

The luminescence properties of **2** are probably the result of Au-Tl interactions. PPNAu(MTP)₂ does not possess any strong absorption band at 320 nm. Tl^I ion is luminescent, but its excitation and emission bands appear at much higher energy than those of AuTl(MTP)₂.²⁰ A simple molecular orbital diagram²¹ for Au-Tl bonding in **2** is given in Figure 2 (lower part). It is proposed that the absorption band at 320 nm which results in the luminescence of **2** is from the σ_1^* to σ_2 transition localized on the Au-Tl bond. The Au-Tl bond may be stabilized by the mixing of the filled 6s level on Tl^I with the empty 6s level on Au(I) and p_z mixing with both levels, a process suggested to occur due to relativistic effects of these heavy metal atoms.

Acknowledgment. We thank the Welch Foundation, the National Science Foundation (CHE 8708625), and the Texas A&M Center for Energy and Minerals Resources for financial support.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and data collection parameters for **2** (3 pages); table of observed and calculated structure factors for **2** (20 pages). Ordering information is given on any current masthead page.

(20) (a) Ranfagni, A.; Mugnai, D.; Bacci, M.; Viliiani, G.; Fontana, M. P. *Adv. Phys.* **1983**, *32*, 823. (b) Edgerton, R.; Teegarden, K.; *Phys. Rev.* **1963**, *129*, 169.

(21) The relative positions of the orbital energies are based on the energies of the atomic orbitals (Herman, F.; Skillman, S.; *Atomic Structure Calculation*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1963).

Stereochemistry of the Addition of Diarylsilylenes to *cis*- and *trans*-2-Butenes

Wataru Ando,* Mikako Fujita, Hitoaki Yoshida, and Akira Sekiguchi

Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan
Received January 25, 1988

The ultraviolet photolysis of linear trisilanes is known to yield silylene. While the reaction of silylenes with olefin has been studied,¹ there seem to be few reports on the stereochemistry of the silylene addition. The scarcity and ambiguity of the stereochemical information are due to the extreme instability of siliranes when attacked by nucleophiles; in such a case they readily give ring-opening products. Ishikawa,² Jones,³ and Seyferth⁴ independently reported the stereospecific addition of silylene to olefins. There is general agreement that normal silylene has singlet ground state⁵ and reacts with olefin in concerted fashion. However, bulky silylenes might find the concerted pathway more difficult than they do their small substituted one and give nonstereospecific products in either singlet or triplet state. We wish to report the results of recent investigations on bulky diorganosilylene reactions with 2-butenes, leading to the first reported examples of nonstereospecific additions of silylenes.

Photolysis of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**1a**) and a large excess of *cis*-2-butene (1:100) in hexane at -5 °C was carried out with a low-pressure mercury lamp for 10 min to give 99% of *cis*-silirane (**3a**)⁶ and only 1% of *trans* isomer **4a**⁷ (Scheme

