Tris(trimethylsilyl)-Substituted Heavy Group 14-Element-Centered Anions: Unsolvated Trimeric Germyllithium and Solvated Dimeric Silyl- and Stannyllithiums

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Keywords: Germanium / Lithium / Silicon / Solid-state structures / Tin

Tris(trimethylsilyl)-substituted group 14-element-centered anion monomers [LiE(SiMe$_3$)$_3$·3THF] (E = Si, Ge, and Sn) can be distilled under reduced pressure to give dimeric silyllithium **4** and stannyllithium **6**, and trimeric germyllithium **5** without pyrolysis products such as dilithiometallanes. The molecular structures of **4**, **5**, and **6** were unequivocally determined by X-ray diffraction. Dimer **4** has a symmetrical bent four-membered-ring structure consisting of two anionic silicon atoms and two cationic lithium atoms with coordinated THF molecules. Dimer **6** has an unsymmetrical distorted four-membered-ring structure consisting of two anionic tin atoms, a bridged unsolvated lithium atom, and a bridged lithium atom solvated by a THF molecule. Interestingly, **6** aggregates to form dimers of dimers by an intermolecular CH$_3$···Li interaction. Trimeric germyllithium **5** forms an equilateral triangular lithium cluster without solvation. Compound **5** has a crystallographic threefold axis with three anionic germanium atoms and three cationic lithium atoms lying in the same plane. The lithium atoms in **5** are stabilized by an intramolecular CH$_3$···Li interaction.

Introduction

Heavy group 14-element-centered anionic species, especially the lithium derivatives, are useful in some applications not only in organic synthesis but also in organometallic chemistry.[1] Despite the large number of reports on syntheses of silyl,[2] germyl,[3] and stannyl[4] anions, much less attention has been paid to their structural studies, which are of special interest for comparing with those of organolithium compounds.[5] Tris(trimethylsilyl)silyllithium (**1**), whose synthesis was first reported by Gilman and Smith in 1967[6] and then modified by Brook in 1982,[7] has been well studied from the viewpoint of its molecular structure,[8] NMR spectroscopic behavior,[9] and its application to the synthesis of the first stable silene species,[10] polysilane dendrimers,[11] and transition metal complexes.[12] Interestingly, thermolysis of **1** leads to the formation of bis(trimethylsilyl)dilithiosilane, which was trapped by [D$_1$]-ethanol and iodomethane to give the corresponding dideuteriosilane and dimethylsilane, respectively.[13] The structural studies on bis(trimethylsilyl)dilithiosilane were performed by mass spectrometry, suggesting that it forms both monomers and dimers, as determined by the molecular-ion peaks. Recently, the crystal structures of dilithiosilanes were revealed by X-ray diffraction method by using more bulky substituents at the anionic silicon center.[14]

Despite the large number of reports on silyllithium compounds, far less attention has been devoted to their germanium and tin analogues. Tris(trimethylsilyl)germyllithium (**2**) was first prepared by Brook et al. in 1986,[15a] and tris(trimethylsilyl)stannyllithium (**3**) by Preuss et al. in 1992.[16a] However, the solvent-separated ion pair [(Me$_3$Si)$_3$Ge][Li·[12]crown-4)$_2$][15b] and the monomeric solvated germyllithiums[15c] have only recently been reported by Stalke et al. More recently still, the solvated monomeric structure of the stannyllithium **3**·3THF has been published.[16b] However, the systematic study of lithium derivatives of the heavy group 14-elements is even more scarce. In the course of the thermolyses of [LiE(SiMe$_3$)$_3$·3THF] (E = Si, Ge, Sn), we found the formation of aggregated structures of heavy group 14-element-centered anionic species, which include a rare trimeric structure of unsolvated germyllithium **5** and an unsymmetrical dimer of stannyllithium **6**. We report herein the structural study of **5** and **6** together with that of a solvated dimer of silyllithium **4**.

Results and Discussion

Synthesis of [LiE(Me$_3$Si)$_3$·3THF] (E = Si, Ge, and Sn)

[LiSi(SiMe$_3$)$_3$·3THF] (**1**), was synthesized by a published procedure,[7] and was purified by recrystallization from *n*-pentane at −20 °C to give colorless crystals. Similarly,

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DOI: 10.1002/ejic.200300919

[$LiGe(SiMe_3)_3$·3THF] (**2**)[15a] and [$LiSn(SiMe_3)_3$·3THF] (**3**)[16a] were also obtained as colorless crystals. The characterization of **1**−**3** was performed by ^{1}H, ^{13}C, ^{29}Si, and ^{7}Li NMR spectroscopy.

