General Preparation of Cyclopentadienyl Molybdenum Dicarbonyl η^3-2-Alkylidene Cyclobutanonyl Complexes

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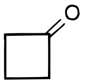
Summary: Cyclopentadienylmolybdenumdicarbonyl anion reacts with a variety of allenic electrophiles to produce η^3*-2-alkylidene cyclobutanoyl complexes. Three of these complexes have been characterized by X-ray crystallography, and the 2-alkylidene cyclobutanone has been removed and recovered from one complex via oxidative demetalation.*

While cyclobutanones (**1**) have been widely utilized in synthesis for a number of years, cyclobutenones (**2**) and 2-alkylidene cyclobutanones (**3**) have only more recently begun to be utilized as synthetic intermediates.[1] Cyclobutenones and 2-alkylidene cyclobutanones are receiving increasing attention 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] Synthetic utilization of cyclobutanones stems from their ready availability via cycloadditions of ketenes with alkenes, but the analogous cycloadditions of ketenes with allenes and alkynes to yield alkylidene cyclobutanones and cyclobutenones have proven more problematic.[3]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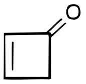
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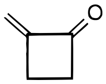
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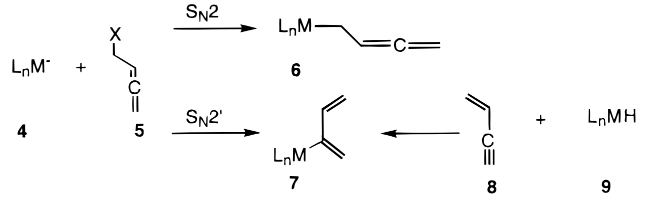
No general transition-metal-mediated routes to cyclobutenones, alkylidene cyclobutanones, and their transition-metal complexes have been reported previously. Brisdon et al. reported the reaction of triphenylbromoallene with a molybdenum complex to produce a complexed cyclobutenone in 1981,[4a] and Hughes et al. have reported that reaction of $Me_5CpM(CO)_3$ anions (M = Cr, Mo, W) with triphenylcyclopropenyl cation and a few other alkyldiphenylcyclopropenyl cations yielded complexed cyclobutenones.[4b,c] 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] Here, we report the synthesis, characterization, and subsequent modification/demetalation of a number of alkylidene cyclobutanonyl complexes.



We have previously described many examples of S_N2' reactions of cobaloxime and cosalen anions with allenic electrophiles (**5**) to yield transition-metal-substituted 1,3 dienes (**7**),[6] but in our experience, S_N2 reactions of transition-metal anions with allenic electrophiles have been rare.[7] Reaction of the $CpMo(CO)_3$ anion (**10**)[8] with tosylate (**11**) initially produced **12**, which can be observed by ^1H NMR (C_6D_6): 5.60 (m, 1H); 4.83 (dt, J = 6.7, 2.6 Hz, 2H), 4.52 (s, 5H), 2.22 (dt, J = 7.4, 2.6 Hz, 2H). However, **12** rapidly undergoes further reaction at 25 °C to produce another air-stable yellow complex.

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[†] Henry Dreyfus Teacher-Scholar Awardee (1994−99).

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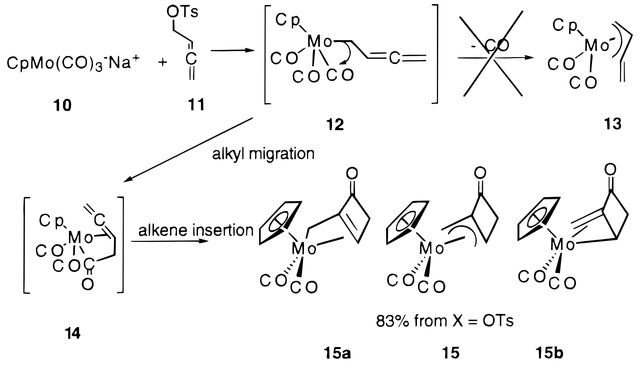
Initially we thought CO loss from **12** to produce a η^3-butadienyl complex (**13**) might be a facile process, but the isolated complex did not have spectroscopic data consistent with that reported for other η^3-butadienyl complexes.[9]



