The structure was solved by the heavy atom method and refined by the block-diagonal least-squares procedure (HBLS-V),[33] the function minimized being $\sum w(|F_o| - |F_c|)^2$. Non-H atoms were refined anisotropically, whereas all H atoms located by stereochemical considerations were refined isotropically. The weighting scheme used is $w = (\sigma_{cs}^2 + a|F_o| + b|F_o|^2)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics, and a and b were 0.0400 and 0.001 in the final refinement cycles. The final R and R_w values, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, are 0.043 and 0.049 for 4150 observed reflections ($|F_o| > 3\sigma(|F_o|)$). The atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[34] Tables of final atomic positional parameters with B_{eq} values[35] and anisotropic temperature factors for non-H atoms, atomic parameters for H atoms, all the bond lengths and angles, and observed and calculated structure factors are available as supplementary materials (Tables S1-S5).

All computations were carried out on an ACOS 930 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research, Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Crystallographic information for **3**-trans including the atom numbering scheme (Figure S1), atomic coordinates and B_{eq} values of non-H atoms (Table S1), anisotropic temperature factors for non-H atoms (Table S2), atomic parameters of H atoms (Table S3), and bond distances and bond angles (Table S4) (6 pages); observed and calculated structure factors for **3**-trans (Table S5) (11 pages). Ordering information is given on any current masthead page.

(33) Ashida, T. *The Universal Crystallographic Computing System—Osaka*, 2nd ed.; The Computation Center, Osaka University: Osaka, 1979; p 53.
(34) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 71.
(35) Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609-610.
(36) Johnson, C. K. ORTEP-II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Cyclization Reactions of Molybdenum and Chromium Carbene Complexes with 1,6- and 1,7-Enynes: Effect of Tether Length and Composition

Daniel F. Harvey,* Kevin P. Lund, and David A. Neil

Contribution from the Department of Chemistry (0506) University of California at San Diego, La Jolla, California 92093-0506. *Received May 26, 1992*

Abstract: It has been observed that the reaction of 1,6- and 1,7-enynes with pentacarbonyl(butylmethoxycarbene)molybdenum(0) (**18**) produces vinylcyclopropanes in good to excellent yield. A systematic investigation into the factors which govern the success of these cyclizations has been performed. Chromium carbene complexes also lead to the formation of vinylcyclopropanes but in significantly lower yields. When the pathway to vinylcyclopropanes is not followed, a number of other distinct types of products are obtained. The pathways leading to these various products are discussed and compared.

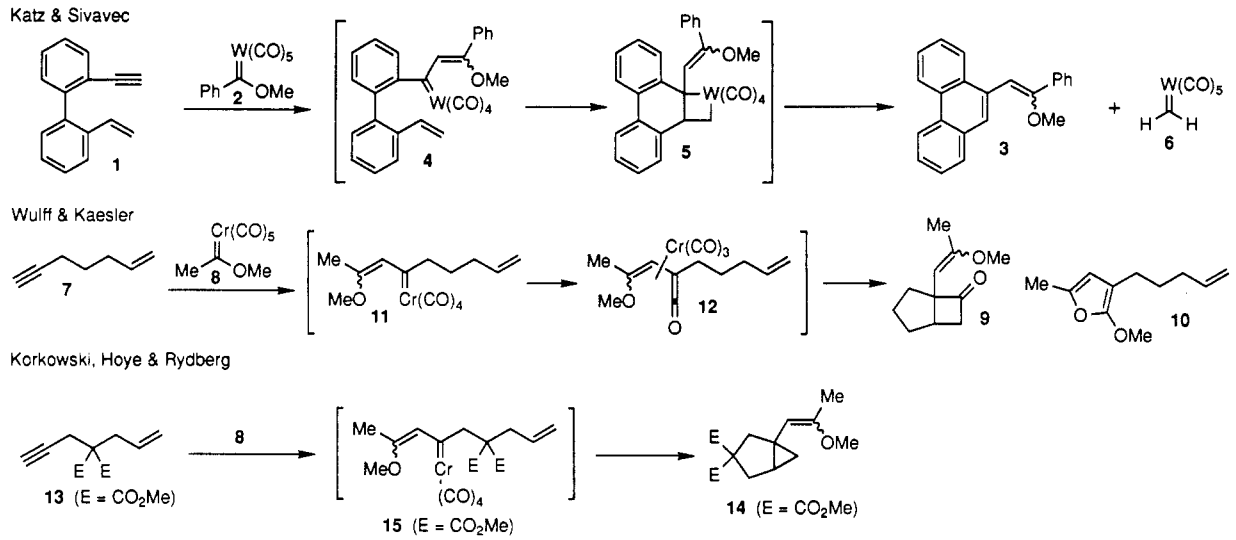
Recently we reported several studies concerning the reactivity of molybdenum carbene complexes.[1,2] Of particular interest has been the ability of these complexes to react with α,ω-enynes to smoothly produce vinylcyclopropanes.[2] Due to our continuing interest in the development of Fischer carbene complex-mediated cyclization strategies for the production of polycyclic ring systems, we have investigated the impact of a variety of olefin substituents on the outcome of this reaction. Herein we report that the reaction pathway followed is highly dependent upon the metal employed as well as the nature of the functionality present on the enyne substrate.

Several groups have recently investigated the reactivity of 1,6- and 1,7-enynes with group VI Fischer carbene complexes. A number of distinct reaction pathways have been described and are shown in Scheme I. Katz and Sivavec have demonstrated that treatment of biphenyl derivative **1** with stoichiometric amounts of tungsten complex **2** gives phenanthrene derivative **3**.[3] This process is believed to occur via the intermediacy of vinylcarbene complex **4** which undergoes an olefin metathesis process with the pendant alkene via metallacyclobutane **5** to give **3** and the unstabilized tungsten carbene complex **6**. In contrast, Wulff and Kaesler have found that alternative reaction pathways are taken when unsubstituted enyne **7** is treated with chromium complex **8**.[4] When performed in acetonitrile, the major product is cyclobutanone **9**, which is suggested to arise via intramolecular 2 + 2 cycloaddition of vinylketene intermediate **12**. In tetrahydrofuran, an additional product, methoxyfuran **10**, is obtained via metal-mediated rearrangement of vinylketene **12**.[5] More recently, Korkowski, Hoye, and Rydberg have demonstrated that vinylcyclopropane formation is the dominant pathway when substituted enyne **13** is treated with chromium carbene complex **8**.[6] This presumably occurs via intramolecular cyclopropanation of the pendant alkene by vinylcarbene complex **15**. In addition, Hoye and co-workers have noted that enynes related to **13**, but with additional substitution on the olefin, give rise to cyclobutanones and/or furans related to **9** and **10** as well as to olefin

(1) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1990**, *31*, 2529-2532. (b) Harvey, D. F.; Brown, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 7806-7807. (c) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066-5068. (d) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 8916-8921. (e) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1991**, *32*, 5223-5226.
(2) For a preliminary account of this work, see: Harvey, D. F.; Lund, K. P.; Neil, D. A. *Tetrahedron Lett.* **1991**, *32*, 6311-6314.
(3) (a) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737-738. (b) For a related reaction of enyne **1** with a tungsten carbyne complex, see: Sivavec, T. M.; Katz, T. J.; Chiang, M. Y.; Yang, G. X.-Q. *Organometallics* **1989**, *8*, 1620-1625.
(4) Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461-1463.
(5) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346-2360 and references cited therein.
(6) (a) Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676-2678. For cyclizations of other carbene complexes with **13** and related enynes, see: (b) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070-2071. (c) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1990**, *9*, 3014-3015. (d) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841-2842.

0002-7863/92/1514-8424$03.00/0 © 1992 American Chemical Society

Scheme I



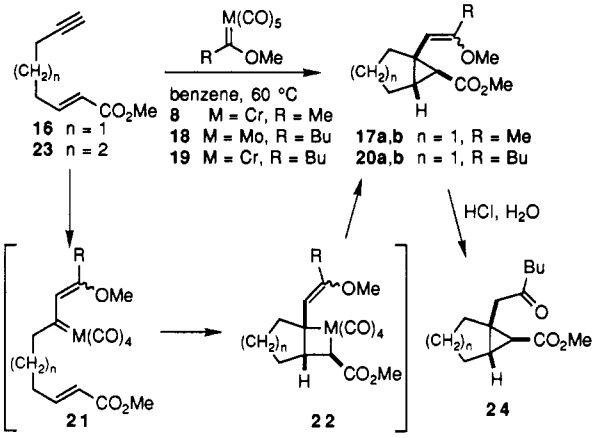
metathesis products related to **3**. It is clear from these three independent studies that relatively minor changes in the substrate, the carbene complex, or the reaction conditions can have a dramatic effect on the outcome of this process.[7,8]

Results

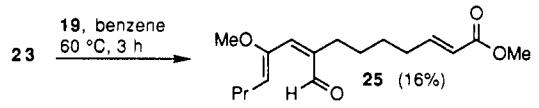
Since it is well-known that Fischer carbene complexes readily cyclopropanate electron-deficient alkenes,[1a,9] the reactivity of enyne **16** was investigated. It was anticipated that the presence of the electron-withdrawing ester would cause the cyclopropanation pathway to be favored over the olefin metathesis or CO insertion processes. Treatment of enyne **16** with chromium carbene complex **8**, used previously in the studies by Wulff[4] and Hoye,[6] did indeed produce vinylcyclopropanes **17a,b** but in only 33% yield. Butyl chromium complex **19** behaved in a similar fashion.

Earlier studies by our group concerning the reactivity of electron-poor olefins[1a] and dienynes[1c] with chromium and molybdenum carbene complexes have demonstrated that molybdenum complexes participate in these reactions at a lower temperature and/or a faster rate than do the analogous chromium complexes. Additionally, molybdenum complexes have been found to significantly favor the cyclopropanation pathways over those involving CO insertion.[1b] When complex **18**[1a] was treated with enyne **16**, vinylcyclopropanes **20a,b** were obtained in 76% yield as a 10:1 mixture of enol ether isomers. Since both **8** and **19** behaved similarly in this reaction, the dramatic improvement in yield does

Scheme II



Carbene	Time	Product	Yield	(E:Z)
8	1.75 h	**17**	33%	(3:1)
18	1.00 h	**20**	76%	(10:1)
19	1.50 h	**20**	34%	(4:1)
18	2.50 h	**24**	52%	



not appear to be associated with the alkyl substituent on the carbene complex. Complex **18** is a stable oil that is easily handled and can be stored at −10 °C for prolonged periods of time. This contrasts quite sharply with the behavior of the analogous methyl molybdenum complex which is relatively unstable and decomposes rapidly during isolation.[10]

This reaction is believed to follow the pathway outlined in Scheme II. Thermolytic dissociation of carbon monoxide opens a coordination site at the metal to which the alkyne can complex.[11] Formal [2 + 2] cycloaddition of the carbene complex with the alkyne leads to a metallacyclobutene which, after electrocyclic ring opening, produces vinylcarbene complex **21**.[12] As demonstrated in previous studies with unsymmetrical alkynes,[13] this

(7) For a recent example of the effect of reaction conditions on this type of process, see: Katz, T. J.; Yang, G. X.-Q. *Tetrahedron Lett.* **1991**, *32*, 5895–5898.

(8) For additional examples of intramolecular reactions of Fischer carbene complexes with alkenes, see: (a) Söderberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113–3121. (b) Alvarez, C.; Parlier, A.; Rudler, H.; Yefsah, R.; Daran, J. C.; Knobler, C. *Organometallics* **1989**, *8*, 2253–2259. (c) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Chem. Soc. Dalton Trans.* **1987**, 1041–1049. (d) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908–4916. (e) Dötz, K. H.; Popall, M.; Müller, G. *J. Organomet. Chem.* **1987**, *334*, 57–75. (f) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736–744. (g) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754–3764. (h) Toledano, C. A.; Levisalles,J.; Rudler, M.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *J. Organomet. Chem.* **1982**, *228*, C7–C11.

(9) (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273–1278. (b) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 1356–1372. c) Cooke, M. D.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *56*, 279–284. For recent examples, see: (d) Hegedus, L. S.; Bates, R. W.; Söderberg, B. C. *J. Am. Chem. Soc.* **1991**, *113*, 923–927. (e) Herndon, J. W.; Tumer, S. U. *J. Org. Chem.* **1991**, *56*, 286–294. (f) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364–4374. (g) Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660–5662. (h) Wienand, A.; Reissig, H.-U. *Organometallics* **1990**, *9*, 3133–3142. (i) Wienand, A.; Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1129–1131. (j) Herndon, J. W.; Tumer, S. U. *Tetrahedron Lett.* **1989**, *30*, 4771. (k) Wienand, A.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2315–2318.

(10) (a) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445–2456. (b) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5833–5838.

(11) For a discussion of the mechanism of the cyclopropanation of alkenes by group VI carbene complexes, see ref 8f.

(12) The intermediacy of metallacyclobutenes in the reaction of Fischer carbene complexes with alkynes has recently been discussed. See: Hofmann, P.; Hammerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908–910.

process is expected to proceed with the regioselectivity shown in order to minimize steric interactions between the carbene ligands and the alkyl chain. The tethered olefin then coordinates to the 16-electron metal center of **21** and participates in a second [2 + 2] cycloaddition process to give metallacyclobutane **22**. Reductive elimination then gives the vinylcyclopropane product.

No products derived from CO insertion or olefin metathesis pathways were observed in any of the reactions with enyne **16**. The electron-withdrawing ester appears to activate the olefin and increase the rate of formation of metallacyclobutane **22**, thus disfavoring the CO insertion pathway. Reaction of unsubstituted enyne **7** with **18** produced a complex mixture of products containing no readily identifiable products.

