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Headline Articles

Tetraanion Tetralithium with 8 Center/12 Electron π-System Stabilized by Silyl Groups. Synthesis and Characterization

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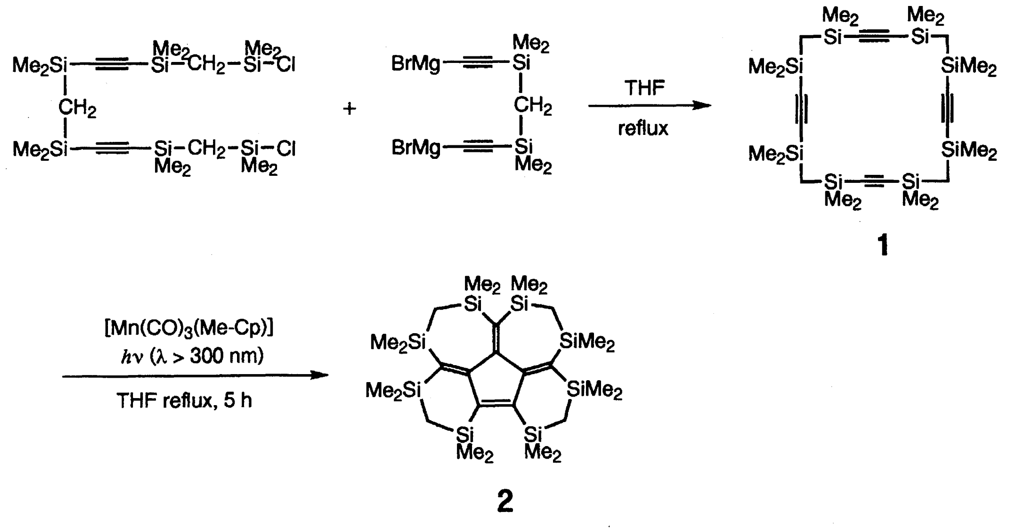
Reduction of octasilyltrimethylenecyclopentene (**2**) with lithium metal in tetrahydrofuran yields orange crystals of the tetraanion tetralithium (**3**) with 8 center/12 electron π-system. The molecular structure of **3** is unequivocally established by X-ray crystallography. The tetralithium **3** has a monomeric structure and forms contact ion pairs (CIP) in the crystals. The two lithium atoms (η^5) are located above and below the center of the five-membered ring, whereas the other two lithium atoms (μ^2) are bonded to the two exocyclic carbon atoms. The structural parameters of **3** are discussed in comparison to that of the neutral starting molecule of **2**. The structure of **3** in solution has also been discussed on the basis of NMR spectroscopic data.

The introduction of a silyl group causes remarkable steric and electronic perturbations to the π-electron system.[1] We have previously reported successful preparations of dianion dilithium derivatives of silyl-substituted ethylenes,[2] silyl-substituted styrenes,[3] silyl-substituted benzenes,[4] silyl-substituted dimethylenecyclobutene,[5] and persilyl-substituted cyclopentadienide.[6] The supercharged anions with extended π-electron systems become of considerable interest owing to their unique structures and electronic properties.[7] The existence of a hexaanionic species in the solid state is inferred from the formation of K_6C_{60} by X-ray powder diffraction data[8] and ^{13}C NMR spectroscopy.[9] Scott et al. have recently reported a tetraanion tetralithium of corannulene ($C_{20}H_{10}$) and its derivatives.[10] The only report on the molecular structure of a rubrene (5,6,11,12-tetraphenyltetracene, $C_{42}H_{28}$) tetraanion tetrasodium determined by X-ray crystallography was recently reported by Bock et al.[11] We wish to report herein a detailed study of tetraanion tetralithium (**3**) as a new silyl-substituted 8 center/12 electron π-system, including the crystal structures of **3** and a precursor of the trimethylenecyclopentene derivative (**2**).[12]

Results and Discussion

Synthesis of 2. Persilylated π-electron systems exhibit quite unusual and interesting physical and chemical properties.[1] Previously, we reported the intramolecular cyclotrimerization of the silacyclotriynes with transition metal complexes to give persilyl-substituted dimethylenecyclobutene derivative.[13] The reaction involves the 1,2-silyl shift in the 1,2-disilyl-substituted acetylene to give 2,2-disilylvinylidene complexes as a reaction intermediate. The intriguing 1,2-silyl shift is a general reaction in cyclic and acyclic bissilylacetylene promoted by (cyclopentadienyl or methylcyclopentadienyl)tricarbonylmanganese.[13,14] The persilylated trimethylenecyclopentene derivative (**2**) has been synthesized in a similar manner via the intramolecular tetramerization of the macrocyclic tetrayne (**1**) with [Mn(CO)$_3$(Me-Cp)].

