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Silyl-Substituted Dilithium Salt of Fulvene Dianion with 6 Center/8 Electron π-System: Synthesis and Characterization

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Treatment of fulvene derivatives bridged by Me_2Si–X–$SiMe_2$ chains (**2a** : X = CH_2, **2b** : X = O) with lithium metal in THF yields yellow crystals of the dilithium salt of fulvene dianion (**3a** and **3b**) with 6 center/8 electron π-system. The molecular structure of the dianion dilithium **3a** has been established by X-ray crystallography. The dianion dilithium **3a** has a monomeric structure and forms a contact ion pair (bis-CIP) in the crystal. One of the lithium atoms is located above the center of the five-membered ring by η^5-coordination, whereas the other one is bonded to the *exo*-cyclic carbon atom by η^2-coordination. The structural parameters of **3a** are discussed in comparison to those of the neutral starting molecule **2a**. The structure of **3a** in solution has also been discussed on the basis of NMR spectroscopic data. The two lithium ions of **3a** are not fixed to the π-skeleton in toluene-d_8, but are fluxional, giving a highly symmetrical bis-CIP structure. The spectral data in THF-d_8 at 298 K also suggest the bis-CIP structure of **3a**. However, the lithium ion on the five-membered ring is dissociated to yield an ion pair (CIP-SSIP) at low temperature in THF-d_8, and two dianion species (bis-CIP and CIP-SSIP) were found in THF-d_8.

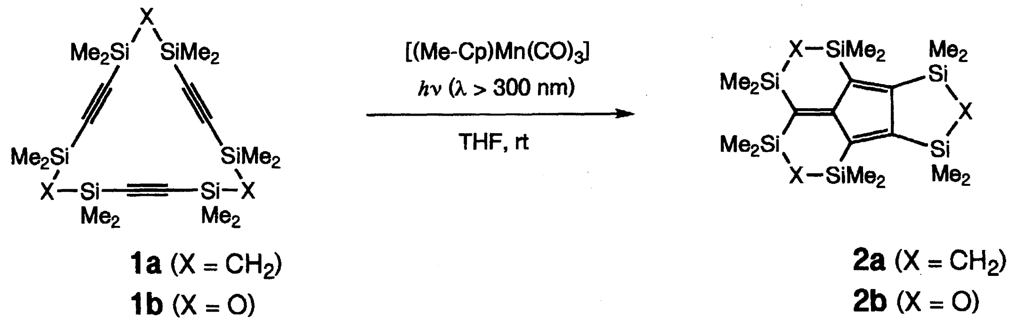
Fulvene is one of the most important cross-conjugated π-electron systems based on a five-membered ring and it reacts with nucleophiles selectively at the 6-position to produce a cyclopentadienide ion.[1] Upon treatment with alkali metals or lithium naphthalenide, fulvene also readily undergoes reduction to afford 6,6′-bifulvenyl through coupling of the anion radical intermediate.[2] Fulvene dianion, 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.[4] Subsequently, Oda et al. reported the NMR observation of 6,6-diphenylfulvene dianion in THF.[5] However, the fulvene dianion has not as yet been isolated and there is no report concerning its molecular structure.

We have shown that the introduction of a silyl group to the π-electron system causes remarkable steric and electronic perturbation.[6] The most remarkable feature of a silyl-substituted π-electron system is the ability to form the corresponding anion species by reduction with alkali metals. We have previously reported successful preparations of dianion dilithium derivatives of silyl-substituted ethylenes,[7] styrenes,[8] benzenes,[9] dimethylenecyclobutene,[10] [4]radialene,[11] and persilyl-substituted cyclopentadienide.[12] Recently, we have reported the tetraanion tetralithium of trimethylenecyclopentene derivatives as a silyl-substituted 8 center 12 electron π-system.[13] Herein, we wish to report a detailed study of fulvene dianion dilithium (**3**) bridged by Me_2Si–X–$SiMe_2$ chains (**3a** : X = CH_2, **3b** : X = O) as a new silyl-substituted 6 center 8 electron π-system, including the crystal structures of fulvene dianion dilithium (**3a**) and a precursor of the fulvene derivative (**2a**).[14]

