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The First Isolation and Full Characterization of Fulvene Dianion. Synthesis and X-ray Structure of Dilithium Hexasilylfulvene Dianion

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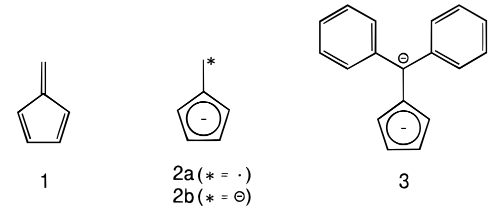
*Summary: Treatment of hexasilylfulvene (**4**) with lithium metal in tetrahydrofuran yields yellow crystals of the dilithium hexasilylfulvene dianion (**5**). The dilithium hexasilylfulvene dianion (**5**) has a monomeric structure and forms a contact ion pair (bis-CIP) in the crystals. One of the lithium atoms is located above the center of the five-membered ring, whereas the other one is bonded to the exocyclic carbon atom. The bis-CIP structure determined by X-ray crystallography is maintained in solution.*

Fulvene (**1**) is one of the most important cross-conjugated π-electron systems; it reacts with nucleophiles selectively at the 6-position to produce a cyclopentadienide ion (Chart 1).[1] Upon treatment with alkali metals or lithium naphthalenide, fulvene also readily undergoes reduction to afford 6,6′-bifulvenyl through coupling of the anion radical intermediate **2a**.[2] Fulvene dianion **2b**, as a result of the two-electron reduction, is an interesting anionic species with regard to its structure, bonding, and delocalization of the negative charge.[3] For electronic and steric reasons, the introduction of the phenyl groups at the 6-position allows the formation of a fulvene dianion. Previously, Oku et al. reported that the alkali-metal reduction of 6,6-diphenylfulvene produced a dihydro compound via dianion **3**.[4] Subsequently, Oda et al. reported the NMR observation of **3** in THF.[5] However, the fulvene dianion has not as yet been isolated and there is no precedent concerning its molecular structure. Herein, we report the first successful isolation, full characterization, and molecular structure of dilithium hexasilylfulvene dianion, which has a novel six-center/eight π-electron system.[6]

Chart 1



Treatment of **4**[7] with excess lithium metal in dry oxygen-free tetrahydrofuran at room temperature af-

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(6) We have previously reported the successful preparations of dilithium derivatives of silyl-substituted six-center/eight π-electron systems. For benzene dianions, see: (a) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 1464. (b) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7081. For the dimethylenecyclobutene dianion, see: (c) Sekiguchi, A.; Matsuo, T.; Ebata, K.; Sakurai, H. *Chem. Lett.* **1996**, 1133.

