.; Kozlowski, J. A. *J. Org. Chem.* **1984**, *49*, 1149. (c) Floyd, D. M.; Fritz, A. W. *Tetrahedron Lett.* **1981**, *22*, 2847.

(14) (a) Nakata, T.; Hata, N.; Iida, K.; Oishi, T. *Tetrahedron Lett.* **1987**, *28*, 5661. (b) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higachi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090.

(15) In our unpublished results, we have determined the molecular structure of the NO salt of **2b**. Reduction of the salt gives the η^2-*trans*-2-pentene in two isomers, which interconvert at low temperature (ΔG^* = 11.2 kcal mol^{-1}).



Similarly, reduction of **7a** gave the same product. This result implies that NO is trans to the $CH(CH_3)OH$ group in the exo isomer of **7a**.

(16) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227.

site for benzaldehyde. In view of the interligand steric hindrance within the metal coordination sphere once benzaldehyde is coordinated, two chairlike transition states are generated. The preferred aldehyde orientation is required by decreased interaction with the CpMo(NO)(Cl) fragment; thus, the η^1-allyl group adds to the *re* face of the aldehyde. The ultimate control of the diastereoselectivity is governed by the transition state B, which places the bulky phenyl and $CH(OH)CH_3$ groups at the equatorial positions to minimize the interligand steric hindrance. In contrast, the insignificant role of state A is attributed to its axial phenyl group, which exerts increased steric interaction with the Cp group; thus, its addition product is not observed in the course of reaction.

Conclusion

Functionalization of the ketone group adjacent to the molybdenum–η^3-allyl unit proceeds in a highly stereoselective manner. Of particular interest, the Mo–*syn*-η^3-1-C_3H_4R unit is effective in directing chiral carbon induction, particularly in the course of *s-trans*-diene formation, aldol condensation, and 1,3-diol and 1,3,5-triol asymmetric synthesis. Stereoselective synthesis of the 1,3-diol skeleton has been a main issue in synthetic organic chemistry. In principle, all the new η^3-allyl functionalized compounds can be further utilized and provide a convenient route in synthesis of 1,3-difunctional homoallyllic alcohols. Studies in this direction are currently in progress.

Experimental Section

All operations were carried out under argon in a Schlenk apparatus or in a glovebox. The solvents benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium/benzophenone and distilled before use. Dichloromethane and chloroform were dried over calcium hydride and distilled. Anhydrous trimethylamine oxide was prepared by subliming its dihydrate (Fluka) at 110 °C without further purification. $Mo(CO)_6$, LiCl, $NOBF_4$, and triphenylphosphine (Strem Chemicals) were used without further purification. $CpMo(CO)_3Na$,[18] 5-chloro-3-penten-2-one, and methyl-4-chloro-2-butenoate[19] were prepared according to procedures in the literature.

All ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker AM-400 spectrometer; the ^1H and ^{13}C spectra were referenced to tetramethylsilane. Microanalyses were performed by the Microanalytic Laboratory at National Taiwan University. Infrared spectra were recorded on a Perkin-Elmer 781 spectrophotometer.

Synthesis of $CpMo(CO)_3(\eta^1$-1-$C_3H_4COOMe)$ (1a). A tetrahydrofuran solution (50 mL) of $CoMo(CO)_3Na$ (5.36 g, 20 mmol) was stirred with methyl 4-chloro-2-butenoate (2.82 g, 21 mmol) at 23 °C for 6 h. The solvent was removed under reduced pressure, leaving a red residue, which was then chromatographed on a silica column with a hexane/ether (4:1) mixture as the eluting solvent. After elution of a purple band of $[CpMo(CO)_3]_2$, **1a** was obtained as a yellow band as a hexane/ether (1:1) eluting solvent was used. Removal of the solvent under reduced pressure afforded an air-stable oil (3.85 g, 11.2 mmol). IR (CH_2Cl_2): ν(CO) 2022 (s), 1934 (s), 1696 (s) cm^{-1}; ν(C=C) 1590 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): *E* isomer (48%) δ 2.26 (d, 2 H, H^1), 3.68 (s, 3 H, OCH_3), 5.28 (s, 5 H, C_5H_5), 5.55 (d, 1 H, H^3), 7.25 (dt, 1 H, H^3), 7.25 (dt, 1 H, H^2), J_{12} = 9.7 Hz, J_{23} = 14.9 Hz; *Z* isomer (48%) δ 2.86 (d, 2 H, H^1), 3.65 (s, 3 H, OCH_3), 5.32 (s, 5 H, C_5H_5), 5.34 (d, 1 H, H^3), 6.61 (q, 1 H, H^2), J_{12} = 10.5 Hz, J_{23} = 11.1 Hz. MS (12 eV): 318 (M^+ – CO), 290 (M^+ – 2CO). Anal. Calcd for $C_{13}H_{12}MoO_5$: C, 45.35; H, 3.94. Found: C, 45.42; H, 3.95.

Synthesis of $CpMo(CO)_3(\eta^1$-1-$C_3H_4COMe)$ (1b). This complex was similarly prepared from the reaction between $CpMo(CO)_3Na$ and 5-chloro-3-penten-2-one; the yield was 58%. IR (CH_2Cl_2): ν(CO) 2022 (s), 1930 (s), 1653 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *E* isomer (81%) δ 2.18 (s, 3 H, $COCH_3$), 2.28 (d, 2 H, H^1), 5.27 (s, 5 H, C_5H_5), 5.87 (d, 1 H, H^3), 7.18 (dt, 1 H, H^2), J_{12} = 9.4 Hz, J_{23} = 15.2 Hz; *Z* isomer (19%) δ 2.95 (s, 3 H, $COCH_3$), 2.30 (d, 2 H, H^1), 5.32 (s, 5 H, C_5H_5), 5.68 (d, 1 H, H^3), 6.42 (q, 1 H, H^2), J_{12} = 10.0 Hz, J_{23} = 10.5 Hz. MS (12 eV): 302 (M^+ – CO), 274 (M^+ – 2CO), 246 (M^+ – 3CO). Anal. Calcd for $C_{13}H_{12}MoO_4$: C, 47.56; H, 3.66. Found: C, 47.38; H, 3.56.

Synthesis of $CpMo(CO)_2(\eta^3$-1-$C_3H_4COOMe)$ (2a). A 25-mL dichloromethane solution of **1a** (3.44 g, 10 mmol) was stirred with anhydrous trimethylamine oxide (0.92 g, 12 mmol) at 25 °C for 2 h. After the solution was evaporated to dryness, the residues were twice extracted with 20 mL of ether. The extract was then evaporated to dryness and the residues were chromatographed through a silica gel column with a hexane/ether (4:1) mixture as the eluting solvent. After the unwanted purple band of $[CpMo(CO)_3]_2$ was eluted, two yellow bands were developed as a hexane/ether (1:1) eluting solvent was used. The syn-η^3 isomer was obtained as a yellow crystalline solid (1.64 g, 5.19 mmol) after removal of the solvent from the first band. The anti-η^3 isomer in the form of an orange oil (1.28 g, 4.05 mmol) was obtained from the second band. IR (CH_2Cl_2): ν(CO) 1958 (s), 1879 (s), 1705 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): syn–exo isomer δ 1.20 (dd, 1 H, H^1), 1.69 (d, 1 H, H^4), 2.92 (dd, 1 H, H^2), 3.68 (s, 3 H, OCH_3), 4.92 (m, 1 H, H^3), 5.27 (s, 5 H, C_5H_5), J_{13} = 11.1 Hz, J_{23} = 7.4 Hz, J_{12} = 1.5 Hz, J_{34} = 9.5 Hz; syn–endo isomer δ 2.08 (d, 1 H, H^1), 2.56 (d, 1 H, H^4), 2.75 (d, 1 H, H^2), 3.68 (s, 3 H, OCH_3), 4.43 (m, 1 H, H^3), 5.30 (s, 5 H, C_5H_5), J_{13} = 10.7 Hz, J_{23} = 6.5 Hz, J_{34} = 9.5 Hz; anti–exo isomer δ 2.74 (d, 1 H, H^1), 3.30 (d, 1 H, H^2), 3.50 (s, 3 H, OCH_3), 3.68 (d, 1 H, H^4), 4.39 (m, 1 H, H^3), J_{13} = 11.6 Hz, J_{23} = 7.9 Hz, J_{34} = 7.8 Hz; anti–endo isomer δ 3.02 (d, 1 H, H^1), 3.58 (s, 3 H, OCH_3), 3.75 (d, 1 H, H^2), 3.85 (d, 1 H, H^4), 4.15 (m, 1 H, H^3), 5.18 (s, 5 H, C_5H_5), J_{13} = 10.3 Hz, J_{23} = 7.2 Hz, J_{34} = 7.0 Hz. MS (12 eV): 318 (M^+), 290 (M^+ – CO), 262 (M^+ – 2CO). Anal. Calcd for $C_{12}H_{12}MoO_4$: C, 45.57; H, 3.80. Found: C, 45.72; H, 3.90.

