Headline Articles

A Novel Tetralithium Salt of a Tetraanion and a Dilithium Salt of a Dianion, Formed by the Reduction of the Tetrasilylethylene Moiety. Synthesis, Characterization, and Observation of an Si–H···Li$^+$ Interaction

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2,3,6,7-Tetrakis(trimethylsilyl)-1,1,4,4,5,5,8,8-octamethyl-1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracene (**3**) was prepared starting from 2,3,6,7-tetrakis(dimethylsilyl)-1,1,4,4,5,5,8,8-octamethyl-1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracene (**1**). The molecular structures of **1** and **3** have been determined by X-ray crystallography. Compound **1** has an almost planar structure, whereas compound **3** exhibits a highly folded structure due to the steric repulsion of the trimethylsilyl groups. Treatment of **1** and **3** with lithium metal yielded the corresponding tetralithium salts of the tetraanions **4** and **5**, in which the two tetrasilylethylene units were subjected to two-electron reduction. 2,3-Bis(dimethylsilyl)-1,1,4,4-tetramethyl-1,4-disila-1,4-dihydronaphthalene (**6**), which has a half unit of **1**, was reacted with lithium metal to give the dilithium salt of the dianion (**7**). Evidence for an interaction between the Si–H and the Li$^+$ ion of **4** and **7** in both solid state and solution is also given.

Over the last decade, structural studies of various carbanions in the solid state and in solution have been reported.[1] Especially, polyanions with extended π-electron systems have attracted considerable interest owing to their unique structures and electronic properties. However, polyanions of polycyclic hydrocarbons have only rarely been observed and they are one of the most attractive synthetic targets. The electron-accepting ability of fullerenes presents an interesting chemistry for polyanions. Several varieties of alkali metal-doped fullerenes, such as hexaanionic species, have been investigated so far.[2] As a related area of chemistry, Scott et al. recently reported on the interesting dimer structure of the tetralithium salt of the corannulene tetraanion and its derivatives in solution.[3] The molecular structure of the tetrasodium salt of the rubrene tetraanion, determined by X-ray crystallography, was first reported by Bock et al.[4]

The introduction of a silyl group to the π-electron systems causes remarkable steric and electronic perturbation.[5] One of the most interesting features of the silyl-substituted π-electron systems is the ability to form the corresponding anion species by reduction with alkali metals.[5] Previously, we have reported successful preparations of dilithium dianion derivatives of silyl-substituted ethylenes,[6] styrenes,[7] benzenes,[8] dimethylenecyclobutene,[9] [4]radialene,[10] fulvene,[11] and persilylated cyclopentadienide.[12] Recently, we have also reported the formation of the tetralithium salt of an octasilyl-substituted trimethylenecyclopentene tetraanion with an eight-center, twelve π-electron system.[13] In this paper, we wish to report a detailed study of the novel tetralithium salt of tetraanions (**4**)[14] and (**5**) formed by the reduction of two units of the tetrasilylethylene moiety, as a new approach to the polyanions. As a related compound, the synthesis and the molecular structure of the dilithium dianion salt (**7**) by the reduction of 2,3-bis(dimethylsilyl)-1,1,4,4-tetramethyl-1,4-disila-1,4-dihydronaphthalene (**6**) are also reported.

Results and Discussion

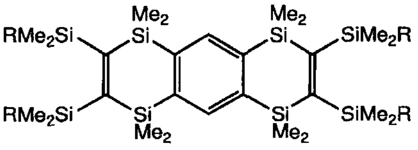
Preparation of Compounds 1 and 3. As a precursor for the novel polyanion species, we have focused on the tricyclic 1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracene skeleton. The dimethylsilyl-substituted derivative, 2,3,6,7-tetrakis(dimethylsilyl)-1,1,4,4,5,5,8,8-octamethyl-1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracene (**1**), was prepared according to the method of Tanaka et al.[15] Starting from **1**, we have prepared the trimethylsilyl-substituted derivative, 2,3,6,7-tetrakis(trimethylsilyl)-1,1,4,4,5,5,8,8-octamethyl-1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracene (**3**). Thus, treatment of **1** with bromine in CCl_4 in the presence of pyridine afforded the tetrakis(bromodimethylsilyl)-substituted derivative (**2**), which was methylated by methylmagnesium bromide to yield colorless crystals of trimethylsilyl-substituted derivative **3** (Scheme 1).

Molecular Structures of 1 and 3. We have determined the molecular structures of compounds **1** and **3** by X-ray diffraction. These molecules have an inversion center at the center of the benzene ring (Figs. 1 and 2). Selected bond lengths, bond angles, and dihedral angles are listed in Tables 1 and 2, respectively. Molecule **1** has an almost planar skeleton, as shown in Fig. 1. Four dimethylsilyl groups have a "gear meshed" structure in the crystals, as found in tetrakis(dimethylsilyl)ethylene.[16] The dihedral angle between the Si1–C4–Si3 and Si2–C5–Si4 planes is only 0.7°. On the other hand, molecule **3** has an extensively folded and twisted structure, as shown in Fig. 2. The dihedral angle between the Si1–C4–Si3 and Si2–C5–Si4 planes is 23.4°. The highly twisted conformation of the tetrasilylethylene units of **3** is evidently attributed to the steric repulsion of the four trimethylsilyl groups, as reported in a variety of twisted tetrakis(trialkylsilyl)ethylene derivatives.[17]

Four-Electron Reduction of 1 and 3 with Lithium Metal. All manipulations for the reduction of **1** and **3** were carried out under an inert atmosphere by standard Schlenk and high-vacuum line techniques. Treatment of **1** with excess lithium metal in dry, oxygen-free diethyl ether (Et_2O) at room temperature afforded a red solution of the tetralithium tetraanion (**4**) (Scheme 2). The four-electron reduction was complete within 20 h. The tetralithium salt of tetraanion **4** was isolated as air- and moisture-sensitive dark red crystals from Et_2O at 5 °C.

