Silene Derivatives

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Conversion of a Disilenide into a Silene: Silyl-Anion-Substituted Silene by a Sila-Peterson-Type Reaction from an sp^2-Type Silyl Anion**

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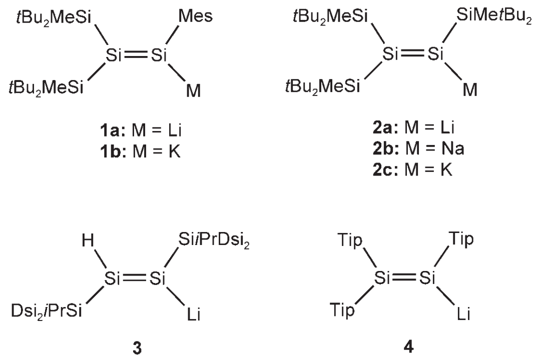
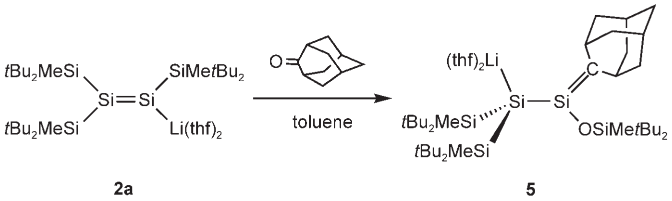
Since the first stable silene was synthesized by Brook et al. in 1981,[1] compounds with a silicon–carbon double bond have attracted attention because of their unique electronic properties and reactivities.[2] Despite intensive study, the chemistry of silenes is still in its infancy owing to the limited number of the isolable silenes. In general, there are several methods for the synthesis of stable silenes: isomerization of acyl polysilanes,[1,2] the sila-Peterson reaction,[2,3] and β elimination of inorganic salts.[2,4] In particular, the sila-Peterson reaction is very useful for synthesizing stable silenes.[3] The Apeloig[3a] and Oehme[3b] groups have reported that transient silenes can be synthesized through a sila-Peterson reaction, and indeed three stable isolable silenes have been reported by this method.[3c–e] However, there have been no reports of a sila-Peterson reaction using an sp^2-type silyl anion, which has recently emerged as a new type of silyl anion. We report herein the synthesis and structure of the first silyl-anion-substituted silene by a sila-Peterson-type reaction starting from an sp^2-type silyl anion.

Silyl anions are powerful reagents for synthesizing various silicon-containing derivatives, and many kinds of sp^3-type silyl anions have been synthesized and characterized.[5] However, the chemistry of compounds with sp^2-type silyl anions has been severely limited until recently because of synthetic difficulties. Recently, we reported the synthesis and isolation of sp^2-type silyl lithium and silyl potassium derivatives **1**[6] by reductive cleavage of the central Si−Si bond of a tetrasila-1,3-butadiene derivative (tBu$_2$MeSi)$_2$Si=Si(Mes)−(Mes)Si=Si(SiMetBu$_2$)$_2$ (Mes = 2,4,6-trimethylphenyl) with tBuLi and KC$_8$, alkali-metal derivatives **2**[7] by the two-electron reduction of (tBu$_2$MeSi)$_2$Si=Si(SiMetBu$_2$)$_2$ with MNp (M = Li, Na, K; Np = naphthalenide) and subsequent elimination of tBu$_2$MeSiM, and hydrogen-substituted disilenyl lithium derivative **3**[8] by the addition of LiH to a silicon–silicon triple bond[9] (Scheme 1). At the same time, Scheschkewitz and coworkers also made the following important contribution in the field of sp^2-type silyl anion chemistry. The disilenyl lithium compound Tip$_2$Si=Si(Tip)Li (**4**) (Tip = 2,4,6-triisopropylphenyl), originally postulated as a key intermediate for the formation of the tetrasilabutadiene derivative (Tip)$_2$Si=Si(Tip)−(Tip)Si=Si(Tip)$_2$[10] by the reaction of tetrakis(2,4,6-triisopropylphenyl)disilene with lithium metal, was later isolated and characterized by the reaction of Tip$_2$SiCl$_2$ with lithium metal (Scheme 1).[11,12] Among these sp^2-type silyl anions, we succeeded in the relatively large scale synthesis of the stable disilenyl lithium derivative **2a** (M = Li)[6] because of the ready accessibility of the disilene precursor (tBu$_2$MeSi)$_2$Si=Si(SiMetBu$_2$)$_2$.[13]



Scheme 1. Isolable sp^2-type silyl anion derivatives **1**–**4**; Mes = 2,4,6-trimethylphenyl; Dsi = bis(trimethylsilyl)methyl; Tip = 2,4,6-triisopropylphenyl.

