Bull. Chem. Soc. Jpn., ***68***, *2981—2988(1995)*

Dianion Dialkali Metals of 2,2′,5,5′-Tetrasilabicyclopentylidene. Synthesis and Crystal Structures

Akira Sekiguchi,* Masaaki Ichinohe, Chizuko Kabuto, and Hideki Sakurai*,#

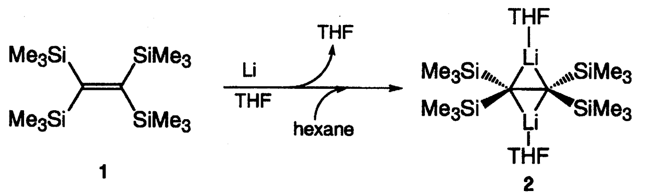
Department of Chemistry and Organosilicon Research Laboratory, Faculty of Science, Tohoku University,
Aoba-ku, Sendai 980-77

(Received May 8, 1995)

The intramolecular bissilylation of 3,3,6,6,7,7,10,10-octamethyl-3,6,7,10-tetrasilacyclodecyne (**4a**) at 110 °C with a catalyst of Pd(OAc)$_2$/1,1,3,3-tetramethylbutyl isocyanide under 5000 bar produced 2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene (**5a**). 2,2,2′,2′,5,5,5′,5′-Octamethyl-2,2′,5,5′-tetragermabicyclopentylidene (**5b**) was also synthesized by the same method. The reaction of **5a** with alkali metals (Li, Na, K, Rb, and Cs) in THF gave the corresponding dianion dialkali metals. The structures of **5a**, (2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene)bis[(tetrahydrofuran)lithium(I)] (**6a**), and (2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene)bis[(tetrahydrofuran)sodium(I)] (**6b**) were studied by X-ray crystallography as well as NMR spectroscopic means. The central anionic C–C bond is not twisted for **6a**, whereas it is twisted by 17.1° for **6b**.

Interest in the reactivity, structure, and bonding of organic alkali metal compounds, especially the organolithium compound, has remarkably increased in recent years.[1,2] We previously reported on the unique structure of [1,1,2,2-tetrakis(trimethylsilyl)ethylene]-bis[(tetrahydrofuran)lithium(I)] (**2**) obtained from the reaction of tetrakis(trimethylsilyl)ethylene (**1**) with lithium metal (Scheme 1).[3] The crystal structures of lithium derivatives of silyl-substituted styrene,[4] silyl-substituted benzenes,[5] and persilyl-substituted cyclopentadienide[6] were also recently reported.

In the dilithium derivative **2**, two lithium cations were bonded to two anionic carbons to give a structure doubly-bridged by lithium. The most interesting feature is that both the dilithium derivative **2** and the precursor ethylene **1**[7] twist along the central C–C bond by 33.6° and 29.5°, respectively. Although the steric and/or electronic factor should be considered, the reason why the dilithium **2** twists by 33.6° still remains unclear. A study of the dilithium derivative from the planar tetrasilyl-substituted ethylene will provide an answer to this question. We thus designed a new 2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene (**5a**) as a planar, or almost planar, ethylene. We wish to report herein on a detailed study of dialkali metals from **5a**, including the crystal structure of 1,2-disodium derivative.[8,9]

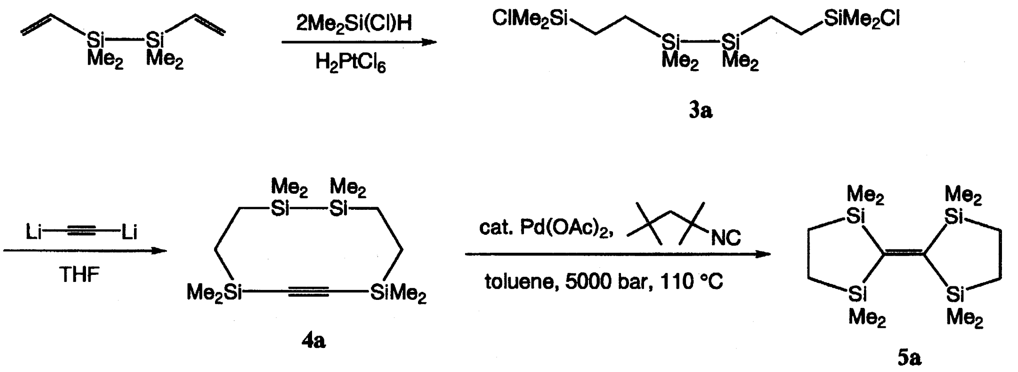


Scheme 1.

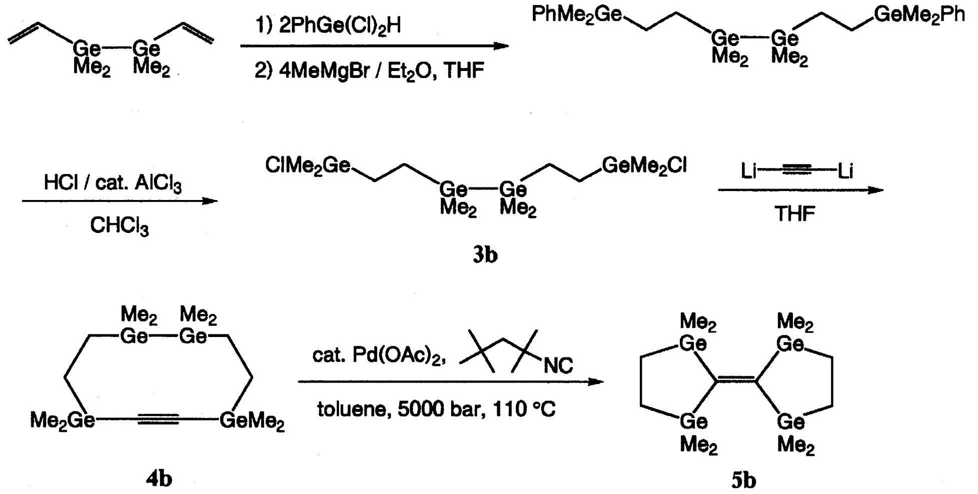
Results and Discussion

Synthesis of 5a and 5b. The introduction of a silyl group causes remarkable steric and electronic perturbations to the π-system.[10] Various per-silyl substituted ethylenes have been synthesized by our laboratory via disilacyclobutene prepared by the addition of the reactive Me$_2$Si=SiMe$_2$ with disilyl-acetylenes.[10a,10b,10c,10d,10e,10f] Thus, tetrakis(trimethylsilyl)-ethylene (**1**) was prepared by heating 7,7,8,8-tetramethyl-1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene with bis(trimethylsilyl)acetylene followed by bromination and subsequent methylation. However, this method has been limited to only the acyclic ones. Recently, Ito et al. reported on the intramolecular bissilylation reaction of the C–C triple bond in the presence of palladium(II) acetate/*tert*-alkyl isocyanide under high pressure.[11] This method was applied to hitherto unknown 2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene and 2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetragermabicyclopentylidene. The cyclic silyl ethylene and its germanium analog were thus prepared as outlined in Schemes 2 and 3.

