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Crystal Structures of Unsolvated Lithiosilanes with Si–Si Bonds

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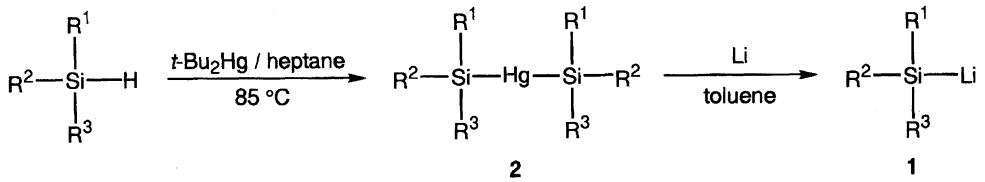
The molecular structures of lithiopentamethyldisilane ($[LiSiMe_2SiMe_3]_4$, **1a**), 2-lithio-1,1,2,3,3-pentamethyl-1,3-diphenyltrisilane ($[LiSi(SiMe_2Ph)_2Me]_2$, **1b**), and 2-lithio-1,1,1,3,3,3-hexamethyl-2-phenyltrisilane ($[LiSi(SiMe_3)_2Ph]_2$, **1c**) have been determined by X-ray diffraction. The silyllithium **1a** is a tetramer in the solid state with intramolecular Li···CH_3 agostic interactions. The silyllithiums **1b** and **1c** are dimers with intramolecular lithium-phenyl interactions. The latter adopts a molecular structure with not only an intramolecular Li–Ph interaction, but also an intermolecular Li···CH_3 agostic interaction. The structures of these organometallic derivatives show novel features not observed in solvent-coordinated lithiosilanes. These features provide valuable insights into structures that differ markedly from those of lithiosilanes containing coordinated donor solvent molecules.

Silyl anions are useful in some applications not only in organosilicon chemistry but also in organic synthesis.[1] Molecular structures of several solvent-coordinated lithiosilanes have been reported: $Me_3SiLi\cdot(TMEDA)_{1.5}$ (TMEDA = *N*,*N*,*N*′,*N*′- tetramethylethylenediamine),[2] $(Me_3Si)_3SiLi\cdot(DME)_{1.5}$ (DME = 1,2-dimethoxyethane),[3] $(Me_3Si)_3SiLi\cdot(THF)_3$,[4] $Ph_3SiLi\cdot(THF)_3$,[5] (*t*-$BuMe_2Si)(Me_3Si)_2SiLi\cdot(THF)_3$,[6] and $[Li(SiPh_2)_4Li]\cdot(THF)_6$.[7] Crystal structure determinations of the solvent-coordinated lithiosilanes have shown them to be monomeric species in which the lithium atom is covalently bonded to the anionic silicon atom and the nitrogen or oxygen atom of TMEDA, DME, or THF. However, much less attention has been devoted to unsolvated lithiosilanes, due to the difficulty of their synthesis and their high reactivity. Only two examples of unsolvated structures of lithiosilanes have been reported so far: hexameric $(Me_3SiLi)_6$[8] and dimeric $[(Me_3Si)_3SiLi]_2$.[9] We wish to report here the detailed molecular structures of a tetramer of lithiopentamethyldisilane ($[LiSiMe_2SiMe_3]_4$, **1a**),[10a] dimers of 2-lithio-1,1,2,3,3-pentamethyl-1,3-diphenyltrisilane ($[LiSi(SiMe_2Ph)_2Me]_2$, **1b**),[10b,c] and 2-lithio-1,1,1,3,3,3-hexamethyl-2-phenyltrisilane ($[LiSi(SiMe_3)_2Ph]_2$, **1c**),[10c] as well as ab initio calculations on the monomer of $LiSiMe_2SiMe_3$.

Results and Discussion

Synthesis. For the preparation of lithiopentamethyldisilane (**1a**), 2-lithio-1,3-diphenylpentamethyltrisilane (**1b**), and 2-lithio-2-phenylhexamethyltrisilane (**1c**), we have adopted a lithium–mercury exchange reaction (Scheme 1). Thus, hydrosilanes (silanes containing Si–H bond) were heated with di-*t*-butylmercury in heptane at 85 °C to produce yellow oils of bis(pentamethyldisilanyl)mercury (**2a**) and bis[bis(dimethylphenylsilyl)methylsilyl]mercury (**2b**), and yellow crystals of bis[bis(trimethylsilyl)phenylsilyl]mercury (**2c**), respectively. The resulting silylmercury derivatives were subjected to the Li–Hg exchange reaction with excess lithium metal in toluene to give the corresponding lithiosilanes. **1a** was recrystallized from pentane at 0 °C as colorless needles. Yellow crystals of **1b** and **1c** were grown from heptane and heptane/toluene (10/1) mixed solvent at 5 °C, respectively.

