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Synthesis and Reduction of Silyl-Substituted [5]Radialene. Characterization and Structure of a [5]Radialene Tetraanion with a Ten-Center, Fourteen-Electron π-System

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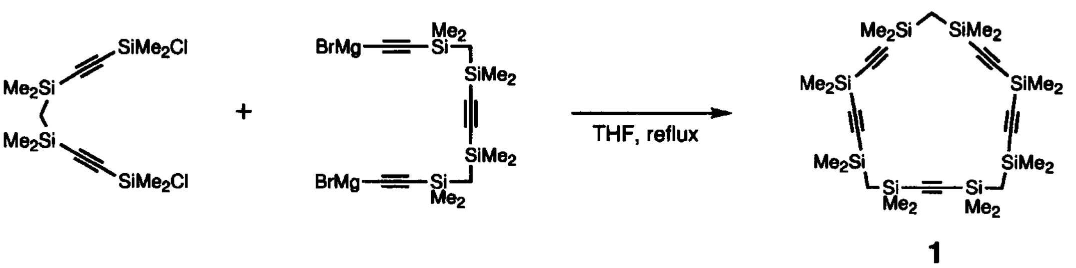
The reaction of 3,3,6,6,8,8,11,11,14,14,16,16,19,19,21,21-hexadecamethyl-3,6,8,11,14,16,19,21-octasilacyclohenicosa-1,4,9,12,17-pentayne with an excess molar amount of [Mn(CO)$_3$(Me-Cp)] in tetrahydrofuran (THF) under photochemical and refluxing conditions produced 2,2,4,4,9,9,11,11,13,13,15,15,17,17,21,21-hexadecamehyl-2,4,9,11,13,15,17,21-octasilahexacyclo[10.5.3.1^{5,8}.0^{6,18}.0^{7,20}.0^{14,19}]henicosa-1(18),5,7,12(20),14(19)-pentaene (**2**) as silyl-substituted [5]radialene derivative. This was reacted with lithium metal in THF to give dark red crystals of the tetralithium salt (**4**) of **2**. The molecular structure of tetraanion of **2** with a novel ten-center, fourteen-electron π-system was established by X-ray crystallography. The tetralithium salt **4** has a monomeric structure and forms contact ion pairs (*tetrakis-CIPs*) in the crystals. The structural parameters of **4** are discussed in comparison with those of the neutral starting molecule **2**. The structure of **4** in solution is also discussed on the basis of NMR spectroscopic data.

The chemistry of polyanions with extended π-electron systems is a subject of considerable interest.[1,2] These polyanions are expected to exhibit unusual structural, electronic, and magnetic properties due to their unusual electronic state. Thus, polyanions have been some of the most attractive synthetic targets in recent years. Fullerene, with a sixty-electron π-system, has a triply-degenerate, low-lying LUMO that can accept up to six electrons to form $C_{60}{}^{6-}$. On the other hand, corannulene, with a twenty-electron π-system, has a doubly-degenerate LUMO that can take up to four electrons to produce corannulene tetraanions.[3,4] [5]Radialene with a cross conjugated ten-electron π-system possesses a central unit of corannulene. However, there have been no studies on the anion species of [5]radialene derivatives, because the synthetic possibilities of the [5]radialene framework are very limited.[5] We previously reported successful preparation and molecular structures of the various dilithium salts of silyl-substituted π-electron systems.[6,7] Subsequently, we also reported the tetralithium salts of tris(methylene)cyclopentene derivative[8] and a 1,4,5,8-tetrasila-1,4,5,8-tetrahydroanthracene derivative.[9] Herein, we report a detailed study of the tetralithium salt of a [5]radialene octasilyl derivative **2** as a new silyl-substituted ten-center, fourteen-electron π-system, together with the crystal structures of the tetralithium salt of **2** and the macrocyclic pentayne **1**. We also report the dynamic behavior of the four lithium cations on the [5]radialene π-skeleton in solution.[10]

Results and Discussion

Synthesis of 2. Radialenes have received considerable interest owing to their special arrangement of π-electrons.[11] Several radialene derivatives have already been prepared, however, there are only a few reports on the synthesis of [5]radialene derivatives with a ten-electron π-system.[5] Previously, we demonstrated the intramolecular cyclooligomerization of the silacyclotriynes with transition metal complexes to give various silyl-substituted π-electron systems, such as hexakis(silyl)-substituted bis(methylene)cyclobutene.[12] More recently, we have reported that the silacyclotetrayne underwent intramolecular cyclization with [Mn(CO)$_3$(Me-Cp)] to form octakis(silyl)-substituted [4]-radialene and tris(methylene)cyclopentene derivatives with an eight-electron π-system.[8] All of these reactions involve a 1,2-silyl shift in the 1,2-disilyl-substituted acetylene to give 2,2-bis(silyl)vinylidene complexes as a key reaction intermediate. The octakis(silyl)[5]radialene derivative **2** has been synthesized in a similar manner via the intramolecular cyclization of the macrocyclic pentayne **1** linked by methylenebis(dimethylsilanediyl) ($Me_2SiCH_2SiMe_2$) and dimethylsilanediyl ($SiMe_2$) chains with [Mn(CO)$_3$(Me-Cp)].

The precursor of 3,3,6,6,8,8,11,11,14,14,16,16,19,19,21,21-hexadecamethyl-3,6,8,11,14,16,19,21-octasilacyclohenicosa-1,4,9,12,17-pentayne (**1**) was prepared by the coupling reaction of 2,10-dichloro-2,5,5,7,7,10-hexamethyl-2,5,7,10-tetrasilaundeca-3,8-diyne with the Grignard reagent prepared from 3,3,5,5,8,8,10,10-octamethyl-3,5,8,10-tetrasiladodeca-1,6,11-triyne and ethylmagnesium bromide in 39% yield (Scheme 1). Compound **1** has a twenty-one-membered ring with five acetylene units and eight silicon atoms. Figure 1 shows the molecular structure of **1** determined by X-ray diffraction. The macrocyclic pentayne **1** has a highly distorted conformation in the crystals. Selected bond lengths and bond angles are listed in Table 1. The C–C triple bond lengths are 1.207(4)—1.219(4) Å (av 1.214(4) Å),



Scheme 1.

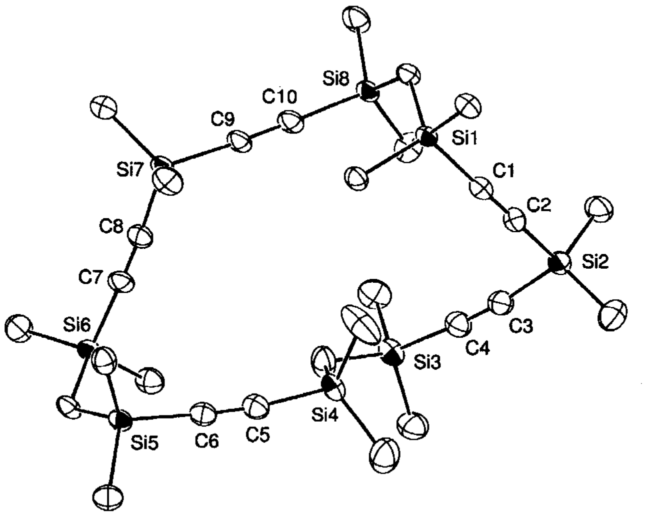


Fig. 1. ORTEP drawing of **1**.

