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Communications to the Editor

The First Stable Cyclic Disilene: Hexakis(trialkylsilyl)tetrasilacyclobutene

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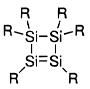
Although a variety of silicon−silicon doubly bonded compounds, disilenes, have been isolated and extensively studied so far,[1] there have been no reports on isolation and characterization of persilacycloalkenes.[2] We report herein the synthesis, structure, and photochemical isomerization of the first stable cyclic disilene, hexakis(*tert*-butyldimethylsilyl)tetrasilacyclobutene (**1**, R = $SiMe_2Bu^t$). The thermal and photochemical pathways involved in the interconversion among **1**, tetrasilabicyclo[1.1.0]butane (**2**), and tetrasila-1,3-butadiene (**3**) may constitute an interesting chemistry as the silicon version of the well-studied electrocyclic interconversion of C_4H_6 (cyclobutene, bicyclobutane, and butadiene).[3] Actually, we observed facile photochemical conversion of **1** to **2** and its thermal reversion to **1**.



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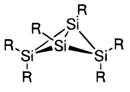

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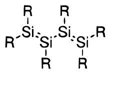

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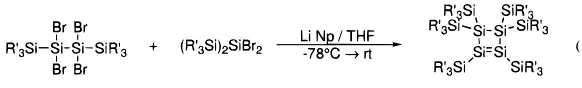
Hexakis(*tert*-butyldimethylsilyl)tetrasilacyclobutene (**1**, $R'_3Si = Bu^tMe_2Si$ in eq 1) was synthesized by reductive coupling of 1,4-di-*tert*-butyl-1,1,4,4-tetramethyl-2,2,3,3-tetrabromotetrasilane (**4**) and 2,2-dibromo-1,3-di-*tert*-butyl-1,1,3,3-tetramethyltrisilane (**5**). To a green suspension of lithium naphthalenide (8.6 mmol) in THF (15 mL) at −78 °C was added a mixture of **4** (0.99 mmol) and **5** (2.21 mmol) in THF (10 mL) over a period of 1 min. The solution was then stirred overnight at room temperature. Removal of the resulting salt by filtration, evaporation of solvents in vacuo, and then removal of naphthalene by sublimation gave a dark orange solid, which contains **1** in 13.6% yield as determined by NMR, together with hexakis(*tert*-butyldimethylsilyl)cyclotrisilane as a major byproduct. Several crystallizations from hexane and heptane gave pure **1** as bright orange crystals in 1.5%. The structure of **1** was determined by MS, ^1H, ^{13}C, and ^{29}Si NMR spectroscopies and X-ray single-crystal analysis.[4] The tetrasilacyclobutene **1** was air-sensitive, similar to other tetrasilyldisilenes; the orange color disappeared immediately when the samples of **1** in solution were exposed to air.



4 **5** **1**

(R'_3Si = *t*-$BuMe_2Si$) (1)

The molecular structure of **1** in the solid state determined by X-ray crystallography[5] is shown in Figure 1 with selected bond lengths and angles. The silicon−silicon double-bond length is 2.174 Å, which is shorter than those of tetrakis(trialkylsilyl)disilenes (2.202−2.251 Å).[6] The Si(3)−Si(4) single bond is unusually long (2.450 Å). The four-membered ring is not planar but folded with the out-of-plane angles of 37.1° and 37.0°, which are the angles between Si(1)−Si(2)−Si(3) and Si(1)−Si(4)−Si(3) planes and the Si(2)−Si(3)−Si(4) and Si(2)−Si(1)−Si(4) planes, respectively. The arrangement around the silicon−silicon double bond is a little trans-bent ($\theta = 13.2°$ (around Si(1)) at 13.3° (around Si(2); bend angle θ is defined as an angle between the $Si(sp^3)-Si(sp^2)-Si(sp^3)$ plane and the $Si(sp^2)-Si(sp^2)$ bond). The twist angle γ determined by the angle between two $Si(sp^3)-Si(Sp^2)-Si(Sp^3)$ planes is 12.3°. Steric repulsion between vicinal Bu^tMe_2Si groups on Si(3) and Si(4) would be the major reason for the folding of the four-membered ring, the long Si(3)−Si(4) bond, and also the deformation around the *soft* Si═Si bond.

