A pathway that is consistent with these results is illustrated in Scheme I. Photolysis of **1** gives cleavage of the benzylic carbon–silicon bond to form the silaallyl 1,6-biradical intermediate A. This intermediate can either dissociate to give the vinylsilene, which leads to products **2**, or ring close to give the ring-expanded cyclic silene B, leading to products **4**. These results indicate the free silene intermediates 1-phenyl-1-vinyl-2-neopentylsilene and the eight-membered bicyclic silene B are formed under our photolysis conditions. The fact that the yields of **2** and **4** increase and that **3** is not found in the photolyses in the presence of methoxytrimethylsilane is consistent with our suggestion that the biradical A is the precursor of all the products observed.[15] The formation of B from A represents the first demonstrated example of a radical ring-closure reaction giving rise to a silene. Attempts to trap B with use of 2,3-dimethyl-1,3-butadiene were unsuccessful, giving rise only to polymeric products. Further investigations of the chemistry of B are in progress.

Table I. Product Yields and Distributions[a] for the Photolysis of 1 in the Presence of Various Trapping Reagents

R–OMe	2	3	(*E*)-4	(*Z*)-4
R = H (a)	3	36[b]	10	7
R = D (b)	4	38[c]	12	8
R = Me_3Si (c)	12[d]	0	23	6

[a] Determined by GLC with use of internal standard methods. [b] A 69:31 mixture of two diastereomers. [c] A 68:32 ratio of two diastereomers. [d] An 83:17 ratio of two diastereomers.

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(14) The numbering for the hydrogens in **4c** is the same as that used for **4a**.[11] Characterization data for (*E*)-**4c** are as follows. ^1H NMR (δ): –0.11, s, 9 H, $Si(CH_3)_3$; 0.47, t, $J^{35} = J^{36} = 6$ Hz, H^3; 1.05, s, 9 H, $C(CH_3)$; 1.87, dd, $J^{82} = 5$, $J^{89} = 17$ Hz, H^8; 2.03, dd, $J^{92} = 2$, $J^{98} = 17$ Hz, H^9; 2.09, ddd, $J^{21} = 2$, $J^{29} = 2$, $J^{28} = 5$ Hz, H^2; 2.52, dd, $J^{63} = 6$, $J^{67} = 5$ Hz, H^6; 2.53, dd, $J^{53} = 6$, $J^{57} = 5$ Hz, H^5; 2.96, s, 3 H, OCH_3; 4.09, t, $J^{75} = J^{76} = 5$ Hz, H^7; 4.22, d, $J^{12} = 2$ Hz, H^1; 6.94–7.48, m, 13 H, aryl hydrogens. ^{13}C NMR (δ): 0.92, $Si(CH_3)_3$; 12.21, $SiCH_2$; 30.22, $C(\mathit{C}H_3)_3$; 33.06, $\mathit{C}(CH_3)_3$; 36.00, $Si–CH_2\mathit{C}H_2$; 40.77, Si–CH; 42.94, $\mathit{C}H_2–C(CH_3)_3$; 47.34 and 49.07, benzyl carbons; 51.62, OCH_3; 126.18–141.28, 16 peaks, aryl and vinyl carbons. Characterization data for (*Z*)-**4c** are as follows. ^1H NMR (δ): –0.26, s, 9 H, $Si(CH_3)_3$; 0.85, dd, $J^{45} = 13$, $J^{46} = 5$ Hz, H^4; 0.87, s, 9 H, $C(CH_3)_3$; 1.45, dd, $J^{82} = 6$, $J^{89} = 10$ Hz, H^8; 1.99, ddd, $J^{21} = 2$, $J^{28} = 6$, $J^{29} = 7$ Hz, H^2; 2.07, dd, $J^{92} = 7$, $J^{98} = 10$ Hz, H^9; 2.37, ddd, $J^{54} = 13$, $J^{56} = 14$, $J^{57} = 2$ Hz, H^5; 2.66, ddd, $J^{64} = 5$, $J^{67} = 8$, $J^{65} = 14$ Hz, H^6; 2.75, s, 3 H, OCH_3; 4.33, dd, $J^{75} = 2$, $J^{76} = 8$ Hz, H^7; 4.48, d, $J^{12} = 2$ Hz, H^1; 6.91–7.53, m, 13 H, aryl hydrogens. ^{13}C NMR (δ): 0.08, $Si(CH_3)_3$; 11.82, $SiCH_2$; 30.78, $C(\mathit{C}H_3)_3$; 32.81, $\mathit{C}(CH_3)_3$; 37.40, $Si–CH_2\mathit{C}H_2$; 39.31, SiCH; 45.78, $\mathit{C}H_2–C(CH_3)_3$; 46.61 and 47.54, benzyl carbons; 51.42, OCH_3; 125.85–143.22, 16 peaks, aryl and vinyl carbons. For a mixture of (*E*)- and (*Z*)-**4c**, data are as follows. MS (*m/z* (relative intensity)): 441 (4) $[M - t\text{-}Bu]^+$, 398 (27), 235 (23), 220 (15), 178 (30), 163 (100), 73 (35), 59 (30). Anal. Calcd for $C_{32}H_{42}Si_2O$: C, 77.05; H, 8.49. Found: C, 77.85; H, 8.36.