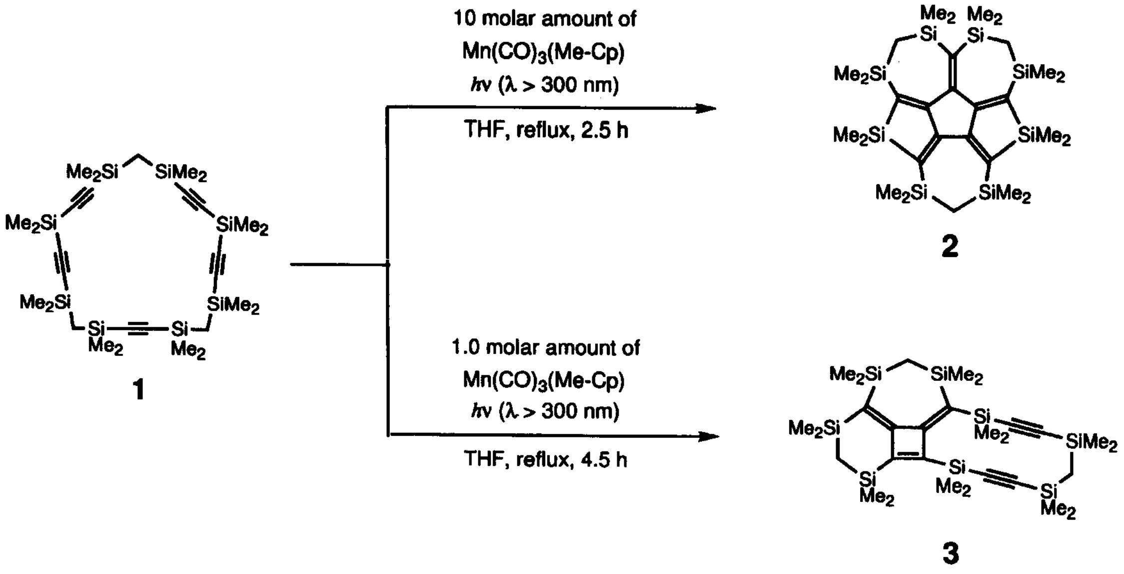
Table 1. Selected Bond Distances (Å) and Angles (deg) of **1**[a)]

	Bond distances		
C1–C2	1.217(4)	C3–C4	1.215(4)
C5–C6	1.214(4)	C7–C8	1.207(4)
C9–C10	1.219(4)	C1–Si1	1.849(3)
C2–Si2	1.836(3)	C3–Si2	1.838(3)
C4–Si3	1.848(3)	C5–Si4	1.845(3)
C6–Si5	1.849(3)	C7–Si6	1.855(3)
C8–Si7	1.840(3)	C9–Si7	1.838(3)
C10–Si8	1.846(3)		
	Bond angles		
C2–C1–Si1	174.0(3)	C1–C2–Si2	171.2(3)
C4–C3–Si2	173.7(3)	C3–C4–Si3	175.9(3)
C6–C5–Si4	173.2(3)	C5–C6–Si5	176.4(3)
C8–C7–Si6	178.9(3)	C7–C8–Si7	174.9(3)
C10–C9–Si7	173.7(3)	C9–C10–Si8	179.5(3)

a) Locative numbers of atoms are given in Fig. 1. Standard deviations are in parentheses.

and the Si–C(sp) single bond lengths are 1.836(3)—1.855(3) Å (av 1.844(3) Å). The bond angles of the acetylene units (Si–C(sp)–C(sp)) are almost linear (171.2(3)—179.5(3)° (av 175.1(3)°)).

A mixture of the pentayne **1** and a large excess molar amount of [Mn(CO)$_3$(Me-Cp)] in THF was irradiated with a 500 W high-pressure mercury lamp at the refluxing temperature of THF to produce orange crystals of the octakis(silyl)[5]radialene derivative **2** in 2.3% yield (Scheme 2). The reaction mechanism remains unclear at this moment. Nevertheless, a quintuple 1,2-silyl shift, which needs a large excess of the manganese complex, must be involved for the formation of **2**. The 1,2-silyl shift was accelerated by heating, and none of the radialene derivative was formed in the reaction at room temperature. However, the use of an equimolar amount



Scheme 2.

of the manganese complex resulted in the formation of the bis(methylene)cyclobutene derivative **3** as pale yellow crystals in 15% yield, arising from a double 1,2-silyl shift. With two molar amounts of [Mn(CO)$_3$(Me-Cp)], **3** was given in 19% yield together with a trace of **2**. The bis(methylene)cyclobutene **3** was not a precursor of [5]radialene **2**, since **3** did not afford **2** under the reaction conditions. The THF refluxing temperature and a large excess of the manganese complex are crucial for the synthesis of the octakis(silyl)[5]radialene **2**. The same results were obtained by using [Mn(CO)$_3$(Cp)]. Although the yield is low, the [5]radialene derivative **2** is the first example of the cyclopentamerization of acetylene units. One of the reasons for the low yield is the photosensitivity of **2**.

The [5]radialene **2** was fully characterized by NMR spectroscopy as well as by X-ray crystallography. In the ^{1}H NMR spectrum of **2**, four sets of methyl groups and two sets of methylene groups were found. In the ^{29}Si NMR spectrum, four sets of signals were observed at $\delta = -12.0, -10.0, -8.4$, and 30.9. The ^{29}Si NMR signal in a silacycle has been reported at lower field than for similar acyclic compounds.[13] Thus, the ^{29}Si NMR signal appearing at 30.9 ppm can be assigned to the silicon of the silacyclopentadiene moiety of **2**. In the ^{13}C NMR spectrum, six sets of quaternary carbon atoms were found: at δ = 143.3, 144.9, 157.0, 163.2, 164.7, and 172.0. In the UV-visible spectrum of **2**, three absorption bands at $\lambda_{\max}$/nm (ε) 264 (44600), 379 (2800), 428 (2700) were observed. The absorption band at 428 nm tails into the visible region until about 500 nm.

Crystal Structure of 2. The molecular structure of **2** was unequivocally determined by X-ray crystallography. An ORTEP drawing of **2** is shown in Fig. 2. Selected bond lengths and bond angles are listed in Table 2. The octakis(silyl)[5]radialene **2** possesses a unique ten-electron π-system; five double bonds are located at the exo positions. Only one example of the crystal structure of a decamethyl[5]radialene is known.[5a] The octakis(silyl)[5]radialene **2** has a distorted structure and the central five-membered ring is not planar, but has an envelope conformation. The angle formed by C2–C3–C4–C5 and C1–C2–C5 planes is 19.0(0)°. The internal bond angles of the five-membered ring are 104.8(2)—110.3(2)° (av 107.2(2)°), the sum of the bond angles being 536.1°. In contrast, the two silacyclopentadiene rings have an almost planar structure. The appreciable bond alternation between the single and double bonds of the π-skeleton of **2** is a characteristic structural feature of a cross-conjugated diene. The single bond lengths are 1.483(4)—1.528(4) Å (av 1.501(4) Å), and the double bond lengths are 1.362(4)—1.375(4) Å (av 1.365(4) Å), respectively.