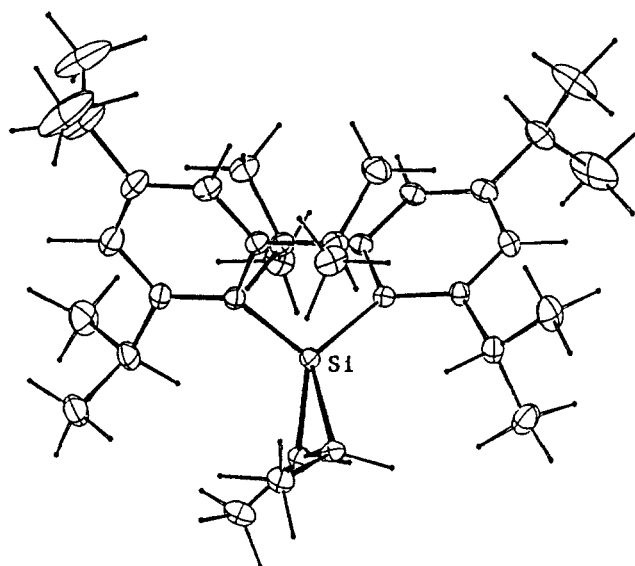


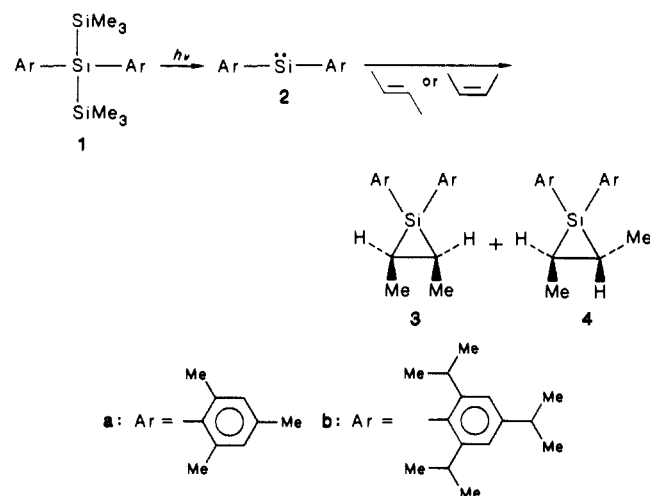
Figure 1. ORTEP drawing of **3b**.

Table I. Product Ratios of Reactions of Dimesitylsilylene and 2-Butene^a

starting materials	irradtn time ^b	product ratios (%)	
		3a (<i>cis</i>)	4a (<i>trans</i>)
1a +	10 min	30	70
	3 h	23	77
	9 h	34	66
	10 min ^c	55	45
1a +	10 min	99	1
	3 h	96	4
	9 h	90	10
	10 min ^c	95	5

^a The product ratios were determined by ¹³C NMR and HPLC (solvent MeOH:H₂O = 9:1). ^b The reaction was carried out at -5 °C. ^c The reaction was carried out at -95 °C.

Scheme I



I). Surprisingly, the photolysis of **1a** in *trans*-2-butene gave a considerable amount of the *cis* isomer **3a** (30%) in addition to **4a** (70%).

2,2-Bis(2,4,6-triisopropylphenyl)-1,1,1,3,3,3-hexamethyltrisilane (**1b**) was synthesized as a precursor of more crowded novel silylene **2b** and irradiated in *trans*-2-butene to afford **3b** (41%) and **4b** (59%); the ratio of nonstereospecific adducts apparently increased.

(1) Gasper, P. P. *Reactive Intermediates*, Jones, M., Jr., Moss, R. A., Eds.; John Wiley & Sons: New York, 1978; Vol. 1, p 229.

(2) Ishikawa, M.; Nakagawa, K.; Kumada, M. *J. Organomet. Chem.* **1979**, *178*, 105.

(3) Tortorelli, V. J.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 1425. Tortorelli, V. J.; Jones, M., Jr.; Wu, S.; Li, Z. *Organometallics* **1983**, *2*, 759.



(4) Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288.

(5) Gordon, M. S. *Chem. Phys. Lett.* **1985**, *114*, 348. Grev, R. S.; Schaefer H. F., III. *J. Am. Chem. Soc.* **1986**, *108*, 5804 and references therein.

(6) Compound **3a**: ¹H NMR (CDCl₃, 500 MHz) 1.07–1.11 (deformed d, 6 H), 1.19–1.25 (deformed q, 2 H), 2.18 (s, 3 H), 2.20 (s, 3 H), 2.52 (s, 6 H), 2.53 (s, 6 H), 6.77 (s, 2 H), 6.80 (s, 2 H); ¹³C NMR (CCl₄, 125 MHz) 10.5, 13.3, 21.00, 21.03, 24.47, 24.50, 127.1, 128.0, 128.4, 139.2, 139.3, 145.6, 145.8; ²⁹Si NMR (CDCl₃, 18 MHz) -83.2; exact MS found 322.2113, calcd for C₂₂H₃₀Si 322.2117.

(7) Compound **4a**: ¹H NMR (CDCl₃, 500 MHz) 0.77–0.83 (deformed q, 2 H), 1.03–1.07 (deformed d, 6 H), 2.19 (s, 6 H), 2.50 (s, 12 H), 6.77 (s, 4 H); ¹³C NMR (CCl₄, 23 MHz) 16.1, 21.0, 21.4, 24.2, 126.7, 128.1, 138.5, 145.2; ²⁹Si NMR (CDCl₃, 18 MHz) -77.4; exact MS found 322.2116, calcd for C₂₂H₃₀Si 322.2117.