We postulated, based on mass spectral, ^{1}H and ^{13}C NMR, and IR data,[8,10,11] that the product of this reaction was a complexed cyclobutenone (**15**). We could account for the formation of **15** via a CO insertion (alkyl migration) to form **14** followed by an alkene insertion. There is ample precedent for a σ-acyl π-alkene complex like **14** in cyclopentadienyl molybdenum, tungsten, and iron chemistry involving other alkenyl or allenyl ligands.[12,13] The proposed cyclobutenone complex **15** has now been characterized by X-ray crystallography.[14] The ORTEP of complex **15** is shown in Figure 1. The molybdenum−C(8) (2.351(8) Å) and molybdenum−C(10) (2.336(6) Å) bond distances are within experimental error of one another, so this complex contains a very symmetrical, with respect to metal−carbon bond distances, complexed π-allyl. The C(8) to C(9) bond (1.390(10) Å) is significantly shorter than the C(9)−C(10) bond (1.440(10) Å), indicating that the σ-bond representation (**15b**) which contains a methylidene cyclobutanone is a better model of this complex than **15a**. The solid-state structure of this complex shows that the π-allyl portion of the molecule is *exo* (**19**) with respect to the CpMo(CO)$_2$ fragment.[15] Faller observed that substituents in the 1 and/or 3 positions of the allyl favor the formation of *exo* complexes (**17**), whereas π-allyls with substituents only in the 2 position favor *endo* complexes (**16**).[10a] Acyclic π-allyls substituted on both the 1 and 2 positions also have high *exo*:*endo* ratios,[10a] and our observations here are consistent with those previous reports.

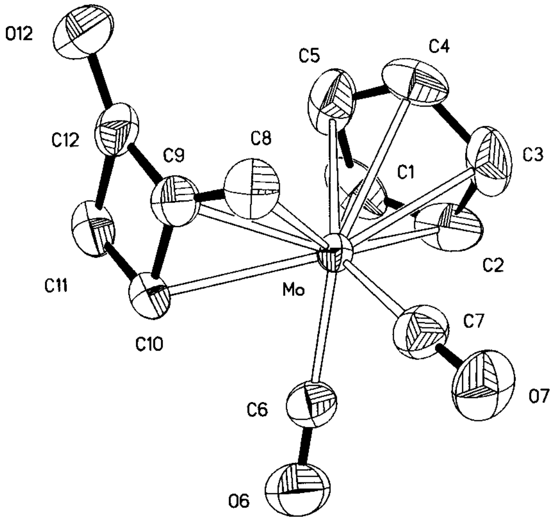
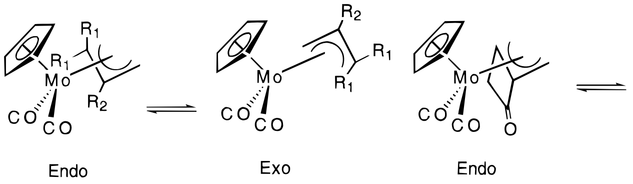
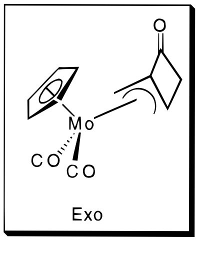


Figure 1. Molecular structure of complex **15** with selected bond distances and angles. Selected bond lengths [Å]: Mo−C7 1.955(7), Mo−C6 1.985(8), Mo−C9 2.221(7), Mo−C10 2.336(6), Mo−C8 2.351(8), O12−C12 1.243(9), C8−C9 1.390(10), C9−C10 1.440(10), C9−C12 1.462(10), C10−C11 1.490(10), C11−C12 1.544(11). Selected bond angles [deg]: C7−Mo−C6 78.8(3), C7−Mo−C9 102.8(3), C6−Mo−C9 104.3(3), C7−Mo−C10 108.7(3), C6−Mo−C10 70.3(3), C9−Mo−C10 36.7(2), C7−Mo−C8 73.5(3), C6−Mo−C8 116.3(3), C10−Mo−C8 66.6(2), C8−C9−C10 130.9(7), C8−C9−C12 138.0(7), C10−C9−C12 90.3(6), C10−C11−C12 85.4(6), O12−C12−C9 135.0(8), O12−C12−C11 133.3(7), C9−C12−C11 90.6(6).



16 **17** **18**



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This initial isolation of complex **15** has now proven general for mono- (**20a**) and dimethylated allenic electrophiles (**20b**). Using Gladysz's LiBH(Et)$_3$ reduction[16] of [CpMo(CO)$_3$]$_2$ to generate anion **10**, we find that complexes **21a**,**b** are more easily obtained in pure form since they do not have to be separated from Hg{Mo(CO)$_3$C$_5$H$_5$}$_2$,[17] which is formed as a byproduct when Na-

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[9] (a) For a review of transition-metal butadienyl complexes see: Brisdon, B. J.; Walton, R. A. *Polyhedron* **1995**, *14*, 1259. (b) Brisdon, B. J.; Deeth, R. J.; Hodson, A. G. W.; Kemp, C. M.; Mahon, M. F.; Molloy, K. C. *Organometallics* **1991**, *10*, 1107. (c) Dema, A. C.; Lukehart, C. M.; McPhail, A. T.; McPhail, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 7229. (d) Bruce, M. I.; Lidell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Organometallics* **1988**, *7*, 343.

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[14] Crystallographic data for **15**: monoclinic, $P2_1/n$, yellow-green plate, $a = 6.9625(4)$ Å, $b = 13.9818(9)$ Å, $c = 11.4410(7)$ Å, $\alpha = 90°$, $\beta = 100.671(2)°$, $\gamma = 90°$, volume = 1094.50(12) Å^3, $Z = 4$, R1 = 0.0611, GOF = 1.035. Complete details of the crystallographic characterization of **15** are included in the Supporting Information.