The reactivity of sp^2-type silyl anions is of considerable interest from the viewpoint of the synthesis of novel silicon compounds.[12] Disilenyl lithium compound **2a** readily reacts with adamantanone in toluene as well as in THF to give silyl-anion-substituted silene **5** (Scheme 2). The choice of carbonyl



Scheme 2. Synthesis of **5**.

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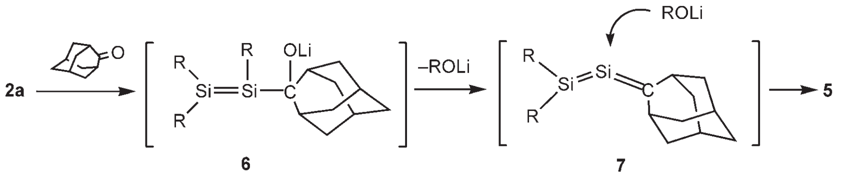
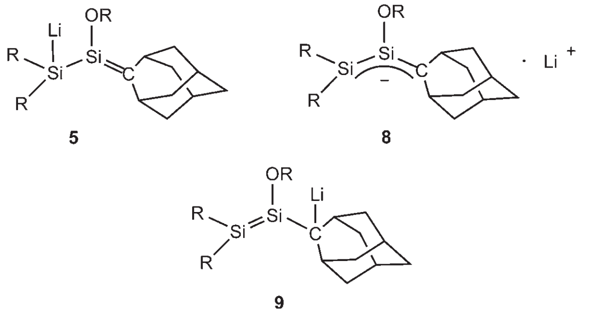
compound is crucial for the sila-Peterson reaction; the reaction was unsuccessful in the case of less hindered ketones. Silene **5** might be formed by the addition of the resulting di-*tert*-butylmethylsiloxylithium to the 1,2-disilaallene intermediate **7** produced in a sila-Peterson-type reaction (Scheme 3). According to this mechanism, **2a** initially reacts with adamantanone to give **6**, then elimination of di-*tert*-butylmethylsiloxylithium from **6** occurs to form the 1,2-disilaallene intermediate **7**. Unfortunately, **7** is unstable toward the siloxy lithium derivative because of insufficient kinetic protection of **7**, which has central sp Si and terminal sp^2 Si atoms. A trapping reaction of the siloxy lithium derivative by chlorotrimethylsilane was not successful. Therefore, addition of the siloxy lithium derivative may result in the formation of three structural isomers: silene **5**, 1,2-disilaallyl anion **8**, and disilene **9** (Scheme 4). Of all these isomers, silene **5** with a Si=C double bond would be stable, and it was actually isolated in the form of air- and moisture-sensitive yellow crystals in 74% yield. Silene **5** was fully characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, as well as by X-ray analysis.



Scheme 3. Reaction pathway to form **5** by the reaction of disilenyllithium **2a** with adamantanone; R = SiMe*t*Bu$_2$.



Scheme 4. Possible structural isomers of **5**, **8**, and **9**; R = SiMe*t*Bu$_2$.