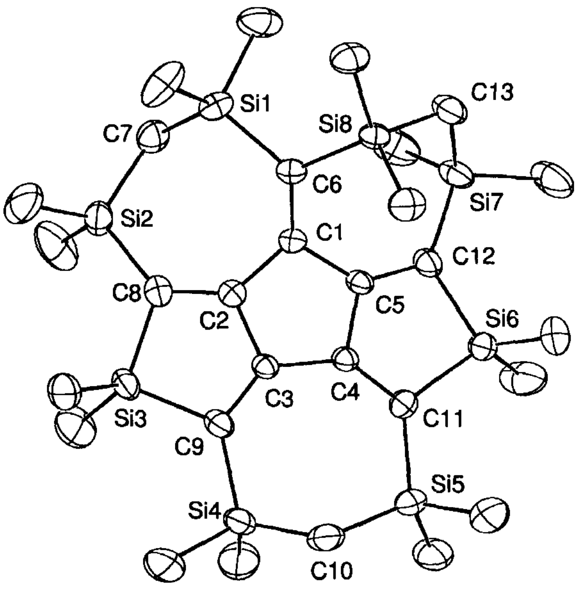


Fig. 2. ORTEP drawing of **2**.

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

	Bond distances		
C1–C2	1.506(4)	C1–C5	1.485(4)
C1–C6	1.375(4)	C2–C3	1.528(4)
C2–C8	1.362(4)	C3–C4	1.483(4)
C3–C9	1.363(4)	C4–C5	1.502(4)
C4–C11	1.363(4)	C5–C12	1.363(4)
C6–Si1	1.881(3)	C6–Si8	1.905(3)
C8–Si2	1.850(3)	C8–Si3	1.878(3)
C9–Si3	1.877(3)	C9–Si4	1.851(3)
C11–Si5	1.861(3)	C11–Si6	1.887(3)
C12–Si6	1.872(3)	C12–Si7	1.864(3)
	Bond angles		
C2–C1–C5	104.8(2)	C2–C1–C6	130.5(3)
C5–C1–C6	123.7(3)	C1–C2–C3	107.0(2)
C1–C2–C8	136.0(3)	C3–C2–C8	116.9(3)
C2–C3–C4	108.2(2)	C2–C3–C9	117.6(3)
C4–C3–C9	133.9(3)	C3–C4–C5	105.8(2)
C3–C4–C11	136.5(3)	C5–C4–C11	117.5(3)
C1–C5–C4	110.3(2)	C1–C5–C12	131.3(3)
C4–C5–C12	118.2(3)		

a) Locative numbers of atoms are given in Fig. 2. Standard deviations are in parentheses.

π-MO and Cyclic Voltammetry of 2. The geometry of **2** determined by X-ray diffraction is successfully reproduced by PM3 calculations.[14] Figure 3 shows the LUMO (−0.27 eV), LUMO+1 (0.66 eV), and LUMO+2 (0.70 eV) of **2** by PM3 calculations and their schematic drawings. The energy of the LUMO is considerably stabilized by the silyl groups. In the LUMO, the exocyclic bonds (C1–C6, C2–C8, C3–C9, C4–C11, and C5–C12) are antibonding, whereas the endocyclic bonds (C1–C2, C2–C3, C3–C4, C4–C5, and C1–C5) are bonding. The π-MO coefficients at the exocyclic carbon atoms are larger than those at the endocyclic carbon atoms. Thus, two-electron reduction of **2** may readily occur to yield the dianion species, which is stabilized by the eight silicon atoms.

Of particular interest in the π-MOs of **2** are LUMO+1 and LUMO+2. The parent [5]radialene ($C_{10}H_{10}$) has degenerate orbitals for LUMO+1 and LUMO+2. The energies of LUMO+1 and LUMO+2 of **2** calculated by PM3 are very close to each other, the energy of LUMO+1 being only slightly lower than that of LUMO+2. This indicates the

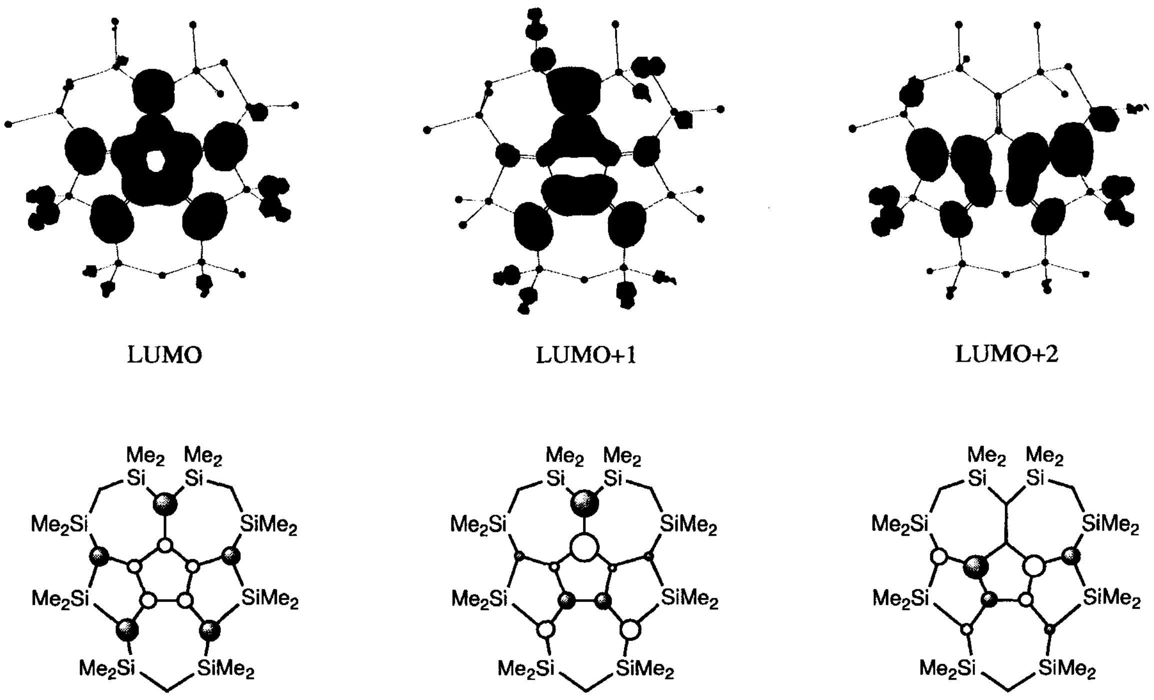


Fig. 3. LUMO, LUMO+1, and LUMO+2 of **2** by PM3 calculation (upper) and their schematic drawings (below).

possibility of forming a hexaanion species by six-electron reduction of **2**. In the LUMO+1, the π-MO coefficients at the C1 and C6 carbon atoms are larger than those at other carbon atoms. Thus, four-electron reduction of **2** may produce a tetrametal tetraanion complex in which the counter cations may strongly interact with the C1 and C6 carbon atoms.

The cyclic voltammogram of **2** in acetonitrile is shown in Fig. 4. The irreversible reduction peak was observed at −0.65 V (vs. SCE) as a very broad peak. The reduction potential of **2** is much lower than that of octakis(silyl)tris(methylene)cyclopentene derivative (−1.38 V).[8b] It is reasonable to consider that the low potential of **2** measured by cyclic voltammetry is consistent with the low LUMO level of **2** calculated by PM3. The broad peak of **2** suggests the possibility of multielectron reduction. The irreversible peak probably is due to the decomposition of **4** under the conditions.

Four-Electron Reduction of 2 with Lithium Metal. Reaction of **2** with excess lithium metal in dry, oxygen-free THF at room temperature led to the formation of a dark red solution of the tetraanion of **2**. The reaction was complete 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 dark red crystals of the tetralithium salt **4** containing four molecules of THF (Scheme 3). The structure of **4** was unequivocally determined by NMR spectroscopy and X-ray crystallography. Several attempts to obtain the dianion species of **2** by two-electron reduction failed due to the facile four-electron reduction. Even with a reaction time longer than 1 h, none of the hexaanion species of **2** could be obtained.

