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Nearly Planar Nonsolvated Monomeric Silyl- and Germyllithiums as a Result of an Intramolecular CH−Li Agostic Interaction

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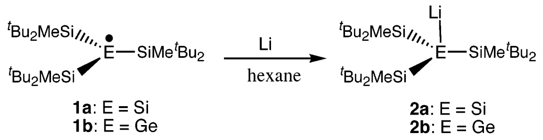
The intra/intermolecular interaction of C−H σ-bonds with transition metals is referred to as an agostic interaction, which is one of the important forces controlling reactivity and structure in transition metal chemistry.[1] In contrast, such an interaction in alkali metal derivatives is not common, owing to complex formation between coordinating solvents such as THF or Et_2O and the alkali metal cations.[2] The CH−Li agostic interaction can be often found in nonsolvated oligomeric lithium derivatives $(RLi)_n$.[2,3] Here we report the synthesis and unusual structural features of nonsolvated monomeric silyl- and germyllithiums with a nearly planar geometry, arising from the intramolecular agostic CH−Li interactions of these silyl- and germyllithiums.

We found that the reaction of tris[di-*tert*-butyl(methyl)silyl]silyl radical **1a**[4] with lithium in hexane at room temperature results in a reduction of the radical **1a** to form tris[di-*tert*-butyl(methyl)silyl]-silyllithium **2a** (Scheme 1).[5] The silyllithium **2a** was isolated as extremely air- and moisture-sensitive pale-yellow crystals in 62% yield.[6] The tris[di-*tert*-butyl(methyl)silyl]germyl radical **1b**[4] also readily reacted with lithium in hexane to produce tris[di-*tert*-butyl-(methyl)silyl]germyllithium (**2b**, 88%).[7,8]

Scheme 1



The molecular structures of **2a** and **2b**, determined by X-ray crystallography, are shown in Figures 1 and 2, respectively.[9] The remarkable features of **2a** are as follows: (a) the central anionic silicon atom is almost planar (av 119.7° for Si−Si−Si bond angles); (b) a nonsolvated monomeric structure is adopted; (c) the Si−Si bond lengths are significantly shortened [av 2.3632(8) Å] relative to those of the neutral species $(^t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{SiH}$ [av 2.450(2) Å] and $(^t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{Si}\cdot$ [av 2.4210(7) Å],[4] because of hyperconjugation of the anionic center with adjacent σ^*-orbitals of Si−C bonds; (d) intramolecular CH−Li agostic interactions are observed (see also Figure 3); and (e) the Si−Li bond length [2.531(6) Å] is somewhat shorter than the typical value of solvated and pyramidal silyllithium compounds (2.67−2.70 Å).[10]

Normally, alkali metal compounds of the group 14 elements prefer a tetrahedral geometry rather than a planar geometry.[2,10] In contrast to a number of planar carbanions in the literature,[2] to the best of our knowledge, no planar alkali metal derivatives of heavier group 14 elements have yet been reported.[10] The introduction of large and electropositive substituents such as silyl groups on the central atom can lead to a planar geometry due to the decrease of inversion barriers,[11] as found in the case of $(Me_3Si)_3CK$[12] and the isoelectronic $(i\text{-}Pr_3Si)_3P$;[13] however, the structure of $[(Me_3Si)_3SiM]_2$ (M = alkali metal) was found to have a significantly pyramidalized geometry.[14]

