4356 *Organometallics* **2000,** *19,* 4356−4368

# Preparation and Subsequent Reaction Chemistry of Cyclopentadienyl Molybdenum Dicarbonyl $\eta^3$-2-Alkylidene Cyclobutanonyl Complexes

N. Ariane Vinson, Cynthia S. Day,[†] and Mark E. Welker*

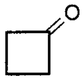
*Department of Chemistry, Wake Forest University, P.O. Box 7486,
Winston-Salem, North Carolina 27109*

*Received June 26, 2000*

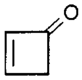
Cyclopentadienylmolybdenumtricarbonyl anion reacts with a variety of allenic electrophiles to produce $\eta^3$-2-alkylidene cyclobutanonyl and/or $\eta^3$-butadienyl complexes. The 2-alkylidene cyclobutanone can be synthetically modified, while still complexed to molybdenum, by nucleophilic addition to the carbonyl or via enolate chemistry. The cyclobutanone can then be removed from the metal via oxidative demetalation. Several of the new complexes reported here have been characterized by X-ray crystallography.

## Introduction

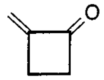
Cyclobutenones (**2**) and 2-alkylidene cyclobutanones (**3**) are receiving increasing attention as synthetic intermediates in part because of their unique physical properties (high ring strain, carbonyl electrophilicity, as well as photochemical and thermal reactivities)[1] and also because of their inclusion in molecules with biomedical science applications.[2] While cyclobutanones (**1**) are readily availabile via cycloadditions of ketenes with alkenes, the analogous cycloadditions of ketenes with allenes and alkynes to yield alkylidene cyclobutanones and cyclobutenones have proven more problematic.[3]



**1**



**2**



**3**

No general transition-metal-mediated routes to cyclobutenones, alkylidene cyclobutanones, and their transition-metal complexes have been reported previously. Isolation of a transition-metal complex containing a cyclobutenonyl or oxocyclobutenyl ligand from the reaction of a metal carbonyl anion with a cyclopropenyl halide was reported as early as 1962,[4a] although the original report incorrectly formulated the complex as an acyl cyclopropene and the product identity was later corrected.[4b,c] Brisdon et al. reported the reaction of triphenylbromoallene with a molybdenum complex to produce a complexed cyclobutenone in 1981,[4d] and Hughes et al. have reported that reaction of Cp*M(CO)$_3$ anions (M = Cr, Mo, W) (Cp* = C$_5$Me$_5$) with triphenylcyclopropenyl cation and other alkyldiphenylcyclopropenyl cations yielded complexed cyclobutenones.[4e,f] While mainly a route to five- and six-membered-ring carbacycles, there are a few reports of carbene complexes reacting with alkynes in a [2 + 1 + 1] cycloaddition to produce cyclobutenones.[5] In 1992, Green et al. reported two examples of complexed cyclobutenone synthesis from the reaction of CpMo(CO)$_3$ anions with 4-chloro-3-ethyl- and 4-chloro-3-methyl-1,2-butadiene.[6] In 1994, we also independently reported one example of complexed cyclobutenone synthesis from the reaction of the CpMo(CO)$_3$ anion with 4-tosyl-1,2-butadiene as part of a general survey of reactions of a number of metal carbonyl anions with this electrophile.[7] Last year, we communicated the results of a number of reactions of methyl-substituted allenic electrophiles with the CpMo(CO)$_3$ anion.[8] Here we give full details of the reactions of a number of methyl- and phenyl-substituted allenic electrophiles with the CpMo(CO)$_3$ anion to produce a number of alkylidene cyclobutanonyl and $\eta^3$-butadienyl complexes, several of which have also been characterized by X-ray crystallography. Details of subsequent demetalation and enolate reaction chemistry of the product alkylidene cyclobutanonyl complexes are also presented.

---

* Corresponding author. E-mail: welker@wfu.edu.

[†] To whom inquiries concerning X-ray crystallography should be addressed.

(1) For reviews of the synthesis and uses of these compounds see: (a) Nemoto, H.; Fukumoto, K. *Synlett* **1997**, 863. (b) Bellus, D.; Ernst, B. *Angew. Chem., Intl. Ed. Engl.* **1988**, *27*, 797.

(2) (a) Prasit, P.; Riendeau, D. *Ann. Rep. Med. Chem.* **1997**, *32*, 211. (b) Friesen, R. W.; Dube, D.; Fortin, R.; Frenette, R.; Prescott, S.; Cromlish, W.; Greig, G. M.; Kargman, S.; Wong, E.; Chan, C. C.; Gordon, R.; Xu, L. J.; Riendeau, D. *Biorg. Med. Chem. Lett.* **1996**, *6*, 2677.

(3) (a) Bertrand, M.; Maurin, R.; Gras, J. L.; Gil, G. *Tetrahedron* **1975**, *31*, 849. (b) Bertrand, M.; Gras, J. L.; Gore, J. *Tetrahedron* **1975**, *31*, 857. (c) Bertrand, M.; Gil, G.; Junino, A.; Maurin, R. *Tetrahedron* **1985**, *41*, 2759. (d) Vidal, J.; Huet, F. *J. Org. Chem.* **1988**, *53*, 611. (e) Nemoto, H.; Ishibashi, H.; Nagamochi, M.; Fukumoto, K. *J. Org. Chem.* **1992**, *57*, 1707. (f) Sugita, H.; Mizuno, K.; Saito, T.; Isagawa, K.; Otsuji, Y. *Tetrahedron Lett.* **1992**, *33*, 2539. (g) Durst, T.; Breau, L. *Compr. Org. Syn.* Trost, B. M., Ed. **1991**, *6*, 675.

(4) (a) Coffey, C. E.; *J. Am. Chem. Soc.* **1962**, *84*, 118. (b) King, R. B.; Efraty, A. *J. Organomet. Chem.* **1970**, *24*, 241. (c) Potenza, J.; Johnson, R.; Mastropalo, D.; Efraty, A. *J. Organomet. Chem.* **1974**, *64*, C13. (d) Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310. (e) Hughes, R. P.; Lambert, J. M. J.; Reisch, J. W.; Smith, W. L. *Organometallics* **1982**, *1*, 1403. (f) Hughes, R. P.; Klaui, W.; Reisch, J. W.; Muller, A. *Organometallics* **1985**, *4*, 1761.

(5) (a) Dotz, K. H.; Dietz, R. E.; Appenstein, C. K.; Neugebauer, D.; Schubert, U. *Chem. Ber.* **1979**, *112*, 3682. (b) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471. (c) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346.

(6) Benyunes, S. A.; Deeth, R. J.; Fries, A.; Green, M.; McPartlin, M.; Nation, C. B. M. *J. Chem. Soc., Dalton Trans.* **1992**, 2453.

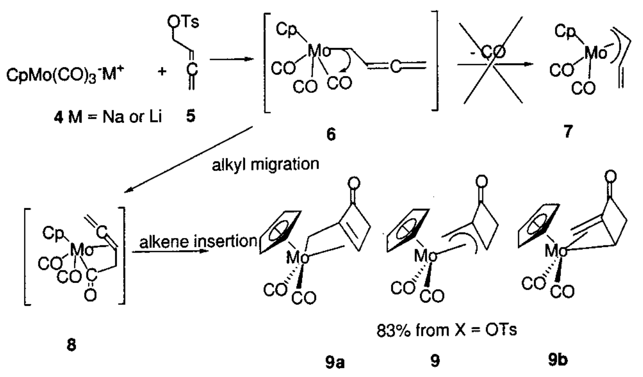
(7) Stokes, H. L.; Smalley, T. L.; Hunter, M. L.; Welker, M. L.; Rheingold, A. L. *Inorg. Chim. Acta* **1994**, *220*, 305.

(8) Vinson, N. A.; Day, C. S.; Welker, M. E.; Guzei, I.; Rheingold, A. L. *Organometallics*, **1999**, *18*, 1824.

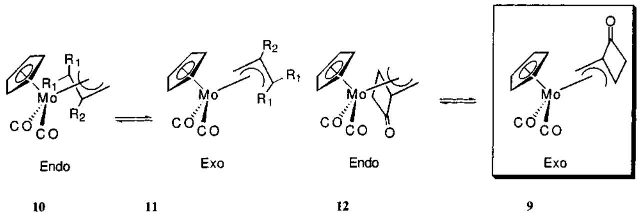
10.1021/om000546u CCC: $19.00
Publication on Web 09/15/2000

## Results and Discussion

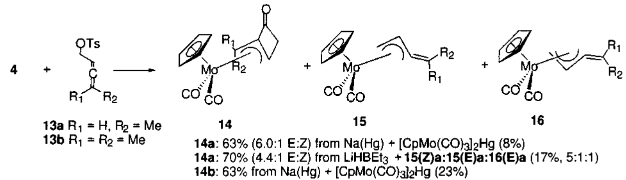
**(i) Reactions of the Cyclopentadienyl Molybdenum Tricarbonyl Anion with Allenic Electrophiles.** We have previously described many examples of $S_N2'$ reactions of cobaloxime and co(salen) anions with allenic electrophiles to yield transition-metal-substituted 1,3-dienes,[9] but in our experience, $S_N2$ reactions of transition-metal anions with allenic electrophiles have been rare.[7,10] Reaction of the $CpMo(CO)_3$ anion **4** (M = Na)[11] with tosylate **5** initially produced **6**; however, **6** rapidly underwent further reaction at 25 °C to produce another air-stable yellow complex, which we identified as alkylidene cyclobutanonyl complex (**9**).[7,8]

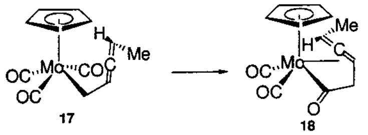


We could account for the formation of **9** via a CO insertion (alkyl migration) from **6** to form **8** followed by an alkene insertion. There is ample precedent for a $\sigma$-acyl $\pi$-alkene complex like **8** in cyclopentadienyl molybdenum, tungsten, and iron chemistry involving other alkenyl or allenyl ligands.[12,13] The X-ray crystal structure of **9** indicated that the $\sigma$-bond representation (**9b**) that contains a methylidene cyclobutanone was a better model of this complex than **9a**.[8] The solid state structure of this complex showed that the $\pi$-allyl portion of the molecule was *exo* (**9**) with respect to the $CpMo(CO)_2$ fragment.[14] Faller had previously observed acyclic $\pi$-allyls substituted on both the 1 and 2 positions also have high *exo:endo* ratios,[15] and our observations here were consistent with those previous reports.

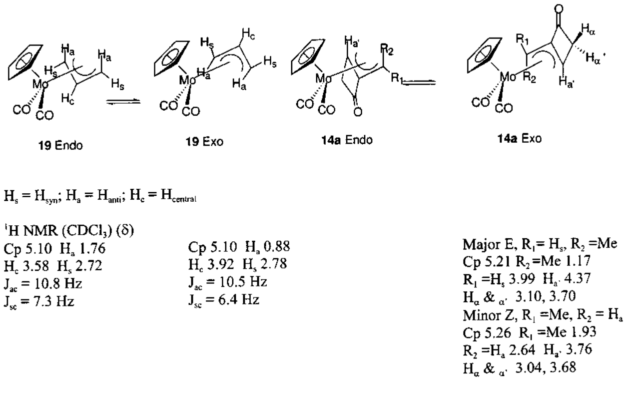


This initial isolation of complex **9** then proved general for mono- (**13a**) and dimethylated allenic electrophiles (**13b**). Using Gladysz's $LiBH(Et)_3$ reduction[16] of $[CpMo(CO)_3]_2$ to generate anion **4** (M = Li), we found that complexes **14a**,**b** were more easily obtained in pure form since they did not have to be separated from $Hg\{Mo(CO)_3C_5H_5\}_2$,[17] which was formed as a byproduct when Na(Hg) was used as reductant. Molybdenum alkylidene cyclobutanonyl complexes **14a**,**b** were also characterized by single-crystal X-ray diffraction, confirming their formulation as *exo* $\pi$-allyl complexes,[8] and **14a** was formed as a 6:1 mixture of *E* and *Z* isomers. Alkene insertion via the least hindered intermediate (**18**) presumably leads to the observed major *E* isomer (**14a**).





The $^1H$ NMR and X-ray crystallographic data used to identify minor isomers from the **14**–**16** series deserve additional discussion. We know the minor isomer observed here for **14a** was the *Z exo* isomer rather than the *E endo* isomer because the cyclobutanone $^1H$ NMR chemical shifts ($H_\alpha$, $H_{\alpha'}$) are almost identical in both isomers, whereas the methyl and $\pi$-allyl proton resonances are dramatically different.[14,15]



Comparison of the **14a** *E* and *Z* $^1H$ NMR chemical shifts with those reported by Faller for **19** *endo* and *exo*

---

(9) For a review of our work in this area see: Welker, M. E.; Wright, M. W.; Stokes, H. L.; Richardson, B. M.; Adams, T. A.; Smalley, T. L.; Vaughn, S. P.; Lohr, G. J.; Liable-Sands, L.; Rheingold, A. L. *Adv. Cycloaddition* **1997**, *4*, 149. For some other recent references to the primary literature see: (a) Hayes, B. L.; Adams, T. A.; Pickin, K. A.; Day, C. S.; Welker, M. E. *Organometallics* **2000**, *19*, 2730. (b) Chapman, J. J.; Day, C. S.; Welker, M. E. *Organometallics* **2000**, *19*, 1615.

(10) Stokes, H. L.; Richardson, B. M.; Wright, M. W.; Vaughn, S. M.; Welker, M. E.; Liable-Sands, L.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5520.

(11) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1963**, 889.

(12) (a) Roustan, J. L.; Benaim, J.; Charrier., C.; Merour, J. Y. *Tetrahedron Lett.* **1972**, 1953. (b) Benaim, J.; Merour, J. Y.; Roustan, J. L. *Tetrahedron Lett.* **1971**, 983. (c) Merour, J. Y.; Roustan, J. L.; Charrier, C.; Benaim, J.; Collin, J.; Cadiot, P. *J. Organomet. Chem.* **1979**, *168*, 337. (d) Roustan, J. L.; Merour, J. Y.; Charrier, C.; Benaim, J.; Collin, J.; Cadiot, P. *J. Organomet. Chem.* **1979**, *169*, 39.

(13) (a) Michelini-Rodriquez, I.; Romero, A. L.; Kapoor, R. N.; Cervantes-Lee, F.; Pannell, K. H. *Organometallics* **1993**, *12*, 1221. (b) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055. (c) Merour, J. Y.; Charrier, C.; Benaim, J.; Roustan, J. L.; Commereuc, D. *J. Organomet. Chem.* **1972**, *39*, 321. (d) Green, M. L. H.; Smith, M. J. *J. Chem. Soc.* (*A*) **1971**, 3220.

(14) Fish, R. W.; Giering, W. P.; Marten, D.; Rosenblum, M. *J. Organomet. Chem*, **1976**, *105*, 101.

(15) (a) Faller, J. W.; Chen, C. C.; Matinna, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361. (b) Faller, J. W.; Whitmore, B. C. *Organometallics* **1986**, *5*, 752.

(16) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

(17) Mickiewicz, M. M.; Raston, C. L.; White, A. H.; Wild, S. B. *Aust. J. Chem.* **1977**, *30*, 1685.

