

## Synthesis and Structure of Ethynylsilyllithiums

Mitsuo Kira,\* Tomoyuki Kadowaki, Dongzhu Yin, and Kenkichi Sakamoto

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku,  
Sendai 980-8578, Japan

Takeaki Iwamoto and Chizuko Kabuto

Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University,  
Aoba-ku, Sendai, 980-8578, Japan

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Ethynylsilyllithiums [ $R^1R^2(R^3CC)SiLi$ :  $R^1 = R^2 = t\text{-BuMe}_2Si$ ,  $R^3 = Me_3Si$  (**5a**);  $R^1 = R^2 = t\text{-BuMe}_2Si$ ,  $R^3 = Ph$  (**5b**);  $R^1 = R^2 = R^3 = Me_3Si$  (**5c**);  $R^1 = t\text{-BuMe}_2Si$ ,  $R^2 = Ph$ ,  $R^3 = Me_3Si$  (**5d**);  $R^1 = t\text{-BuMe}_2Si$ ,  $R^2 = Me_3SiCC$ ,  $R^3 = Me_3Si$  (**5e**)] were prepared by the sila-metalation reactions of the corresponding hydrosilanes using *tert*-butyllithium in THF and trapped by MeI,  $Me_3SiCl$ , and *i*- $Pr_3SiCl$  in high yields. X-ray structural analysis of a single crystal of **5a** has revealed that **5a** adopts a dimer form (**7a**) containing one THF molecule per dimer. Dimer **7a** is a syn dimer with a planar four-membered ring made by two lithium atoms and two anionic silicon atoms; one lithium atom is coordinated by two ethynyl  $\pi$  groups and the other by a THF molecule, indicative of the importance of the coordination of ethynyl  $\pi$  groups for the stabilization of the silyllithium.  $^7Li$  NMR analysis indicates that the dimeric structure of **5a** (**7a**) is maintained in toluene, but **5a** is monomeric in THF. Rates and activation parameters of facile intramolecular exchange of the two lithium atoms in **7a** observed in toluene- $d_8$  were determined by the dynamic  $^7Li$  NMR. The DFT calculations of a model ethynylsilyllithium [ $(H_3Si)_2(H_3SiCC)SiLi$ , **12**] have shown that dimer **13**, with a similar geometry to **7a**, is more stable than the monomeric form. The optimized monomeric form of **12** (**12'**) has an ethynylsilyllithium-type structure with a largely bent Si–CC skeleton, suggesting significant intramolecular  $\pi^+$  coordination to  $Li^+$ .

### Introduction

Much attention has been focused on the structure and reactions of allenyl-propargyllithium (A/P-Li).<sup>1</sup> Theoretical calculations predict that parent monomeric A/P-Li adopts a nonclassically 1,3-bridged allenyl-like arrangement **1** with a bent CCC angle and different C–C bond lengths. Two anti dimers with two equivalent lithium atoms, A-Li dimer **2** and P-Li **3**, are located as energy minima; **2** is 1.33 kcal mol<sup>-1</sup> more stable than **3** (Chart 1).<sup>2</sup> Experimentally, both types of A/P-Li dimers have been known to date.<sup>3</sup> However, structural characteristics of A/P-Li are strongly dependent on substituents and on the oligomerization in solution<sup>4</sup> and in the solid state.<sup>3</sup> Although similar structural diversity is expected for a silicon congener of A/P-Li, silaallenyl-ethynylsilyllithium (SA/ES-Li) derivatives (Chart 1), their preparation, and characteristics have never been studied until now.<sup>5</sup> Recently, Marschner et al. have reported the unique synthesis and application of ethynylsilylpotassium compounds.<sup>6</sup> We wish herein to report the synthesis of various ethynylsilyllithiums via the sila-metalation<sup>7</sup> of the corresponding

hydrosilanes with *tert*-butyllithium and the first structural study of an SA/ES-Li that is dimeric with significant 1,3-bridged ethynylsilyllithium character both in the solid state and in a toluene solution.

### Results and Discussion

#### Preparation of Ethynylsilyllithiums via Sila-Metalation.

Typically, treatment of ethynylhydrosilane **4a** in THF with 1.2 equiv of *tert*-butyllithium in pentane at  $-40$  °C afforded immediately a yellow solution. Stirring for 1 h at  $-40$  °C and then addition of excess methyl iodide gave the corresponding methylated silane **6a** in 89% yield. The formation of ethynylsilyllithiums **5b–5e** in good yields from the corresponding hydrosilanes **4b–4e** was also confirmed by trapping using methyl iodide and trimethylchlorosilane as an electrophile (eq

\* Corresponding author. E-mail: mkira@mail.tains.tohoku.ac.jp.

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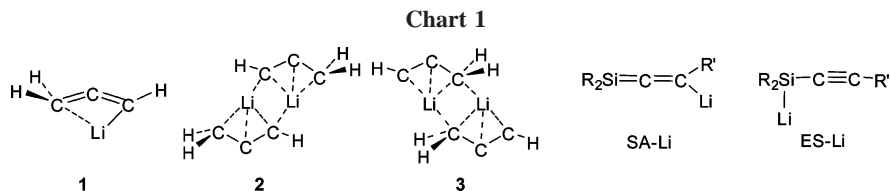
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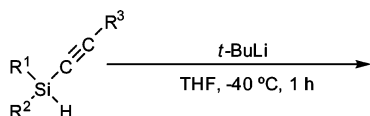


**Table 1. Preparation and Trapping of Various Silylethynyllithiums**

starting hydrosilane	electrophile (EI-X)	product ( <b>6</b> )	yield (%) <sup>a</sup>
<b>4a</b>	MeI	<b>6a</b>	89
<b>4a</b>	<i>i</i> -Pr <sub>3</sub> SiCl	<b>6a'</b>	70
<b>4b</b>	MeI	<b>6b</b>	70
<b>4c</b>	Me <sub>3</sub> SiCl	<b>6c</b>	93
<b>4d</b>	MeI	<b>6d</b>	91
<b>4e</b>	MeI	<b>6e</b>	74

<sup>a</sup> Isolated yield.