The precursor of 3,3,5,5,8,8,10,10,13,13,15,15,18,18,20,20-hexadecamethyl-3,5,8,10,13,15,18,20-octasilacycloicosa-1,6,11,16-tetrayne (**1**) linked by silmethylene chains was prepared by the coupling reaction of 2,14-dichloro-2,4,4,7,7,9,9,12,12,14-decamethyl-2,4,7,9,12,14-hexasilapentadeca-5,10-diyne with the Grignard reagent prepared from 3,3,5,5-tetramethyl-3,5-disilahepta-1,6-diyne and ethylmagnesium bromide. A mixture of the macrocyclic tetrayne (**1**) and one molar amount of [Mn(CO)$_3$(Me-Cp)] in THF was irradiated with a 500 W high-pressure mercury lamp under the refluxing temperature of THF to produce pale yellow crystals of the persilylated trimethylenecyclopentene derivative (**2**) in 17% yield (Scheme 1). The reaction mechanism to produce **2** is not clear at this moment, but a triple 1,2-silyl shift can be



Scheme 1.

involved.

Crystal Structure of 2. The trimethylenecyclopentene derivative (**2**) possesses a very unique 8 π-electron system; one double bond is located in the five-membered ring and the three double bonds are located in the exo positions. Since there is no crystal structure of the trimethylenecyclopentene derivative, we have performed the X-ray diffraction of **2**. Figure 1 shows the molecular structure of **2** determined by the X-ray diffraction method. Selected bond lengths, bond angles, and dihedral angle are listed in Table 1. The structural parameters of **2** calculated by PM3 are also given in Table 1. The trimethylenecyclopentene derivative (**2**) is a highly distorted structure and the central five-membered ring is not planar but in an envelope conformation. The angle formed by C1–C2–C3–C5 and C3–C4–C5 plane is 36.2°. The internal bond angles of the five-membered ring are 101.4(4)—109.3(4)° (av 105.2°), and the sum of bond angles is 526.0°. The appreciable bond alternation between the single and double bonds of the π-skeleton of **2** shows the structural feature as a cross-conjugated diene. The geometry of **2** determined by the X-ray diffraction is successfully reproduced by PM3 calculation (Table 1).

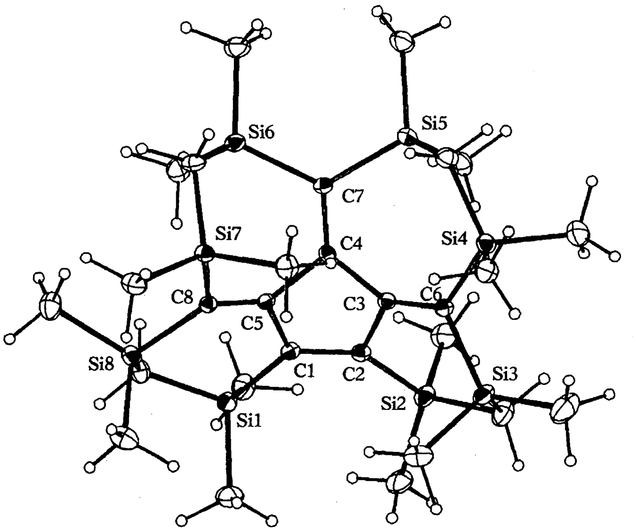


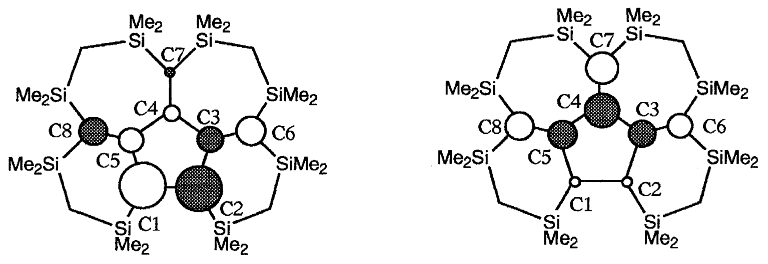
Fig. 1. ORTEP drawing of **2**.

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

Atoms	Exptl (X-ray)	Calcd[b] (PM3)	Atoms	Exptl (X-ray)	Calcd[b] (PM3)
		Bond distances			
C1–C2	1.372(8)	1.350	C1–C5	1.506(7)	1.481
C2–C3	1.520(8)	1.492	C3–C4	1.512(8)	1.496
C3–C6	1.354(8)	1.333	C4–C5	1.523(7)	1.497
C4–C7	1.358(8)	1.334	C5–C8	1.348(7)	1.332
C1–Si1	1.894(6)	1.838	C2–Si2	1.897(6)	1.847
C6–Si3	1.893(6)	1.852	C6–Si4	1.889(6)	1.827
C7–Si5	1.900(6)	1.841	C7–Si6	1.899(6)	1.856
C8–Si7	1.885(6)	1.839	C8–Si8	1.884(6)	1.832
		Bond angles			
C2–C1–C5	108.3(4)	109.0	C1–C2–C3	109.3(4)	109.8
C2–C3–C4	103.4(4)	103.5	C2–C3–C6	125.2(5)	124.2
C4–C3–C6	130.0(5)	131.5	C3–C4–C5	101.4(4)	102.6
C3–C4–C7	132.5(5)	130.9	C5–C4–C7	124.9(4)	125.5
C1–C5–C4	103.6(4)	104.7	C1–C5–C8	128.3(4)	128.0
C4–C5–C8	127.5(4)	126.9			
		Dihedral angle			
C1–C2–C3–C5/C3–C4–C5	36.2 (29.5, calcd)				

a) Atomic numbers are given in Fig. 1. Standard deviations are in parentheses. b) Calculated parameters of **2** by PM3.

