

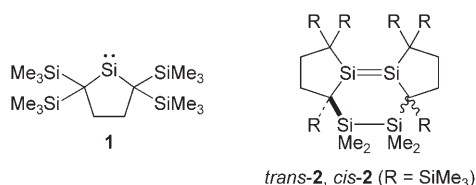
## Si–Si Multiple Bonds

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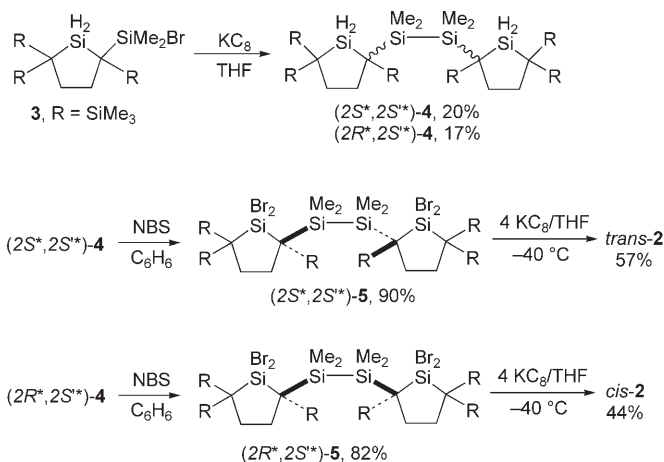
## Fused Tricyclic Disilenes with Highly Strained Si–Si Double Bonds: Addition of a Si–Si Single Bond to a Si–Si Double Bond\*\*

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Dimerization of a silylene (divalent silicon compound) to the corresponding disilene (silicon–silicon doubly bonded compound) and its reverse reaction constitute an important pair of chemical processes in organosilicon chemistry.<sup>[1]</sup> The first stable disilene, tetramesityldisilene, was synthesized by the dimerization of photochemically generated dimesitylsilylene by West et al. in 1981.<sup>[2]</sup> Okazaki, Tokitoh, et al. have reported that a stable tetraaryl disilene dissociates into the corresponding silylene in solution at higher temperatures.<sup>[3,4]</sup> We have found that isolable dialkyl silylene **1**,<sup>[5]</sup> which is protected kinetically by the bulky helmet substituent 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl, does not dimerize to the corresponding disilene either in solution or in the solid state. During our efforts to obtain compounds tethering two dialkyl silylene moieties, we have achieved unexpectedly the synthesis of fused tricyclic disilenes with two dialkyl silylene units, *trans*-**2** and *cis*-**2**. Neither *cis*-**2** nor *trans*-**2** dissociates into the corresponding silylene. Instead, upon heating, *trans*-**2** undergoes unprecedented intramolecular [ $2_s+2_a$ ] cycloaddition of the Si–Si single bond to the Si–Si double bond to give a tetracyclic compound.

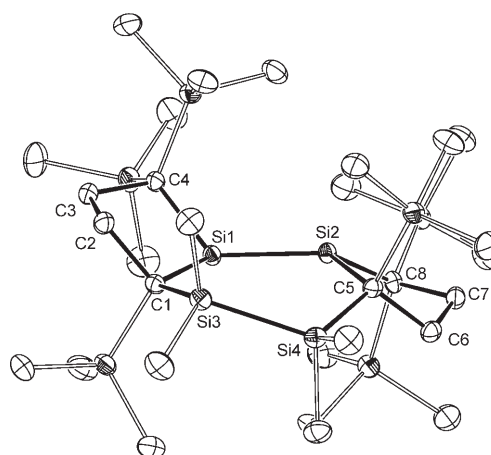


Fused tricyclic disilenes *trans*-**2** and *cis*-**2** were synthesized as red-purple crystals in 57 % yield and yellow crystals in 44 % yield, respectively, according to the reaction sequences shown in Scheme 1.<sup>[6]</sup> Disilenes *trans*-**2** and *cis*-**2** were identified by NMR spectroscopy and X-ray crystallographic analyses.