Tris(trimethylsilyl)silyllithium

The pyrolysis of **1** in an inert atmosphere at 140−150 °C leads to the formation of dilithiosilane $Li_2Si(SiMe_3)_2$ together with $(Me_3Si)_2$, $Si(SiMe_3)_4$, and $[Si(SiMe_3)_3]_2$, as reported by Lagow et al. in 1990.[13] We also examined the thermolysis of **1** under reduced pressure. Crystals of **1** were placed in a reaction vessel attached to vacuum line and heated slowly under reduced pressure (0.01 Torr). The crystals began to melt at 85 °C, and they completely melted at 100 °C. Bubbles from the interior of the liquid were observed. When the oil bath was heated to 150 °C, the oil of **1** boiled and we were able to obtain colorless crystals by distillation in vacuo. No pyrolysis products such as dilithiosilane, disilane, or tetrakis(trimethylsilyl)silane were detected in the ^{1}H NMR spectra. One THF molecule is coordinated to each $LiSi(SiMe_3)_3$ unit, as determined by ^{1}H NMR spectroscopy. The ^{29}Si NMR resonance of the central anionic silicon is observed at $\delta = -183.9$ ppm as a broad signal; this value is intermediate between the value of $\delta = -189.4$ ppm[8b] for monomeric silyllithium **1** and $\delta = -181.7$ ppm[9] for the unsolvated dimer $[(Me_3Si)_3Si(\mu\text{-}Li)]_2$.

The resulting crystals were recrystallized from *n*-hexane to give colorless single crystals. The distilled silyllithium was characterized by X-ray diffraction, and the molecular structure of $[(Me_3Si)_3Si(\mu\text{-}Li\cdot THF)]_2$ (**4**) is shown in Figure 1. The structural parameters are listed in Table 1. The silyllithium **4** is dimeric in the solid state, although the structure is different from that of the unsolvated dimer $[(Me_3Si)_3Si(\mu\text{-}Li)]_2$.[8d] Two lithium atoms bridge two anionic silicon atoms, and each lithium atom is coordinated by one THF molecule with an O(1)−Li(1) distance of 1.914(5) Å. The lithium-lithium distance is 2.695(9) Å. Up to now, six dimeric silyllithiums have been reported: $[(Me_3Si)_3Si(\mu\text{-}Li)]_2$,[8d] $[tBu_3Si(\mu\text{-}Li)]_2$,[17] $[(PhMe_2Si)_2MeSi(\mu\text{-}Li)]_2$,[18] $[(Me_3Si)_2PhSi(\mu\text{-}Li)]_2$,[18] $[(Me_3SiMe_2Si)_3Si(\mu\text{-}Li)]_2$,[19] and $[(tBuMe_2Si)_2HSi(\mu\text{-}Li\cdot THF)]_2$,[20] all of them containing planar four-membered rings consisting of two anionic silicon and two cationic lithium atoms. However, the silyllithium **4** possesses a folded four-membered ring. The sum of the angles of the tetragon is 354.6(4)° and the dihedral angle between the Li(1)−Si(1)−Li(1)* and Li(1)−Si(1)*−Li(1)* planes is 19°. Both the coordinated THF molecules lie on one side of the ring in order to avoid a steric repulsion of the bulky hypersilyl groups. The Li−O distance of 1.914(5) Å is somewhat shorter than that found in [$LiSi(SiMe_3)_3$·3THF] [1.94(1)−1.97(1) Å][8b][8c] and [$LiSi(SiMe_3)_3$·DME]$_2$·(μ-DME) [1.993(6)−2.003(5) Å].[8a] The Si−Si bond lengths of **4** [2.3406(9)−2.3509(9) Å] are normal. The angles around the anionic silicon atom are significantly contracted, the sum of the Si−Si−Si angles being only 307.68(9)°, a value that is closer to that in monomeric [$LiSi(SiMe_3)_3$·3THF] [307.9(3)°] than that in solvent-free dimeric $[LiSi(SiMe_3)_3]_2$ (322.5°).

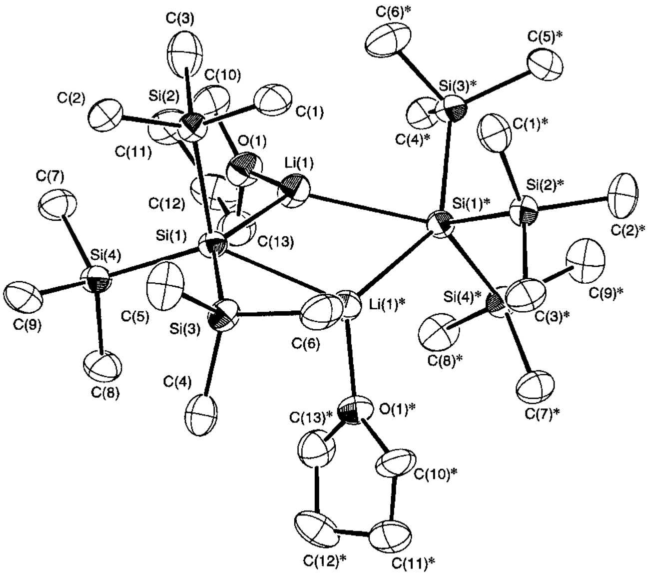

Figure 1. Molecular structure of **4** with 50% probability ellipsoids (H atoms omitted for clarity)