π-MO and Cyclic Voltammetry of 2. As in Table 1, the geometry of **2** by the X-ray diffraction is well reproduced by PM3 calculation. Figure 2 shows the schematic drawings of the LUMO (0.19 eV) and next LUMO (0.41 eV) of **2** by PM3 calculation. In the LUMO, C1–C2, C3–C6, and C5–C8 bonds are antibonding, whereas C1–C5 and C2–C3 bonds are bonding. The π-MO coefficients at the central C1 and C2 carbon atoms are larger than that of other carbon atoms as shown in Fig. 2. Thus, two electron reduction of **2** may produce dianion dimetal complex so that the counter cations may strongly interact with the C1 and C2 carbon atoms. The



LUMO next LUMO

Fig. 2. Schematic drawings of LUMO and next LUMO of **2** calculated by PM3.

resulting dianion may be stabilized by Si1 and Si2 silicon atoms. Of particular interest of the π-MO is the next LUMO; the central five-membered ring has similar π-MO to cyclopentadienide ion with 6π-electron system. In addition, the π-MO of the *exo* carbon–carbon bonds (C3–C6, C4–C7, C5–C8) are all antibonding. Therefore, it is quite reasonable to assume that reduction of **2** may produce the tetraanion by four electron reduction, which will be stabilized by not only cyclopentadienide with 6π-electron system but also six silicon atoms (Si3, Si4, Si5, Si6, Si7, Si8).

The cyclic voltammetry of **2** in acetonitrile is shown in Fig. 3. The irreversible reduction peak was observed at -1.38 V (vs. SCE) as a very broad peak. The reduction peak potential of **2** is close to that of silyl-substituted ethylene derivatives (e.g. -1.20 V for tetrakis(trimethylsilyl)ethylene and -1.22 V for 2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene). The broad peak potential of **2** suggests the possibility of the multiple reduction. Thus, the four electron reduction is reasonably anticipated by means of the MO calculation and the electrochemistry of **2**.

Four Electron Reduction of 2 with Lithium Metal. Reduction of **2** with lithium metal in dry oxygen-free tetrahydrofuran at room temperature led to the formation of an orange solution of the tetraanion of **2**. The reaction completed within 1 h. The solvent was removed in vacuo, and then dry degassed hexane was introduced by vacuum transfer. Crystallization from hexane afforded air and moisture sensitive pale orange crystals of the tetraanion tetralithium (**3**) containing four molecules of THF (Scheme 2). The structure of **3** was unequivocally confirmed by NMR spectroscopy and X-ray crystallography. Several attempts to obtain dianion dilithium of **2** by two electron reduction failed due to the facile four electron reduction.

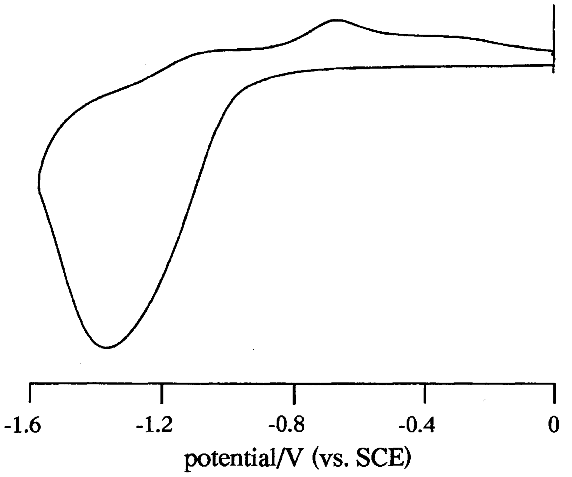


Fig. 3. Cyclic voltammetry of **2** in acetonitrile (scan rate: 200 mV s^{-1}; conditions: room temperature, under argon).

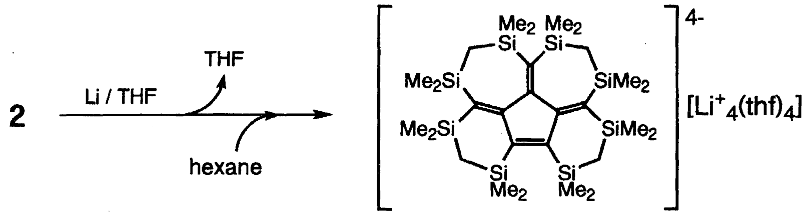
Crystal Structures of 3. Figure 4 shows the molecular structure of **3**, which was confirmed by X-ray diffraction. The structure shows that the molecule has C_2 symmetry and C1–C2 bond is a crystallographic 2-fold axis. The tetralithium **3** has a monomeric structure and forms contact ion pairs (CIP) in the crystals. Selected bond lengths, bond angles, and dihedral angle are listed in Table 2. The structural parameters of $\mathbf{2}^{4-}$ calculated by PM3 are also given in Table 2.