(7) Hexasilylfulvene (**4**) was prepared as red crystals in 26% yield by the intramolecular reaction of 3,3,5,5,8,8,10,10,13,13,15,15-dodecamethyl-3,5,8,10,13,15-hexasilacyclopentadeca-1,6,11-triyne with [Mn(CO)$_3$(Me-Cp)] by irradiation ($\lambda > 300$ nm) in THF. Procedure for the synthesis of the dodecamethylhexasilacyclopentadeca-1,6,11-triyne. 3,3,5,5-tetramethyl-3,5-disilahepta-1,6-diyne (10.97 g, 0.061 mol) in THF (20 mL) was added to a THF solution of ethylmagnesium bromide (100 mL, 0.124 mol) to produce the Grignard reagent of the 1,6-diyne. The THF solution of the resulting Grignard reagent and 2,9-dichloro-2,4,4,7,7,9-hexamethyl-2,4,7,9-tetrasiladeca-5-yne (20.01 g, 0.056 mol) in THF (20 mL) were added dropwise to refluxing THF (500 mL), and the mixture was heated overnight. The reaction mixture was poured into hexane and hydrolyzed with dilute hydrochloric acid, followed by extraction with hexane. The organic layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure to give the triyne (100−150 °C/0.15 mmHg, Kugelrohr distillation). Recrystallization from ethanol gave pure colorless crystals in 38% yield. This compound had already been isolated from the reaction mixture of $BrMgC{\equiv}CMgBr$ and $ClMe_2SiCH_2SiMe_2Cl$ in very low yield; see: Kloster-Jensen, E.; Eliassen, G. A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 565. Mp: 112−113 °C. ^{1}H NMR (CDCl$_3$, δ): −0.08 (s, 6 H), 0.23 (s, 36 H). ^{13}C NMR (CDCl$_3$, δ) 1.2, 2.9, 115.0. ^{29}Si NMR (CDCl$_3$, δ) −19.9. Procedure for the synthesis of **4**: a mixture of the hexasilacyclopentadeca-1,6,11-triyne (227 mg, 0.49 mmol) and [Mn(CO)$_3$(Me-Cp)] (160 mg, 0.73 mmol) in THF (30 mL) was irradiated with a 500 W high-pressure mercury lamp for 8 h through the cutoff filter ($\lambda > 300$ nm) at room temperature. After removal of the manganese complex, the reaction mixture was chromatographed on silica gel to produce red crystals of **4** in 26% yield. Mp: 170 °C. ^{1}H NMR (CDCl$_3$, δ): −0.12 (s, 4 H, CH$_2$), 0.29 (s, 2 H, CH$_2$), 0.30 (s, 12 H, CH$_3$), 0.34 (s, 12 H, CH$_3$), 0.41 (s, 12 H, CH$_3$). ^{13}C NMR (CDCl$_3$, δ) 1.8 (CH$_2$), 1.9 (CH$_3$), 3.2 (CH$_3$), 3.4 (CH$_2$), 3.5 (CH$_3$), 143.8 (C), 167.1 (C), 168.4 (C), 182.9 (C). ^{29}Si NMR (CDCl$_3$, δ) −13.4, −6.7, −2.4. UV (hexane; λ_{max}/nm (ϵ)): 215 (21 000), 298 (19 500); HRMS (m/z): found 462.1894, calcd for $C_{21}H_{42}Si_6$ 462.1902. Crystal data for **4** at 130 K: molecular formula = $C_{21}H_{42}Si_6$, MW = 463.09, triclinic, $a = 11.333(1)$ Å, $b = 11.877(1)$ Å, $c = 20.749(1)$ Å, $\alpha = 94.883(3)°$, $\beta = 97.185(3)°$, $\gamma = 95.948(4)°$, $V = 2773.4(5)$ Å^3, space group $P\bar{1}$, $Z = 4$, $D_{calcd} = 1.109$ g/cm^3. The final R factor was 0.034 ($R_w = 0.040$) for 8231 reflections with $I_o > 3\sigma(I_o)$.

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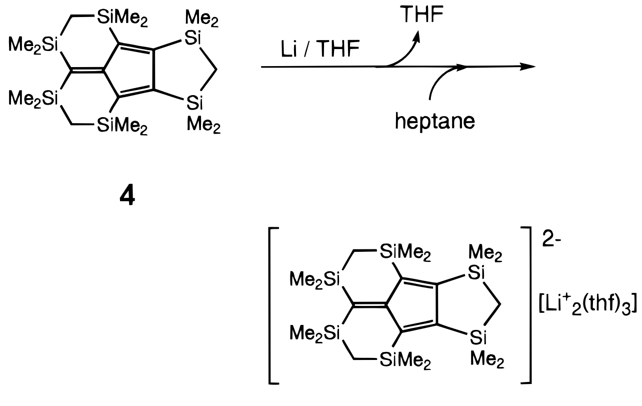
Scheme 1



forded a yellow solution of the dianion **5** within 1 h (Scheme 1). The dilithium hexasilylfulvene dianion (**5**) was isolated as air- and moisture-sensitive yellow crystals, which were recrystallized from heptane.[8]

The molecular structure of **5** has been confirmed by X-ray crystallography (Figure 1).[9] The dilithium hexasilylfulvene dianion **5** has a monomeric structure and forms a contact ion pair (bis-CIP) in the crystals. One THF molecule is coordinated with Li1, and two THF molecules are coordinated with Li2. Li1 and Li2 are located above and below the π-skeleton, respectively. Li1 is situated above the approximate center of the five-membered (Cp) ring. The Li−C distances for the Cp ring range from 2.164(3) to 2.191(3) Å (average 2.179 Å), so that the Li-to-Cp interaction clearly qualifies as η^5. Li2 is bonded to two carbon atoms (C6 and C9) with distances of 2.136(6) Å for Li2−C6 and 2.325(6) Å for Li2−C9 (Figure 2).

