intensities of two standard reflections remeasured every 2 h throughout the experiment. The absorption correction, made by an empirical method,[17] led to transmission factors on F of 0.82-1.10. Of 12099 reflections measured, 2210 were related by symmetry and they were averaged to give 1105 independent ones and R(internal) of 0.023. Only unique reflections with $I \geq 3\sigma(I)$, of which there were 6505, were used in the structure analysis.

The structure was determined by the heavy atom method. The positions of the three nickel atoms were obtained from a Patterson function, and those of the remaining non-hydrogen atoms, as well as of a large number of hydrogen atoms, from the appropriate difference electron density maps. These maps also revealed that in the cationic complex the chloride and carbonyl ligands are disordered, each over two sites lying above opposite faces of the Ni_3 triangle (Figure 2). The disorder was accounted for by assigning occupancy parameters α to Cl(1), C(1), and O(1), and 1 - α to Cl(1'), C(1'), and O(1') atoms. The refinement of this parameter led to $\alpha = 0.70$ (2).

The structure was refined by a three-large-blocks approximation to the normal matrix, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(|F_o|)$. The carbon and oxygen atoms of the disordered carbonyl ligand were allowed isotropic displacement parameters, and all other non-hydrogen atoms anisotropic displacement parameters. In the final calculations the scattering of all 90 hydrogen atoms was accounted for by adding their fixed contribution to the structure factors; they were assigned a common isotropic displacement parameter, fixed at $U = 0.080$ Å^2, and their geometrically deduced positional parameters were constrained to C-H = 1.0 Å. The refinement converged at $R = 0.035$ and $R_w = 0.041$. In the final difference electron density map the highest peak was 0.64 ϵ Å^{-3}. The residual electron density, mostly distributed in the vicinity of the solvent molecule, as well as its high atomic displacement parameters (Table III), suggested that the structure of this molecule may be disordered. The final atomic coordinates are shown in Table III.

All calculations were carried out using the GX program package.[18] Neutral-atom scattering factors were taken from ref 19.

Acknowledgment. We thank the NSERC (Canada) for financial support and NATO for a travel grant.

Supplementary Material Available: Tables of anisotropic displacement parameters (SI), bond lengths (SII), and bond angles (SII) (8 pages). Ordering information is given on any current masthead page.

OM920198Z

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Reaction Chemistry between $CpMo(CO)_2(\eta^3$-2-vinylallyl) and Electrophiles: New Carbon–Carbon Bond Formation through Molybdenum η^4-Trimethylenemethane Cationic Intermediates

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The compound $CpMo(CO)_2(\eta^3$-vinylallyl) (**5**) underwent a novel cyclization with TCNE and PhCHO (BF_3-catalyzed) in CH_2Cl_2 to afford a six-membered ring product. Treatment of **5** with $PhCHO/BF_3{\cdot}Et_2O$ in benzene yielded a Mo-η^4-trimethylenemethane salt, generated from the electrophilic addition of PhCHO to the vinyl group of **5**. Characterization of this cation has been achieved by IR and ^1H NMR spectra and by its subsequent reaction with $NaBH_3CN$ and R_2CuLi (R = Ph, PhC≡C). Formation of this trimethylenemethane cation is also observed for a similar BF_3-catalyzed reaction between methyl vinyl ketone and acetone in benzene. The synthetic utility of this carbon–carbon-forming reaction in organic synthesis has been investigated and is described.

Introduction

The chemistry of electrophilic addition to the unsaturated hydrocarbon ligand on a neutral metal complex is an important topic in organometallic chemistry.[1-5] This reaction generally leads to the formation of metal-stabilized carbocations. Transition-metal η^1-allyl compounds may represent an instance in which the ligand reacts with H^+, Br^+, and CH_3^+ to give η^2-alkene cations.[6,7] If tetracyanoethylene and *p*-toluenesulfonyl isocyanate are used as electrophiles, the reaction pathway follows a [3 + 2] cycloaddition pathway.[8,9] Recently, Green et al. reported[10] that a vinyl group adjacent to a π-Mo–allyl moiety could be protonated to give Mo-η^4-*s-trans*-pentadiene cations. Along this direction, we report here the chemistry of

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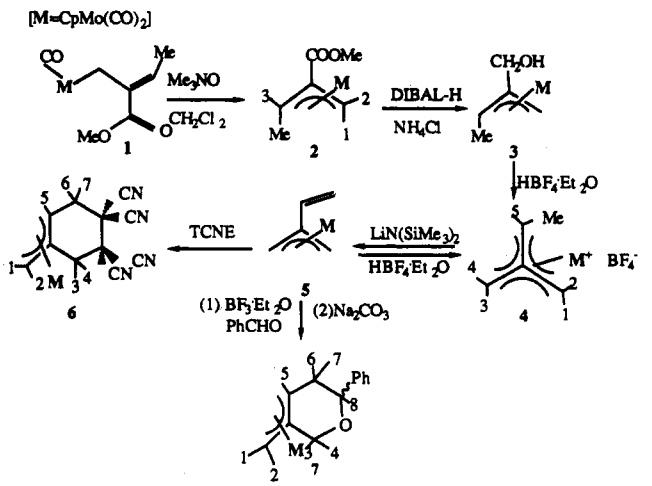
Scheme I

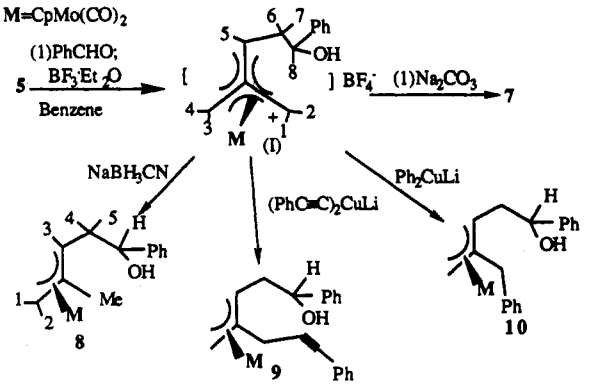


electrophilic addition of the $CpMo(CO)_2(\eta^3$-2-vinylallyl) complex which gives the molybdenum-η^4-trimethylenemethane cation. To make this reaction more useful, the carbon–carbon bond-forming process through generation of this cation is the objective of our work. Part of this paper has been previously communicated.[11]

Results and Discussions

Molybdenum-Mediated Cyclizations. The reaction between $CpMo(CO)_3Na$ and *E*-methyl-2-chloromethyl-2-butenoate[12] in cold THF (−78 °C, 2 h) smoothly delivered the η^1-*E*-2-carbomethoxyl-3-methylallyl compound (**1**) as a pure oil in 65% yield after workup. In contrast with its 2-methyl ketone allyl analogue,[13] complex **1** is stable and no intramolecular cyclization occurs even at elevated temperatures (60 °C, THF, 2 h). Decarbonylation of **1** (Scheme I) with excess anhydrous Me_3NO (10 molar equiv) afforded $CpMo(CO)_2(anti$-η^3-1-methyl-2-carbomethoxyallyl) (**2**) in 71% yield. The chemical shift of H^3 (δ 4.66 ppm) lies more downfield than that of the syn-proton H^2 (δ 3.56 ppm), which indicates that the methyl group is trans to the central carbomethoxyl group. Treatment of **2** with 2.0 molar equiv of DIBAL-H in THF (23 °C, 36 h) produced $CpMo(CO)_2(anti$-η^3-1-methyl-2-(hydroxymethyl)allyl) (**3**) as a yellow oil in 70% yield after workup. Treatment of **3** with HBF_4·Et_2O in anhydrous ether at 0 °C immediately produced a yellow precipitate formulated as the $CpMo(CO)_2(\eta^4$-methyltrimethylenemethane)BF_4 cation (**4**) on the basis of elemental analyses and IR, and ^1H and ^{13}C NMR data. The assignment of ^1H NMR resonances to individual protons was solved by 2D-COSY and NOESY spectra. Exceptional NMR parameters are the long-range coupling magnitudes of J_{15} (3.2 Hz) and J_{24} (4.0 Hz), which are larger than those of the vicinal proton coupling J_{12} (1.5 Hz) and J_{34} (0 Hz). Previously Green et al. have also reported[14] a similar coupling pattern on the related $(C_5Me_5)Mo(CO)_2(\eta^4$-$R_2C_2H_4)^+$ salts. Deprotonation of **4** is best achieved with by $LiN(SiMe_3)_2$ (1.5 molar equiv) in ether, which afforded $CpMo(CO)_2(\eta^3$-2-vinylallyl) (**5**) as yellow crystals after workup. Protonation of **5** by CF_3SO_3H (98%, 1.5 molar equiv) in ether at room temperatures quantitatively regenerated the trimethylenemethane cation **4**.

Scheme II



For an electrophilic carbon–carbon bond-forming reaction, we first examined the reaction between **5** and tetracyanoethylene (TCNE) in CH_2Cl_2 (23 °C, 1 h), which afforded the adduct **6** in 68% yield after purification from a silica column. The elemental analysis is consistent with the given formula. According to a low-temperature ^1H NMR spectrum (−60 °C, d_8-toluene), two conformational isomers, i.e. exo and endo[15] in 1:10 ratio were present in the solution. The anti-proton H^1 resonance at δ 1.35 ppm was assigned to the exo isomer, but the H^1-proton resonance at δ 2.28 ppm was assigned to the endo isomer. With increasing temperatures, the proton resonances of two isomers became broad and eventually coalesced at 16 °C. For both isomers, the four methylene proton resonances $H^{3,4}$ and $H^{6,7}$ were observed within δ 3.0–4.5 ppm, indicating that the two CH^6H^7 and CH^3H^4 carbons are linked to the tetracyanoethylene fragment. Hence a six-membered ring is proposed for **6**. Treatment of **5** with 1 molar equiv of BF_3·OEt_2 and PhCHO in CH_2Cl_2 (0 °C), followed by treatment with aqueous Na_2CO_3 solution, afforded the pyran **7** as a 1:1 mixture of diastereomers (50%) which were separable by fractional crystallization. In a proton NOE experiment, irradiation of the H^4-signal at δ 3.93 ppm of one isomer produced an Overhauser enhancement in the intensity of the methylene proton H^6 (δ 2.62 ppm) by 2.5%; this information confirms a cyclized structure.

