Dilithium 1,4-Disilacyclohexa-2,5-diene-1,4-diide by the Reduction of 1,4-Disilabicyclo[2.2.0]hexa-2,5-diene: Synthesis and Characterization

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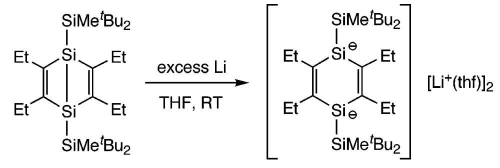
Summary: The dilithium 1,4-bis(di-tert-butylmethylsilyl)-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene-1,4-diide compound $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$ *was prepared by the reduction of 1,4-bis(di-tert-butylmethylsilyl)-2,3,5,6-tetraethyl-1,4-disilabicyclo[2.2.0]-hexa-2,5-diene (**1**) with lithium in THF.* $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$ *has a boat conformation of its six-membered ring with a folding angle of 124.0°.*

The chemistry of dianionic species of Si-containing π-electron systems has attracted a great deal of interest, owing to their unique structures, electronic properties, and potential ferromagnetism.[1] Among them, one can mention the first representatives of the stable tetrasilyl-substituted cyclobutadiene dianions prepared by us, which show a remarkable degree of six-π-electron aromaticity.[1d−f] The doubly reduced derivative of hexakis(trimethylsilyl)benzene, which was appreciably deformed into the boat form,[2−4] and the dianionic derivative of 1,2,4,5-tetrakis(trimethylsilyl)benzene[5] are also worth mentioning as important examples. The dilithium and dipotassium salts of 9,10-dimethyl-9,10-disilaanthracene have also been reported by Ando et al.[6] Recently, we reported the synthesis of a derivative of 1,4-disila-Dewar benzene, 1,4-bis(di-*tert*-butylmethylsilyl)-2,3,5,6-tetraethyl-1,4-disilabicyclo[2.2.0]hexa-2,5-diene (**1**), by the reduction of the corresponding dichloride with KC_8.[7] In this paper, we report the reduction of **1** with metallic lithium, leading to the formation of the dilithium compound 1,4-bis(di-*tert*-butylmethylsilyl)-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene-1,4-diide ($\mathbf{2}^{2-}$), representing a nonaromatic eight-π-electron cyclic system. The dianionic derivative **2**, with an unusual molecular structure, was isolated in pure form as the dilithium salt; it has been fully characterized, including by X-ray crystallography.

Scheme 1



1 $\mathbf{2}^{2-}\cdot[Li^+(thf)]_2$

The reduction of **1** with an excess amount of lithium effectively proceeded in dry THF at room temperature to form the corresponding dianionic derivative $\mathbf{2}^{2-}$, isolated in 84% yield as dark red crystals in the form of its dilithium salt $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$ (Scheme 1).[8] The product $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$, representing the 1,4-dianionic derivative of 1,4-disila-Dewar benzene **1**, can be alternatively considered as a derivative of the 1,4-disilabenzene dianion.

The crystal structure of $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$ was determined by X-ray crystallography and is shown in Figure 1.[9] There are several remarkable structural features of $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$ meriting special discussion. First of all, quite similarly to the known hexakis(trimethylsilyl)benzene dianion,[2a] the six-membered ring of $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$ is not planar (folding angle 124°) and adopts a boat conformation. Consequently, both lithium ions, each of them coordinated with one THF molecule, reside on the same side of the six-membered ring, despite the evident electrostatic repulsion caused by this spatial arrangement. However, such electrostatic loss might be overcompensated by the significant interactions of the Li^+ ions with the two negatively charged silicon atoms and the π-electron density of the C═C double bonds. Indeed, each lithium atom is situated just above the C═C bonds (Li1 is above C1═C2 and Li2 is above C3═C4), thus making their orbital interactions most favorable. This was reflected in the LUMO of the starting compound **1**, which has the major coefficients on both Si atoms and minor, but still important, contributions on both C═C bonds. Such an interaction was demonstrated by the C−Li interatomic contacts of 2.271(4)−2.306(4) Å, the extent of which was, however, smaller than that of the hexakis(trimethylsilyl)benzene dianion (2.099(20)−2.127(18) Å).[2a] As a result of the interaction, both C═C bonds in $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$ are slightly elongated (1.381(3) and 1.385(3) Å) compared with those of the starting **1** (1.356(6) Å), whereas all Si−C skeletal bonds (1.8924(19)−1.9091(19)

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[1] For recent work on the dianion species of π-electron systems, see: (a) Sekiguchi, A.; Matsuo, T.; Ebata, K.; Sakurai, H. *Chem. Lett.* **1996**, 1133. (b) Sekiguchi, A.; Matsuo, T.; Sakurai, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1661. (c) Matsuo, T.; Sekiguchi, A.; Ichinohe, M.; Ebata, K.; Sakurai, H. *Organometallics* **1998**, *17*, 3143. (d) Sekiguchi, A.; Matsuo, T.; Watanabe, H. *J. Am. Chem. Soc.* **2000**, *122*, 5652. (e) Matsuo, T.; Mizue, T.; Sekiguchi, A. *Chem. Lett.* **2000**, 896. (f) Ishii, K.; Kobayashi, N.; Matsuo, T.; Tanaka, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2001**, *123*, 5356.

