Attachment of the New Bulky Ligand $(Me_3Si)_2(Me_2NMe_2Si)C$ to Li, Hg, Al, Ga, and Sn. Crystal Structures of $[Li\{C(SiMe_3)_2(SiMe_2NMe_2)\}(THF)_2]$, $[Hg\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2]$, $[Al\{C(SiMe_3)_2(SiMe_2NMe_2)\}X_2]$ (X = Cl, Ph), and $[Ga\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_2]$

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The organolithium reagent $[Li\{C(SiMe_3)_2(SiMe_2NMe_2)(THF)_2]$ (**1**) is readily obtained by reaction of the chloride $(Me_3Si)_2(Me_2NMe_2Si)CCl$ with LiBu in THF (tetrahydrofuran) at low temperature. Reactions of **1** with $HgBr_2$, $AlCl_3$, $GaCl_3$, and $SnCl_4$ give $[Hg\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2]$ (**2**), $[Al\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_2)]$ (**3**), $Ga\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_2$ (**5**), and $[Sn\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_3]$ (**6**)**,** respectively, and treatment of **3** with LiPh gives $[Al\{C(SiMe_3)_2(SiMe_2NMe_2)\}Ph_2]$ (**4**)**.** Crystal structure determinations have shown that there is intramolecular coordination of the N atom to the metal M, with formation of a planar four-membered C−Si−N−M ring, in **1**, **3**, **4,** and **5** (but not **2**). Engagement of the lone pair on N in coordination with Al in **3** results in an exceptionally long Si−N bond length of 1.875(2) Å, some 0.16 Å longer than that in **2** and in simple silylamines generally; the Si−N bond is possibly shorter in **4** (1.851(2) Å) and **5** (1.858(4) Å), and is markedly so in **1** (1.796(4) Å), but still notably long. The lengths of the N−metal bonds in these compounds are similar to those between alkylamines and the metals in coordination compounds, indicating that at least in these systems the N atoms in the silylamines coordinate as strongly as those in the organic amines. Reaction of **6** with MeOH occurs exclusively at the Si−N bond to give $[Sn\{C(SiMe_3)_2(SiMe_2OMe)\}Cl_3]$, that of **2** with ICl or CF_3CO_2H gives $[Hg\{C(SiMe_3)_2(SiMe_2Cl)\}_2]$ and $[Hg\{C(SiMe_3)_2(SiMe_2O_2CCF_3)\}_2]$, respectively, and that of **1** with ICH_2CH_2I gives the iodide $(Me_3Si)_2(Me_2NMe_2Si)CI$.

Introduction

Attachment of the very bulky ligand $(Me_3Si)_3C$ (the trisyl ligand) or the related ligand $(PhMe_2Si)_3C$ to metal centers has enabled us to isolate a substantial number of novel types of organometallic compounds.[1] Recently the emphasis in our research has moved toward use of ligands of the type $(Me_3Si)_2(XMe_2Si)C$ or $(XMe_2Si)_3C$ that provide comparable bulk around a metal center to which they are attached but also contain donor groups X capable of coordinating intra- or intermolecularly to the metal. Those used previously include $(Me_3Si)_2(XMe_2Si)C$ with X = OMe,[2] SMe[3] and $(XMe_2Si)_3C$ with X = OMe,[4] NMe_2.[5,6] In particular, attachment of the ligand $(Me_2NMe_2Si)_3C$ to Li has given a linear polymeric species with the polymer unit **7**, in which the planar carbanionic center is well removed from the planar lithium ion center,[5a] and attachment of the ligand to Mg has given the highly unusual Grignard reagent $(Me_2NMe_2Si)_3CMgI$, in which there is a planar carban-

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[6] A range of compounds of the type $(Me_3Si)_2(XMe_2Si)CLi$, but not any with X = NR_2, have been prepared in solution; some were isolated as solids but not structurally characterized: Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981,** *114*, 2087.

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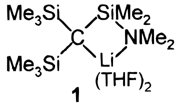
ionic center apparently without specific interaction with the Mg atom.[5b] We have now made available the ligand $(Me_3Si)_2(Me_2NMe_2Si)C$ by preparation of the organolithium reagent **1** and, in order to demonstrate the utility of the latter, have used it to make the organomercury compound **2**, the organoaluminum compound **3** (and hence the corresponding diphenyl compound **4**), the organogallium compound **5**, and the organotin compound **6**. Crystal structure determinations have



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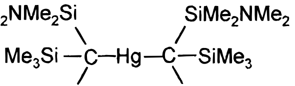

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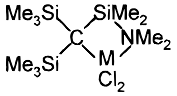
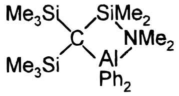


3, M = Al
5, M = Ga



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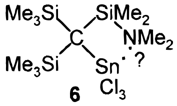

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shown that there is internal coordination of the NMe_2 group to the metal in the lithium, aluminum, and gallium compounds but not in the mercury compound. Spectroscopic data suggest that there is similar internal coordination in the tin compound.

Results and Discussion

The ligand precursors $(Me_3Si)_2(Me_2NMe_2Si)CH$ and $(Me_3Si)_2(Me_2NMe_2Si)CCl$ were respectively made by reaction of $(Me_3Si)_2(BrMe_2Si)CH$ or $(Me_3Si)_2(BrMe_2Si)CCl$ with an excess of NMe_2H in light petroleum. The solvated organolithium reagent **1** was obtained by treatment of $(Me_3Si)_2(Me_2NMe_2Si)CH$ with MeLi at room temperature or of $(Me_3Si)_2(Me_2NMe_2Si)CCl$ with LiBu in THF at low temperature. Reaction of **1** with $HgBr_2$ in THF gave the expected derivative **2**, and similar reactions with $AlCl_3$ (in toluene), $GaCl_3$ (in toluene), or $SnCl_4$ (in THF) gave **3**, **5,** and **6**, respectively. Treatment of **3** with LiPh in toluene gave the diphenylaluminum compound **4**.

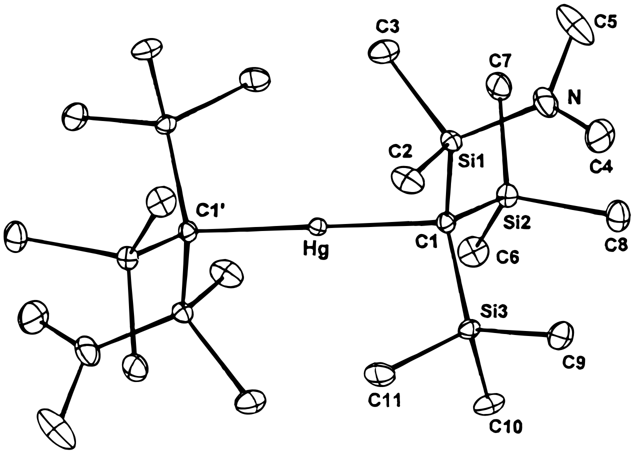

Figure 1. Molecular structure of $[Hg\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2]$ (**2**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Hg\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2]$ (2)

Hg−C1	2.161(4)	Si1−N	1.721(4)
C1−Si1	1.899(4)	N−C4	1.456(8)
C1−Si2	1.881(4)	N−C5	1.441(8)
C1−Si3	1.891(4)	Si−Me (mean)	1.890(3)
Hg−C1−Si1	104.9(2)	Si2−C1−Si3	111.9(2)
Hg−C1−Si2	107.4(2)	C2−Si1−C3	105.2(3)
Hg−C1−Si3	104.2(2)	Si1−N−C4	123.5(4)
Si1−C1−Si2	113.2(2)	Si1−N−C5	124.9(5)
Si1−C1−Si3	114.3(2)	C4−N−C5	110.9(5)
		Me−Si−Me (mean)	105.7(7)