1). Success in the metalation of **4a–4e** is attributed in part to high acidity of ethynyl-substituted hydrosilanes.<sup>8</sup>



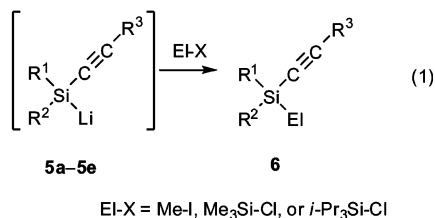
**4a**; R<sup>1</sup> = R<sup>2</sup> = SiMe<sub>2</sub>Bu-*t*, R<sup>3</sup> = SiMe<sub>3</sub>

**4b**; R<sup>1</sup> = R<sup>2</sup> = SiMe<sub>2</sub>Bu-*t*, R<sup>3</sup> = Ph

**4c**; R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = SiMe<sub>3</sub>

**4d**; R<sup>1</sup> = SiMe<sub>2</sub>Bu-*t*, R<sup>2</sup> = Ph, R<sup>3</sup> = SiMe<sub>3</sub>

**4e**; R<sup>1</sup> = SiMe<sub>2</sub>Bu-*t*, R<sup>2</sup> = C≡CSiMe<sub>3</sub>, R<sup>3</sup> = SiMe<sub>3</sub>



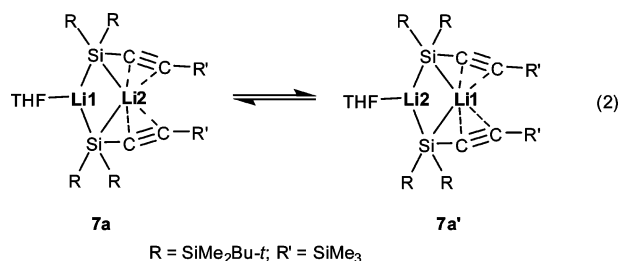
Even when a bulky chlorosilane such as triisopropylchlorosilane is used as an electrophile, **5a** reacts at the silyl anionic center to give the corresponding ethynyl(triisopropylsilyl)silane **6a'** in high yield (Table 1). Similarly to the behavior of ethynylsilylpotassiums reported by Marschner et al.,<sup>6</sup> SA/ES-Li **5a–5e** serve as ES-Li reagents rather than SA-Li reagents. The high regioselectivity of the SA/ES-Li reagents may not be a reflection of the structural characteristics of the lithium reagents but would be ascribed to the thermodynamically more favorable formation of ethynylsilane-type products rather than silylacetylene-type product.

**X-ray Structure of a Dimeric Form of Ethynylsilyllithium 5a (7a).** Warming a solution of **5a** prepared by the reaction of **4a** with *tert*-butyllithium at  $-40\text{ }^{\circ}\text{C}$  to room temperature and then evaporation of solvents in vacuo gave white solids. Recrystallization from hexane gave ethynylsilyllithium **5a** in 54% yield. Rather unexpected structural characteristics were observed for **5a** in the solid state. X-ray structural analysis of a single crystal of **5a** indicates that **5a** adopts a dimer form (**7a**) containing one THF molecule per dimer (Figure 1). Dimer **7a** is a syn dimer, in which two lithium cations are coordinated differently: one coordinated by two ethynyl  $\pi$  groups and the

other coordinated by a THF molecule. The Si1–Li1–Si3–Li2 four-membered ring is nearly planar, with an angle between Si1–Li2–Li1 and Si3–Li2–Li1 of  $0.6^{\circ}$ . The Si(anion)–C(sp) bond length (1.881 Å) is slightly longer than normal Si–C bond lengths (1.84 Å).<sup>9</sup> The average acetylenic C–C bond length is 1.218(12) Å, which is similar to the corresponding length of bisilylacetylenes [1.199(9)–1.217(6) Å].<sup>10</sup> Si1–Li2 and Si3–Li2 distances (av 2.85(4) Å) are longer than Si1–Li1 and Si3–Li1 distances (av 2.65(3) Å). C1(C3)–Li2 (av 2.16(3) Å) and C2(C4)–Li2 distances (av 2.38(6) Å) are similar to the corresponding distances for monomeric triphenylpropargyllithium with two coordinated THF molecules and dimeric [bis(*tert*-butylethynyl)](trimethylsilyl)methylolithium.<sup>3</sup> Geometry around the C≡C bond is not linear but slightly trans bent with a Si(anion)–C–C angle of  $172.2(12)^{\circ}$  (av) and C–C–Si(silyl) angle of  $165.0(8)^{\circ}$ . In the solid state, dimer **7a** is regarded to be an ES-Li dimer with significant interaction of the lithium cation with two ethynyl  $\pi$  systems.

