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Syntheses of Dialkali Metal Complexes of Tetrakis(dimethylsilyl)ethylene: $[(HMe_2Si)_2C{=}C(SiMe_2H)_2]^{2-}[M^+(ligand)_n]_2$. Evidence for SiH–Alkali Metal Agostic Interactions

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A series of dialkali metal complexes, $[(HMe_2Si)_2C{=}C(SiMe_2H)_2]^{2-}[M^+(ligand)_n]_2$ (M = Li, Na, K, Rb, Cs), were prepared by the reaction of tetrakis(dimethylsilylethylene) with alkali metals. These complexes exhibit Si–H alkali metal agostic interactions and have been characterized by spectroscopic and structural methods. Spectroscopic evidence for the interaction of the hydrogen on the silicon atom with alkali metals include (1) an unusually small value of the silicon-hydrogen coupling constant ($^1J_{Si-H}$) in NMR spectra and (2) low-energy Si–H stretching frequency in the infrared spectra. The smallest cation, Li^+, can interact with SiH most strongly.

The transition metal complexes having M–H–Si three center interactions are well known, and have recently attracted considerable interest as intermediates for transition metal-catalyzed hydrosilylation of unsaturated hydrocarbons or polymerization of silanes.[1,2] For the interaction between Si–H and main group metals, Schleyer and Clark predicted by using an ab inito method that the "inverted" C_{3v} structure of LiH_3Si was more stable than the usual "tetrahedral" one, due to the electrostatic interaction between the lithium atom and the three hydrogen atoms on the silicon atom.[3] More recently, an oligomeric sodium alcoholate containing two SiH_3^- groups which are coordinated to a sodium cation with inverted C_{3v} symmetry (Na–H = 2.52—2.67 Å) was reported.[4] Interactions between the hydrogen on a silicon atom and main group metals (Li, Mg) were also found in silyl-substituted amide systems: $\{(Me_3Si)_2NSi(H)[N(Li)\text{-}SiMe_3]_2\}_2$,[5] $\{MeSi(H)[N(Li)\text{-}t\text{-}Bu]_2\}_4$,[6] $[Me_2Si(H)N(Li)\text{-}t\text{-}Bu]_3$,[7] and $\{Mg[Me_2Si(H)N\text{-}t\text{-}Bu]_2\}_2$.[7]

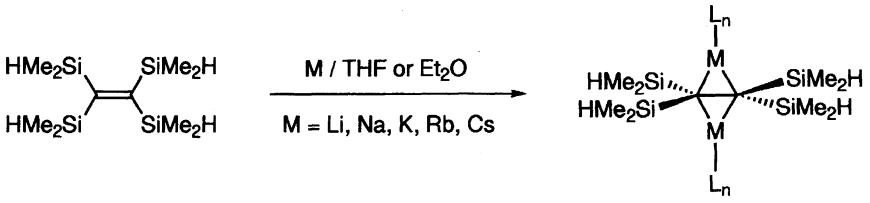
We have studied the unique structures of the silyl-substituted ethylene dialkali metal complexes.[8] We recently reported the preparation, characterization, and molecular structure of tetrakis(dimethylsilyl)ethylene dilithium complex, and demonstrated an SiH–Li interaction by means of spectroscopic and structural methods.[9] In this paper, we wish to describe a detailed study of a series of dialkali metal complexes of tetrakis(dimethylsilyl)ethylene.

Results and Discussion

Synthesis of Dialkali Metal Complexes of Tetrakis(dimethylsilyl)ethylene: $[(HMe_2Si)_2C{=}C(SiMe_2H)_2]^{2-}[M^+(ligand)_n]_2$. We have previously described the reaction of 2,2′-bis(1,3-disilacyclopentylidene) derivative with a series of alkali metals in THF to give the corresponding dialkali metal complexes.[8f] Tetrakis(dimethylsilyl)ethylene (**1**)[10] also gave a series of dialkali metal complexes **2a—e** by reaction with alkali metals in THF (Scheme 1). The dilithium derivative **2a(Et$_2$O)** was also prepared in Et_2O, and good crystals for X-ray crystallography were produced. While **2a** is stable in the solid state and in hydrocarbon solution, the other alkali metal complexes **2b—e** decompose to **1** by the evaporation of THF.