Table 1. Selected atomic distances (Å) and bond angles (°) for **4**; atoms labeled with * are symmetry-equivalent according to the operation *x*, −*y*, −*z* + 1/2

Si(1)−Si(4)	2.3406(9)
Si(1)−Si(3)	2.3464(9)
Si(1)−Si(2)	2.3509(9)
Si(1)−Li(1)	2.689(4)
Si(1)−Li(1)*	2.729(4)
O(1)−Li(1)	1.914(5)
Li(1)−Li(1)*	2.695(9)
Si(4)−Si(1)−Si(3)	102.84(3)
Si(4)−Si(1)−Si(2)	103.98(3)
Si(3)−Si(1)−Si(2)	100.86(3)
Si(4)−Si(1)−Li(1)	108.86(10)
Si(3)−Si(1)−Li(1)	141.29(10)
Si(2)−Si(1)−Li(1)	92.59(10)
Si(4)−Si(1)−Li(1)*	127.60(10)
Si(3)−Si(1)−Li(1)*	83.54(9)
Si(2)−Si(1)−Li(1)*	126.13(10)
Li(1)−Si(1)−Li(1)*	59.66(16)
O(1)−Li(1)−Si(1)	117.8(2)
O(1)−Li(1)−Si(1)*	119.14(19)
Si(1)−Li(1)−Si(1)*	117.64(15)

Tris(trimethylsilyl)germyllithium

Colorless crystals of [$LiGe(SiMe_3)_3$·3THF] (**2**) were placed in a reaction vessel attached to a vacuum line and heated slowly under reduced pressure (0.01 Torr). The crystals began to melt at 90 °C, and they completely melted at 100 °C with bubbling from the interior of the liquid. Similar to the case of **4**, we distilled the liquid at 150 °C under reduced pressure (0.01 Torr) to give colorless crystals. The ^{1}H NMR spectrum of the crystals shows only a singlet at $\delta = 0.41$ ppm assigned to the $SiMe_3$ group; no resonance of coordinated THF molecules was detected. The ^{7}Li NMR signal is observed at $\delta = 2.16$ ppm, which is different from that of **2** ($\delta = 0.58$ ppm), suggesting that the distillate is a solvent-free germyllithium. The resulting crystals were recrystallized from *n*-pentane at −20 °C to give single crystals suitable for X-ray crystallographic analysis.

The molecular structure of $[(Me_3Si)_3Ge(\mu\text{-}Li)]_3$ (**5**) is shown in Figure 2 and the structural parameters are listed in Table 2. Surprisingly, unsolvated germyllithium **5** is a trimeric aggregate in the solid state. The crystal system is hexagonal with the space group $P6_3/m$, and the trimer has a crystallographic threefold axis and a mirror plane. It should be noted that such a trimeric structure is the first such example among all structurally characterized heavy group 14-element-centered anionic species. Trimeric organolithium compounds in the solid state are scarcely known, to the best of our knowledge only three aryllithiums — 2,6-bis(dimethylamino)phenyllithium,[21a] 2,6-di-*tert*-butoxyphenyllithium,[21b] and 2-dimethylamino-6-*tert*-butoxyphenyllithium[21c] — have been characterized by X-ray diffraction. Each lithium atom in **5** is bridging, and three lithium atoms form an equilateral triangle with a Li···Li distance of 3.29(2) Å, which is somewhat longer than those in trimeric aryllithiums (2.96−3.17 Å). Substitution of a carbon in trimeric aryllithiums for a germanium should lead to expansion of the lithium core due to the increased bond length of Li−Ge compared with that of Li−C. Interestingly, each of the lithium atoms is coordinated by carbon atoms on the trimethylsilyl groups, with a C−Li distance of 2.587(10) Å. Although this value is longer than covalent C−Li bond lengths (2.13−2.48 Å) of typical organolithium compounds,[22] it is short enough to be a true CH_3···Li interaction between the lithium and carbon atoms. This is in contrast to the case of trimeric aryllithiums, which are stabilized by coordination of a lone pair of the alkoxy or amino group to the cationic lithium atoms. In **5** the three cationic lithium atoms and three anionic germanium atoms lie in the same plane and one of the trimethylsilyl groups (Si2) is also located in this plane as shown in Figure 2 (bottom). The geometry of the anionic germanium atoms is distorted trigonal bipyramid. The apical Si(2)−Ge(1)−Li(1)** bond angle is 177.6(3)° and equatorial Si(1)−Ge(1)−Li(1), Si(1)′−Ge(1)−Li(1), and Si(1)−Ge(1)−Si(1)′ bond angles are 120.1 (1)°, 120.1 (1)°, and 104.7 (1)°, respectively. The Si(1)−Ge(1)−Si(1)′ angle is very small due to a contribution of the *s*-characteristic anionic charge. The apical bonds Ge(1)−Si(2) and Ge(1)−Li(1)** are slightly longer than the equatorial bonds Ge(1)−Si(1) and Ge(1)−Li(1). The Ge(1)−Li(1) bond of 2.613(10) Å is slightly longer than that found in the monomeric germyllithium **2**.

