under high vacuum. This produced (±)-**1** which exhibited a very clear ^{1}H NMR spectrum (no CH_2Cl_2 present) but which analyzed 0.5% low in carbon. This material was used in the binding studies: dec >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$; see **8** for proton labels) δ 2.19 (s, 18 H, Ar CH_3), 3.49 (d, 6 H, H^e, J = 13.6 Hz), 4.65 (d, 6 H, H^f, J = 13.5 Hz), 4.66 (d, 6 H, CH_2, J = 16.6 Hz), 4.83 (d, 6 H, CH_2, J = 16.6 Hz), 6.70 (s, 6 H, Ar H^c), 7.05 (s, 6 H, Ar H^d); MS (Xenon FAB, NOBA matrix) m/e 943 (M^+, 10%). Anal. Calcd for $C_{66}H_{54}O_6 \cdot 2CH_2Cl_2$: C, 73.38; H, 5.49. Found: C, 73.37; H, 5.24. Calcd for $C_{66}H_{54}O_6 \cdot CH_2Cl_2$: C, 78.28; H, 5.49. Found: C, 78.58; H, 5.43. Anal. Calcd for $C_{66}H_{54}O_6$: C, 84.05; H, 5.77. Found: C, 83.55; H, 5.61.

The crude *meso*-**1** was chromatographed (6.5:3.5 CH_2Cl_2/CCl_4) a second time, producing 45 mg (2%) of *meso*-**1** as a white powder. Recrystallization from $MeOH/CH_2Cl_2$ gave 32 mg of *meso*-**1** as thin, long crystals. X-ray-quality crystals were grown from $CHCl_3$/hexanes: dec >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$; see **8** for proton labels) δ 2.17 (s, 18 H, Ar CH_3), 3.53 (d, 6 H, H^e, J = 13.7 Hz), 4.55 (d, 6 H, CH_2, J = 16.3 Hz), 4.67 (d, 6 H, H^f, J = 13.6 Hz), 4.79 (d, 6 H, CH_2, J = 16.3 Hz), 6.78 (s, 6 H, Ar H^c), 7.07 (s, 6 H, Ar H^d); MS (Xenon FAB, NOBA matrix) m/e 943 (M^+, 100%). Anal. Calcd for $C_{66}H_{54}O_6$: C, 84.05; H, 5.77. Found (sample dried 48 h under high vacuum, 55 °C): C, 83.54; H, 6.06.

Hexachloroacetone Purification. Reagent grade $(CCl_3)_2CO$ (70 mL, Aldrich Chemical Co.) was dissolved in 250 mL of pentane in a 500-mL flask equipped with a drying tube. This was cooled to −78 °C in a dry ice/acetone bath. The pentane was decanted from the resulting large white crystals. This process was repeated three more times. The recrystallized $(CCl_3)_2CO$ was passed through filter paper, and the residual pentane was removed in vacuo. The resulting liquid was distilled through a Vigreux column (~40 Torr, 110 °C) to produce 35 mL of $(CCl_3)_2CO$ of suitable purity for use in the binding studies. This solvent purified in this manner contains very little water and must be stored in a desiccator to prevent it from absorbing atmospheric moisture.

Complexation Studies. Solutions were prepared in volumetric glassware using solvent purified as indicated above. All studies were performed on a 500-MHz spectrometer. The temperature of the probe was calibrated using the differences in chemical shifts between the two peaks of methanol as a standard. A coaxial insert containing "100 atom %" $CDCl_3$ (Aldrich Chemical Co.) was employed for locking purposes. All chemical shifts in $(CCl_3)_2CO$ are reported relative to the external, residual $CHCl_3$ set to 7.26 ppm.

Crystal Structure Data. Compound (±)-**1** crystallizes from CH_2Cl_2/C_2H_5OH as colorless parallelepipeds in the orthorhombic system *Pbca*. Unit cell dimensions are as follows: a = 20.493 (3) Å, b = 26.341 (3) Å, c = 21.568 (3) Å, V = 11 643 Å^3, Z = 8. The crystal was examined on a modified Syntex P$\bar{1}$ diffractometer (Cu Kα radiation) at 25 °C. The structure was determined by direct methods. Refinement of 347 parameters (2034 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.126.

Compound *meso*-**1** crystallizes from $CHCl_3$/hexanes as colorless parallelepipeds in the triclinic system P$\bar{1}$. Unit cell dimensions are as follows: a = 11.767 (2) Å, b = 13.874 (2) Å, c = 20.069 (3) Å, α = 95.736 (5)°, β = 102.525 (5)°, γ = 111.157 (4)°, V = 2930 Å^3, Z = 2. The crystal was examined on a modified Syntex P$\bar{1}$ diffractometer (Cu Kα radiation) at 25 °C. The structure was determined by direct methods. Refinement of 367 + 77 parameters (2 blocks, 3848 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.102.

Further crystallographic details will be published elsewhere.

Cyclopropanation of Unactivated 1,3-Dienes by Fischer Carbene Complexes

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Contribution from the Department of Chemistry-0506, University of California—San Diego, La Jolla, California 92093-0506. *Received May 28, 1991*

Abstract: Though Fischer carbene complexes do not, in general, react with unactivated alkenes, Fischer carbene complexes of molybdenum and chromium have been found to readily monocyclopropanate many simple 1,3-dienes in good-to-excellent yields, with high levels of chemo-, regio-, and stereoselectivity. A mechanism involving the intermediacy of an η^1-alkyl, η^3-allyl complex is proposed to account for this selectivity.

Introduction

Since their initial preparation in the early 1960s, Fischer carbene complexes have been widely investigated, and a variety of novel and synthetically useful transformations have been developed.[1] Some of the earliest studies of their reactivity focused on reactions with substituted alkenes. Fischer and co-workers demonstrated that alkenes with either electron-donating[2] or electron-withdrawing[3] substituents were readily cyclopropanated by phenylmethoxycarbene complexes of chromium, molybdenum, and tungsten. These findings have led to a variety of more recent investigations of the reactivity of Fischer carbene complexes with both electron-rich and electron-poor olefins.[4]

Studies of intramolecular cyclopropanation reactions with Fischer carbene complexes have shown much less reliance on the presence of donor or acceptor substituents on the alkene component.[5] Though occasionally complicated by competing olefin

(1) For recent reviews, 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.

(2) (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966–3973. (b) Dorrer, B.; Fischer, E. O.; Kalbfus, W. *J. Organomet. Chem.* **1974**, *81*, C20–C22.

(3) (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.