Molecular Structure of $[(HMe_2Si)_2C{=}C(SiMe_2H)_2]^{2-}[Li^+(Et_2O)]_2$. Structural characterization of complexes **2** has been limited by the availability of suitable single crystals, and X-ray analysis of only the dilithium complex **2a(Et$_2$O)** was possible. The ORTEP drawings of **2a(Et$_2$O)** are shown in Fig. 1. The atomic distances, bond angles, and dihedral angles are listed in Table 1. A geometrical comparison of **1** and **2a(Et$_2$O)** is made in Table 2.

Several interesting features for the structure of **2a(Et$_2$O)** can be pointed out. The lithium cations are connected to two anionic carbons each to give a doubly-bridged structure. The length of the central C–C bond of **2a(Et$_2$O)** (1.597(5) Å) is significantly longer than that of the precursor ethylene **1** (1.367(9) Å). In contrast, the bond lengths of Si–C(sp^2) bond of **2a(Et$_2$O)** (1.818(4) and 1.815(4) Å) are somewhat shortened with respect to **1** (1.901(av.) Å) due to the interaction of anionic carbon with silicon by $p\pi$–σ^* conjugation.[8b,8c,8e—g] The C–Li bond lengths of **2a(Et$_2$O)** (2.125(9) and 2.128(9) Å) are very close to those of dilithium complexes of tetrasi-



1

2a(THF): M = Li, L_n = THF
2a(Et_2O): M = Li, L_n = Et_2O
2b: M = Na, L_n = THF
2c: M = K, L_n = THF
2d: M = Rb, L_n = THF
2e: M = Cs, L_n = THF

Scheme 1.

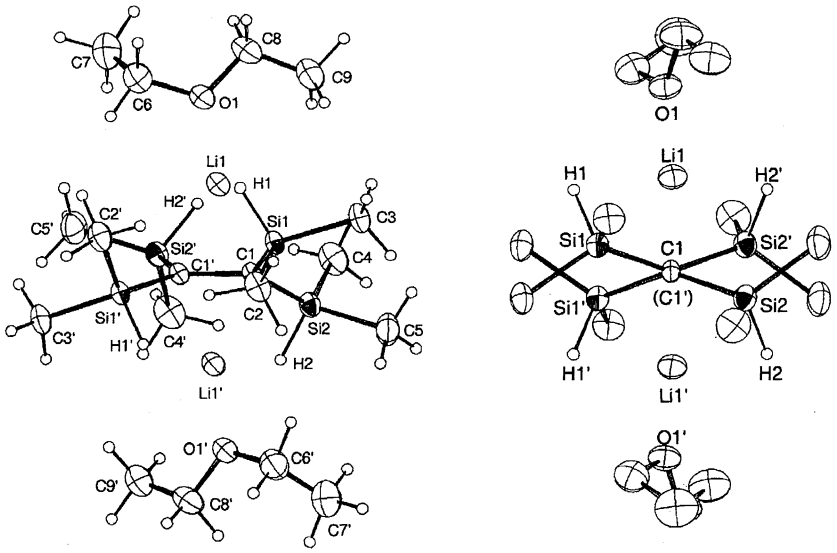


Fig. 1. ORTEP drawing of **2a(Et_2O)**: left, whole view; right, view along C1–C1′ bond (hydrogens other than the hydrogens on silicon atoms are omitted for clarity).

lylethylenes.

However, the significant difference between the dilithium compounds **2a(Et_2O)** and **1** lies in the twist angle of the central C–C bond. The precursor tetrasilylethylene **1** is a completely planar and gear-meshed structure in which four Si–H bonds and two olefinic carbon atoms are essentially coplanar, determined by the dihedral angle of C–C–Si–H = 0°. However, **2a(Et_2O)** is strongly twisted, with a dihedral angle of 41.0°. This is contrasted to the almost planar tetrasilylethylene, 1,1,1′,1′,3,3,3′,3′-octamethyl-2,2′-bis(1,3-disilacyclopentylidene), which gives a completely planar dilithium complex.[8e,8f] For the dilithium compound **2a(Et_2O)**, the hydrogen atom on the silicon atom can interact with the lithium atom, as determined by the dihedral angle of Li–C–Si–H = 19.0(av.)°. As a result, the closest distances between a hydrogen atom and the lithium atom are 2.25(4) Å for Li1–H1 and 2.14(4) Å for Li1–H2′. This SiH–Li nonbonded distance is much shorter than the sum of the van der Waals radii of the hydrogen atom and the lithium atom (1.20 and 1.82 Å respectively), and somewhat longer than the Li–H distance in the crystal of lithium hydride (2.04 Å).[11] Apparently, the highly twisted structure of **2a(Et_2O)** can be attributed to the interaction of the hydrogen atom on the silicon atom with the lithium cations.