Crystal Structure of 1a. Lithiopentamethyldisilane **1a** is a tetramer in the solid state as determined by X-ray diffraction, and its molecular structure is shown in Fig. 1. The structural parameters of **1a** are also listed in Table 1. There are two crystallographically independent molecules of **1a** in the unit cell and the tetramer is crystallographically generated through a two-fold axis. The structural parame-



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a: $R^1 = SiMe_3$, $R^2 = R^3 = Me$; **b:** $R^1 = R^2 = SiMe_2Ph$, $R^3 = Me$; **c:** $R^1 = R^2 = SiMe_3$, $R^3 = Ph$

Scheme 1.

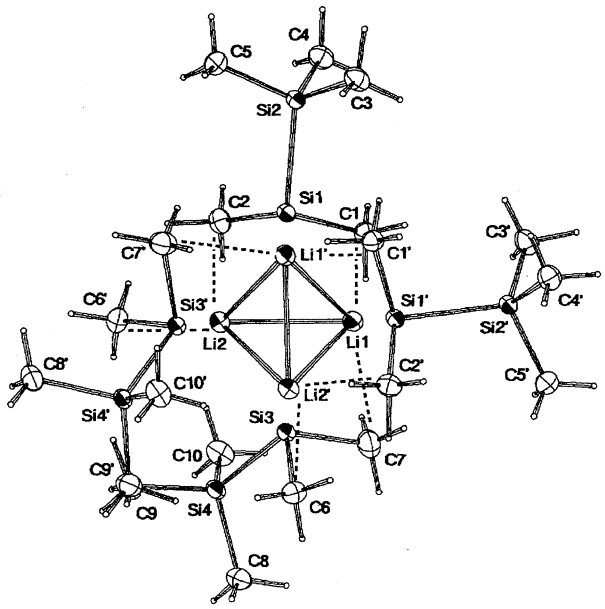


Fig. 1. Molecular structure of **1a** (ellipsoids at the 50% probability level). Dotted lines indicate short intramolecular Li···CH_3 contacts.

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

	Atomic distances		
Si1–Si2	2.348(0)	Si3–Li2′	2.650(5)
Si1–C1	1.944(2)	Si4–C8	1.883(4)
Si1–C2	1.919(4)	Si4–C9	1.871(4)
Si1–Li1	2.662(4)	Si4–C10	1.886(4)
Si1–Li1′	2.687(5)	C1–Li1	2.392(6)
Si1–Li2	2.683(6)	C2–Li2	2.792(6)
Si2–C3	1.871(4)	C6–Li2′	2.348(6)
Si2–C4	1.875(4)	C7–Li1	2.879(6)
Si2–C5	1.880(4)	Li1–Li2	2.749(7)
Si3–Si4	2.344(0)	Li1–Li1′	2.795(7)
Si3–C6	1.944(4)	Li1–Li2′	2.783(7)
Si3–C7	1.928(4)	Li2–Li1′	2.783(7)
Si3–Li1	2.715(6)	Li2–Li2′	2.819(8)
Si3–Li2	2.700(6)	Li1′–Li2′	2.749(7)
	Bond angles		
Si2–Si1–C1	101.9(1)	Si4–Si3–Li2	102.2(1)
Si2–Si1–C2	103.6(1)	Si4–Si3–Li2′	138.5(1)
Si2–Si1–Li1	138.9(1)	C6–Si3–C7	101.6(1)
Si2–Si1–Li2	147.1(1)	Li1–Si3–Li2	61.0(1)
Si2–Si1–Li1′	101.2(1)	Si3–Si4–C8	110.9(1)
C1–Si1–C2	102.5(1)	Si3–Si4–C9	112.3(1)
Li1–Si1–Li2	61.9(1)	Si3–Si4–C10	109.5(1)
Si1–Si2–C3	111.8(1)	C8–Si4–C9	107.4(1)
Si1–Si2–C4	111.4(1)	C8–Si4–C10	108.3(1)
Si1–Si2–C5	110.7(1)	C9–Si4–C10	108.3(1)
C3–Si2–C4	107.3(1)	Li2–Li1–Li1′	60.2(1)
C3–Si2–C5	107.6(1)	Li2–Li1–Li2′	61.3(2)
C4–Si2–C5	107.7(1)	Li1′–Li1–Li2′	59.1(1)
Si4–Si3–C6	101.8(1)	Li1–Li2–Li1′	60.7(1)
Si4–Si3–C7	102.6(1)	Li1–Li2–Li2′	60.0(1)
Si4–Si3–Li1	147.3(1)	Li1′–Li2–Li2′	58.8(1)

a) Atomic numbers are given in Fig. 1. Standard deviations are in parentheses.