#### NMR Study of Dimeric Ethynylsilyllithium **7a** in Solution.

The <sup>7</sup>Li NMR spectrum of dimer **7a** in toluene-*d*<sub>8</sub> is remarkably temperature dependent, as shown in Figure 2. A sharp singlet observed at 2.15 ppm at 273 K splits into two sharp singlets with resonances of 1.77 and 2.93 ppm at 223 K, suggesting that the structure of dimer **7a** is maintained at low temperatures in a nonpolar solvent, while a facile exchange between Li1 and Li2 occurs at higher temperatures, as shown in eq 2. The exchange rate constant (*k*) and its temperature dependence were determined by a line-shape analysis using the two-site model (eq 2). The Eyring parameters for the exchange are  $\Delta H^{\ddagger} = 22.5\text{ kcal mol}^{-1}$  and  $\Delta S^{\ddagger} = 43.0\text{ cal K}^{-1}\text{ mol}^{-1}$ . The large positive  $\Delta S^{\ddagger}$  for the exchange suggests that the rate-determining step is the dissociation of a THF molecule from **7a**. The  $\Delta H^{\ddagger}$  of 22.5 kcal mol<sup>-1</sup> is in accord with this mechanism because the theoretical stabilization energy for coordination of a THF molecule to a model ethynylsilyllithium is 18.6 kcal mol<sup>-1</sup> (vide infra). In THF-*d*<sub>8</sub>, the <sup>7</sup>Li NMR resonance appears at 0.25 ppm as a singlet, suggesting that **5a** is monomeric in THF.<sup>11</sup>

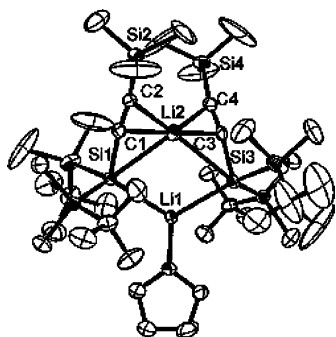


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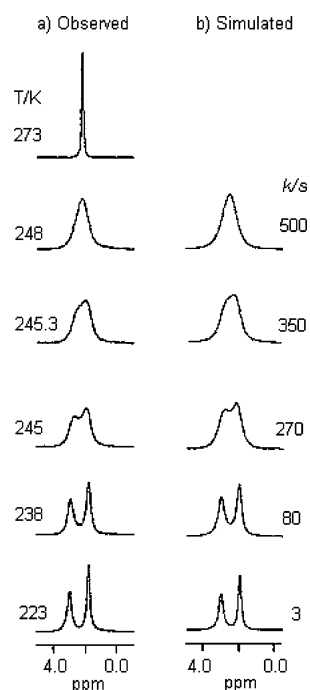
(10) The C≡C bond length in (Me<sub>3</sub>Si)<sub>3</sub>SiC≡CSi(SiMe<sub>3</sub>)<sub>3</sub> was reported to be 1.217(6) Å.<sup>6c</sup> The average C≡C bond length of 1,1,10,10-tetraphenyl-1,4,7,10,13,16-hexasilylacetylenecyclooctadeca-2,5,8,11,14,17-hexayne is 1.199(9) Å: Kwon, E.; Sakamoto, K.; Kabuto, C.; Kira, M. *Silicon Chem.* **2002**, *1*, 391.

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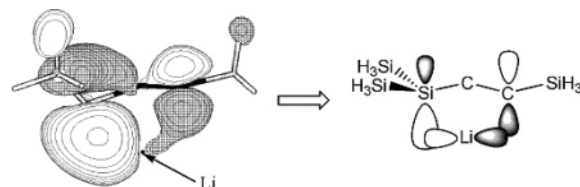
**Figure 1.** ORTEP drawing of ES-Li dimer **7a**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Si1–C1 1.877(6), C1–C2 1.220(9), Si3–C3 1.885(7), C3–C4 1.215(10), Si1–Li1 2.63(1), Si1–Li2 2.82(1), Si3–Li1 2.66(1), Si3–Li2 2.88(1), C3–Li2 2.15(2), C4–Li2 2.33(1), Si1–C1–C2 171.6(7), C1–C2–Si2 164.8(6), Si3–C3–C4 172.7(6), C3–C4–Si4 165.1(6), Li1–Si1–Li2 68.0, Li1–Si3–Li2 67.3, Si1–Li1–Si3 118.7, Si1–Li2–Si3 106.0.



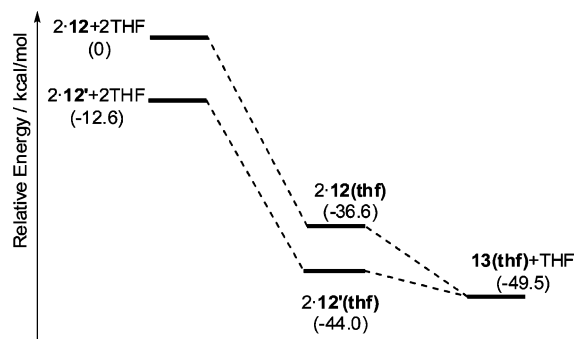
**Figure 2.** Temperature-dependent  $^7\text{Li}$  NMR spectra of **7a** in toluene- $d_8$ : (a) observed; (b) simulated. Intrinsic half line-widths for signals at 1.770 and 29.27 ppm were taken to be 32.84 and 51.10 Hz, respectively.

The  $^{29}\text{Si}$  NMR resonance of the anionic silicon nucleus of **5a** appears at  $-158.2$  and  $-160.1$  ppm in toluene- $d_8$  and THF- $d_8$ , which are about 60 ppm higher than that of **4a**, being in accord with large ES-Li character of **5a**. The  $^{13}\text{C}$  NMR resonance of central carbon nuclei of **5a** (C1 and C3 in **7a**) appears at around 136 ppm in both toluene- $d_8$  and THF- $d_8$ . The  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR data for **5a** are similar to those for ethynylsilylpotassium compounds investigated by Marscher et al.<sup>6c</sup> Obviously, less effective Si–C  $\pi$  bonding is responsible in part for a larger contribution of ES-Li character to monomeric and dimeric SA/ES-Li compounds than that of SA-Li character.

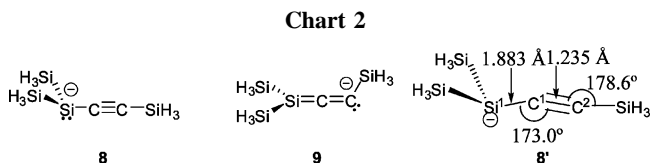
**Theoretical Study of Ethynylsilyllithiums.** First, we would like to discuss the structure of a free AS/ES anion. Geometry optimization at the B3LYP/6-31(d) level<sup>12</sup> of free ethynylsilyl anion **8** and silyallenyl anion **9** afforded the same structure **8'** (Chart 2), whose structural parameters are shown in the chart.



