1,3-Disila-2-gallata- and -indataallenic Anions [>Si⋯M⋯Si<]⁻·Li⁺ (M = Ga, In): Compounds Featuring Double Bonds between Elements of Groups 13 and 14

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Since the isolation of the first stable silene (>Si=C<)[1] and disilene (>Si=Si<)[2] in 1981, several species with a double bond between a silicon and a main group element, such as >Si=Pn— (Pn = N[3], P,[4] and As[5]) and >Si=Ch (Ch = S[6]), have been synthesized as stable compounds by taking advantage of kinetic stabilization with bulky substituents.[7] As cumulative doubly bonded compounds containing silicon atoms, several stable 1-silaallenes (>Si=C=C<)[8] and trisilaallene (>Si=Si=Si<)[9] have also been prepared and isolated. In sharp contrast, doubly bonded compounds consisting of a silicon and group 13 elements have not been synthesized until recently due to the lack of an appropriate synthetic approach. Meanwhile, we have recently reported 1,1-dilithiosilane **1** as an effective reagent for the synthesis of a variety of doubly bonded derivatives of heavier group 14 elements, such as disilenes (>Si=Si<), germasilene (>Si=Ge<), and silastannene (>Si= Sn<).[10,11] The successful preparation of these new doubly bonded systems of heavier group 14 elements using **1** prompted us to extend this method to the synthesis of new systems featuring double bonds between a silicon and group 13 elements. In this contribution, we present the first isolation of stable 1,3-disila-2-gallata- and -indataallenic anions having the [>Si⋯Ga⋯Si<]⁻ or [>Si⋯In⋯Si<]⁻ units, representing a novel allenic anion species of main group elements consisting of two silicon atoms and a gallium or indium atom.

The reactions of bis(di-*tert*-butylmethylsilyl)dilithiosilane **1**[10] with GaCl₃ in dry THF at room temperature resulted in the immediate formation of 1,1,3,3-tetrakis(di-*tert*-butylmethylsilyl)-1,3-disila-2-gallataallenic anion (**2⁻**), which was isolated in the form of lithium salt in 94% yield as dark red crystals (Scheme 1).[12] Dark brown— red crystals of the lithium salt of indium analogue (**3⁻**) were also obtained in 95% yield when InCl₃ was used, as shown in Scheme 1.[13] Gallata- and -indataallenic anions, representing the first examples of compounds with an [>Si⋯M⋯Si<]⁻ unit (M = main group element), are air- and moisture-sensitive, but thermally stable with melting points of 153−155 °C for **2⁻**·[Li(thf)₄]⁺ and 146− 148 °C for **3⁻**·[Li(thf)₄]⁺.

The molecular structures of **2⁻**·[Li(thf)₄]⁺ and **3⁻**·[Li(thf)₄]⁺ determined by X-ray crystallographic analysis are shown in Figures 1 and 2, respectively.[13,14] The lithium cation of both **2⁻** and **3⁻** is coordinated by four THF molecules. Consequently, the closest distances between the lithium ion and a silicon atom of **2⁻** or **3⁻** are greater than 6 Å, showing no interactions between them. These results indicate that allenic anions **2⁻** and **3⁻** are free anion species in the solid state. Both Si⋯M (M = Ga, In) bond lengths [**2⁻**: 2.2828(9) and 2.2775(9); **3⁻**: 2.4849(9) and 2.4792(9) Å] in the anion fragments are almost the same and about 9% shorter than the typical Si−M single bonds in gallium and indium clusters, such as Ga₄(Si^{t}Bu₃)₄ [2.4532(9)−2.567(10) Å],[15a] Ga₁₀[Si(SiMe₃)₃]₆ [2.401(1)−2.468(1) Å],[15b] In₁₂(Si^{t}Bu₃)₈ [2.668(3)−2.685(3) Å],[16a] and In₈(Si^{t}Bu₃)₆ [2.615(1)−2.683(1) Å].[16b] The Si1⋯M1⋯Si4