ters of the two independent molecules are rather similar. No interaction among tetramers was found, as shown in the perspective view in the unit cell down the *a* axis (Fig. 2). The lithium atoms form a tetrahedral arrangement with Li–Li distances of 2.749(7)—2.819(8) Å. The Li–Li distance of the framework is somewhat longer than those of three unsolvated alkyllithium tetramers: Li–Li = 2.56 Å (av), 2.55 Å (av), and 2.41 Å (av) for $(MeLi)_4$,[11a)] $(EtLi)_4$,[11b)] and $(t\text{-}BuLi)_4$,[11c)] respectively. Substitution of a carbon in tetrameric alkyllithiums for a silicon should lead to expansion of the lithium core due to the increased bond length of Li–Si compared with that of Li–C. The pentamethyldisilanyl group caps each face of the Li_4 tetrahedron with three nearly equal Li–Si distances of 2.650(5)—2.715(6) Å, while the Li–C bond lengths for the tetrameric alkyllithiums are in the range of 2.25—2.27 Å (av). The equivalence of the Li–Si bonds implies that each silicon participates equally in bonding to the three lithium atoms. In **1a**, one trimethylsilyl group and two methyl groups are arranged so as to give the eclipsed conformation relative to the Li_3 triangle, whereas one methyl group and two hydrogen atoms in $(EtLi)_4$ are staggered. As a result, the eclipsed conformation in **1a** leads to remarkably short Li–C ($Si_{anionic}$) distances (e.g. Li1–C1 = 2.392(6) Å, Li2′–C6 = 2.348(6) Å) due to an agostic interaction between the lithium atom and a C–H bond (Li–H(C1) = 2.08 Å).[12,13)]

The C–$Si_{anionic}$ bond lengths of 1.919(4)—1.944(4) Å are considerably longer than the normal length (1.88 Å). Of particular interest is the fact that the angles around the anionic silicon atom are significantly contracted, the sum of the an-

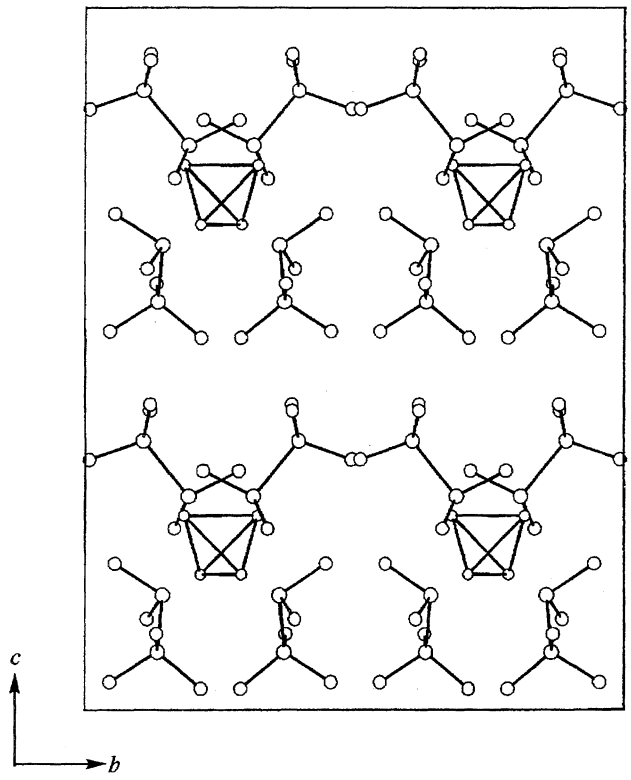
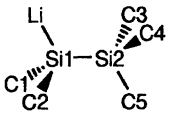


Fig. 2. Perspective view of **1a** in the unit cell down the *a* axis (hydrogen atoms are omitted for clarity).

gles being only 306.0° and 308.0° for the two independent molecules, respectively. This contraction is explained by noting that the anionic charge in silyllithium **1a** is mostly contained in the 3s-orbital. The Si–Si bond lengths of 2.348(0) and 2.344(0) Å are normal, suggesting no dative bonding between the anionic silicon atom and the neighboring silicon atom. As in **1a**, the Si–Si bond lengths of $LiSi(SiMe_3)_3 \cdot (DME)_{1.5}$ and $LiSi(SiMe_3)_3 \cdot (THF)_3$ were reported to be in the normal ranges of 2.342 and 2.330—2.331 Å, respectively.[3,4,5] The ab initio calculations on $LiSiMe_2SiMe_3$ (monomer) show a notable C–$Si_{anionic}$ bond elongation (1.930 Å) and a contraction of the bond angles around the anionic silicon atom (the sum of the angles is 313.8°, Table 2).[14] The calculated Si–Si bond length (2.356 Å) is in close agreement with the experimental value (2.348(0), 2.344(0) Å).

Crystal Structure of 1b. 2-Lithio-1,1,2,3,3-pentamethyl-1,3-diphenyltrisilane **1b** is a dimer in the solid state and the dimeric structure possesses a crystallographic inversion symmetry (Fig. 3). The structural parameters are listed in Table 3. The two lithium and two anionic silicon atoms constitute a planar four-membered ring with Li–Si distances of 2.664(5) and 2.778(7) Å and a Li–Si–Li bond angle of 58.1(2)°. The Li–Li distance is 2.645(10) Å. The most striking point of the structure is that the two lithium atoms are surrounded by the four phenyl groups. No interaction among the dimers is observed, as demonstrated in Fig. 4, which shows the perspective view of the unit cell. One lithium atom apparently contacts two of the four neighboring benzene rings (Fig. 3, side view). The lithium atom is in rather close contact with the *ipso* and *ortho* carbon atoms of the nearby phenyl group (e.g. Li1′–C12: 2.348(6) Å, Li1′–C13: 2.483(7) Å, Li1′–C17: 2.730(8) Å). Although these distances are typical

