1,3-Digerma-2-gallata- and -indataallenic Anions: The First Compounds with Ge=Ga or Ge=In Double Bonds

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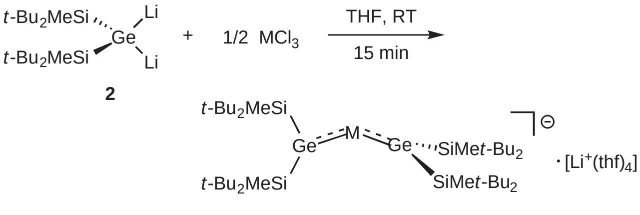
The novel allenic anions consisting of two germanium atoms and a gallium or indium atom, 1,3-digerma-2-gallata- and -indataallenic anions, $[(t\text{-Bu}_2\text{MeSi})_2\text{Ge}{\cdots}\text{M}{\cdots}\text{Ge}(\text{SiMe}t\text{-Bu}_2)_2]^- \cdot [\text{Li}^+(\text{thf})_4]$ (**3a**: M = Ga, **3b**: M = In) were synthesized by the reaction of the dilithiogermane, $(t\text{-Bu}_2\text{MeSi})_2\text{GeLi}_2$ (**2**) with 0.5 equiv of $GaCl_3$ or $InCl_3$. A crystal structure analysis of **3b** showed that the >Ge–In–Ge< framework is *bent* (158.451(14)°) with the two Ge=In bond lengths (2.5453(4) and 2.5387(4) Å).

The synthesis of unsaturated species of heavier main group elements is one of the greatest challenges in organometallic chemistry.[1] In the case of germanium, since the isolation of the first stable digermenes (>Ge=Ge<) achieved by kinetic stabilization with bulky substituents,[2] many studies have been performed on germanium-containing unsaturated species, featuring the $>\text{Ge}=\text{E}_{14}<$ (E_{14} = C,[3] Si,[4] and Sn[5]), $>\text{Ge}=\text{E}_{15}-$ (E_{15} = N[6] and P[7]), and $>\text{Ge}=\text{E}_{16}$ (E_{16} = S, Se, and Te)[8] double bonds. Furthermore, stable heavy allene analogues containing germanium atoms, 1-germaallene (>Ge=C=C<),[9] 1,3-digerma-2-silaallene (>Ge=Si=Ge<),[10] 2-germa-1,3-disilaallene (>Si=Ge=Si<),[11] and trigermaallene (>Ge=Ge=Ge<)[10] have also been prepared and isolated. However, compounds with double bonds between germanium and group 13 element have not been synthesized until recently, because of the lack of appropriate synthetic methods. Very recently, we succeeded in the synthesis and characterization of 1,3-disila-2-gallata- and -indataallenic anions $[(t\text{-Bu}_2\text{MeSi})_2\text{Si}{\cdots}\text{M}{\cdots}\text{Si}(\text{SiMe}t\text{-Bu}_2)_2]^- \cdot [\text{Li}^+(\text{thf})_4]$ (**1a**: M = Ga, **1b**: M = In),[12,13] by the coupling reaction of 1,1-dilithiosilane[14] with $GaCl_3$ or $InCl_3$, representing the first examples of compounds featuring double bonds between the heavier group 13 and 14 elements. In this paper, we report the first isolation of stable 1,3-digerma-2-gallata- and -indataallenic anionic compounds **3a** and **3b** consisting of two germanium atoms and a gallium or indium atom, together with the crystal structure of **3b**, which is the first structurally characterized compound containing a Ge–In bond.