The success of this type of cyclization has previously been shown to be highly dependent upon the length and composition of the tether between the alkyne and the alkene.[1c,2-4,6] A three-atom tether produces the best results, and any increase or decrease in the tether length generally causes a significant reduction in the efficacy of this reaction. In agreement with these earlier studies, treatment of enyne **23**, having a four-methylene tether, with **18** gave a mixture of vinylcyclopropane enol ether isomers (crude yield ≈57%) which was hydrolyzed directly to the corresponding ketone **24** (52% overall yield from **23**). The lower yield of cyclization product from **23**, as compared to **16**, is likely due to the slightly slower rate of olefin coordination with the longer four-atom tether. Treatment of **23** with chromium complex **19** gave none of the desired cyclopropanation products. Instead, only aldehyde **25** was obtained, in 16% yield (vide infra).

Having observed the successful cyclization of enynes with electron-deficient olefins, we next turned our attention to the possibility of preparing bicyclic heterocycles from enynes wherein the requisite electron-withdrawing group comprised part of the tether itself. Accordingly, ester **26** was prepared and treated with **18**.[14] From this reaction, vinylcyclopropanes **27a,b** were obtained in 24% yield. Despite the relatively low yield of the desired cyclization product, no other TLC-mobile products were observed, suggesting that oligomerization or polymerization processes were competing with the desired pathway.

When **26** was treated with chromium complexes **19** and **8**, olefin metathesis products **28a** (9%) and **28b** (10%) were isolated as well as small amounts of cyclopropanation products **27a,b** (5:1, 5%) and **27c** (4%). The isolation of olefin metathesis products with this substrate is not unexpected, as the methylene carbene complex that would be produced via this pathway would be more stable than the carbomethoxy methylene carbene complex produced via metathesis with substrates **16** or **23** (vide infra).[3]

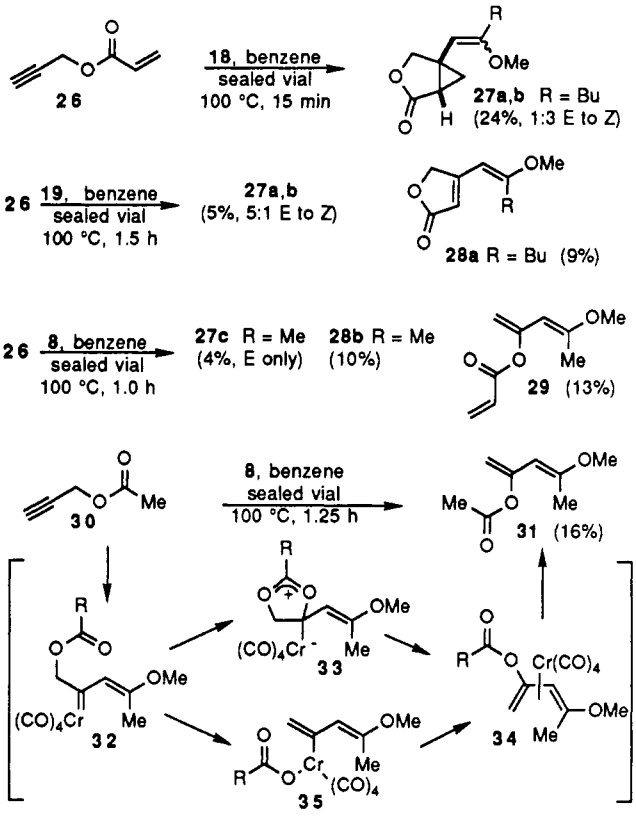
Interestingly, upon treatment of **26** with **8**, an unexpected dienyl acrylate derivative (**29**) was also obtained in 13% yield. An analogous reaction pathway was followed by propargyl acetate (**30**), which gave acetoxy diene **31** in 16% yield upon treatment with **8**, demonstrating that the acrylate double bond is not involved in this transformation. Two possible mechanisms for the formation of **29** and **31** are suggested in Scheme III. Following formation of the intermediate vinylcarbene complex **32**, addition of the oxygen of the carboxylate to the chromium–carbon double bond leads to zwitterionic intermediate **33**, which might then undergo formal β-elimination to give the 18-electron $Cr(CO)_4$–diene complex **34**. Decomplexation of the metal from **34** leads to **29** (when R = $CH{=}CH_2$) or **31** (when R = Me). Alternatively, six-electron electrocyclic rearrangement of **32** might lead to vinyl chromium carboxylate derivative **35**. Reductive elimination from **35** would then give diene complex **34**.[11,15]

(13) For general reviews of the reactivity of Fischer carbene complexes, see: (a) Wulff, W. D. In *Advances in Metal–Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, CT, 1989; Vol. 1, pp 209–393. (b) Casey, C. P. *React. Intermed. (Wiley)* **1985**, *3*, 109. (c) Dötz, K. H. In *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983; pp 191–226.

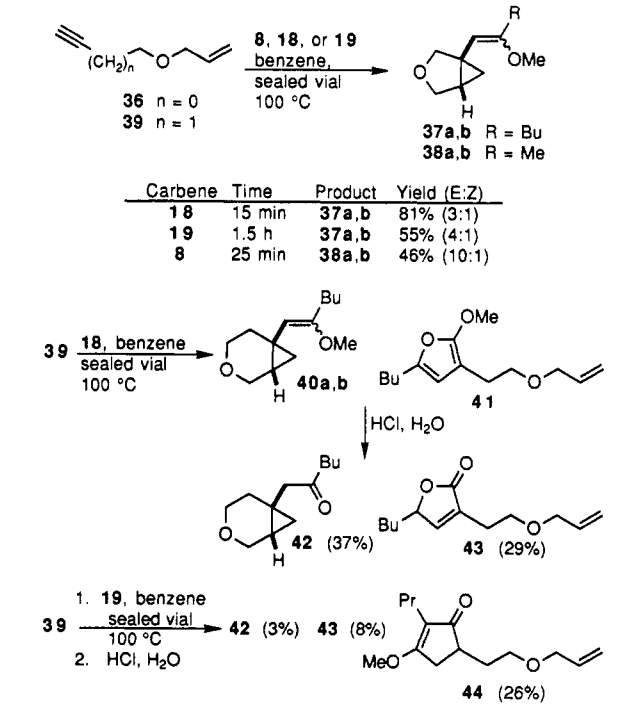
(14) Because of the volatility of **26**, **30**, **36**, **39**, **45**, and **54**, cyclization studies with these substrates were conducted in a sealed vial at 100 °C. Sealed vial reactions at 60 °C were found to give essentially identical product ratios but in some cases required significantly longer reaction times.

(15) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809–7811.

Scheme III



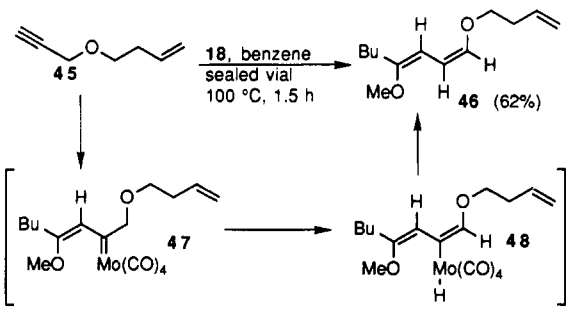
Scheme IV



Carbene	Time	Product	Yield (E:Z)
18	15 min	37a,b	81% (3:1)
19	1.5 h	37a,b	55% (4:1)
8	25 min	38a,b	46% (10:1)

As the ester linkage was only a limited success, we next attempted to prepare bicyclic heterocycles by utilizing an ether linkage between the alkyne and the alkene. The change from ester to ether was expected to eliminate the rearrangement pathway to dienes **29** and **31** seen with esters **26** and **30** and to reduce the polymerizability of the substrate. However, it was not clear whether the allylic oxygen would be a strong enough electron-withdrawing group to activate the alkene. Treatment of **36** with **18** gave vinylcyclopropanes **37a,b** in excellent yield (81%). With chromium complexes **8** and **19**, **36** also produced cyclopropanation products exclusively but in significantly lower yields.[7] Unlike ester

Scheme V



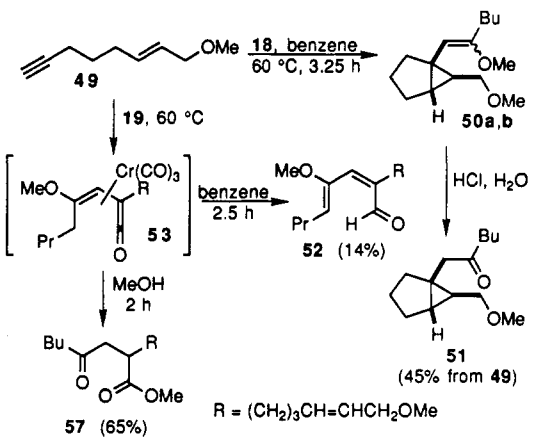
26, no CO insertion or olefin metathesis products were observed. In addition, no other products were isolated when the cyclization was run in THF or acetonitrile.

In order to further probe the effect of an allylic ether on this process, several additional enyne substrates were prepared and their reactivity was studied. Treatment of homopropargyl allyl ether (**39**) with **18** gave approximately equal amounts of cyclopropanated and noncyclized products (see Scheme IV). The crude mixture of enol ethers **40a,b** and furan **41** was hydrolyzed to the corresponding ketone **42** (37% yield) and butenolide **43** (29% yield). Treatment of **39** with **19** produced only small amounts of **42** and **43**. Instead, the major product was cyclopentenone derivative **44** in 26% yield. The production of cyclopentenones has been previously reported by Wulff and co-workers.[16,17] As with **36**, no olefin metathesis products were observed with **39**.

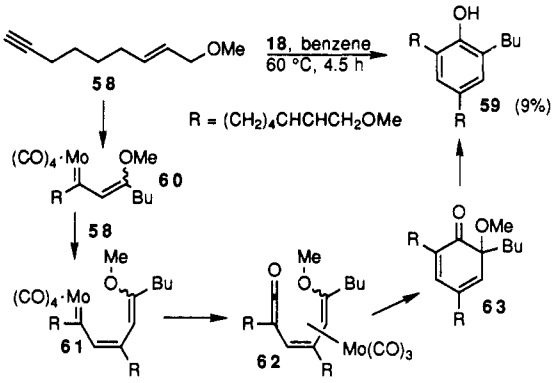
The importance of the position of the oxygen substituent in the four-atom tether case was further investigated with propargyl homoallyl ether (**45**) (see Scheme V). Treatment of **45** with **18** gave none of the expected cyclopropanation or furan products. Instead, the sole product was diene **46** as a single stereoisomer in 62% yield. Treatment of **45** with **19** resulted in the formation of a complex mixture of products containing less than 5% of **46**. Formation of **46** is believed to occur via initial addition of the molybdenum carbene complex to the alkyne to give vinylcarbene complex **47**. Subsequent 1,3-hydrogen shift to give vinyl hydride intermediate **48** appears to be facilitated by the presence of the ether substituent and is favored over CO insertion, olefin metathesis, or cyclopropanation pathways. The stereochemistry of the dienyl substituent of complex **48** would be expected to be as shown in order to avoid steric interaction between the $M(CO)_4H$ unit and the alkoxy substituent.[18] Reductive elimination and decomplexation from vinyl hydride complex **48** then leads to **46** with the stereochemistry indicated. Related processes for the formation of 1,3-dienes by the thermolysis of tungsten carbene complexes with alkynes have previously been reported by Macomber[19] and Rudler,[8c] though the overall reaction pathway is considerably different. The development of this reaction pathway as an expeditious method for the formation of substituted 1,4-dialkoxy-1,3-butadienes will be reported separately.[20]

Since the incorporation of an allylic oxygen into the tether had such a dramatic impact on the outcome of this process, we next sought to determine the effect of an allylic oxygen outside of the tether. Ether **49**, prepared by reduction and methylation of **16**, was treated with **18**, and enol ethers **50a,b** were obtained as a 15:1 mixture. Since **50a,b** were found to readily hydrolyze during isolation, this mixture was directly treated with dilute HCl in H_2O and smoothly converted to ketone **51** in 45% overall yield from

Scheme VI

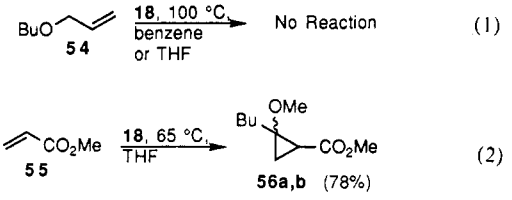


Scheme VII



49. No metathesis or CO insertion products were isolated. It therefore appears that an allylic ether located either in the tether or as a substituent on the olefin significantly increases the propensity of the olefin to participate in the cyclopropanation pathway.

It is interesting to note that no reaction was observed when butyl allyl ether (**54**) was heated with **18**, while thermolysis of methyl acrylate (**55**) with **18** gives the cyclopropanation products **56a,b** in 78% yield.[1a] It appears that while the *intramolecular* cyclo-



propanation process is enhanced by the presence of the allylic ether, this effect does not extend to the analogous *intermolecular* cyclopropanation reaction.

Treatment of **49** with **19** did not follow the expected cyclopropanation pathway. Instead, aldehyde **52** was obtained in 14% yield (see Scheme VI). This aldehyde is analogous to **25**, obtained upon treatment of enyne **23** with **19**. In both cases it appears that CO insertion occurs to give a vinylketene intermediate such as **53**. Subsequent 1,5-hydrogen shift then gives the aldehydes **25** and **52**. This hydrogen migration step is most likely metal-assisted, since a free ketene would be expected to rapidly undergo [2 + 2] cycloaddition with the tethered alkene to give cyclobutanone products such as those seen in the case of enyne **7**.[4] Treatment of **49** with **19** in methanol instead of benzene, produced keto ester **57** in 65% yield.[4,5] Ester **57** is the product expected from reaction of the ketene moiety with methanol and subsequent enol ether hydrolysis. The isolation of **57** further supports the intermediacy of vinylketene complex **53**.