Results and Discussion

Synthesis of 2. Hexasilylfulvene derivatives bridged by Me_2Si–X–$SiMe_2$ chains (**2a** : X = CH_2, **2b** : X = O) were prepared by the intramolecular cyclotrimerization of the macrocyclic silyltriynes. Thus, the fulvene **2a** linked by silmethylene chains was prepared as red crystals in 26% yield by the intramolecular reaction of dodecamethyl-3,5,8,10,13,15-hexasilacyclopentadeca-1,6,11-triyne (**1a**) with [(MeCp)Mn $(CO)_3$] by irradiation ($\lambda > 300$ nm) in THF at room temperature (Scheme 1).[15] In a similar manner, the fulvene **2b** bridged by siloxane chains has also been synthesized by the reaction of dodecamethyl-3,5,8,10,13,15-hexasila-4,9,14-trioxacyclopentadeca-1,6,11-triyne (**1b**).[16] In the reaction of the triyne **1b**, the intermediate vinylidene complex was successfully isolated; its molecular structure was confirmed by X-ray crystallography.[16]

Molecular Structure of 2a. We have performed the X-ray diffraction of the fulvene **2a**. There are two independent molecules in the unit cell (Molecule 1 and Molecule 2). The two molecules have almost same geometry. The molecular



Scheme 1.

structure of **2a** (Molecule 2) is shown in Fig. 1. Selected bond distances, bond angles, and dihedral angle are listed in Table 1. The π-skeleton of **2a** is an almost planar structure. The internal bond angles of the central five-membered ring are 106.7(2)—109.5(2)° (av 108.0°), and the sum of the bond angles is 539.9°. The angle formed by C22–C23–C24–C26 and C24–C25–C26 planes is 2.4(3)°. The substantial bond alternation between the single and double bonds of the π-skeleton of **2a** shows the structural feature as a conjugated diene. The C–C single bond lengths (av 1.510 Å) range from 1.508(4) to 1.511(4) Å, whereas the double bond lengths (av 1.377 Å) range from 1.376(4) to 1.378(4) Å. The five- and two six-membered rings containing the $Me_2SiCH_2SiMe_2$ fragments have almost envelope conformations.

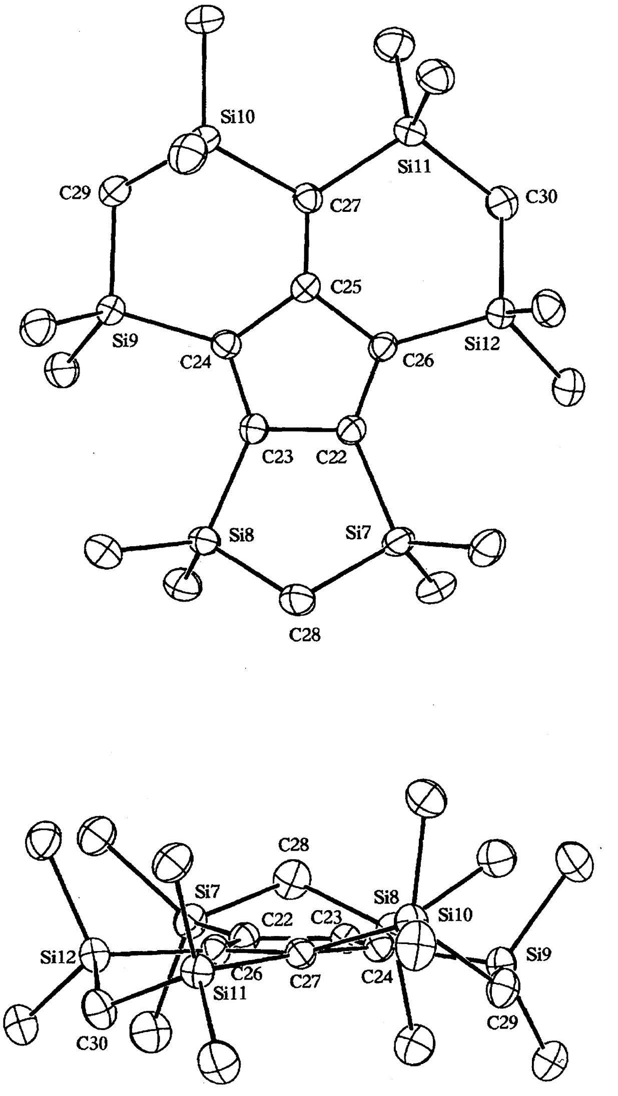


Fig. 1. ORTEP drawing of **2a**: upper, top view; below, side view.

Table 1. Selected Bond Distances (Å), Angles (deg), and Dihedral Angle (deg) of **2a**[a]

Atoms	Exptl (X-ray)	Atoms	Exptl (X-ray)
	Bond distances		
C22–C23	1.508(4)	C22–C26	1.377(4)
C23–C24	1.378(4)	C24–C25	1.510(4)
C25–C26	1.511(4)	C25–C27	1.376(4)
Si7–C22	1.879(3)	Si8–C23	1.883(3)
Si9–C24	1.873(3)	Si10–C27	1.897(3)
Si12–C26	1.866(3)	Si11–C27	1.888(3)
	Bond angles		
C23–C22–C26	109.5(2)	C22–C23–C24	109.3(3)
C23–C24–C25	107.3(3)	C24–C25–C26	106.7(2)
C24–C25–C27	126.9(3)	C26–C25–C27	126.3(3)
C22–C26–C25	107.1(3)		
	Dihedral angle		
C22–C23–C24–C26/C24–C25–C26			2.4(3)

a) Atomic numbers are given in Fig. 1. Standard deviations are in parentheses.