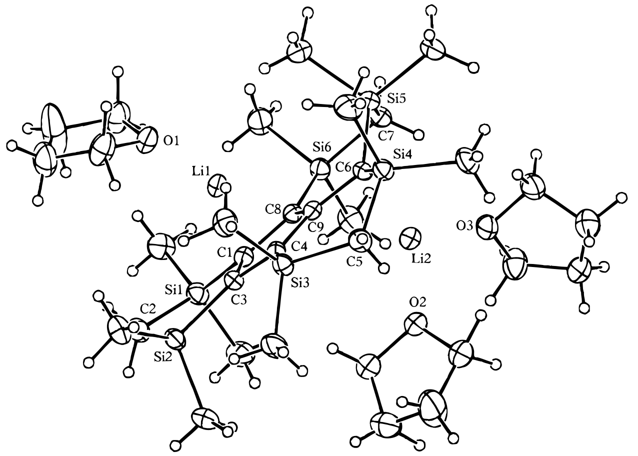


Figure 1. Molecular structure of **5**, with 50% probability ellipsoids. Selected bond distances (Å): C1−C3, 1.441(4); C3−C4, 1.456(4); C4−C9, 1.442(4); C8−C9, 1.463(4); C1−C8, 1.451(4); C6−C9, 1.511(4); C1−Si1, 1.862(3); C3−Si2, 1.861(3); C4−Si3, 1.852(3); C6−Si4, 1.820(3); C6−Si5, 1.827(3); C8−Si6, 1.864(3); Li1−C1, 2.174(3); Li1−C3, 2.164(3); Li1−C4, 2.176(3); Li1−C9, 2.191(3); Li1−C8, 2.189(3); Li2−C6, 2.136(6); Li2−C9, 2.325(6). Selected bond angles (deg): C3−C1−C8, 108.2(3); C1−C3−C4, 108.1(3); C3−C4−C9, 108.2(2); C4−C9−C8, 107.7(3); C1−C8−C9, 107.8 (3); C4−C9−C6, 127.7(3); C6−C9−C8, 124.6(3).

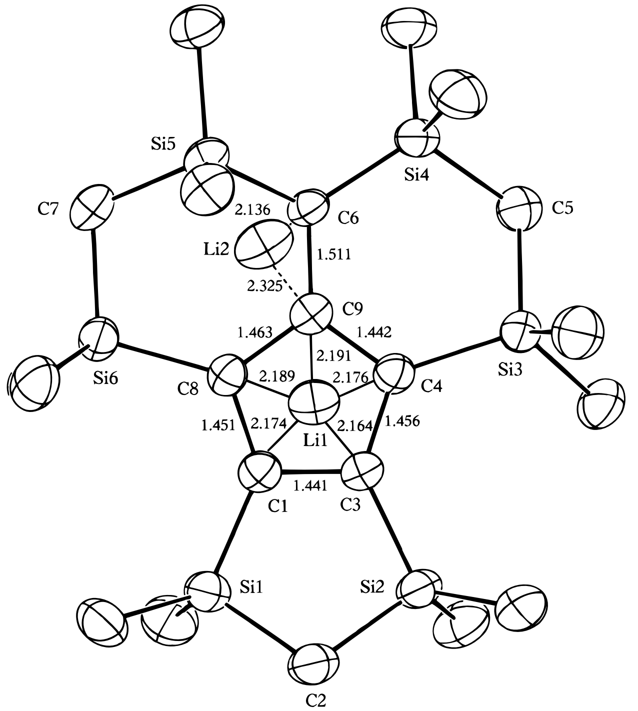


Figure 2. Section from the structure of **5** with selected distances (Å).

