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Lithiosilanes with Si–Si Bonds: Synthesis and ^{6}Li, ^{7}Li, and ^{29}Si NMR Studies

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Lithiopentamethyldisilane ($LiSiMe_2SiMe_3$, **1a**), two isomer of lithioheptamethyltrisilane ($LiSiMe_2SiMe_2SiMe_3$, **1b**; $LiSi(SiMe_3)_2Me$, **1c**), lithio[tris(trimethylsilyl)]silane ($LiSi(SiMe_3)_3$, **1d**), 2-lithio-1,3-diphenylpentamethyltrisilane ($LiSi(SiMe_2Ph)_2Me$, **1e**), 2-lithio-2-phenylhexamethyltrisilane ($LiSi(SiMe_3)_2Ph$, **1f**), 3-lithio-1,5-diphenylnonamethylpentasilane ($LiSi(SiMe_2SiMe_2Ph)_2Me$, **1g**), lithio[bis(dimethlphenylgermyl)]methylsilane ($LiSi(GeMe_2Ph)_2Me$, **1h**), and lithiotrimethylsilane ($LiSiMe_3$, **3**) were prepared by lithium–mercury exchange reactions. The unsolvated lithiosilanes exist as the aggregated oligomers in non-polar solvents, whereas those solvated by THF or Et_2O exist as monomers. Synthesis and detailed spectroscopic studies of the lithiosilanes with Si–Si bonds are reported.

The nature of the carbon–lithium bond has been a subject of considerable interest in recent years.[1] A very unique feature of organolithiums is their tendency to form aggregated structures $(RLi)_n$ in solution as well as in the solid state. The degree of the aggregation of organolithiums is strongly dependent on the nature of the solvents. The aggregation number (n) decreases with increasing polarity of the solvent, and NMR spectroscopy is a very powerful tool to investigate the structural feature in solution. Despite numerous reports on the synthesis of lithiosilanes, far less attention has been devoted to their spectroscopic properties.[2,3] Recently, we have reported the isolation and characterization of the first unsolvated dimeric and tetrameric lithiosilanes.[4,5] Herein, we wish to report the detailed spectroscopic properties of various lithiosilanes with Si–Si bonds, including chemical shifts of ^{6}Li, ^{7}Li, and ^{29}Si NMR spectra together with the scalar couplings of ^{29}Si–^{6}Li or ^{29}Si–^{7}Li, and ^{29}Si–^{29}Si.

Results and Discussion

Synthesis. For the preparation of lithiosilanes with Si–Si bonds, we have adopted the lithium–mercury exchange reaction.[6] Thus, hydrosilane (used for silanes containing Si–H bond) was heated with di-*t*-butylmercury in heptane at 85 °C to produce bis(oligosilanyl)mercury as a yellow oil or yellow crystals with the concomitant formation of isobutane. The bis(oligosilanyl)mercury derivatives are extremely air-, light-, and moisture-sensitive, but can be characterized satisfactorily by NMR. The ^{29}Si NMR signals of $Me_3SiSiMe_2HgSiMe_2SiMe_3$, for example, are observed at $\delta = -5.7$ and 34.9, the latter being attributed to the silicon attached to the mercury. The bis(oligosilanyl)mercury was subjected to the Li–Hg exchange reaction with excess lithium metal in toluene to give the corresponding lithiosilanes with Si–Si bonds (Scheme 1).[7]

^{29}Si NMR Spectra in Hydrocarbon Solvent. Although there are a large number of reports on lithiosilanes,[3] no NMR information on the unsolvated lithiosilanes has been reported. Figure 1 shows the ^{29}Si NMR signal of the anionic silicon of ^{6}Li*Si*Me_3 (**3**) and ^{6}Li*Si*Me_2SiMe_3 (**1a**) in toluene-d_8 at 298 K. The ^{29}Si signal of **3** ranges from $\delta = -37$ to -39 as an unresolved multiplet due to the coupling with several lithium atoms. The anionic silicon of **1a** is also observed as an unresolved multiplet, ranging from $\delta = -79.6$ to -80.4. The NMR spectra suggest that these lithiosilanes are aggregated in hydrocarbon solvent: A hexameric structure for **3**[8] and a tetrameric one for **1a**[5] may be involved. The ^{29}Si NMR spectra of ^{6}Li*Si*$Me_2SiMe_2SiMe_3$ (**1b**), ^{6}Li*Si*$(SiMe_3)_2Me$ (**1c**), ^{6}Li*Si*$(SiMe_3)_3$ (**1d**), ^{6}Li*Si*$(SiMe_2Ph)_2Me$ (**1e**), and ^{6}Li*Si*$(SiMe_3)_2Ph$ (**1f**) also exhibit unresolved multiplets due to their aggregated structures in hydrocarbon solvent.[9]

^{29}Si NMR Spectra in Polar Solvent. Subsequently, we have investigated the spectroscopic properties of the lithiosilanes in THF. In a polar solvent such as THF, the degree of the aggregation of organolithiums decreases due to the

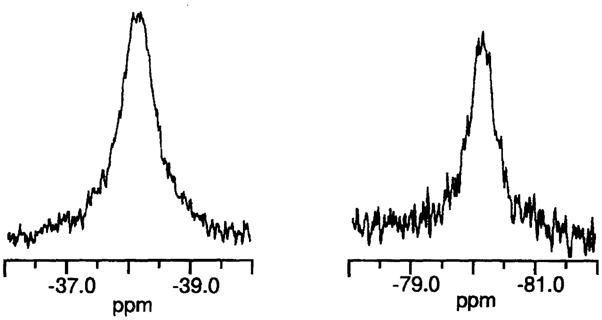
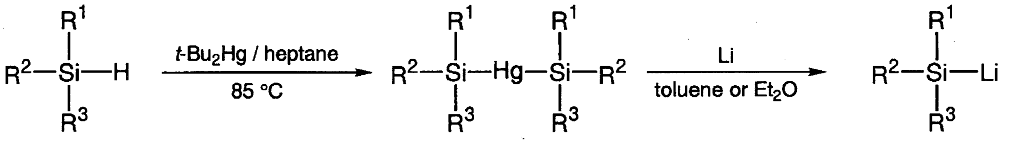


Fig. 1. Anionic silicon ^{29}Si NMR signals of lithiosilanes in toluene-d_8 at 298 K. Left: **3** (^{6}Li*Si*Me_3); right: **1a** (^{6}Li*Si*Me_2SiMe_3).



