

Syntheses and Characterization of Bis(silacyclopropene) and Disilabenzvalene

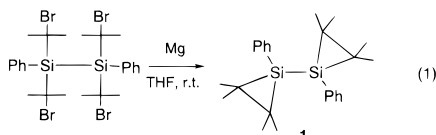
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In continuation of our program on the syntheses and studies of small-ring silicon compounds,¹ we were desired to prepare 1,2-bissilylene, which is an equivalent of disilyne. Earlier papers have described the isolation of trapped products believed to arise from disilyne² and 1,4-disilabenzene^{3,4} in the decomposition of di(7-silanorbornadin-7-yl) derivatives. However, there is no unambiguous evidence on the intermediacy of the disilynes. Herein, we report the syntheses and structural characterizations of the first isolable bis(silacyclopropene) and disilabenzvalene.

The synthesis of the precursor bis(silacyclopropane) **1** is carried out as follows: diphenyltetrakis(1-bromo-1-methylethyl)disilane was allowed to react with magnesium by using a modification of the method of Seyferth.⁵ Pure, neat **1**^{6,7} is stable but slowly decomposes or polymerizes in solution (half-life of 17 min at 65 °C) (eq 1, Figure 1).



Thermolysis of **1** with bis(trimethylsilyl)acetylene at 60 °C affords bis(silacyclopropene) **2** (61%, unstable with respect to hydrolysis and oxidation) (Scheme 1):⁸ *m/e* 550.2215, calcd for C₂₈H₄₆Si₆, *m/e* 550.2215, mp 72–75 °C; ¹H NMR (C₆D₆, 300 MHz) δ 0.30 (s, 36H), 7.05–7.07 (m, 6H), 7.54–7.57 (m, 4H); ¹³C NMR (C₆D₆, 75 MHz) δ –0.1 (q), 128.0 (d), 129.2 (d), 134.6 (d), 137.9 (s), 173.8 (s); ²⁹Si NMR (C₆D₆, 60 MHz) δ –143.2, –9.4; *m/e* 550 (M⁺), 535 (M⁺ – Me). The ²⁹Si

(1) (a) Kabe, Y.; Ando, W. *Adv. Strain Org. Chem.* **1993**, 3, 59. (b) Hojo, F.; Ando, W. *Synlett* **1995**, 880. (c) Ando, W. *Bull. Chem. Soc. Jpn.* **1996**, 69, 1.

(2) Sekiguchi, A.; Zigler, S. S.; West, R. *J. Am. Chem. Soc.* **1986**, 108, 4241.

(3) Sekiguchi, A.; Gillet, G. R.; West, R. *Organometallics* **1988**, 7, 1226.

(4) Rich, J. D.; West, R. *J. Am. Chem. Soc.* **1982**, 104, 6884.

(5) (a) Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, 97, 2273.

(b) Seyferth, D.; Lambert, R. L., Jr.; Annarelli, D. C. *J. Organomet. Chem.* **1976**, 122, 311.

(6) A solution of 8.26 g (11.8 mmol) of diphenyltetrakis(1-bromo-1-methylethyl)disilane in 50 mL of THF was added dropwise to an excess of pure magnesium (99.95% from Aldrich, 895 mg, 36.8 mmol) in 10 mL of THF. Upon workup, **1** was isolated a white solid (1.48 g, 33 %); the pure compound was obtained by recrystallization from hexane/benzene (mp 124 °C (dec.), unstable for air and water).

(7) The crystal structure of **1** is shown in Figure 1. Crystal data for **1**: fw = 378.1, monoclinic, *a* = 39.096(6) Å, *b* = 6.766(2) Å, *c* = 17.125(3) Å, β = 97.81(1)°, *V* = 4581.3 Å³, space group C2/c, *Z* = 8, μ (Mo Kα) = 1.5 cm⁻¹, ρ (calcd) = 1.01 g/cm³. The 4541 independent reflections ($|F_o| > 3.0\sigma|F_o|^2$, 2θ ≤ 50.0°) were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an ω – 2θ scan. An empirical absorption correction based on a series of ψ scans were applied to the data 0.88/1.00. The structure was solved by direct methods, and hydrogen atoms were added to the structure factor calculations but their positions were not refined anisotropically to *R* = 0.052 (*R*_w = 0.065).

