# Novel Chelated Diorganolithate Ion $[\overline{\mathrm{CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMe_2C}}\mathrm{H_2}]^-$ and Highly Crowded Chelated Organomercury Compound $[\overline{\mathrm{CH_2SiMe_2C(SiMe_3)_2HgC(SiMe_3)_2SiMe_2C}}\mathrm{H_2}]$

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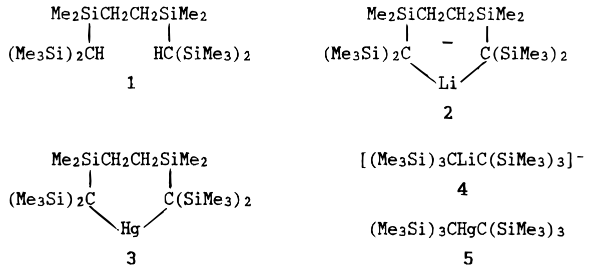
The compound $\{(\mathrm{Me_3Si})_2\mathrm{CHSiMe_2CH_2}\}_2$ has been prepared and metalated with MeLi to give the chelated lithate ion $[\overline{\mathrm{CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMe_2C}}\mathrm{H_2}]^-$, which was isolated as its $[\mathrm{Li(TMEDA)_2}]$ salt (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). The potential of this salt as a source of the very bulky dicarbanionic ligand $\{(\mathrm{Me_3Si})_2\bar{\mathrm{C}}\mathrm{SiMe_2CH_2}\}_2$ was demonstrated by its reaction with $\mathrm{HgBr_2}$ in THF to give the chelated mercury compound $[\overline{\mathrm{CH_2SiMe_2C(SiMe_3)_2HgC(SiMe_3)_2SiMe_2C}}\mathrm{H_2}]$. The crystal structures of the salt and the mercurial compound were determined.

## Introduction

Use of the very bulky "trisyl" ligand $(\mathrm{Me_3Si})_3\mathrm{C}$ [strictly the anionic $(\mathrm{Me_3Si})_3\mathrm{C}^-$], $\mathrm{R}^1$, and the related ligand $(\mathrm{PhMe_2Si})_3\mathrm{C}$, $\mathrm{R}^2$, has made possible the isolation of many unusual organometallic species,[1] including several of previously unknown types such as the following: (a) The first examples of the long-sought but previously unknown diorganolithate and -sodate ions, viz. $[\mathrm{MR}^1{}_2]^-$, M = Li[2] or Na,[3] and the novel polymeric ionic compounds $(\mathrm{MR}^1)_n$, M = K[4] or Rb,[5] and $(\mathrm{MR}^2)_n$, M = Na[3] or K;[4] (b) the first diorganoargentate, $\mathrm{AgR}^1{}_2$,[6] and first dialkylcuprate, $\mathrm{CuR}^1{}_2$;[7] (c) the compounds $\mathrm{MgR}^1{}_2$ and $\mathrm{MnR}^1{}_2$,[8,9] the first derivatives of these metals shown to be two-coordinate in the solid phase; (d) the first structurally-characterized organotrihydro-, trifluoro-, and tris(alkanethiolato)aluminates, $\{[\mathrm{Li(THF)_2}][\mathrm{AlR^2H_3}]\}_2$,[10a] $\{[\mathrm{Li(THF)}][\mathrm{AlR^1F_3}]\}_4$,[10a] and $(\mathrm{THF})\mathrm{LiAlR^1(SMe)_3}$;[10b] (e) the first organomanganese and -cobalt halides, $\mathrm{R^1MCl}$ (as their lithium chloride complexes $[\mathrm{Li(THF)_4}][\mathrm{R^1{}_3M_3Cl_4(THF)}]$;[11] (f) the first solvent-free σ-bonded diorganolanthanides $\mathrm{MR}^1{}_2$, M = Yb[12a] or Eu,[12b] and the first lanthanide metal analogue of a Grignard reagent, $\mathrm{YbR^1I}$;[12a] (g) the first σ-bonded organolead(II) compounds $[(\mathrm{PbR^1Cl})_3]$[13a] and $[(\mathrm{PbR^2Cl})_2]$;[13b] (h) the first silicon cyanate, $\mathrm{SiR^1Me_2OCN}$.[14] It seemed to us likely that a potentially chelating dicarbanionic ligand with similar bulk around both ligating carbon atoms would provide a new range of interesting species, and so we synthesized the compound **1** (Chart 1) and metalated it to give the chelated lithate anion **2**, which was isolated as its $[\mathrm{Li(TMEDA)_2}]$ salt (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). In order to demonstrate the potential of $[\mathrm{Li(TMEDA)_2}][\mathbf{2}]$ as a source of the chelating ligand $(\mathrm{Me_3Si})_2\bar{\mathrm{C}}\mathrm{SiMe_2CH_2CH_2SiMe_2}\bar{\mathrm{C}}(\mathrm{SiMe_3})_2$, we used it to prepare the corresponding chelated organomercury compound **3**.

