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Isolable Silylene Anion Radical: Structural Characteristics in the Solid State and in Solution

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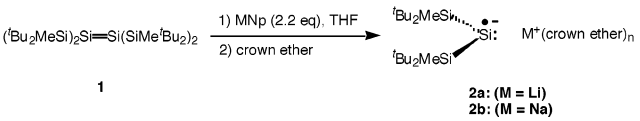
The chemistry of stable free radicals and ion radicals of heavier group 14 elements is one of the most fascinating topics of recent years.[1] Several group 14 element-centered radical species, as well as anion radicals of alkene and alkyne analogues of the heavier group 14 elements have been synthesized and characterized.[2−4] Although only a few examples of metal-substituted silyl radical and silylene anion radical species have been reported,[5a,6,7] the isolation and structural characterization of these species has been missing until now,[1] owing to their high reactivities and instability.[8] Recently, Apeloig et al. reported ESR spectroscopic evidence for the lithium-substituted silyl radicals by the photochemical reactions of the silylmercury compound $[\mathrm{Li}(^i\mathrm{Pr_3Si})_2\mathrm{Si{-}Hg{-}Si(Si}^i\mathrm{Pr_3})_2\mathrm{Li}]$[6a] and hydridosilyllithium $(\mathrm{R_2SiHLi})_2$ ($\mathrm{R} = \mathrm{SiMe}^t\mathrm{Bu}_2$).[6b] The reaction of the isolable silylenoid with alkali metals was also reported to generate alkali metal-substituted silyl radicals.[6c] On the other hand, the anion radicals of the heavy carbene analogues ($\mathrm{R_2E}{:}^{\bullet-}$, E = Si, Ge, Sn) were observed by ESR spectroscopy upon the one-electron reduction of the corresponding divalent species.[5]

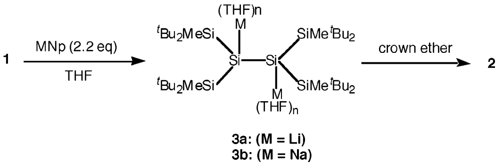
Recently, we reported the one-electron reduction of tetrakis(di-*tert*-butylmethylsilyl)disilene (**1**) by ^{t}BuLi to produce an isolable disilene anion radical of **1**.[3b] In addition, we reported the two-electron reduction of **1** in THF to produce the dianion, which was converted to $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si{=}Si(Li)SiMe}^t\mathrm{Bu}_2$, by changing the solvent from THF to aromatic solvents.[9,10] In this work, we have examined the reduction of disilene **1** by 2.2 equiv of MNp (metal naphthalenide, M = Li, Na) and the subsequent addition of crown ethers, resulting in the unexpected formation of the silylene anion radical. We report here the first isolation and structural characterization of silylene anion radical, which was isolated and characterized by X-ray crystallography and ESR spectroscopy. In addition, we have found interesting structural characteristics of the silylene anion radical: it exists as a solvent-separated ion pair in polar solvents, whereas it forms a contact ion pair in toluene.

First, we examined the reaction of disilene **1** 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 **1** completely disappeared, and a red solution was produced during the reaction. Unexpectedly, when 4.3 equiv of 12-crown-4 were added to the resulting reaction mixture, bis(di-*tert*-butylmethylsilyl)silylene anion radical **2a** was obtained as the lithium salt, which was isolated as air- and moisture-sensitive red crystals in 56% yield (Scheme 1).[11] The reduction of disilene **1** by NaNp (sodium naphthalenide) also proceeded similarly to produce the corresponding anion radical **2b** (56%), which was also isolated as red crystals.[11]

