# Thermal Equilibrium between a Lattice-Framework Disilene and the Corresponding Silylene

Shinobu Tsutsui,*,† Hiromasa Tanaka,† Eunsang Kwon,† Shigeki Matsumoto,† and Kenkichi Sakamoto*,†,‡

*Photodynamics Research Center, The Institute of Physical and Chemical Research (RIKEN), 519-1399 Aoba, Aramaki, Aoba-ku, Sendai 980-0845, Japan, and Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan*

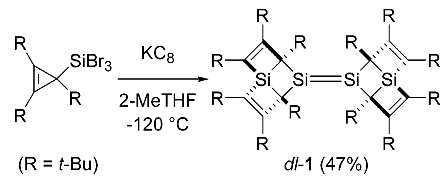
*Received September 7, 2004*

*Summary: The existence of the thermal equilibrium between 2,3,4,6,7,8,2′,3′,4′,6′,7′,8′-dodeca-tert-butyl[5,5′]-bi{1,5-disilatricyclo[4.2.0.0[1,4]]octylidene}-2,7,2′,7′-tetraene and the corresponding silylene was revealed by trapping experiments. The equilibrium was investigated by DFT calculations.*

Dimerization of a silylene to the corresponding disilene usually is irreversible because of the thermal stability of the disilene.[1] Okazaki and co-workers reported the reversible dissociation of a crowded tetraaryldisilene, Tbt(Mes)Si=Si(Mes)Tbt, into Tbt(Mes)Si: (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = 2,4,6-trimethylphenyl).[2,3] The thermal equilibrium between amino-substituted disilenes and the corresponding silylenes also has been reported.[4,5] While the photochemical dissociation of tetrakis[bis(trimethylsilyl)methyl]disilene to the corresponding silylene is known,[6] the thermal dissociation of a tetraalkyldisilene has not been reported.

Very recently we reported that the reduction of (tri-*tert*-butylcyclopropenyl)tribromosilane with $KC_8$ gave a $C_2$-chiral tetraalkyldisilene, a racemate of (4*R*,6*R*,4′*R*,6′*R*)-**1** and (4*S*,6*S*,4′*S*,6′*S*)-**1**, as stable red-orange crystals (Scheme 1).[7] We abbreviate it as *dl*-**1**. The longer Si=Si bond length of *dl*-**1** (2.262 Å) compared with that of Tbt(Mes)Si=Si(Mes)Tbt (trans, 2.228 Å; cis, 2.195 Å)[2,8] implied that *dl*-**1** would dissociate thermally to the corresponding $C_2$-symmetric silylene (4*R*,6*R*)- and (4*S*,6*S*)-2,3,4,6,7,8-hexa-*tert*-butyl-1,5-disilatricyclo[4.2.0.0[1,4]]octa-2,7-diene-5-diyl (**2**). The chirality should be maintained during the dissociation because the tricyclic skeleton of **2** is rigid. We now report experimental evidence for the thermal equilibrium between *dl*-**1** and **2** in solution at room temperature. The theoretical investigation of the equilibrium also is described.

**Scheme 1. Synthesis of *dl*-1**




As shown in Scheme 2, the reaction of the disilene *dl*-**1** with methanol in toluene solution at room temperature for 6 days gave **3** in an isolated yield of 94%. The structure of **3** was determined by mass spectrometry and $^1H$, $^{13}C$, and $^{29}Si$ NMR spectroscopy.[9] Adduct **3**, which is a methanol reaction product of the chiral silylene **2**,[10] also was a racemic mixture of (4*R*,6*R*)-**3** and (4*S*,6*S*)-**3**. The formation of **3** confirmed that the thermal equilibrium between *dl*-**1** and **2** exists under such conditions. Since the direct observation of **2** has not been successful using $^1H$ NMR and UV spectroscopy,[11] the equilibrium constant ($K = [\mathbf{2}]^2/[dl\text{-}\mathbf{1}]$) must be small. A significant temperature dependence of the absorption spectrum of *dl*-**1** was not observed in 3-methylpentane (3-MP) or methylcyclohexane between −196 and 100 °C. The meso isomer of **1**, (4*R*,6*R*,4′*S*,6′*S*)-**1**, could possibly be generated by the heterogeneous combination of (4*R*,6*R*)-**2** with (4*S*,6*S*)-**2** in equilibrium. However, *meso*-**1** has not been detected.

* To whom correspondence should be addressed. E-mail: stsutsui@riken.jp (S.T.); sakamoto@si.chem.tohoku.ac.jp (K.S.).
† RIKEN.
‡ Tohoku University.