π-MO of 2. Consideration of π-MO of **2a** is important to understand the nature of π-electron system. The level of LUMO (−0.19 eV) is remarkably lowered by silyl groups. The schematic drawing of the LUMO of **2a** is shown in Fig. 2. In the LUMO, C2–C3, C1–C5, and C4–C5 bonds are bonding, while C1–C2, C3–C4, and C5–C6 bonds are antibonding. The π-MO coefficient at the *exo* carbon atom (C6) is larger than that of five-membered carbon atoms (C1, C2, C3, C4, and C5). The central five-membered ring has similar π-MO to cyclopentadienide ion with 6π-electron system. Thus, it is reasonable to expect that reduction of **2a** may yield the dianion species; one negative charge is delocalized over the five-membered ring to form a 5 center/6π-electron aromatic cyclopentadienide ion, and the other one is almost localized on the *exo*-cyclic carbon atom stabilized by two silicon atoms.

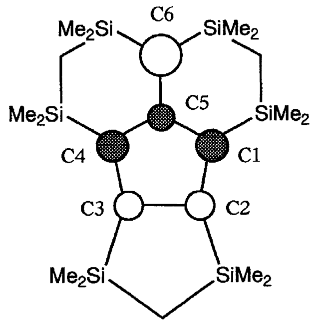


Fig. 2. Schematic drawing of LUMO of **2a** calculated by PM3.

Two Electron Reduction of 2 with Lithium Metal. The reaction of **2a** with excess lithium metal in dry oxygen-free THF at room temperature led to the formation of a yellow solution of the dianion **3a**. The two electron reduction occurred quantitatively and was completed within 1 h (Scheme 2). After the solvent was removed in vacuo, dry degassed heptane was introduced by vacuum transfer. Crystallization from a heptane solution afforded air- and moisture-sensitive yellow crystals of the dilithium salt of fulvene dianion (**3a**) containing three molecules of THF. Fulvene **2b**, bridged by siloxane chains, also underwent a two electron reduction in THF to yield a yellow solution of the dianion dilithium (**3b**) quantitatively.

Molecular Structure of 3a. The molecular structure of dianion **3a** has been confirmed by X-ray crystallography (Fig. 3). The dilithium salt **3a** has a monomeric structure and forms a contact ion pair (bis-CIP) in the crystals. Selected bond distances, bond angles, and dihedral angle are listed in Table 2. One THF molecule is coordinated to Li1 and two THF molecules are coordinated to Li2. Li1 and Li2 are located above and below the π-skeleton, respectively. Li1 is located 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 (av 2.179 Å), so that the Li-to-Cp interaction clearly qualifies as η^5-coordination. Li2 is bonded to two carbon atoms (C6 and C9) with distances of 2.136(6) for Li2–C6 and 2.325(6) Å for Li2–C9 by η^2-coordination. The five- and two six-membered rings linked by $Me_2SiCH_2SiMe_2$ fragments have the envelope conformation.

