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Si$_3$C$_2$-Rings: From a Nonconjugated Trisilacyclopentadiene to an Aromatic Trisilacyclopentadienide and Cyclic Disilenide

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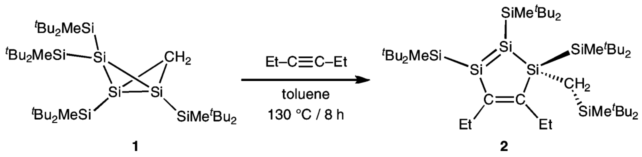
Cyclopentadiene and its derivatives are among the most important reagents in organic chemistry, being readily transformed into the 6π-electron aromatic cyclopentadienides, which in turn are commonly used for the preparation of a variety of transition metal complexes featuring cyclopentadienyl ligands.[1] The chemistry of the cyclopentadienes, incorporating heavy group 14 elements in the ring, is greatly dominated by that of metalloles with the Si, Ge, or Sn atoms at the sp^3-position.[2] Anions and dianions, generated from them, were in some cases recognized as aromatic species.[3] The sole representative of heavy cyclopentadienes, featuring Si and Ge atoms at the sp^2-positions, is the recently reported disilagermacyclopentadiene,[4] the reduction of which produced an aromatic disilagermacyclopentadienide ion derivative.[5]

In this contribution, we report on a totally different approach for the synthesis of a novel heavy cyclopentadiene, namely, trisilacyclopentadiene, currently representing the closest approach to the highly challenging pentasilacyclopentadiene, as well as its reduction forming aromatic trisilacyclopentadienide and unprecedented cyclic disilenide derivatives.

Thermolysis of the recently reported 1,2,3-trisilabicyclo[1.1.0]butane derivative **1**[6] at 130 °C for 8 h in the presence of excess hex-3-yne[7] as a trapping reagent afforded 1,2,3-trisilacyclopenta-1,4-diene **2** isolated as air-sensitive red crystals in 43% yield (Scheme 1).[8,9] Because of the lack of molecular symmetry, **2** exhibits nonequivalence of all substituents in both ^{1}H and ^{13}C NMR spectra. The presence of both C═C and Si═Si unsaturations in **2** was evident from its low-field NMR resonances: 159.4 and 162.0 ppm (^{13}C NMR), 95.6 (*Si*═Si−C═C) and 166.4 ppm (Si═*Si*−C═C) (^{29}Si NMR). The latter values were reasonably reproduced by GIAO calculations on the Me$_3$Si-substituted model: 86.6 and 171.9 ppm (B3LYP/6-31G(d) level).

Scheme 1



The five-membered ring in **2** is planar, with the sum of the interior bond angles being 539.9° and the angle between the mean planes Si3−C1−C2−Si1 and Si1−Si2−Si3 being 3.2° (Figure 1).[8] The Si═Si double bond is highly twisted (torsion angle Si6−Si2−Si3−Si7 = 59.4°) because of the severe steric repulsion between the bulky substituents. A Si2═Si3 bond length of 2.1808(5) Å is typical for Si═Si double bonds, which range from 2.138 to 2.289 Å.[10] Likewise, the lengths of all other skeletal bonds Si3−C1 (1.8947(16) Å), Si1−C2 (1.9082(15) Å), Si1−Si2 (2.3520(5) Å), and C1═C2 (1.367(2) Å) were also quite normal.

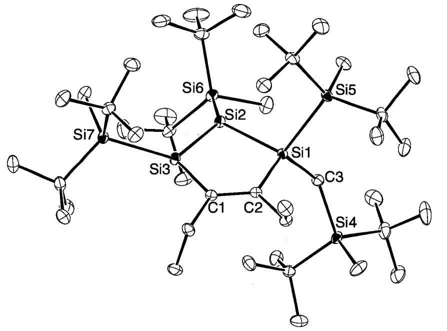
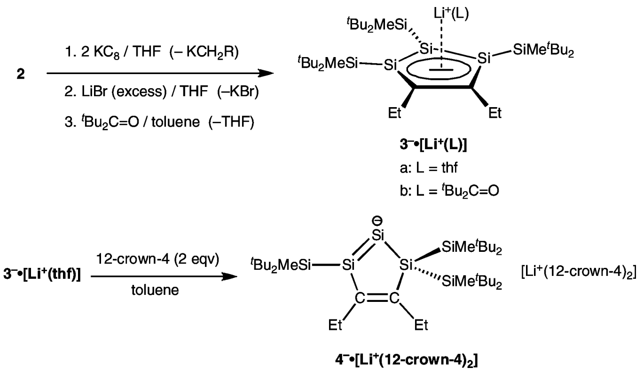


Figure 1. ORTEP drawing of **2** (30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.3520(5), Si2−Si3 = 2.1808(5), Si1−Si5 = 2.4247(5), Si2−Si6 = 2.3622(6), Si3−Si7 = 2.3789(5), Si3−C1 = 1.8947(16), Si1−C2 = 1.9082(15), C1−C2 = 1.367(2). Selected bond angles (deg): C2−Si1−Si2 = 100.97(5), Si1−Si2−Si3 = 92.79(2), Si2−Si3−C1 = 105.67(5), Si3−C1−C2 = 120.03(11), C1−C2−Si1 = 120.47(11).