Crystal Structures of Compounds 1−5. The crystal structures of compounds **1**−**5** were determined by X-ray diffraction studies. It is convenient to consider first the mercury compound **2,** in which the amino group is not involved in coordination. The structure is shown in Figure 1, and relevant bond lengths and angles are given in Table 1. The form of the molecule is very similar to that observed for the corresponding methoxy compound $Hg\{C(SiMe_3)_2(SiMe_2OMe)\}_2$, with the NMe_2 group, like the OMe group in the latter, pointing outward away from the metal.[7] (In contrast, in the corresponding MeO-containing Zn and Cd compounds the OMe groups point inward toward the metal.[7]) The most important feature in the present context is that the Si−N bond length of 1.721(4) Å falls in the normal range of ca. 1.71−1.72 Å for trialkylaminosilanes,[8] and there is a planar geometry at the nitrogen atom, as is usual in the latter species. However, as a consequence of the crowding, the Me−N−Me angle is lowered to 110.9(5)° and the Si1−N−Me angles are correspondingly raised to 124.9(4) and 123.5(4)°. The other relevant geometrical data for **2**, viz. the C−Hg and C1−Si distances and the mean Si−C−Si angle (113.1(4)°), are essentially identical with those in $Hg\{C(SiMe_3)_3\}_2$[9] and $Hg\{C(SiMe_3)_2(SiMe_2OMe)\}_2$.[7]

There are marked changes in some of the geometrical features of the $(Me_3Si)_2(Me_2NMe_2Si)C$ ligand on going to the aluminum compound **3** (see Figure 2 and Table 2), in which the N atom is strongly coordinated to the Al atom to give a near-planar $\overline{\text{Si−N−Al−C}}$ ring, the sum of the internal angles being 358.2° and the fold angle being 14°. The angle at Si, viz. 95.13(7)°, is significantly larger than those at N, Al, and C, viz. 87.42(7), 88.28(7), and 87.33(7)°, respectively. The Si−N bond length (1.875(2) Å) is, as far as we can ascertain, the longest such bond ever observed for silicon attached to an amine center, although it is not much longer than the Si−$NHBu^t$ bond (1.861(2) Å) in the four-membered-ring species **8**.[10] The corresponding bond, Si−$NMe_2(AlCl_3)$, in the acyclic species **9** is, at 1.832(5) Å,[11] markedly shorter (but still much longer than the Si−NMe_2 bonds

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for [$M\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_2$] (M = Al (3), Ga (5))

	M = Al	M = Ga		M = Al	M = Ga
M−Cl(1)	2.134(1)	2.197(1)	C1−Si3	1.865(2)	1.870(5)
M−Cl(2)	2.145(1)	2.200(1)	N−Si3	1.875(2)	1.858(4)
M−C1	1.987(2)	2.000(4)	N−C10	1.491(2)	1.489(6)
M−N	1.975(2)	2.057(4)	N−C11	1.498(2)	1.484(6)
C1−Si2	1.902(2)	1.905(4)	Si−C in $SiMe_3$ (mean)	1.878(1)	1.877(3)
C1−Si1	1.894(2)	1.895(5)	Si−C in $SiMe_2$ (mean)	1.859(2)	1.854(5)
C1−M−N	88.28(7)	86.4(2)	Cl1−M−Cl2	106.74(3)	105.63(5)
M−C1−Si3	87.33(7)	88.3(2)	Cl1−M−C1	122.20(6)	124.70(13)
C1−Si3−N	95.13(7)	96.4(2)	Cl2−M−C1	118.47(5)	119.73(13)
Si3−N−M	87.42(7)	87.0(2)	Cl1−M−N	113.17(5)	112.09(12)
C8−Si3−N	106.44(9)	107.1(2)	Cl2−M−N	105.49(5)	104.68(11)
C9−Si3−N	109.15(9)	109.0(2)	M−N−C10	118.21(12)	116.5(3)
M−C1−Si1	109.86(8)	108.6(2)	M−N−C11	112.83(12)	112.5(3)
M−C1−Si2	114.13(8)	112.5(2)	N−Si3−C8	106.44(9)	107.1(2)
Si1−C1−Si2	109.99(8)	110.4(2)	N−Si3−C9	109.15(9)	109.0(2)
Si1−C1−Si3	120.70(9)	121.3(2)	C10−N−C11	107.5(2)	108.1(4)
Si2−C1−Si3	113.10(9)	113.5(2)	Me−Si−Me (mean)	105.5(8)	105.8(9)

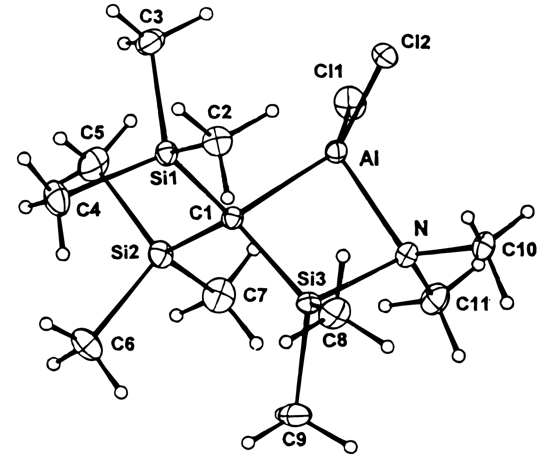
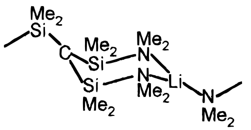


Figure 2. Molecular structure of [$Al\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_2$] (**3**).

from Si to the uncoordinated N atoms; mean 1.679(2) Å). The length of the Si−N bond in **3** indicates that the



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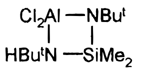

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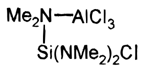

$\begin{array}{l}Me_2N\text{—}AlCl_3\\ \quad|\\ Si(NMe_2)_2Cl\end{array}$

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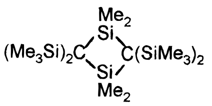

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lone pair on the nitrogen atom is very firmly engaged in bonding to Al. The increase of ca. 0.15 Å over the (normal) Si−N bond length of 1.721(4) Å in **2** is comparable to that of 0.14 Å for the Si−O bond on going to the protonated species $Bu^t_3SiOH_2^+$ [12] and raises the Si−N distance to that corresponding to the sum (1.87 Å) of the covalent radii of Si and N.

The $Me_3Si{-}C{-}SiMe_3$ angle (110.0(1)°) is notably small relative to the corresponding angles of 123.2° in $(Me_3Si)_2CH_2$[13a] and 114.4(2)° in $(Me_3Si)_3CH$,[13b] but it is significantly larger than that (106°) in the 1,3-disilacyclobutane **10**.[14] In both **3** and **10** one Me group (C2 and C7 in **3**) of each Me_3Si points in toward the ring and the other two point outward. (There is an analogous disposition in neutral species $M\{C(SiMe_3)_3\}_2$.[1a,b]) It was concluded in the case of the disilacyclobutane **10** that widening of the $Me_3Si{-}C{-}SiMe_3$ angle is inhibited by interactions between the inward-pointing Me groups and the substituents on the ring atoms (the distance between the inward-pointing Me groups and the Me groups of the $SiMe_2$ fragment is 3.4 Å) that force the Me_3Si groups together,[14] and the analogous interactions between C2 and C8 (C···C 3.27 Å) and to a lesser extent between C7 and C9 (C···C 3.67 Å) as well as between C2 and Cl2 or C7 and Cl1 (C···Cl = 3.65 and 3.64 Å, respectively) appear to do the same in **3**. However, the sum of these interactions is evidently smaller than that in **10**, allowing the $Me_3Si{-}C{-}SiMe_3$ angle to be some 4° larger than in the latter. Other close contacts, reflecting the inevitable crowding about a four-membered ring, are as follows: C8···C10, 3.09 Å; C9···C11, 3.17 Å; Cl1···C11, 3.49 Å.