**Chart 1**



$[(\mathrm{Me_3Si})_3\mathrm{CLiC(SiMe_3)_3}]^-$ **4**

$(\mathrm{Me_3Si})_3\mathrm{CHgC(SiMe_3)_3}$ **5**

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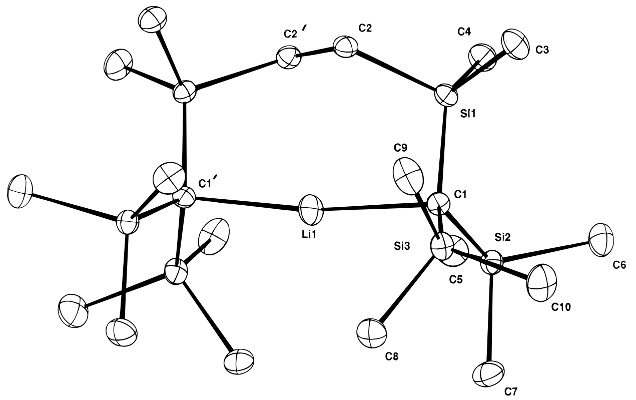

**Figure 1.** Structure of the anion **2**.

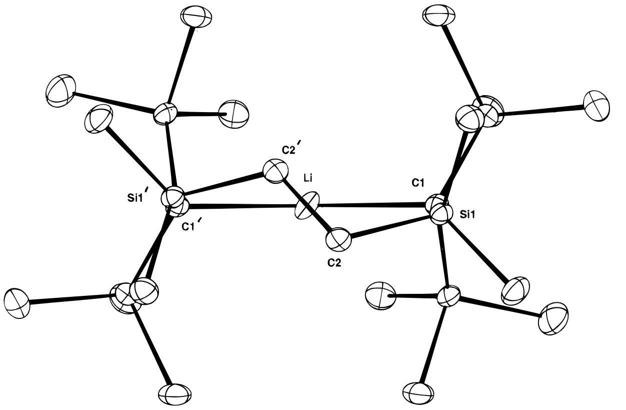

**Figure 2.** Conformation of the seven-membered ring in the anion **2**.

## Results and Discussion

Compound **1** was prepared, as a low melting solid, by the reaction shown in eq 1.

$$2(Me_3Si)_2CHLi + ClMe_2SiCH_2CH_2SiMe_2Cl \rightarrow (Me_3Si)_2CHSiMe_2CH_2CH_2SiMe_2CH(SiMe_3)_2 \quad (1)$$

**1**

It was metalated with MeLi in THF (the method used to prepare the anion **4** from $(Me_3Si)_3CH$[15]), and the resulting lithium compound was treated in diethyl ether with TMEDA to give the solid salt $[Li(TMEDA)_2]$[**2**], which was recrystallized from diethyl ether to give crystals in 66% yield. The same product was obtained directly when the metalation with MeLi in THF was carried out in the presence of TMEDA.

An X-ray diffraction study showed that the product was the lithate $[Li(TMEDA)_2]$[**2**], and the structure of the anion **2** is shown in Figures 1 and 2, the latter included to display the form of the ring system. As far as we are aware, **2** is only the second example of a simple lithate anion. (A more complex tetraaryllithate ion, in the salt $[Na(TMEDA)]_3[LiPh_4]$, has been reported.[16]) In THF-$d_8$, $[Li(TMEDA)_2]$[**2**] showed two (overlapping) $^7Li$ NMR signals, as would be expected if it retained its identity in solution. Surprisingly, crystals of $[Li(TMEDA)_2]$[**2**] showed no visible change on exposure to the air for ca. 10 min.

