

## An Unexpected Reaction of Silacyclopropene To Form an Organodilithiosilane: Isolation and Characterization of a 1,1-Dilithiosilane Derivative

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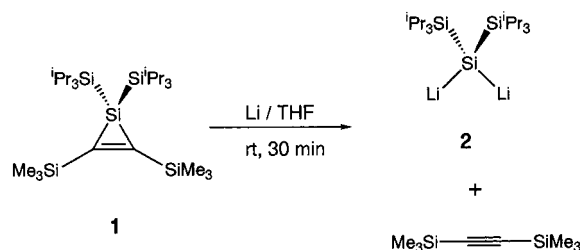
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1,1-Dilithiosilanes ( $R_2SiLi_2$ ) are of interest in view of their synthetic utility, structure, and reactivity. Despite numerous reports on the synthesis of lithiosilanes ( $R_3SiLi$ ), far less attention has been devoted to dilithiosilanes due to synthetic difficulties.<sup>1,2</sup> After the initial report on the generation of tetraphenylsilole dianion by Joo and co-workers, a number of investigations concerned with the study of the structural and chemical properties of silole dianions have been reported, and the unusual interesting structures of  $[Li(THF)_2][Li(THF)_3][\eta^1, \eta^5-C_4Ph_4Si]$  and  $[K(18-crown-6)][\eta^5, \eta^5-C_4Me_4Si]$  have been determined by X-ray crystallography.<sup>3</sup> On the other hand, Lagow et al. reported generation of the 1,1-dilithiosilane derivative, 2,2-dilithio-1,1,1,3,3,3-hexamethyltrisilane, by pyrolysis of  $(Me_3Si)_3SiLi-THF$  at 140–150 °C with a low yield, and it was identified only by a trapping reaction.<sup>4</sup> However, until now, no spectroscopic and crystallographic characterization of 1,1-dilithiosilane derivatives has been reported, except for silole dianions and the related compounds.<sup>3,5</sup>

We have studied a variety of silyl-substituted  $\pi$ -electron systems that readily undergo reduction with alkali metals to produce their alkali metal derivatives.<sup>6</sup> As a part of this study, we have examined the reaction of the persilyl-substituted silacyclopropene **1** with lithium metal and found an unexpected reaction, which gives dilithiosilane **2** and bis(trimethylsilyl)acetylene by cleavage of the two Si–C bonds in the three-membered ring. In this paper, we report the first successful

### Scheme 1



isolation and characterization of dilithiosilane **2** by X-ray analysis as well as by NMR spectroscopy.<sup>7,8</sup>

The reaction of **1**<sup>9</sup> (40 mg, 0.078 mmol) with an excess amount of lithium metal (ca. 100 mg, 14 mmol) in dry, oxygen-free tetrahydrofuran at room temperature gave a red solution of the dilithiosilane within 30 min (Scheme 1).<sup>10</sup> The solution was hydrolyzed with heavy water to give 1,1,1,3,3,3-hexaisopropyltrisilane-2,2-*d*<sub>2</sub> and bis(trimethylsilyl)acetylene in quantitative yield.<sup>11</sup> Since the first isolation of stable silacyclopropene by Gaspar et al.,<sup>12</sup> there has been an explosive growth in the area of three-membered ring systems involving Group 14 elements. However, there is no precedent for the alkali metal induced fragmentation of the silirenes to dianionic silicon derivatives. The reaction mechanism to form **2** is obscure; however, the introduction of silyl groups to the C=C double bond plays an important role by lowering the LUMO of **1** for reduction.

The dilithiosilane **2** was isolated as a pure compound. After removal of the solvent and the resulting bis(trimethylsilyl)acetylene in vacuo, a pale yellow powder, which is slightly soluble in hydrocarbon solvents such as hexane, benzene, and toluene, was obtained and recrystallized from hexane–THF (v/v 30/1) mixed solvent at –40 °C to give moisture- and air-sensitive pale yellow crystals of **2**.

