A Novel Reactivity of a Silylene: The First Examples of [1 + 2] Cycloaddition with Aromatic Compounds

Hiroyuki Suzuki, Norihiro Tokitoh, and Renji Okazaki*

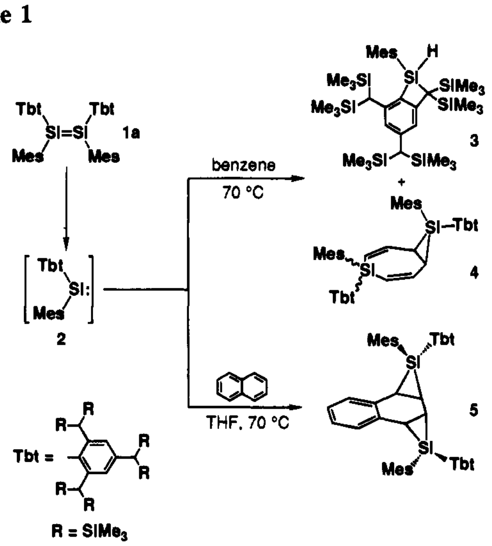
Department of Chemistry, Graduate School of Science
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Received August 8, 1994

Divalent silicon species (silylenes) are among important reactive intermediates in organosilicon chemistry.[1] Much interest has been focused on their reactivities such as addition to olefins,[2] heteroalkynes,[3] isocyanides,[4] and a transition metal complex[5] in connection with the reactivities of carbenes. Although there have been reported several methods of generating silylenes,[1] there is a severe limitation in the study of the reactivities of silylenes using these methods since almost all of these reactions are carried out either at high temperature or under irradiation conditions. Recently we reported the synthesis and structure of air stable disilenes Tbt(Mes)Si=Si(Mes)Tbt (**1**) (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl,[6] Mes = 2,4,6-trimethylphenyl; **1a**: cis form, **1b**: trans form) by taking advantage of kinetic stabilization.[7] The most remarkable feature of **1** is that it undergoes thermal dissociation into a silylene, Tbt(Mes)Si (**2**), under very mild conditions (ca. 70 °C). Since this method for the generation of a silylene is very mild and clean, we anticipated that it would enable us to isolate reaction products which are unstable under the reaction conditions of conventional methods. We delineate here novel [1 + 2] cycloaddition reactions of a silylene to benzene and naphthalene by utilizing this method together with X-ray structural analyses of their addition products.[8]

Previously we reported the thermolysis of *cis*-disilene **1a** in benzene-d_6 at 90 °C.[7] The main product was benzosilacyclobutene **3** (65%), which resulted from the intramolecular C−H insertion reaction of intermediary silylene **2**. We have now found that lowering the reaction temperature only by 20 °C leads to a dramatic change in the reaction path; thermolysis of **1a** in benzene at 70 °C gave the bis(silylene) adduct of benzene **4**[9] [(*E*)-**4**, 42%; (*Z*)-**4**, 16%] as a main product along with 16% **3**[7] (Scheme 1).

Scheme 1



The molecular structures of (*E*)- and (*Z*)-**4** were definitively determined by X-ray crystallographic analysis.[10] Figure 1 shows the ORTEP drawing of (*Z*)-**4**. The adduct (*Z*)-**4** has a bicyclic structure with one silylene silicon atom being in the three-membered ring and the other in the seven-membered ring and with the two Mes groups facing to each other. The seven-membered ring is almost planar, and the dihedral angle between the seven-membered and three-membered ring planes is 125.6°. In the structure of (*E*)-**4**, the two Mes groups are situated in a trans position and the seven-membered ring is folded to relieve the steric repulsion between the two bulky aryl groups (Tbt and Mes).

Thermal reaction of silylene **2** with naphthalene proceeded in a different way. Reaction of **1a** with 10 molar equiv of naphthalene in THF afforded bis(silylene) adduct **5**[9] (81%), the structure of which was determined by X-ray crystallographic analysis[10] as shown in Figure 2. Unlike bis(silylene) adduct **4**, **5** has two silacyclopropyl units, and one aromatic ring of naphthalene remains intact. The two silacyclopropyl units are situated in a trans position, and the Tbt groups are directed toward the outside of the naphthalene ring to avoid steric repulsion.

---

[1] Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1978; Vol. 1, pp 229−277. *Ibid.* 1981; Vol. 2, pp 335−385. *Ibid.* 1985; Vol. 3, pp 333−427. Very recently, the synthesis of the first isolable silylene was reported: Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.

[2] (a) Ando, W.; Fujita, M.; Yoshida, H., Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310. (b) Zhang, S.; Conlin, R. T. *J. Am. Chem. Soc.* **1991**, *113*, 4272. (c) Zhang, S.; Wagenseller, P. E.; Conlin, R. T. *J. Am. Chem. Soc.* **1991**, *113*, 4278. (d) Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281. (e) Boudjouk, P.; Black, E.; Kumarathasan, R. *Organometallics* **1991**, *10*, 2095.

