Disilenyl Anions Derived from Reduction of Tetrakis(di-*tert*-butylmethylsilyl)disilene with Metal Naphthalenide through a Disilene Dianion Intermediate: Synthesis and Characterization

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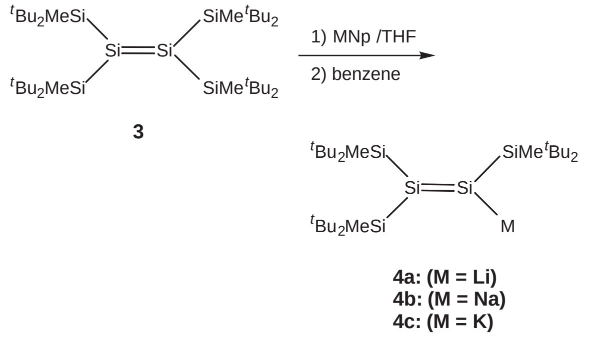
Tetrakis(di-*tert*-butylmethylsilyl)disilene (**3**) was treated with 2 equiv. of metal naphthalenide (M = Li, Na, and K) in THF to give the disilenyl anion by elimination of one $^t\mathrm{Bu_2MeSi}$ group, through the intermediate formation of a disilene dianion upon two-electron reduction. The red crystals of sp^2-type silyl anions were isolated as the corresponding alkali metal derivatives, which were characterized by NMR spectra and X-ray crystallography.

Silylanions, the carbanion analogues, are very useful reagents for synthesizing various silicon-containing derivatives. After the preparation of triphenylsilyllithium by Gilman et al.,[1] various kinds of sp^3-type silylanions have been synthesized and characterized.[2,3] Since then, a variety of organosilicon compounds have been prepared by using the silylanions, which have become very powerful synthetic tools in organosilicon chemistry.[2] However, the chemistry of compounds having sp^2-type silylanions was severely limited due to their synthetic difficulty until recently. Very recently, we reported the first synthesis and characterization of an sp^2-type silyllithium, 1,1-bis(di-*tert*-butylmethylsilyl)-2-lithio-2-mesityldisilene (**1**), by the reaction of 1,1,6,6-tetra-*tert*-butyl-2,5-(di-*tert*-butylmethylsilyl)-3,4-dimesityl-1,6-dimethylhexasila-2,4-diene with ^{t}BuLi, which caused the cleavage of the central Si–Si bond connecting two Si=Si double bond units.[4] At the same time, Scheschkewitz independently succeeded in isolating $\mathrm{Tip_2Si{=}Si(Tip)Li}$ (**2**) by the reduction of $\mathrm{Tip_2SiCl_2}$ with lithium,[5] a compound whose existence was postulated by Weidenbruch et al.[6] Herein, we report the synthesis and isolation of a novel 1,1,2-tri(di-*tert*-butylmethylsilyl)disilenyl anion with three different alkali metals by the reaction of tetrakis(di-*tert*-butylmethylsilyl)disilene (**3**) with 2 equiv. of metal naphthalenide (M = Li, Na, and K) in THF by the elimination of one $^t\mathrm{Bu_2MeSi}$ group, through the intermediate formation of a disilene dianion. This provides a method for the novel synthesis of an sp^2-type silylanion, including not only sp^2-type silyllithium but also sp^2-type silylsodium and silylpotassium, whose synthesis and structural characteristics we report.

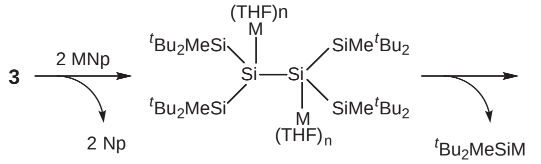
Disilenes are known to undergo easy reduction because their LUMOs are low-lying compared with those of the corresponding alkene analogues. Recently, we reported the synthesis and unusual structure of tetrakis(di-*tert*-butylmethylsilyl)disilene **3**. Because of the extremely twisted structure, **3** shows very unusual reactivity toward reducing reagents. Thus, we have reported that the one-electron reduction of the disilene **3** with ^{t}BuLi in THF results in the formation of a stable disilene anion radical.[7] This result prompted us to study the two-electron reduction of disilene **3** in the hope of synthesizing the corresponding disilene 1,2-dianion.

