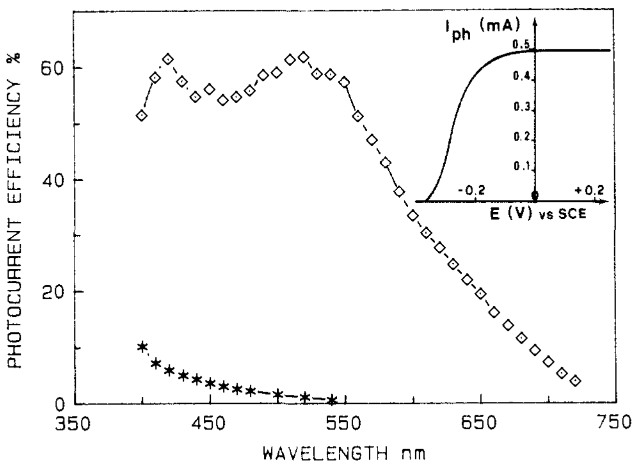

Figure 2. Photocurrent action spectrum for *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$-coated TiO_2 films in 0.1 M aqueous NaI (pH 4.6). Inset: photocurrent-potential curve obtained with the same system under white light ($\lambda > 420$ nm, intensity 23 W/m^2) illumination. Solutions are deaerated with Ar. The lower curve shows the photoresponse of the TiO_2 layer in the absence of sensitizer.

in the conduction band of TiO_2 was tested in photoelectrochemical experiments which employed a high surface area (roughness factor ca. 200) fractal anatase film deposited onto a 2 × 2 cm Ti sheet.[7] The dye was coated onto the TiO_2 layer by dipping the electrode for 4 h in an aqueous solution (pH 4.85) of 10^{-3} M *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$. The TiO_2 film assumed an intensely violet coloration due to adsorption of the dye. Photoelectrochemical experiments employed a standard cell equipped with a flat pyrex window. The regenerative photocell consisted of the dye-loaded TiO_2 sheet immersed in the electrolyte and a 3 × 3 cm-sized Pt flag as counterelectrode. All solutions were degassed with Ar. An Oriel 450 W Xe lamp served as a light source in conjunction with a water filter and a Bausch & Lomb 300 nm blaze high intensity monochromator. The incident photon flux was determined by a thermopile and by chemical actinometry with ferrioxalate.[8] The value at 420 nm was $(5 \pm 0.25) \times 10^{-10}$ Einstein cm^{-2} s^{-1}.

Figure 2 shows the photocurrent action spectrum for *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$-coated TiO_2 films in 0.1 M aqueous NaI (pH 4.6). For comparison, results obtained prior to dye coating are also presented. The incident monochromatic photon to current conversion efficiency (IPCE), defined as the ratio of the number of electrons generated by light in the external circuit divided by the number of incident photons, shows a wavelength dependency

$$\mathrm{IPCE}(\%) = \frac{[(1.24 \times 10^3) \times \text{photocurrent density } (\mu\text{A/cm}^2)]}{[\text{wavelength (nm)} \times \text{photon flux } (\text{W/cm}^2)]} \qquad (1)$$

matching the spectrum of *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ except that the features are red-shifted and broadened. It attains values exceeding 60% close to the maximum and falls gradually toward longer wavelengths. Even with red light ($\lambda \approx 700$ m), sensitization currents are still clearly discernable.

Inserted in Figure 2 is the current-potential curve measured under white light ($\lambda > 420$ nm) illumination under similar conditions as in Figure 1. The photocurrent onset is at -0.3 V from where it rises sharply reaching a plateau value at -0.1 V. Preliminary tests of the *cis*-$Ru^{II}L_2(H_2O)_2$-coated electrodes in a regenerative photoelectrochemical cell containing 0.1 M KI/10^{-3} M I_3^- redox electrolyte gave under white light ($\lambda > 420$ nm, incident photon flux 70 W/m^2) a short circuit current of 0.38 mA/cm^2, an open circuit potential of 0.52 V, and a fill factor of 0.7 corresponding to a light to electrical power conversion efficiency of 2%. The photocurrent remained stable during 4 days of illumination (turnover number of *cis*-$Ru^{II}L_2(H_2O)_2^{2-} > 50\,000$) confirming the high stability of this sensitizer.

