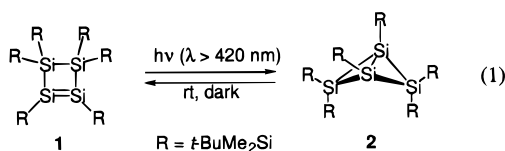# The First Stable Cyclotrisilene

Takeaki Iwamoto, Chizuko Kabuto, and Mitsuo Kira*

*Department of Chemistry, Graduate School of Science
Tohoku University, Aoba-ku, Sendai 980-8578, Japan*

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Among a variety of doubly bonded compounds of group-14 metallic elements ($R_2M=MR_2$; M = Si, Ge, Sn),[1] very few permetallacycloalkenes have been isolated and characterized,[2−6] and unique chemistry of their endocyclic metal−metal double bonds needs to be investigated. We have synthesized the first stable cyclotetrasilene, hexakis(*tert*-butyldimethylsilyl)cyclotetrasilene (**1**), and found an unprecedented interconversion between **1** and the corresponding skeletal isomer, hexakis(*tert*-butyldimethylsilyl)bicyclo[1.1.0]tetrasilane (**2**) (eq 1).[2] Stable cyclo-

trigermene derivatives,[5a] which have been prepared by the reactions of $GeCl_2$−dioxane with *t*-Bu$_3$SiNa and *t*-Bu$_3$GeLi, cyclotrigermenium ions,[5b−d] and a cyclotrigermenyl radical[6] have been synthesized within a short time of one another. However, the silicon analogues of cyclopropene have not been known to date, probably because of the unavailability of the functional silylenes as a reagent. We report herein the synthesis and characterization of the first stable cyclotrisilene, 1-tris(*tert*-butyldimethylsilyl)silyl-2,3,3-tris(*tert*-butyldimethylsilyl)cyclotrisilene (**3**, R = *t*-BuMe$_2$Si), by a reduction of 1,1-dibromo-3-(*tert*-butyl)-2,2-di(*tert*-butyldimethylsilyl)-1-chloro-3,3-dimethyltrisilane (**4**) with potassium graphite (KC_8) in THF. The major product of reduction of **4** depends significantly on the reaction conditions; a reaction of **4** with sodium metal in toluene did not give **3** but **1** in good yield. Interestingly, the reaction of **3** with carbon tetrachloride gave the corresponding 1,2-dichlorinated cyclotrisilane in a trans-addition manner.

Cyclotrisilene **3** was obtained in good yield by the following process (eq 2): To a suspension of KC_8 (8.6 mmol) in THF (15

mL) was added a solution of **4** (0.99 mmol) in THF (10 mL) at −78 °C.[7] The solution was then stirred overnight at room temperature. Removal of the resulting salt and graphite by filtration and evaporation of solvents in vacuo gave a dark orange solid, which contained **3** in 65% yield together with tris(*tert*-butyldimethylsilyl)chlorosilane as the sole byproduct as determined by NMR. After removal of the chlorosilane by distillation, recrystallization from pentane gave pure **3** as dark red crystals in 11%.[8] The structure of **3** was determined by MS and ^1H, ^{13}C, and ^{29}Si NMR spectroscopies as well as the product analysis of a reaction with carbon tetrachloride (vide infra). Cyclotrisilene **3** was air-sensitive similar to other cyclic and acyclic tetrasilyldisilenes; the dark red color disappeared immediately when a solution of **3** was exposed to air.

It is interesting to compare the UV−vis spectra of **3** and cyclotetrasilene **1** in 3-methylpentane. The absorption maxima of **3** were observed at 482 (ϵ 2600) and 401 nm (ϵ 1300), which were red shifted from those for **1** (λ_{max}/nm (ϵ): 465 (6800) and 359 (1060))[2] consistent with the greater ring strain in **3**.

Two ^{29}Si NMR resonances of the three-coordinated silicon atoms ($\delta(Si_u)$) in **3** appeared at +81.9 (*t*-BuMe$_2$Si-*Si*=) and +99.8 ppm ((*t*-BuMe$_2$Si)$_3$Si-*Si*=),[9] which are significantly high-field shifted relative to those for the acyclic tetrasilyldisilenes (142−154 ppm)[10] and **1** (160.4 ppm).[2a,11] The tendency of the $\delta(Si_u)$ values among the corresponding tetrasilyldisilene, **3**, and **1** is quite parallel to that of the ^{13}C NMR chemical shifts of the unsaturated carbons ($\delta(C_u)$) among ethylene, cyclopropene, and cyclobutene;[13] the high-field shift of $\delta(Si_u)$ of **3** and $\delta(C_u)$ of cyclopropene would have the same origin.