(4) For recent examples, please see: (a) Hegedus, L. S.; Bates, R. W.; Söderberg, B. C. *J. Am. Chem. Soc.* **1991**, *113*, 923–927. (b) Herndon, J. W.; Tumor, S. U. *J. Org. Chem.* **1991**, *56*, 286–294. (c) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1990**, *31*, 2529. (d) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364–4374. (e) Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660–5662. (f) Wienand, A.; Reissig, H.-U. *Organometallics* **1990**, *9*, 3133–3142. (g) Wienand, A.; Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1129–1131. (h) Herndon, J. W.; Tumer, S. U. *Tetrahedron Lett.* **1989**, *30*, 4771. (i) Wienand, A.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2315–2318.

0002-7863/91/1513-8916$02.50/0

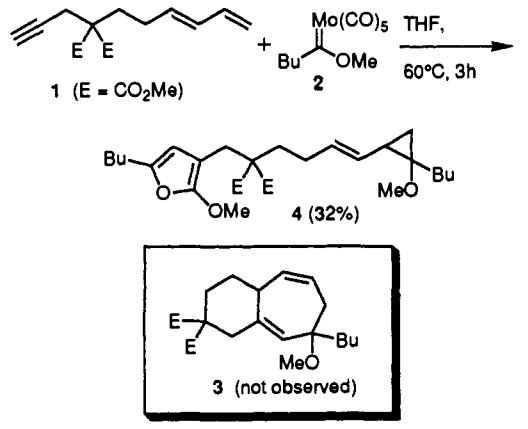
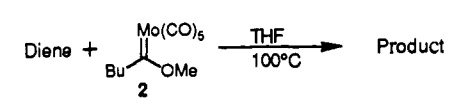


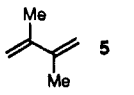
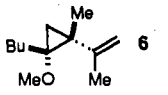
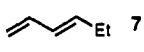
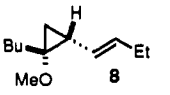
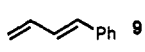
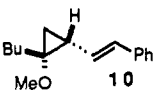
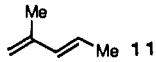
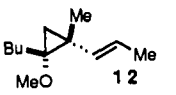
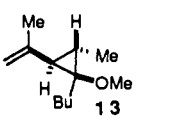
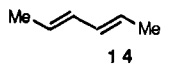
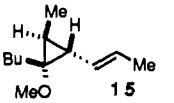
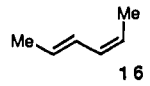
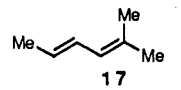
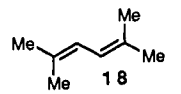
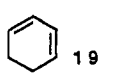
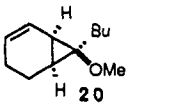
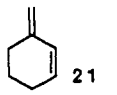
Figure 1.

metathesis processes,[5a] numerous examples of the intramolecular cyclopropanation of unactivated olefins have been described. Very few examples of the cyclopropanation of 1,3-dienes with Fischer carbene complexes have been reported. Intermolecular versions of this reaction with both electron-rich[6] and electron-poor[7] 1,3-dienes have been presented. However, to the best of our knowledge, only one example of the reaction of an electronically neutral 1,3-diene with a Fischer carbene complex has been described.[4b,h,8]

As part of a program directed toward the development of transition metal mediated methodology for the preparation of polycyclic frameworks,[9] we investigated the reactivity of dienyne **1** with (butylmethoxycarbene)molybdenum complex **2**[4c] (Figure 1).[10] The desired cyclization product (**3**), derived from the intramolecular cyclopropanation of an in situ generated vinylcarbene complex and subsequent divinylcyclopropane rearrangement, was not observed. Instead, when this reaction was conducted in THF, the vinylcyclopropane–methoxyfuran system **4** was obtained in 32% yield. The reaction of Fischer carbene complexes with alkynes to give alkoxyfurans is well-precedented,[11] however, the intermolecular cyclopropanation of 1,3-dienes is not. Because of the importance of this finding with respect to our ultimate synthetic goals and the potential synthetic utility of such a process, we chose to conduct a general survey of the reactivity of Fischer carbene complexes with simple substituted 1,3-dienes. The results of these studies are described herein.

Table I



diene	product	yield, %
 **5**	 **6**	71
 **7**	 **8**	76
 **9**	 **10**	76
 **11**	 **12**  **13**	75 (6.3:1)
 **14**	 **15**	65[a]
 **16**	no reaction	
 **17**	no reaction	
 **18**	no reaction	
 **19**	 **20**	67
 **21**	no reaction	

[a] By NMR, **15** appears to contain approximately 12% of a minor diastereomer that could not be separated or characterized.

Results

We began by investigating the reactivity of (butylmethoxycarbene)molybdenum complex **2** with a variety of simple 1,3-dienes. The results are summarized in Table I. In THF at reflux, this reaction was relatively slow for the more substituted dienes (**5**, **11**, **14**, and **19**), requiring 24–48 h for complete consumption of the starting material. Optimum conditions were found to be 0.025 M diene in THF in a sealed flask at 100 °C with 1.25 equiv of carbene **2**. Under these conditions, all of the successful examples in Table I were complete within several hours.

High levels of both regio- and diastereoselectivity were observed for this process. From dienes **5**, **7**, **9**, **14**, and **19** only a single diastereomer was obtained. Cyclopropanation of diene **11** produced a 6.3:1 mixture of regioisomeric vinylcyclopropanes **12** and **13**, each of which was found to be a single diastereomer. Spectroscopic studies (vide infra) indicated that the methoxy group in each case is cis to the vinyl substituent.

Of particular interest was the surprisingly high level of chemoselectivity. The *E,E* isomer of 2,4-hexadiene (**14**) was readily cyclopropanated to give vinylcyclopropane **15**, but the *E,Z* isomer (**16**), which was expected to function as a test of the selectivity

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(6) (a) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653–2655. (b) Wulff, W. D.; Yang, D. C.; Murray, C. K. *Pure Appl. Chem.* **1988**, *60*, 137–144.

(7) (a) Buchert, M.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2319–2320.

(8) For a recent report of the cyclopropanation of 1,3-dienes by benzylidene complexes of chromium and tungsten, see: Fischer, H.; Hofmann, J. *Chem. Ber.* **1991**, *124*, 981–988.

(9) (a) Harvey, D. F.; Brown, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 7806–7807. (b) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066–5068.