Scheme 1



Scheme 2



The mechanism for the formation of anion radical **2** is not clear at this moment, but we propose the following picture. The treatment of **1** with two equiv of LiNp in THF led to the formation of the 1,2-dianionic species $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si(Li)\text{-}Si(Li)(SiMe}^t\mathrm{Bu}_2)_2$ (**3a**), which was spectroscopically observed.[9,11,12] Indeed, hydrolysis of the resulting reaction mixture produced $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si(H)\text{-}Si(H)\text{-}(SiMe}^t\mathrm{Bu}_2)_2$ (**4**) in 71% yield. Upon addition of the crown ether, the dianionic species would dissociate into two molecules of the anion radical $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si}{:}^{\bullet-}$ and the complexed Li(crown ether)$_n^+$, because of the increased electrostatic repulsion at the neighboring positions. This observation is in marked contrast to that of the reduction of the stable diaminosilylene by West et al.[7] They reported that the reduction of the diaminosilylene with $\mathrm{KC_8}$ in THF gives the 1,2-dianionic species, formed by the dimerization of the resulting silylene anion radical.[7] Our present study demonstrates the opposite process: the dissociation of the central Si−Si bond of the 1,2-dianionic species **3** readily occurs by the addition of the crown ethers, leading to the formation of silylene anion radical **2** (Scheme 2).

The structures of **2a** and **2b** were unequivocally characterized by X-ray crystallographic analysis and ESR spectroscopic data.[11] The X-ray crystal structure of **2a** is shown in Figure 1.[13] The lithium counter cation of **2a** is coordinated by two molecules of 12-crown-4, and the shortest distance between the lithium and silicon atom (6.7 Å) is much longer than the sum of the van der Waals radii of Si and Li. Thus, silylene anion radical **2a** is a free anion in the

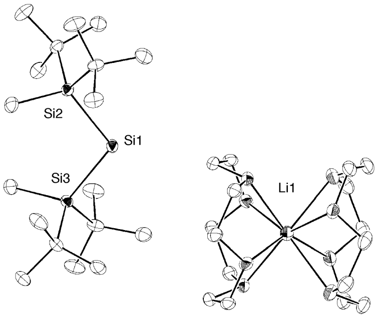


Figure 1. ORTEP drawing of **2a** (30% thermal ellipsoids). Two crystallographically independent Li(12-crown-4)$_2$ units with an occupancy factor of 0.5 were observed and one of them is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.3735(5), Si1−Si3 = 2.3698(5). Selected bond angle (deg): Si2−Si1−Si3 = 107.75(2).

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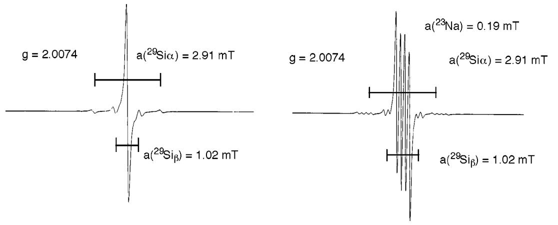
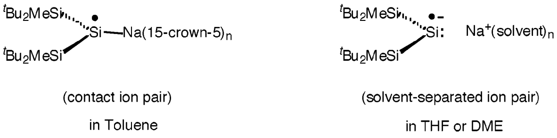


Figure 2. ESR spectra of **2b** in DME (left) and toluene (right) at room temperature.

Scheme 3



solid state. The Si−Si bond lengths are 2.3735(5) Å for Si1−Si2 and 2.3698(5) Å for Si1−Si3. The Si(2)−Si(1)−Si(3) bond angle is slightly contracted to 107.75(2)°, because of its anionic character.[14] The structure of silylene anion radical **2b** in the solid state also represents a free anion;[15] the sodium counter cation of **2b** is coordinated by two molecules of 15-crown-5 and separated from the anionic center, similar to that of **2a**.