Synthesis of $CpMo(CO)_2(\eta^3$-1-$C_3H_4COCH_3)$ (2b). Preparation of this compound was conducted like that of **2a**. The syn and anti isomers were separated by means of a silica column; the yields were 52% and 8%, respectively. IR (CH_2Cl_2): 1956 (s), 1876 (s), 1622 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): syn–exo isomer δ 1.23 (dd, 1 H, H^1), 1.89 (d, 1 H, H^4), 2.19 (s, 3 H, CH_3), 2.96 (dd, 1 H, H^2), 4.95 (m, 1 H, H^3), 5.19 (s, 5 H, C_5H_5), J_{13} = 11.5 Hz, J_{23} = 7.2 Hz, J_{34} = 9.5 Hz; syn–endo isomer δ 2.09 (s, 3 H, CH_3), 2.14 (d, 1 H, H^1), 2.77 (d, 1 H, H^2), 2.88 (s, 1 H, H^4), 4.35 (m, 1 H, H^3), 5.28 (s, 5 H, C_5H_5), J_{13} = 11.2 Hz, J_{23} = 7.6 Hz, J_{34} = 9.6 Hz; anti–exo isomer δ 1.93 (s, 3 H, $COCH_3$), 2.76 (d, 1 H, H^1), 3.36 (d, 1 H, H^2), 3.92 (d, 1 H, H^4), 4.43 (m, 1 H, H^3), 5.30 (s, 5 H, C_5H_5), J_{13} = 12.0 Hz, J_{23} = 8.2 Hz, J_{34} = 7.0 Hz; anti–endo isomer δ 2.08 (s, 3 H, $COCH_3$), 3.10 (d, 1 H, H^2), 3.78 (d, 1 H, H^1), 4.07 (d, 1 H, H^4), 4.15 (m, 1 H, H), 5.13 (s, 5 H, C_5H_5), J_{13} = 11.2 Hz, J_{23} = 7.0 Hz, J_{34} = 7.2 Hz. MS (12 eV): 302 (M^+), 274 (M^+ – CO), 246 (M^+ – 2CO). Anal. Calcd for $C_{12}H_{12}MeO_3$: C, 48.00; H, 4.00. Found: C, 47.98; H, 4.04.

Synthesis of $CpMo(CO)_2(syn$-η^3-1-$C_3H_4COOH)$ (2c). The syn isomer of **2a** (0.52 g, 1.6 mmol) in 20 mL of THF was refluxed with 2.4 mL of aqueous Bu_4NOH (20% wt) for 0.5 h. To the resulting dark red solution was slowly added 2 M HCl to produce a yellow precipitate. After collection of the precipitate by filtration, the yellow power was washed with 5 mL of H_2O and then 5 mL of CH_2Cl_2 and was further recrystallized from CH_3CN under slow evaporation to produce orange crystals (0.39 g, 1.30 mmol). IR (Nujol): ν(CO) 1955 (s), 1877 (s), 1713 (s) cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): exo isomer δ 1.18 (d, 1 H, H^1), 1.67 (d, 1 H, H^4), 3.00 (d, 1 H, H^2), 5.0 (ddd, 1 H, H^3), J_{13} = 11.0 Hz, J_{23} = 7.8 Hz, J_{34} = 9.8 Hz; endo isomer δ 2.33 (d, 1 H, H^1), 2.74 (d, 1 H, H^4), 2.78 (d, 1 H, H^2), 4.35 (m, 1 H, H^3), 5.50 (3, 5 H, C_5H_5), J_{13} = 11.0 Hz, J_{23} = 6.6 Hz, J_{34} = 9.8 Hz. ^{13}C NMR (100 MHz, acetone-d_6): exo isomer δ 38.8 (CH^1H^2), 48.1 (CH^4), 72.8 (CH^3), 93.7 (C_5H_5), 174.1 (COOH), 238.5, 239.3 (2 Mo–CO) endo isomer δ 35.9 (CH^1H^2), 44.4 (CH^4), 89.5 (CH^3), 91.5 (C_5H_5), 175.2 (COOH), 235.5, 237.5 (2Mo–CO). MS (12 eV): 304 (M^+), 276 (M^+ – CO), 248 (M^+ – 2CO). Anal. Calcd for $C_{11}H_{10}MoO_4$: C, 43.71; H, 3.31. Found: C, 43.64; H, 3.37.

Synthesis of $CpMo(CO)_2(syn$-η^3-1-$C_3H_4COCl)$ (2d). Oxalyl chloride (0.024 g, 0.18 mmol) was added to a dichloromethane (10 mL) solution of **2c** (0.10 g, 0.33 mmol) at 23 °C and stirred for 30 min. After removal of the solvent in vacuo, the dark brown residues were twice washed with pentane at −40 °C. After recrystallization from ether at −40 °C produced a red crystalline solid (0.06 g, 0.18 mmol). ^1H NMR spectrum (400 MHz, $CDCl_3$): exo isomer δ 1.33 (dd, 1 H, H^1), 1.83 (d, 1 H, H^4), 2.92 (dd, 1 H, H^2), 4.92 (m, 1 H, H^3), 5.26 (s, 5 H, C_5H_5), J_{13} = 11 Hz, J_{23} = 7.4 Hz, J_{34} = 9.0 Hz; endo isomer δ 2.20 (d, 1 H, H^1), 2.65 (d, 1 H, H^4), 2.69 (d, 1 H, H^2), 4.39 (m, 1 H, H^3), 5.33 (s, 5 H, C_5H_5), J_{13} = 10.6 Hz, J_{23} = 6.5 Hz, J_{34} = 9.6 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): exo isomer δ 40.1 (CH^1H^2), 52.3 (CH^4), 12.3 (CH^3), 93.8 (C_5H_5), 173.0 (COCl), 235.9, 235.7 (2Mo–CO): endo isomer δ 35.3 (CH^1H^2), 50.3 (CH^4), 72.3 (CH^3), 91.2 (C_5H_5), 172.4 (COCl), 236.7, 236.9 (2Mo–CO). Anal. Calcd for $C_{11}H_9MoO_3Cl$: C, 41.20; H, 2.80. Found: C, 42.00; H, 2.94.

Synthesis of $CpMo(CO)_2(syn$-η^3-1-$C_3H_4CONEt_2)$ (2e). Diethylamine (5 mL) was added to a dichloromethane solution of **2d** (0.11 g, 0.34 mmol) at 0 °C, resulting in a color change from red to yellow. The solution was evaporated to dryness, and the residues were crystallized from ether at −40 °C to produce red needle crystals (0.09 g, 0.25 mmol).

(17) Faller, J. W.; Shuo, Y.; Chao, K. H.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251.

(18) Eisch, J. J.; King, R. B. Eds. *Organometallic Synthesis*; Academic Press: New York, 1965; Vol. 1, p 114.

(19) House, H. O.; John, U. K.; Frank, J. A. *J. Org. Chem.* **1964**, *29*, 3327.

IR: ν(CO) 1947 (s), 1862 (s), 1710 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): exo isomer δ 1.11 and 1.17 (t, t, 3 H, 3 H, NCH_2CH_3), 1.22 (dd, 1 H, H^1), 2.04 (d, 1 H, H^4), 3.06 (dd, 1 H, H^2), 3.18 (m, 2 H, NCH_2), 3.58, 3.74 (m, m, 1 H, 1 H, NCH_2), 5.07 (ddd, 1 H, H^3), 5.27 (5 H, s, C_5H_5), J_{13} = 11.5 Hz, J_{23} = 7.2 Hz, J_{34} = 9.2 Hz; endo isomer (selected peak) δ 2.03 (1 H, d, H^1), 2.65 (1 H, d, H^4), 2.85 (d, 1 H, H^2), 4.55 (d, 1 H, H^3). Anal. Calcd for $C_{15}H_{19}NMoO_3$: C, 5.042; H, 3.92. Found: C, 50.55; H, 4.10.