Table 2. Calculated Parameters of $LiSiMe_2SiMe_3$ by HF/3-21G*



	Bond distances (Å)		
Si1–Si2	2.356	Si2–C3	1.905
Si1–C1	1.930	Si2–C4	1.905
Si1–C2	1.930	Si2–C5	1.903
Si1–Li1	2.566		
	Bond angels (deg)		
Si2–Si1–C1	104.7	Si1–Si2–C5	112.3
Si2–Si1–C2	104.7	C3–Si2–C4	107.5
C1–Si1–C2	104.4	C3–Si2–C5	107.3
Si1–Si2–C3	111.1	C4–Si2–C5	107.3
Si1–Si2–C4	111.1		

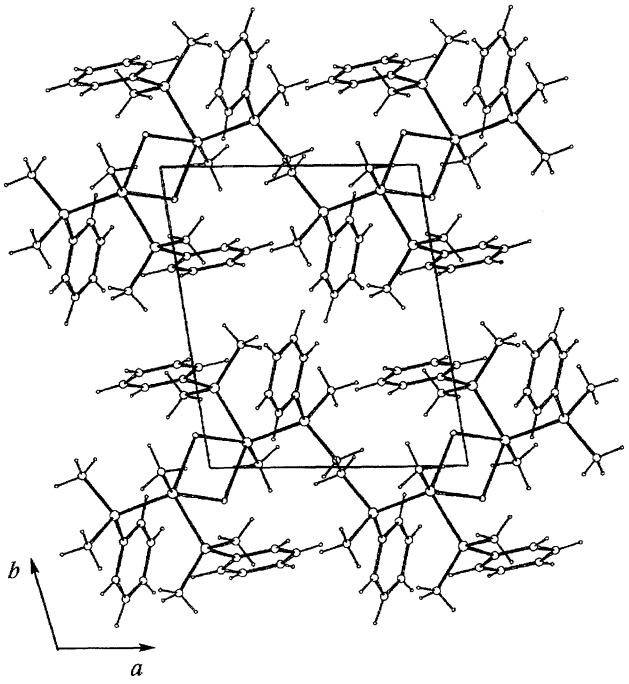


Fig. 4. Perspective view of **1b** in the unit cell down the *c* axis.

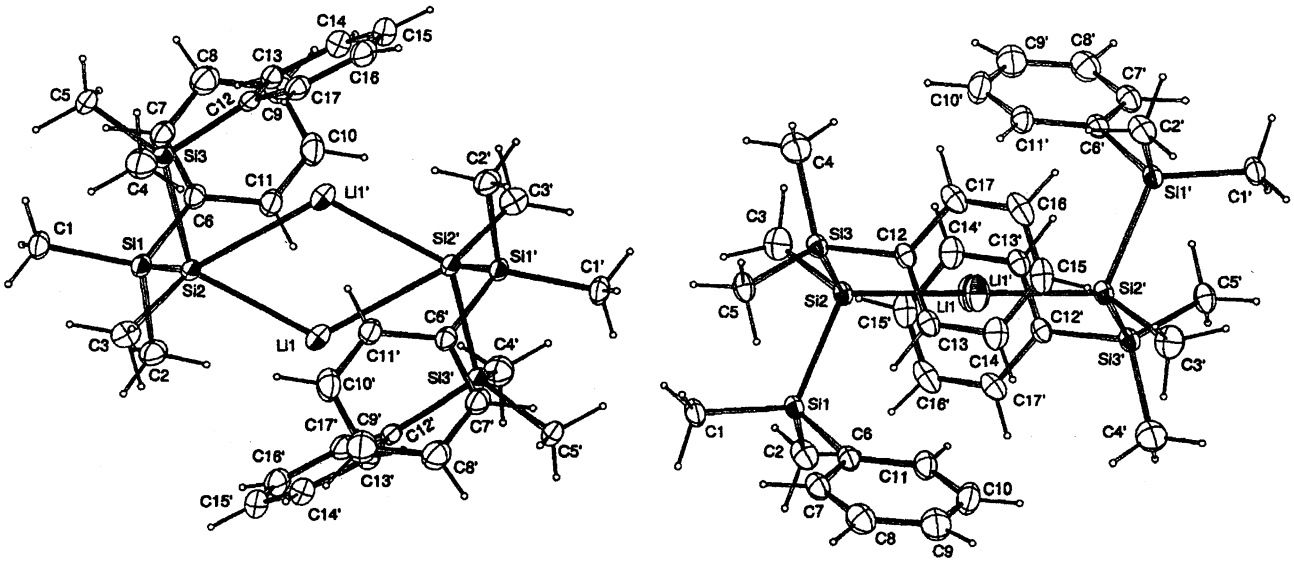


Fig. 3. Molecular structure of **1b** (ellipsoids at the 30% probability level): left, top view; right, side view.