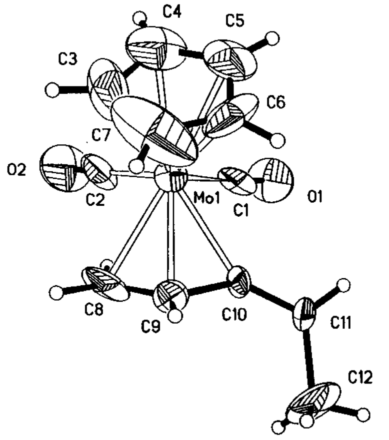


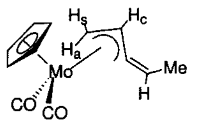
**Figure 1.** Molecular structure of complex **15a** (*Z*) *exo* (molecule 1) using 50% probability thermal ellipsoids.

lends additional support for this assignment of *E* and *Z* versus *endo* and *exo*.[15a] In the CpMo(CO)$_2$($\eta^3$-allyl) complexes (**19** *endo* and *exo*), the *syn* protons are less shielded by the magnetic anisotropy of the metal Cp ring system than the *anti* protons.[15a] This effect is much more pronounced in the *exo* conformation than the *endo*, and it produces a readily identifiable pattern in the $^1$H NMR. In comparing the $^1$H NMR data of the major and minor isomers of **14a**, H$_{a'}$ does shift significantly from 4.37 ppm in the known major *E exo* isomer (X-ray)[8] to 3.76 ppm in the minor isomer, but this shift is upfield, not downfield as would be expected if this minor isomer were the **14a** *E endo* isomer rather than the **14a** *Z exo* isomer. Additionally, the resonance for H$_s$ in the major isomer (**14a** *E exo*) moved considerably upfield from 3.99 to 2.64 ppm in the minor isomer (H$_a$). This shift would be expected on going from the *E* to *Z* isomer, since this proton would become more shielded by the Cp ligand. If the minor isomer was the *E endo* isomer, the chemical shift of H$_s$ would be expected to remain essentially constant between isomers. The methyl group's downfield shift from 1.17 ppm in the major isomer to 1.93 ppm in the minor isomer is also consistent with a minor isomer *Z exo* configuration.

In both of the cases where we used LiBH(Et)$_3$ as reductant, we also observed small amounts of the $\pi$-allyl complexes (**15** and **16**), which we did not see for the unsubstituted electrophile (**5**). This observation indicates that (at least in the presence of Li$^+$ or BEt$_3$) as allene substitution increases, ligand substitution (CO loss) becomes competitive with alkyl migration (CO insertion). Assignment of the *endo*, *exo*, *E*, and *Z* $\pi$-allyl orientations of the $\eta^3$-butadienyl complexes (**15(*Z*)a, 15(*E*)a,** and **16(*E*)a**) was performed by analogy with the method described above for **14a** (*E*) *exo* and **14a** (*Z*) *exo*. Assignment of H$_a$ versus H$_s$ in the **15**/**16** series is possible due to their differing coupling constants to Hc; $J_{HsHc}$ is 6–8 Hz, while $J_{HaHc}$ is 10–11 Hz. Compounds **15a** (*Z*) *exo* and **15a** (*E*) *exo* were assigned as *exo* isomers based on their upfield H$_a$ resonances ($\delta$1.42 and 1.60). Complex **16a** (*Z*) *endo* was assigned as an *endo* isomer based on its downfield H$_a$ ($\delta$2.37). The **15a** *Z* and *E* configurations were assigned based on their differences in Me and H absorptions. The major *Z* isomer had the most upfield alkene H ($\delta$5.50) and the most downfield Me ($\delta$2.03). The *endo* isomer **16a** was assigned the *Z* alkene configuration because its Me and alkene H absorptions most closely resembled those of **15a** (*E*) *exo*, and the methyl and alkene H are in similar magnetic environments in those two isomers.

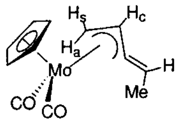
**Table 1. Crystal Data and Structure Refinement for [C$_5$H$_5$]Mo(CO)$_2$[C$_5$H$_7$] (15a *Z exo*)**

| | |
|---|---|
| empirical formula | C$_{12}$H$_{12}$MoO$_2$ |
| fw | 284.16 |
| temp, wavelength | 293(2) K, 0.71073 Å |
| cryst syst, space group | monoclinic, *Pn* (an alternate setting of *Pc* − $C_s^2$ (No. 7)) |
| unit cell dimens | $a$ = 10.952(1) Å<br>$b$ = 7.8742(6) Å, $\beta$ = 97.907(6)°<br>$c$ = 26.970(2) Å |
| volume, Z | 2303.7(3) Å$^3$, 8 |
| density (calcd) | 1.639 g/cm$^{-3}$ |
| abs coeff | 1.115 mm$^{-1}$ |
| *F*(000) | 1136 |
| crystal size | 0.30 × 0.40 × 0.40 mm |
| $\theta$ range for data collection | 1.93–25.35° |
| limiting indices | $-1 \leq h \leq 13$, $-9 \leq k \leq 1$, $-32 \leq l \leq 32$ |
| no. of reflns collected | 5694 |
| no. of ind reflns | 4939 [$R_{int}$ = 0.0209] |
| abs corr | semiempirical from $\psi$-scans |
| max. and min. transmsn | 0.7347 and 0.6372 |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 4938/12/544 |
| goodness-of-fit on $F^2$ | 1.010 |
| final *R* indices | |
| [3148 $I > 2\sigma(I)$ data] | R1 = 0.0372, wR2 = 0.0675 |
| [all 4939 data] | R1 = 0.0789, wR2 = 0.0828 |
| absolute structure param | 0.55(8) |
| extinction coeff | 0.00046(5) |
| largest diff peak and hole | 0.567 and −0.348 e$^-$/Å$^3$ |



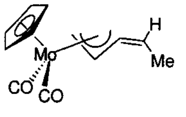
**15a (Z)exo**

$^1$H NMR (CDCl$_3$) ($\delta$)
Cp 5.27 H 5.50
H$_c$ 3.64 H$_a$ 1.42
H$_s$ 2.88 Me 2.03



**15a (E) exo**

Cp 5.28 H 6.79
H$_c$ 3.63 H$_a$ 1.60
H$_s$ 3.24 Me 1.90



**16a (Z) endo**

Cp 5.28 H 6.65
H$_c$ 3.43 H$_a$ 2.37
H$_s$ 2.76 Me 1.79

The *Z exo* configuration for the major isomer of **15a** was ultimately confirmed by X-ray crystallography. The ORTEP of this complex is provided in Figure 1. Crystal data and structure refinement parameters are in Table 1. Bond lengths are provided in Table 2, and bond angles in Table 3.

The crystal structure of the related unsubstituted $\eta^3$-butadienyl complex [C$_5$H$_5$]Mo(CO)$_2$[C$_4$H$_5$] was reported by Green and co-workers back in 1992.[6] As was noted for the unsubstituted complex, the terminal alkene carbon (C11) in **15a** *Z* (*exo*) is bent away from the molybdenum atom (the nonbonding Mo−C11 distance in **15a** is 3.43 Å). The angle between the terminal alkene carbon and the $\pi$-allyl central carbon (C9) is 137.8(5)°, similar to what was noted for Green's butadienyl complex (139°).[6]

**Table 2. Bond Lengths in Crystalline $[C_5H_5]Mo(CO)_2[C_5H_7]$ (15a *Z exo*, molecule 1)[a]**

| type[b] | length, Å | type[b] | length, Å |
|---|---|---|---|
| $Mo_1-C_1$ | 1.992(7) | $Mo_1-C_3$ | 2.255(9) |
| $Mo_1-C_2$ | 1.961(8) | $Mo_1-C_4$ | 2.267(9) |
| $Mo_1-C_8$ | 2.246(8) | $Mo_1-C_5$ | 2.385(9) |
| $Mo_1-C_9$ | 2.229(6) | $Mo_1-C_6$ | 2.342(9) |
| $Mo_1-C_{10}$ | 2.213(6) | $Mo_1-C_7$ | 2.364(12) |
| $O_1-C_1$ | 1.133(8) | $Mo_1-Cp$[c] | 2.023(−) |
| $C_3-C_4$ | 1.360(14) | $O_2-C_2$ | 1.157(9) |
| $C_3-C_7$ | 1.34(2) | $C_8-C_9$ | 1.263(10) |
| $C_4-C_5$ | 1.307(13) | $C_9-C_{10}$ | 1.460(8) |
| $C_5-C_6$ | 1.373(13) | $C_{10}-C_{11}$ | 1.327(8) |
| $C_6-C_7$ | 1.33(2) | $C_{11}-C_{12}$ | 1.576(9) |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] This is one-third of the trace of the orthogonalized $U_{ij}$ tensor.

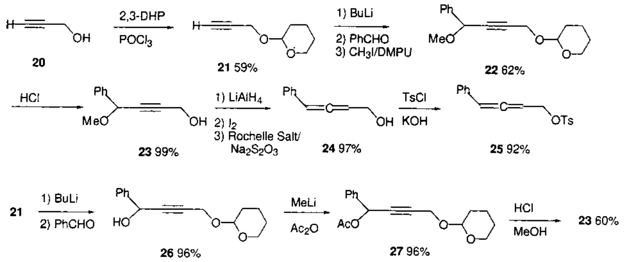
**Table 3. Bond Angles in Crystalline $[C_5H_5]Mo(CO)_2[C_5H_7]$ (15a *Z exo*, molecule 1)[a]**

| type[b,c] | angle, deg | type[b,c] | angle, deg |
|---|---|---|---|
| $C_2-Mo_1-C_1$ | 80.8(3) | $C_2-Mo_1-C_{10}$ | 112.7(3) |
| $C_1-Mo_1-C_8$ | 111.8(3) | $C_1-Mo_1-C_p$[c] | 123.1(−) |
| $C_2-Mo_1-C_8$ | 76.8(3) | $C_2-Mo_1-C_p$[c] | 121.0(−) |
| $C_1-Mo_1-C_9$ | 104.1(2) | $C_8-Mo_1-C_p$[c] | 123.8(−) |
| $C_2-Mo_1-C_9$ | 106.9(3) | $C_9-Mo_1-C_p$[c] | 115.3(−) |
| $C_1-Mo_1-C_{10}$ | 68.2(2) | $C_{10}-Mo_1-C_p$[c] | 126.1(−) |
| $C_9-Mo_1-C_8$ | 32.8(3) | $C_{10}-Mo_1-C_8$ | 63.5(3) |
| $C_{10}-Mo_1-C_9$ | 38.4(2) | $C_3-Mo_1-C_6$ | 54.9(3) |
| $C_3-Mo_1-C_4$ | 35.0(4) | $C_4-Mo_1-C_6$ | 54.8(3) |
| $C_3-Mo_1-C_7$ | 33.7(4) | $C_3-Mo_1-C_5$ | 56.1(3) |
| $C_6-Mo_1-C_7$ | 32.8(4) | $C_4-Mo_1-C_7$ | 56.5(4) |
| $C_4-Mo_1-C_5$ | 32.5(3) | $C_7-Mo_1-C_5$ | 56.0(4) |
| $C_6-Mo_1-C_5$ | 33.8(3) | $C_{10}-Mo_1-C_6$ | 98.2(3) |
| $C_1-Mo_1-C_3$ | 143.1(3) | $C_8-Mo_1-C_7$ | 95.3(4) |
| $C_2-Mo_1-C_3$ | 97.1(4) | $C_9-Mo_1-C_7$ | 87.0(3) |
| $C_8-Mo_1-C_3$ | 103.3(4) | $C_{10}-Mo_1-C_7$ | 108.8(3) |
| $C_9-Mo_1-C_3$ | 111.5(3) | $C_1-Mo_1-C_4$ | 108.2(3) |
| $C_{10}-Mo_1-C_3$ | 141.8(3) | $C_2-Mo_1-C_4$ | 95.0(3) |
| $C_8-Mo_1-C_4$ | 137.0(4) | $C_2-Mo_1-C_6$ | 149.1(3) |
| $C_9-Mo_1-C_4$ | 143.3(3) | $C_1-Mo_1-C_6$ | 112.7(3) |
| $C_{10}-Mo_1-C_4$ | 150.4(3) | $C_2-Mo_1-C_7$ | 127.7(4) |
| $C_8-Mo_1-C_5$ | 151.1(3) | $C_1-Mo_1-C_7$ | 145.5(4) |
| $C_9-Mo_1-C_5$ | 129.8(3) | $C_2-Mo_1-C_5$ | 122.3(3) |
| $C_{10}-Mo_1-C_5$ | 118.2(3) | $C_1-Mo_1-C_5$ | 93.8(3) |
| $C_8-Mo_1-C_6$ | 119.1(3) | $O_2-C_2-Mo_1$ | 173.6(8) |
| $C_9-Mo_1-C_6$ | 96.8(3) | $C_8-C_9-C_{10}$ | 118.9(7) |
| $O_1-C_1-Mo_1$ | 176.0(5) | $C_{11}-C_{10}-C_9$ | 137.8(5) |
| $C_4-C_3-C_7$ | 108.4(9) | $C_{10}-C_{11}-C_{12}$ | 119.5(6) |
| $C_5-C_4-C_3$ | 109.9(8) | $C_6-C_7-Mo_1$ | 72.7(7) |
| $C_4-C_5-C_6$ | 104.8(9) | $C_3-C_7-Mo_1$ | 68.7(6) |
| $C_7-C_6-C_5$ | 111.4(9) | $C_9-C_8-Mo_1$ | 72.9(5) |
| $C_6-C_7-C_3$ | 105.2(10) | $C_8-C_9-Mo_1$ | 74.3(4) |
| $C_4-C_3-Mo_1$ | 73.0(6) | $C_{10}-C_9-Mo_1$ | 70.2(3) |
| $C_7-C_3-Mo_1$ | 77.6(7) | $C_{11}-C_{10}-Mo_1$ | 147.8(5) |
| $C_5-C_4-Mo_1$ | 78.7(6) | $C_9-C_{10}-Mo_1$ | 71.4(3) |
| $C_3-C_4-Mo_1$ | 72.0(5) | | |
| $C_4-C_5-Mo_1$ | 68.8(5) | | |
| $C_6-C_5-Mo_1$ | 71.4(5) | | |
| $C_7-C_6-Mo_1$ | 74.6(6) | | |
| $C_5-C_6-Mo_1$ | 74.9(5) | | |

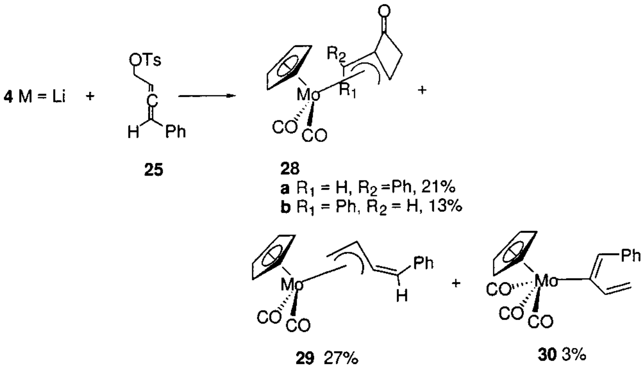
[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] The symbol $C_p$ is used to represent the center of gravity for the cyclopentadienyl ring, and these values are therefore listed without estimated standard deviations.

Assignment of the *exo* and *endo* configurations to the minor $\pi$-allyl products **15b** and **16b** was also done by $^1$H NMR. The chemical shifts of the terminal $\pi$-allyl hydrogens in the *exo* complex **15b** are widely separated at 3.22 ($H_s$) and 1.58 ppm ($H_a$). In the *endo* complex **16b** the chemical shifts are much closer (2.76 ($H_s$) and 2.40 ppm ($H_a$)), consistent with the *endo* configuration as noted above. Complexes **15b** and **16b** are apparently not intermediates involved in the formation of the alkylidene cyclobutanone complex (**14b**). Prolonged stirring of the **15b**/**16b** mixture under an atmosphere of CO in THF resulted in slow decomposition rather than formation of **14b**. Additionally, if the **4**/**13b** reaction was run under an atmosphere of CO, none of the $\eta^3$-butadienyl complexes (**15b**/**16b**) were isolated, indicating that CO loss is competitive with CO insertion and that CO loss is essentially irreversible (as expected) under our standard reaction conditions.

To continue to investigate the effect of allenic electrophile substituent size on the ratio of alkylidene cyclobutanonyl complex to $\eta^3$-butadienyl complex, we first needed to prepare a phenyl-substituted allenic electrophile (**25**). Allenic tosylate **25** was synthesized by two different routes, both of which begin with the preparation of 3-tetrahydropyranyl-1-propyne (**21**).[18] Keck and Webb had communicated[19] the preparation of the methyl, THP ether **22**, but we sometimes had difficulty removing the DMPU from the desired product (**22**). To prepare larger quantities of **23**, we ended up treating protected propynol **21** with BuLi followed by PhCHO to yield 1-phenyl-4-tetrahydropyranyl-2-butyn-1-ol (**26**) followed by acetylation and deprotection in methanol.[20]



The reaction between this phenyl-substituted allenic tosylate (**25**) and the $LiBEt_3H$ generated $CpMo(CO)_3$ anion (**4**, M = Li) led to an essentially 1:1 mixture of alkylidene cyclobutanonyl complexes **28** and $\eta^3$-butadienyl complex **29**. The major *Z* (*exo*) alkylidene cyclobutanone complex (**28a**) was characterized by X-ray crystallography, confirming the *Z* (*exo*) configuration. The ORTEP of this complex is provided in Figure 2. Crystal data and structure refinement parameters are in Table



---

[18] Henbest, H. B.; Jones, E. R. H.; Walls, I. M. S. *J. Chem. Soc.* **1950**, 3646.