Similar to the experimental conditions for 1,3-disila-2-gallata- and -indataallenic anions,[12] the reactions of bis(di-*tert*-butylmethylsilyl)dilithiogermane (**2**)[15] with 0.5 equiv of $GaCl_3$ or $InCl_3$ in dry THF at room temperature proceeded quickly to give 1,1,3,3-tetrakis(di-*tert*-butylmethylsilyl)-1,3-digerma-2-gallata- and -indataallenic anions (**3a** and **3b**), which were obtained in the form of lithium salts as dark brown-red crystals in 83% and 81% yields, respectively (Scheme 1).[16] These allenic anions are air- and moisture-sensitive but thermally stable with a melting point of 160–162 °C for **3a** and 180–182 °C for **3b**, respectively. The molecular structures of **3a** and **3b** were determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and X-ray crystallographic analysis for **3b**. The NMR spectra of **3a** and **3b** are very simple, in agreement with their highly symmetrical structure. The ^{29}Si NMR resonance signals of the $t\text{-Bu}_2\text{MeSi}$ groups are slightly shifted downfield (**3a**: 30.8; **3b**: 32.0 ppm) compared with the silicon derivatives (**1a**: 25.7; **1b**: 26.0 ppm),[12] owing to the higher electronegativity of Ge.



3a: M = Ga, **3b**: M = In

Scheme 1.

The crystal structure of **3b** was determined by X-ray crystallographic analysis, and an ORTEP drawing of **3b** is shown in Figure 1.[17] The crystal structure of **3a** was also revealed by X-ray diffraction; however, we do not discuss it because of insufficient refinement. The lithium cation in both **3a** and **3b** is coordinated with four THF molecules, the closest distances Li···Ge and Li···In are 6.7 and 8.0 Å, respectively, indicating no interactions between them. The two Ge–In bond lengths in **3b** are almost the same [2.5453(4) and 2.5387(4) Å], being about 7% shorter than the sum of the germanium and indium covalent radii

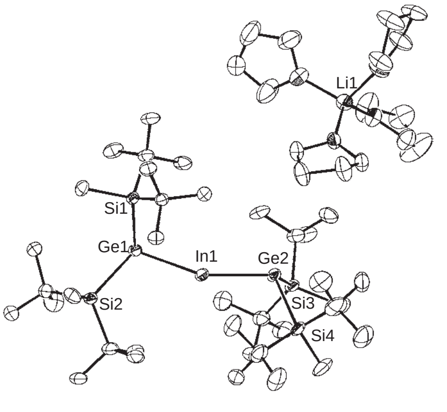
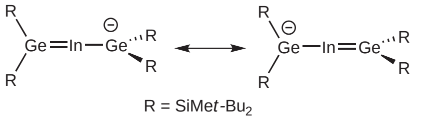


Figure 1. ORTEP drawing of **3b** (major fragment, 30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): In1–Ge1 = 2.5453(4), In1–Ge2 = 2.5387(4), Ge1–Si1 = 2.4268(9), Ge1–Si2 = 2.4306(12), Ge2–Si3 = 2.3885(11), Ge2–Si4 = 2.4288(16); Selected bond angles (°): Ge1–In1–Ge2 = 158.451(14), In1–Ge1–Si1 = 100.98(2), In1–Ge1–Si2 = 107.66(3), Si1–Ge1–Si2 = 108.69(4), In1–Ge2–Si3 = 104.65(3), In1–Ge2–Si4 = 110.97(4), Si3–Ge2–Si4 = 105.50(8); Dihedral angle (°): Si1–Ge1–Si2/Si3–Ge2–Si4 = 62.5.

(2.72 Å).[18] Similarly to other known metallaallenes,[10–12] the Ge1–In1–Ge2 framework is not linear but bent, with a bend angle of 158.451(14)°. The terminal Ge atoms are pyramidalized, the sums of the bond angles about atoms Ge1 and Ge2 being 317.33 and 321.12°, respectively. Indeed, the bending angles, which are defined by the In–Ge vectors and Si–Ge–Si mean planes, are 64.9 (Ge1) and 59.7° (Ge2), indicating a highly pronounced trans bent arrangement of the substituents around the Ge1–In1 and Ge2–In1 double bonds.