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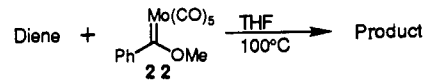
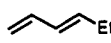
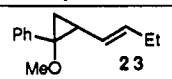
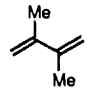
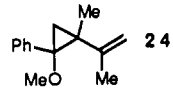
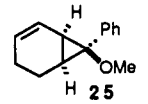
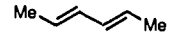
(11) (a) Dötz, K. H.; Tiriliomis, A.; Harms, K. *J. Chem. Soc., Chem. Commun.* **1989**, 788–790. (b) McCallum, J. S.; Kunng, F.-A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346–2360.

Table II

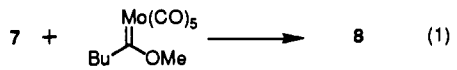


diene	product	yield, %
 7	 23	95 (1.4:1)
 5	 24	72 (1.3:1)
 19	 25	48
 14	no reaction	

of cis versus trans double bonds, failed to react at either position. Additional methyl substituents, as found in dienes **17** and **18**, failed to alter the reactivity. One possible explanation for this result is that only 1,3-dienes with a readily accessible s-cis conformation can participate in this reaction. This behavior is analogous to the reactivity of substituted dienes in the Diels–Alder and other cycloaddition reactions wherein dienes that cannot comfortably exist in the s-cis conformation do not readily participate.[12] The s-cis conformation of diene **14** lacks any severe steric interactions, whereas the s-cis conformation of diene **16** would be greatly disfavored because of the presence of an "inside" methyl substituent. Dienes **17** and **18** would have similar disfavorable steric interactions in their s-cis conformations.

As a further test of the s-cis conformation hypothesis, the reactivity of 1,3-cyclohexadiene (**19**), which is locked in an s-cis conformation, and methylenecyclohexene (**21**), which is locked in an s-trans conformation, were investigated. Indeed, as anticipated, the s-cis locked diene (**19**) led to vinylcyclopropane **20** as a single diastereomer in 67% yield, whereas the s-trans locked diene (**21**) failed to react.

The effect of solvent on this cyclization was briefly investigated. Cyclopropanation was observed in hexane, methanol, and acetonitrile, however, the yields in these solvents were considerably lower than in THF. No reaction was observed in benzene. Representative examples with molybdenum carbene complex **2** and diene **7** are presented in eq 1.



Solvent	Yield
hexane	49%
MeOH	11%
MeCN	33%
benzene	0%

The reactivity of (methoxyphenylcarbene)molybdenum complex **22** was also investigated. Its reactivity was similar to that seen with methoxybutyl complex **2**, however, the diastereoselectivity was considerably lower (see Table II). With (*E*,*E*)-2,4-hexadiene (**14**) no reaction was observed. The reactivity of molybdenum carbene complexes was compared to the analogous chromium and tungsten complexes. The (butylmethylcarbene)chromium complex **26**, using the conditions previously developed for molybdenum carbene complexes, was found to monocyclopropanate (*E*)-1,3-hexadiene (**7**) in 43% yield. Although this system exhibited the same high levels of regioselectivity and diastereoselectivity that were seen with molybdenum complex **2**, the yield was significantly lower.

(12) For a discussion of the effect of diene stereochemistry on the rate of the Diels–Alder reactions, please see: (a) Stewart, C. A., Jr. *J. Org. Chem.* **1963**, *28*, 3320–3323.

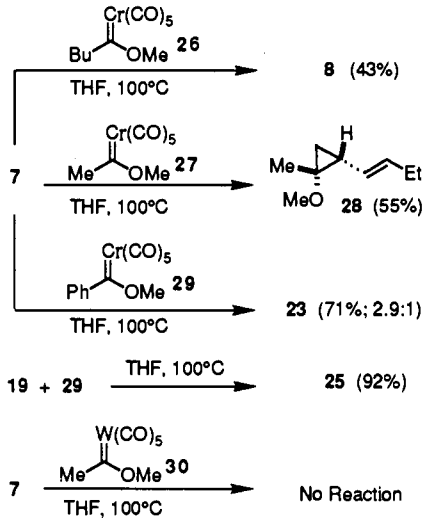


Figure 2.

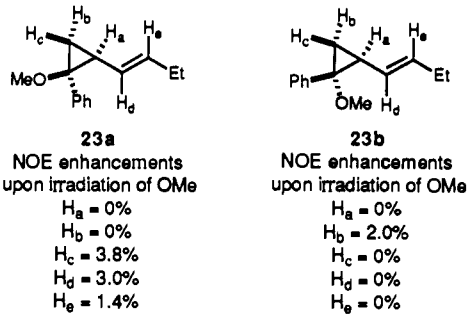


Figure 3.

Chromium complex **27** behaved in a similar fashion to give vinylcyclopropane **28** in 55% yield, again with excellent regio- and diastereoselectivity. Since the analogous (methoxymethylcarbene)molybdenum complex is relatively unstable and difficult to handle,[13] the chromium-based system would be the method of choice for the production of compounds in this series. The (methoxyphenylcarbene)chromium complex **29** behaved in a fashion similar to that seen with the analogous molybdenum complex, though resulting in slightly better diastereoselectivity (Figure 2). Tungsten complex **30** was found to be inert under these reaction conditions.

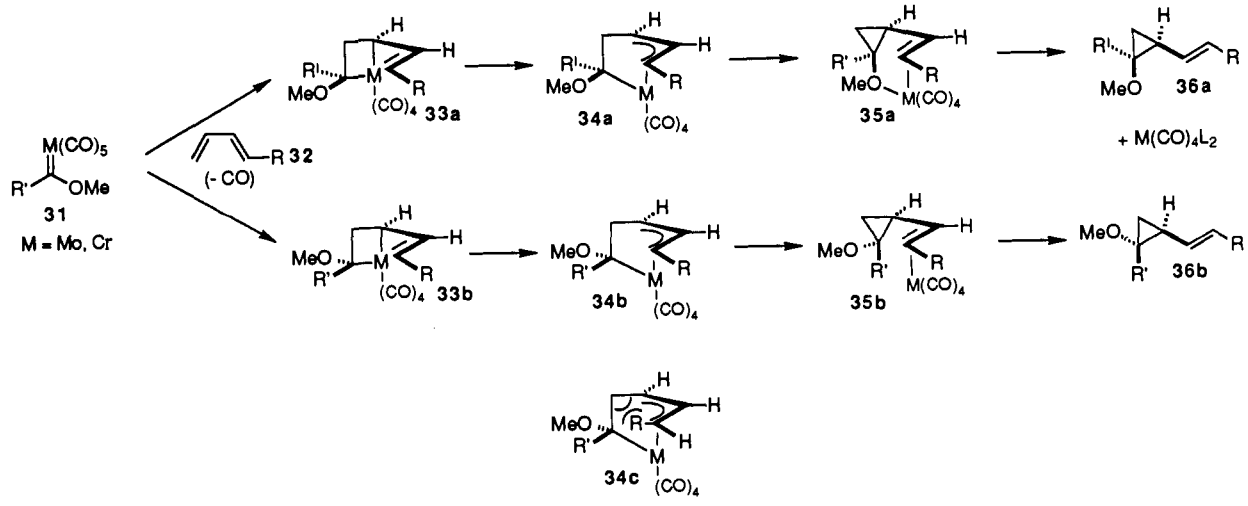
Stereochemical assignments for the cyclopropanes described above were based on the analysis of coupling constants of the cyclopropane protons and NOE enhancement studies. A full analysis of phenyl derivatives **23a** and **23b** was performed, and assignments for other systems were supported by additional NOE studies and comparison to **23a** and **23b**. The assignments of the cyclopropyl protons (H_a, H_b, and H_c) were based on their chemical shifts and coupling constants. For example, for **23a**, H_a was shifted downfield to 1.84 ppm because of its proximity to the olefin substituent. H_b and H_c were assigned as being cis and trans, respectively, on the basis of the observed coupling constants of 9.5 Hz between H_a and H_b and 6.8 Hz between H_a and H_c. In cyclopropanes, cis coupling constants are generally larger than trans.[14] A coupling of 5.6 Hz was observed between H_b and H_c.