The reaction of **3** with excess lithium metal in THF at room temperature afforded a dark purple solution of the tetralithium tetraanion (**5**) (Scheme 2). However, the resulting tetralithium salt of the tetraanion **5** is only slightly soluble in THF. The structure of **5** in solution was characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{6}Li NMR spectroscopies at high temperature (323 or 333 K). In the ^{1}H NMR spectrum of **5**, two sets of methyl groups were observed at 0.09 and 0.28 ppm, and aryl protons at 7.64 ppm. Two sets of ^{29}Si signals were found at −25.3 and −8.9 ppm. The ^{6}Li NMR spectrum of **5** yielded only one signal, appearing at 1.03 ppm. The carbon atoms assigned to the methyl groups were observed at 6.1 and 8.3 ppm. The signal for the carbon atoms attached to the lithium atoms was observed at 6.6 ppm, which was considerably shifted to higher field relative to that of **3** (189.6 ppm) by $\Delta\delta = -183.0$. On the other hand, the ^{13}C signals for the benzene ring of **5** (146.2 (C) and 134.0 (CH) ppm) have almost identical chemical shifts compared with **3** (145.2 (C) and 135.4 (CH) ppm). Thus, it is apparent that the negative charges are largely delocalized over the four quaternary carbon atoms of the two ethylene dianion units. No scalar coupling between ^{6}Li and the anionic carbons was observed.

Molecular Structure of 4. The molecular structure of the tetraanion **4** has been unequivocally confirmed by X-ray crystallography (Fig. 3). This molecule also has an inversion center at the center of the benzene ring. Selected bond lengths, bond angles, and dihedral angles are listed in Table 3. The tetralithium salt **4** has a monomeric structure and forms contact ion pairs (*tetrakis-CIP*) in the crystals. The two lithium atoms are located above and below the olefinic C–C double bond (C4–C5), with distances of 2.09(1) to



1: R = H
2: R = Br
3: R = Me

Scheme 1.

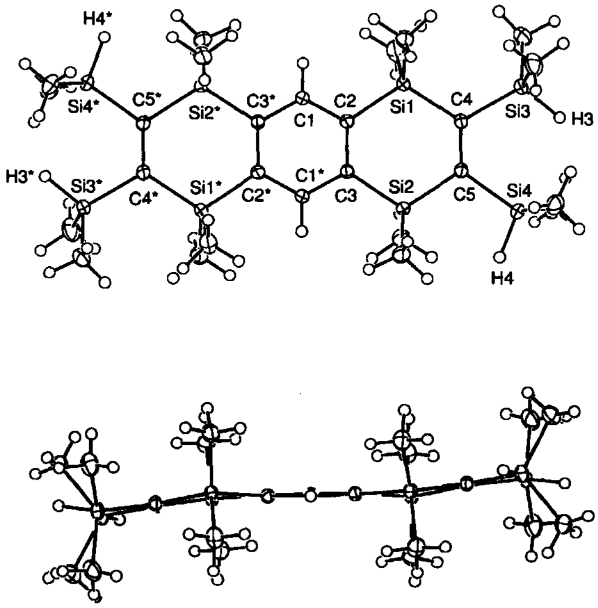


Fig. 1. ORTEP drawing of **1** with thermal ellipsoids shown at the 50% probability level: upper, top view; below, side view.

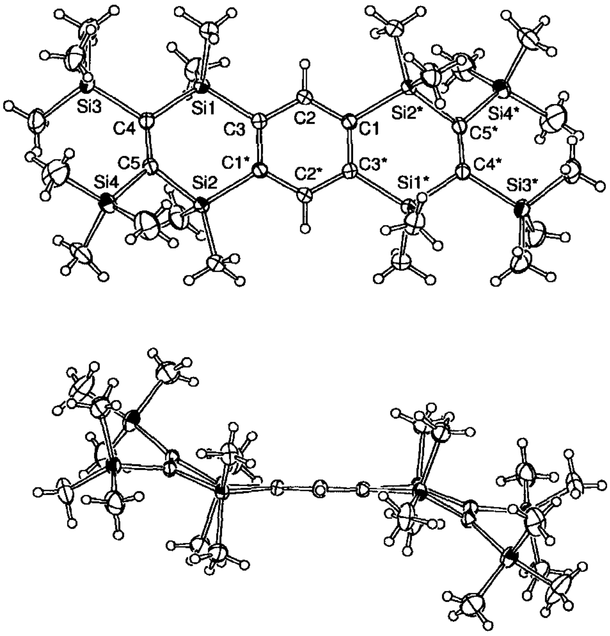


Fig. 2. ORTEP drawing of **3** with thermal ellipsoids shown at the 50% probability level: upper, top view; below, side view.