Lengthening the tether caused an even more dramatic change in reactivity. Treatment of **58** with **18** produced phenol **59** in 9%

(16) Wulff, W. D.; Challener, C. A.; Yang, D. C.; Faron, K. L.; Kim, O. K.; Xu, Y. C. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989; American Chemical Society: Washington, DC, 1989; ORG 185.

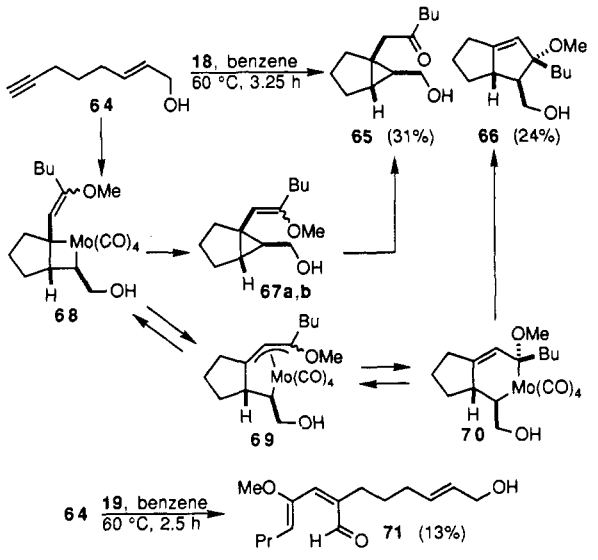
(17) For an alternative Fischer carbene based approach to cyclopentenones, see: (a) Herndon, J. W.; Turner, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334–3335. (b) Herndon, J. W.; Matasi, J. J. *J. Org. Chem.* **1990**, *55*, 786–788.

(18) For a recent example of a related thermal rearrangement of a chromium (acyloxy)carbene complex to an enolacetate, see: Söderberg, B. C.; Turbeville, M. J. *Organometallics* **1991**, *10*, 3951–3953.

(19) Macomber, D. W. *Organometallics* **1984**, *3*, 1589–1591.

(20) Harvey, D. F.; Neil, D. A. Manuscript in preparation.

Scheme VIII



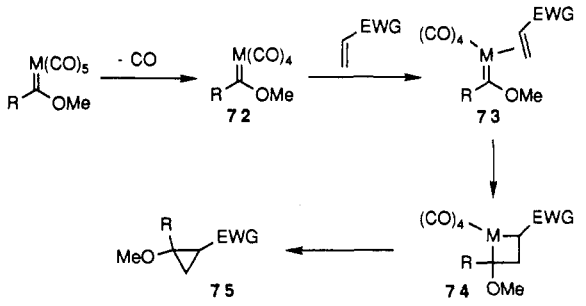
yield rather than the expected cyclopropanation product (see Scheme VII). The phenol results from the addition of a second equivalent of alkyne to the initially generated vinylcarbene complex **60** to give transient dienylcarbene **61**. Subsequent CO insertion gives dienylketene complex **62**, which, upon electrocyclic ring closure, produces methoxycyclohexadienone **63**. Metal-mediated reduction of the cyclohexadienone and loss of methanol leads to phenol **59**. This route to phenols has previously been described by Wulff and co-workers.[21]

The possibility of using an external alcohol rather than an ether to activate the olefin was also investigated. Treatment of alcohol **64** with **18** in benzene for 3.25 h at 60 °C gave cyclopropanation product **65** in 31% yield along with bicyclooctene derivative **66** in 24% yield. The enol ether precursors to ketone **65**, vinylcyclopropanes **67a,b** were not observed and are believed to have been hydrolyzed directly to the ketone during the reaction due to the prolonged reaction times and/or the presence of the alcohol substituent. The formation of **65** and **66** indicates that the effect of the alcohol substituent on the reactivity of the olefin is similar to the effect of the methoxy substituent of **49**. Bicyclooctene **66** is of interest since it can be viewed as resulting from vinylcyclopropane to cyclopentene rearrangement of **67**. Though a similar pathway has recently been reported by Hoye and coworkers to occur with aminocarbene complexes,[6b] it is unlikely that the free vinylcyclopropane **67** will undergo vinylcyclopropane-to-cyclopentene rearrangement under these reaction conditions since significantly higher temperatures or strong Lewis acids are usually required to induce this rearrangement.[22] Since closely related ether-substituted vinylcyclopropanes have previously been cleanly isolated without any cyclopentene-derived products being produced, it appears that the alcohol substituent is inducing the formation of bicyclooctene **66**. A possible mechanistic rationale for this behavior is presented in Scheme VIII. After formation of the expected intermediate vinylcarbene complex, intramolecular [2 + 2] cyclization results in the formation of metallacyclobutane **68**. Reductive elimination from **68** leads to vinylcyclopropanes **67a,b**, which upon hydrolysis go on to ketone **65**. Alternatively, the 16-electron η^1-allyl complex **68** can isomerize via the 18-electron η^3-allyl complex **69** to the 16-electron η^1-allyl complex **70**. In **70**, complexation of the alcohol substituent to the metal

(21) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. *J. Am. Chem. Soc.* **1985**, *107*, 1060–1062.

(22) (a) Corey, E. J.; Myers, A. G. *J. Am. Chem. Soc.* **1985**, *107*, 5574–5576. (b) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1991**, *32*, 2871–2874. (c) Davies, H. M. L.; Hu, B. *Tetrahedron Lett.* **1992**, *33*, 453–456. For recent reviews, see: (d) Wong, H. N. C.; Hon, M. Y.; Hon, M. Y.; Tse, C. H.; Yip, Y. C.; Taniko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165–198. (e) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229–267. (f) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247–335.

Scheme IX



might provide additional stabilization, causing it to be favored over **68**. The alcohol would be expected to coordinate to the metal and stabilize this intermediate more readily than the analogous ether. Subsequent reductive elimination from **70** could then produce a metal complex of **66** where the $Mo(CO)_4$ unit is coordinated to both the hydroxyl substituent and the double bond, allowing the metal to have an 18-electron configuration before it decomplexes from the organic substrate and coordinates to the solvent. As with **49**, when alcohol **64** was treated with **19** the only isolable product obtained was aldehyde **71** in 13% yield.

Discussion

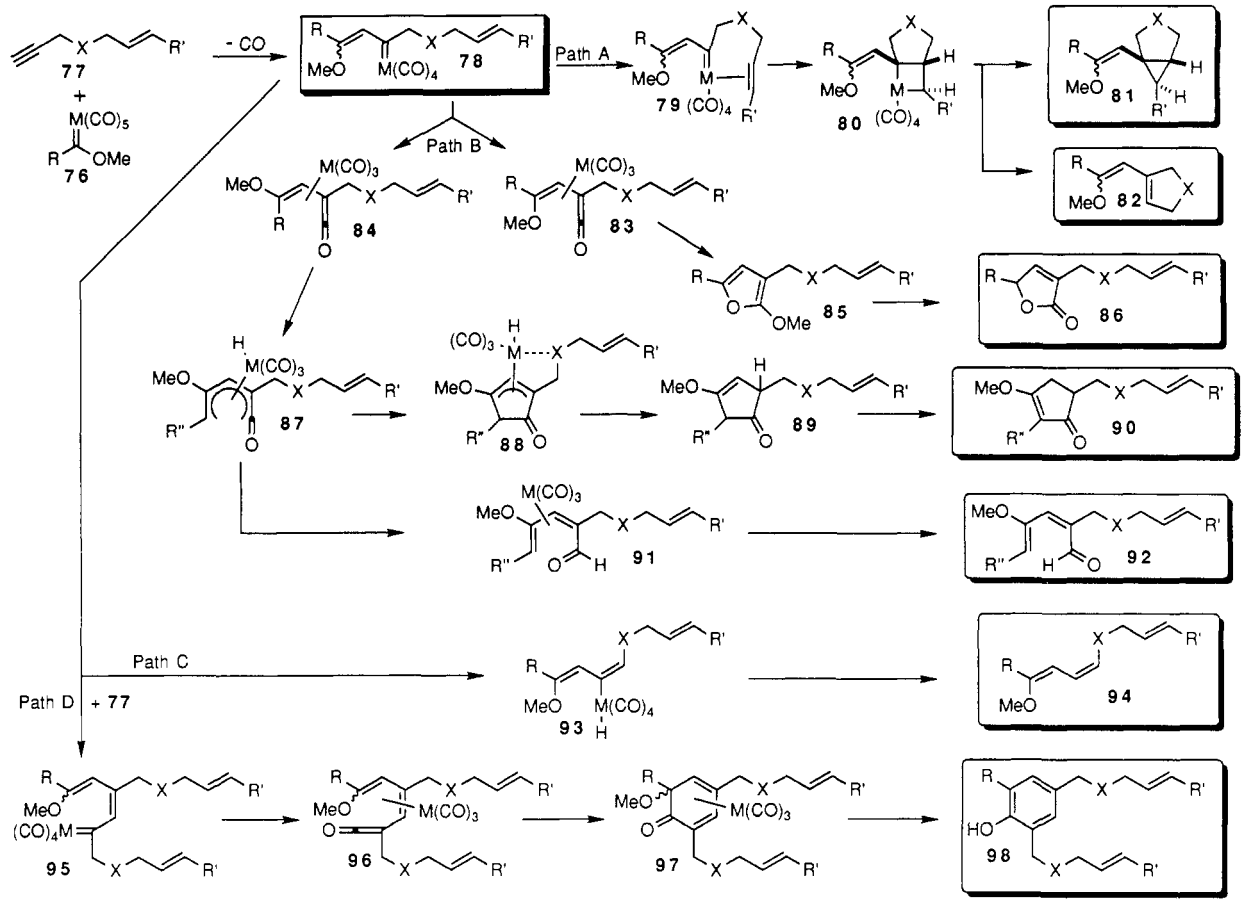
The intermolecular reaction of Fischer carbene complexes with electron-deficient alkenes has been found to produce substituted cyclopropanes in good to excellent yield.[1a,9] This reaction is believed to proceed via a dissociative substitution pathway involving loss of carbon monoxide, to give a coordinatively unsaturated 16-e⁻ complex (**72**), followed by coordination of the alkene to give complex **73** (see Scheme IX). Subsequent metallacyclobutane formation and reductive elimination gives cyclopropane **75**. Electron-rich alkenes react with Fischer carbene complexes to give either cyclopropane or olefin metathesis products, depending on the conditions employed, but the mechanism involved is thought to be quite different than that seen with electron-deficient alkenes.[11] Alkenes without electron-donating or electron-withdrawing groups are, in general, relatively unreactive toward Fischer carbene complexes.[1d,9]

The key step in the reaction of electron-deficient alkenes with Fischer carbene complexes is coordination of the olefin to the 16-e⁻ complex **72**. As the bonding of olefins to zero-valent transition metals is primarily via d-π^* back-bonding, electron-withdrawing groups on the olefin significantly lower the energy of π^*, thus increasing the strength of the metal–olefin bond in **73**. Since the reaction of α,ω-enynes with Fischer carbene complexes involves a closely related intramolecular variation of this reaction, we sought to determine to what extent appropriately situated electron-withdrawing groups might induce the cyclopropanation pathway to be favored.

The studies described herein, as well as previous studies by others, have demonstrated that group VI Fischer carbene complexes can react with α,ω-enynes via several different pathways. As presented in Scheme X, all of the products produced in our studies are derived from vinylcarbene intermediate **78**. Path A, involving reaction of the pendant alkene with the vinylcarbene moiety, leads to either vinylcyclopropane **81** or diene **82**. When the tethered alkene does not react with the vinylcarbene complex, three other reaction pathways have been observed. Path B, involving insertion of carbon monoxide into **78**, leads to vinylketene complexes **83** and **84** which go on to produce either butenolide **86**, cyclopentenone **90**, or dienal **92**. Path C, involving hydrogen migration to produce the intermediate vinyl hydride complex **93**, leads to diene **94**. Alternatively, path D, involving reaction of **78** with a second equivalent of alkyne followed by insertion of carbon monoxide, leads to phenol **98**. Vinylcyclobutanones, though previously reported in related studies by Wulff[4] and Hoye,[6] were not obtained in our studies.

In solution,[7] path A has not been observed with the parent unsubstituted enyne, 1,6-heptenyne (**7**). Previous studies have demonstrated that appropriately positioned substituents on the

Scheme X



tether increase the rate of reaction with the pendant alkene, causing the cyclopropanation process to be the dominant pathway.[1c,6] This is thought to be caused primarily by the substituents reducing the conformational freedom of the tether, though more subtle electronic or coordination effects cannot be ruled out.

The *E* and *Z* isomers of **78** are expected to have quite distinct reactivities. The *E* isomer is expected to coordinate more readily to the pendant olefin to give **79** since the methoxy group is not able to coordinate to the metal. The *Z* isomer is expected to be less likely to form (*Z*)-**79** since the methoxy group can coordinate to the metal and stabilize the vinylcarbene intermediate. Related differences in reactivity have been noted in previous studies.[1e]

The studies reported herein have demonstrated that the desired cyclopropanation process is also favored when the olefin is rendered electron-deficient by the presence of electron-withdrawing groups. The attachment of electron-withdrawing groups to the olefin significantly lowers the energy of the olefin π^* molecular orbital, which increases the stability of the metal–olefin complex **79**, thus causing path A to be favored. The electron-withdrawing functionality on the alkene can be varied quite extensively since both esters and ethers, either as part of the tether or as a substituent on the olefin, have been found to suitably activate the alkene and lead to preferential formation of cyclopropanation products.

The efficacy of this process has also been found to be highly dependent upon both the length of the tether and the metal employed. With a three-atom tether between the alkyne and the alkene, both **18** and **19** readily produced the desired vinylcyclopropanes. However, molybdenum complex **18** consistently gave significantly higher yields than did chromium complex **19**. Several different factors may be responsible for this behavior. In general, ligand coordination to second-row metals is stronger than to first-row metals because of the greater basicity of the second-row elements. As olefin coordination appears to be the key product-determining step, complexation of the olefin when M = Mo would provide greater stabilization of intermediate **79** than would complexation of the olefin when M = Cr. Alternatively, associative pathways involving transient 20-e$^-$ intermediates may be operative with molybdenum but not with chromium.[23] In addition, other reaction pathways, such as those involving CO insertion (vide infra), may be less likely to occur with molybdenum than with chromium because of the greater metal/carbon monoxide bond strength of molybdenum.