**Table 1. Bond Lengths (Å) and Angles (deg) in the Anion 2**[a]

| | | | |
|---|---|---|---|
| | Bond Lengths | | |
| Li(1)−C(1) | 2.156(4) | Si(1)−C(1) | 1.831(4) |
| Si(1)−C(2) | 1.894(4) | Si(1)−C(3) | 1.899(5) |
| Si(1)−C(4) | 1.887(5) | Si(2)−C(1) | 1.823(4) |
| Si(2)−C(5) | 1.882(5) | Si(2)−C(6) | 1.881(5) |
| Si(2)−C(7) | 1.889(4) | Si(3)−C(1) | 1.833(4) |
| Si(3)−C(8) | 1.885(5) | Si(3)−C(9) | 1.890(5) |
| Si(3)−C(10) | 1.884(5) | C(2)−C(2)′ | 1.551(8) |
| | Bond Angles | | |
| C(1)′−Li(1)−C(1) | 171.4(7) | C(1)−Si(1)−C(4) | 115.7(2) |
| C(1)−Si(1)−C(2) | 110.8(2) | C(4)−Si(1)−C(2) | 103.2(2) |
| C(1)−Si(1)−C(3) | 115.7(2) | C(4)−Si(1)−C(3) | 103.3(2) |
| C(2)−Si(1)−C(3) | 107.0(2) | C(1)−Si(2)−C(5) | 114.2(2) |
| C(1)−Si(2)−C(6) | 114.2(2) | C(5)−Si(2)−C(6) | 105.9(2) |
| C(1)−Si(2)−C(7) | 115.3(2) | C(5)−Si(2)−C(7) | 102.7(2) |
| C(6)−Si(2)−C(7) | 103.1(2) | C(1)−Si(3)−C(8) | 111.4(2) |
| C(1)−Si(3)−C(10) | 116.8(2) | C(8)−Si(3)−C(10) | 105.8(2) |
| C(1)−Si(3)−C(9) | 114.7(2) | C(8)−Si(3)−C(9) | 102.8(2) |
| C(10)−Si(3)−C(9) | 104.0(2) | Si(2)−C(1)−Si(3) | 114.1(2) |
| Si(2)−C(1)−Si(1) | 116.1(2) | Si(3)−C(1)−Si(1) | 117.5(2) |
| Si(1)−C(1)−Li(1) | 96.6(4) | Si(2)−C(1)−Li(1) | 115.3(2) |
| Si(3)−C(1)−Li(1) | 93.5(2) | C(2)′−C(2)−Si(1) | 115.8(4) |

[a] Symmetry transformations used to generate equivalent atoms: ′, $-x$, $-y$, $z$.

The bond distances and angles in **2** are shown in Table 1. (Data for the cation, a well-known species, are provided as Supporting Information.) Except for the chelation, the overall structure of **2** is superficially similar to that of **4** but with the obvious difference that the C−Li−C linkage is bent, at an angle of 171.4(7)°, whereas in **4** it is linear. However, there is another significant difference in that in **4** (as in the related ions $[\{(Me_3Si)_3C\}_2M]^-$ with M = Na,[3] Ag,[6] or Cu[7]) two Me groups on each Si point slightly inward toward the metal and one directly outward, whereas in **2** one carbon atom on Si(1) necessarily points inward forcing the other two outward, and two of the Me groups on Si(3) still point inward but only one of those on Si(2).

The low quality of the crystallographic data for **4**[2] rules out a detailed comparison with the parameters for **2**, but the following features are noteworthy: (a) Whereas in **4** the Li−C−Si angles are in the range 101−107° with a mean of ca. 104.3° (over two independent anions), in **2** the endocyclic Li−C−Si angle is constrained to 96.6(4)°. However, the configuration of the $CSi_3$ system remains much as in **4**, the mean Si−C(1)−C angle being 115.9° in **2** and 114.4° in **4**, but because of the chelation it is tilted with respect to the Li−C(1) axis, and it is also twisted to give a Li−C(1)−Si(3) angle of only 93.5(2)° and an Li−C−Si(2) angle of 115.3(2)°. (This brings C(8) to within 3.04 Å of the Li atom; there is an even shorter nonbonded contact of 2.80 Å across the ring between Li and C(2)). The $C-SiMe_3$ bonds in **2** are short in both **2** (mean 1.83 Å) and **4** (mean 1.82 Å), and this feature is discussed below.

Reaction of the salt $[Li(TMEDA)_2]$[**2**] with $HgBr_2$ in THF gave **3** in good yield. It melted at 216−218 °C (cf. 263−265 °C for **5**[17]); the liquid began to give off gas bubbles at ca. 310 °C (cf. ca. 300 °C for **5**[18]) and darkened above ca. 330 °C, with deposition of Hg beads.