2 **1**

a: $R^1 = SiMe_3$, $R^2 = R^3 = Me$; **b**: $R^1 = SiMe_2SiMe_3$, $R^2 = R^3 = Me$; **c**: $R^1 = R^2 = SiMe_3$, $R^3 = Me$; **d**: $R^1 = R^2 = R^3 = SiMe_3$; **e**: $R^1 = R^2 = SiMe_2Ph$, $R^3 = Me$; **f**: $R^1 = R^2 = SiMe_3$, $R^3 = Ph$; **g**: $R^1 = R^2 = SiMe_2SiMe_2Ph$, $R^3 = Me$; **h**: $R^1 = R^2 = GeMe_2Ph$, $R^3 = Me$

Scheme 1.

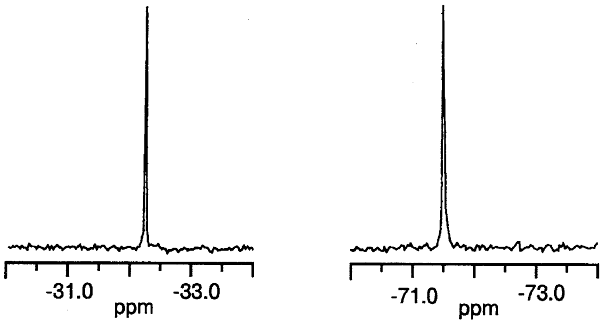


Fig. 2. Anionic silicon ^{29}Si NMR signals of lithiosilanes in THF-d_8 at 298 K. Left: **3** ($^6LiSiMe_3$); right: **1a** ($^6LiSiMe_2SiMe_3$).

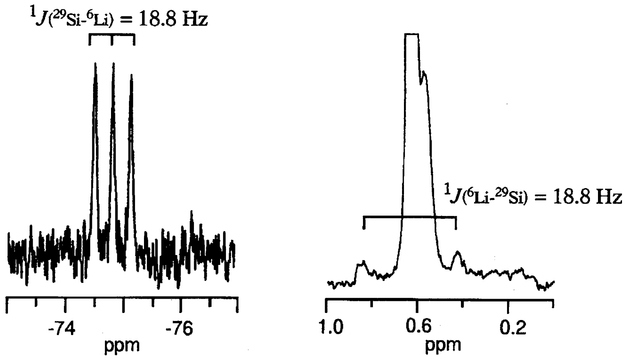


Fig. 3. Low-temperature ^{29}Si NMR (180 K, left) and ^6Li NMR (173 K, right) of anionic silicon of **1a** ($^6LiSiMe_2SiMe_3$) in THF-d_8.

solvation.[1] The solvent THF-d_8 was transferred to the unsolvated lithiosilanes through a vacuum line, and the solution was sealed in an NMR tube. For the NMR experiment, ^6Li ($I = 1$) was used to detect the scalar coupling between ^{29}Si and ^6Li nuclei. Figure 2 depicts the ^{29}Si NMR signals of the anionic silicon of **3** ($^6LiSiMe_3$) appearing at $\delta = -32.2$ and of **1a** ($^6LiSiMe_2SiMe_3$) appearing at $\delta = -71.5$ in THF-d_8 at 298 K. The anionic silicon of **1c** and **1d** can be seen at $\delta = -127.7$ and -190.7, respectively. It should be noted that all anionic ^{29}Si NMR signals are very sharp singlets in THF-d_8 at 298 K, implying that the lithium exchange reaction occurs in THF at room temperature within the NMR time scale.

The ^{29}Si and ^6Li NMR spectra were measured at low temperature to suppress the lithium exchange. Due to the coupling with one ^6Li ($I = 1$), the ^{29}Si NMR signal of **1a** at 180 K splits into a triplet signal ($\delta = -74.9$) with a coupling constant of 18.8 Hz (Fig. 3). Furthermore, in the ^6Li NMR spectrum of **1a**, the satellite signals due to ^{29}Si nucleus can be observed with the same coupling constant. Similar to **1a**, the anionic ^{29}Si NMR signal in THF-d_8 appears as a triplet at $\delta = -62.7$ ($^1J(^{29}Si-^6Li) = 18.6$ Hz, 180 K) for **1b** and at $\delta = -32.8$ ($^1J(^{29}Si-^6Li) = 21.1$ Hz, 223 K) for **3**. This spectroscopic evidence reveals that the lithiosilanes exist as a monomer in THF.

As the anionic silicon center is substituted by the trimethylsilyl groups, the negative charge is largely stabilized by the trimethylsilyl groups to facilitate lithium exchange through the ionic character.[10] This is indicated by the lack of scalar coupling between silicon and lithium. Thus, the ^{29}Si NMR signal of **1c** in THF-d_8 at 180 K shows a broad singlet signal at $\delta = -133.8$, suggesting that the lithium exchange still occurs even at 180 K. In order to suppress the lithium exchange, the solvent THF-d_8 was replaced by toluene-d_8. The ^{29}Si NMR signal of **1c** now splits into a triplet one, appearing at $\delta = -130.1$ (223 K) with the coupling constant of 16.5 Hz. NMR spectrum shows that the silyllithium **1c** has THF molecules coordinated to the lithium atom in toluene-d_8.