The maximum IPCE value of 62% observed in Figure 2 corresponds to the product of the light harvesting efficiency of the *cis*-$Ru^{II}L_2(H_2O)_2$-loaded TiO_2 at 520 nm and the quantum yield for electron injection Assuming that each adsorbed *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ molecule occupies a surface of 100 Å^2, which is the area determined for $Ru^{II}L_3$,[8] and using $\epsilon = 11\,900$ M^{-1} cm^{-1}, 60% light harvesting efficiency is derived. Thus, $\phi_{inj} \approx 1$. Admitting that multiple reflection in the TiO_2 layer may result in complete absorption of incident 520 nm photons by *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$, ϕ_{inj} would still be 0.62.

$$\mathrm{IPCE}(\%) = 100\,(1 - I/I_0)\phi_{inj} \qquad (2)$$

In view of the extremely short excited-state lifetime of *cis*-$Ru^{II}L_2(H_2O)_2$, such high efficiencies require injection rates in the picosecond domain, hence intimate contact of the dye with the semiconductor surface. Strong electronic coupling between electronically excited *cis*-$Ru^{II}L_2(H_2O)_2$ and the Ti-3d wave function manifold could be explained by the formation of Ru-O-Ti surface bonds. $Cu^{II}(bipy)_2$ complexes are bound in a similar fashion on silica.[9] The present discovery of efficient sensitization of TiO_2 by *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ identifies a new class of heterogeneous redox sensitizers covering a broad spectral range in the visible which should be particularly useful for light energy conversion with oxide semiconductor devices.

Acknowledgment. This work was supported by the Gas Research Institute, Chicago, IL (subcontract with the Solar Energy Research Institute, Golden, CO), the Nationaler Energie-Forschungs-Fonds (NEFF), Switzerland, and the Office Fédéral de l'Energie, Switzerland. M.K.N. thanks the Government of India for financial assistance.

Registry No. *cis*-$Ru^{II}L_2(H_2O)_2^{2-}$ (L = 2,2'-bipyridyl-4,4'-dicarboxylate), 114199-00-7; TiO_2, 13463-67-7.

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(12) Geselowitz, D. A.; Kutner, W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2015.

Criteria for Concertedness in Cycloadditions

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Discriminating between a concerted and a stepwise mechanism continues to be a significant challenge. Stereochemistry may not be a sufficiently sensitive probe, i.e., stereospecific reactions may involve nonconcerted processes. Kinetics offers an additional probe. Huisgen states that "the ratio of the trans/cis rates offers an elegant and theoretically clear criterion for concerted additions leading to five- and six-membered rings".[1,2] In our study of the palladium-catalyzed cycloadditions of 2-(trimethylsilylmethyl)allyl acetate (**1**) with electron-deficient olefins, we became concerned with the question of concertedness.[3] In this communication, we record our systematic study of this question with use of both the stereochemical and kinetic probes. These results suggest an ambiguity can arise regarding a conclusion of concertedness based upon the trans/cis rate ratio leading to five-membered carbocyclic rings.

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(1) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633.

