cis-2-butene over *trans*-2-butene and syn selectivity in trisubstituted olefins in terms of barriers to rotation of the methyl groups. The lower the calculated barrier to rotation, the higher the reactivity. For example, they showed that the cis methyl group of 2-butene, which has a lower rotational barrier than the trans, is more reactive than the trans olefin. The geminal methyl groups of 2-methylpropene, which have a higher barrier to rotation, are rather deactivated. Similar trends hold with 2-methyl-2-butene. These useful arguments, which are valid for methylated di- and trisubstituted ethylenes, are insufficient to rationalize the present results. For example, the neopentyl group is expected to have an appreciably higher barrier to rotation than the methyl groups in olefins **11** and **12**, yet it is more reactive. We suggest that nonbonded interactions in the isomeric transition states are far better indicators of product distributions than barriers to rotation.

Further work to clarify the various types of regioselectivity on tri- and tetrasubstituted alkenes is in progress.[17]

Acknowledgment. We thank Professors G. J. Karabatsos and C. S. Foote for valuable comments and discussions. This work was supported by Greek General Secretariat of Research and Technology Grant No. ΠΣ 64. NATO Grant No. 880120 for travel expenses is also acknowledged.

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(17) After completion of this manuscript, we were informed by Prof. E. Clennan of some results similar to those reported here. We thank him for a prepublication copy of his manuscript: Clennan, E. L.; Chen, X.; Koola, J. J. *J. Am. Chem. Soc.*, in press.

Ene versus [2 + 2] Cycloaddition Reactions of Fischer Carbene Complexes: An Unusual Effect of Silicon on the Product Partition and the Stereospecificity

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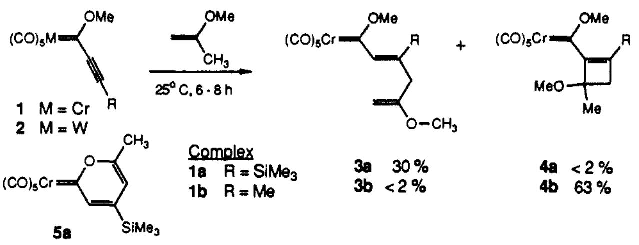
The propensity of a triple bond to participate in a [2 + 2] cycloaddition with an enol ether is greatly facilitated if the triple bond is appended to a chromium or tungsten carbene complex[2] such as in complexes **1** or **2**.[3,4] Further investigations of reactions in this class led to the discovery of ene reactions mediated by a transition metal carbene complex and is the subject of this communication. Additionally, an unusual effect of silicon on the distribution between ene and [2 + 2] cycloaddition products and on the stereospecificity of the [2 + 2] cycloadditions was found which has not yet been observed in organic systems.



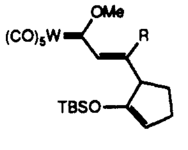
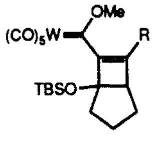
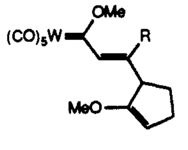
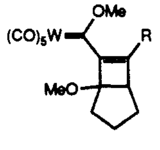
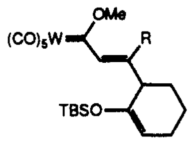
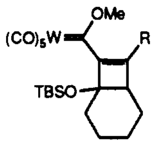
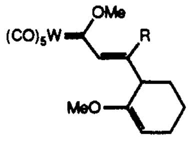
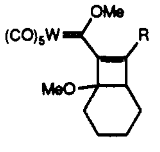
Time	Ene Product[b]		[2 + 2] Product	Ene/[2 + 2]
				
24 h	**10a** 39%	R = $SiMe_3$	**11a** 12%	3.25
12 h	**10b** 28%	R = Me	**11b** 62%	0.45 [c]
				
8 h	**13a** 10%	R = $SiMe_3$	**14a** 64%	0.16
1 h	**13b** 2%	R = Me	**14b** 87%	0.02
3 h	**13c** <2%	R = iPr	**14c** 90%	< 0.02
9 h	**13d** <2%	R = tBu	**14d** 59%	< 0.02
				