With longer four-atom tethers, only **18** gave vinylcyclopropanes in good yield, while **19** gave products derived from path B rather than the desired path A. This is not unexpected as cyclization processes to form five-membered rings are generally faster than those that form six-membered rings. With 1,7-enynes and chromium carbene complexes, insertion of carbon monoxide into **78** is faster than intramolecular cyclization with the pendant alkene, whereas with 1,6-enynes, intramolecular olefin cyclization is faster than CO insertion. However, in the molybdenum series intramolecular cyclization, as well as several other reaction pathways (vide infra), are more favorable than CO insertion for both 1,6- and 1,7-enynes, provided that the olefin is activated toward metal complexation by the presence of appropriate electron-withdrawing groups.

The location of the electron-withdrawing group appears to play an important role in determining whether cyclopropanation or olefin metathesis products are obtained. For example, with **16**, where R′ of Scheme X is a carbomethoxy group, olefin metathesis product **82** is not observed. However, when the electron-withdrawing group is part of the tether, as in **26**, the metathesis pathway leading to diene **82** competes with the cyclopropanation process. The carbene complex produced via metathesis with **16** would be the very unstable carbomethoxy carbene complex **99**, whereas that derived from **26** would be the considerably more stable, though still quite reactive, methylidene carbene complex

(23) For a general discussion of ligand substitution process, see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 247–253 and references cited therein.

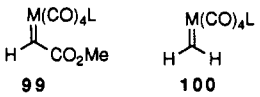


Figure 1.

100 (see Figure 1). It is likely that the high instability of **99** causes the metathesis pathway to be disfavored with this substrate.

With chromium carbene complexes when pathway A is not followed, **78** instead inserts carbon monoxide to give vinylketene complexes **83** and **84**. The *Z*-enol ether **83** can rearrange to give furan **85**. This metal-mediated vinylketene-to-furan rearrangement process has previously been studied by others.[5] The corresponding *E*-enol ether **84** cannot rearrange to furn **85**. Instead, C–H insertion into R gives complex **87**, which can then either undergo a formal metal-mediated electrocyclic ring closure to give allyl hydride complex **88** or reductively eliminate to give dienal complex **91**. Reductive elimination from **88** leads to cyclopentenone **89**, which upon acid- or base-catalyzed olefin isomerization, goes on to cyclopentenone **90**. Though the isolated yields of these products are consistently low, it does appear that the pathway from **87** to **88** is favored over the pathway from **87** to **91** when X = O. The oxygen in the tether may be inducing the η^5-to-η^3 isomerization of **87** to **88** by intramolecularly coordinating to chromium, as shown in Scheme X, producing the transient 18-e$^-$ complex **88**.

With molybdenum carbene complexes when path A is not followed, CO insertion to form a vinylketene complex does not readily occur. Instead, two alternative pathways have been observed.

With substrates having a propargylic oxygen but no olefin activating group, as in enyne **45**, formation of diene **94** occurs in good yield. It appears that the oxygen substituent activates the α-hydrogens, causing rearrangement to vinyl hydride complex **93** to be favored.[20]

The second alternative pathway with molybdenum carbene complexes leads to the low-yield (9%) formation of phenol **98** from enyne **58**.[21] It appears that when the alkene is relatively unreactive because of the length of the tether and absence of strongly activating groups, **78** reacts with a second equivalent of alkyne to give **95** rather than inserting CO to give **83** and **84**.

In summary, we have demonstrated that enynes with an electron-withdrawing substituent on the olefin give vinylcyclopropane products in good to excellent yield when treated with molybdenum carbene complex **18**. Notable examples are enynes **16**, **36**, and **49**, which represent a facile, high-yield route into the substituted bicyclo[3.1.0]hexane ring system. Variation of the length and composition of the tether as well as the substituents on the alkyne leads to a variety of other products, several of which represent new reaction pathways.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 500-MHz or G.E. 300-MHz spectrometers. IR spectra were recorded on a Mattson Galaxy 2020 FT-IR spectrophotometer. Low resolution mass spectra were recorded on a Hewlett-Packard 5970 mass-selective detector (20 eV) interfaced with a Hewlett-Packard 5890 gas chromatograph equipped with a 12-m × 0.2-mm HP-1 fused silica capillary column. High resolution mass spectra were performed at the University of California at Riverside Mass Spectrometry Facility on a VG-ZABZFHF or VG-7070EHF mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. Column chromatography was performed with Fischer Scientific Florisil (100–200 mesh) or silica gel (200–425 mesh). All reagents were obtained from commercial suppliers and used as received unless otherwise indicated. Reactions were performed under a nitrogen atmosphere in flame-dried glassware. A general procedure for reactions involving a sealed vial is provided below. Benzene, tetrahydrofuran, and diethyl ether were distilled from benzophenone ketyl under a nitrogen atmosphere. Methylene chloride and acetonitrile were distilled over calcium hydride. When appropriate, the disappearance of starting material was monitored by thin layer chromatography.

General Procedure for the Cyclizations of 26, 30, 36, 39, 45, and 54. The enyne and the carbene complex were dissolved in benzene (22 mL) and, behind a blast shield, heated at 100 °C in a glass vial sealed with a rubber-lined screw cap and aluminum foil. After being cooled to room temperature, the solution was filtered through a pad of Celite, concentrated in vacuo, and chromatographed on Florisil.

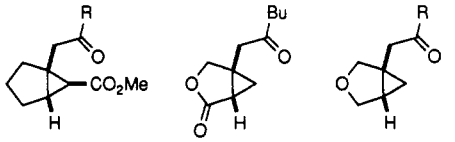


Figure 2.

Methyl *trans*-2-Octen-7-ynoate (16). Using the procedure of Swern,[24] oxalyl chloride (1.0 mL, 11 mmol) was dissolved in CH_2Cl_2 (25 mL) and cooled to −60 °C. DMSO (1.7 mL, 22 mmol) was added and, after 2 min, 5-hexyn-1-ol (1.1 mL, 10 mmol) was added. Stirring was continued for an additional 15 min. Triethylamine (7.0 mL, 50 mmol) was then added, and the solution was allowed to warm to room temperature. The reaction mixture was poured into H_2O (50 mL) and extracted with CH_2Cl_2. The organic phases were combined, washed with H_2O followed by saturated NaCl solution, and dried over $MgSO_4$. The combined organics were then concentrated in vacuo to approximately 5 mL. Due to its instability and volatility, the aldehyde was used directly without further purification.

Methyl (diethylphosphono)acetate (2.00 mL, 11.0 mmol) was dissolved in THF (25 mL) and cooled to −78 °C. *n*-BuLi (7.25 mL, 1.6 M in hexanes, 11.6 mmol) was added, and the mixture was stirred for 5 min. The crude aldehyde solution was added, and the mixture was stirred for 10 min at −78 °C and then allowed to warm to room temperature. H_2O (30 mL) was added, and the reaction mixture was extracted with Et_2O. The combined organics were dried over $MgSO_4$ and concentrated in vacuo. Chromatography on silica gel gave 0.21 g (14%) of methyl *cis*-2-octen-7-ynoate and 1.13 g (74%) of **16**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.68 (p, J = 7.3 Hz, 2 H), 1.97 (t, J = 2.6 Hz, 1 H), 2.22 (dt, J = 2.6, 7.0 Hz, 2 H), 2.33 (qd, J = 1.1, 7.3 Hz, 2 H), 3.72 (s, 3 H), 5.85 (d, J = 15.6 Hz, 1 H), 6.94 (dt, J = 15.7, 7.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 26.6, 30.9, 51.4, 69.0, 83.4, 121.6, 148.1, 166.9; IR (CH_2Cl_2) 3300, 2940, 2110, 1715, 1650, 1430 cm^{-1}; MS (EI, 70 eV) m/e 152 (M$^+$, 1); HRMS for $C_9H_{11}O_2$ (M$^+$ − H) calcd 151.0790, found 151.0763.

Methyl (5β)-1β-(2(*E*)-Methoxyprop-1-enyl)bicyclo[3.1.0]hexane-6β-carboxylate (17a) and Methyl (5β)-1β-(2(*Z*)-Methoxyprop-1-enyl)bicyclo[3.1.0]hexane-6β-carboxylate (17b) from Carbene 8. To a solution of **16** (0.095 g, 0.625 mmol) in benzene (250 mL, 2.5 mM) was added **8** (0.312 g, 1.25 mmol). After being heated at 70 °C for 1.75 h, the reaction mixture was concentrated in vacuo and chromatographed on Florisil (1% EtOAc/Hex) to give a 3:1 mixture (43.2 mg, 33%) of the *E* (**17a**) and *Z* (**17b**) enol ether isomers, respectively. Isomers **17a** and **17b** could only be partially separated by chromatography on Florisil. The enol ether stereochemistry of **17a** and **17b** was assigned on the basis of NOE enhancements of 3.1 and 1.0% to the vinyl methoxy and vinyl methyl of **17a** from the vinyl hydrogen. Also observed was a 28.4% enhancement to the vinyl hydrogen **17a** from the vinyl methoxy. For **17b**, NOE enhancements of 0 and 2.3% were observed from the vinyl hydrogen to the vinyl methoxy and the vinyl methyl, respectively. **17a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10–1.22 (m, 1 H), 1.56–1.91 (m, 6 H), 1.79 (s, 3 H), 1.94–2.05 (m, 1 H), 3.45 (s, 3 H), 3.61 (s, 3 H), 4.55 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.1, 20.9, 27.55, 27.61, 33.7, 35.3, 36.4, 51.2, 54.4, 95.1, 157.8, 172.3; IR ($CDCl_3$) 2945, 2860, 1720, 1660, 1435 cm^{-1}; LRMS (EI, 70 eV) m/e 210 (M$^+$, 24). Because of decomposition during transport, elemental analysis and HRMS of **17a** were not feasible. Full spectral data were obtained for ketone **101**, obtained upon exposure of **17a** (10.0 mg) to wet silica gel in hexane for 3 h at room temperature, followed by silica gel chromatography (7.6 mg, 82%). **17b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75–0.95 (m, 2 H), 1.05–1.95 (m, 5 H), 1.82 (s, 3 H), 2.10–2.20 (m, 1 H), 3.52 (s, 3 H), 3.63 (s, 3 H), 4.60 (s, 1 H). These are the only spectral data available due to low yield, instability, and similar R_f to the major enol ether isomer. By TLC, **17b** was found to hydrolyze to the corresponding ketone (**101**), which is fully characterized below.

Methyl (5β)-1β-(2-oxopropanyl)bicyclo[3.1.0]hexane-6β-carboxylate (101): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16–1.23 (m, 1 H), 1.57–1.67 (m, 3 H), 1.75–1.97 (m, 4 H), 2.07 (s, 3 H), 2.77 (d, J = 17.4 Hz, 1 H), 3.05 (d, J = 17.4 Hz, 1 H), 3.61 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 24.7, 27.5, 29.9, 33.1, 33.4, 35.0, 43.6, 51.5, 173.4, 207.7; IR (CCl_4) 2940, 2850, 1720, 1435, 1410 cm^{-1}; MS (EI, 70 eV) m/e 196 (M$^+$, 31); HRMS for $C_{11}H_{16}O_3$ calcd 196.1099, found 196.1111.

(24) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165–185.

Methyl (5β)-1β-(2(*E*)-Methoxyhex-1-enyl)bicyclo[3.1.0]hexane-6β-carboxylate (20a) and Methyl (5β)-1β-(2(*Z*)-Methoxyhex-1-enyl)bicyclo[3.1.0]hexane-6β-carboxylate (20b) from 18. To a solution of **16** (0.066 g, 0.434 mmol) in benzene (174 mL, 2.5 mM) was added **18** (0.292 g, 0.869 mmol). After being heated at 60 °C for 1 h, the reaction mixture was concentrated in vacuo and chromatographed on Florisil (1% EtOAc/Hex) to give 0.143 g (49%) of recovered **18** and 0.083 g (76%) of **20** as a 10:1 mixture of enol ethers. The major enol ether isomer (**20a**) was assigned the *E* geometry on the basis of comparison to **17a** and **17b** (vide supra).

20a,b from 19. To a solution of **16** (0.086 g, 0.565 mmol) in benzene (225 mL, 2.5 mM) was added **19** (0.330 g, 1.13 mmol). After being heated at 60 °C for 1.5 h, the reaction mixture was concentrated in vacuo and chromatographed on Florisil (1% EtOAc/Hex) to give 0.149 g (45%) of recovered carbene **19** and 48.1 mg (34%) of **20** as a 4:1 (*E*/*Z*) mixture of enol ethers. **20a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.3 Hz, 3 H), 1.14–1.20 (m, 1 H), 1.31 (sextet, *J* = 7.3 Hz, 2 H), 1.38–1.47 (m, 2 H), 1.62–1.89 (m, 5 H), 1.91 (q, *J* = 3.9 Hz, 1 H), 2.01 (dd, *J* = 13.2, 8.3 Hz, 1 H), 2.07–2.13 (m, 1 H), 2.18–2.24 (m, 1 H), 3.45 (s, 3 H), 3.60 (s, 3 H), 4.53 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 20.9, 22.8, 27.5, 27.7, 29.5, 30.9, 34.0, 36.0, 36.4, 51.2, 54.4, 95.0, 161.5, 172.2; IR (CH_2Cl_2) 2940, 2850, 1720, 1650, 1460, 1430 cm^{-1}; MS (EI, 70 eV) *m/e* 252 (M^+, 26). Isomer **20b** could not be separated from **20a**. The presence of **20b** in **20a** was confirmed by comparison of the NMR spectrum of **17b** to the NMR spectrum of the 10:1 mixture of **20a** and **20b**. Enol ethers **20a** and **20b** were unstable to silica gel chromatography. Upon exposure to silica gel, rapid hydrolysis to the corresponding ketone (**102**) was found to occur. Because of decomposition during transport, elemental analysis and HRMS of **20a** and **20b** were not feasible. Full spectral data were obtained for ketone **102**, obtained upon exposure of a mixture (10:1) of **20a** and **20b** (66.5 mg) to wet silica gel in hexane for 3 h at room temperature, followed by silica gel chromatography (56.0 mg, 90%).