**Scheme 1.** Synthesis of tricyclic disilenes *trans*-**2** and *cis*-**2**. NBS = *N*-bromosuccinimide.

Figures 1 and 2 show ORTEP drawings of *trans*-**2** and *cis*-**2**, respectively.<sup>[7]</sup> The geometry around the Si=Si bond in *trans*-**2** is highly distorted. The Si=Si bond length of *trans*-**2** (2.2687(7) Å) is the second largest among all the reported disilenes; the largest was observed in (*Z*)-diaminodisilyl disilene **6** (2.2890(14) Å), reported by West and co-workers.<sup>[8]</sup> The Si=Si bond in *trans*-**2** adopts a strongly *trans*-bent and twisted geometry with bent angles  $\theta$  of 32.9 and 30.9° and a twist angle  $\tau$  of 42.5°.<sup>[9,10]</sup> The central six-membered ring of *trans*-**2** adopts a twist-boat conformation. In contrast, the



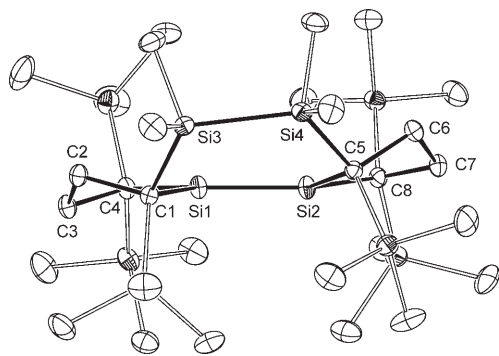
**Figure 1.** ORTEP drawing of *trans*-**2**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30 % probability level. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.2687(7), Si3–Si4 2.3745(8), Si1–C4 1.916(2), Si1–C1 1.937(2), Si2–C5 1.916(2), Si2–C8 1.936(2); Si1–Si2–C5 122.26(6), Si1–Si2–C8 126.31(6), Si2–Si1–C1 125.84(6), Si2–Si1–C4 120.62(6), C1–Si1–C4 98.58(9), C5–Si2–C8 97.93(9).

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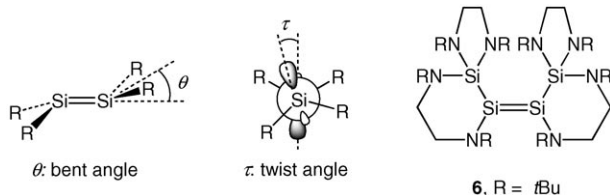
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**Figure 2.** ORTEP drawing of *cis*-**2**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.1767(6), Si3–Si4 2.3752(7), Si1–C4 1.919(2), Si1–C1 1.920(2), Si2–C5 1.917(2), Si2–C8 1.924(2); Si1–Si2–C5 119.96(5), Si1–Si2–C8 137.21(6), Si2–Si1–C1 120.12(5), Si2–Si1–C4 139.38(5), C1–Si1–C4 100.26(7), C5–Si2–C8 100.57(7).

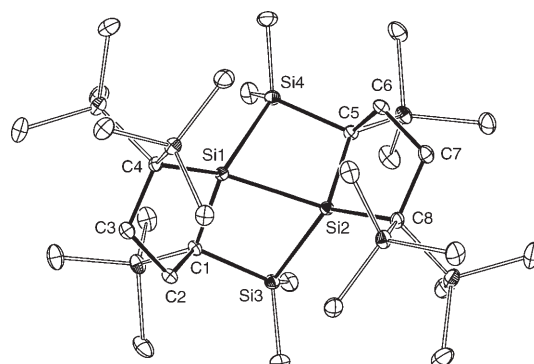
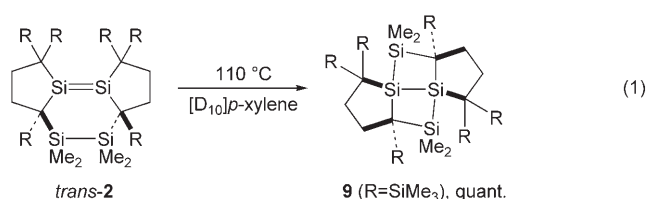
distortion around the Si=Si bond in *cis*-**2** is relatively small. In *cis*-**2**, the Si=Si bond length (2.1767(6) Å) is typical, and the  $\theta$  and  $\tau$  values are rather small ( $\theta = 3.9^\circ$  (Si1) and  $12.4^\circ$  (Si2);  $\tau = 3.9^\circ$ ). The central six-membered ring of *cis*-**2** exhibits a boat conformation.