Table II. Product Ratios of Reactions of Bis(2,4,6-triisopropylphenyl)silylene and 2-Butene^a

starting materials	irradtn time ^b	product ratios (%)	
		3b (cis)	4b (trans)
1b + 	10 min	41	59
	3 h	34	66
	9 h	32	68
	10 min ^c	79	21
	1 h ^d	84	16
1b + 	10 min	93	7
	3 h	96	4
	9 h	86	14
	10 min ^c	97	3
	1 h ^d	99	1

^aThe product ratios were determined by ¹³C NMR and HPLC (solvent MeOH:H₂O = 9:1). ^bThe reaction was carried out at -5 °C. ^cThe reaction was carried out at -95 °C. ^dThe photolysis in 3MP matrix at 77 K, the addition reaction of the silylene occurred during the annealing.

The siliranes **3** and **4** are extremely stable at room temperature, and **3b**⁸ and **4b**⁹ were recrystallized from ethanol. Stereochemistry of siliranes **3** and **4** could be clearly distinguished by ¹H and ¹³C NMR; cis isomer **3** has nonequivalent aryl groups. The key product **3b** was also confirmed by X-ray crystal analysis (Figure 1).

Appropriate control experiments show that cis-trans isomerization of olefins is inefficient and that silirane **4b** does not isomerize to the cis isomer **3b** under the reaction conditions.¹⁰

The reaction was monitored by HPLC as functions of reaction time and temperature. The ratios of *cis*- and *trans*-siliranes were nearly constant with reaction time (Tables I and II). The most marked change was observed in the addition of silylenes to *trans*-2-butene at -95 °C; unexpectedly, nonstereospecific adduct **3b** became a major product.

On the analogy of the reactivity of triplet carbene,¹¹ triplet silylenes may add to the olefin to produce a diradical in which rotation about a carbon-carbon single bond competes with spin inversion and closure. On the other hand, if rotation prevailed sufficiently over closure, one would expect that the stepwise addition of singlet silylene might occur.

It is possible that nonstereospecificity is a result peculiar to an electronically excited silylene. To examine this, we investigated the reaction in a glass matrix.

When **1b** was photolyzed in 3-methylpentane (3MP) at 77 K, the resulting matrix turned to intense blue, and the absorption spectrum assigned to silylene **2b** was observed at 584 nm.¹² On melting the matrix, **2b** dimerized to give tetrakis(2,4,6-triisopropylphenyl)disilene ($\lambda_{\max} = 433$ nm, ²⁹Si NMR in C₆D₆ 52.9 ppm).¹³ Similarly, in the irradiation of **1b** in 3-MP matrices

(8) Compound **3b**: mp 134-135 °C; ¹H NMR (CDCl₃, 500 MHz) 0.9-1.5 (br, 12 H), 1.15 (br d, 12 H), 1.22-1.24 (deformed d, 6 H), 1.26 (d, 6 H; *J* = 6.9 Hz), 1.27 (d, 6 H; *J* = 7.0 Hz), 1.39-1.43 (deformed q, 2 H), 2.87 (sep, 1 H; *J* = 7.0 Hz), 2.89 (sep, 1 H; *J* = 6.9 Hz), 3.57 (sep, 2 H; *J* = 6.7 Hz), 3.79 (sep, 2 H; *J* = 6.7 Hz), 6.96 (s, 2 H), 7.01 (s, 2 H); ¹³C NMR at 58 (CDCl₃, 25 MHz) 11.2, 15.6, 23.8, 24.5, 25.1, 34.2, 34.6, 35.4, 121.0, 121.2, 128.0, 130.9, 150.0, 150.3, 155.3, 156.2; ²⁹Si NMR (CDCl₃, 18 MHz) -85.2; mass *m/e* 490 (M⁺). Anal. Calcd for C₃₄H₅₄Si: C, 83.19; H 11.08. Found: C, 82.98; H, 11.17.

(9) Compound **4b**: mp 151-152 °C; ¹H NMR (CDCl₃, 500 MHz) 0.6-0.9 (br, 6 H), 0.97-1.03 (deformed q, 2 H), 1.09-1.13 (deformed d, 6 H), 1.2-1.4 (br, 18 H), 1.269 (d, 6 H; *J* = 6.9 Hz), 1.270 (d, 6 H; *J* = 6.9 Hz), 2.89 (sep, 2 H; *J* = 6.9 Hz), 3.4-3.7 (br, 2 H), 4.1-4.3 (br, 2 H), 6.8-7.2 (br, 4 H); ¹³C NMR at 58 (CDCl₃, 25 MHz) 16.5, 19.8, 23.8, 25.4, 34.2, 34.8, 121.1, 127.0, 150.3, 156.3; ²⁹Si NMR (CDCl₃, 18 MHz) -81.4; mass *m/e* 490 (M⁺). Anal. Calcd for C₃₄H₅₄Si: C, 83.19; H, 11.08. Found: C, 82.90; H, 11.21.