Recently, we have found that tetrasilyldisilenes readily react with carbon tetrachloride to give the corresponding 2,3-dichlo-

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(2) (a) Kira, M.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1996,** *118,* 10303. (b) Iwamoto, T.; Kira, M. *Chem. Lett.* **1998,** 277.
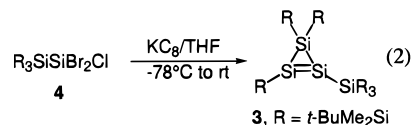
(3) Very recently, Wiberg et al. reported that the novel cyclotetrasilene, 1,2,3,4-tetrakis(tri-*tert*-butylsilyl)-1,2-diiodo-3,4-cyclotetrasilene, was obtained by a simple reaction of tetrakis(tri-*tert*-butylsilyl)tetrahedrane with iodine. Wiberg, N.; Auer, H.; Nöth, H.; Knizek J.; Polborn K. *Angew. Chem., Int. Ed. Engl.* **1998,** *36,* 2869.

(4) 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.

(5) Cyclotrigermenes: (a) Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H.; Nagase, S. *J. Am. Chem. Soc.* **1995,** *117,* 8025. Cyclotrigermenium ions: (b) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997,** *275,* 60. (c) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M.; Fukaya, N. *Phosphorous, Sulfur, Silicon Relat. Elem.* **1997,** *124* and *125,* 323. (d) Ichinohe, M.; Fukaya, N.; Sekiguchi, A. *Chem. Lett.* **1998,** 1045.

(6) A cyclotrigermenyl radical: Olmstead, M. M.; Pu, L.; Simons, R. S.; Power, P. P. *Chem. Commun.* **1997,** 1595.

(7) For the applications of potassium graphite to reduction of organosilicon compounds, see: (a) Fürstner, A.; Weidmann, H. *J. Organomet. Chem.* **1988,** *354,* 15. (b) Cleij, T. J.; Tsang, S. K. Y.; Jenneskens, L. W. *Chem. Commun.* **1997,** 329 and references therein. See also ref 6.

(8) **3**: air-sensitive dark red crystals; mp 150 °C dec; ^1H NMR (C_6D_6) δ 0.40 (s, 6 H, SiMe$_3$), 0.42 (s, 6 H, SiMe$_3$), 0.47 (s, 6 H, SiMe$_3$), 0.51 (s, 18 H, SiMe$_3$), 1.109 (s, 9 H, *t*-Bu), 1.113 (s, 27 H, *t*-Bu), 1.18 (s, 18 H, *t*-Bu); ^{13}C NMR (C_6D_6) δ −1.7, −1.5, −1.2 0.8 (SiCH$_3$), 19.5, 20.0, 20.5 (C(CH$_3$)$_3$), 27.7, 28.8, 29.3 (C(CH$_3$)$_3$); ^{29}Si NMR (C_6D_6) δ −117.2 ((*t*-BuMe$_2$Si)$_2$Si), −105.7 ((*t*-BuMe$_2$Si)$_3$Si), 0.4 ((*t*-BuMe$_2$Si)$_2$Si), 6.4 ((*t*-BuMe$_2$Si)$_3$Si), 14.0 (*t*-BuMe$_2$SiSi=), 81.9 (*t*-BuMe$_2$SiSi=), 99.8 ((*t*-BuMe$_2$Si)$_3$SiSi=); MS (EI, 70 eV) 802 (5.9, M$^+$), 687 (57.2), 515 (32.2), 147 (41.0), 131 (33.2), 115 (38.5), 73 (100), 59 (68.5); UV−vis (3-methylpentane) λ_{max}/nm (ϵ) 482 (2640), 401 (1340), 315 (sh, 7690), 245 (sh, 3670), 217 (5210).

(9) The assignment of the two ^{29}Si signals for unsaturated silicons was confirmed by two-dimensional NMR. The details were given in the Supporting Information.

(10) Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 1489.