The ^{29}Si NMR signals of anionic silicon of 2-lithio-1,3-diphenylpentamethyltrisilane ($LiSi(SiMe_2Ph)_2Me$, **1e**) and 2-lithio-2-phenylhexamethyltrisilane ($LiSi(SiMe_3)_2Ph$, **1f**) were observed as sharp singlets at $\delta = -124.8$ for **1e** and $\delta = -99.4$ for **1f** in THF-d_8 at 298 K and these signals did not split into triplet ones by lowering temperature, as found with **1c**.

Lithiosilanes, **1e**$\cdot(Et_2O)_n$, **1f**$\cdot(Et_2O)_n$, **1g**$\cdot(Et_2O)_n$, and **1h**$\cdot(Et_2O)_n$, coordinated with ethers were also prepared by the reaction of bis(oligosilanyl)mercury and ^6Li metal in diethyl ether. The anionic ^{29}Si NMR spectra of **1e**$\cdot(Et_2O)_n$, **1f**$\cdot(Et_2O)_n$, **1g**$\cdot(Et_2O)_n$, and **1h**$\cdot(Et_2O)_n$ in toluene-d_8 provide triplet signals at $\delta = -124.7$ ($^1J(^{29}Si-^6Li) = 20.0$ Hz, 213 K), -99.2 ($^1J(^{29}Si-^6Li) = 19.0$ Hz, 193 K), -121.4 ($^1J(^{29}Si-^6Li) = 21.9$ Hz, 223 K), -100.9 ($^1J(^{29}Si-^6Li) = 19.7$ Hz, 223 K), respectively. Therefore, these ether-coordinated lithiosilanes exist as monomers with a covalent Si–Li bond. The values of $^1J(^{29}Si-^6Li)$ for lithiosilanes are summarized in Table 1 together with the phenyl-substituted ones reported so far.[11] The values of $^1J(^{29}Si-^6Li)$ range from 15 to 21.9 Hz, implying that the monomeric lithiosilanes have

Table 1. ^{29}Si NMR Chemical Shifts and Values of $^{1}J(^{29}\mathrm{Si}-^{6}\mathrm{Li})$ for Lithiosilanes

Lithiosilane	Chemical shift/δ	$^{1}J(^{29}\mathrm{Si}-^{6}\mathrm{Li})$/Hz	Multiplicity	Temperature/K	Solvent
3	−32.8	21.1	3	223	THF-d_8
1a	−74.9	18.8	3	180	THF-d_8
1b	−62.7	18.6	3	180	THF-d_8
1c·(THF)$_n$	−130.1	16.5	3	223	Toluene-d_8
1e·(Et$_2$O)$_n$	−124.7	20.0	3	213	Toluene-d_8
1f·(Et$_2$O)$_n$	−99.2	19.0	3	193	Toluene-d_8
1g·(Et$_2$O)$_n$	−121.4	21.9	3	223	Toluene-d_8
1h·(Et$_2$O)$_n$	−100.9	19.7	3	223	Toluene-d_8
Ph_3SiLi[a]	−9.3	17	3	173	Me–THF[b]
$Ph_2MeSiLi$[a]	−22.2	16	3	193	Me–THF[b]
$PhMe_2SiLi$[a]	−28.7	18	3	193	Me–THF[b]

a) Taken from Ref. 11. b) 2-Methyltetrahydrofuran.

a similar silicon–lithium bond nature (i.e., similar Si–Li bond distances). Actually, the Si–Li bond distances of $Ph_3SiLi\cdot(THF)_3$ and $(Me_3Si)_3SiLi\cdot(THF)_3$ are reported to be 2.672(9) and 2.669(13) Å, respectively.[12]

Comparison of ^{29}Si NMR in Polar and Nonpolar Solvents. The ^{29}Si NMR chemical shifts of anionic silicon for lithiosilanes in toluene-d_8 and in THF-d_8 are significantly different. Thus, the anionic ^{29}Si NMR signals of **1a**, **1b**, **1c**, and **3** in toluene-d_8 are shifted upfield (ca. 10 ppm) compared to those in THF-d_8. This marked difference was observed for the coupling constants of ^{29}Si–^{29}Si. The values of $^{1}J(^{29}\mathrm{Si}-^{29}\mathrm{Si})$ for **1a**, **1c**, **1d**, **1e**, and **1f** were measured by the INEPT-INADEQUATE technique.[13] Figure 4 shows a typical chart of the INEPT-INADEQUATE NMR of **1a** in toluene-d_8 and in THF-d_8. The values of $^{1}J(^{29}\mathrm{Si}-^{29}\mathrm{Si})$ for the lithiosilanes are listed in Table 2 together with those of some related neutral compounds.[14] The value of $^{1}J(^{29}\mathrm{Si}-^{29}\mathrm{Si})$ has been found to correlate with the substituent electronegativity. Thus, the very small values of $^{1}J(^{29}\mathrm{Si}-^{29}\mathrm{Si})$ for the lithiosilanes are apparently caused by the attachment of the electropositive lithium to the silicon atom. The interesting fact is that the values in THF-d_8 are much smaller than those in toluene-d_8, suggesting that lithiosilanes in THF-d_8 have a more ionic and a less covalent character.

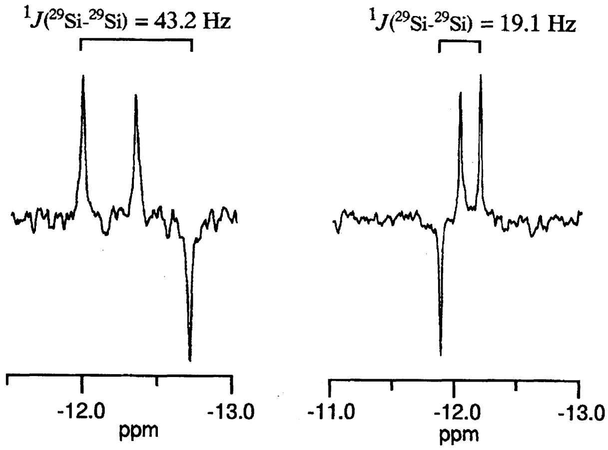


Fig. 4. ^{29}Si INEPT-INADEQUATE NMR of **1a**. Left: in toluene-d_8; right: in THF-d_8.