Several interesting features of the structures of **3** can be pointed out. One THF molecule is coordinated to each

Table 2. Selected Bond Distances (Å), Angles (deg), and Dihedral Angle (deg) of $\mathbf{3}^{a)}$

Atoms	Exptl (X-ray)	Calcd$^{b)}$ (PM3)	Atoms	Exptl (X-ray)	Calcd$^{b)}$ (PM3)
		Bond distances			
C1–C2	1.537(7)	1.424	C2–C3	1.443(5)	1.442
C3–C4	1.464(5)	1.429	C3–C6	1.534(5)	1.427
C4–C4*	1.470(7)	1.425	C1–Si1	1.832(3)	1.758
C6–Si2	1.809(4)	1.764	C6–Si3	1.832(4)	1.742
C4–Si4	1.878(4)	1.795	Li1–C2	2.335(7)	
Li1–C3	2.248(7)		Li1–C4	2.132(7)	
Li1–C3*	2.287(8)		Li1–C4*	2.169(8)	
Li2–C1	2.255(7)		Li2–C6	2.092(8)	
Li2–Si1	2.813(7)		Li2–Si2	3.231(7)	
Li2–Si3	3.263(7)				
		Bond angles			
C1–C2–C3	125.6(2)	126.4	C3–C2–C3*	108.8(4)	107.6
C2–C3–C4	108.2(3)	107.7	C2–C3–C6	123.3(3)	128.7
C4–C3–C6	128.5(3)	123.6	C3–C4–C4*	107.4(2)	108.4
		Dihedral angle			
C3–C4–C4*–C3*/C3–C2–C3*				0.0 (1.2, calcd)	

a) Atomic numbers are given in Fig. 4. Standard deviations are in parentheses. b) Calculated parameters of $\mathbf{2}^{4-}$ by PM3.



3

Scheme 2.

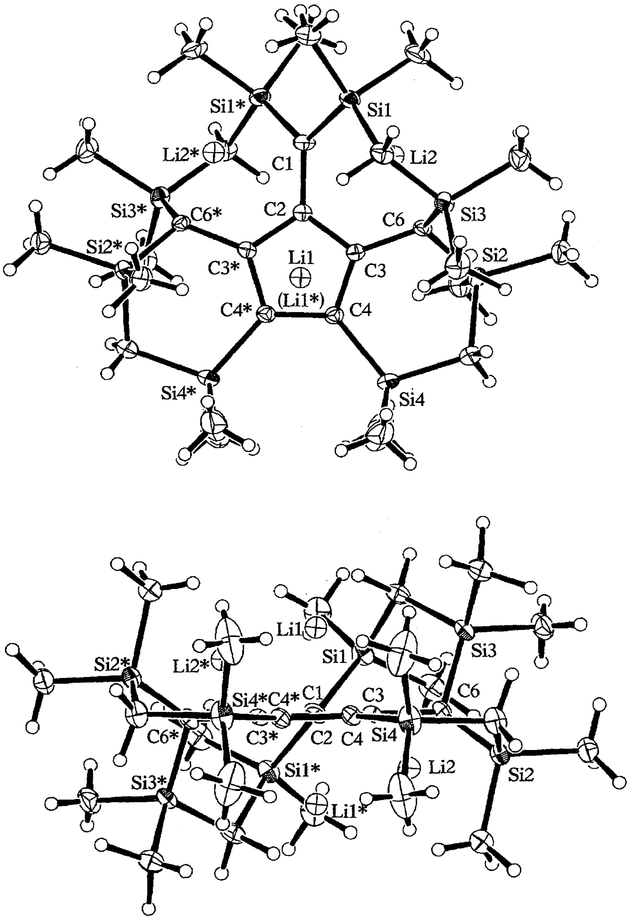


Fig. 4. ORTEP drawing of **3** (THF molecules are omitted for the clarity): upper, top view; below, side view.

lithium atom. Li1 and Li1* are located above and below the center of the five-membered ring (η^5-coordination). The distances between Li1 and the five-membered carbon atoms (C2, C3, C4, C4*, and C3*) range from 2.132(7) to 2.335(7) Å (av 2.234 Å), which are somewhat longer than those of lithium pentakis(dimethylsilyl)cyclopentadienide [$(Ph_2C{=}O)Li\cdot\{C_5(SiMe_2H)_5\}$] (av 2.186Å).[6] Li2 and Li2* are bonded to the two exocyclic carbon atoms (C1, C6 and C1, C6*) (μ^2-coordination).

Comparison of the structural parameters of **2** and **3** is quite interesting. Eight carbon atoms of the π-skeleton of **3** become completely coplanar by the four electron reduction. The distances of C3–C6, C3*–C6*, and C1–C2 of **3** are elongated by 0.18—0.19 Å (av 0.18 Å) relative to those of **2**. As well, the distance of C4–C4* of **3** is stretched by 0.10 Å. By contrast, the distances of C3–C4, C3*–C4*, C2–C3, and C2*–C3* of **3** are shortened by 0.04 —0.08 Å (av 0.06 Å). That is, the C–C double bonds of **2** are elongated whereas the C–C single bonds are shortened by the reduction. Therefore, the geometry of **3** reflects the nature of the next LUMO of **2** (Fig. 2). The five-membered ring is planar and almost an equilateral pentagon, as determined by the internal bond angles of 107.4(2)—108.8(4)° (av 108.0°) and the sum of the bond angles (540.0°). The C–C distances of the five-membered ring are 1.443(5)—1.470(7) Å (av 1.457 Å). The bond lengths of the Si–C bonds (C1–Si1, 1.832(3); C6–Si2, 1.809(4); C6–Si3, 1.832(4) Å) of **3** are remarkably shortened compared to those of **2** (1.900(6), 1.893(6), and 1.889(6), respectively), due to the delocalization of the negative charge onto the silicon centers by $p\pi$–σ^* conjugation. The bond lengths of the Si–C (Si–Me and Si–CH_2) bonds of **3** are slightly elongated (about 0.01 Å) relative to those of **2**. The geometry of $\mathbf{2}^{4-}$ (counter ion free) calculated by PM3 is very close to that of **3** (Fig. 5, Table 2).