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[8] Spectral and characterization data for $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$: dark red crystals; mp 157−159 °C; ^1H NMR (toluene-d_8, δ) 0.45 (s, 6 H), 1.27 (t, J = 7.3 Hz, 12 H), 1.30 (m, 8 H, THF), 1.42 (s, 36 H), 2.78 (dq, J = 7.2, 13.0 Hz, 4 H), 3.07 (dq, J = 7.2, 13.0 Hz, 4 H), 3.42 (m, 8 H, THF); ^{13}C NMR (toluene-d_8, δ) −2.9, 19.2, 21.9, 25.4 (THF), 28.5, 31.2, 69.2 (THF), 148.3; ^{29}Si NMR (toluene−d_8, δ) −47.6 (skeletal Si), 7.1 (substituents Si); ^7Li NMR (toluene−d_8, δ) −1.54.

[9] Crystal data for $\mathbf{2}^{2-}\cdot 2[Li^+(thf)]$ at 120 K: $C_{38}H_{78}Li_2O_2Si_4$, mol wt 693.24, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 10.8090(2)$ Å, $b = 18.5430(7)$ Å, $c = 22.7350(8)$ Å, $\beta = 97.8140(2)°$, $V = 4514.5(2)$ Å^3, $D_{calcd} = 1.020$ g cm^{-3}, $2\theta_{max} = 51.50°$, $R1(I > 2\sigma(I)) = 0.0499$, wR2(all data) = 0.1382 for 8056 reflections and 433 parameters, GOF = 1.060.

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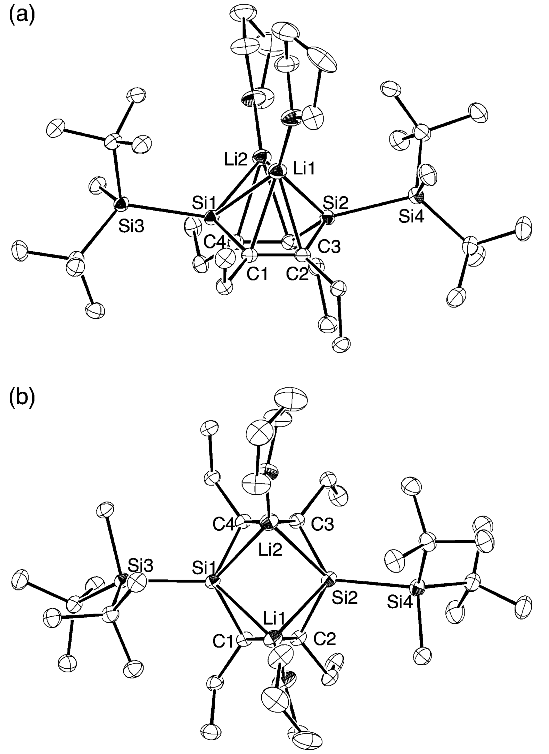


Figure 1. ORTEP drawing of **2**$^{2-}$·2[Li$^+$(thf)] (30% thermal ellipsoids, hydrogen atoms are not shown): (a) side view; (b) top view. Selected bond lengths (Å): Si1−Si3 = 2.3689(7), Si2−Si4 = 2.3582(7), Si1−C1 = 1.9009(18), Si1−C4 = 1.9091(19), Si2−C2 = 1.8924(19), Si2−C3 = 1.8932(18), C1−C2 = 1.381(3), C3−C4 = 1.385(3), Si1−Li1 = 2.529(3), Si1−Li2 = 2.527(3), Si2−Li1 = 2.510(3), Si2−Li2 = 2.567(3), Li1−C1 = 2.281(4), Li1−C2 = 2.271(4), Li2−C3 = 2.306(4), Li2−C4 = 2.284(4), Li1−Li2 = 3.020(5), Selected bond angles (deg): C1−Si1−C4 = 105.93(8), C2−Si2−C3 = 105.98(8), Si1−C1−C2 = 114.84(13), Si1−C4−C3 = 115.07(13), Si2−C2−C1 = 115.83(13), Si2−C3−C4 = 115.31(14), Si3−Si1−C1 = 120.32(6), Si3−Si1−C4 = 117.66(6), Si4−Si2−C2 = 115.99(6), Si4−Si2−C3 = 126.47(6).