Table 3. List of Atomic Distances (Å) and Angles (deg) of **1b**[a)]

	Atomic distances		
Si1–Si2	2.336(1)	C9–C10	1.386(7)
Si1–C1	1.881(4)	C10–C11	1.393(6)
Si1–C2	1.876(4)	C12–C13	1.402(4)
Si1–C6	1.886(4)	C12–C17	1.403(4)
Si2–Si3	2.361(1)	C12–Li1′	2.348(6)
Si2–C3	1.923(4)	C13–C14	1.389(6)
Si2–Li1	2.664(5)	C13–Li1′	2.483(7)
Si2–Li1′	2.778(7)	C14–C15	1.387(6)
Si3–C4	1.879(4)	C14–Li1′	2.964(8)
Si3–C5	1.876(4)	C15–C16	1.373(4)
Si3–C12	1.895(4)	C15–Li1′	3.296(8)
C6–C7	1.400(4)	C16–C17	1.383(6)
C6–C11	1.399(4)	C16–Li1′	3.193(8)
C7–C8	1.389(6)	C17–Li1′	2.730(8)
C8–C9	1.368(7)	Li1–Li1′	2.645(10)
	Bond angels		
Si2–Si1–C1	115.7(1)	C4–Si3–C5	106.9(1)
Si2–Si1–C2	111.2(1)	C4–Si3–C12	107.9(1)
Si2–Si1–C6	107.3(1)	C5–Si3–C12	106.0(1)
C1–Si1–C2	105.4(1)	Si1–C6–C7	123.1(2)
C1–Si1–C6	109.4(1)	Si1–C6–C11	119.6(2)
C2–Si1–C6	107.7(1)	C7–C6–C11	117.1(3)
Si1–Si2–Si3	103.6(0)	C6–C7–C8	121.4(3)
Si1–Si2–C3	103.8(1)	C7–C8–C9	120.5(4)
Si1–Si2–Li1	110.6(2)	C8–C9–C10	119.9(4)
Si1–Si2–Li1′	108.4(1)	C9–C10–C11	119.8(4)
Si3–Si2–C3	104.7(1)	C6–C11–C10	121.4(3)
Si3–Si2–Li1	128.3(1)	Si3–C12–C13	120.2(2)
Si3–Si2–Li1′	75.2(0)	Si3–C12–C17	123.0(2)
C3–Si2–Li1	103.3(2)	C13–C12–C17	116.5(3)
C3–Si2–Li1′	146.9(2)	C12–C13–C14	121.6(3)
Li1–Si2–Li1′	58.1(2)	C13–C14–C15	120.1(3)
Si2–Si3–C4	110.4(1)	C14–C15–C16	119.5(4)
Si2–Si3–C5	119.3(1)	C15–C16–C17	120.5(4)
Si2–Si3–C12	105.9(1)	C12–C17–C16	121.8(3)

a) Atomic numbers are given in Fig. 3. Standard deviations are in parentheses.

for π-complexed organolithiums,[15)] the lithium atoms are not located directly over the centers of the benzene rings. Recently, Power et al. reported the syntheses and structures of two aryllithiums stabilized by a weak Li–benzene π interaction, in which the lithium atoms are located almost over the centers of the benzene rings.[16)] Since these aryllithiums are monomeric, the benzene rings freely interact with lithium atoms. Because **1b** has a dimeric structure, the benzene rings are not able to interact strongly with lithium atoms for structural reasons. In addition, the bond lengths of C_{ipso}–C_{ortho} (e.g. C12–C13: 1.402(4) Å, C12–C17: 1.403(4) Å) are slightly longer than the other benzene C–C distances. Similar Li–Ph interactions are observed in the molecular structures of $LiC(SiMe_3)_2(SiMe_2Ph)\cdot Et_2O$ and $[\{LiCH(SiMe_2Ph)_2\}_2]$.[17)]

The two Si–Si bond lengths of 2.336(1) and 2.361(1) Å range around the normal value for the Si–Si single bond (2.34 Å). However, one of the Si–Si bonds is slightly elongated due to the Li–Ph interaction. The Si2–C3 bond length of 1.923(4) Å is longer than the normal value (1.88 Å), apparently due to the influence of the negative charge on the silicon atom. Thus, the bond angles around the anionic silicon atom are contracted (the sum of the angles is 312°).

