P-074 to W.H.W.), and the University of North Texas and Texas Christian University Faculty Research Committees for financial support of this study. We thank Mr. Peng Yuan, Department of Chemistry, University of North Texas, for having obtained the Raman spectra of 2 and 7. We also thank Dr. Thomas Archibald (Fluorchem, Inc., Azusa, CA) for a generous gift of 5,9-dibromopentacyclo-[5.3.0.0^{2,5}.0^{3,9}.O^{4,8}]decane-6,10-dione mono(ethylene acetal) that was used to synthesize 1. Helpful discussions with Dr. G. K. Surya Prakash are gratefully acknowledged.

Registry No. 1, 15291-18-6; 2, 130670-16-5; 3, 130670-17-6; 4, 130670-18-7; 5, 130670-19-8; 6, 130670-20-1; 7, 130670-21-2; 8, 130670-22-3; 9, 130670-23-4.

Supplementary Material Available: Figures 1-4 (structure drawings for 2, 6, 7, and 9, respectively), Figure 5 (22.5-MHz ^{13}C NMR spectrum of 6), Figure 6 (300-MHz ^{1}H NMR spectrum of 9), Table II (X-ray data for 2, 6, 7, and 9), and Tables III-VII, VIII-XII, XIII-XVII, and XVIII-XXII (tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic displacement parameters for 2, 6, 7, and 9, respectively) (27 pages). Ordering information is given on any current masthead page.

Synthesis of Bicyclopropyl Derivatives from the Reaction of Cyclopropylcarbene-Chromium Complexes with Alkenes

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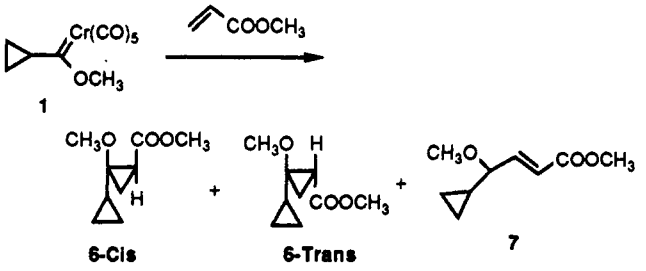
The reaction of cyclopropylcarbene-chromium complexes with alkenes has been examined. The reaction leads to cyclopropylcyclopropane derivatives in good yield, accompanied by minor amounts of ring-opened products. Conjugated dienes and α,β-unsaturated esters and amides appear to be suitable substrates for the reaction. The products of the reaction are donor-acceptor substituted cyclopropanes and are further susceptible to transformations typical of this class of compounds.

Introduction

Recently, cyclopropylcarbene-chromium complexes (1) have emerged as valuable reagents for organic synthesis, by coupling with alkynes to give cyclopentenones (2) in good to excellent yields[1] (Scheme I). During this transformation, a net ring opening of the original cyclopropane ring occurs and ethylene is expelled. At 100 °C in the absence of alkynes, carbene complex 1 does not undergo any ring-opening reaction after 1 h. The cyclopropane ring in this complex is apparently reluctant to undergo ring-opening processes. In some cases, such as when the ring is activated by the presence of alkenyl substituents (compound 3), a facile ring-opening reaction occurs and cyclopentenone 4 is formed.[2] Since the cyclopropane rings in simple complexes such as 1 are somewhat robust, these complexes are potentially useful for cyclopropylcarbene-transfer processes.[3] Free cyclopropylcarbenes are often unstable and undergo ring-opening and/or ring-expansion processes,[4] but typically do not undergo cyclopropanation reactions with alkenes. Cationic cyclopropylcarbene-iron complexes undergo cyclopropanation reactions with electron-rich alkenes with no complications from opening of the cyclopropane ring.[5] As a possible complement to this method, we have investigated the reaction of cyclopropylcarbene-chromium complexes with electron-deficient alkenes.[6]

Table I. Reaction of Complex 1 with Methyl Acrylate



entry	solvent	temp, °C	additive	yield of 6, %	trans:cis 6	yield of 7
1[a]	THF	65	none	64	46:54	5
2	THF	65	none	63	48:52	9
3	THF	65	PPh_3	39	26:74	7
4	dioxane	101	none	52	48:52	7
5	dioxane	101	PPh_3	58	47:53	12

[a] Methyl acrylate was added to a refluxing solution of carbene complex 1 in THF.

If carbene complex 1 functions as a cyclopropanating reagent, donor-acceptor-substituted cyclopropanes (e.g., 5) would be provided (Scheme II). The reaction of pentacarbonyl[phenyl(methoxy)methylene]chromium with electron-deficient alkenes leads to donor-acceptor-substituted cyclopropanes in good yields.[7] Donor-acceptor-

(1) (a) Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334-3335. (b) Herndon, J. W.; Tumer, S. U. *Tetrahedron Lett.* **1989**, 295-296.

(2) Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 6854-6856.

(3) (a) Doetz, K. H.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 1273-1278. (b) Doetz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356-1367. (c) Doetz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 3966-3973. (d) Dorrer, B.; Fischer, E. O.; Kalbfus, W. *J. Organomet. Chem.* **1974**, *81*, C20-C22. (e) Cooke, M. D.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *56*, 279-284. (f) For a review, see: Brookhart, M.: Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411-432. (g) For a comparison of group 6 metal-carbenes in the cyclopropanation reaction, see: Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1990**, *31*, 2529-2532.

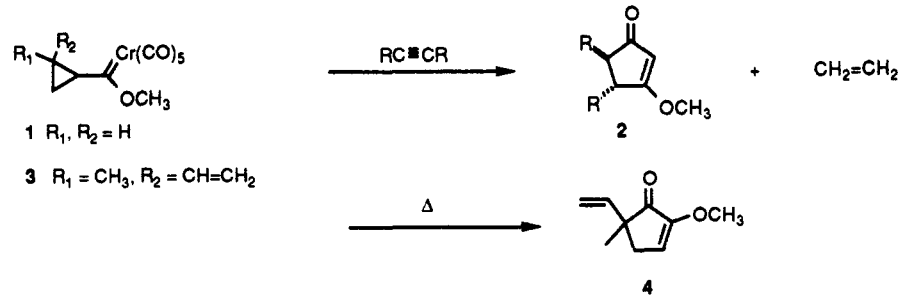
(4) Ho, G.-J.; Krogh-Jesperson, K.; Moss, R. A.; Shen, S.; Sheridan, R. S.; Subramanian, R. *J. Am. Chem. Soc.* **1989**, *111*, 6875-6877.

(5) Brookhart, M.; Studabaker, W. B.; Husk, R. G. *Organometallics* **1987**, *6*, 1141-1145.

(6) For a preliminary report of this work, see: Herndon, J. W.; Tumer, S. U. *Tetrahedron Lett.* **1989**, *30*, 4771-4774.

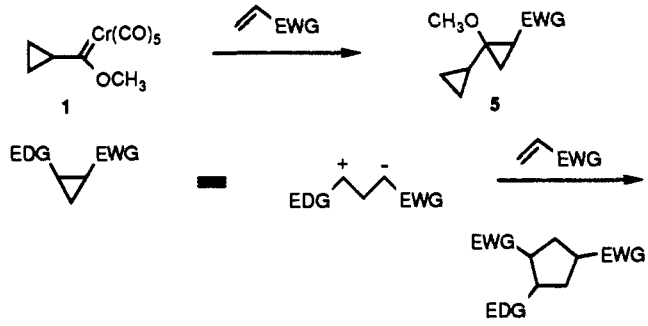
0022-3263/91/1956-0286$02.50/0

Scheme I



2 4

Scheme II



1 5

substituted cyclopropanes are synthetically useful compounds[8] and can serve as a synthon for an all-carbon 1,3-dipole. Compound **5** contains two carbocation-stabilizing substituents at the donor carbon, a methoxy and a cyclopropyl group. The presence of an additional donor substituent at this carbon might enhance the donor aspect of these compounds, and the possibility for opening of the unactivated cyclopropane ring might lead to new types of products from classical reactions of donor–acceptor-substituted cyclopropanes.

Results and Discussion

In initial studies, the reaction between cyclopropylcarbene complex **1** and methyl acrylate was investigated. Under all conditions examined (Table I), a mixture of the expected cyclopropylcyclopropanes **6-*trans*** and **6-*cis***, and the C–H insertion product **7** was obtained. The reaction of vinylcyclopropylcarbene complex **3** with methyl acrylate afforded only cyclopentenone **4** in 48% yield; apparently this ring-expansion process occurs considerably faster than the cyclopropanation reaction.

In general, the yield of **6** was slightly higher if the reaction was concluded in refluxing THF (65 °C) instead of refluxing dioxane (101 °C). The yield was not significantly affected by concentration but was slightly higher if the reaction was conducted under high-dilution conditions, achieved by syringe-pump addition of a solution of the alkene and carbene complex over a period of 2.5 h to refluxing THF. The trans:cis[9] ratio of the products was virtually 1:1 except when the reaction was conducted at 65 °C in the presence of triphenylphosphine. Treatment of cyclopropylcyclopropane **6-*trans*** or **6-*cis*** with chromium hexacarbonyl, which was a byproduct of the cyclopropanation reaction, in refluxing dioxane led to trans–cis isomerization (**6-*trans*:6-*cis*** = 48:52), but compound **7** could not be detected. There was no isomerization in the absence of chromium hexacarbonyl. The stereochemical preferences in the cycloaddition reaction itself cannot be assessed since product formation is most likely accompanied by isomerization. In one case, entry 3, the reaction leads to primarily the cis isomer. In this case, the triphenylphosphine could tie up a coordination site in the chromium(0) byproduct, preventing the trans–cis isomerization.

