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Isolable Alkali-Metal-Substituted Silyl Radicals ($(^t\mathrm{Bu}_2\mathrm{MeSi})_2\mathrm{SiM}$ (M = Li, Na, K): Electronically and Sterically Accessible Planar Silyl Radicals

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*Summary: Tetrakis(di-tert-butylmethylsilyl)disilene (***1***) was treated with 2.2 equiv of MNp (metal naphthalenide, M = Na, K) in THF followed by addition of 2 equiv of a crown ether (***2b***, 15-crown-5;* **2c***, 18-crown-6), resulting in the formation of the first isolable alkali-metal-substituted silyl radicals* **2***, which were characterized by both EPR spectra and X-ray crystallography. The lithium-substituted silyl radical* **2a** *was also synthesized as an isolable compound by the reaction of free silylene anion radical with LiBr, and it has a monomeric structure in solution but a dimeric structure in the solid state.*

The heavier analogues of radical species, such as silyl radicals, are one of the most important reactive intermediates in organometallic chemistry.[1] The tricoordinate radicals of the heavier group 14 elements can be generated in one of the following ways: (1) by the photolysis or thermolysis of the corresponding hydrides R_3EH (E = heavier group 14 elements) in the presence of the radical initiators, (2) by the γ-irradiation of R_4E or photolysis of $R_3E{-}Hg{-}ER_3$, or (3) by the thermolysis or photolysis of either $R_3E{-}ER_3$ or $R_3E{-}ER_2{-}ER_3$.[1f] Considered just several decades ago as phantom species, the heavier group 14 element centered radicals quickly became a class of observable, spectroscopically detectable, and isolable compounds.[1–3] The first persistent radicals of the heavy group 14 elements ($[(\mathrm{Me_3Si})_2\mathrm{CH}]_3\mathrm{E}^\bullet$; E = Si, Ge, Sn) were reported by Lappert et al. in the mid-1970s.[2] An isolable Ge-centered radical, cyclotrigermenyl radical, was reported by Power et al. in 1997[3c] and isolable Sn- and Pb-centered radicals were also reported.[3e,f] We recently reported some isolable silyl radicals: e.g., cyclotetrasilenyl radical,[3a] a silyl radical lacking stabilization by π-conjugation,[3b] a disilene anion radical,[4] a disilyne anion radical,[5] and a silylene anion radical.[6] However, the crystal structures of silyl radicals that have other substituents, except for a silyl group, such as alkyl, aryl, or alkali-metal substituents, have remained elusive. Apeloig et al. recently reported the EPR spectrum of a lithium-substituted silyl radical generated by the photochemical reaction of silyl−mercury compounds and hydrosilyllithium.[7a,b] The reaction of the silylenoid with alkali metals was also reported to generate lithium- and sodium-substituted silyl radicals.[7d] However, all attempts to isolate alkali-metal-substituted silyl radicals have failed until now because of their extremely high reactivity. In this paper, we present the synthesis and molecular structures determined by X-ray crystallography of the isolable alkali-metal-substituted silyl radicals $(^t\mathrm{Bu_2MeSi})_2\mathrm{SiM}$ (M = Li, Na, K).

Tetrakis(di-*tert*-butylmethylsilyl)disilene (**1**)[4] was treated with MNp (metal naphthalenide, M = Li, Na, K) in dry THF at −78 °C, and the reaction mixture was warmed to room temperature over 2 h, accompanied by a rapid color change from dark blue to intense red due to the formation of the 1,2-dianionic species of **1**.[6] When 2 equiv of a crown ether (sodium derivative, 15-crown-5; potassium derivative, 18-crown-6) was added to the reaction mixture, the alkali-metal-substituted silyl radicals **2b**,**c** (**b**, M = Na; **c**, M = K) crystallized out as red crystals in 70 and 76% yields, respectively (Scheme 1).[8] These radicals are extremely air- and moisture-sensitive; however, they are thermally stable with melting points of 143−144 °C dec for **2b** and 140−141 °C dec for **2c**. These radical products **2b**,**c** were characterized by EPR spectroscopy. The molecular structures of **2b**,**c** were finally characterized by X-ray crystallographic analysis.[8] In the case of the lithium derivative, use of 12-crown-4 produced a mixture of **1** and free silylene anion radical **2a′**

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(8) For the experimental procedures and crystal data of **2a**−**c**, see the Supporting Information.