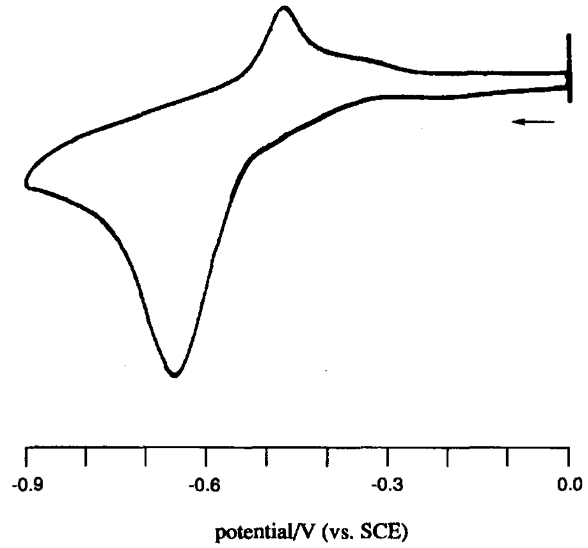
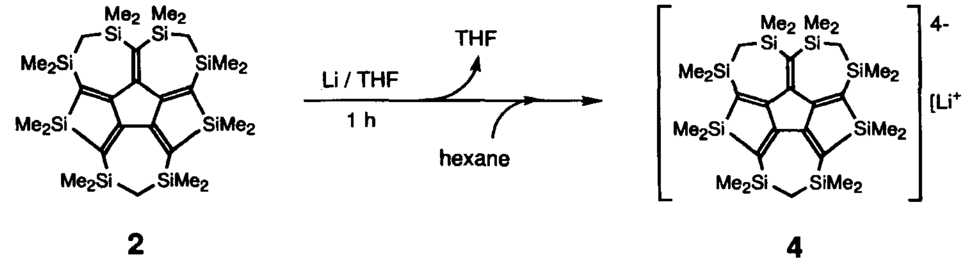


Fig. 4. Cyclic voltammetry of **2** in acetonitrile (scan rate: 200 mV s^{-1}; conditions: room temperature, under argon).

Crystal Structure of 4. The molecular structure of **4** was unequivocally determined by X-ray diffraction, as shown in Fig. 5. The perspective view of the unit cell of **4** down the *b* axis is shown in Fig. 6. The crystal structure can be described as being composed of 2^{4-} and Li^+ ions alternating along the *b* axis (Fig. 6). The tetralithium salt **4** is monomeric and forms contact ion pairs (*tetrakis-CIPs*) in the crystals. Selected bond lengths and bond angles are listed in Table 3. All four lithium ions are bonded to the four quaternary carbon atoms of the [5]radialene π-skeleton as well as to the oxygen atoms of THF. Li1 and Li2 are located above and below the adjacent seven-membered rings (denoted **A** for the C1–C5–C10–Si7–CH$_2$–Si8–C6 ring and **B** for the C1–C2–C7–Si2–CH$_2$–Si1–C6 ring, respectively),



Scheme 3.

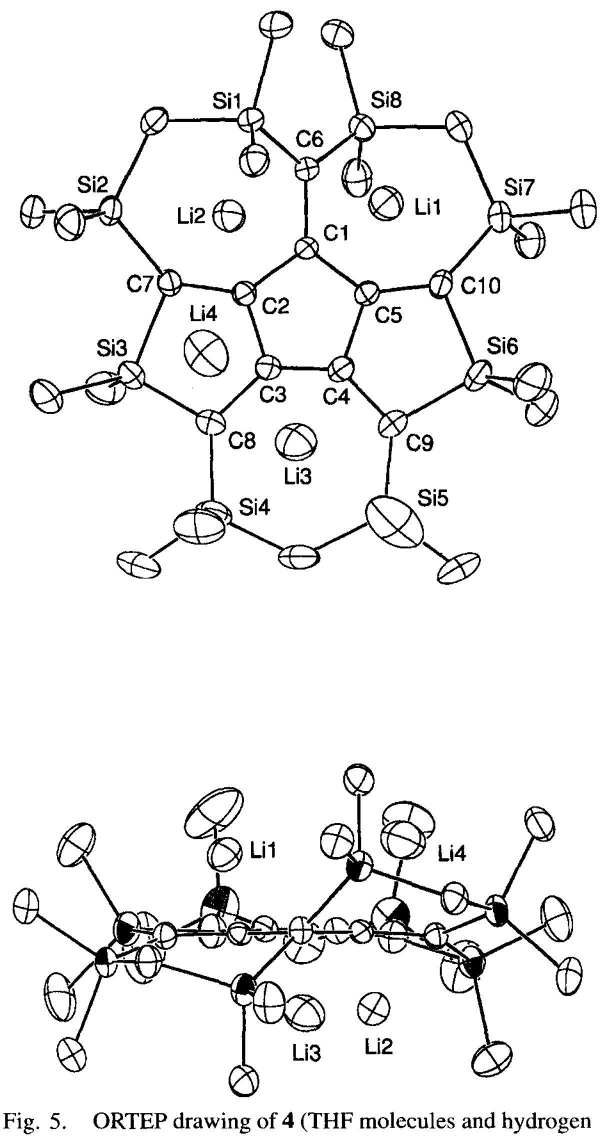


Fig. 5. ORTEP drawing of **4** (THF molecules and hydrogen atoms are omitted for the clarity): upper, top view; below, side view.

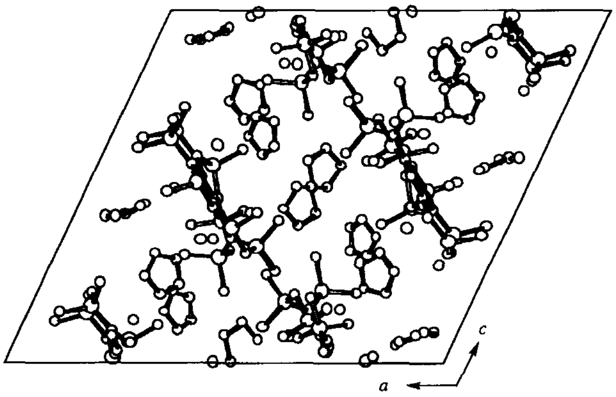


Fig. 6. Perspective view of the unit cell of **4** down the *b* axis.

whereas Li3 is located below the isolated seven-membered ring (denoted **C** for the C4–C3–C8–Si4–CH$_2$–Si5–C9 ring). The remaining Li4 is situated above one of the two silacyclopentadiene rings (denoted **D** for the C2–C3–C8–Si3–C7 ring and **E** for the C5–C4–C9–Si6–C10 ring, respectively). The distances between lithium and carbon atoms range from 2.10(1) to 2.44(2) Å (av 2.23 Å). The two seven-membered rings **A** and **B** have highly twisted conformations about the C1–C6 bond, whereas the other seven-membered ring **C** and the two five-membered rings **D** and **E** are almost planar.