Structure of 3 in Solution. The structure of **3** in benzene-d_6 was deduced by ^1H, ^{13}C, ^{29}Si, and ^6Li NMR spectroscopies. The two methyl groups of $SiMe_2$ and two hydrogen atoms of CH_2 were magnetically nonequivalent due to the fixed six- or seven-membered ring, as well as due to the coordination of lithiums. Thus, in the ^1H NMR spectrum of **3** in benzene-d_6, eight sets of methyl groups and four sets of doublet signals of methylene groups with the geminal couplings (13.2 and 13.7 Hz) were found. In the ^{29}Si NMR spectrum, four sets of signals were observed at −16.1, −15.1, −14.5, and −13.2 ppm, shifted to upper field relative to those of **2**. In the ^{13}C NMR spectrum, five sets of quaternary carbon atoms were found at 9.62, 19.7, 107.0, 132.1, and 148.2 ppm. The signal appearing at 19.7 ppm splits into a triplet ($J_{^{13}C-^{6}Li} = 6.2$ Hz) due to the coupling with one ^6Li ($I = 1$), whereas the signal at 9.62 ppm splits into a quintet ($J_{^{13}C-^{6}Li} = 2.3$ Hz) due to the coupling with two equivalent ^6Li. Thus, the triplet signal is assigned to C6 and C6* carbons, and the quintet signal is assigned to C1 carbon. It is apparent that the negative charge is largely delocalized of the three exocyclic carbon atoms (C1, C6, and C6*) in the π-skeleton of **3**, as evidenced by the ^{13}C NMR spectral data. These carbons are remarkably shifted to upper field by 169.3 ppm for C1 and 152.9 ppm for C6 and C6* relative to those of **2**.

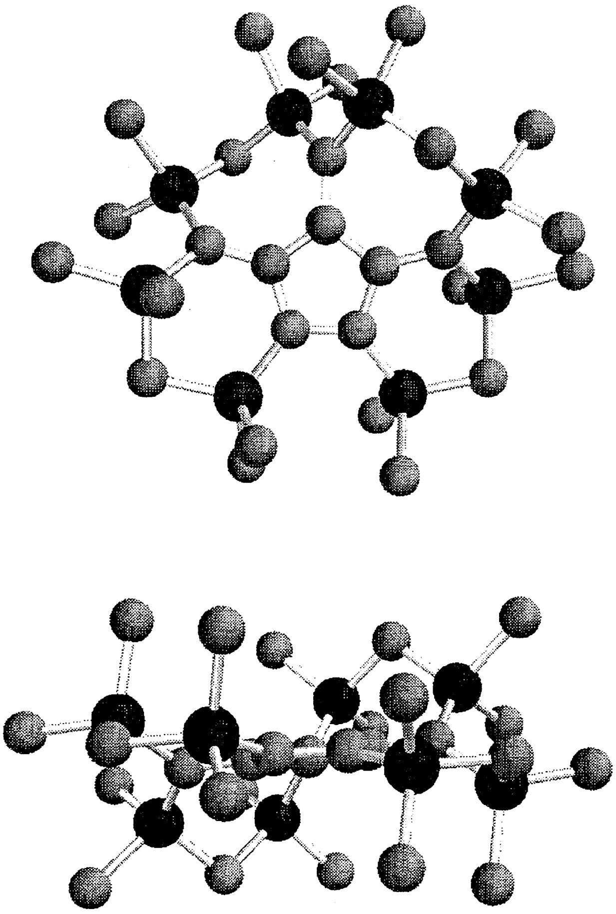


Fig. 5. Calculated structure of $\mathbf{2}^{4-}$ by PM3 (hydrogen atoms are omitted for the clarity): upper, top view; below, side view.

Interestingly, the ^{6}Li NMR spectrum of **3** yielded two signals appearing at −6.27 and 2.47 ppm with the same intensity as shown in Fig. 6. The appreciable upfield shift at −6.27 ppm is evidently caused by the strong shielding effect by the diamagnetic ring current resulting from the 6π aromatic system. Thus, this ^{6}Li signal is reasonably assigned to Li1 and Li1*, locating at the center of the five-membered ring. Thus, the molecular structure of **3** found in the crystals is maintained in non-polar solvents such as benzene-d_6 and toluene-d_8 to give a contact ion pair (CIP) (left in Fig. 7).