(1) For recent reviews on disilenes, see: (a) Sekiguchi, A.; Lee, V. Y. *Chem. Rev.* **2003**, *103*, 1429. (b) Weidenbruch, M. *J. Organomet. Chem.* **2002**, *646*, 39. (c) Kira, M.; Iwamoto, T. *J. Organomet. Chem.* **2000**, *611*, 236. (d) Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds,* 2nd ed.; Rappoport, Z.; Apeloig, Y., Eds.; Wiley: New York, 1999; Part 3, p 2463. (e) Tokioth, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251.

(2) Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428.

(3) Suzuki, H.; Tokitoh, N.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2471.

(4) Tsutsui, S.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 9955.

(5) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T., Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479.

(6) Masamune, S.; Eriyama, Y.; Kawase, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 584.

(7) Matsumoto, S.; Tsutsui, S.; Kwon, E.; Sakamoto, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 4610.

(8) Suzuki, H.; Tokitoh, N.; Okazaki, R. *Organometallics* **1995**, *14*, 1016.

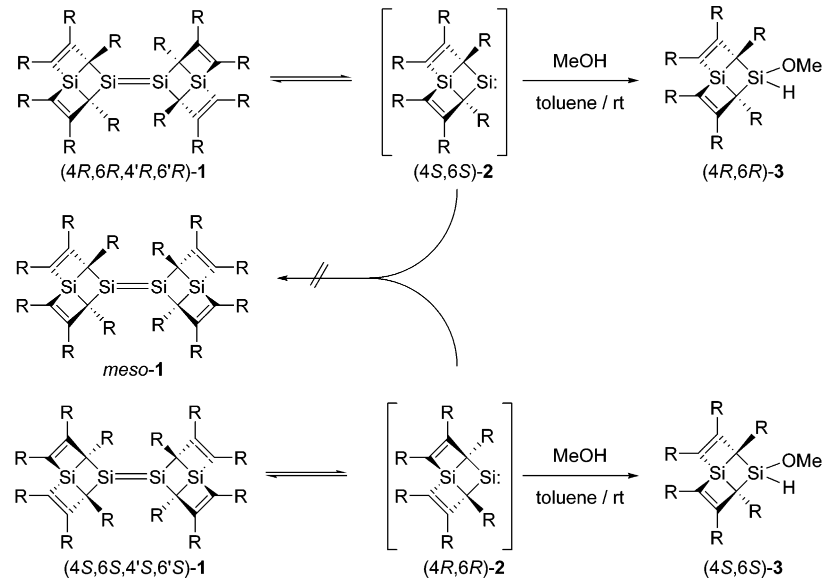
(9) Dry methanol (25 mg, $7.8 \times 10^{-4}$ mol) was added to a toluene (15 mL) solution of *dl*-**1** (25 mg, $2.6 \times 10^{-5}$ mol) at room temperature under an argon atmosphere. After the mixture was stirred for 6 days at room temperature in the dark until the dark red color had disappeared, the solvent was removed under reduced pressure. Separation using a recycling GPC (toluene as eluent) gave adduct **3** (25 mg, $4.9 \times 10^{-5}$ mol, 94%). **3**: colorless crystals; mp 186–189 °C; $^1H$ NMR ($C_6D_6$, $\delta$) 1.339 (s, 9H), 1.345 (s, 9H), 1.38 (s, 9H), 1.39 (s, 9H), 1.40 (s, 9H), 1.41 (s, 9H), 3.49 (s, 3H), 5.55 (s, $^1J_{Si-H}$ = 200 Hz, 1H); $^{13}C$ NMR ($C_6D_6$, $\delta$) 32.93, 33.53, 33.63, 33.75, 33.81, 34.84, 35.07, 35.20, 35.87, 35.95, 38.14, 38.68, 53.32, 57.25, 59.61, 165.51 (overlapped), 166.22, 166.88; $^{29}Si$ NMR ($C_6D_6$, $\delta$) −42.04, −8.62; MS (70 eV; *m/z* (%)) 502 ($M^+$, 20), 235 (100), (57). Anal. Calcd for $C_{31}H_{58}OSi_2$: C, 74.03; H, 11.62. Found: C, 73.77; H, 11.53.

(10) The reaction of a cyclic silylene that contains an asymmetric chiral carbon with alcohols has been reported. See: Sanji, T.; Fujiyama, H.; Yoshida, K.; Sakurai, H. *J. Am. Chem. Soc.* **2003**, *125*, 3216.