(15) In response to a reviewer's suggestion an attempt to intercept the biradical intermediate A with tri-*n*-butyltin hydride was carried out. When the photolysis was carried out to 75% decomposition in the presence of excess hydride, only polymeric products were obtained, as is the case for the photolysis of **1** in the absence of a trap. The rate of decomposition was faster in the presence of tri-*n*-butyltin hydride, suggesting that ring closure to re-form **1** is another competing reaction of A.

Novel Pathway of a Molybdenum-Mediated Cyclization Reaction

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Summary: **Synthesis of the new molybdenum η^4-trimethylene cationic complex $CpMo(CO)_2(\eta^4\text{-}MeC_4H_5)BF_4$ (4) has been described. Deprotonation of 4 gives $CpMo(CO)_2(\eta^3\text{-}2\text{-vinylallyl})$, which undergoes an unusual cyclization with TCNE and PhCHO (BF_3 catalyzed) to afford six-membered-ring products. The molecular structure of a bicyclic product based on this cyclization has been described.**

Transition-metal-mediated cyclization of organic substrates is recognized to be an important methodology in modern organic chemistry.[1-6] This synthetic approach has proved effective in the construction of basic skeletons of complex pericyclic natural products. Recently, there has been considerable interest in the utilization of organomolybdenum complexes in organic reactions;[6-9] complexes of the type $CpMoL_2(\eta^3\text{-allyl})$ represent one case in which the organic moiety has exhibited interesting chemical reactivity. Nevertheless, as noted in early papers,[9-11] the scope of investigation has been limited mainly to use of a metal fragment as a chiral auxiliary, and the aspect of the chemistry of cyclization has been neglected.[12] In this paper, we wish to report a novel pathway of molybde-

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[†] National Tsing Hua University.

[‡] National Taiwan University.

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(11) (a) Green, M.; Greenfield, S.; Grimshire, M. J.; Kersting, M.; Orpen, A. G.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 97. (b) Green, M.; Greenfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18. (c) Allen, S. R.; Barnes, S. G.; Green, M.; Moran, G.; Murrall, N. W.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1175.

(12) Reports of molybdenum-mediated cyclizations are few; see: (a) Davidson, J. L.; Green, M.; Nyathi, J. N.; Scott, C.; Stone, F. G. A.; Welch, J. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1976**, 714. (b) Roustan, J. L.; Merour, J. Y.; Charrier, C.; Cadiot, P. *J. Organomet. Chem.* **1979**, *169*, 39. (c) Bailey, N. A.; Chell, P. L.; Manuel, C. P.; Mukhopadhyay, A.; Rodgers, D.; Tabbron, H. E.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2397.

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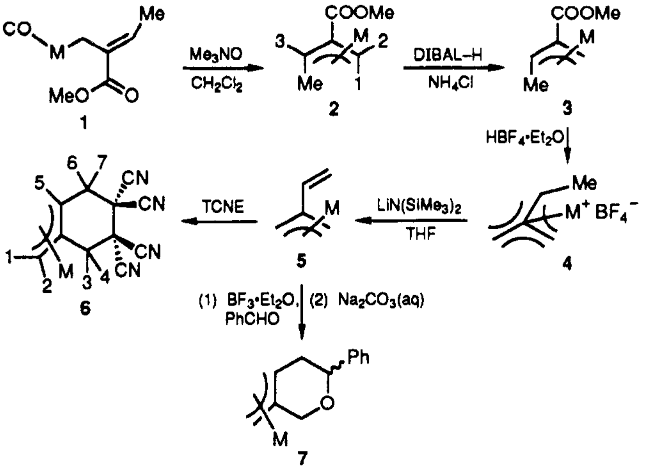
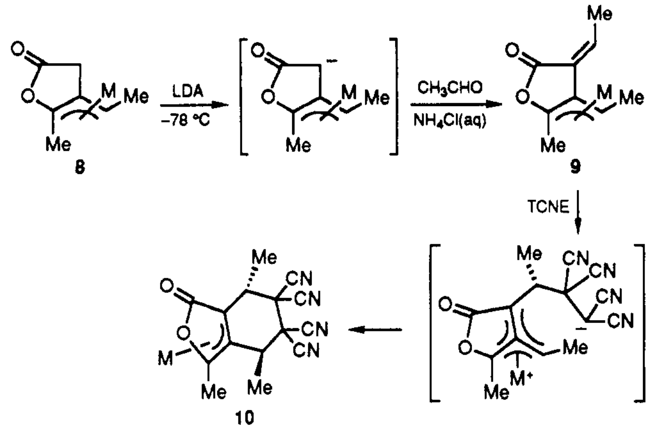
Scheme I