The stereochemical assignments of the other substituents of **23a** and **23b** were based on the NOE studies shown below. For **23a**, NOE enhancements were observed from the methoxy signal to both the olefinic protons and H_c. Isomer **23b** showed no NOE enhancement from the methoxy signal to the olefinic protons and

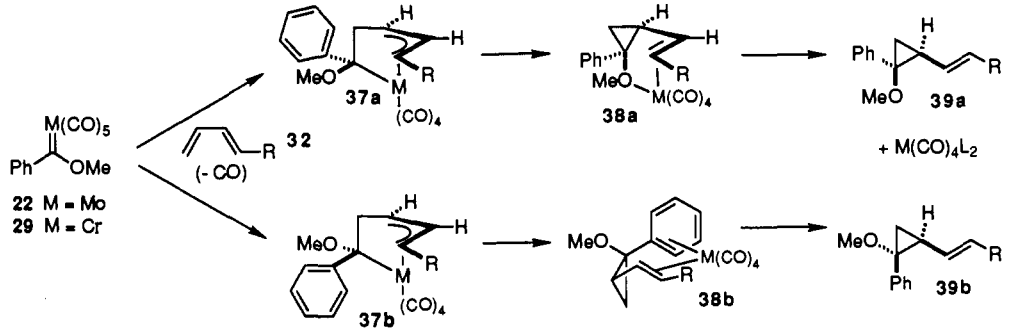
(13) (a) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445–2456. (b) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5833–5838.

(14) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, 1983; p H185.

Scheme I



Scheme II



H_c but did show a significant NOE effect to H_b (Figure 3). Further support for the assignment of stereochemistry comes from comparison of the chemical shifts of the olefinic protons. The major diastereomer **23a** has olefin signals at 5.67 ppm (dt) and 5.40 ppm (dd). The minor diastereomer **23b** has olefin signals at 5.52 ppm (dt) and 4.62 ppm (dd). With the aromatic ring cis to the olefin, the nearest olefinic proton is shifted upfield by 0.78 ppm.

NOE studies of the vinylcyclopropanes produced from the alkylmethoxycarbene complexes were hampered by the high diastereoselectivity of this process and the absence of the minor diastereomer for comparison purposes. Butylmethoxycyclopropane **8** showed significant NOE effects from the methoxy group to the nearest olefinic proton and H_c and no NOE effect to H_b. NOE effects of a similar magnitude were seen for cyclopropanes **10**, **20**, **25**, and **28**.

Discussion

From the above results several key observations can be made. First of all, this process shows a surprisingly high degree of diastereoselectivity. Previous intermolecular cyclopropanation processes have produced mixtures of diastereomers and/or lower overall yields.[2-4,7] In all of the examples of reactions with alkylmethoxycarbene complexes presented herein, only a single diastereomer was isolated. Second, for unsymmetrically substituted 1,3-dienes, cyclopropanation occurs preferentially at the least sterically hindered double bond. Even more intriguing is the high level of chemoselectivity and the apparent trend toward reactions with 1,3-dienes having readily accessible s-cis conformations. A plausible mechanism that explains all of these results is presented in Scheme I.

From complex **31** (M = Mo or Cr), loss of CO and cyclization with one of the diene double bonds leads to metallacyclobutanes **33a** or **33b**. Metallacyclobutane formation would be expected to preferentially occur at the less substituted or less sterically encumbered double bond of the 1,3-diene. As drawn, **33a** and **33b** are 16-e$^-$ complexes. Though the C_2–C_3 bond (original diene numbering) of **33a** and **33b** can freely rotate, these η^1-allyl complexes would be expected to rapidly convert to, or be in rapid equilibrium with, the 18-e$^-$ η^3-allyl species **34a** and **34b**, respectively. Allyl molybdenum complexes have previously been both isolated[15] and proposed as reactive intermediates[16] in other ligand environments. Allyl alkyl complexes analogous to **34a** and **34b** have been implicated as intermediates in transition metal catalyzed vinylcyclopropane rearrangements.[17] If the double bond geometry of **33a,b** were cis rather than trans, as shown, the isomeric η^3-allyl complex with R syn rather than anti to the original carbene carbon would have severe steric interactions that would significantly disfavor its formation (see **34c**). This type of steric interaction would exist with dienes **16**, **17**, and **18**, all of which were found to not participate in this reaction.

Reductive elimination from **34a** and **34b** then leads to the vinylcyclopropane products. From **34a**, reductive elimination can produce the 18-e$^-$ complex **35a** wherein the $Mo(CO)_4$ unit is complexed to both the olefin and the methoxy substituents. From **34b**, reductive elimination would likely result in the formation of the 16-e$^-$ complex **35b** wherein the $Mo(CO)_4$ fragment is coordinated only to the olefin of the vinylcyclopropane. In **35b**, the methoxy substituent on the cyclopropane ring is anti to the

(15) (a) Hansson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9660–9661. (b) Benyunes, S. A.; Green, M.; McPartlin, M.; Nation, C. B. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1887–1888. (c) Benyunes, S. A.; Green, M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268–2270. (d) Brisdon, B. J.; Hodson, A. G. W.; Mahon, M. F.; Molloy, K. C. *J. Organomet. Chem.* **1988**, *344*, C8–C10. (e) Drew, M. G. B.; Brisdon, B. J.; Brown, D. W.; Willis, C. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1510–1512. (f) Brisdon, B. J.; Day, A. *J. Organomet. Chem.* **1981**, *221*, 279–285.