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

	Bond distances		
C1–C2	1.406(1)	C1–C3*	1.404(1)
C2–C3	1.413(1)	C4–C5	1.377(1)
C2–Si1	1.878(1)	C3–Si2	1.871(1)
C4–Si1	1.899(1)	C5–Si2	1.892(1)
C4–Si3	1.897(1)	C5–Si4	1.911(1)
	Bond angles		
C2–C1–C3*	123.1(1)	C1–C2–C3	118.2(1)
C1–C2–Si1	118.5(1)	C3–C2–Si1	123.1(1)
C1*–C3–C2	118.7(1)	C1*–C3–Si2	118.2(1)
C2–C3–Si2	123.1(1)	C5–C4–Si1	123.1(1)
C5–C4–Si3	121.0(1)	Si1–C4–Si3	115.9(1)
C4–C5–Si2	123.9(1)	C4–C5–Si4	125.6(1)
Si2–C5–Si4	110.6(1)	C2–Si1–C4	112.4(1)
C3–Si2–C5	112.9(1)		
	Dihedral angles		
Si1–C4–C5–Si2	0.0(1)	Si3–C4–C5–Si4	0.1(1)
Si1–C4–Si3/Si2–C5–Si4			0.68(2)

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

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

	Bond distances		
C1–C2	1.397(3)	C1–C3*	1.404(3)
C2–C3	1.402(3)	C4–C5	1.369(3)
C1*–Si2	1.876(2)	C3–Si1	1.870(2)
C4–Si1	1.898(2)	C5–Si2	1.906(2)
C4–Si3	1.906(2)	C5–Si4	1.909(2)
	Bond angles		
C2–C1–C3*	118.7(2)	C2–C1–Si2*	120.9(2)
C3*–C1–Si2*	120.4(1)	C1–C2–C3	123.3(2)
C1*–C3–C2	118.0(2)	C1*–C3–Si1	121.8(1)
C2–C3–Si1	119.9(1)	C5–C4–Si1	122.7(1)
C5–C4–Si3	123.3(2)	Si1–C4–Si3	114.0(1)
C4–C5–Si2	117.4(2)	C4–C5–Si4	129.7(2)
Si2–C5–Si4	112.7(1)	C3–Si1–C4	111.78(9)
C1*–Si2–C5	111.08(9)		
	Dihedral angles		
Si1–C4–C5–Si2	24.5(2)	Si3–C4–C5–Si4	19.8(3)
Si1–C4–Si3/Si2–C5–Si4			23.4(2)

a) Atomic numbers are given in Fig. 2. Standard deviations are in parentheses.

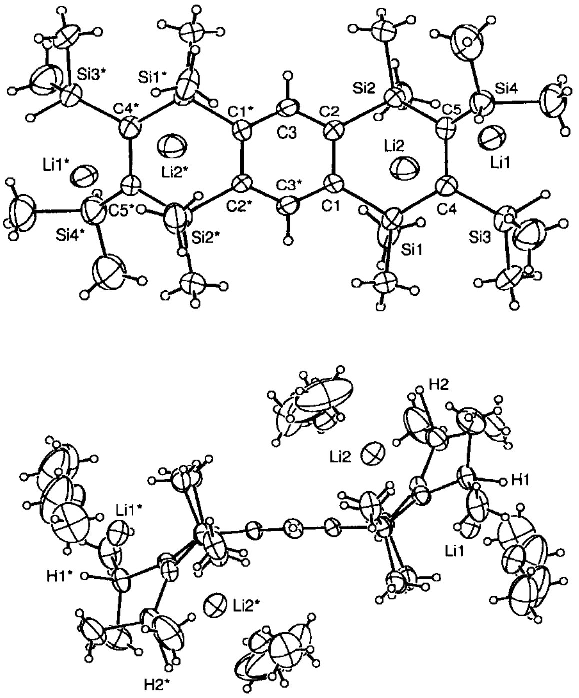
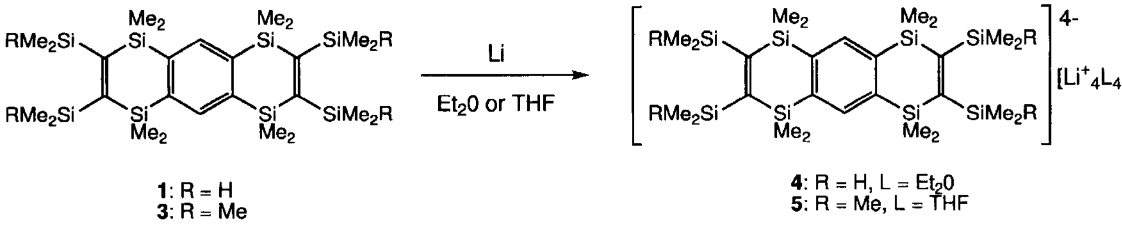


Fig. 3. ORTEP drawing of **4** with thermal ellipsoids shown at the 30% probability level: upper, top view (Et_2O molecules are omitted for the clarity); below, side view.