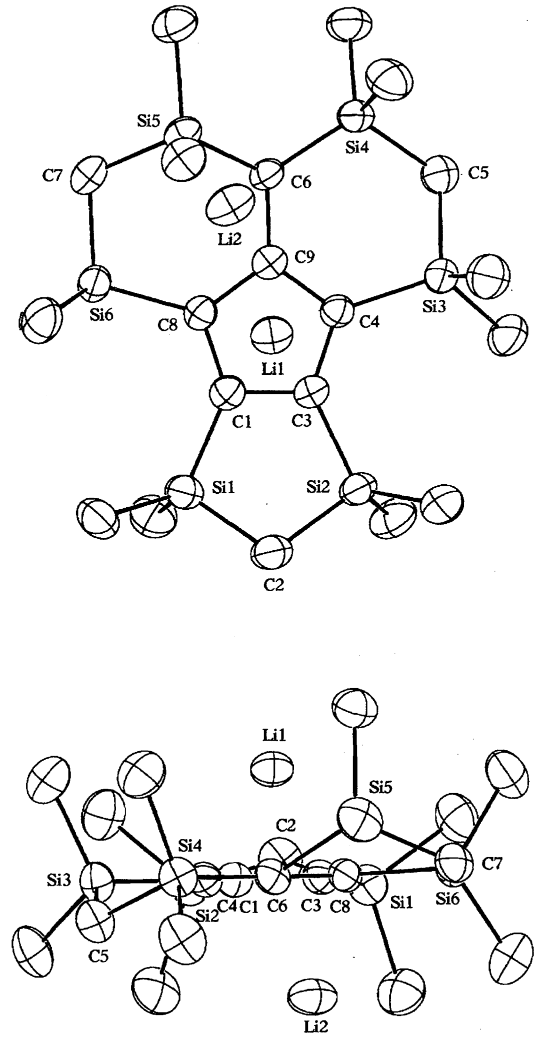
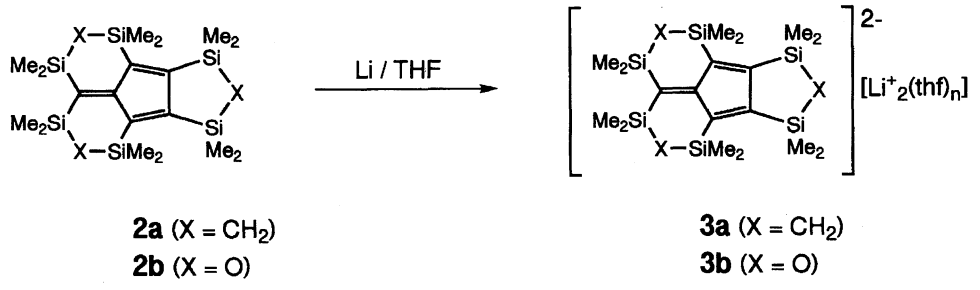


Fig. 3. ORTEP drawing of **3a** (THF moleules are omitted for the clarity): upper, top view: below, side view.

The Li distance from the ring centroid (1.795 Å) is comparable to that observed in $[(Ph_2C{=}O)Li\cdot\{C_5(SiMe_2H)_5\}]$ (1.818 Å),[12] and somewhat shorter than those observed in $Li(C_5H_4Me)TMEDA$ (1.92 Å),[17] $Li[C_5H_4SiMe_3]TMEDA$ (1.93 Å),[18] $[(isodiCp)_2Li]^-$ (1.91 Å),[19] $LiCp_2^-$ (2.008 Å),[20] and $[Li_2(TMEDA)_2(C_5H_4Me)]^-$ (2.00 Å).[21] The Li distance from the Cp ring of the tetralithium octasilyltrimethylenecyclopentene tetraanion,[13] bridged by Me_2SiCH_2SiMe, is also slightly short (1.827 Å), as was the Li distance in **2a**. The relatively short Li distance of **2a** compared with the reported Li distances may be due to the bridged structure comprising $Me_2SiCH_2SiMe_2$ chains.

Comparison of the structural parameters of **2a** and **3a** is



2a (X = CH_2)
2b (X = O)

3a (X = CH_2)
3b (X = O)

Scheme 2.

Table 2. Selected Bond Distances (Å), Angles (deg), and Dihedral Angle (deg) of **3a**[a)]

Atoms	Exptl (X-ray)	Atoms	Exptl (X-ray)
	Bond distances		
C1–C3	1.441(4)	C1–C8	1.451(4)
C3–C4	1.456(4)	C4–C9	1.442(4)
C6–C9	1.511(4)	C8–C9	1.463(4)
Si1–C1	1.862(3)	Si2–C3	1.861(3)
Si3–C4	1.852(3)	Si4–C6	1.820(3)
Si5–C6	1.827(3)	Si6–C8	1.864(3)
Li1–C1	2.174(3)	Li1–C3	2.164(3)
Li1–C4	2.176(3)	Li1–C8	2.189(3)
Li1–C9	2.191(3)	Li2–C6	2.136(6)
Li2–C9	2.235(6)		
	Bond angles		
C3–C1–C8	108.2(3)	C1–C3–C4	108.1(3)
C3–C4–C9	108.2(2)	C1–C8–C9	107.8(3)
C4–C9–C8	107.7(3)	C4–C9–C6	127.7(3)
C6–C9–C8	124.6(3)		
	Dihedral angle		
	C1–C3–C4–C8/C4–C8–C9		0.2(3)

