The Heavy Analogue of CpLi: Lithium 1,2-Disila-3-germacyclopentadienide, a 6π-Electron Aromatic System

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The cyclopentadienide ion (Cp$^-$), a five-membered cyclic 6π-electron system, is one of the most fundamental aromatic compounds. It has been known for more than 100 years and exhaustively studied both experimentally and theoretically.[1] The CpM (M = alkali metal) derivatives have become very useful organometallic reagents that are widely used in organic chemistry, particularly in the field of transition metal complexes. The great importance of Cp$^-$ derivatives stimulated a great deal of interest in the chemistry of their nearest homologues containing heavier group 14 elements (Si, Ge), that is, silole and germole anions.[2] The first attempt to generate such species was made by Gilman in 1958 by the reduction of bis(dibenzosilole) with lithium to form, presumably, the lithium salt of the dibenzosilole anion.[3] The story of silole and germole anions experienced a renaissance in the early 1990s, when Joo,[4a] Boudjouk,[4b] West,[4c,d] and Tilley[4e,f] reported the generation and isolation of several silole and germole anions and dianions. Detailed experimental[4a−f] and theoretical[4g−i] studies revealed that some of them possess a delocalized aromatic structure with the characteristic η^5-coordination of countercation to the five-membered ring. Recently, we have synthesized 1,2-disila-3-germacyclopenta-2,4-diene **1**, incorporating the Si=Ge−C=C diene system.[5] Here, we report the reduction of this compound with alkali metals, resulting in the formation of the heavy analogue of Cp$^-$, and discuss its aromatic nature on the basis of crystal structure and NMR data.

The reduction of **1** was smoothly achieved by its treatment with 2 equiv of KC$_8$ in THF. The color of the reaction mixture immediately changed from bright orange to very dark red because of the apparent formation of the potassium derivative **2$^-$·K$^+$** (Scheme 1). The only identifiable side product formed along with **2$^-$·K$^+$** was ^{t}Bu$_2$MeSiK, detected by NMR spectroscopy.[6] Although the reduction of **1** with KC$_8$ proceeded relatively cleanly, the isolation of **2$^-$·K$^+$** was prevented by its poor crystallinity. However, treatment of **2$^-$·K$^+$** with an excess of dry LiBr in THF resulted in the clean formation of the corresponding Li derivative, lithium 1,2,3-tris(di-*tert*-butylmethylsilyl)-4-phenyl-1,2-disila-3-germa-cyclopentadienide, **2$^-$·Li$^+$**, which was isolated as bright orange plates by recrystallization from hexane in 23% yield (Scheme 1).[7]

The crystal structure of **2$^-$·Li$^+$** as a THF solvate was determined by X-ray crystallography (Figure 1).[8] The structural changes taking place upon reduction of **1** with alkali metal to form **2$^-$·[Li$^+$(THF)]** are particularly instructive, and the structural features of **2$^-$·[Li$^+$(THF)]** are discussed below (Figures 1 and 2). First, the five-membered ring of **2$^-$·[Li$^+$(THF)]** is close to planarity (similar to starting **1**), with the sum of the interior bond angles being 536.32° (cf. 539.86° in **1**). Second, the Li$^+$ ion has η^5-coordination to the anionic part, being directly bonded to all skeletal atoms of **2$^-$**. Third, the tendency of changes of the skeletal bond lengths upon reduction is as follows: all double bonds of the starting **1**[5] are *elongated* compared with those in the resulting **2$^-$·[Li$^+$(THF)]** (Ge1−Si1
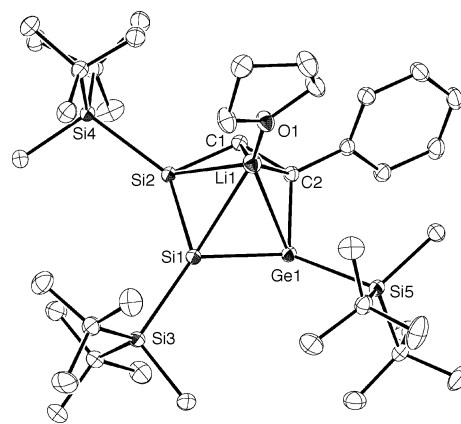