Plausible mechanisms for the trans–cis isomerization by chromium are outlined in Scheme III. The donor–acceptor-activated C–C bond of the cyclopropane is weak and might be susceptible to oxidative addition reactions,[10] leading to metallacyclobutane **8A**. In the mechanism in Scheme IIIA, retrometallacyclobutane formation gives intermediate carbene complex **9**, which, after rotation of the carbene ligand,[11] can then reform the metallacyclobutane with the opposite stereochemistry; this mechanism suggests that the cyclopropanation reaction is reversible. In the mechanism in Scheme IIIB, metallacyclobutane **8A** converts to the zwitterionic species **10A**, which after rotation about the C_2–C_3 bond (giving **10B**) can provide metallacyclobutane **8B**, which is the precursor to **6-*cis***. If a carbene complex such as **9** were present in the reaction, then it might be possible to exchange the alkene ligand with external ligands. Reaction of **6-*trans*** with large excesses of ethyl acrylate, diphenylacetylene, or dimethyl fumarate failed to provide any of the expected exchange products (Scheme IIIC). This result suggests that the mechanism in Scheme IIIA does not account for the cis–trans isomerization; however, the possibility that **9** converts to **8** faster than any exchange with external ligands cannot be ruled out.

The reactivity of complex **1** with a variety of alkenes was examined. As can be seen in Table II, the reaction appears to be quite general for ester-substituted alkenes. The reaction appears to be stereoselective;[12] crotonate, cinnamate, tiglate, and fumarate esters result in products that retain the stereochemistry of the original alkene substituents. In one reaction, dimethyl maleate with complex **1** (entry C), a mixture of stereoisomers was obtained: both cyclopropane **11B** and the expected cyclopropane **11C**, in which the ester groups are in the cis relationship[12b] were obtained. Maleate to fumarate isomerization occurs under the conditions of the reaction. ^{1}H NMR analysis of the

(7) (a) Wienand, A.; Reissig, H. U. *Tetrahedron Lett.* **1988**, *29*, 2315–2318. (b) Buchert, M.; Reissig, H. U. *Tetrahedron Lett.* **1988**, *29*, 2319–2320.

(8) Reissig, H. U. *Top. Curr. Chem.* **1988**, *144*, 73–136.

(9) These compounds have been designated as cis or trans to conform with IUPAC nomenclature. Thus these compounds are derivatives of bicyclopropyl, and the cis–trans designation refers to the relative stereochemistry between the ester and methoxy substituents.

(10) Doyle, M. P.; van Leusen, D. *J. Org. Chem.* **1982**, *47*, 5326–5339.

(11) Rotation about the C–Cr bond should be facile at 100 °C. Beck, H. J.; Fischer, E. O.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, *26*, C41–C44.

(12) Reactions between carbene complexes and electron-deficient alkenes have been reported to be stereoselective and to proceed through metallacyclobutane intermediates. See ref 3a,b,e. Reactions involving electron-rich alkenes are not always stereoselective and proceed via zwitterionic intermediates. (a) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908–4916. (b) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653–2655.

Scheme III

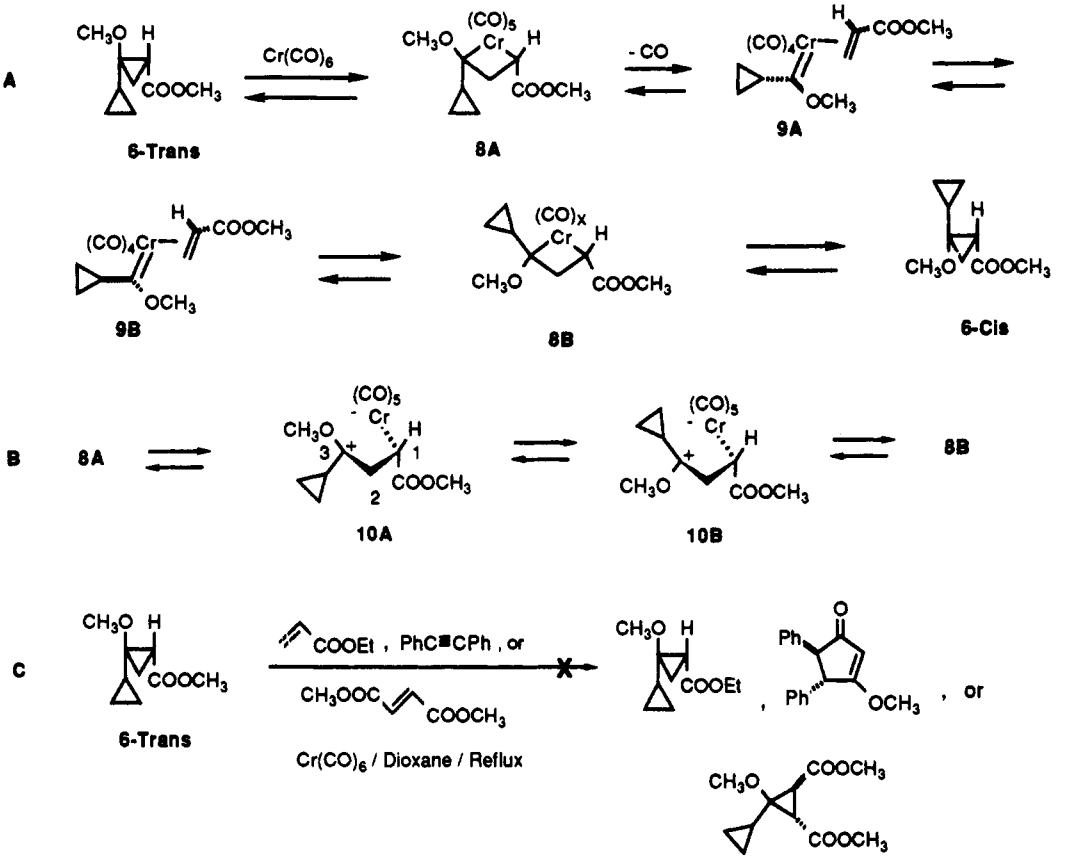
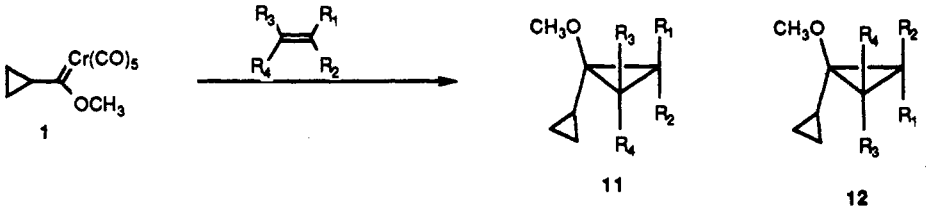


Table II. Reaction of Complex 1 with Alkenes

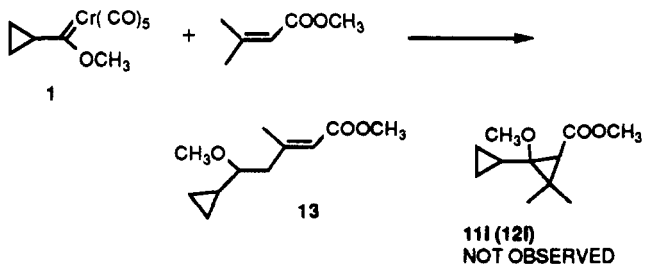


entry[a]	R_1	R_2	R_3	R_4	% yield (11 + 12)[b]	12:11
A	$COOCH_3$	H	H	H	63[c]	48:52
B	$COOCH_3$	H	H	$COOCH_3$	62[d]	
C	$COOCH_3$	H	$COOCH_3$	H	37[e]	
D	$COOCH_3$	CH_3	H	H	69	22:78
E	$COOCH_3$	H	H	CH_3	66	>95% 11[f]
F	$CON(CH_3)_2$	H	H	H	81	21:79
G	1-cyclopenten-1-yl	H	H	H	66	40:60[g]
H	$COOCH_3$	H	H	Ph	5	0:100
I	$COOCH_3$	H	CH_3	CH_3	0[h]	
J	$COOCH_3$	CH_3	H	CH_3	50	14:86

[a] Table entry letters define substituents for compounds 11 and 12. [b] The yield refers to compounds which are pure by combustion analysis and/or spectroscopic data. [c] A 9% yield of compound 7 was also obtained. [d] A 18% yield of compound 17 was also obtained. [e] A 12% yield of compound 17 was also obtained; the total yield refers to an 89:11 mixture of 11C:11B. [f] The relative stereochemistry of the methyl and carbomethoxy groups was trans. [g] The stereochemistry could not be assigned reliably; the major product has been suggested as cis by analogy with the other systems. [h] A 7% yield of C-H insertion product 13 was obtained.

mixture before completion of the reaction showed that both dimethyl maleate and dimethyl fumarate were present. Presumably this accounts for the lack of stereoselectivity in the reaction of 1 with dimethyl maleate. In addition, treatment of cyclopropylcyclopropane 11C with chromium hexacarbonyl led to isomerization to cyclopropylcyclopropane 11B. The reaction appears to be quite sensitive to steric effects since the product yields are reduced as the number of substituents on the double bond increases. Also, substituents on the β-carbon of the alkene are more detrimental to the yield than are substituents on the α-carbon. For example, the product yields are greater for the reaction of 1 with methyl tiglate (entry J) than for the corresponding reaction with methyl 3,3-dimethylacrylate (entry I). The reaction of carbene complex 1 with methyl 3,3-dimethylacrylate afforded only the allylic C-H insertion product 13 in 7% yield. The reaction of methyl cinnamate with carbene complex 1 led to a low yield of the expected cyclopropylcyclopropane (11H) accompanied by η^6-(methylcinnamate)tricarbonylchromium(0) in 5% yield.