Synthesis of $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4CH_2OH$) (2f). Complex **2a** (0.30 g, 0.96 mmol) in 20 mL of ether was treated with 1.60 mL of 1.2 N DIBAL-H in hexane at −78 °C and the resultant mixture stirred for 2 h. The solution was warmed to room temperature and added to a saturated aqueous Na_2CO_3 solution. The ether layer was decanted and the aqueous solution was twice extracted with 20 mL of ether. The combined extract were concentrated and eluted on a silica column with a hexane/ether (1:1) mixed solvent. Two yellow bands were developed. The first band consisted of unreacted **3a**. Evaporation of the second band to dryness produced a yellow solid **2f** (0.19 g, 0.66 mmol). IR (Nujol): ν(OH) 3562 (s) cm^{-1}; ν(CO) 1947 (s) cm^{-1}; 1860 (s) cm^{-1}; 1860 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): exo isomer δ 0.80 (dd, 1 H, H^1), 1.68 (ddd, 1 H, H^4), 2.55 (dd, 1 H, H^2), 3.62 (dd, 1 H, CHH^1OH), 4.05 (dd, 1 H, $CHH'OH$), 4.08 (m, 1 H, H^3), J_{13} = 10.3 Hz, J_{23} = 6.8 Hz, J_{34} = 6.8 Hz, J_{4H} = 4 Hz, $J_{4H'}$ = 8.8 Hz, $J_{CHH'}$ = 12.0 Hz; endo isomer (selected peak) δ 1.76 (d, 1 H, H^1), 2.56 (d, 1 H, H^2), 2.76 (m, 2 H, H^4+$CHH'OH$), 3.90 (dd, 1 H, $CHH'OH$), 4.00 (m, 1 H, H^3), J_{13} = 10.4 Hz, J_{23} = 6.6 Hz, J_{4H} = 7.0 Hz, $J_{HH'}$ = 11.0 Hz. Anal. Calcd for $C_{11}H_{12}MoO_3$: C, 45.83; H, 4.17. Found: C, 45.71; H, 4.09.

Synthesis of $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4CH(OH)CH_3$) (2g). Complex **2b** (1.0 g, 3.33 mmol) was stirred with $NaBH_4$ (0.70 g, 18.0 mmol) in CH_3OH (20 mL) at room temperature for 0.5 h. As the solution turned from orange to light yellow, 2 N HCl was added to achieve neutralization. The solution was evaporated to dryness and the residues were extracted with ether. Further eluting through silica gel with a Et_2O/hexane (1:1) solvent produced a yellow oil. Removal of the solvent gave a yellow oil **2g** (0.93 g, 3.05 mmol). IR (in Nujol): ν(OH) 3502 (s) cm^{-1}; ν(CO) 1948 (s), 1872 (s) cm^{-1}. ^1H NMR (400 MHz): exo isomer δ 0.81 (dd, 1 H, H^1), 1.47 (d, 3 H, CH_3), 1.82 (dd, 1 H, H^4), 2.72 (dd, 1 H, H^2), 3.95 (m, 1 H, CH(OH)), 4.06 (m, 1 H, H^3), 5.33 (s, 5 H, C_5H_5), J_{13} = 10.4 Hz, J_{23} = 6.8 Hz, J_{34} = 9.0 Hz, J_{4H} = 8.0 Hz, J_{CH_3-CH} = 6.2 Hz; endo isomer δ 1.46 (d, 3 H, CH_3), 1.78 (d, 1 H, H^1), 2.67 (d, 1 H, H^2), 2.77 (dd, 1 H, H^4), 3.64 (m, 1 H, H^3), 3.95 (m, 1 H, H^5), 5.26 (s, 5 H, C_5H_5), J_{CH_3-H} = 6.0 Hz, J_{13} = 10.6 Hz, J_{23} = 6.5 Hz, J_{34} = 9.8 Hz, J_{4H} = 6.8 Hz. MS (12 eV): 304 (M^+), 248 (M^+ − 2CO). Anal. Calcd for $CH_{12}H_{14}MoO_3$: C, 47.68; H, 4.64. Found: C, 47.58; H, 4.58.

Synthesis of $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4COH(CH_3)R$) (R = CH_3 (2h), Ph (2i)). Complex **2b** (0.15 g, 0.50 mmol) in 20 mL of THF was treated with 0.3 mL of CH_3Li (1.6 M in hexane) at −78 °C and the resultant mixture was stirred for 2 h. As the solution was warmed to room temperature, 10 mL of aqueous NH_4Cl was added for neutralization. The solution was concentrated to 10 mL, followed by addition of 20 mL of ether. The ether layer was decanted, and the remaining aqueous solution was twice extracted with 20 mL of ether. The combined ether solution was evaporated to dryness, and the residues were eluted through a silica column with a hexane/ether (7:3) mixture as solvent. A yellow band was developed, collected, and evaporated to dryness, to afford a yellow viscous solid **2h** (0.09 g, 0.28 mmol). IR (in Nujol): ν(OH) 3512 (s) cm^{-1}; ν(CO) 1950 (s), 1880 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): exo isomer δ 0.72 (dd, 1 H, H^1), 1.48, 1.55 (s, s, 3 H, 3 H, 2 *s*-CH_3), 1.85 (d, 1 H, H^4), 2.65 (d, 1 H, H^2), 4.15 (m, 1 H, H^3), 5.34 (m, 1 H, C_5H_5); endo isomer δ J_{12} = 10.8 Hz, J_{23} = 6.8 Hz, J_{34} = 10.2 Hz, J_{CH_3H} = 9.0 Hz; endo isomer δ 1.43 (s, 3 H, CH_3), 1.78 (d, 1 H, H^1), 2.95 (d, 1 H, H^4), 3.78 (m, 1 H, H^3), 5.26 (s, 5 H, C_5H_5), J_{13} = 10.4 Hz, J_{23} = 6.8 Hz, J_{34} = 10.0 Hz, J_{H-CH_3} = 9.2 Hz. MS (12 eV): 318 (M^+), 262 (M^+ − 2CO). Anal. Calcd for $C_{13}H_{16}MoO_3$: C, 49.37; H, 5.06. Found: C, 49.20; H, 4.92. Compound **2i** was obtained similarly from PhLi addition to **2b**; the yield was 52%. IR (in Nujol): ν(OH) 3523 (m) cm^{-1}; ν(OH) 1922 (s) cm^{-1}; 1834 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): exo isomer δ 0.70 (dd, 1 H, H^1), 1.86 (d, 1 H, H^4), 2.59 (dd, 1 H, H^2), 4.16 (m, 1 H, H^3), 5.26 (s, 5 H, C_5H_5), 7.34–7.55 (m, 5 H, C_6H_5), J_{13} = 10.3 Hz, J_{23} = 6.2 Hz, J_{34} = 10.1 Hz; endo isomer δ 1.13 (d, 1 H, H^1), 1.80 (s, 3 H, CH_3), 3.06 (d, 1 H, H^4), 3.89 (m, 1 H, H^3), 7.35–7.55 (m, 5 H, C_6H_5), J_{13} = 10.2 Hz, J_{23} = 6.2 Hz, J_{34} = 10.4 Hz. MS (12 eV): 380 (M^+), 324 (M^+ − 2CO). Anal. Calcd for $C_{18}H_{18}MoO_3$: C, 57.14; H, 4.76. Found: C, 57.41; H, 4.48.

Synthesis of [$CpMo(CO)_2$(*s-trans*-η^4-butadiene)]CF_3SO_3 (3a). Complex **2f** (0.15 g, 0.52 mmol) in 30 mL of ether was treated with $(CF_3SO_2)_2O$ (0.15 g, 0.53 mmol) at −78 °C, resulting in formation of a yellow precipitate (0.19 g, 0.45 mmol), which was collected by filtration. IR (Nujol): ν(CO) 2033 (s), 1971 (s) cm^{-1}. ^1H NMR (400 MHz, acetone-d_6, −40 °C): δ 4.15 (ddd, 1 H, H^4), 4.18 (d, 1 **H**, H^1), 4.25 (d, 1 H, H^5), 4.32 (d, 1 H, H^2), 4.82 (ddd, 1 H, H^3), 4.89 (d, 1 H, H^6), J_{13} = 12.1 Hz, J_{23} = 6.8 Hz, J_{34} = 8.2 Hz, J_{45} = 6.4 Hz, J_{56} = 13.1 **Hz**. ^{13}C NMR (100 MHz, acetone-d_6, −40 °C): δ 66.1, 67.1, 84.9, 96.2, 96.8 (C_5H_5), 211.1, 232.7. Anal. Calcd for $C_{12}H_{11}MoO_5SF_3$: C, 34.29; H, 2.62. Found: C, 34.36; H, 2.58.

Synthesis of [($CpMo(CO)_2$(*s-trans*-η^4-*cis*-pentadiene)]CF_3SO_3 (3b). This cation was prepared similarly from the reaction between $(CF_3SO_2)_2O$ and **2g**; the yield was 87%. IR (Nujol): ν(CO) 2035 (s), 1973 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{13}MoO_5SF_3$: C, 35.94; H, 3.00. Found: C, 35.10; H, 3.31. Characterization of this complex by NMR spectra was unsuccessful because of its facile conversion to η^4-*s-cis*-pentadiene **3d**. The s-trans configuration was proved by its reaction with diverse nucleophiles.