Other features of the structure of **3** are as follows. (a) The Al−N bond length of 1.975(2) Å is fairly close to that of 1.96 Å in, for example, the trialkylamine derivative $Me_3N{\cdot}AlCl_3$[16] and is significantly shorter than that of 2.02 Å in $Me_3N{\cdot}AlMe_2I$.[17] It is also significantly shorter than that of the $Al{-}NH^tBuSi$ bond (1.994(2) Å) in **8**.[10] The mean Al−Cl bond length of 2.139(1) Å compares with the mean value of 2.138 Å for the Al−Cl bonds in **8** and 2.116(4) Å for those in **9**.[11] (b) To minimize interaction between the $SiMe_3$ groups and the Cl atoms, the Al−Cl bonds lie over toward the NMe_2 group to give a mean C1−Al−Cl angle of ca. 120° and a

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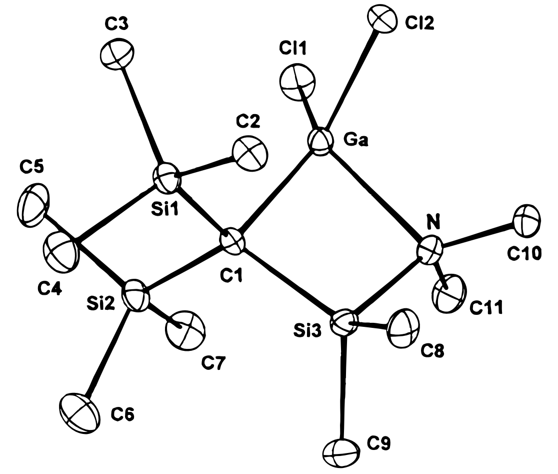

Figure 3. Molecular structure of $[Ga\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_2]$ (**5**).

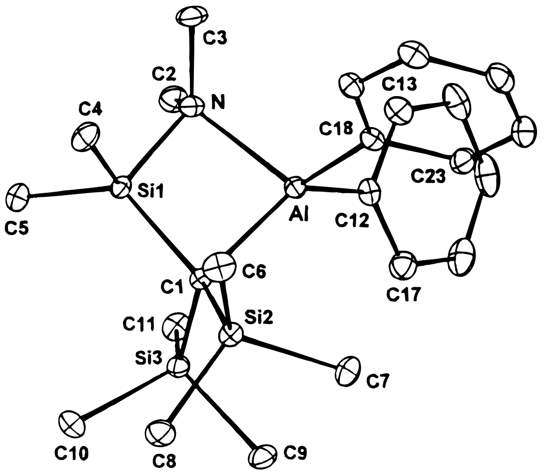

Figure 4. Molecular structure of $[Al\{C(SiMe_3)_2(SiMe_2NMe_2)\}Ph_2]$ (**4**).

mean Cl−Al−N angle of ca. 109°. (c) The endocyclic Si−C1 bond, 1.865(2) Å, is significantly shorter than the exocyclic Si−C1 bonds (mean 1.898(2) Å); there is a similar shortening of the intra-ring Si−C1 bond in **4** (1.857(3) Å), compared with a mean of 1.890(2) Å for the other two Si−C1 bonds. No such shortening of the $C-SiMe_2NMe_2$ bond is observed in the acyclic compound **2,** and in the case of the cyclic lithium compound **1** (see below) the intra-ring C1−Si1 bond, while clearly shorter than the C1−Si3 bond, is not significantly shorter than the C1−Si2 bond. (d) The Si−Me bonds in the $SiMe_3$ groups (mean 1.878(1) Å) are longer than those in the $SiMe_2$ group (mean 1.859(2) Å); this is true also for compound **5** and probably for compound **4**, although in this case the observed difference is within the limits implied by the estimated standard deviations. (There is no such effect in compounds **1** and **2**.) (e) The mean of the Si−C1−Si angles (114.6°) and the angle of 113.10(9)° between the Si3−C1 and Si2−C1 bonds are similar to those in a $(Me_3Si)_3C$ group attached to Al,[15] but the involvement of Si3 in the four-membered ring leads to a large difference between the Si1−C1−Si3 and Si2−C1−Si3 angles, which are 109.99(8) and 120.70(9)°, respectively. The Al−C bond lengths are normal.

The structure of the gallium compound **5** is shown in Figure 3, and relevant bond lengths and angles are given in Table 2 alongside those for **3**. The compound is closely isomorphous with its aluminum analogue **3**, and so the comments made above on the structure of the latter apply equally to that of **5**. It is noteworthy, however, that the metal−C bond lengths are not significantly different in the two compounds but the metal−N and metal−Cl bonds are slightly longer in **5**. The ring angle at the metal in **5** (86.4(2)°) is slightly smaller than that in **3** (88.28(7)°). The other parameters are virtually identical in the two compounds; the sum of the ring angles is 358.1° in **5** and 358.8° in **3**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Al\{C(SiMe_3)_2(SiMe_2NMe_2)\}Ph_2]$ (4)

Al−C12	1.984(3)	C1−Si3	1.893(3)
Al−C18	2.000(3)	N−Si1	1.851(2)
Al−C1	2.057(3)	N−C2	1.494(4)
Al−N	2.038(2)	N−C3	1.484(3)
C1−Si1	1.857(3)	Si−C in $SiMe_3$ (mean)	1.879(2)
C1−Si2	1.887(3)	Si−C in $SiMe_2$ (mean)	1.866(3)

C1−Al−N	85.20(10)	C12−Al−C18	104.26(12)
Al−C1−Si1	87.38(11)	C12−Al−C1	125.57(11)
C1−Si1−N	96.75(11)	C18−Al−C1	119.35(11)
Si1−N−Al	88.13(10)	C12−Al−N	109.04(11)
C4−Si1−N	106.73(13)	C18−Al−N	110.99(11)
C5−Si1−N	108.61(13)	Al−N−C2	110.7(2)
Al−C1−Si2	110.40(12)	Al−N−C3	120.2(2)
Al−C1−Si3	115.20(12)	N−Si1−C4	106.73(13)
Si1−C1−Si2	120.46(14)	N−Si1−C5	108.61(13)
Si1−C1−Si3	113.30(13)	C2−N−C3	106.8(2)
Si2−C1−Si3	108.86(12)	Me-Si−Me (mean)	104.6(8)

The structure of **4** is shown in Figure 4, and relevant bond lengths and angles are given in Table 3. The four-membered ring is a little further from planarity than that in **3**, the sum of the internal angles being 357.5° and the fold angle being 17°. The $Me_3Si-C-SiMe_3$ angle (108.9(1)°) is slightly smaller than that in **3**, probably because the larger size of the substituents on Al slightly increases the overall crowding around the ring in **4**. The fact that the Si−N bond length is, at 1.851(2) Å, somewhat shorter than that in **3** is consistent with the suggestion that as electron withdrawal from Al by Ph is weaker than that by Cl, the resulting N−Al coordination is slightly weaker. Other features of the structure are closely similar to those in **3** and require no further comment.