Scheme IV



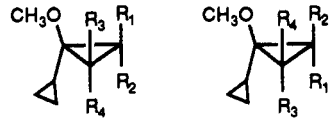
In reactions employing maleate and fumarate esters, the reduction products dimethyl succinate and compound **17**, in which both of the cyclopropane rings have been opened, were also observed. The extra hydrogens in the open-chain product **17** both came from proton sources. When the reaction between complex **1** and dimethyl fumarate was conducted in THF/D_2O, 99:1, compound **17** was obtained with deuteriums at the 2- and 7-positions. No deuterium incorporation was detected in compound **11B**, confirming that epimerization is not due to deprotonation. In the absence of the added proton source, the cyclopropylcarbene complex itself might function as the proton source since the α-hydrogen would be quite acidic.[13] Possible mechanisms for formation of **17** are outlined in Schemes V and VI. Protonolysis of the chromium–carbon bonds in intermediate **16** provides compound **17**. Treatment of cyclopropylcyclopropane **11C** with chromium hexacarbonyl leads to isomerization to **11B**, but does not provide compound **17**.

Why is compound **17** only formed in reactions involving 1,2-diesters? Perhaps this is due to the greater backbonding ability to these alkenes relative to simple α,β-unsaturated esters. In complex **14**, the fumarate would be more strongly bound to the chromium than in the analogous complex containing an acrylate ester. This slows the step involving metallacyclobutane formation and perhaps allows other processes such as cyclopropane ring opening (e.g., **14** → **18**, Scheme V) to compete. Alternatively, the formation of **17** might be a reflection of the relative stabilities of carbocation intermediates. A comparison of zwitterions **10** and **19** (Scheme VI) suggests that the carbocation portion of **19** is inductively destabilized by the presence of the carbomethoxy group. Thus the carbocation in **19** will require more electron donation by the methoxy and cyclopropyl groups, thus activating the cyclopropane with respect to ring-opening reactions. A final point of divergence involves the regiochemistry of metallacyclobutane ring formation. Recently, it has been shown that when alkynes having strongly electron-withdrawing groups react with carbene complexes, there is enhanced control of the regiochemistry by electronic effects.[14] Thus for alkenes with a single electron-withdrawing group, the predicted regiochemistry should be as shown in Scheme VII, and metallacyclobutane **20** should be the more likely intermediate in the reaction. Metallacyclobutane **15** differs from **20** in that an electron-withdrawing group is present at the chromium-containing carbon. Thus, the carbene–chromium bond is stabilized by this interaction and should be less likely to undergo reductive elimination reactions. This might then allow ring-opening processes to compete with reductive elimination to form cyclopropanes. Compound **7** provides a possible clue as to the regiochemistry of metallacyclobutane formation; C–H insertion product **7** could arise via β-hydride elimination and reductive elimination from a metallacyclobutane such as **21**, but not from **20**. Compounds such as **22** have never been reported from the reaction of chromium(0) carbene complexes and electron-deficient alkenes. Trans–cis isomerization of **6-*trans*** or **6-*cis*** and **11C** proceeds without isomerization to ring-opened products **7** and **17**, respectively, suggesting that these compounds do not arise from metallacyclobutane intermediates. We thus suggest that the different reaction pathways are due to the different ligating abilities of fumarates (maleates) vs acrylates.

Cyclopropylcyclopropanes were also obtained from the reaction of complex **1** with α,β-unsaturated amides. Complex reaction mixtures were obtained from the reaction of **1** with α,β-unsaturated ketones. Although none of the desired cyclopropanation products could be isolated from the reaction of complex **1** and methyl vinyl ketone, we were able to isolate 2,7-octanedione from the reaction in low yield. The reaction appears to be restricted to activated alkenes since norbornene, a highly strained alkene which complexes readily to metals,[15] and styrene both fail to react with complex **1**. Interestingly, 1-vinylcyclopentene couples readily with carbene complex **1**, giving the bicyclopropane **11(12)G** in 66% yield. Previously only electron-deficient[7b] and highly electron-rich dienes were reported to couple with chromium–carbene complexes.[12b] We are currently examining the generality of the reaction of chromium carbene complexes with simple 1,3-dienes.

Stereochemical assignments were made on the basis of NOE studies or through the use of chemical shift additivity predictions established by Reissig[16] (Table III). In compound **11C** there is an 11% enhancement of the signals

Table III. Chemical Shifts for Protons on the Donor–Acceptor-Substituted Cyclopropane Rings

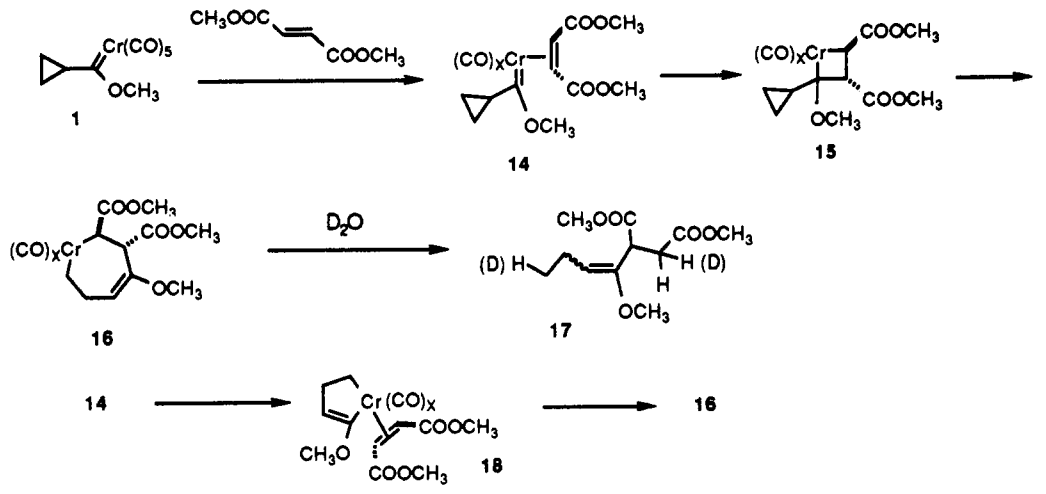


compd no.	R_1	R_2 (δ)	R_3 (δ)	R_4 (δ)
6-*cis* (**11A**)	$COOCH_3$	H (1.46)	H (1.63)	H (0.81)
6-*trans* (**12A**)	$COOCH_3$	H (1.97)	H (1.15)	H (1.15)
11B	$COOCH_3$	H (2.33)	H (2.72)	$COOCH_3$
11C	$COOCH_3$	H (1.83)	$COOCH_3$	H (1.83)
11D[a]	$COOCH_3$	CH_3	H (1.63)	H (0.45)
12D	$COOCH_3$	CH_3	H (1.26)	H (0.64)
11E[b]	$COOCH_3$	H (1.16)	H (1.89)	CH_3
11F	$CON(CH_3)_2$	H (1.43)	H (1.66)	H (0.49)
12F	$CON(CH_3)_2$	H (1.98)	H (1.07)	H (1.07)
11H[c]	$COOCH_3$	H (2.06)	H (3.25)	C_6H_5
11J	$COOCH_3$	CH_3	H (2.12)	CH_3
12J	$COOCH_3$	CH_3	H (1.51)	CH_3

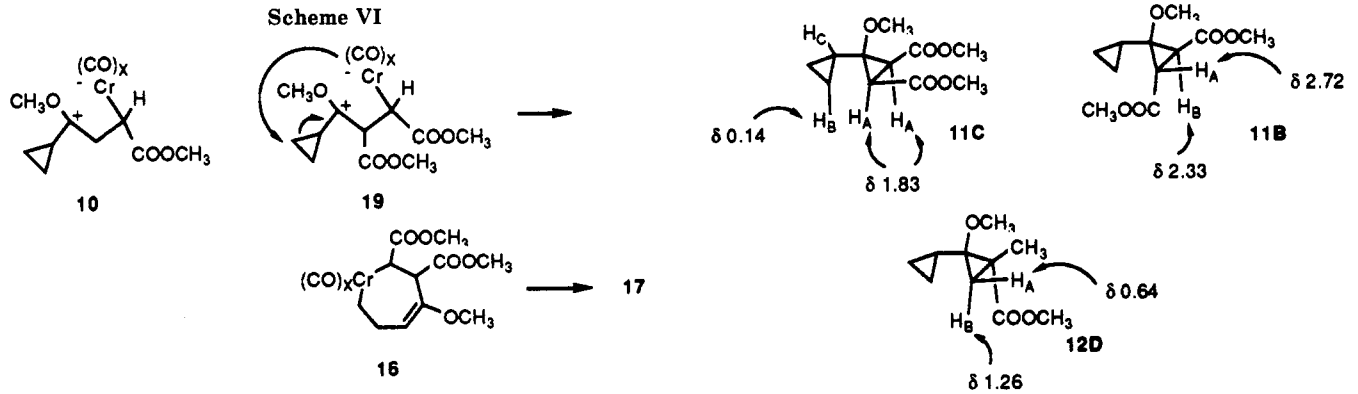
[a] An exact assignment between R_3 and R_4 cannot be made. The chemical shift difference between these protons should be greater in **11D** (1.18 ppm) than in **12D** (0.62 ppm). [b] Only this isomer was obtained; the unusually low chemical shift for R_2 is consistent only with the cis isomer (**11E**) (compare with the same proton in **6-*cis*** and **11F**). [c] Only this isomer was obtained; the stereochemistry has been suggested as cis by analogy to the reaction in Table II, entry E.

(13) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947–8948.
(14) Brandvold, T. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 645–647.
(15) For example, norbornene is one of only a few alkenes which participate efficiently in the intermolecular Pauson-Khand cyclization. Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. E. *J. Chem. Soc., Perkin Trans. 1*, **1973**, 977–981.
(16) (a) Reichelt, I.; Reissig, H. U. *Chem. Ber* **1983**, *116*, 3895–3914. (b) Kunkel, E.; Reichelt, I.; Reissig, H. U. *Liebigs Ann. Chem.* **1984**, 512–530.