(11) The preparation of an isolable dialkylsilylene has been reported. See: Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722.

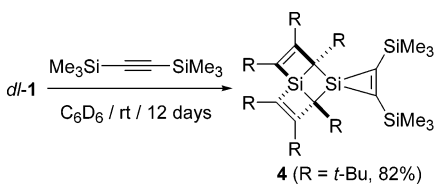
10.1021/om049306v CCC: $27.50 
Publication on Web 10/28/2004

**Scheme 2. Reaction Mechanism of *dl*-1 with Methanol (R = *t*-Bu)[a]**




[a] The absolute configurations of the chiral carbon atoms are formally changed during the reactions.

**Scheme 3. Reaction of *dl*-1 with Bis(trimethylsilyl)acetylene**




As shown in Scheme 3, the reaction of *dl*-**1** with bis(trimethylsilyl)acetylene in $C_6D_6$ at room temperature for 12 days gave **4** in 82% yield, as determined by $^1$H NMR spectroscopy. The structure of **4** was established by mass spectrometry and $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy and was confirmed by X-ray crystallography.[12,13,14a] The ORTEP drawing of **4** is shown in Figure 1. The generation of **4** also indicates the existence of the equilibrium between *dl*-**1** and **2** in solution at room temperature. While the thermal reaction takes a long time, it is noteworthy that the dissociation of *dl*-**1** was significantly activated photochemically.[14] The irradiation ($\lambda$ > 440 nm) of *dl*-**1** in the presence of bis(trimethylsilyl)acetylene in $C_6D_6$ at room temperature for 3 h gave **4** in 90% yield.[14b]

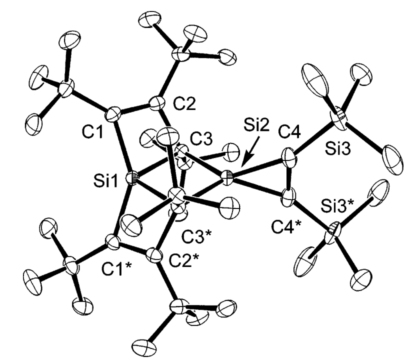



**Figure 1.** (a) ORTEP view of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−C1, 1.8497(14); Si1−C3, 1.9154(14); Si2−C4, 1.8347(16); Si2−C3, 1.9030(14); Si3−C4, 1.8722(16); C1−C2, 1.376(2); C2−C3, 1.5821(19); C4−C4*, 1.357(3); C1−Si1−C1*, 146.05(10); C1−Si1−C3, 78.93(6); C1−Si1−C3*, 126.37(6); C3−Si1−C3*, 93.24(9); C1−Si1−C2*, 164.18(6); C3−Si1−C2*, 110.58(6); C4*-Si2−C3, 127.90(6); C4−Si2−C3, 130.74(6); C3−Si2−C3*, 94.03(9); C4−Si2−C4*, 43.40(10); Si2−C4−C4*, 68.30(5).

Why was only *dl*-**1** experimentally observed? To answer this question, we have investigated the structures and energetics of *dl*-**1** and *meso*-**1** by DFT calculations.[15,16] Two model disilenes, *dl*- and *meso*-**5**, in which all of the *tert*-butyl groups in *dl*- and *meso*-**1** are replaced by hydrogen atoms, were investigated (Table 1).[17] The present calculations using the B3LYP method gave stable structures (i.e., those having no imaginary vibrational frequencies) for *dl*-**1**, *meso*-**1**, *dl*-**5**, and *meso*-**5**.

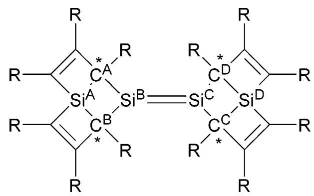
As summarized in Table 1, the stable structure of *dl*-**5** has a 143.6° average Si- - -Si═Si angle and 2.220 Å Si═Si bond distance. The geometric parameters in *dl*-**5**

(12) A mixture of disilene *dl*-**1** (0.29 mg, 3.1 × $10^{-7}$ mol) and bis(trimethylsilyl)acetylene (7.2 $\mu$L, 3.2 × $10^{-5}$ mol) was dissolved in $C_6D_6$ (0.8 mL) in a Pyrex NMR tube, and the tube was allowed to stand in the dark at room temperature for 12 days. A $^1$H NMR spectrum of the reaction mixture showed the formation of **4**[14a] in 82% yield.

