spin density at C_3, and correspondingly divergent hfc's for $H(C_1)$ and $H(C_3)$, is foreshadowed in the preferred structure (**7b**) calculated for the monomethyl derivative (ρ_1 = 0.51, hfc = −18.8 G; ρ_3 = 0.74, hfc = −28.2 G). Clearly, **7b** and **7c** are unusual and unprecedented cyclopropane radical cations; their structures merit experimental verification. Appropriate experiments for the dimethyl derivative are under way.

Concluding Remarks

We conclude that even simple alkyl substituents are capable of significantly altering the shapes of the potential energy surfaces of cyclopropane radical cations, always preferentially stabilizing the "$^2A_1$-type" states possessing a long, one-electron C–C bond.[28] Localization of the UHF/6-31G* wave function using the natural bond orbital analysis procedures developed by Weinhold et al.[29] progresses smoothly; in **4a**, for example, this procedure predicts that a C_2–C_3 bond orbital containing 0.97 electron is formed almost exclusively (>95%) by C(2p) atomic orbitals. Despite the bonding characteristics exemplified by cyclopropane orbital **3**, all "$^2B_2$-type" states are low-energy transition states for interconversion of equivalent "$^2A_1$-type" minima. The predicted fine-tuning of the preferred geometry and resulting charge and spin distributions for substituted cyclopropane cations should be qualitatively verifiable by a combination of chemical (e.g., nucleophilic substitution) and spectroscopic (principally ESR and CIDNP) experiments. Such experiments are under way in our laboratories.

Acknowledgment. The computational work was made possible by equipment grants from the National Science Foundation, the National Institutes of Health, and the New Jersey Commission on Science and Technology.

Supplementary Material Available: The optimized geometries of all stationary points for species **4**, **5**, **7**, and **8** in Z-matrix format (20 pages). Ordering information is given on any current masthead page.

(28) A referee has questioned whether diffuse functions should have been added to the basis set to properly describe this long C–C bond. We have used the 6-31G* basis set throughout our geometry optimizations. This basis set is of split-valence quality on all the atoms and contains d-type polarization functions on the carbon atoms as well. In **4a** at the UHF/6-31G* level, we obtained C_1–C_2 and C_2–C_3 bond lengths of 1.477 and 1.875 Å, respectively (Table I). Addition of diffuse valence functions to the basis set on the carbon atoms only (6-31G* → 6-31+G*) and reoptimization leads to equilibrium C_1–C_2 and C_2–C_3 bond lengths of 1.477 and 1.877 Å, respectively. These values are unchanged upon addition of diffuse functions to the hydrogen atoms (6-31+G* → 6-31++G*). Addition of p-type polarization functions on the hydrogen atoms (6-31++G* → 6-31++G**) and reoptimization gives C_1–C_2 and C_2–C_3 bond lengths of 1.476 and 1.876 Å, respectively, for **4a**. We conclude that the 6-31G* basis set is adequate for the description of the structural features of cyclopropane cations and that the role played by diffuse basis functions is minimal.

(29) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct.: THEOCHEM* **1988**, *169*, 41–62. Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

Reaction of Alkynes with Cyclopropylcarbene–Chromium Complexes: A Versatile [4 + 2 + 1 − 2] Cycloaddition Reaction for the Construction of Cyclopentenones

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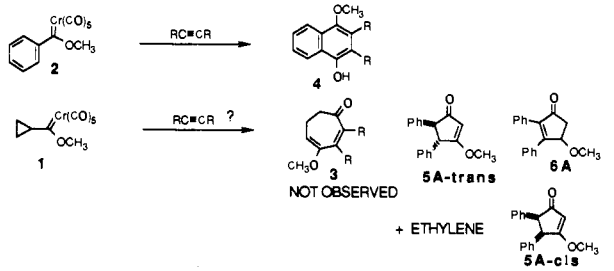
Abstract: The scope and limitations of the reaction between cyclopropylcarbene–chromium complexes and alkynes have been examined. A variety of cyclopropylcarbene complexes and alkynes have been employed in these studies. The reaction appears to be general for most simple alkynes, producing cyclopentenones. A mechanism has been proposed involving metallacyclobutene formation, electrocyclic ring opening, electrocyclic ring closure, CO insertion, alkene insertion, metallacyclopentene fragmentation, and cyclopentadienone reduction. The presence of these intermediates has been inferred from the structure of products obtained when the reaction was conducted in acetonitrile instead of dioxane. A trapping experiment employing 1,6-heptadiyne supports the intermediacy of vinylcarbene or vinylketene complexes.

Introduction

The reaction between alkynes and α,β-unsaturated carbene–chromium complexes, which produces aromatic rings[1] in addition to other types of products, has emerged as a powerful tool for the synthetic organic chemist. A diverse array of natural products has been synthesized using this reaction, including anthraquinone anticancer agents,[2] naphthoquinone antibiotics,[3] vitamin E,[4] khellin,[5] and psoralen derivatives.[6] In all of these reactions, a carbene complex containing an unsaturated substituent at the carbene carbon (e.g., complex **2**) was employed, and the unsaturated substituent and the carbene carbon were later incorporated into the newly-formed aromatic ring system. As part of a program to develop a general cycloaddition reaction for the synthesis of carbocyclic seven-membered rings, we have examined the reaction

Scheme I. Reaction of Alkynes with α,β-Unsaturated Carbene Complexes and Cyclopropylcarbene Complexes



(1) (a) For a review of metal–carbene complexes, see: Doetz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587–608. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1.
(2) Wulff, W. D.; Xu, Y.-C. *J. Am. Chem. Soc.* **1988**, *110*, 2312–2314.
(3) Semmelhack, M. F.; Zask, A. *J. Am. Chem. Soc.* **1983**, *105*, 2034–2043.
(4) Doetz, K. H.; Kuhn, W. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 732.
(5) Yamashita, A.; Toy, A.; Scahill, T. A. *J. Org. Chem.* **1989**, *54*, 3625–3634.
(6) Wulff, W. D.; McCallum, J. S.; Kunng, F.-A. *J. Am. Chem. Soc.* **1988**, *110*, 7419–7434.

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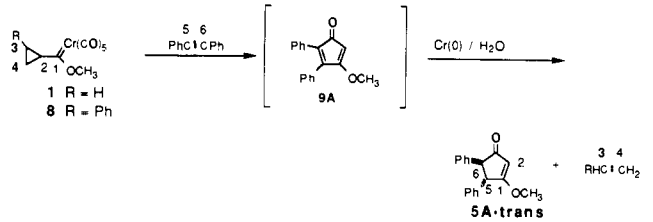
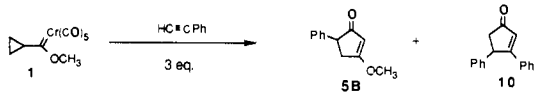
Scheme II. Correlation between Reactants and Products in the [4 + 2 + 1 − 2] Cycloaddition Reaction



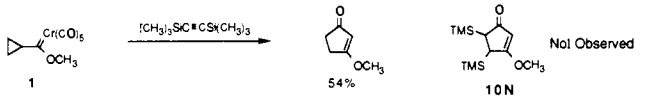
Scheme III. Byproducts in the [4 + 2 + 1 − 2] Cycloaddition Reaction Employing Phenylacetylene



of cyclopropylcarbene–chromium complexes with alkynes. In many organic reactions, the ability of a cyclopropane ring to mimic the chemistry of an alkene is well-documented,[7] and thus if complexes **1** and **2** react similarly with alkynes, then cycloheptadienone derivatives such as compound **3** would be produced (Scheme I). As we reported in our preliminary communication,[8] the reaction of cyclopropylcarbene complex **1** and diphenylacetylene did not produce cycloheptadienone **3A** (Table I entry letters correlate with R groups for compounds **3**, **5–7**, and **9**), but gave exclusively the cyclopentenone derivatives **5A** and **6A** plus ethylene. This reaction was found to be general for a variety of alkynes. The tungsten analog of complex **1** did in fact produce the desired seven-membered-ring derivative **3A** upon reaction with diphenylacetylene.[9] The conversion of complex **1** and alkynes to cyclopentenone derivatives allows for the construction of highly-functionalized five-membered rings from readily available components. The development of cycloaddition approaches for the construction of five-membered rings has become a very active area of research in recent years, and only a few actual one-pot reactions have been developed.[10] As such, the overall conversion represented by this [4 + 2 + 1 − 2] cycloaddition reaction is a potentially powerful reaction for cyclopentane ring construction.

The most reasonable correlation between compound **5** and the reactants is outlined in Scheme II. The carbonyl carbon arises from a CO ligand of the carbene complex, and carbons 1 and 2 of cyclopentenone **5** are from carbons 1 and 2 of the carbene complex. Carbons 5 and 6 correspond to the alkyne carbons of diphenylacetylene. This implies that carbons 3 and 4 of the carbene complex are lost as some two-carbon fragment. When complex **8** was reacted with diphenylacetylene under identical conditions, compound **5A** (53%) was obtained along with styrene (35%). To balance the equation for formation of **5** from **1** or **8**, an external source of hydrogen must be involved. Previously we had verified that cyclopentadienones were intermediates in the reaction, which were converted to cyclopentenones by the combination of chromium hexacarbonyl and water.[8b,11] The best yields of **5A-trans** (78%) were obtained using 1% aqueous dioxane as the solvent and using high-dilution conditions generated by the addition of a solution of the carbene complex and the alkyne to a solution of refluxing aqueous dioxane over a period of 2 h. High yields of cyclopentenone derivatives require that the alkyne be kept at low concentration to prevent polymerization.[12] Mixtures of cis and trans isomers are typically obtained, but the proportion of trans isomer increases with increasing reaction time. In this article, we report on the scope, limitation, and mechanism of this highly useful new five-membered-ring-forming reaction.

Scheme IV. Protiodesilylation in the Reaction of Bis(trimethylsilyl)acetylene with Complex **1**



Scheme V. Competing Cycloaddition and Ring Expansion in the Reaction of Complex **12** and Diphenylacetylene

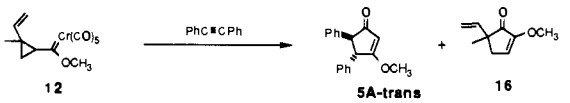
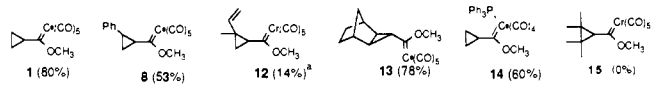


Chart I. Yield of Cyclopentenones **5–7** from Reaction of Diphenylacetylene with Various Cyclopropylcarbene–Chromium Complexes[b]



[a] A 37% yield of cyclopentenone **16** was also obtained.
[b] Total yields of **5A** and **6A** are in parentheses.

Scope and Limitations

As can be seen in Table I, the reaction is general for a wide variety of alkynes. With monosubstituted alkynes (entries B and G–M), the only regioisomer obtained was that in which the substituent on the alkyne was α to the carbonyl group in the product. When using phenylacetylene, it is critical that no more than 1.3 equiv of alkyne per carbene complex is used. When large excesses of monosubstituted alkyne were used, cyclopentenones such as **10** (Scheme III) were obtained in low yield, which might have resulted from a Reppe-type coupling of the alkynes with CO.[13] The reaction was not regioselective when the unsymmetrically-disubstituted alkynes 1-phenylpropyne (entry C) and 4-methyl-2-pentyne (entry F) were employed, but the major products obtained were those where the larger substituent was

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(8) (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**, *30*, 295–296. (c) Herndon, J. W.; Turner, S. U.; McMullen, L. A.; Maiasi, J. J.; Schnatter, W. F. K.; Daitch, C. E. *Comments Inorg. Chem.* **1990**, *10*, 1–24.

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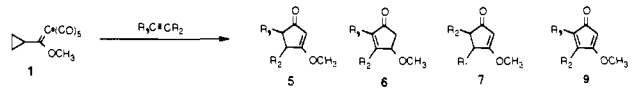
(10) Some examples of the use of organotransition-metal reagents to effect one-step, five-membered-ring-forming cycloaddition reactions are as follows: (a) Herndon, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 3165–3166. (b) Semmelhack, M. F.; Herndon, J. W.; Liu, J. K. *Organometallics* **1983**, *2*, 1885–1888. (c) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1–20. (d) Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77–151. (e) Rosenblum, M. A. *J. Organomet. Chem.* **1986**, *300*, 191–218. (f) Welker, M. E. *Chem. Rev.* **1992**, *92*, 97–112. (g) Wojcicki, A.; Schuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35–60. (h) Lee, G.-H.; Peng, S.-M.; Yang, G.-M.; Lush, S. F.; Liu, R.-S. *Organometallics* **1989**, *8*, 1106–1111. (i) For a recent reference to the Pauson Khand reaction, see: Schore, N. E. *Org. React.* **1991**, *40*, 1–90. (j) Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025–5026. (k) Aumann, R. A.; Weiderhaupt, H. J. *Chem. Ber.* **1987**, *120*, 23–27. (l) Alper, H.; Brandes, D. A. *Organometallics* **1991**, *10*, 2457–2467. (m) O'Connor, J. M.; Pu, L.; Uhrhammer, R.; Johnson, J. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 1889–1891. (n) Hayakawa, Y.; Yokoyama, K.; Noyori, R. *J. Am. Chem. Soc.* **1978**, *100*, 1791–1798. (o) Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915–5918. (p) Xu, Y.-C.; Challener, C. A.; Dragisch, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269–7271. (q) Brandvold, T. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem.* **1990**, *112*, 1645–1647. (r) Stein, F.; Deutsch, M.; Lackmann, R.; Noltemeyer, M.; de Meijre, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1658–1660. For a listing of other five-membered-ring-forming cycloaddition reactions and sequences, see: Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691–6707.

(11) For a similar reduction using tetraphenylcyclopentadienone, see: Brown, D. A.; Hargaden, J. P.; McMullin, C. M.; Gogan, N.; Sloan, H. *J. Chem. Soc.* **1963**, 4914–4918. (b) Dolcetti, G.; Hoffmann, N. W. *Inorg. Chim. Acta* **1974**, *9*, 269–303.

(12) (a) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422–424. (b) The polymerization can be suppressed if the concentration of alkyne is kept low. Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P.-C. *J. Am. Chem. Soc.* **1985**, *107*, 1060–1062.