The dilithiosilane **2** has a monomeric structure, as evidenced by X-ray crystallography, and its molecular structure is shown in Figure 1.<sup>13</sup> Each lithium atom is coordinated with two tetrahydrofuran molecules and the central silicon atom. The central silicon atom has nearly tetrahedral geometry, and the bond angles of Si1–Si2–Si3 and Li1–Si2–Li2 are somewhat expanded [112.0(1) and 114.8(3)°, respectively], due to the steric bulkiness

(7) Very recently, Tokitoh and Okazaki have reported the generation of bulky aryl-substituted 1,1-dilithiosilane,  $[Tbt(Dip)SiLi_2]$  (Tbt = 2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl), by the reaction of the corresponding dibromosilane with a 5 equivolar amount of lithium naphthalene (LiNp) in THF at –78 °C. However, no spectroscopic and crystallographic characterization of the dilithiosilane has been given; see: Tokitoh, N.; Hatano, K.; Sadahiro, T.; Okazaki, R. *Chem Lett.* **1999**, 931.

(8) We have learned that the 1,1-dilithiosilane **2** has independently been prepared by the reaction of  $[(t-BuHg)Si\{Si(i-Pr)_3\}_2]_2Hg$  with lithium metal in hydrocarbon solvent. We thank Prof. Y. Apeloig for informing us prior to publication.

(9) Silacyclopropene **1** was prepared by the reaction of 2,2-dibromo-1,1,1,3,3,3-hexaisopropyltrisilane with sodium in bis(trimethylsilyl)acetylene under refluxing conditions in 78% yield; colorless crystals; mp 157 °C; MS *m/z* (%) 512 ( $M^+$ , 5), 469 (12), 355 (21), 57 (100); <sup>1</sup>H NMR ( $C_6D_6$ ,  $\delta$ ) 0.37 (s, 18 H), 1.14–1.21 (m, 42 H); <sup>13</sup>C NMR ( $C_6D_6$ ,  $\delta$ ) 0.7, 13.5, 20.2, 166.4; <sup>29</sup>Si NMR ( $C_6D_6$ ,  $\delta$ ) –186.5, –8.6, 7.6; Anal. Calcd for  $C_{26}H_{60}Si_3$ : C, 60.85; H, 11.78. Found: C, 60.80; H, 11.95.

(10) 1,1-Dilithiosilane **2** and related bisilyl-substituted 1,1-dilithiosilanes,  $(t-Bu_2Si)_2SiLi_2$  and  $(t-BuMe_2Si)_2SiLi_2$ , can also be generated by the reaction of the corresponding 2,2-dibromotrisilane,  $(R_3Si)_2SiBr_2$  ( $R_3Si = i-Pr_3Si$ ,  $t-Bu_3Si$ ,  $t-BuMe_2Si$ ) with a 4 equivolar amount of LiNp in THF at –78 °C.

(11) 1,1,1,3,3,3-Hexaisopropyltrisilane-2,2-*d*<sub>2</sub>: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>,  $\delta$ ) 1.10–1.20 (m, 42 H); <sup>13</sup>C NMR (THF-*d*<sub>8</sub>,  $\delta$ ) 13.5, 20.2; <sup>29</sup>Si NMR (THF-*d*<sub>8</sub>,  $\delta$ ) –132.5 (quint, <sup>1</sup>*J*<sub>Si–D</sub> = 25.1 Hz), 11.3; MS *m/z* (%) 346 ( $M^+$ , 0.1), 303 ( $M^+ - 43$ , 0.8), 56 (100).

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(13) Crystal data of **2**:  $C_{34}H_{74}Li_2Si_3O_4$ , FW = 645.10, monoclinic, space group  $P2_1/n$ ,  $a = 11.093(1)$  Å,  $b = 22.899(1)$  Å,  $c = 16.130(2)$  Å,  $\beta = 97.450(5)^\circ$ ,  $V = 4063(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{calc} = 1.055$  g·cm<sup>–3</sup>, temperature 120 K,  $R = 0.086$ ,  $R_w = 0.164$ , 5019 reflections ( $I > 3\sigma(I)$ ), 388 parameters.