#Present address: Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278.



Scheme 2.



Scheme 3.

1,1,2,2-Tetramethyl-1,2-divinyldisilane was subjected to hydrosilylation by chlorodimethylsilane followed by a treatment with dilithioacetylene to produce 3,3,6,6,7,7,10,10-octamethyl-3,6,7,10-tetrasilacyclodecyne (**4a**), a precursor of the intramolecular bissilylation. Heating of the cyclic acetylene at 110 °C with a catalyst of Pd(OAc)$_2$/1,1,3,3-tetramethylbutyl isocyanide under 5000 bar cleanly gave rise to **5a**. Chromatography by silica gel with hexane followed by sublimation and recrystallization afforded pure **5a** as pale-yellow crystals in 60% yield. A high pressure of 5000 bar is crucial for this reaction.

The germanium analog **5b** was also prepared in a similar manner. 1,1,2,2-Tetramethyl-1,2-divinyldigermane was reacted with dichlorophenylgermane followed by methylation to give 1,2-bis[2-(dimethylphenylgermyl)-ethyl]-1,1,2,2-tetramethyldigermane. Dephenylative chlorination of the digermane afforded 1,2-bis[2-(chlorodimethylgermyl)ethyl]-1,1,2,2-tetramethyldigermane (**3b**), which was treated with dilithioacetylene to afford cyclic 3,3,6,6,7,7,10,10-octamethyl-3,6,7,10-tetragermacyclodecyne (**4b**). The intramolecular bisgermylation of **4b** at 110 °C with Pd(OAc)$_2$/1,1,3,3-tetramethylbutyl isocyanide under 5000 bar led to the formation of **5b** as pale-yellow crystals.

The structure of **5b** was confirmed by spectroscopic data. The mass spectrum showed the molecular ion peaks in the range of m/z 482—500, in agreement with the calculated formula of $C_{14}H_{32}Ge_4$. The ^{1}H and ^{13}C NMR spectra are fully consistent with the highly symmetrical structure: ^{1}H NMR (CDCl$_3$) δ=0.26 (s, 24 H, CH$_3$), 1.03 (s, 8 H, CH$_2$); ^{13}C NMR (CDCl$_3$) δ=−0.1 (CH$_3$), 13.2 (CH$_2$), 182.0 (C=C). The ^{13}C chemical shift of the olefinic carbon of **5b** (δ=182.0) is close to that of the silyl analog **5a** (δ=189.5).

The intramolecular bissilylation and bisgermylation of the cyclic acetylenes with palladium(II) acetate/1,1,3,3-tetramethylbutyl isocyanide catalyst under high pressure was successful for **5a** and **5b**. However, attempts to synthesize tetrakis(trimethylsilyl)ethylene (**1**) by an intermolecular reaction of hexamethyldisilane and bis(trimethylsilyl)acetylene with Pd(OAc)$_2$/1,1,3,3-tetramethylbutyl isocyanide failed. Several attempts to prepare tetrakis(trimethylgermyl)ethylene also failed.

Crystal Structure of 5a. Figure 1 shows the molecular structure of **5a** determined by the X-ray diffraction method. The molecule has a crystallographic 2-fold axis. Selected bond lengths, bond angles, and dihedral angle are listed in Table 1. The bond lengths of **5a** are almost similar to those of **1**.[7] However, be-

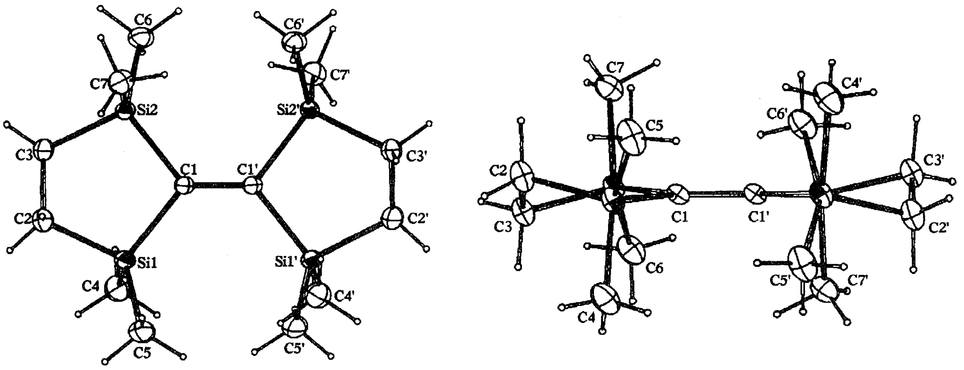


Fig. 1. ORTEP drawing of **5a**: left, top view; right, side view.

Table 1. Selected Bond Distances (Å), Angles (deg), and Dihedral Angle (deg) of **5a**

	Bond distances		
Si1–C1	1.906(2)	Si1–C2	1.879(2)
Si1–C4	1.872(2)	Si1–C5	1.867(2)
Si2–C1	1.905(2)	Si2–C3	1.887(2)
Si2–C6	1.868(4)	Si2–C7	1.874(2)
C1–C1′	1.369(2)	C2–C3	1.548(4)
	Bond angles		
C1–Si1–C2	100.7(1)	C1–Si1–C4	109.5(1)
C1–Si1–C5	117.7(1)	C2–Si1–C4	108.2(1)
C2–Si1–C5	109.0(1)	C4–Si1–C5	111.0(1)
C1–Si2–C3	100.9(1)	C1–Si2–C6	117.3(1)
C1–Si2–C7	109.8(1)	C3–Si2–C6	110.0(1)
C3–Si2–C7	107.0(1)	C6–Si2–C7	111.0(1)
Si1–C1–Si2	104.5(1)	Si1–C1–C1′	127.4(1)
Si2–C1–C1′	128.1(1)	Si1–C2–C3	107.0(1)
Si2–C3–C2	106.4(2)		
	Dihedral angle		
Si(1)–C(1)–Si(2)/Si(1′)–C(1′)–Si(2′)	4.8		

cause of the fixed structure due to 5-membered rings, the bond angles of **5a** are slightly different from those of **1**, and the Si–C=C angles (127.4° and 128.1°) are enlarged compared with **1** (124.1°). Atoms Si1, Si2, C1, and C1′, and Si1′, Si2′, C1′, and C1 are strictly coplanar. Neither twisting along the C–C double bond nor pyramidalization of the sp^2 carbons was observed. Thus, the dihedral angle between the planes Si1–C1–Si2 and Si1′–C1′–Si2′ is 4.8°.

