

Synthesis, Structure, and Reactivity of Extremely Hindered Disilenes: The First Example of Thermal Dissociation of a Disilene into a Silylene

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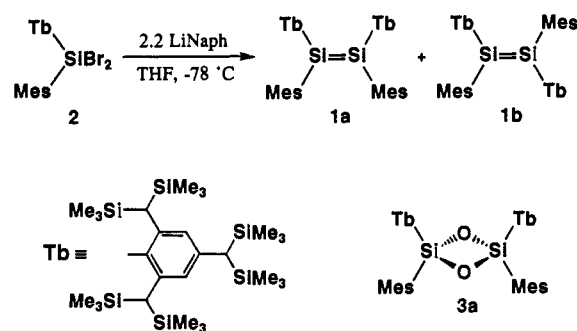
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Since the first isolation of a stable disilene derivative (tetramesityldisilene) by West et al. in 1981,¹ introduction of bulky groups on silicon atoms has been an approved method for the synthesis of stable disilenes.² Although remarkable progress has been made in the chemistry of disilenes,³ the intrinsic nature of a Si-Si double bond has not been fully disclosed. For example, there have been no reports on the thermal dissociation of disilenes into silylenes, in contrast to the known dissociations for digermenes and distannenes.⁴ The high thermodynamic stability of the Si-Si double bond relative to those for the Ge-Ge and Sn-Sn double bonds is in good agreement with computed dissociation energies for the process $H_2E=EH_2 \rightarrow 2H_2E$ (52-58 kcal mol⁻¹ for E = Si,⁵ 30-45 kcal mol⁻¹ for E = Ge,^{5b,6} and 22-28 kcal mol⁻¹ for E = Sn^{5b,7}).

We now report the synthesis of extremely hindered and kinetically stable disilenes $Tb(Mes)Si=Si(Mes)Tb$ { $Tb = 2,4,6$ -tris[bis(trimethylsilyl)methyl]phenyl,⁸ Mes = mesityl; **1a**, *cis*-isomer and **1b**, *trans*-isomer} and their ready thermal dissociation into silylene $Tb(Mes)Si$: under very mild conditions.

Disilenes **1** were readily synthesized as a mixture of *cis*- and *trans*-isomers (ca. 40% in total) by the reductive coupling reaction of dibromosilane **2**⁹ with lithium naphthalenide in THF followed by chromatographic separation (flash column chromatography,

Scheme I



SiO_2 /pentane) (Scheme I). Pure *cis*-disilane **1a** (30%) was isolated as lemon yellow microcrystals by filtration of the concentrated pentane suspension of the crude mixture of the disilenes, while a mixture of *trans*-disilene **1b** and naphthalene was obtained as an orange oil (ca. 10%) by concentration of the filtrate. Careful recrystallization of this orange oil from benzene gave reddish orange crystals of **1b** including naphthalene.¹⁰

Both disilenes **1a** and **1b** were found to be quite stable in the open air in the solid state (even in microcrystalline form) for weeks, while they underwent very slow decomposition (half-life ca. 84 h) in an aqueous THF solution (containing 200 mol equiv of water) at room temperature (ca. 20 °C). The remarkable stability of disilenes **1a** and **1b** relative to that of previously reported hindered disilenes² is apparently due to the high steric demand of the Tb group.

trans-Disilene **1b** showed satisfactory spectral and analytical data,¹¹ and the molecular structure was finally determined by X-ray crystallographic analysis as shown in Figure 1.¹² Disilene **1b** showed a remarkable elongation of the Si-Si double bond [2.228(2) Å],¹³ most likely reflecting the large steric repulsion between the Tb and Mes groups.

(8) We have recently found that the Tb group is a useful steric protection group for the kinetic stabilization of a variety of highly reactive chemical species containing heavier typical elements. (a) Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047. (b) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1993**, 407. (c) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351. (d) Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065.

(9) Dibromosilane **2** was prepared by treatment of the corresponding dihydrosilane $Tb(Mes)SiH_2$ ^{8a} with *N*-bromosuccinimide (2.0 equiv) in the presence of a catalytic amount of benzoyl peroxide in benzene at 80 °C.

(10) Removal of naphthalene by exhaustive sublimation under reduced pressure gave almost pure **1b** as orange crystals. Since they are not single crystals with the quality for the X-ray diffraction, the single crystal containing naphthalene (1:1) was used for the X-ray analysis.

(11) All the reaction products here obtained showed satisfactory spectral and analytical data, which are described in the supplementary material. For example, λ_{max} (hexane) **1a**, 378 (ϵ , 15 000), 403 (16 000) nm; **1b**, 368 (12 000), 425 (11 000), 460 (sh, 8800) nm.