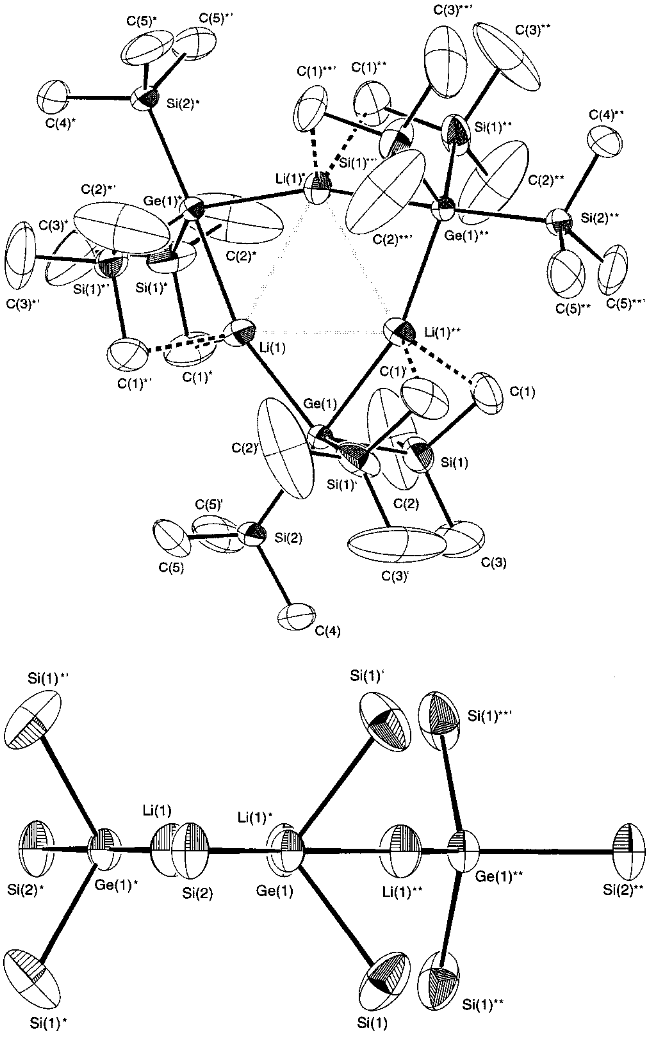

Figure 2. Molecular structure of **5** with 50% probability ellipsoids (H atoms omitted for clarity); dotted lines indicate short intramolecular CH_3···Li interaction

Table 2. Selected atomic distances (Å) and bond angles (°) for **5**; atoms labeled with *, **, and ′ are symmetry-equivalent according to the operations $-y + 1$, $x - y$, z; $-x + y + 1$, $-x + 1$, z; and x, y, $-z + 3/2$; respectively

Ge(1)−Si(1)	2.3801(15)
Ge(1)−Si(1)′	2.3801(15)
Ge(1)−Si(2)	2.3909(17)
Ge(1)−Li(1)	2.613(10)
Ge(1)−Li(1)**	2.623(10)
C(1)−Li(1)**	2.587(10)
C(1)′−Li(1)**	2.587(10)
Li(1)−Li(1)*	3.29(2)
Li(1)−Li(1)**	3.29(2)
Si(1)′−Ge(1)−Si(1)	104.73(12)
Si(1)′−Ge(1)−Si(2)	102.23(4)
Si(1)−Ge(1)−Si(2)	102.23(4)
Si(1)′−Ge(1)−Li(1)	120.12(12)
Si(1)−Ge(1)−Li(1)	120.12(12)
Si(2)−Ge(1)−Li(1)	104.4(3)
Si(1)′−Ge(1)−Li(1)**	76.38(16)
Si(1)−Ge(1)−Li(1)**	76.38(16)
Si(2)−Ge(1)−Li(1)**	177.6(3)
Li(1)−Ge(1)−Li(1)**	77.9(5)
Ge(1)−Li(1)−Ge(1)*	162.1(5)
Li(1)*−Li(1)−Li(1)**	60.001(4)