48 h	**16a** 42%	R = $SiMe_3$	**17a** <3%	> 14.0
12 h	**16b** 86%	R = Me	**17b** 10%	8.8
				
48 h	**19a** 67%	R = $SiMe_3$	**20a** <2%	> 33.0
4 h	**19b** 21%	R = Me	**20b** 69%	0.35
12 h	**19c** 24%	R = iPr	**20c** 69%	0.35

Table I. Ene versus [2 + 2] Cycloaddition Reactions of Carbene Complexes[a]

[a] All reactions were carried out in neat enol ether (10–20 equiv) at 25 °C under argon for the indicated time. All products were purified on silica gel. [b] A single double-bond isomer was obtained in each case which is assumed to be that resulting from syn addition since this was shown to be the case for **19a** by NOE experiments (see supplementary material). [c] Compounds **10b** and **11b** could not be separated by silica gel chromatogrpahy.

The first ene reaction of a transition metal carbene complex was encountered in the reaction of the chromium carbene complex **1a** with methyl isopropenyl ether. The ene product **3a** slowly cyclizes to the pyranylidene complex **5a**[5] upon hydrolysis on silica gel but can be isolated if eluted rapidly. The nature of the substituent R in the reaction of **1** was found to be crucial to the outcome; the trimethylsilyl complex **1a** gave only the ene product **3a** whereas the methyl complex **1b** led only to the [2 + 2] cycloadduct **4b**. The Lewis acid mediated reactions of acetylenic esters and alkenes are known to give mixtures of ene and [2 + 2] cycloadducts where the ratio of products has been shown to have a strong dependence on the olefin substitution pattern and on the conformations of the starting materials.[6,7] However, this

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(1) National Institutes of Health Predoctoral Fellow.

(2) For recent reviews, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (d) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990, Vol. 5. (e) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Boston, MA, 1989. (f) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

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(6) (a) Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5283. (b) Snider, B. B.; Roush, D. M.; Rodini, D. J.; Gonzalez, D.; Spindell, D. *J. Org. Chem.* **1980**, *45*, 2773. (c) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.

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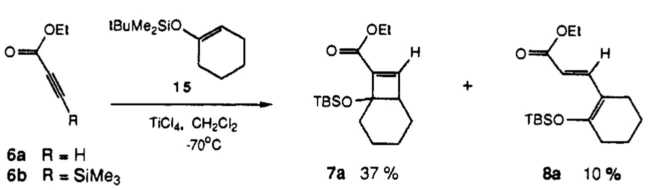
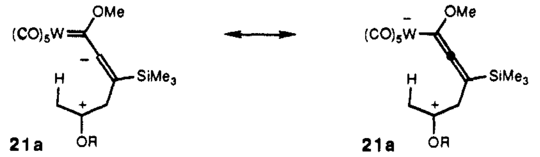
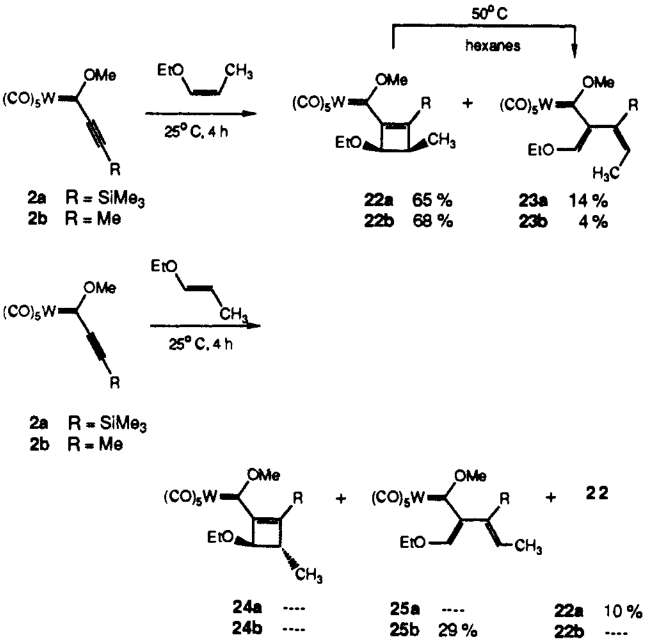
effect of silicon has not been reported for the Lewis acid mediated ene reactions of olefins with either β-silyl-substituted acetylenic esters (such as **6b**) or β-silyl-substituted alkenyl esters.