ab initio Calculation of $[(H_3Si)_2C{=}C(SiH_3)_2]^{2-}[Li^+(H_2O)]_2$. In order to assess the effects of electrostatic interactions between the hydrogen atom on the silicon atom and the lithium atom computationally, we optimized $[(H_3Si)_2C{=}C(SiH_3)_2]^{2-}[Li^+(H_2O)]_2$, using both **3-twist** (D_2 symmetry) as a model compound for **2a(Et_2O)** and **3-planar** (D_{2h} symmetry) as a noninteracting model (Fig. 2, Table 3). Although the parent complex, $[H_2C{=}CH_2]^{2-}[Li^+(H_2O)]_2$, has no minimum geometry at the twisted D_2 symmetry,[12] the **3-twist** in which the central C–C bond is twisted by 35.0° is 3.93 kcal mol^{-1} more stable than the **3-planar** one. The calculated structural parameters for **3-twist** are very similar to those experimentally observed in **2a(Et_2O)**. The Li–H(Si) distance in **3-twist** (2.360 Å) compares well to that in **2a(Et_2O)**.

Spectroscopic Evidence for SiH–Alkali Metal Interactions. The SiH–alkali metal interactions have been also evidenced by spectroscopic means. In ^{1}H NMR spectra of **2a(THF)** in toluene-d_8, methyl protons appeared at δ = 0.54 as a doublet due to the coupling with the proton on the same silicon atom ($^3J_{HH}$ = 3.1 Hz). The signal of SiH was observed at δ = 4.65 as a broad singlet, and the coupling with

Table 1. Selected Atomic Distances (Å), Bond Angles (deg), and Dihedral Angles (deg) of **2a(Et$_2$O)**

		Atomic distances			
Si1–C1	1.818(4)	O1–C6	1.468(7)	C6–C7	1.45(1)
Si1–C2	1.892(6)	O1–C8	1.397(9)	C8–C9	1.46(1)
Si1–C3	1.888(6)	O1–Li1	1.908(9)	Si1–H1	1.41(4)
Si2–C1	1.815(4)	C1–C1′	1.597(5)	Si2–H2	1.44(4)
Si2–C4	1.888(7)	C1–Li1	2.125(9)	Li1–H1	2.25(4)
Si2–C5	1.881(7)	C1–Li1′	2.128(9)	Li1–H2′	2.14(4)
		Bond angles			
C1–Si1–C2	120.2(2)	C8–O1–Li1	126.9(5)	C1′–C1–Li1	68.0(3)
C1–Si1–C3	116.9(2)	Si1–C1–Si2	121.2(2)	C1′–C1–Li1′	67.9(3)
C2–Si1–C3	103.6(2)	Si1–C1–C1′	119.2(2)	Li1–C1–Li1′	135.9(3)
C1–Si2–C4	119.1(2)	Si1–C1–Li1	84.8(3)	O1–C6–C7	112.4(6)
C1–Si2–C5	117.4(2)	Si1–C1–Li1′	118.4(3)	O1–C8–C9	112.5(7)
C4–Si2–C5	103.6(3)	Si2–C1–C1′	119.7(2)	O1–Li1–C1	167.6(5)
C6–O1–C8	116.7(5)	Si2–C1–Li1	117.3(3)	O1–Li1–C1′	146.8(4)
C6–O1–Li1	116.0(4)	Si2–C1–Li1′	83.9(3)	C1–Li1–C1′	44.1(2)
		Dihedral angles			
		Si1–C1–C1′–Si1′	40.8(4)		
		Si1–C1–C1′–Si2′	139.0(2)		
		Si2–C1–C1′–Si1′	139.0(2)		
		Si2–C1–C1′–Si2′	41.3(4)		

Table 2. Selected Bond Lengths (Å) and Twist Angles (deg) of **1**[a] and **2a(Et$_2$O)**

	1	**2a (Et$_2$O)**
C–C	1.367 (9)[b]	1.597 (5)[c]
C–Li	—	2.127 (av.)
C–Si	1.901 (av.)	1.817 (av.)
Si–CH$_3$	1.856 (av.)	1.887 (av.)
ω[d]	0.0	41.0

a) Ref. 10. b) C–C double bond. c) Anionic C–C bond. d) Twist angle along central C–C bond.