The structures of **2** in solution were deduced by ESR spectroscopy. The ESR spectra of **2a** and **2b** in a polar solvent (THF) show the characteristic signal expected for the free silylene anion radical. Indeed, the ESR spectrum of **2a** showed signals with a g value of 2.0074, $a(^{29}\mathrm{Si}_\alpha) = 2.91$ mT, $a(^{29}\mathrm{Si}_\beta) = 1.02$ mT, and hyperfine coupling with the lithium atom was not observed. Therefore, the solution structure of **2a** in THF is determined to be a metal-free silylene anion radical (solvent-separated ion pair), that is, the same as the solid-state structure. To see the possible interaction between the anionic silicon atom and the M^+ ion, we tried to measure the ESR spectrum of **2a** in toluene; unfortunately, this was hampered by its insolubility. However, we were able to measure the ESR spectrum of **2b** in toluene, which showed a very characteristic signal of a central quartet at $g = 2.0074$, due to the coupling with the ^{23}Na nucleus ($I = {}^3/_2$) with hfcc value $a(^{23}\mathrm{Na}) = 0.19$ mT, accompanied by satellites with $a(^{29}\mathrm{Si}_\alpha) = 2.91$ mT, $a(^{29}\mathrm{Si}_\beta) = 1.02$ mT (Figure 2, right). The observed hyperfine interaction of the unpaired electron with the ^{23}Na nucleus indicates the presence of an Si−Na bond in **2b** (contact ion pair).[16] However, when the solvent was changed from toluene to dimethoxyethane (DME) or THF, the coupling with ^{23}Na disappeared, as shown in Figure 2 (left). These results suggest that the structure of **2b** in toluene is represented by a contact ion pair (Scheme 3, left), as proposed for $\mathrm{M(R_3Si)_2Si^\bullet}$ (M = Li, Na, $\mathrm{R_3Si} = \mathrm{Si}^i\mathrm{Pr_3}$, $\mathrm{SiMe}^t\mathrm{Bu_2}$) in hexane by Apeloig.[6a,b] Thus, the conversion of the structure of **2b** in solution from the solvent-separated ion pair to contact ion pair of the silylene anion radical is possible by changing the solvent polarity (Scheme 3). The reaction of **2a** with water produced $(^t\mathrm{Bu_2MeSi})_2\mathrm{SiH_2}$ in 87% yield.

Supporting Information Available: The experimental procedures of **2a** and **2b**, table of crystallographic data including atomic positional and thermal parameters for **2a** (PDF/CIF), optimized geometries of bis(di-*tert*-butylmethyl)silylene and its anion radical **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For the experimental procedures and spectral data, see the Supporting Information.

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(13) Crystal data for **2a** at 120 K: $\mathrm{C_{34}H_{74}LiO_8Si_3}$, MW = 702.14, monoclinic, $C2/c$, $a = 17.1250(5)$, $b = 13.9720(4)$, $c = 34.8770(9)$ Å, $\beta = 91.236(2)°$, $V = 8343.1(4)$ Å^3, $Z = 8$, $D_{\mathrm{calcd}} = 1.118$ g cm^{-3}. $R = 0.0479$ ($I > 2\sigma(I)$), $R_w = 0.1446$ (all data), GOF = 1.025.

(14) A DFT calculation on the silylene anion radical **2** predicts the contraction of the bond angle upon the one electron reduction of the silylene. The calculated Si−Si−Si bond angle is 105.2° for $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si}:^{\bullet-}$ at the UB3LYP/6-31(G) level, whereas 109.9° for $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si}:$ at B3LYP/6-31G(d) level (see the Supporting Information).

(15) The structure of **2b** was unambiguously determined by X-ray crystallography; however, we do not discuss its structural features because the refinement is not sufficiently good at this moment.

(16) The hfcc value $a(^{23}\mathrm{Na}) = 0.19$ mT of **2b** in toluene is a little bit smaller than that of $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si^\bullet\text{-}Na(thf)}_n$ ($a(^{23}\mathrm{Na}) = 0.28$ mT) in hexane (Supporting Information of ref 6c) owing to the complexation of sodium ion by the crown ether.

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