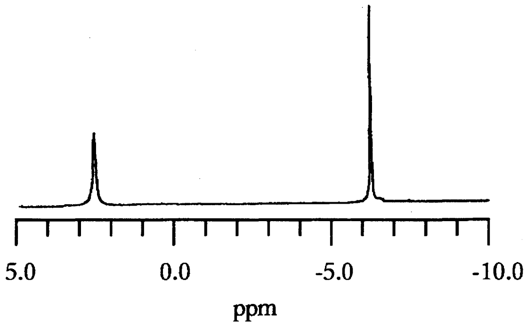


Fig. 6. ^{6}Li NMR of **3** in benzene-d_6 at 298 K.

The structure in a solvating media such as THF-d_8 is quite different from that found in non-polar solvents. In ^{6}Li NMR of **3** in THF-d_8, four signals were observed at −6.56, −0.37, 0.17, and 1.72 ppm with the same intensity as shown in Fig. 8. The exchange between the four ^{6}Li signals did not occur even at 60 °C. The satellite signals due to the coupling with ^{13}C were observed for the signals of 0.17 ($J_{^{13}\mathrm{C}-^{6}\mathrm{Li}} = 4.7$ Hz) and 1.72 ppm ($J_{^{13}\mathrm{C}-^{6}\mathrm{Li}} = 5.7$ Hz), assignable to the Li^{+} ion bonded to the π-skeleton. It should be noted that none of the satellite signals for −6.56 and −0.37 ppm were found. The ^{6}Li signal at −6.56 ppm is reasonably assigned to the Li^{+} ion located above the cyclopentadienide ring. The chemical shift and the lack of the satellite signals due to ^{13}C suggest that the ^{6}Li signal at −0.37 ppm is assignable to the THF solvated species, Li^{+}(thf)$_n$. Thus, one of the two Li^{+} ions (either Li1 or Li1*) of above the cyclopentadienide ring is dissociated to yield a solvent separated ion pair (SSIP) in a solvating media such as THF-d_8 (right in Fig. 7). In ^{1}H and ^{13}C NMR spectra of the tetraanion **3** in THF-d_8, sixteen different protons and carbons due to SiMe$_2$ can be observed because of the lack of the symmetry. Four different methylene carbons can also be found. As well, eight different ^{29}Si signals can be seen.

Conclusion. The X-ray crystallography and the NMR data presented here indicate that the structure of **3** is a stable, closed-shell supercharged tetraanion, which is stabilized not only by the eight silicon atoms but also by the aromatic cyclopentadienyl anion. The geometry of **3** reflects the nature of the next LUMO of **2**. The four Li^{+} ions of **3** are fixed to the π-skeleton in non-polar solvents, giving a contact ion

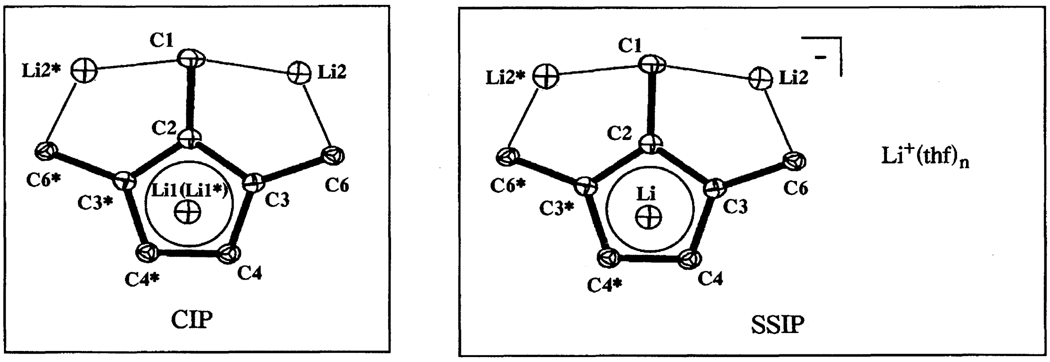


Fig. 7. Structures of CIP and SSIP.

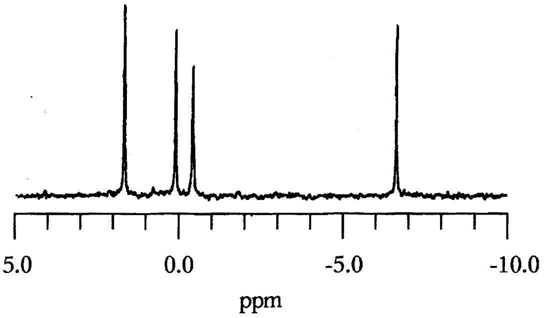


Fig. 8. ^{6}Li NMR of **3** in THF-d_8 at 298 K.

pair (CIP) with a highly symmetrical structure. However, in a solvating media such as THF-d_8, one of the Li^+ ions above the cyclopentadienide ring is dissociated to yield a solvent separated ion pair (SSIP) due to the solvation of the lithium cation.

