

# Communications to the Editor

## The First Isolable Dialkylsilylene

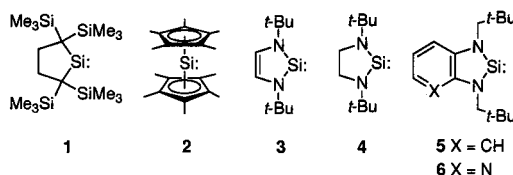
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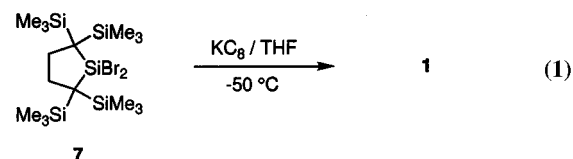
Divalent silicon species (silylenes) corresponding to carbenes in organic chemistry are key intermediates in numerous thermal and photochemical reactions of organosilicon compounds.<sup>1</sup> For a long time, silylenes as well as carbenes were considered only as short-lived species to be observed by spectroscopic methods either in the gas phase or in low-temperature matrixes, with an exception of dodecamethylsilicocene (**2**) having pentahapto-cyclopentadienyl ligands,<sup>2</sup> while the divalent dicoordinate species of germanium, tin, and lead have been well characterized as stable molecules.<sup>3</sup> Crystalline silylenes (**3**–**6**) with two amino substituents have been isolated very recently, and their characteristic structure and reactivity have been investigated extensively.<sup>4,5</sup> These silylenes as well as related *N*-heterocyclic carbenes<sup>6</sup> are stabilized, however, by the strong interaction between the vacant  $p\pi$ -orbital at the divalent atom and filled  $\pi$ -type orbitals of nitrogen or phosphorus atoms, and therefore, their electronic nature is strongly modified from the parent divalent species.<sup>7</sup> We wish herein to report the first isolable dialkylsilylene, 2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl (**1**), which is well-protected sterically from dimerization but least perturbed electronically; the intrinsic properties of silylene are entirely embodied in **1**. Interestingly, **1** is storable at 0 °C in the solid state but

Chart 1



isomerizes slowly to the corresponding silaethene via an apparent 1,2-silyl migration at room temperature in solution.

Dialkylsilylene **1**<sup>8</sup> was synthesized as air- and moisture-sensitive orange crystals in 74.5% yield by the reduction of dibromosilane **7**<sup>9</sup> (0.98 g, 1.84 mmol) with potassium graphite (KC<sub>8</sub>, 0.57 g, 4.22 mmol) in THF at –50 °C for 8 h (eq 1).



The molecular structure of **1** determined by a single-crystal X-ray diffraction study is shown in Figure 1 with selected bond lengths and angles.<sup>10</sup> The shortest distance between the divalent silicon atoms in the crystal is 7.210(1) Å, indicating that **1** is monomeric in the solid states. The averaged C–Si1 bond length of 1.908(6) Å in **1**, which is longer than the normal Si–C single bond lengths (~1.87 Å), and the relatively small C–Si–C angle of 93.88(7)° are suggestive of the larger *p*-character of the silicon hybrid orbitals used in the C–Si1 bonds.

The most remarkable structural characteristics of **1** were obtained by UV–vis and <sup>29</sup>Si NMR spectroscopies. A UV–vis spectrum of **1** in hexane shows band maxima at 260 nm ( $\epsilon$  1700) and 440 nm ( $\epsilon$  500); the latter band is weak and broad and assignable to the  $n(\text{Si})\text{-}3p\pi(\text{Si})$  transition. Although the  $n(\text{Si})\text{-}3p\pi(\text{Si})$  transition of silylene is known to be strongly affected by the substituents,<sup>11,12</sup> the maximum at 440 nm is close to that for dimethylsilylene ( $\lambda_{\text{max}}$  453 nm)<sup>13</sup> and 1-silacyclopentane-1,1-diyl ( $\lambda_{\text{max}}$  436 nm)<sup>12</sup> observed in matrixes at 77 K. In contrast, the  $n(\text{Si})\text{-}3p\pi(\text{Si})$  bands of diaminosilylenes **5** and **6** have been found at much shorter wavelengths (344 nm (sh) and 302 nm ( $\epsilon$  3300)),

