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An Isolable Disilyne Anion Radical and a New Route to the Disilenide Ion upon Reduction of a Disilyne

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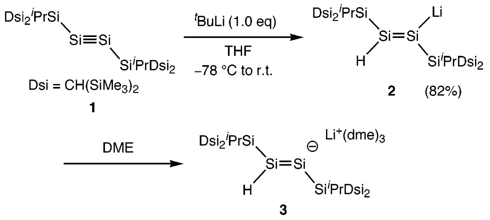
The synthesis, characterization, and reactivity of compounds with multiple bonds between heavier main group elements are of considerable interest due to their unusual structures and bonding. Numerous alkene analogues of heavier group 14 elements have been isolated and characterized.[1] On the other hand, much less is known about the heavier group 14 congeners of alkynes, although a few papers have described the synthesis and structure of alkyne analogues.[2] In particular, very recently, considerable interest has been focused on the silicon−silicon triple bond species, disilyne, since we[3] and Wiberg's group[4] reported the synthesis of stable disilynes, which in our case was isolated as crystalline compound **1** bearing two bulky substituents, $Si^{i}Pr[CH(SiMe_3)_2]_2$ groups, at the triply bonded silicon atoms. Of particular interest in the structure of **1** is that the geometry around the silicon−silicon triple bond is not linear, but *trans*-bent, which results in splitting of the two occupied MOs (π_{in} for HOMO − 1 and π_{out} for HOMO) and splitting of the two unoccupied MOs (π^*_{in} for LUMO and π^*_{out} for LUMO + 1).[3] Upon bending, the energy of the HOMO is raised, whereas the energy of the LUMO is significantly lowered. Therefore, it is expected that the disilyne **1** is prone to easy reduction of its low-lying LUMO. In this paper, we report the reduction of **1** with $^{t}BuLi$, leading to isolation of the disilenyllithium, which provides a new route to the disilenide derivatives by the formal addition of LiH to the silicon−silicon triple bond.[5] In addition, we also report here the isolable disilyne anion radical upon the reduction of **1** by KC_8,[6] representing the first example of the stable compounds of such class, which has been fully characterized including by X-ray crystallography.

The reactivity of disilyne **1** toward organolithium compounds was first examined. The reaction of **1** with an equivalent amount of $^{t}BuLi$ in dry THF at −78 °C resulted in the immediate development of a red color. Disilenyllithium **2** was isolated as air- and moisture-sensitive red crystals in 82% isolated yield (Scheme 1).[7] The disilenide ion was also obtained as a solvent-separated ion pair **3** by the addition of 1,2-dimethoxyethane (DME) to **2** and was purified by recrystallization from pentane, benzene, and DME at −30 °C.[7]

The chemistry of sp^3-silyl anions has been greatly developed during the past decade.[8] In contrast, the chemistry of disilenides, that is, silicon analogues of vinyl anions, has remained poorly explored because of synthetic difficulties.[5] The present method provides an entirely new method for the preparation of disilenide derivatives by taking advantage of the reactivity of the silicon−silicon triple bond. The formation of **2** can be rationalized by assuming an initial single electron transfer process involving intermediate formation of the anion radical of **1** and *tert*-butyl radical as a key radical pair, followed by fast hydrogen abstraction by the anion radical of **1** with the formation of disilenyllithium.[9] Indeed, we have observed the simultaneous formation of an equivalent amount of isobutene as the sole side product by ^1H and ^{13}C NMR spectroscopy. Therefore, disilenyllithium **2** is the product of a formal 1,2-addition of lithium hydride across the Si≡Si triple bond of **1**.