Tris(trimethylsilyl)stannyllithium

Colorless crystals of $[LiSn(SiMe_3)_3{\cdot}3THF]$ (**3**) were placed in a reaction vessel attached to a vacuum line and heated slowly under reduced pressure (0.01 Torr). The crystals began to melt with bubbling from the interior of the liquid and the colorless oil gradually changed to pale yellow. Colorless crystals were obtained by distillation under reduced pressure. From the ^{1}H NMR spectrum it was concluded that only one THF molecule is coordinated to the two $LiSn(SiMe_3)_3$ units. The ^{119}Sn NMR resonance is observed at $\delta = -878.2$ ppm as an unresolved multiplet due to coupling with the ^{7}Li nuclei. The resulting crystals were recrystallized from *n*-hexane at room temperature for an X-ray analysis. We also succeeded in the structural characterization of the distilled stannyllithium (**6**). The structural parameters are listed in Table 3.

Table 3. Selected atomic distances (Å) and bond angles (°) for **6**; atoms labeled with * are symmetry-equivalent according to the inversion center at $-x + 2$, $-y$, $-z$

Sn(1)−Si(1)	2.558(2)	Sn(2)−Si(5)	2.582(3)
Sn(1)−Si(2)	2.573(3)	Sn(2)−Li(1)	2.764(15)
Sn(1)−Si(3)	2.583(3)	Sn(2)−Li(2)	2.857(17)
Sn(1)−Li(1)	2.796(15)	O(1)−Li(2)	1.907(17)
Sn(1)−Li(2)	2.926(18)	C(3)−Li(1)*	2.392(17)
Sn(2)−Si(4)	2.570(3)	Li(1)−C(3)*	2.392(17)
Sn(2)−Si(6)	2.575(3)	Li(1)−Li(2)	2.74(2)
Si(1)−Sn(1)−Si(2)	102.48(9)	Si(4)−Sn(2)−Li(2)	118.8(4)
Si(1)−Sn(1)−Si(3)	101.70(10)	Si(6)−Sn(2)−Li(2)	136.4(4)
Si(2)−Sn(1)−Si(3)	99.63(12)	Si(5)−Sn(2)−Li(2)	88.3(4)
Si(1)−Sn(1)−Li(1)	127.4(3)	Li(1)−Sn(2)−Li(2)	58.2(4)
Si(2)−Sn(1)−Li(1)	125.5(3)	C(19)−O(1)−C(22)	111.2(10)
Si(3)−Sn(1)−Li(1)	91.2(3)	C(19)−O(1)−Li(2)	119.1(11)
Si(1)−Sn(1)−Li(2)	109.6(3)	C(22)−O(1)−Li(2)	129.7(10)
Si(2)−Sn(1)−Li(2)	89.1(4)	Si(1)−C(3)−Li(1)*	175.7(7)
Si(3)−Sn(1)−Li(2)	144.8(3)	C(3)*−Li(1)−Li(2)	133.2(9)
Li(1)−Sn(1)−Li(2)	57.1(5)	C(3)*−Li(1)−Sn(2)	114.2(6)
Si(4)−Sn(2)−Si(6)	101.24(10)	C(3)*−Li(1)−Sn(1)	116.2(6)
Si(4)−Sn(2)−Si(5)	101.79(9)	Sn(2)−Li(1)−Sn(1)	122.8(5)
Si(6)−Sn(2)−Si(5)	100.38(10)	O(1)−Li(2)−Sn(2)	117.8(9)
Si(4)−Sn(2)−Li(1)	125.7(3)	O(1)−Li(2)−Sn(1)	122.3(8)
Si(6)−Sn(2)−Li(1)	85.3(3)	Sn(2)−Li(2)−Sn(1)	115.2(5)
Si(5)−Sn(2)−Li(1)	130.2(3)		