Mechanistic Studies. Compounds **6** and **7** represent the cases of a novel $2\pi + 2\pi$ + 2allyl-π cyclization, and their formation mechanism deserves further investigation. We placed **5** under CO (2 atm) and with PPh_3 (1.0 molar equiv), which produced no corresponding η^1-2-vinylallyl complex. Therefore the new cyclization here cannot be attributed to a Diels–Alder reaction between η^1-allyl and dienophiles. By the fact that the vinyl group of **5** can be protonated, it is rational to propose a trimethylenemethane zwitterion as an intermediate during cyclization. To verify this proposal, **5** was treated with a mixture of PhCHO/BF_3·Et_2O (1:1 molar equiv) in benzene at 23 °C (Scheme II), which gradually deposited a yellow semisolid quite stable to air. Its IR spectra in Nujol mull exhibited ν(CO) bands at 2058 (s) and 2008 (s) cm^{-1}, indicative of a cationic salt (I). The ^{19}F NMR spectra showed a single resonance at δ 149 ppm corresponding to a free BF_4^- ion.[16] Additional evidence to support this hydrated BF_4^- salt is the

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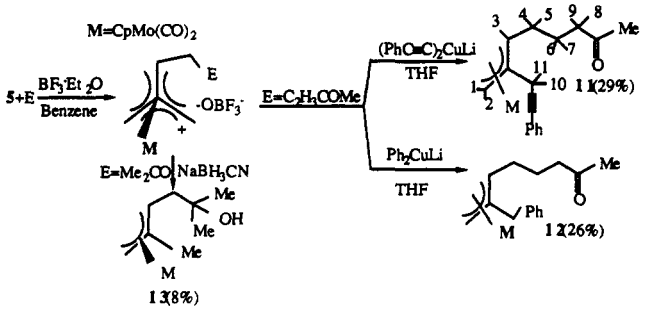
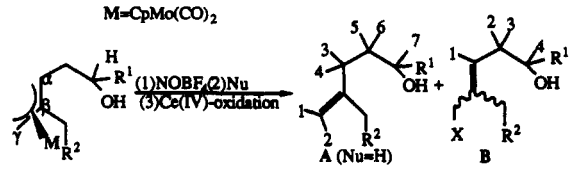
(16) Although in recent papers[16a,b] zwitterions with the BF_3O^- anion were believed to be primary products in this acid-catalyzed reaction. From the contamination of **4**, it is clear that H^+ has been generated during the reaction. This may cause further hydrolysis of this OBF_4^- ion to give I as the BF_4^- salt. (a) Agoston, G. E.; Cabal, M. P.; Turos, E. *Tetrahedron Lett.* **1991**, *32*, 3001. (b) Jiang, S.; Turos, E. *Ibid.* **1991**, *32*, 4639.

Scheme III



Scheme IV



Entry	Complex	R^1	R^2	Nu	Products	(yields[a])
1	8	Ph	H	$NaBH_3CN$	X=H(17)	A/B=2.0 (58%)
2	8	Ph	H	$NaBH_3CN$ (-25°C)	X=H(17)	A/B=0.54 (61%)
3	9	Ph	PhC≡C	$NaBH_3CN$	X=H(18)	A/B= 5.2(56%)
4	10	Ph	Ph	$NaBH_3CN$	X=H(19)	A/B= 4.6(58%)
5	14	$PhCH_2$	H	$NaBH_3CN$	X=H(20)	A/B=1.5 (69%)
6	15	$PhCH_2$	Ph	$NaBH_3CN$	X=H(21)	A/B= 3.9(60%)
7	16	$PhCH_2$	PhC≡C	$NaBH_3CN$	X=H(22)	A/B= 4.2(58%)
8	8	Ph	H	PhSNa	X=PhS (23)	B (E)only (60%)
9	10	Ph	Ph	NaOH	X=OH (24)	B(E)only (43%)
10	14	$PhCH_2$	H	NaOH	X=OH (25)	B (E)only (45%)

[a] Nucleophilic additions at the molybdenum nitrosyl salts were operated at 23°C except for entry 2.

ν(OH) band at 3580 cm^{-1} in Nujol mull. The ^1H NMR spectra of I showed that two diastereomers are present; part of their resonances are overlapped with those of 4 (ca. 10% by ^1H NMR integral). The latter is inseparable from I by fractional crystallization. ^1H NMR assignment of the observed resonances of I was aided by 2D-NOSEY and COSY spectra. Likewise, the coupling parameters J_{15}, J_{24} (3–4 Hz) are significantly larger than those of J_{12} and J_{34} (1–0 Hz). The η^4-trimethylenemethane structure of I can be also deduced from its subsequent reaction with nucleophiles such as $NaBH_3CN$, $(PhC{\equiv}C)_2CuLi$, and Ph_2CuLi in cold THF (0 °C, 2 h), which afforded the η^3-allyl compounds 8–10 (52%–60%) as a mixture of 1:1 diastereomers, further separable by preparative TLC plates. In all cases, no efforts were made to isolate and characterize the small amount of allyl compounds which resulted from nucleophilic addition to the cation 4. The *syn*-CH^4H^5 configurations of 8–10 were indicated by their chemical shifts of H^3 (δ 2.8–3.0 ppm) and H^1 (δ 1.7–1.8 ppm), very close to those (H^3, δ 2.76; H^1, δ 1.60) of *endo*-$CpMo(CO)_2(\eta^3\text{-}1\text{-}MeC_3H_4)$.[15] Treatment of I with Na_2CO_3 in THF (0 °C, 2 h), followed by hydrolysis gave the pyran 7 in 50% yield. This result provides direct experimental evidence to support I as the cyclization intermediate.

We extended this new acid-catalyzed carbon–carbon formation to other electrophiles such as methyl vinyl ketone and acetone. Similarly, a cationic salt was generated under the same conditions which reacted further with $(PhC{\equiv}C)_2CuLi$ and Ph_2CuLi in THF (–78 °C, 2 h) to give the products 11 and 12, respectively, in 29% and 26% yields. Likewise, 5 reacted with acetone in the presence of $BF_3{\cdot}Et_2O$ to give a cationic salt which was reduced with $NaBH_3CN$ in THF to yield 13 (8%). For other electrophiles such as alkyl halides, acyl halides, and anhydrides, no BF_3-catalyzed carbon–carbon formation occurred under the same conditions, which nevertheless gave yellow precipitates identified as 4 by ^1H NMR spectra. Notably, treatment of the zwitterions shown in Scheme III with Na_2CO_3 or $LiN(SiMe_3)_2$ in CH_2Cl_2 failed to give the corresponding cyclized compounds.

Decomplexation of Mo–π-Allyl Complexes. Although numerous transition-metal–η^4-trimethylenemethane complexes have been reported, they were prepared exclusively from the reaction between an unsaturated metal fragment with methylenecyclopropane or $CH_2{=}C(CH_2X)CH_2Y$ (X = Y = halides, OAc, Y = Me_3Si).[14,17,18] Among them, only (η^3-trimethylenemethane)PdL_2[19] is synthetically useful for organic reactions. It has long been recognized that metal-mediated carbon–carbon formation is one of the most important topics in modern synthetic chemistry. The fact that the new trimethylenemethane cations in our system are easily transformed to useful Mo–π-allyl complexes[20] by nucleophilic attack should make this reaction of much use in organic synthesis once the metal fragment is removed. The η^3-allyl compounds 14–16 given in Scheme IV were prepared in a similar fashion which involved the nucleophilic attack of $NaBH_3CN$, Ph_2CuLi, and $(PhC{\equiv}C)_2CuLi$ on the trimethylenemethane cation derived from 5 and $PhCH_2CHO$; the yields are 50%–55%. In a typical procedure for metal decomplexation, the η^3-allyl compounds were treated with an equimolar amount of $NOBF_4$ in CH_3CN to generate an electrophilic allyl cation,[21–23] which reacted in situ with nucleophiles to liberate an olefin after Ce(IV) oxidation. The results are summarized in Scheme IV. In entries 8–10, nucleophiles RS^- and OH^- add only at the C_γ carbon (CH_2) to produce internal olefins (B), consistent with the nucleophilic regiochemistry observed for $CpMo(CO)NO(\eta^3\text{-}syn\text{-}R\text{-}C_3H_4)^+$.[22] Compounds 23–25 are assumed to have the *E*-configuration, which is determined by a proton NOE difference experiment. For example, the H^1-proton (δ 5.76 ppm) of 25 has an Overhauser enhancement on the CH_2OH proton resonances (δ 4.84 ppm) as indicated by a 2.7% increase in intensities, but there is no effect on the CH_2Ph protons. Although H^- may add to both allylic cationic carbons at room temperature, C_α addition is preferred for bulky R^2 (R^2 = Ph, PhC≡C; entries 3, 4, 6, 7), which gives more external olefins (A). As a comparison of the results in entries 1 and 2, the hydride is envisaged to attack the C_γ carbon kinetically preferentially at –25 °C. Whereas at 23 °C C_α addition becomes the major pathway, which is presumably ther-

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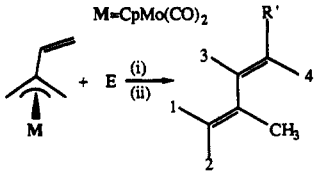
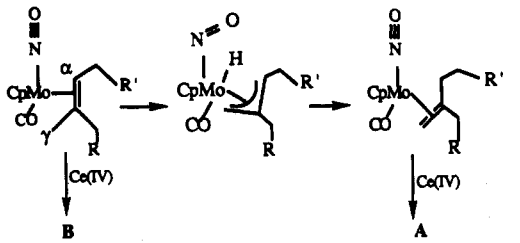
Scheme V



Entry	E	R'	(product no.)	yields[iii]
1	PhCHO	PhCH(OH)	26	58%
2	$PhCH_2CHO$	$PhCH_2CH(OH)$	27	54%
3	Me_2CHCHO	$Me_2CHCH(OH)$	28	55%
4	$t\text{-}C_4H_9CHO$	$t\text{-}C_4H_9CH(OH)$	29	50%
5	Me_2CHCH_2CHO	$Me_2CHCH_2CH(OH)$	30	45%
6	$CH_2CHCOC_2H_5$	$(CH_2)_2COC_2H_5$	31	22%
7	$CH_2CHCOCH_3$	$CH_2CH_2COCH_3$	32	18%

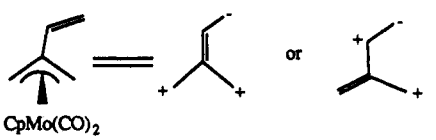
M=CpMo(CO)$_2$; reagents and conditons (i) $BF_3{\cdot}Et_2O$(1.0 equiv.), E(1.0 equiv.), benzene, 23°C, 2 h (ii) Me_3NO(5.0 equiv.), CH_3CN, 23°C, 24 h (iii) products were isolated and purified by preparative SiO_2-TLC-plate, and the yields were calculated based on the amount of 5 used.

modynamically favored. In principle, the isomerization of external olefin (B) to internal olefin (A) can be achieved



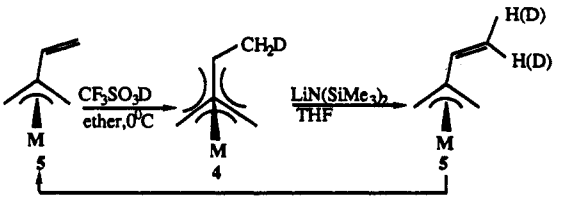
by low-valent metals through formation of metal hydride intermediates.[1] In our proposal, we believe that the initial η^2-internal olefin intermediate undergoes C_γ–H bond activation to give a Mo–η^3-allyl hydride intermediate, which may have a bent NO group to support 18 electrons. Further, hydride migration to the C_α carbon of this species will give a sterically more favorable η^2-external olefin.