Methyl (5β)-1β-(2-oxohexanyl)bicyclo[3.1.0]hexane-6β-carboxylate (102): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.3 Hz, 3 H), 1.23–1.31 (m, 3 H), 1.51 (p, *J* = 7.7 Hz, 2 H), 1.58–1.69 (m, 3 H), 1.76 (t, *J* = 3.6 Hz, 1 H), 1.81–1.94 (m, 3 H), 2.33 (dt, *J* = 7.3, 1.5 Hz, 2 H), 2.76 (d, *J* = 17.3 Hz, 1 H), 3.03 (d, *J* = 17.4 Hz, 1 H), 3.62 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 20.9, 22.3, 24.8, 25.8, 27.5, 33.2, 33.3, 35.1, 42.4, 42.6, 51.5, 173.5, 210.0; IR (CCl_4) 2955, 2860, 1715, 1435, 1410 cm^{-1}; MS (EI, 70 eV) *m/e* 238 (M^+, 12); HRMS for $C_{14}H_{22}O_3$ calcd 238.1569, found 238.1558.

Methyl *trans*-2-Nonen-8-ynoate (23). 6-Heptynal[25] (1.681 g, 15.2 mmol) was dissolved in THF (150 mL) and methyl (triphenylphosphoranylidene)acetate (5.11 g, 15.28 mmol) was added. After the solution was stirred for 3.5 h at room temperature, H_2O (300 mL) was added and the solution was extracted with Et_2O (5 × 50 mL) and dried over $MgSO_4$. Chromatography on silica gel gave 1.250 g (49%) of **23**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52–1.63 (m, 4 H), 1.95 (t, *J* = 2.4 Hz, 1 H), 2.19–2.25 (m, 4 H), 3.72 (s, 3 H), 5.83 (dt, *J* = 15.6, 1.5 Hz, 1 H), 6.96 (dt, 15.6, 7.1 Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 18.1, 26.9, 27.7, 31.5, 51.3, 68.5, 84.0, 121.1, 148.9, 167.0; IR (CCl_4) 3314, 2948, 2863, 1727, 1659, 1436 cm^{-1}; MS (EI, 20 eV) *m/e* 166 (M^+, 1); HRMS for $C_{10}H_{13}O_2$ (M^+ − H) calcd 165.0916, found 165.0920.

Methyl (6β)-1β-(2-Oxoheptanyl)bicyclo[4.1.0]heptane-7β-carboxylate (24) from Carbene 8. To a solution of **23** (0.062 g, 0.373 mmol) in benzene (150 mL) was added **18** (0.138 g, 0.411 mmol). After being heated at 60 °C for 2.5 h, the reaction mixture was cooled to room temperature, concentrated in vacuo, and chromatographed on silica gel to give 48.7 mg (52%) of **24**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.79 (t, *J* = 7.3 Hz, 3 H), 0.85–0.97 (m, 2 H), 1.04–1.20 (m containing sextet at 1.14, *J* = 7.3 Hz, 4 H), 1.41–1.50 (m, 4 H), 1.55 (dt, *J* = 1.2, 6.8 Hz, 1 H), 1.65 (d, *J* = 5.4 Hz, 1 H), 1.72–1.82 (m, 2 H), 1.95–2.07 (m, 2 H), 2.68 (apparent q, *J* = 17 Hz, 2 H), 3.41 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.0, 20.7, 21.2, 22.6, 22.9, 26.1, 27.6, 27.9, 29.5, 30.3, 42.4, 47.6, 51.1, 173.8, 207.9; IR (CCl_4) 2935, 2863, 1722, 1448, 1438 cm^{-1}; MS (EI, 20 eV) *m/e* 252 (M^+, 2); HRMS for $C_{15}H_{24}O_3$ calcd 252.1725, found 252.1732.

Methyl (*E*,*Z*,*Z*)-8-Formyl-10-methoxy-2,8,10-tetradecatrienoate (25) from Carbene 19. To a solution of **23** (62 mg, 0.373 mmol) in benzene (150 mL) was added **19** (119.6 mg, 0.411 mmol). After being heated at 60 °C for 3 h, the reaction mixture was cooled to room temperature, concentrated in vacuo, and immediately chromatographed on silica gel to give 17.6 mg (16%) of **25**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.88 (t, *J* = 7.3 Hz, 3 H), 1.25–1.35 (m, 4 H), 1.44 (p, *J* = 7.8 Hz, 2 H), 1.86 (q, *J* = 6.8 Hz, 2 H), 2.11 (q, *J* = 7.3, 2 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 3.19 (s, 3 H), 3.46 (s, 3 H), 5.04 (t, *J* = 7.6 Hz, 1 H), 5.87 (d, *J* = 15.6 Hz, 1 H), 6.07 (s, 1 H), 7.03 (dt, *J* = 15.6, 7.1 Hz, 1 H), 9.32 (s, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 13.9, 22.5, 24.0, 28.1 (2×), 28.7, 31.9, 51.3, 59.7, 120.9, 129.5, 140.7, 145.8, 149.5, 154.1, 167.1, 195.2; IR (CCl_4) 2940, 2935, 2863, 1727, 1687, 1659, 1626, 1462, 1436 cm^{-1}; MS (EI, 20 eV) *m/e* 294 (M^+, 9); HRMS (CI, NH_3) for $C_{17}H_{27}O_4$ calcd (MH^+) 295.1909, found 295.1913. Irradiation of the methoxy signals at δ 3.19 and 3.46 showed no enhancement of the olefin signal at δ 5.04.

2-Propynyl Propenoate (26). To a stirred solution of propargyl alcohol (0.75 mL, 13 mmol) and triethylamine (2.5 mL) in CH_2Cl_2 (70 mL) at 0 °C was added acryloyl chloride (1.2 mL, 14 mmol). The reaction mixture was allowed to warm to room temperature and then quenched with a saturated $NaHCO_3$ solution. The organic layer was extracted with 10% HCl (3 × 15 mL), saturated $NaHCO_3$ solution (1 × 15 mL), and H_2O (1 × 15 mL), dried over $MgSO_4$, filtered through neutral alumina, and concentrated in vacuo to give **26** (1.28 g, 90%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.49 (t, *J* = 2.4 Hz, 1 H), 4.77 (d, *J* = 2.4 Hz, 2 H), 5.90 (dd, *J* = 10.7, 1.0 Hz, 1 H), 6.16 (dd, *J* = 17.3, 10.5 Hz, 1 H), 6.47 (dd, *J* = 17.1, 1.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.0, 74.9, 77.5, 127.5, 131.9, 165.2; IR (CCl_4) 3314, 2947, 1733, 1636, 1622, 1451, 1435, 1406 cm^{-1}; MS (EI, 20 eV) *m/e* 111 (MH^+, 1); HRMS for $C_6H_5O_2$ (M^+ − H), calcd 109.0290, found 109.0281.

(5β)-1β-(2(*E*)-Methoxy-1-hexenyl)-3-oxabicyclo[3.1.0]hexan-4-one (27a) and (5β)-1β-(2(*Z*)-Methoxy-1-hexenyl)-3-oxabicyclo[3.1.0]hexan-4-one (27b) from Carbene 18. According to the general procedure, **26** (112.1 mg, 1.02 mmol) and **18** (196.4 mg, 0.58 mmol) were heated for 15 min to give 30 mg (24%) of a 1:3 mixture (by ^{1}H NMR) of **27a** and **27b**. Because of difficulty in separating the isomers, the mixture was hydrolyzed to ketone **103** for complete characterization.

27a,b and 4-(2(*E*)-Methoxy-1-hexenyl)-2(5*H*)-furanone (28a) from Carbene 19. According to the general procedure, **26** (97 mg, 0.88 mmol) and **19** (199 mg, 0.68 mmol) were heated for 1.5 h to give 7.0 mg (5%) of a 5:1 mixture (by ^{1}H NMR) of **27a** and **27b** and 11.8 mg (9%) of **28a**. **27a**: ^{1}H NMR (300 MHz, C_6D_6, from 5:1 mixture) δ 0.60 (t, *J* = 3.9 Hz, 1 H), 0.74 (dd, *J* = 9.1, 4.3, 1 H), 0.81 (t, *J* = 7.2 Hz, 3 H), 1.08–1.19 (m, 2 H), 1.26–1.39 (m, 2 H), 1.54 (dd, *J* = 9.1, 3.4 Hz, 1 H), 1.95–2.00 (m, 2 H), 3.00 (s, 3 H), 3.57 (d, *J* = 8.9 Hz, 1 H), 3.67 (d, *J* = 9.0 Hz, 1 H), 3.95 (s, 1 H); ^{13}C NMR (125 MHz, C_6D_6, from 1:3 mixture) δ 14.1, 19.7, 22.7, 25.1, 26.6, 29.8, 30.9, 54.2, 73.0, 92.3 (signal for minor isomer at ∼164 not observed), 175.1. **27b**: ^{1}H NMR (500 MHz, C_6D_6, from 1:3 mixture) δ 0.68 (t, *J* = 3.9 Hz, 1 H), 0.79–0.85 (m containing triplet at 0.81, *J* = 7.1 Hz, 4 H), 1.11–1.17 (m, 4 H), 1.69–1.73 (m, 3 H), 2.91 (s, 3 H), 3.90 (s, 1 H), 3.92–3.97 (AB, 2 H); ^{13}C NMR (125 MHz, C_6D_6, from 1:3 mixture) δ 14.0, 18.9, 22.4, 25.5, 26.7, 29.4, 30.5, 54.9, 72.6, 103.2, 159.7, 175.2. **27a,b**: IR (CCl_4, of 5:1 mixture) 2959, 2932, 2899, 2873, 2862, 1772, 1653, 1452 cm^{-1}; MS (EI, 20 eV) *m/e* 210 (M^+, 16). Stereochemistry was assigned by NOE difference spectroscopy on the 1:3 mixture. Irradiation of the methoxy signal at 3.00 ppm (**27a**) produced a 7.3% enhancement of the olefin proton signal at 3.95 ppm (**27a**), while irradiation of the methoxy signal at 2.91 ppm (**27b**) produced no enhancement of the olefin proton signal at 3.90 ppm (**27b**). **28a**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.74 (t, *J* = 7.2 Hz, 3 H), 1.06 (sextet, *J* = 7.5, Hz, 2 H), 1.28 (p, *J* = 7.6 Hz, 2 H), 1.92 (t, *J* = 7.7 Hz, 2 H), 2.93 (s, 3 H), 4.23 (s, 2 H), 4.54 (s, 1 H), 5.58 (s, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 13.9, 22.5, 29.2, 32.7, 54.8, 72.2, 91.0, 110.9, 160.9, 169.0, 173.6; IR ($CDCl_3$) 2962, 2935, 2876, 1780, 1750, 1722, 1646, 1616, 1447, 1437 cm^{-1}; MS (EI, 20 eV) *m/e* 196 (M^+, 8); HRMS for $C_{11}H_{16}O_3$ calcd 196.1099, found 196.1100.

(5β)-1β-(2-Oxohexanyl)-3-oxabicyclo[3.1.0]hexan-4-one (103) from 27a,b. A mixture of **27a,b** (24.0 mg, 0.11 mmol) was dissolved in acetone (5 mL), and 2 drops of 10% HCl were added. After being stirred for 30 min at room temperature, the solution was concentrated in vacuo, taken up in Et_2O (10 mL), and extracted with H_2O (10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to give 19.5 mg of ketone **103** (87%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.3 Hz, 3 H), 1.14 (t, *J* = 4.2 Hz, 1 H), 1.20 (dd, *J* = 9.3, 4.9 Hz, 1 H), 1.30 (sextet, *J* = 7.5 Hz, 2 H), 1.55 (p, *J* = 7.6 Hz, 2 H), 1.92 (dd, *J* = 9.3, 3.4 Hz, 1 H), 2.40 (t, *J* = 7.6 Hz, 2 H), 2.59 (d, *J* = 18.1 Hz, 1 H), 2.94 (d, *J* = 18.1 Hz, 1 H), 4.11 (d, *J* = 9.8 Hz, 1 H), 4.43 (d, *J* = 9.3 Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.0, 17.6, 22.41, 22.46, 25.2, 25.8, 42.1, 44.3, 72.3, 175.1, 206.5; IR (CCl_4) 2961, 2933, 2875, 1783, 1721, 1466, 1456, 1414 cm^{-1}; MS (EI, 20 eV) *m/e* 196 (M^+, 6); HRMS for $C_{11}H_{16}O_3$ calcd 196.1099, found 196.1102. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.16; H, 8.04.

(5β)-1β-(2(*E*)-Methoxy-1-propenyl)-3-oxabicyclo[3.1.0]hexan-4-one (27c), 4-(2(*E*)-Methoxy-1-propenyl)-2(5*H*)-furanone (28b), and 2-(4-Methoxy-1,3-pentadienyl) Propenoate (29) from Carbene 8. According to the general procedure, **26** (222 mg, 2.0 mmol) and **8** (343 mg, 1.4 mmol) were heated for 1.0 h to give 8.5 mg (4%) of **27c**, 22.0 mg (10%) of **28b**, and 29.3 mg (13%) of **29**. **27c**: ^{1}H NMR (300 MHz, $CDCl_3$)

(25) (a) Lee, S. L.; Cameron, A. M.; Warkentin, J. *Can. J. Chem.* **1972**, *50*, 2326–2331. (b) Knittel, P.; Lee, S. L.; Warkentin, J. *Can. J. Chem.* **1972**, *50*, 3248–3250.