Figure 1. ORTEP drawing of **2$^-$·[Li$^+$(THF)]**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge1−Si1 = 2.3220(5), Si1−Si2 = 2.2403(7), Ge1−C2 = 1.9303(17), Si2−C1 = 1.8269(18), C1−C2 = 1.402(2), Ge1−Si5 = 2.4092(5), Si1−Si3 = 2.3558(7), Si2−Si4 = 2.3550(7), Ge1−Li1 = 2.760(4), Si1−Li1 = 2.692(3), Si2−Li1 = 2.677(4), C1−Li1 = 2.259(4), C2−Li1 = 2.284(4), Li1−O1 = 1.869(4). Selected bond angles (deg): Ge1−Si1−Si2 = 94.49(2), Si1−Si2−C1 = 101.48(6), Si2−C1−C2 = 122.74(13), C1−C2−Ge1 = 119.72(13), C2−Ge1−Si1 = 97.89(5).

Scheme 1
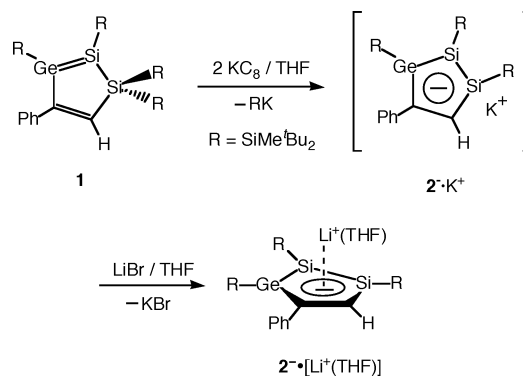
2.250(1) vs 2.3220(5) Å, C1−C2 1.343(5) vs 1.402(2) Å), whereas all single bonds are *shortened* upon reduction (Ge1−C2 1.972(3) vs 1.9303(17) Å, Si1−Si2 2.364(1) vs 2.2403(7) Å, Si2−C1 1.888(3) vs 1.8269(18) Å) (Figure 2). Definitely, such structural features give evidence for delocalization of the electron density over the five-membered ring of **2$^-$·[Li$^+$(THF)]**, which in turn means some degree of aromaticity.[9] Indeed, the nucleus-independent chemical shift (NICS),[10] recognized as a most efficient aromaticity probe, was calculated for the model compound of **2$^-$·Li$^+$** at 1 Å above the center of the ring:[11] NICS(1) = −12 (for comparison, NICS(1) for benzene = −10.6[12]). The optimized geometry[11] for **2$^-$·[Li$^+$(THF)]** reproduced the real structure well, with the char-
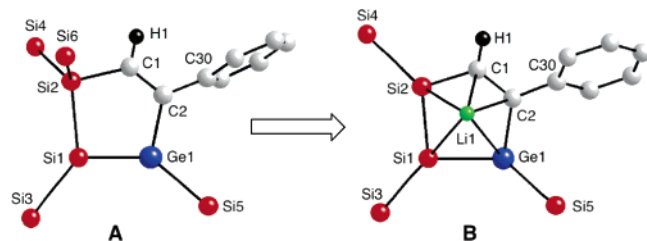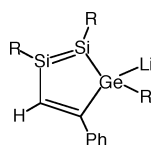
Figure 2. Structural changes taking place upon reduction of **1** (H and C atoms of *t*Bu₂MeSi substituents, H atoms of the Ph group, and the THF molecule are not shown): (A) **1**, (B) **2⁻·[Li⁺(THF)]**.

Chart 1

acteristic η^5-coordination of the Li⁺ ion and similar trends for the skeletal bond lengths.