The molecular structure of **5** was unequivocally determined by X-ray crystallography (Figure 1).[14] The lithium atom is solvated by two thf molecules, and the Si–Li bond length is 2.685(3) Å. The Si=C bond length is 1.7431(17) Å, which is a typical Si=C bond length.[2c,15] The Si–O bond length (1.6560(12) Å) is normal for Si–O single bonds.[16] The geometry about the sp^2 Si and C atoms is essentially planar, as determined by the sum of the bond angles for Si2 (359.97(6)°) and C28 (359.80(13)°). The Si=C bond is nearly planar; the dihedral angle between the mean planes of C28-C29-C33 and Si1-Si2-O1 is 6.37°. The sum of the bond angles around Si1 ($\sphericalangle$Si2-Si1-Si3 + $\sphericalangle$Si2-Si1-Si4 + $\sphericalangle$Si3-Si1-Si4) is 337.14(2)°, suggesting that the negative charge is mainly localized on Si1. The central Si1–Si2 bond length (2.3246(6) Å) is shorter than Si1–Si3 (2.3855(6) Å) and Si1–Si4 (2.3734(6) Å), a result of the steric hindrance of the two bulky $t\mathrm{Bu}_2\mathrm{MeSi}$ substituents and probably because of some contribution from the increased s character of sp^2 Si2. Thus, these X-ray crystallographic data suggest the silene structure **5** with a silicon–carbon double bond, with no contribution from the 1,2-disilaallyl-anion-type structure **8** and the disilene-type structure **9** (Scheme 4).

The spectral data of **5** are also consistent with a structure containing a silicon–carbon double bond. The ^{29}Si NMR spectrum of **5** in [D$_6$]benzene showed a signal for an sp^2 silicon atom at $\delta = 78.6$ ppm, whereas the sp^2 carbon atom was observed at $\delta = 130.9$ ppm in the ^{13}C NMR spectrum.[17] These resonances are shifted to higher and lower fields, respectively, relative to other silenes[2c,15] because of the presence of the oxygen atom on the sp^2 silicon atom. This Si=C bond is strongly polarized in a $\mathrm{Si}^{\delta+}{=}\mathrm{C}^{\delta-}$ manner; the sp^2 silicon atom has a positive charge because of the substituted oxygen atom, whereas the sp^2 carbon atom has a relatively negative charge. Therefore, these chemical shifts (sp^2 Si: upfield shift of about 35 ppm; sp^2 C: downfield shift of about 80 ppm) are reasonable compared with Brook-type silenes.[1,2] The anionic silicon atom was observed at $\delta = -188.3$ ppm, a value that is similar to that of [($t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{SiLi(thf)}_4$] ($\delta = -198.8$ ppm).[18] A

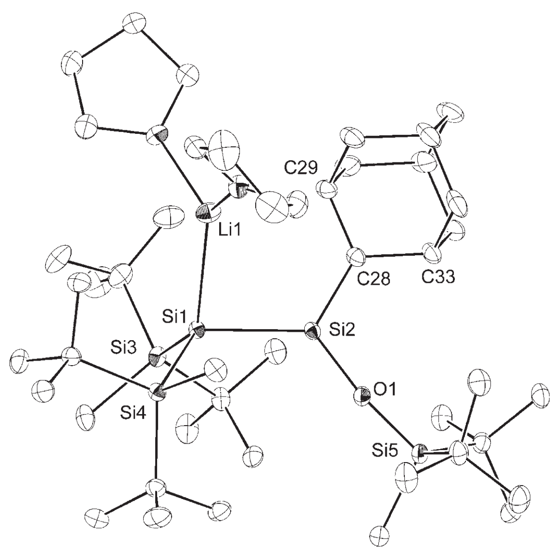


Figure 1. Crystal structure of **5** (ORTEP plot; thermal ellipsoids are shown at the 30% probability; hydrogen atoms are omitted). Selected bond lengths [Å] and angles [°]: Si1-Si2 2.3246(6), Si1-Si3 2.3855(6), Si1-Si4 2.3734(6), Si1-Li1 2.685(3), Si2-C28 1.7431(17), Si2-O1 1.6560(12); O1-Si2-C28 112.50(7), O1-Si2-Si1 127.70(5), C28-Si2-Si1 119.77(6), C29-C28-C33 109.87(14), C29-C28-Si2 126.60(13), C33-C28-Si2 123.33(13), Si2-Si1-Si4 109.98(2), Si2-Si1-Si3 108.74(2), Si3-Si1-Si4 118.42(2), Si5-O1-Si2 171.47(8), Si2-Si1-Li1 85.97(8), Si3-Si1-Li1 131.13(7), Si4-Si1-Li1 97.56(7).