The bent structure of **3b** is similar to that of the silicon derivatives **1a** and **1b**. However, bending of the >E–M–E< fragment (E = Si, Ge; M = Ga, In), and the consequent pyramidalization about the terminal E centers become more important on going from Si to Ge. Thus, in the case of germanium derivative **3b**, the bending angle is 62.3 vs. 55.9° (av) for **1b**, the sum of the bond angles about the terminal atoms in **3b** is 319.2 (av) vs. 326.6° (av) in **1b**. This is in line with the general tendency for alkene analogues of the heavy group 14 elements,[19] for which trans bent geometry clearly dominates over the classical planar geometry because of the increasing difference in size of the s and p orbitals. This causes the increased p contribution to the Ge–Si(subst.) bonds as well as the Ge=In bond, resulting in the highly pronounced pyramidalization at the Ge centers.

This was supported by a theoretical calculation for the model compound, $[(Me_3Si)_2Ge\overset{\cdots}{-}M\overset{\cdots}{-}Ge(SiMe_3)_2]^-$ (**4a**: M = Ga; **4b**: M = In) performed at the B3LYP/LANL2DZ level.[20] The calculated Ge–In–Ge bond angle (157.8°) for **4b** is in fairly good agreement with that experimentally obtained for **3b** (158.451(14)°), but the calculated Ge=In bond lengths (av 2.635 Å) are longer than the experimental values, owing to the large bending angle (av 71.1°) and the significant pyramidalization around the Ge atoms (the sum of the bond angles: av 306.5°), which results in lengthening of the Ge=In bond. The model compound has Me_3Si substituents on Ge atoms, whereas the real compound has two bulky t-Bu_2MeSi groups, which suppress the bending for steric reasons. The anionic character at the terminal Ge atoms is shown by the natural population analysis (NPA); both germanium atoms are negatively charged (−0.754 and −0.754 for **4a**, −0.805 and −0.807 for **4b**), whereas the gallium and indium atoms are positively charged (+0.603 for **4a**, +0.818 for **4b**). This indicates that the allenic $[>Ge\overset{\cdots}{-}M\overset{\cdots}{-}Ge<]^-$ fragments are highly polarized and that the negative charge is preferentially located at the two terminal Ge atoms. Thus, the structures of **3a** and **3b** could be represented as the hybrid of the two allylic germyl anion resonance structures, as depicted in Scheme 2.



Scheme 2.

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16 Spectral data for **3a**: dark brown-red crystals. Mp 160–162 °C. ^{1}H NMR (THF-d_8, δ) 0.08 (s, 12H, Me), 1.06 (s, 72H, ^{t}Bu); ^{13}C NMR (THF-d_8, δ) −0.2, 23.4, 32.2; ^{29}Si NMR (THF-d_8, δ) 30.8; UV–vis (hexane) λ_{max}/nm (ε) 248 (20900), 282sh (9200), 429 (2400), 471 (2400). Spectral data for **3b**: dark brown-red crystals. Mp 180–182 °C. ^{1}H NMR (THF-d_8, δ) 0.07 (s, 12H, Me), 1.04 (s, 72H, ^{t}Bu); ^{13}C NMR (THF-d_8, δ) 0.8, 23.5, 32.2; ^{29}Si NMR (THF-d_8, δ) 32.0; UV–vis (hexane) λ_{max}/nm (ε) 256 (26200), 297sh (10300), 397 (1300), 481 (3200), 612 (1200).

17 Crystal data for **3b** at 120 K: $C_{52}H_{116}Ge_2InLiO_4Si_4$, MW 1184.75, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 13.7790(3)$ Å, $b = 22.6560(6)$ Å, $c = 21.7260(4)$ Å, $\beta = 101.9040(10)°$, $V = 6636.5(3)$ Å^3, $D_{calcd} = 1.186$ g cm^{-3}, R_1 ($I > 2\sigma(I)$) = 0.0425, wR_2 (all data) = 0.1169 for 12340 reflections, 857 parameters, and 55 restraints, GOF = 1.037.

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