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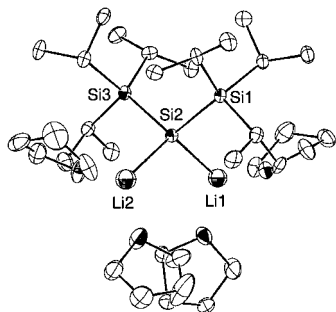
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(6) For silyl-substituted ethylenes and their alkali metal derivatives, see: (a) Sekiguchi, A.; Nakanishi, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, 111, 3748. (b) Sekiguchi, A.; Ichinohe, M.; Kabuto, C.; Sakurai, H. *Organometallics* **1995**, 14, 1092. (c) Sekiguchi, A.; Ichinohe, M.; Takahashi, M.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 1533. For silyl-substituted benzenes and their alkali metal derivatives, see: (d) Sakurai, H.; Ebata, K.; Kabuto, C.; Sekiguchi, A. *J. Am. Chem. Soc.* **1990**, 112, 1799. (e) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, 113, 1464. (f) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, 113, 7081. For other silyl-substituted  $\pi$ -electron compounds and their alkali metal derivatives, see: (g) Sekiguchi, A.; Sugai, Y.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, 115, 1144. (h) Sekiguchi, A.; Matsuo, T.; Kabuto, C. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 2462. (i) Sekiguchi, A.; Matsuo, T.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 1662. (j) Matsuo, T.; Sekiguchi, A.; Ichinohe, M.; Ebata, K.; Sakurai, H. *Organometallics* **1998**, 17, 3143.



**Figure 1.** ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2, 2.337(2); Si2–Si3, 2.335(2); Si2–Li1, 2.549(7); Si2–Li2, 2.55(1). Selected bond angles (deg): Si1–Si2–Si3, 112.0(1); Si1–Si2–Li1, 106.3(2); Si1–Si2–Li2, 107.4(2); Si3–Si2–Li1, 108.6(2); Si3–Si2–Li2, 107.8(3); Li1–Si2–Li2, 114.8(3).

of the two *i*-Pr<sub>3</sub>Si groups and the electrostatic repulsion of the two lithium atoms. The Si–Si bond lengths of **2** are 2.335(2) and 2.337(2) Å, which lie in the normal range. However, the Si–Li bond lengths of **2** [2.549(7) and 2.55(1) Å] are significantly shorter than those of usual silyllithiums that have a solvated monomeric structure [2.67–2.70 Å].<sup>14,15</sup>

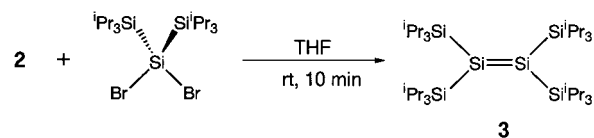
The structure of **2** in solution was also investigated by NMR spectroscopy. The THF-*d*<sub>8</sub> solution of **2**-<sup>6</sup>Li<sub>2</sub> was prepared by the reaction of **1** with lithium-6 in THF, and subsequently the solvent was replaced by THF-*d*<sub>8</sub>.<sup>16</sup> In the <sup>29</sup>Si NMR spectrum at 298 K, a broad signal assignable to the central silicon atom was observed at –282.0 ppm. At a lower temperature (200 K), the signal for the central silicon atom was slightly shifted to higher field, appearing at –292.0 ppm as a quintet (<sup>1</sup>*J*<sub>Si–<sup>6</sup>Li</sub> = 15.0 Hz) due to coupling with two equivalent <sup>6</sup>Li (*I* = 1). In <sup>6</sup>Li NMR at 200 K, one signal can be observed at 2.18 ppm with the satellite