Table 2. Values of $^{1}J(^{29}\mathrm{Si}-^{29}\mathrm{Si})$ for Lithiosilanes with Si–Si Bonds and Some Oligosilanes

Lithiosilane	$^{1}J(^{29}\mathrm{Si}-^{29}\mathrm{Si})$/Hz		
	Toluene-d_8	THF-d_8	$CDCl_3$
1a	43.2	19.1	
1c	33.4	18.8	
1d	28.6	17.4	
1e	27.5	15.3	
1f	33.3	21.4	
$Me_3SiSiMe_2Cl$[a]			94.0
$Me_3SiSiMe_2Ph$[a]			86.1[b]
$(Me_3Si)_2SiMe_2$[a]			73.2
$(Me_3Si)_4Si$[a]			52.5

a) Taken from Ref. 14. b) In acetone-d_6.

Li NMR Spectra. The ^{6}Li and ^{7}Li chemical shifts provide a useful probe for evaluating the bonding nature, ie. covalent, ion pairing, π-complex, and so on. Figure 5 shows the Li NMR chemical shifts of the lithiosilanes. The Li NMR signals of unsolvated **1a**, **1b**, **1c**, and **3** are typically observed at around $\delta = 2.3$ in hydrocarbon solvents, whereas these resonances appear at around $\delta = 0.5$ in THF due to the disruption of the aggregates by complexation with THF. However, unsolvated **1d** ($\delta = 1.18$), **1e** ($\delta = -0.54$), and **1f** ($\delta = -0.42$) show quite unusual ^{7}Li NMR chemical shifts. The anionic silicon atoms in **1a** (tetramer in the solid state)[5] and **3** (hexamer in the solid state)[8] interact with the three lithium atoms, whereas those of **1d**, **1e**, and **1f** (dimer in the solid state)[4,9] interact with two lithium atoms. Of particular interest is the fact that the ^{7}Li signals of **1e** and **1f** are shifted significantly upfield, compared with other ones; $\delta = -0.54$ in toluene-d_8 and $\delta = -0.36$ in cyclohexane-d_{12} for **1e**, $\delta = -0.42$ in toluene-d_8 and $\delta = -0.97$ in cyclohexane-d_{12} for **1f**. These upfield shifts are caused by the shielding effect of the phenyl groups. The lithiosilanes **1e** and **1f** are dimeric structures in the solid state and each lithium atom is surrounded by the phenyl groups, due to electrostatic attraction between the lithium ion and benzene rings.[4] It is quite reasonable to assume similar electrostatic interactions in the hydrocarbon solvents. In fact, the ^{7}Li signal of **1e** is ob-

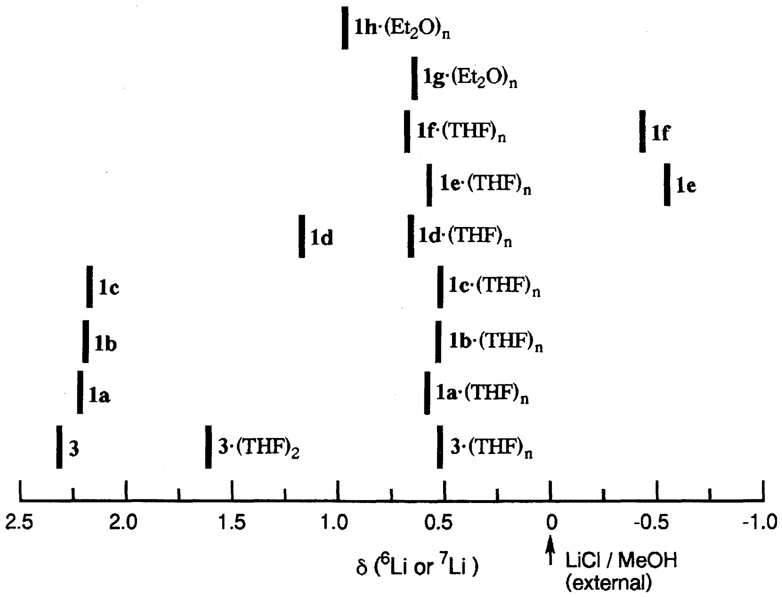


Fig. 5. Li NMR chemical shifts of lithiosilanes. Li NMR spectra were taken by using ^{6}Li or ^{7}Li nucleus. The unsolvated **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **3**, and the solvated **1g**·$(Et_2O)_n$, **1h**·$(Et_2O)_n$, **3**·$(THF)_2$ were measured in toluene-d_8 at room temperature. The solvated **1a**·$(THF)_n$, **1b**·$(THF)_n$, **1c**·$(THF)_n$, **1d**·$(THF)_n$, **1e**·$(THF)_n$, **1f**·$(THF)_n$, and **3**·$(THF)_n$ were measured in THF-d_8 at room temperature.

served at $\delta = 0.58$ for a THF-d_8 solution, indicating that the dimeric structure is destroyed completely by complexation with THF. Consequently, the lithium atom can no longer be shielded by the phenyl groups. The lithiosilane **1f** in THF-d_8 provided a similar ^{7}Li NMR signal appearing at 0.69.

For the preparation of **3**·$(THF)_2$, the solvent THF was removed in vacuo and pentane was introduced to give colorless crystals with two THF molecules.[15] The ^{6}Li signal is observed at $\delta = 1.61$, which is intermediate between the unsolvated **3** ($\delta = 2.33$) and the completely solvated monomer ($\delta = 0.53$).