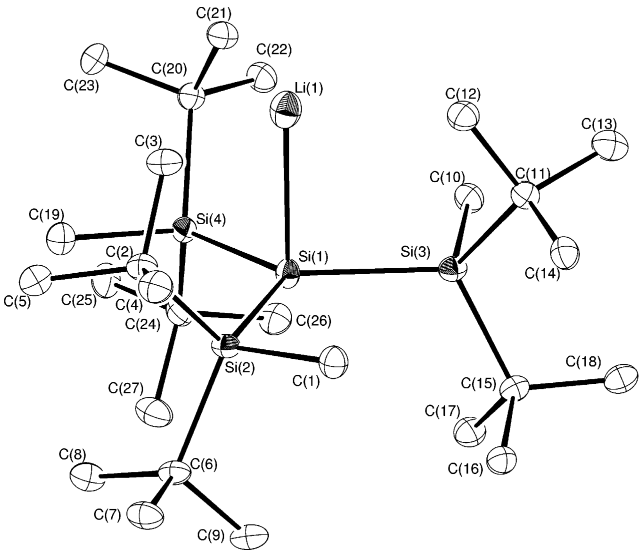


Figure 1. ORTEP drawing of tris[di-*tert*-butyl(methyl)silyl]silyllithium **2a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si(1)−Li(1) 2.531(6), Si(1)−Si(2) 2.3608(8), Si(1)−Si(3) 2.3629(8), Si(1)−Si(4) 2.3660(8), Li(1)−C(3) 2.595(6), Li(1)−C(12) 2.518(5), Li(1)−C(21) 2.574(5). Selected bond angles (deg): Si(2)−Si(1)−Si(3) 119.96(3), Si(2)−Si(1)−Si(4) 119.31(3), Si(3)−Si(1)−Si(4) 119.89(3).

The unusual structure of **2a** is ascribed to severe steric repulsion by the three bulky $^t\mathrm{Bu}_2\mathrm{MeSi}$ groups, which can force the molecule into a monomeric and planar structure. All of the methyl substituents at the Si atoms are arranged in a "gear"-type fashion to minimize steric hindrances. Of further interest is the fact that **2a** has intramolecular $\mathrm{Li}\cdots\mathrm{CH}_3$ interactions, as determined by $\mathrm{Li}-\mathrm{CH}_3$ distances [Li(1)−C(3), 2.595(6); Li(1)−C(12), 2.518(5); Li(1)−C(21), 2.574(5) Å]. Thus, the planarity of the central silicon atom is a consequence of the combination of both the intramolecular CH−Li agostic interaction and the steric factor (Figure 3). Indeed, the crystal structure of free silyl anion $[(^t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{Si}^-][\mathrm{Li}^+(\mathrm{THF})_4]$ **3a**, which was prepared by the reaction of **1a** with lithium in THF, no longer showed planar geometry, because of the absence of the intramolecular CH−Li agostic interaction.[15]

Tris[di-*tert*-butyl(methyl)silyl]germyllithium (**2b**) has structural features similar to those of **2a** (Figure 2), that is, a nonsolvated, monomeric, and nearly planar structure with CH−Li interactions ([Li(1)−C(3), 2.588(9); Li(1)−C(12), 2.597(8); Li(1)−C(21), 3.511(9) Å; av 117.5° for Si−Ge−Si bond angles). As with **3a**, the geometry of the free anion $[(^t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{Ge}^-][\mathrm{Li}^+(\mathrm{THF})_n]$ (n = 3, 4) (**3b**) changed to a pyramidal structure.[15]

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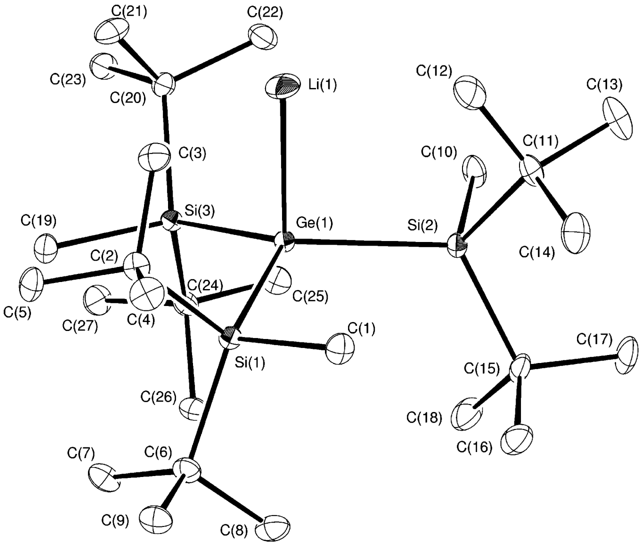

Figure 2. ORTEP drawing of tris[di-*tert*-butyl(methyl)silyl]germyllithium **2b**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge(1)−Li(1) 2.518(7), Ge(1)−Si(1) 2.4500(11), Ge(1)−Si(2) 2.4357(10), Ge(1)−Si(3) 2.4140(10), Li(1)−C(3) 2.588(9), Li(1)−C(12) 2.597(8), Li-(1)−C(21) 3.511(9). Selected bond angles (deg): Si(1)−Ge(1)−Si(2) 116.00(3), Si(1)−Ge(1)−Si(3) 116.96(3), Si(2)−Ge(1)−Si(3) 119.40(3).