Scheme 1



The disilenyllithium **2** was fully characterized spectroscopically. Eight signals at −0.8, −0.74, −0.7, −0.5, 2.3, 12.8, 124.7, and 165.0 ppm were observed in the ^{29}Si NMR spectrum in benzene-d_6. The last two were assigned as follows: the peak at 165.0 ppm corresponds to the Li-substituted sp^2-Si atom, and the peak at 124.7 ppm corresponds to the H-substituted sp^2-Si atom with the $Si(sp^2)-H$ coupling constant of 155 Hz.[10,11] The Si−Li coupling for **2** was not observed, as in the cases of $Tip_2Si{=}Si(Tip)Li$[5a] and $(^tBu_2MeSi)_2Si{=}Si(Mes)Li$[5b] in toluene-$d_8$. In the ^1H NMR spectrum, the signal due to hydrogen on the sp^2-silicon atom appeared at 7.10 ppm; this is obviously the result of the deshielding effect of the Si=Si π-electrons. The UV spectrum of **2** in hexane shows an absorption band with a maximum at 390 nm (ϵ 5440), which is assigned to the $\pi-\pi^*$ electronic transition of the Si=Si double bond.

The molecular structure of the solvent-separated ion pair of disilenide **3** as determined by X-ray crystallographic analysis is shown in Figure 1.[12] The lithium countercation is coordinated by three DME molecules. Consequently, the distance between the lithium ion and Si1 is greater than 7 Å, showing no interactions

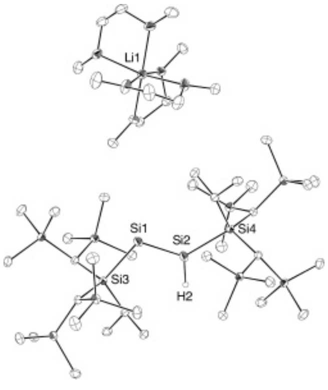


Figure 1. ORTEP drawing of **2** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity except for H2. Selected bond lengths (Å): Si1−Si2 = 2.2034(9), Si1−Si3 = 2.4201(8), Si2−Si4 = 2.3642(8). Selected bond angles (deg): Si2−Si1−Si3 = 102.69(3), Si1−Si2−Si4 = 121.45(3).

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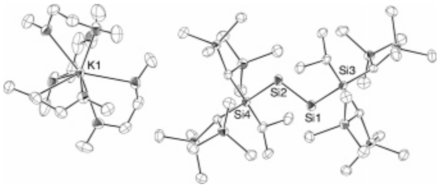
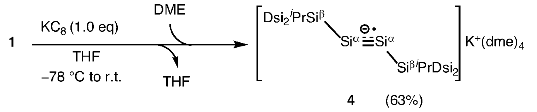


Figure 2. ORTEP drawing of **4** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.1728(14), Si1−Si3 = 2.3639(13), Si2−Si4 = 2.3714(13), Selected bond angles (deg): Si2−Si1−Si3 = 113.97(6), Si1−Si2−Si4 = 112.84(6).

Scheme 2



4 (63%)

between them. The four Si atoms (Si4, Si2, Si1, Si3) are almost coplanar, and the bulky $\mathrm{Si^{\mathit{i}}Pr[CH(SiMe_3)_2]_2}$ groups at Si═Si are arranged in the *trans* orientation, due to their extreme bulkiness. The Si═Si double bond length is 2.2034(9) Å, which is elongated by 7% relative to the precursor **1** (2.0622(9) Å).[3,13] The bond angle of Si1−Si2−Si4 is 121.45(3)°, whereas Si2−Si1−Si3 is significantly contracted to 102.69(3)°, due to the influence of the negative charge on the Si1 atom.