That is, from the structural viewpoint, heavy cyclopentadiene **2** showed no notable conjugation between the Si═Si and C═C bonds, in contrast to organic cyclopentadienes, despite the planarity of the five-membered ring. On the other hand, the π(HOMO)−π*(LUMO) absorption in the UV−vis spectrum of **2** was observed at 493 nm, which is red-shifted compared with the previously reported disilagermacyclopentadiene (472 nm),[4] thus pointing to a slightly higher extent of π−π conjugation in **2**.

Reduction of the heavy cyclopentadiene **2** with KC$_8$ in THF produced the 1,2,3-trisilacyclopentadienide derivative **3**$^-$•**K**$^+$, which was isolated as the Li salt **3**$^-$•**[Li**$^+$**(thf)]** after exchange of the countercation from K$^+$ to Li$^+$ by treatment with an excess of LiBr (Scheme 2).[8] Because the crystal structure refinement of **3**$^-$•**[Li**$^+$**(thf)]** suffered from disorder problems, we exchanged the coordinating ligand from THF to ^{t}Bu$_2$C═O to form the ketone-

Scheme 2



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coordinated derivative $\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$, which was isolated as air- and moisture-sensitive orange crystals in 61% yield.

The X-ray crystal structure of $\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$ is shown in Figure 2.[8] There are several prominent structural features worthy of discussion. First, the Li$^+$ cation is coordinated by di-*tert*-butyl ketone with an O1—Li1 distance of 1.869(5) Å, a C34═O1 bond length of 1.222(3) Å, and a Li1—O1—C34 bond angle of 164.3(3)°. More importantly, the Li$^+$ cation is coordinated to its anionic counterpart in a diagnostic η^5-fashion. Second, the Si_3C_2 five-membered ring retained its planarity upon reduction: 539.9° in the starting **2** vs 538.5° in the resulting $\mathbf{3}^-$. Third, the general trend in the change of the skeletal bond lengths taking place upon reduction is exactly that expected for a cyclically conjugated system: namely, all double bonds of **2** are stretched upon reduction to form **3** (Si2—Si3: 2.1808(5) vs 2.2438(10) Å, C1—C2: 1.367(2) vs 1.418(4) Å), whereas all single bonds are shortened (Si1—Si2: 2.3520(5) vs 2.2508(10) Å, Si3—C1: 1.8947(16) vs 1.844(3) Å, Si1—C2: 1.9082(15) vs 1.829(3) Å). Overall, the structural peculiarities of $\mathbf{3^{-}\bullet Li^{+}}$ definitely point to its aromaticity.

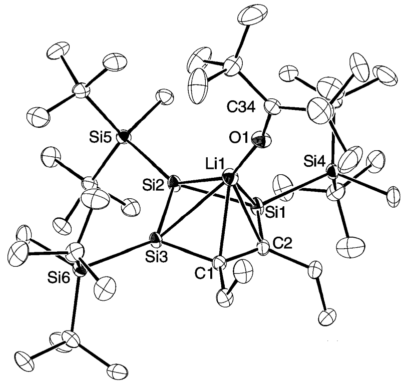

Figure 2. ORTEP drawing of $\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$ (30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1—Si2 = 2.2508(10), Si2—Si3 = 2.2438(10), Si3—C1 = 1.844(3), Si1—C2 = 1.829(3), C1—C2 = 1.418(4), Si1—Si4 = 2.3703(11), Si2—Si5 = 2.3670(10), Si3—Si6 = 2.3695(10), Si1—Li1 = 2.656(5), Si2—Li1 = 2.774(5), Si3—Li1 = 2.677(5), C1—Li1 = 2.305(6), C2—Li1 = 2.275(6), O1—Li1 = 1.869(5), O1—C34 = 1.222(3). Selected bond angles (deg): C2—Si1—Si2 = 102.42(9), Si1—Si2—Si3 = 93.14(4), Si2—Si3—C1 = 102.61(9), Si3—C1—C2 = 119.70(19), C1—C2—Si1 = 120.62(19), Li1—O1—C34 = 164.3(3).

The delocalized nature of both $\mathbf{3^{-}\bullet[Li^{+}(thf)]}$ and $\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$ in solution was manifested in their characteristic NMR resonances. Thus, the signals of the skeletal silicons were observed at 22.0, 29.9 (for $\mathbf{3^{-}\bullet[Li^{+}(thf)]}$) and at 22.4, 28.3 (for $\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$). Significantly, all of these resonances were found in the region between those of the neutral precursor **2**: −10.9 ppm (sp^3-Si) and 95.6/166.4 ppm (sp^2-Si's); that is, the skeletal sp^3-Si was deshielded upon reduction, whereas the sp^2-Si's were significantly shielded. Particularly important was the observation of the ^{7}Li NMR signals in the high-field region of −5.8 ($\mathbf{3^{-}\bullet[Li^{+}(thf)]}$) and −5.0 ($\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$) ppm. Such great shielding of the Li atoms is indicative of the aromatic ring current effects inside the Si_3C_2 ring of $\mathbf{3}^-$, typical for the aromatic cyclopentadienides.[11]