Reaction of 3b with Nucleophiles. (i) H_2O (5 mL) was added to **3b** (0.43 g, 0.99 mmol) in 30 mL of ether at −40 °C with rapid stirring. After the solid **3b** was completely dissolved, aqueous $NaHCO_3$ solution was added. The solution was evaporated to dryness. Elution through a silica column produced a yellow band, which was collected and evaporated to dryness to yield an oil (0.22 g, 0.70 mmol), identified to be **2g**. The η^3-allyls below were obtained similarly. Type A represents (*RR*-(*SS*))-$CpMo(CO)_2$(*syn*-CH_2CHCHC(Nu)HCH_3) and type B for $CpMo(CO)_2$(*syn,anti*-η^3-CH_2Nu$CHCHCH$C$H(CH_3)$). (ii) Compound **4a** (type A, Nu = OCH_3, 73% yield). IR (Nujol): ν(CO) 1950 (s), 1872 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): exo isomer only δ 0.72 (dd, 1 H, H^1), 1.30 (d, 1 H, CH_3), 1.71 (dd, 1 H, H^4), 2.66 (dd, 1 H, H^2), 3.36 (s, 3 H, OCH_3), 3.89 (m, 1 H, H^5), 4.09 (m, 1 H, H^3), 5.28 (s, 5 H, C_5H_5), J_{12} = 10.5 Hz, J_{23} = 7.2 Hz, J_{34} = 10.8 Hz, J_{45} = 6.8 Hz. MS (12 eV): 318 (M^+), 287 (M^+ − OMe), 262 (M^+ − 2CO). Anal. Calcd for $C_{13}H_{16}MoO_3$: C, 43.37; H, 5.06. Found: C, 43.24; H, 5.12. (iii) Compound **4b** (type A, Nu = EtO, 72% yield). IR (Nujol): ν(CO) 1942 (s), 1864 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): exo isomer δ 0.72 (dd, 1 H, H^1), 1.18 (t, 3 H, CH_2CH_3), 1.30 (d, 3 H, $CHCH_3$), 1.75 (dd, 1 H, H^4), 2.66 (dd, 1 H, H^2), 3.44, 3.63 (m, m, 2 H, $OCHH^1$), 4.05 (m, 1 H, H^5), 4.09 (m, 1 H, H^3), 5.23 (s, 5 H, C_5H_5), J_{12} = 1.5 Hz, J_{13} = 10.6 Hz, J_{23} = 7.2 Hz, J_{34} = 10.3 Hz, J_{45} = 3.8 Hz, $J_{5\text{-}CH_3}$ = 6.2 Hz; endo isomer (selected peak) δ 1.18 (t, 3 H, CH_2CH_3), 1.37 (d, 3 H, $CHCH_3$), 1.70 (d, 1 H, H^1), 2.52 (d, 1 H^1, H^2), 2.75 (dd, 1 H, H^4), 3.58 (m, 1 H, H^3), 3.70 (m, 1 H, $CHCH_3$), 5.23 (s, 5 H, C_5H_5), J_{13} = 10.3 Hz, J_{23} = 6.2 Hz, J_{34} = 10.1 Hz, J_{45} = 3.9 Hz. Anal. Calcd for $C_{14}H_{18}MoO_3$: C, 50.91; H, 5.45. Found: C, 50.62; H, 5.84. (iv) **4c** (type A, Nu = C_2H_5S, yield 34%, type B, R = C_2H_5S, yield 24%). IR (Nujol): ν(CO) 1944 (s), 1868 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): type A, exo isomer δ 0.77 (dd, 1 H, H^1), 1.25 (m, 3 H, CH_2CH_3), 1.33 (d, 3 H, $CHCH_3$), 1.85 (dd, 1 H, H^4), 2.53 (d, 1 H, H^2), 2.60 (m, 2 H, $SCHH'$), 3.38 (m, 1 H, H^5), 4.10 (m, 1 H, H^3), 5.27 (s, 5 H, C_5H_5), J_{12} = 1.8 Hz, J_{13} = 10.4 Hz, J_{23} = 6.8 Hz, J_{34} = 9.8 Hz, J_{12} = 1.5 Hz, J_{45} = 5.1 Hz; endo isomer δ 1.25 (m, 3 H, CH_2CH_3), 1.53 (d, 3 H, $CHCH_3$), 11.65 (d, 1 H, H^1), 2.53 (d, 1 H, H^2), 2.60–2.63 (m, 3 H, H^4 + SCH_2), 3.12 (m, 1 H, H^5), 3.62 (m, 1 H, H^3), J_{13} = 10.2 Hz, J_{23} = 7.2 Hz, J_{34} = 9.8 Hz, J_{CH_3-H} = 6.2 Hz; type B δ 1.00 (d, 3 H, anti-CH_3), 1.28 (m, 3 H, CH_2CH_3), 2.18 (t, 1 H, H^3), 2.31 (dd, 1 H, H^4), 2.66 (m, 2 H, SCH_2), 2.70 (dd, 1 H, H^5), 3.50 (m, 1 H, H^1), 4.00 (dd, 1 H, H^2), 5.24 (s, 5 H, C_5H_5), $J_{1\text{-}CH_3}$ = 6.6 Hz, J_{12} = 7.3 Hz, J_{23} = 10.0 Hz, J_{34} = 10.0 Hz, J_{35} = 3.6 Hz, J_{45} = 13.2 Hz; MS (12 eV): 348 (M^+), 292 (M^+ − 2CO). Anal. Calcd for $C_{14}H_{18}MoO_2S$: C, 48.55; H, 5.20. Found: C, 48.72; H, 5.32. (v) **4d** (type A, R = Me_2CHNH, yield 57%): IR (CH_2Cl_2): ν(CO) 1960 (s), 1890 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): exo isomer δ 0.72 (dd, 1 H, H^1), 1.06 (d, d, 3 H, 3 H, $NCHMe_2$), 1.24 (d, 3 H, $CHCH_3$), 1.78 (dd, 1 H, H^4), 2.04 (dd, 1 H, H^2), 2.91 (m, 1 H, NCH), 3.00 (m, 1 H, H^5), 4.04 (m, 1 H, H^3), 5.25 (s, 5 H, C_5H_5), J_{12} = 10.4 Hz, J_{23} = 7.2 Hz, J_{34} = 10.4 Hz, J_{45} = 6.5 Hz, $J_{5\text{-}CH_3}$ = 6.4 Hz; endo isomer δ 1.06 (d, d, 3 H, 3 H, $NCHMe_2$), 1.30 (d, 3 H, $CHCH_3$), 1.68 (d, 1 H, H^1), 2.62 (d, 1 H, H^2), 2.64 (t, 1 H, H^4), 2.91 (m, 1 H, $NCHMe_2$), 3.00 (m, 1 H, H^5), 3.60 (m, 1 H, H^3), 5.24 (s, 5 H, C_5H_5), J_{13} = 10.3 Hz, J_{23} = 6.7 Hz, J_{34} = 9.8 Hz, $J_{5\text{-}CH_3}$ = 6.2 Hz. MS (12 eV): 345 (M^+), 317 (M^+ − CO). Anal. Calcd for $C_{15}H_{21}NMoO_2$: C, 52.48; H, 6.12. Found: C, 52.32; H, 6.30. (vi) **4e** (type B, R = $N(CHMe_2)$, yield 58%). IR (Nujol): ν(CO) 1944 (s), 1870 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): exo isomer δ 1.00 (d, 3 H, anti-CH_3), 1.09, 1.06 (d, d, 6 H, 6 H, $CHMe_2$), 2.42 (dd, 1 H, H^4), 2.85 (ddd, 1 H, H^3), 3.20 (m, 2 H, NCH), 3.33 (dd, 1 H, H^5), 3.42 (m, 1 H, H^1), 3.92 (dd, 1 H, H^2), 5.24 (s, 5 H, C_5H_5), $J_{1\text{-}CH_3}$ = 6.6 Hz, J_{12} = 6.8 Hz, J_{23} = 10.3 Hz, J_{34} = 10.3 Hz, J_{35} = 2.4 Hz, J_{45} = 14.2 Hz, J_{HCH_3} = 6.6 Hz. MS (12 eV): 387 (M^+). Anal. Calcd for $C_{17}H_{25}NMoO_2$: C, 52.99; H, 6.49; N, 3.64. Found: C, 52.88; H, 6.50; N, 3.82. (vii) **4f** (type A, R = CH_3, yield 62%). IR (CH_2Cl_2): ν(CO) 1952 (s), 1878 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): exo isomer δ 0.66 (dd, 1 H, H^1), 1.11, 1.19 (d, d, 3 H, 3 H, CH_3), 1.63 (dd, 1 H, H^4), 1.76 (m, 1 H, H^5), 2.66 (dd, 1 H, H^2), 3.92 (m, 1 H, H^3), 5.24 (s, 5 H, C_5H_5), J_{12} = 1.8 Hz, J_{13} = 10.5 Hz, J_{23}