(13) A similar type of side reaction has been previously suggested. Yamashita, A.; Timko, J. M.; Watt, W. *Tetrahedron Lett.* **1988**, *29*, 2513–2516. For a similar reaction in cobalt chemistry, see: Doyama, K.; Fujiwara, K.; Joh, T.; Maeshima, K. S. *Chem. Lett.* **1988**, 901–904.

Table I. Reaction of Complex 1 with Alkynes in Refluxing Aqueous Dioxane[a,b]



entry[b]	R_1	R_2	yield 5 (%)[c]	*trans*:*cis* (5)	yield 7 (%)
A	Ph	Ph	78 (2)	85:15	
B	Ph	H	62		0
C	Ph	CH_3	75	73:27	10[d]
D	Ph	*p*-$PhOCH_3$	40	52:48[e]	37[e,f]
E	*n*-C_3H_7	*n*-C_3H_7	60	50:50[e]	0
F	i-C_3H_7	CH_3	48	53:47[e]	14[d,g]
G	*n*-C_3H_7	H	68		0
H	c-C_3H_5	H	51		0
I	$(CH_2)_4OH$	H	68		0
J	$(CH_2)_4OTBDMS$[h]	H	58		0
K	$(CH_2)_4OSO_2CH_3$	H	38[i]		0
L	*cis*-$CH{=}CHOCH_3$	H	37[j]		0
M	COOEt	H	0		0
N	$Si(CH_3)_3$	$Si(CH_3)_3$	54[k]		0

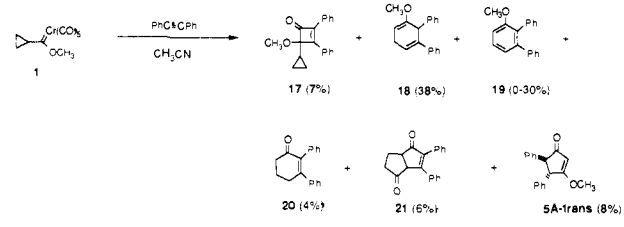
[a] In all cases, the alkyne and complex 1 (0.1 M in dioxane) were added to a refluxing 1% aqueous dioxane solution via syringe pump over a period of 2 h, and reflux was continued for a 6-h period. Note: Since trans:cis ratios are a function of reflux time, the ratios in Table I may differ from values quoted in the text where longer reflux times were employed. [b] Entry letters define R_1 and R_2 for compounds 5–7 and 9. [c] The yield in parentheses refers to the yield of compound 6. [d] Only the compound having the double bond between the phenyl and methyl substituents was obtained. [e] The regioisomer ratio was determined by examination of the crude ^1H NMR spectrum; these compounds were isomerized to the pure trans isomer by treatment with sodium methoxide and methanol prior to characterization. [f] The trans:cis ratio was 52:48. [g] The trans:cis ratio was 9:1. [h] TBDMS = *tert*-butyldimethylsilyl. [i] A 16% yield of compound 5I was also obtained from the reaction. [j] The product was obtained as a 3:2 trans/cis mixture about the enol ether double bond. [k] This is the yield for the desilylation product, 3-methoxy-2-cyclopentenone.

α to the carbonyl group. The reaction appears to proceed in a way such that the larger substituent will end up α to the carbonyl group in the final product. When an alkyne having similar steric properties at both carbons but different electronic properties (e.g., (*p*-methoxyphenyl)phenylacetylene) was treated with complex 1 (entry D), a 52:48 mixture of the two regioisomers was obtained.

The scope and limitations of the reaction have been explored using a variety of functionalized alkynes. The reaction is tolerant of an alcohol functionality (entry I), and similar yields were obtained when the alcohol functionality was protected (entry J). Even a mesylate functionality can be tolerated in the reaction; hex-5-yn-1-yl mesylate couples with carbene complex 1 to give a mixture of the expected mesylate 5K and the corresponding alcohol 5I, which might result from solvolysis of the mesylate under the conditions of the reaction.[14] In one case, the reaction of carbene complex 1 with alkynes failed to produce any of the cyclopentenones 5–7. The five-membered-ring-forming reaction did not proceed using the electron-deficient alkyne, ethyl propiolate; alkynes of this type often exhibit abnormal behavior in reactions with Fischer carbene complexes.[15] The reaction of bis(trimethylsilyl)acetylene with complex 1 led to 3-methoxy-2-cyclopentenone in 54% yield. Protiodesilylation of compound 5N could lead to 3-methoxy-2-cyclopentenone since all of the trimethylsilyl groups are capable of being hydrolyzed (Scheme IV).[16]

In most cases, the major alkene isomer obtained from the reaction mixture was the thermodynamically more stable vinylogous esters 5 or 7,[17] where the original alkyne substituents have the trans relative stereochemistry in the product. The trans:cis ratio increased with increasing reflux time, and chromium hexacarbonyl was an effective isomerization catalyst for conversion of 5A-cis to 5A-trans but did not catalyze the interconversion of alkene regioisomer 6A to 5A. Sodium methoxide/methanol was an effective reagent for conversion of 5A-cis or 6A to 5A-trans. All of the products in Table I (except for regioisomer 7 of entry C) could be rearranged to essentially pure vinylogous ester trans isomers by the action of sodium methoxide and methanol.

Scheme VI. Reaction of Complex 1 and Diphenylacetylene in Acetonitrile or DMF



We have briefly examined the reaction of other cyclopropylcarbene–chromium complexes with diphenylacetylene. As can be seen in Chart I, the simple cyclopropylcarbene complex 1 was the optimal carbene complex for use in the cyclization reaction. A comparable yield of cyclopentenones was obtained using norbornane-fused cyclopropylcarbene complex 13; however, this complex is considerably more difficult to obtain than complex 1. Lower overall yields of the cyclopentenones were obtained with the phenyl-substituted carbene complex 8. The vinyl-substituted carbene complex 12 reacted with diphenylacetylene to afford a mixture of cyclopentenones 5 and 16 (Scheme V). Cyclopentenone 16 results from a rearrangement–carbonylation reaction of starting carbene complex 12.[18] Compound 16 was also obtained from the thermolysis of complex 12 in the absence of an alkyne, and this reaction was found to be general for a wide variety of (2-vinylcyclopropyl)carbene–chromium complexes. The triphenylphosphine-substituted carbene complex 14 was also reactive with diphenylacetylene, giving cyclopentenone 5 as the major product of the reaction. Although reactions from this species seemed to be much more facile,[19] the overall yield from this complex was disappointing. (Tetramethylcyclopropyl)carbene complex 15 was unreactive to alkynes.

The effect of various solvents and temperatures on the reaction has also been examined. Refluxing aqueous dioxane seems to be the optimal solvent since the highest yields of cyclopentenones are obtained under these conditions and since under these conditions almost complete isomerization to the trans product is observed. THF and benzene also provide primarily cyclopentenone

(14) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674.

(15) The formation of abnormal products from the reaction of arylcarbene–chromium complexes and propiolate esters is precedented: Yamashita, A.; Scahill, T. A. *Tetrahedron Lett.* **1982**, *23*, 3765–3768.

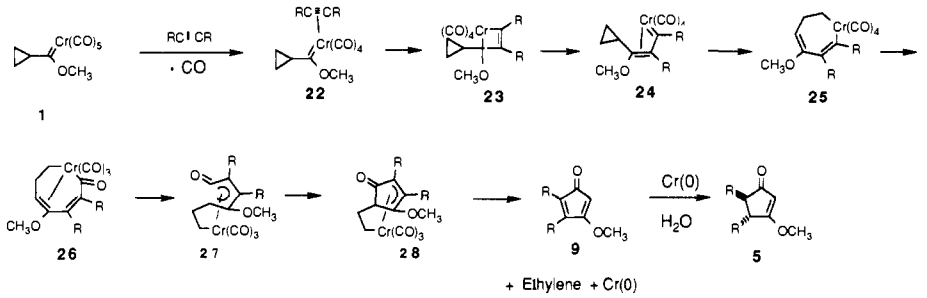
(16) For a similar desilylation, see: Stork, G.; Ganem, B. *J. Am. Chem. Soc.* **1973**, *95*, 6152–6153.

(17) Taskinen, E.; Mukkala, V. M. *Tetrahedron* **1982**, *38*, 613–616.

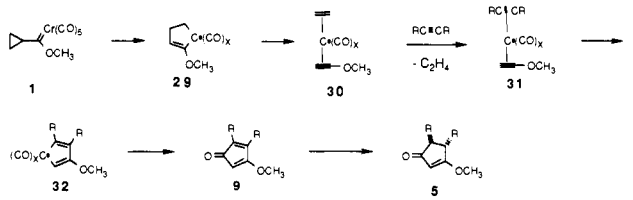
(18) Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 6854–6856.

(19) For a similar phosphine-substitution effect, see: Xu, Y.-C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263–3275.

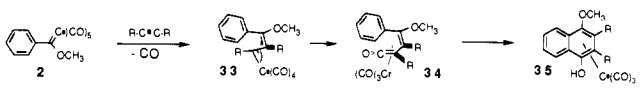
Scheme VII. Mechanism for the [4 + 2 + 1 − 2] Cycloaddition Reaction Involving Alkyne Insertion as an Early Event



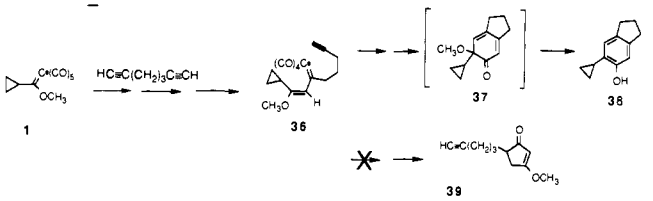
Scheme VIII. Mechanism for the [4 + 2 + 1 − 2] Cycloaddition Reaction Involving Ring Expansion and Fragmentation as an Early Event



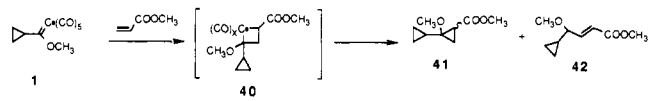
Scheme IX. Mechanism for the Dötz Reaction as Suggested by Reference 21b



Scheme X. Trapping of Vinylcarbene Intermediates Involved in the [4 + 2 + 1 − 2] Cycloaddition Reaction



Scheme XI. Reaction of Complex **1** with Alkenes



5A from the reaction of **1** and diphenylacetylene. The proportion of **5A-cis** was considerably higher in THF and benzene than in dioxane, probably due to the lower reflux temperature. When acetonitrile or DMF was used as the solvent of the reaction, a diverse array of products (**5A-trans**, **17–21**) containing different ring systems was obtained (Scheme VI). The formation of these products relates to the mechanism of the reaction and will be discussed later.

Mechanism of the Cycloaddition Reaction

a. Fragmentation vs Alkyne Insertion. In earlier publications, two general classes of mechanism accounting for formation of cyclopentadienones from cyclopropylcarbene complexes and alkynes were proposed. The mechanism in Scheme VII[20] is similar to the mechanism for the Dötz reaction[21] (hereafter referred to as the alkyne-insertion mechanism). The involvement of metallacyclobutenes in these processes has recently been questioned, thus complex **22** might be directly converted to **24** without the involvement of metallacyclobutene **23**.[21d] For conversion of vinylcarbene complex **24** to cyclopentadienone **9**, many alternatives are possible; for reasons discussed in this section, we currently favor the mechanism in Scheme VII. The mechanism in Scheme VIII is drastically different and involves ring expansion and fragmentation, followed by assembly of the cyclopentadienone ring system via the highly precedented oxidative ligand coupling reaction[22] (hereafter this mechanism is referred to as the fragmentation mechanism). Compound **10** of Scheme III is presumably formed via this mechanism. A key difference in the two mechanisms is the timing of the cyclopropane ring opening and ethylene loss steps. Intellectual arguments in favor of an alkyne insertion mechanism were presented in previous publications, the most notable argument being that a fragmentation mechanism was not operative since thermolysis of the carbene complex did not appear to produce fragmentation products. Loss of ethylene upon thermolysis of the acylate analog of complex **1** has been reported.[23] Since these are not the real conditions for the reaction (i.e., the alkyne is not present), this cannot be considered definitive proof against the fragmentation mechanism.

The mechanism in Scheme VII is identical to that proposed for the Dötz reaction (Scheme IX) up to vinylcarbene intermediate **24**. Others have reported that non-heteroatom-stabilized carbene complex intermediates such as **24** can be trapped with alkynes or alkenes, ultimately producing cyclohexadienones and phenols (from reaction with alkynes)[12b] or cyclopropanes and cyclobutenones (from reaction with alkenes).[24] The reaction of complex **1** with 1,6-heptadiyne led to phenol **38** in 51% yield as the only product of the reaction (Scheme X). This result suggests very strongly that vinylcarbene complexes (e.g., **24** and **36**) are intermediates in the reaction. Further indirect evidence can be found in ref 25, where the reaction of carbene complex **1** with alkenes leads only to cyclopropylcyclopropane derivatives (Scheme XI). This is another example of a reaction process for complex **1** where an organic ligand is inserted without opening the cyclopropane ring.[26]

b. Mechanism for Cyclopropane Ring Opening and Ethylene Loss. The experiment in Scheme X establishes that vinylcarbene complexes are intermediates in the reaction, as required in Scheme VII. Final conversion into cyclopentadienones then occurs via a 1,5-alkyl shift (**24** → **25**), followed by CO insertion (**25** → **26**), conversion to the pentadienyl complex (**26** → **27**), ring closure (**27** → **28**),[27] and fragmentation with ethylene loss (**28** → **9**).[28]

(20) This mechanism differs slightly from that presented in ref 8a,c, in that we suggest alkene coordination in order to stabilize coordinatively-unsaturated intermediates. We thank a reviewer for suggesting this alternative mechanism.

(21) (a) Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615–8617. (b) Bos, M. A.; Wulff, W. D.; Miller, R. A.; Shamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293–9319. (c) The cyclopropane ring opening step (**24** → **25**) is analogous to a similar step in the mechanism proposed by Casey. Casey, C. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; John Wiley and Sons: New York, 1985; Vol. 3, pp 109–150. (d) Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908.

(22) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–556.