(16) (a) Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9590 and references cited therein. (b) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257 and references cited therein. (c) Trost, B. M.; Lautens, M. *Tetrahedron* **1987**, *43*, 4817.

(17) (a) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229–267 and references cited therein. (b) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React. (NY)* **1985**, *33*, 247–335.

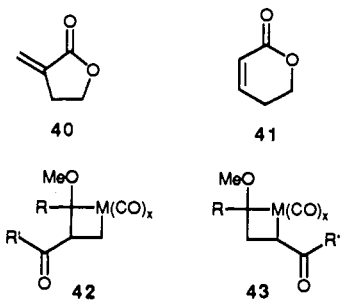


Figure 4.

olefin substituent and both of these substituents cannot coordinate to the metal center at the same time. Subsequent decomplexation, presumably with incorporation of the solvent as L, leads to vinylcyclopropanes **36a** and **36b**. If one presumes that all steps prior to the reductive elimination are reversible, the ability of **36a** to coordinate in a bidentate fashion to $Mo(CO)_4$ (as in **35a**) would cause its production to be favored over the isomeric **36b** and explain why only vinylcyclopropanes with the methoxy group cis to the olefin are produced in this transformation.

As outlined in Scheme II, a similar rationale can be used to explain why the stereoselectivity is severely eroded when phenylcarbene complexes **22** and **29** are used in place of alkylcarbene complexes **2**, **26**, and **27**. Carbenes **22** and **29** would be expected to form allyl complexes **37a** and **37b**. Reductive elimination from **37a** leads to **38a** wherein the $Mo(CO)_4$ unit is coordinated to both the olefin and the methoxy substituents as previously proposed with **35a**. Alternatively, reductive elimination from **37b** can produce **38b** wherein the $Mo(CO)_4$ fragment is complexed to both the arene, in an η^2 fashion, and the olefin substituents. The 18-e$^-$ complex **38b** would certainly be more stable than the 16-e$^-$ complex **35b**. If one presumes that an ether group coordinates to an $Mo(CO)_4$ fragment about as well as a phenyl ring coordinates in an η^2 fashion, then an approximately 1:1 ratio of **38a** to **38b** would be expected.[18] Formation of η^3-benzylic intermediates is also possible[19] and would lead to a similar conclusion; however, it is anticipated that η^3-coordination to the allyl substituent would be strongly preferred. As before, decomplexation leads to free vinylcyclopropanes **39a** and **39b**. Steric interactions between the aromatic ring and the additional methyl group of diene **14** are the probable explanation for the absence of any reaction with this substrate.

In surveying previous reports of cyclopropanation processes with Fischer carbene complexes, it is interesting to note the absence of reports of successful intermolecular cyclopropanation reactions with alkenes in which a neighboring group would not be available for coordination to and stabilization of a metallacyclobutane intermediate. Indeed, Reissig and co-workers have recently reported that α-methylene lactone **40**, which is locked in a pseudo-s-cis conformation was readily cyclopropanated by carbene complex **29** but that butenolide **41**, which is locked in a pseudo-s-trans conformation, was not (Figure 4).[4f,j] A mechanistic pathway similar to that proposed above may be operative in this system as well.

It has previously been assumed that, in the cyclopropanation of olefins with electron-withdrawing substituents, metallacyclobutane **42** is favored over metallacyclobutane **43**.[3a,b,4b] If an acrylate group behaves in a fashion similar to that of the 1,3-dienes reported herein, metallacyclobutane **43** would be favored because of its ability to form an η^3-metalloenolate intermediate. The possible intermediacy of such a complex is in full agreement with the pathways leading to CH insertion products that have previously been isolated as minor products from the chromium carbene based cyclopropanation reaction of acrylate esters.[4b,f,g,l]

Conclusion

The studies reported herein demonstrate that several simple 1,3-dienes without electron-donating or electron-withdrawing groups are readily cyclopropanated by molybdenum- and chromium-based Fischer carbene complexes. High levels of chemo-, regio-, and diastereoselectivity have been observed for this process, and a mechanism that accounts for this selectivity has been suggested.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 500-MHz or G.E. 300-MHz spectrometers and referenced relative to the solvent signal present. 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—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).

General Procedure. All cyclizations were performed under a nitrogen atmosphere in flame-dried glassware. THF was freshly distilled from sodium–benzophenone ketyl. The dienes (except **9** and **21**) were purchased from Aldrich and used as received. Dienes were dissolved in THF (0.025 M), and the carbene complex was then added. Behind a blast shield, the solutions were heated at 100 °C in a sealed glass vial equipped with a rubber-lined cap and aluminum foil. After thermolysis, the solution was cooled to room temperature and concentrated in vacuo, and the residue was chromatographed on Florisil to give the vinylcyclopropane product(s).

***cis*-1-Butyl-1-methoxy-2-methyl-2-(1-methylethenyl)cyclopropane (6).** Following the general procedure, 2,3-dimethyl-1,3-butadiene (**5**) (41.6 mg, 0.496 mmol) and **2**[4c] (0.208 g, 0.619 mmol) were heated in 20 mL of THF at 100 °C for 1.25 h to give 64.3 mg (71%) of **6** as a single diastereomer: ^{1}H NMR (500 MHz, C_6D_6) δ 0.10 (d, J = 5 Hz, 1 H), 0.92 (t, J = 7.3 Hz, 3 H), 1.02 (d, J = 5 Hz, 1 H), 1.04–1.09 (m, 1 H), 1.11 (s, 3 H), 1.34 (sextet, J = 7.3 Hz, 2 H), 1.41–1.46 (m, 1 H), 1.63–1.71 (m, 1 H), 1.86–1.92 (m, 1 H), 1.91 (s, 3 H), 3.00 (s, 3 H), 4.96 (s, 2 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.3, 20.8, 21.6, 22.7, 23.3, 28.6, 29.8, 33.9, 53.6, 68.0, 111.4, 148.5; IR (CH_2Cl_2) 3076, 2958, 2927, 2872, 2858, 1648, 1467, 1377, 1365, 1310, 1231, 1166, 1141, 1078, 1027, 956; LRMS EI *m/e* 182 (M^+, 0.2), 167 (3), 153 (2), 126 (9), 125 (100), 111 (7), 108 (6), 107 (12), 97 (5), 95 (13), 93 (19), 91 (14), 81 (5), 79 (9), 77 (8), 67 (11), 57 (10), 55 (9), 53 (5). Anal. ($C_{12}H_{22}O$) Calcd: C, 79.06; H, 12.16. Found: C, 79.91; H, 12.29. NOE data supported the assignment of stereochemistry as shown. For example, upon irradiation of the vinyl methyl group, a 2% NOE effect to the methoxy group was observed.