Table V. Summary of Crystal Data and Data Collection

compound	**6b**	**2e**	**2b**
empirical formula	$C_{19}H_{18}O_4Mo$	$C_{15}H_{19}NO_3Mo$	$C_{12}H_{12}O_3Mo$
color, habit	orange, needle	red, chunky	orange, chunky
crystal size, mm	0.05 × 0.12 × 0.25	0.20 × 0.20 × 0.40	0.35 × 0.40 × 0.50
space group	monoclinic; $P2_1/c$	tetragonal; $P4$	triclinic; $P\bar{1}$
cell dimens			
a, Å	14.901 (7)	11.113 (1)	7.040 (2)
b, Å	8.611 (4)		7.891 (3)
c, Å	13.830 (6)	12.614 (3)	11.716 (8)
α, deg			98.67 (4)
β, deg	104.57 (3)		92.50 (4)
γ, deg			112.93 (3)
vol, Å^3	1717.5 (13)	1557.6 (4)	558.8 (5)
Z	4	4	2
form wt	406.3	357.26	293.11
density$_{calcd}$, mg/m^3	1.571	1.523	1.653
abs coeff, mm^{-1}	0.762	0.83	1.07
$F(000)$	824	727.74	299.89
diffractometer used	Nicolet R3m/V	Enraf-Nonius, CAD4	Enraf-Nonius, CAD4
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.7093)	Mo Kα (0.7093)
temp, K	room	room	room
monochromator	highly oriented graphite crystal	highly oriented graphite crystal	highly oriented graphite crystal
2θ range, deg	2.5–50.0	2.0–50.0	2.0–50.0
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg/min	2.93–14.65	1.03–8.24	1.37–8.24
scan range, deg	1.00 + Kα separation	0.65 + 0.35 tan θ	0.85 + 0.35 tan θ
bgd meas	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time	time spent on background at each ends is quarter of peak scan time	time spent on background at each ends is quarter of peak scan time
std reflctns	3 measd/50 ref	3 measd/2 h	3 measd/2 h
index ranges	$-17\le h\le 17$, $-10\le k\le 0$, $0\le l\le 16$	$0\le h\le 13$, $0\le k\le 13$, $0\le l\le 14$	$-8\le h\le 7$, $0\le k\le 9$, $-13\le l\le 13$
no of reflctns collcted	2972 (1300 > 3.0$\sigma(I)$)	1585 (1211 > 2$\sigma(I)$)	2259 (2006 > 2$\sigma(I)$)
no. of independ reflctns	2623 (1215 > 3.0$\sigma(I)$)	1432 (1211 > 2$\sigma(I)$)	2076 (2006 > 2$\sigma(I)$)
T_{min}/T_{max}	0.920/0.858	0.979/0.996	0.950/0.999
solution	Patterson methods	Patterson methods	Patterson methods
extctn corrctn	x = −0.000 10 (5)[a]	g = 3.4 (4)[b]	g = 0.32 (6)[b]
hydrogen atom	fixed isotropic U	fixed refinement flag	fixed refinement flag
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0003F^2$	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$
final R indices, %	R = 3.50, R_w = 3.21	R = 2.4, R_w = 2.3	R = 2.3, R_w = 2.8
goodness of fit	1.24	1.74	1.68
largest and mean σ	0.118, −0.001	0.040, 0.001	0.034, 0.001
data to parameter ratio	5.6:1	6.7:1	13.74:1
largest diff peak, e/Å^3	0.45	0.27	0.41
largest diff hole, e/Å^3	−0.42	0.21	0.56

[a] Where $F^* = F(1 + 0.002F^2 \sin 2\theta)^{-1/4}$. [b] Where $F_c = kF_c/(1 + g\beta F_c^2)^{1/4}$.

= 7.3 Hz, J_{34} = 10.0 Hz, J_{45} = 1.8 Hz; endo isomer δ 1.11, 1.19 (d, d, 3 H, CH_3), 1.60 (d, 1 H, H^1), 2.02 (m, 1 H, H^5), 2.57 (t, 1 H, H^4), 2.60 (d, 1 H, H^2), 3.50 (m, 1 H, H^3), 5.20 (s, 5 H, C_5H_5), $J_{5\text{-}CH_3}$ = 6.6 Hz, J_{13} = 10.3 Hz, J_{23} = 6.6 Hz, $J_{34} = J_{45}$ = 9.9 Hz. Anal. Calcd for $C_{13}H_{16}MoO_2$: C, 52.00; H, 5.33. Found: C, 52.32; H, 5.68.

Reaction of 3d with CH_3OH and H_2O. This reaction was conducted in a procedure similar to that in the section above, and $CpMo(CO)_2$-(*anti*-η^3-1-$C_3H_4CH(Nu)CH_3$) (Nu = OCH_3 (**5g**), OH (**5h**)) were obtained in 62% and 51% yields, respectively. Complex **4g**. IR (Nujol): ν(CO) 1953 (s), 1872 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): exo isomer δ 1.07 (d, 3 H, CH_3), 1.40 (dd, 1 H, H^1), 2.33 (m, 1 H, C*H*(CH_3), 2.98 (dd, 1 H, H^2), 3.19 (s, 3 H, OCH_3), 3.76 (dd, 1 H, H^4), 3.89 (m, 1 H, H^3), 5.30 (s, 5 H, C_5H_5), J_{13} = 11.5 Hz, J_{23} = 7.2 Hz, J_{34} = 7.4 Hz, $J_{4CH(CH_3)}$ = 2.0 Hz, $J_{CH_3\text{-}CH(CH_3)}$ = 6.0 Hz. MS (12 eV): 318 (M$^+$), 262 (M$^+$ − 2CO). Anal. Calcd for $C_{13}H_{16}MoO_3$: C, 43.37; H, 5.00. Found: C, 43.20; H, 5.11. Complex **4h**. IR (Nujol): ν(CO) 1956 (s), 1876 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 1.22 (d, 3 H, CH_3), 1.45 (dd, 1 H, H^1), 2.94 (m, 1 H, $CHCH_3$), 3.04 (dd, 1 H, H^2), 3.83 (t, 1 H, H^4), 3.99 (m, 1 H, H^3), 5.29 (s, 5 H, C_5H_5), J_{13} = 11.7 Hz, J_{23} = 7.8 Hz, J_{34} = 8.1 Hz, $J_{4\text{-}CH(CH_3)}$ = 8.0 Hz, $J_{CH_3\text{-}H}$ = 6.4 Hz. Anal. Calcd for $C_{12}H_{14}MoO_3$: C, 47.68; H, 4.64. Found: C, 47.40; H, 4.62.

Synthesis of $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4C(CH_3)NCHMe_2$) (5a) and Its Iminium Salt (5b). (i) Compound **2b** (3.0 g, 10 mmol) was treated with 4 mL of BF_3·OEt_2 in THF at −78 °C. Immediately the solution turned dark red; isopropylamine (5.9 g, 100 mmol) was added, with stirring for 0.5 h. The solution was warmed to room temperature and evaporated to dryness. Elution of the residues through a silica column produced an orange band, which was collected and evaporated to dryness. Recrystallization of the residue produced block-shaped red crystals (1.62 g, 5.0 mmol). IR (CH_2Cl_2): ν(CO), 1949 (s), 1874 (s), ν(C=N) 1601 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): exo isomer only δ 0.98 (d, 1 H, H^1), 1.04, 1.08 (d, d, 3 H, 3 H, 2CH_3), 1.67 (d, 1 H, H^4), 1.94 (s, 3 H, $CNCH_3$), 2.85 (m, 1 H, NCH), 5.05 (m, 1 H, H^3), 5.22 (s, 5 H, C_5H_5), J_{13} = 12.0 Hz, J_{23} = 7.0 Hz, J_{34} = 10.1 Hz, $J_{H\text{-}CH_3}$ = 6.0 Hz. MS (12 eV): 315 (M$^+$ − CO), 287 (M$^+$ − 2CO). Anal. Calcd for $C_{15}H_{19}NMoO_2$: C, 52.79; H, 5.59; N, 4.11. Found: C, 52.94; H, 5.50; N, 3.88.