2.23(1) Å. Each lithium atom is coordinated with one Et_2O molecule. Thus, the two olefinic units connected with the HMe_2Si groups in **1** are subjected to a two-electron reduction, although the benzene ring is not reduced. The Li–C distances (av 2.139 Å) are close to those of the dilithium tetrasilylethylene dianion derivatives (e.g. dilithium tetrakis(trimethylsilyl)ethylene dianion (av 2.105 Å),[6a] dilithium 2,2′-bis(1,1,3,3-tetramethyl-1,3-disilacyclopentylidene) dianion (av 2.063 Å),[6c] and dilithium tetrakis(dimethylsilyl)ethylene dianion (av 2.127 Å).[6e] The X-ray results of these nonconjugated 1,2-dilithioethanes clearly show the "doubly-bridged structure" of lithiums.

A comparison of the structural parameters of the neutral starting molecule **1** and its tetraanion **4** is quite interesting. The molecular structure of **4** becomes considerably folded and twisted after the four-electron reduction, as shown in Fig. 3. The twisting along the C4–C5 bond is attributed to the interaction of the hydrogen atom on the silicon atom with the Li^+ ion. Indeed, the dihedral angle of **4** between the Si1–C4–Si3 and Si2–C5–Si4 planes is 28.4°, which is remarkably increased relative to that of **1** (0.7°). A similar Si–H···Li^+ interaction has been observed in the crystals



Scheme 2.

Table 3. Selected Bond Distance (Å), Angles (deg), and Dihedral Angles (deg) of **4**[a)]

	Bond distances		
C1–C2	1.413(9)	C1–C3*	1.398(9)
C2–C3	1.406(10)	C4–C5	1.585(10)
C1–Si1	1.890(7)	C2–Si2	1.887(7)
C4–Si1	1.825(8)	C5–Si2	1.827(8)
C4–Si3	1.825(8)	C5–Si4	1.808(8)
C4–Li1	2.233(17)	C5–Li1	2.097(18)
C4–Li2	2.135(18)	C5–Li2	2.091(17)
	Bond angles		
C2–C1–C3*	116.9(6)	C2–C1–Si1	121.8(6)
C3*–C1–Si1	121.2(5)	C1–C2–C3	117.1(6)
C1–C2–Si2	119.8(5)	C3–C2–Si2	123.0(5)
C2–C3–C1*	126.0(6)	C5–C4–Si1	123.4(5)
C5–C4–Si3	119.6(5)	Si1–C4–Si3	116.8(4)
C4–C5–Si2	113.0(5)	C4–C5–Si4	121.4(5)
Si2–C5–Si4	124.3(4)	C1–Si1–C4	107.0(3)
C2–Si2–C5	108.0(3)		
	Dihedral angles		
Si1–C4–C5–Si2	19.8(8)	Si3–C4–C5–Si4	37.5(9)
Si1–C4–Si3/Si2–C5–Si4		28.4(6)	

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

Table 4. The Coupling Constant of Si–H Bond ($^1J_{^1H-^{29}Si}$) and the Wavenumber of Si–H Stretching Vibration (ν_{Si-H})

Compound	^{29}Si NMR $^1J_{^1H-^{29}Si}$/Hz	IR ν_{Si-H}/cm^{-1}
1	181[a)]	2158[d)] 2116
4	146[b)]	1957[e)]
6	180[a)]	2164[f)] 2122
7	145[c)]	1942[f)]

a) In $CDCl_3$ at 298 K. b) In C_7D_8 at 298 K. c) In C_6D_6 at 298 K. d) In THF at 298 K. e) In toluene at 298 K. f) In hexane at 298 K.

of dilithium tetrakis(dimethylsilyl)ethylene dianion.[6e] The folded structure into the boat form (C1–C2–Si2–C5–C4–Si1 ring) is probably caused by the interaction of the Li$^+$ ion with the benzene ring (e.g., C1–Li2: 2.74(1), C2–Li2: 2.92(1) Å).

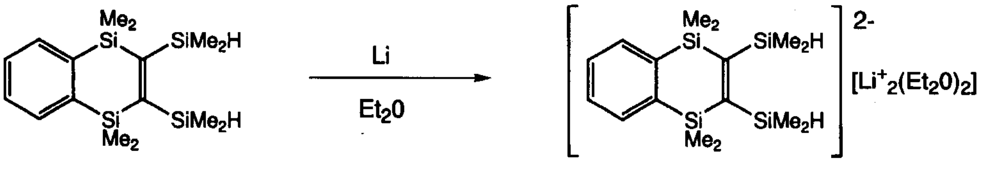
The bond length of the dianionic C–C bond increases significantly from 1.377(1) Å in **1** to 1.585(10) Å in **4**. The Si–C (anionic carbon) bonds (e.g., C4–Si1, C4–Si3, C5–Si2, and C5–Si4) in **4** (av 1.821 Å) are shorter than those in **1** (av 1.900 Å), because of the delocalization of the negative charge onto the silicon centers by pπ–σ* conjugation. In contrast, the bond lengths of the C1–Si1 and C2–Si2 (av 1.889(7) Å for **4**) are almost unchanged after the reduction (1.874(1) Å for **1**).