The longest-wavelength absorption band which was assignable to the  $\pi \rightarrow \pi^*$  transition of *trans*-**2** ( $\lambda_{\max} = 517$  nm,  $\epsilon = 4800$  mol $^{-1}$  L cm $^{-1}$ ) is remarkably red-shifted from that of *cis*-**2** ( $\lambda_{\max} = 433$  nm,  $\epsilon = 8580$  mol $^{-1}$  L cm $^{-1}$ ) and that of structurally similar  $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Si}=\text{Si}\{\text{CH}(\text{SiMe}_3)_2\}_2$  (**8**;  $\lambda_{\max} = 393$  nm,  $\epsilon = 12600$  mol $^{-1}$  L cm $^{-1}$ ).<sup>[11]</sup> The small  $\pi \rightarrow \pi^*$  transition energy of *trans*-**2** can be explained by poor  $3p\pi$ – $3p\pi$  overlap as a result of the significant twist and elongation of the Si=Si bond. The distortion would be responsible for the smaller molar extinction coefficient of *trans*-**2** compared to that of *cis*-**2**. A similar tendency is observed between highly distorted (*t*Bu $_2$ MeSi) $_2$ Si=Si(SiMe $_2$ tBu) $_2$  (**7**;  $\tau = 54.5^\circ$ ,  $\lambda_{\max} = 612$  nm,  $\epsilon = 1300$  mol $^{-1}$  L cm $^{-1}$ )<sup>[10]</sup> and less distorted (*t*Bu–Me $_2$ Si) $_2$ Si=Si(SiMe $_2$ tBu) $_2$  ( $\tau = 8.9^\circ$ ,  $\lambda_{\max} = 420$  nm,  $\epsilon = 2800$  mol $^{-1}$  L cm $^{-1}$ ).<sup>[12]</sup>

The NMR resonances for the unsaturated  $^{29}\text{Si}$  nuclei,  $\delta(\text{Si}_u)$ , of these disilenes ( $\delta = 135.9$  ppm (*trans*-**2**), 128.1 ppm (*cis*-**2**)) are considerably low-field-shifted compared with that for **8** ( $\delta = 87.4$  ppm).<sup>[13]</sup> Because  $\delta(\text{Si}_u)$  values in disilenes are known to be proportional to the reciprocal of the energy difference between the  $\sigma$  and  $\pi^*$  orbitals of the Si=Si bond,<sup>[13]</sup> it is reasonable that the order of  $\delta(\text{Si}_u)$ , *trans*-**2** > *cis*-**2** > **8**, is the same as that of  $\lambda_{\max}$  of the  $\pi$ – $\pi^*$  transition bands among these disilenes.

Although both *trans*-**2** and *cis*-**2** are intramolecular dimers of two apparently isolable dialkyl silylene units, they do not dissociate into the corresponding tethered bis(dialkyl silylene) compounds upon heating at 100 °C or upon irradiation with a monochromated Xe lamp. The results indicate that the dissociation of the Si=Si bond in *trans*- and *cis*-**2** to give the bis(dialkyl silylene) compounds is energetically unfavorable though the disilenes have twisted Si=Si bonds and strained rings. In comparison with the steric repulsion between the trimethylsilyl groups for the hypothetical dimer of **1**, this repulsion for *trans*- and *cis*-**2** would be significantly reduced by tethering. However, upon heating at 110 °C in [D $_{10}$ ]p-xylene or in the solid state, *trans*-**2** isomerized stereospecifically into tetracyclic compound **9** in quantitative yield [Eq. (1)]. The structure of product **9** was determined by NMR spectroscopy and X-ray analysis (Figure 3). To the best of our knowledge, compound **9** is the first tetracyclo[7.3.0.0 $^{3,6}$ .0 $^{3,9}$ ]dodecane derivative.