(ii) HBF_4 in ether (0.10 mL) was added to **5a** (0.15 g, 0.44 mmol) in 20 mL of ether with rapid stirring. A red precipitate gradually formed after stirring for 3 h; the precipitate was collected by filtration and washed twice with ether. Recrystallization from an acetone/ether solution produced red block crystals (0.18 g, 0.41 mmol). IR (Nujol): ν(CO) 1963 (s), 1888 (s), ν(C=N) 1612 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): exo isomer δ 1.37, 1.39 (d, d, 3 H, 3 H, 2 CH_3), 1.70 (dd, 1 H, H^1), 1.92 (d, 1 H, H^4), 2.27 (s, 3 H, CH_3), 3.00 (dd, 1 H, H^2), 4.73 (m, 1 H, H^3), 5.59 (s, 5 H, C_5H_5), J_{13} = 10.1 Hz, J_{23} = 7.3 Hz, J_{34} = 9.8 Hz; endo isomer δ 1.36, 1.37 (d, d, 3 H, 3 H, 2 CH_3), 2.30 (s, 3 H, CH_3), 2.78 (d, 1 H, H^1), 3.08–3.10 (complex m, 2 H, H^2 + C*H*Me_2), 4.20 (d, 1 H, H^2), 4.74 (m, 1 H, H^3), 5.63 (s, 5 H, C_5H_5), J_{13} = 10.7 Hz, J_{23} = 6.4 Hz, J_{34} = 9.8 Hz, $J_{CH_3\text{-}CHMe_2}$ = 6.2 Hz. Anal. Calcd for $C_{15}H_{20}NMoO_2BF_4$: C, 41.99; H, 4.66; N, 3.26. Found: C, 42.11; H, 4.88; N, 3.50.

Reaction of 5b with $NaBH_4$. Compound **5b** (0.10 g, 0.23 mmol) in 25 mL of THF was added to $NaBH_4$ (0.02 g, 0.53 mmol) and the resultant mixture was stirred for 5 min. During this period, the red solution immediately turned from red to yellow. The solution was concentrated and 1 mL of 1 M HCl/H_2O was added and evaporated to dryness; the residues were eluted through a silica column with a THF/hexane (1:1) mixture as the eluting solution. A yellow band was developed, collected, and evaporated to dryness to yield a yellow oil (0.07 g, 0.47 mmol). The product was confirmed to be **4d** by its mass and ^{1}H NMR spectral data.

Synthesis of $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4COC_2H_5$) (6a). Complex **2b** (0.20 g, 0.67 mmol) in 30 mL of THF was treated with an ether solution (1.0 mL, 0.70 mmol) of LDA at −78 °C. As the solution turned deep yellow, CH_3I (0.15 g, 1.06 mmol) was added and the resultant mixture

was stirred for 0.5 h. The solution was warmed to room temperature and evaporated to dryness. Elution through a silica column with hexane/ether (1:1) solvent produced a yellow band. Upon concentration, an orange viscous oil of **6a** was obtained in 85% yield (0.18 g, 0.57 mmol). IR (Nujol): ν(CO) 1958 (s), 1886 (s), 1671 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (q, 3 H, CH_3), 1.24 (d, 1 H, H^1), 1.91 (d, 1 H, H^4), 2.47, 2.54 (m, m, COH_2), 2.99 (d, 1 H, H^2), 4.98 (m, 1 H, H^3), 5.52 (m, 1 H, H^3), J_{13} = 11.4 Hz, J_{23} = 7.2 Hz, J_{34} = 9.8 Hz, J_{H-CH_3} = 6.5 Hz. MS (12 eV): 316 (M$^+$), 260 (M$^+$ - 2CO). Anal. Calcd for $C_{13}H_{14}O_3$: C, 49.68; H, 4.46. Found: C, 49.82; H, 4.72.

Synthesis of $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4COCH_2CH(OH)R$) (R = Ph (6b), CH_3 (6c), $(CH_3)_2CH$ (6a)). (i) In a typical reaction, the enolate prepared above (1.0 mmol) was treated with PhCHO (0.20 g, 1.99 mmol) at −78 °C and the resultant mixture was stirred for 0.5 h. A 20-mL aqueous NH_4Cl (6 M) solution was added, and the solution was concentrated to 10 mL. Ether (30 mL) was added and stirred rapidly. The organic layer was decanted, and the aqueous solution was twice extracted with 30 mL of ether. The combined extracts were evaporated to dryness to produce a yellow oil **6b**, which was further purified through a silica column (0.30 g, 0.74 mmol). IR (400 MHz, $CDCl_3$): ν(CO) 1954 (s), 1882 (s), 1665 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): major diastereoisomer (87%) δ 1.35 (dd, 1 H, H^1), 1.85 (d, 1 H, H^4), 2.84 (dd, 1 H, COH*H'*), 3.00 (dd, 1 H, CO*H*H'), 3.02 (dd, 1 H, H^2), 5.04 (m, 1 H, H^3), 5.10 (dd, 1 H, C*H*OH), 5.08 (s, 5 H, C_5H_5), 7.2–7.5 (m, 5 H, C_6H_5), J_{12} = 1.3 Hz, J_{13} = 11.3 Hz, J_{23} = 7.1 Hz, J_{34} = 9.5 Hz, J_{COHH} = 16.7 Hz, $J_{H'CH(OH)}$ = 8.8 Hz, $J_{HCH(OH)}$ = 4.0 Hz; minor diastereoisomer (13%, selected peak) δ 1.33 (dd, 1 H, H^1), 2.89 (dd, 1 H, COH*H'*), 2.91 (dd, 1 H, CO*H*H'), 3.20 (dd, 1 H, H^2), 5.05 (m, 1 H, H^3), 5.16 (dd, 1 H, C*H*OH), 5.18 (s, 5 H, C_5H_5). ^{13}C NMR (100 MHz, $CDCl_3$): major diastereoisomer δ 40.2 (CH^1H^2), 48.9 (CHH^1), 50.0 (CH^4), 70.7, 71.1 (CH(OH) + CH^3), 126.0, 127.7, 128.5, 143.2 (C_6H_5), 207.4 ($COCH^4$). MS (12 eV): 408 (M$^+$), 380 (M$^+$ - CO), 352 (M$^+$ - 2CO). Anal. Calcd for $C_{19}H_{18}MoO_4$: C, 56.16; H, 4.43. Found: C, 56.00; H, 4.04.

(ii) Complex **6c** (R = CH_3, 70% yield). IR (CH_2Cl_2): ν(CO) 1954 (s), 1882 (s), 1665 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): major diastereoisomer (78%), exo form δ 1.32 (d, 1 H, H^1), 1.21 (d, 3 H, CH_3), 1.84 (d, 1 H, H^4), 2.51 (dd, 1 H, COH*H'*), 2.73 (dd, 1 H, CO*H*H'), 3.03 (d, 1 H, H^2), 4.16 (m, 1 H, C*H*(OH)), 5.02 (m, 1 H, H^3), 5.21 (s, 5 H, C_5H_5), J_{13} = 11.2 Hz, J_{23} = 7.2 Hz, J_{34} = 9.8 Hz, $J_{COHH'}$ = 17.2 Hz, $J_{H'CHMe}$ = 9.3 Hz, J_{HCHMe} = 2.8 Hz, J_{CHMe} = 6.3 Hz; minor isomer (22%, selected peak) δ 1.87 (d, 1 H, H^1), 2.65 (dd, 1 H, COH*H'*), 2.68 (dd, 1 H, CO*H*H'), 4.18 (m, 1 H, C*H*COH), 5.32 (s, 5 H, C_5H_5), J_{13} = 10.0 Hz, $J_{H'CHMe}$ = 9.4 Hz, J_{HCHMe} = 1.8 Hz. MS (12 eV): 346 (M$^+$), 318 (M$^+$ - CO), 290 (M$^+$ - 2CO). Anal. Calcd for $C_{14}H_{16}MoO_3$: C, 48.84; H, 4.65. Found: C, 48.90; H, 4.72.

(iii) Complex **6d**. IR (Nujol): ν(CO) 1956 (s), 1880 (s), 1665 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): major diastereoisomer (53%) δ 0.91, 0.93 (d, d, 3 H, 3 H, C*H*Me), 1.65 (m, 1 H, C*H*Me$_2$), 1.84 (dd, 1 H, COH*H'*), 2.70 (d, 1 H, CO*H*H'), 2.99 (d, 1 H, H^2), 3.69 (m, 1 H, C*H*OH), 5.01 (m, 1 H, H^3), 5.21 (s, 5 H, C_5H_5), J_{13} = 11.3 Hz, J_{23} = 7.4 Hz, J_{34} = 9.4 Hz, $J_{COHH'}$ = 16.5 Hz, $J_{H'(CHOH)}$ = 9.8 Hz, $J_{H(CHOH)}$ = 2.3 Hz; minor diastereoisomer (47%) δ 0.91, 0.93 (d, d, 3 H, 3 H, CH*Me*$_2$), 1.27 (d, 1 H, H^1), 1.65 (m, 1 H, C*H*Me$_2$), 1.88 (d, 1 H, H^4), 2.60 (dd, 1 H, COH*H'*), 2.62 (dd, 1 H, CO*H*H'), 2.99 (d, 1 H, H^2), 3.76 (m, 1 H, C*H*(OH)), 5.0 (m, 1 H, H^3), 5.21 (s, 5 H, C_5H_5), J_{13} = 11.3 Hz, J_{23} = 7.4 Hz, J_{34} = 9.4 Hz, $J_{H'CH(OH)}$ = 11.3 Hz, $J_{H(CHOH)}$ = 1.1 Hz. MS (12 eV): 372 (M$^+$), 316 (M$^+$ - 2CO). Anal. Calcd for $C_{16}H_{20}MoO_4$: C, 51.61; H, 5.38. Found: C, 51.48; H, 5.26.