(14) (a) [(Me<sub>3</sub>SiLi)<sub>2</sub>(TMEDA)<sub>3</sub>]: Teclé, B.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1982**, *1*, 875. (b) [Ph<sub>3</sub>SiLi(THF)<sub>3</sub>] and [(Me<sub>3</sub>Si)<sub>3</sub>SiLi(THF)<sub>3</sub>]: Dias, H. V. R.; Olmstead, M. M.; Ruhlandt-Senge, K.; Power, P. P. *J. Organomet. Chem.* **1993**, *462*, 1. (c) [(Me<sub>3</sub>Si)<sub>3</sub>SiLi(THF)<sub>3</sub>]: Heine, A.; Herbst-Imer, R.; Sheldrick, G. M.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 2694. (d) [(THF)<sub>3</sub>Li–(SiPh<sub>2</sub>)<sub>4</sub>–Li(THF)<sub>3</sub>]: Becker, G.; Hartmann, H.-M.; Hengge, E.; Schrank, F. *Z. Anorg. Allg. Chem.* **1989**, *572*, 63.

(15) 1,2-Dilithiodisilane and 1,3-dilithiotrisilane derivatives, (THF)Li–(Ar<sub>2</sub>Si)<sub>2</sub>–Li(THF)<sub>2</sub> [2.55(1) and 2.54(1) Å] and (1,4-dioxane)Li–(Ar<sub>2</sub>Si)<sub>3</sub>–Li(1,4-dioxane) [2.542(8), 2.550(8), 2.589(8), and 2.590(8) Å] [Ar = 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>], have short Si–Li distances due to the coordination of intramolecular amino groups. See: Belzner, J.; Dehnert, U.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2450.

(16) **2**-<sup>6</sup>Li<sub>2</sub>: pale yellow powder; <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 298 K, δ) 0.96 (sept, *J* = 6.2 Hz, 6 H), 1.08 (d, *J* = 6.2 Hz, 36 H); <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 298 K, δ) 18.0, 22.5; <sup>29</sup>Si NMR (THF-*d*<sub>8</sub>, 200 K, δ) –292.0 (quint, *J*<sub>Si–<sup>6</sup>Li</sub> = 15.0 Hz), 29.4; <sup>6</sup>Li NMR (THF-*d*<sub>8</sub>, 200 K, δ) 2.18.

## Scheme 2



signals due to the <sup>29</sup>Si nucleus. Since the central silicon atom is substituted by two electropositive lithium atoms and two *i*-Pr<sub>3</sub>Si groups, the chemical shift of the anionic silicon atom is largely shifted upfield compared with that of (Me<sub>3</sub>Si)<sub>3</sub>SiLi, which shows the signal of anionic silicon at –189.4 ppm.<sup>14d</sup> The one-bond coupling between silicon and lithium-6 of **2** (15.0 Hz) lies in the normal range for monomeric silyllithiums (15–22 Hz).<sup>17</sup> The splitting patterns and coupling constant of the anionic silicon of **2** in the <sup>29</sup>Si NMR spectrum suggest that two lithium atoms connect to the silicon atom with sp<sup>3</sup> hybridization and the monomeric tetrahedral structure found in the solid state is maintained in solution. Although a theoretical calculation of dilithiosilane has been reported,<sup>18</sup> our results provide the first structural characterization of dilithiosilane, except for silole dianion dilithium.

Reactions of **2** with some electrophiles have also been carried out. Dilithiosilane **2** reacted with methyl iodide to give the corresponding 2,2-dimethyltrisilane in almost quantitative yield. However, the reaction with chlorotrimethylsilane did not give the disubstituted compound (*i*-Pr<sub>3</sub>Si)<sub>2</sub>Si(SiMe<sub>3</sub>)<sub>2</sub>, probably due to steric reasons, but gave a monosubstituted one, (*i*-Pr<sub>3</sub>Si)<sub>2</sub>Si(H)SiMe<sub>3</sub>, after hydrolysis. Of particular interest is that the reaction of **2** with 2,2-dibromo-1,1,1,3,3,3-hexaisopropyltrisilane as a difunctional electrophile afforded tetrakis(triisopropyl)disilene **3**<sup>19</sup> in almost quantitative yield (Scheme 2).

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**Supporting Information Available:** Tables of crystallographic data including atomic positional and thermal parameters for **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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