The anion radical of **1** was obtained when the reaction was carried out in the absence of the hydrogen atom source. Thus, the reaction of **1** with an equivalent amount of KC_8 in THF produced the disilyne anion radical **4**, which was isolated by recrystallization from pentane and DME as dark brown crystals in 63% yield (Scheme 2).[7] The ESR spectrum of **4** showed a triplet signal with a g value of 1.99962 (hfcc = 0.23 mT), which is one of the smallest values for silyl radicals.[14] The triplet splitting of the signal arises from coupling with the two δ-H of isopropyl groups; however, no coupling with the four δ-H of $\mathrm{CH(SiMe_3)_2}$ groups was observed.[15] The signal is accompanied by the two pairs of satellite signals (3.92 and 2.24 mT), due to coupling of the unpaired electron with the α- and β-^{29}Si nuclei, respectively. The magnitude of the spin coupling by the α-^{29}Si nuclei is smaller than that in the tris(di-*tert*-butylmethylsilyl)silyl radical (5.80 mT),[16] due to the delocalization of unpaired electron over the two central α-Si atoms.[17] The magnitude of the spin coupling by the β-^{29}Si nuclei, however, is the largest for all observed silyl-substituted silyl radicals.[14]

X-ray crystallography unambiguously revealed the *trans*-bent structure of disilyne anion radical **4** (Figure 2).[18] The countercation, potassium, is solvated by four DME molecules, and the distance between Si1 and K1 is greater than 11 Å, showing that anion radical **4** is free. The central Si−Si bond length is 2.1728(14) Å, which is 5% longer than that of **1** (2.0622(9) Å)[3] because of the half-occupied π_{in}*-orbital with antibonding character. The characteristic bond angles (112.84(6) and 113.97(6)°) of the tetrasilane unit are smaller than the corresponding bond angle (137.44°) of **1**.[19] These bond angles are found to be essentially equal to each other, indicating the delocalization of the unpaired electron between the two central α-silicon atoms.

Supporting Information Available: Experimental procedures of **2**−**4**, tables of crystallographic data including atomic positional and thermal parameters for **3** and **4** (PDF/CIF), optimized geometries and GIAO calculations on $\mathrm{H_3Si(H)Si{=}Si(SiH_3)Li(OMe_2)_3}$, π-MO diagram, and energies of molecular orbitals of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Unexpectedly, $^1J_{\mathrm{Si(sp^2)-H}}$ value in **2** (155 Hz) is smaller than that of $^1J_{\mathrm{Si(sp^3)-H}}$ (172 Hz) in the related compound $\mathrm{Dsi_2{}^{\mathit{i}}PrSiSi(H_2)Si(H_2)Si^{\mathit{i}}PrDsi_2}$. However, the reason is not clear at this moment.

(11) The calculated ^{29}Si NMR chemical shifts of the model compound $\mathrm{H_3Si(H)Si{=}Si(SiH_3)Li(OMe_2)_3}$ are 132.9 ppm (H-substituted sp^2-Si atom) and 178.5 ppm (Li-substituted sp^2-Si atom) at the B3LYP/6-31G(d) level, which agree well with the experimental values.

(12) For the crystal data of **3**, see the Supporting Information.

(13) The Si═Si bond lengths of disilenyllithium derivatives: 2.192(1) Å for $\mathrm{Tip_2Si{=}Si(Tip)Li}$ (ref 5a), 2.2092(7) Å for $\mathrm{(^{\mathit{t}}Bu_2MeSi)_2Si{=}Si(Mes)Li}$ (ref 5b), and 2.1983(18) Å for $\mathrm{(^{\mathit{t}}Bu_2MeSi)_2Si{=}Si(SiMe^{\mathit{t}}Bu_2)Li}$ (ref 5c).

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(15) The lack of coupling with these four protons is due to the almost orthogonal position of these protons toward the Si(4)−Si(2)−Si(1)−Si(3) plane, whereas the two δ-H of ^{i}Pr groups lie in this plane.

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(17) A DFT calculation on the disilyne anion radical **4** at the UB3LYP/6-31(G) level confirmed that SOMO is represented by π^*_{in}-orbital, and unpaired electron is delocalized over the two central α-Si atoms, resulting in a decrease of α-^{29}Si hfcc.

(18) For the crystal data of **4**, see the Supporting Information.

(19) A similar widening of the bond angles was observed for the anion radicals of the alkyne analogues of Ge and Sn; see ref 6.

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