[3] (a) Weidenbruch, M.; Schäfer, A.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1986**, *314*, 25. (b) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 776.

[4] Weidenbruch, M.; Brand-Roth, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 90.

[5] Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33.

[6] Since the abbreviation "Tb" for 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl, which we used so far in our previous papers, may confuse it with the symbol for the element terbium, we denote this bulky aryl group hereafter as Tbt.

[7] Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428. For the first stable disilene, see: West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

[8] The [1 + 4] cycloaddition of silylenes to anthracene derivatives was previously reported: (a) Schäfer, A.; Weidenbruch, M.; Peters, K.; von Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302. (b) Sekiguchi, A.; West, R. *Organometallics* **1986**, *5*, 1911.

[9] Compounds **4** and **5** were satisfactorily confirmed by analytical and spectral data. ^{29}Si NMR spectra (53.45 MHz, in $CDCl_3$) which are characteristic of these structures follow. (*Z*)-**4**: δ −93.28, −36.43, 1.54, 1.72, 2.16, 2.37. (*E*)-**4**: δ −81.99, −29.81, 1.54, 1.78, 2.37, 2.54. **5**: δ −79.11, 1.72, 2.13, 2.30. The other physical properties (^{1}H and ^{13}C NMR and FAB-MS) are described in the supplementary material.

[10] Crystallographic data for **4** and **5**. (*Z*)-**4**: $C_{78}H_{146}Si_{14}$, MW = 1477.21, monoclinic, space group $P2_1/a$, $a = 20.739(4)$ Å, $b = 22.862(5)$ Å, $c = 22.529(4)$ Å, $\beta = 115.43(1)°$, $V = 9646(3)$ Å^3, $Z = 4$, $D_c = 1.017$ g cm^{-3}, $\mu = 2.43$ cm^{-1}. (*E*)-**4**: $C_{78}H_{146}Si_{14}$, MW = 1477.21, monoclinic, space group $P\bar{1}$, $a = 13.24(3)$ Å, $b = 39.95(6)$ Å, $c = 9.52(2)$ Å, $\alpha = 90.0(1)°$, $\beta = 108.9(2)°$, $\gamma = 88.5(2)°$, $V = 4763(16)$ Å^3, $Z = 2$, $D_c = 1.030$ g cm^{-3}, $\mu = 2.23$ cm^{-1}. **5**: $C_{82}H_{148}Si_{14}$, MW = 1527.27, triclinic, space group $P2_1/n$, $a = 14.155(9)$ Å, $b = 22.124(4)$ Å, $c = 31.726(6)$ Å, $\beta = 93.36(3)°$, $V = 9919(7)$ Å^3, $Z = 4$, $D_c = 1.023$ g cm^{-3}, $\mu = 2.11$ cm^{-1}. The final cycle of the full-matrix least-squares refinement was based on 3704 [(*Z*)-**4**], 1893 [(*E*)-**4**], and 3311 (**5**) observed reflections [$I > 3\sigma(I)$ for (*Z*)-**4** and (*E*)-**4** and $I > 2.5\sigma(I)$ for **5**] and 911 [(*Z*)-**4**], 359 [(*E*)-**4**], and 865 (**5**) variable parameters with R (R_w) = 0.057 (0.032) [(*Z*)-**4**], 0.155 (0.147) [(*E*)-**4**], and 0.075 (0.070) (**5**). Although the refinement for (*E*)-**4** has not yet been converged with satisfactory agreement factors because of the inferiority of the single crystal used, the crystallographic data described here sufficiently support the presupposed molecular structure of (*E*)-**4**. Full details for the crystallographic analyses of (*Z*)-**4**, (*E*)-**4**, and **5** are described in the supplementary material.

0002-7863/94/1516-11572$04.50/0

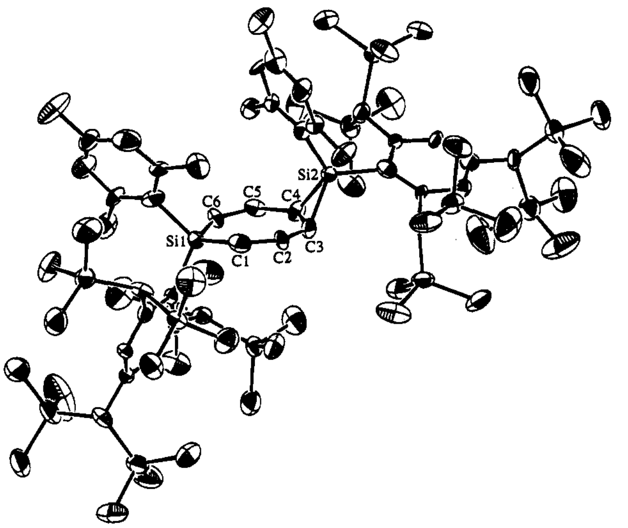
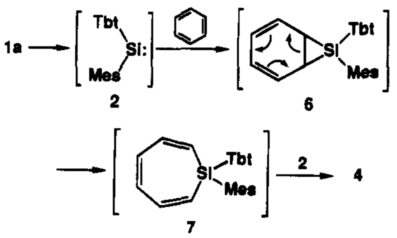