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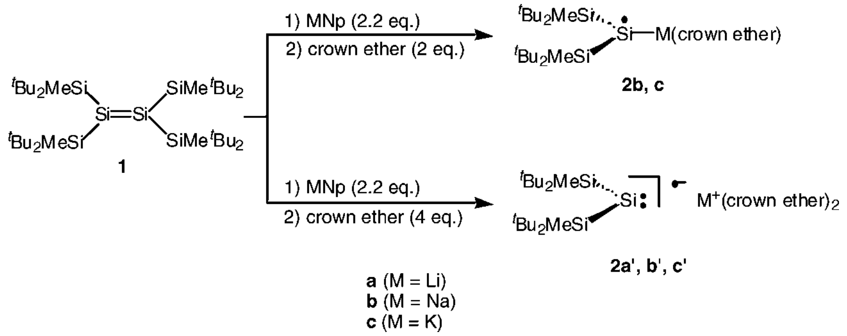
Scheme 1. Synthesis of the Alkali-Metal-Substituted Silyl Radicals 2b,c and the Metal-Free Silylene Anion Radicals 2a′,b′,c′ from Tetrakis(di-*tert*-butylmethylsilyl)disilene (1)



(Scheme 1). The reaction products highly depend on stoichiometry and the type of coordination ligand. When 4 equiv of crown ether was added, the metal-free silylene anion radical species **2a′**,**b′**,**c′** (**a′**, M = Li; **b′**, M = Na; **c′**, M = K) were formed (Scheme 1).[6]

The X-ray crystal structure of **2b** showed a sodium to central silicon bonding interaction with a bond length of 3.0744(8) Å,[9] indicating that **2b** is a sodium-substituted silyl radical (Figure 1).[8] The geometry of the central silicon atom is almost planar (sum of the angles 358.02(3)°; 104.66(2)° for Si2−Si1−Si3, 129.65(3)° for Si2−Si1−Na1, 123.71(3)° for Si3−Si1−Na1), and the lengths of Si1−Si2 and Si1−Si3 are 2.3728(6) and 2.3685(7) Å, respectively. The molecular structure of **2c** was also determined by X-ray crystallography (Figure 2),[8] and it showed the presence of a Si−K bond with a bond length of 3.5442(8) Å,[10] which is an ordinary Si−K bond length. The structural properties of **2c** are similar to those of the sodium derivative **2b**. The geometry of the central silicon atom is almost planar (sum of the angles 359.95(3)°), the lengths of Si1−Si2 and Si1−Si3 are 2.3655(9) and 2.3736(8) Å, respectively.

In the solid state, the geometry of silyl radicals **2b**,**c** is trigonal planar around the sp^2-Si radical center, implying that **2** is a true π radical with the SOMO represented by the central silicon 3p$_z$ orbital. The hyperconjugative delocalization of the unpaired electron over the antibonding σ^*(Si−C$_{t\text{-Bu}}$) orbitals notably contributes to the overall stabilization of **2**, leading to elongation of the Si−C$_{t\text{-Bu}}$ bond lengths (average 1.9454(19) Å for **2b** and average 1.950(2) Å for **2c**), in comparison with the Si−C$_{\text{Me}}$ bond lengths (average 1.8960(19) Å for **2b** and average 1.909(2) Å for **2c**), which lie in the plane. As expected, the introduction of two ^{t}Bu$_2$MeSi substituents with low electronegativity and one extremely electropositive substituent such as Li, Na, or K to the central silicon atom in **2** promotes flattening at the Si radical center.

The EPR spectrum of **2b** in toluene at room temperature showed a very characteristic signal of a central quartet with a *g* value of 2.0074, due to the coupling with the ^{23}Na nucleus ($I = {}^3/_2$) with an hfcc value a(^{23}Na) = 0.19 mT, accompanied by satellite signals with a(α-^{29}Si) = 2.91 mT and a(β-^{29}Si) = 1.02 mT (Figure 3).[6] The extremely small value of 2.91 mT for hfcc(α-^{29}Si) is indicative of the high p character of its SOMO, as found in the solid state. These EPR results indicate that the planar structure with an interaction between sodium and the radical center silicon atom is retained in solution. On the other hand, the EPR spectrum of **2c** in toluene showed no coupling with K (*g* value = 2.0075, a(α-^{29}Si) = 2.91 mT, a(β-^{29}Si) = 1.02 mT), probably due to the rapid intermolecular exchange reaction of **2c** in solution on the EPR time scale. Measurement