Table 3. Computed Energies,[a] and Si and Li Chemical Shifts δ[b] of **3-twist** (D_2) and **3-planar** (D_{2h})

	3-twist (D_2)	**3-planar** (D_{2h})
Total energy (au)	−1405.3569491	−1405.3506778
Relative energy (kcal mol^{-1})	−3.93	0.0
δ_{Si} (ppm)	−47.87	−53.49
δ_{Li} (ppm)	3.10	3.56

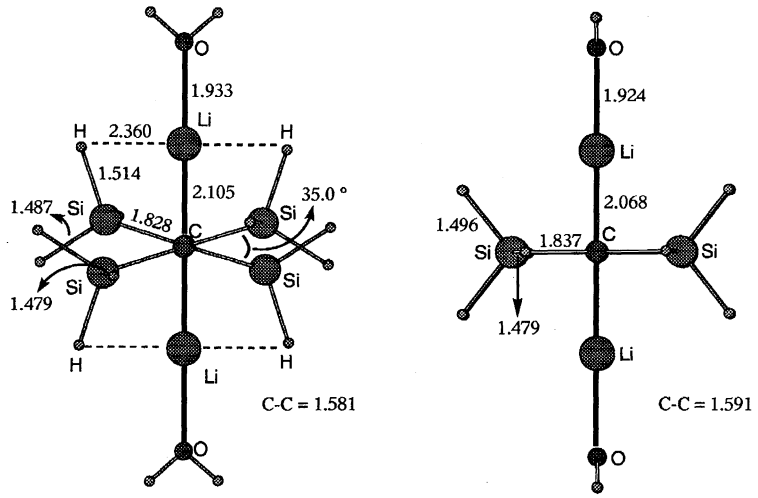
a) HF/6-31+G* optimizations, b) HF/6-31+G*-GIAO computations, the δ values of Si and Li are relative to the computed absolute chemical shielding of Si (32.83) in TMS and Li$^+$ (95.39), respectively.

six methyl protons was unclear since SiH protons are coupled with ^{6}Li. ^{1}H, as well as ^{13}C NMR spectra of **2a(THF)**, reveals that one molecule of tetrahydrofuran binds to the lithium cation. The ^{13}C NMR spectrum exhibits signals for $SiMe_2$ (δ = 6.5), CLi–CLi (δ = 15.1, quintet, $J_{^{13}C-^6Li}$ = 2.5 Hz), and THF (δ = 25.6 and 68.8). The signal of anionic carbon observed at δ = 15.1 split into a quintet signal due to coupling with two equivalent ^{6}Li (I = 1), indicating the lithium doubly-bridged structure of **2a(THF)**.

^{29}Si resonance was observed at δ = −12.9 for **2a(THF)** in toluene-d_8, which shifted downfield from that of the precursor ethylene **1** (δ = −24.4). For the dilithium complexes of tetrakis(trialkylsilyl)ethylene, the negative charge is partially delocalized on the silicon atoms by the pπ–σ^*(Si–CH$_3$) conjugation and consequently, the upfield shift of ^{29}Si resonance can be observed by the complexation with lithium.[8b—g] The downfield shift of ^{29}Si resonance for **2a(THF)** is quite unusual. This unusual downfield shift of ^{29}Si resonance for **2a(THF)** with SiH–Li interaction compared to that of **1** is supported by the GIAO calculation. The chemical shifts of silicon for **3-twist** and **3-planar** are δ = −47.87 and −53.49, respectively. The SiH–Li interaction causes the downfield shifted δ_{Si} value in **3-twist** relative to **3-planar** [$\Delta(\delta_{Si})$ = 5.62].