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 (1 M = 1 mol dm^{-3}) in methanol/benzene-d_6 or 1 M LiCl in THF-d_8. Mass spectra were obtained on a Shimadzu QP-1000. Electronic spectra were recorded on a Shimadzu UV-2100 spectrometer. Cyclic Voltammetry was carried out with a conventional CV cell with a platinum disk as a working electrode, a platinum wire as a counter electrode, and a saturated calomel electrode as a reference electrode in acetonitrile. A Hokuto HA501 Potentiostat/Galvanostat, a Hokuto HB 104 Function Generator, and a YEW Model XY recorder were used for the measurement. Commercially available anhydrous lithium perchlorate (Kishida Kagaku Chameleon Reagent) as a supporting electrolyte was used as received. The sampling of **3** for X-ray crystallography was carried out by using a Giken Engineering Service GBX-1200 gas-replacement type glove box. Tetrahydrofuran and hexane were dried and distilled from sodium benzophenone ketyl. These solvents were further dried and degassed over a potassium mirror in vacuo prior to use. Benzene-d_6 and THF-d_8 were dried over molecular sieves, and then transferred into a tube covered with potassium mirror prior to use. Lithium-6 (95 atom%) metal was commercially available (Aldrich Chemical Company).

3,3,5,5,8,8,10,10,13,13,15,15,18,18,20,20-Hexadecamethyl-3,5,8,10,13,15,18,20-octasilacycloicosa-1,6,11,16-tetrayne (1).[15] 3,3,5,5-tetramethyl-3,5-disilahepta-1,6-diyne (7.45 g, 0.041 mol) in THF (20 ml) was added to a THF solution of ethylmagnesium bromide (80 ml, 0.086 mol) to produce Grignard reagent of the 1,6-diyne. The THF solution of the resulting Grignard reagent and 2,14-dichloro-2,4,4,7,7,9,9,12,12,14-decamethyl-2,4,7,9,12,14-hexasilapentadeca-5,10-diyne (21.57 g, 0.042 mol) in THF (20 ml) were added dropwise slowly to the refluxing THF (500 ml). After the addition, the reaction mixture was heated overnight. The mixture was poured in 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 crude **1** as colorless crystals (100—120 °C/0.2 mmHg, 1 mmHg = 133.322 Pa). Recrystallization from ethanol gave pure colorless crystals of **1** in 25% yield. Compound **1** had already been isolated from the reaction mixture of $BrMgC{\equiv}CMgBr$ and $ClMe_2Si{-}CH_2{-}SiMe_2Cl$ in very low yield.[15]

Octasilyltrimethylenecyclopentene (2). A mixture of **1** (201 mg, 0.33 mmol) and $[Mn(CO)_3(Me\text{-}Cp)]$ (93 mg, 0.43 mmol) in THF (30 ml) was irradiated with a 500 W high-pressure mercury lamp for 5 h through the cut off filter ($\lambda > 300$ nm) under the refluxing temperature of THF. After removal of the manganese complex, the reaction mixture was chromatographed on silica gel to produce pale yellow crystals of **2** in 17% yield. Mp 229—230 °C; ^{1}H NMR (C_7D_8) $\delta = -0.28$ (d, $J = 13.4$ Hz, 2 H, CH_2), -0.16 (d, $J = 13.4$ Hz, 2 H, CH_2), 0.05 (s, 6 H, CH_3), 0.05 (d, $J = 13.6$ Hz, 2 H, CH_2), 0.18 (s, 6 H, CH_3), 0.21 (s, 6 H, CH_3), 0.23 (s, 6H, CH_3), 0.26 (s, 6H, CH_3), 0.29 (s, 6 H, CH_3), 0.30 (s, 6 H, CH_3), 0.31 (s, 6 H, CH_3), 0.43 (d, $J = 13.6$ Hz, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) $\delta = 1.00$ (CH_3), 1.13 (CH_3), 1.76 (CH_2), 2.54 (CH_3), 3.52 (CH_3), 3.69 (CH_3), 3.99 (CH_3), 4.77 (CH_3), 6.45 (CH_3), 12.0 (CH_2), 134.1 (C4), 135.7 (C3,C5), 158.6 (C1, C2), 172.6 (C6, C8), 178.9 (C7); ^{29}Si NMR ($CDCl_3$) $\delta = -13.3, -10.2, -10.0, -9.1$; UV (hexane) λ_{max}/nm (ε) 229 (19500), 268 (15500), 309 (11000), 351 (5600). Found: C, 54.37; H 9.35%. Calcd for $C_{28}H_{56}Si_8$: C, 54.47; H 9.14%.

Octasilyltrimethylenecyclopentene Tetraanion Tetralithium (3). The crystals of **2** (51 mg, 0.083 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 (3 ml) was introduced by vacuum transfer and stirred at room temperature to give an orange solution of the tetraanion of **2** within 1 h. After the solvent was removed in vacuo, degassed hexane was introduced by vacuum transfer. Then, after removing the lithium metal, the solution was cooled to afford orange crystals of **3** quantitatively. ^{1}H NMR (C_6D_6) $\delta = -0.72$ (d, $J = 13.7$ Hz, 2 H, CH_2), -0.20 (d, $J = 13.7$ Hz, 2 H, CH_2), 0.05 (s, 6 H, CH_3), 0.08 (s, 6 H, CH_3), 0.12 (d, $J = 13.2$ Hz, 2H, CH_2), 0.29 (s, 6 H, CH_3), 0.34 (d, $J = 13.2$ Hz, 2 H, CH_2), 0.54 (s, 6 H, CH_3), 0.56 (s, 6 H, CH_3), 0.61 (s, 6 H, CH_3), 0.62 (s, 6 H, CH_3), 0.63 (s, 6 H, CH_3), 1.32 (m, 16 H, THF), 3.56 (m, 16 H, THF); ^{13}C NMR (C_6D_6) $\delta = 5.37$, 5.67 ($CH_3 \times 2$), 6.65, 6.90, 6.96, 7.37, 7.53, 9.20, 9.62 (quint, $J_{^{13}C-^{6}Li} = 2.3$ Hz), 11.6, 19.7 (t, $J_{^{13}C-^{6}Li} = 6.2$ Hz), 25.4 (THF), 68.9 (THF), 107.0, 132.1, 148.2; ^{29}Si NMR (C_6D_6) $\delta = -16.1, -15.1, -14.5, -13.2$; ^{6}Li NMR ($C_6D_6$) $\delta = -6.27, 2.47$.