(8) The benzene solution of **1** (200 mg, 0.53 mmol) with bis(trimethylsilyl)acetylene (1.3 g, 7.6 mmol) in a degassed sealed tube was stirred at 60 °C for 15 h. The volatile materials were removed under reduced pressure, and the residue was chromatographed with a Florisil column eluted by hexane to give **2** (170 mg). The solid **2** was recrystallized from hexane at –20 °C.

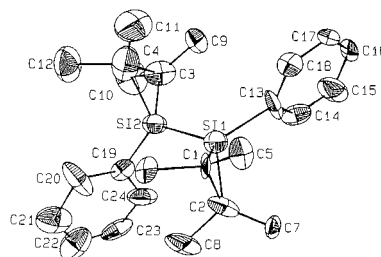


Figure 1. Crystal structure of **1**. Selected bond distances (Å) and angles (deg): 2.313(5) [Si(1)–Si(2)], 1.877(5) [Si(1)–C(1)], 1.880(5) [Si(1)–C(2)], 1.560(7) [C(1)–C(2)], 1.520(8) [C(1)–C(5)], 1.504(7) [C(1)–C(6)], 1.522(7) [C(2)–C(7)], 1.513(6) [C(2)–C(8)], 49.1 [C(1)–Si(1)–C(2)], 65.6 [Si(1)–C(1)–C(2)], 65.4 [Si(1)–C(2)–C(1)].

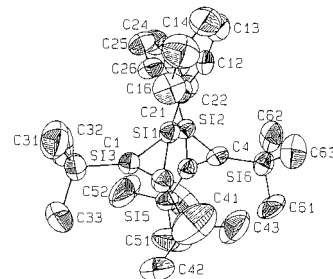
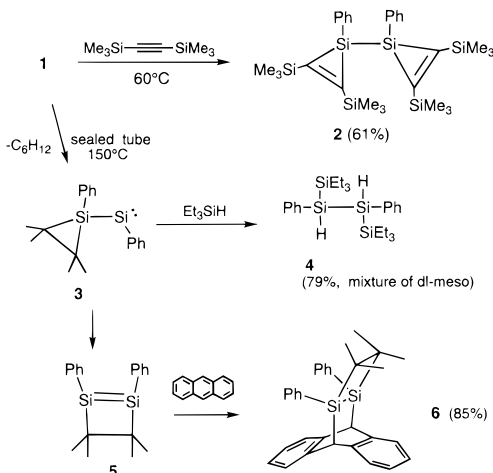


Figure 2. Crystal structure of **2**. Selected bond distances (Å) and angles (deg): 2.296(3) [Si(1)–Si(2)], 1.835(9) [Si(1)–C(1)], 1.835(9) [Si(1)–C(2)], 1.84(1) [Si(2)–C(3)], 1.80(1) [Si(1)–C(4)], 1.32(1) [C(1)–C(2)], 1.33(1) [C(3)–C(4)], 119.2(3) [Si(2)–Si(1)–C(1)], 116.3(3) [Si(2)–Si(1)–C(2)], 116.3(3) [Si(2)–Si(1)–C(3)], 120.3(3) [Si(2)–Si(1)–C(4)], 68.9(6) [Si(1)–C(1)–C(2)], 68.8(6) [Si(1)–C(2)–C(1)], 67.3(6) [Si(2)–C(3)–C(4)], 70.0(6) [Si(2)–C(4)–C(3)], 42.3(5) [C(1)–Si(2)–C(2)], 42.7(5) [C(3)–Si(2)–C(2)].

Scheme 1

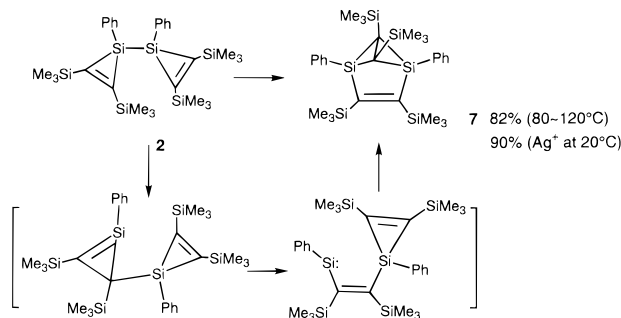


chemical shifts for the ring silicon atoms are highly unusual.⁹ The crystal structure was solved by direct methods, and the molecular structure of **2** is shown in Figure 2.¹⁰ The observed silicon–silicon bond distance is significantly shorter than found for a normal silicon–silicon single bond. Bis(trimethylsilyl)-

(9) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Am. Chem. Soc.* **1976**, 98, 6382.