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(3) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

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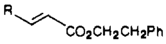
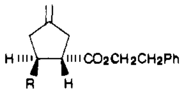
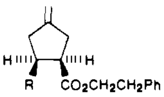
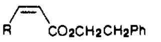
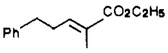
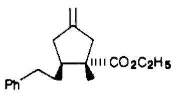
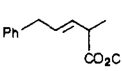
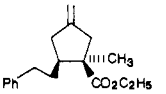
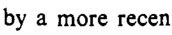
Table I. Stereocontrol of TMM–PdL$_2$ Cycloadditions[a]

entry	acceptor[b,c]	TMM precursor	temp (°C)	cycloadduct[b]		yield[d] (%)
						
1	R = CH_3	**1**	65–70	95	5	95
2	R = CH_3	**3**	25	>99	<1	59
3	R = n-C_4H_9[e]	**1**	65–70	97	3	90
4	R = i-C_3H_7	**1**	65–70	94	6	80
						
5	R = CH_3	**1**	65–70	30	70	86
6	R = CH_3	**3**	25	12	88	57
7	R = n-C_4H_9	**1**	65–70	22	78	89
8	R = i-C_3H_7	**1**	65–70	16	84	65
9		**1**	65–70			44 (95)[f,g]
10		**1**	65–70			41 (93)[f,h]

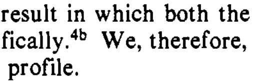
[a] All reactions were performed in THF with 5 mol% palladium acetate, 25 mol% triisopropyl phosphite, and 10 mol% n-butyllithium on a 1-mmol scale. [b] Ratios were determined by capillary VPC with a J and W Scientific DB-1 megabore column, 15-m long and 1.5-μm film thickness on a Varian Model 3700 instrument or by using a Hewlett Packard HP-17 megabore column, 10-m long and 2.0-μm film thickness on a Hewlett Packard Model 5730A instrument. All new compounds have been fully characterized spectrally and elemental composition established by combustion analysis and/or high resolution mass spectrometry. [c] VPC analysis indicates each olefin isomer to be >99% geometrically pure unless otherwise indicated. [d] Isolated yields. [e] VPC indicates 98.2:1.8 E:Z. [f] Yields in parentheses are corrected for recovered starting material. [g] VPC indicates product to be >99:<1 E:Z. [h] VPC indicates product to be 98:2 Z:E.

In examining the question of concertedness, we initially considered the stereochemical course of the reaction. In our early work, we established that disubstituted electron deficient E olefins reacted to give E cycloadducts but that the corresponding Z isomer showed partial to complete stereochemical scrambling.[4a] Whether such scrambling arose as a consequence of a stepwise pathway involving an intermediate that can lose its stereochemical integrity or of equilibration of the starting material was not rigorously established. That the latter explanation may be correct was suggested by a more recent result in which both the E and Z acceptors reacted stereospecifically.[4b] We, therefore, turned to examining the trans/cis rate profile.

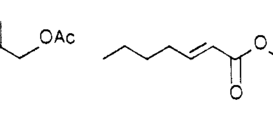
To facilitate analysis of both starting materials and products, the cis/trans pair **2a,b**, each one of which was >99% isomerically pure, was reacted with the silyl acetate **1** in THF at 66 °C. The



1



2a



2b

catalyst was generated in situ from 5.15 mol% palladium acetate, 25.7 mol% triisopropyl phosphite, and 10.3 mol% n-butyllithium. The reactions exhibit excellent second-order kinetics for disappearance of starting materials with $k_{trans} = 7.09 \times 10^{-4}$ M^{-1} s^{-1} and $k_{cis} = 1.50 \times 10^{-4}$ M^{-1} s^{-1} with R-Sq values of 0.9965 and 0.9925. Our k_{trans}/k_{cis} of 4.72 compares to the ratio of 2.6 determined by Huisgen for the 1,3-dipolar cycloaddition of diphenyldiazomethane with the E and Z isomers of ethyl crotonate.[2a]

The product analyses of these reactions are summarized in Table I. The observation of some stereochemical scrambling would be consistent with a concerted mechanism only if the starting materials isomerized under the reaction conditions. Careful examination of the geometrical integrity of the starting materials over the course of the reaction revealed no detectable isomerization. In the case of the Z olefin isomer of starting material where such isomerization would have had to occur the greatest, the lack of buildup of the E olefin isomer might have arisen by the faster rate of cycloaddition of the latter. However, the k_{trans}/k_{cis} rate factor of 4.72 is not sufficiently large to lend credence to this proposal. Furthermore, the cis/trans ratio of products remains invariant over the entire course of the reaction. Thus, isomerization of the starting materials under the conditions of the cycloaddition does not appear consistent with our experimental observations.