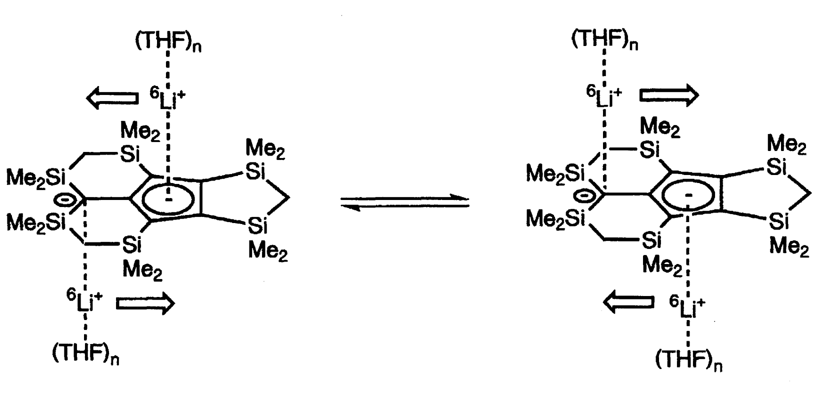
a) Atomic numbers are given in Fig. 3. Standard deviations are in parentheses.

quite interesting (Figs. 1 and 3). In **3a**, the central five-membered ring, the *exo* carbon atom (C6), and Si1, Si2, Si3, Si4, Si6, and C7 atoms become completely coplanar by the two electron reduction. The distance of C6–C9 (1.511(4) Å) is elongated by 0.135 Å relative to that of **2a** (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 and 0.073 Å compared with **2a** (1.377(4) and 1.378(4) Å for **2a**, respectively). In contrast, the distances of C1–C3 (1.441(4) Å), C4–C9 (1.442(4) Å), and C8–C9 (1.463(4) Å) of **3a** are shortened by 0.047—0.069 Å (1.508(4), 1.511(4), and 1.510(4) Å, respectively, for **2a**). That is, the C–C double bonds of **2a** are elongated, whereas the C–C single bonds are shortened by the reduction. Therefore, the geometry of **3a** reflects the nature of the LUMO of **2a** (Fig. 2).

The Cp ring is an almost planar equilateral pentagon, as determined by the internal bond angles of 107.7(3)—108.2(3)° (av 108.0°) and the sum of the bond angles (540.0°). The C–C distances of the five-membered ring are 1.441(4)—1.463(4) Å (av 1.451 Å), which are close to those of tetralithium trimethylenecyclopentene tetraanion (av 1.457 Å),[13)] but somewhat longer than those of [$(Ph_2C{=}O)$-Li·{$C_5(SiMe_2H)_5$}] (av 1.424 Å).[12)] 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 (1.820(3) Å) and the C6–Si5 (1.827(3) Å) bonds in **3a** are shortened markedly compared with those of **2a** (1.888(3) and 1.897(3) Å, respectively) by $p\pi$-σ^* conjugation. The other negative charge is delocalized over the Cp ring to form the cyclopentadienide ion.

Structure of 3 in Toluene-d_8. The structure of **3a** in solution was characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{6}Li NMR spectroscopies. The NMR data in toluene-d_8 indicate a highly symmetric bis-CIP structure, as found by the X-ray crystallography. However, the two Li$^+$ ions of **3a** are not fixed to the π-skeleton and undergo rapid exchange with each other on the NMR time scale, as depicted in Fig. 4. Thus, the ^{6}Li NMR spectrum of **3a** in toluene-d_8 yielded only one signal, appearing at $\delta = -3.18$. The exchange of the Li$^+$ ions was not suppressed in the temperature range of 193—298 K. The ^{6}Li NMR chemical shift of **3a** ($\delta = -3.18$) is intermediate of $(Me_3Si)_2CHLi$ ($\delta = 2.46$) and [$(Ph_2C{=}O)$-Li·{$C_5(SiMe_2H)_5$}] ($\delta = -7.51$). This also supports the facile interconversion of Li$^+$ ions, as depicted in Fig. 4.

In the ^{13}C NMR spectrum, three sets of methyl carbons (δ = 4.4, 5.34, and 6.0) and two sets of methylene carbons (δ = 3.4 and 5.27) were observed, as well as four sets of quaternary carbons at δ = 30.2 (C6), 112.1 (C4 and C8), 138.6 (C1 and C3), and 164.9 (C9). The ^{13}C signal of the C6 atom was observed at δ = 30.2, which is markedly shifted to upper field by 152.7 ppm relative to that of **2a** (δ = 182.9). This shift is due to the negative charge at the exocyclic C6 carbon atom of **3a**. The ^{29}Si NMR spectrum showed three sets of signals at $\delta = -14.4$, -12.5, and -5.4, shifting to upper field relative to those of **2a**. This suggests that



n = 1 or 2

Fig. 4. Lithium interconversion of **3a**.

the negative charge is stabilized by the six silyl groups in **3a**. The same highly symmetric bis-CIP formation in toluene-d_8 was also deduced for the dianion dilithium **3b**. The interconversion of the two Li^+ ions of **3** in solution readily occurs due to the planar structure of the π-system.