[19] Keck, G. E.; Webb, R. R. *Tetrahedron Lett.* **1982**, *23*, 3051.

[20] *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: Singapore, 1989; p 552.

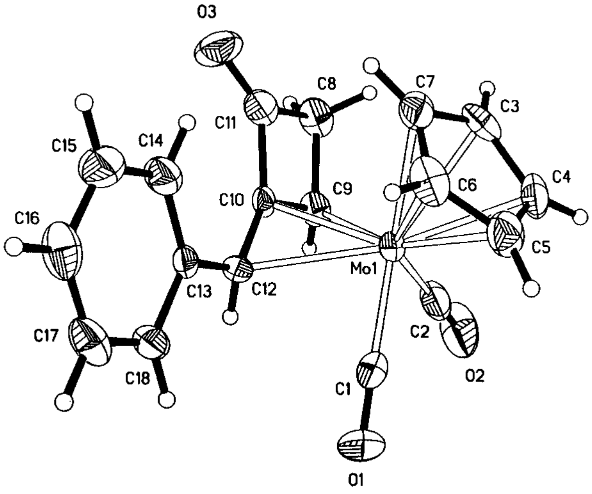


**Figure 2.** Molecular structure of complex **28a** (*Z*) *exo* using 50% probability thermal ellipsoids.

**Table 4. Crystal Data and Structure Refinement for $[C_5H_5]Mo(CO)_2[C_5H_4O(C_6H_5)]$ (28a)**

| | |
|---|---|
| empirical formula | $C_{18}H_{14}MoO_3$ |
| fw | 374.23 |
| temp | 228(2) K |
| wavelength | 0.71073 Å |
| cryst syst, space group | triclinic, $P\bar{1} - C_i^1$ (No. 2) |
| unit cell dimens | $a = 8.127(1)$ Å, $\alpha = 97.39(1)°$ |
| | $b = 8.4278(7)$ Å, $\beta = 105.72(1)°$ |
| | $c = 11.516(2)$ Å, $\gamma = 96.63(1)°$ |
| volume | 743.62(15) Å$^3$ |
| Z, calcd density | 2, 1.671 g/cm$^{-3}$ |
| abs coeff | 0.891 mm$^{-1}$ |
| *F*(000) | 376 |
| cryst size | 0.12 × 0.20 × 0.20 mm |
| $\theta$ range for data collection | 2.47–26.40° |
| limiting indices | $-1 \leq h \leq 10, -10 \leq k \leq 10, -14 \leq l \leq 14$ |
| no. of reflns collected/unique | 3707/3038 [$R_{int} = 0.0181$] |
| completeness to $\theta = 26.40°$ | 99.6% |
| abs corr | semiempirical from $\psi$-scans |
| max. and min. transmsn | 0.7449 and 0.6761 |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/params | 3038/215 |
| goodness-of-fit on $F^2$ | 1.031 |
| final *R* indices | |
| [2619 $I > 2\sigma(I)$ data] | R1 = 0.0279, wR2 = 0.0566 |
| [all 3038 data] | R1 = 0.0376, wR2 = 0.0592 |
| largest diff peak and hole | 0.462 and −0.439 e/Å$^3$ |

**Table 5. Bond Lengths in Crystalline $[C_5H_5]Mo(CO)_2[C_5H_4O(C_6H_5)]$ (28a)[a]**

| type[b] | length, Å | type[b] | length, Å |
|---|---|---|---|
| $Mo_1{-}C_1$ | 1.955(3) | $Mo_1{-}C_3$ | 2.365(3) |
| $Mo_1{-}C_2$ | 1.945(3) | $Mo_1{-}C_4$ | 2.350(3) |
| | | $Mo_1{-}C_5$ | 2.342(3) |
| $Mo_1{-}C_9$ | 2.293(3) | $Mo_1{-}C_6$ | 2.352(3) |
| $Mo_1{-}C_{10}$ | 2.221(2) | $Mo_1{-}C_7$ | 2.367(3) |
| $Mo_1{-}C_{12}$ | 2.410(3) | $Mo_1{-}Cp^c$ | 2.030(−) |
| $O_1{-}C_1$ | 1.153(4) | $O_3{-}C_{11}$ | 1.198(4) |
| $O_2{-}C_2$ | 1.149(4) | | |
| | | $C_{13}{-}C_{14}$ | 1.392(4) |
| $C_3{-}C_7$ | 1.409(4) | $C_{13}{-}C_{18}$ | 1.396(4) |
| $C_3{-}C_4$ | 1.402(4) | $C_{14}{-}C_{15}$ | 1.380(4) |
| $C_4{-}C_5$ | 1.392(4) | $C_{15}{-}C_{16}$ | 1.382(5) |
| $C_5{-}C_6$ | 1.406(4) | $C_{16}{-}C_{17}$ | 1.381(5) |
| $C_6{-}C_7$ | 1.412(4) | $C_{17}{-}C_{18}$ | 1.384(4) |
| $C_8{-}C_9$ | 1.544(4) | $C_9{-}C_{10}$ | 1.441(4) |
| $C_8{-}C_{11}$ | 1.535(4) | $C_{10}{-}C_{11}$ | 1.508(4) |
| $C_{10}{-}C_{12}$ | 1.406(4) | $C_{12}{-}C_{13}$ | 1.474(4) |
| $C_8{-}H_{8a}$ | 0.98(3) | $C_9{-}H_9$ | 1.00(3) |
| $C_8{-}H_{8b}$ | 0.94(3) | $C_{12}{-}H_{12}$ | 0.93(3) |

[a,b,c] See footnotes in Table 3.

**Table 6. Bond Angles in Crystalline $[C_5H_5]Mo(CO)_2[C_5H_4O(C_6H_5)]$ (28a)[a]**

| type[b,c] | angle, deg | type[b,c] | angle, deg |
|---|---|---|---|
| $C_2{-}Mo_1{-}C_1$ | 80.01(14) | | |
| $C_1{-}Mo_1{-}C_9$ | 110.68(12) | $C_2{-}Mo_1{-}C_9$ | 70.35(13) |
| $C_1{-}Mo_1{-}C_{10}$ | 102.58(11) | $C_2{-}Mo_1{-}C_{10}$ | 104.16(12) |
| $C_1{-}Mo_1{-}C_{12}$ | 70.86(10) | $C_2{-}Mo_1{-}C_{12}$ | 111.90(11) |
| $C_1{-}Mo_1{-}C_p{}^c$ | 120.7(−) | $C_2{-}Mo_1{-}C_p{}^c$ | 119.8(−) |
| $C_9{-}Mo_1{-}C_p{}^c$ | 128.5(−) | $C_{12}{-}Mo_1{-}C_p{}^c$ | 128.1(−) |
| $C_{10}{-}Mo_1{-}C_p{}^c$ | 121.2(−) | | |
| $C_{10}{-}Mo_1{-}C_9$ | 37.20(10) | $C_4{-}Mo_1{-}C_6$ | 57.88(11) |
| $C_{10}{-}Mo_1{-}C_{12}$ | 35.04(9) | $C_4{-}Mo_1{-}C_7$ | 57.68(11) |
| $C_4{-}Mo_1{-}C_3$ | 34.60(11) | $C_5{-}Mo_1{-}C_3$ | 57.40(11) |
| $C_5{-}Mo_1{-}C_4$ | 34.52(11) | $C_6{-}Mo_1{-}C_3$ | 57.77(11) |
| $C_5{-}Mo_1{-}C_6$ | 34.85(11) | $C_5{-}Mo_1{-}C_7$ | 57.63(11) |
| $C_6{-}Mo_1{-}C_7$ | 34.81(11) | $C_9{-}Mo_1{-}C_{12}$ | 65.48(10) |
| $C_3{-}Mo_1{-}C_7$ | 34.64(11) | | |
| $C_1{-}Mo_1{-}C_3$ | 147.62(12) | $C_2{-}Mo_1{-}C_3$ | 103.02(12) |
| $C_1{-}Mo_1{-}C_4$ | 114.41(12) | $C_2{-}Mo_1{-}C_4$ | 89.68(12) |
| $C_1{-}Mo_1{-}C_5$ | 91.13(12) | $C_2{-}Mo_1{-}C_5$ | 111.29(13) |
| $C_1{-}Mo_1{-}C_6$ | 101.68(13) | $C_2{-}Mo_1{-}C_6$ | 145.50(12) |
| $C_1{-}Mo_1{-}C_7$ | 135.81(13) | $C_2{-}Mo_1{-}C_7$ | 137.40(12) |
| $C_{10}{-}Mo_1{-}C_3$ | 107.69(10) | $C_{10}{-}Mo_1{-}C_7$ | 90.85(10) |
| $C_9{-}Mo_1{-}C_3$ | 100.42(11) | $C_9{-}Mo_1{-}C_7$ | 105.34(11) |
| $C_{10}{-}Mo_1{-}C_4$ | 142.29(11) | $C_5{-}Mo_1{-}C_{12}$ | 128.82(11) |
| $C_9{-}Mo_1{-}C_4$ | 126.01(11) | $C_4{-}Mo_1{-}C_{12}$ | 158.41(10) |
| $C_{10}{-}Mo_1{-}C_5$ | 143.72(11) | $C_6{-}Mo_1{-}C_{12}$ | 100.86(10) |
| $C_9{-}Mo_1{-}C_5$ | 157.81(11) | $C_3{-}Mo_1{-}C_{12}$ | 133.29(10) |
| $C_{10}{-}Mo_1{-}C_6$ | 108.93(11) | $C_7{-}Mo_1{-}C_{12}$ | 103.24(10) |
| $C_9{-}Mo_1{-}C_6$ | 136.65(11) | | |
| $O_1{-}C_1{-}Mo_1$ | 179.0(3) | $O_2{-}C_2{-}Mo_1$ | 179.6(4) |
| $C_4{-}C_3{-}C_7$ | 108.1(3) | $C_{14}{-}C_{13}{-}C_{18}$ | 117.5(3) |
| $C_5{-}C_4{-}C_3$ | 108.0(3) | $C_{14}{-}C_{13}{-}C_{12}$ | 123.2(2) |
| $C_4{-}C_5{-}C_6$ | 108.8(3) | $C_{18}{-}C_{13}{-}C_{12}$ | 119.2(2) |
| $C_5{-}C_6{-}C_7$ | 107.3(3) | $C_{15}{-}C_{14}{-}C_{13}$ | 121.2(3) |
| $C_3{-}C_7{-}C_6$ | 107.8(3) | $C_{14}{-}C_{15}{-}C_{16}$ | 120.5(3) |
| | | $C_{17}{-}C_{16}{-}C_{15}$ | 119.3(3) |
| $C_4{-}C_3{-}Mo_1$ | 72.13(17) | $C_{16}{-}C_{17}{-}C_{18}$ | 120.1(3) |
| $C_7{-}C_3{-}Mo_1$ | 72.77(16) | $C_{17}{-}C_{18}{-}C_{13}$ | 121.3(3) |
| $C_5{-}C_4{-}Mo_1$ | 72.41(17) | | |
| $C_3{-}C_4{-}Mo_1$ | 73.27(16) | $C_{10}{-}C_9{-}Mo_1$ | 68.69(15) |
| $C_4{-}C_5{-}Mo_1$ | 73.07(17) | $C_8{-}C_9{-}Mo_1$ | 111.2(2) |
| $C_6{-}C_5{-}Mo_1$ | 72.99(17) | $C_{12}{-}C_{10}{-}Mo_1$ | 79.86(15) |
| $C_5{-}C_6{-}Mo_1$ | 72.17(18) | $C_9{-}C_{10}{-}Mo_1$ | 74.11(15) |
| $C_7{-}C_6{-}Mo_1$ | 73.17(17) | $C_{11}{-}C_{10}{-}Mo_1$ | 111.39(17) |
| $C_3{-}C_7{-}Mo_1$ | 72.58(17) | $C_{10}{-}C_{12}{-}Mo_1$ | 65.10(14) |
| $C_6{-}C_7{-}Mo_1$ | 72.01(17) | $C_{13}{-}C_{12}{-}Mo_1$ | 120.51(18) |
| $C_{11}{-}C_8{-}C_9$ | 85.5(2) | $O_3{-}C_{11}{-}C_{10}$ | 134.6(3) |
| $C_{10}{-}C_9{-}C_8$ | 93.3(2) | $O_3{-}C_{11}{-}C_8$ | 133.2(3) |
| $C_{12}{-}C_{10}{-}C_9$ | 126.8(3) | $C_{10}{-}C_{11}{-}C_8$ | 91.0(2) |
| $C_{12}{-}C_{10}{-}C_{11}$ | 142.8(3) | $C_{10}{-}C_{12}{-}C_{13}$ | 126.1(2) |
| $C_9{-}C_{10}{-}C_{11}$ | 90.2(2) | | |
| | | $C_{10}{-}C_9{-}H_9$ | 125(2) |
| $C_{11}{-}C_8{-}H_{8a}$ | 116(2) | $C_8{-}C_9{-}H_9$ | 125(2) |
| $C_9{-}C_8{-}H_{8a}$ | 117(2) | $Mo_1{-}C_9{-}H_9$ | 119(2) |
| $C_{11}{-}C_8{-}H_{8b}$ | 109(2) | $C_{10}{-}C_{12}{-}H_{12}$ | 115(2) |
| $C_9{-}C_8{-}H_{8b}$ | 117(2) | $C_{13}{-}C_{12}{-}H_{12}$ | 115(2) |
| $H_{8a}$-$C_8{-}H_{8b}$ | 111(3) | $Mo_1{-}C_{12}{-}H_{12}$ | 105(2) |

[a,b,c] See footnotes in Table 3.