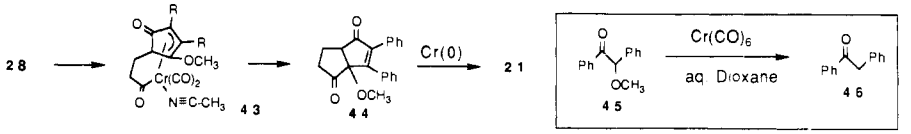
(23) Connor, J. A.; Jones, E. M. *J. Organomet. Chem.* **1973**, *60*, 77–86.

(24) (a) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070–2071. (b) Hoye, T. R.; Korkowski, P. F.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676–2678. (c) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066–5068.

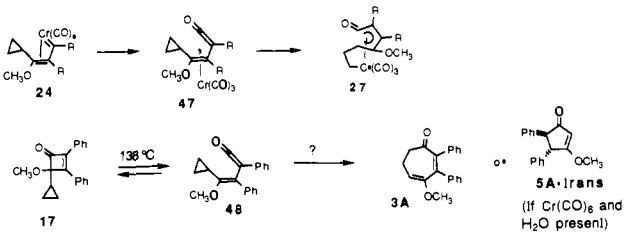
(25) (a) Herndon, J. W.; Tumer, S. U. *Tetrahedron Lett.* **1989**, *30*, 4771–4774. (b) Herndon, J. W.; Tumer, S. U. *J. Org. Chem.* **1991**, *56*, 286–94.

(26) Fischer, H.; Munlemeier, J.; Markl, R.; Doetz, K. H. *Chem. Ber.* **1982**, *115*, 1355–1362.

Scheme XII. Mechanism for Formation of Bicyclic Compound **21**



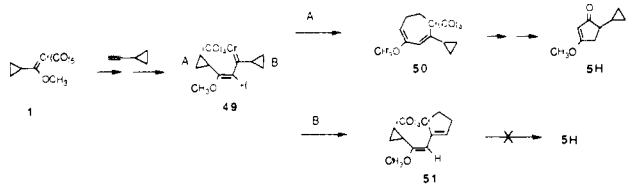
Scheme XIII. Alternative Mechanism for Formation of Metallacyclooctadienone **27** where CO Insertion Precedes Ring Opening



The primary evidence for this mechanism is that products in Scheme VI appear to be derived from the intermediates **24–28**. Cyclobutenones such as **17** are often minor byproducts in the reactions of alkynes and chromium–carbene complexes, and their existence supports the intermediacy of metallacyclobutenes (e.g., **23**), vinylcarbenes (e.g., **24**), or vinylketenes (see ahead). Interestingly, the maximum yield of cyclobutenones is typically obtained in acetonitrile.[29] Cyclohexadiene **18** would most likely arise via reductive elimination from metallacycloheptadiene **25**, followed by metal-catalyzed alkene isomerization. Dehydrogenation of **18** could provide terphenyl derivative **19**. The combined yield of **18** and **19** was nearly constant at 40%; however, the yield of the individual compounds varied widely between different experiments. Hydrolysis of **18**, possibly during purification, would provide cyclohexenone **20**. These results suggest that cyclopropane ring opening occurs from vinylcarbene intermediate **24**.

Bicyclic compound **21** of Scheme VI is most likely derived from bicyclic intermediate **28** of Scheme VII. CO insertion and reductive elimination from intermediate **28** would provide bicyclic compound **44**. Reductive removal of methoxy groups by chromium hexacarbonyl has a precedent (see Scheme X, **37** → **38**, ref 12b). The conversion of **37** to **38** has considerably more thermodynamic driving force than the conversion of **44** to **21**. In order to determine whether this reductive removal of methoxy happens in systems which do not lead to aromatization, the reaction of *O*-methylbenzoin with chromium hexacarbonyl and water was examined. The methoxy group of *O*-methylbenzoin (**45**) is replaced by hydrogen under these conditions (30% yield of **46**), suggesting that a similar reaction might have occurred in compound **44** to provide **21**. Only a mixture of compounds **5A** and **6A** was obtained from the reaction of bicyclic carbene complex **13** with diphenylacetylene (Chart I). Since the strained alkene norbornene must be ejected in this reaction, it was anticipated that a bicyclic derivative similar to **21** would be obtained in this process (Scheme XII).[30]

Scheme XIV. Reaction of Cyclopropylacetylene with Complex **1**



c. Timing of CO Insertion. A notable problem with the mechanism in Scheme VII is that it requires CO insertion to occur selectively into an sp^2 carbon–metal bond over an sp^3 carbon–metal bond (**25** → **26**). Though there are examples where this selectivity is observed, they tend to be the exception more than the rule.[31] Results from cycloaddition reactions in acetonitrile and DMF do not rule out the possibility of CO insertion prior to ring expansion, although they definitely establish that (cyclopropylvinyl)carbene–chromium complexes can undergo the 1,5-alkyl shift. In the Dötz reaction, it appears that CO insertion of the intermediate vinylcarbene complex occurs prior to electrocyclic ring closure.[21b] A possible variant of the mechanism in Scheme VII which invokes vinylketene intermediates is shown in Scheme XIII. Here CO insertion into the vinylcarbene complex occurs to produce vinylketene complex **47**, and oxidative addition into the cyclopropane carbon–carbon bond[32] gives rise to pentadienyl complex **27**. This mechanism cannot account for the formation of the six-membered-ring derivatives **18–20** of Scheme VII. Since the products of Scheme VII are formed under different conditions than the optimal conditions for cyclopentenone formation, this result does not rule out the alternate pathway of Scheme XIII, but formation of **18–20** does show that direct conversion of (cyclopropylvinyl)carbene complexes (e.g., **24**) to metallacycloheptadienes is a reasonable pathway.

The chemistry of vinylketene complexes derived from insertion of alkynes into metal–carbene complexes can often be imitated by free vinylketenes.[33] If this similarity holds true for our case, then alternative generation of (2-cyclopropylvinyl)ketenes or their transition-metal complexes might lead to some of the products we have previously observed. It was therefore predicted that thermolysis of 4-cyclopropyl-2-cyclobutenone derivatives such as **17** (which should produce a (cyclopropylvinyl)ketene upon thermolysis at greater than 138 °C)[33] might provide seven-membered rings such as **3A**, while thermolysis in the presence of chromium hexacarbonyl might provide five-membered rings, provided that vinylketene **48** is converted to chromium complex **47** under the reaction conditions. Thermolysis of **17** in the presence of tungsten hexacarbonyl should also provide cycloheptadienone **3**. Thermolysis of **17** in the presence (101 °C) or absence (138 °C) of chromium hexacarbonyl did not provide any new compounds. We currently favor the mechanism in Scheme VII since there is evidence that cyclopropane ring opening reactions can arise from 2-cyclopropylvinylcarbene complexes but no evidence

(27) For similar conversions of pentadienyl complexes to five-membered-ring derivatives, see: (a) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463–465. (b) Bleeke, J. R.; Peng, W.-J.; Xie, Y.-F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113–1119. (c) Egan, W. J., Jr.; Hughes, R. P.; Rheingold, A. R. *Organometallics* **1987**, *6*, 1578–1581. (d) Donovan, B. T.; Hughes, R. P.; Trujillo, H. A. *J. Am. Chem. Soc.* **1990**, *112*, 7077–7079. (e) Hughes, R. P.; Robinson, D. J. *Organometallics* **1989**, *8*, 1015–1019. (f) Sivavec, T. M.; Katz, T. U.; Chiang, M. Y.; Wang, G. X.-Q. *Organometallics* **1989**, *8*, 1620–1625.

(28) (a) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739–777. (b) For examples involving chromium complexes, see: Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodard, P. *J. Chem. Soc., Dalton Trans.* **1982**, 173–185. (c) Michman, M.; Zeiss, H. H. *J. Organomet. Chem.* **1970**, *25*, 161–166.

(29) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9–56.

(30) For a dramatic alteration of the course of an organometallic reaction by the presence of a norbornyl system, see: (a) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 1370–1373. (b) Stille, J. R.; Santaserio, B. D.; Grubbs, R. H. *J. Org. Chem.* **1990**, *55*, 843–862.

(31) For a more detailed discussion of metal–vinyl vs metal–alkyl insertion reactions, see: Doxsee, K. M.; Mouser, J. K. M. *Organometallics* **1990**, *9*, 3012–3014.

(32) (a) For a similar process, see: Sarel, S. *Acc. Chem. Res.* **1978**, *11*, 204–211. (b) The oxidative addition is analogous to other previously-observed C–H oxidative addition reactions: Macomber, D. W. *Organometallics* **1984**, *3*, 1589–1591. (c) Wulff, W. D.; Challener, C. A.; Yang, D. C.; Faron, K. L.; Kim, O. K.; Xu, Y. C. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989; American Chemical Society: Washington, DC, 1989; ORGN 185.

(33) (a) Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093–3110. (b) Perri, S. T.; Moore, H. W. *J. Am. Chem. Soc.* **1990**, *112*, 1897–1905. (c) Liebeskind, L. S.; Iyer, S.; Jewell, C. F., Jr. *J. Org. Chem.* **1986**, *51*, 3065–3067.

of ring-opening reactions resulting from (2-cyclopropylvinyl)-ketenes. This cannot be considered definitive evidence since there is no guarantee that a metal-complexed ketene was ever formed. Nonetheless, if a vinylketene intermediate is present, it must be metal-complexed, and this vinylketene–metal complex must thus behave very differently from a free vinylketene.[34]

The cyclopropane ring appears to open only after the alkyne insertion reaction. This could conceivably be due to the lack of heteroatom stabilization[35] for intermediate carbene complex **24**. To determine the ring-opening selectivity in an unbiased system, the reaction with cyclopropylacetylene was examined. Reaction of complex **1** with cyclopropylacetylene leads to the cyclopropylcyclopentenone derivative **5H** in 51% yield, which is very similar to the yield of cyclopentenone adduct obtained from complex **1** and 1-pentyne (68%). According to the mechanism in Scheme VII, the intermediate carbene complex **49** would be present in the reaction between cyclopropylacetylene and complex **1** (Scheme XIV). Compound **49** can undergo two possible cyclopropane ring opening reactions, and only by opening the A ring can the observed product of the reaction (**5H**) be obtained. This preference might be due to a more favorable orientation for interaction between the metal and the cyclopropane ring. Alternatively, this preference might be due to orbital symmetry considerations.[36] The observed pathway is a 1,5-alkyl shift, whereas the alternate pathway is a 1,3-alkyl shift. In all-carbon systems, the 1,3-shift is forbidden suprafacially while the 1,5-shift is allowed.[37]

With the exception of the conversion of **1** to **29**, all of the steps of the mechanism in Scheme VIII have ample precedent in organometallic chemistry. In order to test for the likelihood of this ring expansion as a first step of the reaction, we examined thermolysis reactions of cyclopropylcarbene–chromium complexes. When complex **1** was heated to reflux in dioxane for a period of 2 h, no reaction was observed. This process cannot be the first step of the reaction with alkynes unless the alkyne tremendously accelerates the ring expansion. If the system is activated by placement of an alkene at the 2-position of the cyclopropane ring (i.e., complex **12** of Scheme V), then net ring expansion occurs to give the cyclopentenone derivative **16**. This process was found to be general for a wide variety of (2-alkenylcyclopropyl)carbene complexes.[18] The ring-expansion reaction is competitive with alkyne cocyclization; a mixture of **16** (37% yield) and cyclopentenone **5A-trans** (14% yield) was obtained from the reaction of complex **12** and diphenylacetylene. Mechanistic investigations of this reaction are presently in progress.

d. Regiochemistry of Alkyne Insertion. The overall regiochemistry of the reaction is set in the metallacyclobutene ring forming (or alkyne insertion) step (**22** → **23** or **24**, Scheme VII) of the reaction. Investigations by others in this area have shown that the larger group ends up α to the chromium in the metallacyclobutene.[38] By following these substituents through the mechanism in Scheme VII, it is predicted that the larger substituent will be α to the carbonyl group in the final product. This is exactly the case when monosubstituted alkynes and unsymmetrically-disubstituted alkynes are used in the reaction. A comparison of regioselectivities observed in this reaction with those observed between the reaction of arylcarbene–chromium complexes and alkynes reveals that the regioselectivity in this reaction is slightly lower. That these processes are controlled by steric effects can be seen by viewing the examples in Table I (entries B, C, F–L), where the larger group does end up α to the carbonyl group in the product. Also, little regioselectivity is observed in the reaction of complex **1** with phenyl(*p*-methoxyphenyl)acetylene, indicating that there is only a minor electronic effect in the reaction. The reaction is completely regioselective with monosubstituted alkynes, but mixtures are usually obtained when unsymmetrically-disubstituted alkynes are used in the reaction. A method to control the overall regioselectivity of the reaction through an intramolecular version has recently been reported.[39]

Conclusions

We have studied the scope, limitation, and mechanism of the reaction between alkynes and cyclopropylcarbene–chromium complexes. The overall conversion represents a versatile one-step method for the synthesis of highly-substituted five-membered rings. The reaction appears to proceed by the intermediacy of metallacyclobutene intermediates, which eventually provide the product cyclopentenones by the mechanism in Scheme VII. The simplicity and availability of the reacting components, alkynes and cyclopropylcarbene-chromium complexes, coupled with the high regioselectivity and functional group toleration make this reaction a powerful method for carbocyclic five-membered-ring construction.