**Figure 3.** HOMO of **12'** showing significant contribution of the ethynyl  $\pi^*$  orbital in the HOMO and significant interaction between the lithium 2p orbital and the ethynyl  $\pi$  system.



**Figure 4.** Relative energies of dimeric ethynylsilyllithium **13** and related monomeric ethynylsilyllithium derivatives at the B3LYP/6-31G(d) level ( $\text{kcal mol}^{-1}$ ).



Silyl anion **8'** is slightly bent but has largely the structural characteristics of the ES anion.

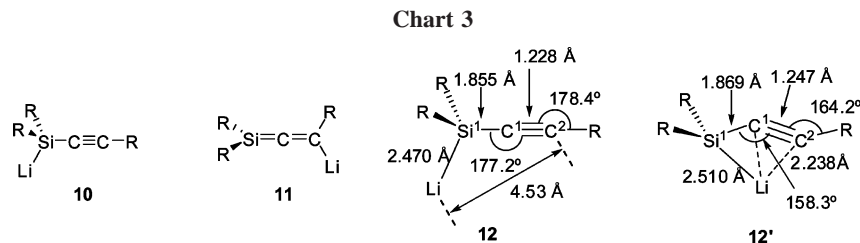
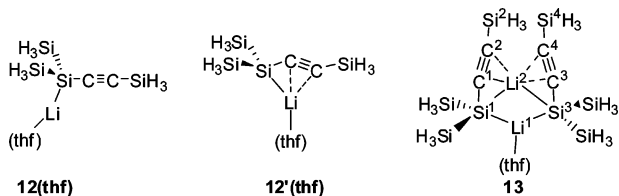
When the structural optimization was carried out starting from model ethynylsilyllithium **10** and silyallenylithium **11**, **12** having an approximately linear Si–C–C skeleton and **12'** having a bent Si–C–C skeleton were located as the local minima, respectively, where **12'** is 6.3  $\text{kcal mol}^{-1}$  more stable than **12** (Chart 3). Although the bent skeletal structure of **12'** is similar to that of A/P-Li **1** optimized at the MP2(FU)/6-31G(d) level,<sup>13</sup> the Si1–C1 length (1.869 Å) is even longer than the normal Si–C single bond lengths.<sup>9</sup> Both **12** and **12'** should be assigned as ES-Li, although **12'** is significantly stabilized by the interaction between a vacant 2p orbital of lithium and the ethynyl  $\pi$  system, as representatively shown in the shape of the HOMO of **12'** (Figure 3). Monomer **12'** is regarded as an ES-Li with a significant intramolecular coordination of an ethynyl  $\pi$  group.

Structural characteristics of dimeric ethynylsilyllithium **7a** are well reproduced by the calculations for model dimer **13**; selected

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(13) Selected structural parameters reported for allenylithium  $[\text{H}(\text{Li})\text{C}^1=\text{C}^2=\text{C}^3\text{H}_2]^-$ :  $\text{C}^1-\text{C}^2 = 1.373 \text{ \AA}$ ,  $\text{C}^2-\text{C}^3 = 1.276 \text{ \AA}$ ,  $\angle\text{C}^1-\text{C}^2-\text{C}^3 = 156.5^\circ$ ,  $\angle\text{H}-\text{C}^1-\text{C}^2 = 135.7^\circ$ .



**Chart 4**

bond lengths (Å) and bond and dihedral angles (deg): Si<sup>1</sup>–C<sup>1</sup> 1.871, C<sup>1</sup>–C<sup>2</sup> 1.238, Si<sup>1</sup>–Li<sup>2</sup> 2.872, Si<sup>1</sup>–Li<sup>1</sup> 2.656, C<sup>1</sup>–Li<sup>2</sup> 2.183, C<sup>2</sup>–Li<sup>2</sup> 2.317, Si<sup>1</sup>–C<sup>1</sup>–C<sup>2</sup> 169.7, C<sup>1</sup>–C<sup>2</sup>–Si<sup>2</sup> 170.6, C<sup>2</sup>–C<sup>1</sup>–C<sup>3</sup>–C<sup>4</sup> 43.46.

In Figure 4, relative energies are compared among pertinent monomeric and dimeric ethynylsilyllithiums. Coordination of a THF molecule to **12** and **12'** causes 18.3 and 18.9 kcal mol<sup>−1</sup> (av 18.6 kcal mol<sup>−1</sup>) of stabilization of the systems to form **12**(thf) and **12'**(thf), respectively.<sup>14</sup> The stabilization energy by the bent-ethynyl coordination is reduced from 6.3 to 3.7 kcal mol<sup>−1</sup>, when **12** is coordinated by THF, as estimated by the energy difference between **12**(thf) and **12'**(thf). The energy of dimeric ES-Li **13** + a free THF is 5.5 kcal mol<sup>−1</sup> lower than twice the energy of **12'**(thf), although a Li<sup>+</sup>–THF interaction is missing in the former.