**Figure 3.** ORTEP drawing of **9**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.4536(9), Si2–Si3 2.3601(8), Si1–Si4 2.3677(8); Si1–Si2–C8 141.65(3), Si2–Si1–C4 142.05(7), Si4–Si1–Si2–Si3 –115.20(3).

The X-ray analysis of **9** shows that two terminal five-membered rings in **9** are fused to the central bicyclo[2.2.0]hexane skeleton in an *anti* fashion, thus indicating that the isomerization is the *antarafacial* [2+2] addition of the Si–Si bond to the Si=Si bond. The central Si1–Si2 bond is considerably elongated (2.4536(9) Å) compared with the peripheral Si–Si bonds (2.3601(8) and 2.3677(8) Å). The Si1–Si2–C8 (141.65(3)) and Si2–Si1–C4 (142.05(7)°) bond angles are unusually large. These structural distortions could be caused by the steric repulsion between the trimethylsilyl groups on the C4 and C8 atoms. The tetrasilene unit in **9** adopts an almost eclipsed conformation with an Si4–Si1–Si2–Si3 dihedral angle of 115.20(3)°.

The first-order rate constants and the activation parameters for the isomerization of *trans*-**2** to **9** were determined by monitoring the decrease of the UV/Vis absorbance at 517 nm of *trans*-**2** at various temperatures:  $k = 2.68 \pm 0.02 \text{ s}^{-1}$  at 351 K,  $\Delta H^\ddagger = 19.0 \pm 1.2 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -21 \pm 3 \text{ cal mol}^{-1} \text{ K}^{-1}$ . The  $\Delta H^\ddagger$  value is slightly smaller than that for the bond dissociation of the Si=Si bond in Tbt(Mes)Si=Si(Mes)Tbt (Tbt = 2,4,6-[(Me<sub>3</sub>Si)<sub>2</sub>-CH]<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) reported by Suzuki, Tokitoh, and Okazaki (ca. 26 kcal mol<sup>-1</sup>)<sup>[4]</sup> and much smaller than that of the Si-Si bond in hexamethyldisilane (79 kcal mol<sup>-1</sup>).<sup>[14]</sup> The large negative  $\Delta S^\ddagger$  value suggests that the transition-state structure of the thermal isomerization is considerably restricted, and therefore, multistep mechanisms involving dissociation into the corresponding silylenes or the Si-Si bond cleavage may be ruled out. Stereospecific formation of **9** and the activation parameters indicate that the thermal isomerization is regarded as the first symmetry-allowed thermal [2<sub>s</sub>+2<sub>s</sub>] intramolecular cycloaddition between Si-Si double and single bonds as proposed for the thermal isomerization of cyclobutene to bicyclo[1.1.0]butane.<sup>[15]</sup>

Further work on the reactivity of *cis*- and *trans*-**2** are currently in progress.

## Experimental Section

*trans*-**2**: A mixture of (2*S*\*,2'*S*'\*)-**5** (273 mg, 0.264 mmol) and K<sub>2</sub>C<sub>8</sub> (157 mg, 1.16 mmol) in dry THF (25 mL) was stirred at -40°C for 48 h, and a brown solution was obtained. The solvent was removed in vacuo, and dry hexane was added to the resulting residue. Filtration of the resulting mixture and concentration of the filtrate under -20°C gave pure *trans*-**2** as red-purple crystals (107 mg, 57% yield). M.p. 182°C (decomp); <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]benzene):  $\delta = 0.306$  (s, overlap, 24H, 2SiMe<sub>3</sub> + SiMe<sub>2</sub>), 0.357 (s, overlap, 36H, 4SiMe<sub>3</sub>), 0.396 (s, 6H, SiMe<sub>2</sub>), 1.80–1.97 (m, 4H), 2.13–2.20 ppm (m, 4H); <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]benzene):  $\delta = 2.75$ , 3.47 (SiMe<sub>2</sub>), 4.37, 4.88, 5.07 (SiMe<sub>3</sub>), 17.62, 22.34 (C), 34.89, 35.43 ppm (CH<sub>2</sub>); <sup>29</sup>Si NMR (79 MHz, [D<sub>6</sub>]benzene):  $\delta = -19.51$  (SiMe<sub>2</sub>), 2.44, 3.48, 3.61 (SiMe<sub>3</sub>), 135.90 ppm (Si=Si); MS (30 eV):  $m/z$  (%): 714 (100) [*M*<sup>+</sup>]; UV/Vis (hexane)  $\lambda_{\text{max}}$  ( $\epsilon$  in mol<sup>-1</sup> L cm<sup>-1</sup>): 517 (4800), 334 nm (6830). Elemental analysis (%) calcd for C<sub>30</sub>H<sub>74</sub>Si<sub>10</sub>: C 50.34, H 10.42; found: C 50.36, H 10.18.