A comparison of the structural parameters of neutral molecule **2** and tetraanion **4** is quite interesting. The ten carbon atoms (C1–C10) that constitute the π-electron system of the skeleton of **4** are almost coplanar as a consequence of the delocalization of the negative charge. The C1–C6 distance in **4** (1.523(8) Å) is considerably elongated by 0.148 Å relative to that of **2** (1.375(4) Å). The C3–C8 and C4–C9 distances in **4** are also elongated by 0.143 and 0.066 Å, compared with those of **2** (1.363(4) Å). The C2–C7 and C5–C10 distances in **4** are also stretched by 0.059 and 0.044 Å, relative to those of **2** (1.362(4) and 1.363(4) Å). By contrast, the C3–C4 distance in **4** (1.377(8) Å) is remarkably shortened by 0.106 Å with respect to that of **2** (1.483(4) Å). The C1–C2 and C1–C5 distances in **4** are shortened by 0.056 and 0.044 Å compared with those in **2** (1.506(4) and 1.485(4) Å). These structural features are reflected by the LUMO and LUMO+1 of **2** (Fig. 3).

The central five-membered ring (C1–C2–C3–C4–C5) of **4** has an almost planar conformation, as determined by the sum of the bond angles (539.9°). However, this five-membered ring does not form an equilateral pentagon, as observed in the lithium pentakis(dimethylsilyl)cyclopentadienide,[15] the dilithium salt of hexakis(silyl)fulvene with a six-center, eight-electron π-system,[7m,n] and the tetralithium salt of octakis(silyl)tris(methylene)cyclopentene with an eight-center, twelve-electron π-system.[8] This suggests that the [5]-radialene tetraanion **4** has no aromatic character resulting from the cyclopentadienide ion. The bond lengths of the Si–C (quaternary carbons) bonds of **4** (av 1.835 Å) are shorter than those of **2** (av 1.873 Å) due to delocalization of the negative

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

	Bond distances		
C1–C2	1.450(7)	C1–C5	1.441(8)
C1–C6	1.523(8)	C2–C3	1.484(8)
C2–C7	1.421(8)	C3–C4	1.377(8)
C3–C8	1.506(8)	C4–C5	1.526(8)
C4–C9	1.429(8)	C5–C10	1.407(8)
C6–Si1	1.824(6)	C6–Si8	1.815(6)
C7–Si2	1.830(6)	C7–Si3	1.898(6)
C8–Si3	1.823(7)	C8–Si4	1.798(7)
C9–Si5	1.812(7)	C9–Si6	1.829(7)
C10–Si6	1.876(6)	C10–Si7	1.841(6)
Li1–C1	2.18(1)	Li1–C5	2.20(1)
Li1–C6	2.19(1)	Li1–C10	2.36(1)
Li2–C1	2.17(1)	Li2–C2	2.24(1)
Li2–C6	2.17(1)	Li2–C7	2.33(1)
Li3–C3	2.10(1)	Li3–C4	2.15(1)
Li3–C8	2.23(2)	Li3–C9	2.37(2)
Li4–C2	2.32(2)	Li4–C3	2.11(2)
Li4–C7	2.44(2)	Li4–C8	2.17(1)
	Bond angles		
C2–C1–C5	106.2(5)	C2–C1–C6	126.5(5)
C5–C1–C6	127.3(5)	C1–C2–C3	109.1(5)
C1–C2–C7	134.4(5)	C3–C2–C7	116.4(5)
C2–C3–C4	109.0(5)	C2–C3–C8	116.2(5)
C4–C3–C8	134.5(5)	C3–C4–C5	107.1(5)
C3–C4–C9	135.1(6)	C5–C4–C9	117.4(5)
C1–C5–C4	108.5(5)	C1–C5–C10	135.5(5)
C4–C5–C10	116.0(5)		

a) Locative numbers of atoms are given in Fig. 5. Standard deviations are in parentheses.

charge onto the silicon centers by pπ–σ* conjugation.[6]

Structure of 4 in Solution. The structure of **4** in toluene-d_8 was deduced by ^{1}H, ^{13}C, ^{29}Si, and ^{6}Li NMR spectroscopy. The NMR data of **4** in toluene-d_8 indicate formation of highly symmetric *tetrakis-CIPs* with C_2 group symmetry, the C1–C6 bond being a two-fold axis. The four methyls of the two SiMe$_2$ groups and the two hydrogen atoms of CH$_2$ in the rings **A** and **B** are magnetically nonequivalent, due to the fixed five- and seven-membered rings. On the other hand, the two hydrogen atoms of CH$_2$ in the ring **C** are magnetically equivalent. Thus, the ^{1}H NMR spectrum of **4** in toluene-d_8 reveals the presence of eight signals for the methyl groups, two doublets for the ring **A** and **B** methylene groups with a geminal coupling constant of 13.2 Hz, and one singlet for the ring **C** methylene group. In the ^{29}Si NMR spectrum, four signals are observed at $\delta = -20.1, -16.7, -15.0$, and 18.5, which are shifted to higher field in comparison to those of **2** ($\delta = -12.0, -10.0, -8.4$, and 30.9). The ^{13}C NMR spectrum shows six signals for quaternary carbon atoms at $\delta = 15.1$, 40.8, 81.0, 93.1, 131.8, and 178.9. The signal appearing at 15.1 ppm can be assigned to the C6 carbon atom, which is shifted considerably up-field relative to that of **2** ($\delta = 164.7$) by $\Delta\delta = -149.6$. The other exocyclic carbons (C7, C8, C9, and C10) are also shifted to higher field by the four-electron reduction ($\delta = 40.8$ and 81.0 for **4**; $\delta = 163.2$ and 172.0 for **2**). Apparently, the negative charge is largely delocalized over the five exocyclic carbon atoms in the π-skeleton of **4** and is stabilized by the eight silyl groups.

Interestingly, the ^{6}Li NMR spectrum of **4** displays only one signal at $\delta = -0.18$. This indicates that the four Li$^+$ ions of **4** are not fixed to the π-skeleton, but are fluxional; the four Li$^+$ ions migrate over the π-skeleton of [5]radialene on the NMR time scale (Fig. 7, left). As the temperature was lowered, the ^{6}Li NMR signal broadened and eventually yielded two very sharp signals at $\delta = -0.55$ and 0.08 with the same intensity at 187 K. However, the C_2 symmetry of **4** in toluene-d_8 was completely retained in the temperature range 187—298 K. Thus, the temperature-dependent change of the ^{6}Li NMR signals must result from the dynamics of four Li$^+$ ions on the [5]radialene framework. Experimental and simulated spectra for the ^{6}Li NMR signals are shown in Fig. 8. From the Arrhenius and Eyring plots, the values of $E_a = 10.7$ kcal mol^{-1}, $\Delta H^\ddagger = 10.3$ kcal mol^{-1}, and $\Delta S^\ddagger = 0.3$ cal mol^{-1} K^{-1} can be estimated for the dynamic behavior of the four Li$^+$ ions. This can be explained by assuming that two Li$^+$ ions (Li1 and Li2) are fixed to the seven-membered

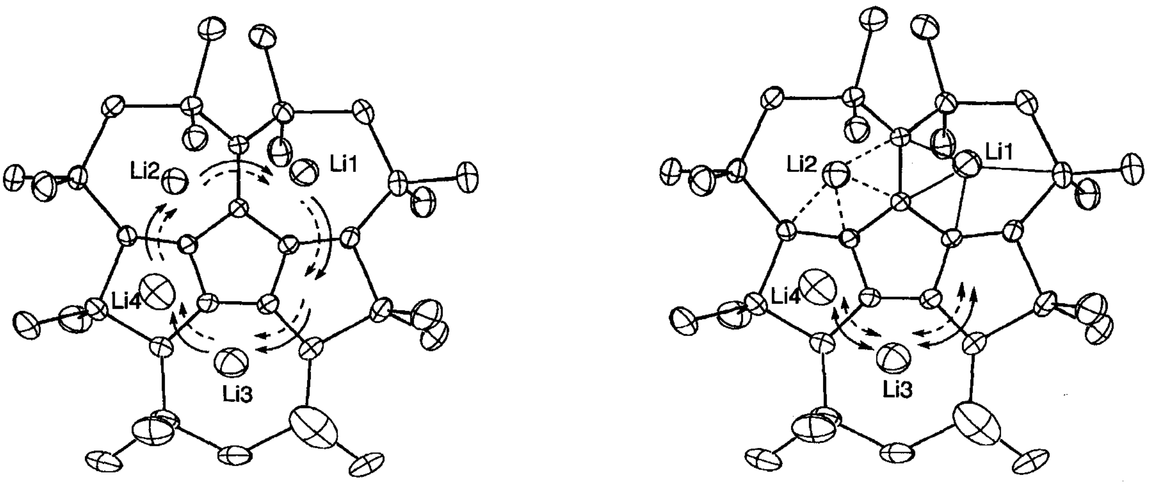


Fig. 7. Schematic representation of the dynamic behavior of lithium cations on the π-skeleton of **4** (*tetrakis-CIPs*) in toluene-d_8: left, 298 K; right, 187 K.