Scheme V



Scheme VI

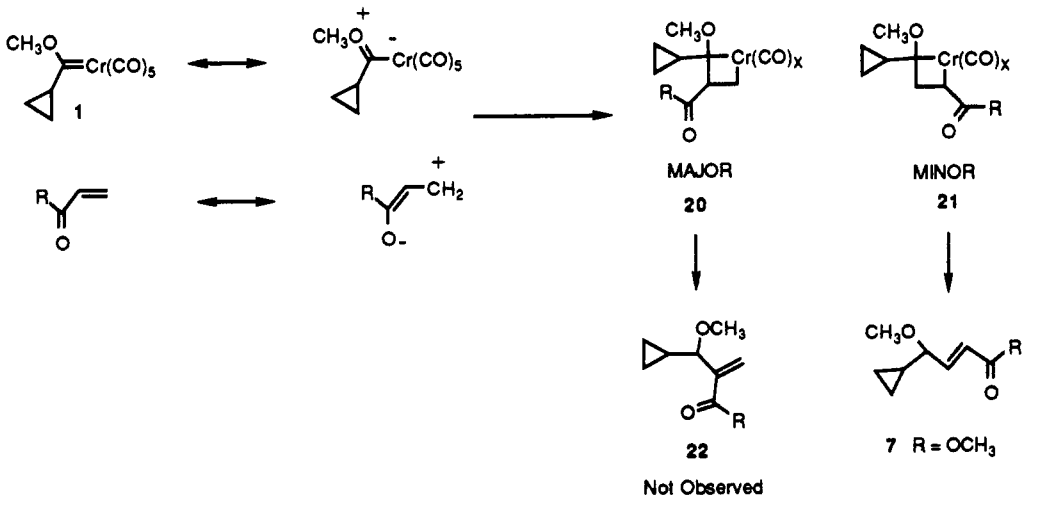


at δ 0.14 (H_B) when the signal at δ 1.83 (H_A) was irradiated (Figure 1). A comparison of compound **11C** and **11B** reveals an application of these rules, where alkoxy groups and carbonyl groups induce a strong downfield shift to a proton cis on the cyclopropane ring, while alkyl groups induce an upfield shift for a cis proton. In **11C**, the chemical shift of H_A is δ 1.83; this proton is not cis to the methoxy or the ester group. In compound **11B**, the analogous protons, H_A and H_B, exhibit higher chemical shifts since each is cis either to a carbomethoxy group and/or a methoxy group. Interestingly, there is a strong NOE interaction between protons H_A and H_B in **11C**, but no detectable NOE between H_A and H_C. This suggests that compound **11C** exists predominately in the conformation depicted in Figure 1. Similarly, the NOESY

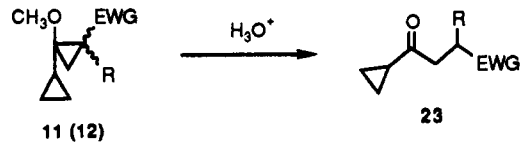
Figure 1. Stereochemical determination for **11C**, **11B**, and **12D**.

spectrum for compound **12** shows NOE interactions between H_A and methoxy and between H_B and carbomethoxy, which is consistent with the stereochemical assignment determined from chemical shift effects. A greater chemical shift difference is predicted between H_A and H_B in **11D** ($\Delta\delta$ = 1.18) than in **12D** ($\Delta\delta$ = 0.62). A similar application of these rules has been used for other structures in this paper. As can be seen in Table III, in all cases where R_2 and R_4 = H, the chemical shift is higher in compound **12** than in compound **11** (R_1 is the carbonyl group). In compound **12** these protons are always cis to methoxy, whereas they are cis neither to methoxy nor carbomethoxy in **11**. In cases where R_3 = H, the chemical

Scheme VII



Scheme VIII



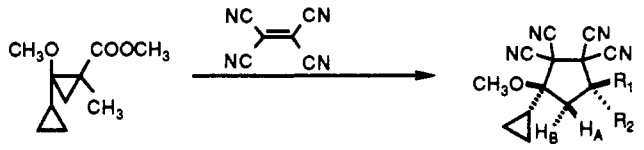
11 (12) 23

A. EWG = $CON(CH_3)_2$, R = H: 100%

B. EWG = $COOCH_3$, R = H: 93%

C. EWG = $COOCH_3$, R = CH_3: 88%

Scheme IX



11D (12D) 24

A. $R_1 = COOCH_3$, $R_2 = CH_3$

B. $R_1 = CH_3$, $R_2 = COOCH_3$

shift is higher in compound **11** than in compound **12**. In compound **11**, this proton is cis to methoxy and carbomethoxy, while it is cis only to carbomethoxy in compound **12**.

Reactions of Cyclopropylcyclopropanes. The reactivity of donor–acceptor-substituted cyclopropanes has recently been reviewed.[8] As predicted,[17] the cyclopropanes **11** and **12** are very susceptible to acid-catalyzed hydrolysis reactions, which give the compounds shown in Scheme VIII. In this reaction, only the donor–acceptor-activated cyclopropane opens, while the unactivated cyclopropane ring is untouched. The product of the reaction is a 1,4-dicarbonyl compound. Thus carbene complex **1** can be viewed as a synthon for the cyclopropylcarbonyl anion. The cyclopropyl ketone functionality is further susceptible to a variety of synthetically useful transformations.[18]

Donor–acceptor-substituted cyclopropanes have been reported to undergo [3 + 2] cycloaddition reactions with some electron-deficient alkenes.[8,19] Compound **11D** reacts with the electron-deficient alkene tetracyanoethylene in acetonitrile to give the five-membered ring containing compounds **24A** and **24B** as a 72:28 mixture (Scheme IX). This is presumably a stepwise reaction, and both of the cyclopropane stereosiomers give identical ratios of the five-membered ring adducts. The minor stereoisomer obtained was the one depicted by structure **24A**. In this compound the methyl and cyclopropyl substituents are on the same side; since these substituents produce a strong upfield shift for cis hydrogens vicinal on the cyclopentane ring,[20] a greater difference in the chemical shifts of H_A and H_B would be predicted. In the major isomer these shifts are δ 2.46 and 1.86 ($\Delta\delta$ = 0.60), and in the minor isomer these are δ 3.14 and 1.43 ($\Delta\delta$ = 1.71). In this conversion as well, there is no complication from a ring-opening reaction of the unactivated cyclopropane ring. Less electrophilic alkenes such as dimethyl fumarate did not undergo this conversion.

Conclusions

The reaction of cyclopropylcarbene–chromium complexes and electron-deficient alkenes provides cyclopropylcyclopropanes in good yield. The reaction proceeds readily for ester and amide-substituted alkenes, and in one case for an electroneutral 1,3-diene, but is quite sensitive to steric effects. More highly activated alkenes such as methyl vinyl ketone enter into other reaction pathways and do not give cyclopropanation products. The products of the reaction participate in the standard reactions of donor–acceptor-substituted cyclopropanes with no complications from ring opening of the original cyclopropane ring.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on 200- or 400-MHz spectrometers. Mass spectra (MS) were obtained using electron ionization or chemical ionization. Flash column chromatography was performed using thick-walled glass columns and "flash grade" silica (American scientific products 230–400 mesh). Preparative thin-layer chromatography was performed using precoated 1.0-mm 20 × 20 silica gel plates purchased from Analtech. Routine thin-layer chromatography was done using precoated 0.25-mm silica gel plates purchased from Whatman. The relative ratios in mixed chromatography solvents refers to the volume:volume ratio. All reactions were performed in an inert atmosphere created by a slight positive pressure (ca. 0.1 psi) of nitrogen.

Cyclopropyl bromide,[21] methyl 3,3-dimethylacrylate,[22] methyl tiglate,[22] 1-vinylcyclopentene,[23] and cyclopropyl(methoxy)-methylenepentacarbonylchromium(0) (complex 1)[24] were prepared according to known procedures. Methyl acrylate, methyl methacrylate, 3,3-dimethylacrylic acid, tiglic acid, methyl cinnamate, methyl crotonate, methyl vinyl ketone, *N,N*-dimethylacrylamide, styrene, methyl vinyl ketone, dimethyl maleate, dimethyl fumarate, and tetracyanoethylene were purchased from Aldrich Chemical Company and were used without further purification. Tetrahydrofuran (THF), diethyl ether, and 1,4-dioxane were distilled from sodium/benzophenone ketyl. Acetonitrile was distilled from calcium hydride before use. All other commercially available reagents and reactants were obtained as reagent grade and used without further purification.

General Procedure for the Reaction of Carbene Complexes with Alkenes. A. Complex 1 (0.276 g, 1.00 mmol) and alkene (2.0 mmol) were dissolved in THF (20 mL). This solution was added dropwise via syringe pump over a period of 5 h to refluxing THF (100 mL) under nitrogen. **B.** Complex 1 (0.276 g, 1.00 mmol) was dissolved in THF (100 mL) and heated to reflux under nitrogen while a solution of alkene (2.00 mmol) in THF (10–15 mL) was added dropwise over a period of 3–5 h.

Following either procedure A or procedure B, the solution was refluxed for an additional 12 h after the addition was complete, and the solvent was removed on a rotary evaporator. The residue after evaporation was then dissolved in ethyl acetate (10 mL), and the resulting suspension was filtered through Celite. The solvent was removed on a rotary evaporator, and the residue after evaporation was treated as outlined in subsequent sections.