(12) Crystallographic data for **1b**·C₁₀H₈: C₃₂H₁₄₈Si₁₄, MW = 1527.27, monoclinic, space group $P2_1/c$, $a = 18.130(3)$, $b = 18.466(3)$, and $c = 28.522(2)$ Å, $\beta = 95.976(9)^\circ$, $V = 9497(2)$ Å³, $Z = 4$, $D_c = 1.068$ g cm⁻³, $\mu = 2.09$ mm⁻¹. The intensity data were collected on a Rigaku AFC6A diffractometer with graphite-monochromated Cu K α radiation ($\lambda = 1.54184$ Å) at 120 K using an Oxford Cryostream cooler. The structure was solved by direct method with SHELXS-86¹⁸ and refined by the block-diagonal least-squares method using XTAL3.2.¹⁹ All the non-hydrogen atoms except for the naphthalene carbons were refined anisotropically. The final cycle of the least-squares refinement was based on 7950 observed reflections [$I > 2\sigma(I)$] and 776 variable parameters with $R(R_w) = 0.080$ (0.081). Full details for the crystallographic analysis of **1b** are described in the supplementary material.

(13) The values of Si-Si double bond lengths previously reported varied within a range from 2.138 to 2.160 Å (nine examples of disilenes have been crystallographically analyzed, and the mean value of their Si-Si double-bond lengths is 2.146 Å; Cambridge Structural Database (CSD) Ver 5.05 (March, 1993)); see also ref 2. Very recently, Sakurai et al. reported the synthesis and crystal structure analysis of tetrakis(triisopropylsilyl)disilene, which showed an unusual elongation of the central Si-Si double bond [2.251(1) Å]. Maruyama, T.; Kira, M.; Sakurai, H. *39th Symposium on Organometallic Chemistry, Japan*; Tokyo, 1992; Abstr. PA-109; Kinki Chemical Society, Japan; Osaka, 1992.

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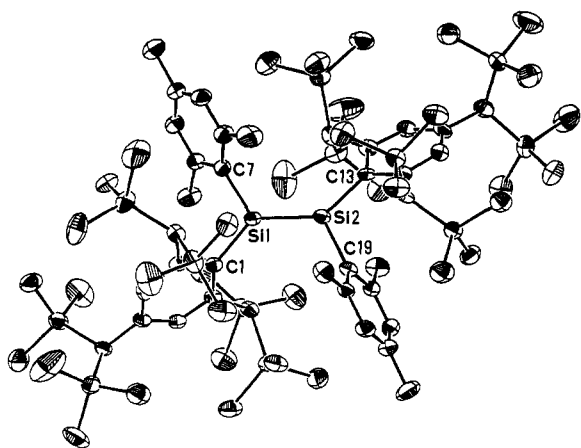


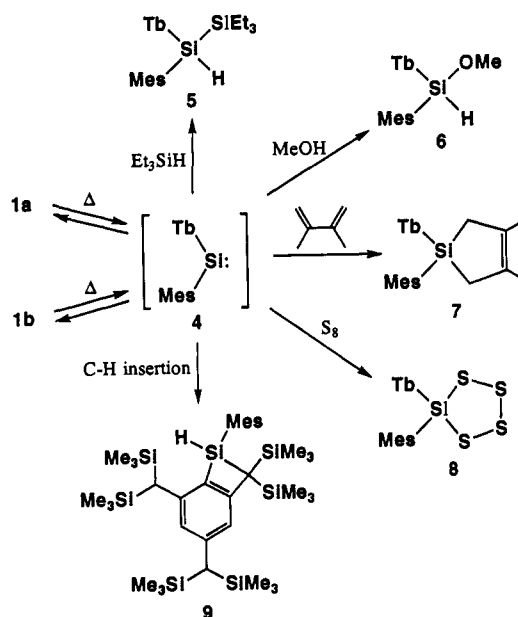
Figure 1. ORTEP drawing of *trans*-disilene (**1b**) with thermal ellipsoid plot (50% probability for nonhydrogen atoms). Selected bond lengths (Å) and angles (deg): Si(1)–Si(2) 2.228(3), Si(1)–C(1) 1.922(7), Si(1)–C(7) 1.895(8), Si(2)–C(13) 1.927(7), Si(2)–C(19) 1.894(7), Si(2)–Si(1)–C(1) 130.0(2), Si(2)–Si(1)–C(7) 120.1(2), C(1)–Si(1)–C(7) 108.8(3), Si(1)–Si(2)–C(13) 132.2(2), Si(1)–Si(2)–C(19) 115.8(2), C(13)–Si(2)–C(19) 109.2(3).