*cis*-**2**: Similarly to the synthesis of *trans*-**2**, reaction of (2*R*\*,2'*S*'\*)-**5** (94 mg, 91 mmol) and K<sub>2</sub>C<sub>8</sub> (54 mg, 400 mmol) in dry THF (10 mL) gave pure *cis*-**2** as yellow crystals (29 mg, 44% yield). M.p. 208°C (decomp); <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]benzene):  $\delta = 0.281$  (s, 18H, SiMe<sub>3</sub>), 0.323 (s, 6H, SiMe<sub>2</sub>), 0.351 (s, 18H, SiMe<sub>3</sub>), 0.375 (s, 6H, SiMe<sub>2</sub>), 0.398 (s, 18H, SiMe<sub>3</sub>), 1.75–2.20 ppm (m, 8H); <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]benzene):  $\delta = 1.73$ , 3.30 (SiMe<sub>2</sub>), 4.40, 5.03, 5.08 (SiMe<sub>3</sub>), 15.64, 19.05, 35.38, 36.56 ppm (CH<sub>2</sub>); <sup>29</sup>Si NMR (79 MHz, [D<sub>6</sub>]benzene):  $\delta = -11.78$  (SiMe<sub>2</sub>), 2.98, 3.10, 3.84 (SiMe<sub>3</sub>), 128.07 ppm (Si=Si); MS (30 eV)  $m/z$  (%): 714 (93) [*M*<sup>+</sup>], 357 (70), 73 (100); UV/Vis (hexane)  $\lambda_{\text{max}}$  ( $\epsilon$  in mol<sup>-1</sup> L cm<sup>-1</sup>): 433 (8580), 353 nm (12800). Elemental analysis (%) calcd for C<sub>30</sub>H<sub>74</sub>Si<sub>10</sub>: C 50.34, H 10.42; found: C 50.35, H 10.39.

**9**: A solution of *trans*-**2** (1.9 mg) in [D<sub>10</sub>]p-xylene (0.4 mL) was sealed in an NMR tube and was heated at 110°C for 3 h. Removal of the solvent from the resulting solution gave **9** as colorless crystals (1.9 mg, 100% yield). M.p. 243–245°C; <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]benzene):  $\delta = 0.221$  (s, 18H, SiMe<sub>3</sub>), 0.282 (s, 36H, SiMe<sub>3</sub>), 0.401 (s, 6H, SiMe<sub>2</sub>), 0.854 (s, 16, SiMe<sub>2</sub>), 1.80–2.25 ppm (m, 8H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]benzene):  $\delta = 0.95$ , 2.96, 3.85, 4.16,

5.33, 13.55, 17.63, 34.65, 36.36 ppm; <sup>29</sup>Si NMR (79 MHz, [D<sub>6</sub>]benzene):  $\delta = 0.72$ , 2.23, 2.35, 2.64, 37.99 ppm; UV/Vis (hexane)  $\lambda_{\text{max}}$  ( $\epsilon$  in mol<sup>-1</sup> L cm<sup>-1</sup>): 301 (8310), 242 (16500), 234 nm (16600). Elemental analysis (%) calcd for C<sub>30</sub>H<sub>74</sub>Si<sub>10</sub>: C 50.34, H 10.42; found: C 50.12, H 10.12.

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