**Scheme 1**

2⁻: M = Ga, **3⁻**: M = In
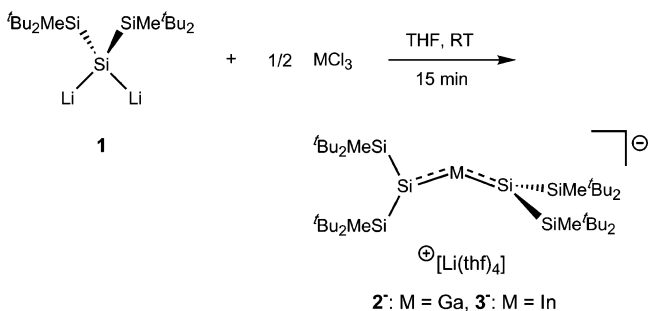
frameworks (M = Ga, In) are not linear but are somewhat bent with bending angles of 161.60(3) and 161.35(3)°, respectively. The sum of the bond angles at Si1 and Si4 atoms (**2⁻**: 341.26 and 342.96; **3⁻**: 324.39 and 328.87°) reveal the pyramidal geometry around the two terminal silicon atoms in the Si⋯M⋯Si (M = Ga, In) frameworks. In addition, the bending angles around Si1 and Si4 atoms (**2⁻**: 41.63 and 45.35; **3⁻**: 53.17 and 58.63°) indicate a highly pronounced *trans*-bent arrangement of substituents around the Si1=M and Si4=M double bonds (M = Ga, In) (Figure 3). Indeed, this was supported by a theoretical calculation for the model compound, [(Me₃Si)₂Si⋯Ga⋯Si(SiMe₃)₂]⁻ (**4⁻**) performed at the B3LYP/6-31G(d) level. The two theoretically calculated Si=Ga
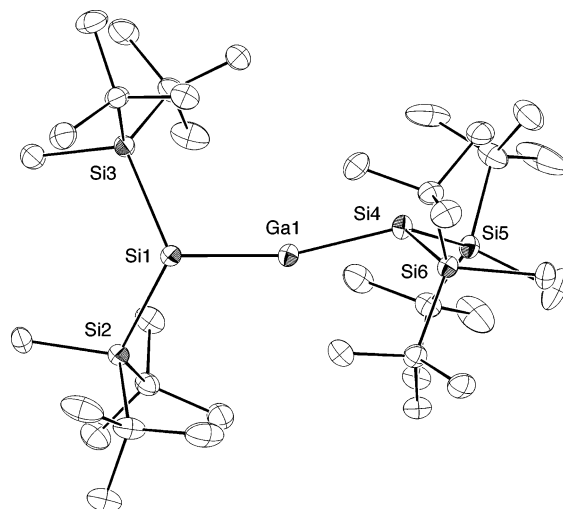
Figure 1. ORTEP drawing of **2⁻**·[Li(thf)₄]⁺ (30% thermal ellipsoids). Hydrogen atoms and the cationic fragment [Li(thf)₄]⁺ are omitted for clarity. Selected bond lengths (Å): Ga1−Si1 = 2.2828(9), Ga1−Si4 = 2.2775(9), Si1−Si2 = 2.3627(11), Si1−Si3 = 2.3621(11), Si4−Si5 = 2.3615(11), Si4−Si6 = 2.3568(11). Selected bond angles (deg): Si1−Ga1−Si4 = 161.61(3), Ga1−Si1−Si2 = 112.67(4), Ga1−Si1−Si3 = 110.46(4), Si3− Si1−Si2 = 118.13(4), Ga1−Si4−Si5 = 112.10(4), Ga1−Si4−Si6 = 113.84(3), Si6−Si4−Si5 = 117.02(4). Dihedral angle (deg): Si2−Si1− Si3/Si5−Si4−Si6 = 82.9.

Chart 1

M = Ga, In ; R = SiMe^{t}Bu$_2$

Scheme 2
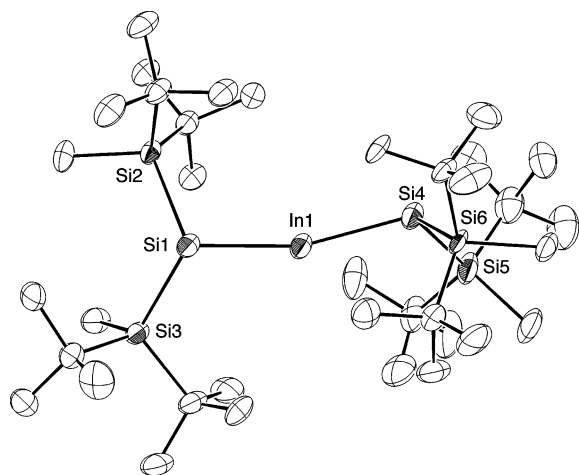
Figure 2. ORTEP drawing of **3**$^-$·[Li(thf)$_4$]$^+$ (major fragment, 30% thermal ellipsoids). Hydrogen atoms and the cationic fragment [Li(thf)$_4$]$^+$ are omitted for clarity. Selected bond lengths (Å): In1–Si1 = 2.4849(9), In1–Si4 = 2.4792(9), Si1–Si2 = 2.3662(11), Si1–Si3 = 2.3801(14), Si4–Si5 = 2.325(2), Si4–Si6 = 2.3761(17). Selected bond angles (deg): Si1–In1–Si4 = 161.35(3), In1–Si1–Si2 = 103.85(4), In1–Si1–Si3 = 110.43(4), Si3–Si1–Si2 = 110.11(5), In1–Si4–Si5 = 107.85(6), In1–Si4–Si6 = 113.03(5), Si6–Si4–Si5 = 107.99(7). Dihedral angle (deg): Si2–Si1–Si3/Si5–Si4–Si6 = 75.4.
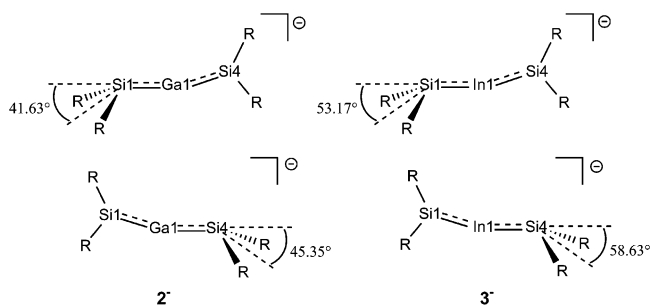