Due to the interaction between ^{6}Li and SiH, the ^{6}Li NMR signal of **2a(THF)** was observed at δ = 0.53 as a quintet with the coupling constant 0.4 Hz (Fig. 3). The splitting of ^{6}Li resonance was caused by the coupling with four SiH protons, which suggests a flipping along the central C–C bond in solution.[13] Moreover, the ^{6}Li chemical shift of **2a(THF)** is observed at field strength higher by ca. 1 ppm than those of dilithium compounds derived from tetrakis(trialkylsilyl)-ethylene (1.42—1.72 ppm). This is also supported by GIAO calculation of **3-twist** and **3-planar**; the $\Delta(\delta_{Li})$ between **3-twist** and **3-planar** is −0.46 ppm. Similar NMR spectral features were also observed for **2a(Et$_2$O)**.

The ^{1}H NMR spectra of the other alkali metal complexes **2b—e** in THF-d_8 display resonances for the $SiMe_2$ and SiH



3-twist, D_2 **3-planar**

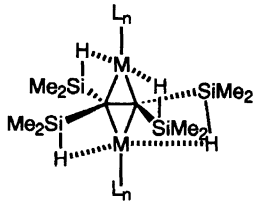
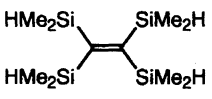
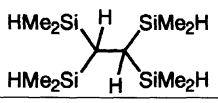
Fig. 2. HF/6-31+G* optimized geometries (Å) (Table 3) of $[(H_3Si)_2C{=}C(SiH_3)_2]^{2-}\cdot[Li^+(H_2O)]_2$ (**3-twist**, D_2; **3-planar**, D_{2h}) as viewed along the C–C bond.

protons in the normal regions of the spectrum, and the chemical shifts of SiH are almost unchanged by the different alkali metals (see Table 4).

The most striking feature of the ^{29}Si NMR spectra of **2** is the magnitude of the ^{29}Si–^{1}H coupling constants. Although the coupling between Si and methyl protons is normal for two-bond couplings ($^2J_{Si-H}\approx$6.0 Hz), the one-bond coupling is unusually small ($^1J_{Si-H}\approx$140—149 Hz; see Table 4). Hydrosilanes generally display a value in the range of 160—200 Hz.[14] For example, the $^1J_{SiH}$ values are 181 for **1** and 183 Hz for $(HMe_2Si)_2CH$–$CH(SiMe_2H)_2$.[15] The decrease of the one-bond coupling constant in dialkali metal complexes suggests a significant interaction of Si–H with the alkali metals. The dilithium complex **2a** displays the smallest value of $^1J_{Si-H}$ (140 Hz in THF-d_8, 141 Hz in toluene-d_8) for a series of dialkali metal derivatives, and the value of $^1J_{Si-H}$ increases with the change to heavier alkali metal derivatives. This suggests that the magnitude of interaction between SiH and an alkali metal in $[(HMe_2Si)_2C{=}C(SiMe_2H)_2]^{2-}[M^+(ligand)_n]_2$ decreases in the order of M = Li > Na ≈ K ≈ Rb ≈ Cs.

Similarly, evidence for SiH–alkali metal interaction in **2** is found in the infrared spectra. For example, the infrared spectra of **2a(THF)** in hexane exhibit a weak and broad band at 1938 cm^{-1} assignable to the Si–H stretching mode (ν_{Si-H}). Normally, ν_{Si-H} for hydrosilanes is observed at ca. 2100 cm^{-1} (for example, ν_{Si-H} = 2145, 2103 cm^{-1} for **1** and 2108, 2123 cm^{-1} for $(HMe_2Si)_2CH$–$CH(SiMe_2H)_2$, respectively). The frequencies of **2a(THF)** and **2a(Et$_2$O)** (1937 cm^{-1}) are significantly lower and indicate a distinct weakening of the Si–H bond. The lower energy Si–H stretching frequencies of

Table 4. Spectroscopic Data for a Series of Tetrakis(dimethylsilyl)ethylene Dialkali Metal Complexes and Related Compounds