***cis*-2-((*E*)-1-Butenyl)-1-butyl-1-methoxycyclopropane (8).** From **2**: Following the general procedure, (*E*)-1,3-hexadiene (**7**) (41.6 mg, 0.456 mmol) and **2** (0.191 g, 0.568 mmol) were heated in 20 mL of THF at 100 °C for 1 h to give 62.6 mg (76%) of **8** as a single diastereomer. From **26**: Following the general procedure, (*E*)-1,3-hexadiene (**7**) (38.6 mg, 0.423 mmol) and **26** (0.165 g, 0.565 mmol) were heated in 19 mL of THF at 100 °C for 4 h to give 33.1 mg (43%) of **8** as a single diastereomer: ^{1}H NMR (500 MHz, C_6D_6) δ 0.59 (dd, J = 9, 5 Hz, 1 H), 0.74 (t, J = 5 Hz, 1 H), 0.88 (t, J = 7 Hz, 3 H), 0.96 (t, J = 7 Hz, 3 H), 1.27–1.33 (m, 4 H), 1.42–1.48 (m, 3 H), 2.03 (p, J = 7 Hz, 2 H), 3.11 (s, 3 H), 5.48 (ddd, J = 15, 9, 1 Hz, 1 H), 5.63 (dt, J = 15, 6 Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.28, 14.35, 19.9, 23.0, 26.2, 28.1, 28.5, 33.4, 53.7, 65.7, 128.8, 131.1; IR (CH_2Cl_2) 2995, 2960, 2932, 2872, 2661, 1457, 1315, 1260, 1085, 1062, 1028, 967, 798; LRMS EI *m/e* 182 (M^+, 7), 153 (20), 126 (8), 125 (100), 97 (17), 95 (12), 93 (48), 91 (19), 85 (8), 81 (7), 79 (21), 77 (14), 72 (34), 67 (18), 59 (7), 57 (17), 55 (11), 53 (9). Anal. ($C_{12}H_{22}O$) Calcd: C, 79.06; H, 12.16. Found: C, 79.84; H, 12.27. NOE studies supported the assignment of stereochemistry as shown. For example, irradiation of the methoxy group produced 2.2% enhancement of the olefin signal at δ 5.48 and 2.0% enhancement of the cyclopropane H syn to the olefin.

***cis*-1-Butyl-1-methoxy-2-((*E*)-2-phenylethenyl)cyclopropane (10).** Following the general procedure, (*E*)-1-phenyl-1,3-butadiene (**9**) (64.5 mg, 0.496 mmol) and **2** (0.204 g, 0.607 mmol) were heated in 19 mL of THF at 100 °C for 2 h to give 88.1 mg (77%) of **10** as a single diaste-

(18) For a discussion of ether versus alkene coordination in chromium carbene complexes, please see ref 5h.

(19) (a) Winter, M. J.; Woodward, S. *J. Chem. Soc., Chem. Commun.* **1989**, 457–458. (b) Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 845–850. (c) Colton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339–1346. (d) Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90* 5418–5422. (e) King, R. B.; Fronzaglia, A. *J. Am. Chem. Soc.* **1966**, *88*, 709–712.

reomer: ^{1}H NMR (500 MHz, C_6D_6) δ 0.68 (dd, J = 9.3, 5.4 Hz, 1 H), 0.84–0.92 (m, 4 H, containing a triplet at 0.89, J = 7.3 Hz, 3 H), 1.22–1.37 (m, 3 H), 1.39–1.52 (m, 4 H), 3.08 (s, 3 H), 6.23 (dd, J = 16, 9 Hz, 1 H), 6.53 (d, J = 16 Hz, 1 H), 6.99–7.34 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 20.8, 22.6, 27.6, 28.8, 33.1, 54.2, 66.7, 125.6, 126.4, 128.4, 128.6, 130.0, 137.9; IR (CCl_4) 3068, 3063, 3027, 3020, 2959, 2933, 2874, 2870, 2827, 1647, 1602, 1494, 1451, 1390, 1314, 1261, 1216, 1091, 1065, 1029, 964; LRMS EI m/e 230 (M^+, 23), 174 (14), 173 (100), 157 (9), 155 (11), 143 (8), 141 (19), 130 (12), 129 (22), 128 (14), 117 (16), 116 (8), 115 (33), 105 (8), 91 (27), 85 (20), 77 (11), 74 (8), 59 (13), 57 (46), 45 (31), 43 (12); HRMS ($C_{16}H_{22}O$) calcd 230.1671, found 230.1677. NOE studies supported the assignment of stereochemistry as shown. Irradiation of the methoxy group produced a 2.5% enhancement of both of the olefinic signals.

***cis*-2-((*E*)-1-Butenyl)-1-butyl-1-methoxy-2-methylcyclopropane (12).** Following the general procedure, (*E*)-2-methyl-1,3-pentadiene (**11**) (41.1 mg, 0.495 mmol) and **2** (0.208 g, 0.568 mmol) were heated in 20 mL of THF at 100 °C for 5 h to give 68.0 mg (75%) of cyclopropanes **12** and **13** as an inseparable 6.3:1 mixture. All data below is of this mixture. **12** and **13**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.31 (d, J = 4.9 Hz, 1 H), 0.86–0.94 (m, 5 H), 1.08 (s, 3 H), 1.25–1.36 (m, 3 H), 1.41–1.59 (m, 2 H), 1.70 (dd, J = 6.3, 1.5 Hz, 3 H), 3.06 (s, 3 H), 5.46 (dq, J = 15.6, 6.4 Hz, 1 H), 5.75 (dd, J = 15.6, 1.5 Hz, 1 H), the structure of **13** was suggested by the presence of a doublet at δ 4.93; ^{13}C NMR (125 MHz, C_6D_6) δ 14.4, 18.3, 23.2, 26.8, 28.0, 28.3, 29.6, 39.7, 53.6, 69.5, 121.1, 137.9, the structure of **13** was suggested by the presence of ^{13}C NMR signals at 142.5, 110.6, 39.7, 29.2, 28.3, 22.8, 14.0; IR (of mixture, CH_2Cl_2) 3030, 2958, 2933, 2874, 2860, 2824, 1465, 1452, 1441, 1378, 1313, 1225, 1222, 1205, 1076, 1034, 977; LRMS of **12** EI m/e 182 (M^+, 3), 167 (14), 153 (6), 139 (5), 126 (9), 125 (100), 111 (10), 110 (4), 109 (5), 107 (7), 95 (14), 94 (5), 93 (45), 91 (16), 85 (11), 81 (7), 79 (11), 77 (12), 72 (6), 71 (4), 69 (7), 67 (16), 65 (4), 59 (3), 57 (21), 55 (9), 53 (7), LRMS of **13** EI m/e 182 (M^+, 1), 167 (8), 139 (5), 126 (9), 125 (100), 111 (13), 110 (6), 109 (7), 107 (12), 97 (6), 95 (22), 94 (8), 93 (74), 91 (26), 85 (16), 83 (5), 81 (13), 79 (21), 77 (24), 72 (8), 71 (8), 69 (13), 67 (34), 65 (9), 59 (9), 57 (32), 55 (25), 53 (16). Anal. ($C_{12}H_{22}O$): C, H. Assignment of stereochemistry was based on the comparison of ^{1}H NMR data to **8** and **23a**.