Conclusion. Unsolvated and aggregated lithiosilanes have been synthesized by lithium–mercury exchange reaction in toluene. The ^{29}Si, ^{6}Li, and ^{7}Li NMR spectra indicate that lithiosilanes in the hydrocarbon solvents prefer the aggregated structures to the monomeric ones as found in RLi, whereas the aggregated structures are completely destroyed in a polar solvent such as THF or Et_2O. The formation of the only monomer in the polar solvent is markedly different compared with organolithium (RLi). The ^{6}Li and ^{7}Li chemical shifts provide a useful probe for evaluating the structure of lithiosilanes in solution.

Experimental

General Procedure. ^{1}H NMR spectra were recorded on a Bruker AC-300 FT spectrometer. ^{6}Li, ^{7}Li, ^{13}C, and ^{29}Si NMR spectra were collected on the Bruker AC-300 at 44.2, 116.6, 75.5, and 59.6 MHz, respectively. The chemical shifts of ^{1}H, ^{13}C, and ^{29}Si NMR spectra were referenced to external tetramethylsilane. The chemical shifts of ^{6}Li and ^{7}Li NMR spectra were referenced to external lithium chloride (1.0 M in methanol, 1 M = 1 mol dm^{-3}). The low-temperature ^{6}Li and ^{29}Si NMR experiments were carried out by using a Bruker variable temperature unit with a CKD Co. heatless air dryer model HD-0.5. The sampling of lithiosilanes for NMR experiments was carried out by using a Giken Engineering Service GBX-1200 gas-replacement type glove box. Diethyl ether, tetrahydrofuran (THF), pentane, and heptane were dried and distilled from sodium benzophenone ketyl. These solvents were further dried and degassed over a potassium mirror in vacuo prior to use. Toluene-d_8, benzene-d_6, and THF-d_8 were dried over molecular sieves (4 Å), and then transferred into a tube covered with a potassium mirror prior to use. Lithium-6 (95 atom %) metal was obtained commercially (Aldrich Chemical Company). Unsolvated lithiotrimethylsilane (**3**),[8] bis(trimethylsilyl) mercury,[16] and di-*t*-butylmercury[17] were prepared according to the published procedures. Elementary analyses of bis(oligosilanyl)mercury derivatives and lithiosilanes are not available due to their instability.

Bis(1,1,2,2,2-pentamethyldisilanyl)mercury (2a). Pentamethyldisilane (130 mg, 0.985 mmol) and dry heptane (2.0 ml) were placed into a glass reaction vessel, and then di-*t*-butylmercury (135 mg, 0.429 mmol) was added to the solution. The mixture was immediately stirred under argon atmosphere for 4 h at 85 °C. The solvent was removed in vacuo to give **2a** as a yellow oil in 79% yield. ^{1}H NMR (benzene-d_6) $\delta = 0.21$ (s, 18 H), 0.41 (s, 12 H); ^{13}C NMR (benzene-d_6) $\delta = -0.1$, 0.6; ^{29}Si NMR (benzene-d_6) $\delta = -5.7$, 34.9.

Lithiopentamethyldisilane (1a). Some pieces of lithium-6 metal wire (ca. 80 mg, 12 mmol) were added to **2a**. Dry degassed toluene-d_8 (0.6 ml) was introduced by a vacuum transfer, and the vessel was sealed. The mixture was stirred for 12 h at room temperature. The solution of the unsolvated **1a** was decanted into a NMR tube and sealed. ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.22$ (s, 9 H), 0.33 (s, 6 H); ^{6}Li NMR (toluene-d_8, 298 K) $\delta = 2.22$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = -2.51$, -0.56; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -80.0$ (m), -12.4 ($^1J(^{29}\text{Si}-^{29}\text{Si}) = 43.2$ Hz).

The sampling in THF-d_8 was also carried out in a similar manner. Some pieces of lithium-6 metal wire (ca. 80 mg, 12 mmol) were added to **2a**, and then dry degassed THF-d_8 (0.6 ml) was introduced by a vacuum transfer. After 6 h, the solution was discolored. The solution of **1a** was decanted into an NMR tube and sealed.

1a·(THF)$_n$: ^{1}H NMR (THF-d_8, 298 K) $\delta = -0.17$ (s, 9 H), -0.04 (s, 6 H); ^{6}Li NMR (THF-d_8, 298 K) $\delta = 0.58$; ^{13}C NMR (THF-d_8, 298 K) $\delta = -0.15$, 1.31; ^{29}Si NMR (THF-d_8, 298 K) $\delta = -71.5$, -12.0 ($^{1}J(^{29}\text{Si–}^{29}\text{Si}) = 19.1$ Hz); ^{29}Si NMR (THF-d_8, 180 K) $\delta = -74.9$ (t, $^{1}J(^{29}\text{Si–}^{6}\text{Li}) = 18.8$ Hz), -10.6.

Bis(1,1,2,2,3,3,3-heptamethyltrisilanyl)mercury (2b). This was obtained as a yellow oil in 78% yield by a procedure similar to the synthesis of **2a**. ^{1}H NMR (benzene-d_6) $\delta = 0.19$ (s, 18 H), 0.29 (s, 12 H), 0.46 (s, 12 H); ^{13}C NMR (benzene-d_6) $\delta = -5.2$, -1.0, 1.5; ^{29}Si NMR (benzene-d_6) $\delta = -33.5$, -14.3, 38.3.

1-Lithio-1,1,2,2,3,3,3-heptamethyltrisilane (1b). This was prepared by a procedure similar to the synthesis of **1a**.