For compounds **18**, **19** and **21**, **22**, we were unable to determine the geometries of internal olefins B as being in the *E* or *Z* configuration because the NOE experiments were hampered by the overwhelming amount of external olefins A in the mixture. In synthetic utility, the functional equivalence of **5** can be represented by the following two forms:

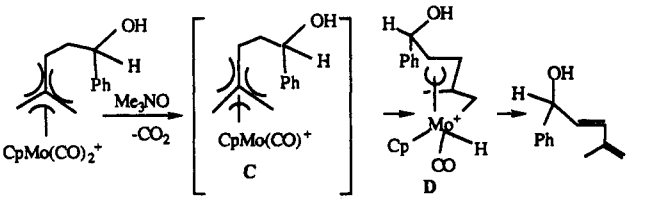


Decomplexation of Trimethylenemethane Cations. Pettit et al.[17] reported that transient biradical trimethylenemethane species were generated from Ce(IV)-oxidative decomposition of $(\eta^4\text{-}(CH_2)_3C)Fe(CO)_3$, which reacted in situ with TCNE to give a [3 + 2] cycloaddition adduct in small yield (4%). In order to find the possible functional equivalence of the trimethylenemethane diradical in our system, we treated our new molybdenum–trimethylenemethane cations with excess TCNE and anhydrous Me_3NO (5.0 molar equiv), which however produced complicated mixtures of organic compounds. Notably, as shown in Scheme V, treatment of the cations with anhydrous Me_3NO alone in CH_3CN gave 1-substituted-3-methyl-1,3-butadienes. When RCHO (R = Ph, $PhCH_2$, Me_2CH, $n\text{-}C_3H_7$) compounds were used as electrophiles, the yields were 45%–60%. For α,β-unsaturated ketones (entries 6 and 7), the corresponding 1,3-dienes were obtained in 20%–25% yields. Direct Ce(IV) oxidation of all

Scheme VI



Scheme VII



the cations above in CH_3CN failed to give any significant organic compound.

In functional equivalence, complex **4** is virtually identical to the 3-methyl-1,3-butadien-1-yl anion (CH_2=CMeCH=CH^-). We performed a deuterium-labeling experiment according to Scheme VI. A ca. 50% deuterium content on the vinylic CH_2 end of **5** was attained by repeated protonation (D^+)/deprotonation twice. ^2H NMR spectra of diene **26**, derived from the deuterated **5** and PhCHO revealed that both CH_3 and =CHC(OH)Ph were deuterated at a ca. 1:1 ratio, indicative of a hydrogen-migration process. We propose a mechanism shown in Scheme VII. After loss of CO by Me_3NO-promoted decarbonylation, the newly generated 16e C undergoes a β-hydrogen abstraction to give a 18e-η^5-isopentadienyl cation D, which after reductive elimination is expected to liberate the diene **26**. No evidence for formation of the trimethylenemethane diradical was observed in our system, which according to early reports[24] is expected to give the derivatives of methylenecyclopropanes and 1,4-dimethylenecyclohexane.

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 (Aldrich) at 110 °C. $Mo(CO)_6$, $NOBF_4$, CF_3SO_3H (98%), $HBF_4{\cdot}Et_2O$, $H(NSiMe_3)_2$, BuLi (1.6 M, hexane), methyl vinyl ketone, ethyl vinyl ketone, tetracyanoethylene, phenylacetylene, phenyl bromide, and aldehydes RCHO (R = Ph, $PhCH_2$, Me_2CH, $n\text{-}C_3H_7$, Me_2CHCH_2, Me_3C) (Aldrich) were used without further purification. $CpMo(CO)_3Na$[25] and *E*-methyl-2-(chloromethyl)-butenoate[12] were prepared according to procedures in the literature.

All ^1H (400 MHz, 300 MHz) ^2H (61.4 MHz), and ^{13}C NMR (100 MHz, 75.5 MHz) spectra were obtained on either a Brucker AM-400 or Varian Gemini-300 spectrometer; the chemical shifts of ^1H, ^{13}C, and ^{19}F NMR spectra were referenced to tetramethylsilane and CCl_3F. Microanalyses were performed at National Chengkung University, Tainan, ROC. Infrared spectra were recorded on a Perkin-Elmer 781 spectrophotometer.

(a) Synthesis of $CpMo(CO)_3(\eta^1$-*anti*-1-methyl-2-carbomethoxyallyl) (1). A tetrahydrofuran solution (50 mL) of $CpMo(CO)_3Na$ (5.36 g, 20.0 mmol) was stirred with *E*-methyl-2-(chloromethyl)-2-butenoate (2.97 g, 20.0 mmol) at 23 °C for 6 h. The solvent was removed under reduced pressure, leaving a

(24) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242 and references therein.
(25) Eisch, J. J., King, R. B., Eds. *Organometallic Synthesis*; Academic Press: New York, 1965; Vol. 1, p 114.

red residue, which was then chromatographed on a silica column with a hexane/ether (4:1) mixture as eluting solvent. After elution of a purple band of $[CpMo(CO)_3]_2$, 1 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 (4.65 g, 13.0 mmol). IR (Nujol): ν(CO) 2013 (s), 1918 (s), and 1706 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.62 (d, J = 7.2 Hz, CH_3), 2.37 (s, CH_2), 3.67 (OCH_3), 5.34 (s, 5 H, C_5H_5), 6.48 (q, J = 7.2 Hz, =$CHCH_3$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ -8.6 (Mo-CH_2), 14.4 (=CCH_3), 51.2 (O-CH_3), 93.0 (C_5H_5), 130.8, 140.5 (C=C), 169.3 (CO-OCH_3), 228.4, 240.6 (2 Mo-CO). Mass (12 eV): m/e 356 (M^+). Anal. Calcd for $C_{14}H_{14}MoO_5$: C, 46.94; H, 3.94. Found: C, 46.80; H, 4.05.

(b) Synthesis of $CpMo(CO)_2(\pi^3$-*anti*-1′-methyl-2′-carbomethoxyallyl) (2). A dichloromethane solution (25 mL) of 1 (7.16 g, 20.0 mmol) was stirred with anhydrous trimethylamine oxide (6.0 g, 80.0 mmol) at 0 °C for 18 h. After the solution was evaporated to dryness, the residues were twice extracted with ether (20 mL). 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 off, compound 2 was obtained as a yellow band as a hexane/ether eluting solvent was used. Removal of the solvent under reduced pressure, followed by crystallization from a saturated hexane/ether solution at 0 °C afforded a yellow crystalline solid (4.68 g, 14.2 mmol). IR (Nujol): ν(CO) 1954 (s), 1877 (s), and 1706 (s) cm^{-1}. ^1H NMR (400 MHz, 273 K, $C_6D_5CD_3$): δ 1.27 (d, J = 6.6 Hz, 3 H, CH_3), 1.49 (d, J = 1.0 Hz, H^1), 3.51 (s, 3 H, OMe), 3.56 (d, J = 1.0 Hz, 1 H, H^2), 4.66 (q, J = 6.6 Hz, 1 H, H^3), 4.80 (s, 5 H, C_5H_5). ^{13}C NMR (100 MHz, 253 K, $C_6D_5CD_3$): δ 18.2 (CH_3), 39.4 (CH^1H^2), 53.5 (OCH_3), 62.4 (*C*Me), 71.4 (*C*CO), 96.0 (C_5H_5), 172.3 (*C*O-OCH_3), 230.4, 238.2 (2 Mo-CO). Mass (12 eV): m/e 332 (M^+). Anal. Calcd for $C_{13}H_{14}MoO_4$: C, 47.29; H, 4.27. Found: C, 47.15; H, 4.38.

(c) Synthesis of $CpMo(CO)_2(\eta^3$-*anti*-1′-methyl-2′-hydroxyallyl) (3). Compound 2 (6.60 g, 20.0 mmol) in CH_2Cl_2 (20 mL) was treated with DIBAL-H (40 mmol, 1.2 M in 33.3 mL) in hexane at -78 °C, and the resulting mixture was stirred for 8 h. The solution was warmed to room temperatures and added to a saturated aqueous Na_2CO_3 solution. The ether layer was decanted, and the aqueous solution was twice extracted with ether (20 mL). The combined extracts 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 oil (4.28 g, 14.0 mmol). IR (Nujol): ν(CO) 1948 (s), 1868 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.23 (d, J = 5.0 Hz, 3 H, CH_3), 1.80 (s, 1 H, H^1), 1.84 (s, 1 H, H^2), 1.90 (s, OH), 2.65 (d, J = 2.9 Hz, 1 H, C*H*H′(OH)), 3.19 (d, J = 2.9 Hz, 1 H, CH*H*′(OH)), 3.42 (q, J = 5.0 Hz, H^3), 5.17 (s, 5 H, C_5H_5). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 25.9 (CH_3), 31.1 (CH^1H^2), 34.1 (*C*H^{3}Me), 70.8 (CHH′(OH)), 97.0 (C_5H_5), 114.5 (*C*CH^{3}Me), 242.3, 240.6 (2 Mo-CO). Mass (12 eV): m/e 302 (M^+). Anal. Calcd for $C_{12}H_{14}MoO_3$: C, 47.70; H, 4.67. Found: C, 47.58; H, 4.82.