The stannyllithium $\{[(Me_3Si)_3Sn]_2(\mu\text{-}Li)(\mu\text{-}Li{\cdot}THF)\}$ (**6**) is dimeric in the solid state and the dimer has an unsymmetrical structure, as shown in Figure 3. Although each lithium atom is coordinated by a THF molecule in the case of silyllithium **4**, stannyllithium dimer **6** has only one THF molecule bound to Li(2), with an O(1)−Li(2) bond length of 1.907(17) Å. The two anionic tin and two cationic lithium atoms make a four-membered ring, which has a bent structure with a dihedral angle of 21° between the Sn(1)−Li(1)−Li(2) and Sn(2)−Li(1)−Li(2) planes. The Li(1)−Sn(1)−Li(2) and Li(1)−Sn(2)−Li(2) bond angles are 57.1(5)° and 58.2(4)°, respectively. These values are smaller than that found in silyllithium **4**. The sum of the three Si−Sn−Si angles in **6** is 303.8(3)° at Sn(1) and 303.4(2)° at Sn(2); these values are significantly contracted from the ideal tetrahedral value of 328.5° and are less than that found in silyllithium **4** [the sum of three angles of Si−Si−Si is 307.68(9)°]. However, they are larger than that found in the monomeric structure of **3** (total 296.2°).[16b] Of particular interest is the fact that two $[(Me_3Si)_3Sn(\mu\text{-}Li)]_2$ dimers construct aggregates through short Li(1)···C(3)* and C(3)···Li(1)* interactions, as shown in Figure 4. The Li(1)···C(3)* distance of is 2.392(17) Å and the Si(1)−C(3)−Li(1)* angle is 175.7(7)°. These structures are therefore so-called "super-dimers"; super-dimeric structures of group 14-element-centered anionic species have also been observed in the series $[(Me_3Si)_3Si(\mu\text{-}M)]_2$ (M = Li, Na, K, Rb, and Cs)[8d] and $[Ph(Me_3Si)_2Si(\mu\text{-}Li)]_2$.[23] In his paper[8d] Klinkhammer described $CH_3{\cdots}M$ interactions, which include a dipole-ion component and C−H donor/M^+ − acceptor component. Although these $CH_3{\cdots}M$ interactions are weaker than the coordination of solvent molecules, they are strong enough to stabilize a naked lithium atom Li(1) in the case of **6**. The conformation of the trimethylsilyl groups at the anionic Sn(1) and Sn(2) centers is eclipsed. The Sn(1)−Li(2) [2.926(18) Å] and Sn(2)−Li(2) [2.857(17) Å] bond lengths are somewhat longer than those of Sn(1)−Li(1) [2.796(15) Å] and Sn(2)−Li(1) [2.764(17) Å] for steric reasons. The Sn(1)−Li(1)−Sn(2) angle of 122.8(5)° is larger than that of Sn(1)−Li(**2**)−Sn(2) [115.2(5)°].

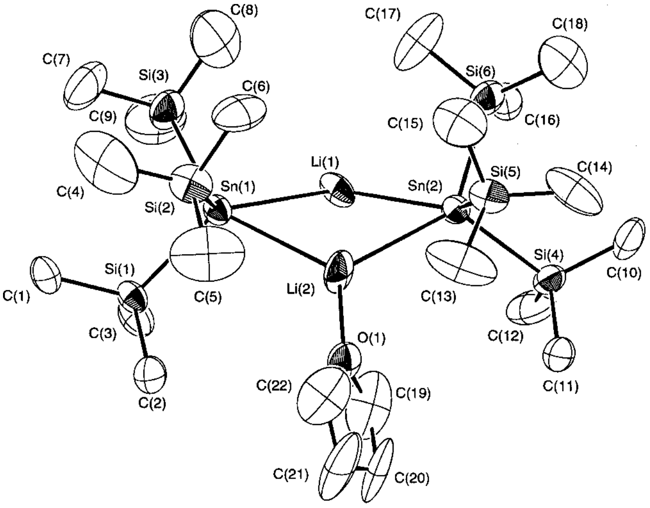

Figure 3. Molecular structure of **6** with 50% probability ellipsoids (H atoms omitted for clarity)

It is interesting that all three group 14-element-centered anionic species $LiE(SiMe_3)_3$ (E = Si, Ge, and Sn) **4**−**6** represent different aggregates in the solid state. It is not clear for the moment why they form different types of clusters. One of the possible reasons might be associated with the difference in Allred−Rochow electronegativities[24] of the central elements (Si = 1.74, Ge = 2.02, Sn = 1.72): the more electronegative germanium atom forms amore stable germyllithium, which does not require additional stabilization by a polar solvent (THF).

Conclusion

Tris(trimethylsilyl)-substituted group 14-element-centered anionic species $[LiE(SiMe_3)_3{\cdot}3THF]$ (E = Si, Ge, Sn)