Structure of 3 in THF-d_8. The structure of **3a** in a solvating medium such as THF-d_8 was also deduced on the basis of the NMR spectra. The spectral data indicate that bis-CIP formation of **3a** is maintained in THF-d_8 at 298 K. The ^{6}Li NMR spectrum shows one signal at $\delta = -3.05$ (298 K, Fig. 5a). Upon lowering the temperature, this ^{6}Li signal ($\delta = -3.05$) was decreasing, whereas two peaks were growing (193 K, Fig. 5b). The ^{6}Li NMR spectrum at 163 K yielded two new peaks, appearing at $\delta = 0.79$ and -0.29 with the same intensity (Fig. 5c). The signal at $\delta = 0.79$ is assigned to the Li^+ ion bonded to the π-skeleton (CIP-Li^+). The other signal ($\delta = -0.29$) is assignable to the THF solvated species, $[Li^+(THF)_n]$.[7b)] Thus, at low temperature, CIP-SSIP species (**3a′**) is formed in THF-d_8. There is equilibrium between the two dianion species, **3a** (bis-CIP structure) and **3a′** (CIP-SSIP structure) in THF-d_8.

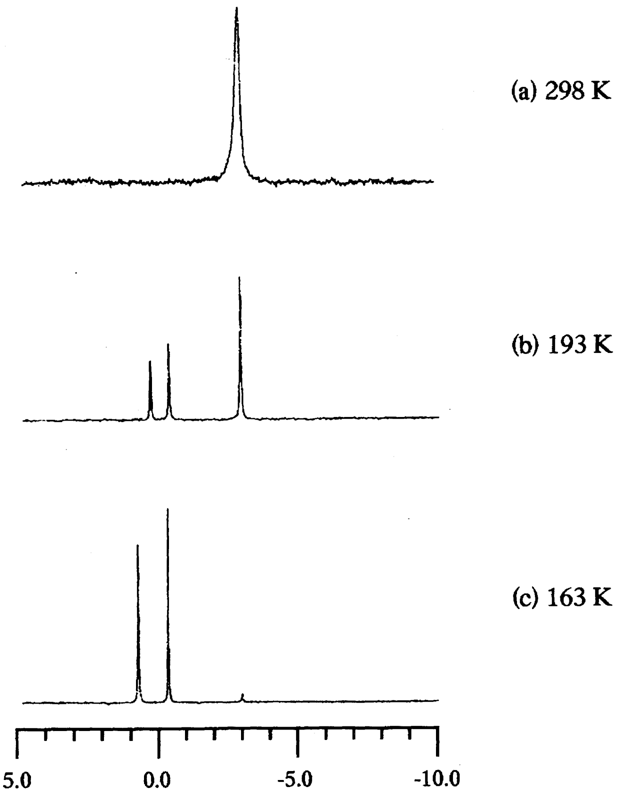


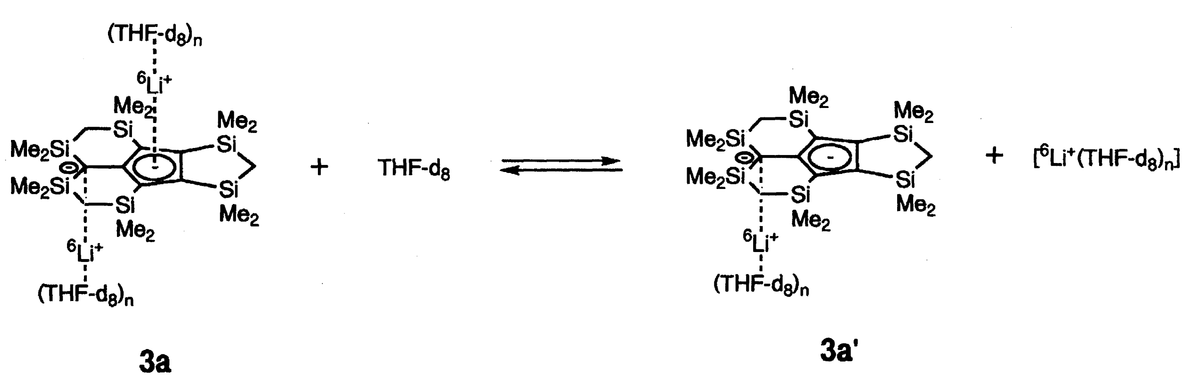
Fig. 5. ^{6}Li NMR spectra of **3a** and **3a′** in THF-d_8: (a) at 298 K, (b) at 193 K, and (c) at 163 K.