As can be seen from Figure 5, there is also coordination of the N atom to the metal in the lithium compound **1**, bond lengths and angles for which are given in Table 4. The four-membered ring is again almost planar, the sum of the internal angles being 358.8° and the fold angles across the N/C1 and Si1/Li axes being 13 and 11°. These fold angles differ because the endocyclic Li−C and Li−N bonds (2.287(9) and 2.162(8) Å, respectively) are substantially longer than the Si−C and Si−N bonds (1.796(4) and 1.806(4) Å, respectively). The same effect allows the endocyclic angle at Si (108.1(2)°) to be markedly larger than that in **3** or **4**.

There are striking differences between the geometry of the $(Me_3Si)_2C$ system in **1** and that in the aluminum compound **3** (and so also in **4** or **5**): the C1−Si bonds (mean 1.819 Å) are markedly shorter, the mean Si−C1−Si angle (116.9°) is markedly larger, and the mean Me-Si−Me angle (103.6°) is significantly smaller than those in **3** (1.878 Å, 114.6°, and 105.5°, respectively), and these are attributed to the greater carbanionic character at

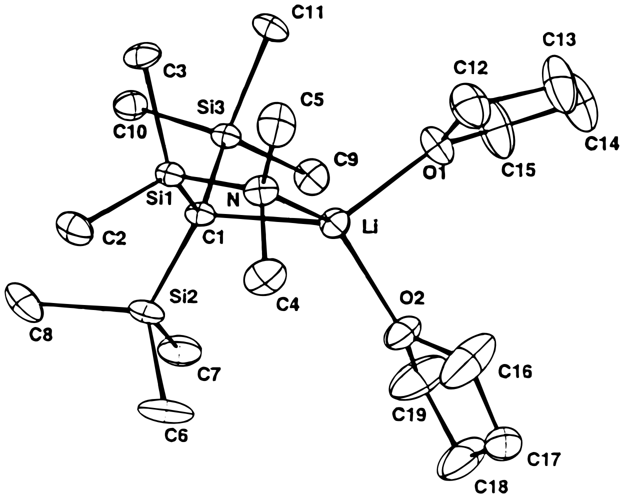

Figure 5. Molecular structure of $[Li\{C(SiMe_3)_2(SiMe_2NMe_2)\}(THF)_2]$ (**1**).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Li\{C(SiMe_3)_2(SiMe_2NMe_2)\}(THF)_2]$ (1)

Li−O1	1.980(8)	C1−Si2	1.815(4)
Li−O2	1.980(8)	C1−Si3	1.835(4)
Li−C1	2.287(9)	N−C4	1.469(6)
Li−N	2.162(8)	N−C5	1.468(6)
N−Si1	1.796(4)	Si−Me (mean)	1.886(3)
C1−Si1	1.806(4)		
C1−Li−N	81.8(3)	Si1−C1−Si2	117.4(2)
Li−N−Si1	86.4(2)	Si1−C1−Si3	119.2(2)
N−Si1−C1	108.1(2)	Si2−C1−Si3	114.0(2)
Si1−C1−Li	82.5(2)	C4−N−C5	108.3(4)
O1−Li−O2	95.7(3)	Li−N−C4	96.5(3)
O1−Li−N	110.4(4)	Li−N−C5	131.0(4)
O2−Li−N	119.8(4)	Si2−C1−Li	119.8(3)
O1−Li−C1	129.8(4)	Si3−C1−Li	98.6(3)
O2−Li−C1	120.8(4)	Me−Si−Me (mean)	103.2(5)

the C1 center in the lithium compound.[1b,15a] Especially noteworthy is that the $Me_3Si{-}C{-}SiMe_3$ angle in **1** (114.0(2)°) is larger than that in **3** (110.0(1)°), and in view of the discussion above of cross-ring Me···Me interactions in **3** it is appropriate to consider why the angle in **1** can open so far. As in **3**, and neutral $M\{C(SiMe_3)_3\}_2$ compounds, one Me group of each Me_3Si lies toward the center of the molecule. However, because the plane through the Si2, C1, and Si3 atoms lies well away from perpendicularity to that through Si1, C1, and Li (the Li−C1−Si2 and Li−C1−Si3 angles are 119.8(3) and 98.6(3)°, respectively) and the plane through the C5, N, and C4 atoms similarly lies well away from perpendicularity to the Si1, N, Li plane (the Li−N−C4 and Li−N−C5 angles being 96.5(3) and 131.0(4)°, respectively), inward-pointing Me groups at C6 and C11 are well removed (by >5 Å) from the Me groups at C4 and C5. The closest nonbonding Me···Me contacts around the ring are C2···C4 (3.14 Å) and C3···C5 (3.05 Å), and other close contacts are C4···O2 (3.34 Å), Si2···C2 (3.50 Å), and Si3···C3 (3.56 Å); all of these contacts involve near-eclipsed substituents in 1,2-dispositions in the four-membered ring.

The Li−N bond length of 2.162(8) Å in **1** (cf. 2.094(7) and 2.133(11) Å in the unit **7**) is not significantly longer than that of 2.125(9) Å in $[Li(TMEDA)_2]^+$.[18] The Si−N bond length of 1.796(4) Å is ca. 0.08 Å shorter than that in **3**, perhaps implying a somewhat weaker N−metal coordination than in the latter; however, it is still markedly longer than that in **2** or those in $R_3SiNR'_2$ compounds.[8]

The Compound $Sn\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_3$ (6). Reaction of the lithium reagent **1** with $SnCl_4$ in THF at −12 °C gave after workup a white solid which was shown from its analysis and spectroscopic data to have the formula $Sn\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_3$. Good crystals were obtained from heptane, but they proved to be cubic, with $a = 12.95$ Å, the cell volume indicating that the compound is monomeric. Unfortunately the structure could not be resolved, possibly because of extensive disorder. However, the position of the signal in the ^{119}Sn NMR spectrum, at δ −182 for a solution in C_6D_6, is more consistent with five- than four-coordinate tin,[19] again pointing to N−Sn coordination. (The position of the ^{15}N NMR signal is considered below.)

Treatment of **5** with MeOH in Et_2O gave, as colorless crystals, the methoxy derivative $Sn\{C(SiMe_3)_2(SiMe_2OMe)\}Cl_3$, identical with a sample that had been made previously from $[Li\{C(SiMe_3)_2(SiMe_2OMe)(THF)_2]$ and $SnCl_4$.[20]

Reactions of the Mercury Derivative 2. Treatment of compound **2** with ICl in THF gave a moderately good yield of the chloro derivative $Hg\{C(SiMe_3)_2(SiMe_2Cl)\}_2$ without any observable attack on the C−Hg bond. Treatment with 2 mol equiv of CF_3CO_2H in the hope of obtaining the ammonium salt $[Hg\{C(SiMe_3)_2(SiMe_2NMe_2H)\}_2][CF_3CO_2]_2$ gave the bis(trifluoroacetate) $Hg\{C(SiMe_3)_2(SiMe_2O_2CCF_3)\}_2$, the zinc analogue of which was obtained earlier by reaction of $Zn\{C(SiMe_3)_2(SiMe_2I\}_2$ with CF_3CO_2H and Ag_2O in CCl_4.[21]

The Iodide $(Me_3Si)_2(Me_2NMe_2Si)CI$. Treatment of **1** with ICH_2CH_2I gave the iodide $(Me_3Si)_2(Me_2NMe_2Si)CI$, which has the potential to react directly with appropriate metals to give the corresponding organometallic iodides; compare the reaction of $(Me_2NMe_2Si)_3CI$ with Mg to give $(Me_2NMe_2Si)_3CMgI$[5b] and that of $(Me_3Si)_2(MeOMe_2Si)CI$ with Yb or Mg to give $Yb\{C(SiMe_3)_2(SiMe_2OMe)\}_2{\cdot}OEt_2$[1d] or $Mg\{C(SiMe_3)_2(SiMe_2OMe)\}_2$.[2]