Reaction with Alkali Metals. The reaction of **5a** with excess lithium metal in dry oxygen-free THF at room temperature gave a yellow solution of the ethylene dianion within one hour. The two-electron reduction occurred quantitatively.[12] After the solvent was removed in vacuo, degassed toluene was introduced by vacuum transfer. Crystallization from a toluene solution afforded (2,2′,5,5′-tetrasilabicyclopentylidene)bis[(tetrahydrofuran)lithium(I)] (**6a**) as extremely air and moisture sensitive yellow crystals (Scheme 4).

NMR data are most informative concerning the structure in solution, and particularly observations of ^{13}C–^{6}Li scalar coupling are useful. The anionic carbons of **6a** in toluene-d_8 appeared at $\delta=11.0$ as a quintet ($J_{^{13}\mathrm{C}-^{6}\mathrm{Li}}=3.1$ Hz) due to coupling with two equivalent ^{6}Li ($I=1$). A ^{6}Li NMR signal was observed at $\delta=1.72$ with satellite signals due to ^{13}C. The quintet signal of the anionic carbons implies the lithium doubly-bridged structure for **6a**.

The NMR spectra of **6a** in THF-d_8 are very similar to that in toluene-d_8. The anionic carbons in THF-d_8 appeared at $\delta=10.7$ as a broad signal at 298 K; however, this signal was split into a quintet ($J_{^{13}\mathrm{C}-^{6}\mathrm{Li}}=2.7$ Hz) at 230 K. ^{6}Li NMR resonance was observed at $\delta=1.71$. Thus, the doubly-bridged structure of lithium is maintained even in THF-d_8, in contrast to **2**.[13]

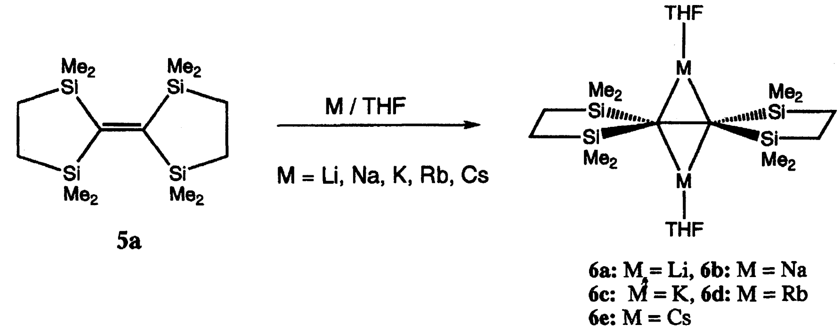
The cyclic ethylene **5a** also underwent a two electron reduction, not only by lithium, but also by sodium, potassium, rubidium, and cesium in THF to give dark-red solutions of the dianions of **6b** (Na), **6c** (K), **6d** (Rb), and **6e** (Cs). The first 1,2-disodium ethylene derivative without an aromatic ring was isolated as dark-red crystals.[9] Thus, the reduction of **5a** with excess sodium in THF at room temperature gave a dark-red solution of the ethylene dianion within one hour. Crystallization from a toluene solution afforded (2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene)bis[(tetrahydrofuran)sodium(I)] (**6b**).

The ^{13}C and ^{29}Si NMR data of **6a** (Li), **6b** (Na), **6c** (K), **6d** (Rb), and **6e** (Cs) with those of the precursor **5a** are summarized in Table 2. These chemical shifts provide good information which can be used to estimate the localized negative charge on carbon and silicon of the resulting dianions. Thus, the anionic carbons

Table 2. NMR Spectral Data of **5a** and **6a**—**6e** at 298 K

		5a[a]	**6a**[b]	**6b**[b]	**6c**[b]	**6d**[b]	**6e**[b]
^{13}C NMR	C$^-$	189.5[c]	10.7	13.9	22.4	24.7	29.5
	CH_3	0.1	5.3	6.0	6.2	6.2	6.0
	CH_2	10.5	14.1	13.9	14.6	14.7	14.8
^{29}Si NMR		−3.9	−6.5	−10.9	−13.7	−14.8	−15.5

a) $CDCl_3$. b) THF-d_8. c) Olefinic carbon.



Scheme 4.

appreciably shift to a higher field (δ=10.7—29.5) from $\delta=189.5$ of the olefinic carbon by reduction. Methyl and methylene carbons of the dianions shift slightly to a lower field. The ^{29}Si resonance ranges from $\delta=-6.5$ in **6a** (Li) to $\delta=-15.5$ in **6e** (Cs). This higher field change of the ^{29}Si chemical shift accounts for an increase of the ionic character; also the four silicon atoms can stabilize the negative charge by a pπ–σ^* interaction. In contrast, the ^{13}C resonance of the anionic carbons moves in the opposite direction from $\delta=10.7$ in **6a** (Li) to $\delta=29.5$ in **6e** (Cs). This is reasonably explained by the fact that the polarizing effect of the counter cation on the electron density at the anionic carbons is proportional to the size of the cation.[14)]

Crystal Structures of 6a (Li) and 6b (Na). Figures 2 and 3 show the molecular structures of **6a** and **6b**, which were confirmed by X-ray diffractions. The molecule of **6a** has a crystallographic 2-fold axis and mirror symmetry, whereas that of **6b** has only a crystallographic 2-fold axis. Oxygen atoms of THF in **6a** are crystallographically disordered. The bond lengths, bond angles, and dihedral angle are listed in Tables 3 and 4. A geometrical comparison of **5a**, **6a**, and **6b** is made in Table 5.