4. Bond lengths are provided in Table 5, and bond angles in Table 6. The $\pi$-allyl C–C bond within the ring ($C_9{-}C_{10}$, 1.441(4) Å) is considerably longer than the external $\pi$-allyl bond ($C_{10}{-}C_{12}$, 1.406(4) Å), indicating **28a** also strongly resembles a complexed 2-alkylidene cyclobutanone. The Mo–$\pi$-allyl carbon bonds are also not equivalent, with the distance from the metal to $C_{10}$ being the shortest (2.221(2) Å) and Mo–$C_{12}$ the longest (2.410(3) Å), similar to the asymmetry we had noted for the methyl analogues previously.[8]

The minor alkylidene cyclobutanonyl complex **28b** was assigned the *E* (*exo*) rather than *Z* (*endo*) configuration because $R_1 = H_a$ shifts dramatically from $\delta$ 3.7 in the major isomer to $\delta$ 5.1 in the minor isomer. If the minor isomer were *Z* (*endo*), this chemical shift would

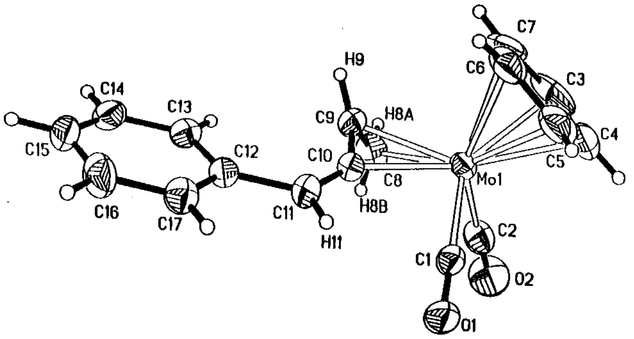


**Figure 3.** Molecular structure of complex **29** using 50% probability thermal ellipsoids.

**Table 7. Crystal Data and Structure Refinement for $\mathrm{Mo(CO)_2(C_5H_5)(C_4H_4(C_6H_5))}$ (29)**

| | |
|---|---|
| Empirical formula | $\mathrm{C_{17}H_{14}MoO_2}$ |
| fw | 346.22 |
| temp | 293(2) K |
| wavelength | 0.71073 Å |
| cryst syst, space group | monoclinic, $P2(1)/n$, an alternate setting of $P2_1/c - C_{2h}{}^5$ (No. 14) |
| unit cell dimens | $a = 6.302(2)$ Å<br>$b = 7.609(1)$ Å, $\beta = 90.865(14)°$<br>$c = 29.721(3)$ Å |
| volume | 1425.1(5) Å$^3$ |
| $Z$, calcd density | 4, 1.614 g/cm$^3$ |
| abs coeff | 0.918 mm$^{-1}$ |
| $F(000)$ | 696 |
| cryst size | 0.10 × 0.17 × 0.65 mm |
| $\theta$ range for data collection | 2.74−27.49° |
| limiting indices | $-1 \le h \le 8$, $-1 \le k \le 9$, $-38 \le l \le 38$ |
| no. of reflns collected/unique | 4743/3262 [$R_{\mathrm{int}} = 0.0260$] |
| completeness to $\theta = 27.49$ | 99.9% |
| abs corr | empirical |
| max. and min. transmsn | 0.8868 and 0.7033 |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/params | 3262/194 |
| goodness-of-fit on $F^2$ | 1.050 |
| final $R$ indices | |
| [2445 $I > 2\sigma(I)$ data] | R1 = 0.0311, wR2 = 0.0618 |
| [all 3262 data] | R1 = 0.0569, wR2 = 0.0707 |
| extinction coeff | 0.0007(3) |
| largest diff peak and hole | 0.432 and −0.616 e/Å$^3$ |

**Table 8. Bond Lengths in Crystalline $\mathrm{Mo(CO)_2(C_5H_5)(C_4H_4(C_6H_5))}$ (29)[a]**

| type[b] | length, Å | type[b] | length, Å |
|---|---|---|---|
| $\mathrm{Mo_1{-}C_8}$ | 2.345(4) | $\mathrm{Mo_1{-}C_3}$ | 2.329(3) |
| $\mathrm{Mo_1{-}C_9}$ | 2.239(3) | $\mathrm{Mo_1{-}C_4}$ | 2.309(3) |
| $\mathrm{Mo_1{-}C_{10}}$ | 2.223(3) | $\mathrm{Mo_1{-}C_5}$ | 2.332(4) |
| | | $\mathrm{Mo_1{-}C_6}$ | 2.371(4) |
| $\mathrm{Mo_1{-}C_1}$ | 1.939(3) | $\mathrm{Mo_1{-}C_7}$ | 2.367(4) |
| $\mathrm{Mo_1{-}C_2}$ | 1.950(4) | $\mathrm{Mo_1{-}C_p}{}^c$ | 2.024(−) |
| $\mathrm{O_1{-}C_1}$ | 1.151(4) | $\mathrm{C_3{-}C_4}$ | 1.385(6) |
| $\mathrm{O_2{-}C_2}$ | 1.146(4) | $\mathrm{C_3{-}C_7}$ | 1.399(6) |
| | | $\mathrm{C_4{-}C_5}$ | 1.374(6) |
| $\mathrm{C_8{-}C_9}$ | 1.390(5) | $\mathrm{C_5{-}C_6}$ | 1.372(6) |
| $\mathrm{C_9{-}C_{10}}$ | 1.396(4) | $\mathrm{C_6{-}C_7}$ | 1.397(6) |
| $\mathrm{C_{10}{-}C_{11}}$ | 1.321(4) | | |
| $\mathrm{C_{11}{-}C_{12}}$ | 1.475(4) | $\mathrm{C_8{-}H_{8a}}$ | 0.92(4) |
| $\mathrm{C_{12}{-}C_{13}}$ | 1.387(4) | $\mathrm{C_8{-}H_{8b}}$ | 0.81(4) |
| $\mathrm{C_{12}{-}C_{17}}$ | 1.392(4) | $\mathrm{C_{11}{-}H_{11}}$ | 0.91(3) |
| $\mathrm{C_{13}{-}C_{14}}$ | 1.389(4) | | |
| $\mathrm{C_{14}{-}C_{15}}$ | 1.373(5) | | |
| $\mathrm{C_{15}{-}C_{16}}$ | 1.374(5) | | |
| $\mathrm{C_{16}{-}C_{17}}$ | 1.384(4) | | |

[a,b,c] See footnotes in Table 3.

**Table 9. Bond Angles in Crystalline $\mathrm{Mo(CO)_2(C_5H_5)(C_4H_4(C_6H_5))}$ (29)[a]**

| type[b,c] | angle, deg | type[b,c] | angle, deg |
|---|---|---|---|
| $\mathrm{C_1{-}Mo_1{-}C_8}$ | 108.94(15) | $\mathrm{C_2{-}Mo_1{-}C_8}$ | 74.00(16) |
| $\mathrm{C_1{-}Mo_1{-}C_9}$ | 103.64(12 | $\mathrm{C_2{-}Mo_1{-}C_9}$ | 107.15(14) |
| $\mathrm{C_1{-}Mo_1{-}C_{10}}$ | 70.19(12) | $\mathrm{C_2{-}Mo_1{-}C_{10}}$ | 113.82(12) |
| $\mathrm{C_1{-}Mo_1{-}C_p}{}^c$ | 122.3(−) | $\mathrm{C_2{-}Mo_1{-}C_p}{}^c$ | 119.7(−) |
| $\mathrm{C_8{-}Mo_1{-}C_p}{}^c$ | 128.2(−) | $\mathrm{C_9{-}Mo_1{-}C_p}{}^c$ | 117.6(−) |
| $\mathrm{C_{10}{-}Mo_1{-}C_p}{}^c$ | 126.3(−) | | |
| $\mathrm{C_{10}{-}Mo_1{-}C_9}$ | 36.46(11) | $\mathrm{C_3{-}Mo_1{-}C_5}$ | 57.25(16) |
| $\mathrm{C_4{-}Mo_1{-}C_3}$ | 34.74(16) | $\mathrm{C_4{-}Mo_1{-}C_7}$ | 57.36(15) |
| $\mathrm{C_4{-}Mo_1{-}C_5}$ | 34.43(15) | $\mathrm{C_5{-}Mo_1{-}C_7}$ | 56.72(15) |
| $\mathrm{C_9{-}Mo_1{-}C_8}$ | 35.20(13) | $\mathrm{C_4{-}Mo_1{-}C_6}$ | 57.14(14) |
| $\mathrm{C_3{-}Mo_1{-}C_7}$ | 34.64(14) | $\mathrm{C_3{-}Mo_1{-}C_6}$ | 57.39(14) |
| $\mathrm{C_5{-}Mo_1{-}C_6}$ | 33.90(14) | | |
| $\mathrm{C_7{-}Mo_1{-}C_6}$ | 34.30(14) | $\mathrm{C_1{-}Mo_1{-}C_2}$ | 79.79(15) |
| $\mathrm{C_{10}{-}Mo_1{-}C_4}$ | 149.93(15) | $\mathrm{C_4{-}Mo_1{-}C_8}$ | 140.80(17) |
| $\mathrm{C_1{-}Mo_1{-}C_3}$ | 139.35(16) | $\mathrm{C_3{-}Mo_1{-}C_8}$ | 107.83(17) |
| $\mathrm{C_1{-}Mo_1{-}C_4}$ | 105.01(16) | $\mathrm{C_5{-}Mo_1{-}C_8}$ | 155.04(17) |
| $\mathrm{C_2{-}Mo_1{-}C_4}$ | 93.67(15) | $\mathrm{C_1{-}Mo_1{-}C_7}$ | 147.25(15) |
| $\mathrm{C_9{-}Mo_1{-}C_4}$ | 147.06(14) | $\mathrm{C_2{-}Mo_1{-}C_7}$ | 125.09(16) |
| $\mathrm{C_2{-}Mo_1{-}C_3}$ | 94.31(14) | $\mathrm{C_{10}{-}Mo_1{-}C_7}$ | 110.22(14) |
| $\mathrm{C_{10}{-}Mo_1{-}C_3}$ | 144.46(15) | $\mathrm{C_9{-}Mo_1{-}C_7}$ | 89.71(14) |
| $\mathrm{C_9{-}Mo_1{-}C_3}$ | 116.39(16) | $\mathrm{C_8{-}Mo_1{-}C_7}$ | 99.23(16) |
| $\mathrm{C_1{-}Mo_1{-}C_5}$ | 92.66(15) | $\mathrm{C_1{-}Mo_1{-}C_6}$ | 113.48(15) |
| $\mathrm{C_2{-}Mo_1{-}C_5}$ | 123.61(15) | $\mathrm{C_2{-}Mo_1{-}C_6}$ | 149.63(13) |
| $\mathrm{C_{10}{-}Mo_1{-}C_5}$ | 115.55(14) | $\mathrm{C_{10}{-}Mo_1{-}C_6}$ | 96.52(12) |
| $\mathrm{C_9{-}Mo_1{-}C_5}$ | 128.72(15) | $\mathrm{C_9{-}Mo_1{-}C_6}$ | 96.39(14) |
| $\mathrm{C_{10}{-}Mo_1{-}C_8}$ | 63.30(12) | $\mathrm{C_8{-}Mo_1{-}C_6}$ | 122.12(17) |
| $\mathrm{O_1{-}C_1{-}Mo_1}$ | 179.3(3) | $\mathrm{O_2{-}C_2{-}Mo_1}$ | 177.9(3) |
| $\mathrm{C_4{-}C_3{-}C_7}$ | 107.5(4) | $\mathrm{C_8{-}C_9{-}C_{10}}$ | 118.9(3) |
| $\mathrm{C_5{-}C_4{-}C_3}$ | 108.1(4) | $\mathrm{C_{11}{-}C_{10}{-}C_9}$ | 142.7(3) |
| $\mathrm{C_6{-}C_5{-}C_4}$ | 109.3(4) | $\mathrm{C_{11}{-}C_{10}{-}Mo_1}$ | 144.5(2) |
| $\mathrm{C_5{-}C_6{-}C_7}$ | 107.5(4) | $\mathrm{C_{10}{-}C_{11}{-}C_{12}}$ | 126.8(3) |
| $\mathrm{C_6{-}C_7{-}C_3}$ | 107.7(4) | $\mathrm{C_{13}{-}C_{12}{-}C_{17}}$ | 118.2(3) |
| | | $\mathrm{C_{13}{-}C_{12}{-}C_{11}}$ | 123.6(3) |
| $\mathrm{C_4{-}C_3{-}Mo_1}$ | 71.8(2) | $\mathrm{C_{17}{-}C_{12}{-}C_{11}}$ | 118.2(3) |
| $\mathrm{C_7{-}C_3{-}Mo_1}$ | 74.2(2) | $\mathrm{C_{12}{-}C_{13}{-}C_{14}}$ | 120.4(3) |
| $\mathrm{C_5{-}C_4{-}Mo_1}$ | 73.7(2) | $\mathrm{C_{15}{-}C_{14}{-}C_{13}}$ | 120.7(3) |
| $\mathrm{C_3{-}C_4{-}Mo_1}$ | 73.4(2) | $\mathrm{C_{14}{-}C_{15}{-}C_{16}}$ | 119.6(3) |
| $\mathrm{C_6{-}C_5{-}Mo_1}$ | 74.6(2) | $\mathrm{C_{15}{-}C_{16}{-}C_{17}}$ | 120.2(3) |
| $\mathrm{C_4{-}C_5{-}Mo_1}$ | 71.9(2) | $\mathrm{C_{16}{-}C_{17}{-}C_{12}}$ | 121.0(3) |
| $\mathrm{C_5{-}C_6{-}Mo_1}$ | 71.5(2) | | |
| $\mathrm{C_7{-}C_6{-}Mo_1}$ | 72.7(2) | $\mathrm{Mo_1{-}C_8{-}H_{8a}}$ | 119(2) |
| $\mathrm{C_6{-}C_7{-}Mo_1}$ | 73.0(2) | $\mathrm{Mo_1{-}C_8{-}H_{8b}}$ | 108(3) |
| $\mathrm{C_3{-}C_7{-}Mo_1}$ | 71.2(2) | $\mathrm{C_9{-}C_8{-}H_{8a}}$ | 119(3) |
| $\mathrm{C_9{-}C_8{-}Mo_1}$ | 68.26(19) | $\mathrm{C_9{-}C_8{-}H_{8b}}$ | 123(3) |
| $\mathrm{C_8{-}C_9{-}Mo_1}$ | 76.5(2) | $\mathrm{H_{8a}\text{-}C_8{-}H_{8b}}$ | 112(4) |
| $\mathrm{C_{10}{-}C_9{-}Mo_1}$ | 71.11(17) | $\mathrm{C_{10}{-}C_{11}{-}H_{11}}$ | 119(2) |
| $\mathrm{C_9{-}C_{10}{-}Mo_1}$ | 72.43(17) | $\mathrm{C_{12}{-}C_{11}{-}H_{11}}$ | 114(2) |

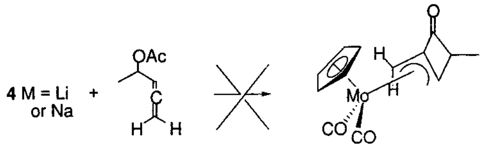
[a,b,c] See footnotes in Table 3.

be expected to shift downfield by less than 1 ppm between isomers, as described above. Complex **29** was assigned the *Z* (*exo*) configuration because its allyl proton chemical shifts were almost identical with those of the methyl *Z* (*exo*) complex (**15a**) described above. This postulate based on $^1$H NMR data for **29** was also confirmed by X-ray crystallography. The ORTEP of this complex (**29**) is provided in Figure 3. Crystal data and structure refinement parameters are in Table 7. Bond lengths are provided in Table 8, and bond angles in Table 9.

We also isolated a small amount of the $\mathrm{S_N2'}$ addition product (**30**), which we had not seen previously for any of the other allenic electrophiles. The $^1$H NMR of the dienyl portion of **30** was analogous to what we have reported previously for a number of cobalt- and iron-substituted 1,3-dienes[7,9,10] [$^1$H NMR (CDCl$_3$): 5.80 (dd, $J = 17.1$, 10.4 Hz, 1H), 5.38 (d, $J = 17.1$ Hz, 1H), 5.18 (s, 1H), 5.00 (d, $J = 10.4$ Hz, 1H)]. We presume that this complex (**30**) has the *E* alkene stereochemistry shown based on analogy with our previously reported cobalt work, which gave *E* dienes for similarly substituted allenic electrophiles.[10] Switching to the larger phenyl substituent on the allene **25** has resulted in a situation where CO insertion and CO loss yield almost identical amounts of product. We presume that the electron-withdrawing inductive effect of the phenyl group is responsible for the fact that $S_N2'$ attack has started to become competitive with $S_N2$ here.

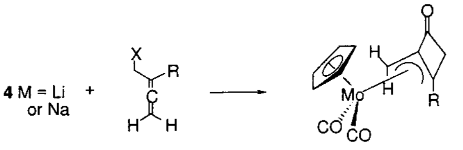
All the reactions of allenic electrophiles with molybdenum anion (**4**, M = Na or Li) described above were run under conditions that should yield thermodynamic products: several hours of stirring at 25 °C or above. Since the reaction of **4** with **25** proved to be unusual in product composition, we also decided to try to look at the kinetic product mixture from this reaction. Molybdenum anion (**4**) was allowed to react with **25** at 25 °C in THF for only 15 min before workup. Somewhat surprisingly, we isolated a 1:1:1 mixture of **28a**/**29**/**30** (isolated yields, 10%, 10%, 9%). None of the *E* isomer (**28b**) was present, and the relative amount of **30** present was larger than the thermodynamic result. Our earlier experiments run under CO would indicate that **29** is an unlikely precursor to **28** or **30**. Complex **30**, however, could serve as a precursor to **29** via CO loss and could also serve as a precursor to the *E* isomer (**28b**) via CO insertion and alkene insertion. However, since **30** was never isolated in large amount from any experiment, it is unlikely to be synthetically useful compared with our other previously reported 1,3-dienyl complexes,[7,9,10] and its reaction chemistry was not pursued further.