Initially, we examined the reaction of disilene **3** with 2.2 equiv. of LiNp (lithium naphthalenide) in THF at −78 °C. The reaction mixture was slowly warmed to room temperature; the dark blue color of **3** completely disappeared, and a red solution was produced during the reaction. Unexpectedly, when the THF solvent was replaced by benzene, 1,1,2-tris(di-*tert*-butylmethylsilyl)-2-lithiodisilene **4a** was produced as a red precipitate in 42% yield (Scheme 1).[8] $^t\mathrm{Bu_2MeSiLi}$ was also formed in the benzene solution. The disilenyllithium **4a** is extremely air and moisture sensitive, but is a thermally stable compound. Reduction of disilene **3** by NaNp (sodium naphthalenide) and KNp (potassium naphthalenide) also proceeded similarly to produce the corresponding disilenylanions, disilenylsodium (**4b**, 27%), and disilenylpotassium (**4c**, 14%), which were isolated as red crystals and characterized in a pure form.[9,10] In the ^{29}Si NMR spectrum, two signals of the unsaturated Si atoms were observed (77.6 and 328.4 ppm for **4a**, 79.5 and 325.6 ppm for **4b**, and 81.7 and 323.1 ppm for **4c**).[8,9] Extremely low field signals at 328.4 ppm for **4a**, 325.6 ppm for **4b**, and 323.1 ppm for **4c** were assigned to the alkali metal-substituted sp^2-Si atom. In general, the signals of sp^2-Si atoms substituted with an electropositive group are shifted to lower field. The same tendency was observed in the disilenyllithiums **1** and **2**.[4,5]

Now, we consider the mechanism for the formation of disilenyl anions. After the treatment of **3** with two equiv. of LiNp in THF-d_8, the dilithium compound **5a** was spectroscopically observed instead of the sp^2-type silylanion **4a**.[11] In the ^{29}Si NMR spectrum, the characteristic signal of anionic silicon atoms at −199.4 ppm was observed, which was reasonably assigned to **5a** compared with the reported values of −185.9 ppm for $(^t\mathrm{BuMe_2Si})_2\mathrm{SiLi{-}Si(Li)(SiMe_2}^t\mathrm{Bu})_2$ and −190.9 ppm for $(^i\mathrm{Pr_2MeSi})_2\mathrm{SiLi{-}Si(Li)(SiMe}^i\mathrm{Pr_2})_2$.[12] Indeed, the corresponding 1,2-dihydrosilane derivative was isolated in 49% yield by hydrolysis of the reaction mixture. In THF solution, **5a** is enough stabilized with the solvation by THF molecules on lithium over the large steric congestion. On the other hand, **5a** would be un-



Scheme 1.



5a: (M = Li)
5b: (M = Na)
5c: (M = K)

Scheme 2.

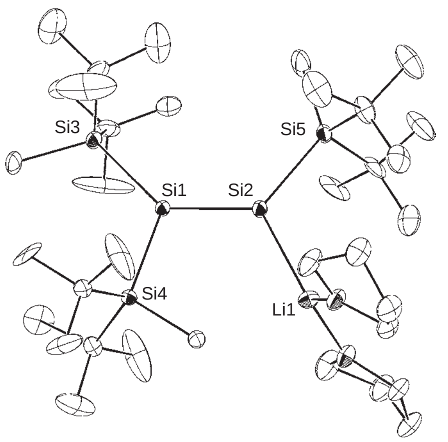


Figure 1. ORTEP drawing of **4a** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2 = 2.1983(18), Si1–Si3 = 2.3792(19), Si1–Si4 = 2.3792(18), Si2–Si5 = 2.383(2), Si2–Li1 = 2.598(9). Selected bond angles (deg): Si2–Si1–Si3 = 132.85(8), Si2–Si1–Si4 = 106.50(7), Si3–Si1–Si4 = 120.64(7), Si1–Si2–Si5 = 125.48(8), Si1–Si2–Li1 = 117.3(2), Si5–Si2–Li1 = 117.2(2).

stable due to the lack of solvation in less coordinating solvent such as aromatic hydrocarbons. As a result, one of the substituents was eliminated as ^{t}Bu$_2$MeSiLi, and disilenyllithium **4a** was produced (Scheme 2).