(10) Photolysis of **4b** gave silylene and only *trans*-2-butene. Photolysis of **3b**, however, gave silylene and a mixture of *cis*- and *trans*-2-butenes in the molar ratio ca. 2.5:1. The silylene was trapped by triethylsilane.

(11) Bethell, D. *Organic Reactive Intermediates*; McManus, S. P.; Ed.; Academic Press: New York, 1973; pp 61-126.

(12) Dimethylsilylene have absorption bands at 577 nm. West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. West, R. *Science (Washington, D.C.)* **1984**, *225*, 1109.

(13) Watanabe, H.; Takeuchi, K.; Fukawa, N.; Kato, M.; Goto, M.; Nagai, Y. *Chem. Lett.* **1987**, 1341.

containing *cis*- or *trans*-2-butenes, initially only bands due to the silylene were observed. After the light was interrupted for 1 h, the intensity of the absorption bands did not change at all, but upon annealing these bands disappeared. Warming the matrix, no disilene could be found although two products were **3b** and **4b**, respectively (Table II). The ratios obtained are independent of secondary reaction of siliranes. These results show that the electronically excited silylenes do not participate in these addition reactions.¹⁴

Since the most important factor is the spin state of silylene, we tried to measure an ESR spectrum of silylene at 77 K. Although the ESR sample showed the silylene to be an intense color, no signal could be observed in 0.02-1.2 T.

Apparently the reaction of silylene **2** gives a nonstereospecific adduct, which largely depends on the bulkiness of the silylene. These results suggest especially difficult and interesting problems as other divalent singlet species of the IVb group might also be expected to add to olefin nonstereospecifically.

Acknowledgment. We are grateful to Dr. Chizuko Kabuto, Analytical Center of Tohoku University for X-ray analysis, and to Shin-etsu Chemical Co., Ltd. for the gift of chlorosilanes. This work was supported by a Grant-in-Aid for Special Project Research (no. 62115002) from the Ministry of Education, Science, and Culture of Japan.

Supplementary Material Available: Spectroscopic data for **1b** and listings of final atomic coordinates and temperature factors and bond lengths and angles (9 pages); listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

(14) Nearly the same product ratio was obtained in a methylcyclohexane matrix, which is ca. 10⁴ times as hard as the 3MP matrix: Ling, A. C.; Willard, J. E. *J. Phys. Chem.* **1968**, *72*, 1918.

Preparation and Catalytic Activity of a New Solid Acid Catalyst

R. S. Drago* and E. E. Getty

Department of Chemistry, University of Florida
Gainesville, Florida 32611

Received August 6, 1987

The preparation and use of strong solid acid catalysts and superacids are active areas of research for isomerization, cracking, hydrocracking, dehydration, alkylation, acylation, methanol to gasoline, etc.¹ Because of the reported advantages of solid catalysts,² recent research has focused on the preparation and characterization²⁻⁴ of stronger solid acids. In view of the higher activity associated with tetrahedral compared to octahedral aluminum Lewis acids, we are interested in preparing solids containing stable tetrahedral aluminum sites. In this paper we report the synthesis, characterization, and catalytic activity for these new solid acid catalyst systems.⁵

Our catalyst is prepared by reacting an inorganic oxide with aluminum chloride (Al₂Cl₆) in refluxing carbon tetrachloride (CCl₄), Scheme I. The reaction of aluminum chloride with silicon

(1) Tanabe, K. In *Heterogeneous Catalysis; Catalysis by Novel Solid Strong Acids and Superacids*; Shapiro, B. L., Ed.; Texas A & M University Press: College Station, TX, 1984; pp 71-94.

(2) Vedrine, J. C.; Auroux, A.; Bolis, V.; Dejaifve, P.; Naccache, C.; Wierzchowski, P.; Derovane, E. G.; Nagy, J. B.; Gilson, J.; Van Hooff, J. H. C.; Van Den Berg, J. P.; Wolthoizen, J. *J. Catal.* **1979**, *59*, 248-262.

(3) Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversion*; Academic Press: New York/London, 1981; pp 100-122.

(4) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*; Wiley: New York, 1985; p 53.

(5) Drago, R. S.; Getty, E. E.; US Patent 4 719 190, January 12, 1988.