Reaction of Complex 1 with Methyl Acrylate (Table II, Entry A). General procedure A was followed using complex 1 (0.828 g, 3.00 mmol) and methyl acrylate (0.54 mL, 6.00 mmol). The residue after evaporation was distilled (Kugelrohr, 25–55 °C, 0.025 mmHg). The distillate was subjected to flash chromatography (silica gel, 9:1 hexane–ethyl acetate). The product in the

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first fraction (R_f 0.53 in 4:1 hexane–ethyl acetate) was identified as methyl *trans*-1-methoxy-[1,1′-bicyclopropyl]-2-carboxylate (**6-*trans***) (0.155 g, 30%). The product in the second fraction (R_f 0.51 in 4:1 hexane–ethyl acetate) was identified as methyl 4-cyclopropyl-4-methoxy-2-butenoate (**7**) (0.047 g, 9%). The product in the third fraction (R_f 0.38 in 4:1 hexane–ethyl acetate) was identified as methyl *cis*-1-methoxy-[1,1′-bicyclopropyl]-2-carboxylate (**6-*cis***) (0.166 g, 33%).

6-*trans*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.67 (s, 3 H), 3.36 (s, 3 H), 1.97 (dd, 1 H, J = 7.3, 8.9 Hz), 1.09–1.23 (m, 3 H), 0.43–0.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 171.3, 69.4, 54.5, 51.6, 28.2, 18.7, 9.8, 5.8, 3.2; IR ($CDCl_3$) 3110 (w), 3012 (w), 2954 (m), 2840 (w), 1728 (vs), 1439 (m), 1374 (m), 1224 (m), 1195 (m), 1170 (m), 1156 (s), 1069 (m), 1040 (w) cm^{-1}; MS (CI) m/z 171 (M + 1), 139, 112, 99, 95, 85, 81, 79, 71, 69 (100); HRMS (EI) calcd for $C_9H_{14}O_3$ 170.0943, found 170.0939.

6-*cis*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.68 (s, 3 H), 3.33 (s, 3 H), 1.63 (dd, 1 H, J = 6.6, 8.6 Hz), 1.35–1.51 (m, 2 H), 0.81 (dd, 1H, J = 5.8, 8.6 Hz), 0.44–0.59 (m, 2 H), 0.25 (m, 1 H), 0.07 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 170.3, 69.2, 55.2, 51.6, 26.0, 16.4, 13.4, 3.1, 2.8; IR ($CDCl_3$) 3087 (w), 3012 (m), 2954 (m), 2833 (w), 1733 (vs), 1440 (m), 1396 (w), 1366 (w), 1354 (w), 1288 (m), 1223 (m), 1197 (m), 1170 (s), 1066 (m), 1026 (w) cm^{-1}; MS (EI) m/z 170 (M$^+$), 155, 139, 127, 123, 111 (100), 95, 81, 79, 69. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.28; H, 7.99.

7: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.87 (dd, 1 H, J = 6.2, 15.8 Hz), 5.97 (dd, 1 H, J = 1.2, 15.8 Hz), 3.73 (s, 3 H), 3.33 (s, 3 H), 3.12 (ddd, 1 H, J = 1.2, 6.2, 7.7 Hz), 0.91 (m, 1 H), 0.37–0.70 (m, 3 H), 0.22 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 166.7, 147.3, 121.2, 83.9, 56.8, 51.5, 14.6, 4.0, 1.2; IR ($CDCl_3$) 3088 (w), 3009 (w), 2953 (m), 2874 (w), 1722 (vs), 1438 (m), 1306 (s), 1282 (s), 1254 (m), 1195 (m), 1173 (m), 1082 (m), 1060 (w) cm^{-1}; MS (EI) m/z 170 (M$^+$), 142, 134, 130, 123, 111 (100) 95, 91, 79, 77; HRMS (EI) calcd for $C_9H_{14}O_3$ 170.0943, found 170.0939.

Reaction of Complex 1 with Dimethyl Fumarate (Table II, Entry B). A solution of cyclopropylcarbene complex **1** (0.276 g, 1.00 mmol) in 1,4-dioxane (100 mL) was heated to reflux while a solution of dimethyl fumarate (0.288 g, 2.00 mmol) in 1,4-dioxane (10 mL) was added to the refluxing solution over a 2-h period. After the addition was complete, the reaction was refluxed an additional 4 h. The solvent was then removed on a rotary evaporator. The residue after evaporation was diluted with 4:1 hexane–ethyl acetate (20 mL) and filtered through Celite. This solution was subjected to flash chromatography (silica gel, 19:1 hexane–ethyl acetate). The product in the first fraction (R_f 0.45 in 4:1 hexane–ethyl acetate) was assigned as methyl 3-carbomethoxy-4-methoxy-4-heptenoate (**17**) (0.041 g, 18%). The product in the second fraction (R_f 0.42 in 4:1 hexane–ethyl acetate) was concentrated and placed under vacuum (0.04 mmHg) for 2 h to remove the dimethyl succinate impurity to give dimethyl 1α-methoxy-[1,1′-bicyclopropyl]-2α,3β-dicarboxylate (**11B**) (0.142 g, 62%) as colorless crystals, mp 81–82 °C (sublimed at 60 °C and 0.025 mmHg).

17: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (t, 1 H, J = 7.2 Hz), 3.71 (s, 3 H), 3.66 (s, 3 H), 3.58 (s, 3 H, overlapping with m, 1 H), 2.93 (dd, 1 H, J = 9.5, 16.8 Hz), 2.59 (dd, 1 H, J = 5.5, 16.8 Hz), 2.09 (quintet, 2 H, J = 7.4 Hz), 0.93 (t, 3 H, J = 7.5 Hz); irradiation at 3.59 resulted in 2.93 (d, J = 16.8 Hz), 2.59 (d, J = 16.8 Hz); ^{13}C NMR ($CDCl_3$) δ 172.4, 172.0, 151.8, 116.2, 59.1, 52.1, 51.6, 45.5, 34.9, 18.6, 14.1; IR ($CDCl_3$) 3001 (w), 2967 (m), 2955 (m), 2936 (m), 2876 (w), 2846 (w), 1736 (vs), 1673 (m), 1438 (s), 1342 (m), 1266 (m), 1230 (m), 1199 (m), 1165 (s), 1075 (w), 1053 (w), 1007 (w); MS (EI) m/z (relative intensity) 230 (M$^+$), 170, 155, 125, 111, 95, 79, 69, 59, 55 (100); HRMS (EI) calcd for $C_{11}H_{18}O_5$ 230.1154, found 230.1160. Compound **17** was contaminated with a minor alkene stereoisomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.50 (t, 1 H, J = 7.3 Hz), 3.99 (dd, 1 H, J = 5.7, 8.9 Hz), 3.68 (s, 3 H), 3.66 (s, 3 H), 3.44 (s, 3 H), 3.04 (dd, 1 H, J = 8.9, 16.9 Hz), 2.48 (dd, 1 H, J = 5.7, 16.9 Hz), 2.09 and 2.08 (two quintets, 2 H, J = 7.5 Hz), 1.00 (t, 3 H, J = 7.5 Hz).

11B: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.68 (s, 3 H), 3.66 (s, 3 H), 3.35 (s, 3 H), 2.72 (d, 1 H, J = 6.8 Hz), 2.33 (d, 1 H, J = 6.8 Hz), 1.16 (m, 1 H), 0.50–0.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 169.0, 167.8, 72.1, 55.7, 51.9, 51.8, 33.1, 32.7, 10.7, 4.8 3.4; IR ($CDCl_3$) 3005 (w), 2955 (m), 2836 (w), 1729 (vs), 1438 (s), 1319 (m), 1283 (w), 1259 (w), 1195 (m), 1169 (m), 1065 (w), 1031 (w) cm^{-1}; MS (CI) m/z (relative intensity) 229 (M + 1, 100), 207, 197, 169, 165, 137, 109, 85, 71, 69. Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.89; H, 7.06. Found: C, 57.79; H, 7.15.

Reaction of Complex 1 with Dimethyl Fumarate in the Presence of D_2O. To a solution of D_2O (1 mL) in THF (100 mL) at 100 °C was added a solution of complex **1** (0.276 g, 1.00 mmol) and dimethyl fumarate (0.288 g, 2.00 mmol) in THF (20 mL) over a period of 2 h. The above procedure was then followed to obtain the open-chain product methyl 3-carbomethoxy-2,7-dideuterio-4-methoxy-4-heptenoate (**17-d_2**) and cyclopropanation product **11B**. The ^{1}H NMR spectrum for cyclopropanation product **11B** was identical with that reported in the previous experiment. Compound **17** showed labeling in the 2- and 7-positions: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.72 (t, 1 H, J = 7.2 Hz), 3.71 (s, 3 H), 3.66 (s, 3 H), 3.57 (s, 3 H, overlapping with m, 1 H), 2.90 (br d, 0.5 H, J = 9.4 Hz), 2.57 (br td, 0.5 H, J = 2.8, 5.5 Hz), 2.08 (br q, 2 H, J = 7.3 Hz), 0.91 (m, 2.4 H).

Reaction of Complex 1 with Dimethyl Maleate (Table II, Entry C). General procedure B was followed using complex **1** (0.276 g, 1.00 mmol) and dimethyl maleate (0.5 mL, 4.00 mmol). The residue after evaporation was dissolved in 3:2 hexane–ethyl acetate (20 mL) and filtered through silica gel. Final purification was achieved by flash chromatography (silica gel, 4:1, then 3:2 hexane–ethyl acetate). The product in the first fraction collected was identified as compound **17** (0.027 g, 12%). The product in the second fraction was identified as cyclopropylcyclopropane **11B** (0.009 g, 4%). The product in the third fraction (R_f 0.40 in 3:2 hexane–ethyl acetate) was identified as dimethyl 1α-methoxy-[1,1′-bicyclopropyl]-2α,3α-dicarboxylate (**11C**) (0.075 g, 33%).