Structure of 4 in Solution. The structure of **4** in solution was also characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{6}Li NMR spectroscopies. The NMR spectroscopic data of **4** in toluene-d_8 indicate the highly symmetric *tetrakis-CIP* structure. The spectral data are consistent with a doubly-bridged structure; the signal in the ^{13}C NMR for the anionic carbon atoms at 7.6 ppm appears as a quintet ($^1J_{^6Li-^{13}C}$ = 2.6 Hz) due to the coupling with two ^{6}Li nuclei (I = 1). This signal of **4** is shifted remarkably upfield relative to that of **1** (185.6 ppm) by $\Delta\delta = -177.8$. On the other hand, the ^{13}C signals for the benzene ring of **4** (146.0 (C) and 134.2 (CH) ppm) have almost identical chemical shifts to **1** (144.3 (C) and 136.4 (CH) ppm). Thus, the negative charges are largely delocalized over the four quaternary carbon atoms of the two ethylene dianion units and can be stabilized by eight silicon atoms.

The Si–H···Li$^+$ interaction found in the crystals of **4** is clearly observed by NMR and IR spectroscopies in solution. The ^{6}Li NMR signal of **4** is a triplet at δ = 0.41 ($^1J_{^1H-^6Li}$ = 0.35 Hz). The splitting of the ^{6}Li signal is caused by coupling with two SiH protons, which suggests a flipping along the C–C bond in solution. The coupling constant of the Si–H bond ($^1J_{^1H-^{29}Si}$) is considerably decreased on going from **1** (181 Hz) to **4** (146 Hz) due to the Si–H···Li$^+$ interaction. The infrared spectrum of **4** in hexane exhibits a broad Si–H stretching band at 1957 cm^{-1}, which is at a lower wavenumber than those of **1** (2158 and 2116 cm^{-1}). These spectroscopic data are summarized in Table 4.

Two-Electron Reduction of 6 with Lithium Metal. We have also examined the two-electron reduction of 2,3-bis(dimethylsilyl)-1,1,4,4-tetramethyl-1,4-disila-1,4-dihydronaphthalene (**6**),[15] which has a half unit of **1**. Compound **6** was reacted with excess lithium metal in Et_2O at room temperature to give a red solution of the dianion (**7**) (Scheme 3). Crystallization from heptane afforded air- and moisture-sensitive dark red crystals of the dilithium salt of dianion **7**.

Figure 4 shows the molecular structure of **7**, which was determined by X-ray diffraction. Selected bond lengths, bond angles, and dihedral angles are listed in Table 5. The dilithium salt **7** has a monomeric structure and forms contact ion pairs (*bis-CIP*) in the crystals. The two lithium atoms



6 **7**

Scheme 3.

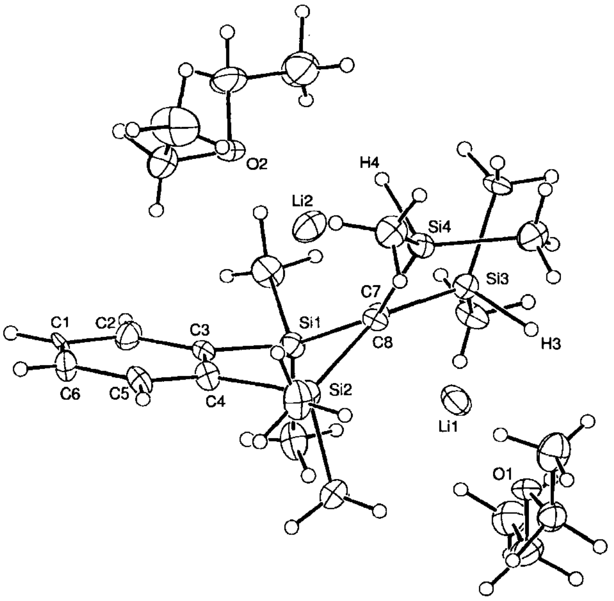


Fig. 4. ORTEP drawing of **7** with thermal ellipsoids shown at the 30% probability level.

Table 5. Selected Bond Distance (Å), Angles (deg), and Dihedral Angles (deg) of **7**[a)]

	Bond distances		
C1–C2	1.368(12)	C1–C6	1.387(13)
C2–C3	1.403(9)	C3–C4	1.431(11)
C4–C5	1.387(11)	C5–C6	1.408(10)
C7–C8	1.588(10)	C3–Si1	1.886(8)
C4–Si2	1.902(8)	C7–Si1	1.832(8)
C8–Si2	1.801(10)	C7–Si3	1.828(9)
C8–Si4	1.828(9)	C7–Li1	2.169(16)
C8–Li1	2.073(16)	C7–Li2	2.140(15)
C8–Li2	2.158(16)		
	Bond angles		
C2–C1–C6	119.2(7)	C1–C2–C3	123.6(9)
C2–C3–C4	116.9(7)	C2–C3–Si1	120.7(6)
C4–C3–Si1	122.3(5)	C3–C4–C5	119.5(7)
C3–C4–Si2	119.0(6)	C5–C4–Si2	121.5(6)
C4–C5–C6	121.2(8)	C1–C6–C5	119.5(8)
C8–C7–Si1	122.1(6)	C8–C7–Si3	120.1(5)
Si1–C7–Si3	117.7(4)	C7–C8–Si2	113.6(6)
C7–C8–Si4	118.5(7)	Si2–C8–Si4	126.4(4)
C3–Si1–C7	108.7(3)	C4–Si2–C8	108.4(4)
	Dihedral angles		
Si1–C7–C8–Si2	26.5(5)	Si3–C7–C8–Si4	42.0(5)
Si1–C7–Si3/Si2–C8–Si4	35.04(2)		

a) Atomic numbers are given in Fig. 4. Standard deviations are in parentheses.