(8) **1**: air- and moisture-sensitive orange crystals; mp 91–92 °C (decomp); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.26 (s, 36 H), 2.08 (s, 4 H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.8 (SiMe<sub>3</sub>), 37.1 (CH<sub>2</sub>), 61.8 (C); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  –2.8, 567.4; UV–vis (hexane)  $\lambda_{\text{max}}$ /nm ( $\epsilon$ ) 440 (500), 260 (1700); MS (EI, 70 eV)  $m/z$  (%) 372 (8, M<sup>+</sup>), 357 (11), 299 (7), 73 (100); HRMS calcd for C<sub>16</sub>H<sub>40</sub>Si<sub>5</sub>, 372.1977; found, 372.1967.

(9) Dibromosilane **7** was synthesized by the reaction of the corresponding dihydrosilane with bromoform in 79% yield: Kira, M.; Hino, T.; Kubota, Y.; Matsuyama, N.; Sakurai, H. *Tetrahedron Lett.* **1988**, 29, 6939.

(10) X-ray analysis of **1**: C<sub>16</sub>H<sub>40</sub>Si<sub>5</sub>; orange prism; monoclinic; space group *P2<sub>1</sub>/a*;  $a = 13.483(3)$  Å,  $b = 11.304(4)$  Å,  $c = 16.667(2)$  Å,  $\beta = 113.28(1)^\circ$ ,  $V = 2333.3(9)$  Å<sup>3</sup>;  $Z = 4$ ;  $\rho_{\text{calcd}} = 1.061$  g/cm<sup>3</sup>;  $\mu(\text{MoK}\alpha) = 3.01$  cm<sup>–1</sup>. The reflection intensities were collected on a Rigaku AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å) at 150 K. The structure was solved by direct method, using SIR-92, and refined by full-matrix least squares on  $F$ . A total of 6204 reflections were measured, and of these, 4909 reflections [ $F_o > 3.0\sigma(F_o)$ ] were used in refinement:  $R = 0.034$ ,  $R_w = 0.036$ .

(11) (a) Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1048. (b) Apeloig, Y.; Karni, M.; West, R.; Welsh, K. *J. Am. Chem. Soc.* **1994**, 116, 9719.

(12) (a) Michalczyk, M. J.; Fink, M. J.; DeYoung, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. *Silicon, Germanium, Tin, Lead Compd.* **1986**, 9, 75. (b) Gillette, G. R.; Noren, G.; West, R. *Organometallics* **1990**, 9, 2925. (c) Belzner, J.; Ihmels, H. *Adv. Organomet. Chem.* **1998**, 43, 1.

(13) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1979**, 101, 5427.

(1) For a recent review of silylenes, see: Gaspar, P. P.; West R. In *The Chemistry of Organic Silicon Compounds*, 2nd ed.; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1999; Part 3, pp 2463–2568.

(2) (a) Jutzi, P.; Kanne, K.; Krueger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 164. (b) Jutzi, P.; Holtmann, U.; Kanne, D.; Krüger, C.; Blom, R.; Gleiter, R.; Hyla-Krypsin, I. *Chem. Ber.* **1989**, 122, 1629.

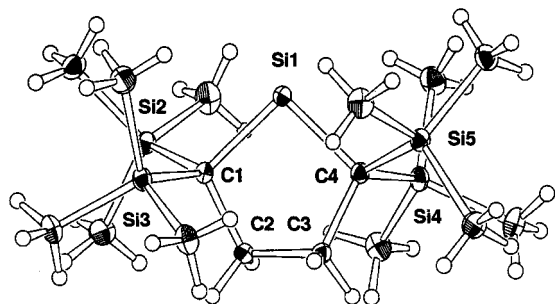
(3) For recent reviews of isolable divalent species of Ge, Sn, and Pb, see: (a) Barrau, J.; Escudé, J.; Satgé, J. *Chem. Rev.* **1990**, 90, 283. (b) Lappert, M. F. *Coord. Chem. Rev.* **1990**, 100, 267. (c) Neumann, W. P. *Chem. Rev.* **1991**, 91, 311. (d) Lappert, M. F. *Main Group Met. Chem.* **1994**, 17, 183. (e) Barrau, J.; Rima, G. *Coord. Chem. Rev.* **1998**, 178–180, 593.