NMR Spectra. Some significant chemical shift data for solutions in C_6D_6 of the RX compounds with $R = (Me_3Si)_2(Me_2NMe_2Si)C$ are given in Table 5 for compounds **1**−**5** and the compounds RH, RCl, and RI. The features are as follows. (i) Neither the ^{29}Si data for the $SiMe_3$ groups nor the ^{13}C data appear to show any systematic variation that might help in indicating whether the nitrogen atom of the NMe_2 group is coordinated to a metal in relevant compounds in solution. The relatively large negative value of the chemical shift for ^{29}Si of the $SiMe_3$ group in the lithium compound can be associated with the high carbanionic character of the central carbon; compare the corresponding shift of δ −16.8 for the ^{29}Si nuclei in the salt $[Li(THF)_4][C(SiMe_2$-

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Table 5. NMR Data: Selected Chemical Shifts in C_6D_6 for Compounds Containing the Ligand $(Me_3Si)_2(Me_2NMe_2Si)C$ (R)[a]

	δ(Si)		δ(C)			
compd	$SiMe_3$	$SiNMe_2$	NMe_2	$SiMe_3$	$SiMe_2$	δ(N)
RH	−1.5	4.9	38.3	3.3	1.6	−380
RCl	2.7	3.4	39.5	1.0	0.18	−378
RI	3.2	3.5	39.9	3.2	3.0	*a*
RLi·2THF	−10.6	7.0	38.8	8.1	3.3	−373
R_2Hg	−5.1	2.3	40.0	6.6	5.6	−378
$RAlC1_2$	−2.4	30.0	41.1	2.4	2.5	−373
$RAlPh_2$	−3.5	29.0	42.5	7.8	3.5	*a*
$RGaC1_2$	−1.1	31.8	41.5	6.5	2.4	*a*
$RSnCl_3$	−0.04	18.3	42.6	5.6	4.8	−335

[a] Not recorded.

C_6H_4Me-*o*)$_3$][22] and δ −10.8 for the $SiMe_3$ groups in the cyclic anion $[\overline{CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMeCH_2}]^-$.[18] (ii) In contrast, the ^{29}Si shifts for the $SiMe_2NMe_2$ groups do show a clear separation between those in the range δ 2−5 for the compounds in which there can be no N−metal coordination and those in the range δ 29−32 for the Al and Ga compounds in which there is such coordination in the solid state, and this strongly suggests that in these compounds the coordination persists in solution. The shift of δ 18.3 for the tin compound **6**, although distinctly smaller than those for the Al and Ga compounds, also strongly favors the presence of such coordination. The shift for the lithium compound at first sight may seem anomalous, but in the absence of coordination a substantial negative value would be expected and the observed positive shift of δ 7.0 can be attributed to persistence of the N−metal coordination in solution in this case also. (iii) With one exception the ^{15}N shifts lie within a remarkably narrow range, but this is perhaps not surprising, since even protonation of amines normally results in only small upfield shifts.[23] In this light it seems likely that the change in the shift from δ −378 to −380 for the compounds in which there can be no coordination to the δ −373 observed for RLi and $RAlC1_2$ reflects the persistence of the coordination in these cases, but the effect is too small to be regarded as diagnostic. The exceptional shift is that of δ −335 for the tin compound **6,** and we are unable to account for it, but we note that a shift of δ −357 was recorded for the related compound $Sn\{C(SiMe_2NMe_2)_3\}Cl_3$ (compared with δ −380 for the corresponding aluminum compound $\overline{Al\{C(SiMe_2N}Me_2)_3\}_2$).[24]

Concluding Comments. An important feature of the results described above is that the lengths (and so presumably the strengths) of the $SiMe_2N−M$ bonds in the cyclic species with M = Li, Al, Ga are not appreciably different from those between organic amines and these metals, which is somewhat surprising in view of the fact that silylamines are much less basic than alkylamines.[25]

Experimental Section

Air and moisture were excluded as rigorously as possible by use of Schlenk techniques, flame-dried glassware, and argon as blanket gas. Solvents were dried by standard procedures and distilled immediately before use. C, H analyses were by Medac Ltd.

Spectra. Unless otherwise stated, the NMR spectra were determined for solutions in C_6D_6. The frequencies (MHz) used for the various nuclei were as follows: ^1H, 300.1; ^{13}C, 125.8; ^{29}Si, 99.4; ^{119}Sn, 186.6; ^7Li, 194.5; ^{199}Hg, 89.5; ^{15}N 50.7. Chemical shifts are relative to $SiMe_4$ for H, C, and Si, to $SnMe_4$ for Sn, to $HgMe_2$ for Hg, and to aqueous LiCl for ^7Li. Signals from quaternary ^{13}C and from ^{29}Si and ^{15}N were enhanced by polarization transfer. Mass spectra were obtained by EI at 70 eV; *m*/*z* values refer to ^{28}Si, ^{35}Cl, ^{120}Sn, and ^{202}Hg. It is noteworthy that in the case of compounds **3**, **4**, and **5** the base peak was that at *m*/*z* 230, corresponding to the ion produced by loss of Me from the silene $Me_2Si{=}C(SiMe_2NMe_2)SiMe_3$ or an isomer.

$(Me_3Si)_2(Me_2NMe_2Si)CCl$. Dimethylamine (1.0 g, 22 mmol) was added dropwise with stirring to a stirred solution of $(Me_3Si)_2(BrMe_2Si)CCl$ (3.7 g, 13 mmol)[7] in light petroleum (bp 40−60 °C, 40 mL) at −117 °C. The mixture was allowed to warm to room temperature and the solvent then removed under vacuum to leave a white solid, which was extracted with light petroleum (3 × 25 mL). The extract was filtered and the solvent evaporated from the filtrate to leave a white solid, which was sublimed at 60 °C/0.05 mmHg to give $(Me_3Si)_2(Me_2NMe_2Si)CCl$ (3.0 g, 92%), mp 95 °C. Anal. Calcd for $C_{11}H_{30}ClNSi_3$: C, 44.6; H, 10.2; Cl, 12.0; N, 4.7. Found: C, 44.0; H, 10.1; Cl, 11.2; N, 4.6. ^1H NMR: δ 0.20 (s, 18H, $SiMe_3$), 0.29 (s, 6H, $SiMe_2$), 2.40 (s, 6H, NMe_2). ^{13}C NMR: δ 0.18 ($SiMe_2$), 1.0 ($SiMe_3$), 39.5 (NMe_2), 44.2 (^1J(CSi) 37 Hz, CSi_3). ^{15}N NMR (C_6D_6): δ −378. ^{29}Si NMR: δ 2.7 ($SiMe_3$), 3.4 ($SiMe_2$). MS: *m*/*z* 295 (15, M^+), 280 (25, M − Me), 237 (30), 187 (10, $Me_2Si{=}C(SiMe_2H)SiMe_2$), 129 (25, $Me_2Si{=}CHSiMe_2$), 102 (100, $SiMe_2NMe_2$].