(10) Crystal data for **2**: fw = 551.20, triclinic, *a* = 9.797(1) Å, *b* = 10.310(7) Å, *c* = 19.188(9) Å, α = 87.24(5)°, β = 79.49(6)°, γ = 72.94(7)°, *V* = 4581.3 Å³, space group *P*-1, *Z* = 2, μ (Mo Kα) = 2.4 cm⁻¹, ρ (calcd) = 1.00 g/cm³. The 6787 independent reflections ($|F_o| > 3.0\sigma|F_o|^2$, 2θ ≤ 50.0°) were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an ω – 2θ scan. An empirical absorption correction based on a series of ψ scans were applied to the data 0.78/1.00. The structure was solved by direct methods, and hydrogen atoms were added to the structure factor calculations but their positions were not refined anisotropically to *R* = 0.078 (*R*_w = 0.088).

Scheme 2



acetylene is an efficient trapping reagent for silylene **3**. Evidence for the intermediacy of silylene **3** was obtained by thermolyzing **1** in the presence of triethylsilane or anthracene, which afforded the 2,3-diphenyltetrasilane **4** (79%) or the adduct **6** (101 mg, 85%).¹¹ Silylene **3**, in the presence of an inefficient trapping reagent undergoes the ring expansion to disilene **5** which upon Diels–Alder reaction affords **6**. The possible involvement of disilyne may not be considered under the reaction conditions.

Bis(silacyclopropene) **2** is expected to be an intermediate in a number of interesting isomerizations of disilabenzene. Thermolysis of **2** in a degassed sealed tube at 120°C in benzene afforded the disilabenzvalene **7** (82%) (Scheme 2). The structure of **7** (mp $161\text{--}164^\circ\text{C}$, air and moisture sensitive) was initially deduced from its HRMS (calcd for $\text{C}_{28}\text{H}_{46}\text{Si}_6$ 550.2203, found 550.2215): ^1H NMR (C_6D_6 , 300 MHz) δ 0.08 (s, 18H), 0.20 (s, 18H), 7.15–7.17 (m, 6H), 7.96–7.99 (m, 4H); ^{13}C NMR (C_6D_6 , 75 MHz) δ 2.39 (q), 2.83 (q), 37.9 (s), 128.1 (d), 130.7 (d), 131.3 (s), 137.6 (d), 182.8 (s); ^{29}Si NMR (C_6D_6 , 60 MHz) δ –61.9, –6.5, –4.5; UV 312 nm (ϵ 4495). The crystal structure was solved by direct methods, and the molecular structure of **7** is shown in Figure 3.¹² The silicon–silicon internuclear distance is 2.549 Å, which due to a transannular bond between two silicon atoms.

The isomerization of **2** could be considered as occurring via the initial formation of an intermediate Dewar silabenzene or 1,4-disilabenzene and their subsequent isomerization to disilabenzvalene. To evaluate the stabilities of **2**, the relative energies of the corresponding valence isomers (**2a**, **7a–10a**) were determined by 6-31G* molecular orbital calculations (Scheme

(11) A mixture of **1** (100 mg, 0.264 mmol) and anthracene (471 mg, 2.64 mmol) in 5 mL of benzene was heated in a degassed sealed tube at 150°C for 2 h, producing tetramethylethylene (~70%) as well as of 1,2-diphenyl-1,2-disilacyclobutene **5** (Scheme 1). Compound **6**: yellow crystal, mp 145°C (dec.); ^1H NMR (C_6D_6 , 300 MHz) δ 0.53 (s, 6H), 0.8 (s, 6H), 4.60 (s, 2H), 6.74–6.87 (m, 2H), 7.08–7.46 (m, 14H); ^{13}C NMR (C_6D_6 , 75 MHz) δ 21.8 (q), 24.8 (q), 34.3 (s), 43.8 (d), 124.6 (d), 125.0 (d), 125.7 (d), 126.3 (d), 127.7 (d), 129.5 (d), 131.6 (s), 136.1 (d), 139.9 (s), 140.1 (s); ^{29}Si NMR (C_6D_6 , 60 MHz) δ 9.3.