Compound		^{1}H NMR	^{29}Si NMR		IR
		$\delta_{H(Si)}$/ppm	δ_{Si}/ppm	$^1J_{Si-H}$/Hz	ν_{Si-H}/cm^{-1}
	**2a(Et$_2$O)** (M = Li)	4.50[a]	−19.7[a]	141[a]	1937[b]
	2a(THF) (M = Li)	4.65[a]	−12.9[a]	141[a]	1938[b]
	2b (M = Na)	4.47[c]	−29.0[c]	146[c]	
	2c (M = K)	4.48[c]	−30.3[c]	149[c]	
	2d (M = Rb)	4.58[c]	−30.3[c]	147[c]	
	2e (M = Cs)	4.56[c]	−28.9[c]	149[c]	
	**1**	4.34[d]	181[d]	181[d]	2145[b] 2103
		4.05[d]	183[d]	183[d]	2123[b] 2108

a) NMR spectra recorded in toluene-d_8. b) IR spectra recorded in hexane solution. c) NMR spectra recorded in THF-d_8. d) NMR spectra recorded in $CDCl_3$.

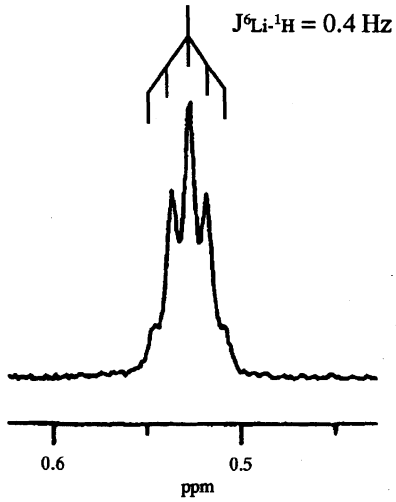


Fig. 3. ^{6}Li NMR spectrum (C_6D_8, 298 K) of **2a(THF)**.

2 relative to that of **1** suggest the presence of an interaction between SiH and alkali metals (Table 4).

The SiH–alkali metal agostic interaction is based on electrostatic interaction ($Si^{\delta+}$–$H^{\delta-}\cdots M^{+}$).[3,7] Therefore, the degree of interaction between SiH and alkali metals in $[(HMe_2Si)_2C{=}C(SiMe_2H)_2]^{2-}[M^{+}(ligand)_n]_2$ is dependent on the surface charge density of the alkali metal cation. The dilithium complex **2a** displays the strongest SiH–M interaction among a series of dialkali metal derivatives.

Conclusion. The spectroscopic and structural features for the series of dialkali metal complexes **2a—e** clearly demonstrate the presence of SiH–alkali metal agostic interaction. Diminished values of $^{1}J_{SiH}$ in **2a—e**, compared to those observed for normal hydrosilanes, suggest that the order of the strength of the agostic interaction between SiH and alkali metal in $[(HMe_2Si)_2C{=}C(SiMe_2H)_2]^{2-}[M^{+}(ligand)_n]_2$ is as follows: M = Li > Na ≈ K ≈ Rb ≈ Cs. This interaction is dominated by electrostatic interaction between the negatively charged hydrogen atom on the silicon atom and the alkali metal cation, since the Si–H bond is polarized as $Si^{\delta+}$–$H^{\delta-}$.[3,7] Thus, the degree of the SiH–alkali metal interaction is dependent on the size of the alkali metal cation. The smallest cation, Li^{+}, can interact with SiH most strongly. The hydrogen atom on the silicon atom is coordinated to the lithium cation in the dilithium complex **2a(Et$_2$O)** to make the twisted structure the more stable one.

Experimental

General Procedure. All manipulations were carried out under an inert atmosphere in a Giken Engineering Service GBX-1200 gas-replacement type glove box or by standard Schlenk and high-vacuum line techniques. ^{1}H NMR spectra were recorded at 300.1 MHz on a Bruker AC-300 FT NMR spectrometer. ^{13}C, ^{29}Si, ^{6}Li, ^{23}Na, and ^{133}Cs NMR spectra were collected on a Bruker AC-300 at 75.5, 59.6, 44.2, 79.4, 39.4 MHz, respectively. ^{6}Li, ^{23}Na, and ^{133}Cs NMR spectra are referenced to external 1 M LiCl (1 M = 1 mol dm^{-3}) in methanol/toluene-d_8 or 1 M LiCl in THF-d_8, saturated NaCl in THF-d_8, and saturated $CsNO_3$ in water/THF-d_8, respectively. Infrared spectra were recorded on a JEOL JIR-3510 FT IR spectrometer. All solvents were dried and degassed over potassium mirror in vacuo prior to use for the preparation of dialkali metal complexes. Lithium-6 (95 atom%) metal was commercially available (Aldrich Chemical Company). Tetrakis(dimethylsilyl)-ethylene was prepared according to the literature procedure.[10]