11C: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.64 (s, 6 H), 3.44 (s, 3 H), 1.83 (s, 2 H), 1.44 (m, 1 H), 0.56 (m, 2 H), 0.14 (m, 2 H); irradiation at δ 1.83 ppm resulted in 11% NOE enhancement at 0.14 ppm multiplet; ^{13}C NMR ($CDCl_3$) δ 166.9, 69.1, 55.6, 51.7, 28.4, 13.2, 3.1; IR ($CDCl_3$) 3087 (w), 3007 (w), 2954 (m), 2841 (w), 1743 (vs), 1439 (s), 1351 (m), 1264 (m), 1226 (m), 1198 (m), 1156 (s), 1058 (m), 1023 (m) cm^{-1}; MS (CI) m/z (relative intensity) 229 (M + 1), 197, 169 (100), 137, 109, 86, 84, 77, 69, 59. Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.89; H, 7.06. Found: C, 57.61; H, 6.92.

Reaction of Complex 1 with Methyl Methacrylate (Table II, Entry D). General procedure A was followed using complex **1** (0.276 g, 1.00 mmol) and methyl methacrylate (0.200 g, 2.00 mmol). The residue after evaporation was distilled (Kugelrohr, 25–45 °C, 0.025 mmHg). The distillate was purified by flash chromatography (silica gel, 9:1 hexane–ethyl acetate). The product in the first fraction (R_f 0.59 in 4:1 hexane–ethyl acetate) was identified as methyl 1α-methoxy-2α-methyl-[1,1′-bicyclopropyl]-2β-carboxylate (**12D**) (0.028 g, 15%). The product in the second fraction (R_f 0.51 in 4:1 hexane–ethyl acetate) was identified as methyl 1α-methoxy-2β-methyl-[1,1′-bicyclopropyl]-2α-carboxylate (**11D**) (0.099 g, 54%).

12D: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 3 H), 3.35 (s, 3 H), 1.38 (s, 3 H), 1.26 (d, 1 H, J = 5.9 Hz), 1.09 (m, 1 H), 0.64 (d, 1 H, J = 5.9 Hz), 0.42-0.61 (m, 3 H), 0.33 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 173.3, 70.2, 54.6, 51.5, 32.8, 22.4, 15.4, 10.7, 5.6, 3.2; IR ($CDCl_3$) 3090 (w), 3008 (m), 2953 (m), 2833 (w), 1720 (vs), 1461 (m), 1436 (s), 1320 (s), 1303 (s), 1210 (s), 1197 (s), 1154 (s), 1135 (vs), 1086 (m), 1040 (m) cm^{-1}; MS (EI) m/z (relative intensity) 184 (M$^+$), 137, 129, 111, 91, 87, 83, 74 (100), 69, 59; HRMS (EI) calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1095.

11D: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.67 (s, 3 H), 3.25 (s, 3 H), 1.63 (d, 1 H, J = 6.0 Hz), 1.34 (s, 3 H), 1.22 (m, 1 H), 0.47–0.75 (m, 3 H), 0.45 (d, 1 H, J = 6.0 Hz), 0.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 172.2, 70.7, 54.4, 51.5, 32.0, 21.3, 16.3, 10.6, 4.7, 3.1; IR ($CDCl_3$) 3088 (w), 3011 (m), 2953 (m), 2832 (w), 1721 (vs), 1462 (m), 1437 (s), 1336 (m), 1316 (m), 1296 (s), 1232 (m), 1197 (s), 1184 (m), 1146 (vs), 1072 (m), 1041 (m) cm^{-1}; MS (CI) m/z (relative intensity) 185 (M + 1, 100), 169, 153, 141, 137, 125, 109, 97, 93, 69. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.07; H, 8.60.

Reaction of Complex 1 with Methyl *trans*-Crotonate (Table II, Entry E). General procedure B was followed using complex **1** (0.276 g, 1.00 mmol) and methyl crotonate (0.200 g, 2.00 mmol). The residue after evaporation was distilled (Kugelrohr, 25–60 °C, 0.025 mmHg). The distillate was purified by flash chromaatography (silica gel, 85:15 hexane–ethyl acetate). The fraction collected (R_f 0.47 in ($CDCl_3$) was distilled (Kugelrohr,, 25–45 °C, 0.025 mmHg) to give methyl 1α-methoxy-3β-methyl-

[1,1'-bicyclopropyl]-2α-carboxylate (**11E**) (0.121 g, 66%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.57 (s, 3 H), 3.23 (s, 3 H), 1.89 (quintet, 1 H, J = 6.5 Hz), 1.16 (d, 1 H, J = 6.3 Hz), 1.07 (d, J = 6.6 Hz) overlaps with 1.08 (m, 4 H), 0.40–0.70 (m, 3 H), 0.19 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 170.3, 72.2, 55.0, 51.4, 31.3, 26.4, 12.5, 10.2, 3.4, 3.3; IR ($CDCl_3$) 3088 (w), 3001 (m), 2953 (m), 2937 (m), 2835 (w), 1729 (vs), 1440 (s), 1319 (s), 1282 (m), 1266 (m), 1195 (s), 1169 (vs) 1068 (m) cm^{-1}; MS (EI) m/z (relative intensity) 184 (M^+), 169, 153, 141, 125 (100), 109, 93, 77, 69, 59. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.92; H, 8.88.

Reaction of Complex 1 with *N,N*-Dimethylacrylamide (Table II, Entry F). General procedure B was followed using *N,N*-dimethylacrylamide (0.198 g, 2.00 mmol) and complex 1 (0.276 g, 1.00 mmol). The residue after evaporation was purified by chromatography (silica gel, 9:1 ethyl acetate–hexane). The product in the first fraction (R_f 0.30 in ethyl acetate) was assigned as *N,N*-dimethyl-*trans*-1-methoxy-[1,1'-bicyclopropyl]-2-carboxamide (**12F**) (0.032 g, 17%). The product in the second fraction (R_f 0.28 in ethyl acetate) was assigned as *N,N*-dimethyl-*cis*-1-methoxy-[1,1'-bicyclopropyl]-2-carboxamide (**11F**) (0.118 g, 64%). Compound **11F** was further purified by distillation (Kugelrohr, 70–80 °C, 0.15 mmHg).

12F: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.32 (s, 3 H), 3.14 (s, 3 H), 2.92 (s, 3 H), 1.98 (dd, 1 H, J = 6.7, 9.8 Hz), 0.89–1.11 (m, 3 H), 0.52 (m, 1 H), 0.16–0.42 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.0, 67.7, 54.4, 37.3, 35.4, 29.3, 14.2, 9.9, 3.1, 2.6; IR ($CDCl_3$) 3085 (w), 3011 (m), 2936 (m), 2831 (w), 1633 (vs), 1498 (m), 1447 (m), 1413 (m), 1402 (s), 1204 (m), 1260 (w), 1161 (m), 1081 (w), 1060 (m), 1030 (w) cm^{-1}; MS (CI) m/z (relative intensity) 184 (M + 1), 170, 154, 127, 113, 95, 85, 81, 71, 69 (100). Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35. Found: C, 65.50; H, 9.07.

11F: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.21 (s, 3 H), 3.02 (s, 3 H), 2.86 (s, 3 H), 1.66 (dd, 1 H, J = 6.7, 8.9 Hz), 1.18–1.36 (m, 2 H), 0.45–0.60 (m, 2 H), 0.23–0.42 (m, 2 H), –0.13 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 168.1, 67.2, 55.1 36.9, 35.3, 28.1 13.3, 12.2, 3.7, 1.2; IR ($CDCl_3$) 3087 (w), 3011 (m), 2936 (m), 2832 (m), 1636 (vs), 1498 (m), 1449 (m), 1412 (s), 1403 (s), 1275 (w), 1258 (w), 1217 (m), 1152 (m), 1062 (s), 1022 (w) cm^{-1}; MS (CI) m/z (relative intensity) 184 (M + 1, 100), 168, 152, 139, 123, 111, 100, 89, 72, 69; HRMS (CI) calcd for $C_{10}H_{18}NO_2$ 184.1338, found 184.1344.

Reaction of Complex 1 with 1-Vinylcyclopentene (Table II, Entry G). General procedure A was followed using complex 1 (0.276 g, 1.00 mmol) and 1-vinylcyclopentene[19] (0.188 g, 2.00 mmol). The residue after evaporation was subjected to flash chromatography (silica gel, 19:1 hexane–ethyl acetate). The fraction with R_f 0.60 (in 9:1 hexane–ethyl acetate) was collected and distilled (Kugelrohr 25–50 °C, 0.025 mmHg) to give *cis*- and *trans*-1-methoxy-2-cyclopenten-1-yl-[1,1'-bicyclopropyl] (**11G** and **12G**) (0.117 g, 66%) as a 60:40 cis:trans mixture as calculated from ^{1}H NMR. These compounds were not completely separable, but analytical samples for the two isomers were obtained through preparative TLC (9:1 hexane–ethyl acetate) where the major isomer was collected at R_f 0.62 and minor isomer at R_f 0.58.

Major Isomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.46 (m, 1 ($CDCl_3$) 3 H), 2.20–2.37 (m, 4 H), 1.75–1.91 (m, 2 H), 1.30–1.46 (m, 2 H), 0.80 (dd, 1 H, J = 5.6, 7.1 Hz), 0.38–0.62 (m, 3 H), 0.23 (m, 1 H), 0.03 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 141.2, 124.8, 67.5, 54.6, 35.2, 32.5, 24.4, 24.4, 23.5, 14.9, 13.2, 2.8, 2.6; IR ($CDCl_3$) 3084 (w), 3008 (m), 2953 (s), 2935 (s), 2897 (m), 2847 (s), 1445 (m), 1273 (w), 1223 (m), 1160 (w), 1062 (vs), 1041 (m), 1023 (m) cm^{-1}; MS (EI) m/z (relative intensity) 178 (M^+), 163, 149, 135, 121, 105, 91, 79, 77, 69 (100); HRMS (EI) calcd for $C_{12}H_{18}O$ 178.1358, found 178.1358.