Synthesis of 6e. Complex **6b** (0.16 g, 0.40 mmol) in 25 mL of THF was added to $NaBH_4$ (0.02 g, 0.53 mmol) and the resultant mixture was stirred for 40 min. A 1 M HCl/H_2O solution was added until the solution reached pH = 7.0. After removal of the solvent, the residues were eluted through a silica column with THF/hexane (1:1) as the eluting solvent. A yellow band was developed, collected, and evaporated to dryness to give a yellow oil (0.14 g, 0.35 mmol). IR (Nujol): ν(CO) 1939 (s), 1854 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): exo isomer (72%) δ 0.76 (dd, 1 H, H^1), 1.78 (t, 1 H, H^4), 2.08 (m, 2 H, CHH'), 2.47 (br s, 1 H, OH), 2.69 (dd, 1 H, H^2), 3.12 (br s, 1 H, OH), 3.90 (m, 1 H, C*H*(OH)), 3.99 (m, 1 H, H^3), 5.07 (d, 1 H, C*H*(OH)Ph), 5.28 (s, 5 H, C_5H_5), 7.35–7.60 (m, 5 H, C_6H_5), J_{13} = 10.5 Hz, J_{23} = 7.4 Hz, J_{12} = 2.0 Hz, J_{34} = J_{4H} = 9.6 Hz, $J_{H'CHPh}$ = 7.9 Hz; endo isomer (28%) δ 2.08–2.20 (m, 2 H, CHH'), 2.63 (d, 1 H, H^2), 2.78 (t, 1 H, H^4), 3.58 (m, 1 H, H^3), 3.92 (m, 1 H, C*H*Ph), 5.20 (s, 5 H, C_5H_5), 7.34–7.60 (m, 5 H, C_6H_5), J_{13} = 9.2 Hz, J_{23} = 6.5 Hz, J_{34} = J_{4H} = 9.2 Hz. MS (FAB): 410 (M$^+$). Anal. Calcd for $C_{19}H_{20}MoO_4$: C, 55.61; H, 4.88. Found: C, 55.72; H, 4.92.

Synthesis of 7a and 7b. (i) $NOBF_4$ (0.40 g, 3.7 mmol) was added to **2g** (1 g, 3.3 mmol) in 10 mL of CH_3CN, and the resultant solution was stirred for 5 min; 80 mL of ether was added to the solution to yield an orange precipitate. After filtration, the crude product was recrystallized from CH_3CN/ether to give a dark red crystalline solid **7a** (1.0 g, 2.5 mmol). IR (CH_3CN): ν(CO) 2100 (s) cm^{-1}; ν(CO) 1660 (s) cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN): δ 1.50 (d, 3 H, CH_3), 3.03 (d, 1 H, H^1), 4.53 (m, 1 H, H^5), 4.86 (m, 2 H, H^2 + H^4), 5.52 (td, 1 H, H^3), 6.45 (s, 5 H, C_5H_5), J_{13} = 13.9 Hz, J_{23} = 7.7 Hz, J_{34} = 11.7 Hz, J_{45} = 6.4 Hz, J_{5CH_3} = 6.4 Hz. Anal. Calcd for $C_{11}H_{14}MoO_3NBF_4$: C, 33.79; H, 3.60; N, 3.58. Found: C, 34.00; H, 3.72; N, 3.69.

(ii) LiCl (0.12 g, 2.8 mmol) in 5 mL of THF was added to **7a** (1.0 g, 2.56 mmol) in 20 mL of acetone, at 23 °C, and the mixture was stirred for 30 min. After evaporation of the solution to dryness, the residue was eluted through a silica column with CH_2Cl_2 as the eluting solvent. A red band was collected and evaporated to dryness to yield **7b** as an orange solid (0.32 g, 1.02 mmol). IR (CH_3CN): ν(NO) 1660 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (d, 3 H, CH_3), 2.38 (dd, 1 H, H^1), 2.71 (br s, 1 H, OH), 2.99 (ddd, 1 H, H^2), 4.22 (d, 1 H, H^5), 5.06 (q, 1 H, H^4), 5.84 (s, 5 H, C_5H_5), 6.04 (m, 1 H, H^3), J_{13} = 12.8 Hz, J_{23} = 6.8 Hz, J_{12} = 2.1 Hz, J_{2Cp} = 1.2 Hz, J_{34} = 10.8 Hz, J_{5CH_3} = 6.5 Hz. MS (12 eV): 297 (M$^+$ - OH). Anal. Calcd for $C_{10}H_{14}MoO_2NCl$: C, 38.54; H, 4.53; N, 4.50. Found: C, 38.43; H, 4.41; N, 4.44.

Decomplexation of 7b with Benzaldehyde. **7b** (0.30 g, 0.96 mmol) was dissolved in CH_2Cl_2 (3.0 mL) containing PhCHO (0.25 g, 2.34 mmol) and CH_3OH (0.13 g, 4.06 mmol) and the mixture was stirred at 23 °C for 60 h. After removal of solvent, the residues were eluted with a TLC plate using Et_2O/hexane (1:4) as solvent; 0.14 g (0.50 mmol) of **7c** was obtained after removal of the solvent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (d, 3 H, CH_3), 2.26 (ddd, 1 H, H^3), 4.24 (td, 1 H, H^4), 4.65 (dd, 1 H, H^7), 4.96 (dd, 1 H, H^6), 5.06 (d, 1 H, H^2), 5.76 (s, 1 H, H^1), 5.90 (ddd, 1 H, H^5), 7.20–7.30 (m, 5 H, C_6H_5), J_{23} = 2.3 Hz, J_{34} = 2.1 Hz, $J_{4\text{-}CH_3}$ = 6.2 Hz, J_{35} = 10.0 Hz, J_{56} = 19.0 Hz, J_{57} = 10.4 Hz. MS (12 eV): 281 (M + 1). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.54; H, 7.24.

Hydrolysis of 7c. A 0.15-g sample of **7c** (0.535 mmol) was dissolved in 40 mL of THF/MeOH (1:1 volume ratio) containing with 0.21 g of *p*-toluenesulfonic acid (0.11 mmol). The mixture was stirred for 5 h, followed by addition of 30 mL of Et_2O. The organic layer was twice washed with 10 mL of H_2O and evacuated to dryness. The residues were chromatographed on a silica column to give **7d** (50 mg, 0.30 mmol). IR (Nujol): ν(OH) 3377 (s), ν(C=C) 1637 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (d, 3 H, CH_3), 2.10 (ddd, 1 H, H^2), 3.96 (qd, 1 H, H^3), 4.87 (dd, 1 H, H^5), 4.93 (d, 1 H, H^1), 5.20 (dd, 1 H, H^6), 5.92 (ddd, 1 H, H^4), J_{12} = 4.9 Hz, J_{23} = 2.5 Hz, J_{24} = 9.7 Hz, J_{45} = 17.2 Hz, J_{46} = 10.4 Hz. Anal. Calcd for $C_{12}H_{19}O_2$: C, 73.87; H, 9.80. Found: C, 73.92; H, 9.73.

Synthesis of 8a–8c. These complexes were prepared by procedures similar to those described in the above sections. (i) Complex **8a** (48% yield). IR: ν(NO) 1648 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97 (complex, 2 H, CH_2), 2.33 (d, 1 H, H^1, J = 9.9 Hz), 2.94 (dd, 1 H, C*H*(OH), J = 6.8, 2.2 Hz), 2.98 (s, 1 H, OH), 4.36 (d, 1 H, H^2, J = 6.0 Hz), 4.92 (d, 1 H, H^4, J = 10.0 Hz), 5.04 (dd, 1 H, C*H*(OH)Ph), 5.81 (s, 5 H, C_5H_5), 5.91 (m, 1 H, H^3, J = 10.0, 9.9, 6.0 Hz). Anal. Calcd for $C_{17}H_{20}NO_3ClMo$: C, 48.87; H, 4.82; N, 3.35. Found: C, 48.94; H, 4.92; N, 3.45. (ii) Complex **8b** (51% yield). IR (Nujol): 3414 (br), 1639 (w), 1603 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (ddd, 1 H, J = 14.8, 8.8, 2.4 Hz), 2.10 (ddd, 1 H, J = 14.8, 10.3, 2.8 Hz), 2.31 (ddd, 1 H, J = 10.0, 2.3, 2.3 Hz), 4.45 (ddd, 1 H, J = 10.3, 2.4, 2.3 Hz), 4.77 (dd, 1 H, J = 17.4, 2.0 Hz), 4.97 (dd, 1 H, J = 10.5, 2.0 Hz), 5.03 (dd, 1 H, J = 8.8, 2.8 Hz), 5.13 (d, 1 H, J = 2.3 Hz), 5.84 (s, 1 H), 5.98 (m, 1 H), 7.24–7.63 (m, 15 H, PhH). MS (12 eV): 387 (M - H). Anal. Calcd for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78. Found: C, 81.00; H, 6.80. (iii) Complex **8c** (43% yield). IR (CH_2Cl_2): 3372 (br), 1637 (w), 1602 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67 (ddd, 1 H, J = 14.5, 7.6, 2.7 Hz), 1.96 (ddd, 1 H, J = 14.5, 10.0, 3.3 Hz), 2.07 (ddd, 1 H, J = 9.8, 4.0, 2.4 Hz), 2.57 (s, 1 H, OH), 2.83 (s, 1 H, OH), 3.15 (s, 1 H, OH), 4.52 (m, 1 H), 4.75 (dd, 1 H, J = 17.4, 2.0 Hz), 4.97 (m, 2 H), 5.12 (dd, 1 H, J = 10.4, 2.0 Hz), 5.97 (m, 1 H), 7.45–7.14 (m, 10, PhH). MS (12 eV): 299 (M + 1). Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.72; H, 7.52.