(1α,2α,3β)-1-Butyl-1-methoxy-3-methyl-2-((*E*)-1-propenyl)cyclopropane (15). Following the general procedure, (*E*,*E*)-2,4-hexadiene (**14**) (47.2 mg, 0.569 mmol) and **2** (0.228 g, 0.678 mmol) were heated in 19 mL of THF at 100 °C for 4 h to give 67.1 mg (65%) of **15**. Both ^{1}H and ^{13}C NMR data suggested the presence of a minor isomer that could not be cleanly separated or characterized. Spectral data are reported only for the major product **15**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.90 (t, J = 7.3 Hz, 3 H), 0.93 (d, J = 7 Hz, 3 H), 1.00 (q, J = 6.4 Hz, 1 H), 1.24–1.61 (m, 7 H), 1.67 (d, J = 5 Hz, 3 H), 3.10 (s, 3 H), 5.47–5.57 (m, 2 H); ^{13}C NMR (125 MHz, C_6D_6) δ 13.7, 14.4, 18.3, 23.1, 26.1, 28.1, 29.0, 36.0, 53.4, 68.9, 123.3, 131.1; IR (CH_2Cl_2) 2959, 2933, 2873, 2860, 2825, 1465, 1460, 1439, 1377, 1242, 1215, 1116, 1103, 1091, 1078, 1062, 999, 966; LRMS EI m/e 182 (M^+, 10), 167 (15), 126 (8), 125 (100), 111 (5), 95 (9), 93 (14), 91 (6). Anal. ($C_{12}H_{22}O$): C, H. NOE data supported the stereochemical assignment as shown. For example, upon irradiation of the methoxy group, a 3.4% NOE enhancement was observed at the syn H of the cyclopropane ring.

***endo*-7-Butyl-7-methoxybicyclo[4.1.0]hept-2-ene (20).** Following the general procedure, 1,3-cyclohexadiene (**19**) (51.5 mg, 0.630 mmol) and **2** (0.277 g, 0.824 mmol) were heated in 19 mL of THF at 100 °C for 2 h to give 0.076 g (67%) of **20**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.74 (ddd, J = 14.2, 9.8, 6.3 Hz, 1 H), 0.90 (t, J = 7.3 Hz, 3 H), 0.94–1.01 (m, 2 H), 1.24–1.36 (m, 2 H), 1.39–1.53 (m, 2 H), 1.57–1.64 (m, 1 H), 1.92–2.05 (m, 3 H), 2.21–2.30 (m, 1 H), 3.04 (s, 3 H), 5.70 (ddd, J = 9.8, 5.9, 2.4 Hz, 1 H), 5.95–5.99 (m, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.1, 16.4, 21.4, 22.7, 23.2, 25.0, 28.0, 34.1, 54.4, 72.1, 122.1, 125.7; IR (CH_2Cl_2) 3027, 3011, 2957, 2930, 2872, 2860, 2827, 1643, 1455, 1433, 1316, 1269, 1265, 1066, 1032; LRMS EI m/e 180 (M^+, 13), 137 (3), 124 (8), 123 (100), 109 (3), 108 (3), 105 (5), 93 (5), 92 (3), 91 (3), 91 (24), 79 (6), 77 (5). Anal. ($C_{12}H_{20}O$): C, H. NOE data supported the stereochemical assignment as shown. For example, irradiation of the methoxy group resulted in 2% NOE enhancement of the olefinic hydrogens.

***cis*-2-((*E*)-1-Butenyl)-1-methoxy-1-phenylcyclopropane (23a) and *trans*-2-((*E*)-1-Butenyl)-1-methoxy-1-phenylcyclopropane (23b).** From **22**: Following the general procedure, (*E*)-1,3-hexadiene (**7**) (39.4 mg, 0.431 mmol) and **22** (0.237 g, 0.666 mmol) were heated in 20 mL of THF at 100 °C for 3 h to give 0.083 g (95%) of a 1.4:1 mixture of **23a** and **23b**. **23a** and **23b** from **29**: Following the general procedure, (*E*)-1,3-hexadiene (**7**) (42.4 mg, 0.465 mmol) and **29** (0.202 g, 0.647 mmol) were heated in 19 mL of THF at 100 °C for 4 h to give 66.3 mg (71%) of a 2.9:1 mixture of **23a** to **23b**. **23a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (t, J = 7.3 Hz, 3 H), 1.11 (t, J = 6.1 Hz, 1 H), 1.36 (dd, J = 9.5, 5.6 Hz, 1 H), 1.84 (q, J = 9.0 Hz, 1 H), 2.09 (dq, J = 7.3, 6.4 Hz, 2 H), 3.26 (s, 3 H), 5.40 (dd, J = 15.6, 8.8 Hz, 1 H), 5.67 (dt, J = 15.6, 6.4 Hz, 1 H), 7.22–7.25 (m, 1 H), 7.29–7.36 (m, 4 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 13.8, 20.4, 25.8, 31.6, 55.3, 67.4, 126.1, 126.6, 126.7, 128.3, 133.1, 141.1. **23b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (t, J = 7.3 Hz, 3 H), 1.08 (t, J = 6.1 Hz, 1 H), 1.31 (dd, J = 10.0, 5.6 Hz, 1 H), 1.84 (p, J = 7.2 Hz, 2 H), 2.07 (q, J = 9.3 Hz, 1 H), 3.13 (s, 3 H), 4.62 (dd, J = 15.1, 8.0 Hz, 1 H), 5.52 (dt, J = 15.1, 6.4 Hz, 1 H), 7.26–7.29 (m, 1 H), 7.32–7.38 (m, 4 H); ^{13}C NMR (500 MHz, C_6D_6) δ 13.8, 17.2, 25.4, 29.6, 54.1, 68.9, 126.6, 127.3, 128.0, 129.5, 132.6, 136.9; IR (mixture of **23a** and **23b**, CH_2Cl_2) 3025, 2964, 2935, 2874, 2828, 1495, 1462, 1449, 1282, 1241, 1201, 1077, 1057, 1027, 971; LRMS (mixture of **23a** and **23b**) EI m/e 202 (M^+, 12), 173 (63), 159 (12), 155 (15), 143 (11), 141 (40), 134 (54), 133 (55), 129 (24), 128 (33), 121 (12), 115 (35), 105 (88), 104 (14), 103 (12), 91 (44), 78 (14), 77 (100), 51 (24). Anal. ($C_{14}H_{18}O$): C, H. See the Results section for assignment of stereochemistry.