Experimental Section

General Experimental. Nuclear magnetic resonance spectra (^{1}H and ^{13}C) spectra were recorded on a Bruker AF200 (200 MHz) or a Bruker AF400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded on a Nicolet FT-IR spectrometer. Band positions are reported in reciprocal centimeters. Band intensities are reported relative to the most intense band and are listed as follows: br (broad), vs (very strong), s (strong), m (medium), w (weak). Mass spectra (MS) were obtained on a VG 7070E spectrometer using elcctron impact ionization or on a Hewlett-Packard GC-Mass Spec 5970B with mass selection detector; m/e values are reported. Melting points were taken on a Fisher-Johns melting point apparatus (Model 12-144) equipped with a calibrated thermometer. Gas chromatography (GC) was performed on a Hewlett-Packard Model 5890A gas chromatograph equipped with a flame ionization detector and Hewlett-Packard integrator, Model 3390A. All runs were made using a variable-temperature program. The column used in all runs was a 3% OV-17 on Chromosorb W, 6 ft × $^1/_8$ in. stainless steel column. In all runs, helium was used as the carrier gas. Routine flash column chromatography was performed using thick-walled glass columns and "flash grade" silica (Bodman 230–400 mesh). Routine thin-layer chromatography was effected by using precoated 0.25-mm silica gel plates purchased from Whatman. The relative proportion of solvents in mixed chromatography solvents refers to the volume:volume ratio. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

General Procedure I. Synthesis of Carbene Complexes. To a solution of the monobromocyclopropane (1.0 equiv) under nitrogen at −78 °C in diethyl ether was added by syringe *tert*-butyllithium (2.0 equiv of a 1.7 M hexane solution) over a period of 10 min. This solution was stirred at −78 °C for a period of 30 min and then transferred by cannula to a suspension of chromium hexacarbonyl (1.0 equiv) in diethyl ether at 0 °C. This mixture was warmed to 25 °C and was allowed to stir for 1.5–2 h. The reaction mixture was cooled to 0 °C, and methyl fluorosulfonate (5.0 equiv) was added. The reaction mixture was warmed to 25 °C and stirred for 30 min. After the extraction with sodium bicarbonate solution, sodium chloride solution, and water, the organic layer was dried with

(34) For a recent discussion concerning the difference of free vs metal-bound ketenes, see: Hegedus, L. S.; Montgomery, J.; Narukawa, Y.; Snustad, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 5784–5791.

(35) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533–2539.

(36) For a recent reference to pericyclic reactions of organometallic systems, see: Goldschmidt, Z.; Hezroni, Langerman, D.; Gottlieb, H. E.; Bakal, Y. *Isr. J. Chem.* **1990**, *30*, 385–390. (b) For an example, see: Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M.; Silvestre, J.; Hoffmann, R. *Organometallics* **1986**, *5*, 1733–1741. (c) It has been suggested that the $Cr(CO)_5$ fragment is isolobal to the CH_2 fragment. Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711–724. (d) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. (e) For an interesting discussion of [2 + 2] cycloadditions vs [4 + 2] cycloadditions in a transition-metal system, see: Doxsee, K. M.; Farahi, J. B.; Hope, H. *J. Am. Chem. Soc.* **1991**, *113*, 8889–8898.

(37) Cyclopropyl-substituted dienes typically do not react via this pathway. (a) Doering, W. v. E.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 115–122. (b) Frey, H. M.; Krantz, Z. *J. Chem. Soc. A* **1969**, 1159–1161.

(38) (a) Wulff, W. D.; Tang, P.-C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677–7678. (b) Dötz, K. H.; Muhlemeier, J.; Schubert, U.; Orama, O. *J. Organomet. Chem.* **1983**, *247*, 187–201. (c) In some cases, there is an electronic effect on the regioselectivity of the reaction between alkynes and cyclopropylcarbene–chromium complexes. For an example, see reference 10p. (d) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471–3474.

(39) Herndon, J. W.; Matasi, J. J. *J. Org. Chem.* **1990**, *55*, 786–788.

magnesium sulfate. Concentrated crude product was purified by flash chromatography.

Synthesis of Carbene Complex 1. General procedure I was followed using cyclopropyl bromide (4.80 g, 39.7 mmol), *tert*-butyllithium (36.4 mL of a 2.2 M hexane solution 80.1 mmol), chromium hexacarbonyl (8.80 g, 40.0 mmol), and methyl fluorosulfonate (25.2 g, 153 mmol). Final purification was achieved by flash chromatography on silica gel using pure hexane as the eluent. A single yellow fraction was isolated and identified as complex **1** (8.10 g, 74%).

Pentacarbonyl[(cyclopropyl)methoxymethylene]chromium (1): ^{1}H NMR (C_6D_6) δ 3.78 (s, 3 H), 3.01 (tt, 1 H, J = 7.6, 3.2 Hz), 0.85 (m, 2 H), 0.48 (m, 2 H); ^{1}H NMR ($CDCl_3$) δ 4.65 (s, 3 H), 3.46 (m, 1 H), 1.36 (m, 2 H), 1.18 (m, 2 H). The spectral data were in agreement with those reported previously for this compound.[40]

Synthesis of Carbene Complex 12. General procedure I was followed using 1-bromo-2-ethenyl-2-methylcyclopropane[41] (1.85 g, 11.5 mmol), *tert*-butyllithium (13.5 mL of a 1.7 M hexane solution), chromium hexacarbonyl (2.5 g, 11.4 mmol), and methyl fluorosulfonate (8.27 g, 72.5 mmol). Final purification was achieved by flash chromatography on silica gel using pure hexane as the eluent. A yellow oil identified as complex **12** was obtained (8.47 g, 68%). Spectral data showed this to be a cis/trans mixture; the isomers could not be separated.

Pentacarbonyl[(2-ethenyl-2-methylcyclopropyl)methoxymethylene]chromium (12, cis/trans mixture); ^{1}H NMR ($CDCl_3$) δ major isomer 5.55 (dd, 1 H, J = 18.0, 13.0 Hz), 5.10 (m, 2 H), 4.65 (s, 3 H), 3.65 (t, 1 H, J = 8.4 Hz), 2.15 (dd, 1 H, J = 10.9, 9.5 Hz), 1.50 (s, 3 H), 1.25 (m, 1 H), minor isomer 5.65 (dd, 1 H, J = 18.0, 12.0 Hz), 5.10 (m, 2 H), 4.75 (s, 3 H), 3.55 (t, 1 H, J = 8.2 Hz), 1.95 (dd, 1 H, J = 10.8, 9.3 Hz), 1.25 (m, 1 H), 1.15 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 351.2, 350.4, 223.4, 216.5, 143.6, 136.9, 115.5, 113.1, 66.3, 66.1, 57.5, 55.9, 40.6, 40.3, 27.5, 26.2, 23.7, 14.3; IR($CDCl_3$) 2060 (s), 1980 (s), 1950 (vs), 1645 (w), 1460 (m), 1390 (m), 1250 (s), 1050 (m), 980 (m), 920 (s) cm^{-1}; MS (CI) m/z 316 (M, 100), 288, 260, 232, 204, 176, 153, 125; HRMS (EI) calcd for $C_{13}H_{12}O_6Cr$ 316.0039, found 316.0043. Anal. Calcd for $C_{13}H_{12}O_6Cr$: C, 49.37; H, 3.80. Found: C, 49.35; H, 4.01. From the integration values in the ^{1}H NMR spectrum, the cis:trans ratio was determined to be 58:42. Irradiation of the peak at δ 1.50 produces an 18% enhancement of the peak at δ 3.65.

Synthesis of Carbene Complex 8. General procedure I was followed using (2-bromocyclopropyl)benzene[42] (0.43 g, 2.2 mmol), *tert*-butyllithium (2.60 mL of a 1.7 M hexane solution), chromium hexacarbonyl (0.48 g, 2.2 mmol), and methyl fluorosulfonate (1.02 g, 8.9 mmol). Final purification was achieved by flash chromatography on silica gel using 19:1 hexane/ethyl acetate as the eluent. A single yellow fraction was isolated and identified as complex **8** (0.49 g, 63%). The ^{1}H NMR spectrum suggested that this was a mixture of the cis and trans isomers. A small sample of the cis isomer was separated and characterized; however, in subsequent transformations the cis/trans mixture was employed. The trans isomer could not be obtained free of the cis isomer.

***cis*-Pentacarbonyl[methoxy(2-phenylcyclopropyl)methylene]chromium (8-cis)**: ^{1}H NMR ($CDCl_3$) δ 7.26–7.14 (m, 5 H), 4.10 (s, 3 H), 3.95 (ddd, 1 H, J = 5.6, 6.9, 8.9 Hz), 3.23 (q, 1 H, J = 8.4 Hz), 2.25 (ddd, 1 H, J = 4.8, 5.4, 7.8 Hz), 1.45 (ddd, 1 H, J = 4.8, 6.9, 8.4 Hz), minor isomer 7.32–7.10 (m, 5 H), 4.71 (s, 3 H), 3.63 (ddd, 1 H, J = 3.9, 5.2, 7.8 Hz), 2.85 (ddd, 1 H, J = 3.8, 7.2, 9.1 Hz), 2.00 (ddd, 1 H, J = 4.2, 5.2, 9.2 Hz), 1.66 (dt, 1 H, J = 4.1, 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ major isomer 350.2, 223.5, 216.6, 135.3, 129.6, 127.9, 127.0, 65.5, 48.9, 36.9, 17.5; IR ($CDCl_3$) 2060 (s), 1980 (s), 1945 (vs), 1600 (w), 1500 (w), 1215 (vs), 1190 (s) cm^{-1}; MS (CI) 352 (M, 100), 323, 295, 268, 240, 212, 177, 161, 91, 69; HRMS (CI) calcd for $C_{16}H_{12}O_6Cr$ 352.0039, found 352.0043. The major compound was assigned as the cis isomer because the chemical shift for the methoxy group, δ 4.10, is significantly lower than those for all other carbene complexes reported here and can be attributed to anisotropic interaction with the phenyl group.

***trans*-Pentacarbonyl[methoxy(2-phenylcyclopropyl)methylene]chromium (8-trans)**: ^{1}H NMR ($CDCl_3$) (this was obtained from the cis/trans mixture, factoring out the peaks previously attributed to the cis isomer) δ 7.32–7.10 (m, 5 H), 4.71 (s, 3 H), 3.63 (ddd, 1 H, J = 3.9, 5.2, 7.8 Hz), 2.85 (ddd, 1 H, J = 3.8, 7.2, 9.1 Hz), 2.00 (ddd, 1 H, J = 4.2, 5.2, 9.2 Hz), 1.66 (dt, 1 H, J = 4.1, 7.5 Hz). From the integration values in the ^{1}H NMR spectrum, the cis:trans ratio was determined to be 54:46.

Synthesis of Carbene Complex 13. General procedure I was followed using 3-bromotricyclo[3.2.1.0^{2,4}]octane[43] (0.94 g, 5.0 mmol), *tert*-butyllithium (5.90 mL of a 1.7 M hexane solution, 10.0 mmol), chromium hexacarbonyl (1.32 g, 6.0 mmol), and methyl fluorosulfonate (3.0 g, 26.0 mmol). Final purification was achieved by flash chromatography on silica gel using hexane as the eluent. The yellow band with R_f value 0.72 in 9:1 hexane/ethyl acetate was collected, giving a yellow oil identified as complex **13** after solvent removal (1.14 g, 67%); this compound was assigned as the exo isomer due to the small coupling (2.5 Hz) between the hydrogens on the cyclopropane ring.

***exo*-Pentacarbonyl[methoxy(tricyclo[3.2.1.0^{2,4}]oct-3-yl)methylene]chromium (13)**: ^{1}H NMR ($CDCl_3$) δ 4.59 (s, 3 H), 3.42 (t, 1 H, J = 2.5 Hz), 2.38 (br s, 2 H), 1.71 (br d, 2 H, J = 2.5 Hz), 1.47 (m, 2 H), 1.23 (m, 3 H), 0.80 (br d, 1 H, J = 11.5 Hz); ^{13}C NMR ($CDCl_3$) δ 351.2, 223.5, 216.8, 66.7, 46.3, 36.6, 36.0, 29.0, 28.4; IR ($CDCl_3$) 2963 (m), 2912 (w), 2875 (w), 2060 (s), 1981 (s), 1937 (vs), 1452 (m), 1377 (m), 1266 (m), 1239 (m), 1193 (m), 1016 (m) cm^{-1}; MS (CI) m/z 342 (M$^+$), 314, 286, 236, 230, 219, 202, 178, 167 (100), 151; HRMS (CI) calcd for $C_{15}H_{14}CrO_6$ 342.0195, found 342.0193.

Synthesis of Carbene Complex 14. Carbene complex **1** (1.76 g, 6.38 mmol) and triphenylphosphine (2.01 g, 7.68 mmol) were dissolved in 60 mL of a benzene/hexane (1:1) mixture and heated to reflux for 5 h. The solvent was removed on a rotary evaporator, and the residue was subjected to flash chromatography on silica gel using hexane/benzene (4:1) as the eluent. The orange component with R_f value 0.33 (4:1 hexane/benzene) was collected and identified as carbene complex **14** (1.96 g, 60%). The ^{1}H NMR spectrum revealed that this was an 89:11 cis/trans mixture according to ^{1}H NMR integration of the methoxy peaks at δ 4.24 and 4.18.

Tetracarbonyl[(cyclopropyl)methoxymethylene](triphenylphosphine)chromium (14, cis/trans mixture): ^{1}H NMR (C_6D_6) δ 6.90–7.80 (m, 15 H), 4.24 (s, 3 H, trans isomer), 4.18 (s, 3 H, cis isomer), 3.11 (m, 1 H), 0.98–1.08 (m, 2 H), 0.37–0.57 (m, 2 H); ^{13}C NMR (C_6D_6) δ 357.4 (d, J = 12.1 Hz) (the carbene carbon for the minor (trans) isomer could not be detected), 230.4 (d, J = 12.0 Hz), 227.3 (s), 223.9 (d, J = 11.7 Hz), 222.1 (d, J = 12.4 Hz), 137.0–127.8 (15 lines), 65.4 (s), 41.1 (s), 16.9 (s); MS (EI) m/z 510 (M$^+$), 314, 277, 263 (100), 262, 201, 183, 152, 108, 84, 69; HRMS (EI) calcd for $C_{27}H_{23}CrO_5P$ 510.0688, found 510.0728.

General Procedure II. Reaction of Alkynes with Cyclopropylcarbene–Chromium Complexes. To a three-neck round-bottom flask equipped with reflux condenser, stopper, and septum, under nitrogen, was added 20 mL of 1% aqueous dioxane solution. The dioxane solution was heated to reflux. To this refluxing solution was added a solution of 1 equiv of carbene complex **1** (0.1 M) and 1.5–2 equiv of the alkyne in dioxane by syringe pump over a period of 2 h. After the addition was complete, the mixture was allowed to reflux for a period of 6 h. The mixture was then allowed to cool to 25 °C, and the solvent was removed on a rotary evaporator. Ethyl acetate (50 mL) was added, and the solution was filtered through Celite. The solvent was removed on a rotary evaporator, and final purification was achieved through flash chromatography on silica gel.

Equilibration Procedure. The solution of the substrate (0.07 M) and sodium methoxide (0.02 M) in methanol was allowed to stir under nitrogen for a period of 24 h. The reaction mixture was poured into a mixture of water and ether in a separatory funnel. The ether layer was washed two times with water and once with saturated sodium chloride solution and dried over magnesium sulfate, and the solvent was removed on a rotary evaporator. In most cases the crude product was pure when checked with TLC and ^{1}H NMR. Otherwise the crude material was purified via flash chromatography on silica gel.