## Conclusion

Various SA/ES-Li reagents are able to be prepared by the sila-metalation of the corresponding hydrosilanes. Electrophiles such as methyl iodide and chlorosilanes react with the SA/ES-Li reagents at the anionic silicon center to give the corresponding methylated and silylated silanes in a highly regioselective manner. Both in the solid state and in a nonpolar solvent, SA/ES-Li **5a** exists as a syn dimer incorporating one THF molecule (**7a**). Dimer **7a** has a planar four-membered ring made by two lithium atoms and two anionic silicon atoms; the environments of the two lithiums are remarkably different from each other, where one lithium atom is coordinated by two ethynyl  $\pi$  groups and the other is coordinated by a THF molecule. Deformation from linear arrangement of the Si(anion)–C≡C–Si skeleton in **7a** is small, and hence, **7a** is regarded as an ES-Li dimer with significant intramolecular ethynyl  $\pi$ –Li<sup>+</sup> interaction. Dynamic <sup>7</sup>Li NMR analysis indicates that two lithium ions exchange with each other in the dimeric structure of **7a** in a nonpolar solvent. The DFT calculations of model SA/ES-Li **12** have revealed that in a dimer of **12** (**13**) as a model of **7a**, the coordination of two ethynyl  $\pi$  systems to a Li<sup>+</sup> more than offsets the loss of a Li<sup>+</sup>–THF interaction. Although the Si–C(sp)–C(sp) bent angle of the optimized monomeric structure of **12** (**12'**, 158.3°) is similar to that for theoretical allenyl/propargyl-lithium (156.5°),<sup>3,13</sup> the shortening of the Si–C(sp) bond and elongation of the C(sp)–C(sp) bond are not observed in **12'**,

indicating that **12'** is regarded as ES-Li having remarkable intramolecular coordination of the bent-ethynyl  $\pi$  group to the Li<sup>+</sup> ion.

## Experimental Section

All operations were performed in flame-dried glassware under an atmosphere of dry argon. All solvents were distilled from appropriate drying agents before use. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz), <sup>29</sup>Si (79 MHz), and <sup>7</sup>Li (155 MHz) NMR were recorded on a Bruker Avance 400 NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to residual <sup>1</sup>H and <sup>13</sup>C of the solvents; benzene-*d*<sub>6</sub> (<sup>1</sup>H  $\delta$  7.15 and <sup>13</sup>C  $\delta$  128.0). <sup>29</sup>Si NMR chemical shifts were given in ppm relative to externally referenced tetramethylsilane ( $\delta_{\text{Si}}$  0). Mass spectra were obtained on a JEOL JMS MS-600W mass spectrometer.

A gNMR (ver. 4.1) program supplied by Cherwell Scientific, Co. Ltd. was used for simulation of temperature-dependent <sup>7</sup>Li NMR spectra of **7a** in toluene-*d*<sub>8</sub>. The activation enthalpy ( $\Delta H^\ddagger$ ) and activation entropy ( $\Delta S^\ddagger$ ) of the exchange (eq 2) were determined as the slope and intercept of the linear relationship obtained by an Eyring plot of the exchange rate constants determined by the <sup>7</sup>Li NMR line shape analysis.

All DFT calculations were performed using the Gaussian 98 program<sup>12</sup> on an HIS HPC-SCC workstation. All model compounds were optimized at the B3LYP/6-31(d) level.

**Synthesis and Reactions of Hydrosilanes 4a–4e.** Ethynylhydrosilanes **4a–4e** were synthesized by protodephenylation of the corresponding phenylsilanes using trifluoromethanesulfonic acid followed by ethynylation using the corresponding ethynyl Grignard reagents. The following are the synthesis of **4a** and the physical data of **4a–4e**.

**(*t*-BuMe<sub>2</sub>Si)<sub>2</sub>PhSiH.** To an ice-cooled mixture of 1,3-di-*tert*-butyl-1,1,3,3-tetramethyl-2,2-diphenyltrisilane<sup>15</sup> (8.00 g, 19.4 mmol) and toluene (70 mL) in a Schlenk flask (100 mL) was added dropwise trifluoromethanesulfonic acid (1.80 mL, 20.4 mmol), and then the mixture was stirred at rt for 2 h. The mixture was added dropwise to an ice-cooled mixture of LiAlH<sub>4</sub> (0.550 g, 14.5 mmol) and ether (80 mL) and then stirred at rt for 5 h. After hydrolysis of the mixture using dilute HCl, extraction with hexane, and washing the organic layer using water, aqueous NaHCO<sub>3</sub>, and then saturated NaCl solution, the mixture was dried over MgSO<sub>4</sub>. Evaporation of the solvent and then Kugelrohr distillation afforded the title compound as a colorless oil 92% yield (6.01 g, 17.9 mmol). (*t*-BuMe<sub>2</sub>Si)<sub>2</sub>PhSiH: bp 90 °C/0.15 mmHg; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 0.17 (s, 6H), 0.21 (s, 6H), 0.90 (s, 18H), 4.21 (s, 1H), 7.09–7.11 (m, 3H), 7.53–7.55 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ) −4.3, −3.8, 18.3, 27.2, 127.70, 127.72, 135.6, 136.0; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) −67.5, −2.9; MS (EI, 70 eV) *m/z* (%) 336 (25, M<sup>+</sup>), 279 (42), 223 (31), 164 (33), 135 (69), 73 (100). Anal. Calcd for C<sub>18</sub>H<sub>36</sub>Si<sub>3</sub>: C, 64.20; H, 10.78. Found: C, 64.42; H, 11.03.

**(Me<sub>3</sub>Si)<sub>2</sub>PhSiH.**<sup>16</sup> A similar protodephenylation of (Me<sub>3</sub>Si)<sub>2</sub>SiPh<sub>2</sub> (7.20 g, 21.9 mmol) in toluene (70 mL) using trifluoromethanesulfonic acid (2.13 mL, 24.1 mmol) followed by the reduction with

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$\text{LiAlH}_4$  (0.590 g, 15.5 mmol) in ether (70 mL) afforded the title compound as a colorless oil in 69% yield (3.80 g, 15.0 mmol).  $(\text{Me}_3\text{Si})_2\text{PhSiH}$ : bp 55 °C/0.2 mmHg;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.19 (s, 18H), 4.07 (s, 1H), 7.09–7.17 (m, 3H), 7.52–7.59 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –0.1, 128.3, 128.4, 134.1, 136.2;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –60.6, –14.9.