Having investigated the effect of terminal allene substitutents on reaction outcome, we proceeded to substituent changes at other points in the allenic electrophiles we used. We had prepared secondary allenic acetate **31** earlier for use in our cobaloxime chemistry.[21] We found this secondary, rather than primary, allenic acetate to be unreactive toward both the sodium and lithium salts of **4**. In each case (even heating the anion (**4**) with **31** for several hours), we observed only $[CpMo(CO)_3]_2$ and the electrophile **31** by TLC. We presume from this result that only primary allenic electrophiles are viable substrates for the $S_N2$ reaction. However, since we used an allenic acetate rather than a tosylate here, we cannot rule out the idea that the leaving group has an impact on reaction outcome. We can note that in our previously reported cobaloxime dienyl complex synthesis, allenic acetates and tosylates were interchangeable.[10,21] The fact that we did not see any $S_N2'$ product here also lends additional support to the suggestion that electron-withdrawing substituents are needed on the allene to promote this mode of attack.



**31**

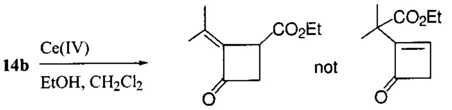
Green et al. had reported reactions of the $CpMo(CO)_3$ anion with the methyl- and ethyl-substituted chlorides (**32a**,**b**).[6] However when we tried using α-methyl allenic acetate (**32c**) in this reaction, we isolated only trace amounts of alkylidene cyclobutanone complex (**33a**), again recovering mostly molybdenum starting material $[CpMo(CO)_3]_2$.



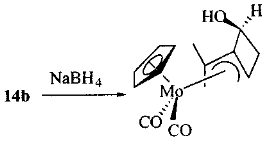
**32a** R = Me, X = Cl
**32b** R = Et, X = Cl
**32c** R = Me, X = OAc

**33a** R = Me
**33b** R = Et

**(ii) Demetalation, Nucleophilic Addition, and Enolate Reactions of the Cyclopentadienyl Molybdenum Dicarbonyl Complexed Alkylidene Cyclobutanones.** We have successfully oxidatively demetalated **14b** to yield functionalized alkylidene cyclobutanone **34** (67%). Compound **34** presumably arises via Ce(IV) oxidation of the molybdenum in **14b**, thereby activating the π-allyl for CO insertion followed by nucleophilic attack of ethanol. Isolation of alkylidene cyclobutanone **34** rather than cyclobutenone **35** was expected based on the X-ray structure of **14b**.[8] Additionally, we have found that nucleophilic addition to the cyclobutanone carbonyl is also possible. Complex **14b** was treated with $NaBH_4$ using Liu's protocol,[22] and a single new complex (**36**) was isolated in high yield (92%).



**34** **35**



**36**

Oxidative demetalation of **36** somewhat unexpectedly yielded an essentially 1:1 mixture of diastereomers **37** and **38**. The crude product of this reaction was a quantitative amount of the **37**/**38** mixture by $^1H$ NMR, but even rapid filtration through silica resulted in isolation of only the *anti* isomer **38** (50% yield). Assignment of *syn* and *anti* to **37** and **38** was done based on analysis of their $^1H$ NMR spectra. Methylene protons $H_a$ and $H_b$ are magnetically inequivalent in the *syn* isomer **37**, so they show geminal coupling. These same protons in **38** are made magnetically equivalent via ring flip, hence no geminal coupling. Cerium(IV) is known to rapidly complex alcohols.[23] Such a complexation could both facilitate replacement of the hydroxyl by ethanol in **36** and slow CO insertion enough to allow EtOH nucleophilic attack at the least substituted π-allyl terminus to become competitive.

Treatment of **36** with Ce(IV) in ethanol followed by aqueous base workup unexpectedly yielded cyclobutene **39** (46%). Compounds **37** and **38** are present in solution (by TLC) prior to the addition of the 10% $Na_2CO_3$.

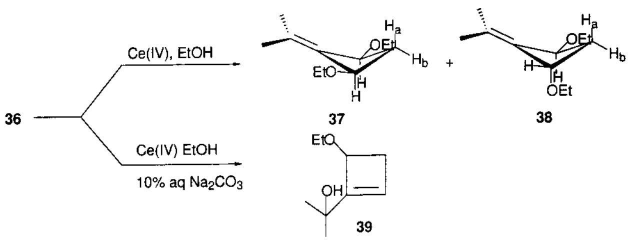
---

[21] Wright, M. W.; Smalley, T. L.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6777.

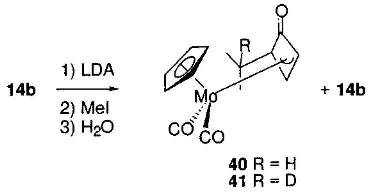
[22] (a) Lin, S. H.; Lush, S. F.; Cheng, W. J.; Lee, G. H.; Peng, S. M.; Liao, Y. L.; Wang, S. L.; Liu, R. S. *Organometallics* **1994**, *13*, 1711. (b) Vong, W. J.; Peng, S. M.; Lin, S. H.; Lin, W. J.; Liu, R. S. *J. Am. Chem. Soc.* **1991**, *113*, 573.

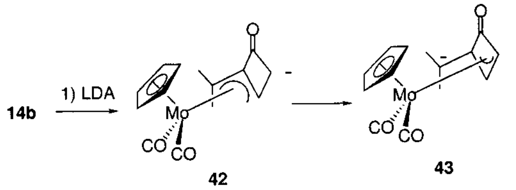
[23] Trahanovsky, W. S.; Young, L. B. *J. Chem. Soc.* **1965**, 5777.

Addition of base in the presence of cerium and molybdenum then causes conversion to **39**. Attempts to convert the **37**/**38** mixture into **39** with just base and with base plus cerium proved unsuccessful. Oxidized molybdenum byproduct is thus presumably playing a role in this conversion. The production of **39** can be rationalized as a formal $S_N2'$ replacement of ethoxide in **37** or **38** by hydroxide under these basic reaction conditions.



As noted for the reaction of **4** with **31** above, attempts to synthesize alkylidene cyclobutanonyl complexes with substituents α to the carbonyl failed. An alternative approach to such complexes would be to form the enolate of a complexed cyclobutanone such as **9**, **14a**, or **14b** and alkylate it by analogy with chemistry previously reported by both Pearson[24] and Liu.[25] Use of Pearson's enolate generation method[24] on **14b** followed by addition of MeI and aqueous workup yielded a 1:1 mixture of recovered starting material (**14b**, 26%) and a new endocyclic $\eta^3$-cyclobutenonyl or oxocyclobutenyl complex (**40**, 25%). The first hint that the $\pi$-allyl in **40** was now endocyclic came from the IR spectrum, where the cyclobutanone C=O stretch had shifted from 1745 cm$^{-1}$ in **14b** down to 1678 cm$^{-1}$ in **40**. This lower wavenumber absorption is similar to those observed by Brisdon[4d] (1680 cm$^{-1}$) and Hughes[4e,f] (1677 cm$^{-1}$) in related complexes discussed in the Introduction. The proton in the isopropyl group of **40** apparently comes from the aqueous workup since repetition of this experiment using MeI followed by $D_2O$ or simply enolate generation followed by $D_2O$ quench yielded **14b** and the deuterated isopropyl complex **41**. Increasing the amount of THF used for LDA generation and increasing the equivalents of LDA used for enolate generation to 2.2 followed by MeI addition and aqueous workup yielded a crude product that by $^1$H NMR was a 3:1 mixture of **40** (57%) and **14b** (19%) in good mass balance (76%). However, **40** must be sensitive to chromatographic purification since after chromatography the isolated yield of **40** remained 26%. Treatment of **14b** with LDA presumably generates enolate **42** initally, which rapidly isomerizes to the endocyclic vinylogous enolate **43**. Steric hindrance in **43** presumably prevents alkylation and the enolate is simply protonated (**40**) or deuterated (**41**) on workup. We do not think the enolate is a mixture of **42** and **43** since we do not isolate any **14b** deuterated α to the carbonyl after $D_2O$ quench.





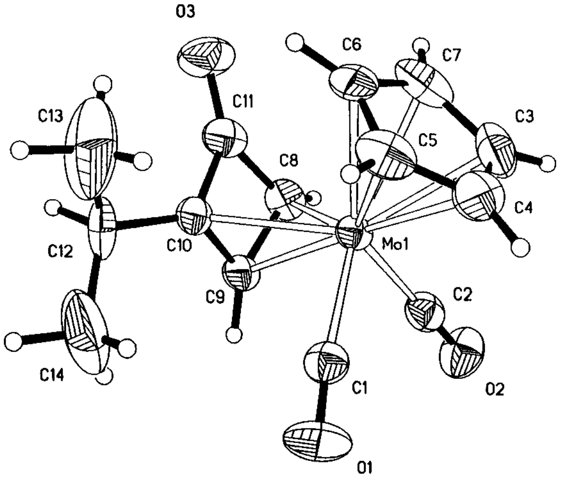


**Figure 4.** Molecular structure of complex **41** using 50% probability thermal ellipsoids.

**Table 10. Crystal Data and Structure Refinement for $[C_5H_5]Mo(CO)_2[C_4H_2O(CMe_2D)]$ (41)**

| | |
|---|---|
| empirical formula | $C_{14}H_{13}DMoO_3$ |
| fw | 327.21 |
| temp | 228(2) K |
| wavelength | 0.71073 Å |
| cryst syst, space group | orthorhombic, $Pbca-D_{2h}{}^{15}$ (No. 61) |
| unit cell dimens | $a = 13.561(1)$ Å<br>$b = 11.168(1)$ Å<br>$c = 17.159(2)$ Å |
| volume | 2598.9(5) Å$^3$ |
| $Z$, calcd density | 8, 1.672 g/cm$^{-3}$ |
| abs coeff | 1.006 mm$^{-1}$ |
| $F$(000) | 1312 |
| cryst size | 0.03 × 0.15 × 0.30 mm |
| $\theta$ range for data collection | 2.37−24.11° |
| limiting indices | $-15 \le h \le 1, -12 \le k \le 1, -1 \le l \le 19$ |
| no. of reflns collected/unique | 2681/2064 [$R_{int} = 0.0352$] |
| completeness to $\theta = 24.11°$ | 99.9% |
| refinement method | full-matrix least-squares on $F^2$ |
| abs corr | semiempirical from $\psi$-scans |
| max. and min. transmsn | 0.6810 and 0.6511 |
| no. of data/params | 2064/176 |
| goodness-of-fit on $F^2$ | 1.007 |
| final $R$ indices | |
| [1285 $I > 2\sigma(I)$ data] | R1 = 0.0419, wR2 = 0.0563 |
| [all 2064 data] | R1 = 0.0930, wR2 = 0.0670 |
| extinction coeff | 0.00028(9) |
| largest diff peak and hole | 0.415 and −0.407 e$^-$/Å$^3$ |

The formulation of these complexes (**40** and **41**) as endocyclic $\eta^3$-cyclobutenonyl or oxocyclobutenyl complexes was confirmed by X-ray crystallographic characterization of **41**. The ORTEP of this complex is provided in Figure 4. Crystal data and structure refinement parameters are in Table 10. Bond lengths are provided in Table 11, and bond angles in Table 12. This

---

(24) (a) Pearson, A. J.; Mortezaei, R. *Tetrahedron Lett.* **1989**, *30*, 5049. (b) Pearson, A. J.; Mallik, A.; Pinkerton, A.; Adams, J. P.; Zheng, S. *J. Org. Chem.* **1992**, *57*, 2910.

(25) Lin, S.-H.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1993**, *12*, 2591.

**Table 11. Bond Lengths in Crystalline $[C_5H_5]Mo(CO)_2[C_4H_2O(CMe_2D)]$ (41)[a]**

| type[b] | length, Å | type[b] | length, Å |
|---|---|---|---|
| $Mo_1-C_1$ | 1.979(6) | $Mo_1-C_3$ | 2.321(6) |
| $Mo_1-C_2$ | 1.995(6) | $Mo_1-C_4$ | 2.312(6) |
|  |  | $Mo_1-C_5$ | 2.314(7) |
| $Mo_1-C_8$ | 2.248(6) | $Mo_1-C_6$ | 2.333(6) |
| $Mo_1-C_9$ | 2.203(6) | $Mo_1-C_7$ | 2.336(6) |
| $Mo_1-C_{10}$ | 2.295(5) | $Mo_1-Cp^c$ | 1.997(−) |
|  |  | $Mo_1\cdots C_{11}$ | 2.610(6) |
| $O_1-C_1$ | 1.143(6) | $O_3-C_{11}$ | 1.208(7) |
| $O_2-C_2$ | 1.132(6) |  |  |
| $C_8-C_9$ | 1.430(8) | $C_3-C_7$ | 1.378(9) |
| $C_8-C_{11}$ | 1.482(8) | $C_3-C_4$ | 1.383(9) |
| $C_9-C_{10}$ | 1.443(8) | $C_4-C_5$ | 1.400(8) |
| $C_{10}-C_{11}$ | 1.495(8) | $C_5-C_6$ | 1.392(9) |
|  |  | $C_6-C_7$ | 1.421(9) |
| $C_{10}-C_{12}$ | 1.502(8) |  |  |
|  |  | $C_8-H_8$ | 0.89(5) |
| $C_{12}-C_{14}$ | 1.480(10) | $C_9-H_9$ | 0.96(5) |
| $C_{12}-C_{13}$ | 1.529(10) | $C_{12}\text{-}D_{12}$ | 0.97(5) |

[a,b,c] See footnotes in Table 3.