(d) Synthesis of $[CpMo(CO)_2(\eta^4$-(methylmethylene)dimethylenemethane)]BF_4 (4). Complex 3 (6.12 g, 20.0 mmol) in ether (30 mL) was treated with HBF_4·Et_2O (3.23 g, 20.0 mmol) at -78 °C, resulting in formation of a yellow precipitate (5.15 g, 14.0 mmol), which was collected by filtration. Recrystallization from a saturated CH_2Cl_2/ether solution produced yellow crystalline solid 4 (4.11 g, 11.2 mmol). IR (Nujol): ν(CO) 2064 (s), 2015 (s) cm^{-1}. ^1H NMR (300 MHz, CD_3CN): δ 1.23 (d, J = 6.7 Hz, 3 H, CH_3), 2.64 (d, J = 4.3 Hz, 1 H, H^4), 2.88 (s, 1 H, H^3), 3.21 (dd, J = 3.2, 1.5 Hz, 1 H, H^1), 3.59 (dd, J = 4.3, 1.5 Hz, 1 H, H^2), 4.27 (dq, J = 6.7, 3.2 Hz, 1 H, H^5), 5.68 (s, 5 H, C_5H_5). ^{13}C NMR (75.5 MHz, CD_3CN): δ 17.5 (CH_3), 49.5 (CH_2), 56.3 (C′H_2), 60.9 (*C*CH$_3$), 90.1 (C_5H_5), 111.4 (*C*CH$_2$), 215.3, 215.5 (2 Mo-CO). Anal. Calcd for $C_{12}H_{13}O_2BF_4Mo$: C, 38.75; H, 3.53. Found: C, 38.81; H, 3.70.

(e) Synthesis of $CpMo(CO)_2(\eta^3$-2-vinylallyl) (5). A hexane solution (20 mL) of $LiN(SiMe_3)_2$ (60.0 mmol) was added to 4 (7.36 g, 20.0 mmol) in 20 mL of THF at 23 °C and stirred for 1 h, which led to complete dissolution of 4. The solution was evaporated to dryness, and the residues were extracted twice with ether (20 mL). Further elution through a silica column with a hexane/ether (4:1) mixture produced a yellow band, which was collected, concentrated, and recrystallized from a saturated hexane solution to produce a yellow crystalline solid (4.26 g, 15.0 mmol). IR (Nujol): ν(CO) 1950 (s), 1857 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.16 (s, 2 H, anti-H), 3.29 (s, 2 H, syn-H), 5.03 (d, J = 16.5 Hz, =C*H*H′), 5.55 (d, J = 10.3 Hz, =CH*H*′), 5.60 (s, 5 H, C_5H_5), 6.13 (dd, 1 H, J = 16.5, 10.3 Hz, C*H*=CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 33.8 (*C*H$_2$), 90.1 (C_5H_5), 100.8 (*C*CH=C), 109.7 (=CH_2), 138.5 (*C*=CH_2), 239.6 (2 Mo-CO). Mass (12 eV): m/e 286 (M^+). Anal. Calcd for $C_{12}H_{12}MoO_2$: C, 50.72; H, 4.26. Found: C, 50.65; H, 4.37.

(f) Reaction of 5 with Tetracyanoethylene. Complex 5 (0.30 g, 1.05 mmol) was stirred with tetracyanoethylene (0.130 g, 1.05 mmol) in benzene (10 mL) for 1 h. During this period, a yellow precipitate gradually deposited and was collected by filtration. Recrystallization from a saturated THF/hexane solution afforded yellow crystalline solid 6 (2.96 g, 0.71 mmol). IR (Nujol): ν(CO) 1953 (s), 1877 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 213 K, 400 MHz): endo isomer, δ 2.28 (s, 1 H, H^1), 2.77 (s, 1 H, H^2), 3.12 (d, 1 H, J = 15.6 Hz, H^6), 3.22 (d, 1 H, J = 5.1 Hz, H^5), 3.54 (d, 1 H, J = 17.8 Hz, 1 H, H^3), 3.77 (dd, J = 15.6, 5.1 Hz, 1 H, H^7), 3.92 (d, 1 H, J = 17.8 Hz, H^4), 5.50 (s, 5 H, C_5H_5); exo isomer (selected peaks), δ 1.35 (s, 1 H, H^1), 2.87 (s, 1 H, H^2), 2.98 (d, 1 H, J = 15.6 Hz, H^5), 4.08 (d, 1 H, J = 17.8 Hz, H^4), 4.30 (d, 1 H, J = 17.8 Hz, H^3), 5.35 (s, 5 H, C_5H_5); the rest of the resonances were masked by those of the major isomer within δ 3.20-3.92 ppm. Mass (12 eV): m/e 414 (M^+). Anal. Calcd for $C_{18}H_{12}MoN_4O_2$: C, 52.44; H, 2.93. Found: C, 52.33; H, 3.04.

(g) Cyclization Reaction of 5 with PhCHO. A mixture of PhCHO (110 mg, 1.05 mmol) and BF_3·Et_2O (0.149 g, 1.05 mmol) in CH_2Cl_2 (8 mL) was added to a CH_2Cl_2 solution (25 mL) of 5 (0.30 g, 1.05 mmol) at 23 °C, and the resulting solution was stirred for 2 h before addition of an aqueous Na_2CO_3 solution (0.5 M, 5 mL). After the mixture was stirred for 30 min, the aqueous layer was decanted away and concentrated (15 mL) in vacuo. The residues were chromatographed through a silica column with a hexane/ether (1:1) mixture. A yellow band was developed, collected, and evaporated to dryness to give the yellow solid 7 (0.21 g, 0.53 mmol) as two diastereomers in equal amounts. The mixture was dissolved in ether/hexane (4/3, 2.0 mL) mixed solvent and cooled at 0 °C for 24 h, which gave pure the form of diastereomer a (90 mg). Further cooling of the remaining mother solution at 0 °C for 12 h gave the second crop of solid as a mixture of two diastereomers (20 mg). Removal of solvent from the last mother solution afforded the pure form of diastereomer b. IR (Nujol): ν(CO) 1945 (s), 1866 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): diastereomer a, δ 1.69 (s, 1 H, H^1), 2.40-2.60 (m, 3 H, H^5 + H^6 + H^7), 2.68 (s, 1 H, H^2), 3.23 (d, J = 11.6 Hz, 1 H, H^3), 4.05 (d, J = 11.6 Hz, 1 H, H^4), 4.69 (d, J = 9.3 Hz, 1 H, H^8), 5.14 (s, 5 H, C_5H_5), 7.18-7.32 (m, 5 H, Ph*H*); diastereomer b, δ 1.50 (s, 1 H, H^1), 2.26 (dd, J = 12.4, 6.2 Hz, 1 H, H^7), 2.62 (d, J = 12.4 Hz, 1 H, H^6), 2.69 (s, 1 H, H^2), 2.78 (br d, J = 6.2 Hz, 1 H, H^5), 3.21 (d, J = 11.6 Hz, 1 H, H^3), 3.93 (d, J = 11.6 Hz, 1 H, H^4), 4.69 (d, J = 9.3 Hz, 1 H, H^8), 5.06 (s, 5 H, C_5H_5), 7.18-7.32 (m, 5 H, Ph-H). Mass (12 eV): m/e 392 (M^+). Anal. Calcd for $C_{19}H_{18}MoO_3$: C, 58.16; H, 4.59. Found: C, 57.96; H, 4.72.

(h) Characterization of Trimethylenemethane Cation (I). To a benzene solution (20 mL) of 5 (0.30 g, 1.05 mmol) was added PhCHO (0.111 g, 1.05 mmol) and BF_3·Et_2O (0.149 g, 1.05 mmol), which immediately deposited a yellow viscous solid. After 30 min of stirring, the benzene was decanted away and the residues were dissolved in CH_3CN (2 mL). Ether (25 mL) was added to produce a viscous precipitate, which was collected by filtration and dried in vacuo (8 h). Examination of the solid by ^1H NMR spectroscopy revealed a contamination of 4 by 10%. IR (Nujol): ν(OH) 3580 cm^{-1}; ν(CO) 2064 (s), 2011 (s) cm^{-1}. ^1H NMR (CD_3CN, 300 MHz): diastereomer a, δ 2.25 (m, 1 H, H^6), 2.45 (m, 1 H, H^7), 2.60 (d, 1 H, J = 4.0 Hz, H^4), 2.87 (s, 1 H, H^3), 3.25 (dd, 1 H, J = 3.5, 1.5 Hz, H^1), 3.45 (dd, 1 H, J = 4.0, 1.5 Hz, H^2), 4.19 (m, 1 H, H^5), 4.67 (dd, 1 H, J = 7.2, 5.6 Hz, H^8), 5.68 (s, 5 H, C_5H_5), 7.20-7.37 (m, 5 H, Ph*H*); diastereomer b, δ 2.18 (m, 1 H, H^6), 2.35 (m, 1 H, H^7), 2.62 (d, 1 H, J = 3.5 Hz, H^4), 2.96 (s, 1 H, H^3), 3.17 (dd, 1 H, J = 3.8, 1.5 Hz, H^1), 3.52 (dd, J = 3.5, 1.5 Hz, H^2), 4.08 (m, 1 H, H^5), 4.60 (dd, 1 H, J = 8.6, 3.5 Hz, H^8), 5.71 (s, 5 H, C_5H_5), 7.20-7.37 (m, 5 H, Ph*H*). ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ 149. Elemental analyses were unsatisfactory because of the contamination of 4.