**$(t\text{-BuMe}_2\text{Si})\text{Ph}_2\text{SiH}$ .** In a three-necked flask (100 mL) equipped with a dropping funnel (50 mL) and a magnetic stirrer bar, lithium powder (477 mg, 68.7 mmol) and THF (30 mL) were placed. To the suspension was added chloro(diethylamino)diphenylsilane (9.61 g, 33.2 mmol) in THF (10 mL) within 30 min at 0 °C. After stirring overnight at 0 °C, a dark brown solution of (diethylamino)-diphenylsilyllithium<sup>17</sup> was obtained. Then, *tert*-butyldimethylchlorosilane (5.03 g, 33.4 mmol) in THF (15 mL) was added to the solution of aminosilyllithium at 0 °C. After stirring at 0 °C for 3 h, acetyl chloride (2.76 g, 35.1 mmol) was added to the mixture. After further stirring overnight at room temperature, solvent was removed in vacuo and dry hexane was added to the residue. Removal of the resulting salt with Celite, evaporation of hexane, and then Kugelrohr distillation gave the corresponding chlorosilane. The reduction of the crude chlorosilane using  $\text{LiAlH}_4$  in ether gave the title compound in 61% yield.  $(t\text{-BuMe}_2\text{Si})\text{Ph}_2\text{SiH}$ : colorless oil;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.11 (s, 6H), 0.92 (s, 9H), 4.39 (s, 1H), 7.12–7.16 (m, 6H), 7.74–7.67 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –5.1, 18.1, 27.7, 128.3, 129.3, 135.0, 136.3;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –60.6, –6.4; MS (EI, 70 eV)  $m/z$  (%) 298 (11,  $\text{M}^+$ ), 183 (17), 115 (100), 57 (65). Anal. Calcd for  $\text{C}_{18}\text{H}_{26}\text{Si}_2$ : C, 72.41; H, 8.78. Found: C, 72.37; H, 9.02.

**$(t\text{-BuMe}_2\text{Si})_2(\text{Me}_3\text{Si}-\text{C}\equiv\text{C})\text{SiH}$  (4a).** To an ice-cooled mixture of 1,3-di-*tert*-butyl-1,1,3,3-tetramethyl-2-phenyltrisilane (2.78 g, 8.26 mmol) and toluene (35 mL) in a Schlenk flask (50 mL) was added dropwise trifluoromethanesulfonic acid (0.77 mL, 8.7 mmol), and then the mixture was stirred at rt for 2 h. To the mixture was transferred trimethylsilylethynyl Grignard reagent, which was prepared by the reaction of trimethylsilylacetylene (1.01 g, 10.3 mmol) in THF (30 mL) with 0.95 M ethylmagnesium bromide in THF (10.0 mL, 9.5 mmol). The mixture was stirred overnight at room temperature. After hydrolysis of the mixture using dilute HCl, extraction with hexane, and washing the organic layer using water, aqueous  $\text{NaHCO}_3$ , and then saturated NaCl solution, the mixture was dried over  $\text{MgSO}_4$ . Evaporation of the solvent and then Kugelrohr distillation afforded the title compound as colorless solids 92% yield (2.71 g, 7.59 mmol). **4a**: colorless crystals; mp 41 °C; bp 65 °C/0.01 mmHg;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.14 (s, 9H), 0.16 (s, 6H), 0.29 (s, 6H), 1.07 (s, 18H), 3.94 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –4.2, –4.5, –0.2, 18.6, 27.4, 108.0, 120.5;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –99.1, –19.4, –1.9; MS (EI, 70 eV)  $m/z$  (%) 356 (41,  $\text{M}^+$ ), 299 (28), 225 (29), 183 (28). Anal. Calcd for  $\text{C}_{17}\text{H}_{40}\text{Si}_4$ : C, 57.22; H, 11.30. Found: C, 57.08; H, 11.27.

Hydrosilanes **4b–4e** were synthesized similarly as above and purified by silica gel column chromatography (eluent, hexane).

**$(t\text{-BuMe}_2\text{Si})_2(\text{Ph}-\text{C}\equiv\text{C})\text{SiH}$  (4b)**: yellow oil;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.21 (s, 6H), 0.32 (s, 6H), 1.10 (s, 18H), 4.11 (s, 1H), 6.91–6.93 (m, 3H), 7.39–7.42 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –4.4, –4.1, 18.5, 27.4, 88.2, 110.9, 124.4, 128.4, 128.5, 131.9;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –98.1, –1.6; MS (EI, 70 eV)  $m/z$  (%) 360 (10,  $\text{M}^+$ ), 303 (25), 247 (21), 187 (31), 173 (40), 159 (49), 115 (100). Anal. Calcd for  $\text{C}_{20}\text{H}_{36}\text{Si}_3$ : C, 66.59; H, 10.06. Found: C, 66.87; H, 9.94.

**$(\text{Me}_3\text{Si})_2(\text{Me}_3\text{Si}-\text{C}\equiv\text{C})\text{SiH}$  (4c)**: colorless oil;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.14 (s, 9H), 0.25 (s, 18H), 3.84 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –0.6, 0.0, 106.1, 119.6;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –90.5, –19.3, –14.3. Anal. Calcd for  $\text{C}_{11}\text{H}_{28}\text{Si}_4$ : C, 48.45; H, 10.35. Found: C, 48.43; H, 10.06.

**$(t\text{-BuMe}_2\text{Si})\text{Ph}(\text{Me}_3\text{Si}-\text{C}\equiv\text{C})\text{SiH}$  (4d)**: colorless oil; bp 65 °C/0.01 mmHg;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.09 (s, 3H), 0.14 (s, 9H), 0.17 (s, 3H), 0.98 (s, 9H), 4.85 (s, 1H), 7.13–7.15 (m, 3H), 7.66–7.69 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –4.0, –0.2, 18.2, 27.5, 107.5, 120.9,

128.4, 129.5, 132.1, 135.3;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –58.8, –18.5, –5.7. Anal. Calcd for  $\text{C}_{17}\text{H}_{30}\text{Si}_3$ : C, 64.07; H, 9.49. Found: C, 64.12; H, 9.61.