**Table 12. Bond Angles in Crystalline $[C_5H_5]Mo(CO)_2[C_4H_2O(CMe_2D)]$ (41)[a]**

| type[b,c] | angle, deg | type[b,c] | angle, deg |
|---|---|---|---|
| $C_1-Mo_1-C_2$ | 83.1(2) |  |  |
| $C_1-Mo_1-C_9$ | 82.8(2) | $C_2-Mo_1-C_9$ | 82.0(2) |
| $C_1-Mo_1-C_8$ | 119.3(2) | $C_2-Mo_1-C_8$ | 79.9(2) |
| $C_1-Mo_1-C_{10}$ | 87.3(2) | $C_2-Mo_1-C_{10}$ | 119.3(2) |
| $C_1-Mo_1-C_p{}^c$ | 117.7(−) | $C_2-Mo_1-C_p{}^c$ | 118.0(−) |
| $C_8-Mo_1-C_p{}^c$ | 121.8(−) | $C_9-Mo_1-C_p{}^c$ | 151.7(−) |
| $C_{10}-Mo_1-C_p{}^c$ | 119.4(−) | $C_{11}-Mo_1-C_p{}^c$ | 102.5(−) |
| $C_8-Mo_1-C_{11}$ | 34.5(2) | $C_8-Mo_1-C_{10}$ | 54.2(2) |
| $C_{10}-Mo_1-C_{11}$ | 34.74(19) | $C_9-Mo_1-C_{11}$ | 49.3(2) |
| $C_9-Mo_1-C_8$ | 37.5(2) | $C_5-Mo_1-C_3$ | 58.2(2) |
| $C_9-Mo_1-C_{10}$ | 37.3(2) | $C_4-Mo_1-C_6$ | 58.2(2) |
| $C_4-Mo_1-C_3$ | 34.7(2) | $C_3-Mo_1-C_6$ | 58.2(2) |
| $C_4-Mo_1-C_5$ | 35.2(2) | $C_4-Mo_1-C_7$ | 57.8(2) |
| $C_5-Mo_1-C_6$ | 34.9(2) | $C_5-Mo_1-C_7$ | 58.2(2) |
| $C_3-Mo_1-C_7$ | 34.4(2) |  |  |
| $C_6-Mo_1-C_7$ | 35.4(2) |  |  |
| $C_1-Mo_1-C_3$ | 122.1(3) | $C_2-Mo_1-C_3$ | 87.7(2) |
| $C_1-Mo_1-C_4$ | 91.7(2) | $C_2-Mo_1-C_4$ | 100.9(2) |
| $C_1-Mo_1-C_5$ | 92.0(2) | $C_2-Mo_1-C_5$ | 135.9(2) |
| $C_1-Mo_1-C_6$ | 122.9(2) | $C_2-Mo_1-C_6$ | 144.2(2) |
| $C_1-Mo_1-C_7$ | 148.1(2) | $C_2-Mo_1-C_7$ | 109.5(3) |
| $C_1-Mo_1-C_{11}$ | 121.7(2) | $C_2-Mo_1-C_{11}$ | 114.4(2) |
| $C_9-Mo_1-C_3$ | 151.8(3) | $C_{10}-Mo_1-C_5$ | 104.1(2) |
| $C_8-Mo_1-C_3$ | 114.9(3) | $C_9-Mo_1-C_6$ | 122.2(2) |
| $C_{10}-Mo_1-C_3$ | 143.5(3) | $C_8-Mo_1-C_6$ | 103.2(2) |
| $C_9-Mo_1-C_4$ | 173.5(2) | $C_{10}-Mo_1-C_6$ | 88.7(2) |
| $C_8-Mo_1-C_4$ | 148.6(2) | $C_9-Mo_1-C_7$ | 127.0(2) |
| $C_{10}-Mo_1-C_4$ | 139.3(2) | $C_8-Mo_1-C_7$ | 92.1(2) |
| $C_9-Mo_1-C_5$ | 141.0(2) | $C_{10}-Mo_1-C_7$ | 109.4(3) |
| $C_8-Mo_1-C_5$ | 137.3(3) | $C_4-Mo_1-C_{11}$ | 132.8(2) |
| $C_5-Mo_1-C_{11}$ | 105.4(2) | $C_3-Mo_1-C_{11}$ | 114.1(3) |
| $C_6-Mo_1-C_{11}$ | 75.1(2) | $C_7-Mo_1-C_{11}$ | 80.7(2) |
| $O_1-C_1-Mo_1$ | 174.5(6) | $O_2-C_2-Mo_1$ | 179.3(6) |
| $C_7-C_3-C_4$ | 108.8(6) | $C_9-C_8-C_{11}$ | 89.0(5) |
| $C_3-C_4-C_5$ | 108.1(6) | $C_8-C_9-C_{10}$ | 92.1(5) |
| $C_6-C_5-C_4$ | 108.1(6) | $C_9-C_{10}-C_{11}$ | 88.0(5) |
| $C_5-C_6-C_7$ | 107.1(7) | $C_9-C_{10}-C_{12}$ | 132.5(6) |
| $C_3-C_7-C_6$ | 107.9(7) | $C_{11}-C_{10}-C_{12}$ | 129.6(6) |
|  |  | $O_3-C_{11}-C_8$ | 135.1(7) |
| $C_8-C_{11}-Mo_1$ | 59.2(3) | $O_3-C_{11}-C_{10}$ | 136.9(7) |
| $C_{10}-C_{11}-Mo_1$ | 61.0(3) | $C_8-C_{11}-C_{10}$ | 88.0(5) |
| $C_7-C_3-Mo_1$ | 73.4(4) | $C_3-C_7-Mo_1$ | 72.2(4) |
| $C_4-C_3-Mo_1$ | 72.3(4) | $C_6-C_7-Mo_1$ | 72.2(4) |
| $C_3-C_4-Mo_1$ | 73.0(4) | $C_9-C_8-Mo_1$ | 69.6(3) |
| $C_5-C_4-Mo_1$ | 72.4(4) | $C_{11}-C_8-Mo_1$ | 86.3(4) |
| $C_6-C_5-Mo_1$ | 73.3(4) | $C_8-C_9-Mo_1$ | 73.0(3) |
| $C_4-C_5-Mo_1$ | 72.3(4) | $C_{10}-C_9-Mo_1$ | 74.8(3) |
| $C_5-C_6-Mo_1$ | 71.8(4) | $C_9-C_{10}-Mo_1$ | 67.9(3) |
| $C_7-C_6-Mo_1$ | 72.4(4) | $C_{11}-C_{10}-Mo_1$ | 84.2(3) |
| $C_{12}-C_{10}-Mo_1$ | 133.2(5) | $C_{14}-C_{12}-C_{10}$ | 114.5(6) |
| $O_3-C_{11}-Mo_1$ | 134.7(5) | $C_{14}-C_{12}-C_{13}$ | 113.0(7) |
|  |  | $C_{10}-C_{12}-C_{13}$ | 109.9(6) |
| $C_9-C_8-H_8$ | 129(4) | $Mo_1-C_9-H_9$ | 123(3) |
| $C_{11}-C_8-H_8$ | 136(4) | $C_{14}-C_{12}\text{-}D_{12}$ | 113(3) |
| $Mo_1-C_8-H_8$ | 124(4) | $C_{10}-C_{12}\text{-}D_{12}$ | 105(3) |
| $C_8-C_9-H_9$ | 132(3) | $C_{13}-C_{12}\text{-}D_{12}$ | 101(3) |
| $C_{10}-C_9-H_9$ | 134(3) |  |  |

[a,b,c] See footnotes in Table 3.

complex **41** is similar to other $\eta^3$-oxocyclobutenyl complexes characterized by X-ray crystallography previously.[4] The complex has an *endo* configuration for the $\pi$-allyl, and the four-member ring is approximately square (all C−C−C bond angles within the ring within 2° of 90°). The isopropyl group is bent away from the metal center ($Mo-C_{10}-C_{12}$ is 133.2(5)°). The deuterium is at a 105° angle facing away from the metal center, with the two methyl groups occupying the other two $sp^3$ positions in an almost linear plane perpendicular to the $CpMo(CO)_2$ moiety.

In conclusion, we have now investigated the reaction of the $CpMo(CO)_3$ anion with a variety of allenic electrophiles. For reactions with primary, allenic electrophiles this represents a new, general route to alkylidene cyclobutanonyl complexes. Metal complexation of the alkylidene cyclobutanones can be used to direct stereoselective addition reactions to the cyclobutanone carbonyl, and the alkylidene cyclobutane framework can be recovered via demetalation. Enolate generation from the complexed alkylidene cyclobutanone resulted in a shift from an exocyclic $\pi$-allyl complex to an endocyclic $\pi$-allyl. Efforts to extend this chemistry from the $CpMo(CO)_2$ series to the more stable $TpMo(CO)_2$ series will be reported in due course.

## Experimental Section

**General Comments.** All nuclear magnetic resonance (NMR) spectra were obtained using a Varian VXR-200 FT NMR or a Bruker AVANCE 300 FT NMR. All absorptions were expressed in parts per million relative to residual protonated solvent. Infrared (IR) spectra were obtained using a Perkin-Elmer 1620 FTIR. All elemental analyses were performed by Atlantic Microlab, Inc. of Norcross, GA. Low-resolution mass spectral analyses were performed by the Midwest Center for Mass Spectrometry, University of Nebraska−Lincoln, the Duke University Mass Spectrometry Facility, or with a Hewlett-Packard 5989 GC/MS system. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone under nitrogen immediately prior to use. Dichloromethane was distilled from calcium hydride immediately prior to use. All reactions were carried out under an atmosphere of dry nitrogen. Alumina adsorption (80−200 mesh) for column chromatography was purchased from Fisher Scientific and deactivated with an acetone/water mixture (90:10) immediately prior to use. Cyclopentadienylmolybdenum tricarbonyl dimer was purchased from Strem Chemicals and used as received. 4-(*p*-Tolylsulfonyl)-1,2-butadiene (**5**),[21] 1-(*p*-tolylsulfonyl)-2,3-pentadiene (**13a**),[21] 5-(*p*-tolylsulfonyl)-2-methyl-2,3-pentadiene (**13b**),[10a] 4-acetoxy-1,2-pentadiene (**31**),[10a] 4-acetoxy-3-methyl-1,2-pentadiene (**32c**),[10a] and cyclopentadienylmolybdenum dicarbonyl-$\eta^3$-2-methylene-2-cyclobuten-1-one (**9**)[7] were prepared according to previously described methods.

**Cyclopentadienylmolybdenum Dicarbonyl-$\eta^3$-3-methyl-2-methylene-2*E*-cyclobuten-1-one (14a) Using Sodium Amalgam.** The molybdenum complex **14a** was synthesized according to an adaptation of a procedure we have described.[7] Cyclopentadienylmolybdenum tricarbonyl dimer (1.03 g, 2.10

mmol) was used to prepare anion **4** (M = Na), which was added via a double-ended needle under nitrogen to a cooled (0 °C) solution of 1-(*p*-tolylsulfonyl)-2,3-pentadiene (**13a**) (1.00 g, 4.48 mmol) in THF (10 mL). This mixture was stirred for 1 h at 25 °C, followed by 4 h at 45−50 °C. The solvent was removed under reduced pressure and high vacuum. The residue was washed with 50:1 pentane/ether until the washings were clear. These extracts were concentrated and yielded a combination of three molybdenum complexes, which were separated by preparative TLC (alumina, 20:1, pentane/EtOAc) (a 6:1 ratio of major *E* regioisomer (**14a**) (0.17 g, 0.54 mmol, 54%) to minor *Z* isomer (0.03 g, 0.09 mmol, 9%), and $[Hg\{Mo(CO)_3(C_5H_5)\}_2]$[17] (0.03 g, 0.04 mmol, 8%)). Major regioisomer (**14a**, $R_1$ = H, $R_2$ = Me): Mp: 101 °C dec. $^1H$ NMR ($CDCl_3$): 5.21 (s, 5H), 4.37 (d, *J* = 3.0 Hz, 1H), 3.99 (q, *J* = 6.5 Hz, 1H), 3.70 (dd, *J* = 15.5, 3.0 Hz, 1H), 3.10 (d, *J* = 15.5 Hz, 1H), 1.17 (d, *J* = 6.5 Hz, 3H). $^{13}C$ NMR ($CDCl_3$): 235.98, 234.20, 198.72, 95.04, 94.31, 75.42, 54.98, 47.61, 17.17. IR ($CDCl_3$): 1961, 1883, 1746 $cm^{-1}$. LRMS: (*m/z* reported for $Mo^{98}$ isotope) 314(17), 286(2), 258(4), 228(100). Anal. Calcd for $C_{13}H_{12}MoO_3$: C, 50.01; H, 3.88. Found: C, 49.96; H, 4.25. Minor regioisomer (**14a**, $R_1$ = Me, $R_2$ = H): $^1H$ NMR ($CDCl_3$): 5.26 (s, 5H), 3.76 (s, 1H), 3.68 (d, *J* = 15 Hz, 1H), 3.04 (d, *J* = 15 Hz, 1H), 2.64 (q, *J* = 6.7 Hz, 1H), 1.93 (d, *J* = 6.7 Hz, 3H). IR ($CDCl_3$): 1948, 1867, 1745 $cm^{-1}$. HRMS: *m/z* calcd for $C_{13}H_{12}Mo^{98}O_3$ 313.9840, found 313.9854.

**Cyclopentadienylmolybdenum Dicarbonyl-$\eta^3$-3-methyl-2-methylene-2*E*-cyclobuten-1-one (14a) Using Lithium Triethylborohydride.** Cyclopentadienylmolybdenum tricarbonyl dimer (0.245 g, 0.50 mmol) was dissolved in tetrahydrofuran (25 mL) and degassed with dry nitrogen. Lithium triethylborohydride (1.55 mmol of a 1.0 M solution in THF, 1.55 mmol) was added quickly via syringe, and the solution was degassed and stirred for 15 min. 1-(*p*-Tolylsulfonyl)-2,3-pentadiene (**13a**) (0.43 g, 1.80 mmol) in THF (5 mL) was then added quickly, and the solution was degassed. The mixture was heated to 60−70 °C for 2 h. TLC (4:1 pentane/ethyl acetate, alumina) showed two yellow spots ($R_f$ 0.78 and 0.51). The solution was cooled to 25 °C and concentrated under reduced pressure. Chromatography on deactivated alumina with 100% pentane eluted the $\pi$-allyl complexes **15(*Z*)a/15(*E*)a/16(*E*)a** (5:1:1) (0.05 g, 0.17 mmol, 17%). IR (all isomers) ($CDCl_3$): 1957, 1876 $cm^{-1}$. LRMS (FAB): *m/z* for $C_{12}H_{12}{}^{98}MoO_2$ $M^+$ 286 (100), $M^+$ − CO 258 (27), $M^+$ −2CO 230 (20). Anal. Calcd for $C_{12}H_{12}MoO_2$: C, 50.72; H, 4.26. Found: C, 50.47; H, 4.38. The second yellow band (eluted with 10:1 pentane/ethyl acetate) contained a 4.4:1 ratio of the two regioisomers described above (**14a**) (0.22 g, 0.70 mmol, 70%). The $\pi$-allyl complexes were then rechromatographed on an alumina prep plate (1.0 mm, pentane), and the *Z* and *E* isomers were separated. **15(*Z*)a** (major *Z exo* allyl isomer ($R_1$ = H, $R_2$ = Me)): $^1H$ NMR ($CDCl_3$): 5.50 (m, 1H), 5.27 (s, 5H), 3.64 (m, 1H), 2.88 (d, *J* = 7.7 Hz, 1H), 2.03 (dd, *J* = 6.5, 1.5 Hz, 3H), 1.42 (m, 1H). **15(*E*)a** (minor *E exo* allyl isomer ($R_1$ = Me, $R_2$ = H)): $^1H$ NMR ($CDCl_3$): 6.79 (m, 1H), 5.28 (s, 5H), 3.63 (m, 1H), 3.24 (d, *J* = 7.6 Hz, 1H), 1.90 (dd, *J* = 6.6, 1.9 Hz, 3H), 1.60 (d, *J* = 11.0 Hz, 1H). **16(*E*)a** (minor *E endo* allyl isomer ($R_1$ = Me, $R_2$ = H)): $^1H$ NMR ($CDCl_3$): 6.65 (m, 1), 5.28 (s, 5H), 3.43 (m, 1H), 2.76 (dd, *J* = 6.7, 1.1 Hz, 1H), 2.37 (d, *J* = 11.0 Hz, 1H), 1.79 (dd, *J* = 6.5, 1.7 Hz, 3H).

**Cyclopentadienylmolybdenum Dicarbonyl-$\eta^3$-3,3-dimethyl-2-methylene-2-cyclobuten-1-one (14b) Using Sodium Amalgam.** Molybdenum anion (**4**, M = Na) generated from cyclopentadienylmolybdenum tricarbonyl dimer (0.26 g, 0.53 mmol) was added to 5-(*p*-tolylsulfonyl)-2-methyl-2,3-pentadiene (**13b**) (0.25 g, 0.99 mmol) by analogy with the procedure reported for **14a** to synthesize **14b** (0.22 g, 0.67 mmol, 63%) along with $[Hg\{Mo(CO)_3(C_5H_5)\}_2]$[17] (0.08 g, 0.12 mmol, 23%). **14b**: Mp: 89−91 °C dec. $^1H$ NMR ($CDCl_3$): 5.23 (s, 5H), 3.84 (d, *J* = 3.4 Hz, 1H), 3.67 (dd, *J* = 15.5, 3.4 Hz, 1H), 3.05 (d, *J* = 15.5 Hz, 1H), 1.94 (s, 3H), 1.19 (s, 3H). $^{13}C$ NMR ($CDCl_3$): 237.97, 234.57, 198.48, 96.09, 93.77, 77.87, 66.21, 54.48, 25.54, 25.47. IR ($CDCl_3$): 1953, 1876, 1744 $cm^{-1}$. Anal. Calcd for $C_{14}H_{14}MoO_3$: C, 51.55; H, 4.33. Found: C, 51.41; H, 4.47.