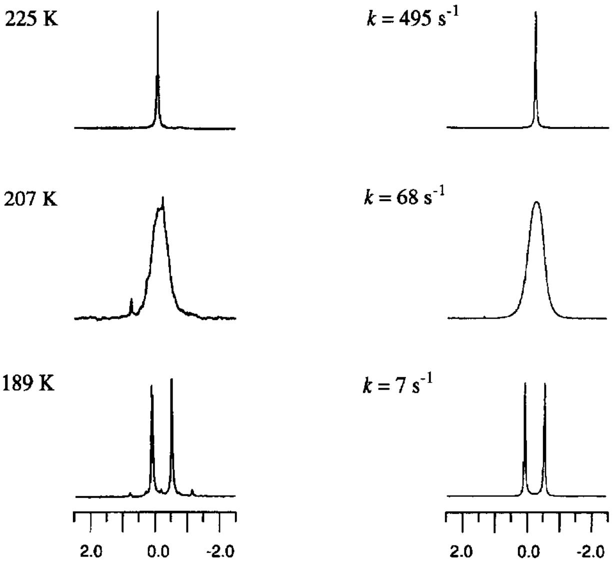


Fig. 8. Observed (left) and simulated (right) ^{6}Li (44.2 MHz) line shapes of **4** in toluene-d_8.

rings (**A** and **B**), whereas the other two Li$^+$ ions (Li3 and Li4) are still fluxional over two five-membered rings (**D** and **E**) and one seven-membered ring (**C**) (Fig. 7, right). Since the latter three rings are almost coplanar, the fluxional behavior of the two Li$^+$ ions (Li3 and Li4) is not hindered even at 187 K. The possibility of producing a solvent-separated ion pair (*SSIP*) in toluene-d_8 is unlikely.

The structure of **4** in THF-d_8 was also deduced on the basis of the NMR spectroscopic data. The ^{6}Li NMR spectrum of **4** in THF-d_8 at room temperature shows one broad signal at -0.22 ppm. Interestingly, upon lowering the temperature, the ^{6}Li signal split into four signals ($\delta = -0.85$, -0.67, -0.06, and -0.01) with the same intensity. This suggests that one of the four lithium cations is dissociated to yield a solvent separated ion pair (*SSIP*). In the ^{13}C NMR spectrum of the tetraanion **4** in THF-d_8 at 173 K, sixteen different carbons due to the SiMe$_2$ can be observed because of the lack of symmetry. Three different methylene carbons and eight different ^{29}Si signals were also observed.

Conclusion. We performed a four-electron reduction of octakis(silyl)[5]radialene derivative **2** to form the hitherto unknown [5]radialene tetraanion **4**. Six-electron reduction does not proceed, presumably because of the significant electrostatic repulsion due to the negative charge. The X-ray crystallographic and the NMR spectroscopic data presented here indicate that the structure of the [5]radialene tetraanion **4** is a stable tetraanion, which is stabilized by the eight silicon atoms. The geometry and properties of **4** reflect the nature of the LUMO and LUMO + 1 of the precursor **2**. In toluene-d_8, the four Li$^+$ ions of **4** are not fixed to the π-skeleton at room temperature, but are fluxional, giving highly symmetric contact ion pairs. The fluxional behavior of the four Li$^+$ ions is partially suppressed at low temperature.

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 (1 M = 1 mol dm^{-3}) LiCl 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** for X-ray crystallography was carried out by using a Giken Engineering Service GBX-1200 gas-replacement type glove box. 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 as a supporting electrolyte was used as received. Tetrahydrofuran and hexane were dried and distilled from sodium diphenylketyl. 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 potassium mirror prior to use. Lithium-6 (95 atom%) metal was commercially available (Aldrich Chemical Company).

3,3,6,6,8,8,11,11,14,14,16,16,19,19,21,21-Hexadecamethyl-3,6,8,11,14,16,19,21-octasilacyclohenicosa-1,4,9,12,17-pentayne (1). 3,3,5,5,8,8,10,10-Octamethyl-3,5,8,10-tetrasiladodeca-1,6,11-triyne (10.04 g, 0.030 mol) in THF (20 ml) was added to a THF solution of ethylmagnesium bromide (180 ml, 0.067 mol) to produce the Grignard reagent. The THF solution of the resulting Grignard reagent and 2,10-dichloro-2,5,5,7,7,10-hexamethyl-2,5,7,10-tetrasilaundeca-3,8-diyne (10.97 g, 0.030 mol) in THF (180 ml) were added dropwise slowly to 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 pentayne (**1**) (120—200 °C/0.1 mmHg, Kugelrohr distillation). Recrystallization from ethanol gave pure colorless crystals of **1** in 39% yield. Mp 68—69 °C; ^{1}H NMR (CDCl$_3$) $\delta = 0.00$ (s, 4 H, CH$_2$), 0.03 (s, 2 H, CH$_2$), 0.22 (s, 12 H, CH$_3$), 0.25 (s, 24 H, CH$_3$), 0.28 (s, 12 H, CH$_3$); ^{13}C NMR (CDCl$_3$) $\delta = 0.1$ (CH$_3$), 0.9 (CH$_3$×2), 1.0 (CH$_3$), 3.2 (CH$_2$×2), 110.1 (C), 110.2 (C), 114.8 (C), 115.7 (C×2); ^{29}Si NMR (CDCl$_3$) $\delta = -42.7$, -19.6, -18.9, -18.8; UV (hexane) $\lambda_{\max}$/nm (ε) 209 (5800), 218 (3900). Found: C, 55.22; H 8.66%. Calcd for $C_{29}H_{54}Si_8$: C, 55.52; H 8.67%.