Reaction of Diphenylacetylene with Complex 1 (Entry A). General proceudre II was followed using diphenylacetylene (0.356 g, 2.00 mmol) and complex **1** (0.276 g, 1.00 mmol). After chromatography on silica gel using 3:2 hexane/ethyl acetate as eluent, three components were isolated. The first component that eluted (R_f value 0.53 in 3:2 hexane/ethyl acetate, 0.005 g, 2%) was identified as cyclopentenone **6A**. The second component that eluted (R_f value 0.33 in 3:2 hexane/ethyl acetate 0.174 g, 66%) was identified as cyclopentenone **5A-trans**. The third component that eluted (R_f value 0.22 in 3:2 hexane/ethyl acetate, 0.031 g, 12%) was identified as cyclopentenone **5A-cis**. Integration of the crude ^{1}H NMR spectrum in the region 4.5–6.0 ppm confirmed the relative ratios of the three isomers.

4-Methoxy-2,3-diphenyl-2-cyclopentenone (6A): ^{1}H NMR ($CDCl_3$) δ 7.15–7.36 (m, 10 H), 5.04 (dd, 1 H, J = 2.0, 5.9 Hz), 3.39 (s, 3 H), 2.96 (dd, 1 H, J = 5.9, 18.3 Hz), 2.66 (dd, 1 H, J = 2.0, 18.3 Hz); ^{13}C NMR ($CDCl_3$) δ 203.1, 165.1, 141.5, 134.0, 131.3, 129.6, 128.8, 128.3,

(40) Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2119–2124.

(41) The requisite bromide was prepared from isoprene via the sequence isoprene + dibromocarbene → 2-methyl-2-vinyl-1,1-dibromocyclopropane (A), A + Bu_3SnH → 2-methyl-2-vinyl-1-bromocyclopropane (B). (a) Skattebol, L. *J. Org. Chem.* **1964**, *29*, 2591–2956. (b) Seyferth, D.; Yamazaki, H.; Alleston, D. L. *J. Org. Chem.* **1963**, *28*, 703–706.

(42) For synthesis of (2-bromocyclopropyl)benzene, see: Hausser, J. W.; Grubber, M. J. *J. Org. Chem.* **1972**, *37*, 2648–2650.

(43) Martel, B.; Hiriat, J. M. *Synthesis* **1972**, 201–202.

128.2, 78.1, 56.6, 41.1; IR ($CDCl_3$) 3060 (m), 2930 (m), 1705 (s), 1600 (m), 1440 (m), 1350 (m), 1260 (m), 1210 (m), 1180 (s) cm^{-1}; MS (EI) m/z 264 (M^+), 248, 233, 205, 191, 178 (100), 152, 105, 88, 77; HRMS (EI) calcd for $C_{18}H_{16}O_2$ 264.1150, found 264.1156. This compound was subjected to the equilibration procedure, and only **5A-trans** was isolated according to TLC and ^1H NMR analysis.

***trans*-3-Methoxy-4,5-diphenyl-2-cyclopentenone (5A-trans)**: ^1H NMR ($CDCl_3$) δ 7.25–7.38 (m, 6 H), 7.11–7.18 (m, 4 H), 5.58 (d, 1 H, J = 1.1 Hz), 3.98 (dd, 1 H, J = 1.1, 3.3 Hz), 3.83 (s, 3 H), 3.59 (d, 1 H, J = 3.3 Hz); ^{13}C NMR ($CDCl_3$) δ 203.7 (s), 190.0 (s), 139.3 (s), 138.8 (s), 128.9, 128.7, 127.6, 127.4, 127.2, 127.0 (overlapping in SFORD spectrum), 104.5 (d), 62.4 (d), 59.0 (q), 56.4 (d); IR ($CDCl_3$) 3040 (m), 2945 (m), 1694 (s), 1598 (s), 1500 (m), 1457 (m), 1443 (m), 1358 (s), 1347 (s), 1170 (s) cm^{-1}; MS (EI) m/z 264 (M^+, 100), 233, 205, 187, 159, 128, 115, 102, 91, 69. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.93; H, 6.24.

***cis*-3-Methoxy-4,5-diphenyl-2-cyclopentenone (5A-cis)**: ^1H NMR ($CDCl_3$) δ 6.95–7.06 (m, 6 H), 6.77–6.83 (m, 4 H), 5.75 (d, 1 H, J = 0.7 Hz), 4.48 (d, 1 H, J = 7.8 Hz), 4.25 (d, 1 H, J = 7.8 Hz), 3.89 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 204.4, 189.3, 136.4, 135.8, 130.1, 130.0, 128.8, 127.8, 127.6, 126.7, 126.3, 106.2, 58.8, 58.0, 52.8; IR ($CDCl_3$) 3068 (w), 2942 (m), 1691 (s), 1599 (m), 1455 (m), 1354 (m), 1335 (m), 1232 (m), 1133 (s), 1101 (s), 996 (m) cm^{-1}; MS (EI) m/z 264 (M^+, 100), 249, 231, 203, 187, 178, 165, 115, 91, 73; HRMS (EI) calcd for $C_{18}H_{16}O_2$ 264.1150, found 264.1156. This compound was subjected to the equilibration procedure. Only compound **5A-trans** was isolated from the reaction as judged by ^1H NMR and TLC analysis.

Reaction of Phenylacetylene (1.3 equiv) with Complex 1 (Entry B). General procedure II was followed using phenylacetylene (0.040 g, 0.39 mmol) and complex **1** (0.083 g, 0.30 mmol). After chromatography on silica gel using hexane/ethyl acetate (1:1) as eluent, a minor component was isolated having an R_f value of 0.61 in 1:1 hexane/ethyl acetate (0.005 g, 3%). It was assigned the structure cyclopentenone **10**, which has the same spectral data as the authentic sample prepared.[44] The major component was isolated having an R_f value of 0.28 in 1:1 hexane/ethyl acetate (0.034 g, 61%). This compound was assigned as cyclopentenone **5B**.

3-Methoxy-5-phenyl-2-cyclopentenone (5B): ^1H NMR ($CDCl_3$) δ 7.07–7.35 (m, 5 H), 5.38 (t, 1 H, J = 1.1 Hz), 3.38 (s, 3 H), 3.69 (dd, 1 H, J = 7.7, 3.1 Hz), 3.12 (ddd, 1 H, J = 17.9, 7.7, 1.1 Hz), 2.69 (ddd, 1 H, J = 17.9, 3.1, 1.1 Hz); irradiated at δ 5.38 δ 3.12 (dd, J = 17.9, 7.7 Hz), 2.69 (dd, J = 17.9, 3.1 Hz); IR (CH_2Cl_2) 3060 (m), 3020 (m), 2930 (m), 1685 (s), 1595 (s), 1493 (m), 1450 (m), 1430 (m), 1350 (s), 1238 (m), 1183 (s), 1165 (s), 980 (s), 830 (s) cm^{-1}; MS (EI) m/z 188 (M^+, 100), 173, 159, 145, 128, 115, 102, 91, 77, 69. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.53; H, 6.50.

3,4-Diphenyl-2-cyclopentenone (10): ^1H NMR ($CDCl_3$) δ 7.49–7.53 (m, 2 H), 7.12–7.31 (m, 8 H), 6.74 (d, 1 H, J = 1.3 H), 4.62 (ddd, 1 H, J = 7.3, 2.2, 1.7 Hz), 3.11 (dd, 1 H, J = 18.8, 7.3 Hz), 2.44 (dd, 1 H, J = 18.8, 2.2 Hz); IR (CH_2Cl_2) 3040 (w), 3020 (w), 2900 (w), 1700 (s), 1680 (s), 1590 (s), 1560 (m), 1482 (m), 1435 (w), 1398 (w), 1315 (w), 1273 (w), 1180 (s), 1020 (w), 1065 (w) cm^{-1}; MS (EI) m/z 234 (M^+, 100), 205, 191, 178, 157, 128, 102, 91, 77, 63.

Reaction of Phenylacetylene (2 equiv) with Complex 1. General procedure II was followed using phenylacetylene (0.065 g, 0.64 mmol) and carbene complex **1** (0.083 g, 0.30 mmol). After chromatography on silica gel using 1:1 hexane/ethyl acetate as eluent, three components were isolated. The first component was assigned the structure 2,5-diphenyl-2-cyclopentenone (R_f 0.71 in hexane/ethyl acetate, 1:1, 0.011 g, 4%), the second component was compound **10** (0.016 g, 5%), and the third component was identified as compound **5B** (0.035 g, 62%).

2,5-Diphenyl-2-cyclopentenone: ^1H NMR ($CDCl_3$) δ 7.96 (t, 1 H, J = 3.0 Hz), 7.74 (dd, 2 H, J = 1.8, 7.7 Hz), 7.42–7.17 (m, 8 H), 3.76 (dd, 1 H, J = 2.6, 7.0 Hz), 3.26 (ddd, 1 H, J = 3.0, 7.0, 19.8 Hz), 2.82 (ddd, 1 H, J = 2.6, 3.0, 19.8); IR ($CDCl_3$) 1690 cm^{-1}. The spectral data were in agreement with those previously reported for this compound.[45]

Reaction of 1-Phenylpropyne with Complex 1 (Entry C). General procedure II was followed using 1-phenylpropyne (0.25 mL, 2.0 mmol) and complex **1** (0.276 g, 1.0 mmol). After chromatography on silica gel using 3:2 hexane/ethyl acetate as eluent, three components were isolated. The first component that eluted (R_f value, 0.51 in 3:2 hexane/ethyl acetate, 0.021 g, 10%) was assigned as 4-methoxy-2-methyl-3-phenyl-2-cyclopentenone [**6C** (R_1 = CH_3, R_2 = Ph)]. The second component that eluted (R_f value, 0.28 in 3:2 hexane/ethyl acetate, 0.112 g, 55%) was assigned as cyclopentenone **5C-trans**. The third component that eluted (R_f value, 0.21 in 3:2 hexane/ethyl acetate, 0.041 g, 20%) was assigned as cyclopentenone **5C-cis**. Integration of the crude ^1H NMR spectrum in the region 4.4–5.5 ppm confirmed the relative ratios of the three isomers.

4-Methoxy-2-methyl-3-phenyl-2-cyclopentenone [6C (R_1 = CH_3, R_2 = Ph)]: ^1H NMR ($CDCl_3$) δ 7.26–7.43 (m, 5 H), 4.44 (ddd, 1 H, J = 5.9, 2.2, 0.9 Hz), 3.45 (s, 3 H), 2.80 (dd, 1 H, J = 18.2, 5.9 Hz), 2.46 (dd, 1 H, J = 18.2, 2.2 Hz), 2.17 (d, 3 H, J = 0.9 Hz), irradiated at δ 2.17, δ 4.44 (dd, J = 5.9, 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 203.0, 168.1, 141.8, 130.9, 129.1, 128.2, 128.0, 79.7, 57.2, 41.0, 14.9; IR ($CDCl_3$) 3063 (w), 2992 (m), 2934 (m), 1702 (s), 1600 (m), 1380 (m), 1345 (m), 1244 (m), 1195 (m), 1164 (s), 1137 (s), 1099 (s), 1047 (m) cm^{-1}; MS (EI) m/z 202 (M^+), 187, 174, 159, 143, 128, 115 (100), 105, 99, 77; HRMS (EI) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.1005. This compound did not convert to **5C-trans** when subjected to the equilibration procedure.

***trans*-3-Methoxy-4-methyl-5-phenyl-2-cyclopentenone (5C-trans)**: ^1H NMR ($CDCl_3$) δ 7.09–7.32 (m, 5 H), 5.32 (d, 1 H, J = 1.0 Hz), 3.83 (s, 3 H), 3.19 (d, 1 H, J = 3.2 Hz), 2.86 (ddq, 1 H, J = 3.2, 1.0, 7.1 Hz), 1.28 (d, 3 H, J = 7.1 Hz), irradiated at δ 5.32, δ 2.86 (dq, J = 3.2, 7.1 Hz), irradiated at δ 2.86, δ 5.32 (s), 3.19 (s), 1.28 (s), irradiated at δ 1.28, δ 2.86 (dd, J = 3.2, 1.0 Hz); ^{13}C NMR ($CDCl_3$) δ 203.4, 192.3, 139.1, 128.5, 127.7, 126.8, 102.5, 60.8, 58.6, 44.8, 16.9; IR ($CDCl_3$) 3067 (m), 3031 (m), 2960 (m), 1686 (s), 1594 (s), 1467 (m), 1458 (m), 1380 (m), 1352 (s), 1169 (s), 1134 (s), 991 (s) cm^{-1}; MS (EI) m/z 202 (M^+), 187, 173, 159, 144, 125, 112, 91, 69 (100); HRMS (EI) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0979.

***cis*-3-Methoxy-4-methyl-5-phenyl-2-cyclopentenone (5C-cis)**: ^1H NMR ($CDCl_3$) δ 7.00–7.30 (m, 5 H), 5.44 (d, 1 H, J = 0.9 Hz), 3.92 (d, 1 H, J = 7.6 Hz), 3.87 (s, 3 H), 3.20 (d of quintets, 1 H, J = 7.5, 0.9 Hz), 0.76 (d, 3 H, J = 7.4 Hz), irradiated at δ 3.20, δ 5.44 (s), 3.92 (s); ^{13}C NMR ($CDCl_3$) δ 205.1, 193.4, 136.9, 129.8, 128.2, 126.8, 103.6, 58.7, 56.2, 39.9, 14.5; IR ($CDCl_3$) 3062 (w), 3027 (m), 2978 (m), 2943 (m), 1685 (s), 1594 (s), 1458 (m), 1350 (s), 1243 (s), 1170 (m) cm^{-1}; MS (EI) m/z 202 (M^+, 100), 187, 173, 159, 155, 141, 131, 128, 125, 115; HRMS (EI) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0989. This compound was converted to **10C-trans** when subjected to the equilibration procedure.