**$(t\text{-BuMe}_2\text{Si})(\text{Me}_3\text{Si}-\text{C}\equiv\text{C})_2\text{SiH}$  (4e)**: colorless oil; bp 80 °C/0.37 mmHg;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.04 (s, 18H), 0.22 (s, 6H), 1.02 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –6.2, –0.4, 18.3, 27.3, 104.7, 120.1;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –84.9, –18.2, –4.9. Anal. Calcd for  $\text{C}_{16}\text{H}_{34}\text{Si}_4$ : C, 56.72; H, 10.12. Found: C, 56.73; H, 9.91.

**Preparation and Trapping of Ethynylsilyllithiums 5a–5e.** Metalation of ethynylhydrosilanes **4a–4e** was applied for the preparation of the corresponding ethynylsilyllithiums **5a–5e**, which were trapped by methyl iodide, trimethylchlorosilane, and triisopropylchlorosilane to afford the corresponding methylated and silylated products **6a–6e** and **6a'**. The following are the preparation of **5a**, its trapping giving **6a** and **6a'**, and physical data of **6b–6e**.

**$(t\text{-BuMe}_2\text{Si})_2(\text{Me}_3\text{Si}-\text{C}\equiv\text{C})\text{SiLi}$  (5a)/MeI.** Addition of a 1.41 M pentane solution of *tert*-butyllithium (1.43 mL, 2.02 mmol) at –40 °C to a mixture of **4a** (0.597 g, 1.67 mmol) and THF (5 mL) afforded immediately a yellow solution. After magnetic stirring for 1 h, an excess amount of methyl iodide was added to the mixture at the same temperature. Stirring for 1 h, hydrolysis using dilute HCl solution, extraction of an organic layer with hexane, washing with aqueous  $\text{NaHCO}_3$  and aqueous NaCl, drying overnight over anhydrous  $\text{MgSO}_4$ , and then Kugelrohr distillation afforded 1,3-di-*tert*-butyl-1,1,2,3,3-pentamethyl-2-(trimethylsilylethynyl)trisilane (**6a**) in 89% yield (0.555 g, 1.50 mmol). **6a**: colorless oil; bp 80 °C/0.02 mmHg;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.15 (s, 9H), 0.16 (s, 6H), 0.25 (s, 6H), 0.42 (s, 3H), 1.08 (s, 18H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –5.0, –4.6, –4.3, –0.1, 19.3, 27.9, 113.4, 119.3;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –67.5, –19.8, –4.2; MS (EI, 70 eV)  $m/z$  (%) 370 (81,  $\text{M}^+$ ), 313 (81), 257 (31), 183 (39), 155 (53), 73 (100). Anal. Calcd for  $\text{C}_{18}\text{H}_{42}\text{Si}_4$ : C, 58.29; H, 11.41. Found: C, 57.93; H, 11.58.

**$(t\text{-BuMe}_2\text{Si})_2(\text{Me}_3\text{Si}-\text{C}\equiv\text{C})\text{SiLi}$  (5a)/*i*-Pr<sub>3</sub>SiCl.** To a yellow solution of **5a** prepared as above from **4a** (0.380 g, 1.06 mmol) in THF (5 mL) and 1.41 M *tert*-butyllithium in pentane (0.91 mL, 1.28 mmol) was added an excess amount of chlorotriisopropylsilane at rt. No color change was observed after stirring at rt for 6 h. Refluxing for 2 days and then usual workup gave a colorless oil of the corresponding triisopropylsilyl-substituted ethynylsilane **6a'** in 74% yield (0.38 g, 0.74 mmol). **6a'**: colorless oil;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.14 (s, 9H), 0.33 (s, 6H), 0.34 (s, 6H), 1.19 (s, 18H), 1.30 (d,  $J = 7.3$  Hz, 18H), 1.45 (sept,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –1.2, –1.0, –0.4, 15.9, 20.8, 21.3, 28.3, 114.3, 121.7;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –107.8, –20.7, –0.5, 9.6; MS (EI, 70 eV)  $m/z$  (%) 512 (79,  $\text{M}^+$ ), 455 (59), 340 (25), 283 (37). Anal. Calcd for  $\text{C}_{26}\text{H}_{60}\text{Si}_5$ : C, 60.85; H, 11.78. Found: C, 60.62; H, 12.02.

**$(t\text{-BuMe}_2\text{Si})_2\text{MeSi}(\text{C}\equiv\text{C}-\text{Ph})$  (6b)**: 70% yield; colorless oil;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.19 (s, 6H), 0.28 (s, 6H), 0.51 (s, 3H), 1.10 (s, 18H), 6.93–6.94 (m, 3H), 7.42–7.44 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –4.9, –4.5, –4.1, 19.2, 27.9, 93.2, 110.5, 124.5, 128.5 (overlapped), 131.8;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –66.5, –4.0; MS (EI, 70 eV)  $m/z$  (%) 374 (100,  $\text{M}^+$ ), 317 (69), 229 (33), 159 (59). Anal. Calcd for  $\text{C}_{21}\text{H}_{38}\text{Si}_3$ : C, 67.30; H, 10.22. Found: C, 67.44; H, 10.52.