**Cyclopentadienylmolybdenum Dicarbonyl-$\eta^3$-3,3-dimethyl-2-methylene-2-cyclobuten-1-one (14b) Using Lithium Triethylborohydride.** The $LiB(Et)_3H$ procedure was used to prepare **14b** as described above for the preparation of **14a**, using 5-(*p*-tolylsulfonyl)-2-methyl-2,3-pentadiene (**13b**) (0.45 g, 1.78 mmol) as the electrophile, except the reaction was stirred 24 h at 25 °C (rather than heating) after mixing the Mo anion (**4**, M = Li) and the electrophile (**13b**). Anion **4** (M = Li) was formed from $[CpMo(CO)_3]_2$ (0.245 g, 0.50 mmol) and lithium triethylborohydride (1.55 mL of a 1.0 M solution in THF, 1.55 mmol). Chromatography on deactivated alumina again provided two yellow bands (TLC, 4:1, pentane/EtOAc, $R_f$ 0.79, 0.59); the first (eluted with pentane) contained the two $\pi$-allyl regioisomers (**15b/16b**) (1.5:1 *exo*:*endo*) (0.072 g, 0.24 mmol, 24%), and the second (10:1 pentane/EtOAc) contained **14b** (0.238 g, 0.73 mmol, 73%), identical by spectroscopic comparison with the material reported above. **15b** and **16b** isomers: IR ($CDCl_3$): 1954, 1873 $cm^{-1}$. Major *exo* allyl isomer (**15b**): $^1H$ NMR ($CDCl_3$): 5.26 (s, 5H), 3.59 (m, 1H), 3.22 (d, *J* = 7.6 Hz, 1H), 2.12 (d, *J* = 0.9 Hz, 3H), 1.90 (d, *J* = 1.7 Hz, 3H), 1.58 (d, *J* = 11.2 Hz, 1H). $^{13}C$ NMR ($CDCl_3$): 238.26, 230.54, 151.61, 126.88, 91.35, 65.13, 48.10, 30.04, 23.38. Minor *endo* allyl isomer (**16b**): $^1H$ NMR ($CDCl_3$): 5.25 (s, 5H), 3.36 (m, 1H), 2.76 (dd, *J* = 6.7, 1.1 Hz, 1H), 2.40 (dd, *J* = 11.1, 1.0 Hz, 1H), 2.10 (s, 3H), 1.81 (d, *J* = 1.4 Hz, 3H). $^{13}C$ NMR ($CDCl_3$): 238.26, 230.54, 157.59, 124.03, 90.31, 49.07, 39.26, 29.46, 24.06. LRMS (FAB): *m/z* for $C_{13}H_{14}{}^{98}MoO_2$ $M^+$ 300 (100), $M^+$ − CO 272 (31), $M^+$ −2CO 244 (48). Both isomers: Anal. Calcd for $C_{13}H_{14}O_2Mo$: C, 52.36; H, 4.73. Found: C, 52.38; H, 4.79.

**3-Tetrahydropyranyl-1-propyne (21).** This compound was prepared according to the method of Henbest.[18] Bp: 76 °C/18 mmHg. Spectroscopic data not reported previously: $^1H$ NMR ($CDCl_3$): 4.80 (t, *J* = 3.1 Hz, 1H), 4.23 (m, 2H), 3.82 (m, 1H), 3.52 (m, 1H), 2.39 (t, *J* = 2.4 Hz, 1H), 1.68 (m, 6H). $^{13}C$ NMR ($CDCl_3$): 96.8, 79.8, 73.9, 62.0, 54.0, 30.2, 25.3, 19.0. LR EIMS: $M^+$ 140 (0.6), 101 (5), 85 (100), 55 (44), 39 (40).

**1-Methoxy-1-phenyl-4-tetrahydropyranyl-2-butyne (22).** This compound was prepared in a manner analogous to part of a synthesis reported by Keck and Webb for 3-methoxyundec-2-yn-1-ol.[19]

*n*-Butyllithium (15.7 mL, 2.5 M in hexanes, 0.0393 mol) in THF (100 mL) was cooled to −78 °C. Compound **21** (5.00 g, 0.0357 mol) in THF (20 mL) was added dropwise. Benzaldehyde (3.63 mL, 0.0357 mol) in THF (10 mL) was also added dropwise, and the solution was stirred 20 min at −78 °C. MeI (8.89 mL, 0.1428 mol) was added, and the solution was warmed to −20 °C. As recommended by Friesen,[26] DMPU (10 mL) was added instead of HMPA. The solution was then warmed to 25 °C and stirred for 1 h. The solvent was removed under reduced pressure. Saturated aqueous NaCl (75 mL) was added, and the water layer was extracted with ether (3 × 30 mL). The ether layers were washed with 1 × $H_2O$ (30 mL), then saturated aqueous NaCl (30 mL). The ether layers were combined and dried with anhydrous $K_2CO_3$, and the solvent was removed under reduced pressure. The crude product can be immediately deprotected as described below, or it can be purified by distillation with a 4 in. Vigareux column at 3.5 mmHg. Compound **22** was collected between 175 and 178 °C (5.734 g, 0.0220 mol, 62%). $^1H$ NMR ($CDCl_3$): 7.47 (m, 2H), 7.37 (m, 3H), 5.11 (s, 1H), 4.82 (t, *J* = 3.2 Hz, 1H), 4.35 (m, 2H), 3.83 (m, 1H), 3.50 (m, 1H), 3.41 (s, 3H), 1.67 (m, 6H). $^{13}C$ NMR ($CDCl_3$): 138.4, 128.5, 128.4, 127.4, 96.9, 83.9, 83.4, 73.1, 62.0, 55.9, 54.3, 30.3, 25.4, 19.1. IR (NaCl): 2941, 1025 $cm^{-1}$. HREIMS: *m/z* calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1407.

---

(26) Friesen, R. W.; Giroux, A.; Cook, K. L. *Tetrahedron Lett.* **1993**, *34*, 5983.

**1-Methoxy-1-phenyl-2-butyn-4-ol (23).** This compound was reported by Keck and Webb,[19] but no specific procedural or spectroscopic data were reported. Since the representative procedures using pyridinium *p*-toluene sulfonate (PPTS) did not deprotect the alcohol, concentrated hydrochloric acid was used instead.[20] Compound **22** (5.734 g, 0.022 mol) was deprotected using methanol (22 mL) and concentrated hydrochloric acid (3.30 mL). The solution was heated to 76 °C over 1 h, then cooled to 0 °C, and excess aqueous $NaHCO_3$ (60 mL) was added. The water layer was extracted with ether (3 × 30 mL), and the ether layers were combined and dried with $MgSO_4$. After removal of the solvent under reduced pressure, compound **23**, a dark red oil, remained in pure enough form for further reactions (quantitative yield of crude product, 3.95 g, 0.022 mol). $^1$H NMR ($CDCl_3$): 7.47 (m, 2H), 7.32 (m, 3H), 5.09 (s, 1H), 4.34 (s, 2H), 3.40 (s, 3H), 2.45 (bs, 1H). $^{13}$C NMR ($CDCl_3$): 137.9, 128.2, 128.1, 127.1, 86.2, 82.3, 72.8, 55.6, 50.3. IR (NaCl): 3412, 2935, 2361, 10756 cm$^{-1}$. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 73.82; H, 6.49. HREIMS: *m*/*z* calcd for $C_{11}H_{12}O_2$ 176.0837, found 176.0837.

**4-Phenyl-2,3-butadien-1-ol (24).** This compound was synthesized by Keck and Webb in 70% yield.[19] The following procedures are based upon their representative procedure for 2,3-undecadien-1-ol. Lithium aluminum hydride (0.74 g, 0.0195 mol) was added to diethyl ether (340 mL) and cooled to −20 °C. Compound **23** (0.86 g, 4.88 mmol) in ether (20 mL) was added dropwise, and the reaction mixture was stirred 15 min as it warmed to −12 °C. The solution was cooled to −78 °C, iodine was added (3.72 g, 0.0146 mol), and the mixture was stirred for 2 h. After warming to 0 °C, saturated aqueous Rochelle salt (20 mL) and saturated aqueous sodium thiosulfate (20 mL) were added. After stirring 1 h, the water layer was extracted with ether (3 × 20 mL). The ether layers were combined and dried with anhydrous potassium carbonate, then the solvent was removed under reduced pressure and high vacuum to yield **24** (0.69 g, 4.72 mmol, 97%). $^1$H NMR ($CDCl_3$): 7.26 (m, 5H), 6.31 (m, 1H), 5.78 (q, *J* = 6.0 Hz, 1H), 4.25 (m, 2H), 1.60 (bs, 1H). $^{13}$C NMR ($CDCl_3$): 204.3, 133.7, 128.5, 127.1, 126.7, 96.7, 95.6, 60.2. IR (NaCl): 3366, 2930, 1950, 1020 cm$^{-1}$. HREIMS: *m*/*z* calcd for $C_{10}H_{10}O$ 146.0732, found 146.0735.

**4-(*p*-Tolylsulfonyl)-1-phenyl-1,2-butadiene (25).** This compound was prepared in a manner analogous to that for the methyl and dimethyl tosylates (**13a** and **13b**).[10a,21] *p*-Toluenesulfonyl chloride (0.933 g, 4.89 mmol) was added to compound **24** (0.744 g, 5.09 mmol) in diethyl ether (15 mL), and the mixture was immediately cooled to −14 °C. Potassium hydroxide (2.54 g, 0.0453 mol) was added over 25 min in four increments, and the solution was stirred for 1.5 h at −14 °C. The reaction was quenched with ice water (14 mL), then the water layer was extracted three times with ether (15 mL). The ether layers were combined and dried with anhydrous magnesium sulfate. Solvent was removed under reduced pressure, and the oil was stored under nitrogen in the freezer until it crystallized. If desired, the crude product could be used for further reactions (1.349 g, 4.49 mmol, 92%), or it can be purified further by trituration. The compound was dissolved in diethyl ether (7 mL), then pentane (90 mL) was added, and the cloudy mixture was swirled. After 20 min at −15 °C the pentane was decanted off, and any remaining solvent was removed under high vacuum. A pale off-white precipitate remained (**25**, 0.770 g, 2.56 mmol, 52%). $^1$H NMR ($CDCl_3$): 7.79 (d, *J* = 8.3 Hz, 2H), 7.27 (m, 7H), 6.24 (m, 1H), 5.63 (q, *J* = 7.0 Hz, 1H), 4.62 (dd, *J* = 7.0, 2.1 Hz, 2H), 2.42 (s, 3H). $^{13}$C NMR ($CDCl_3$): 207.3, 144.9, 133.2, 132.5, 129.9, 128.7, 127.9, 127.6, 127.1, 96.9, 89.8, 68.0, 21.6. IR (NaCl): 3155, 2987, 1383, 1177 cm$^{-1}$. HREIMS: *m*/*z* calcd for $C_{17}H_{16}O_3S$ 300.0837, found 300.0839.

**1-Phenyl-4-tetrahydropyranyl-2-butyn-1-ol (26).** 3-tetrahydropyranyl-propyne (**21**, 4.00 g, 0.0285 mol) in diethyl ether (17 mL) was cooled to −78 °C. *n*-Butyllithium (12.6 mL, 2.5 M in hexanes, 0.0314 mol) was added dropwise, and the solution was stirred 30 min. Benzaldehyde (2.99 mL, 0.0294 mol) was added, and the mixture was stirred for 30 min at 25 °C. After cooling to 0 °C, ice water (10 mL) was added. The water layer was extracted with ether (3 × 5 mL), whereupon the ether layers were combined and dried with anhydrous magnesium sulfate. After removing the solvent under reduced pressure, **26** (6.723 g, 0.0273 mol, 96%) remained as an orange oil. $^1$H NMR ($CDCl_3$): 7.52 (m, 2H), 7.35 (m, 3H), 5.49 (d, *J* = 6.0 Hz, 1H), 4.80 (t, *J* = 3.1 Hz, 1H), 4.34 (m, 2H), 3.82 (m, 1H), 3.49 (m, 1H), 2.37 (1H), 1.61 (m, 6H). $^{13}$C NMR ($CDCl_3$): 140.4, 128.6, 128.4, 126.6, 96.9, 85.6, 82.8, 64.6, 62.0, 54.3, 30.2, 25.3, 19.0. IR (NaCl): 3391, 2944, 2868, 1024 cm$^{-1}$. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.24; H, 7.18.

**1-Acetoxy-1-phenyl-4-tetrahydropyranyl-2-butyne (27).** This compound was synthesized in a manner analogous to that of Wright et al. for 2-acetoxy-3,4-pentadiene.[21] Methyllithium (7.19 mL, 1.4 M in diethyl ether, 10.1 mmol) was added dropwise to a solution of **26** (1.952 g, 7.93 mmol) in THF (25 mL) at −45 °C. After stirring 45 min, acetic anhydride (0.845 mL, 9.0 mmol) was added. The solution was stirred at 25 °C for 2 h, then quenched with saturated aqueous sodium bicarbonate (30 mL). The water layer was extracted with ether (3 × 20 mL), then the ether layers were combined and dried with anhydrous magnesium sulfate. After removing the solvent under reduced pressure, **27** (2.190 g, 7.60 mmol, 96%) remained. $^1$H NMR ($CDCl_3$): 7.49 (m, 2H), 7.36 (m, 3H), 6.49 (d, *J* = 1.1 Hz, 1H), 4.79 (s, 1H), 4.33 (m, 2H), 3.81 (m, 1H), 3.49 (m, 1H), 2.08 (s, 3H), 1.68 (m, 6H). $^{13}$C NMR ($CDCl_3$): 169.7, 136.9, 128.9, 128.6, 127.7, 96.9, 83.4, 82.4, 65.6, 62.0, 54.2, 30.2, 25.3, 21.0, 19.0. IR (NaCl): 2943, 1742, 1227, 1027 cm$^{-1}$. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 69.84; H, 7.04.

**Deprotection of 1-Acetoxy-1-phenyl-4-tetrahydropyranyl-2-butyne (27) To Yield 1-Methoxy-1-phenyl-2-butyn-4-ol (23).** Using the same procedures described for **22**, compound **27** (3.1869 g, 0.0111 mol) was deprotected using methanol (11 mL) and concentrated hydrochloric acid (1.66 mL). Chromatography on silica gel with 1:1 pentane/ethyl acetate yielded **23** (1.1664 g, 6.62 mmol, 60%). This compound was identical by spectroscopic comparison with material prepared by the alternate route above.

**Synthesis of Cyclopentadienylmolybdenum Dicarbonyl $\eta^3$-3-phenyl-2-methylenecyclobuten-1-one (28a, 28b) Using Lithium Triethylborohydride.** The $LiBEt_3H$ procedure was used to prepare the *Z* and *E* complexes **28a** and **28b**, respectively, as described above for the preparation of **14**, using 5-(*p*-tolylsulfonyl)-2-phenyl-2,3-pentadiene (**25**, 0.345 g, 1.15 mmol) as the electrophile. Anion **4** (M = Li) (0.643 mmol) was formed from $[CpMo(CO)_3]_2$ (0.1577 g, 0.322 mmol) and lithium triethylborohydride (1.10 mL of a 1.0 M solution in THF, 1.10 mmol). The solution was warmed to 60 °C over 1 h and then stirred between 70 and 75 °C for an additional 3 h. Chromatography was performed on deactiviated alumina using 100% pentane, then 10:1 pentane/ethyl acetate to remove the yellow band, gradually increasing the amount of ethyl acetate to remove the orange band. From the $^1$H NMR, it was determined that the yellow band (0.1109 g) contained the $\eta^3$-butadienyl complex **29** (0.0606 g, 0.175 mmol, 27%) and the *Z* cyclobutanone complex **28a** (0.0503 g, 0.134 mmol, 21%). The orange residue after the yellow band consisted of the *E* cyclobutanone complex **28b** (0.0305 g, 0.082 mmol, 13%). Complexes **29** and **28a** were separated by preparative TLC (20:1 pentane/ethyl acetate, alumina). A small amount of the $\eta^1$-butadienyl complex (**30**) was also obtained from this TLC (0.0070 g, 0.019 mmol, 3%). $\eta^3$-Butadienyl complex (**29**, Z, *exo*): Mp: 120 °C (dec). $^1$H NMR ($CDCl_3$): 7.49 (d, *J* = 6.7 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.57 (s, 1H), 5.33 (s, 5H), 4.10 (m, 1H), 3.08 (d, *J* = 6.4 Hz, 1H), 1.58 (d, *J* = 8.7 Hz, 1H). $^{13}$C NMR ($CDCl_3$): 234.8, 231.4, 162.0, 137.4, 128.5, 126.2, 122.0, 92.2, 47.3, 41.0. IR ($CDCl_3$): 1949, 1873 cm$^{-1}$. HRMS

(FAB+): *m*/*z* calcd for $C_{17}H_{14}O_2{}^{98}Mo$ 348.0048, found 348.0040. *E* cyclobutanone isomer (**28b**): $^1H$ NMR ($CDCl_3$): 7.12 (t, *J* = 7.6 Hz, 2H), 6.97 (m, 1H), 6.65 (d, *J* = 7.4 Hz, 2H), 5.29 (s, 5H), 5.15 (d, *J* = 3.0 Hz, 1H), 5.13 (s, 1H), 3.92 (dd, *J* = 15.5, 3.0 Hz, 1H), 3.25 (d, *J* = 15.5 Hz, 1H). $^{13}C$ NMR ($CDCl_3$): 236.4, 233.1, 198.2, 140.7, 128.5, 126.6, 125.7, 95.2, 93.5, 80.5, 56.5, 55.0. IR (CDCl3): 1957, 1882, 1750 $cm^{-1}$. *Z* cyclobutanone isomer (**28a**): $^1H$ NMR ($CDCl_3$): 7.80 (d, *J* = 7.4 Hz, 2H), 7.28 (m, 2H), 7.17 (m, 1H), 5.03 (s, 5H), 3.83 (s, 1H), 3.81 (dd, *J* = 15.5, 0.68 Hz, 1H), 3.47 (s, 1H), 3.13 (d, *J* = 15.5 Hz, 1H). $^{13}C$ NMR ($CDCl_3$): 236.7, 235.2, 196.1, 139.1, 128.6, 127.1, 127.0, 113.8, 97.0, 68.5, 60.7, 54.5. IR ($CDCl_3$): 1947, 1874, 1742 $cm^{-1}$. Anal. Calcd for $C_{18}H_{14}O_2Mo$: C, 57.77; H, 3.77. Found: C, 58.32; H, 4.00. HRMS (FAB+): *m*/*z* calcd for $C_{18}H_{14}O_2{}^{98}Mo$ 375.9997, found 376.0006. $\eta^1$-Butadiene complex (**30**): $^1H$ NMR ($CDCl_3$): 7.14 (m, 4H), 6.97 (m, 1H), 5.80 (dd, *J* = 17.1, 10.4 Hz, 1H), 5.38 (d, *J* = 17.1 Hz, 1H), 5.18 (s, 1H), 5.00 (d, *J* = 10.4 Hz, 1H), 4.75 (s, 5H). $^{13}C$ NMR ($CDCl_3$): (CO peaks not visible) 146.1, 134.7, 128.7, 125.6, 125.2, 114.6, 94.3. IR[1] (NaCl): 1991, 1932 $cm^{-1}$. HRMS: *m*/*z* calcd for $C_{17}H_{14}O_2{}^{92}Mo$ ($M^+ - CO$) 342.0062, found 342.0062. Anal. Calcd for $C_{18}H_{14}O_3$-Mo: C, 57.77; H, 3.77. Found: C, 59.04; H, 4.35.

