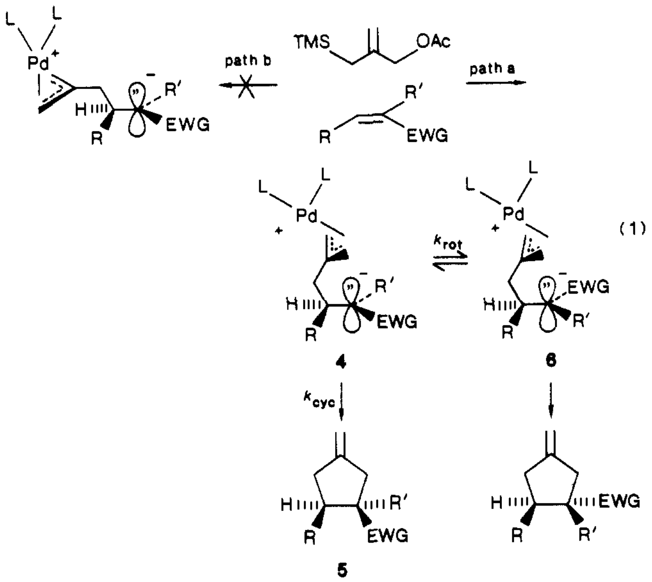

proposed to account for the stereochemical observations of some [2 + 2] cycloadditions.[7] The partitioning of **4** as a function of structure accounts for the stereospecificity. The greater relief of the steric compression between R and EWG, which arises in the zwitterion from the *Z* acceptor, accounts for the increased stereochemical crossover in the cycloaddition of *Z* acceptors compared to *E* acceptors. The smaller molecular motion required for cyclization (i.e., **4** to **5**) compared to rotation (i.e., **4** to **6**) accounts for the increased degree of stereospecificity as the temperature is lowered.

The lower degree of stereospecificity for R' = H compared to R' = CH_3 suggests that rotation to interconvert **4** and **6** whereby a hydrogen brushes against the π-allylpalladium moiety is feasible but that insufficient space exists to accommodate a methyl group. A rotation whereby the EWG group must swing past the π-allylpalladium moiety would be disfavored in any case.

The kinetic criterion of Huisgen may also be accounted for in this picture. This intermediate approaches the geometry of the lopsided concerted cycloaddition whereby the R group may move as much as 0.3 Å closer to the oxygen of the ester carbonyl group in **4**, EWG = CO_2R'', due to the limited flexibility to rotate in order to minimize this interaction. Of course, such an interaction does not exist when R and EWG are anti as they would be starting from the *E* acceptor. The absence of such a destabilizing interaction in this latter case decreases k_{rot} compared to k_{cyc}—a fact that leads to enhanced stereospecificity. It would appear that the interpretation of the kinetic criterion for concertedness requires an expansion in which a $k_{trans}/k_{cis} > 1$ signifies either concerted reactions or stepwise processes whose transition-state geometries closely resemble highly lopsided concerted cycloadditions. The magnitude of this rate ratio should provide a differentiation of these two cases. In this regard, it is interesting to note that, in the cycloadditions of diphenyldiazomethane, this ratio varied from 36 for the fumarate/maleate pair to 2.6 for the (*E*)-crotonate/(*Z*)-crotonate pair. The fact that the latter value is smaller than our value of 4.7 may have significance regarding the mechanistic implications of this data.[8]

Acknowledgment. We thank the National Science Foundation and Monsanto Co. for their generous support of this work. We thank the University of Missouri at St. Louis for their hospitality for M.L.M.

Supplementary Material Available: A figure plotting the rate data (1 page). Ordering information is given on any current masthead page.

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(7) Huisgen, R.; Steiner, G. *J. Am. Chem. Soc.* **1973**, *95*, 5055. Huisgen, R.; Graf, H. *J. Org. Chem.* **1979**, *44*, 2595.

(8) For an opposing view regarding the concertedness of the cycloadditions of diazoalkanes, see: Firestone, R. A. *J. Org. Chem.* **1976**, *41*, 2212.