Several interesting features of the structures of **6a** and **6b** can be pointed out. The cations in **6a** and **6b** are three-coordinated, being bonded to THF in addition to two anionic carbons. The bond length of the central C–C bond is significantly stretched from 1.369 Å in **5a** to 1.575 Å in **6a** and 1.579 Å in **6b**. The bond lengths of the Si–C(sp^2) bonds (1.825 Å for **6a** and 1.807 Å for **6b**) are remarkably shortened compared to **5a** (1.906 Å) by pπ-σ^* conjugation. In contrast, the bond lengths of the Si–CH_3 bonds (1.901 Å for **6a** and 1.919 Å for **6b**) are somewhat elongated with respect to **5a** (1.870

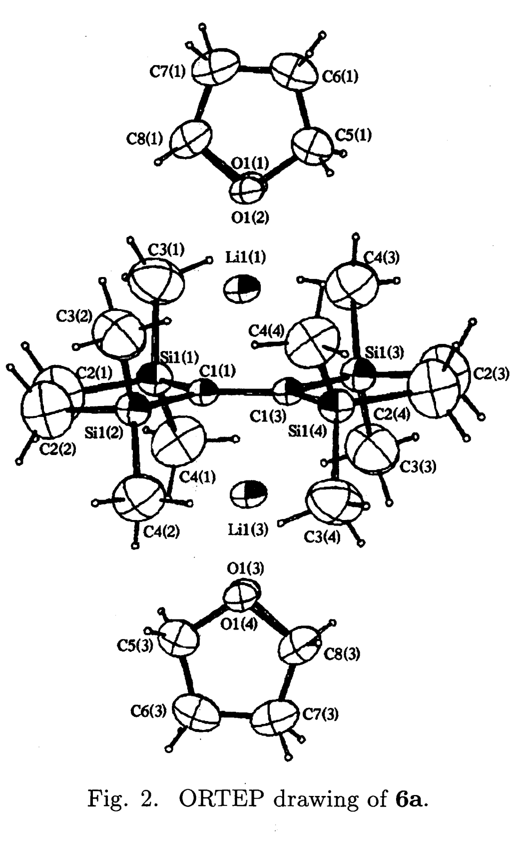


Fig. 2. ORTEP drawing of **6a**.

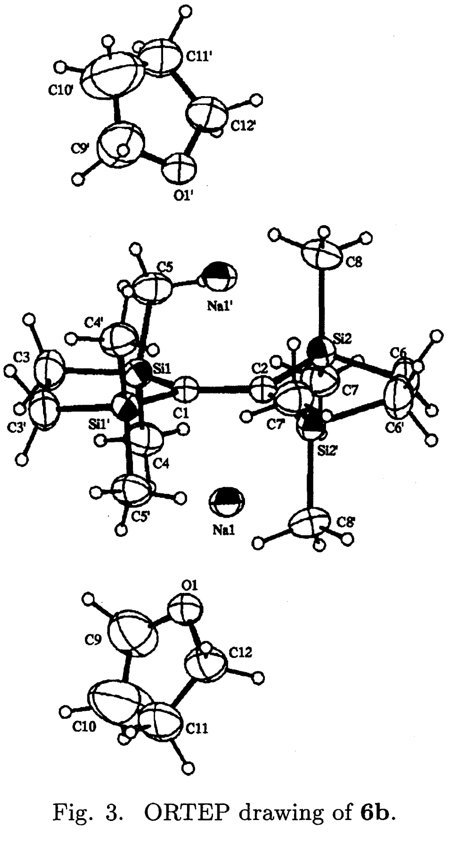


Fig. 3. ORTEP drawing of **6b**.

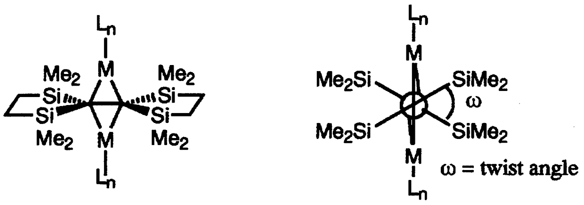
Table 3. Selected Bond Distances (Å), Angles (deg), and Dihedral Angle (deg) of **6a**

Bond distances			
Si1(1)–C1(1)	1.825(4)	Si1(1)–C2(1)	1.868(9)
Si1(1)–C3(1)	1.913(8)	Si1(1)–C4(1)	1.889(7)
O1(1)–Li1(1)	1.871(11)	C1(1)–C1(3)	1.575(9)
C1(1)–Li1(1)	2.061(12)	C1(1)–Li1(3)	2.065(12)
Bond angles			
C1(1)–Si1(1)–C2(1)	103.2(3)	C1(1)–Si1(1)–C3(1)	117.1(3)
C1(1)–Si1(1)–C4(1)	117.2(3)	C2(1)–Si1(1)–C3(1)	105.1(3)
C2(1)–Si1(1)–C4(1)	108.4(3)	C3(1)–Si1(1)–C4(1)	105.0(4)
Si1(1)–C1(1)–Si1(2)	106.0(4)	Si1(1)–C1(1)–C1(3)	127.0(1)
C1(3)–C1(1)–Li1(1)	67.7(4)	C1(3)–C1(1)–Li1(3)	67.4(4)
C1(1)–Li1(1)–C1(3)	44.9(3)		
Dihedral angle			
Si1(1)–C1(1)–Si1(2)/Si1(3)–C1(3)–Si1(4)	0.0		

Table 4. Selected Bond Distances (Å), Angles (deg), and Dihedral Angle (deg) of **6b**

Bond distances			
Si1–C1	1.807(6)	Si1–C3	1.879(11)
Si1–C4	1.919(9)	Si1–C5	1.923(9)
Si2–C2	1.806(7)	Si2–C6	1.866(10)
Si2–C7	1.907(10)	Si2–C8	1.927(8)
C1–C2	1.579(15)	O1–Na1	2.293(6)
C1–Na1	2.487(4)	C2–Na1	2.501(4)
Bond angles			
C1–Si1–C3	103.5(4)	C1–Si1–C4	116.7(3)
C1–Si1–C5	118.5(3)	C3–Si1–C4	108.7(5)
C3–Si1–C5	105.5(4)	C4–Si1–C5	103.3(4)
C2–Si2–C6	104.1(5)	C2–Si2–C7	118.9(3)
C2–Si2–C8	116.5(3)	C6–Si2–C7	105.7(5)
C6–Si2–C8	108.8(5)	C7–Si2–C8	102.1(4)
C1–Na1–C2	36.9(3)	Si1–C1–Si1′	106.5(5)
Si1–C1–C2	126.8(3)	Na1–C1–C2	72.0(2)
Si2–C2–Si2′	106.0(5)	Si2–C2–C1	127.0(2)
Na1–C2–C1	71.1(2)		
Dihedral angle			
Si1–C1–Si1′/Si2–C2–Si2′	17.1		

Table 5. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) of **5a**, **6a**, and **6b**[a]



	5a	**6a** (Li)	**6b** (Na)
C–C	1.369 (2)[b]	1.575 (9)[c]	1.579 (15)[c]
C–M	—	2.063 (12)	2.494 (4)
C–Si	1.906 (2)	1.825 (4)	1.807 (6)
Si–CH$_3$	1.870 (2)	1.901 (7)	1.919 (9)
Si–CH$_2$	1.883 (2)	1.868 (9)	1.873 (10)
Si–C–C	127.8 (1)	127.0 (1)	126.9 (2)
Si–C–Si	104.5 (1)	106.0 (4)	106.3 (5)
ω	4.8	0.0	17.1

a) Standard deviations are in parentheses. b) C–C double bond. c) Anionic C–C bond.