Crystal Structure of 1c. The dimeric structure of 2-lithio-1,1,1,3,3,3-hexamethyl-2-phenyltrisilane **1c** was also established by X-ray diffraction (Fig. 5). The structural parameters are listed in Table 4. A planar four-membered ring is made up of two lithium atoms and two anionic silicon atoms with Li–Si distances of 2.63(1) and 2.78(1) Å and a Li–Si–Li bond angle of 68.3(3)°. The Li–Li distance of 3.03(1) Å in **1c** is longer than those of dimers **1b** (2.65 Å) and tris(trimethylsilyl)silyllithium (2.76 Å), probably due to steric reasons. For **1c**, the electrostatic repulsion between the lithium atoms is increased, since only two benzene rings serve as electron donors to the electron deficient lithium atoms. As found in **1b**, the two lithium atoms are associated with the two phenyl groups. The lithium atom interacts moderately with the *ipso* and *ortho* carbon atoms of the nearby phenyl group (e.g. Li1′–C4: 2.36(1) Å, Li1′–C9: 2.56(1) Å). Of further interest is the fact that **1c** not only has an intramolecular Li–Ph interaction, but also an intermolecular Li···CH_3 agostic interaction. Thus, an intermolecular interaction among the dimers with a Li···CH_3 distance of 2.64(1) Å and Li···H–C distance of 2.25(4) Å is observed, as shown in the perspective view of **1c** (Fig. 6). Since the dimer of **1c** has only two phenyl groups available for the intramolecular interaction with the electron deficient lithium atoms, the C–H bond may serve as an intermolecular donor. Recently, Klinkhammer reported the structure of the super-dimers in tris(trimethylsilyl)silyllithium with an intermolecular Li···CH_3 distance of 2.49 Å,[9)] as found for **1c**.

The Si2–C4 bond length of 1.939(6) Å is considerably longer than the normal value due to the negative charge on the anionic silicon atom. The bond angles around the anionic silicon atom are compressed (the sum of the angles is 312°), as found in **1a** and **1b**. The Si–Si bond lengths of 2.343(2) and 2.346(2) Å are normal.

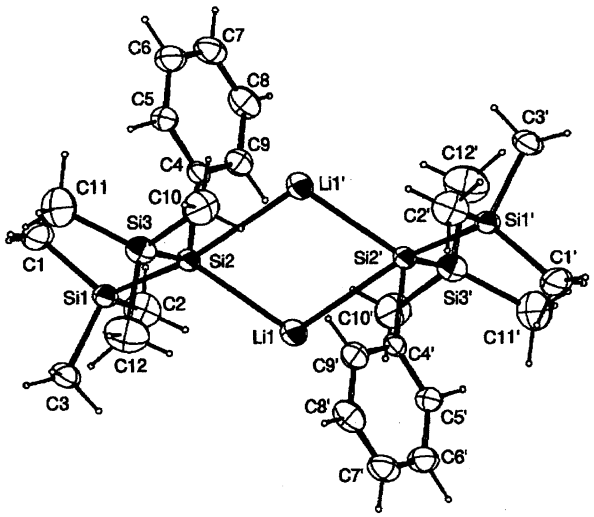


Fig. 5. Molecular structure of **1c** (ellipsoids at the 30% probability level).

Table 4. List of Atomic Distances (Å) and Angles (deg) of **1c**[a)]

	Atomic distances		
Si1–Si2	2.343(2)	C4–C9	1.411(9)
Si1–C1	1.874(9)	C4–Li1′	2.361(12)
Si1–C2	1.877(9)	C5–C6	1.380(9)
Si1–C3	1.886(7)	C5–Li1′	3.173(13)
Si2–Si3	2.346(2)	C6–C7	1.369(10)
Si2–C4	1.939(6)	C6–Li1′	3.929(12)
Si2–Li1	2.630(12)	C7–C8	1.389(10)
Si2–Li1′	2.775(11)	C7–Li1′	4.061(11)
Si3–C10	1.880(9)	C8–C9	1.400(9)
Si3–C11	1.929(9)	C8–Li1′	3.479(12)
Si3–C12	1.884(10)	C9–Li1′	2.556(12)
C4–C5	1.403(9)	Li1–Li1′	3.038(16)
	Bond angles		
Si2–Si1–C1	112.6(3)	Li1–Si2–Li1′	68.3(3)
Si2–Si1–C2	109.1(2)	Si2–Si3–C10	108.9(2)
Si2–Si1–C3	113.8(2)	Si2–Si3–C11	119.0(3)
C1–Si1–C2	107.3(4)	Si2–Si3–C12	107.3(3)
C1–Si1–C3	107.2(3)	C10–Si3–C11	106.6(4)
C2–Si1–C3	106.6(3)	C10–Si3–C12	108.2(4)
Si1–Si2–Si3	107.6(1)	C11–Si3–C12	106.4(4)
Si1–Si2–C4	97.3(2)	Si2–C4–C5	124.6(4)
Si1–Si2–Li1	115.1(2)	Si2–C4–C9	119.8(4)
Si1–Si2–Li1′	146.8(2)	C5–C4–C9	115.5(5)
Si3–Si2–C4	107.3(2)	C4–C5–C6	122.0(6)
Si3–Si2–Li1	111.7(2)	C5–C6–C7	120.9(7)
Si3–Si2–li1′	100.5(2)	C6–C7–C8	120.3(7)
C4–Si2–Li1	116.7(3)	C7–C8–C9	118.3(6)
C4–Si2–Li1′	56.8(2)	C4–C9–C8	122.9(6)

a) Atomic numbers are given in Fig. 5. Standard deviations are in parentheses.