1,1,2,2-Tetrakis(dimethylsilyl)ethane-1,2-diyldilithium (2a). The colorless crystals of **1** (200 mg, 0.767 mmol) and some pieces of excess lithium metal (30 mg, 4.3 mmol) were placed in a Schlenk tube with a magnetic stirrer. After degassing, dry-oxygen free THF or Et_2O (3 ml) was introduced by vacuum transfer. The solution was stirred at room temperature to give a red solution of the dilithium complex within 20 min. The solvent was removed in vacuo, and then degassed pentane was introduced by vacuum transfer. The resulting yellow pentane solution was transferred to another Schlenk tube to remove the remaining lithium metal. Concentration and cooling of the pentane solution afforded yellow crystals of **2a(THF)** or **2a(Et$_2$O)**.

2a(THF): Yellow crystals; ^{1}H NMR (C_7D_8, 298 K) δ = 0.54 (d, J = 3.1 Hz, 24 H, $SiMe_2$), 1.34—1.42 (m, 8 H, THF), 3.53—3.61 (m, 8 H, THF), 4.65 (br s, 4 H, SiH); ^{13}C NMR (C_7D_8, 298 K) δ = 6.5 ($SiMe_2$), 15.1 (quintet, $J_{^{13}C-^{6}Li}$ = 2.5 Hz, CLi), 25.6 (THF), 68.8 (THF); ^{29}Si NMR (C_7D_8, 298 K) δ = −12.9 (d of septet, $^{1}J_{Si-H}$ = 141 Hz, $^{2}J_{Si-H}$ = 6.3 Hz); ^{6}Li NMR (C_7D_8, 298 K) δ = 0.53 (quint, $J_{^{6}Li-^{1}H}$ = 0.40 Hz); IR (hexane) 1938 cm^{-1} (ν_{Si-H}).

2a(Et$_2$O): Yellow crystals; ^{1}H NMR (C_7D_8, 298 K) δ = 0.45 (d, J = 4.0 Hz, 24 H, $SiMe_2$), 1.12 (t, J = 7.0 Hz, 12 H, CH_3CH_2O), 3.30 (q, J = 7.0 Hz, 8 H, CH_3CH_2O), 4.50 (br s, 4 H, SiH); ^{13}C NMR (C_7D_8, 298 K) δ = 6.3 ($SiMe_2$), 14.6 (quint, $J_{^{13}C-^{6}Li}$ = 2.3 Hz, CLi), 15.7 (CH_3CH_2O), 66.0 (CH_3CH_2O); ^{29}Si NMR (C_7D_8, 298 K) δ = −19.7 (d of septet, $^{1}J_{Si-H}$ = 141 Hz, $^{2}J_{Si-H}$ = 6.3 Hz); ^{6}Li NMR (C_7D_8, 298 K) δ = 0.10 (quintet, $J_{^{6}Li-^{1}H}$ = 0.49 Hz); IR (hexane) 1937 cm^{-1} (ν_{Si-H}).

Preparation of THF-d_8 Solution of 1,1,2,2-Tetrakis(dimethylsilyl)ethane-1,2-diyldialkali Metal (2b—e). The colorless crystals of tetrakis(dimethylsilyl)ethylene **1** (ca. 30 mg) and excess alkali metal were put into the reaction glass vessel which had been previously dried, degassed, and filled with argon. Then dry degassed THF-d_8 (0.6 ml) was introduced by vacuum transfer. The upper part of the reaction glass vessel was sealed. The mixture was stirred for several hours at room temperature to give a dark red solution of the corresponding dialkali metal complexes **2**. The resulting dark red THF-d_8 solution was sealed in an NMR tube for the NMR measurement.