Å). The pπ-σ* interaction is apparently enhanced in **6b** due to an increased ionic character. The bond angles of Si–C(sp^2)–C(sp^2) (127.0° for **6a** and 126.9° for **6b**) and C(sp^2)–Si–C(sp^2) (106.0° for **6a** and 106.3° for **6b**) are almost the same as those of **5a** (127.8° and 104.5°, respectively). The dilithium derivative **6a** has a completely planar structure, which is similar to that of the precursor olefin **5a** (4.8°); therefore, the geometry of the bicyclopentylidene **5a** is essentially retained after lithiation. On the other hand, disodium derivative **6b** is twisted by 17.1°, resulting from an increased electronic repulsion.[15] The twisting angle is evidently influenced by the counter cation. The dianion halves of **6a** and **6b** are unexpectively not twisted perpendicularly to each other, due to a Coulombic attraction between the anion and cation centers. The magnitude of such an attractive interaction depends on the distance between the anion and cation centers, as well as the radii of the cations. The distances of Li$^+$ and Na$^+$ from the anionic carbons are 2.063 and 2.494 Å, respectively. It can therefore be concluded that the group 1 complexes of **5a** prefer a planar geometry to the perpendicular structure, but larger cations tend to have more twist structures along the central C–C bond. It is interesting to note that in this respect the dianion halves for the charge-transfer salt of decamethylcobaltcene tetracyanoethylene, $\{[Co(C_5Me_5)_2]\}^{2+}[(NC)_2CC(CN)_2]^{2-}$, are reported to be twisted by 87.1° due to a rather weak interaction between the anion and cation centers.[16]

Conclusion. Owing to the electronic repulsion of the adjacent negative charge in ethylene dianion, the central C–C bond should be stretched and twisted. Indeed, an MNDO calculation predicts a perpendicular structure with a dihedral angle of 90°.[9b] However, an ab initio calculation takes into consideration the fact that the effect of counter cations is important.[17] A theoretical calculation of 1,2-dilithioethane suggests that a *trans* structure with partially or symmetrically lithium-bridged geometry is most stable, whereas the perpendicular structure is calculated to be much higher in energy than the *trans* bridged planar one.[17a] The present studies provide clear evidence for a planar lithium-doubly bridged structure based on the X-ray crystallography as well as the NMR characteristics. In addition, it has been revealed that the twisting angle is influenced by the counter cation. Thus, the sodium derivative twists to yield a dihedral angle of 17.1° caused by the significant ionic character, whereas the dilithium one is planar in order to maintain the effective Coulombic attraction between the anion and cation centers. For [1,1,2,2-tetrakis(trimethylsilyl)ethylene]bis[(tetrahydrofuran)lithium(I)] (**2**), it undergoes twisting in order to relieve the steric repulsion rather than the electronic one.

Experimental

General Procedure. ^{1}H NMR spectra were recorded on a Bruker AC-300 FT spectrometer. ^{13}C, ^{29}Si, ^{6}Li, ^{23}Na, ^{39}K, and ^{133}Cs NMR spectra were collected on a Bruker AC-300 at 75.5, 59.6, 44.2, 79.4, 14.0, and 39.4 MHz, respectively. ^{6}Li, ^{23}Na, ^{39}K, and ^{133}Cs NMR spectra are referenced to 1 M LiCl in methanol/toluene-d_8 (1 M=1 mol dm^{-3}) or 1 M LiCl in THF-d_8, saturated NaCl in water/toluene-d_8 or saturated NaCl in THF-d_8, saturated KBr in water/THF-d_8, and saturated CsNO$_3$ in water/THF-d_8, respectively. Mass spectra and high-resolution mass spectra were obtained on a Shimadzu QP-1000 or a JEOL JMS D-300 mass spectrometer. Electronic spectra were recorded on a Shimadzu UV-2100 spectrometer. A high-pressure synthesis was carried out by using a Hikari-kouatsukiki Co., Model 0235. The sampling of **6a** and **6b** for X-ray crystallography was carried out by using a Giken Engineering Service GBX-1200 gas-replacement type glove box. Tetrahydrofuran, hexane, and toluene were dried and distilled from sodium benzophenone ketyl. Pentane was treated with concentrated sulfuric acid, dried, and then distilled from sodium benzophenone ketyl. These solvents were further dried and degassed over a potassium mirror in vacuo prior to use. Benzene-d_6, 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).

1,2-Bis[2-(chlorodimethylsilyl)ethyl]-1,1,2,2-tetramethyldisilane (3a). A 2-propanol solution of dihydrogen hexachloroplatinate(IV) hydrate (0.6 M, 8 ml, 0.005 mol%) as a catalyst was added to a mixture of 1,1,2,2-tetramethyl-1,2-divinyldisilane (17.2 g, 101 mmol) and chlorodimethylsilane (38.0 g, 402 mmol) with stirring under argon. An exothermic reaction occurred. The excess chlorosilane was removed in vacuo, and distillation afforded 33.7 g (93.7 mmol, 92.8%) of **3a** as a colorless oil, bp 100—120 °C/0.08 mmHg (1 mmHg=133.322 Pa). ^{1}H NMR (CDCl$_3$) δ=0.04 (s, 12 H), 0.38 (s, 12 H), 0.52—0.63 (m, 4 H), 0.64—0.75 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ=−4.2, 1.0, 6.5, 12.2; ^{29}Si NMR (CDCl$_3$) δ=−15.0, 32.4. HRMS Found: m/z 358.0980. Calcd for $C_{12}H_{32}Cl_2Si_4$: M, 358.0958.

3,3,6,6,7,7,10,10-Octamethyl-3,6,7,10-tetrasilacyclodecyne (4a). To a mixture of butyllithium (1.71 M, 90 ml, 154 mmol), THF (50 ml), and Et$_2$O (50 ml) was added dropwise trichloroethylene (6.75 g, 51.4 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature to give a solution of dilithioacetylene. THF solution of **3a** (18.5 g, 51.4 mmol) and the solution of dilithioacetylene were added dropwise simultaneously in THF (500 ml) over 5 h at room temperature. The reaction mixture was stirred overnight. The usual workup followed by Kugelrohr distillation afforded 10.0 g (32.0 mmol, 62.2%) of **4a** as a colorless oil, bp 70—110 °C/0.08 mmHg. ^{1}H NMR (CDCl$_3$) δ=0.05 (s, 12 H), 0.11 (s, 12 H), 0.50—0.59 (m, 4 H), 0.72—0.81 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ=−2.9, −2.7, 7.5, 10.5, 116.0; ^{29}Si NMR (CDCl$_3$) δ=−14.6, −12.0. HRMS Found: m/z 312.1575. Calcd for $C_{14}H_{32}Si_4$: M, 312.1581.