The structure of **3** is shown in Figure 3, and the bond distances and angles are in Table 2. (The form of the

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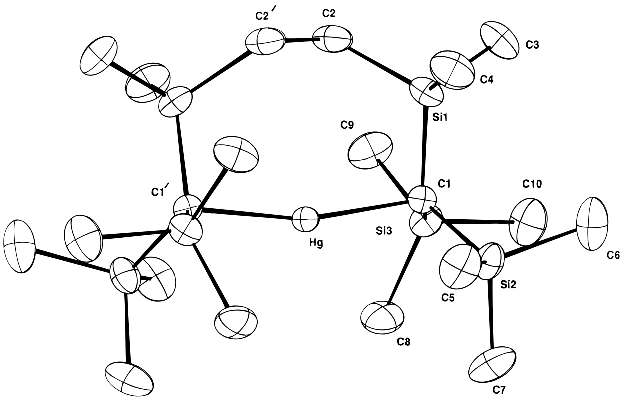

**Figure 3.** Structure of **3**.

**Table 2. Bond Lengths (Å) and Angles (deg) in 3**[a]

| | | | |
|---|---|---|---|
| **Bond Lengths** | | | |
| Hg−C(1) | 2.132(3) | Si(1)−C(3) | 1.871(4) |
| Si(1)−C(2) | 1.887(5) | Si(1)−C(4) | 1.885(5) |
| Si(1)−C(1) | 1.901(3) | Si(2)−C(7) | 1.867(6) |
| Si(2)−C(5) | 1.875(4) | Si(2)−C(1) | 1.873(4) |
| Si(2)−C(6) | 1.884(5) | Si(3)−C(9) | 1.863(5) |
| Si(3)−C(10) | 1.876(4) | Si(3)−C(8) | 1.875(5) |
| Si(3)−C(1) | 1.881(3) | C(2)−C(2)′ | 1.562(7) |
| **Bond Angles** | | | |
| C(1)′−Hg−C(1) | 165.8(2) | C(3)−Si(1)−C(2) | 105.2(2) |
| C(3)−Si(1)−C(4) | 106.7(2) | C(2)−Si(1)−C(4) | 104.7(3) |
| C(3)−Si(1)−C(1) | 111.9(2) | C(2)−Si(1)−C(1) | 114.1(2) |
| C(4)−Si(1)−C(1) | 113.5(2) | C(7)−Si(2)−C(5) | 103.9(3) |
| C(7)−Si(2)−C(1) | 114.0(2) | C(5)−Si(2)−C(1) | 112.7(2) |
| C(7)−Si(2)−C(6) | 106.8(3) | C(5)−Si(2)−C(6) | 106.3(3) |
| C(1)−Si(2)−C(6) | 112.4(2) | C(9)−Si(3)−C(10) | 107.4(2) |
| C(9)−Si(3)−C(8) | 104.2(3) | C(10)−Si(3)−C(8) | 106.5(3) |
| C(9)−Si(3)−C(1) | 113.7(2) | C(10)−Si(3)−C(1) | 112.0(2) |
| C(8)−Si(3)−C(1) | 112.5(2) | Si(2)−C(1)−Si(3) | 113.6(2) |
| Si(2)−C(1)−Si(1) | 114.9(2) | Si(3)−C(1)−Si(1) | 112.9(2) |
| Si(2)−C(1)−Hg | 109.4(2) | Si(3)−C(1)−Hg | 106.8(2) |
| Si(1)−C(1)−Hg | 97.6(2) | C(2)′−C(2)−Si(1) | 121.4(5) |

[a] Symmetry transformations used to generate equivalent atoms: ′, $-x$, $y$, $-z + {}^{3}/_{2}$.

ring is, after allowance for the fact that it has the hand opposite to that observed for **2**, very similar to that of **2** and need not be shown separately.) Again the most obvious feature is that the C−M−C bond is bent, at an angle of 165.8(2)°, in contrast to that in **5**; the bending is somewhat larger than that in **2**. The C−Hg bond length, 2.132(3) Å, is not significantly different from that in **5**, 2.142(4) Å,[17] or $\{(MeOMe_2Si)(Me_3Si)_2C\}_2Hg$, 2.07(2) Å.[19] The endocyclic C(1)−Si(1) bond, 1.901(3) Å, is possibly slightly longer than the exocyclic C(1)−Si bonds (1.873(4) and 1.881(3)°) and than the C−SiMe$_3$ bonds in **5** (mean 1.887(4) Å). The angle Hg−C(1)−Si(1) is constrained by the chelation to 97.6(1)°; as in **2** the CSi$_3$ system overall retains its configuration, the mean of the Si−C(1)−Si angles being 113.8° compared with 112.6° in **5**. In contrast to the situation for **2**, there is no significant twisting, the Hg−C(1)−Si(3) and Hg−C−Si(2) angles being 106.8(2) and 109.4(2)°, respectively (compared with a mean of 106.0° for the Hg−C−Si angles in **5**).