(4) (a) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, 116, 2691. (b) Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2405. (c) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1931. (d) Heinicke, J.; Opera, A.; Kindermann, M. K.; Karbati, T.; Nyulászi, L.; Veszprémi, T. *Chem. Eur. J.* **1998**, 4, 541.

(5) For reviews of stable cyclic diaminosilylenes, see: (a) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, 68, 785. (b) Denk, M.; West, R.; Hayashi, R.; Apeloig, Y.; Pauncz, R.; Karni, M. In *Organosilicon Chemistry II*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; pp 251–261. (c) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (d) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 828. (e) Gehrhus, B.; Lappert, M. F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1997**, 124 & 125, 537.

(6) For reviews on stable carbenes, see: (a) Arduengo, A. J., III.; Krafczyk, R. *Chem.-Ztg.* **1998**, 32, 6. (b) Bertrand, G.; Reed, R. *Coord. Chem. Rev.* **1994**, 137, 323. (c) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 2162.

(7) The electronic nature of heteroatom-substituted carbenes and silylenes remains a controversial topic. (a) Dixon, D. A.; Dobbs, K. B.; Arduengo, A. J., III.; Bertrand, G. *J. Am. Chem. Soc.* **1991**, 113, 8782. (b) Dagani, R. *Chem. Eng. News* **1991**, 69 (4), 19. (c) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 674. (d) Dagani, R. *Chem. Eng. News* **1994**, 72 (18), 20. (e) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwartz, H. *J. Am. Chem. Soc.* **1996**, 118, 2023. (f) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, 118, 2039. (g) Veszprémi, T.; Nyulászi, L.; Hajgató, B.; Heinicke, J. *THEOCHEM* **1998**, 431, 1. (h) West, R.; Buffy, J. J.; Haaf, M.; Müller, T.; Gehrhus, B.; Lappert, M. F.; Apeloig, Y. *J. Am. Chem. Soc.* **1998**, 120, 1639.



**Figure 1.** ORTEP drawing of silylene **1**. The thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and bond angles (deg) are Si(1)–C(1) 1.911(2); Si(1)–C(4) 1.904(2); C(1)–C(2) 1.569(2); C(2)–C(3) 1.530(2); C(3)–C(4) 1.568(2); C(1)–Si(2) 1.911(2); C(1)–Si(3) 1.901(2); C(4)–Si(4) 1.897(2); C(4)–Si(5) 1.915(2); C(1)–Si(1)–C(4) 93.88(7); Si(2)–C(1)–Si(3) 120.2(1); Si(4)–C(4)–Si(5) 119.1(1); Si(1)–C(1)–C(2) 106.0(1); C(1)–C(2)–C(3) 108.9(1); C(2)–C(3)–C(4) 109.6(1); C(3)–C(4)–Si(1) 106.2(1).

respectively),<sup>4c,d</sup> indicative of the substantial orbital interaction between nitrogen lone-pair orbitals and the silicon vacant  $p\pi$  orbital.

Quite interestingly, the <sup>29</sup>Si resonance for the divalent silicon in **1** was found at +567.4 ppm in benzene-*d*<sub>6</sub>, which is the lowest-field resonance reported to date.<sup>14,15</sup> The low-field <sup>29</sup>Si resonance is characteristic of divalent dicoordinate silylene as shown by the GIAO calculations; the <sup>29</sup>Si resonances for SiH<sub>2</sub>,<sup>16</sup> silacyclopentane-1,1-diyl,<sup>17</sup> and 2,2,5,5-tetrakis(trihydrosilyl)silacyclopentane-1,1-diyl<sup>17</sup> are calculated to be 817, 754, and 602 ppm, respectively. On the other hand, the <sup>29</sup>Si resonances for stable diaminosilylenes **3**, **4**, and **5** appear at +78, +117, and +97 ppm,<sup>4a-c</sup> respectively, which are much higher than the calculated values for the parent silylene.