X-ray Diffraction of 2b, 2e, and 6b. Single crystals of **2b**, **2e**, and **6b** were sealed in glass capillaries under an inert atmosphere. Data for **2b** and **2e** were collected on a Nonius CAD4 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 NRCCSDP package. Data for **6b** were collected on a Nicolet R3M/V diffractometer, using graphite-monochromated Mo Kα radiation. The structure of **6b** was solved by the Patterson superposition method; all data reduction and structure refinement were performed with the SHELXTL

PLUS package. Crystal data, details of the data collection, and structure analysis are summarized in Table V. For all structures, all nonhydrogen atoms were refined with anisotropic parameters. All hydrogen atoms included in the structure factor calculations were placed in idealized positions.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support of this work.

Supplementary Material Available: Crystal data and full tables of bond lengths and angles and final atomic coordinates (14 pages); observed and calculated structural factors for **2b**, **2e**, and **6b** (25 pages). Ordering information is given on any current masthead page.

Molecular Semiconductors from Bifunctional Dithia- and Diselenadiazolyl Radicals. Preparation and Solid-State Structural and Electronic Properties of 1,4-[$(E_2N_2C)C_6H_4(CN_2E_2)$] (E = S, Se)

A. Wallace Cordes,[1a,*] Robert C. Haddon,[1b,*] Richard T. Oakley,*[,1c] Lynn F. Schneemeyer,[1b] Joseph V. Waszczak,[1b] Kelly M. Young,[1c] and Neil M. Zimmerman[1b]

Contribution from the Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, AT&T Bell Laboratories, Murray Hill, New Jersey 07974, and Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.
Received June 7, 1990

Abstract: The reactions of 1,4-phenylenebis[*N,N,N'*-tris(trimethylsilyl)amidine] with sulfur and selenium dichlorides yield, respectively, the 1,4-phenylenebis(dithiadiazolium) and bis(diselenadiazolium) dichlorides 1,4-[$(E_2N_2C)C_6H_4(CN_2E_2)$]Cl_2 (E = S, Se). Reduction of these materials with triphenylantimony affords the corresponding diradical species 1,4-[$(E_2N_2C)C_6H_4(CN_2E_2)$], which can be purified by high vacuum sublimation. The crystal structures of 1,4-[$(E_2N_2C)C_6H_4(CN_2E_2)$] (E = S, Se) are both monoclinic, space group $P2_1/n$. The crystal packing consists of sheets of interleaved columns of weakly associated diradical units (dimers); the mean intradimer separation is 3.34/3.37 Å (E = S/Se), and the mean interdimer separation is 3.68/3.71 Å (E = S/Se). The sulfur compound is an insulator, but the selenium material has a room temperature pressed pellet resistivity of about 100 Ω cm. Magnetic susceptibility measurements show the solids to be predominantly diamagnetic with variable amounts of paramagnetic defects in the lattice. While the exact mechanism of conduction remains to be established, these systems represent the first structurally characterized conducting materials constructed from neutral molecular radicals. Extended Hückel band structure calculations reveal band gaps of 0.84/0.69 eV (E = S, Se) for the crystalline solids. The calculated band dispersions show a high degree of three-dimensionality; to our knowledge these are the most isotropic organic molecular solids yet to be reported.

Introduction

Research into the development of low-dimensional molecular conductors and superconductors has focused heavily on the use of charge-transfer salts,[2] e.g., TTF TCNQ, or radical ion (Bechgaard) salts such as those based on the TMTSF and BEDT-TTF donors.[3] Conductivity in these materials depends on efficient overlap between the π-systems of the molecular building blocks, which are often stacked in uniform one-dimensional columns. The susceptibility of these columns to undergo a Peierls distortion[4] with consequent loss of conductivity requires designing structures in which intercolumnar interactions are optimized. Considerable effort has therefore been directed toward modifying both the size and shape of the counterion.

An alternative approach to molecular conductors, one which obviates the need for counterions, involves the use of neutral rather than charged π-radicals. Several variations[5] on the originally proposed phenalenyl framework[6] have been pursued, but a paucity of structural data has hindered progress. Recent advances in heterocyclic sulfur nitrogen chemistry,[7] however, particularly the characterization of a number of stable radical systems,[8] have

(1) (a) University of Arkansas. (b) AT&T Bell Laboratories. (c) University of Guelph.

(2) See, for example: (a) Garito, A. F.; Heeger, A. J. *Acc. Chem. Res.* **1974**, *7*, 232. (b) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79. (c) Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519.

(3) (a) Wudl, F. *Acc. Chem. Res.* **1984**, *17*, 227. (b) Williams, J. M.; Beno, M. A.; Wang, H. H.; Leung, P. C. W.; Emge, T. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.* **1985**, *18*, 261. (c) Williams, J. M.; Wang, H. H.; Emge, T. J.; Gieser, U.; Beno, M. A.; Leung, P. C. W.; Carlson, K. D.; Thorn, R. J.; Schultz, A. J.; Whangbo, M.-H. *Prog. Inorg. Chem.* **1987**, *35*, 51. (d) Inokuchi, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1747.

(4) Peierls, R. E. *Quantum Theory of Solids*; Oxford, London, 1953; p 108.

(5) (a) Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629. (b) Kaplan, M. L.; Haddon, R. C.; Hirani, A. M.; Schilling, F. C.; Marshall, J. H. *J. Org. Chem.* **1981**, *47*, 675. (c) Haddon, R. C.; Chichester, S. V.; Stein, S. M.; Marshall, J. H.; Mujsce, A. M. *J. Org. Chem.* **1987**, *52*, 711. (d) Canadell, E.; Shaik, S. S. *Inorg. Chem.* **1987**, *26*, 3797. (e) Nakasuji, K.; Yamaguchi, M.; Murata, I.; Yamaguchi, K.; Fueno, T.; Ohya-Nishiguchi, H.; Sugano, T.; Kinoshito, M. *J. Am. Chem. Soc.* **1989**, *111*, 9265.

(6) (a) Haddon, R. C. *Nature (London)* **1975**, *256*, 394. (b) Haddon, R. C. *Aust. J. Chem.* **1975**, *28*, 2343.

(7) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299.

(8) (a) Wolmershäuser, G.; Schnauber, M.; Wilhelm, T. *J. Chem. Soc., Chem. Commun.* **1984**, 573. (b) Wolmershäuser, G.; Schnauber, M.; Wilhelm, T.; Suicliffe, L. H. *Synth. Met.* **1986**, *14*, 239. (c) Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O., Jr.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594. (d) Wolmershäuser, G.; Wortmann, G.; Schnauber, M. *J. Chem. Res. Synop.* **1988**, 358. (e) Wolmershäuser, G.; Johann, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 920. (f) Hayes, P. J.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 1346. (g) Boerè, R. T.; Cordes, A. W.; Hayes, P. J.; Oakley, R. T.; Reed, R. W. *Inorg. Chem.* **1986**, *25*, 2445. (h) Oakley, R. T.; Reed, R. W.; Cordes, A. W.; Craig, S. L.; Graham, J. B. **1987**, *109*, 7745. (i) Boerè, R. T.; French, C. L.; Oakley, R. T.; Cordes, A. W.; Privell, J. A. J.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 7710. (j) Awere, E. G.; Burford, N.; Haddon, R. C.; Parsons, S.; Passmore, J.; Waszczak, J. V.; White, P. S. *Inorg. Chem.* In press. (k) Wolmershäuser, G.; Krafl, G. *Chem. Ber.* **1990**, *123*, 881.

0002-7863/91/1513-582$02.50/0