The UV−vis spectrum of **1** in 3-methylpentane is similar to that of tetrakis(*tert*-butyldimethylsilyl)disilene (**6**),[6] but the maximum for **1** at 465 nm is red shifted by 45 nm relative to that for **6** due to the high strain in the cyclic four-membered ring.

During photolysis of **1** in 3-methylpentane with a high-pressure Hg arc lamp (λ > 420 nm), the solution turned from the original bright orange to red brown; the absorbance at 465 nm decreased with two clear isosbestic points at 424 and 515 nm. Leaving the photolysate for 12 h in the dark at room temperature, **1** was reproduced quantitatively. In the photostationary state at 288 K, 91% of **1** was converted to the photoproduct, as determined by UV−vis spectroscopy. The structure of the photoproduct[7] was characterized as the corresponding tetrasilabicyclo[1.1.0]butane (**2**) by ^1H NMR spec-

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[1] For reviews, see: (a) West, R. *Pure Appl. Chem.* **1984**, *56*, 163. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (d) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Part 2, Chapter 17. (e) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (f) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (g) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125.

[2] The formation of a Dewar hexasilabenzene by the photolysis of the corresponding hexasilaprismane was evidenced spectroscopically: (a) Sekiguchi, A.; Yatabe, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 5853. (b) Sekiguchi, A.; Yatabe, T.; Doi, S.; Sakurai, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *93/94*, 193. An interesting cyclic pergermacycloalkene, tetrakis(tri-*tert*-butylsilyl)trigermacyclopropene, was isolated very recently: Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H.; Nagase, S. *J. Am. Chem. Soc.* **1995**, *117*, 8025.

[3] Woodward, R. B.; Hoffmann, R. *The conservation of orbital symmtery*; Verlag-Chemie: Weinheim, 1970. See also: (a) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3412. (b) Nguyen, K. A.; Gordon, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 3835 and references cited therein. (c) Leigh, W. J.; Postigo, J. A.; Venneri, P. C. *J. Am. Chem. Soc.* **1995**, *117*, 7826 and references cited therein.

[4] **1**: air-sensitive orange crystals; mp 263−265 °C; ^1H NMR (C_6D_6) δ 0.40 (s, 12H), 0.44 (s, 12H), 0.48 (s, 12H), 1.15 (brs, 54H); ^{13}C NMR (C_6D_6) δ −1.6, 0.9, 1.2, 19.8, 20.5, 28.0, 29.8; ^{29}Si NMR (C_6D_6) δ −71.4, 1.48, 5.01, 160.4; MS (DEI) *m/z* (%) 802 (2.2), 687 (10.6), 402 (19.4), 73 (100); UV (hexane) λ_{max}/nm ($\epsilon \times 10^{-3}$) 465 (6.81), 359 (1.06), 308 (sh, 4.07), 271 (sh, 10.6).

[5] Crystal data of **1**: $Si_{10}C_{36}H_{90}\cdot C_7H_{16}$, MW = 803.92 + 100.20, orange prism, triclinic, space group $P1$, a = 12.567(2) Å, b = 23.459(3) Å, c = 10.396(1) Å, α = 101.25(1)°, β = 100.64(1)°, γ = 74.72(1)°, V = 2871(1) $Å^3$, Z = 2, D_{calcd} = 0.93 g/cm^3, μ(Mo Kα) = 2.429 cm^{-1}. The reflection intensities were collected on a Rigaku AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). A total of 10 117 reflections were measured, and of these, 5012 reflections [$F_o > 3.5\sigma(F_o)$] were used in refinement: R = 0.0893, R_w = 0.0940. All calculations were performed by an ACOS-3900 computer at Tohoku University with the applied library program UNICS III system and RANTAN81 program.

[6] Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1489.