(12) Crystal data for **7**: fw = 551.20, monoclinic space group $P2_1/n$, $a = 9.251(3)$ Å, $b = 11.884(4)$ Å, $c = 16.814(6)$ Å, $\beta = 101.54(3)^\circ$, $V = 1811.1$ Å³, $Z = 2$, $\rho = 1.01$ g/cm³, μ (Mo $K\alpha$) = 4.6 cm⁻¹. The 3448 independent reflections ($|F_o| > 3.0\sigma|F_o|$, $2\theta \leq 50.0^\circ$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo $K\alpha$ irradiation and an $\omega - 2\theta$ scan. An empirical absorption correction based on a series of ψ scans were applied to the data 0.78/1.00. The structure was solved by direct methods, and hydrogen atoms were added to the structure factor calculations but their positions were not refined anisotropically to $R = 0.054$ ($R_w = 0.058$).

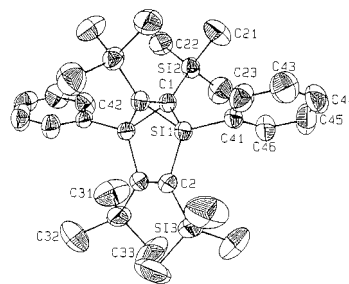
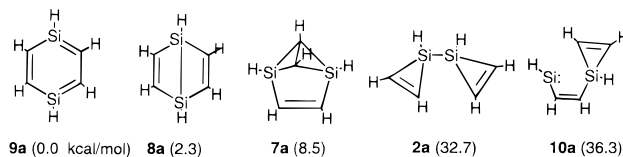


Figure 3. Crystal structure of **7**. Selected bond distances (Å) and angles (deg): 1.858(5) [Si(1)–C(1)], 1.897(5) [Si(1)–C(2)], 1.680(7) [C(1)–C(1')], 1.344 [C(2)–C(2')], 2.549 [Si(1)–Si(1')], 108.5 [C(1)–Si(1)–C(2)], 54.2 [C(1)–Si(1)–C(1')], 108.5 [Si(1)–C(2)–C(2')], 62.0 [Si(1)–C(1)–C(1')], 87.4 [Si(1)–C(1)–Si(1')].

Scheme 3



3). Thus, the disilabenzvalene **7a** and the Dewar benzene **8a** have been found to have similar energies and are slightly less stable than 1,4-disilabenzene (**9a**).^{13,14} Since large basis sets and inclusion of electron correlation generally tend to favor tricyclic over bicyclic or monocyclic geometries,¹⁵ **7a**, **8a**, and **9a** may have quite similar energies; the stability order may even be reversed. An alternative mechanism involving the 1,2-migration of silyl group to adjacent olefinic carbon and formation of silylene **10a** is proposed to account for bis(silacyclopropene) rearrangement. Since the structure retains one silacyclopropene ring, the true energy change involved in the silacyclopropene by silylene is expected to be very small. This is supported by HF/6-31G* calculations.¹³ Interestingly, the isomerization of **2** to **7** proceeds much more rapidly in AgBF_4 which functions as a catalyst (half-life of 5 min at 20°C). The reaction is proposed as an alternative route for the silylene intermediate via a cationic species. We are continuing to explore this system in search of new information.

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Supporting Information Available: Crystallographic details tables of atomic positional parameters with estimated standard deviations (54 pages). See any current masthead page for ordering and Internet access instructions.

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(13) Calculated relative energies of 1,4-disilabenzene isomers by HF/6-31G* (for optimized structures in Scheme 2): **2a** is 32.7 kcal/mol higher than a planar form of 1,4-disilabenzene (**9a**), while the disilabenzvalene (**7a**) and the Dewar form (**8a**) are only 8.5 and 2.3 kcal/mol higher than **9a**. Isomers, **7a**, **8a**, and **9a** have quite similar energies; the stabilities order may even be reversed. Silylene (**10a**) is less stable by 3.6 kcal/mol than **2a** (Scheme 3).

(14) Chandrasekhar, J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, 289, 51.

(15) Witeside, R. A.; Krishnan, R.; Defrees, D. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, 78, 538.