Reaction of (*p*-Methoxyphenyl)phenylacetylene with Complex 1 (Entry D). General procedure II was followed using carbene complex **1** (0.212 g, 0.77 mmol) and (*p*-methoxyphenyl)phenylacetylene[46] (0.192 g, 0.92 mmol). After chromatography on silica gel using 3:2 ethyl acetate/hexane as eluent, two components were isolated. The first component (R_f value 0.45 in 3:2 ethyl acetate/hexane) was assigned as the mixture of trans isomers of the two regioisomers (**5D-trans** and **7D-trans**) (0.091 g, 40%). The second component (R_f value 0.35 in 3:2 ethyl acetate/hexane) was assigned as the cis isomers of the two regioisomers (0.084 g, 37%). ^1H NMR of both components showed that the two regioisomers (**5D-cis** and **7D-cis**) are an approximately 52:48 mixture.

The cis component was subjected to the equilibration procedure, which converted the two cis isomers to pure trans isomers of the two regioisomers in the same ratio. Under the same equilibration conditions the trans component did not change. Further attempts to separate the two regioisomers were not successful.

***trans*-3-Methoxy-4-(4-methoxyphenyl)-5-phenyl-2-cyclopentenone (5D-trans) and *trans*-3-methoxy-5-(4-methoxyphenyl)-4-phenyl-2-cyclopentenone (7D-trans)** (inseparable—integral values are reported relative to other peaks in the same isomer): ^1H NMR ($CDCl_3$) δ 7.12–7.25 (m, 6 H), 7.04 (m, 4 H), 6.98 (d, 2 H, J = 8.3 Hz), 6.96 (d, 2 H, J = 8.3 Hz), 6.78 (d, 4 H, J = 8.3 Hz), 6.76 (d, 2 H, J = 8.3 Hz), 5.50 (d, 1 H, J = 1.0 Hz), 5.49 (d, 1 H, J = 1.0 Hz), 3.89 (dd, 1 H, J = 3.0, 1.0 Hz), 3.88 (dd, 1 H, J = 3.0, 1.0 Hz), 3.76 (s, 6 H), 3.69 (s, 3 H), 3.67 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 204.0, 203.8, 190.2, 190.0, 158.9, 158.7, 139.4, 138.9, 131.2, 130.8, 128.9, 128.7, 128.6, 128.2, 127.6, 127.3, 127.2, 127.0, 114.3, 114.2, 104.4, 104.3, 67.0, 62.5, 61.7, 59.0, 58.9, 56.5, 55.7, 55.1; IR ($CDCl_3$) 3031 (w), 2941 (m), 2840 (w), 1691 (s), 1597 (vs), 1513 (s), 1455 (m), 1440 (m), 1354 (m), 1335 (m), 1251 (s), 1168 (m), 1035 (m) cm^{-1}; MS (EI) m/z 294 (M^+, 100), 279, 265, 263, 235, 217, 189, 159, 145, 135, 105, 84, 69; HRMS (EI) calcd for $C_{19}H_{18}O_3$ 294.1256, found 294.1269.

***cis*-3-Methoxy-4-(4-methoxyphenyl)-5-phenyl-2-cyclopentenone (5D-cis) and *cis*-3-methoxy-5-(4-methoxyphenyl)-4-phenyl-2-cyclopentenone (7D-cis)** (inseparable—integral values are reported relative to other peaks in the same isomer): ^1H NMR ($CDCl_3$) δ 6.93–7.07 (m, 6 H), 6.78 (m, 4 H), 6.72 (d, 2 H, J = 9.0 Hz), 6.71 (d, 2 H, J = 9.0 Hz), 6.56 (d, 2 H, J = 9.0 Hz), 6.51 (d, 2 H, J = 9.0 Hz), 5.21 (br s, 2 H), 4.41 (br d, 1 H, J = 8.0 Hz), 4.40 (br d, 1 H, J = 8.0 Hz), 4.20 (d, 1 H, J = 8.0 Hz), 4.19 (d, 1 H, J = 8.0 Hz), 3.88 (s, 6 H), 3.62 (s, 3 H), 3.60 (s, 3

(44) For spectral data for compound **9**, see: Freeman, B. H.; Gagan, J. M. F. *Tetrahedron* **1973**, *29*, 4307–4312.

(45) Khand, I. U.; Pauson, P. L. *J. Chem. Res., Miniprint* **1977**, 168–180.

(46) (*p*-Methoxyphenyl)phenylacetylene was prepared according to a literature procedure. Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280–2286.

H); ^{13}C NMR ($CDCl_3$) δ 204.9, 204.7, 189.6, 189.3, 158.3, 158.0, 136.5, 136.0, 131.0, 130.0, 129.7, 128.8, 128.4, 128.2, 127.9, 127.6, 126.7, 126.3, 114.3, 113.3, 106.0, 105.9, 58.7, 58.0, 57.4, 55.0, 52.9, 52.1; IR ($CDCl_3$) 3034 (w), 2959 (w), 2940 (m), 2840 (w), 1695 (s), 1598 (vs), 1513 (s), 1456 (m), 1440 (m), 1355 (s), 1338 (m), 1250 (s), 1180 (m), 1037 (m) cm^{-1}; MS (EI) m/z 294 (M^+, 100), 279, 263, 235, 217, 189, 165, 151, 135, 121; HRMS (EI) calcd for $C_{19}H_{18}O_3$ 294.1256, found 294.1264.

Reaction of 4-Octyne with Complex 1 (Entry E). General procedure II was followed using 4-octyne (0.44 mL, 3 mmol) and complex **1** (0.414 g, 1.5 mmol). After chromatography on silica gel using 3:2 hexane/ethyl acetate as eluent, one component was isolated having an R_f value of 0.43 in 3:2 hexane/ethyl acetate (0.176 g, 60%). Analysis of this component by ^{1}H NMR revealed that a mixture of isomers was obtained. Integration of the ^{1}H NMR spectrum in the olefinic region suggested that a 9:1 mixture of two isomers (**5E-trans** and **5E-cis**) was present. A sample of this mixture was subjected to the equilibration procedure, and only a single compound, corresponding to the major isomer, was obtained. The structure of this compound was assigned as the cyclopentenone **5E-trans**. The minor isomer from this reaction was assumed to be the cis stereoisomer.

***trans*-4,5-Dipropyl-3-methoxy-2-cyclopentenone (5E-trans)**: ^{1}H NMR ($CDCl_3$) δ 5.16 (d, 1 H, J = 1.0 Hz), 3.76 (s, 3 H), 2.43 (m, 1 H), 2.08 (m, 1 H), 1.57–1.69 (m, 2 H), 1.19–1.43 (m, 6 H), 0.82–0.90 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 206.9, 191.8, 102.6, 58.2, 51.4, 46.2, 34.3, 33.8, 19.8, 19.5, 13.8; IR ($CDCl_3$) 2934 (s), 2860 (s), 1670 (s), 1585 (s), 1450 (m), 1436 (m), 1348 (s), 1305 (m), 1190 (s), 1165 (s) cm^{-1}; MS (EI) m/z 196 (M^+), 167, 154, 125 (100), 112, 91, 77, 69, 59, 55; HRMS (EI) calcd for $C_{12}H_{20}O_2$ 196.1438, found 196.1463.

Reaction of 4-Methyl-2-pentyne with Complex 1 (Entry F). General procedure II was followed using 4-methyl-2-pentyne (0.164 g, 2 mmol) and carbene complex **1** (0.276 g, 1 mmol). After chromatography on silica gel using 3:2 hexane/ethyl acetate, the mixture of products with R_f value 0.45 (3:2 hexane/ethyl acetate) was collected (0.104 g, 62%). The 400-MHz ^{1}H NMR spectrum (integration of the alkene peaks) showed the ratio of the products to be 41:36:21:2 for **5F-trans/5F-cis/7F-trans/7F-cis**.

The mixture of four compounds from above was divided into two parts. From one part, analytical samples were obtained by preparative TLC with the eluent 7:3 hexane/ethyl acetate. The UV-active band was cut into slices to obtain enriched isomers. The rest of the mixture was subjected to the equilibration procedure for 2 days. After this operation, it was observed by ^{1}H NMR that the reaction mixture is composed of two isomers (**5F-trans/7F-trans**) in 77:23 ratio. The product of the equilibration reaction was subjected to flash chromatography with 7:3 hexane/ethyl acetate as eluent. The first and last fractions were found to be **5F-trans** (R_f 0.45 in 3:2 hexane/ethyl acetate) and pure **7F-cis** (R_f 0.41 in 3:2 hexane/ethyl acetate), respectively.

***trans*-3-Methoxy-4-methyl-5-(1-methylethyl)-2-cyclopentenone (5F-trans)**: ^{1}H NMR ($CDCl_3$) δ 5.18 (d, 1 H, J = 1.0 Hz), 3.78 (s, 3 H), 2.57 (br qd, 1 H, J = 7.1, 2.6 Hz), 2.21 (m, 1 H), 2.00 (dd, 1 H, J = 4.2, 2.6 Hz), 1.17 (d, 3 H, J = 7.1 Hz), 0.96 (d, 3 H, J = 7.0 Hz), 0.75 (d, 3 H, J = 6.8 Hz), irradiated at δ 5.18, δ 2.57 become sharp; ^{13}C NMR ($CDCl_3$) δ 206.5, 192.9, 103.5, 59.9, 58.6, 37.0, 28.4, 20.5, 18.3, 17.3; IR ($CDCl_3$) 3020 (w), 2963 (s), 2941 (m), 2875 (m), 1680 (s), 1596 (vs), 1459 (m), 1380 (m), 1355 (s), 1340 (m), 1320 (m), 1298 (w), 1243 (m), 1194 (w), 1170 (m) cm^{-1}; MS (EI) m/z 168 (M^+), 167, 149, 126 (100), 111, 95, 83, 69; HRMS (EI) calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1156. **5F-cis**: ^{1}H NMR ($CDCl_3$) δ 5.17 (d, 1 H, J = 1.0 Hz), 3.78 (s, 3 H), 2.98 (d of quintet, 1 H, J = 1.0, 7.2 Hz), 2.39 (dd, 1 H, J = 7.2, 4.3 Hz), 2.00 (m, 1 H), 1.23 (d, 3 H, J = 7.2 Hz), 1.13 (d, 3 H, J = 6.9 Hz), 0.94 (d, 3 H, J = 6.8 Hz), irradiated at δ 5.17, δ 2.98 become sharper.

***trans*-3-Methoxy-5-methyl-4-(1-methylethyl)-2-cyclopentenone (7F-trans)**: ^{1}H NMR ($CDCl_3$) δ 5.24 (d, 1 H, J = 0.9 Hz), 3.80 (s, 3 H), 2.39 (ddd, 1 H, J = 0.9, 2.6, 3.9 Hz), 2.18 (m, 1 H), 1.17 (d, 3 H, J = 7.4 Hz), 0.96 (d, 3 H, J = 6.9 Hz), 0.76 (d, 3 H, J = 6.9 Hz), irradiated at δ 5.24, δ 2.39 (dd, J = 2.6, 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ 207.9, 191.0, 103.5, 58.5, 54.8, 41.9, 28.1, 20.2, 17.3, 17.0; IR ($CDCl_3$) 2964 (m), 2934 (w), 2875 (w), 1683 (s), 1592 (vs), 1457 (w), 1440 (w), 1374 (w), 1355 (m), 1326 (w), 1242 (w), 1231 (w), 1194 (w), 1170 (w), 1004 (w) cm^{-1}; MS (EI) m/z 168 (M^+), 167, 149 (100), 129, 112, 101, 83, 71, 57; HRMS (EI) calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1153. **7F-cis**: ^{1}H NMR ($CDCl_3$) δ 5.29 (d, 1 H, J = 0.5 Hz), 3.79 (s, 3 H), 2.80 (ddd, 1 H, J = 0.5, 2.2, 7.2 Hz), 2.64 (quintet, 1 H, J = 7.2 Hz), 2.01 (d of septet, 1 H, J = 2.2, 7.0 Hz), 1.12 (d, 3 H, J = 7.2 Hz), 1.11 (d, 3 H, J = 7.0 Hz), 0.67 (d, 3 H, J = 7.0 Hz), irradiated at δ 5.29, δ 2.80 (dd, J = 2.2, 7.2 Hz).

Reaction of 1-Pentyne with Complex 1 (Entry G). General procedure II was followed using 1-pentyne (0.20 mL, 2.0 mmol) and complex **1** (0.276 g, 1.00 mmol). After chromatography on silica gel using 1:1 hexane/ethyl acetate as eluent, one component was isolated having an R_f value of 0.41 in 1:1 hexane/ethyl acetate (0.105 g, 68%). This compound was assigned as cyclopentenone **5G**.

3-Methoxy-5-propyl-2-cyclopentenone (5G): ^{1}H NMR ($CDCl_3$) δ 5.25 (t, 1 H, J = 1.0 Hz), 3.81 (s, 3 H), 2.73 (ddd, 1 H, J = 17.4, 7.0, 1.0 Hz), 2.42–2.54 (m, 1 H), 2.27 (ddd, 1 H, J = 17.4, 2.6, 1.0 Hz), 1.72–1.86 (m, 1 H), 1.23–1.43 (m, 3 H), 0.90 (t, 3 H, J = 7.0 Hz), irradiated at δ 5.25, δ 2.73 (dd, J = 17.4, 7.0 Hz), 2.27 (dd, J = 17.4, 2.6 Hz); ^{13}C NMR ($CDCl_3$) δ 207.6, 189.5, 103.6, 58.3, 45.4, 34.8, 33.6, 20.2, 13.8; IR ($CDCl_3$) 3024 (w), 2962 (m), 2907 (s), 2875 (m), 1684 (s), 1596 (m), 1457 (m), 1430 (m), 1356 (s), 1287 (m), 1245 (s), 1193 (s), 1169 (s), 1001 (s) cm^{-1}; MS (EI) m/z 154 (M^+), 139, 125, 112 (100), 97, 83, 69, 55, 53. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.96; H, 9.03.

Reaction of Cyclopropylacetylene with Complex 1 (Entry H). General procedure II was followed using cyclopropylacetylene[47] (0.180 g, 2.73 mmol) and complex **1** (0.284 g, 1.03 mmol). After chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent, the product was isolated (0.80 g, 51%) and identified as cyclopentenone **5H**.