Three trends of significance can be seen from the data presented in Table I. First, the reactions of alkynyl carbene complexes with silyl enol ethers give mainly ene products while alkyl enol ethers give predominately [2 + 2] cycloadducts. Second, it was found that six-membered-ring enol ethers give a greater proportion of ene products than their five-membered-ring analogues, and this has also been observed in reactions of esters.[7a] Third, the effect of a β-silyl substituent was not an isolated phenomenon; in each case in Table I the silyl-substituted carbene complexes give a greater proportion of ene product than do the corresponding alkyl complexes. Furthermore, the effect of silicon on these reactions can be judged to be electronic since the steric bulk of R does not affect the product partition between **13** and **14**. This suggests that either (a) silicon stabilizes an intermediate of the type **21** for a period of time sufficient to allow for conformation changes required for proton transfer or (b) silicon destabilizes intermediate **21** relative to a concerted ene reaction.



This issue was probed with the reactions of complexes **2a** and **2b** with the cis and trans isomers of ethyl propenyl ether. In these reactions, ene products are not possible, but the question of whether silicon stabilizes or destabilizes the zwitterionic intermediate **21** could be approached in a study of the stereospecificity of the [2 + 2] cycloadditions, an issue that has not been previously examined.[3] The reactions of both the silyl- and methyl-substituted complexes **2a** and **2b** were stereospecific with *cis*-propenyl ethyl ether giving the *cis*-cyclobutene complex **22** and its ring-opened dienyl complex **23**. The reaction of *trans*-propenyl ethyl ether with the methyl complex **2b** gave only the dienyl complex **25b**. The only reaction where there was crossover in the stereochemistry was that of the trimethylsilyl complex **2a** with *trans*-propenyl ethyl ether, where only the *cis*-cyclobutenyl complex **22a** was observed.[8] This is the first piece of evidence indicating that the [2 + 2] cycloaddition of alkynyl carbene complexes with enol ethers occurs by a stepwise mechanism. Taken together, the above results suggest that the role that silicon plays in affecting the partition between ene and [2 + 2] cycloaddition product is also played in stabilizing zwitterionic intermediates of the type **21**. Silicon is known to stabilize cationic centers in a variety of situations;[9-11] however, it is not clear how silicon stabilizes **21**, and this issue and the scope of the ene reactions of carbene complexes are currently being investigated.



Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8821326). The National Institutes of Health has provided a predoctoral training grant for K.L.F. (GM 07151). Some of the mass spectral data were obtained at the Midwest Center for Mass Spectrometry, an NSF Regional Instrument Facility (CHE-8211164). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (5 P30 CA-14599-17).

Supplementary Material Available: Spectral data for all new compounds (11 pages). Ordering information is given on any current masthead page.

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[8] It was determined that the recovered *trans*-propenyl ether had not isomerized and that this was not the source of the stereochemical crossover. The reason for the low mass balance has not been determined.

[9] α-Stabilization: Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

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Nucleophilic Addition of Enolates to the Central Carbon of Transition-Metal η^3-Allyl Complexes. Metallacyclobutane Formation, Reversibility of Nucleophilic Addition, and Synthesis of α-Cyclopropyl Ketones

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Nucleophilic addition to the central carbon of the π-allyl ligand has been observed in reactions of a limited class of transition-metal π-allyl complexes, leading to the formation of metallacyclobutane complexes.[1] Originally reported for the addition of hard nucleophiles to $[(C_5H_5)_2M(\eta^3\text{-allyl})]^+PF_6^-$ (M = Mo, W),[1a] this regioselectivity is in marked contrast to the terminal carbon addition generally observed in such reactions.[2] Two theoretical

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[1] (a) Mo, W: Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; MacKenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. Ephritikhine, M.; Green, M. L. H.; MacKenzie, R. *J. Chem. Soc., Chem. Commun.* **1976**, 619. (b) Rh: Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. (c) Ir: McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388.

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