1,1,2,2-Tetrakis(dimethylsilyl)ethane-1,2-diyldisodium (2b): ^{1}H NMR (THF-d_8, 298 K) δ = 0.05 (d, 24 H, J = 3.1 Hz, $SiMe_2$), 4.47 (septet, 4 H, J = 3.1 Hz, SiH); ^{13}C NMR (THF-d_8, 298 K) δ = 6.4 ($SiMe_2$), 17.1 (CNa); ^{29}Si NMR (THF-d_8, 298 K) δ = −29.0 (d of septet, $^{1}J_{Si-H}$ = 146 Hz, $^{2}J_{Si-H}$ = 6.3 Hz); ^{23}Na NMR (THF-d_8, 298 K) δ = −11 ($\nu_{1/2}$ = 1200 Hz).

1, 1, 2, 2- Tetrakis(dimethylsilyl)ethane- 1, 2- diyldipotassium (2c): ^{1}H NMR (THF-d_8, 240 K) δ = 0.02 (d, J = 3.0 Hz, 24 H, $SiMe_2$), 4.57 (septet, J = 3.0 Hz, 4 H, SiH); ^{13}C NMR (THF-d_8, 240 K) δ = 6.9 ($SiMe_2$), 22.9 (CK); ^{29}Si NMR (THF-d_8, 240 K) δ = −30.3 ($^{1}J_{Si-H}$ = 149 Hz, $^{2}J_{Si-H}$ = 6.3 Hz).

1, 1, 2, 2- Tetrakis(dimethylsilyl)ethane- 1, 2- diyldirubidium (2d): ^{1}H NMR (THF-d_8, 220 K) δ = 0.00 (d, 24 H, J = 3.0 Hz, $SiMe_2$), 4.57 (septet, 4 H, J = 3.0 Hz, SiH); ^{13}C NMR (THF-d_8, 240 K) δ = 6.9 ($SiMe_2$), 22.9 (CRb); ^{29}Si NMR (THF-d_8, 240 K) δ = −30.3 ($^{1}J_{Si-H}$ = 147 Hz, $^{2}J_{Si-H}$ = 5.4 Hz).

1,1,2,2-Tetrakis(dimethylsilyl)ethane-1,2-diyldicesium (2e): ^{1}H NMR (THF-d_8, 220 K) δ = 0.01 (d, J = 2.8 Hz, 24 H, $SiMe_2$), 4.42 (br s, 4 H, SiH); ^{13}C NMR (THF-d_8, 220 K) δ = 6.1 ($SiMe_2$),

27.6 (CCs); ^{29}Si NMR (THF-d_8, 220 K) δ = −28.9 (d of septet, $^1J_{Si-H}$ = 149 Hz, $^2J_{Si-H}$ = 5.9 Hz); ^{133}Cs NMR (THF-d_8, 298 K) δ = 17.8 ($\nu_{1/2}$ = 17 Hz).

X-Ray Crystallography of 1,1,2,2-Tetrakis(dimethylsilyl)ethane-1,2-diyldilithium-bis(diethyl ether) (2a(Et$_2$O)). A single crystal (0.25×0.30×0.40 mm) of **2a(Et$_2$O)** was sealed in a capillary glass tube, and diffraction data collected at 150 K on a Rigaku Denki AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) employing graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71069 Å). A total of 3247 reflections with $3 < 2\theta < 55°$ were collected. Crystal data: MF = $C_{18}H_{48}Li_2O_2Si_4$, MW = 422.80, monoclinic, a = 18.551(7), b = 9.890(8), c = 17.183(6) Å, β = 113.61(2)°, V = 2889(2) Å^3, space group $C2/c$, Z = 4, D_c = 0.972 g cm^{-3}. The positions of hydrogen atoms connected to silicon atoms were revealed by a difference Fourier calculation, and those of other hydrogen atoms were calculated. When the hydrogen atoms were included in the refinement, the final R factor was 0.0698 (R_w = 0.0717) for 2114 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. 72027 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 124998.

Computational Methods. Calculations at Hatree–Fock (HF) level were performed by using the Gaussian 94 computer programs.[16] 6-31+G* basis sets were used for all geometry optimization. The structures of 1,1,2,2-tetrakis(dimethylsilyl)ethane-1,2-diyldilithium-bis(water) were completely optimized within each assumed symmetry. Absolute chemical shieldings were computed with the 6-31+G*-GIAO method.[17]

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