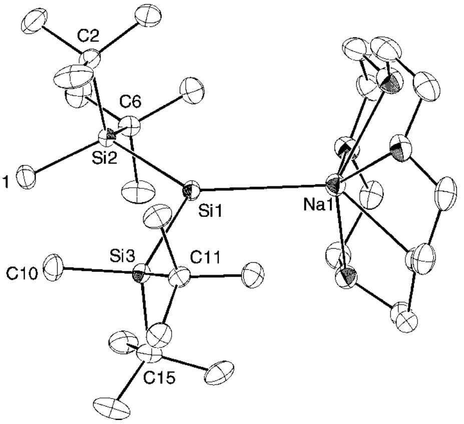


Figure 1. ORTEP drawing of **2b** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.3728(6), Si1−Si3 = 2.3685(7), Si1−Na1 = 3.0744(8), Si2−C1 = 1.8959(19), Si2−C2 = 1.9436(19), Si2−C6 = 1.9448(19), Si3−C10 = 1.8961(19), Si3−C11 = 1.9467(18), Si3−C15 = 1.9463(19). Selected bond angles (deg): Si2−Si1−Si3 = 104.66(2), Si2−Si1−Na1 = 129.65(3), Si3−Si1−Na1 = 123.71(3).

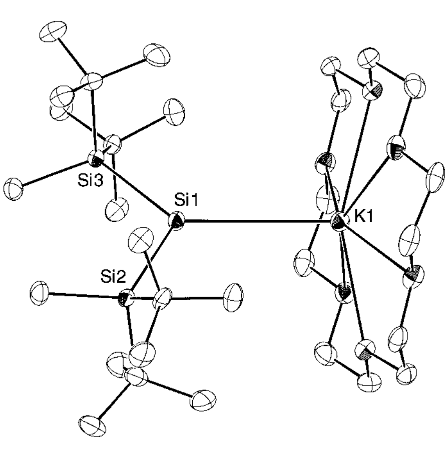


Figure 2. ORTEP drawing of **2c** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.3655(9), Si1−Si3 = 2.3636(8), Si1−K1 = 3.5442(8). Selected bond angles (deg): Si2−Si1−Si3 = 105.80(3), Si2−Si1−K1 = 119.67(3), Si3−Si1−K1 = 134.48(3).

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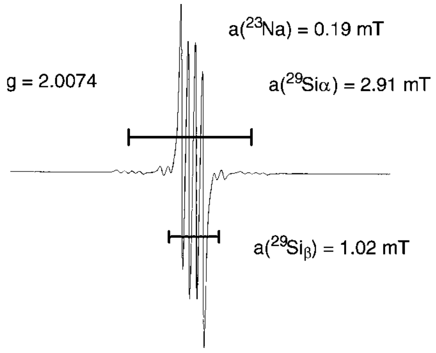


Figure 3. EPR spectrum of **2b** in toluene at room temperature.

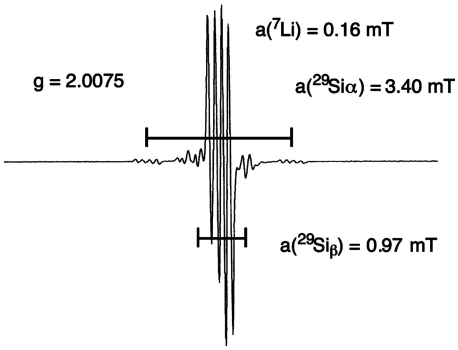
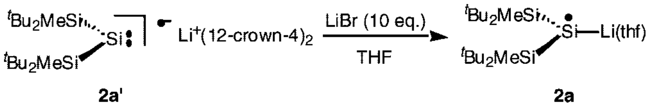


Figure 4. EPR spectrum of **2a** in toluene at room temperature.

Scheme 2. Synthesis of the Lithium-Substituted Silyl Radical 2a



of the EPR spectrum at low temperature in toluene (200 K) produced the same spectrum as that at room temperature.