The Li distance from the ring centroid (1.795 Å) is comparable to that observed in [(Ph$_2$C=O)Li·{C$_5$(SiMe$_2$H)$_5$}] (1.818 Å),[10] and somewhat shorter than those observed in Li(C$_5$H$_4$Me)TMEDA (1.92 Å),[11] Li[C$_5$H$_4$SiMe$_3$]TMEDA (1.93 Å),[12] [(isodiCp)$_2$Li]$^-$ (1.91 Å),[13] LiCp$_2$$^-$ (2.008 Å),[14] [Li$_2$(TMEDA)$_2$(C$_5$H$_4$Me)]$^-$ (2.00 Å).[15] The Li distance from the Cp ring of the tetralithium octasilyltrimethylenecyclopentene tetraanion,[16] bridged by Me$_2$SiCH$_2$SiMe$_2$, is also slightly short (1.827 Å), as was the Li distance in **5**. The relatively short Li distance of **5** compared with the reported Li distances may be due to the bridged structure consisting of Me$_2$SiCH$_2$SiMe$_2$ chains.

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(8) Procedure for the synthesis of **5**: the crystals of **4** (22 mg, 0.05 mmol) and lithium metal (30 mg, 4.3 mmol) were placed in a reaction tube with a magnetic stirrer. After degassing, dry oxygen-free THF (1.5 mL) was introduced by vacuum transfer and the mixture was stirred at room temperature to give a yellow solution of the dianion **5** within 1 h. After the solvent was removed in vacuo, degassed heptane was introduced by vacuum transfer. Then, after the lithium metal was removed, the solution was cooled to afford yellow crystals of **5** quantitatively. ^{1}H NMR (C$_7$D$_8$, δ): 0.04 (s, 4 H, CH$_2$), 0.18 (s, 2 H, CH$_2$), 0.49 (s, 12 H, CH$_3$), 0.55 (s, 24 H, CH$_3$), 1.39 (br s, 12 H, THF), 3.42 (br s, 12 H, THF). ^{13}C NMR (C$_7$D$_8$, δ): 3.4 (CH$_2$), 4.4 (CH$_3$), 5.27 (CH$_2$), 5.34 (CH$_3$), 6.0 (CH$_3$), 25.3 (THF), 30.2 (C), 66.4 (THF), 112.1 (C), 138.6 (C), 164.9 (C). ^{29}Si NMR (C$_7$D$_8$, δ) −14.4, −12.5, −5.4. ^{6}Li NMR (C$_7$D$_8$, δ): −3.18 (from LiCl in MeOH).

(9) Crystal data for **5** at 180 K: molecular formula = C$_{33}$H$_{66}$Li$_2$O$_3$Si$_6$, MW = 693.29, monoclinic, $a = 11.579(1)$ Å, $b = 11.652(1)$ Å, c = 31.332(2) Å, $\beta = 95.805\ (4)°$, $V = 4205.58\ (3)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_{\text{calcd}} = 1.095$ g/cm^3. The final R factor was 0.045 ($R_w = 0.054$) for 5783 reflections with $I_o > 3\sigma(I_o)$.

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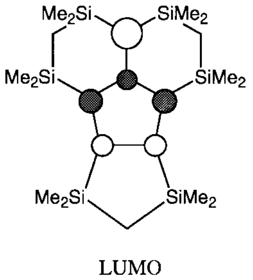

Figure 3. Schematic representation of the LUMO of **4** calculated by PM3.

The distance C6−C9 (1.511(4) Å) is considerably elongated by 0.135(4) Å relative to that of **4** (1.376(4) Å). The distances of C3−C4 (1.456 (4) Å) and C1−C8 (1.451(4) Å) are also stretched by 0.079(4) and 0.073(4) Å compared with **4** (1.377(4) and 1.378 (4) Å for **4**, respectively). In contrast, the distances C1−C3 (1.441(4) Å), C4−C9 (1.442(4) Å), and C8−C9 (1.463(4) Å) of **5** are shortened by 0.047−0.069 Å (1.508(4), 1.511(4), and 1.510(4) Å, respectively, for **4**). That is, the C−C double bonds of **4** are elongated, whereas the C−C single bonds are shortened by the reduction. Therefore, the geometry of **5** reflects the nature of the LUMO of **4** (Figure 3).[17] Thus, the C6−C9, C3−C4, and C1−C8 bonds are antibonding, whereas the C1−C3, C4−C9, and C8−C9 bonds are bonding.