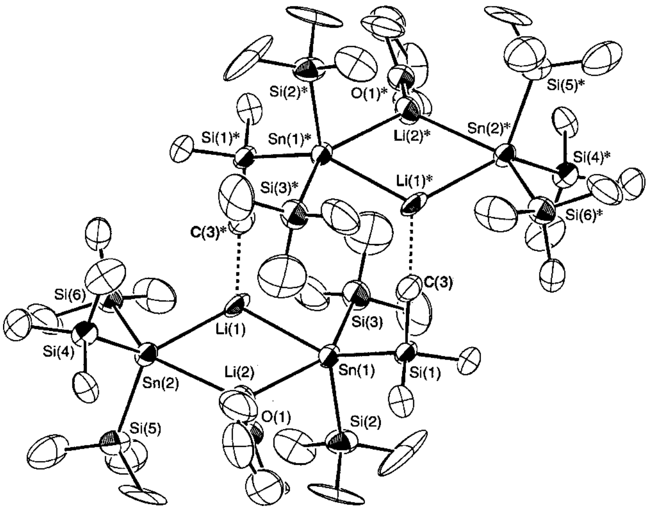

Figure 4. Formation of a dimer of dimers found in **6**; dotted lines indicate short intermolecular $CH_3\cdots Li$ interactions; C−Li distances are listed in Table 3

were heated at 150 °C under reduced pressure to give the corresponding aggregated anionic species with loss of coordinated THF molecules. The dimeric structures of silyllithium $[(Me_3Si)_3Si]_2(\mu\text{-}Li\cdot THF)_2$ (**4**) and stannyllithium $[(Me_3Si)_3Sn]_2(\mu\text{-}Li)(\mu\text{-}Li\cdot THF)$ (**6**) and the trimeric strucrture of unsolvated germyllithium $[(Me_3Si)_3Ge]_3(\mu\text{-}Li)_3$ (**5**) were unequivocally determined by X-ray crystallographic analyses. Silyllithium **4** and stannyllithium **6** contain distorted four-membered rings consisting of two anionic center atoms and two bridged lithium atoms. Both lithium atoms in **4** are coordinated by a THF molecule; **6** has only one coordinated THF molecule connected to a lithium atom and forms a dimer of dimers by an intermolecular $CH_3\cdots Li$ interaction. Trimeric germyllithium **5** has a crystallographic threefold axis and three anionic germanium atoms and three cationic lithium atoms lying in the same plane. The lithium atoms in **5** are stabilized by an intramolecular $CH_3\cdots Li$ interaction.

Experimental Section

General Procedure: All experiments were performed under an inert atmosphere of argon by standard vacuum-line techniques. *n*-Pentane and *n*-hexane were dried over potassium mirrors and degassed by freeze-pump-thaw cycles and then distilled prior to use. ^1H (400 MHz), ^{13}C (100 MHz), and ^7Li (155 MHz) NMR spectra were recorded on a Varian Inova 400 spectrometer, and ^{29}Si (60 MHz) and ^{119}Sn (112 MHz) NMR spectra were recorded on a JEOL AL-300 spectrometer. ^1H, ^{13}C, and ^{29}Si chemical shifts are referenced to $SiMe_4$ as an external standard. The chemical shifts in the ^7Li NMR spectra are referenced to external LiCl (1.0 M in methanol). The ^{119}Sn NMR chemical shifts are referenced to $SnMe_4$ as an external standard. Elemental analyses could not be performed because of the high instability of the anion species in air.

Preparation of $[(Me_3Si)_3Si(\mu\text{-}Li\cdot THF)]_2$ (4): Tris(tetrahydrofuran)tris(trimethylsilyl)silyllithium (**1**)[7] (0.110 g, 0.234 mmol) was placed in a dry 6-mm diameter reaction vessel equipped with a side tube. After evacuation of the tube with a rotary pump, it was heated slowly in an oil bath to 150 °C in vacuo. Melting of **1** was observed at 85 °C, and bubbling from the interior of the liquid was observed at 100 °C. When the temperature of the oil bath had reached 150 °C, the vapor went to the top of the vessel and was cooled in the side tube to become a colorless oil, and then colorless crystals of **4** were obtained (0.066 g, 86%) at room temperature. The resulting crystals were recrystallized from *n*-hexane (0.15 mL) to give single crystals suitable for an X-ray crystallographic analysis. ^1H NMR ($[D_6]$benzene): $\delta = 0.46$ (s, 54 H), 1.3−1.4 (m, 9.4 H, THF), 3.4−3.5 (m, 9.4 H, THF) ppm. ^7Li NMR ($[D_6]$benzene): $\delta = 1.99$ ppm. ^{13}C NMR ($[D_6]$benzene): $\delta = 6.5$, 25.2 (THF), 68.7 (THF) ppm. ^{29}Si NMR ($[D_6]$benzene): $\delta = -5.9$ (Me_3Si), −183.9 (br., SiLi) ppm.