(13) Crystal data for **4**: $C_{38}H_{72}Si_4$; $M$ = 641.32; $T$ = 123 K; colorless plate; monoclinic; $C2/c$; $a$ = 21.118(5) Å; $b$ = 13.125(3) Å; $c$ = 17.174(4) Å; $\beta$ = 121.528(3)°; $V$ = 4057.5(17) Å$^3$; $Z$ = 4; $D_c$ = 1.050 g/cm$^3$; 0.40 × 0.32 × 0.27 mm$^3$; 3971 independent reflections; 203 parameters; GOF = 1.068; final $R$ indices ($I > 2\sigma(I)$) R1 = 0.0443, wR2 = 0.1195; $R$ indices (all data) R1 = 0.0493, wR2 = 0.1238; largest difference peak and hole 0.533 and −0.295 e Å$^{-3}$.

(14) (a) A hexane (50 mL) solution of the disilene *dl*-**1** (21.0 mg, 2.23 × $10^{-5}$ mol) and bis(trimethylsilyl)acetylene (528 mg, 3.10 mmol) was irradiated ($\lambda$ > 440 nm) for 2 h at room temperature under an argon atmosphere. In vacuo evaporation of the solvent resulted in a colorless solid. Recrystallization from hexane gave colorless crystals of silacyclopropene **4** (13.0 mg, 2.03 × $10^{-5}$ mol, 45%). Separation of the mother liquor by using a recycling GPC (toluene as an eluent) gave an additional amount of **4** (8.8 mg, 1.4 × $10^{-5}$ mol, 31%). **4**: total 76% yield; colorless crystals; mp 241.9−242.3 °C; $^1$H NMR ($C_6D_6$, $\delta$) 0.40 (s, 18H), 1.31 (s, 18 H), 1.35 (s, 18H), 1.37 (s, 18H); $^{13}$C NMR ($C_6D_6$, $\delta$) 1.42, 33.46, 34.11, 34.34, 34.75, 35.61, 38.86, 61.70, 161.34, 167.02, 192.19; $^{29}$Si NMR ($C_6D_6$, $\delta$) −119.0, −37.6, −12.1; UV (hexane; $\lambda_{max}$/nm ($\epsilon$)) 288 (5790); MS (40 eV; $m/z$ (%)) 640 ($M^+$, 3), 568 (8), 470 (35), 207 (100), 155 (77). Anal. Calcd for $C_{38}H_{72}Si_4$: C, 71.17; H, 11.32. Found: C, 70.87; H, 11.18. (b) A $C_6D_6$ (0.8 mL) solution of the disilene *dl*-**1** (0.35 mg, 3.7 × $10^{-7}$ mol) and bis(trimethylsilyl)acetylene (7.2 $\mu$L, 3.2 × $10^{-5}$ mol) was irradiated ($\lambda$ > 440 nm) for 3 h at room temperature under an argon atmosphere. A $^1$H NMR spectrum of the reaction mixture showed the formation of **4** in 90% yield.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) of Optimized Structures of 1 and 5**



| R | | $Si^B{=}Si^C$ | bent angle[c] | twist angle[d] | $\Delta E$[e] |
|---|---|---|---|---|---|
| *t*-Bu[a] | *dl*-**1** | 2.274 (2.262)[f] | 179.1 (177.8)[f] | 15.5 (12.1)[f] | (0) |
| | *meso*-**1** | 2.335 | 159.9 | 0.9 | 54.5 |
| H[b] | *dl*-**5** | 2.220 | 143.6 | 4.5 | (0) |
| | *meso*-**5** | 2.220 | 143.6 | 0.1 | 0 |

[a] References 15 and 16. [b] Reference 17. [c] The angle of $Si^A$- - -$Si^B{=}Si^C$. [d] The angle between the $Si^A-C^A-Si^B-C^B$ plane and the $Si^C-C^C-Si^D-C^D$ plane. [e] Energies in kJ $mol^{-1}$ relative to the respective lowest-energy structure (*dl*-**1** for the "real" system and *dl*-**5** for the model system). [f] X-ray crystallographic data in ref 7.

are similar to those in *meso*-**5**. Also, *dl*-**5** and *meso*-**5** are energetically degenerate. The dissociation energy of *dl*-**5** and *meso*-**5** for splitting into two molecules of the corresponding silylene is calculated to be 188.5 kJ $mol^{-1}$, which is close to that of $Me_2Si{=}SiMe_2$ (209.4 kJ $mol^{-1}$ at the B3LYP/6-311+G(d,p) level). The calculated results for the model disilenes *dl*-**5** and *meso*-**5** do not reproduce the experimental result.