2,2,2′,2′,5,5,5′,5′-Octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene (5a). The cell (4 ml) used for high-pressure synthesis was charged with **4a** (650 mg, 2.08 mmol), 1,1,3,3-tetramethylbutyl isocyanide (140 μl, 15 mmol), palladium(II) acetate (22.0 mg, 98 mmol), and toluene (3 ml). The mixture was heated under 5000 bar at 110 °C for 12 h. The reaction mixture was chromatographed on silica gel with hexane, and then sublimation followed by recrystallization from ethanol afforded 392 mg (1.25 mmol, 60.3%) of **5a** as pale-yellow crystals, mp 118—119 °C. ^{1}H NMR (CDCl$_3$) δ=0.13 (s, 24 H), 0.76 (s, 8 H); ^{13}C NMR (CDCl$_3$) δ=0.1, 10.5, 189.5; ^{29}Si NMR (CDCl$_3$) δ=−3.9; UV (hexane) $\lambda_{\max}$/nm (ε) 235 (15400), 379 (160). HRMS Found: m/z 312.1589. Calcd for $C_{14}H_{32}Si_4$: M, 312.1581.

1,2-Bis[2-(dimethylphenylgermyl)ethyl]-1,1,2,2-tetramethyldigermane. Dichlorophenylgermane (2.7 g, 12.2 mmol) was slowly added to 1,1,2,2-tetramethyl-1,2-divinyldigermane (1.56 g, 6.00 mmol) at 0 °C and stirred overnight at room temperature to give 1,2-bis[2-(dichlorophenylgermyl)ethyl]-1,1,2,2-tetramethyldigermane (4.2 g, 6.00 mmol) as colorless solids. Without purification, this was treated with methylmagnesium bromide. The usual workup followed by Kugelrohr distillation afforded 2.9 g (4.67 mmol, 78.1%) of the title compound, bp 170—190 °C/0.04 mmHg. ^{1}H NMR (CDCl$_3$) δ=0.15 (s, 12 H), 0.33 (s, 12 H), 0.76—0.97 (m, 8 H), 7.27—7.35 (m, 6 H), 7.38—7.47 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ=−4.1, 10.4, 11.5, 128.2, 128.5, 133.6, 141.7. HRMS Found: m/z 626.0135. Calcd for $C_{24}H_{42}Ge_4$: M, 626.0134.

1,2-Bis[2-(chlorodimethylgermyl)ethyl]-1,1,2,2-tetramethyldigermane (3b). A dry hydrogen chloride was introduced to a chloroform solution of 1,2-bis[2-(dimethylphenylgermyl)ethyl]-1,1,2,2-tetramethyldigermane (4.67 mmol, 2.9 g) and a catalytic amount of aluminum chloride (ca. 10 mg) at room temperature. The reaction was followed by gas chromatography and ^{1}H NMR. After completion of the reaction, acetone (1 ml) was added to the mixture. The solvent was removed in vacuo, and then hexane (15 ml) was added. Removal of the resulting aluminum chloride–acetone complex followed by Kugelrohr distillation afforded 2.1 g (3.91 mmol, 83.6%) of **3b**, bp 110—130 °C/0.04 mmHg. ^{1}H NMR (CDCl$_3$) δ=0.21 (s, 12 H), 0.66 (s, 12 H), 0.86—0.97 (m, 4 H), 1.10—1.20 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ=−4.4, 2.5, 8.8, 17.1; MS (rel intensity) m/z 527 for $C_{11}H_{29}Cl_2{}^{74}Ge_4$ (M^+-Me; 4), 525 for $C_{11}H_{29}Cl_2{}^{72}Ge_1{}^{74}Ge_3$ (M^+-Me; 6), 523 for $C_{11}H_{29}Cl_2{}^{72}Ge_2{}^{74}Ge_2$ (M^+-Me; 7), 521 for $C_{11}H_{29}Cl_2{}^{72}Ge_3{}^{74}Ge_1$ (M^+-Me; 6), 519 for $C_{11}H_{29}Cl_2{}^{72}Ge_4$ (M^+-Me; 4), 507 (15), 505 (24), 503 (29), 501 (28), 499 (21), 375 (5), 373 (7), 371 (8), 369 (6), 273 (35), 271 (80), 269 (100), 267 (82), 265 (40), 139 (25), 137 (19), 119 (47), 117 (36). HRMS Found: m/z 526.8511. Calcd for $C_{11}H_{29}Cl_2Ge_4$: (M^+-Me), 526.8493.

3,3,6,6,7,7,10,10-Octamethyl-3,6,7,10-tetragermacyclodecyne (4b). This was obtained in 23% yield by a procedure similar to the synthesis of **4a**; bp 100—150 °C/0.04 mmHg (Kugelrohr). ^{1}H NMR (CDCl$_3$) δ=0.21 (s, 12 H), 0.29 (s, 12 H), 0.82—0.94 (m, 4 H), 1.07—1.19 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ=−3.5, −2.6, 10.0, 13.7, 114.1.

HRMS Found: m/z 495.9359. Calcd for $C_{14}H_{32}Ge_4$: M, 495.9351.

2,2,2′,2′,5,5,5′,5′-Octamethyl-2,2′,5,5′-tetragermabicyclopentylidene (5b). This was obtained in 59% yield by a procedure similar to the synthesis of **5a**; mp 165—166 °C. ^{1}H NMR ($CDCl_3$) δ=0.26 (s, 24 H), 1.03 (s, 8 H); ^{13}C NMR ($CDCl_3$) $\delta=-0.1$, 13.2, 182.0; UV-vis (hexane) λ_{max}/nm (ε) 198 (18100), 226 (14200), 314 (sh, 20), 351 (80). HRMS Found: m/z 495.9344. Calcd for $C_{14}H_{32}Ge_4$: M, 495.9351.