Preparation of $[(Me_3Si)_3Ge(\mu\text{-}Li)]_3$ (5): Tris(tetrahydrofuran)tris(trimethylsilyl)germyllithium (**2**)[15] (0.105 g, 0.204 mmol) was placed in a dry 7-mm diameter reaction vessel equipped with a side tube. After evacuation of the tube with a rotary pump, it was heated slowly in an oil bath to 150 °C in vacuo. Melting of **2** was observed at 90 °C, and bubbling from the interior of the liquid was observed at 100 °C. When the temperature of the oil bath had reached 140 °C, the vapor went to the top of the vessel and was cooled in the side tube to become a colorless oil, and then colorless crystals of **5** were obtained (0.060 g, 98%) at room temperature. The resulting crystals were recrystallized from *n*-pentane (0.3 mL) to give single crystals suitable for an X-ray crystallographic analysis. ^1H NMR ($[D_6]$benzene): $\delta = 0.41$ (s, 27 H) ppm. ^7Li NMR ($[D_6]$benzene): $\delta = 2.16$ ppm. ^{13}C NMR ($[D_6]$benzene): $\delta = 6.4$ ppm. ^{29}Si NMR ($[D_6]$benzene): $\delta = -4.9$ ppm.

Preparation of $\{[(Me_3Si)_3Sn]_2(\mu\text{-}Li)(\mu\text{-}Li\cdot THF)\}$ (6): Tris(tetrahydrofuran)tris(trimethylsilyl)stannyllithium (**3**)[16] (0.130 g, 0.232 mmol) was placed in a dry 6-mm diameter reaction vessel equipped with a side tube. After evacuation of the tube with a rotary pump, it was heated slowly in an oil bath to 150 °C in vacuo. Melting of **3** was observed at 100 °C, and bubbling from the interior of the liquid was observed. When the temperature of the oil bath had reached 140 °C, the vapor went to the top of the vessel and was cooled in the side tube to become a colorless oil, and then colorless crystals of **6** were obtained (0.056 g, 63%) at room temperature. The resulting crystals were recrystallized from *n*-pentane (0.1 mL) to give single crystals suitable for an X-ray crystallographic analysis. ^1H NMR ($[D_6]$benzene): $\delta = 0.56$ (s, 54 H). 1.2−1.3 (m, 4.6 H, THF), 3.5−3.6 (m, 4.6 H, THF) ppm. ^7Li NMR ($[D_6]$benzene): $\delta = 1.20$ ppm. ^{13}C NMR ($[D_6]$benzene): $\delta = 7.3$, 25.1 (THF), 69.2 (THF) ppm. ^{29}Si NMR ($[D_6]$benzene): $\delta = -12.4$ ppm. ^{119}Sn NMR ($[D_6]$benzene): $\delta = -878.2$ (br) ppm.

X-ray Crystal Structure Analyses for 4, 5, and 6: Crystal data for all structures are presented in Table 4. Data were collected with a MacScience DIP2030 imaging plate diffractometer employing graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods by means of SIR-92[25] (for **4** and **5**) and Multan78[26] (for **6**) refined with all data on F^2 by means of SHELXL-97.[27]
CCDC-225267, -225265, and -225266 (for **4**, **5**, and **6**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Summary of crystallographic data for **4**, **5**, and **6**

	4	**5**	**6**
Formula	$C_{32}H_{82}Li_2O_2Si_8$	$C_9H_{27}GeLiSi_3$	$C_{22}H_{62}Li_2OSi_6Sn_2$
Mol. mass	737.58	299.11	762.52
Cryst system	orthorhombic	hexagonal	monoclinic
Space group	*Pcan*	$P6_3/m$	$P2_1/n$
a (Å)	15.8010(7)	13.8490(8)	14.136(1)
b (Å)	16.4830(8)	13.849	19.776(2)
c (Å)	18.6960(5)	16.3550(8)	15.246(1)
α (°)	90	90	90
β (°)	90	90	97.608(6)
γ (°)	90	120	90
V (Å^3)	4869.3(3)	2716.5(2)	4224.6(7)
Z	4	6	4
T (K)	295	200	295
$\rho_{\mathrm{calcd.}}$ (g cm^{-3})	1.006	1.097	1.199
F(000)	1632	948	1568
θ range (deg)	2.80−26.45	2.11−27.96	2.70−26.45
No. of unique reflns	5000	4358	8550
No. of reflns used for refinement	4101	2261	4564
No. of refined params	201	71	299
$R1$ [$I > 2\sigma(I)$]	0.0581	0.0570	0.0732
$wR2$ (all data)	0.1790	0.1901	0.1636
GOF	1.345	1.412	1.407
Max/min $\Delta\rho$ (e·Å^{-3})	0.763/−0.383	0.627/−0.539	0.596/−0.597

Acknowledgments

We thank the Ministry of Education, Culture, Sports, Science and Technology, Japan, for Grants-in Aid for Scientific Research (Grant No. 13740359). We wish to thank Dr. V. Ya. Lee of the University of Tsukuba for helpful discussions and for comments on this manuscript.

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Received December 10, 2003
Early View Article
Published Online May 13, 2004