Disilene *dl*-**1** apparently differs from *meso*-**1** in its geometry around the Si=Si bonds, as summarized in Table 1. The optimized structures of *dl*- and *meso*-**1** are shown in Figure 2. The stable structure of *dl*-**1** has a 179.1° average Si- - -Si=Si angle, indicating that the geometry around the Si=Si bond is almost planar. This structure nicely reproduces the X-ray crystallographic structure.[7] On the other hand, *meso*-**1** adopts the trans-bent structure, in which the average Si- - -Si=Si angle is as small as 159.9°. Disilene *dl*-**1** is 54.5 kJ $mol^{-1}$ more stable in energy than *meso*-**1**. The dissociation energy of *dl*-**1** for splitting into two molecules of silylene **2** is calculated to be 94.0 kJ $mol^{-1}$. These results suggest

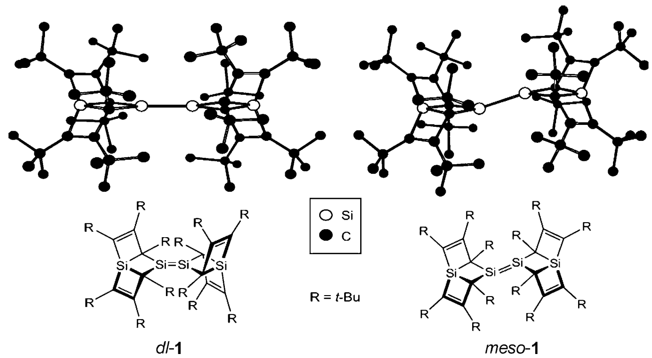



**Figure 2.** Optimized structures of *dl*-**1** and *meso*-**1**. Hydrogen atoms are omitted for clarity.

that the stabilization by forming the Si=Si bond is less effective in *meso*-**1** than in *dl*-**1**. The reason for the reduced stability of *meso*-**1** could be explained by the steric repulsion between the *tert*-butyl groups surrounding the Si=Si bond. This repulsion elongates the Si=Si bond in *meso*-**1** (2.335 Å) by 0.061 Å compared to that in *dl*-**1** (2.274 Å), making the Si=Si bond weaker.

It is known that disilenes such as $Me_2Si{=}SiMe_2$ favor a trans-bent geometry due to the donor−acceptor bond character of the Si=Si bond.[20,21] The structures of *dl*- and *meso*-**5** are also trans-bent.[22] In contrast, the geometry around the Si=Si bond of *dl*-**1** is planar. Obviously, the planarity of *dl*-**1** is ascribed to the steric repulsion by the bulky *tert*-butyl groups. The introduction of *tert*-butyl groups elongates the Si=Si bond length in *dl*-**1** compared to *dl*-**5** by 0.054 Å.

In conclusion, we have succeeded in presenting experimental evidence for the thermal equilibrium between the racemic tetraalkyldisilene *dl*-**1** and the corresponding racemic dialkylsilylene *dl*-**2** in solution at room temperature; no *meso*-**1** has been observed. The theoretical calculation nicely reproduced the experimental results and suggests that employing model compounds in which bulky substituents are replaced by small ones is insufficient for discussing the structure and stability of the disilene evaluated in this study.

**Supporting Information Available:** Tables giving the details of the X-ray structure determination, thermal ellipsoid plots, fractional atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for **4**, as both PDF and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049306V

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, M. A.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, D. K.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andress, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc., Pittsburgh, PA, 1998. The computational method is based on a DFT calculation with Becke's three-parameter hybrid functional incorporating the Lee−Yang−Parr correlation functional (B3LYP).[18,19]

(16) The 6-31G(d) basis sets were used for the Si and C atoms, except for the atoms consisting of the 12 *tert*-butyl groups. For the C and H atoms in these substituents, the 3-21G basis sets were employed.

(17) The calculation was carried out at the B3LYP/6-311+G(d,p) level.

(18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(19) Lee, C.; Yang, W.; Parr, R. *Phys. Rev. B* **1988**, *37*, 785.

(20) For a review, see: Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 2, p 129.

(21) Karsten, K.-J. *J. Am. Chem. Soc.* **1985**, *107*, 537.

(22) For *dl*-**5** and *meso*-**5**, the planar structures are the transition states and are 11.8 kJ $mol^{-1}$ less stable than the corresponding trans-bent structures.