To further probe the stereochemical criteria, variation of the size of the β-substituent to a smaller (i.e., CH_3) as well as a larger (i.e., i-C_3H_7) group was examined. Similar results were obtained.

To explore the effect of temperature in THF, we developed a new TMM–PdL$_2$ precursor. 2-(Trimethoxysilylmethyl)allyl chloride (**3**)[5] reacts with E and Z phenethyl crotonate in THF at room temperature in the presence of tetra-n-butylammonium acetate in the presence of the standard Pd(0) catalyst.[6] It is to be noted that no cycloaddition occurs with the chloride **3** in the absence of acetate ion at any temperature and that 2-(trimethoxysilylmethyl)allyl acetate or methyl carbonate does not participate in cycloadditions under these conditions. Stereospecificity of the reactions of both the E and Z isomers does increase (see Table I, entries 2 and 6).

Converting the disubstituted olefin to a trisubstituted one by introducing an alkyl substituent at the α-position produces a virtually completely stereospecific reaction.

The kinetic and stereochemical criteria of concertedness are in conflict with respect to this reaction. Particularly noteworthy is the fact that the stereospecificity of the reaction varies from complete to poor depending upon substrate.

An explanation that resolves this dilemma proposes a highly ordered nonconcerted reaction (eq 1). The stereochemical profile of the cycloaddition suggests formation of the cisoid zwitterion (path a) which minimizes charge separation rather than the transoid one (path b). A related cisoid intermediate has been

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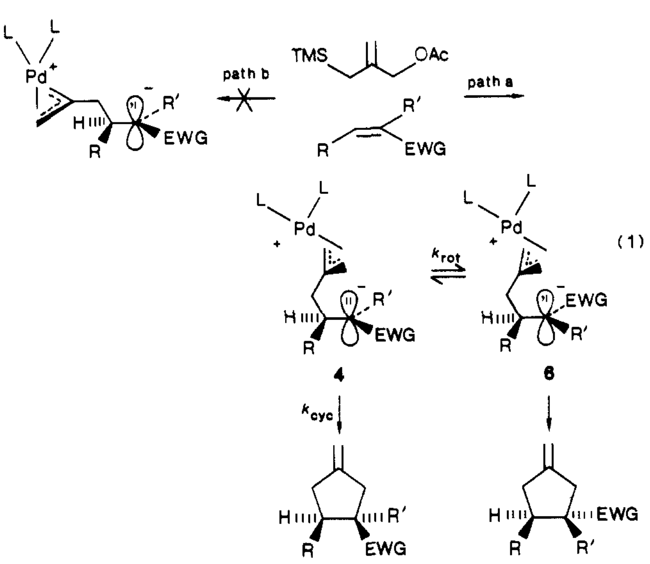

(1)

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$_2$R'', 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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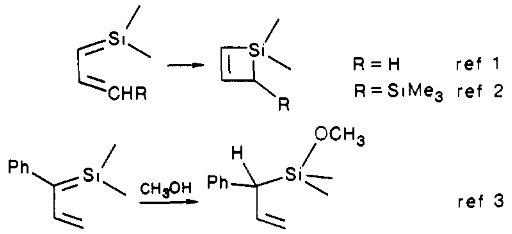
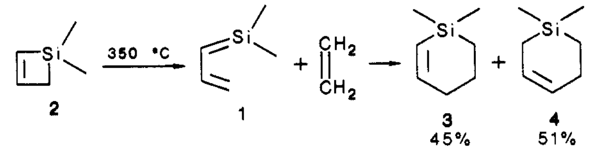
Received February 5, 1988

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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