The η^5-coordinated Li^+ ion of bis-CIP species (**3a**) is solvated by THF-d_8 to form CIP-SSIP species (**3a′**) at low temperature. Therefore, the π-skeleton of **3a′** has different environments above and below the plane. The six resonances of $SiMe_2$ were found in both ^{1}H and ^{13}C spectra of **3a′** at 163 K. In the ^{13}C NMR spectrum of **3a′**, the signal appearing at $\delta = 23.4$ split into a triplet ($J_{^{13}C-^6Li} = 3.5$ Hz) due to the coupling with one ^{6}Li ($I = 1$). The triplet signal is assigned to the exocyclic carbon atom. From the van't Hoff plot, the value of $\Delta H = -38.3$ kJ mol^{-1} for the equilibrium of the two dianion species (**3a** and **3a′**) can be estimated. The negative enthalpy suggests that the CIP-SSIP structure **3a′** is favored at low temperature due to the solvation of Li^+ ion by THF.

Experimental

General Procedure. ^{1}H NMR spectra were recorded on a Bruker AC-300 FT spectrometer. ^{13}C, ^{29}Si, and ^{6}Li NMR spectra were collected on a Bruker AC-300 at 75.5, 59.6, and 44.2 MHz, respectively. ^{6}Li NMR spectra are referenced to 1 M LiCl in methanol/toluene-d_8 or 1 M LiCl in THF-d_8 (1 M = 1 mol dm^{-3}). Mass spectra were obtained on a Shimadzu QP-1000. Electronic spectra were recorded on a Shimadzu UV-2100 spectrometer. The sampling of **3a** for X-ray crystallography was carried out by using a Giken Engineering Service GBX-1200 gas-replacement type glove box. Tetrahydrofuran and heptane were dried and distilled from sodium benzophenone ketyl. These solvents were further dried and degassed over a potassium mirror in vacuo prior to use. Toluene-d_8 and THF-d_8 were dried over molecular sieves, and then transferred into a tube covered with a potassium mirror prior to use. Lithium-6 (95 atom%) metal was commercially available (Aldrich Chemical Company). 3,3,5,5,8,8,10,10,13,13,15,15-Dodecamethyl-3,5,8,10,13,15-hexasilacyclopentadeca-1,6,11-triyne (**1a**) and 3,3,5,5,8,8,10,10,13,13,15,15-dodecamethyl-3,5,8,10,13,15-hexasila-4,9,14-trioxacyclopentadeca-1,6,11-triyne (**1b**) were prepared by the reported method.[15,16)] Hexasilylfulvene (**2b**) was prepared by the reported method.[16)]

Hexasilylfulvene (2a).[15)] A mixture 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 (**1a**) (227 mg, 0.49 mmol) and $[Mn(CO)_3(Me\text{-}Cp)]$ (160



Scheme 3.

mg, 0.73 mmol) in THF (30 ml) was irradiated with a 500 W high-pressure mercury lamp for 8 h through the cut off 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 **2a** in 26% yield, along with the hexasilyldimethylenecyclobutene derivative (16% yield). Mp 170 °C; ^{1}H NMR ($CDCl_3$) $\delta = -0.12$ (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 ($CDCl_3$) $\delta = 1.8$ (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 ($CDCl_3$) $\delta = -13.4, -6.7, -2.4$; UV (hexane) λ_{max}/nm (ε) 215 (21000), 298 (19500); HRMS Found: *m*/*z* 462.1894. Calcd for $C_{21}H_{42}Si_6$: M, 462.1902.

Hexasilylfulvene Dianion Dilithium (3a). The crystals of **2a** (22 mg, 0.05 mmol) and lithium metal (30 mg, 4.3 mmol) were put in a sealed 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 **3a** within 1 h. After the solvent was removed in vacuo, degassed heptane was introduced by vacuum transfer. Then after removing the lithium metal, the solution was cooled to afford yellow crystals of **3a** quantitatively. ^{1}H NMR (C_7D_8) $\delta = 0.04$ (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_7D_8) $\delta = 3.4$ (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_7D_8) $\delta = -14.4, -12.5, -5.4$; ^{6}Li NMR ($C_7D_8$) $\delta = -3.18$.

NMR Spectral Data of 3a in THF-*d*$_8$ at 298 K. ^{1}H NMR (THF-d_8) $\delta = -0.34$ (s, 4 H, CH_2), -0.15 (s, 2 H, CH_2), 0.02 (s, 12 H, CH_3), 0.17 (s, 12 H, CH_3), 0.21 (s, 12 H, CH_3); ^{13}C NMR (THF-d_8) $\delta = 4.4$ (CH_3), 4.6 (CH_2), 5.2 (CH_2), 5.4 (CH_3), 5.9 (CH_3), 30.5 (C), 112.0 (C), 138.7 (C), 164.7 (C); ^{29}Si NMR (THF-d_8) $\delta = -15.0, -13.2, -6.3$; ^{6}Li NMR (THF-$d_8$) $\delta = -3.05$.