[7] The ^1H NMR data of **2** was as follows: δ 0.44 (s, 12H), 0.45 (s, 24H), 1.18 (s, 36H), 1.19 (s, 18H). Existence of only two kinds of *t*-$BuMe_2$-Si groups suggests the facile ring flipping as indicated for a tetrasilabicyclo[1.1.0]butane by Masamune et al.[8] The UV−vis spectrum of **2** showed a tailing into 600 nm with no appreciable band, which is responsible for the red brown color. The tetrasilabicyclobutane **2** may have a structure assigned to the “long-bond” isomer as predicted theoretically.[9]

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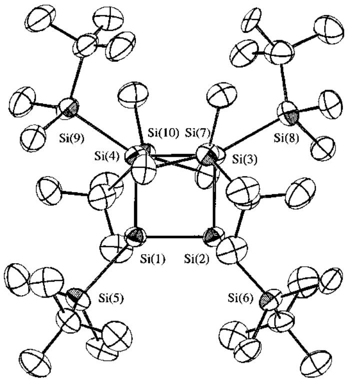

Figure 1. ORTEP view of **1**, showing the atom-numbering scheme. Hydrogen atoms were omitted for clarity. Selected bond distances (Å): Si(1)−Si(2), 2.174(4); Si(2)−Si(3), 2.353(4); Si(3)−Si(4), 2.450(4); Si(4)−Si(1), 2.349(4); Si(1)−Si(5), 2.366(4); Si(2)−Si(6), 2.384(4); Si(3)−Si(7), 2.417(4); Si(3)−Si(8), 2.388(8); Si(4)−Si(9), 2.415(4); Si(4)−Si(10), 2.419(4). Selected bond angles (deg): Si(4)-Si(1)-Si(2), 90.0(1); Si(1)−Si(2)−Si(3), 90.3(1); Si(2)−Si(3)−Si(4), 83.5(1); Si(3)−Si(4)−Si(1), 84.0(1); Si(2)−Si(1)−Si(5), 132.1(1); Si(4)−Si(1)−Si(5), 136.5(1).

troscopy and by the product analysis of hydrolysis of the photoproduct of **1**. Thus, the hydrolysis at 0 °C gave the cis isomer of 1-hydrido-3-hydroxy-1,2,2,3,4,4-hexakis(*tert*-butyldimethylsilyl)cyclotetrasilane (**7**) in 81.7% yield based on the starting **1** as determined by NMR. The structure of **7** was confirmed by the NMR[10] and X-ray analyses.[11] The direct measurements of the ^{29}Si and ^{13}C NMR spectra of **2** failed because **2** was obtained only in a low concentration in solution and was converted to **1** during sample concentration.

The photochemical conversion of **1** to **2** and the thermal reversion were repeated more than 10 times without appreciable side reactions (eq 2). The present results indicate that **1** is

$$\mathbf{1} \underset{\text{rt, dark}}{\overset{h\nu\ (\lambda > 420\ \text{nm})}{\rightleftarrows}} \mathbf{2} \qquad (2)$$

thermodynamically more stable than **2**, in contrast to a previous experimental study of a tetrasilabicyclo[1.1.0]butane[8] and a theoretical study of parent Si_4H_6.[12]

The first-order rates and the activation parameters for the thermal reversion of **2** to **1** were determined by monitoring the absorbance at 465 nm at various temperatures: $k = 5.67 \times 10^{-5}$ s^{-1} at 288 K, $\Delta H^{\ddagger} = 16.5$ kcal/mol, $\Delta S^{\ddagger} = -20.8$ cal mol^{-1} K^{-1}.

Further work is in progress to elucidate the detailed mechanisms including the possible intermediacy of the corresponding tetrasila-1,3-butadiene **3** during the interconversion between **1** and **2**.

Acknowledgment. This work was supported by the Ministry of Education, Science, and Culture of Japan (Grand-in-Aid for Scientific Research on Priority Areas nos. 06227207 and 07216207).

Supporting Information Available: The photochemical and thermal interconversion between **1** and **2** followed by UV−vis spectroscopy and crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **1** and **7** (47 pages). See any current masthead page for ordering and Internet access instructions.

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(8) (a) Jones, R.; Williams, D. J.; Kabe, Y.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 173. (b) Masamune, S.; Kabe, Y.; Collins, S.; Williams, D. J.; Jones, R. *J. Am. Chem. Soc.* **1987**, *107*, 5552. (c) Kawase, T.; Batcheller, S. A.; Masamune, S. *Chem. Lett.* **1987**, 227.