are bonded to the two anionic carbon atoms with a doubly-bridged structure. The Li–C distances range from 2.07(2) to 2.17(2) Å (av 2.14 Å). The bond length of the dianionic C–C bond is 1.588(10) Å and the average Si–C (anionic carbon) bond length is 1.822 Å. The dihedral angle of **7** between the Si1–C7–Si3 and Si2–C8–Si4 planes is 35.0° due to the Si–H···Li^+ interaction. These structural parameters indicate that dianion **7** can be regarded as a half unit of tetraanion **4**.

The NMR spectral data of **7** in benzene-d_6 are consistent with the highly symmetrical doubly-bridged *bis-CIP* structure. The ^{13}C signal for the anionic carbon atoms at 7.3 ppm appears as a quintet ($^1J_{^6\mathrm{Li}-^{13}\mathrm{C}}$ = 2.4 Hz) due to the coupling with two ^6Li nuclei. This signal of **7** is considerably shifted to a higher field relative to that of **6** (185.5 ppm) by $\Delta\delta = -178.2$. The ^{6}Li NMR signal of **7** is a triplet at $\delta = 0.28$ ($^1J_{^1\mathrm{H}-^6\mathrm{Li}}$ = 0.42 Hz) resulting from the coupling with two SiH protons. The coupling constant of the Si–H bond ($^1J_{^1\mathrm{H}-^{29}\mathrm{Si}}$) is decreased from **6** (180 Hz) to **7** (145 Hz). The infrared spectrum of **7** in hexane exhibits a broad Si–H stretching band at 1942 cm^{-1}, which is at a lower wavenumber than those for **6** (2164 and 2122 cm^{-1}). These spectroscopic data clearly show the presence of an Si–H···Li^+ interaction in dianion **7** in solution (Table 4).

Conclusions. The reaction of **1** and **3** with lithium metal produced a novel tetralithium salt of the tetraanions **4** and **5**, in which the two tetrasilylethylene units were reduced. The dilithium salt of the tetrasilylethylene dianion **7** can be regarded as a half unit of **4**. The spectroscopic and structural features of **4** and **7** clearly show the presence of an Si–H···Li^+ interaction, which leads to the highly twisted structure.

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/toluene-d_8 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. The sampling of **4** and **7** for X-ray crystallography were carried out by using a MBRAUN MB-150 B-G gas-replacement type glove box. Tetrahydrofuran, diethyl ether, 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, 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. Carbon tetrachloride and pyridine were dried and distilled from calcium hydride. Lithium-6 (95 atom%) metal was commercially available (Aldrich Chemical Company).

2,3,6,7-Tetrakis(dimethylsilyl)-1,1,4,4,5,5,8,8-octamethyl-1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracene (1). Compound **1** was prepared by the dehydrogenative double silylation reported by Tanaka et al.[15] Spectral data for **1**; mp 235 °C; ^{1}H NMR ($CDCl_3$) δ = 0.28 (d, J = 3.9 Hz, 24 H, CH_3), 0.37 (s, 24 H, CH_3), 4.49 (sept, J = 3.9 Hz, 4 H, SiH), 7.66 (s, 2 H, CH); ^{13}C NMR ($CDCl_3$) δ = -1.4 (CH_3), 0.7 (CH_3), 136.4 (CH), 144.3 (C), 185.6 (C); ^{29}Si NMR ($CDCl_3$) δ = $-27.3, -24.4$.

2,3,6,7-Tetrakis(trimethylsilyl)-1,1,4,4,5,5,8,8-octamethyl-1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracene (3). Bromine (0.54 g, 3.3 mmol) in CCl_4 (5 ml) was added to a solution of **1** (0.50 g, 0.84 mmol) in CCl_4 (15 ml) and pyridine (4.5 ml) at 0 °C for 2 h. The reaction mixture was stirred for an additional 3 h at room temperature, and then the solvent was removed in vacuo. Dry benzene (20 ml) was introduced, and then the resulting pyridinium bromide salt was filtered off. After the filtrate was evaporated in vacuo, dry THF (20 ml) was added to the residue. Without purification of

2,3,6,7-tetrakis(bromodimethylsilyl)-1,1,4,4,5,5,8,8-octamethyl-1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracene (**2**), an ether solution of methylmagnesium bromide (4.0 ml, 3.76 mmol) was added to this solution. The reaction mixture was stirred for 2 d and then 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 chromatographed on silica gel with hexane to give the crude **3** as colorless crystals. Recrystallization from hexane gave pure colorless crystals of **3** in 7% yield. Compound **3**: Colorless crystals; mp 254—256 °C; ^{1}H NMR ($CDCl_3$) $\delta = 0.27$ (s, 36 H, CH_3), 0.41 (s, 24 H, CH_3), 7.61 (s, 2 H, CH); ^{13}C NMR ($CDCl_3$) $\delta = 2.8$ (CH_3), 4.2 (CH_3), 135.4 (CH), 145.2 (C), 189.6 (C); ^{29}Si NMR ($CDCl_3$) $\delta = -27.4$, -9.9; UV (hexane) λ_{max}/nm (ε) 224 (45100), 294 (65600), 356 (900). Found: C, 55.21; H, 9.46%. Calcd for $C_{30}H_{62}Si_8$: C, 55.65; H, 9.65%.