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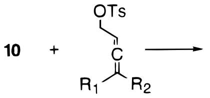
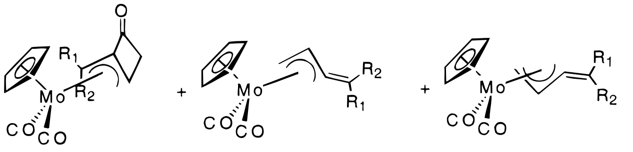
(Hg) is used as reductant. Molybdenum π-allyl complexes **21a**,**b** are also *exo*, and complex **21a** is formed as a 6:1 mixture of *E*:*Z* isomers. We know the minor isomer observed here is the *Z* isomer rather than the *endo* isomer because the cyclobutanone ^{1}H NMR chemical shifts are almost identical in both isomers, whereas the methyl and adjacent π-allyl proton resonances are dramatically different in the two isomers.[10,15] Alkene insertion via the least hindered intermediate (**25**) leads to the observed major *E* isomer (**21a**). In both of these cases where we have used LiBH(Et)$_3$ as reductant, we also observe small amounts of the π-allyl complexes (**22** and **23**), which we did not see for the unsubstituted electrophile (**11**). This observation indicates that as allene substitution increases, ligand substitution (CO loss) becomes competitive with alkyl migration (CO insertion). Complexes **21a**,**b** have also been characterized by single-crystal X-ray diffraction, confirming their formulation as *exo* π-allyl complexes.[18]

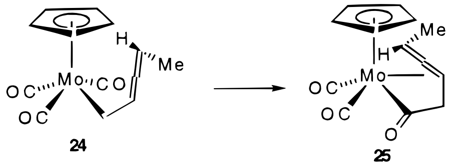


20a R$_1$ = H, R$_2$ = Me
20b R$_1$ = R$_2$ = Me



21 **22** **23**

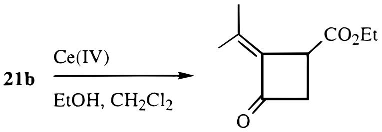
21a: 63% (6.0:1 E:Z) from Na(Hg) + [CpMo(CO)$_3$]$_2$Hg (8%)
21a: 70% (4.4:1 E:Z) from LiHBEt$_3$ + **22(Z)a:22(E)a:23(E)a** (17%, 5:1:1)
21b: 63% from Na(Hg) + [CpMo(CO)$_3$]$_2$Hg (23%)
21b: 73% from LiHBEt$_3$ + **22b:23b** (24%, 3.9:1)



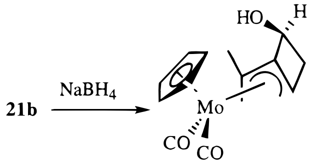
24 **25**

We have successfully oxidatively demetalated **21b** to yield functionalized alkylidene cyclobutanone **26**. Compound **26** presumably arises via Ce(IV) oxidation of the molybdenum in **21b**, thereby activating the π-allyl for CO insertion followed by nucleophilic attack of ethanol. Additionally, we have found that nucleophilic addition to the cyclobutanone carbonyl is also possible, indicating we will be able to stereoselectively manipulate these new complexes. Complex **21b** was treated with NaBH$_4$ using Liu's protocol,[19] and a single new complex (**27**) was isolated in high yield.

In conclusion, we have discovered a new, general transition-metal-mediated route to alkylidene cyclobutanones. Metal complexation of the alkylidene cyclobutanones can be used to direct stereoselective addition reactions, and the alkylidene cyclobutane framework can be recovered via demetalation. Efforts to extend this new transition-metal complex forming reaction into a method for 2-alkylidene cyclobutanone synthesis will be reported in due course.



26 (67%)



27 (92%)

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Supporting Information Available: Tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, and anisotropic displacement parameters for **15**, **21a**, and **21b** in addition to spectroscopic and characterization data on all new compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Crystallographic data for **21a** and **21b**. **21a**: monoclinic, $P2_1/n$, yellow plate, $a = 7.229(1)$ Å, $b = 21.195(5)$ Å, $c = 8.107(2)$ Å, $\alpha = 90°$, $\beta = 97.70(2)°$, $\gamma = 90°$, volume $= 1230.9(5)$ Å^3, $Z = 4$, R1 = 0.035, GOF = 1.045. **21b**: monoclinic, $P2_1/c$, yellow rectangular parallelepiped, $a = 12.270(1)$ Å, $b = 11.747(1)$ Å, $c = 18.377(2)$ Å, $\alpha = 90°$, $\beta = 90.981(6)°$, $\gamma = 90°$, volume $= 2648.5(4)$ Å^3, $Z = 8$, R1 = 0.059, GOF = 1.060. The ORTEP plots and complete details of the crystallographic characterization of **21a** and **21b** are included in the Supporting Information.

[19] (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.