Figure 3. The *trans*-bent angles around the Si and M atoms (M = Ga, In) in **2**$^-$ and **3**$^-$ (R = SiMe^{t}Bu$_2$).

bond lengths (2.330 and 2.331 Å) and the Si⋯Ga⋯Si bond angle (161.66°) for **4**$^-$ are in fairly good agreement with those experimentally obtained for **2**$^-$.

These structural features of **2**$^-$ and **3**$^-$ are reflected by the ^{29}Si NMR spectra. The ^{29}Si NMR chemical shifts of **2**$^-$ and **3**$^-$ in THF-d_8 appeared as two signals (**2**$^-$: 25.7 and −79.9; **3**$^-$: 26.0 and −77.6 ppm). The unusual upfield shifted signals for the Si atoms attached to a gallium or indium atom can be explained in terms of preferential localization of the negative charge on the terminal Si atoms caused by the difference in the electronegativities of Si, Ga, and In atoms. Indeed, the NPA (natural population analysis) charge distribution for **4**$^-$ showed a large part of the negative charge localizing on the two terminal silicon atoms (−0.736 and −0.729), whereas the gallium atom has a positive charge (+0.627), which implies that the allenic [>Si⋯Ga⋯Si<]$^-$ fragment is highly polarized. Thus, the structures of **2**$^-$ and **3**$^-$ might be better described as allyl-type silyl anion resonance structures **I** and **I'** rather than the formal ate-type anion **II**, as depicted in Chart 1.

As expected, **2**$^-$ is highly reactive toward electrophiles. The reaction of **2**$^-$·[Li(thf)$_4$]$^+$ with MeI gave the corresponding iodogallane **5** in almost quantitative yield (Scheme 2).[17] Thus, the
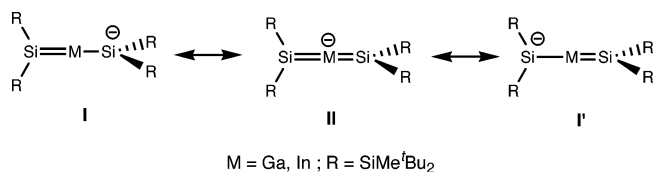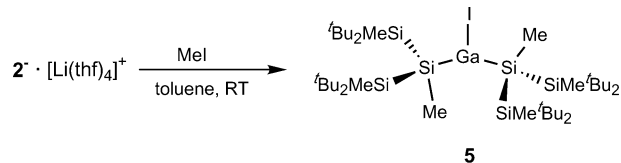
regioselective addition of MeI to **2**$^-$ reflects the polarity of the Si═Ga double bond.

Supporting Information Available: Experimental procedures of **2**$^-$, **3**$^-$, and **5**, calculated geometry for **4**$^-$, table of crystallographic data including atomic positional and thermal parameters for **2**$^-$·[Li(thf)$_4$]$^+$ and **3**$^-$·[Li(thf)$_4$]$^+$ (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Spectral data for **2**$^-$·Li$^+$: dark red crystals; mp 153−155 °C; ^{1}H NMR (THF-d_8, δ) 0.02 (s, 12 H), 1.04 (s, 72 H); ^{13}C NMR (THF-d_8, δ) −1.3 (Si*Me*), 23.0 (C*Me*$_3$), 32.1 (C*Me*$_3$); ^{29}Si NMR (THF-d_8, δ) −79.9 (*Si*═Ga), 25.7 (*Si*Me^{t}Bu$_2$); UV/vis (hexane) λ_{max}/nm (ϵ) 237 (10100), 282 (sh, 3700), 456 (1400).
(13) For the experimental procedure, spectral data, and crystal data of **3**$^-$·[Li(thf)$_4$]$^+$, see the Supporting Information.
(14) Crystal data for **2**$^-$·[Li(thf)$_4$]$^+$ at 120 K: C$_{58}$H$_{122}$GaLiO$_4$Si$_6$, FW = 1128.76, monoclinic, space group $P2/n$, a = 22.2290(12) Å, b = 12.0770-(5) Å, c = 24.5730(11) Å, β = 104.763(3)°, V = 6953.0(5) Å^3, Z = 4, D_{calcd} = 1.078 g·cm^{-3}. R$_1$ (I > 2σ(I)) = 0.0564, wR$_2$ (all data) = 0.1516 for 15933 reflections. GOF = 0.926.
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(17) For the experimental procedure and spectral data of **5**, see the Supporting Information.

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