Minor Isomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.26 (m, 1 H), 3.33 (s, 3 H), 2.22–2.36 (m, 4 H), 1.77–1.92 (m, 2 H), 1.68 (m, 1 H), 1.09 (m, 1 H), 0.88 (ddd, 1 H, J = 0.7, 5.5, 10.2 Hz), 0.37–0.62 (m, 4 H), 0.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) (INEPT) δ 141.9 (0), 125.1 (+), 67.5 (0), 54.1 (+), 35.8 (–), 32.4 (–), 26.6 (+), 23.8 (–), 16.2 (–), 10.0 (+), 5.0 (–), 3.0 (–); IR ($CDCl_3$) 3086 (w), 3008 (m), 2988 (m), 2951 (s), 2935 (s), 2896 (m), 2846 (s), 1605 (w), 1445 (m), 1290 (w), 1208 (s), 1159 (s), 1082 (m), 1055 (s), 1024 (m) cm^{-1}; MS (EI) m/z (relative intensity) 178 (M^+), 163, 149, 134, 121, 105, 91, 79, 77, 69 (100); HRMS (EI) calcd for $C_{12}H_{18}O$ 178.1358, found 178.1358.

Reaction of Complex 1 with Methyl Cinnamate (Table II, Entry H). To a solution of complex 1 (0.276 g, 1.00 mmol) in 1,4-dioxane (50 mL) at reflux was added a solution of methyl *trans*-cinnamate (0.324 g, 2.00 mmol) in 1,4-dioxane (10 mL) over a period of 5 h. After the addition was complete, the reaction mixture was refluxed for an additional 20 h. The mixture was cooled to 25 °C, and the solvent was removed on a rotary evaporator. The residue was dissolved in ethyl acetate (20 mL) and filtered through Celite. The solvent was removed on rotary evaporator, and the residue was subjected to flash chromatography (silica gel, 9:1 hexane–ethyl acetate). The product in the first fraction was the starting ester. The product in the second fraction (R_f 0.48 in 4:1 hexane–ethyl acetate) was assigned as methyl 1α-methoxy-3β-phenyl-[1,1'-bicyclopropyl]-2α-carboxylate (**11H**) (0.12 g, 5%). The orange product in the third fraction (R_f 0.20 in 4:1 hexane–ethyl acetate) was identified as tricarbonyl(η^6-(methyl cinnamate))chromium (0.014 g, 5%).

11H: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.16–7.33 (m, 5 H), 3.72 (s, 3 H), 3.44 (s, 3 H), 3.25 (d, 1 H, J = 6.9 Hz), 2.06 (d, 1 H, J = 6.9 Hz), 0.87 (m, 1 H), 0.49–0.62 (m, 2 H), 0.06–0.34 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 169.8, 136.1, 128.6, 128.3, 126.6, 72.6, 55.6, 51.8, 36.6, 31.5, 11.4, 4.3, 3.8; IR ($CDCl_3$) 3089 (w), 3007 (m), 2954 (m), 2832 (w), 1733 (vs), 1605 (w), 1440 (m), 1305 (w), 1272 (m), 1250 (s), 1216 (m), 1197 (m), 1167 (s), 1070 (w), 1051 (m), 1028 (w) cm^{-1}; MS (CI) m/z (relative intensity) 247 (M + 1), 215, 187 (100), 155, 131, 115, 103, 91, 77, 69; HRMS (CI) calcd for $C_{15}H_{19}O_3$ 247.1334, found 247.1338.

Chromium complex: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.73 (d, 1 H, J = 15.6 Hz), 5.77 (d, 1 H, J = 15.6 Hz), 4.81–5.09 (m, 5 H), 3.32 (s, 3 H); IR ($CDCl_3$) 2954 (w), 1979 (vs), 1907 (vs), 1720 (m), 1638 (w), 1438 (w), 1320 (m), 1284 (w), 1205 (m), 1177 (m) cm^{-1}.

Reaction of Complex 1 with Methyl 3,3-Dimethylacrylate (Table II, Entry I). General procedure A was followed using complex 1 (0.276 g, 1.00 mmol) and methyl 3,3-dimethylacrylate[20] (0.228 g, 2.00 mmol); in this case, the reflux was continued for 24 h. The residue after evaporation was subjected to flash chromatography (silica gel, 19:1 hexane–ethyl acetate). Only one fraction was isolated (R_f 0.47 in 9:1 hexane–ethyl acetate), which was identified as methyl 5-cyclopropyl-5-methoxy-3-methyl-2-pentenoate (**13**) (0.014 g, 7%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.70 (br s, 1 H), 3.64 (s, 3 H), 3.37 (s, 3 H), 2.71–2.92 (ABX pattern, 3 H), 1.96 (d, 3 H, J = 1.4 Hz), 0.82 (m, 1 H), 0.25–0.64 (m, 3 H), 0.20 (m, 1H); irradiate δ 5.70, δ 1.96 (s); irradiate δ 0.82, the splitting pattern at 2.71–2.92 (m), 0.25–0.64 (m), and 0.20 (m) changes; ^{13}C NMR ($CDCl_3$) δ 166.7, 158.6, 116.8, 85.1, 56.7, 50.6, 39.0, 26.8, 15.0, 4.4, 1.2; IR ($CDCl_3$) 3090 (w), 3010 (m), 2990 (m), 2995 (m), 2950 (m), 2825 (w), 1705 (s), 1645 (m), 1455 (m), 1440 (m), 1260 (m), 1215 (m), 1190 (m), 1175 (m), 1160 (s), 1100 (m), 1075 (m), 1025 (w) cm^{-1}; MS (CI) m/z (relative intensity) 199 (M + 1), 177, 171, 167 (100), 153, 139, 135, 107, 85, 69; HRMS (EI) calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1256.

Reaction of Complex 1 with Methyl Tiglate (Table II, Entry J). General procedure A was followed using complex 1 (0.458 g, 1.66 mmol) and methyl tiglate[20] (0.378 g, 3.32 mmol); the total reflux was 24 h in this case. The residue after evaporation was distilled (Kugelrohr, 25–60 °C, 0.025 mmHg), and final purification was achieved by flash chromatography (silica gel, 19:1 hexane–ethyl acetate). The product in the first fraction (R_f 0.44 in 9:1 hexane–ethyl acetate) was assigned as methyl 1α-methoxy-2α,3α-dimethyl-[1,1'-bicyclopropyl]-2β-carboxylate (**12J**) (0.023 g, 7%). The product in the second fraction (R_f 0.35 in 9:1 hexane–ethyl acetate) was assigned as methyl 1α-methoxy-2β,3β-dimethyl-[1,1'-bicyclopropyl]-2α-carboxylate (**11J**) (0.142 g, 43%).

12J: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.62 (s, 3 H), 3.38 (s, 3 H), 1.51 (q, 1 H, J = 6.5 Hz), 1.25 (s, 3 H), 1.12 (m, 1 H), 0.92 (d, 3 H, J = 6.5 Hz), 0.35–0.60 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 174.1, 70.4, 54.3, 51.5, 33.9, 24.6, 11.4, 9.6, 6.5, 6.3, 3.7; IR ($CDCl_3$) 3088 (w), 3005 (m), 2952 (m), 2883 (w), 2833 (w), 1716 (vs), 1470 (w), 1449 (w), 1436 (m), 1295 (m), 1276 (m), 1226 (w), 1196 (s), 1136 (m), 1090 (m), 1058 (s), 1030 (w) cm^{-1}; MS (EI) m/z (relative intensity) 198 (M^+), 183, 167, 155, 139 (100), 123, 107, 91, 79, 69; HRMS (EI) calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1246. The ^{1}H and ^{13}C NMR spectra revealed a trace amount (ca. 5–10%) of another isomer.

11J: ^{1}H NMR (200 MHz, $CDCl_3$), δ 3.61 (s, 3 H), 3.11 (s, 3 H), 2.12 (q, 1 H, J = 6.7 Hz), 1.18 (s, 3 H), 1.03 (d, 3 H, J = 6.7 Hz), 0.44–0.58 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 173.0, 70.7, 55.3, 51.7, 34.8,

25.0, 10.6, 8.4, 7.3, 3.2, 2.7; IR ($CDCl_3$) 3094 (w), 2998 (m), 2952 (m), 2936 (m), 2830 (w), 1718 (vs), 1452 (m), 1436 (m), 1296 (s), 1230 (s), 1196 (s), 1165 (m), 1150 (m), 1080 (s) cm^{-1}; MS (CI) m/z (relative intensity) 199 (M + 1, 100), 185, 177, 167, 155, 153, 145, 139, 85, 69; HRMS (CI) calcd for $C_{11}H_{19}O_3$ 199.1334, found 199.1318.

Chromium Hexacarbonyl Catalyzed Isomerization of 6-*cis* and 6-*trans*. A solution of **6-*trans*** (0.046 g, 0.27 mmol) and $Cr(CO)_6$ (0.297 g, 1.35 mmol) in 1,4-dioxane (10 mL) was heated to reflux for 15 h. The solvent was removed on rotary evaporator. The residue after evaporation was diluted with ethyl acetate, and the black suspension was filtered through Celite. The residue after evaporation was analyzed by 200-MHz NMR, and the approximate ratio of cis:trans was calculated as 52:48. The above procedure was repeated using **6-*cis***, and an identical ratio of isomers was obtained.