1b (unsolvated): ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.15$ (s, 9 H), 0.18 (s, 6 H), 0.36 (s, 6 H); ^{6}Li NMR (toluene-d_8, 298 K) $\delta = 2.21$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = -4.19$, -1.21, -0.49; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -73.5$ (m), -40.4, -14.2;

1b·(THF)$_n$: ^{1}H NMR (THF-d_8, 298 K) $\delta = -0.09$ (s, 9 H), -0.04 (s, 6 H), 0.04 (s, 6 H); ^{6}Li NMR (THF-d_8, 298 K) $\delta = 0.53$; ^{13}C NMR (THF-d_8, 298 K) $\delta = -4.17$, 0.13, 2.19; ^{29}Si NMR (THF-d_8, 298 K) $\delta = -61.5$, -40.6, -14.6; ^{29}Si NMR (THF-d_8, 180 K) $\delta = -62.7$ (t, $^{1}J(^{29}\text{Si–}^{6}\text{Li}) = 18.6$ Hz), -40.6, -14.6.

Bis(1,1,1,2,3,3,3-heptamethyltrisilan-2-yl)mercury (2c). A yellow oil, 88% yield. ^{1}H NMR (benzene-d_6) $\delta = 0.27$ (s, 36 H), 0.45 (s, 6 H); ^{13}C NMR (benzene-d_6) $\delta = -7.4$, 2.1; ^{29}Si NMR (benzene-d_6) $\delta = -5.5$, -4.2.

2-Lithio-1,1,1,2,3,3,3-heptamethyltrisilane (1c). **1c** (unsolvated): ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.32$ (s, 18 H), 0.36 (s, 3 H); ^{6}Li NMR (toluene-d_8, 298 K) $\delta = 2.18$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = -1.6$, 2.8; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -137$ (m), -8.3 ($^{1}J(^{29}\text{Si–}^{29}\text{Si}) = 33.4$ Hz);

1c·(THF)$_n$: ^{1}H NMR (THF-d_8, 298 K) $\delta = -0.07$ (s, 18 H), 0.11 (s, 3 H); ^{6}Li NMR (THF-d_8, 298 K) $\delta = 0.58$; ^{13}C NMR (THF-d_8, 298 K) $\delta = 0.5$, 3.4; ^{29}Si NMR (THF-d_8, 298 K) $\delta = -127.7$, -7.4 ($^{1}J(^{29}\text{Si–}^{29}\text{Si}) = 18.8$ Hz).

Bis[tris(trimethylsilyl)silyl]mercury (2d). Yellow crystals, 82% yield. ^{1}H NMR (benzene-d_6) $\delta = 0.35$; ^{13}C NMR (benzene-d_6) $\delta = 4.7$; ^{29}Si NMR (benzene-d_6) $\delta = -54.4$, -2.9.

Lithio[tris(trimethylsilyl)]silane (1d). **1d** (unsolvated); ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.27$; ^{7}Li NMR (toluene-d_8, 298 K) $\delta = 1.18$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = 5.8$; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -181.7$, -7.0 ($^{1}J(^{29}\text{Si–}^{29}\text{Si}) = 28.6$ Hz);

1d·(THF)$_n$: ^{1}H NMR (THF-d_8, 298 K) $\delta = 0.06$; ^{7}Li NMR (THF-d_8, 298 K) $\delta = 0.67$; ^{13}C NMR (THF-d_8, 298 K) $\delta = 6.7$; ^{29}Si NMR (THF-d_8, 298 K) $\delta = -190.7$, -5.1 ($^{1}J(^{29}\text{Si–}^{29}\text{Si}) = 17.4$ Hz).

Bis[1,1,2,3,3-pentamethyl-1,3-diphenyltrisilan-2-yl]mercury (2e). A yellow oil, 95% yield. ^{1}H NMR (benzene-d_6) $\delta = 0.42$ (s, 6 H, Ph*Me*MeSi), 0.43 (s, 6 H, PhMe*Me*Si), 0.44 (s, 3 H), 7.12—7.27 (m, 6 H), 7.45—7.50 (m, 4 H); ^{13}C NMR (benzene-d_6) $\delta = -6.82$, 0.18 (Ph*Me*MeSi), 0.23 (PhMe*Me*Si), 128.4, 128.9, 134.1, 142.0; ^{29}Si NMR (benzene-d_6) $\delta = -7.8$, -6.7.

2-Lithio-1,1,2,3,3-pentamethyl-1,3-diphenyltrisilane (1e). **1e** (unsolvated): ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.23$ (s, 3 H), 0.47 (s, 6 H, Ph*Me*MeSi), 0.53 (s, 6 H, PhMe*Me*Si), 7.04—7.08 (m, 2 H), 7.11—7.20 (m, 4 H), 7.36—7.40 (m, 4 H); ^{7}Li NMR (toluene-d_8, 298 K) $\delta = -0.54$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = -11.1$, 0.16 (Ph*Me*MeSi), 0.25 (PhMe*Me*Si), 128.5, 129.4, 133.0, 147.2; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -123.3$ (m), -9.7;

1e·(THF)$_n$: ^{1}H NMR (THF-d_8, 298 K) $\delta = 0.06$ (s, 3 H), 0.16 (s, 12 H), 7.05—7.16 (m, 6 H), 7.40—7.45 (m, 4 H); ^{7}Li NMR (THF-d_8, 298 K) $\delta = 0.58$; ^{13}C NMR (THF-d_8, 298 K) $\delta = -8.92$, 1.24 (Si*Me*MePh), 1.41 (SiMe*Me*Ph), 126.6, 127.3, 134.5, 150.3; ^{29}Si NMR (THF-d_8, 298 K) $\delta = -124.8$, -8.6 ($^{1}J(^{29}\text{Si–}^{29}\text{Si}) = 15.3$ Hz).