(11) The $\delta(Si_u)$ values for the tetrasilyldisilenes, **3**, and **1** are good in accord with those for the model compounds, **6**, **7**, and **8**, calculated with the GIAO method (GIAO/B3LYP/6-311+G(2df, p)//HF/6-31G(d)); those are +147.5,[12] +103.1, and +187.8, respectively.
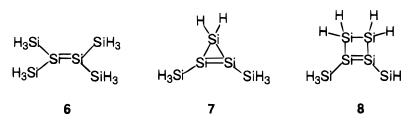
(12) West, R.; Cavalieri, J. D.; Buffy, J. J.; Fry, C.; Zilm, K. W.; Duchamp, J. C.; Kira, M.; Iwamoto, T.; Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **1997,** *119,* 4972.

rotetrasilanes through chlorine abstraction of the tetrasilyldisilenes.[14] Expectedly, a reaction of **3** with an excess amount of carbon tetrachloride completed within 1 min even at −70 °C to afford the corresponding *trans*-1,2-dichloro-1-tris(*tert*-butyldimethylsilyl)silyl-2,3,3-tris(*tert*-butyldimethylsilyl)cyclotrisilane (**5**) quantitatively without cleavage of the Si−Si single bonds in the ring (eq 3).[15] The X-ray analysis of a single crystal of **5** disclosed that the two chlorine atoms were arranged in a trans fashion as shown in Figure 1.[16,17] The formation of **5** from **3** confirms the three-membered-ring structure and the existence of an endocyclic silicon−silicon double bond in **3**.

$$\textbf{3} \xrightarrow[\text{-70°C}]{\text{CCl}_4,\ \text{dark}} \quad \text{(3)}$$

5
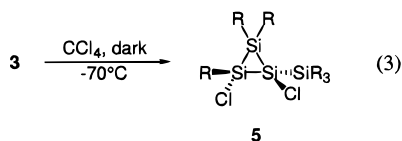
The mechanism of the formation of **3** by the reductive coupling of **4** remains open at present. A possible and attractive mechanism is the production of the corresponding disilyne, $(t\text{-BuMe}_2\text{Si})_3\text{SiSi}\equiv\text{SiSi}(\text{SiMe}_2\text{Bu-}t)_3$, through the reductive coupling followed by the 1,2-migration of a $(t\text{-BuMe}_2\text{Si})_3$Si group to give the corresponding disilavinylidene, $[(t\text{-BuMe}_2\text{Si})_3\text{Si}]_2\text{Si}=\text{Si}:$, which rearranges to **3** through intramolecular silylene insertion into a Si−Si bond.[20]

The major product of the reduction of **4** depended remarkably

(13) The ^{13}C chemical shifts of the unsaturated carbons $\delta(C_u)$ for ethylene, cyclopropene, and cyclobutene are reported to be 123.5, 108.7, and 137.2 ppm, respectively. (a) Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; John Wiley & Sons: New York, 1988. See also for cyclopropene: (b) Günther, H.; Seel, H. *Org. Magn. Reson.* **1976**, *8*, 299. For cyclobutene: (c) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757. For ethylene: Savitsky, G. B.; Ellis, P. D.; Namikawa, K.; Maciel, G. E. *J. Chem. Phys.* **1968**, *49*, 2395.

(14) Iwamoto, T.; Sakurai, H.; Kira, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2741.

(15) **5**: air-sensitive pale yellow crystals; mp 152−154 °C. ^{1}H NMR (C_6D_6) δ 0.40 (s, 3 H, SiMe₃), 0.41 (s, 3 H, SiMe₃), 0.43 (s, 3 H, SiMe₃), 0.47 (s, 6 H, SiMe₃), 0.50 (s, 9 H, SiMe₃), 0.54 (s, 9 H, SiMe₃), 0.61 (s, 3 H, SiMe₃), 1.11 (s, 9 H, *t*-Bu), 1.13 (s, 27 H, *t*-Bu), 1.14 (s, 9 H, *t*-Bu), 1.18 (s, 9 H, *t*-Bu); ^{13}C NMR (C_6D_6) δ −2.6, −2.5, 1.9, 2.2, 2.4, 3.5, 3.6 (Si*C*H₃), 19.5, 19.9, 20.6, 20.8 (*C*(CH₃)₃), 28.5, 29.0, 29.2, 29.6 (C(*C*H₃)₃); ^{29}Si NMR (C_6D_6) δ −119.2 ((t-BuMe₂Si)₂*Si*), −95.3 ((t-BuMe₂*Si*)₃Si), −40.0 (t-BuMe₂Si*Si*Cl), −20.0 ((t-BuMe₂Si)₃Si*Si*Cl), 7.1 ((t-BuMe₂*Si*)₃Si), 9.4 ((t-BuMe₂*Si*)₂Si), 11.3 (t-BuMe₂*Si*SiCl), 12.4 ((t-BuMe₂*Si*)₂Si).