(9) (a) Schleyer, P. v. R.; Sax, A. F.; Kalcher, J.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364. (b) Schoeller, W. W.; Dabisch, T.; Busch, T. *Inorg. Chem.* **1987**, *26*, 4383. (c) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1988**, 54. (d) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1992**, *96*, 9189. (e) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 2888. (f) Boatz, J. A.; Gordon, M. S. *Organometallics* **1996**, *15*, 2118.

(10) **7**: colorless crystals; mp 198−200 °C; ^{1}H NMR (C_6D_6, 313 K) δ 0.37 (s, 6H), 0.38 (s, 6H), 0.39 (s, 1H), 0.41 (s, 6H), 0.44 (s, 6H), 0.47 (s, 6H), 0.56 (s, 6H), 1.08 (s, 9H), 1.10 (s, 18H), 1.14 (s, 18H), 1.16 (s, 9H), 4.64 (s, 1H); ^{13}C NMR (C_6D_6, 313 K) δ −2.2, −1.0, 0.5, 0.7, 1.6, 1.9, 19.6, 19.7, 20.2, 20.7, 28.7, 29.1, 29.2; ^{29}Si NMR (C_6D_6, 313 K) δ −97.8 (*Si*H), −69.8 (*Si*(SiMe$_2$Bu^t)$_2$), −3.0, 4.6, 5.7, 7.2, 46.4 (*S*iOH); MS (EI, 70 eV) *m/z* (%) 820 (1.3, M$^+$), 703 (12.2), 588 (13.7), 116 (26.0), 44 (100). The NMR spectra showed that there exists neither the other geometrical isomer nor the hydrolysis products from **1** in the isolated solid. The NMR spectra of **7** are completely different from those for the hydrolysis product of **1**: ^{1}H NMR (C_6D_6, 313 K) δ 0.36 (s, 3H), 0.39 (s, 1H), 0.43 (s, 3H), 0.45 (brs, 6H), 0.49 (s, 3H), 0.50 (s, 3H), 0.54−0.55 (m, 12H), 0.67 (s, 3H), 0.91 (s, 3H), 1.09 (s, 9H), 1.11 (s, 9H), 1.12 (s, 9H), 1.15 (s, 9H), 1.19 (s, 9H), 1.21 (s, 9H), 4.90 (s, 1H); ^{13}C NMR (C_6D_6, 313 K) δ −1.6, −1.1, −0.3, −0.1, 1.8, 2.4, 2.6, 2.9, 3.4, 3.8, 4.2, 4.5, 19.4, 20.3, 20.5, 20.8, 21.2, 21.3, 28.0, 29.3, 30.0, 30.1, 30.2, 30.8; ^{29}Si NMR (C_6D_6, 313 K) δ −82.8 (*Si*H), −66.0 (*Si*(SiMe$_2$Bu^t)$_2$), −60.2 (*Si*(SiMe$_2$Bu^t)$_2$), 4.1, 5.2, 6.1, 6.3, 7.6, 9.1, 18.9 (*S*iOH).

(11) Crystal data of **7**: $Si_{10}C_{36}H_{92}O$, MW = 821.98, colorless prism, monoclinic, space group $P2_1/c$, $a = 12.512(4)$ Å, $b = 35.584(7)$ Å, $c = 12.782(3)$ Å, $\beta = 110.69(1)°$, $V = 5323(2)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.025$ g/cm^3, μ(Cu Kα) = 25.03 cm^{-1}. The reflection intensities were collected on a Rigaku AFC-5R diffractometer with a rotating anode (5 kV, 180 mA) using graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å). A total of 8998 reflections were measured, and of these, 5959 reflections [$F_o > 4\sigma(F_o)$] were used in refinement: $R = 0.066$, $R_w = 0.071$. The X-ray analysis revealed a disordered structure which had an approximate, noncrystallographic, 2-fold axis normal to the plane of the cyclotetrasilane ring. The disorder is confined to the axial hydroxy group which has 37 and 63% site occupancies on Si(1) and Si(3), respectively. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Coorporation.

(12) Ab initio MO calculations for Si_4H_6 isomers have shown that tetrasilabicyclo[1.1.0]butane is more stable than tetrasilacyclobutene with the small energy difference of 3.4 kcal/mol: Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1988**, *92*, 3037.