2,2,4,4,9,9,11,11,13,13,15,15,17,17,21,21-Hexadecamethyl-2,4,9,11,13,15,17,21-octasilahexacyclo[10.5.3.$1^{5,8}$.$0^{6,18}$.$0^{7,20}$.$0^{14,19}$]-henicosa-1(18),5,7,12(20),14(19)-pentaene (2). A mixture of **1** (400 mg, 0.64 mmol) and [Mn(CO)$_3$(Me-Cp)] (1396 mg, 6.40 mmol) in THF (35 ml) was irradiated with a 500 W high-pressure mercury lamp for 2.5 h through the cutoff filter ($\lambda > 300$ nm) in the refluxing THF. After removal of the manganese complex, the reaction mixture was chromatographed on silica gel to produce orange crystals of **2** in 2.3% yield. Mp 140—142 °C; ^{1}H NMR (CDCl$_3$) $\delta = 0.10$ (s, 2 H, CH$_2$), 0.13 (s, 12 H, CH$_3$), 0.14 (s, 12 H, CH$_3$), 0.15 (s, 12 H, CH$_3$), 0.286 (s, 12 H, CH$_3$), 0.290 (s, 4 H, CH$_2$); ^{13}C NMR (CDCl$_3$) $\delta = -2.3$ (CH$_3$), 1.1 (CH$_3$), 1.5 (CH$_3$), 3.0 (CH$_3$), 4.9 (CH$_2$), 11.7 (CH$_2$), 143.3 (C), 144.9

(C), 157.0 (C), 163.2 (C), 164.7 (C), 172.0 (C); ^{29}Si NMR ($CDCl_3$) $\delta = -12.0, -10.0, -8.4, 30.9$; UV (hexane) λ_{max}/nm (ε) 264 (44600), 379 (2800), 428 (2700). Found: C, 55.28; H 8.68%. Calcd for $C_{29}H_{54}Si_8$: C, 55.52; H 8.67%.

2,2,5,5,7,7,10,10,13,13,15,15,17,17,19,19-Hexadecamethyl-2,5,7,10,13,15,17,19-octasilatetracyclo[9.8.1.1^{12,16}.0^{20,21}]henicosa-1(20),11,16(21)-triene-3,8-diyne (3). A mixture of **1** (198 mg, 0.32 mmol) and [$Mn(CO)_3$(Me-Cp)] (69 mg, 0.32 mmol) in THF (35 ml) was irradiated with a 500 W high-pressure mercury lamp for 4.5 h through the cutoff filter ($\lambda > 300$ nm) in the refluxing THF. After removal of the manganese complex, the reaction mixture was chromatographed on silica gel to produce pale yellow crystals of **3** in 15% yield. Mp 130—131 °C; ^{1}H NMR ($CDCl_3$) $\delta = -0.17$ (s, 2 H, CH_2), -0.16 (s, 2 H, CH_2), 0.01 (s, 2 H, CH_2), 0.13 (s, 6 H, CH_3), 0.15 (s, 6 H, CH_3), 0.17 (s, 6 H, CH_3), 0.18 (s, 6 H, CH_3), 0.22 (s, 6 H, CH_3), 0.31 (s, 6 H, CH_3), 0.38 (s, 6 H, CH_3), 0.41 (s, 6 H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta = 0.9$ (CH_3), 1.1 (CH_2), 1.2 (CH_3), 1.7 (CH_3), 1.8 (CH_2), 2.7 (CH_3), 2.8 (CH_3), 3.2 (CH_3), 3.6 (CH_3), 3.7 (CH_3), 7.6 (CH_2), 114.5 (C), 116.1 (C×2), 116.5 (C), 119.6 (C), 121.5 (C), 172.6 (C), 173.0 (C), 176.4 (C), 184.2 (C); ^{29}Si NMR ($CDCl_3$) $\delta = -33.7, -28.6, -19.3, -19.2, -16.5, -7.6, -6.8, -6.3$; UV (hexane) λ_{max}/nm (ε) 250 (26500), 280 (sh. 9600), 324 (sh. 5100). Found: C, 55.44; H, 8.92%. Calcd for $C_{29}H_{54}Si_8$: C, 55.52; H, 8.67%.

The Tetralithium Salt of 2 (4). The crystals of **2** (21 mg, 0.033 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 (0.8 ml) was introduced by vacuum transfer and the mixture was stirred at room temperature to give a dark red 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 the lithium metal was removed, the solution was cooled to afford dark red crystals of **2** quantitatively. ^{1}H NMR (C_7D_8) $\delta = -0.15$ (d, $J = 13.2$ Hz, 2 H, CH_2), -0.11 (s, 6 H, CH_3), 0.14 (s, 2 H, CH_2), 0.28 (s, 6 H, CH_3), 0.30 (s, 6 H, CH_3), 0.33 (s, 6 H, CH_3), 0.35 (s, 6 H, CH_3), 0.36 (s, 6 H, CH_3), 0.49 (s, 6 H, CH_3), 0.54 (d, $J = 13.2$ Hz, 2 H, CH_2), 0.62 (s, 6 H, CH_3), 1.35 (br.s, 16 H, THF), 3.52 (br.s, 16 H, THF); ^{13}C NMR (C_7D_8) $\delta = 2.8$ (CH_3), 5.6 (CH_3), 6.0 (CH_3), 6.6 (CH_3), 7.0 (CH_3), 7.3 (CH_3), 7.5 (CH_3), 7.7 (CH_3), 15.1 (C), 15.9 (CH_2), 16.5 (CH_2), 25.4 (THF), 40.8 (C), 66.6 (THF), 81.0 (C), 93.1 (C), 131.8 (C), 178.9 (C); ^{29}Si NMR (C_7D_8) $\delta = -20.1, -16.7, -15.0, 18.5$; ^{6}Li NMR ($C_7D_8$) $\delta = -0.18$.

NMR Spectral Data of 4 in THF-d_8 at 173 K. ^{13}C NMR (THF-d_8) $\delta = 5.3$ (CH_3×2), 6.1 (CH_3), 6.5 (CH_3×2), 6.6 (CH_3), 7.2 (CH_3), 7.5 (CH_3), 7.7 (CH_3), 7.8 (CH_3×2), 7.9 (CH_3), 8.1 (CH_3), 9.0 (CH_3), 9.2 (CH_3×2), 16.4 (CH_2), 18.3 (C), 19.0 (CH_2), 21.2 (CH_2), 49.5 (C), 51.0 (C), 98.5 (C×2), 106.9 (C), 109.1 (C), 155.8 (C), 166.7 (C), 186.4 (C); ^{29}Si NMR (THF-d_8) $\delta = -24.6, -20.8, -20.5, -18.8, -17.0, -15.1, 11.3, 20.0$; ^{6}Li NMR (THF-$d_8$) $\delta = -0.85, -0.67, -0.06, -0.01$.

X-Ray Crystallography. Single crystals of **1** and **2** for X-ray diffractions were grown from an ethanol solution. A single crystal of **4** for X-ray diffraction was grown from a hexane solution. The X-ray crystallographic experiments of **1**, **2**, and **4** were performed on a DIP2020 or DIP2030K image plate diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71070$ Å). Crystal data for **1** at 120 K: MF = $C_{29}H_{54}Si_8$, MW = 627.44, triclinic, $a = 8.9940(6)$, $b = 11.9830(5)$, $c = 19.761(1)$ Å, $\alpha = 77.372(4)$, $\beta = 86.223(3)$, $\gamma = 82.040(4)°$, $V = 2056.8(3)$ Å^3, space group = $P\bar{1}$, $Z = 2$, $D_{calcd} = 1.01$ g cm^{-3}. The final R factor was 0.107 ($R_w = 0.192$) for 7428 reflections with $I > 3\sigma(I)$. Crystal data for **2** at 180 K: MF = $C_{29}H_{54}Si_8$, MW = 627.44, monoclinic, $a = 12.831(1)$, $b = 14.975(1)$, $c = 19.943(1)$ Å, $\beta = 93.902(3)°$, $V = 3823.0(2)$ Å^3, space group = $P2_1/n$, $Z = 4$, $D_{calcd} = 1.090$ g cm^{-3}. The final R factor was 0.046 ($R_w = 0.048$) for 6750 reflections with $I > 3\sigma(I)$. Crystal data for **4** at 180 K: MF = $C_{45}H_{86}Li_4O_4Si_8$, MW = 943.63, monoclinic, $a = 48.328(3)$, $b = 13.470(1)$, $c = 21.676(1)$ Å, $\beta = 115.003(3)°$, $V = 12788(1)$ Å^3, space group = $C2/c$, $Z = 8$, $D_{calcd} = 0.981$ g cm^{-3}. The final R factor was 0.0775 ($R_w = 0.2358$) for 6183 reflections with $I > 3\sigma(I)$. Some of the carbon atoms of the THF molecules have elongated thermal ellipsoids due to disorder. Tables of positional and thermal parameters and complete interatomic distances and angles for **1**, **2**, and **4** have been deposited as Document No. 73047 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 CCDC 146330 for **1**, 146331 for **2**, and 182/1394 for **4**.