(i) Synthesis of $CpMo(CO)_2[\eta^3$-*syn*-1-(2′-hydroxyl-2′-phenylethyl)-2-methylallyl] (8). The trimethylenemethane cation (I) generated in section h [5 (0.30 g, 1.05 mmol), PhCHO (0.11 g, 1.05 mmol), and $BF_3{\cdot}Et_2O$ (0.148 g, 1.05 mmol)] was stirred with $NaBH_3CN$ (0.314 g, 5.00 mmol) in CH_3CN (10 mL) at 23 °C. After 1 h of stirring, the solution was evaporated to dryness and the residues were extracted with ether twice (2 × 10 mL). Chromatography on a silica column with a ether/hexane eluting solvent gave two yellow bands (R_f = 0.95, 0.52). The second band (R_f = 0.52) was collected and evaporated to dryness to give a yellow viscous solid of 8 (0.24 g, 0.62 mmol). Further separation of the two diastereomers was conducted by elution through a preparative TLC plate on SiO_2 (ether/hexane = 1/2). IR (Nujol): ν(CO) 1940 (s), 1860 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): diastereomer a, δ 1.65 (s, 3 H, Me), 1.70 (s, 1 H, H^1), 2.44 (m, 1 H, H^5), 2.59 (m, 1 H, H^4), 2.69 (s, 1 H, H^2), 2.87 (dd, J = 8.3, 4.8 Hz, 1 H, H^3), 4.84 (dd, 1 H, J = 9.2, 3.6 Hz, C*H*(OH)), 5.12 (s, 5 H, C_5H_5), 7.28–7.40 (m, 5 H, C_6H_5); diastereomer b, δ 1.60 (s, 3 H, Me), 1.65 (s, 1 H, H^1), 2.59–2.62 (m, 2 H, H^4 + H^5), 2.65 (s, 1 H, H^2), 2.72 (dd, J = 7.6, 5.2 Hz, 1 H, H^3), 4.79 (dd, 1 H, J = 9.0, 4.2 Hz, C*H*(OH)), 5.15 (s, 5 H, C_5H_5), 7.30–7.38 (m, 5 H, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): diastereomer a, δ 18.8 (Me), 36.3, 40.1 (CH^1H^2 + CH^4H^5), 57.5 (CH^3), 76.4 (CH(OH)), 90.7 (C_5H_5), 105.1 (CCH^1H^2), 125.7–145.0 (Ph–C), 229.9, 235.8 (Mo–2 CO); diastereomer b, δ 18.8 (Me), 36.7, 40.3 (CH^1H^2 + CH^4H^5), 55.3 (CH^3), 76.1 (CH(OH)), 90.9 (C_5H_5), 104.9 (CCH^1H^2), 126.3–144.2 (Ph–C), 240.7, 241.6 (Mo–2 CO). Mass (12 eV): m/e 394 (M^+). Anal. Calcd for $C_{19}H_{20}MoO_3$: C, 58.17; H, 5.14. Found: C, 57.86; H, 5.26.

(j) Synthesis of $CpMo(CO)_2[\eta^3$-*syn*-1-(2′-hydroxyl-2′-phenylethyl)-2-(3′-phenyl-2′-propynyl)allyl] (9). This compound was prepared similarly from the reaction between I (ca. 1.05 mmol, see section h) and $(PhC{\equiv}C)_2CuLi$ [PhC≡CH (0.32 g, 3.15 mmol)/BuLi (1.60 N, 1.96 mL) and CuI (0.30 g, 1.58 mmol)] in THF (10 mL, −40 °C); the yield is 55% (0.28 g, 0.58 mmol). The resulting two diastereomers (1:1) were further separated on a preparative silica TLC plate (ether/hexane = 1:2). IR (Nujol): ν(CO) 1943 (s), 1864 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): diastereomer a, δ 1.77 (s, 1 H, H^1), 2.45 (m, 1 H, H^4), 2.65 (m, 1 H, H^5), 2.77 (dd, 1 H, J = 9.1, 5.4 Hz, H^3), 2.90 (d, 1 H, J = 18.0 Hz, C*H*H′CPh), 2.99 (s, 1 H, H^2), 3.25 (d, J = 18.0 Hz, 1 H, CH*H′CPh*), 5.02 (dd, 1 H, J = 7.7, 4.2 Hz, C*H*(OH)), 5.25 (s, 5 H, C_5H_5), 7.26–7.43 (complex, m, 10 H, 2 Ph-*H*); diastereomer b, δ 1.74 (s, 1 H, H^1), 2.80 (complex m, 3 H, H^3 + H^4 + H^5), 2.86 (d, 1 H, J = 17.6 Hz, C*H*H′CPh), 2.95 (s, 1 H, H^2), 3.23 (d, J = 17.6 Hz, 1 H, CH*H′*Ph), 4.91 (dd, 1 H, J = 9.2, 3.4 Hz, C*H*OH), 5.16 (s, 5 H, C_5H_5), 7.26–7.43 (complex m, 10 H, 2 Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): diastereomer a, δ 31.1, 35.1 (CH^4H^5 + CH^1H^2), 39.9 (*C*HH′Ph), 56.8 (CH^3), 76.3 (CH(OH)), 81.9, 87.7 (C≡C), 90.8 (C_5H_5), 102.9 (CCH^1H^2), 124.0–127.0 (2 Ph–C), 209.7 (C═O), 240.5, 241.5 (Mo–2 CO); diastereomer b, δ 31.1, 34.6 (CH^4H^5 + CH^1H^2), 39.9 (*C*HH′Ph), 54.7 (CH^3), 75.7 (CH(OH)), 81.9, 87.7 (C≡C), 90.7 (C_5H_5), 103.0 (CCH^1H^2), 124.0–127.0 (2 Ph–C), 209.7 (C═O), 240.5, 241.5 (Mo–2 CO). Mass (12 eV): 494 (M^+). Anal. Calcd for $C_{27}H_{24}MoO_3$: C, 65.86; H, 4.90. Found: C, 65.59; H, 5.02.

(k) Synthesis of $CpMo(CO)_2[\eta^3$-*syn*-1-(2′-hydroxy-2′-phenylethyl)-2-(phenylmethyl)allyl] (10). This compound was prepared similarly from the reaction between I (ca. 1.05 mmol; see section h) and Ph_2CuLi [PhBr (0.49 g, 3.15 mmol)/BuLi (1.60 N, 1.96 mL) and CuI (0.30 g, 1.58 mmol)] in THF (10 mL, −78 °C), which gave 10 in 55% yield (0.28 g, 0.58 mmol). The two diastereomers were further separated by a preparative silica TLC plate (ether/hexane = 1/2). IR (Nujol): ν(CO) 1941 (s), 1862 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): diastereomer a, δ 1.84 (s, 1 H, H^1), 2.49 (m, 1 H, H^5), 2.57 (m, 1 H, H^4), 2.84 (s, 1 H, H^2), 2.98 (d, J = 15.0 Hz, 1 H, C*H*H′Ph), 3.00 (dd, J = 5.2, 3.6 Hz, 1 H, H^3), 3.41 (d, J = 15.0 Hz, 1 H, CH*H′*Ph), 4.77 (dd, J = 8.3, 5.2 Hz, 1 H, C*H*(OH), 5.19 (s, 5 H, C_5H_5), 7.23–7.37 (complex m, 10 H, 2 Ph–H); diastereomer b, δ 1.83 (s, 1 H, H^1), 2.68 (dd, J = 5.2, 3.7 Hz, 1 H, H^3), 2.70–2.73 (complex m, 2 H, H^4 + H^5), 2.82 (s, 1 H, H^2), 2.92 (d, J = 14.9 Hz, 1 H, C*H*H′Ph), 3.36 (d, J = 14.9 Hz, 1 H, CH*H′*Ph), 4.48 (dd, J = 8.1, 6.2 Hz, 1 H, C*H*(OH)), 5.29 (s, 5 H, C_5H_5), 7.23–7.37 (complex m, 10 H, 2 Ph–*H*). ^{13}C NMR (75.5 MHz, $CDCl_3$): diastereomer a, δ 31.1, 36.6 (CH^1H^2 + CH^4H^5), 40.8 (*C*HH′Ph), 58.3 (CH^3), 76.7 (CH(OH)), 90.8 (C_5H_5), 106.4 (CCH^1H^2), 124.3–145.0 (2 Ph–C), 240.6, 242.6 (Mo–2 CO); diastereomer b, δ 35.9, 39.5, 39.9 (CH^1H^2 + CH^4H^5 + CH^7H^8), 55.6 (CH^3), 75.7 (CH^6), 90.7 (C_5H_5), 106.3 (CCH^1H^2), 124–147 (2 Ph–C), 240.3, 241.7 (Mo–2 CO). Mass (12 eV): 470 (M^+). Anal. Calcd for $C_{25}H_{24}MoO_3$: C, 64.11; H, 5.16. Found: C, 63.89; H, 5.26.

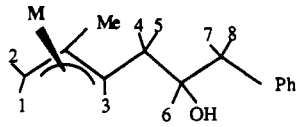
(l) Synthesis of $CpMo(CO)_2[\eta^3$-*syn*-1-(4′-pentanonyl)-2-(3′-phenyl-2′-propargyl)allyl] (11). To a benzene solution (10 mL) of 5 (0.30 g, 1.05 mmol) was added methyl vinyl ketone (0.070 g, 1.05 mmol) and then $BF_3{\cdot}Et_2O$ (0.149 g, 1.05 mmol), which gradually deposited a greenish viscous solid. After 30 min of stirring, the benzene was decanted and the residues were evaporated to dryness under vacuo (0.1 Torr). Addition of $(PhC{\equiv}C)_2CuLi$ [PhC≡CH (0.32 g, 3.15 mmol)/BuLi (1.60 N, 1.96 mL) and CuI (0.30 g, 1.58 mmol) in 10 mL of THF] to this salt in THF (20 mL) at −78 °C resulted in the rapid development of a bright yellow color. After 1 h of stirring, the solution was warmed to room temperature and evaporated to dryness. Chromatography of the residues through a silica column with the hexane/ether (3:1) eluting solvents gave two yellow bands (R_f = 0.89 and 0.58). Collection of the second band from the column (R_f = 0.58), followed by of removal solvent afforded 11 as a yellow oil (0.13 g, 0.31 mmol). IR (Nujol): ν(CO) 1942 (s), 1862 (s), 1709 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.67 (s, 1 H, H^1), 1.85 (m, 2 H, H^6 + H^7), 2.09 (m, 1 H, H^4), 2.13 (s, 3 H, CH_3), 2.25–2.50 (m, 3 H, H^5 + H^8 + H^9), 2.69 (t, J = 6.5 Hz, 1 H, H^3), 2.80 (d, 1 H, J = 17.7 Hz, H^{11}), 2.93 (s, 1 H, H^2), 3.23 (d, 1 H, J = 17.7 Hz, H^{10}), 5.21 (s, 5 H, C_5H_5), 7.24–7.39 (m, 5 H, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.9 (Me), 25.7, 29.6, 30.0 (CH^6H^7 + CH^4H^5 + CH^8H^9), 34.5 (CH^1H^2), 43.4 ($CH^{10}H^{11}$), 59.9 (CH^3), 81.1, 87.9 (C≡C), 90.5 (C_5H_5), 102.4 (CCH^1H^2), 127.9–131.7 (Ph–C), 209.2 (C═O), 240.7, 242.0 (Mo–2 CO). Mass (12 eV): m/e 458 (M^+). Anal. Calcd for $C_{24}H_{24}MoO_3$: C, 63.16; H, 5.30. Found: C, 62.98; H, 5.40.