(2,2,2′,2′,5,5,5′,5′-Octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene)bis[(tetrahydrofuran)lithium(I)] (6a). The pale yellow-crystals of **5a** (200 mg, 0.64 mmol) and lithium metal (30 mg, 4.3 mmol) were put in a Schlenk 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 a yellow solution of the dianion within 1 h. After the solvent was removed in vacuo, degassed toluene was introduced by vacuum transfer. Then after removing the lithium metal, the solution was concentrated and cooled to afford yellow crystals of **6a**. ^{1}H NMR (toluene-d_8) δ=0.41 (s, 24 H), 1.13 (s, 8 H), 1.30—1.38 (m, 8 H), 3.52—3.59 (m, 8 H); ^{1}H NMR (THF-d_8) δ=0.06 (s, 24 H), 0.63 (s, 8 H); ^{13}C NMR (toluene-d_8) δ=5.7 (CH_3), 11.0 (quint, $J_{^{13}C-^{6}Li}$=3.1 Hz, CLi), 14.5 (CH_2), 25.6 (THF), 69.2 (THF); ^{13}C NMR (THF-d_8) δ=5.3 (CH_3), 10.7 (CLi), 14.1 (CH_2); ^{29}Si NMR (toluene-d_8) $\delta=-6.2$; ^{29}Si NMR (THF-d_8) $\delta=-6.5$; ^{6}Li NMR (toluene-d_8) δ=1.72; ^{6}Li NMR (THF-d_8) δ=1.71.

(2,2,2′,2′,5,5,5′,5′-Octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene)bis[(tetrahydrofuran)sodium(I)] (6b). This was obtained by a procedure similar to the synthesis of **6a** as dark red-crystals. ^{1}H NMR (toluene-d_8) δ=0.35 (s, 24 H), 1.03 (s, 8 H), 1.26—1.34 (m, 8 H), 3.32—3.40 (m, 8 H); ^{1}H NMR (THF-d_8) δ=0.05 (s, 24 H), 0.60 (s, 8 H); ^{13}C NMR (toluene-d_8) δ=6.8 (CH_3), 13.9 (CH_2), 14.7 (CNa), 25.5 (THF), 68.6 (THF); ^{13}C NMR (THF-d_8) δ=6.0 (CH_3), 13.9 (CH_2 and CNa); ^{29}Si NMR (toluene-d_8) $\delta=-10.6$; ^{29}Si NMR (THF-d_8) $\delta=-10.9$; ^{23}Na NMR (toluene-d_8) $\delta=-2.8$ ($\nu_{1/2}$=2120 Hz); ^{23}Na NMR (THF-d_8) $\delta=-6.1$ ($\nu_{1/2}$=2100 Hz).

Dipotassium (6c). ^{1}H NMR (THF-d_8) δ=0.04 (s, 24 H), 0.54 (s, 8H); ^{13}C NMR (THF-d_8) δ=6.2 (CH_3), 14.6 (CH_2), 22.4 (CK); ^{29}Si NMR (THF-d_8) $\delta=-13.7$; ^{39}K NMR (THF-d_8) δ=0.04.

Dirubidium (6d). ^{1}H NMR (THF-d_8) δ=0.04 (s, 24 H), 0.52 (s, 8 H); ^{13}C NMR (THF-d_8) δ=6.2 (CH_3), 14.7 (CH_2), 24.7 (CRb); ^{29}Si NMR (THF-d_8) $\delta=-14.8$.

Dicesium (6e). ^{1}H NMR (THF-d_8) δ=0.06 (s, 24 H), 0.53 (s, 8 H); ^{13}C NMR (THF-d_8) δ=6.0 (CH_3), 14.8 (CH_2), 29.5 (CCs); ^{29}Si NMR (THF-d_8) $\delta=-15.5$; ^{133}Cs NMR (THF-d_8) δ=87.0 ($\nu_{1/2}$=70 Hz).

X-Ray Crystallography. Single crystals of **6a** and **6b** for X-ray diffractions were grown from a toluene solution. A single crystal was selected, cut to a suitable size, and sealed in a capillary glass tube. The X-ray crystallographic experiments were performed on a Rigaku-Denki AFC 5R diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å) or Cu $K\alpha$ radiation (λ=1.54178 Å).

Crystal data of **5a**: MF=$C_{14}H_{32}Si_4$, MW=312.76, monoclinic, a=18.274(3), b=9.200(1), c=13.145(2) Å, β=116.38(1) °, V=1979.7(6) Å^3, space group=$C2/c$, Z=4, D_{calcd}=1.049 g cm^{-3}. The final R factor was 0.0448 (R_w=0.0456) for 2259 reflections with $F_o>3\sigma(F_o)$.

Crystal data of **6a**: MF=$C_{22}H_{48}Li_2O_2Si_4$, MW=470.85, monoclinic, a=17.551(18), b=9.438(7), c=9.520(4) Å, β=108.89(4) °, V=1492.1(20) Å^3, space group=$C2/m$, Z=2, D_{calcd}=1.048 g cm^{-3}. The final R factor was 0.0923 (R_w=0.0913) for 1606 reflections with $F_o>3\sigma(F_o)$.

Crystal data of **6b**: MF=$C_{22}H_{48}Na_2O_2Si_4$, MW=502.94, monoclinic, a=9.715(1), b=11.383(4), c=13.728(3) Å, β=99.06(1) °, V=1499.1(6) Å^3, space group=$P2/c$, Z=2, D_{calcd}=1.114 g cm^{-3}. The final R factor was 0.0880 (R_w=0.0921) for 1698 reflections with $F_o>3\sigma(F_o)$. Tables of positional and thermal parameters and complete interatomic distances and angles have been deposited as Document No. 68053 at the Office of the Editor of Bull. Chem. Soc. Jpn.

This work was supported by the Grant-in-Aid for Specially Promoted Research No. 02102004 and for Scientific Research on Priority Area of Reactive Organometallics No. 05236102 from the Ministry of Education, Science and Culture. One of the authors (M. I.) thanks the Japan Society for Promotion of Science for the Fellowship for Japan Junior Scientists.

References

1) For reviews, see: a) B. J. Wakefield, "The Chemistry of Organolithium Compounds," Pergamon Press, New York (1974); b) J. L. Wardell, "Alkali Metals," in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, New York (1982), Vol. 1, p. 43; c) P. v. R. Schleyer, *Pure Appl. Chem.*, **55**, 355 (1983); d) P. v. R. Schleyer, *Pure Appl. Chem.*, **56**, 151 (1984); e) W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, **24**, 353 (1985); f) H. Günther, D. Moskau, P. Bast, and D. Schmalz, *Angew. Chem., Int. Ed. Engl.*, **26**, 1212 (1987).