Reaction of Compound 12F with Aqueous Acid. General Procedure for Hydrolysis of Cyclopropylcyclopropanes. To a solution of bicyclopropane **12F** (0.090 g, 0.50 mmol) in THF–H_2O (10 mL of a 1:1 mixture) was added aqueous hydrochloric acid (0.015 mL of a 1M solution), and the mixture was stirred for 2 h at 25 °C. Diethyl ether (20 mL) was added, and the organic phase was washed with saturated aqueous sodium bicarbonate solution, water, and saturated aqueous sodium chloride solution, dried over magnesium sulfate, and filtered through Celite. The solvent was removed on a rotary evaporator, and the residue was subjected to flash chromatography (silica gel, ethyl acetate). The fraction with an R_f value of 0.34 (ethyl acetate) was collected (0.083 g, 100%) and assigned as *N,N*-dimethyl-4-cyclopropyl-4-oxobutanamide (**23A**): ^1H NMR (200 MHz, $CDCl_3$) δ 2.97 (s, 3 H), 2.86 (s, 3 H) overlaps with 2.84 (t, 2 H, J = 6.4 Hz), 2.51 (t, 2 H, J = 6.4 Hz), 1.93 (m, 1 H), 0.91–0.98 (m, 2 H), 0.77–0.88 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 209.1, 171.6, 37.3, 36.6, 35.0, 26.6, 20.2, 10.0; IR ($CDCl_3$) 3013 (w), 2936 (m), 1699 (s), 1636 (vs), 1500 (w), 1417 (m), 1402 (s), 1391 (s), 1264 (w), 1198 (w), 1150 (w), 1105 (w), 1086 (m), 1020 (w) cm^{-1}; MS (EI) m/z (relative intensity) 169 (M^+), 128, 125, 113, 100, 97, 86, 84 (100), 72, 69; HRMS (EI) calcd for $C_9H_{15}NO_2$ 169.1103, found 169.1101.

Reaction of Compound 6-*cis* with Aqueous Acid. The general procedure for hydrolysis of cyclopropylcyclopropanes was followed using compound **6-*cis*** (0.049 g, 0.30 mmol). Final purification was achieved by flash chromatography (silica gel, 4:1 hexane–ethyl acetate). The collected fraction (R_f 0.30 in 4:1 hexane–methyl acetate, 0.042 g, 93% yield) was assigned as methyl 4-cyclopropyl-4-oxobutanoate (**23B**): ^1H NMR (200 MHz, $CDCl_3$) δ 3.63 (s, 3 H), 2.86 (t, 2 H, J = 6.6 Hz), 2.54 (t, 2 H, J = 6.6 Hz), 1.93 (m, 1 H), 0.96–1.04 (m, 2 H), 0.79–0.93 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 208.2, 173.1, 51.5, 37.5, 27.9, 20.4, 10.3; IR ($CDCl_3$) 3014 (w), 2955 (m), 2913 (w), 1736 (vs), 1702 (vs), 1439 (s), 1392 (w), 1367 (s), 1264 (w), 1221 (m), 1210 (m), 1196 (m), 1172 (m), 1108 (w), 1087 (s), 1023 (w) cm^{-1}; MS (EI) m/z (relative intensity) 156 (M^+), 128, 125, 115, 97, 86, 84, 79, 69 (100), 59; HRMS (EI) calcd for $C_8H_{12}O_3$ 156.0786, found 156.0781.

Reaction of Compound 11D with Aqueous Acid. The general procedure for hydrolysis of cyclopropylcyclopropanes was followed using compound **11D** (0.088 g, 0.48 mmol); total reaction time was 3 h for this case. Final purification was achieved by flash chromatography (silica gel, 4:1 hexane–ethyl acetate) to give a single compound (R_f 0.41 in 4:1 hexane:ethyl acetate, 0.071 g, 88%) which is assigned the structure methyl 4-cyclopropyl-2-methyl-4-oxobutanoate (**23C**): ^1H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3 H), 3.02 (dd, 1 H, J = 7.9, 17.2 Hz), 2.93 (m, 1 H), 2.60 (dd, 1 H, J = 5.4, 17.2 Hz), 1.90 (m, 1 H), 1.16 (d, 3 H, J = 7.0 Hz), 0.97–1.02 (m, 2 H), 0.82–0.88 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 208.2, 176.0, 51.6, 46.2, 34.6, 20.5, 16.9, 10.4; IR ($CDCl_3$) 3013 (m), 2978 (m), 2955 (m), 2908 (w), 2882 (w), 1733 (vs), 1700 (vs), 1437 (m), 1394 (s), 1268 (w), 1227 (s), 1195 (m), 1175 (s), 1144 (m), 1085 (m), 1046 (m) cm^{-1}; MS (EI) m/z (relative intensity) 170 (M^+), 139, 129, 111, 101, 88, 86, 84, 69 (100), 59; HRMS (EI) calcd for $C_9H_{14}O_3$ 170.0943, found 170.0939.

Reaction of 11D and 12D with Tetracyanoethylene. To a solution of cyclopropylcyclopropanes **11D** and **12D** (0.106 g, 0.58 mmol, 78:22 mixture) in acetonitrile (4 mL) at 0 °C was added all at once a solution of tetracyanoethylene (0.074 g, 0.58 mmol) in acetonitrile (2 mL). The reaction mixture was stirred for 1 h at 0 °C and for 2 h at 25 °C. The solvent was removed on a rotary evaporator, and the residue was subjected to flash chromatography (silica gel; 3:2 hexane–ethyl acetate). The product in the first fraction (R_f 0.39 in 3:2 hexane–ethyl acetate) was identified as methyl 4β-cyclopropyl-4α-methoxy-1β-methyl-2,2,3,3-tetracyanocyclopentane-1α-carboxylate (**24A**) (0.049 g, 27%). The product in the second fraction (R_f 0.32 in 3:2 hexane–ethyl acetate) was identified as methyl 4α-cyclopropyl-4β-methoxy-1β-methyl-2,2,3,3-tetracyanocyclopentane-1α-carboxylate (**24B**) (0.121 g, 67%).

24B: ^1H NMR (200 MHz, $CDCl_3$) δ 3.86 (s, 3 H), 3.49 (s, 3 H), 2.46 (d, 1 H, J = 15.0 Hz), 1.86 (d, 1 H, J = 15.0 Hz), 1.77 (s, 3 H), 1.31 (m, 1 H), 0.86–0.98 (m, 2 H), 0.77 (m, 1 H), 0.53 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 170.0, 110.6, 109.6, 109.4, 109.2, 91.6, 60.1, 56.7, 53.9, 52.0, 51.5, 36.5, 24.7, 13.3, 4.1, 3.8; IR (neat) 3094 (w), 3008 (m), 2958 (m), 2843 (w), 2254 (vw), 1745 (vs), 1457 (m), 1437 (m), 1286 (s), 1244 (s), 1148 (s), 1086 (s), 1048 (m), 970 (w), 921 (w) cm^{-1}; MS (CI) m/z (relative intensity) 313 (M + 1, 100), 286, 281, 270, 253, 184, 169, 137, 125, 100; HRMS (CI) calcd for $C_{16}H_{17}N_4O_3$ 313. 1301, found 313.1299.

24A: ^1H NMR (200 MHz, $CDCl_3$) δ 3.88 (s, 3 H), 3.44 (s, 3 H), 3.14 (d, 1 H, J = 15.1 Hz), 1.80 (s, 3 H), 1.43 (d, 1 H, J = 15.1 Hz), 1.23 (m, 1 H), 0.89–0.98 (m, 2 H), 0.52–0.74 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 170.0, 110.5 (br), 110.1, 108.8, 91.2, 56.8, 55.6, 54.0, 51.5, 51.2, 35.5, 27.4, 12.7, 3.8, 3.3; IR ($CDCl_3$) 3094 (w), 3028 (m), 3009 (w), 2984 (w), 2958 (m), 2843 (w), 2258 (vw), 1750 (vs), 1464 (m), 1438 (m), 1390 (w), 1298 (s), 1165 (m), 1148 (s), 1094 (s), 1079 (m), 980 (w), 928 (w), 889 (w) cm^{-1}; MS (CI) m/z (relative intensity) 313 (M + 1, 100), 286, 281, 270, 229, 184, 169, 114, 100, 85; HRMS (CI) calcd for $C_{16}H_{17}N_4O_3$ 313.1301, found 313.1295.

The above procedure was repeated with pure **11D** and **12D** to give 89% yield, 2.5:1 isomer ratio, and 75% yield, 2:1 isomer ratio, respectively (isomer ratios were calculated from NMR), where in all cases the major isomer is **24B**.

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Registry No. **1**, 52149-50-5; **3**, 130694-25-6; **4**, 122235-73-8; **6-*trans***, 126909-14-6; **6-*cis***, 130574-63-9; **7**, 126909-13-5; **11B**, 126909-22-6; **11C**, 127000-56-0; **11D**, 126909-17-9; **11E**, 126909-21-5; **11F**, 126925-21-1; **11G**, 126909-20-4; **11H**, 130574-67-3; **11J**, 130694-24-5; **12D**, 126909-16-8; **12F**, 126909-18-0; **12G**, 126909-19-1; **12J**, 130574-69-5; **13**, 130574-68-4; (*E*)-**17**, 130574-64-0; (*Z*)-**17**, 130574-65-1; **17-d_2**, 130574-66-2; **23A**, 130574-70-8; **23B**, 130574-71-9; **23C**, 130574-72-0; **24A**, 130574-73-1; **24B**, 130574-74-2; $Cr(CO)_6$, 13007-92-6; methyl acrylate, 96-33-3; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6; methyl methacrylate, 80-62-6; methyl *trans*-crotonate, 623-43-8; *N,N*-dimethylacrylamide, 2680-03-7; 1-vinylcyclopentene, 28638-58-6; methyl *trans*-cinnamate, 1754-62-7; methyl 3,3-dimethylacrylate, 924-50-5; methyl tiglate, 6622-76-0; tricarbonyl(η^6-(methyl cinnamate))chromium, 130574-75-3; tetracyanoethylene, 670-54-2.

Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra for compounds **6-*trans***, **7**, **12D**, **11F**, **11G**, **12G**, **11H**, **11J**, **12J**, **11I**, **17**, **23A**, **23B**, **23C**, **24A**, and **24B** and NOESY spectra for compound **12D** (34 pages). Ordering information is given on any current masthead page.