(m) Synthesis of $CpMo(CO)_2[\eta^3$-*syn*-1-(4′-pentanonyl)-2-(phenylmethyl)allyl] (12). This compound was prepared similarly from the reaction between Ph_2CuLi and the cation generated in section l; the yield was 26%. IR (Nujol): ν(CO) 1940 (s), 1861 (s), 1705 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.68 (m, 2 H, H^6 + H^7), 1.70 (s, 1 H, H^1), 2.06 (s, 3 H, CH_3), 2.09 (m, 2 H, H^4 + H^5), 2.36 (m, 2 H, H^8 + H^9), 2.62 (dd, 1 H, J = 8.2, 4.8 Hz, H^3), 2.72 (s, 1 H, H^2), 2.82 (d, 1 H, J = 14.8 Hz, H^{11}), 3.30 (d, 1 H, J = 14.8 Hz, H^{10}), 5.18 (s, 5 H, C_5H_5), 7.25–7.43 (m, 5 H, Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 25.8, 29.6 (CH^6H^7 + CH^4H^5), 29.9 (Me), 35.7, 39.5 (CH^8H^9 + CH^1H^2), 43.4 ($CH^{10}H^{11}$), 60.8 (CH^3), 90.7 (C_5H_5), 105.9 (CCH^1H^2), 115.4–141.6 (Ph–C), 209.7 (C═O), 241.3, 242.7 (Mo–2 CO). Mass (12 eV): m/e 434 (M^+). Anal. Calcd for $C_{22}H_{24}MoO_3$: C, 61.11; H, 5.59. Found: C, 60.70; H, 5.68.

(n) Synthesis of $CpMo(CO)_2[\eta^3$-*syn*-1-(2′-hydroxyisobutyl)-2-methylallyl] (13). To a benzene solution (10 mL) of 5 (0.30 g, 1.05 mmol) was added acetone (0.010 g, 10.5 mmol) and then $BF_3{\cdot}Et_2O$ (0.149 g, 1.05 mmol), which gradually deposited a dark greenish viscous solid. The benzene layer was decanted, and the residues were dissolved in THF and dried again in vacuo for 2 h. Addition of $NaBH_3CN$ (0.30 g, 6.25 mmol) to this salt in 20 mL of THF at 23 °C gradually led to appearance of a bright yellow color. After 6 h of stirring, the solution was evaporated to dryness in vacuo and the residues were chromatographed through a silica column with hexane/ether (2:1) eluting solvents. Two yellow bands (R_f = 0.86 and 0.51) were developed, and the second band (R_f = 0.51) was collected and evaporated to dryness to give 13 (27 mg, 0.080 mmol) as a yellow oil. IR (Nujol): ν(CO) 1940 (s), 1859 (s) cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 1.03 (s, 3 H, Me), 1.04 (s, 3 H, Me), 1.40 (s, 1 H, H^1), 1.72 (s, 3 H, Me), 2.31 (dd, 1 H, J = 14.7, 9.2 Hz, H^5), 2.39 (dd, 1 H, J = 14.7, 4.0 Hz, H^4), 2.61 (s, 1 H, H^2), 2.72 (dd, 1 H, J = 9.2, 4.0 Hz, H^3), 4.66 (s, 5 H, C_5H_5). Mass (12 eV): m/e 346 (M^+). Anal. Calcd for $C_{15}H_{20}MoO_3$: C, 52.33; H, 5.86. Found: C, 52.02; H, 5.93.

(o) Synthesis of $CpMo(CO)_2[\eta^3$-*syn*-1-(2′-hydroxyl-3′-phenylpropyl)-2-methylallyl] (14). This complex was prepared similarly according to the procedure in section i except that phenylacetaldehyde was used in the reaction. Two diastereomers in a 1:1 ratio were obtained in 51% yield, which were further separated by a preparative silica TLC plate (SiO_2, $60F_{254}$, 20 × 20 cm, hexane/ether = 1/1). IR (Nujol): ν(CO) 1945 (s), 1865 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): diastereomer a, δ 1.63 (s, 1 H, H^1), 1.66 (s, 3 H, Me), 2.35 (m, 2 H, H^4 + H^5), 2.68 (m, 2 H,

$H^7 + H^8$), 2.72 (s, 1 H, H^2), 2.97 (dd, 1 H, J = 13.5, 4.4 Hz, H^3), 3.89 (m, 1 H, H^6), 5.15 (s, 5 H, C_5H_5), 7.12–7.35 (m, 5 H, Ph*H*); diastereomer b, δ 1.66 (s, 3 H, Me), 1.71 (s, 1 H, H^1), 2.38 (m, 1 H, H^5), 2.48 (s, 1 H, H^4), 2.70 (m, 2 H, $H^7 + H^8$), 2.72 (s, 1 H, H^2), 2.97 (dd, 1 H, J = 13.6, 3.8 Hz, H^3), 3.89 (m, 1 H, H^6), 5.21 (s, 5 H, C_5H_5), 7.22–7.34 (m, 5 H, Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): diastereomer a, δ 19.0 (Me), 36.3, 37.6 ($CH^1H^2 + CH^4H^5$), 44.4 (CH^7H^8), 57.9 (CH^3), 74.7 (CH^6), 90.8 (C_5H_5), 105.0 (CCH^1H^2), 126.9–138.5 (Ph–C), 242.0, 243.4 (Mo–2 CO); diastereomer b, δ 19.0 (Me), 35.0, 40.7 ($CH^1H^2 + CH^4H^5$), 43.9 (CH^7H^8), 57.9 (CH^3), 72.0 (CH^6), 90.8 (C_5H_5), 105.0 (CCH^1H^2), 126.9–138.5 (Ph–C), 242.0, 243.4 (Mo–2 CO). Mass (12 eV): m/e 408 (M^+). Anal. Calcd for $C_{20}H_{22}MoO_3$: C, 59.12; H, 5.48. Found: C, 58.90; H, 5.54.



(p) Synthesis of CpMo(CO)$_2$[η^3-*syn*-1-(2′-hydroxyl-3′-phenylpropynyl)-2-(phenylmethyl)allyl] (15). Synthesis of this complex was conducted similarly to the procedure in section i except that $PhCH_2CHO$ and Ph_2CuLi were used in the reaction. Two diastereomers in equal proportions were obtained in 49% yield, which were further separated by preparative TLC plate (SiO_2, $60F_{254}$, 20 × 20 cm, hexane/ether = 1/1). IR (Nujol): ν(CO) 1945 (s), 1865 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): diastereomer a, δ 1.88 (s, 1 H, H^1), 2.38 (m, 2 H, $H^4 + H^5$), 2.68 (dd, 1 H, J = 13.5, 4.1 Hz, H^8), 2.79 (s, 1 H, H^2), 2.85 (d, 1 H, J = 14.8 Hz, C*H*H′Ph), 2.88 (dd, 1 H, J = 13.5, 4.1 Hz, H^7), 2.91 (dd, 1 H, J = 8.1, 6.2 Hz, H^3), 3.32 (d, 1 H, J = 14.8 Hz, C*H*H′Ph), 3.51 (m, 1 H, H^6), 5.24 (s, 5 H, C_5H_5), 7.03–7.29 (complex m, 10 H, 2Ph*H*); diastereomer b, δ 1.80 (s, 1 H, H^1), 2.38 (m, 2 H, $H^4 + H^5$), 2.55 (dd, 1 H, J = 13.6, 8.7 Hz, H^8), 2.78 (s, 1 H, H^2), 2.86 (dd, 1 H, J = 13.6, 6.2 Hz, H^7), 2.91 (d, 1 H, J = 14.8 Hz, CH*H*′Ph), 2.96 (dd, 1 H, J = 10.4, 4.7 Hz, H^3), 3.34 (d, J = 14.8 Hz, 1 H, C*H*H′Ph), 3.89 (m, 1 H, H^6), 5.24 (s, 5 H, C_5H_5), 7.04–7.33 (complex m, 10 H, 2 Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): diastereomer a, δ 36.0, 37.6 (*C*HH′Ph + CH^4H^5), 40.0, 44.9 ($CH^7H^8 + CH^1H^2$), 58.3 (CH^3), 74.8 (CH^6), 90.9 (C_5H_5), 129.5–141.4 (2 Ph–C), 241.5, 242.6 (Mo–2 CO); diastereomer b, δ 36.1, 36.8, 38.3 (*C*CH′Ph + CH^4H^5 + CH^7H^8), 44.3 (CH^1H^2), 56.2 (CH^3), 74.3 (CH^6), 91.1 (C_5H_5), 106.3 (CCH^1H^2), 129.5–141.4 (2 Ph–C), 241.5, 242.6 (Mo–2 CO). Mass (12 eV): m/e 484 (M^+). Anal. Calcd for $C_{26}H_{26}MoO_3$: C, 64.73; H, 5.43. Found: C, 64.34; H, 5.52.

(q) Synthesis of CpMo(CO)$_2$[η^3-*syn*-1-(2′-hydroxyl-3′-phenylpropyl)-2-(3′-phenyl-2′-propargyl)allyl] (16). This compound was prepared similarly to the procedure in section h except that $PhCH_2CHO$ and $(PhC{\equiv}C)_2CuLi$ were used. Two diastereomers (1:1) were obtained in 52%, which were further separated by preparative TLC plate (SiO_2, $60F_{254}$, 20 × 20 cm, ether/hexane = 1/1). ^1H NMR (400 MHz, $CDCl_3$): diastereomer a, δ 1.83 (s, 1 H, H11), 2.45 (m, 2 H, $H^4 + H^5$), 2.75–2.80 (complex m, 2 H, $H^7 + H^8$), 2.84 (s, 1 H, H^2), 3.00 (m, 2 H, H^3 + C*H*H′), 3.38 (d, J = 17.3 Hz, CH*H*′), 4.15 (m, 1 H, H^6), 5.23 (s, 5 H, C_5H_5), 7.18–7.38 (m, 10 H, 2 Ph–H); diastereomer b, δ 1.83 (s, 1 H, H^1), 2.55 (m, 2 H, $H^4 + H^5$), 2.65–2.69 (m, 2 H, $H^7 + H^8$), 2.83 (s, 1 H, H^2), 2.96 (d, 1 H, J = 17.4 Hz, C*H*H′), 3.01 (dd, 1 H, J = 9.2, 6.1 Hz, H^3), 3.29 (d, J = 17.3 Hz, CH*H*′), 4.07 (m, 1 H, H^6), 5.17 (s, 5 H, C_5H_5), 7.18–7.30 (m, 10 H, 2 Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): diastereomer a, δ 29.9 (CH^4H^5), 35.1, 38.1, 44.6 (CH^1H^2 + CHH′ + CH^7H^8), 57.0 (CH^3), 74.0 (CH^6), 82.9, 88.6 (C≡C), 90.9 (C_5H_5), 103.0 (CCH^1H^2), 124–147 (2 Ph–C), 240.5, 241.5 (Mo–2 CO); diastereomer b, δ 29.8 (CH^4H^5), 35.1, 37.9, (CH^1H^2 + CHH′), 44.0 (CH^7H^8), 55.4 (CH^3), 74.3 (CH^6), 81.6, 87.9 (C≡C), 90.5 (C_5H_5), 102.8 (CCH^1H^2), 124–147 (2 Ph–C), 239.7, 240.5 (Mo–2 CO). Mass (12 eV): m/e 508 (M^+). Anal. Calcd for $C_{28}H_{26}MoO_3$: C, 66.40; H, 5.16. Found: C, 66.02; H, 5.27.