The Cp ring is an almost planar equilateral pentagon, as determined by the internal bond angles of 107.7(3)−108.2(3)° (average 108.0°) and the sum of the bond angles (540.0°). One of the negative charges is largely localized at the exocyclic C6 carbon atom and is stabilized by both the Si4 and Si5 atoms, so that this carbon atom is slightly pyramidalyzed (351.4° for the sum of the bond angles). Consequently, the bond lengths of the C6−Si4 bond (1.820(3) Å) and the C6−Si5 bond (1.827(3) Å) in **5** are shortened markedly compared with those of **4** (1.888(3) and 1.897(3) Å, respectively) by $p\pi-\sigma^*$ conjugation. The other negative charge is delocalized over the Cp ring to form the cyclpentadienide ion. The X-ray structure of the related dianionic derivative dilithium acepentalenediide has been reported.[18]

The structure of **5** in solution was characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{6}Li NMR spectroscopy. The NMR data of **5** in toluene-d_8 indicate the highly symmetric bis-CIP structure, as found by X-ray crystallography. However, the two Li$^+$ ions of **5** are not fixed to the π-skeleton and undergo rapid exchange with each other on the NMR time scale, as depicted in Figure 4.[19] Thus, the ^{6}Li NMR spectrum of **5** in toluene-d_8 yielded only one signal, appearing at −3.18 ppm. The exchange of the Li$^+$ ions was not suppressed in the temperature range of 193−298 K. In the ^{13}C NMR spectrum, three sets of methyl carbons (4.4, 5.34, and 6.0 ppm) and two sets of methylene carbons (3.4 and 5.27 ppm) were observed, as well as four sets of quaternary carbons at 30.2 (C6), 112.1 (C4 and C8), 138.6 (C1 and C3), and 164.9 (C9) ppm. The ^{13}C signal of the C6 atom was observed at 30.2 ppm, which is a marked shift to upper field by 152.7 ppm relative to that of **4** (182.9 ppm). This shift is due to the negative charge at the exocyclic C6 carbon atom of **5**. The ^{29}Si NMR spectrum showed three sets of signals at −14.4, −12.5, and −5.4 ppm shifting to upper field, relative to those of **4**.

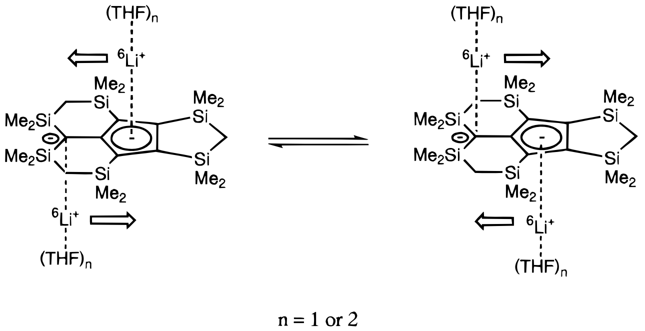

Figure 4. Lithium interconversion of **5**.

The negative charge of the present dilithium hexasilylfulvene dianion is stabilized not only by the six silicon atoms but also by the aromatic cyclopentadienide ion. The interconversion of the two Li$^+$ ions in solution readily occurs due to the planar structure of the π-system.

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Supporting Information Available: Figures giving thermal ellipsoid plots and tables giving the details of the X-ray structure determination, fractional atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for **4** and **5** (24 pages). Ordering information is given on any current masthead page.

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(17) The geometry of **4** by X-ray diffraction was successfully reproduced by PM3 calculation. The PM3 calculation of 4^{2-} has also been carried out. The details of the calculation will be reported elsewhere.

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(19) The ^{6}Li NMR chemical shift of **5** (δ −3.18) is intermediate between those of (Me$_3$Si)$_2$CHLi (δ 2.46) and [(Ph$_2$C=O)Li·{C$_5$(SiMe$_2$H)$_5$}] (δ −7.51). This also supports the facile interconversion of Li$^+$ ions as depicted in Figure 4.