Reactions of 1,1-Dimethylsilabutadiene. Stereospecific 4 + 2 and Nonstereospecific 2 + 2 Cycloadditions

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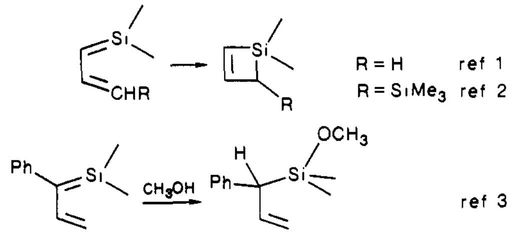
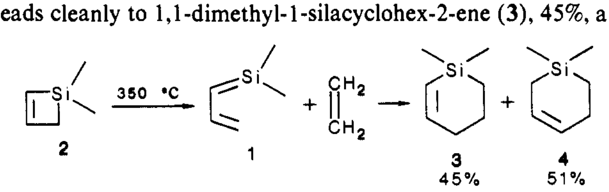
Silabutadienes **1**, dimethylated on silicon, have been implicated as short-lived intermediates in several gas-phase flow pyrolyses when 1-silacyclobutenes **2** have been isolated as the isomerization product.[1,2] In other studies, but in solution, bimolecular reactions of 1,1-dimethyl-1-sila-2-phenyl-1,3-butadiene, generated photochemically from the corresponding silacyclobutene, have been reported.[3,4] Exclusive addition of the O–H bond of methanol across the silene end of the siladiene was reported to be the primary product. When acetone was the coreactant in the photolysis, evidence for a 4 + 2 cycloaddition was presented[5] although the interpretation of that result has been questioned.[6] Bimolecular reactions of the formally conjugated siladiene with organic π systems, however, have not been described. We consider such reactions and address the mechanisms of both 2 + 2 and 2 + 4 cycloadditions.



Isomerization of 1,1-dimethylsilacyclobutene (**2**) in a closed pyrolysis vessel containing a 20-fold excess of ethylene at 350 °C leads cleanly to 1,1-dimethyl-1-silacyclohex-2-ene (**3**), 45%, and the cyclic 3-ene **4**, 51%, in nearly quantitative yield.[7] Formation of the 2-ene might be anticipated from a Diels–Alder type cycloaddition between ethylene and the siladiene, but observation of the 3-ene raises mechanistic concerns about the primary thermal pathways. A possible path leading to **4** is the 2 + 2 addition of ethylene to the silene π system to form the unknown 2-vinylsilacyclobutane. A facile ring expansion via a 1,3-silyl shift to the terminal methylene of the allyl group could yield the cyclic 3-ene. Since the Si–C bond enthalpy (89 kcal/mol) is slightly greater than corresponding C–C bond (87 kcal/mol),[8] it is conceivable that some, if not all, of **3** is produced by cleavage of the weaker C–C bond of the 2-vinylsilacyclobutane.



The predication from orbital symmetry, here expanded to the row including silicon, is that a 4 + 2 path would preserve the stereochemical arrangement of the reactants in the products but the 2 + 2 path would not. Pyrolysis of **2** with a 20-fold excess of *trans*-2-butene produces four major adducts of **1** and the butene:

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(1) Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1976**, *100*, 1630.

(2) Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *216*, C5.

(3) Tzeng, D.; Fong, R. H.; Dilanjan Soysa, H. S.; Weber, W. P. *J. Organomet. Chem.* **1981**, *219*, 153. The product of a thermal 4 + 2 and evidence for 2 + 2 cycloaddition between the siladiene and acetone were also described.

(4) Fink, M. J.; Puranik, D. B.; Pointer Johnson, M. *J. Am. Chem. Soc.* **1988**, *110*, 1315.

(5) Valkovich, P. B.; Weber, W. P. *Tetrahedron Lett.* **1975**, 2153.

(6) Okazaki, R.; Kang, K. T.; Inamoto, N. *Tetrahedron Lett.* **1981**, 235.

(7) The experimental apparatus has been described previously: Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1986**, *5*, 1205.

(8) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

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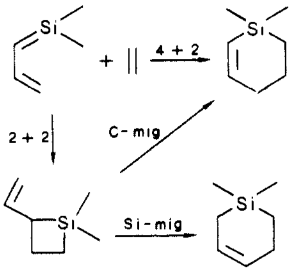
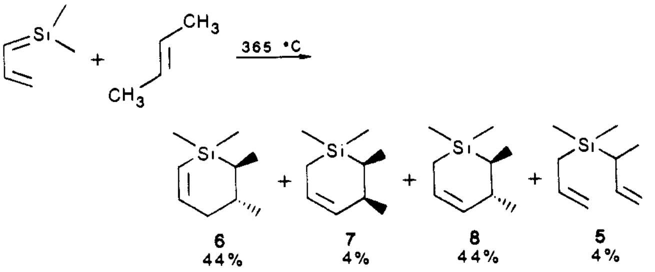
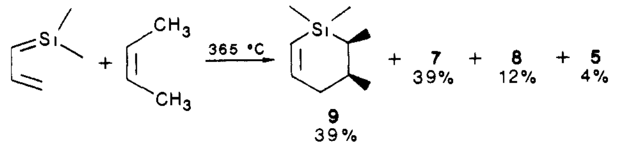


the acyclic 3,4,4-trimethyl-4-silahepta-1,6-diene (**5**) (4%), *trans*-1,1,5,6-tetramethyl-1-silacyclohex-2-ene (**6**) (44%), and *cis*- and *trans*-1,1,5,6-tetramethyl-1-silacyclohex-3-enes (**7**) and (**8**) (4% and 44%), respectively. Reaction of **1** with *cis*-2-butene also provides four adducts: **5** (4%) and *cis*-1,1,5,6-tetramethyl-1-silacyclohex-2-ene (**9**) (39%) along with **7** and **8** (39% and 12%), respectively.