The diethyl ether complex of **1e** was prepared as follows. Some pieces of lithium-6 metal wire (ca. 80 mg, 12 mmol) were added to **2e**, and then dry degassed Et_2O (0.6 ml) was introduced by a vacuum transfer. The mixture was stirred under an argon atmosphere at 0 °C for 24 h. After the solvent was removed in vacuo, dry degassed toluene-d_8 (0.6 ml) was introduced by a vacuum transfer. The solution of **1e**·(Et_2O)$_n$ was decanted to the NMR tube and sealed. **1e**·(Et_2O)$_n$: ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.59$ (s, 3 H), 0.66 (s, 6 H, Si*Me*MePh), 0.68 (s, 6 H, SiMe*Me*Ph), 0.93 (t, Et_2O, 12 H), 3.13 (q, Et_2O, 8 H), 7.20—7.35 (m, 6 H), 7.80—7.90 (m, 4 H); ^{6}Li NMR (toluene-d_8, 298 K) $\delta = 1.10$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = -6.93$, 0.05 (Si*Me*MePh), 0.43 (SiMe*Me*Ph), 15.2 (Et_2O), 65.9 (Et_2O), 126.3, 127.4, 134.1, 151.7; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -120.1$, -8.6; ^{29}Si NMR (toluene-d_8, 213 K) $\delta = -124.7$ (t, $^{1}J(^{29}\text{Si–}^{6}\text{Li}) = 20.0$ Hz), -7.4.

Bis[1,1,1,3,3,3-hexamethyl-2-phenyltrisilan-2-yl]mercury (2f). Yellow crystals, 82% yield. ^{1}H NMR (benzene-d_6) $\delta = 0.35$ (s, 18 H), 7.04—7.13 (m, 1 H), 7.21—7.14 (m, 2 H), 7.64—7.58 (m, 2 H); ^{13}C NMR (benzene-d_6) $\delta = 2.5$, 128.3, 128.4, 137.6, 140.4; ^{29}Si NMR (benzene-d_6) $\delta = -5.9$, 5.2.

2-Lithio-1,1,1,3,3,3-hexamethyl-2-phenyltrisilane (1f). **1f** (unsolvated): ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.29$ (s, 18 H), 6.61 (t, 1 H, $J = 7.4$ Hz), 6.82 (dd, 2H, $J = 7.4$ Hz, $J = 7.7$ Hz), 7.50 (d, 2 H, $J = 7.7$ Hz); ^{7}Li NMR (toluene-d_8, 298 K) $\delta = -0.42$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = 3.5$, 125.0, 129.2, 136.1, 151.8; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -94.0$ (m), -9.9;

1f·(THF)$_n$: ^{1}H NMR (THF-d_8, 298 K) $\delta = 0.06$ (s, 18 H), 6.73 (t, $J = 7.4$ Hz, 1 H), 6.83 (dd, $J = 7.4$ Hz, $J = 7.7$ Hz, 2 H), 7.40 (d, $J = 7.7$ Hz, 1 H); ^{7}Li NMR (THF-d_8, 298 K) $\delta = 0.69$; ^{13}C NMR (THF-d_8, 298 K) $\delta = 4.3$, 122.8, 126.4, 137.9, 155.0; ^{29}Si NMR (THF-d_8, 298 K) $\delta = -99.4$, -10.0 ($^{1}J(^{29}\text{Si–}^{29}\text{Si}) = 21.4$ Hz);

1f·(Et_2O)$_n$: ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.52$ (s, 18 H), 0.98 (t, Et_2O, 12 H), 3.13 (q, Et_2O, 8 H), 7.05—7.14 (m, 1 H), 7.20—7.28 (m, 2 H), 7.85—7.90 (m, 2 H); ^{6}Li NMR (toluene-d_8, 298 K) $\delta = 1.22$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = 3.9$, 14.6 (Et_2O), 65.8 (Et_2O), 124.2, 127.5, 136.9, 151.0; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -97.2$, -9.5; ^{29}Si NMR (toluene-d_8, 193 K) $\delta = -99.2$ (t, $^{1}J(^{29}\text{Si–}^{6}\text{Li}) = 19.0$ Hz), -9.5.

1,1,2,2,3,4,4,5,5-Nonamethyl-1,5-diphenylpentasilane. Trifluoromethanesulfonic acid (25.0 g, 167 mmol) was added dropwise to a toluene solution of 1,1,2,3,3-pentamethyl-1,3-diphenyltrisilane (25.70 g, 81.69 mmol) under a nitrogen atmosphere at 0 °C. The mixture was stirred for 5 h, and then to the mixture was added a toluene solution (100 ml) of Me_2PhSiLi (91.65 mmol). The reaction mixture was hydrolyzed with 1 M hydrochloric acid, followed by extraction with toluene. The organic layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residual oil was distilled to give the title compound (17.94 g, 41.63 mmol) as a colorless oil in 51% yield. Bp 158 °C/0.2 mmHg (1 mmHg = 133.322 Pa); ^{1}H NMR (CDCl_3) $\delta = -0.06$ (d, 3 H, $J = 5.1$ Hz), 0.09 (s, 6 H), 0.10 (s, 6 H), 0.35 (s, 12, H), 3.26 (q, 1 H, $J = 5.1$ Hz), 7.24—7.33 (m, 6 H), 7.40—7.44 (m, 4 H); ^{13}C NMR (CDCl_3) $\delta = -11.0$, -5.3, -4.5, -3.4, 127.7, 128.4, 133.8, 139.5; ^{29}Si NMR (CDCl_3) $\delta = -70.1$, -43.0, -18.2; Anal. Calcd for $\text{C}_{21}\text{H}_{38}\text{Si}_5$: C, 58.53; H, 8.89%. Found: C, 58.85; H, 8.73%.

Bis[1,1,2,2,3,4,4,5,5-nonamethyl-1,5-diphenylpentasilan-3-yl]mercury (2g). A yellow oil, 88% yield. ^{1}H NMR (benzene-d_6) $\delta = 0.326$ (s, 12 H), 0.334 (s, 12 H), 0.380 (s, 6 H), 0.457 (s, 6 H), 0.465 (s, 12 H), 7.13—7.28 (m, 12 H), 7.44—7.53 (m, 8 H); ^{13}C NMR (benzene-d_6) $\delta = -4.88$, -2.53, -2.45, -2.34, -1.68, 128.2, 128.8, 134.0, 139.8; ^{29}Si NMR (benzene-d_6) $\delta = -29.5$,

−17.4, −4.2.