5-Cyclopropyl-3-methoxy-2-cyclopentenone (5H): ^{1}H NMR ($CDCl_3$) δ 5.19 (t, 1 H, J = 1.1 Hz), 3.76 (s, 3 H), 2.65 (dd, 1 H, J = 17.6, 7.4, 1.1 Hz), 2.20 (ddd, 1 H, J = 17.6, 2.8, 1.1 Hz), 2.08 (ddd, 1 H, J = 7.4, 7.4, 2.8 Hz), 0.83 (m, 1 H), 0.51 (m, 1 H), 0.34 (m, 2 H), 0.09 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 206.6, 189.4, 103.5, 58.4, 48.2, 34.0, 12.7, 3.1, 1.2; IR ($CDCl_3$) 3080 (m), 2990 (m), 2970 (m), 2935 (m), 2860 (m), 1682 (s), 1600 (s), 1460 (m), 1440 (m), 1430 (m), 1355 (s), 1295 (m), 1245 (s), 1195 (m), 1165 (s), 1025 (m), 995 (m) cm^{-1}; MS (EI) m/z 152 (M^+), 137, 124, 121, 111, 109, 94, 91, 77, 69; HRMS (EI) calcd for $C_9H_{12}O_2$ 152.0837, found 152.0836.

Reaction of 5-Hexyn-1-ol with Complex 1 (Entry I). General procedure II was followed using 5-hexyn-1-ol (0.392 g, 4.00 mmol) and complex **1** (0.552 g, 2.00 mmol). After chromatography on silica gel using 5:1:14 hexane/methanol/ethyl acetate as eluent, one component was isolated (0.251 g, 68%) having an R_f value of 0.24 (5:1:14 hexane/methanol/ethyl acetate), which was identified as cyclopentenone **5I**.

5-(4-Hydroxybutyl)-3-methoxy-2-cyclopentenone (5I): ^{1}H NMR ($CDCl_3$) δ 5.25 (t, 1 H, J = 1.0 Hz), 3.80 (s, 3 H), 3.62 (t, 2 H, J = 6.3 Hz), 2.73 (ddd, 1 H, J = 17.4, 7.1, 1.0 Hz), 2.41–2.53 (m, 1 H), 2.27 (ddd, 1 H, J = 17.4, 2.7, 1.0 Hz), 1.73–1.88 (m, 1 H), 1.31–1.64 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 208.1, 190.0, 103.4, 62.0, 58.4, 45.2, 34.5, 32.3, 30.9, 23.0; IR ($CDCl_3$) 3622 (m), 3622 (m), 3190–3560 (s, broad), 2942 (s), 2907 (s), 2879 (m), 1682 (s), 1594 (s), 1457 (m), 1441 (m), 1359 (s), 1247 (m), 1194 (m), 1135 (m), 1002 (m) cm^{-1}; MS (EI) m/z 184 (M^+), 167, 153, 125, 112, 97, 84, 74, 69, 60; HRMS (EI) calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1096.

Reaction of 6-[(*tert*-butyldimethylsilyl)oxy]hex-1-yne with Complex 1 (Entry J). General procedure II was followed using 6-[(*tert*-butyldimethylsilyl)oxy]hex-1-yne[48] (0.127 g, 0.60 mmol) and complex **1** (0.083 g, 0.30 mmol) in dioxane containing 0.1 mL (6 mmol) of water. After chromatography on silica gel using 3:2 hexane/ethyl acetate as eluent, one component was isolated having an R_f value of 0.18 in 3:2 hexane/ethyl acetate (0.052 g, 58%). This compound was identified as cyclopentenone **5J**.

5-[4-[(*tert*-butyldimethylsilyl)oxy]butyl]-3-methoxy-2-cyclopentenone (5J): ^{1}H NMR ($CDCl_3$) δ 5.21 (t, 1 H, J = 1.0 Hz), 3.77 (s, 3 H), 3.54 (t, 2 H, J = 6.3 Hz), 2.70 (ddd, 1 H, J = 17.4, 7.1, 1.0 Hz), 2.36–2.48 (m, 1 H), 2.23 (ddd, 1 H, J = 17.4, 2.7, 1.0 Hz), 1.72–1.86 (m, 1 H), 1.29–1.53 (m, 5 H), 0.82 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 207.8, 189.7, 103.7, 62.9, 58.5, 45.6, 34.7, 32.8, 31.2, 26.0, 23.5, 18.3, −5.3; IR ($CDCl_3$) 2931 (s), 2897 (m), 2885 (m), 2859 (s), 1684 (s), 1596 (s), 1472 (m), 1462 (m), 1441 (m), 1359 (s), 1250 (s), 1189 (m), 1170 (m), 1088 (m), 1005 (m), 836 (s) cm^{-1}; MS (EI) m/z 298 (M^+), 283, 255, 242, 227, 199, 167, 112, 101, 75; HRMS (EI) calcd for $C_{16}H_{30}O_3Si$ 298.1964, found 298.1975.

Reaction of Hex-5-yn-1-yl Methanesulfonate with Complex 1 (Entry K). General procedure II was followed using carbene complex **1** (0.276 g, 1.00 mmol) and hex-5-yn-1-yl methanesulfonate[49] (0.352 g, 2.00 mmol) in dioxane containing 0.36 mL (20 mmol) of water. After chromatography on silica gel using 5:1:14 hexane/methanol/ethyl acetate, the first fraction was isolated having an R_f value of 0.34 (5:1:14 hexane/methanol/ethyl acetate) and identified as **5K** (0.099 g, 38%). The second fraction isolated was hydrolyzed product **5I** (0.029 g, 16%).

(47) For synthesis of cyclopropylacetylene, see: Salaün, J. *J. Org. Chem.* **1976**, *41*, 1237–1240.

(48) This compound was prepared from 5-hexyn-1-ol and *tert*-butyldimethylsilyl chloride according to the procedure of Corey. Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190–6191.

(49) Bell, R.; Cottam, P. D.; Davies, J.; Jones, D. N. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2106–2115.

5-[4-[(Methylsulfonyl)oxy]butyl]-3-methoxy-2-cyclopentenone (5K): ^{1}H NMR ($CDCl_3$) δ 5.19 (t, 1 H, J = 1.0 Hz), 4.14 (t, 2 H, J = 6.4 Hz), 3.76 (s, 3 H), 2.93 (s, 3 H), 2.69 (ddd, 1 H, J = 17.5, 7.2, 1.0 Hz), 2.40 (m, 1 H), 2.21 (ddd, 1 H, J = 17.5, 2.8, 1.0 Hz), 1.64–1.81 (m, 3 H), 1.31–1.51 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 207.3, 189.7, 103.5, 69.6, 58.5, 44.9, 37.1, 34.4, 30.5, 28.9, 22.8; IR ($CDCl_3$) 3024 (w), 2943 (m), 2862 (w), 2850 (w), 1684 (s), 1596 (vs), 1358 (s), 1248 (m), 1176 (m), 1000 (m) cm^{-1}; MS (EI) m/z 263 (M + 1), 183, 167, 153, 139, 125, 112 (100); HRMS (CI) calcd for $C_{11}H_{19}SO_5$ 263.0953, found 263.0938.

Reaction of *cis*-1-Methoxy-1-buten-3-yne with Complex 1 (Entry L). *cis*-1-Methoxy-1-buten-3-yne was purchased from Aldrich Chemical Company as a 50% solution in methanol. This solution was placed in a separatory funnel and washed two times with ether. The ether layer was dried over sodium sulfate, and the solvent was removed by fractional distillation; the temperature of the heat source, an oil bath, did not exceed 50 °C. At temperatures greater than 65 °C, a violently exothermic polymerization reaction ensued. A single high-boiling fraction was collected (bp 55–60 °C, 50 mmHg). Then general procedure II was followed using *cis*-1-methoxy-1-buten-3-yne (0.164 g, 2.00 mmol) and complex **1** (0.276 g, 1.00 mmol) in aqueous THF, and the reaction mixture was refluxed for 14 h. After chromatography on silica gel using 3:2 hexane/ethyl acetate as eluent, one component isolated with an R_f value of 0.61 in 3:7 hexane/ethyl acetate was identified as cyclopentenone **5L** (0.062 g, 37%). ^{1}H NMR analysis revealed that this was a mixture of two isomers (isomer ratio from ^{1}H NMR 78:22). The major isomer was assigned as the cis configuration at the vinyl group due to coupling constants of the alkene hydrogens. The minor isomer showed peaks indicative of the trans isomer.

The same reaction was carried out using carbene complex **1** (0.276 g, 1 mmol) and *cis*-1-methoxy-1-buten-3-yne (0.45 mL, 5 mmol) for 8 h of reaction time. Flash chromatography of the reaction mixture yielded **5L** (0.048 g, 28%). ^{1}H NMR analysis showed that this was the pure cis isomer.

***cis*-3-Methoxy-5-(2-methoxyethenyl)-2-cyclopentenone [5L (cis alkene isomer)]**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (dd, 1 H, J = 1.1, 6.0 Hz), 5.25 (t, 1 H, J = 1.0 Hz), 4.31 (dd, 1 H, J = 6.0, 8.7 Hz), 3.79 (s, 3 H), 3.57 (s, 3 H), 3.55 (dddd, 1 H, J = 1.1, 3.3, 7.6, 8.7 Hz), 2.88 (ddd, 1 H, J = 1.0, 7.6, 17.7 Hz), 2.36 (ddd, 1 H, J = 1.0, 3.3, 17.7 Hz), irradiated at δ 3.58, δ 6.11 (d, J = 6.0 Hz), 4.37 (d, J = 6.0 Hz), 2.93 (dd, J = 1.1, 17.7 Hz), 2.41 (dd, J = 1.1, 17.7 Hz); ^{13}C NMR ($CDCl_3$) δ 206.2, 189.7, 149.0, 103.4, 103.2, 59.7, 58.4, 42.0, 36.2; IR ($CDCl_3$) 3043 (w), 2942 (m), 2896 (m), 2875 (m), 2851 (w), 1687 (s), 1595 (s), 1457 (w), 1441 (w), 1358 (s), 1244 (m), 1189 (w), 1170 (m), 1114 (w), 997 (m) cm^{-1}; MS (EI) m/z 168 (M$^+$), 153, 139, 125, 109, 97, 83, 69, 75; HRMS (EI) calcd for $C_9H_{12}O_3$ 168.0786, found 168.0773.

***trans*-3-Methoxy-5-(2-methoxyethenyl)-2-cyclopentenone [5L (trans alkene isomer)]**: ^{1}H NMR ($CDCl_3$) δ 6.49 (d, 1 H, J = 12.6 Hz), 5.31 (br s, 1 H), 4.64 (dd, 1 H, J = 6.0, 12.6 Hz), 3.85 (s, 3 H), 3.62 (s, 3 H), 3.04 (ddd, 1 H, J = 3.1, 6.0, 6.0 Hz), 2.89 (dd, 1 H, J = 6.0, 17.8 Hz), 2.42 (dd, 1 H, J = 3.1, 17.8 Hz). The trans isomer could not be obtained free of the cis isomer.

Reaction of Bis(trimethylsilyl)acetylene with Complex 1 (Entry N). General procedure II was followed using carbene complex **1** (0.276 g, 1.00 mmol) and bis(trimethylsilyl)acetylene (0.341 g, 2.00 mmol) where the reaction mixture was refluxed for 12 h. At the end of the reaction, the solvent was distilled at atmospheric pressure. The residue was partitioned between chloroform–water phases. The chloroform phase was dried over magnesium sulfate and concentrated. Purification by flash chromatography with ethyl acetate/hexane (7:3) as eluent yielded 3-methoxy-2-cyclopentenone (0.60 g, 54%).

3-Methoxy-2-cyclopentenone: ^{1}H NMR ($CDCl_3$) δ 5.38 (br s, 1 H), 3.78 (s, 3 H), 2.30–2.64 (A_2B_2 pattern 2.58, 2 H; 2.41, 2 H), irradiated at δ 5.38, δ 2.58 (the lines become sharper), 2.41 (unaffected); IR ($CDCl_3$) 3020 (w), 2940 (m), 2860 (w), 1703 (s), 1679 (s), 1595 (vs), 1359 (s), 1254 (s) cm^{-1}; MS (EI) m/z 112 (M$^+$), 97, 82, 69, 54. The spectral data were in agreement with those reported previously for this compound.[50]

Reaction of Diphenylacetylene with Complex 1 in Anhydrous Acetonitrile. Carbene complex **1** (0.276 g, 1.00 mmol) and diphenylacetylene (0.356 g, 2.00 mmol) were dissolved in 20 mL of acetonitrile and added to 100 mL of refluxing acetonitrile over 2 h. The mixture was refluxed for 5 h more after the addition was complete. Solvent was evaporated under vacuum. The residue was dissolved in ethyl acetate and filtered through Celite. Concentrated filtrate was chromatographed on silica gel: The first fraction was unreacted diphenylacetylene, which was collected with hexane/ethyl acetate (19:1) as eluent.

The second fraction (R_f 0.6 in hexane/ethyl acetate 9:1) was assigned as cyclohexadiene derivative **18** (0.099 g, 38%). Further purification of this compound could not be achieved due to the partial conversion to the terphenyl derivative **19** upon attempted purification.

The third fraction with R_f 0.43 (hexane/ethyl acetate, 9:1) was rechromatographed with hexane/dichloromethane (1:1) to give cyclobutenone **17** (0.019 g, 7%).

The yellow colored fourth fraction, which was eluted with hexane/ethyl acetate (4:1), was treated with iodine in ether. After extraction with sodium thiosulfate solution, solvent evaporation, and column chromatography (R_f 0.38 in hexane/ethyl acetate (4:1), cyclohexenone **20** (0.010 g, 4%) was obtained.

Elution was carried out with 3:2 hexane/ethyl acetate to give bicyclic compound **21** (R_f 0.37 in hexane/ethyl acetate 3:2, 0.017 g, 6%). The last two fractions contained **5A-trans** (0.013 g, 5%) and **5A-cis** (0.008 g, 3%).