As in the case of the lithium derivatives, the cyclic and acyclic compound differ in respect of the dispositions of the Me groups. Whereas in **5** (as in the other $\{(Me_3Si)_3C\}_2M$ compounds with M = Mg,[9] Zn,[20] or Mn[9]) one methyl group from each SiMe$_3$ ligand points inward toward the metal to cover the latter very effectively (see ref 1), in **3** one C−Si bond on Si(1) necessarily points inward and the others outward, two Me groups on Si3 point slightly inward and one directly outward, and one Me on Si(2) points inward and two outward. That is, the orientation of the Me groups in **3** is like that in **2**, the chelation resulting in each case in a compromise between the usual orientation in the anions $[\{(Me_3Si)_3C\}_2M]^-$ and that in the neutral species $\{(Me_3Si)_3C\}_2M$.

Although the structures of the anion **2** and the neutral **3** are in general remarkably similar (distinctly more so than those of **4** and **5**), detailed comparison reveals some interesting features additional to those noted above, viz.:

(a) The M−C bond is a little longer in **2** than in **3**; that the metal from the second row of the periodic table should appear to be larger than that from the sixth row can be attributed to the low nuclear charge on Li and to relativistic effects in Hg which contract the inner electrons.

(b) The C(1)−Si bond lengths in **2**, mean 1.829 Å, are much shorter than those in **3**, mean 1.885 Å, and the Si−C−Si angles in **2** significantly larger than those in **3**. These differences can be attributed to the fact that the negative charge in the anion is shared between the C(1) and C(1′) atoms and from there delocalized into organosilyl groups attached to those atoms, either by d($\pi$)−p($\pi$) bonding or, more likely, by negative hyperconjugation, to give some double-bond character to the C(1)−Si bonds.[1a] It is perhaps surprising that the bond shortening in **2** is only a little less than that at the fully carbanionic center in $[(FMe_2Si)(Bu^t_2MeSi)(Me_3Si)C]^-$ (mean for C−SiMe$_3$ and C−SiMeBu$^t_2$, 1.81 Å; C−SiMe$_2$F, 1.78 Å)[21] or at that in the polymeric species $\{(Me_2NMe_2Si)_3CLi\}_n$ (mean for C−SiMe$_2$NMe$_2$ bonds 1.79 Å),[22] in which some of the shortening can be attributed to the effect of the electronegative NMe$_2$ substituent.

(c) In contrast, the Si−Me bonds in both **2** and **3** are of normal lengths (mean 1.887 Å in **2** and 1.875 Å in **3**). Thus the electronic effect that causes the C(1)−Si bond shortening in **2** has no significant effect on the Si−Me bonds, perhaps because any influence is dispersed over so many bonds. However this influence may be responsible for the fact that the Me−Si−Me angles in **2** (mean 103.9°) are somewhat smaller than those in **3** (mean 106.0°). Both sets of angles are narrowed significantly below the tetrahedral values, as they are in the acyclic **4** and **5**.

(d) Accommodation of the steric strain in the ring system causes the Si−C(2)−C(2′) angle to open to 115.8(4)° in **2** and, markedly further, to 121.4(5)°, in **3**.

The main significance of the present work lies in the synthetic potential of the reagent [Li(TMEDA)$_2$][**2**]. From consideration of the structures of several compounds $\{(Me_3Si)_3C\}_2M$, for some years we thought it likely that the steric interaction between the SiMe$_3$ groups on opposite sides of the metal would prevent a contraction of the C−M−C angle much below 180°, and so it would be very improbable that two $(Me_3Si)_3C$ ligands could be attached to a three- or four-coordinate

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metal center. However, we recently observed C−M−C angles of 137.0(4) and 136.0(2)°, respectively, in the lanthanide derivatives $\{(Me_3Si)_3C\}_2M$ with M = Yb or Eu,[12] the steric interactions (in addition to being somewhat reduced compared with those in other $\{(Me_3Si)_3C\}_2M$ species as a result of the greater length of the C−M bonds) being accommodated by large bond angle distortions within the $(Me_3Si)_3C$ ligands. We thus now think that it may be possible to make, for example, three-coordinate compounds of B or Al containing the chelated ligand from **1**.