**$(\text{Me}_3\text{Si})_3\text{Si}(\text{C}\equiv\text{C}-\text{SiMe}_3)$  (6c)**: 93% yield; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 0.11 (s, 9H), 0.18 (s, 27H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 0.18, 0.21, 107.8, 117.6;  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) –101.2, –20.3, –11.9; MS (EI, 70 eV)  $m/z$  (%) 344 (87,  $\text{M}^+$ ), 329 (40), 271 (31), 241 (49), 174 (91), 73 (100).  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are in accord with those reported by Ishikawa et al.<sup>18</sup>

**$(t\text{-BuMe}_2\text{Si})\text{PhMeSi}(\text{C}\equiv\text{C}-\text{SiMe}_3)$  (6d)**: 91% yield; colorless oil; bp 65 °C/0.01 mmHg;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.04 (s, 3H), 0.06 (s, 3H), 0.20 (s, 9H), 0.50 (s, 3H), 0.90 (s, 9H), 7.32–7.33 (m, 3H), 7.56–7.58 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –6.1, –3.1, –0.2, 18.2, 27.4, 111.2, 119.0, 127.8, 128.7, 134.2, 136.2;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) –39.5, –18.9, –7.6; MS (EI, 70 eV)  $m/z$  (%) 332 (49,

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M<sup>+</sup>), 275 (100). Anal. Calcd for C<sub>18</sub>H<sub>32</sub>Si<sub>3</sub>: C, 64.98; H, 9.69. Found: C, 65.23; H, 9.93.

(*t*-BuMe<sub>2</sub>Si)MeSi(C≡C–SiMe<sub>3</sub>)<sub>2</sub> (**6e**): 74% yield; colorless oil; bp 56 °C/0.01 mmHg; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.08 (s, 18H), 0.25 (s, 6H), 0.47 (s, 3H), 1.11 (s, 9H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ) –6.4, –0.4, –1.6, 18.5, 27.6, 109.5, 118.4. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, δ) –59.6, –18.5, –6.7; MS (EI, 70 eV) *m/z* (%) 352 (31, M<sup>+</sup>), 337 (8), 295 (100), 73 (59). Anal. Calcd for C<sub>17</sub>H<sub>36</sub>Si<sub>4</sub>: C, 57.87; H, 10.28. Found: C, 58.17; H, 10.38.

**Isolation of (*t*-BuMe<sub>2</sub>Si)<sub>2</sub>(Me<sub>3</sub>Si–C≡C)SiLi (**5a**).** To a mixture of **4a** (1.20 g, 3.36 mmol) and THF (10 mL) was added a 1.41 M pentane solution of *tert*-butyllithium (2.86 mL, 4.04 mmol) at –40 °C. The mixture that turned immediately yellow was stirred overnight to warm to ambient temperature. Removal of solvents from the mixture in vacuo gave a white residue. Addition and then evaporation of hexane (7 mL) resulted in a white solid. Drying the solid under vacuum and then recrystallization from hexane gave the title compound coordinated by a THF molecule in 54% yield (654 mg, 1.64 mmol). **5a**: colorless crystals; mp 195 °C. NMR data in benzene-*d*<sub>6</sub>: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.23 (s, 9H), 0.30 (brs, 6H), 0.51 (brs, 6H), 1.17 (s, 18H), 1.26–1.30 (m, 2H, 1/2 THF), 3.54–3.58 (m, 2H, 1/2 THF); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ) –1.8, 0.8, 19.5, 25.3 (THF), 28.5, 69.6 (THF), 120.1, 136.0; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, δ) –158.0 (brs), –19.9, 6.5; <sup>7</sup>Li NMR (C<sub>6</sub>D<sub>6</sub>, δ) 2.16. NMR data in toluene-*d*<sub>8</sub>: <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, δ) 0.22 (s, 9H), 0.25 (brs, 6H), 0.45 (brs, 6H), 1.13 (s, 18H), 1.36–1.39 (m, 2H, 1/2 THF), 3.59–3.62 (m, 2H, 1/2 THF); <sup>13</sup>C NMR (C<sub>7</sub>D<sub>8</sub>, δ) –1.9, 0.8, 19.5, 25.2 (THF), 28.4, 69.5 (THF), 120.0, 136.0; <sup>29</sup>Si NMR (C<sub>7</sub>D<sub>8</sub>, δ) –158.2 (brs), –20.0, 6.4; <sup>7</sup>Li NMR (C<sub>7</sub>D<sub>8</sub>, δ) 2.15. NMR data in THF-*d*<sub>8</sub>: <sup>1</sup>H NMR (C<sub>4</sub>D<sub>8</sub>O, δ) –0.04 (s, 9H), 0.03 (brs, 12H), 0.92 (s, 18H);

<sup>13</sup>C NMR (C<sub>4</sub>D<sub>8</sub>O, δ) –1.1, –0.1, 19.8, 28.9, 111.0, 135.4; <sup>29</sup>Si NMR (C<sub>4</sub>D<sub>8</sub>O, δ) –160.1, –27.2, 5.1; <sup>7</sup>Li NMR (C<sub>4</sub>D<sub>8</sub>O, δ) 0.25.

**X-ray Crystallographic Analysis.** Single crystals of **7a** suitable for X-ray diffraction study were obtained by recrystallization from hexane. X-ray data were collected on a Rigaku/MS Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ 0.71073 Å). The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares against *F*<sup>2</sup> using the SHELXL-97 program.<sup>19</sup> Crystallographic data for **7a**: C<sub>38</sub>H<sub>86</sub>Si<sub>8</sub>Li<sub>2</sub>O, *M* = 797.66, colorless, prism; monoclinic, space group, *P*2<sub>1</sub>/*n* (No. 14), *a* = 12.469(2) Å, *b* = 19.335(2) Å, *c* = 23.561(3) Å, β = 105.534(6)°, *V* = 5473(1) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 0.968 g/cm<sup>3</sup>. The final *R* value calculated for 4669 reflections (2σ < 54.97°) was 0.082, and the *wR*<sub>2</sub> for all of the reflections was 0.316. GOF = 0.71.

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**Supporting Information Available:** The X-ray crystallographic data of **7a** are supplied in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Germany, 1997.