In order to obtain the lithium-substituted silyl radical **2a**, the silylene anion radical **2a′** was first synthesized by the addition of 4 equiv of 12-crown-4 to the 1,2-dianionic species of **1**.[6] Dry oxygen-free THF was added to a mixture of **2a′** and 10-fold excess LiBr by vacuum transfer, and then the reaction mixture was stirred at room temperature for 6 h. After removal of THF in vacuo, hexane was added, and the reaction mixture was filtered to remove Li$^+$−12-crown-4. The lithium-substituted silyl radical **2a** with a melting point of 136−137 °C dec was crystallized from hexane as air- and moisture-sensitive red crystals in 75% yield (Scheme 2).[8]

The EPR spectrum of **2a** in toluene showed a very characteristic picture of quartet signals due to coupling with the ^{7}Li nucleus ($I = {}^3/_2$) with the hfcc value $a(^7\text{Li}) = 0.16$ mT (g value 2.0075, $a(\alpha\text{-}^{29}\text{Si}) = 3.40$ mT, $a(\beta\text{-}^{29}\text{Si}) = 0.97$ mT), as depicted in Figure 4. As in **2b**, the very small value of 3.40 mT for $a(\alpha\text{-}^{29}\text{Si})$ is also observed in **2a**. The lithium-substituted radical **2a** has already been reported by Apeloig et al., generated by the reaction of the silylenoid with ^{t}BuLi or Li,[7d] whose EPR spectrum in hexane was identical with the spectrum observed by us.

After recrystallization of **2a** from toluene, we obtained red crystals suitable for X-ray analysis. The molecular structure of **2a** is shown in Figure 5.[8] There is a four-membered-ring bridged structure consisting of two lithium atoms and two silicon atoms. The Si−Li bond lengths (2.703(5)−2.728(5) Å) are the longest among all Si−Li bonds reported so far.[11] The bond angles of Si2−Si1−Si3 and Si5−Si4−Si6 are 110.18(4) and 110.31(4)°, which are wider than that of the free silylene anion radical $(^t\text{Bu}_2\text{MeSi})_2\text{Si}^{\bullet-}$ in **2a′** (107.75(12)°).[6] These results indicate that silyl radical **2a** has a monomeric structure (EPR study) in solution but has a dimeric structure (X-ray study) in the solid state, as depicted in Scheme 3. This may be due to the weak and long Si−Li bond lengths in the dimeric structure, and dissociation into two molecules of the lithium-substituted silyl radical occurs in solution.

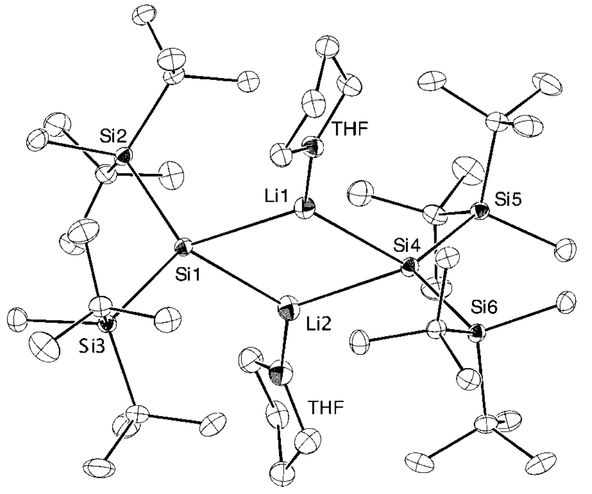
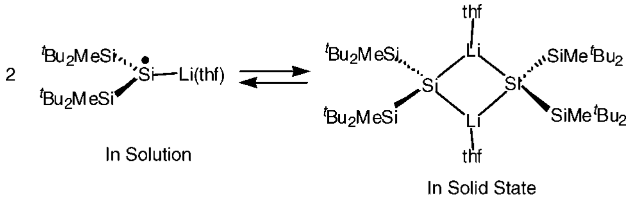


Figure 5. ORTEP drawing of **2a** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.3817(11), Si1−Si3 = 2.3845(10), Si1−Li1 = 2.712(5), Si1−Li2 = 2.715(5), Si4−Si5 = 2.3836(10), Si4−Si6 = 2.3753(11), Si4−Li1 = 2.728(5), Si4−Li2 = 2.703(5). Selected bond angles (deg): Si2−Si1−Si3 = 110.18(4), Li1−Si1−Li2 = 67.67(16), Si5−Si4−Si6 = 110.31(4), Li1−Si4−Li2 67.60(16), Si1−Li1−Si4 = 112.00(19), Si1−Li2−Si4 = 112.7(2).

Scheme 3. Monomeric (Solution) and Dimeric Structures (Solid State) of the Lithium-Substituted Silyl Radical 2a



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Supporting Information Available: For **2a**−**c**, text giving experimental procedures and tables and CIF files giving crystallographic data, including atomic positional and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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