3-Lithio-1,1,2,2,3,4,4,5,5-nonamethyl-1,5-diphenylpentasilane (1g). **1g**·$(Et_2O)_n$: ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.29$ (s, 6 H), 0.35 (s, 3 H), 0.43 (s, 6 H), 0.456 (s, 6 H), 0.462 (s, 6 H), 0.80 (t, 12 H, Et_2O), 3.04 (q, 8 H, Et_2O), 7.03—7.18 (m, 6 H), 7.52—7.60 (m, 4 H); ^{7}Li NMR (toluene-d_8, 298 K) $\delta = 0.65$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = -8.0$, −2.0, −1.9, −1.3, −0.6, 14.6 (Et_2O), 65.8 (Et_2O), 127.6, 134.4, 143.9; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -116.8$, −34.0, −17.1; ^{29}Si NMR (toluene-d_8, 223 K) $\delta = -121.4$ (t, $^1J(^{29}Si-^6Li) = 21.9$ Hz), −34.0, −17.1.

Bis(dimethylphenylgermyl)methylsilane. A toluene solution (50 ml) of $Me_2PhGeLi$ (55.99 mmol) was added dropwise to dichloromethylsilane (3.20 g, 27.8 mmol) in hexane (300 ml). The reaction mixture was hydrolyzed with 1 M hydrochloric acid, followed by extraction with hexane/toluene. The organic layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residual oil was distilled to give the title compound (8.19 g, 20.3 mmol) as a colorless oil in 73% yield. Bp 103 °C/0.035 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 0.22$ (d, 3 H, $J = 5.3$ Hz), 0.44 (s, 12 H), 4.00 (q, 1 H, $J = 5.3$ Hz), 7.15—7.25 (m, 6 H), 7.40—7.45 (m, 4 H); ^{13}C NMR ($CDCl_3$) $\delta = -10.8$, −2.6, −2.4, 128.48, 128.52, 133.9, 141.9; ^{29}Si NMR ($CDCl_3$) $\delta = -59.4$; Anal. Calcd for $C_{17}H_{26}Ge_2Si$: C, 50.58; H, 6.49%. Found: C, 50.48; H, 6.48%.

Bis[bis(dimethylphenylgermyl)methylsilyl]mercury (2h). A yellow oil, 87% yield. ^{1}H NMR (benzene-d_6) $\delta = 0.47$ (s, 6 H), 0.54 (s, 24 H), 7.15—7.28 (m, 12 H), 7.45—7.50 (m, 8 H); ^{13}C NMR (benzene-d_6) $\delta = -5.0$, −0.38, −0.33, 128.2, 128.5, 133.7, 144.4; ^{29}Si NMR (benzene-d_6) $\delta = 10.7$.

Lithio[bis(dimethylphenylgermyl)methyl]silane (1h). **1h**·$(Et_2O)_n$: ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.68$ (s, 3 H), 0.70 (s, 6 H, Ge*Me*MePh), 0.73 (s, 6 H, GeMe*Me*Ph), 1.09 (t, 12 H, Et_2O), 3.27 (q, 8 H, Et_2O), 7.18—7.32 (m, 6 H), 7.72—7.78 (m, 4 H); ^{6}Li NMR (toluene-d_8, 298 K) $\delta = 0.98$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = -6.9$, 0.0 (Ge*Me*MePh), 0.4 (GeMe*Me*Ph), 15.2 (Et_2O), 65.9 (Et_2O), 126.3, 127.4, 134.1, 151.7; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -96.5$; ^{29}Si NMR (toluene-d_8, 223 K) $\delta = -100.9$ (t, $^1J(^{29}Si-^6Li) = 19.7$ Hz).

Lithiotrimethylsilane (3). The crystals of bis(trimethylsilyl)mercury (ca. 60 mg) and some pieces of lithium-6 metal wire (ca. 80 mg, 12 mmol) were placed in glass vessel in a glove box with a nitrogen atmosphere. Dry degassed toluene-d_8 (0.6 ml) was introduced by a vacuum transfer, and then the mixture was stirred for 12 h. The solution of **3** was decanted into an NMR tube and sealed. **3** (unsolvated): ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.21$; ^{6}Li NMR (toluene-d_8, 298 K) $\delta = 2.33$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = 5.1$; ^{29}Si NMR (toluene-d_8, 298 K) $\delta = -38.0$.

The preparation of **3** in THF-d_8 was also carried out in a similar manner. **3**·$(THF)_n$: ^{1}H NMR (THF-d_8, 298 K) $\delta = -0.29$; ^{7}Li NMR (THF-d_8, 298 K) $\delta = 0.53$; ^{13}C NMR (THF-d_8, 298 K) $\delta = 11.3$; ^{29}Si NMR (THF-d_8, 298 K) $\delta = -32.2$; ^{29}Si NMR (THF-d_8, 223 K) $\delta = -32.8$ (t, $^1J(^{29}Si-^6Li) = 21.1$ Hz).

3·$(THF)_2$ was prepared by a procedure similar to the synthesis of **1e**·$(Et_2O)_n$. **3**·$(THF)_2$: ^{1}H NMR (toluene-d_8, 298 K) $\delta = 0.33$ (s, 9 H), 1.38 (m, 8 H, THF), 3.58 (m, 8 H, THF); ^{6}Li NMR (toluene-d_8, 298 K) $\delta = 1.61$; ^{13}C NMR (toluene-d_8, 298 K) $\delta = 9.2$, 25.5 (THF), 68.7 (THF); ^{29}Si NMR (toluene-d_8, 200 K) $\delta = -38.4$ (m).

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