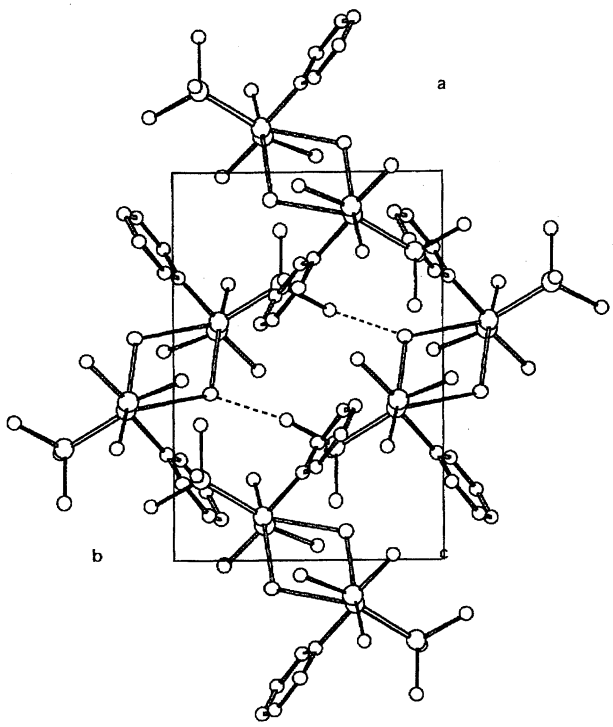


Fig. 6. Perspective view of **1c** in the unit cell down the *a* axis (hydrogen atoms are omitted for clarity). Dotted lines indicate short intermolecular Li···CH_3 contacts.

Conclusion. Unsolvated and aggregated lithiosilanes are available by a lithium–mercury exchange reaction. The tetrameric structure of **1a** and dimeric structures of **1b** and **1c** have been established by single crystal X-ray diffraction. The unsolvated silyllithium derivatives adopt an astonishing range of structures. From results presented here, a common feature of unsolvated silyllithiums would be that there are significant interactions between the lithium atoms and the methyl groups attached to the anionic silicon atom, as shown in **1a**. The structure of the silyllithium adjusts to maximize these interactions. Electrostatic interactions between lithium atoms and aromatic rings are especially strong and appear to play a dominant role in determining the structures, as shown in **1b** and **1c**. However, in **1c**, the phenyl groups do not interact sufficiently with the lithium atoms due to steric reasons, so that intermolecular Li···CH_3 agostic interactions among the dimers are also involved. These structural differences may be due mainly to the steric and electronic nature of substituents.

Experimental

General Procedure. ^{1}H (300 MHz), ^{7}Li (116.6 MHz), ^{13}C (75.5 MHz), and ^{29}Si (59.6 MHz) NMR spectra were recorded on a Bruker AC-300 FT spectrometer. The chemical shifts of ^{1}H, ^{13}C, and ^{29}Si NMR spectra were referenced to external tetramethylsilane. The chemical shifts of ^{7}Li NMR spectra were referenced to external lithium chloride (1.0 M in methanol, 1 M = 1 mol dm^{-3}). Pentane, heptane, and toluene were dried and distilled from sodium benzophenone ketyl. Di-*t*-butylmercury was prepared according to the reported procedure.[18)] Elementary analyses of lithiosilanes are not available due to their instability.

Lithiopentamethyldisilane (1a). A mixture of pentamethyldisilane (3.92 g, 29.6 mmol) and di-*t*-butylmercury (4.23 g, 13.4 mmol) in heptane (ca. 50 ml) was heated at 85 °C for 6 h until the evolution of isobutane gas was ceased. After the solvent was removed in vacuo, bis(pentamethyldisilanyl)mercury (**2a**) was obtained as a yellow oil. Excess lithium metal (ca. 1 g, 140 mmol) in toluene was added to the resulting **2a**. After the mixture was stirred at room temperature for 24 h, the mercury and the remaining lithium metal were separated by decantation. The solvent was removed in vacuo, and the title compound **1a** was obtained (2.16 g, 15.7 mmol) as colorless crystals in 58% yield. The single crystals for X-ray diffraction were obtained by recrystallization from pentane at 0 °C. ^{1}H NMR (toluene-d_8) δ = 0.22 (s, 9 H), 0.33 (s, 6 H); ^{7}Li NMR (toluene-d_8) δ = 2.22 ($\nu_{1/2}$ = 8.5 Hz); ^{13}C NMR (toluene-d_8) δ = −2.51, −0.56; ^{29}Si NMR (toluene-d_8) δ = −80.0 (m), −12.4.