The *cis*-disilene **1a** exhibited a very complicated ^1H NMR spectrum,¹¹ suggesting greater steric congestion around the silicon atoms than in the *trans*-isomer **1b**. The ^{29}Si NMR spectrum of **1b** measured in benzene- d_6 showed only one signal at 66.49 ppm in the sp^2 silicon region, while that of **1a** exhibited four peaks with roughly equal intensities at 56.16, 56.74, 57.12, and 58.12 ppm, most likely due to the existence of two or more conformational isomers. Although we have not obtained good crystals of **1a** suitable for X-ray structural analysis yet, the *cis*-geometry of **1a** was evidenced by the stereospecific formation of the corresponding *cis*-1,3,2,4-dioxadisilene **3a**^{11,14} upon treatment of **1a** with molecular oxygen in hexane at room temperature.¹⁵

Of particular note among the properties of the extremely hindered disilenes **1a** and **1b** is their ready thermal dissociation into silylene **4** under very mild conditions. When *cis*-disilene **1a** was heated in toluene at 70 °C in the presence of an excess amount of triethylsilane (100 equiv), **1a** was quantitatively converted into disilane **5**,¹¹ the insertion product of the intermediary silylene **4** into the Si–H bond of triethylsilane (Scheme II). *trans*-Disilene **1b** also gave disilane **5** under the same reaction conditions, though the rate of dissociation of **1b** into **4** was found to be much slower than that of **1a** due to its smaller steric demand around the Si–Si double bond as compared with that of **1a** (Scheme II). The half-lives of **1a** and **1b** [70 °C in toluene in the presence of Et_3SiH (100 equiv)] were found to be about 13 and 85 min, respectively, by monitoring of the consumption of the starting disilenes by UV-vis spectroscopy. Silylene **4** thus generated was also allowed to react with various reagents such as methanol, 2,3-dimethyl-1,3-butadiene, and elemental sulfur to afford the corresponding adducts **6**, **7**, and **8**^{8a} in good yields (**6**, 71%; **7**, 47%; **8**, 60% from **1a**) as shown in Scheme II.¹¹

In the absence of such trapping reagents, the thermolysis of **1a** (90 °C, 24 h, benzene in a sealed tube) gave a silacyclobutabenzene derivative (**9**, 65%) which most likely resulted from the intramolecular C–H insertion reaction of the intermediary

Scheme II



silylene **4**. Interestingly, the monitoring of the thermolysis of **1a** in benzene- d_6 at 50 °C by ^1H and ^{29}Si NMR revealed a competitive formation of the isomerized *trans*-isomer **1b** and the cyclization product **9**, suggesting the possible occurrence of *cis*–*trans* isomerization via a dissociation–association mechanism (Scheme II).¹⁶

The formation of silylene **4** by the thermolysis of disilenes **1a** and **1b** as described here is important as the first example of thermal dissociation of a Si–Si double-bond compound, though there have been a few reports on the photochemical formation of silylenes from disilenes.¹⁷ The remarkable thermal fragility of the Si–Si double bonds in **1a** and **1b** as compared with that of the previously reported hindered disilenes is obviously due to the extremely strong steric demand of a combination of Tb and Mes groups on the Si–Si double bonds. The formation of silylene **4** under very mild conditions and its versatile reactivity will provide us with useful synthetic methods for a variety of interesting organosilicon compounds. Investigation along this line is currently under way.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 04403005) from the Ministry of Education, Science and Culture, Japan. We are grateful to Mr. J. Harada, the University of Tokyo, for his kind assistance on the X-ray structural analysis of **1b**. We also thank Central Glass Co., Ltd., Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd. for the generous gifts of tetrafluorosilane, chlorosilanes, and alkylolithiums, respectively.

Supplementary Material Available: Physical properties of the starting material and reaction products **1**–**7** and **9**; crystallographic data with complete tables of bond lengths, angles, and thermal and positional parameters for **1b** (33 pages). Ordering information is given on any current masthead page.

(14) The *cis* configuration of **3a** was determined by X-ray crystallographic analysis, the details of which will be described elsewhere.

(15) *trans*-Disilene **1b** afforded the corresponding *trans*-1,3,2,4-dioxadisilene under reaction conditions similar to those for **1a**. Retention of the stereochemistry in the air-oxidation of disilenes has already been described. (a) Michalczyk, M. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1525. (b) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Organometallics* **1986**, *5*, 531.

(16) At present, we cannot rule out rigorously the possibility that the *trans*-isomer **1b** resulted from the rotational isomerization of **1a** without dissociation into silylene **4**.

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