Å) in **2**$^{2-}$·2[Li$^+$(thf)] are shortened by 0.017−0.026 Å relative to those of **1**. Moreover, the Si−Li bond distances of 2.510(3)−2.567(3) Å are somewhat shorter than those of the typical solvated silyllithium derivatives (2.67−2.70 Å).[10]

Depending on the position of the Li$^+$ ion, the four isomers for the dianion are possible; the boat form **3a**$^{2-}$, the inverse sandwich **3b**$^{2-}$, and syn and anti forms (**3c**$^{2-}$ and **3d**$^{2-}$, respectively). A theoretical study on dilithium 1,4-bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-disilacyclohexa-2,5-diene-1,4-diide (**3**$^{2-}$·2[Li$^+$]) suggests that the boat form **3a**$^{2-}$ is preferred over the inverse sandwich **3b**$^{2-}$ (+6.7 kcal/mol), syn (+39.3 kcal/mol), and anti (38.3 kcal/mol) derivatives (Figure 2),[11] which agrees well with the present experimental results for **2**$^{2-}$·2[Li$^+$(thf)]. The significant folding of the six-membered ring of **2**$^{2-}$ into a boat form results from interactions between the two Li$^+$ ions with the two negatively charged Si atoms and the π-electron density of the C=C double bonds. Apparently the steric factors are not important for the deformation into a boat form in **2**$^{2-}$.

The ^{29}Si NMR signals of **2**$^{2-}$·2[Li$^+$(thf)] in toluene-d_8 were observed at −47.6 ppm (skeletal Si atoms) and 7.1 ppm (substituent Si atoms); the former resonance is in the same range as that of the dianion in dilithium 9,10-dimethyl-9,10-disilaanthracene (−45.4 ppm in THF-d_8).[6b] The ^{13}C NMR resonances of the doubly bonded C atoms appeared at 148.3 ppm, being greatly shifted upfield compared with those in the starting compound **1** (168.4 ppm), indicating a significant transfer of the negative charge density from the Si atoms to the C=C double bonds through their conjugative interaction (this was also seen in the crystal structure of **2**$^{2-}$·2[Li$^+$(thf)]). A single ^{7}Li NMR resonance of **2**$^{2-}$·2[Li$^+$(thf)] was observed at −1.54 ppm, in a range similar to that of the dilithium salt of the nonaromatic hexakis(trimethylsilyl)benzene dianion (−1.48 ppm),[2a] suggesting a localized nonaromatic structure for **2**$^{2-}$·2[Li$^+$(thf)] as well. Thus, all structural, spectral and computational data of **2**$^{2-}$·2[Li$^+$(thf)] support its localized nonaromatic structure.

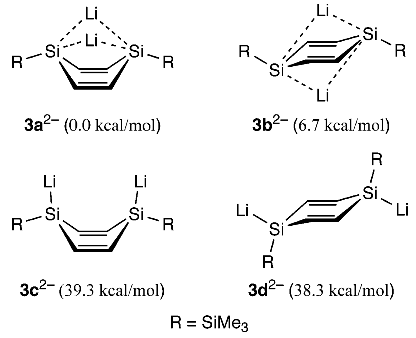
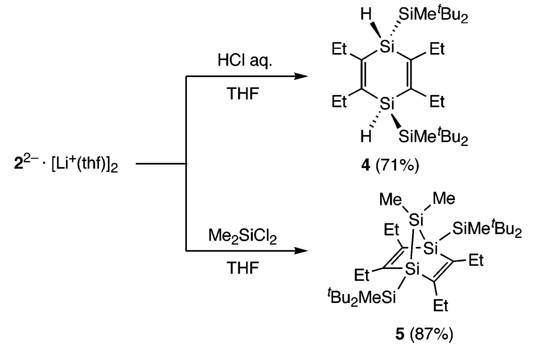


Figure 2. Relative energies for the isomers of dilithium 1,4-bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-disilacyclohexa-2,5-diene-1,4-diide **3**$^{2-}$·2[Li$^+$] (kcal/mol) calculated at the B3LYP/6-31G(d) level (methyl groups on the C=C bonds are omitted for clarity).

Scheme 2



The quenching reactions of **2**$^{2-}$·2[Li$^+$(thf)] with HCl/H$_2$O and Me$_2$SiCl$_2$ expectedly produced the corresponding mono- and bicyclic derivatives *anti*-**4** and **5** in good yields (Scheme 2).[12]

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Supporting Information Available: Experimental procedures and spectral data for **2**$^{2-}$·2[Li$^+$(thf)], *anti*-**4**, and **5**, optimized geometries of **3a**−**d**$^{2-}$·2[Li$^+$], and tables of crystallographic data, including atomic positional and thermal parameters, for **2**$^{2-}$·2[Li$^+$(thf)] (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Geometry optimizations for **3a**−**d**$^{2-}$·2[Li$^+$] and the NPA charge distributions for **3a**$^{2-}$·2[Li$^+$] were performed with the GAUSSIAN 98 program package at the B3LYP/6-31G(d) calculation level.

(12) For the experimental procedures and spectral data for *anti*-**4** and **5**, see the Supporting Information.