The Li$^+$ countercation plays a decisive role in the stabilization of the aromatic derivative $\mathbf{3^{-}\bullet Li^{+}}$. Thus, adding 12-crown-4 to $\mathbf{3^{-}\bullet[Li^{+}(thf)]}$ in toluene, we were able to isolate a totally unexpected anionic compound $\mathbf{4^{-}\bullet[Li^{+}(12\text{-}crown\text{-}4)_{2}]}$ isolated as an air- and moisture-sensitive orange powder in 71% yield, which was formed as a result of a 1,2-migration of the silyl substituent and existed as a separated ion pair (Scheme 2).[8] $\mathbf{4^{-}\bullet[Li^{+}(12\text{-}crown\text{-}4)_{2}]}$, being isomeric to aromatic delocalized $\mathbf{3^{-}\bullet[Li^{+}(thf)]}$, has a dramatically different structure, featuring two localized Si═Si and C═C bonds with an anionic charge residing on one of the sp^2-Si atoms.[8] The preliminary crystal structure analysis of $\mathbf{4^{-}\bullet[Li^{+}(12\text{-}crown\text{-}4)_{2}]}$ showed no bonding cation—anion interaction, confirming the free status of the cyclic disilenide $\mathbf{4}^-$.[12] As the most prominent feature of $\mathbf{4}^-$, one should stress a significant reduction of the skeletal bond angle around the doubly bonded Si═*Si*—Si silicon atom on going from the neutral **2** to the anionic $\mathbf{4}^-$. Such appreciable narrowing of the bond angle can be reasonably attributed to the high s-contribution of the anionic orbital of $\mathbf{4}^-$, giving rise to a higher p-character of the Si—Si bonds in the Si═Si^-—Si fragment. The high s-fraction of the anionic orbital of $\mathbf{4}^-$ can also be taken as the reason for the selective formation of an sp^2, but not sp^3, Si anion. Overall, anionic $\mathbf{4^{-}\bullet[Li^{+}(12\text{-}crown\text{-}4)_{2}]}$ represents the first example of a cyclic disilenide derivative.[13]

Supporting Information Available: Experimental procedures and spectral data for compounds **2**, $\mathbf{3^{-}\bullet[Li^{+}(thf)]}$, $\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$, and $\mathbf{4^{-}\bullet[Li^{+}(12\text{-}crown\text{-}4)_{2}]}$, proposed mechanism for the formation of **2**, relative stabilities of sp^3- and sp^2-anions of trisilacyclopentadienide $\mathbf{4}^-$, preliminary X-ray data of $\mathbf{4^{-}\bullet[Li^{+}(12\text{-}crown\text{-}4)_{2}]}$, tables of crystallographic data, including atomic positional and thermal parameters for **2** and $\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$ (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The choice of alkyne was quite crucial: no cyclopentadiene adducts were formed when PhC≡CPh or $Me_3SiC{\equiv}CSiMe_3$ was used as a trapping reagent. On the other hand, thermolysis of **1** in the presence of PhC≡CH resulted in the formation of a messy reaction mixture.

(8) For the experimental procedure and the spectral data of compounds **2**, $\mathbf{3^{-}\bullet[Li^{+}(thf)]}$, $\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$, $\mathbf{4^{-}\bullet[Li^{+}(12\text{-}crown\text{-}4)_{2}]}$ and crystal data of compounds **2** and $\mathbf{3^{-}\bullet[Li^{+}(O{=}C^{\mathit{t}}Bu_{2})]}$, relative stabilities of sp^3-and sp^2-anions of trisilacyclopentadienide $\mathbf{4}^-$, see the Supporting Information.

(9) For the mechanism of **2**, apparently involving initial formation of the three-membered ring cyclotrisilene bearing a $CH_2SiMe^tBu_2$ group at one of the doubly bonded Si atoms, following [2 + 2] cycloaddition with Et—C≡C—Et and a subsequent series of isomerizations, see the Supporting Information.

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(11) ^{7}Li NMR resonances of the aromatic cyclopentadienide derivatives: (a) −8.37 ppm for C_5H_5Li (ref 1). (b) −7.51 ppm for $(HMe_2Si)_5C_5Li$ (Sekiguchi, A.; Sugai, Y.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 1144). (c) −5.63 ppm for $[\eta^5\text{-Li(TMEDA)}][\eta^5\text{-Li}]_{1/2}[\eta^1\text{-Li}]_{1/2}[Et_4C_4Ge]$ (Choi, S.-B.; Boudjouk, P.; Hong, J.-H. *Organometallics* **1999**, *18*, 2919). −5.4 ppm for Li$^+$-disilagermacyclopentadienide (ref 5).

(12) The structure of $\mathbf{4^{-}\bullet[Li^{+}(12\text{-}crown\text{-}4)_{2}]}$ was unambiguously determined by X-ray crystallographic analysis; however, the X-ray data were not sufficiently good for further discussion (see the Supporting Information).

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