[2,3,6,7-Tetrakis(dimethylsilyl)-1,1,4,4,5,5,8,8-octamethyl-1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracenato]tetrakis[(diethyl ether)lithium(I)] (4). The crystals of **1** (28 mg, 0.047 mmol) and lithium metal (30 mg, 4.4 mmol) were placed in a reaction tube with a magnetic stirrer. After degassing, dry oxygen-free Et_2O (0.8 ml) was introduced by vacuum transfer and the mixture was stirred at room temperature to give a red solution of the tetraanion **4**. The four electron reduction was complete in about 20 h. Additional degassed Et_2O (3.0 ml) was introduced by vacuum transfer. Then, after the lithium metal was removed, the solution was cooled to afford dark red crystals of **4**, quantitatively. ^{1}H NMR (C_7D_8) $\delta = 0.52$ (d, $J = 3.4$ Hz, 24 H, CH_3), 0.60 (s, 24 H, CH_3), 1.02 (t, $J = 7.0$ Hz, 24 H, CH_3, Et_2O), 3.16 (q, $J = 7.0$ Hz, 16 H, CH_2, Et_2O), 4.77 (br s, 4 H, SiH), 7.96 (s, 2 H, CH); ^{13}C NMR (C_7D_8) $\delta = 6.0$ (CH_3), 6.2 (CH_3), 7.8 (quint, $J_{^6Li-^{13}C} = 2.3$ Hz, C), 15.1 (CH_3, Et_2O), 65.9 (CH_2, Et_2O), 134.2 (CH), 146.0 (C); ^{29}Si NMR (C_7D_8) $\delta = -24.3$, -23.9; ^{6}Li NMR (C_7D_8) $\delta = 0.41$ (t, $J_{^1H-^6Li} = 0.35$ Hz) (from LiCl in MeOH).

[2,3,6,7-Tetrakis(trimethylsilyl)-1,1,4,4,5,5,8,8-octamethyl-1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracenato] tetrakis[(tetrahydrofuran)lithium(I)] (5). The crystals of **3** (23 mg, 0.035 mmol) and lithium metal (30 mg, 4.4 mmol) were placed in a reaction tube with a magnetic stirrer. After degassing, dry oxygen-free THF (0.8 ml) was introduced by vacuum transfer and the mixture was stirred at room temperature to give a dark purple solution of the tetraanion **5**. The four-electron reduction was complete in about 20 h. ^{1}H NMR (THF-d_8, 333 K) $\delta = 0.09$ (s, 36 H, CH_3), 0.28 (s, 24 H, CH_3), 7.64 (s, 2 H, CH); ^{13}C NMR (THF-d_8, 323 K) $\delta = 6.1$ (CH_3), 6.6 (C), 8.3 (CH_3), 134.0 (CH), 146.2 (C); ^{29}Si NMR (THF-d_8, 323 K) $\delta = -25.3$, -8.9; ^{6}Li NMR (THF-d_8, 323 K) $\delta = 1.03$ (from LiCl in MeOH).

2,3-Bis(dimethylsilyl)-1,1,4,4-tetramethyl-1,4-disila-1,4-dihydronaphthalene (6). Compound **6** was prepared by the dehydrogenative double silylation reported by Tanaka et al.[15] Spectral data for **6**; ^{1}H NMR ($CDCl_3$) $\delta = 0.29$ (d, $J = 3.9$ Hz, 12 H, CH_3), 0.36 (s, 12 H, CH_3), 4.50 (sept, $J = 3.9$ Hz, 2 H, SiH), 7.33 (dd, $J = 5.4$ and 3.4 Hz, 2 H, CH), 7.52 (dd, $J = 5.4$ and 3.4 Hz, 2 H, CH); ^{13}C NMR ($CDCl_3$) $\delta = -1.3$ (CH_3), 0.7 (CH_3), 128.1 (CH), 132.7 (CH), 145.2 (C), 185.5 (C); ^{29}Si NMR ($CDCl_3$) $\delta = -26.8$, -24.3.