M = CpMo(CO)₂

Scheme II



M = CpMo(CO)₂

num-mediated cyclization in which both the key step and intermediate of the mechanism are of interest in organometallic chemistry.

Conveniently prepared from the reaction of CpMo(CO)$_3$Na and (*E*)-methyl 2-(chloromethyl)-2-butenoate[13] in cold THF (1 equiv, -78 °C, 3 h), complex 1 was obtained as a yellow oil after workup (65% yield). Stirring 1 with excess anhydrous Me$_3$NO (10 equiv) in CH$_2$Cl$_2$ (23 °C, 36 h) gave CpMo(CO)$_2$(*anti*-η^3-1-methyl-2-carbomethoxyallyl) (2) in 71% yield. The anti methyl group is indicated[8] by the chemical shift (δ 4.66 ppm) of H^3 being more downfield than that (δ 3.56 ppm) of the syn proton H^1. The reaction of 2 with DIBAL-H (2 equiv, CH$_2$Cl$_2$) for 36 h produced CpMo(CO)$_2$(*anti*-η^3-1-methyl-2-(hydroxymethyl)allyl) (3) in 70% yield after workup. Slow addition of HBF$_4$·Et$_2$O to 3 in anhydrous ether immediately results in a yellow precipitate of CpMo(CO)$_2$(η^4-trimethylenemethane)BF$_4$ (4), which is fairly stable to air. In the NMR spectra of 4 (CD$_3$CN, 23 °C), the five trimethylene protons resonate at δ 2.64–4.27 ppm and the four trimethylene carbons resonate at δ 49.5, 56.3, 60.9, and 111.4 (central carbon) ppm, respectively. Its IR spectrum in a Nujol mull exhibits the terminal ν(Mo–CO) bands at 2064 (s) and 2015 (s) cm^{-1} indicative of a η^4-trimethylene cation.[11c,14] The methyl group of 4 is highly acidic and is readily deprotonated by LiN(SiMe$_3$)$_2$ to afford CpMo(CO)$_2$(η^3-2-vinylallyl) (5) in 75% yield after workup.

A novel $2\pi + 2\pi + 2$ allyl $- \pi$ cyclization occurs as 5 reacts with TCNE (1 equiv) in CH$_2$Cl$_2$ (23 °C, 1 h), to afford 6 (68%) after workup. A six-membered ring (Scheme I) is assignable to 6 on the basis of its ^{1}H NMR data: δ 2.28 (s, H^1), 2.87 (s, H^2), 3.12 (d, H^6, J = 15.6 MHz), 3.22 (d, H^5, J = 6.1 Hz), 3.54 (d, H^3, J = 17.8 Hz), 3.77 (dd, H^7, J = 15.6, 6.1 Hz), 3.92 (d, H^4, J = 17.8 Hz), 5.50 (s, 5 H, Cp). In the presence of BF$_3$·OEt$_2$, complex 5 undergoes analogous cyclization with PhCHO in CH$_2$Cl$_2$ (0 °C, 0.5 h) to afford pyran 7 as a 1:1 mixture of diastereomers (52%), which are separable by fractional crystallization.

It is possible to construct a bicyclic molecule based on the new cyclization in Scheme I. Complex 9 was readily prepared from the reaction of the enolate of 8[15] with CH$_3$CHO in cold THF (-78 °C, 1 h) in 56% yield (Scheme II). Its further reaction[16] with TCNE (1 equiv, benzene, 2 h) gave 10 in 25% yield after workup. An X-ray structural analysis reveals[17] that each unit cell contains two independent molecules. The ORTEP drawing of one enantiomer (Figure 1) shows that a six-membered ring is linked to the γ-lactone ring to give a bicyclic ring and the CpMo(CO)$_2$ unit has migrated to the C(4A), C(9A), and C(10A) atoms. The two methyls on the six-membered ring are mutually trans. Notably, this cyclization proceeds with high stereospecificity and a single diastereomer was detected in the ^{1}H NMR spectrum. The structure of 10 conforms to that derived from the ionic mechanism in which TCNE attacks twice on the vinyl and allyl groups opposite to the CpMo(CO)$_2$ fragment. An interesting aspect here is the nucleophilic nature of the vinyl carbon, which behaves quite distinctly from its organic counterpart.