theoretical calculation of the NMR chemical shift (GIAO/B3LYP/6-311G(d) (Li, C, H, O), 6-311 + G(3d) (Si)//B3LYP/6-31G(d)) on the model compound of **5** with $SiMe_3$ groups instead of $SiMe\textit{t}Bu_2$ groups agreed well with the experimental values ($\delta = -184.3$ ppm for the anionic Si atom, $\delta = 85.8$ ppm for the sp^2 Si atom, $\delta = 145.0$ ppm for the sp^2 C atom). The UV/Vis spectrum of **5** showed an absorption maximum at 320 nm in hexane, resulting from the π–π* transition of an Si=C double bond; this value is similar to that observed for other silenes.[2c] Both NMR and UV/Vis spectral data do not correspond to the 1,2-disilaallylic resonance structure. All data including X-ray, NMR, UV/Vis, and theoretical calculations concluded that **5** has a silene structure, and is the first isolable silyl-anion-substituted silene.

Experimental Section

5: Dry oxygen-free toluene (1.5 mL) was added by vacuum transfer to a mixture of **2a** (70 mg, 0.01 mmol) and adamantanone (18 mg, 0.012 mmol), and the reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated to give the lithium salt **5** (74 mg) as air- and moisture-sensitive yellow crystals in 74% yield. M.p. 112–113 °C; ^1H NMR (400.2 MHz, $[D_6]$benzene, TMS): $\delta = 0.36$ (s, 3H, Me), 0.50 (s, 6H, 2Me), 1.23 (s, 18H), 1.32 (m, 8H, thf), 1.38 (s, 36H, 2*t*Bu), 1.96–2.17 (m, 12H), 2.18–2.23 (m, 2H, Ad), 3.49 ppm (m, 8H, thf); $^{13}C\{^1H\}$ NMR (100.6 MHz, $[D_6]$benzene, TMS): $\delta = -3.3$ (Me), −0.6 (Me), 21.3 ($\textit{C}Me_3$), 22.0 ($\textit{C}Me_3$), 25.1 (thf), 28.6 ($C\textit{Me}_3$), 30.0, 31.3 ($C\textit{Me}_3$), 34.2, 38.7, 40.8, 41.7, 68.3 (thf), 130.9 ppm (Si=C); $^{29}Si\{^1H\}$ NMR (79.5 MHz, $[D_6]$benzene, TMS); $\delta = -188.3$ (SiLi), 7.7 ($\textit{t}BuMe_2SiO$), 20.0 ($\textit{t}BuMe_2Si$), 78.6 ppm (Si=C); UV/Vis (hexane): λ_{max} (ε): 320 nm (7900 $M^{-1}cm^{-1}$).

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[14] Crystal structure analysis of **5**: The single crystals of **5** for X-ray diffraction were grown from a benzene solution. The X-ray crystallographic experiments were performed on a MacScience DIP2030 image plate diffractometer equipped with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). Crystal data for $\mathbf{5}\cdot(C_6H_6)_{0.5}$ at 120 K: $C_{48}H_{96}LiO_3Si_5$, $M_r = 868.64$, monoclinic, space group $P2_1/c$, $a = 11.6610(2)$, $b = 22.0760(6)$, $c = 23.6650(5)$ Å, $\beta = 117.1191(10)°$, $V = 5422.3(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.064$ g cm^{-3}, GOF = 1.027. The final R factor was 0.0484 ($R_w = 0.1418$ for all data) for 10048 reflections with $I_o > 2\sigma(I_o)$. The structure was solved by direct methods and refined by the full-matrix least-squares method by using SHELXL-97. CCDC-631002 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] The silene $\textit{t}BuMe_2Si(Me_3Si)Si$=Ad (Ad = 2-adamantylidene) was reported to exhibit a shift of $\delta = 51.7$ ppm for the sp^2 silicon atom in the ^{29}Si NMR spectrum and $\delta = 196.8$ ppm for the sp^2 carbon atom in the ^{13}C NMR spectrum. The Si=C bond length for this silene was reported to be 1.741(2) Å (see reference [3c]).

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