The manifestation of the aromaticity of **2⁻·Li⁺** in solution was convincingly demonstrated by its NMR characteristics in toluene-d_8.[7] Thus, in the ^{29}Si NMR spectrum of **2⁻·Li⁺**, the two signals for the skeletal Si atoms were observed at 54.4 and 69.1 ppm, values that lie between those for the starting **1**[5] (−45.7 for sp³-Si and +124.0 ppm for sp²-Si), that is, sp³-Si in **1** is deshielded upon reduction, whereas sp²-Si in **1** is shielded. In the ^{13}C NMR spectrum of **2⁻·Li⁺**, the skeletal olefinic *C*H atom is expectedly shielded compared with that in starting **1**: 143.2 vs 150.0 ppm ($\Delta\delta$ = −6.8 ppm), whereas the olefinic *C*Ph atom is deshielded: 181.4 vs 173.6 ppm ($\Delta\delta$ = +7.8 ppm).[13] In the ^{1}H NMR spectrum of **2⁻·Li⁺**, all *t*Bu groups of the silyl substituents appeared to be nonequivalent because of the η^5-coordination of the Li⁺ ion to the five-membered ring. Most importantly, the ^{7}Li NMR resonance of **2⁻·Li⁺** was observed at −5.4 ppm, a very high-field region that is diagnostic for aromatic lithium cyclopentadienide derivatives.[14]

However, **2⁻·Li⁺** is unable to benefit from such aromatic delocalization in polar solvents, thus changing the coordination from the delocalized η^5- to a localized η^1-mode. Indeed, the NMR spectral data of **2⁻·Li⁺** in THF-d_8 are clearly different from those in toluene-d_8.[7] Thus, the ^{29}Si NMR resonances of the skeletal Si atoms of **2⁻·Li⁺** in THF-d_8 at 97.4 and 104.9 ppm are in the region for doubly bonded Si atoms.[15] In the ^{1}H NMR spectrum, there are only three signals for the *t*Bu groups, and the resonances of one of the *t*Bu₂MeSi substituents are greatly shifted to higher field (−0.33 ppm for Me and 0.80 ppm for *t*Bu), indicating the preferential presence of negative charge on the nearest skeletal atom. The ^{7}Li NMR resonance appeared at −0.6 ppm, the typical region of η^1-germyllithiums,[16] rather than the aromatic cyclopentadienide derivatives.[14] That is, in THF-d_8 solution, the anionic part of **2⁻·Li⁺** acquires the properties of the localized cyclopentadienide derivative, which features Si=Si and C=C double bonds and has a negative charge situated on the Ge atom (Chart 1).

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(6) Presumably, at first, the two-electron reduction of the Si=Ge double bond takes place, followed by the fast elimination of *t*Bu₂MeSiK to produce finally the 6π-electron Cp⁻-type system. The easy accessibility of E=E′ bonds (E, E′ = Si, Ge) for the one- and two-electron reduction with alkali metals is due to their low-lying LUMOs: (a) Lee, V. Ya.; Sekiguchi, A. *Chem. Lett.* **2004**, *33*, 84. (b) Sekiguchi, A.; Inoue, S.; Ichinohe, M.; Arai. Y. *J. Am. Chem. Soc.* **2004**, *126*, 9626.
(7) For the experimental procedure and spectral data for **2⁻·Li⁺** in toluene-d_8 and THF-d_8, see Supporting Information.
(8) For the crystal data of **2⁻·[Li⁺(THF)]**, see Supporting Information.
(9) Obviously, the delocalization of the negative charge in **2⁻·Li⁺** does not imply the even distribution of electron density over all skeletal atoms because of their different electronegativities. The largest part of the negative charge is expected to accumulate on the Ge atom, which is evident from the different degree of the skeletal atoms' pyramidalization: Ge1 (342.89°), Si1 (350.75°), Si2 (357.03°), C1 (359.94°), C2 (359.79°).
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(13) Such trends in the ^{13}C NMR chemical shift changes upon the reduction of siloles were predicted by the recent DFT calculations; see ref 4h.
(14) The delocalized lithium cyclopentadienide derivatives typically exhibit very diagnostic highly upfield shifted ^{7}Li NMR resonances because of their aromatic ring current: (a) −8.37 ppm for C₅H₅Li: Elschenbroich, Ch.; Salzer, A. *Organometallics, A Concise Introduction*, 2nd ed.; VCH: Weinheim, Germany, 1992. (b) −7.51 ppm for (HMe₂Si)₅C₅Li: Sekiguchi, A.; Sugai, Y.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 1144. (c) −5.63 ppm for [η⁵-Li·TMEDA][η⁵-Li]₁/₂[η¹-Li]₁/₂[Et₄C₄-Ge]: Choi, S.-B.; Boudjouk, P.; Hong, J.-H. *Organometallics* **1999**, *18*, 2919.
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