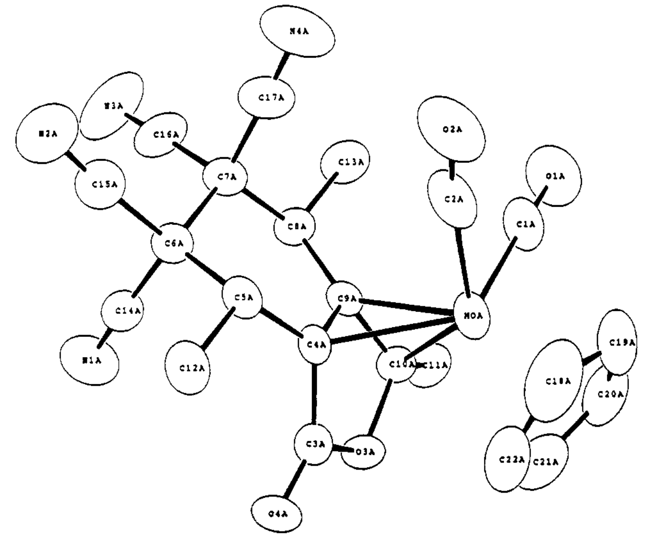


Figure 1. ORTEP drawing of one of the two independent molecules of 10. Pertinent bond distances: Mo(A)–C(4A) = 2.139 (4) Å, Mo(A)–C(9A) - 2.230 (4) Å, Mo(A)–C(10A) = 2.250 (4) Å, C(3A)–O(4A) = 1.208 (5) Å, C(3A)–O(3A) = 1.370 (5) Å.

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[15] The synthesis of 8 has appeared in an earlier paper; see: Yang, G. H.; Peng, S. M.; Lee, G. H.; Liu, R. S. *J. Chem. Soc., Chem. Commun.* **1991**, 478.

[16] In Scheme II, the vinyl methyl of 9 cis to the lactone is inferred from the crystal structure of its phenyl analogue. The latter crystallizes in the monoclinic system, space group $P2_1/c$, with a = 12.081 (2) Å, b = 11.835 (2) Å, c = 12.929 (5) Å, β = 92.08 (1)°, final R = 0.027, and R_w = 0.023 for 2699 reflections $>2\sigma(I)$ out of 3237 unique reflections and 236 parameters.

[17] Complex 10 crystallizes in the monoclinic system, space group $P2_1/c$, with a = 24.253 (3) Å, b = 9.019 (2) Å, c = 19.480 (2) Å, β = 92.09 (1)°, and Z = 8. Each unit cell contains two independent molecules. Crystal data were collected on an Enraf-Nonius CAD-4 diffractometer, using Mo Kα radiation. Final R = 0.032 and R_w = 0.027 for 4116 reflections $>2\sigma(I)$ out of 5559 unique reflections.

In summary, a new molybdenum η^4-trimethylene cation has been synthesized and fully characterized. A novel cyclization involving this cationic intermediate has been demonstrated.[18] Further expansion of this cyclization involving the use of dienophiles such as ketones and α,β-unsaturated ketones will be the focus of future studies.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support of this work; special funds (1990–1993) from National Tsing Hua University are also acknowledged.

Supplementary Material Available: Spectral data and satisfactory elemental analyses of 1–7, 9, and 10, tables of atomic coordinates, thermal parameters, bond lengths and angles, and crystal data for 10, and a drawing of molecule B of 10 (11 pages); a listing of structure factors for 10 (19 pages). Ordering information is given on any current masthead page.

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[18] We have placed 5 and 9 under CO (2 atm), which does not produce their η^1-allyl compounds. Therefore, the cyclization described in this paper cannot be attributed to a Diels–Alder reaction between η^1-allyl and dienophiles.