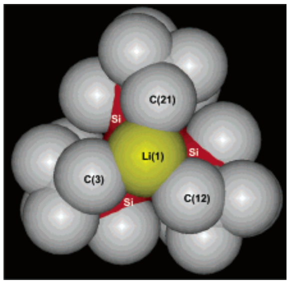

Figure 3. Space-filling representation of **2a**. Hydrogen atoms are omitted for clarity. Gray, carbon; yellow, lithium; red, silicon.

The CH−Li agostic interaction found in **2a** is very weak. Indeed, the ^{1}H NMR spectrum of **2a** in toluene-d_8 shows a very sharp signal for both *tert*-butyl groups at 1.30 ppm and the methyl group at 0.43 ppm. As the temperature was lowered, the ^{1}H NMR signals of the *tert*-butyl groups broadened ($T_c = 240$ K) and split into two singlets (1.46 and 1.06 ppm at 220 K) in a 1:1 ratio, whereas the signal due to the methyl groups (0.38 ppm) remained unsplit. The temperature-dependent change of the ^{1}H NMR signals of the *tert*-butyl groups in toluene-d_8 resulted from the restricted rotation, which is consistent with the presence of a CH−Li agostic interaction in **2a**. At lower temperatures, the two *tert*-butyl groups in the ^{t}Bu$_2$MeSi substituents above and below the Si(1)−Si(2)−Si(3)−Si(4) plane became nonequivalent, as shown in Figure 1, whereas all methyl groups remained equivalent. From the Arrhenius and Eyring plots, the values $E_a = 11.1 \pm 0.3$ kcal mol^{-1}, $\Delta H^{\ddagger} = 10.6 \pm 0.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -2.4 \pm 1$ cal mol^{-1} K^{-1} were estimated for the rotational barrier around the Si−Si bonds. This exceptionally high Si−Si single bond rotational barrier might be caused by the intramolecular CH−Li agostic interaction in **2a**. However, in a polar solvent such as THF-d_8, we did not observe such phenomena, because of the lack of the CH−Li agostic interaction.

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Supporting Information Available: Experimental procedure and spectral data of **3a** and **3b**, temperature-dependent ^{1}H NMR chart of **2a** and kinetic data, tables of crystallographic data including atomic positional and thermal parameters for **2a**, **2b**, **3a**, and **3b** (PDF). A crystallographic file in CIF format is also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Spectral data for **2a**: ^{1}H NMR (C_7D_8, 298 K, δ) 0.43 (s, 9H), 1.30 (s, 54H); ^{13}C NMR (C_7D_8, 298 K, δ) 2.0, 23.2, 32.3; ^{29}Si NMR (C_7D_8, 298 K, δ) −185, 19.5.
(7) Both silyl and germyl radicals **1a** and **1b** also readily reacted with Na and K in hexane to give the corresponding alkali metal derivatives as almost insoluble products. The results will be reported elsewhere.
(8) Spectral data for **2b**: ^{1}H NMR (C_7D_8, 298 K, δ) 0.37 (s, 9H), 1.20 (s, 54H); ^{13}C NMR (C_7D_8, 298 K, δ) 2.5, 23.4, 32.3; ^{29}Si NMR (C_7D_8, 298 K, δ) 24.0.
(9) Crystal data for **2a** at 120 K: MF = $C_{27}H_{63}LiSi_4$, MW = 507.07, monoclinic, $P2_1/n$, $a = 11.3960(5)$, $b = 18.1210(4)$, $c = 16.6950(7)$ Å, $\beta = 104.520(2)°$, $V = 3337.5(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.009$ g cm^{-3}. The final R factor was 0.0669 for 6622 reflections with $Io > 2\sigma(Io)$ ($R_w = 0.1906$ for all data, 7760 reflections), GOF = 1.008. Crystal data for **2b** at 120 K: MF = $C_{27}H_{63}GeLiSi_3$, MW = 551.57, orthorhombic, $Pna2_1$, $a = 16.9060(2)$, $b = 11.4130(6)$, $c = 17.5190(6)$ Å, $Z = 4$, $V = 3380.3(2)$ Å^3, $D_{calcd} = 1.084$ g cm^{-3}. The final R factor was 0.0354 for 3825 reflections with $Io > 2\sigma(Io)$ ($R_w = 0.0948$ for all data, 4163 reflections), GOF = 1.060.
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(15) For the spectral data and crystal structures of **3a** and **3b**, see the Supporting Information.

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