Using the same amounts of reagents as above, the reaction mixture was stirred at 25 °C for 15 min. Chromatography was performed on deactivated alumina (100% pentane to 20:1 pentane/ethyl acetate) to obtain the $\eta^3$-butadiene complex **29** (0.0219 g, 0.063 mmol, 10%) followed by the *Z* cyclobutanone isomer **28a** (0.023 g, 0.061 mmol, 10%) and the $\eta^1$-butadiene complex **30** (0.022 g, 0.059 mmol, 9%).

**Synthesis of Cyclopentadienylmolybdenum Dicarbonyl $\eta^3$-4′-Methyl-2-methylene-2-cyclobuten-1-one (33a) Using Lithium Triethylborohydride.** The same ratios of reagents were used as reported by Green et al.[6] using a different electrophile (**32c**) and possibly a different preparation of the molybdenum anion (**4**, M = Li). Cyclopentadienylmolybdenum tricarbonyl dimer (0.245 g, 0.500 mmol)) was dissolved in THF (10 mL) degassed with dry nitrogen. To this solution was added $LiBEt_3H$ in THF (1.55 mL of a 1.0 M solution, 1.55 mol), and the mixture was degassed. After stirring 15 min, an excess of 1-acetoxy-2-methyl-2,3-butadiene (**32c**, 0.378 g, 3.0 mmol) in THF (10 mL) was added, and the mixture was degassed. The mixture was stirred for 3.5 h at 25 °C, then the solvent was removed under reduced pressure and high vacuum. The residue was chromatographed on deactivated alumina using a pentane/ethyl acetate gradient. The major product was a pink metal complex (unstable in solution in air), which upon evaporation of solvent yielded shiny pink crystals identical with the original dimer ($[CpMo(CO)_3]_2$). We could isolate only trace amounts of **33a** (0.0018 g, 0.0058 mmol, 1%) identical by $^1H$ NMR comparison with material reported by Green.[6]

**3-Carboethoxy-2-isopropylidenecyclobutanone (34).** The molybdenum complex **14b** (0.27 g, 0.83 mmol) was dissolved in dichloromethane and ethanol (1:1, 5.5 mL), and the solution was cooled to −78 °C. Ceric ammonium nitrate (1.13 g, 2.1 mmol) was dissolved in ethanol (17 mL). Both solutions were degassed with dry nitrogen, and then the Ce(IV) solution was transferred to the molybdenum complex solution via cannula under nitrogen. The mixture was then stirred for 30 min at −78 °C followed by 30 min at 25 °C. The solvent was removed under reduced pressure and in vacuo. Chromatography on deactivated alumina (pentane/EtOAc, 4:1) afforded **34** (0.10 g, 0.55 mmol, 67%) as a yellow oil. Bp: 87 °C @ 3 mmHg. $^1H$ NMR ($CDCl_3$): 4.18 (q, *J* = 7.1 Hz, 2H), 3.68 (m, 1H), 3.14 (dd, *J* = 17.1, 5.2 Hz), 3.00 (dd, *J* = 17.1, 8.1 Hz, 1H), 2.09 (d, *J* = 1.5 Hz, 3H), 1.80 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR ($CDCl_3$): 195.3, 172.7, 146.3, 140.6, 60.9, 46.8, 37.4, 21.3, 21.0, 14.1. IR ($CDCl_3$): 1743, 1661 $cm^{-1}$. LR EIMS: $M^+$ 182(11), 154(76), 126 (35), 109 (28). HRMS: *m*/*z* calcd for $C_{10}H_{14}O_3$ 182.0942, found 182.0947. Anal. Calcd for $C_{10}H_{14}O_3$; C, 65.92; H, 7.74. Found: C, 65.37; H, 7.61.

**Cyclopentadienylmolybdenum Dicarbonyl $\eta^3$-3,3-Dimethyl-2-methylene-2-cyclobuten-1-ol (36).** Molybdenum complex **14b** (0.19 g, 0.59 mmol) was dissolved in methanol (3.5 mL), degassed with dry nitrogen, and cooled to 0 °C. Sodium borohydride (0.12 g, 3.2 mmol) was added, and gas immediately evolved. The mixture was stirred 20 min at 0 °C until gas was no longer given off. The solvent was removed under reduced pressure and high vacuum. Chromatography on deactivated alumina (4:1 pentane/EtOAc) yielded **36** (0.18 g, 0.54 mmol, 92%) as a yellow-orange solid. Mp: 116 °C dec. IR (NaCl): 3600, 3400, 1930, 1845 $cm^{-1}$. $^1H$ NMR ($C_6D_6$): 5.02 (s, 5H), 4.62 (m, 1H), 2.94 (m, 1H), 2.61 (m, 1H), 1.85 (m, 1H), 1.71 (s, 3H), 1.09 (s, 3H), 1.04 (s, 1H, exchanges w/$D_2O$). $^{13}C$ NMR ($C_6D_6$): 240.86, 240.57, 103.88, 93.68, 67.52, 67.34, 57.97, 43.31, 27.43, 25.94. LRMS (FAB): *m*/*z* for $C_{14}H_{16}{}^{98}MoO_3$ $M^+$ 330 (100), $M^+ - CO$ 302 (21), $M^+ - 2CO$ 274 (40). Anal. Calcd for $C_{14}H_{16}MoO_3$: C, 51.23; H, 4.91. Found: C, 51.06; H, 4.98.

***cis*- and *trans*-1,3-Diethoxy-2-isopropylidenecyclobutane (37 and 38).** The same procedure used for **34** was followed to demetalate **36** (0.210 g, 0.64 mmol) using 2.5 equiv of ceric ammonium nitrate (0.877 g, 1.60 mmol) in 8 mL of ethanol and 4.27 mL of 1:1 dichloromethane/ethanol. After 30 min at room temperature the solvent was removed under reduced pressure and in vacuo. The residue was filtered through Celite with dichloromethane, which was removed under reduced pressure and in vacuo. This yielded the two compounds **37** and **38** in a 1.1:1 ratio by $^1H$ NMR. The yield of the crude product was quantitative (0.12 g). A pipet was packed with a small amount of silica. The mixture of two compounds was filtered quickly through the silica with $CDCl_3$; however, after this filtration only one of the compounds (**38**) was visible by $^1H$ NMR. Attempts to separate the two compounds by column or preparative TLC were unsuccessful. Cyclobutane **37**: $^1H$ NMR ($CDCl_3$): 4.24 (m, 2H), 3.41 (m, 4H), 2.43 (dt, *J* = 12.4, 6.9 Hz, 1H), 1.90 (dt, *J* = 12.4, 6.9 Hz, 1H), 1.72 (s, 3H), 1.70 (s, 3H), 1.17 (t, *J* = 7.0 Hz, 6H). Cyclobutane **38**: $^1H$ NMR ($CDCl_3$): 4.62 (m, 2H), 3.41 (m, 4H), 2.11 (t, *J* = 5.80 Hz, 2H), 1.70 (s, 3H), 1.69 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 6H). $^{13}C$ NMR ($CDCl_3$): 134.5, 134.2, 76.1, 63.3, 34.7, 19.5, 15.4. IR (NaCl): 2976, 2930, 2869, 1114 $cm^{-1}$. LR EIMS: $M^+$ (*m*/*z*) 184 (6), 155 (100), 139(29).

**1-(2′-Hydroxy-2′-methyl)ethyl-4-ethoxycyclobutene (39).** Complex **36** was demetalated following the same procedure used for **14b** to yield **34**. The reduced complex **36** (0.198 g, 0.28 mmol) was dissolved in dichloromethane and ethanol (1:1, 4.02 mL), and the solution was cooled to −78 °C. Ceric ammonium nitrate (0.826 g, 0.60 mmol) was dissolved in ethanol (6 mL). Both solutions were degassed with dry nitrogen, and then the Ce(IV) solution was transferred to the molybdenum complex solution via cannula under nitrogen. The mixture was then stirred for 10 min at −78 °C followed by 30 min at 25 °C. The reaction was quenched with 10% $Na_2CO_3$ (9 mL). The water layer was extracted three times with ether, and the organic layers were combined and dried with anhydrous potassium carbonate. After removal of the solvent under reduced pressure and in vacuo, the residue was filtered through Celite with ether. The solvent was removed to yield **39** (0.0432 g, 0.28 mmol, 46%). $^1H$ NMR ($CDCl_3$): 5.97 (d, *J* = 0.8 Hz, 1H), 4.70 (m, 1H), 3.38 (m, 2H), 2.66 (dd, *J* = 13.1, 3.8 Hz, 1H), 2.27 (bs, 1H), 2.18 (d, *J* = 13.1 Hz, 1H), 1.31 (s, 3H), 1.29 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 3H). $^{13}C$ NMR ($CDCl_3$): 155.4, 129.0, 73.6, 69.5, 58.0, 37.2, 25.1, 24.0, 15.9. IR (NaCl): 3406 (br), 2976, 2926, 1060 $cm^{-1}$. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.15; H, 9.97. FAB HRMS: *m*/*z* calcd for $C_9H_{17}O_2$ M + H 155.1071, found 155.1072.

**Substituted Cyclopentadienyl ($\eta^3$-2-Isopropyloxocyclobutenyl) Dicarbonyl Molybdenum Complexes (40 and 41).** Lithium diisopropylamide (1.64 mmol) was generated from stirring equimolar amounts of *n*-butyllithium (0.656 mL, 2.5 M in hexane, 1.64 mmol) and diisopropylamine (0.230 mL, 1.64 mmol) in THF (0.25 mL) for 30 min at 0 °C.[24] The LDA solution was cooled to −78 °C, then **14b** (0.5438 g, 1.50 mmol) (in 1−2 mL of THF) was added dropwise. The enolate solution was gradually warmed over 1 h to 0 °C, then cooled to −20 °C to add MeI (0.144 mL, 2.31 mmol) in degassed THF (10 mL). The mixture was stirred at −20 °C for 20 min, then gradually warmed to 25 °C and stirred 2 h. The THF was removed under reduced pressure, then ether and water were added. The water layer was extracted several times with ether, and the ether layers were combined and dried with magnesium sulfate. After removing the ether under reduced pressure, a dark oil remained. This was chromatographed on deactivated alumina using a gradient of pentane/ethyl acetate. The bright yellow band contained unreacted starting material (**14b**) (0.1409 g, 0.432 mmol, 26%). The orange band that followed contained **40** (0.1335 g, 0.409 mmol, 25%, $R_f$ 0.09 in 4:1 pentane/ethyl acetate). Oxocyclobutenyl complex **40**: Mp: 85−87 °C. $^1$H NMR ($CDCl_3$): 5.24 (s, 5H), 4.18 (d, $J = 1.2$ Hz, 1H), 3.51 (d, $J = 1.2$ Hz, 1H), 2.36 (septet, $J = 6.9$ Hz, 1H), 1.21 (d, $J = 6.9$ Hz, 3H), 1.09 (d, $J = 6.9$ Hz, 3H). $^{13}$C NMR ($CDCl_3$): 228.9, 227.5, 170.4, 92.4, 81.9, 68.1, 47.1, 27.9, 24.3, 22.3. IR (NaCl): 1993, 1931, 1678 cm$^{-1}$. Anal. Calcd for $C_{14}H_{14}O_3Mo$: C, 51.55; H, 4.33. Found: C, 52.12; H, 4.66.

The reaction was repeated with equivalent amounts and procedures as described above, but degassed $D_2O$ (1 mL) was added 5 min after adding the 1.5 equiv of MeI at −78 °C. Chromatography yielded **14b** (0.1402 g, 0.430 mmol, 57%) and **41** (0.0367 g, 0.112 mmol, 15%). Oxocyclobutenyl complex **41**: $^1$H NMR ($CDCl_3$): 5.25 (s, 5H), 4.19 (d, $J = 1.1$ Hz, 1H), 3.52 (d, $J = 1.1$ Hz, 1H), 1.22 (s, 3H), 1.10 (s, 3H). $^{13}$C NMR ($CDCl_3$): 228.9, 227.5, 170.5, 92.4, 68.1, 65.8, 47.1, 24.2, 22.2, 15.3. IR (NaCl): 1995, 1933, 1682 cm$^{-1}$. Anal. Calcd for $C_{14}H_{13}O_3DMo$: C, 51.39; H+D as H, 4.31. Found: C, 51.45; H+D as H, 4.50.

The reaction was repeated using degassed THF (10 mL) with 2.2 equiv of LDA. Complex **14b** (0.2051 g, 0.629 mmol) was added over 30 min to the LDA solution (1.38 mmol) at 0 °C, then stirred 1 h. Methyl iodide (122 $\mu$L, 1.95 mmol) was then added at 0 °C. After stirring for 30 min at 0 °C, the mixture was stirred for 2 h at 25 °C. After removal of THF under reduced pressure, ether (10 mL) and water (10 mL) were added. The water layer was extracted several times with ether (10 mL). The ether layers were combined and dried with anhydrous magnesium sulfate, then solvent was removed under reduced pressure and in vacuo. By $^1$H NMR, it was determined that a 3:1 ratio of **41** to starting material (**14b**) was obtained (**41**: 0.1181 g, 0.36 mmol, 58%; **14b**: 0.389 g, 0.12 mmol, 19%). After chromatography on deactivated alumina, the isolated yields were lower than expected, especially for complex **41**, which must be sensitive to chromatography (**41**: 0.0527 g, 0.16 mmol, 26%; **14b**: 0.0257 g, 0.08 mmol, 13%).

**Acknowledgment.** We thank the donors of the Petroleum Research Fund administered by the American Chemical Society and the Camille and Henry Dreyfus Foundation (Henry Dreyfus Teacher-Scholar Award to M.E.W, 1994−1999) for their support. Low-resolution mass spectra were obtained on an instrument purchased with the partial support of NSF (CHE-9007366). High-field NMR spectra were obtained on instruments purchased with the partial support of the NSF (CHE-9708077) and the NCBC (9703-IDG-1007). The Duke University Center for Mass Spectrometry performed high-resolution mass spectral analyses.

**Supporting Information Available:** Tables giving experimental details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, and anisotropic displacement parameters for **15a**, **28a**, **29**, and **41**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000546U