A New Catalyst for the Epimerization of Secondary Alcohols: Carbon–Hydrogen Bond Activation in the Rhenium Alkoxide Complexes (η^5-C_5R_5)Re(NO)(PPh_3)(OCHRR′)

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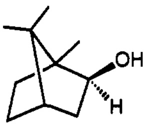
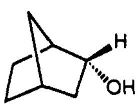
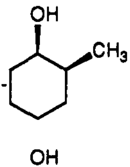
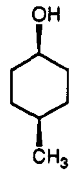
Summary: The methoxide complexes (η^5-C_5R_5)Re(NO)(PPh_3)(OCH_3) (R = H, Me) catalyze the title reaction (65–90 °C, C_6H_5R solvent); intermediate secondary alkoxide complexes undergo PPh_3 dissociation and sequential epimerization at rhenium and carbon.

Unsymmetrical secondary alcohols, RR′CHOH, constitute ubiquitous stereogenic units in organic molecules. Accordingly, the need to manipulate configuration frequently arises. For example, considerable attention has been directed at methods for the catalytic epimerization of secondary alcohols.[1,2] In this communication, we disclose an efficient and mechanistically novel epimerization catalyst that operates in aromatic hydrocarbon solvents at 65–90 °C.

The diastereomerically pure alcohols shown in Table I were dissolved in deuterated benzene or toluene. Then 10 mol % of the racemic chiral rhenium methoxide complex (η^5-C_5H_5)Re(NO)(PPh_3)(OCH_3) (1)[3] was added. The samples were heated, and the organic products were assayed by ^{1}H NMR spectroscopy and in some cases GLC. In each case, the alcohols epimerized to a mixture of diastereomers. Small amounts of the corresponding ketones were usually produced (3–5%).[4] Also, *endo*-borneol gave a product distribution identical with that obtained from *exo*-borneol.

Table I. Data for the Catalytic Epimerization of Secondary Alcohols by (η^5-C_5H_5)Re(NO)(PPh_3)(OCH_3) (1)

Starting alcohol	time (h)	temp (°C)	isomer ratio found[a]	literature ratio[b]
 ((±)-exo-borneol)	48	65[c]	67:33 (endo/exo)	71:29
 ((±)-endo-norborneol)	180	70[c]	76:24 (exo/endo)	80:20
(±)- 	80	80[c]	70:30 (trans/cis)	77:23
	40	90[d]	70:30 (trans/cis)	70:30

[a] Assayed by ^{1}H NMR spectroscopy. The *endo*/*exo*-borneol and -norborneol ratios were confirmed by GLC. [b] These ratios were obtained in benzene with use of Raney Ni or in 2-propanol with use of Al(O-*i*-Pr)$_3$/acetone.[2] Equilibrium ratios in benzene sometimes differ significantly from those in 2-propanol. [c] In benzene-d_6. [d] In toluene-d_8.

Parallel reactions were conducted with the *pentamethyl*cyclopentadienyl complex (η^5-C_5Me_5)Re(NO)(PPh_3)(OCH_3) (1-Me$_5$).[5] Rates were 2–5 times faster. In

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[1] (a) Feghouli, G.; Vanderesse, R.; Fort, Y.; Caubere, P. *Tetrahedron Lett.* **1988**, *29*, 1383. (b) Vanderesse, R.; Feghouli, G.; Fort, Y.; Caubère, P. *J. Org. Chem.* **1990**, *55*, 5916. (c) Choudary, B. M. *Polyhedron* **1986**, *5*, 2117. (d) Nugent, W. A.; Zubyk, R. M. *Inorg. Chem.* **1986**, *25*, 4604.

[2] (a) Eliel, E. L.; Schroeter, S. H.; Brett, T. J.; Biros, F. J.; Richer, J.-C. *J. Am. Chem. Soc.* **1966**, *88*, 3327 and references therein. (b) Wilcox, C. F., Jr.; Sexton, M.; Wilcox, M. F. *J. Org. Chem.* **1963**, *28*, 1079.

[3] (a) Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. (b) Agbossou, S. K.; Smith, W. W.; Gladysz, J. A. *Chem. Ber.* **1990**, *123*, 1293.

[4] Ketone byproducts are also observed with other epimerization catalysts.[1b] A C_6D_6 solution of camphor (formed in the borneol epimerizations) and the hydride complex (η^5-C_5H_5)Re(NO)(PPh_3)(H) was kept at 65 °C for 48 h. No reaction occurred. Also, the epimerization of *exo*-borneol was repeated in the presence of camphor-*d* (1.0 equiv). No deuterium was incorporated in the product borneol, as assayed by ^{1}H NMR spectroscopy and mass spectrometry. Thus, the ketone byproducts form irreversibly.

[5] This compound was prepared by a procedure analogous to that reported for 1 in ref 2a.

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