$(Me_3Si)_2(Me_2NMe_2Si)CH$. Dimethylamine (0.70 g, 15 mmol) was added dropwise with stirring to a stirred solution of $(Me_3Si)_2(BrMe_2Si)CH$ (2.3 g, 8.0 mmol) in light petroleum (bp 40−60 °C, 40 mL) at −120 °C. The mixture was stirred at −120 °C for a further 1 h and then for an additional 2 h without cooling. The solvent was removed under vacuum, and the residue was extracted with light petroleum. The extract was filtered, the solvent evaporated, and the residue distilled to give $(Me_3Si)_2(Me_2NMe_2Si)CH$ (bp 62−65 °C at 0.01 mmHg; 1.84 g, 82%). ^1H NMR: δ −0.56 (s, Si_3CH), 0.11 (s, 18H, $SiMe_3$), 0.12 (s, 6H, $SiMe_2$), 2.30 (s, 6H, NMe_2). ^{13}C NMR: δ 1.6 ($SiMe_2$), 3.3 ($SiMe_3$), 5.05 (CSi_3), 38.3 (NMe_2). ^{15}N NMR (C_6D_6): δ −380. ^{29}Si NMR: δ −1.5 ($SiMe_3$), 4.9 ($SiMe_2$). MS: *m*/*z* 261 (25, M^+), 246 (100, M − Me), 102 (100, $SiMe_2NMe_2$), 73 (95, $SiMe_3$), 59 (65, $SiMe_2H$). The spectra indicated that traces of other species were present in the product, and so it was not sent for analysis but used directly in the reaction with MeLi as described below.

$[\overline{Li\{C(SiMe_3)_2(SiMe_2N}Me_2)(THF)_2]$ (1). (a) From $(Me_3Si)_2(Me_2NMe_2Si)CCl$. A solution of BuLi (1.06 mmol) in hexane (0.43 mL) was added dropwise to a stirred solution of $(Me_3Si)_2(Me_2NMe_2Si)CCl$ (0.25 g, 0.85 mmol) in THF (10 mL) at −78 °C. The mixture was stirred for a further 2 h at −78 °C, and the solvent was then removed under vacuum and the residue crystallized from THF to give colorless crystals of **1** (0.20 g, 87%). Anal. Calcd for $C_{19}H_{46}LiNO_2Si_3$: C, 55.4; H, 11.3; N, 3.4. Found: C, 53.8; H, 10.9; N, 3.8. (Better analytical data could not be obtained because of the sensitivity of the compound.) ^1H NMR: δ 0.34 (s, 18H, $SiMe_3$), 0.36 (s, 6H, $SiMe_2$), 1.3 (s, 8H, THF), 2.2 (s, 6H, NMe_2), 3.4 (s, 8H, THF). ^{13}C NMR: δ 3.3 (^1J(CSi) 53.5 Hz, $SiMe_2$), 3.8 (^1J(CSi) 54 Hz, CSi_3), 8.1 (^1J(CSi) 47.8 Hz, $SiMe_3$), 25.4 (THF), 38.8 (NMe_2). 68.5 (THF). ^{29}Si NMR: δ −10.6 (^1J(CSi) 47.8 Hz, $SiMe_3$), 7.0

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(^{1}J(CSi) 53.5 Hz, SiMe$_2$). ^{7}Li NMR: δ 0.48. ^{15}N NMR: δ −373. The identity of the product was confirmed by an X-ray diffraction study.

(**b) From (Me$_3$Si)$_2$(Me$_2$NMe$_2$Si)CH.** A solution of MeLi (5.0 mmol) in diethyl ether (3.7 mL) was added dropwise to a stirred solution of (Me$_3$Si)$_2$(Me$_2$NMe$_2$Si)CH (1.04 g, 4.0 mmol) in THF (30 mL) at room temperature. The mixture was stirred for a further 5 h at room temperature, and the solvent was then slowly removed under vacuum at 0 °C to deposit colorless crystals. These were washed three times with light petroleum (bp 40−60 °C) and shown to be those of **1** (0.95 g, 59%), with spectroscopic data essentially identical with those presented above.

Hg{C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)}$_2$ (2). A solution of the lithium reagent **1** was made at −78 °C from (Me$_3$Si)$_2$(Me$_2$NMe$_2$Si)CCl (2.4 g, 8.1 mmol) in THF (30 mL) and LiBu (10.2 mmol) in hexane (4.1 mL) by the procedure described above and then added dropwise with stirring to a suspension of HgBr$_2$ (1.60 g, 4.1 mmol) in THF (20 mL) at −110 °C. The mixture was allowed to warm to room temperature, and the solvents were removed under vacuum to leave a solid, which was extracted with light petroleum. The extract was filtered and evaporated and the residue recrystallized from heptane to give **2** (2.9 g, 51%; mp 209−213 °C). Anal. Calcd for C$_{22}$H$_{60}$HgN$_2$Si$_6$: C, 36.6; H, 8.4; N, 3.9. Found: C, 37.6; H, 8.8; N, 3.9. ^{1}H NMR: δ 0.35 (s, 36H, SiMe$_3$), 0.37 (s, 12H, SiMe$_2$), 2.48 (s, 12H, NMe$_2$). ^{13}C NMR: δ 5.6 (^{1}J(CSi) 55 Hz, SiMe$_2$), 6.6 (^{1}J(CSi) 41 Hz, SiMe$_3$), 40.0 (NMe$_2$), 43.5 (^{1}J(HgC) 332 Hz, ^{1}J(CSi) 40.2 Hz (SiMe$_3$) and 34.6 Hz (SiMe$_2$), Si$_3$C). ^{29}Si NMR: δ −5.1 (SiMe$_3$), 2.3 (SiMe$_2$); ^{199}Hg NMR: δ − 531. MS: *m*/*z* 722 (1, M$^+$), 707 (1, M − Me), 635 (1), 520 (30), 504 (70), 477 (30), 462 (20), 201 (95), 129 (70), 102 (100, SiMe$_2$NMe$_2$], 73 (95).

[Al{C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)}Cl$_2$)] (3). A solution of the lithium reagent **1** was made at −78 °C from (Me$_3$Si)$_2$(Me$_2$NMe$_2$Si)CCl (0.80 g, 2.7 mmol) in THF (30 mL) and LiBu (3.4 mmol) in hexane (1.4 mL) by the procedure described above, and the solvent was then removed. A solution of the residue in toluene (25 mL) was added dropwise with stirring to a suspension of AlCl$_3$ (0.40 g, 2.7 mmol) in toluene (15 mL) at −15 °C. The mixture was warmed to room temperature, and the solvents were removed under vacuum to leave a solid, which was extracted with light petroleum. The extract was filtered and evaporated and the residue recrystallized from light petroleum (bp 40−60 °C) to give colorless crystals of **3** (1.1 g, 91%; mp 249−254 °C). Anal. Calcd for C$_{11}$H$_{30}$AlC1$_2$NSi$_3$: C, 36.8; H, 8.4; N, 3.9. Found: C, 36.7; H, 8.3; N, 4.1. ^{1}H NMR: δ −0.02 (s, 6H, SiMe$_2$), 0.36 (s, 18H, SiMe$_3$), 1.91 (s, 6H, NMe$_2$). ^{13}C NMR: δ 2.5 (SiMe$_2$), 7.0 (SiMe$_3$), 41.3 (NMe$_2$); the signal from the quaternary carbon was not observed. ^{15}N NMR: δ −373. ^{29}Si NMR: δ −2.4 (SiMe$_3$), 30.1 (SiMe$_2$). ^{27}Al NMR: δ 126 ($\Delta\nu_{1/2}$ 1200 Hz**).** MS: *m*/*z* 342 (65, M − Me), 322 (15, M − Cl), 230 (100, Me$_2$Si=C(SiMe$_2$NMe$_2$)SiMe$_2$), 102 (30, SiMe$_2$NMe$_2$) 75 (SiMe$_3$).