Molecular Orbital Calculations. PM3 calculations were performed by Power Macintosh G3 with MACSPARTAN plus program (Ver. 1.1.7).[14] All the calculations were performed with geometry optimization.

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References

1 For reviews, see: a) K. Müllen, *Chem. Rev.*, **84**, 603 (1994). b) W. N. Setzer and P. v. R. Schleyer, *Chem. Rev.*, **24**, 353 (1985). c) C. Schade and P. v. R. Schleyer, *Chem. Rev.*, **27**, 169 (1987). d) M. Rabinovitz, *Top. Curr. Chem.*, **14**, 99 (1988). e) A. B. Sannigrahi, T. Kar, B. G. Niyogi, P. Hobza, and P. v. R. Schleyer, *Chem. Rev.*, **90**, 1061 (1990). f) H. Bock, K. Ruppert, C. Näther, Z. Havlas, H. F. Herrmann, C. Arad, I. Gögel, A. John, J. Meuret, S. Nick, A. Rauschenbach, W. Seitz, T. Vaupel, and B. Solouki, *Angew. Chem., Int. Ed. Engl.*, **31**, 550 (1992). g) A. -M. Sapse and P. v. R. Schleyer, in "Lithium Chemistry: A Theoretical and Experimental Overview," Wiley, New York (1995).

2 For recent papers, see: a) H. Bock, K. Gharagozloo-Hubmann, C. Näther, N. Nagel, and Z. Havlas, *Angew. Chem., Int. Ed. Engl.*, **35**, 631 (1996). b) A. Sekiguchi, T. Matsuo, and C. Kabuto, *Angew. Chem., Int. Ed. Engl.*, **36**, 2462 (1997). c) A. Sekiguchi, T. Matsuo, and R. Akaba, *Bull. Chem. Soc. Jpn.*, **71**, 41 (1998). d) H. Bock, Z. Havlas, D. Hess, and C. Näther, *Angew. Chem., Int. Ed. Engl.*, **37**, 502 (1998).

3 A. Ayalon, M. Rabinovitz, P. -C. Cheng, and L. T. Scott, *Angew. Chem., Int. Ed. Engl.*, **104**, 1636 (1992).

4 a) A. Ayalon, A. Sygula, P. -C. Cheng, M. Rabinovitz, P. W. Rabideau, and L. T. Scott, *Science*, **265**, 1065 (1994). b) M. Baumgarten, L. Gherghel, M. Wagner, A. Weitz, M. Rabinovitz, P.-C. Cheng, and L. T. Scott, *J. Am. Chem. Soc.*, **117**, 6254 (1995).

5 a) M. Iyoda, H. Otani, M. Oda, Y. Kai, Y. Baba, and N. Kasai, *J. Chem. Soc., Chem. Commun.*, **1986**, 1794. b) Z. Yoshida and T. Sugimoto, *Angew. Chem., Int. Ed. Engl.*, **27**, 1573 (1988). c) K. Kano, T. Sugimoto, Y. Misaki, T. Enoki, H. Hatakeyama, H. Oka, Y. Hosotani, and Z. Yoshida, *J. Phys. Chem.*, **98**, 252 (1994).

6 A. Sekiguchi and T. Matsuo, *Yuki Gosei Kagaku Kyokai Shi*,

57, 945 (1999).

7 For ethylene dianion, see: a) A. Sekiguchi, T. Nakanishi, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **111**, 3748 (1989). b) A. Sekiguchi, M. Ichinohe, T. Nakanishi, and H. Sakurai, *Chem. Lett.*, **1993**, 267. c) A. Sekiguchi, M. Ichinohe, C. Kabuto, and H. Sakurai, *Organometallics*, **14**, 1092 (1995). d) A. Sekiguchi, M. Ichinohe, C. Kabuto, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **68**, 2981 (1995). e) A. Sekiguchi, M. Ichinohe, C. Kabuto, and H. Sakurai, *Angew. Chem., Int. Ed. Engl.*, **36**, 1533 (1997). For styrene dianion, see: f) A. Sekiguchi, T. Nakanishi, C. Kabuto, and H. Sakurai, *Chem. Lett.*, **1992**, 867. g) A. Sekiguchi, M. Ichinohe, T. Nakanishi, C. Kabuto, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **68**, 3215 (1995). For benzene dianion, see: h) A. Sekiguchi, K. Ebata, C, Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **113**, 1464 (1991). i) A. Sekiguchi, K. Ebata, C, Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **113**, 7081 (1991). For bis(methylene)cyclobutene dianion, see: j) A. Sekiguchi, T. Matsuo, K. Ebata, and H. Sakurai, *Chem. Lett.*, **1996**, 1133. For [4]radialene dianion, see: k) A. Sekiguchi, T. Matsuo, and H. Sakurai, *Angew. Chem., Int. Ed. Engl.*, **37**, 1661 (1998). l) T. Matsuo, A. Sekiguchi, M. Ichinohe, K. Ebata, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **71**, 41 (1998). For fulvene dianion, see: m) T. Matsuo, A. Sekiguchi, M. Ichinohe, K. Ebata, and H. Sakurai, *Organometallics*, **17**, 3143 (1998). n) T. Matsuo, A. Sekiguchi, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **72**, 1115 (1999). For cyclobutadiene dianion, see: o) A. Sekiguchi, T. Matsuo, and H. Watanabe, *J. Am. Chem. Soc.*, **122**, 5652 (2000).

8 a) A. Sekiguchi, T. Matsuo, and C. Kabuto, *Angew. Chem., Int. Ed. Engl.*, **36**, 2462 (1997). b) A. Sekiguchi, T. Matsuo, and R. Akaba, *Bull. Chem. Soc. Jpn.*, **71**, 41 (1998).

9 T. Matsuo, H. Watanabe, M. Ichinohe, and A. Sekiguchi, *Inorg. Chem. Soc.*, **2/10**, 510 (1999).

10 For the preliminary results, see: a) T. Matsuo, H. Fure, and A. Sekiguchi, *Chem. Lett.*, **1998**, 1101. b) T. Matsuo, H. Fure, and A. Sekiguchi, *Chem. Commun.*, **1999**, 1981.

11 Z. Rappoport, in "The Chemistry of Dienes and Polyenes," John Wiley & Sons, New York (1997), Vol. 1.

12 K. Ebata, T. Matsuo, T. Inoue, Y. Otsuka, C. Kabuto, A. Sekiguchi, and H. Sakurai, *Chem. Lett.*, **1996**, 1053.

13 J. Dubac, A. Laporterie, and G. Manuel, *Chem. Rev.*, **90**, 215 (1990).

14 J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209 (1989).

15 A. Sekiguchi, Y. Sugai, K. Ebata, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **115**, 1144 (1993).