[2,3-Bis(dimethylsilyl)-1,1,4,4-tetramethyl-1,4-disila-1,4-dihydronaphthalenato]bis[(diethyl ether)lithium(I)] (7). The crystals of **6** (25 mg, 0.058 mmol) and lithium metal (30 mg, 4.4 mmol) were placed in a reaction tube with a magnetic stirrer. After degassing, dry oxygen-free Et_2O (0.8 ml) was introduced by vacuum transfer and the mixture was stirred at room temperature to give a red solution of the tetraanion **7**. The two electron reduction was complete in about 20 h. After the solvent was removed in vacuo, dry degassed heptane (3.0 ml) was introduced by vacuum transfer. Then, after the lithium metal was removed, the solution was cooled to afford dark red crystals of **7**, quantitatively. ^{1}H NMR (C_6D_6) $\delta = 0.58$ (d, $J = 3.3$ Hz, 12 H, CH_3), 0.63 (s, 12 H, CH_3), 0.89 (t, $J = 7.1$ Hz, 12 H, CH_3, Et_2O), 3.01 (q, $J = 7.1$ Hz, 8 H, CH_2, Et_2O), 4.81 (br s, 2 H, SiH), 7.28 (dd, $J = 5.5$ and 3.3 Hz, 2 H, CH), 7.69 (dd, $J = 5.5$ and 3.3 Hz, 2 H, CH); ^{13}C NMR (C_6D_6) $\delta = 6.0$ (CH_3), 6.3 (CH_3), 7.3 (quint, $J_{^6Li-^{13}C} = 2.4$ Hz, C), 14.7 (CH_3, Et_2O), 65.8 (CH_2, Et_2O), 127.8 (CH), 131.6 (CH), 148.4 (C); ^{29}Si NMR (C_6D_6) $\delta = -23.7$, -23.5; ^{6}Li NMR (C_6D_6) $\delta = 0.28$ (t, $J_{^1H-^6Li} = 0.42$ Hz) (from LiCl in MeOH).

X-Ray Crystallography of 1. Single crystals of **1** for X-ray diffraction were grown from a pentane solution. The X-ray crystallographic experiments were performed on a MacScience DIP-2030K image plate diffractometer with graphite-monochromatized Mo *Kα* radiation. The structure was solved by the direct method using *SIR*92 and refined by the full-matrix least-squares method using maXus. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms except the hydrogen atoms on the silicon atoms were treated as idealized contributions. Crystal data for **1** at 120 K; molecular formula = $C_{26}H_{54}Si_8$, MW = 591.41, triclinic, $a = 6.4890(2)$, $b = 9.3480(6)$, $c = 16.338(1)$ Å, $\alpha = 72.218(3)$, $\beta = 84.077(4)$, $\gamma = 72.346(1)°$, $V = 899.2(1)$ Å^3, space group $P\bar{1}$, $Z = 1$, $D_{calcd} = 1.09$ g cm^{-3}. The final *R* factor was 0.033 ($R_w = 0.114$) for 3603 reflections with $I > 3\sigma(I)$.

X-Ray Crystallography of 3. Single crystals of **3** for X-ray diffraction were grown from a hexane solution. The X-ray crystallographic experiments were performed on a Enraf–Nonius FR590 diffractometer with graphite-monochromatized Mo *Kα* radiation. The structure was solved by the direct method using *SIR*92 and refined by the full-matrix least-squares method using teXsan. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Crystal data for **3** at 298(2) K; molecular formula = $C_{30}H_{62}Si_8$, MW = 647.50, monoclinic, $a = 9.6696(4)$, $b = 16.845(1)$, $c = 13.052(1)$ Å, $\beta = 106.85(0)°$, $V = 2034.7(2)$ Å, space group $P2_1/c$, $Z = 2$, $D_{calcd} = 1.056$ g cm^{-3}. The final *R* factor was 0.0309 ($R_w = 0.0323$) for 2895 reflections with $I > 3\sigma(I)$.

X-Ray Crystallography of 4. Single crystals of **4** for X-ray diffraction were grown from a Et_2O solution. The X-ray crystallographic experiments were performed on a Bruker Smart 1000 CCD area detector with graphite-monochromatized Mo *Kα* radiation. The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELX97. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms except the hydrogen atoms on the silicon atoms were treated as idealized contributions. Some of the carbon atoms of the Et_2O molecules have elongated thermal ellipsoids due to disorder. Crystal data for **4** at 293(2) K; molecular formula = $C_{42}H_{94}Li_4O_4Si_8$, MW = 915.66, triclinic, $a = 9.9924(19)$, $b = 10.473(2)$, $c = 16.695(3)$ Å, $\alpha = 91.238(6)$, $\beta = 102.11(1)$, $\gamma = 117.84(1)°$, $V = 1496.0(5)$ Å, space group $P\bar{1}$, $Z = 1$, $D_{calcd} = 1.016$ g cm^{-3}. The final *R* factor was 0.0844 ($R_w = 0.2391$) for 1562 reflections with $I > 2\sigma(I)$.

X-Ray Crystallography of 7. Single crystals of **7** for X-ray diffraction were grown from a heptane solution. The X-ray crystallographic experiments were performed on a MacScience DIP-2030K image plate diffractometer with graphite-monochromatized Mo *Kα* radiation. The structure was solved by the direct method using *SIR*92 and refined by the full-matrix least-squares method using SHELX97. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms except the hydrogen atoms on the silicon atoms were treated as idealized contributions. Crystal data for **7** at 120 K; molecular formula = $C_{24}H_{50}Li_2O_2Si_4$, MW = 496.88, triclinic, a = 8.984(7), b = 10.443(10), c = 18.738(16) Å, α = 91.79(4), β = 98.23(5), γ = 115.23(6)°, V = 1566(2) Å, space group $P\bar{1}$, Z = 2, D_{calcd} = 1.05 g cm^{-3}. The final R factor was 0.0827 (R_w = 0.1915) for 1771 reflections with $I > 2\sigma(I)$. Tables of positional and thermal parameters and complete interatomic distances and angles for **1, 3, 4,** and **7** have been deposited as Document No. 73038 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 141347, 141348, 143889, and 143890.

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