Stereospecific formation of the cyclic 2-enes **6** and **9** (>99%) requires that **1**, despite the highly polarized and unsymmetrical distribution of four π electrons,[9] produces the six-membered ring without rotation of the central C–C bond of the two-electron component. This is the first example in which a *siladiene* reacts stereospecifically with an olefin in an orbital symmetry allowed 4 + 2 cycloaddition.[10]

The mechanisms by which the cyclic 3-enes **7** and **8** are obtained require a process in which olefin stereochemistry is partially lost. From (*E*)-2-butene, retention of the trans relation between adjacent methyls in the cyclic 3-ene is 92% but only 76% from (*Z*)-2-butene. A likely rationale is that the silene end of **1** reacts with slight nonstereospecificity with the alkene to yield the substituted 2-vinyl-1-silacyclobutane **10**. Although the stereochemistry of the 2 + 2 cycloaddition of silenes to alkenes is not known, it has been reported that (*E*)- and (*Z*)-1,1,2,3-tetramethyl-1-silacyclobutane each fragment with ≥20% loss of starting stereochemistry in the 2-butene product.[11] Microscopic reversibility then dictates that the silene/alkene 2 + 2 cycloaddition also proceeds with some loss of stereochemistry in formation of the four-membered ring.

Expansion of the diastereomeric intermediates **10** by migration of the Si–C bond to the terminal methylene of the vinyl substituent can account for the formation of the *E* and *Z* isomers **7** and **8**. Such a rearrangement may be considered an example of the 1,3-sila-sigmatropic shift previously reported to occur with inversion of configuration at the migrating silicon center.[12] Since **6** and **9** are produced stereospecifically, it appears that they do not derive from any C–C ring expansion of diastereomeric **10**. Curious but also consistent with this interpretation is that facile ring expansion via silicon migration precludes the 1,5-sigmatropic hydrogen shift previously observed for pyrolysis of substituted 3-vinylsilacyclobutanes.[13] Further, **10** does not appear to fragment to silenes and substituted 1,3-dienes.

Relative amounts of the symmetry allowed 4 + 2 cyclic 2-enes and the forbidden 2 + 2 cyclic 3-enes are of theoretical interest. The major cycloaddition path of **1** and ethylene is the 2 + 2 mechanism (51%) and similarly, in reaction with (*E*)- and (*Z*)-2-butene, products from the "biradical" path predominate. Surprisingly, $\Delta G^\ddagger$ of the allowed and stereospecific Diels–Alder path must be slightly higher than that of the forbidden and partially stereospecific 2 + 2 mechanism.[14] Although the rules of orbital symmetry correctly depict the stereochemistry of 4 + 2 and 2 + 2 cycloadditions of 1-silabutadiene, they do not account for the faster rate of the forbidden reaction. Possibly the polarization of **1**, known to have greater negative charge density on C(2) than C(4),[8] may emphasize the importance of coulombic forces in such cycloadditions.[15]

Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation, the Dow Corning Corporation, and the N. T.S.U. Faculty Research Fund for financial support of this work. We thank the Mass Spectrometry Facilities at M.I.T. and Rice University for obtaining high resolution mass spectra.

Supplementary Material Available: Spectroscopic data (^{13}C, ^{1}H NMR, and mass spectra) and experimental methods are available for all new compounds (3 pages). Ordering information is given on any current masthead page.

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A Cu_2–O_2 Complex. Crystal Structure and Characterization of a Reversible Dioxygen Binding System

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In this paper, we describe the first X-ray crystallographic characterization of a copper–dioxygen complex, formed by the addition of O_2 to a copper(I) compound. The detailed structural characterization of a Cu_n–O_2 species has been a longtime goal of researchers investigating copper/dioxygen reactivity, because of (i) interest in copper-containing proteins such as hemocyanin (Hc)[1] (anthropod and mollusc O_2 carrier), the monooxygenases tyrosinase and dopamine β-hydroxylase,[1a,2] oxidases such as laccase[3] and the iron–copper-containing cytochrome *c* oxidase[4] and (ii) the synthetic utility of copper compounds in oxidation reactions.[5]

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