1-Methoxy-2-methyl-2-(1-methylethenyl)-1-phenylcyclopropane (24). Following the general procedure, 2,3-dimethyl-1,3-butadiene (**5**) (39.7 mg, 0.474 mmol) and **22** (0.255 g, 0.632 mmol) were heated in 19 mL of THF at 100 °C for 4 h to give 61.9 mg (72%) of **24** as a 1.3:1 mixture of diastereomers that could be partially separated by chromatography. Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, J = 6.4 Hz, 1 H), 1.28 (s, 3 H), 1.43 (s, 3 H), 1.59 (d, J = 6.4 Hz, 1 H), 3.17 (s, 3 H), 4.62 (s, 1 H), 4.67 (s, 1 H), 7.17–7.20 (m, 1 H), 7.23–7.26 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.9, 20.1, 20.9, 37.8, 54.9, 70.7, 112.4, 126.5, 127.4, 127.5, 138.0, 146.1. Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (s, 3 H), 0.98 (d, J = 6 Hz, 1 H), 1.20 (d, J = 6 Hz, 1 H), 2.08 (s, 3 H), 3.00 (s, 3 H), 5.11 (apparent d, J = 10.0 Hz, 2 H), 7.09–7.18 (m, 5 H). Mixture of diastereomers: IR (CH_2Cl_2) 3080, 3027, 2972, 2933, 2905, 2875, 2826, 1645, 1495, 1447, 1438, 1373, 1261, 1175, 1130, 1078, 1028; LRMS EI m/e 202 (M^+, 8), 201 (14), 187 (97), 172 (46), 171 (61), 170 (89), 155 (61), 129 (52), 128 (31), 115 (25), 105 (89), 91 (34), 77 (100), 51 (24). Anal. ($C_{14}H_{18}O$): C, H.

***endo*-7-Methoxy-7-phenylbicyclo[4.1.0]hept-2-ene (25).** From **22**: Following the general procedure, 1,3-cyclohexadiene (**19**) (39.6 mg, 0.484 mmol) and **22** (0.207 g, 0.581 mmol) were heated in 19 mL of THF at 100 °C for 3 h to give 0.046 g (48%) of **25** as a single diastereomer. **25** from **29**: Following the general procedure, 1,3-cyclohexadiene (**19**) (37.6 mg, 0.460 mmol) and **29** (0.179 g, 0.573 mmol) were heated in 19 mL of THF at 100 °C for 2 h to give 84.3 mg (92%) of **25** as a single diastereomer: ^{1}H NMR (500 MHz, C_6D_6) δ 1.32–1.35 (m, 1 H), 1.60–1.67 (m, 1 H), 1.84 (dd, J = 9.5, 5.6 Hz, 1 H), 2.00–2.06 (m, 1 H), 2.14–2.18 (m, 1 H), 2.33–2.41 (m, 1 H), 3.13 (s, 3 H), 5.82–5.85 (m, 1 H), 6.02–6.06 (m, 1 H), 7.11–7.37 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.9, 22.77, 22.82, 27.3, 56.2, 73.2, 121.0, 125.4, 126.6, 127.4, 128.3; IR (CH_2Cl_2) 3028, 2980, 2928, 2858, 2847, 2827, 1494, 1447, 1098, 1068, 1045; LRMS EI m/e 200 (M^+, 83), 169 (27), 168 (58), 167 (73), 153 (28), 141 (28), 121 (26), 114 (28), 105 (100), 91 (38), 77 (85). Anal. ($C_{14}H_{16}O$): C, H.

***cis*-2-((*E*)-1-Butenyl)-1-methoxy-1-methylcyclopropane (28).** Following the general procedure, (*E*)-1,3-hexadiene (**7**) (40.2 mg, 0.440 mmol) and **27** (0.147 g, 0.588 mmol) were heated in 19 mL of THF at 100 °C for 5 h to give 33.8 mg (55%) of **28**. Both ^{1}H and ^{13}C NMR suggested the presence of a minor isomer. The ratio of **28** to this minor isomer was >10:1. **28**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.55 (dd, J = 9.0, 5.4 Hz, 1 H), 0.75 (t, J = 5.4 Hz, 1 H), 0.96 (t, J = 7.3 Hz, 3 H), 1.15 (s, 3 H), 1.26 (m, 1 H), 2.02 (pd, J = 7.3, 1.5 Hz, 2 H), 3.12 (s, 3 H), 5.46 (ddt, J = 15.6, 9.5, 1.5 Hz, 1 H), 5.60 (dt, J = 15.6, 6.4 Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.3, 20.1, 20.9, 26.2, 29.2, 53.9, 62.3, 128.7, 131.2; IR (CH_2Cl_2) 2963, 2933, 2874, 2851, 2828, 1463, 1442, 1378, 1274, 1266, 1262, 1217, 1096, 1065, 1001, 966, 919, 845; LRMS EI m/e 140 (M^+, 11), 125 (26), 111 (99), 108 (11), 95 (15), 93 (40), 91 (32), 81 (31), 79 (55), 77 (42), 73 (11), 72 (100), 68 (14), 67 (39), 65 (12), 59 (28), 55 (31), 53 (21), 51 (10). NOE studies supported the assignment of stereochemistry as shown. For example, upon irradiation of the methoxy group, 3.6% NOE enhancement of the olefinic protons and 3.7% NOE enhancement of the cyclopropane proton syn to the olefin were observed.

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 Institutes of Health (GM41984) is gratefully acknowledged. The 500-MHz NMR spectrometer was purchased with assistance from NIH (RR04733) and NSF (CHE 8814866).