NMR Spectral Data of 3 in THF-d_8. ^{1}H NMR (THF-d_8) $\delta = -0.90$ (d, $J = 12.6$ Hz, 1 H, CH_2), -0.74 (d, $J = 12.6$ Hz, 1 H, CH_2), -0.62 (d, $J = 12.6$ Hz, 1 H, CH_2), -0.46 (d, $J = 12.6$ Hz, 1 H, CH_2), -0.40 (d, $J = 12.6$ Hz, 1 H, CH_2), -0.36 (d, $J = 12.3$ Hz, 1 H, CH_2), -0.35 (d, $J = 12.6$ Hz, 1 H, CH_2), -0.26 (s, 3 H, CH_3), -0.24 (s, 3 H, CH_3), -0.23 (s, 3 H, CH_3), -0.22 (s, 3 H, CH_3), -0.11 (s, 3 H, CH_3), -0.08 (s, 3 H, CH_3), -0.01 (s, 3 H, CH_3), 0.01 (s, 3 H, CH_3), 0.04 (s, 3 H, CH_3), 0.05 (s, 3 H, CH_3), 0.12 (s, 3 H, CH_3), 0.16 (s, 3 H, CH_3), 0.20 (s, 6 H, $CH_3 \times 2$), 0.22 (s, 3 H, CH_3), 0.27 (s, 3 H, CH_3); ^{13}C NMR (THF-d_8) $\delta = 2.92$ (CH_3), 6.02 (CH_3), 6.56 (CH_3), 6.92 ($CH_3 \times 2$), 6.98 (CH_3), 7.56 (CH_3), 7.57 (CH_3), 7.58 (CH_3), 7.64 (CH_3), 8.18 (CH_3), 8.54 (CLi_2), 8.79 (CH_3), 8.92 (CH_3), 9.25 (CH_3), 9.59 (CH_3), 10.2 (CH_2), 10.8 (CH_3), 11.2 (CH_2), 11.5 (CH_2), 11.7 (CH_2), 17.2 (t, $J_{^{13}C-^{6}Li} = 5.7$ Hz, C), 19.1 (t, $J_{^{13}C-^{6}Li} = 4.7$ Hz, C), 108.5 (C), 109.8 (C), 127.9 (C), 139. 2 (C), 143.0 (C); ^{29}Si NMR (THF-d_8) $\delta = -19.2, -17.1, -15.9, -15.7, -15.2, -14.5, -11.8, -11.1$; ^{6}Li NMR (THF-$d_8$) $\delta = -6.56, -0.37, 0.17, 1.72$. The assignment of ^{1}H and ^{13}C signals were performed by DEPT and C-H COSY experiments, indicating that one doublet signal of CH_2 (ca. -0.22 ppm) was obscured by overlapping signals of methyl groups.

X-Ray Crystallography. Single crystals of **2** and **3** for

X-ray diffractions were grown from an ethanol solution and a hexane solution, respectively. The X-ray crystallographic experiments were performed on a Rigaku-Denki AFC 5R diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) or Cu K_α radiation ($\lambda = 1.54718$ Å). Crystal data for **2**: MF = $C_{28}H_{56}Si_8$, MW = 617.43, monoclinic, $a = 16.194(7)$, $b = 11.963(3)$, $c = 19.581(2)$ Å, $\beta = 97.94(2)°$, $V = 3757(2)$ Å^3, space group = $P2_1/a$, $Z = 4$, $D_{\text{calcd}} = 1.091$ g cm^{-3}. The final R factor was 0.0799 ($R_w = 0.0914$) for 6229 reflections with $F_o > 3\sigma(F_o)$. Crystal data for **3**: MF = $C_{44}H_{88}Li_4O_4Si_8$, MW = 933.62, monoclinic, $a = 22.94(1)$, $b = 12.257(4)$, $c = 20.164(7)$ Å, $\beta = 106.49(3)°$, $V = 5435(3)$ Å^3, space group = $C2/c$, $Z = 4$, $D_{\text{calcd}} = 1.141$ g cm^{-3}. The final R factor was 0.0574 ($R_w = 0.0650$) for 3546 reflections with $I > 3\sigma(I)$. Tables of positional and thermal parameters and complete interatomic distances and angles have been deposited as Document No. 71004 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Molecular Orbital Calculations. PM3 calculations were performed by Silicon Graphics INDY workstation with SPARTAN program (Ver. 4.0).[16] All the calculations were performed with geometry optimization.

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