[Al{C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)}Ph$_2$] (4). A solution of LiPh (5.6 mmol) in C$_6$H$_6$/Et$_2$O (3.1 mL) was added dropwise to a stirred solution of **3** (1.0 g, 2.7 mmol) in toluene (30 mL) at −3 °C. The mixture was stirred at −3 °C for a further 5 h and then set aside at room temperature for 10 h. The solvents were then removed under vacuum, and the sticky residue solid was extracted with light petroleum. The extract was filtered and the solvent removed to leave a white solid, which was recrystallized from toluene to give **4** in ca. 50% yield. ^{1}H NMR: δ 0.20 (s, 6H, SiMe$_2$), 0.31 (s, 18H, SiMe$_3$), 2.10 (s, 6H, NMe$_2$), 7.15−7.30 (m, 6H, *m*- and *p*-H), 7.78 (d, 4H, *o*-H). ^{13}C NMR: δ 3.5 (SiMe$_2$), 7.8 (SiMe$_3$), 42.5 (NMe$_2$), 127.2, 127.6. 128.5, 139.1 (all Ph). ^{29}Si NMR: δ −3.5 (SiMe$_3$), 28.6 (SiMe$_2$). ^{27}Al NMR: δ 142 ($\Delta\nu_{1/2}$ 4000 Hz) MS: *m*/*z* 426.2042 (15, M − Me, C$_{22}$H$_{37}$AlNSi$_3$ calcd 426.2049), 364 (75, M − Ph), 287 (55, M − 2Ph), 230 (50, Me$_2$Si=C(SiMe$_2$NMe$_2$)SiMe$_2$), 102 (80, SiMe$_2$NMe$_2$), 73 (100, SiMe$_3$), 59 (80, SiMe$_2$H).

[Ga{C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)}Cl$_2$] (5). A solution of the lithium reagent **1** (1.10 g, 3.00 mmol) in toluene (35 mL) was added dropwise to a stirred solution of GaCl$_3$ in toluene (15 mL) at −15 °C and the mixture was allowed to warm to room temperature. The solution was then filtered and the solvent removed under vacuum to leave an off-white solid which was recrystallized from heptane to give colorless crystals of **5** (0.95 g, 58%), mp 269−274 °C. Anal. Calcd for C$_{11}$H$_{30}$GaC1$_2$NSi$_3$: C, 32.9; H, 7.5; N, 3.5. Found: C, 32.3, H, 7.5; N, 2.9 ^{1}H NMR: δ − 0.01 (s, 6H, SiMe$_2$), 0.34 (s, 18H, SiMe$_3$), 2.00 (s, 6H, NMe$_2$). ^{13}C NMR: δ 2.4 (SiMe$_2$), 6.5 (SiMe$_3$), 18.8 (CSi$_3$), 41.5 (NMe$_2$). ^{29}Si NMR: δ −1.1 (SiMe$_3$), −32.3 (SiMe$_2$). MS: *m*/*z* 401 (5%, M) 386 (35, M − Me), 366(50, M − Cl), 230 (100, Me$_2$Si=C(SiMe$_2$NMe$_2$)SiMe$_2$), 102 (20, SiMe$_2$NMe$_2$], 73 (65%, SiMe$_3$), 59 (50, SiMe$_2$H).

Sn{C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)}Cl$_3$ (6). A solution of the lithium reagent **1** was made at −78 °C from (Me$_3$Si)$_2$(Me$_2$NMe$_2$Si)CCl (1.1 g, 3.7 mmol) in THF (30 mL) and LiBu (4.6 mmol) in hexane (1.9 mL) by the procedure described above and then added dropwise with stirring to a solution of SnCl$_4$ (0.98 g, 3.7 mmol) in THF (10 mL) at −12 °C. The mixture was allowed to warm to room temperature, and the solvents were removed under vacuum to leave a solid, which was extracted with light petroleum (bp 40−60 °C). The solvent was evaporated from the extract to leave a white solid, which was recrystallized from heptane to give **6** (1.4 g, 78%; mp 247−250 °C). Anal. Calcd for C$_{11}$H$_{30}$Cl$_3$NSi$_3$Sn: C, 27.2; H, 6.2; N, 2.9. Found: C, 27.2; H, 6.3; N, 2.7. ^{1}H NMR: δ 0.04 (s, 6H, SiMe$_2$), 0.34 (s, 18H, SiMe$_3$), 2.13 (s, 6H, NMe$_2$). ^{13}C NMR: δ 4.8 (SiMe$_2$), 5.6 (SiMe$_3$), 42.5**(**^{1}J(C^{119}Sn) 217, ^{1}J(C^{117}Sn**)** 207 Hz; ^{1}J(CSi) 36 Hz (SiMe$_2$), 26 Hz (SiMe$_3$), CSi$_3$), 42.6 (NMe$_2$). ^{29}Si NMR: δ −0.04 (^{2}J(Si^{119}Sn) 87 Hz, SiMe$_3$), 18.3 **(**^{2}J(Si^{119}Sn) 135 Hz, SiMe$_2$). ^{119}Sn NMR: δ −182. MS: *m*/*z* 485 (20, M$^+$), 470 (35, M − Me), 450 (30, M − Cl), 221 (75), 102 (85, SiMe$_2$NMe$_2$), 73 (100).

(Me$_3$Si)$_2$(Me$_2$NMe$_2$Si)CI. A solution of LiBu (13 mmol) in hexane (5 mL) was added dropwise with stirring to a solution of (Me$_3$Si)$_2$(Me$_2$NMe$_2$Si)Cl (3.0 g, 10 mmol) in THF (40 mL) at − 78 °C. The mixture was stirred at − 78 °C for a further 2 h; then a solution of ICCH$_2$CH$_2$I (2.8 g, 10 mmol) in THF (30 mL) was added dropwise. The stirred mixture was kept at −78 °C for 3 h, and the solvents were then removed under vacuum at −60 °C to leave a brown solid. This was extracted with light petroleum, and the solvent was removed from the extract to leave a white solid, which was recrystallized from MeOH to give white crystals of the iodide (Me$_3$Si)$_2$(Me$_2$NMe$_2$Si)CI (3.1 g, 82%; mp 199−204 °C). Anal. Calcd for C$_{11}$H$_{30}$INSi$_3$: C, 34.1; H, 7.8; N, 3.6. Found: C, 34.7; H, 7.4; N, 3.9. ^{1}H NMR: δ 0.28 (s, 18H, SiMe$_3$), 0.38 (s, 6H, SiMe$_2$), 2.45 (s, 6H, NMe$_2$). ^{13}C NMR: δ 3.01 (SiMe$_2$), 3.16 (SiMe$_3$), 16.3 (^{1}J(CSi) 34 Hz (SiMe$_3$), 37 Hz (SiMe$_2$), CSi$_3$), 39.9 (NMe$_2$). ^{29}Si NMR: δ 3.2 (SiMe$_3$), 3.5 (SiMe$_2$). MS: *m*/*z* 387 (15, M$^+$), 372 (20, M − Me), 329 (20, M − SiMe$_2$), 102 (100, SiMe$_2$NMe$_2$), 73 (30, SiMe$_3$).