δ 1.21 (t, J = 3.9 Hz, 1 H), 1.41 (dd, J = 9.2, 4.4 Hz, 1 H), 1.90 (s, 3 H), 1.97 (dd, J = 8.8, 3.7 Hz, 1 H), 3.50 (s, 3 H), 4.09 (d, J = 8.9 Hz, 1 H), 4.23 (d, J = 9.2, 1 H), 4.61 (s, 1 H); IR (CCl_4) 3003, 2958, 2928, 2909, 2854, 1784, 1658, 1465, 1453, 1440 cm^{-1}; MS (EI, 20 eV) m/e 168 (M^+, 30); HRMS for $C_9H_{12}O_3$ calcd 168.0786, found 168.0788. Stereochemistry was assigned by NOE difference spectroscopy. Irradiation of the methoxy signal at 3.50 ppm produced a 16.2% enhancement of the olefin proton signal at 4.61 ppm. **28b**: ^1H NMR (500 MHz, $CDCl_3$) δ 2.09 (s, 3 H), 3.68 (s, 3 H), 4.88 (s, 2 H), 5.25 (s, 1 H), 5.71 (s, 1 H); ^{13}C (125 MHz, $CDCl_3$) 20.1, 55.5, 72.8, 91.2, 109.7, 162.3, 166.4, 174.8; IR ($CDCl_3$) 2969, 2940, 1783, 1746, 1733, 1627, 1597, 1464, 1456, 1447 cm^{-1}; MS (EI, 20 eV) m/e 154 (M^+, 97); HRMS for $C_8H_{10}O_3$ calcd 154.0530, found 154.0631. Stereochemistry was assigned by NOE difference spectroscopy. Irradiation of the methoxy signal at 3.68 ppm produced a 26.5% enhancement of the olefin proton signal at 5.25 ppm. **29**: ^1H NMR (500 MHz, C_6D_6) δ 1.96 (s, 3 H), 3.01 (s, 3 H), 4.63 (s, 1 H), 4.87 (s, 1 H), 4.99 (s, 1 H), 5.24 (dd, J = 10.5, 1.2 Hz, 1 H), 5.98 (dd, J = 17.6, 10.3 Hz, 1 H), 6.30 (dd, J = 17.6, 1.5 Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 18.4 (q), 54.2 (q), 95.1 (d), 102.9 (t), 128.5 (d), 131.3 (t), 152.4 (s), 159.7 (s), 163.8 (s); IR (CCl_4) 3002, 2960, 2938, 1743, 1660, 1652, 1635, 1455, 1440 cm^{-1}; MS (EI, 20 eV) m/e 168 (M^+, 9); HRMS for $C_9H_{12}O_3$ calcd 168.0786, found 168.0778. Stereochemistry was assigned by comparison of olefinic ^1H and ^{13}C chemical shifts with compound **31**.

2-Propynyl Acetate (30). To a stirred solution of propargyl alcohol (0.75 mL, 13 mmol) and triethylamine (2.2 mL) in CH_2Cl_2 (70 mL) at 0 °C was added acetic anhydride (1.85 mL, 20 mmol). The reaction mixture was allowed to warm to room temperature, stirred for 3 h, and then quenched with 5% NaOH (15 mL). The organic layer was extracted with 5% NaOH (1 × 15 mL) followed by 10% HCl (3 × 15 mL) and H_2O (1 × 15 mL), dried over $MgSO_4$, and concentrated in vacuo to give **30** (0.98 g, 78%): ^1H NMR (500 MHz, C_6D_6) δ 2.09 (s, 3 H), 2.46 (t, J = 2.7 Hz, 1 H), 4.65 (d, J = 2.4 Hz, 2 H); ^{13}C NMR (125 MHz, C_6D_6) δ 20.5, 51.7, 74.7, 77.5, 169.9; IR ($CDCl_3$) 3308, 2942, 1766, 1753, 1738, 1450 cm^{-1}; MS (EI, 20 eV) m/e 98 (M^+, 2).

2-(4-Methoxy-1,3-pentadienyl) Acetate (31). According to the general procedure, **30** (106 mg, 1.1 mmol) and **8** (181 mg, 0.72 mmol) were heated for 1.25 h to give 18.3 mg (16%) of **31**: ^1H NMR (500 MHz, C_6D_6) δ 1.69 (s, 3 H), 1.95 (s, 3 H), 3.05 (s, 3 H), 4.62 (s, 1 H), 4.85 (s, 1 H), 4.98 (s, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 18.3, 20.6, 54.2, 95.3, 102.7, 152.5, 159.5, 168.0; IR (CCl_4) 3003, 2960, 2936, 2910, 2835, 1760, 1755, 1661, 1652, 1601, 1466 cm^{-1}; MS (EI, 20 eV) m/e 156 (M^+, 18); HRMS for $C_8H_{12}O_3$ calcd 156.0786, found 156.0787. Stereochemistry was assigned by NOE difference spectroscopy. Irradiation of the methoxy signal at 3.04 ppm produced a 20.0% enhancement of the olefin proton signal at 4.98 ppm.

Allyl Propargyl Ether (36). Propargyl alcohol (1.5 mL, 26 mmol) was slowly added to a suspension of NaH (1.508 g of a 55% dispersion in mineral oil, washed with hexanes, 34.6 mmol) in Et_2O (70 mL) containing HMPA (7.0 mL) at room temperature. After the mixture was stirred at room temperature for 2 h, allyl bromide (2.5 mL, 29 mmol) was added and the mixture was heated at reflux for 12 h. After being cooled to room temperature, the reaction mixture was quenched with a saturated $NaHCO_3$ solution, and the organic layer was extracted with H_2O (3 × 15 mL), dried over $MgSO_4$, filtered through neutral alumina, and concentrated in vacuo to give **36** (1.62 g, 66%): ^1H NMR (300 MHz, $CDCl_3$) δ 2.42 (t, J = 2.2 Hz, 1 H), 4.06 (d, J = 5.8 Hz, 2 H), 4.14 (d, J = 2.2 Hz, 2 H), 5.21 (d, J = 10.3 Hz, 1 H), 5.30 (dd, J = 17.5, 1.1 Hz, 1 H), 5.89 (ddt, J = 16.8, 10.8, 5.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.0, 70.5, 74.3, 79.6, 117.9, 133.8; IR ($CDCl_3$) 3308, 2896, 2858, 1442 cm^{-1}; MS (EI, 20 eV) m/e 96 (M^+, 1); HRMS for C_6H_7O (M^+ − H) calcd 95.0497, found 95.0495.

(5β)-1β-(2(*E*)-Methoxy-1-hexenyl)-3-oxabicyclo[3.1.0]hexane (37a), (5β)-1β-(2(*Z*)-Methoxy-1-hexenyl)-3-oxabicyclo[3.1.0]hexane (37b), and (5β)-1β-(2-Oxohexanyl)-3-oxabicyclo[3.1.0]hexane (104) from 18. According to the general procedure, **36** (79 mg, 0.82 mmol) and **18** (183.6 mg, 0.55 mmol) were heated for 10 min to give 13 mg (7%) of carbene **18**, 64 mg (60%) of **37a**, 22 mg (21%) of **37b**, and 3.0 mg (3%) of **104**.

Synthesis of 37a,b from Carbene 19. According to the general procedure, **36** (77 mg, 0.80 mmol) and **19** (146.0 mg, 0.50 mmol) were heated for 1.5 h to give 42.4 mg (43%) of **37a** and 12.0 mg (12%) of **37b**. **37a**: ^1H NMR (500 MHz, C_6D_6) δ 0.64 (dd, J = 7.8, 4.4 Hz, 1 H), 0.85–0.88 (m containing triplet at 0.86, J = 7.3 Hz, 4 H), 1.13–1.16 (m, 1 H), 1.27 (sextet, J = 7.3 Hz, 2 H), 1.55 (p, J = 7.6 Hz, 2 H), 2.24–2.34 (m, 2 H), 3.16 (s, 3 H), 3.57 (d, J = 8.3 Hz, 1 H), 3.73 (dd, J = 8.1, 2.7 Hz, 1 H), 3.81 (d, J = 8.3 Hz, 1 H), 3.89 (d, J = 7.8 Hz, 1 H), 4.44 (s, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 14.2, 15.2, 23.0, 25.4, 26.1, 30.1, 31.2, 54.0, 70.0, 73.9, 94.0, 163.0; IR (CCl_4) 2960, 2929, 2856, 1652, 1466, 1453 cm^{-1}; MS (EI, 20 eV) m/e 196 (M^+, 26). HRMS for $C_{12}H_{20}O_2$ calcd 196.1463, found 196.1474. **37b**: ^1H NMR (300 MHz, C_6D_6) δ 0.75 (dd, J = 7.8, 4.2 Hz, 1 H), 0.84 (t, J = 7.1 Hz, 3 H), 0.89–0.94 (m, 1 H), 1.16–1.37 (m, 5 H), 1.91 (t, J = 7.3 Hz, 2 H), 3.15 (s, 3 H), 3.71 (dd, J = 8.0, 2.7 Hz, 1 H), 3.80 (d, J = 8.1 Hz, 1 H), 3.89 (d, J = 8.3 Hz, 1 H), 4.17 (d, J = 8.2 Hz, 1 H), 4.40 (s, 1 H); IR (CCl_4) 2960, 2933, 2859, 1674, 1668, 1464, 1456 cm^{-1}; MS (EI, 20 eV) m/e 196 (M^+, 35); HRMS for $C_{12}H_{20}O_2$ calcd 196.1463, found 196.1463. Stereochemistry was assigned by NOE difference spectroscopy. Irradiation of the methoxy signal of **37a** at 3.16 ppm produced a 13.6% enhancement of the olefin proton signal at 4.44 ppm, while irradiation of the methoxy signal of **37b** at 3.15 ppm produced a 1.4% enhancement of the olefin proton signal at 4.40 ppm. **104**: ^1H NMR (500 MHz, $CDCl_3$) δ 0.57 (dd, J = 7.3, 4.9 Hz, 1 H), 0.67 (t, J = 4.6 Hz, 1 H), 0.90 (t, J = 7.3 Hz, 3 H), 1.30 (sextet, J = 7.4 Hz, 2 H), 1.36–1.38 (m, 1 H), 1.55 (p, J = 7.4 Hz, 2 H), 2.41 (t, J = 7.6 Hz, 2 H), 2.58 (d, J = 16.6 Hz, 1 H), 2.72 (d, J = 16.6 Hz, 1 H), 3.52 (d, J = 8.3 Hz, 1 H), 3.78 (d, J = 1.5 Hz, 2 H), 3.89 (d, J = 8.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 13.8, 22.3, 22.7, 24.7, 25.7, 42.6, 45.1, 69.5, 72.6, 209.6; IR (CCl_4) 2961, 2932, 2860, 1721, 1717, 1466, 1456, 1410 cm^{-1}; MS (EI, 20 eV) m/e 182 (M^+, 1); HRMS for $C_{11}H_{18}O_2$ calcd 182.1307, found 182.1311.

(5β)-1β-(2(*E*)-Methoxy-1-propenyl)-3-oxabicyclo[3.1.0]hexane (38a) and (5β)-1β-(2(*Z*)-Methoxy-1-propenyl)-3-oxabicyclo[3.1.0]hexane (38b) from Carbene 8. According to the general procedure, **36** (95 mg, 0.98 mmol) and **8** (164.0 mg, 0.66 mmol) were heated for 25 min to give 42.9 mg (42%) of **38a** and 4.0 mg (4%) of **38b**. **38a**: ^1H NMR (300 MHz, C_6D_6) δ 0.56 (dd, J = 7.7, 4.0 Hz, 1 H), 0.79 (t, J = 4.1 Hz, 1 H), 1.08–1.13 (m, 1 H), 1.77 (s, 3 H), 3.14 (s, 3 H), 3.50 (d, J = 8.0 Hz, 1 H), 3.68 (dd, J = 8.1, 2.5 Hz, 1 H), 3.78 (d, J = 9 Hz, 1 H), 3.82 (d, J = 8 Hz, 1 H), 4.40 (s, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 15.1, 17.4, 25.3, 26.2, 54.0, 69.9, 73.4, 93.9, 159.3; IR (CCl_4) 2997, 2958, 2925, 2852, 1661, 1466, 1452, 1439 cm^{-1}; MS (EI, 20 eV) m/e 154 (M^+, 4); HRMS for $C_9H_{14}O_2$ calcd 154.0994, found 154.0998. **38b**: ^1H NMR (500 MHz, C_6D_6) δ 0.74 (dd, J = 7.8, 3.9 Hz, 1 H), 0.91 (t, J = 4.2 Hz, 1 H), 1.28–1.31 (m, 1 H), 1.48 (s, 3 H), 3.06 (s, 3 H), 3.72 (dd, J = 8.3, 2.4 Hz, 1 H), 3.80 (d, J = 8.3 Hz, 1 H), 3.88 (d, J = 7.8 Hz, 1 H), 4.17 (d, J = 8.3 Hz, 1 H), 4.25 (s, 1 H); MS (EI, 20 eV) m/e 154 (M^+, 25). Stereochemistry was assigned by NOE difference spectroscopy. Irradiation of the methoxy signal of **38a** at 3.14 ppm produced at 14.5% enhancement of the signal from the olefin proton at 4.40 ppm, while irradiation of the methoxy signal of **38b** at 3.06 ppm produced at 0.7% enhancement of the signal from the olefin proton at 4.25 ppm.