Figure 1. ORTEP drawing of bis(silylene) adduct (*Z*)-**4** with thermal ellipsoid plots (30% probability for non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.85(2), Si(1)–C(6) 1.84(1), Si(2)–C(3) 1.88(1), Si(2)–C(4) 1.88(1), C(1)–C(2) 1.32(2), C(2)–C(3) 1.48(2), C(3)–C(4) 1.55(2), C(4)–C(5) 1.44(2), C(5)–C(6) 1.34(1), C(1)–Si(1)–C(6) 110.0(6), C(3)–Si(2)–C(4) 48.7(4), Si(1)–C(1)–C(2) 134(1), C(1)–C(2)–C(3) 130(1), C(2)–C(3)–C(4) 129(1), C(3)–C(4)–C(5) 129(1), C(4)–C(5)–C(6) 134(1), Si(1)–C(6)–C(5) 130.7(9).

Scheme 2



The formations of **4** and **5** represent the first examples of [1 + 2] cycloaddition of a silylene with aromatic compounds.[11] Although there are numerous examples for [1 + 2] cycloaddition of carbenes with aromatic π-bonds,[12] such reactions have not been reported so far, to our knowledge, for silylenes. The formation of **4** is unique in that it most likely involves silanorcaradiene **6** and silacycloheptatriene **7** (Scheme 2). The isolation of **7** was impossible even in the presence of a large excess of benzene because of the higher reactivity of **7** than benzene itself. Silylene **2** would attack **7** with its Mes group directing toward the seven-membered ring for steric reasons to give (*E*)-**4** and (*Z*)-**4**. The formation of **5** is reasonably interpreted in terms of a tandem [1 + 2] addition of the silylene to one of the aromatic rings of naphthalene.

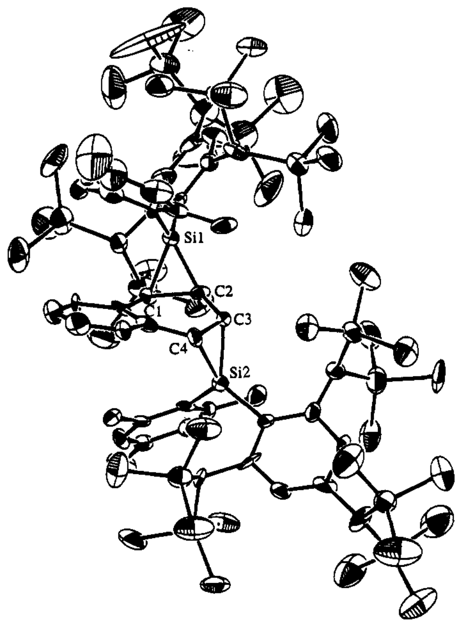


Figure 2. ORTEP drawing of bis(silylene) adduct **5** with thermal ellipsoid plots (30% probability for non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.88(1), Si(1)–C(2) 1.87(1), Si(2)–C(3) 1.89(1), Si(2)–C(4) 1.87(1), C(1)–C(2) 1.56(2), C(3)–C(4) 1.52(2), C(1)–Si(1)–C(2) 49.2(5), C(3)–Si(2)–C(4) 47.6(5), Si(1)–C(1)–C(2) 65.1(7), Si(1)–C(2)–C(1) 65.8(7), Si(2)–C(3)–C(4) 65.4(7), Si(2)–C(4)–C(3) 67.0(8).

It should be noted that **4** and **5** are also good precursors of silylene **2**. When a toluene-d_8 solution of (*E*)-**4** was heated at 120 °C for 30 h in the presence of 10 molar equiv of triethylsilane, benzene and disilane Tbt(Mes)Si(H)SiEt$_3$ (**8**), a product of insertion of silylene **2** into the Si–H bond of triethylsilane, were formed quantitatively. Similar thermolysis of **5** resulted in quantitative formation of **8** and naphthalene. A further investigation on the reactivities of the hindered silylene **2** is currently in progress.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 05236102) from the Ministry of Education, Science and Culture, Japan. We thank Central Glass Co., Ltd., Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd., for the generous gifts of tetrafluorosilane, chlorosilanes, and alkyllithiums, respectively.

Supplementary Material Available: Text describing physical properties of the reaction products **4** and **5** and tables of crystallographic data with complete listings of bond lengths and angles and thermal and positional parameters for **4** and **5** (146 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(11) Reaction of a photochemically generated silylene with C$_{60}$ has been reported: Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 1605.

(12) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; Part 2, pp 821–976.