Hg{C(SiMe$_3$)$_2$(SiMe$_2$Cl)}$_2$. A solution of **2** (0.44 g, 0.60 mmol) in THF (20 mL) was added dropwise with stirring to a solution of ICl (0.19 g, 1.20 mmol) at −78 °C. The mixture was allowed to warm to room temperature, and the solvent was removed under vacuum. The residual solid was extracted with light petroleum (bp 40−60 °C) and the extract filtered. The solvent was removed from the filtrate under vacuum to leave a solid, which was recrystallized from heptane to give Hg{C(SiMe$_3$)$_2$(SiMe$_2$Cl)}$_2$ (mp 270−273 °C). Anal. Calcd for C$_{18}$H$_{48}$C1$_2$HgSi$_6$: C, 30.7; H, 6.9. Found: C, 30.6; H, 6.9. ^{1}H NMR: δ 0.33 (s, 36H, SiMe$_3$), 0.60 (s, 12H, SiMe$_2$). ^{13}C NMR: δ 5.8 (SiMe$_3$), 9.1 (SiMe$_2$). ^{29}Si NMR: δ −3.5 (SiMe$_3$), 25.1 (SiMe$_2$). ^{199}Hg NMR: δ −522. MS: *m*/*z* 704 (1, M), 689 (15, M − Me), 236 (75, Me$_2$Si=C(SiMe$_2$Cl)SiMe$_2$), 221 (35), 201 (100, Me$_2$Si=C(SiMe$_3$)SiMe$_2$), 73 (65, SiMe$_3$).

Hg{C(SiMe$_3$)$_2$(SiMe$_2$O$_2$CCF$_3$)}$_2$. A solution of **2** (0.15 g, 2.1 mmol) in benzene (10 mL) was added dropwise with stirring to a solution of CF$_3$CO$_2$H (0.032 mL, 4.2 mmol) in benzene (5

Table 6. Summary of Crystallographic Data for 1−5

	2	**1**	**3**	**4**	**5**
empirical formula	$C_{22}H_{60}HgN_2Si_6$	$C_{19}H_{46}LiNO_2Si_3$	$C_{11}H_{30}AlC1_2NSi_3$	$C_{23}H_{40}AlNSi_3$	$C_{11}H_{30}GaC1_2NSi_3$
fw	721.9	411.8	358.5	441.8	401.3
cryst size (mm)	0.4 × 0.4 × 0.2	0.4 × 0.3 × 0.1	0.4 × 0.4 × 0.2	0.3 × 0.2 × 0.2	0.2 × 0.24 × 0.1
cryst syst	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\ \bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	9.048(1)	9.270(7)	8.941(2)	8.906(2)	8.941(2)
b (Å)	9.102(1)	9.867(4)	14.093(2)	9.414(4)	14.038(4)
c (Å)	12.580(2)	15.479(6)	15.789(2)	15.956(3)	15.840(4)
α (deg)	69.25(1)	85.63(3)	90	80.75(2)	90
β (deg)	71.32(1)	86.73(5)	90.08(1)	75.66(2)	90.22(2)
γ (deg)	60.49(1)	66.05(5)	90	87.04(3)	90
V (Å^3)	829.5(2)	1289.6(12)	1989.5(6)	1279.1(7)	1988.1(9)
Z	1	2	4	2	4
d_c (Mg m^{-3})	1.45	1.06	1.20	1.15	1.34
F(000)	370	456	768	480	840
μ (mm^{-1})	4.87	0.20	0.54	0.23	1.82
θ range (deg)	2−25	2−25	2−30	2−28	2−28
index range	$0 \leq h \leq 10$	$0 \leq h \leq 11$	$0 \leq h < 12$	$0 < h < 11$	$0 \leq h < 11$
	$-8 \leq k \leq 10$	$-10 \leq k \leq 11$	$0 \leq k \leq 19$	$-12 \leq k \leq 12$	$0 \leq k \leq 18$
	$-13 \leq l \leq 14$	$-18 \leq l \leq 18$	$-22 \leq l \leq 22$	$-19 < l \leq 21$	$-20 \leq l \leq 20$
no. of rflns collected	2907	4522	6114	6160	5059
no. of unique rflns	2907	4522	5790 ($R_{int} = 0.01$)	6160	4777 ($R_{int} = 0.04$)
no. of rflns with $I > 2\sigma(I)$	2892	3060	4803	4420	2976
R1; wR2 ($I > 2\sigma(I)$)	0.027, 0.070	0.070; 0.184	0.032; 0.086	0.049; 0.130	0.054; 0.100
R1; wR2 (all data)	0.027, 0.071	0.111; 0.216	0.043; 0.111	0.080; 0.162	0.109; 0.120
no. of data/restraints/ params	2907/0/142	4522/0/236	5790/0/163	6160/0/253	4777/0/163
GOF on F^2	0.846	1.031	0.430	0.761	1.013
max shift/error	0.001	0.001	0.001	0.001	0.001
largest diff peak/hole (e Å^{-3})	0.96, −1.67	0.47, −0.45	0.32, −0.29	0.37, −0.36	0.68, −0.47
abs cor: T_{max}; T_{min}	1.00, 0.52	not applied	not applied	not applied	not applied

mL) at 0 °C. The mixture was allowed to warm to room temperature, and the solvent was removed under vacuum. The residual solid was extracted with light petroleum (bp 40−60 °C), and the extract was filtered. The solvent was removed from the filtrate under vacuum to leave a solid, which was recrystallized from heptane to give colorless crystals of $Hg\{C(SiMe_3)_2(SiMe_2O_2CCF_3)\}_2$ (0.10 g, 56%; mp 135−137 °C). Anal. Calcd for $C_{22}H_{48}F_6HgO_4Si_6$: C, 30.7; H, 5.6. Found: C, 30.8; H, δ 5.8. ^{1}H NMR: δ 0.20 (s, 36H, $SiMe_3$), 0.50 (s, 12H, $SiMe_2$). ^{13}C NMR: δ 5.2 ($SiMe_2$), 5.6 ($SiMe_3$), 38.6 (^1J(CSi) 32 ($SiMe_3$), 46.3 Hz ($SiMe_2$), CSi_3), 115.3 (q, ^1J(CF) 287 Hz, CF_3), 156.3 (q, ^2J(CF) 42 Hz, CO). ^{29}Si NMR: δ −3.6 ($SiMe_3$), 26.0 ($SiMe_2$).^{199}Hg NMR: δ −531. ^{19}F NMR −76.5. MS: 860 (1, M), 845 (15, M − Me), 747 (5, M − O_2CCF_3), 314 (100, $CH(SiMe_3)_2(SiMe_2COCF_3)$), 205 (45), 73 (60, $SiMe_3$).

Reaction of $Sn\{C(SiMe_3)_2(SiMe_2NMe_2)\}Cl_3$ with MeOH. Methanol (0. 40 mL, 9.9 mmol) was added to a stirred solution of **5** (0.07 g, 1.4 mmol) in Et_2O (10 mL) at −15 °C. The mixture was allowed to warm to room temperature, and the solid present was filtered off and judged from its spectroscopic properties, which were essentially identical with those of an authentic sample,[20] to be $Sn\{C(SiMe_3)_2(SiMe_2OMe)\}Cl_3$. ^{1}H NMR: δ 0.14 (s, 6H, $SiMe_2$), 0.29 (s, 18H, $SiMe_3$), 3.0 (s, 3H, OMe). MS: m/z 457 (35, M − Me), 437 (M − Cl), 237 (100), 129 (25), 59 (40).

Crystal Structure Determinations. Data were collected at 173(2) K on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (λ 0.710 73 Å) and corrected for Lorentz and polarization effects; details are given in Table 6. The structures were determined by direct methods, with SHELXS-86 and SHELXL-93 programs used for structure solution and refinement on F^2 using all reflections. Non-hydrogen atoms were anisotropic. The H atoms were refined in the riding mode with $U_{iso}(H) = 1.5U_{eq}(C)$.

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Supporting Information Available: Tables of crystallographic data, atom coordinates, bond lengths and angles, and anisotropic thermal parameters for **1−5** (15 pages). Ordering information is given on any current masthead page.

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