Exposure of **38b** (4.0 mg, 0.03 mmol) to $CDCl_3$ at room temperature resulted in immediate formation of ketone **105** (2.0 mg, 55%). Overnight exposure of **38a** (30.0 mg, 0.19 mmol) to $CDCl_3$ at room temperature also produced **105** (18.0 mg, 66%): ^1H NMR (300 MHz, $CDCl_3$) δ 0.59 (dd, J = 7.7, 5.0 Hz, 1 H), 0.69 (t, J = 4.5 Hz, 1 H), 1.37–1.42 (m, 1 H), 2.16 (s, 3 H), 2.59 (d, J = 16.8 Hz, 1 H), 2.76 (d, J = 16.8 Hz, 1 H), 3.52 (d, J = 8.0 Hz, 1 H), 3.78 (s, 2 H), 3.89 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 22.8, 24.7, 30.1, 46.1, 69.5, 72.5, 207.2; IR (CCl_4) 2997, 2962, 2926, 2855, 1717, 1419 cm^{-1}; MS (EI, 20 eV) m/e 140 (M^+, 1); HRMS for $C_8H_{12}O_2$ calcd 140.0837, found 140.0848.

5-Oxa-7-octen-1-yne (39). 3-Butyn-1-ol (0.75 mL, 9.9 mmol) was slowly added to a stirred suspension of NaH (0.354 g of an 80% dispersion in mineral oil, washed with hexanes, 11.8 mmol) in Et_2O (60 mL) containing HMPA (2.15 mL) at room temperature. After the mixture was stirred at room temperature for 30 min, allyl bromide (0.95 mL, 11.0 mmol) was added, and the reaction mixture was heated at reflux for 2.5 h. After being cooled to room temperature, the reaction mixture was quenched with a saturated $NaHCO_3$ solution, and the organic layer was extracted with H_2O (3 × 15 mL), dried over $MgSO_4$, filtered through neutral alumina, and concentrated in vacuo to give **39** (0.92 g, 84%): ^1H NMR (500 MHz, $CDCl_3$) δ 1.99 (t, J = 2.4 Hz, 1 H), 2.48 (td, J = 6.8, 2.4 Hz, 2 H), 3.57 (t, J = 6.8 Hz, 2 H), 4.02–4.03 (m, 2 H) 5.19 (dd, J = 10.5, 1.2 Hz, 1 H), 5.29 (dq, J = 17.3, 1.6 Hz, 1 H), 5.91 (ddt, J = 16.9, 10.6, 5.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, 68.1, 69.2, 71.9, 81.3, 117.2, 134.5; IR (CCl_4) 3314, 2940, 2917, 2864, 1420 cm^{-1}; MS (EI, 20 eV) m/e 109 (M^+ − H, 5); HRMS for C_7H_9O (M^+-H) calcd 109.0653, found 109.0652.

(6β)-1β-(2-Oxohexanyl)-4-oxabicyclo[4.1.0]heptane (42) and 5-Butyl-3-(3-oxa-5-hexenyl)-2(5*H*)-furanone (43) from Carbene 18. According to the general procedure, **39** (101.3 mg, 0.920 mmol) and **18** (205.2 mg, 0.610 mmol) were heated for 1.25 h. After being cooled to room temperature, the solution was filtered through a pad of Celite and concentrated in vacuo. The residue was then dissolved in THF (15 mL), and 2 drops (~60 μL) of 10% HCl were added. After the solution was stirred at room temperature for 10 min, Et_2O (15 mL) was added. The organic layer was extracted with H_2O (2 × 15 mL), dried over $MgSO_4$, filtered and concentrated in vacuo, and the residue was chromatographed

on Florisil to give 44.2 mg (37%) of **42** and 39.7 mg (29%) of **43**. **42**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.51–0.57 (m, 2 H), 0.73–0.77 (m, 1 H), 0.89 (t, J = 7.3 Hz, 3 H), 1.29 (sextet, J = 7.5 Hz, 2 H), 1.50–1.57 (m containing pentet at 1.53, J = 7.4 Hz, 3 H), 1.82 (ddd, J = 13.9, 10.3, 6.1 Hz, 1 H), 2.24 (d, J = 16.6 Hz, 1 H), 2.38 (t, J = 7.6 Hz, 2 H), 2.48 (d, J = 16.6 Hz, 1 H), 3.30 (td, J = 11.0, 4.9 Hz, 1 H), 3.51 (ddd, J = 11.2, 6.2, 3.4, 1 H), 3.84–3.90 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.84, 13.93, 16.7, 17.2, 22.3, 25.7, 28.6, 42.6, 53.8, 64.1, 65.6, 210.2; IR (CCl_4) 2960, 2933, 2874, 2854, 1717, 1466 cm^{-1}; MS (EI, 20 eV) m/e 196 (M^+, 2); HRMS for $C_{12}H_{20}O_2$ calcd 196.1463, found 196.1461. **43**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (t, J = 7.1 Hz, 3 H), 1.31–1.46 (m, 4 H), 1.61–1.67 (m, 1 H), 1.69–1.76 (m, 1 H), 2.57 (t, J = 6.1 Hz, 2 H), 3.64 (t, J = 6.1 Hz, 2 H), 3.98 (d, J = 5.4 Hz, 2 H), 4.90–4.93 (m, 1 H), 5.18 (d, J = 9.8 Hz, 1 H), 5.26 (dd, J = 17.3, 1.2 Hz, 1 H), 5.89 (ddt, J = 16.7, 10.7, 5.4 Hz, 1 H), 7.16 (d, J = 1.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.4, 25.8, 27.0, 33.1, 67.3, 71.8, 81.4, 117.1, 131.2, 134.5, 150.0, 173.8; IR (CCl_4) 2960, 2933, 2874, 2863, 1761, 1467, 1456 cm^{-1}; MS (EI, 20 eV) m/e 225 (MH^+, 0.1); HRMS (CI, NH_3) for $C_{13}H_{21}O_3$ (MH^+) calcd 225.1491, found 225.1495.

42, 43, and 1-Methoxy-2-propyl-4-(3-oxa-5-hexenyl)cyclopent-1-en-3-one (44) from Carbene 19. According to the general procedure, **39** (55.7 mg, 0.506 mmol) and **19** (92.8 mg, 0.320 mmol) were heated for 2.5 h to give 9.1 mg of a mixture of enol ethers **40a,b** and furan **41** as well as 20.0 mg (26%) of **44**. The furan/enol ether mixture was dissolved in THF (5 mL), and 10% HCl (60 μL) was added. After the mixture was stirred at room temperature for 5 min, Et_2O (15 mL) was added, and the organic layer was extracted with H_2O (2 × 15 mL), dried over $MgSO_4$, filtered, concentrated in vacuo, and chromatographed on Florisil to give 2.0 mg (3%) of **42** and 5.6 mg (8%) of **43**. **44**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.96 (t, J = 7.3 Hz, 3 H), 1.50–1.57 (m, 1 H), 1.66 (sextet of d, J = 7.3, 1.5 Hz, 2 H), 1.91 (d, J = 17.4 Hz, 1 H), 2.10 (dd, J = 17.3, 7.1 Hz, 1 H), 2.22–2.29 (m, 1 H), 2.35–2.40 (m containing triplet at δ 2.38, J = 7.3 Hz, 3 H), 3.02 (s, 3 H), 3.37 (t, J = 6.1 Hz, 2 H), 3.70–3.78 (m, 2 H), 5.03 (dd, J = 10.7, 1.5 Hz, 1 H), 5.20 (dd, J = 17.3, 1.7 Hz, 1 H), 5.81 (ddt, J = 16.7, 11.0, 5.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 21.2, 23.2, 31.56, 31.59, 42.6, 56.3, 68.8, 71.7, 116.6, 119.8, 134.8, 183.7, 206.9; IR ($CDCl_3$) 2961, 2933, 2872, 1699, 1684, 1653, 1622, 1461, 1429 cm^{-1}; MS (EI, 20 eV) m/e 197 ($M^+ - C_3H_5$, 11): HRMS (CI, NH_3) for $C_{14}H_{23}O_3$ (MH^+) calcd 239.1647, found 239.1645.

4-Oxa-7-octen-1-yne (45). To a suspension of NaH (0.467 g of a 55% dispersion in mineral oil, washed with hexanes, 10.7 mmol) in Et_2O (50 mL) containing HMPA (2.25 mL) at room temperature was slowly added 3-buten-1-ol (0.75 mL, 8.7 mmol). After the solution was stirred at room temperature for 2 h, propargyl bromide (1.0 mL, 80 wt % in toluene, 9.0 mmol) was added, and the mixture was heated at reflux for 12 h. After being cooled to room temperature, the reaction mixture was quenched with a saturated $NaHCO_3$ solution, and the organic layer was extracted with H_2O (3 × 15 mL), dried over $MgSO_4$, filtered through neutral alumina, and concentrated in vacuo to give **45** (0.87 g, 91%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (q, J = 6.7 Hz, 2 H), 2.42 (t, J = 2.4 Hz, 1 H), 3.59 (t, J = 6.6 Hz, 2 H), 4.15 (d, J = 2.4 Hz, 2 H), 5.06 (dd, J = 10.3, 1.0 Hz, 1 H), 5.11 (dq, J = 17.3, 1.6 Hz, 1 H), 5.83 (ddt, J = 17.1, 10.9, 6.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.9, 58.0, 69.3, 74.2, 79.8, 116.5, 134.9; IR (CCl_4) 3313, 3082, 2982, 2949, 2931, 2915, 2891, 2859, 1642, 1441 cm^{-1}; MS (EI, 20 eV) m/e 109 ($M^+ - H$, 2). HRMS for C_7H_9O ($M^+ - H$) calcd 109.0653, found 109.0649.

(*Z,Z*)-1-(4-Butenyloxy)-4-methoxy-1,3-octadiene (46) from Carbene 18. According to the general procedure, **45** (89.9 mg, 0.82 mmol) and **18** (171.6 mg, 0.51 mmol) were heated for 1.5 h to give 66.7 mg (62%) of **46**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.78 (t, J = 7.3 Hz, 3 H), 1.20 (sextet, J = 7.5 Hz, 2 H), 1.38 (pentet, J = 7.7 Hz, 2 H), 2.03 (t, J = 7.6 Hz, 2 H), 2.12–2.17 (m, 2 H), 3.31 (s, 3 H), 3.44 (t, J = 6.8 Hz, 2 H), 4.94–4.99 (m, 2 H), 5.63–5.70 (m containing d at 5.69, J = 6 Hz, 2 H), 5.82 (dd, J = 11.2, 6.3 Hz, 1 H), 5.99 (d, J = 11.7, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.0 (q), 22.6 (t), 29.8 (t), 31.6 (t), 34.5 (t), 55.9 (q), 71.6 (t), 102.2 (d), 103.6 (d), 116.8 (t), 134.7 (d), 143.4 (d), 154.8 (s); IR (C_6D_6) 2957, 2934, 2873, 1643, 1609, 1468, 1432 cm^{-1}; MS (EI, 20 eV) m/e 210 (M^+, 44); HRMS for $C_{13}H_{22}O_2$ calcd 210.1620, found 210.1621. Stereochemistry was assigned by olefinic proton coupling constants and NOE difference spectroscopy. For example, irradiation of the methoxy signal at 3.31 ppm produced less than 3% enhancement of any of the olefin proton signals. Complete assignment will be reported separately.[20]

(*E*)-1-Methoxy-2-octen-7-yne (49). To a solution of (*E*)-2-octen-7-yn-1-ol (**64**) (423 mg, 3.41 mmol) in Et_2O (100 mL) was added NaH (123 mg, 4.10 mmol, 80% in mineral oil). After 5 min, HMPA (0.770 mL, 4.43 mmol) and methyl iodide (0.430 mL, 6.91 mmol) were added, and the reaction mixture was heated at 35 °C for 48 h. After addition of saturated $NaHCO_3$ solution, (50 mL), the organic layer was washed with H_2O (2 × 50 mL) and dried over $MgSO_4$. Chromatography on silica gel gave **49** (0.407 g, 86%): ^{1}H NMR (500 MHz, C_6D_6) δ 1.36 (p, J = 7.3 Hz, 2 H), 1.76 (t, J = 2.4 Hz, 1 H), 1.89–1.95 (m, 4 H), 3.10 (s, 3 H), 3.70 (d, J = 5.4 Hz, 2 H), 5.41–5.52 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.8, 27.8, 31.1, 57.7, 68.4, 73.1, 84.2, 127.2, 133.3; IR (CCl_4) 3314, 2966, 2935, 2846, 1453, 1438 cm^{-1}; MS (EI, 20 eV) m/e 138 (M^+,1); HRMS for $C_9H_{13}O$ ($M^+ - H$) calcd 137.0966, found 137.0965.

(5β)-1β-(2-Oxohexanoyl)-6β-(methoxymethyl)bicyclo[3.1.0]hexane (51) from Carbene 18. Enyne **49** (62.5 mg, 0.453 mmol) was dissolved in benzene (175 mL), treated with **18** (166.0 mg, 0.494 mmol), and heated at 60 °C for 3.25 h. After the solution was concentrated in vacuo, chromatography on silica gel gave the enol ethers **50a,b** and the ketone **51** as a crude mixture. This mixture was dissolved in THF (5 mL) and treated with 5 drops of H_2O and 5 drops of concentrated HCl. After the mixture was stirred for 10 h, Et_2O (10 mL) was added, and the mixture was washed with H_2O (3 × 5 mL), dried over $MgSO_4$, and chromatographed on silica gel to give 45.5 mg (45%) of **51**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.81 (t, J = 7.3 Hz, 3 H), 0.88 (t, J = 3.9 Hz, 1 H), 0.96–0.99 (m, 1 H), 1.02–1.07 (m, 1 H), 1.19 (sextet, J = 7.3 Hz, 2 H), 1.40 (dt, J = 13.5, 8.2 Hz, 1 H), 1.49–1.55 (m, 3 H), 1.63 (dd, J = 12.2, 7.8 Hz, 1 H), 1.67–1.75 (m, 1 H), 1.86 (dd, J = 12.2, 8.3 Hz, 1 H), 2.01–2.22 (m, 2 H), 2.26 (d, J = 16.6 Hz, 1 H), 2.48 (d, J = 16.1 Hz, 1 H), 3.07 (s, 3 H), 3.12 (dd, J = 10.7, 7.8 Hz, 1 H), 3.25 (dd, J = 10.3, 5.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.1, 22.3, 22.7, 26.1, 27.9, 28.7, 29.3, 33.7, 42.4, 44.6, 57.8, 72.4, 208.4; IR (CCl_4) 2959, 2932, 2874, 1715, 1466, 1460 cm^{-1}; MS (EI, 20 eV) m/e 224 (M^+, 0.3). HRMS for $C_{14}H_{24}O_2$ calcd 224.1776, found 224.1765.