(r) Demetalation of Mo–π-Allyl Complexes 8–10 and 14–16. (i) In a typical reaction, to a CH_3CN solution (5 mL) of 8 (0.15 g, 0.38 mmol) was slowly added $NOBF_4$ (46.4 mg, 0.40 mmol) at 0 °C, and the mixture was stirred for 30 min. The solution volume was reduced (0.5 mL) in vacuo, and then ether (10 mL) was added to give a viscous solid. The ether layer was decanted, and the residues were dried in vacuo for 2 h before redissolution in CH_3CN (5 mL). To this solution was added $NaBH_3CN$ (70 mg, 1.14 mmol) at 23 °C and the mixture was kept stirred for 1 h. $(NH_4)_2Ce(NO_3)_6$ (0.30 g, 0.55 mmol) was slowly added to the solution. After being stirred for 20 min, the solution was dried in vacuo, and the residues were extracted with CH_2Cl_2 (5 mL). Elution through a preparative TLC plate (SiO_2, $60F_{254}$, 20 × 20 cm, hexane/ether = 2:1) produced an organic band (R_f = 0.51) which afforded 17 (40.8 mg, 0.23 mmol, 61%) as a mixture of two structural isomers (A/B = 2.0). The following olefins 18–22 were prepared similarly. (ii) Compound 17 was made in 61% yield. IR (neat): ν(OH) 3510 (br s), ν(C=C) 1645 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): A, δ 1.72 (s, 3 H, CH_3), 2.01–2.04 (complex m, 4 H, $H^3 + H^4 + H^5 + H^6$), 4.66 (dd, 1 H, J = 7.50, 5.60 Hz, H^7), 4.70, 4.72 (s, s, 2 H, $H^1 + H^2$), 7.32–7.46 (m, 5 H, Ph–H); B, δ 1.59 (s, 6 H, 2-Me), 2.49 (m, 2 H, $H^2 + H^3$), 5.12 (dd, 1 H, J = 9.1, 6.5 Hz, H^4), 5.17 (t, 1 H, J = 6.6 Hz, H^1), 7.27–7.40 (m, 5 H, Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): A, δ 22.3 (Me), 33.8, 36.7 ($CH^5H^6 + CH^3H^4$), 74.2 (CH^7), 119.9, 145.9 (C=C), 126–138 (Ph–C). Mass (12 eV): m/e 176 (M^+). Anal. Calcd for $C_{12}H_{16}O$: C, 81.81; H, 9.16. Found: C, 81.68; H, 9.27. (iii) Compound 18 was prepared in 56% yield. IR (neat): ν(OH), 3580 (vs), ν(C≡C) 2210 (w), ν(C=C) 1640 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): A, δ 1.96 (m, 2 H, $H^3 + H^4$), 2.18–2.20 (m, 2 H, $H^5 + H^6$), 3.13 (s, 2 H, $CH_2C{\equiv}$), 4.70 (t, 1 H, J = 6.4 Hz, H^7), 4.90, 5.15 (s, s, 2 H, $H^1 + H^2$), 7.23–7.37 (m, 10 H, 2 Ph–H); B, δ 1.97 (s, 3 H, Me), 2.56–2.61 (m, 2 H, $H^2 + H^3$), 3.09 (s, 1 H, C*H*H′C≡), 3.10 (s, 1 H, CH*H*′C≡), 4.68 (t, 1 H, J = 6.4 Hz, H^4), 5.15 (t, 1 H, J = 7.0 Hz, H^1), 7.23–7.37 (m, 10 H, 2 Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): A, δ 26.6 (CH^5H^6), 31.6, 36.6 (CH^3H^4 + *C*HH′C≡), 74.0 (CH^7), 84.1, 86.1 (C≡C), 111.3, 144.1 (C=C), 127.9–131.7 (2 Ph–C). Mass (12 eV): m/e 276 (M^+). Anal. Calcd for $C_{20}H_{20}O$: C, 86.91; H, 7.30. Found: C, 86.82; H, 7.43. (iv) Compound 19 was prepared in 58% yield. IR (neat): ν(OH) 3620 (vs), ν(C=C) 1640 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): A, δ 1.86–1.92 (complex m, 4 H, $H^3 + H^4 + H^5 + H^6$), 3.34 (s, 2 H, CH_2Ph), 4.62 (t, 1 H, J = 7.0 Hz, H^7), 4.77, 4.85 (s, s, 2 H, $H^1 + H^2$), 7.26–7.50 (complex m, 10 H, 2 Ph–H); B, δ 1.50 (s, 3 H, Me), 2.64 (m, 2 H, $H^2 + H^3$), 3.36 (s, 1 H, $PhCH_2$–), 4.73 (dd, 1 H, J = 8.2, 5.3 Hz, H^4), 5.45 (t, 1 H, J = 6.6 Hz, H^1), 7.23–7.50 (m, 10 H, 2 Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): A, δ 31.4 (CH^5H^6), 36.7, 42.9 (CH^3H^4 + CH_2Ph), 74.2 (CH^7), 115.1, 148.6 (C=C), 126–138 (2 Ph–C). Mass (12 eV): m/e 252 (M^+). Anal. Calcd for $C_{18}H_{20}O$: C, 85.66; H, 7.99. Found: C, 85.59; H, 8.05. (v) Compound 20 was prepared in 69% yield. IR (neat): ν(OH) 3592 (vs), ν(C=C) 1640 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): A, δ 1.63 (s, 3 H, CH_3), 1.87 (m, 2 H, $H^5 + H^6$), 2.20 (m, 2 H, $H^3 + H^4$), 2.79 (m, 2 H, C*H*H′Ph), 3.81 (m, 1 H, H^7), 4.69, 4.70 (s, s, 2 H, $H^1 + H^2$), 7.19–7.29 (m, 5 H, Ph–H); B, δ 1.71 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 2.15 (m, 2 H, C*H*H′Ph), 2.65 (m, 2 H, $H^2 + H^3$), 3.80 (m, 1 H, H^4), 5.19 (t, 1 H, J = 7.0 Hz, H^1), 7.19–7.30 (m, 5 H, Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): A, δ 25.6 (CH_3), 35.2, 33.7 ($CH^5H^6 + CH^3H^4$), 43.9 (CHH′Ph), 72.5 (CH^7), 119.9, 145.9 (C=C), 126–138 (Ph–C); B, δ 17.7 (CH_3), 22.1 (CH_3), 38.5, 43.0 ($CH^2H^3 + CH^5H^6$), 72.5 (CH^4), 110.3, 138.8 (C=C), 126–138 (Ph–C). Mass (12 eV): m/e 190 (M^+). Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 81.89; H, 9.65. (vi) Compound 21 was prepared in 60% yield. IR (neat): ν(OH) 3620 (vs), ν(C=C) 1640 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): A, δ 1.53 (m, 2 H, $H^5 + H^6$), 1.96 (ddd, J = 11.2, 8.2, 6.8 Hz, H^3), 2.12 (ddd, J = 11.2, 7.2, 4.2 Hz, H^4), 2.47 (m, 1 H, C*H*H′Ph), 2.62 (m, 1 H, CH*H*′Ph), 3.20 (s, 2 H, $PhCH_2$), 3.48 (m, 1 H, H^7), 4.78 and 4.83 (s, s, 2 H, $H^1 + H^2$), 7.23–7.37 (complex m, 10 H, 2 Ph–H); B, δ 1.60 (s, 3 H, Me), 2.18–2.25 (m, 2 H, $H^2 + H^3$), 2.45–2.53 (m, 2 H, C*H*H′Ph), 3.24 (s, 2 H, CH_2Ph), 3.67 (m, 1 H, H^4), 5.33 (t, 1 H, J = 6.8 Hz, H^1), 7.23–7.37 (complex m, 10 H, 2 Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): A, δ 31.3, 34.3 (CH^3H^4 + CH^5H^6), 42.9 (CHH′), 43.8 (*C*H$_2$Ph), 72.2 (CH^7), 111.6, 134.0 (C=C), 126–129 (2 Ph–C); B, δ 15.0 (Me), 37.8 (CH^2H^3), 42.9 (CHH′), 43.2 (*C*H$_2$Ph), 72.6 (CH^4), 122.1, 138.8 (C=C), 126–129 (2 Ph–C). Mass (12 eV) m/e 266 (M^+). Anal. Calcd for $C_{19}H_{22}O$: C, 85.66; H, 8.33. Found: C, 85.55; H, 8.44. (vii) Compound 22 was prepared in 58% yield. IR (neat): ν(OH) 3610 (vs), ν(C=C) 1648 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): A, δ 2.25 (m, 2 H, $H^5 + H^6$), 2.68 (m, 2 H, $H^3 + H^4$), 2.85 (m, 2 H, CHH′Ph), 3.14 (s, 2 H, $CH_2C{\equiv}$), 3.85 (m, 1 H, H^7), 4.90, 5.15 (s, s, 2 H, $H^1 + H^2$), 7.19–7.33 (complex m, 10 H, 2 Ph–H); B, δ 1.91 (s, 3 H, CH_3), 2.18–2.21 (m, 2 H, $H^2 + H^3$),