Another aspect of interest concerns the question of whether the anion **2** reacts with electrophiles directly or by prior formation of separate CLi centers. (In solution in THF, $[Li(THF)_4][\{(Me_3Si)_3C\}_2Li]$ is thought to be in equilibrium with $(Me_3Si)_3CLi{\cdot}2THF$.[2c])

Finally, we propose to call the dicarbanionic ligand $\{(Me_3Si)_2\bar{C}SiMe_2CH_2\}_2$ (1,1,6,6-tetrakis(trimethylsilyl)-2,2,5,5-tetramethyl-2,5-sila-hexane-1,6-diyl) the *siamyl* ligand, since it can be regarded as a Siamese twin pair of the commonly used $(Me_3Si)_3C^-$ (trisyl) ligands and the two initial letters indicate that it is silicon-containing.

## Experimental Section

Reactions (and in the case of $[Li(TMEDA)_2][\mathbf{2}]$ the isolation and recrysallization) were carried out under Ar in carefully dried solvents.

The following NMR spectrometers were used: for $^1H$, Bruker WM360; for $^{13}C$ (at 62.85 MHz), $^{29}Si$ (at 49.70 MHz), and $^7Li$ (at 97.26 MHz), Bruker AC P250. Mass spectra were obtained by electron impact at 70 eV.

**Preparation of $(Me_3Si)_2CHSiMe_2CH_2CH_2SiMe_2CH(SiMe_3)_2$, 1.** The organolithium compound $LiCH(SiMe_3)_2$ was prepared as described by Wiberg and Wagner[23] and purified by sublimation. To a solution of the reagent (9.0 g, 54 mmol) in THF (30 $cm^3$) at room temperature a solution of (Aldrich) 1,2-bis(chlorodimethylsilyl)ethane (5.0 g, 23 mmol) in THF (20 $cm^3$) was added dropwise with stirring during 30 min. The mixture was refluxed for 4 h and then stirred at room temperature for 3 days. The solvent was removed under vacuum and the residue extracted with pentane. The extract was shaken with water, and the organic layer was separated and dried over $MgSO_4$. The pentane was evaporated and the residue distilled at 134−140°/0.01 mmHg to give a thick oil. This solidified to a white solid, mp 45−46 °C, which was shown to be **1** (8.7 g, 82%). $^1H$ NMR (360 MHz, $C_6D_6$): δ 0.18 (36H, s, $SiMe_3$), 0.21 (12H, s, $SiMe_2$), 0.62 (4H, s, $CH_2$), 0.67 (2H, s, CH). $^{13}C$ NMR ($C_6D_6$): δ 0.64 ($SiMe_2$), 2.3 (CH), 3.6 ($SiMe_3$), 11.8 ($CH_2$). $^{29}Si$ NMR ($C_6D_6$): δ −11.5 ($SiMe_3$), 2.7 ($SiMe_2$). MS (*m*/*z*, relative intensity): 462, 30% (M+); 289, 15% $(M - Me)^+$; 233, 25%; 217, 100% $((Me_3Si)_2CHSiMe_2)^+$; 202, 50%; 187, 30%; 157, 20%; 145, 40%; 129, 65%; 73, 70% $(SiMe_3)^+$.

**Preparation of $[Li(TMEDA)_2][\mathbf{2}]$. Method a.** A 1.4 M solution of MeLi in $Et_2O$ (12 $cm^3$; 16.8 mmol of MeLi) was added to **1** (1.9 g, 4.1 mmol), and the solvent was removed under vacuum. The solid residue was dissolved in THF (30 $cm^3$), and the solution was refluxed with stirring for 6 h at room temperature, becoming yellow. The solvent was removed under vacuum, and the residue was washed with pentane and then dissolved in $Et_2O$. A slight excess of TMEDA (1.2 $cm^3$) was added and colorless crystals separated immediately. The product was recrystallized from $Et_2O$, to give $[Li(TMEDA)_2][\mathbf{2}]$ (1.8 g, 66%) as colorless needles, mp 250−252 °C (dec), some of which were suitable for the crystallographic study. $^1H$ NMR (360 MHz; THF-$d_8$): δ 0.01 (12H, s, $SiMe_2$), 0.03 (36H, s, $SiMe_3$), 0.54 (4H, s, $SiCH_2$), 2.15 (24H, s, $NMe_2$), 2.30 (8H, s, $NCH_2$). $^{13}C$ NMR (THF-$d_8$): δ 1.2 (CLi), 5.8 ($SiMe_2$), 8.1 ($SiMe_3$), 14.7 ($SiCH_2$), 46.7 ($NMe_2$), 58.8 ($NCH_2$). $^{29}Si$ NMR (THF-$d_8$): δ −10.8 ($SiMe_3$), −7.1 ($SiMe_2$). $^7Li$ (THF-$d_8$): δ −1.5 and 2.5 (overlapping).