We also succeeded in characterizing the structure of **4a** by X-ray crystallography (Figure 1).[13] The geometry of two sp^2 Si atoms are planar: the sums of the bond angles are 359.99° for Si1 and 359.98° for Si2. In particular, the sum of the bond angle around lithium-substituted Si2 is nearly ideal sp^2 (117.2(2)° for Si5–Si2–Li1, 117.3(2)° for Si1–Si2–Li1, and 125.48(8)° for Si1–Si2–Si5). Compared with the highly twisted Si=Si double bond of disilene **3** (twisting angle is 54.5°), **4a** is planar due to the decrease in steric repulsion. The Si=Si double bond in **4a** (2.1983(18) Å) is shorter than that in **3** (2.2598(18) Å). The lithium cation in **4a** is solvated by two THF molecules, and the Si–Li bond length is 2.598(9) Å, which is slightly shorter than the typical Si–Li bond length in sp^3-type silyllithium (2.67–2.70 Å).[14] The Si=Si bond length (2.1983(18) Å) of **4a** is similar to those of **1** (2.2092(7) Å)[4] and **2** (2.192(1) Å),[5] whereas the Si–Li bond length (2.598(9) Å) of **4a** is much shorter than those of **1** (2.702(9) Å)[4] and **2** (2.853(3) Å).[5] In contrast to **4a**, the disilenyllithiums **1** and **2** bearing bulky aryl groups on the sp^2 Si atom show a twisted structure because of steric reasons.[4,5]

In summary, we have presented here a new method for the generation of stable sp^2-type silylanions with lithium, sodium, and potassium as counter ions by the two-electron reduction of disilene in THF, followed by spontaneous bond cleavage of the Si–Si bond in benzene solvent.

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8 Procedure for the synthesis of **4a**: A THF solution of lithium naphthalenide (0.79 mmol) was added to disilene **3** (252 mg, 0.37 mmol) in THF (1.5 mL) at −78 °C, and then the reaction mixture was allowed to warm to room temperature over 2 h. There was a rapid color change from the dark blue to a red due to the formation of the dianion **5a**. After removal of THF in vacuo, benzene was added to the reaction mixture. The NMR spectra of the benzene solution showed the formation of **4a** and ^{t}Bu$_2$MeSiLi, and disappearance of **5a**. The solution was cooled to give red crystals of **4a** (104 mg, 42%). mp 159–161 °C; ^{1}H NMR (THF-d_8, δ) 0.24 (s, 3H), 0.27 (s, 3H), 0.29 (s, 3H), 1.08 (s, 18H), 1.12 (s, 18H), 1.22 (s, 18H); ^{13}C NMR (THF-d_8, δ) −3.5, −2.0, −1.7, 22.5, 22.7, 23.1, 31.5, 31.7, 32.2; ^{29}Si NMR (THF-d_8, δ) −1.0, 4.8, 8.8, 77.6, 328.4; ^{7}Li NMR (THF-d_8, δ) −0.6.

9 In a similar manner to **4a**, **4b**, and **4c** were prepared by the reaction of **3** with NaNp or KNp, following the solvent exchange to benzene. **4b**: red crystals; mp 158–159 °C; ^{1}H NMR (THF-d_8, δ) 0.24 (s, 3H), 0.27, (s, 3H), 0.28 (s, 3H), 1.07 (s, 18H), 1.11 (s, 18H), 1.23 (s, 18H); ^{13}C NMR (THF-d_8, δ) −3.0, −2.1, −1.5, 22.9, 22.9, 23.5, 31.0, 32.4, 33.0; ^{29}Si NMR (THF-d_8, δ) 1.0, 5.2, 9.0, 79.5, 325.6. **4c**: red crystals; mp 155–156 °C ^{1}H NMR (THF-d_8, δ) 0.24 (s, 3H), 0.27, (s, 3H), 0.28 (s, 3H), 1.08 (s, 18H), 1.11 (s, 18H), 1.24 (s, 18H); ^{13}C NMR (THF-d_8, δ) −3.5, −2.0, −1.7, 22.5, 22.7, 23.1, 31.5, 31.7, 32.2; ^{29}Si NMR (THF-d_8, δ) 1.4, 5.1, 10.0, 81.7, 323.1.

10 The structures of **4b** and **4c** were determined by X-ray crystallography, however, the refinement was insufficient to discuss their structures in detail.

11 Spectral data of the THF-d_8 solution of the reaction mixture indicate the formation of the dianion **5a**, however, we could not isolate the dianion in a pure form. **5a**: ^{1}H NMR (THF-d_8, δ) 0.28 (s, 12H), 0.89, (s, 72H); ^{13}C NMR (THF-d_8, δ) −2.7, 21.2, 30.3; ^{29}Si NMR (THF-d_8, δ) −199.4, 21.3; ^{6}Li NMR (THF-d_8, 220 K, δ) 0.42.

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13 Crystal data for **4a** at 120 K: $C_{35}H_{79}LiO_2Si_5$, MW = 679.37, Orthorhombic, space group *Pnma*, $a = 18.149(1)$ Å, $b = 16.429(1)$ Å, $c = 14.600(1)$ Å, $V = 4353.3(5)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.037\ \text{g cm}^{-3}$. $R = 0.0830$ ($I > 2\sigma(I)$), wR (all data) = 0.2321. GOF = 1.032.

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