2.42 (dd, 1 H, J = 11.8, 8.2 Hz, C*H*H'Ph), 2.53 (dd, 1 H, J = 11.8, 6.2 Hz, CH*H'Ph*), 3.14 (m, 2 H, $CH_2C{\equiv}$), 3.85 (m, 1 H, H^4), 5.36 (t, 1 H, J = 6.8 Hz, H^1), 7.20–7.40 (complex m, 10 H, 2 Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): A, δ 31.3, 34.2, 34.5 (CH^3H^4 + CH^5H^6 + CHH'Ph), 43.8 ($CH_2C{\equiv}$), 72.0 (CH^7), 82.7, 86.6 (C≡C), 111.3, 144.2 (C=C), 124–131 (2 Ph–C). Mass (12 eV): m/e 290 (M^+). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.74; H, 7.75. (viii) Complex **23** was prepared similarly according to the procedures above except that PhSNa (3.0 molar equiv) was used; the yield was 67%. Similarly, compounds **24** and **25** were prepared from their nitrosonium salts and NaOH (6 M, 1 mL). Compound **23** was prepared in 67% yield. IR (neat): ν(OH) 3630 (vs), ν(C=C) 1650 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.71 (s, 3 H, Me), 2.38 (m, 2 H, H^2 + H^3), 3.48 (s, 1 H, CH*H'*S), 3.49 (s, 1 H, C*H*H'S), 4.50 (dd, 1 H, J = 7.8, 5.2 Hz, H^4), 5.10 (t, 1 H, J = 7.7 Hz, H^1), 7.26–7.34 (complex m, 10 H, 2 Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 25.6 (CH_3), 38.5 (CH^2H^3), 48.5 (CHH'S), 73.9 (CH^4), 124.5, 144.0 (C=C), 126.0–129.1 (2 Ph–C). Mass (12 eV): m/e 284 (M^+). Anal. Calcd for $C_{18}H_{20}OS$: C, 75.72; H, 7.42. Found: C, 75.63; H, 7.53. (ix) Compound **24** was prepared in 43% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 2.65 (m, 2 H, H^2 + H^3), 3.45 (m, 2 H, CH_2Ph), 4.75 (s, 2 H, CH_2OH), 4.85 (t, 1 H, J = 5.9 Hz, H^4), 5.87 (t, 1 H, J = 7.4 Hz, H^1), 7.24–7.38 (complex m, 10 H, 2 Ph*H*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 37.9 (CH^2H^3), 42.3 (CH_2Ph), 73.4 (CH^5H^6), 74.0 (CH^4), 124.5, 144.0 (C=C), 125.8–133.7 (2 Ph–C). Mass (12 eV): m/e 268 (M^+). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.55; H, 7.52. Found: C, 80.44; H, 7.63. (x) Compound **25** was prepared in 45% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 1.86 (s, 3 H, Me), 2.33 (m, 2 H, H^2 + H^3), 2.70 (dd, 1 H, J = 13.6, 8.2 Hz, PhC*H*H'), 2.82 (dd, 1 H, J = 13.6, 4.7 Hz, PhCH*H'*), 3.92 (m, 1 H, H^4), 4.84 (s, 2 H, CH_2–O), 5.76 (t, 1 H, J = 7.3 Hz, H^1), 7.18–7.32 (complex m, 5 H, Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.2 (Me^1), 29.8, 30.8 (CH^2H^3 + PhCHH'), 65.8 (CH^4), 75.7 (CH_2–O), 133.7–142.1 (C=C, Ph–C). Mass (12 eV): m/e 206 (M^+). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.68; H, 8.80. Found: C, 75.57; H, 8.91.

(s) Demetalation of Trimethylene Cations Derived from Aldehydes and α,β-Unsaturated Ketones. (i) In a typical reaction, to a stirred CH_2Cl_2 (3 mL) solution of cation I (section h, ca. 0.35 mmol) was added anhydrous Me_3NO (50 mg, 0.70 mmol) at room temperature, and the mixture was stirred for 8 h. TLC monitoring (SiO_2, ether/hexane = 1:2) showed the formation of a new compound (UV, R_f = 0.56). The solution was washed with water (2 mL), and the CH_2Cl_2 layer was evaporated to dryness. The residues were chromatographed through a preparative TLC plate (SiO_2, $60F_{254}$) using ether/hexane (1:2) as the eluting solvent, which provides **26** (35.32 mg, 58%, 0.20 mmol). The following dienes **27–32** were prepared similarly. IR (neat): ν(OH) 3580 (br vs), ν(C=C) 1610 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.65 (s, 3 H, Me), 4.89, 4.93 (s, s, 2 H, H^1 + H^2), 4.97 (d, 1 H, J = 6.5 Hz, C*H*OH), 5.70 (dd, 1 H, J = 15.5, 6.5 Hz, H^4), 6.35 (d, 1 H, J = 15.5 Hz, H^3), 7.24–7.38 (m, 5 H, Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.2 (Me), 75.0 (CH(OH)), 117.4, 131.7, 133.7, 144.2 (C=C), 126.4–128.7 (Ph–C). Mass (12 eV): m/e 174 (M^+). Anal. Calcd for $C_{12}H_{14}O_2$: C, 82.60; H, 8.10. Found: C, 82.49; H, 8.21. (ii) Compound **27** was prepared in 54% yield. IR (neat): ν(OH) 3570 (vs), ν(C=C) 1605 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.83 (s, 3 H, Me), 2.68 (dd, 1 H, J = 13.6, 8.0 Hz, PhC*H*H'), 2.90 (dd, 1 H, J = 13.6, 4.8 Hz, PhCH*H'*), 4.40 (ddd, 1 H, J = 8.0, 6.5, 4.8 Hz, H^5), 4.96, 4.97 (s, s, 2 H, H^1 + H^2), 5.71 (dd, 1 H, J = 15.8, 6.5 Hz, H^4), 6.31 (d, 1 H, J = 15.8 Hz, H^3), 7.24–7.38 (m, 5 H, Ph–H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.4 (Me), 44.0 (PhCHH'), 73.3 (CH^5), 117.0, 131.5, 132.1, 136.8 (C=C), 126.7–129.5 (Ph–C). Mass (12 eV): m/e 188 (M^+). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.81; H, 8.68. (iii) Compound **28** was prepared in 55% yield. IR (neat): ν(OH) 3610 (br vs), ν(C=C) 1608 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, 3 H, J = 6.0 Hz, Me), 0.95 (d, 3 H, J = 6.0 Hz, Me), 1.76 (m, 1 H, Me_2CH), 1.83 (s, 3 H, Me), 3.89 (dd, 1 H, J = 7.2, 6.8 Hz, C*H*(OH)), 4.95 (s, 2 H, H^1 + H^2), 5.63 (dd, 1 H, J = 15.7, 7.2 Hz, H^4), 6.27 (d, 1 H, J = 15.7 Hz, H^3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 8.4, 17.6, 18.2 (3 Me–C), 33.4 (Me_2CH), 78.0 (CH(OH)), 116.7, 131.0, 134.4, 136.9 (C=C). Mass (12 eV): m/e 140 (M^+). Anal. Calcd for $C_9H_{16}O$: C, 77.08; H, 11.51. Found: C, 76.94; H, 11.62. (vi) Compound **29** was prepared in 50% yield. IR (neat): ν(OH) 3608 (br vs), ν(C=C) 1610 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (s, 9 H, 3 Me), 1.83 (s, 3 H, Me), 3.80 (d, 1 H, J = 7.0 Hz, C*H*(OH)), 4.96 (s, 2 H, H^1 + H^2), 5.70 (dd, 1 H, J = 15.6, 7.0 Hz, H^4), 6.28 (d, 1 H, J = 15.6 Hz, H^3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.3, 25.4 (2 Me–C), 29.4 (CMe), 80.5 (CH(OH)), 116.7, 124.8, 129.5, 134.9 (C=C). Mass (12 eV): m/e 154 (M^+). Anal. Calcd for $C_{10}H_{18}O$: C, 71.43; H, 11.68. Found: C, 71.66; H, 11.55. (v) Compound **30** was prepared in 45% yield. IR (neat): ν(OH) 3610 (br vs), ν(C=C) 1608 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, 3 H, Me), 0.90 (d, 3 H, Me), 1.31 (m, 1 H, CH*H'*), 1.53 (m, 1 H, C*H*H'), 1.83 (s, 3 H, Me), 4.22 (ddd, 1 H, J = 8.6, 7.2, 4.8 Hz, C*H*(OH)), 4.96 (s, 2 H, H^1 + H^2), 5.62 (dd, 1 H, J = 15.6, 7.2 Hz, H^4), 6.28 (d, 1 H, J = 15.6 Hz, H^3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.3, 22.2, 22.8 (3 Me), 24.4 (Me_2CH), 46.4 (CHH'), 71.2 (CH(OH)), 116.8, 133.0, 133.3, 144.6 (C=C). Mass (12 eV): m/e 154 (M^+). Anal. Calcd for $C_{10}H_{18}O$: C, 71.43; H, 11.68. Found: C, 71.62; H, 10.94. (vi) Compound **31** was prepared in 22% yield. IR (neat): ν(CO) 1710 (s), ν(C=C) 1608 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (t, 3 H, J = 7.5 Hz, Me), 1.78 (s, 3 H, Me), 2.37 (q, 2 H, J = 7.1 Hz, CH^4CH_2), 2.41 (q, 2 H, J = 7.5 Hz, $COCH_2$), 2.50 (t, 2 H, J = 7.1 Hz, CH_2CO), 4.96 (s, 2 H, H^1 + H^2), 5.62 (dt, 1 H, J = 15.6, 7.1 Hz, H^4), 6.28 (d, 1 H, J = 15.6 Hz, H^3). Mass (12 eV): m/e 152 (M^+). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.75; H, 10.71. (vii) Compound **32** was prepared in 18% yield. IR (neat): ν(CO) 1710 (s), ν(C=C) 1610 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.78 (s, 3 H, Me), 2.13 (s, 3 H, $COCH_3$), 2.34 (q, 2 H, J = 7.1 Hz, CH^4CH_2), 2.50 (t, 2 H, J = 7.1 Hz, CH_2CO), 4.96 (s, 2 H, H^1 + H^2), 5.62 (dt, 1 H, J = 15.6, 7.1 Hz, H^4), 6.28 (d, 1 H, J = 15.6 Hz, H^3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.2 (Me), 26.5 ($COCH_3$), 42.9, 43.1 (CH_2CH_2CO), 115.1, 124.9, 128.7, 133.9 (C=C), 180.2 (C=O). Mass (12 eV): m/e 138 (M^+). Anal. Calcd for $C_9H_{14}O$: C, 78.20; H, 10.22. Found: C, 78.09; H, 10.34.

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