**Table 3. Crystal Data and Details of Structural Analyses for $[Li(TMEDA)_2][\mathbf{2}]$ and 3**

| | $[Li(TMEDA)_2][\mathbf{2}]$ | **3** |
|---|---|---|
| empirical formula | $C_{32}H_{84}Li_2N_4Si_6$ | $C_{20}H_{52}HgSi_6$ |
| fw | 707.5 | 661.8 |
| cryst system | orthorhombic | orthorhombic |
| unit cell dimens | | |
| a (Å) | 14.015(5) | 9.1280(10) |
| b (Å) | 18.480(3) | 16.0990(1) |
| c (Å) | 17.852(4) | 21.517(2) |
| α (deg) | 90 | 90 |
| *V* ($Å^3$) | 4624(2) | 3162.0(5) |
| *Z* | 4 | 4 |
| *D* (g $cm^{-3}$) | 1.02 | 1.39 |
| μ ($mm^{-1}$) | 0.20 | 5.10 |
| *F*(000) | 1576 | 1344 |
| cryst size (mm) | 0.40 × 0.20 × 0.20 | 0.40 × 0.35 × 0.20 |
| θ range (deg) | 2−25 | 2−30 |
| index ranges | $0 \le h \le 16$<br>$0 \le k \le 21$<br>$-21 \le l \le 21$ | $0 \le h \le 12$<br>$-22 \le k \le 22$<br>$-30 \le l \le 30$ |
| reflcns collcd | 4388 | 9168 |
| indepdt reflctns | 4086 (*R*(int) = 0.507) | 4600 (*R*(int) = 0.0418) |
| reflcns with $I > 2\sigma(I)$ | 1850 | 3999 |
| data/restraints/params | 4086/0/201 | 4599/0/123 |
| goodness of fit on $F^2$ | 1.028 | 0.976 |
| final *R* indices | | |
| $R1$, $wR^2$ ($I > 2\sigma(I)$) | 0.059, 0.134 | 0.026, 0.047 |
| $R1$, $wR^2$ (all data) | 0.084, 0.149 | 0.036, 0.050 |
| abs struct param | 0.0(2) | −0.001(5) |
| largest diff peak and hole (e $Å^{-3}$) | 0.34, −0.35 | 0.36, −0.85 |
| ψ scans ($T_{max}$, $T_{min}$) | | 1.00, 0.55 |
| max shift/esd | 0.001 | 0.001 |

**Table 4. Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2$ × $10^3$) for the Anion 2**

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Li(1) | 0 | 0 | 2293(6) | 35(3) |
| Si(1) | 384(1) | 1170(1) | 3405(1) | 24(1) |
| Si(2) | −656(1) | 1727(1) | 1985(1) | 25(1) |
| Si(3) | 1363(1) | 1103(1) | 1828(1) | 27(1) |
| C(1) | 264(3) | 1146(2) | 2384(2) | 23(1) |
| C(2) | 470(3) | 222(2) | 3802(2) | 26(1) |
| C(3) | 1446(3) | 1696(3) | 3777(3) | 39(1) |
| C(4) | −658(4) | 1573(3) | 3930(3) | 34(1) |
| C(5) | −1910(3) | 1465(3) | 2250(3) | 39(1) |
| C(6) | −532(4) | 2710(2) | 2238(3) | 41(1) |
| C(7) | −707(4) | 1745(3) | 927(2) | 41(1) |
| C(8) | 1214(4) | 503(3) | 982(3) | 37(1) |
| C(9) | 2413(3) | 681(3) | 2328(3) | 44(1) |
| C(10) | 1845(4) | 1987(3) | 1464(3) | 49(1) |

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$.