2) For 1,2-dilithioethane, see: a) J. F. Garst, *J. Am. Chem. Soc.*, **93**, 6312 (1971); b) V. Rautenstrauch, *Angew. Chem., Int. Ed. Engl.*, **14**, 259 (1975); c) M. Walczak and G. D. Stucky, *J. Organomet. Chem.*, **97**, 313 (1975); d) M. Walczak and G. D. Stucky, *J. Am. Chem. Soc.*, **98**, 5531 (1976); e) W. E. Rhine, J. H. Davis, and G. D. Stucky, *J. Organomet. Chem.*, **134**, 139 (1977); f) B. Bogdanović and B. Wermeckes, *Angew. Chem., Int. Ed. Engl.*, **20**, 684 (1981); g) L. Manceron and L. Andrews, *J. Phys. Chem.*, **90**, 4514 (1986); h) A. Maercker and B. Grebe, *J. Organomet. Chem.*, **334**, C21 (1987); i) N. J. R. van E. Hommes, F. Bickelhaupt, and G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, **106**, 514 (1987); j) N. J. R. van E. Hommes, F. Bickelhaupt, and G. W. Klumpp, *Angew. Chem., Int. Ed. Engl.*, **27**, 1083 (1988); k) M. A. Fox and D. Shultz, *J. Org. Chem.*, **53**, 4386 (1988).

3) A. Sekiguchi, T. Nakanishi, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **111**, 3748 (1989).

4) A. Sekiguchi, T. Nakanishi, C. Kabuto, and H. Sakurai, *Chem. Lett.*, **1992**, 867.

5) a) A. Sekiguchi, K. Ebata, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **113**, 1464 (1991); b) A. Sekiguchi, K. Ebata, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **113**,

7081 (1991).

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

7) H. Sakurai, Y. Nakadaira, H. Tobita, T. Ito, K. Toriumi, and H. Ito, *J. Am. Chem. Soc.*, **104**, 300 (1982).

8) For the preliminary results, see: A. Sekiguchi, M. Ichinohe, C. Kabuto, and H. Sakurai, *Organometallics*, **14**, 1092 (1995).

9) For reviews on sodium derivatives, see: a) C. Schade and P. v. R. Schleyer, *Adv. Organomet. Chem.*, **27**, 169 (1987); b) H. Bock, K. Ruppert, C. Näther, Z. Havlas, H. F. Herrmann, C. Arad, I. Göbel, A. John, J. Meuret, S. Nick, A. Rauschenbach, W. Seitz, T. Vaupel, and B. Solouki, *Angew. Chem., Int. Ed. Engl.*, **31**, 550 (1992).

10) a) H. Sakurai, Y. Nakadaira, M. Kira, and T. Tobita, *Tetrahedron Lett.*, **21**, 3077 (1980); b) H. Sakurai, H. Tobita, M. Kira, and Y. Nakadaira, *Angew. Chem., Int. Ed. Engl.*, **19**, 620 (1980); c) H. Sakurai, Y. Nakadaira, and H. Tobita, *Chem. Lett.*, **1982**, 771; d) H. Sakurai, K. Ebata, Y. Nakadaira, and C. Kabuto, *Chem. Lett.*, **1987**, 301; e) H. Sakurai, K. Ebata, K. Sakamoto, Y. Nakadaira, and C. Kabuto, *Chem. Lett.*, **1988**, 965; f) A. Sekiguchi, K. Ebata, C. Kabuto, and H. Sakurai, *Chem. Lett.*, **1990**, 539; g) T. Brennan and H. Gilman, *J. Organomet. Chem.*, **11**, 625 (1968); h) D. Ballard, T. Brennan, F. W. G. Fearon, K. Shiina, I. Haiduc, and H. Gilman, *Pure Appl. Chem.*, **19**, 449 (1969); i) H. Sakurai, K. Ebata, C. Kabuto, and A. Sekiguchi, *J. Am. Chem. Soc.*, **112**, 1799 (1990); j) C. Rudinger, H. Beruda, and H. Schmidtbaur, *Chem. Ber.*, **125**, 1401 (1992).

11) a) Y. Ito, M. Suginome, and M. Murakami, *J. Org. Chem.*, **56**, 1948 (1991); b) M. Murakami, H. Oike, M. Sugawara, M. Suginome, and Y. Ito, *Tetrahedron*, **49**, 3933 (1993); c) M. Murakami, M. Suginome, K. Fujimoto, and Y. Ito, *Angew. Chem., Int. Ed. Engl.*, **32**, 1473 (1993).

12) One of the reviewer has pointed out the possibility of the formation of monometal radical anion salts in the solvents of rather poor metal cation solvation. However, the two-electron reduction of **5a** with lithium in diethy ether occurred smoothly to produce (2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene)bis[(diethyl ether)lithium(I)]: ^{1}H NMR (toluene-d_8) $\delta=0.39$ (s, 24 H, SiMe$_2$), 1.02 (t, J=7.2 Hz, 12 H), 1.10 (s, 8 H, SiCH$_2$), 3.35 (q, J=7.2 Hz, 8 H); ^{13}C NMR (toluene-d_8) $\delta=5.7$ (SiMe$_2$), 10.6 (quint, $J_{^{13}\mathrm{C}-^{6}\mathrm{Li}}=3.0$ Hz, CLi), 14.3 (SiCH$_2$), 14.7, 65.9; ^{29}Si NMR (toluene-d_8) $\delta=-6.3$; ^{6}Li NMR (toluene-d_8) $\delta=1.33$.

13) In marked contrast to **6a**, the dilithium derivative **2** exists as a symmetrically lithium-bridged species in nonpolar solvents, whereas as a singly bridged one in THF. The anionic carbon of **2** in THF-d_8 appeared at $\delta=11.2$ as a triplet signal due to coupling with only one ^{6}Li ($J_{^{13}\mathrm{C}-^{6}\mathrm{Li}}=4.1$ Hz). The most dramatic change was found for ^{6}Li NMR spectrum of **2**, two signals were observed at $\delta=1.43$ and $\delta=-0.39$ at 220 K. These NMR spectra suggest that **2** gives a solvent separated ion pair in THF-d_8, see: A. Sekiguchi, M. Ichinohe, T. Nakanishi, and H. Sakurai, *Chem. Lett.*, **1993**, 267.

14) D. H. O'Brien, C. R. Russell, and A. J. Hart, *J. Am. Chem. Soc.*, **98**, 7427 (1976).

15) There is precedent that (tetraphenylethylene)bis[(diethyl ether)sodium(I)] twists by 56° along the central C–C bond, see: H. Bock, K. Ruppert, and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, **28**, 1685 (1989).

16) D. A. Dixon and J. S. Miller, *J. Am. Chem. Soc.*, **109**, 3656 (1987).

17) a) A. J. Kos, E. D. Jemmis, P. v. R. Schleyer, R. Gleiter, U. Fischbach, and J. A. Pople, *J. Am. Chem. Soc.*, **103**, 4996 (1981); b) S. P. So, *J. Organomet. Chem.*, **361**, 283 (1989).