2-Lithio-1,1,2,3,3-pentamethyl-1,3-diphenyltrisilane (1b). A mixture of di-*t*-butylmercury (3.14 g, 10.0 mmol) and 1,1,2,3,3-pentamethyl-1,3-diphenyltrisilane (6.30 g, 20.0 mmol) in heptane (50 ml) was heated at 85 °C for 86 h. The solution turned yellow due to the formation of bis[bis(dimethylphenylsilyl)methylsilyl]-mercury (**2b**). The solvent was removed in vacuo, and then lithium wire (ca. 1 g, 0.1 mol) and toluene (50 ml) were introduced to the reaction mixture. The mixture was stirred for 180 h. After removal of the resulting mercury and unreacted lithium metal, the solvent was evaporated in vacuo to give yellow crystals of the title compound **1b** (4.52 g, 14.1 mmol) in 70.5% yield. The single

Table 5. Summary of the Crystallographic Data

	1a	**1b**	**1c**
Formula	$(C_5H_{15}LiSi_2)_4$	$(C_{17}H_{25}LiSi_3)_2$	$(C_{12}H_{23}LiSi_3)_2$
MW	553.15	641.17	517.02
Color	Colorless	Yellow	Yellow
Crystal size	$0.10 \times 0.25 \times 0.25$	$0.25 \times 0.30 \times 0.30$	$0.25 \times 0.30 \times 0.35$
Crystal shape	Needle	Rhombic plate	Prism
System	Orthorhombic	Triclinic	Monoclinic
Space group (No.)	*Aba*2 (41)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a/Å	9.354(2)	9.714(9)	12.651(4)
b/Å	17.998(4)	11.840(1)	8.588(9)
c/Å	22.881(5)	9.571(2)	15.786(4)
α/°	90	112.25(2)	90
β/°	90	106.61(4)	101.34(2)
γ/°	90	92.10(3)	90
V/Å^3	3852.1(16)	963.2(18)	1681(2)
Z	4	1	2
Temp/K	200	150	286
ρ_{calcd}/g cm^{-3}	0.954	1.105	1.021
μ/cm^{-1}	2.801	2.311	2.518
2θ range/°	$3 < 2\theta < 62$	$3 < 2\theta < 60$	$3 < 2\theta < 60$
Unique data	3852	5658	3731
Refl. used	2769($> 3\sigma(F_o)$)	3874($> 3\sigma(F_o)$)	2026($> 3\sigma(F_o)$)
Parameters	266	291	238
R[a)]	0.0330	0.0575	0.0663
R_w[b)]	0.0345	0.0612	0.0664

a) $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. b) $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

crystals for X-ray diffraction were obtained by recrystallization from heptane at 5 °C. ^{1}H NMR (toluene-d_8) δ = 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) δ = −0.54 ($\nu_{1/2}$ = 5.2 Hz); ^{13}C NMR (toluene-d_8) δ = −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) δ = −123.3 (m), −9.7.

2-Lithio-1,1,1,3,3,3-hexamethyl-2-phenyltrisilane (1c). A mixture of di-*t*-butylmercury (2.90 g, 9.21 mmol) and 1,1,1,3,3,3-hexamethyl-2-phenyltrisilane (4.70 g, 18.6 mmol) in heptane (50 ml) was heated at 85 °C for 86 h. The solution turned yellow due to the formation of bis[bis(trimethylsilyl)phenylsilyl]mercury (**2c**). The solvent was removed in vacuo, and then lithium wire (ca. 0.6 g) and toluene (50 ml) were introduced to the reaction mixture. The mixture was stirred for 20 h. After removal of the resulting mercury and unreacted lithium, the solvent was evaporated in vacuo to give yellow crystals of the title compound **1c** (2.16 g, 8.36 mmol) in 44.9% yield. The single crystals for X-ray diffraction were obtained by recrystallization from a heptane/toluene mixture (10/1) at 5 °C. ^{1}H NMR (toluene-d_8) δ = 0.29 (s, 18 H), 6.61 (t, 1 H, J = 7.4 Hz), 6.82 (dd, 2 H, J = 7.4 Hz, J = 7.7 Hz), 7.50 (d, 2 H, J = 7.7 Hz); ^{7}Li NMR (toluene-d_8) δ = −0.42 ($\nu_{1/2}$ = 10.5 Hz); ^{13}C NMR (toluene-d_8) δ = 3.5, 125.0, 129.2, 136.1, 151.8; ^{29}Si NMR (toluene-d_8) δ = −94.0 (m), −9.9.

Crystal Structure Analyses for 1a, 1b, and 1c. The handling of the sample for X-ray crystallography was carried out under dry nitrogen atmosphere in a glove box. The single crystal of the lithiosilane was sealed in a 0.5 mmϕ glass capillary tube for data collection. Diffraction data were collected on a Rigaku Denki AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). The structure was solved by direct methods with the applied library program UNICS III[19] system and RANTAN 81[20] direct method program. The details of the X-ray experiment for the lithiosilanes are given in Table 5. Tables of positional and thermal parameters and complete interatomic distances and angles have been deposited as Document No. 72022 at the Office of the Editor of Bull. Chem. Soc. Jpn. The X-ray data of **1a**, **1b**, and **1c** have been deposited in Cambridge Structural Database (refcode: ANCEW, REPKUS, REPLAZ).

Computational Methods. The ab initio calculations (HF/3-21G*) were performed by Power Macintosh 7600/200 with Mac-SPARTAN Plus program.[21]

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