Although the electron donation to the formally vacant Si  $p$ -orbital from the neighboring C–Si  $\sigma$  bonding orbitals ( $\sigma$ – $\pi$  conjugation) may be significant in **1**, the extent is far smaller than the electronic perturbation by amino substituents in **3**–**6**, as indicated by the unperturbed  $n(\text{Si})$ – $3p\pi(\text{Si})$  band maximum and the very low-field <sup>29</sup>Si resonance of the divalent silicon.

Masamune et al. reported that the reduction of structurally similar [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>Si<sub>2</sub> with lithium naphthalenide afforded the corresponding disilene.<sup>18</sup> The major reason silylene **1** is isolated

(14) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Part 1, Chapter 8, pp 511–554.

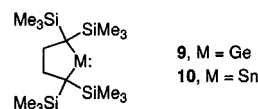
(15) The <sup>29</sup>Si resonance at –398 ppm for dodecamethylsilicocene **2** is the highest among the reported values.<sup>2</sup>

(16) Apeloig, Y.; Karni, M.; Müller, T. In *Organosilicon Chemistry II*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; pp 263–288.

(17) GIAO calculations were performed at the B3LYP/6-311+G(2df, p) level with the geometry optimized at the B3LYP/6-31G(d) level.

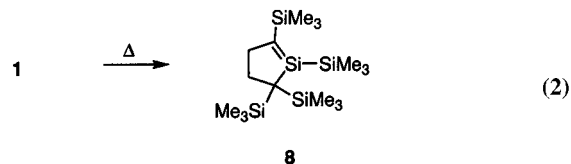
(18) Masamune, S.; Eriyama, Y.; Kawase, T. *Angew. Chem., Int., Ed. Engl.* **1987**, *26*, 584.

## Chart 2



would be ascribed to the effective steric protection from dimerization by a *helmet-like bidentate ligand* with four bulky trimethylsilyl groups.<sup>19</sup>

Silylene **1** reacts with methanol, bis(trimethylsilyl)acetylene, and 2,3-dimethyl-1,3-butadiene to give the corresponding adducts quantitatively. The most intriguing reactivity of **1** is the facile 1,2-migration of the neighboring trimethylsilyl group to give the corresponding silaethene derivative **8** (eq 2),<sup>20</sup> in contrast to the



corresponding stable germylene **9**<sup>21</sup> and stannylene **10**,<sup>19</sup> which show no such isomerization even at 100 °C. The present results give the first experimental evidence for the facile isomerization of silylmethylsilylene to 1-silylsilaethene.<sup>22–24</sup>

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**Supporting Information Available:** UV–Vis spectrum of silylene **1** in hexane and X-ray structural information on **1** (16 pages print/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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(19) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7785.

(20) Silylene **1** isomerizes gradually to **8** at room temperature in hexane, while **1** is rather stable in the solid state. **8**: a pale yellow oil; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.13 (s, 18 H), 0.31 (s, 9 H), 0.33 (s, 9H), 2.17 (t,  $J = 7.1$  Hz, 2H), 2.76 (t,  $J = 7.1$  Hz, 2H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.9, 1.7, 1.9, 19.2, 35.3, 38.8, 145.4 (C=Si); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  –15.9, –9.1, 1.6, 137.3 (Si=C); UV–vis (3-methylpentane)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 338 (~9000).

(21) Kira, M.; Ishida, S.; Iwamoto, T.; Ichinohe, M.; Kabuto, C.; Ignatovich, L.; Sakurai, H. *Chem. Lett.* **1999**, 263.

(22) Theoretically, the isomerization of silylmethylsilylene to 1-silylsilaethene is predicted to occur more facilely than the isomerization of methylsilylene to silaethene. Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1392. See also: Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Part 1, Chapter 2, pp 57–225.

(23) The inverse isomerization from a 1-silylsilaethene to the corresponding silylmethylsilylene at high temperatures in the gas phase has been reported. Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1982**, *1*, 210.

(24) A mechanistic study of the isomerization is in progress. As suggested by a reviewer, the isomerization of **1** to **8** may not occur by an intramolecular 1,2-silyl migration but by an intermolecular process as recently reported in the N-heterocyclic carbene series: Solé, S.; Gornitzka, H.; Gurret, O.; Bertrand, G. *J. Am. Chem. Soc.* **1998**, *120*, 9100.