**Method b.** A mixture of **1** (1.15 g, 2.5 mmol), MeLi (5.6 mmol), and TMEDA (0.75 $cm^3$, 5 mmol) in THF (10 $cm^3$) was stirred at room temperature for 2 h and then at 50 °C for 2 h and finally refluxed for 3 h. The solvent was removed under vacuum, and the residue was washed with pentane and then recrystallized from $Et_2O$ to give $[Li(TMEDA)_2][\mathbf{2}]$ (1.4 g, 79%), with properties identical to those reported above.

The compound is slightly soluble in benzene and toluene and soluble in $Et_2O$ and THF.

**Preparation of 3.** Reagent $[Li(TMEDA)_2][\mathbf{2}]$ (0.70 g, 1.0 mmol) and $HgBr_2$ (0.40 g, 1.1 mmol) were dissolved in THF (30 $cm^3$), and the solution was stirred at room temperature for 48 h. The solvent was removed under vacuum, and the solid residue was extracted with pentane. The extract was filtered and the solvent removed to leave colorless crystals (0.60 g, 91%). The product was recrystallized from heptane to give a solid of mp 216−218 °C. Anal. Calcd for $C_{20}H_{52}$-

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[23] Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1455.

**Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3**

| | $x$ | $y$ | $z$ | $U(\mathrm{eq})^a$ |
|---|---|---|---|---|
| Hg | 0 | 6405.7(1) | 7500 | 35(1) |
| Si(1) | 969.1(13) | 7721.1(7) | 6573.7(5) | 51(1) |
| Si(2) | 2090.0(13) | 5879.3(9) | 6328.4(5) | 52(1) |
| Si(3) | −1204.7(12) | 6343.1(8) | 6090.8(5) | 48(1) |
| C(1) | 516(4) | 6569(2) | 6541(2) | 38(1) |
| C(2) | −179(7) | 8327(2) | 7145(2) | 60(1) |
| C(3) | 672(6) | 8242(3) | 5807(2) | 74(1) |
| C(4) | 2922(6) | 7941(4) | 6807(2) | 79(1) |
| C(5) | 3527(5) | 5832(4) | 6950(2) | 76(2) |
| C(6) | 3050(6) | 6233(4) | 5600(2) | 91(2) |
| C(7) | 1570(7) | 4770(3) | 6205(3) | 86(2) |
| C(8) | −2059(6) | 5328(3) | 6316(3) | 73(1) |
| C(9) | −2689(5) | 7120(3) | 6217(2) | 72(1) |
| C(10) | −855(6) | 6288(4) | 5233(2) | 79(2) |

[a] $U$(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$.

$HgSi_6$: C, 36.3; H, 7.9. Found: C, 36.2; H, 8.1. MS ($m/z$, relative intensity): 662, 13% ($M^+$); 647, 50% ($M - Me^+$), 217, 100% ($(Me_3Si)_2CHSiMe_2^+$). $^1$NMR ($C_6D_6$): $\delta$ 0.28 (36H, s, $SiMe_3$), 0.29 (12H, s, $SiMe_2$), 0.86 (4H, $SiCH_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 3.2 ($SiMe_2$), 6.6 ($SiMe_3$, $^2J(\mathrm{HHg}) = 38.0$ Hz), 14.6 ($SiCH_2$). $^{29}$Si NMR ($C_6D_6$): $\delta$ −2.0 ($SiMe_3$), 0.1 ($SiMe_2$).

**Crystal Structure Determinations.** Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo Kα radiation. Cell dimensions were calculated from the setting angles for 25 reflections with $7 < \theta < 10°$. Intensities were measured by an $\omega{-}2\theta$ scan and corrected for Lorentz and polarization effects. $\psi$-scan measurements were used to apply an absorption correction for the mercury compound **3**. All non-hydrogen atoms were refined anisotropically. H atoms were included in riding mode with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ or $1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl groups. The molecules in **3** and the anions in **2** lie on crystallographic 2-fold axes, and the cations in **2** on sites of crystallographic 222 symmetry. Structure solution was by direct methods using SHELXS-86, and refinement was by full-matrix least squares on $F^2$ using SHELX-93. The CAMERON program was used to prepare the molecular drawings. Crystal structure data and further details are given in Table 3, and atomic coordinates in Tables 4 and 5.

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**Supporting Information Available:** Tables of calculated hydrogen atom coordinates and $U$ values and anisotropic temperature factors for $[Li(TMEDA)_2]$[**2**] and **3** and a full list of bond lengths and angles for the former (6 pages). Ordering information is given on any current masthead page.

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