NMR Spectral Data of 3a′ in THF-*d*$_8$ at 163 K. ^{1}H NMR (THF-d_8) $\delta = -0.61$ (d, $J = 11.9$ Hz, 2 H, CH_2), -0.47 (d, $J = 11.9$ Hz, 2 H, CH_2), -0.36 (br.s, 2 H, CH_2), -0.12 (s, 6 H, CH_3), -0.07 (s, 6 H, CH_3), -0.04 (s, 6 H, CH_3), -0.03 (s, 6 H, CH_3), 0.15 (s, 6 H, CH_3), 0.19 (s, 6 H, CH_3); ^{13}C NMR (THF-d_8) $\delta = 5.2$ (CH_2), 5.6 (CH_3), 5.7 (CH_3), 5.9 (CH_3), 6.4 (CH_2), 6.6 (CH_3), 7.1 (CH_3), 8.6 (CH_3), 23.4 (t, $J_{^{13}C-^6Li} = 3.5$ Hz, C), 109.1 (C), 138.3 (C), 164.5 (C); ^{29}Si NMR (THF-d_8) $\delta = -16.2, -13.9, -9.8$; ^{6}Li NMR (THF-$d_8$) $\delta = -0.29, 0.79$.

Hexasilylfulvene Dianion Dilithium (3b). This was obtained by a procedure similar to the synthesis of **3a** as yellow crystals. ^{1}H NMR (C_7D_8) $\delta = 0.46$ (s, 12 H, CH_3), 0.50 (s, 12 H, CH_3), 0.53 (s, 12 H, CH_3), 1.42 (br. s, 12 H, THF), 3.46 (br. s, 12 H, THF); ^{13}C NMR (C_7D_8) $\delta = 4.1$ (CH_3), 5.2 (CH_3), 5.4 (CH_3), 25.5 (THF), 29.3 (C), 68.5 (THF), 109.4 (C), 135.3 (C), 162.6 (C); ^{29}Si NMR (C_7D_8) $\delta = -2.0, 1.3, 6.6$; ^{6}Li NMR (C_7D_8) $\delta = -3.10$.

NMR Spectral Data of 3b in THF-*d*$_8$ at 298 K. ^{1}H NMR (THF-d_8) $\delta = 0.00$ (s, 12 H, CH_3), 0.14 (s, 12 H, CH_3), 0.17 (s, 12 H, CH_3); ^{13}C NMR (THF-d_8) $\delta = 3.9$ (CH_3), 4.9 (CH_3), 5.1 (CH_3), 29.3 (C), 109.5 (C), 135.2 (C), 163.2 (C); ^{29}Si NMR (THF-d_8) $\delta = -2.7, 0.4, 5.8$; ^{6}Li NMR (THF-d_8) $\delta = -2.89$.

X-Ray Crystallography. Single crystals of **2a** and **3a** for X-ray diffractions were grown from an ethanol solution and a heptane solution, respectively. The X-ray crystallographic experiments of **2a** and **3a** were performed on a DIP2020 image plate diffractometer equipped with graphite-monochromatized Mo *Kα* radiation ($\lambda = 0.71073$ Å). Crystal data for **2a** at 130 K: MF = $C_{21}H_{42}Si_6$, MW = 463.09, triclinic, $a = 11.333(1)$, $b = 11.877(1)$, $c = 20.749(1)$ 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 $I_o > 3\sigma(I_o)$. Crystal data for **3a** at 180 K: MF = $C_{33}H_{66}Li_2O_3Si_6$, MW = 693.29, monoclinic, $a = 11.579(1)$, $b = 11.652(1)$, $c = 31.332(2)$ Å, $\beta = 95.805(4)°$, $V = 4205.58(3)$ Å^3, space group = $P2_1/c$, $Z = 4$, $D_{calcd} = 1.095$ g cm^{-3}. The final *R* factor was 0.045 ($R_w = 0.054$) for 5783 reflections with $I_o > 3\sigma(I_o)$. Tables of positional and thermal parameters and complete interatomic distances and angles have been deposited as Document No. 72017 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Molecular Orbital Calculations. PM3 calculations were performed by Power Macintosh 7600/200 with MACSPARTAN plus program (Ver. 1.1.7).[22] All the calculations were performed with geometry optimization.

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