(*Z,Z,E*)-7-Formyl-5,13-dimethoxy-4,6,11-tridecatriene (52) from Carbene 19. To a solution of **49** (73.5 mg, 0.532 mmol) in benzene (210 mL) was added **19** (0.171 g, 0.585 mmol). After being heated at 60 °C for 2.5 h, the reaction mixture was cooled to room temperature, concentrated in vacuo, and chromatographed on silica gel to give 25.2 mg (18%) of **52**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.96 (t, J = 7.3 Hz, 3 H), 1.43–1.59 (m, 4 H), 2.08 (q, J = 7.3 Hz, 2 H), 2.25 (q, J = 7.3 Hz, 2 H), 2.47–2.51 (m, 2 H), 3.30 (s, 3 H), 3.57 (s, 3 H), 3.85 (d, J = 6.4 Hz, 2 H), 5.45 (t, J = 7.3 Hz, 1 H), 5.56 (dt, J = 15.1, 6.4 Hz, 1 H), 5.70 (dt, J = 15.1, 6.4 Hz, 1 H), 6.50 (s, 1 H), 9.37 (s, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 13.9, 22.5, 24.0, 28.0, 28.6, 32.5, 57.6, 59.7, 73.2, 126.5, 129.2, 134.3, 140.9, 145.7, 154.0, 195.2; IR (CCl_4) 2960, 2933, 2874, 2282, 1729, 1687, 1625, 1451 cm^{-1}; MS (CI, CH_4) m/e 267 (MH^+, 14); HRMS for $C_{16}H_{27}O_3$ (MH^+) calcd 267.1960, found 267.1964.

Methyl (*E*)-2-(2-Oxohexanyl)-8-methoxy-6-octenoate (57). To a solution of **49** (56.5 mg, 0.409 mmol) in methanol (150 mL) was added **19** (190 mg, 0.650 mmol). After heating at 65 °C for 2 h, the reaction mixture was cooled to room temperature, concentrated in vacuo, and chromatographed on silica gel to give 94.2 mg (77%) of a mixture of enol ether isomers. The enol ether mixture (35.8 mg, 0.120 mmol) was readily hydrolyzed by dissolving in THF (5 mL) and adding H_2O (90 μL) followed by concentrated HCl (90 μL). After the mixture was stirred for 30 min at room temperature, H_2O (20 mL) was added, and the reaction mixture was extracted with Et_2O (3 × 5 mL). The combined organics were washed with H_2O (5 mL) and dried over $MgSO_4$. Chromatography on silica gel gave 28.5 mg (84%) of **57**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.79 (t, J = 7.3 Hz, 3 H), 1.15 (sextet, J = 7.3 Hz, 2 H), 1.23–1.38 (m, 3 H), 1.43–1.55 (m, 3 H), 1.86–1.90 (m, 2 H), 1.94–2.07 (m, 3 H), 2.64 (dd, J = 17.6, 9.8 Hz, 1 H), 2.94–2.99 (m, 1 H), 3.13 (s, 3 H), 3.36 (s, 3 H), 3.75 (d, J = 3.9 Hz, 2 H), 5.53–5.56 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 22.3, 25.8, 26.5, 31.5, 32.0, 39.8, 42.6, 44.2, 51.7, 57.7, 73.1, 126.7, 133.8, 175.9, 209.2; IR (CCl_4) 2955, 2933, 2863, 2822, 1736, 1720, 1459, 1436 cm^{-1}; MS (CI, NH_3) m/e 302 ($M + NH_4^+$, 16), 285 (MH^+, 34); HRMS for ($C_{16}H_{32}NO_4$ ($M + NH_4^+$) calcd 302.2331, found 302.2323.

(*E*)-1-Methoxy-2-nonen-8-yne (58). Ester **23** (0.461 g, 2.78 mmol) was dissolved in CH_2Cl_2 (150 mL) and cooled to 0 °C. DIBAL was added (7 mL, 1.0 M solution, 7 mmol) and the reaction mixture was stirred for 5 min before warming to room temperature. Methanol (20 mL), H_2O (100 mL), and concentrated H_2SO_4 (1 mL) were added to dissolve the aluminum salts. The organic layer was washed with H_2O (50 mL) and dried over $MgSO_4$. Chromatography on silica gel gave (*E*)-2-nonen-8-yn-1-ol (0.336 g, 88%). To a suspension of NaH (59 mg, 80%, 2 mmol) in Et_2O (15 mL) was added the alcohol (181.6 mg, 1.315 mmol) followed by HMPA (300 μL, 1.7 mmol) and then MeI (245 μL, 3.9 mmol). In a sealed vial, the solution was heated behind a blast shield at 35 °C for 24 h. After the addition of saturated $NaHCO_3$ solution (10 mL) and H_2O (10 mL) and extraction with ether (2 × 10 mL), the combined organics were dried over $MgSO_4$ and concentrated in vacuo. Chromatography on silica gel gave 324.6 mg (69%) of **58**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48–1.64 (m, 4 H), 1.93 (t, J = 2.4 Hz, 1 H), 2.01

(q, J = 6.8 Hz, 2 H), 2.19 (dt, J = 2.4, 6.8 Hz, 2 H), 3.31 (s, 3 H), 3.86 (d, J = 5.9 Hz, 2 H), 5.56 (dt, J = 15.1, 6.4 Hz, 1 H), 5.69 (dt, J = 15.1, 6.8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.2, 27.9, 28.1, 31.7, 57.7, 68.2, 73.2, 84.4, 126.5, 134.2; IR (CCl_4) 3314, 2986, 2937, 2862, 2822, 1461, 1450, 1432 cm^{-1}; MS (EI, 20 eV) m/e 153 (M^+ + H, 2); HRMS for $C_{10}H_{17}O$, calcd 153.1279, found 153.1277.

2-Butyl-4,6-bis((*E*)-7-methoxy-5-heptenyl)phenol (59) from Carbene 18. To a solution of **58** (73.3 mg, 0.482 mmol) in benzene (150 mL) was added **18** (189 mg, 0.562 mmol). After being heated at 60 °C for 4.5 h, the reaction mixture was concentrated in vacuo. Chromatography on silica gel gave 18.0 mg (9%) of **59**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.94 (t, J = 7.3 Hz, 3 H), 1.37–1.62 (m, 12 H), 2.05–2.12 (m, 4 H), 2.48 (t, J = 7.6 Hz, 2 H), 2.55 (dt, J = 2.4, 7.8 Hz, 4 H), 3.31 (s, 6 H), 3.85 (d, J = 6.3 Hz, 4 H), 4.50 (s, 1 H), 5.51–5.58 (m, 2 H), 5.66–5.73 (m, 2 H), 6.75 (d, J = 4.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.7, 28.8, 29.0, 29.3, 29.9, 30.1, 31.3, 32.0, 32.1, 32.2, 35.0, 57.65, 57.68, 73.23, 73.25, 126.2, 126.3, 127.5 (2×), 127.67, 127.75, 134.2, 134.7, 134.8, 149.3; IR (CCl_4) 3604, 2932, 2857, 1467 cm^{-1}; MS (CI, NH_3) m/e 421 (MH + NH_4^+, 12), 420 (M + NH_4^+, 39), 402 (M^+, 10); HRMS for $C_{26}H_{46}O_3N$ (M + NH_4^+), calcd 420.3478, found 420.3481.

(*E*)-2-Octen-7-yn-1-ol (64). Methyl (*E*)-2-octen-7-ynoate (285.1 mg, 1.875 mmol) was dissolved in CH_2Cl_2 (25 mL) and cooled to −78 °C DIBAL (4.8 mL, 1.0 M in CH_2Cl_2, 4.8 mmol) was added and the solution was stirred for 10 min at −78 °C, warmed to room temperature, and quenched with MeOH (2 mL). H_2O (100 mL) was added followed by several drops of concentrated H_2SO_4 to dissolve the aluminum salts. After the solution was extracted with CH_2Cl_2 (4 × 25 mL), the combined organics were extracted with H_2O (1 × 25 mL) and dried over $MgSO_4$. Concentration in vacuo and chromatography on silica gel gave 189 mg (81%) of **64**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (s, 1 H), 1.62 (p, J = 7.3 Hz, 2 H), 1.95 (t, J = 2.7 Hz, 1 H), 2.15–2.21 (m, 4 H), 4.09 (s, 2 H), 5.67–5.68 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.7, 27.7, 31.0, 63.5, 68.5, 84.1, 129.9, 131.7; IR (CCl_4) 3607, 3490, 3305, 2943, 2866, 1456, 1433 cm^{-1}; MS (EI, 20 eV) m/e 123 (M^+ − H, 11); HRMS for $C_8H_{11}O$ (M^+ − H) calcd 123.0810, found 123.0807.

(5β)-1β-(2-Oxohexanyl)-6β-(hydroxymethyl)bicyclo[3.1.0]hexane (65) and (5β)-3β-Butyl-4β-(hydroxymethyl)-3α-methoxybicyclo[3.3.0]-1-octene (66) from Carbene 18. To a solution of **64** (60 mg, 0.486 mmol) in benzene (195 mL) was added **18** (0.195 g, 0.580 mmol). After being heated at 60 °C for 3.25 h, the reaction mixture was concentrated in vacuo and chromatographed on silica gel to give 31.0 mg (31%) of **65** and 26.5 mg (24%) of **66**. **65**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84–0.87 (m, 1 H), 0.91 (t, J = 7.3 Hz, 3 H), 1.19 (dt, J = 10.3, 4.4 Hz, 1 H), 1.22–1.35 (m containing a sextet at 1.32, J = 7.3 Hz, 3 H), 1.44–1.50 (m, 1 H), 1.53–1.64 (m, 3 H), 1.70–1.74 (m, 2 H), 1.81 (dd, J = 12.0, 8.1 Hz, 1 H), 2.44 (d, J = 16.1 Hz, 1 H), 2.49 (t, J = 7.3 Hz, 2 H), 2.91 (d, J = 16.1 Hz, 1 H), 3.22 (t, J = 11.2 Hz, 1 H), 3.52 (d, J = 9.8 Hz, 1 H), 3.86–3.91 (m, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 13.8, 21.9, 22.2, 25.3, 25.6, 26.5, 27.1, 30.1, 33.2, 44.1, 44.4, 62.6, 214.1; IR (CCl_4) 3614, 3436, 2960, 2935, 2864, 1703, 1467, 1453, 1429 cm^{-1}; MS (EI, 20 eV) m/e 210 (M^+, 9); HRMS for $C_{13}H_{22}O_2$ calcd 210.1620, found 210.1620. **66**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.89 (t, J = 7.3 Hz, 3 H), 1.03 (ddd, J = 14.4, 10.5, 5.9 Hz, 1 H), 1.25–1.40 (m, 4 H), 1.43–1.58 (m, 2 H), 1.64 (br s, 1 H), 1.72–1.84 (m, 3 H), 2.10–2.30 (m, 4 H), 3.00 (s, 3 H), 3.65–3.71 (m, 1 H), 3.94–3.99 (m, 1 H), 5.14 (s, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.1, 22.7, 23.7, 27.5, 28.0, 29.1, 32.4, 32.7, 36.3, 53.4, 61.9, 70.1, 124.4, 141.5; IR (CCl_4) 3603, 2957, 2932, 2860, 1466 cm^{-1}; MS (FAB, 20 eV) m/e 224 (M^+, 0.2); HRMS for $C_{14}H_{24}O_2$ calcd 224.1776, found 224.1765.

(*Z*,*Z*,*E*)-7-Formyl-13-hydroxy-5-methoxy-4,6,11-tridecatriene (71) from Carbene 19. To a solution of **64** (62 mg, 0.500 mmol) in benzene (150 mL) was added **19** (0.159 g, 0.544 mmol), After being heated at 60 °C for 2.5 h, the reaction mixture was cooled to room temperature, concentrated in vacuo, and chromatographed on silica gel to give 16.6 mg (13%) of **71**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.81 (t, J = 7.3, 3 H), 1.01 (br s, 1 H), 1.24 (sextet, J = 7.3 Hz, 2 H), 1.59 (p, J = 7.6 Hz, 2 H), 1.98–2.06 (m, 4 H), 2.59–2.63 (m, 2 H), 3.14 (s, 3 H), 3.85 (d, J = 4.4 Hz, 2 H), 4.99 (t, J = 7.6 Hz, 1 H), 5.43–5.55 (m, 2 H), 6.03 (s, 1 H), 9.26 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 22.4, 23.8, 28.0, 28.4, 32.2, 59.7, 63.8, 129.4, 129.6, 132.9, 140.8, 145.8, 154.0, 195.3; IR (CCl_4) 3620, 3504, 2961, 2934, 2866, 1687, 1625, 1457 cm^{-1}; MS (CI, CH_4) m/e 253 (MH^+, 4); HRMS for $C_{15}H_{25}O_3$ (MH^+) calcd 253.1804, found 253.1793. Irradiation of the methoxy signal (δ 3.14) showed less than a 2% enhancement to the olefin signal at δ 4.99.

Acknowledgment. Support from the Cancer Research Coordinating Committee of the University of California, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the American Cancer Society (Junior Faculty Research Award to D.F.H.) and the National Institute of Health (GM41984) is gratefully acknowledged. The 500-MHz NMR spectrometer was purchased with assistance from NIH (RR04733) and NSF (CHE 8814866).