(16) X-ray analysis of **5**: $C_{36}H_{90}Si_{10}Cl_2$; pale yellow prism; orthorhombic; space group $Pna2_1$; $a = 17.286(7)$ Å, $b = 25.14(1)$ Å, $c = 12.473(8)$ Å, $V = 5419(3)$ Å³; $Z = 4$; $\rho_{calcd} = 1.072$ g/cm³; μ(Mo Kα) = 3.63 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 ($\lambda = 0.71069$ Å) at 150 K. The structure was solved by direct methods, using SIR-92,[18] and refined by full-matrix least squares on F^2, using SHELXL93:[19] $R = 0.049$ (data with $I > 2\sigma(I)$), $Rw = 0.159$ (all data).

(17) A mechanistic study of the reactions of disilenes and haloalkanes is under way. Trans arrangement of two chlorine atoms in **5** can be explained by a stepwise chlorine abstraction mechanism in the reaction of **5** with carbon tetrachloride.

(18) Altomare A.; Burla, M. C.; Camalli, M.; Cascarano G.; Giacovazzo, C.; Guagliardi A. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(19) Sheldrick, G. M. *SHELXL93*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1993.
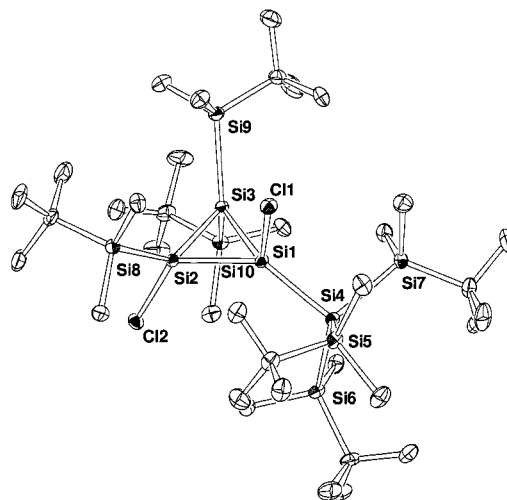
Figure 1. ORTEP drawing of *trans*-1,2-dichlorocyclotrisilane (**5**). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Si1−Cl1, 2.121(2); Si2−Cl2, 2.097(2); Si1−Si2, 2.350(2); Si1−Si3, 2.404(1); Si2−Si3, 2.380(2); Si1−Si4, 2.409(1); Si2−Si8, 2.363(2); Si3−Si9, 2.397(2); Si3−Si10, 2.398(2). Selected bond angles (deg): Cl1−Si1−Si2, 98.34(6); Cl2−Si2−Si1, 119.02(6); Si1−Si2−Si3, 61.08(4); Si2−Si1−Si3, 60.07(4); Si1−Si3−Si2, 58.85(4); Si2−Si1−Si4, 141.46(6); Si3−Si1−Si4, 141.33(6); Si1−Si2−Si8, 126.33(6); Si3−Si2−Si8, 136.91(6).

on the reaction conditions. Thus, treatment of **4** with sodium metal in toluene at room temperature gave cyclotetrasilene **1** in 64% yield without formation of **3** (eq 4). The yield of **1** formed by

$$\textbf{4} \xrightarrow[\text{toluene}]{\text{Na}} \textbf{1},\ R = t\text{-BuMe}_2\text{Si} \quad \text{(4)}$$
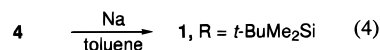
this reaction is much higher than that by our previous method, i.e. the reductive cross coupling of 2,2-dibromo-1,3-di-*tert*-butyl-1,1,3,3-tetramethyltrisilane and 2,2,3,3-tetrabromo-1,4-di-*tert*-butyl-1,1,4,4-tetramethyltetrasilane.[2a] The reduction of **3** with sodium provides an advantageous method for preparation of **1**.

Supporting Information Available: ^{1}H, ^{13}C, and ^{29}Si NMR and their 2D NMR spectra of cyclotrisilene **3** and X-ray structural information on **5** (PDF). An X-ray crystallographic file is also available (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Kobayashi and Nagase have recently reported the relative energies of the two isomers of R_2Si_2 derivatives, $RSi\equiv SiR$ and $R_2Si=Si:$. When R = $(H_3Si)_3Si$, the disilavinylidene isomer is calculated to be 6.2 kcal/mol more stable than the *trans*-bent disilyne isomer. Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489.