4-Methoxy-2,3-diphenyl-1,4-cyclohexadiene (18): ^{1}H NMR ($CDCl_3$) δ 7.22–6.95 (m, 10 H), 6.12 (t, 1 H, J = 3.5 Hz), 4.70 (t, 1 H, J = 3.4 Hz), 4.34 (t, 1 H, J = 5.5 Hz), 3.41 (s, 3 H), 2.98–3.09 (m, 2 H), irradiated at δ 6.12, 4.70, 4.34, and 3.41, δ 2.98–3.09 (pattern altered in each case), irradiated at δ 3.04, δ 6.12 (s), 4.70 (s), 4.34 (s); ^{13}C NMR ($CDCl_3$) δ 156.4, 142.8, 140.8, 138.5, 131.3, 129.8, 128.4, 128.1, 126.7, 126.3, 123.3, 90.1, 54.5, 47.7, 27.3; IR ($CDCl_3$) 3084 (w), 3063 (m), 3029 (m), 2957 (m), 2935 (s), 2855 (w), 2836 (w), 2822 (w), 1688 (m), 1605 (m), 1493 (s), 1466 (m), 1453 (s), 1443 (s), 1254 (s), 1210 (vs), 1165 (vs), 1032 (s) cm^{-1}; MS (EI) m/z 262 (M$^+$), 260 (100), 229, 215, 203, 185, 171, 152, 115, 91, 77; HRMS (EI) calcd for $C_{19}H_{18}O$ 262.1358, found 262.1358.

3′-Methoxy-1,1′:2′,1″-terphenyl (19): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, 1 H, J = 8.0 Hz), 6.90–7.11 (m, 12 H), 3.68 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 157.0, 142.9, 141.5, 136.9, 131.3, 129.8, 128.2, 127.5, 127.4, 126.3, 126.2, 122.8, 110.1, 55.9; IR ($CDCl_3$) 3064 (m), 3030 (w), 2960 (w), 2940 (m), 2840 (w), 1601 (w), 1583 (m), 1568 (m), 1466 (vs), 1431 (s), 1305 (m), 1252 (vs), 1122 (s), 1073 (w), 1040 (m), 1021 (s) cm^{-1}; MS (EI) m/z 260 (M$^+$, 100), 245, 229, 226, 215, 202, 189, 152, 113, 77; HRMS (EI) calcd for $C_{19}H_{16}O$ 260.1201, found 260.1191.

4-Cyclopropyl-4-methoxy-2,3-diphenyl-2-cyclobutenone (17): ^{1}H NMR ($CDCl_3$) δ 7.93 (m, 2 H), 7.82 (m, 2 H), 7.40–7.55 (m, 6 H), 3.42 (s, 3 H), 1.45 (tt, 1 H, J = 8.3, 5.3 Hz), 0.82 (m, 1 H), 0.60 (m, 2 H), 0.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 193.2, 170.8, 145.3, 131.7, 131.2, 129.6, 129.1, 128.8, 128.3, 128.0, 100.1, 53.1, 14.6, 3.4, 2.6; IR ($CDCl_3$) 3080 (w), 3010 (w), 2940 (m), 2825 (w), 1753 (s), 1625 (w), 1600 (w), 1485 (w), 1450 (m), 1355 (m), 1100 (s), 1095 (m), 1030 (w) cm^{-1}; MS (EI) m/z 290 (M$^+$), 262 (100), 247, 234, 191, 152, 115, 69; HRMS (EI) calcd for $C_{20}H_{18}O_2$ 290.1307, found 290.1305.

2,3-Diphenyl-2-cyclohexenone (20): ^{1}H NMR ($CDCl_3$) δ 7.11 (m, 6 H), 7.01 (m, 2 H), 6.92 (m, 2 H), 2.83 (t, 2 H, J = 6.1 Hz), 2.66 (t, 2 H, J = 6.1 Hz), 2.22 (quintet, 2 H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 198.3, 157.7, 140.9, 137.8, 135.6, 131.0, 128.1, 127.9, 127.7, 127.5, 126.7, 38.3, 33.0, 22.6; IR ($CDCl_3$) 3082 (m), 3061 (m), 3031 (m), 3024 (m), 2950 (s), 2871 (m), 1666 (vs), 1594 (m), 1491 (w), 1444 (m), 1361 (m), 1329 (m), 1307 (m), 1182 (m) cm^{-1}; MS (EI) m/z 248 (M$^+$, 100), 220, 205, 191, 178, 165, 115, 77; HRMS (EI) calcd for $C_{18}H_{16}O$ 248.1201, found 248.1207.

3,4-Diphenylbicyclo[3.3.0]oct-3-ene-2,6-dione (21): ^{1}H NMR ($CDCl_3$) δ 7.43 (m, 2 H), 7.05–7.32 (m, 8 H), 3.91 (d, 1 H, J = 6.7 Hz), 3.31 (br dd, 1 H, J = 8.9, 6.7 Hz), 2.35–2.55 (m, 2 H), 2.06–2.34 (m, 2 H), irradiated at δ 3.91, δ 3.31 (br d, J = 8.9 Hz), 2.06–2.55 (unaffected), irradiated at δ 3.31, δ 3.91 (s), 2.35–2.55 (unaffected), 2.06–2.34 (pattern altered); ^{13}C NMR ($CDCl_3$) δ 211.9, 208.1, 164.4, 140.1, 133.6, 131.7, 130.3, 129.5, 129.3, 128.6, 128.3, 54.8, 48.3, 36.0, 22.2; IR ($CDCl_3$) 3030 (m), 2930 (m), 1747 (s), 1701 (s), 1616 (m), 1598 (m), 1557 (w), 1489 (m), 1444 (m), 1346 (m), 1147 (m), 912 (w) cm^{-1}; MS (EI) m/z 288 (M$^+$), 270, 246, 215, 202, 189, 165, 152, 128, 115, 84 (100); HRMS (EI) calcd for $C_{20}H_{16}O_2$ 288.1150, found 288.1150.

Reaction of Diphenylacetylene with Complex 1 in Anhydrous DMF. Carbene complex **1** (0.138 g, 0.5 mmol) and diphenylacetylene (0.178 g, 1 mmol) were dissolved in 10 mL of DMF and added to 50 mL of 1% aqueous DMF at 115 °C. The reaction mixture was stirred for 18 h. Extraction with hexane/ethyl acetate (1:1) and water was performed. The organic phase was concentrated, and flash chromatography was carried for this complex reaction mixture. ^{1}H NMR data of the collected fractions revealed the presence of the compounds **18** and **19** (0.039 g, 30%), **20** (0.006 g, 5%), **21** (0.007 g, 5%), and **5A-trans** (0.013 g, 10%) similar to the reaction with acetonitrile solvent as explained above.

Reaction of Complex 8 with Diphenylacetylene. Carbene complex **8** (0.149 g, 0.42 mmol) and diphenylacetylene (0.150 g, 0.84 mmol) were dissolved in 10 mL of dioxane. This solution was added dropwise to 40 mL of dioxane containing 0.15 mL of water (8.3 mmol) over a 2-h period. The reaction mixture was refluxed for 12 h. The solvent was collected via simple distillation at atmospheric pressure. The distillate was treated with bromine (0.5 mL, 9.7 mmol) at room temperature for 3 h. The

(50) House, H. O.; Rasmussen, G. H. *J. Org. Chem.* **1963**, *29*, 27–30.

solvent was distilled at reduced pressure, and the residue was subjected to flash chromatography. The fraction obtained was assigned as (1,2-dibromoethyl)benzene (0.110 g, 35%). The residue of the original reaction mixture after the distillation was subjected to flash chromatography to yield **5A-trans** (0.111 g, 53%). In a control experiment, carbene complex **8** (0.183 g, 0.5 mmol) in 50 mL of dioxane was heated to reflux for 12 h. The reaction mixture was monitored by GC, and no styrene formation was observed due to decomposition.

(1,2-Dibromoethyl)benzene: ^{1}H NMR ($CDCl_3$) δ 7.41–7.35 (m, 5 H), 5.13 (dd, 1 H, J = 6.1, 10.1 Hz), 4.08 (dd, 2 H, J = 6.1, 10.1 Hz); ^{13}C NMR ($CDCl_3$) δ 138.6, 129.2, 128.9, 127.7, 51.0, 35.1; MS (EI) m/z 266, 264, 262, 185, 183 (100), 104, 103, 77. The spectral data were in agreement with those previously reported for this compound.[51]

Reaction of Complex 12 with Diphenylacetylene. General procedure II was followed using carbene complex **12** (0.318 g, 1.00 mmol) and diphenylacetylene (0.356 g, 2.00 mmol). Purification was achieved with flash chromatography using hexane/ethyl acetate (4:1) as eluent. The first fraction was assigned as cyclopentenone **15** (R_f 0.54 in hexane/ethyl acetate, 3:2, 0.056 g, 37%) and the second fraction as compound **5A-trans** (0.036 g, 14%).

5-Ethenyl-2-methoxy-5-methyl-2-cyclopentenone (15): ^{1}H NMR ($CDCl_3$) δ 6.33 (t, 1 H, J = 3.4 Hz), 5.78 (dd, 1 H, J = 17.6, 10.9 Hz), 5.08 (d, 1 H, J = 17.6 Hz), 5.05 (d, 1 H, J = 10.9 Hz), 3.70 (s, 3 H), 2.60 (dd, 1 H, J = 18.9, 3.4 Hz), 2.39 (dd, 1 H, J = 18.9, 3.4 Hz), 1.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 203.5, 155.5, 140.5, 123.8, 113.8, 56.8, 48.8, 37.5, 23.4; IR ($CDCl_3$) 3100 (w), 2960 (m), 2910 (s), 2820 (w), 1720 (s), 1645 (s), 1470 (m), 1380 (m), 1360 (m), 1305 (m), 1275 (s), 1140 (m), 1060 (m), 1020 (m) cm^{-1}; MS (EI) m/z 152 (M^+), 137, 124, 123, 110, 109, 91, 84, 81 (100), 77. Anal. Calcd for $C_8H_{10}O_2$: C, 71.05; H, 7.89. Found: C, 70.95; H, 7.87.

Reaction of Complex 13 with Diphenylacetylene. General procedure II was followed using carbene complex **13** (0.342 g, 1.00 mmol) and diphenylacetylene (0.356 g, 2.00 mmol). Purification was achieved with flash chromatography using hexane/ethyl acetate (4:1) as eluent. The first fraction collected was a trace amount of compound **6A**. The second and third fractions were **5A-trans** (0.171 g, 64%) and **5A-cis** (0.036 g, 14%).

Reaction of Complex 14 with Diphenylacetylene. General procedure II was followed using carbene complex **14** (0.182 g, 0.360 mmol) and diphenylacetylene (0.128 g, 0.720 mmol). The reaction mixture was refluxed for 14 h, and final purification was achieved by flash chromatography. Three fractions, compounds **6A** (0.003 g, 3%), **5A-trans** (0.031 g, 33%), and **5A-cis** (0.023 g, 24%), were obtained in that order, with hexane/ethyl acetate (4:1) as eluent.

Reaction of Cyclopentenone 5A-cis Chromium Hexacarbonyl. A solution of *cis*-3-methoxy-4,5-diphenyl-2-cyclopentenone (**5A-cis**) (0.031 g, 0.12 mmol) and chromium hexacarbonyl (0.132 g, 0.600 mmol) in 10 mL of dioxane was heated to reflux for 18 h, during which time a yellow colored chromium complex was formed. The solvent was removed under reduced pressure, and the residue was treated with iodine in ether for 3 h and filtered through silica gel. ^{1}H NMR showed that the complete conversion to trans isomer **5A-trans** had occurred.

A control experiment was carried out using **5A-cis** in refluxing aqueous dioxane and in the absence of chromium hexacarbonyl. It was observed that isomerization did not take place. Treating this **5A-cis** with iodine also did not induce isomerization.

Reaction of Cyclopentenone 6A with Chromium Hexacarbonyl. A solution of 4-methoxy-2,3-diphenyl-2-cyclopentenone (**6A**) (0.017 g, 0.060 mmol) and chromium hexacarbonyl (0.073 g, 0.33 mmol) in 5 mL of dioxane was heated to reflux as explained above, and the formation of an orange red chromium complex was observed. After the iodine treatment, compound **6A** was obtained, indicating that alkene migration did not take place.

Reaction of Complex 1 with 1,6-Heptadiyne. General procedure II was followed under anhydrous conditions using carbene complex **1** (0.276 g, 1.00 mmol) and 1,6-heptadiyne (0.100 g, 1.08 mmol). After the 4 h of addition were completed, the mixture was refluxed for 10 h more. Flash chromatography on silica gel with 9:1 hexane/ethyl acetate gave (R_f 0.5 in hexane/ethyl acetate 4:1, 0.895 g, 51%) indanol derivative **38**.

6-Cyclopropyl-5-indanol (38): ^{1}H NMR ($CDCl_3$) δ 6.98 (s, 1 H), 6.82 (s, 1 H), 5.62 (br s, 1 H), 2.88 (t, 2 H, J = 6.8 Hz), 2.83 (t, 2 H, J = 6.8 Hz), 2.07 (quintet, 2 H, J = 6.8 Hz), 1.82 (tt, 1 H, J = 9.5, 4.1 Hz), 0.99 (m, 2 H), 0.66 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 153.9, 143.8, 135.6, 125.2, 124.0, 110.5, 32.8, 25.7, 9.4, 5.4; IR ($CDCl_3$) 3561 (s), 3090 (w), 3010 (m), 2951 (s), 2848 (m), 1595 (m), 1488 (s), 1445 (m), 1328 (s), 1270 (m), 1217 (s), 1153 (m), 1032 (m) cm^{-1}; MS (EI) m/z 174 (M^+, 100), 159, 145, 131, 115, 91, 77, 63; HRMS (EI) calcd for $C_{12}H_{14}O$ 174.1045, found 174.1045.

Reaction of 2-Methoxy-2-phenylacetophenone with $Cr(CO)_6$. The control reaction was performed by refluxing 2-methoxy-2-phenylacetophenone (**45**) (0.113 g, 0.5 mmol) and chromium hexacarbonyl (0.550 g, 2.5 mmol) in 50 mL of acetonitrile for 14 h. The solvent was removed under reduced pressure, and the residue was filtered through Celite by dissolving it in ethyl acetate. The yellow colored filtrate was concentrated, and purification was achieved by preparative TLC with hexane/ethyl acetate (4:1) as eluent. The band with R_f value 0.61 (hexane/ethyl acetate 4:1) was identified as 2-phenylacetophenone (**46**) (0.035 g, 36%), and its spectral data were in agreement with the published data:[51] ^{1}H NMR ($CDCl_3$) δ 7.89–7.99 (m, 2 H), 7.16–7.52 (m, 8 H), 420 (s, 2 H); IR ($CDCl_3$) 1684 cm^{-1}.

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