

A missing allene of heavy Group 14 elements: 2-germadisilaallene†

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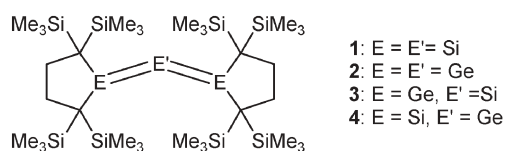
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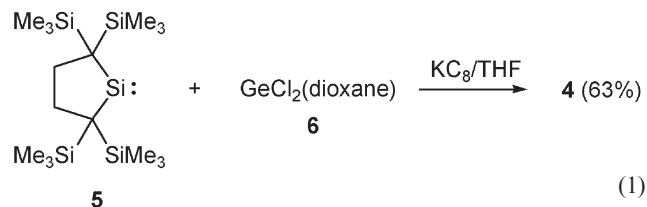
The first stable 2-germadisilaallene was synthesized by the reduction of a 2 : 1 mixture of a stable dialkylsilylene and dichlorogermylene–dioxane complex with KC_8 ; the 2-germadisilaallene showed dynamic disorder similar to the corresponding trisilaallene in the solid state.

Although the chemistry of stable doubly-bonded compounds of heavy Group 14 elements (dimetallenes) like disilenes have been developed extensively,¹ studies of the chemistry of stable unsaturated compounds with formally sp -hybridized heavy Group 14 elements (dimetallynes and trimetallaallenes) have started only recently.^{2–5} We have recently synthesized a set of stable trimetallaallenes composed of silicon and germanium atoms **1**,⁶ **2**⁷ and **3**⁷ and revealed the quite unique bonding nature of the trimetallaallenes. In contrast to rigid linear skeletons of carbon allenes, the skeletons of all these trimetallaallenes are significantly bent with a bond angle of 122.6–136.5° and they are fluxional in solution.^{6,7} However, only trisilaallene **1** shows dynamic disorder in the solid state;⁶ no such disorder was observed in trigermaallene **2** and 1,3-digermasilaallene **3**.⁷ A missing germasilaallene **4** is synthesized with a novel route to elucidate the necessary conditions for the dynamic disorder in the solid state.



2-Germadisilaallene **4** is synthesized by the reduction of a mixture of isolable dialkylsilylene **5**⁸ and GeCl_2 -dioxane complex (**6**, 0.5 equiv) with KC_8 in 63% yield (eqn (1)). Germadisilaallene **4** is formed as oxygen and moisture-sensitive dark-green crystals (mp 200 °C). The structure of **4** was determined by NMR and X-ray analysis.‡ A similar synthetic method used for **1–3**, *i.e.* the insertion of silylene **5** to a Ge–Cl bond of GeCl_4 followed by reduction with KC_8 in THF failed to give **4**.⁹

The central germanium atom in **4** shows remarkable dynamic disorder in the single crystal (Fig. 1), similarly to the corresponding silicon atom in trisilaallene **1**.⁶ The Si–Ge–Si skeleton of **4** is bent



and the central Ge atom (Ge1) is observed at four positions labeled Ge1a–Ge1d in Fig. 1 at –50 °C, indicating that four isomers **4A** to **4D** with Ge1a to Ge1d, respectively, exist in the solid state (Scheme 1). The site occupancy factors (SOF) of the Ge1 atom are independent of the crystal but are significantly temperature-dependent as shown in Table 1. The SOF of the most populated isomer **4A** increases from 0.533 at 0 °C up to 0.950 at –180 °C, while those of isomers **4B** to **4D** decrease with lowering temperature and the least populated isomer **4C** disappears below –100 °C. The reversible temperature-dependence of the SOF suggests a facile equilibrium among the four isomers **4A** to **4D**. Actually, plots of $\ln[\text{4X}]/[\text{4A}]$ ($\text{4X} = \text{4B} - \text{4C}$) vs. $1/T$ show a good linear relationship. The enthalpies and entropies of **4X** relative to **4A** are estimated from the slope and intercept of the linear lines, respectively.† Isomers **4B** to **4D** of 2-germadisilaallene **4** are 0.64, 0.95, and 1.55 kcal mol^{–1} higher in energy than isomer **4A**, respectively. The energy difference between the most-populated and the least-populated isomers in **4** (1.55 kcal mol^{–1}) is slightly larger than that in trisilaallene **1** (1.13 kcal mol^{–1}),

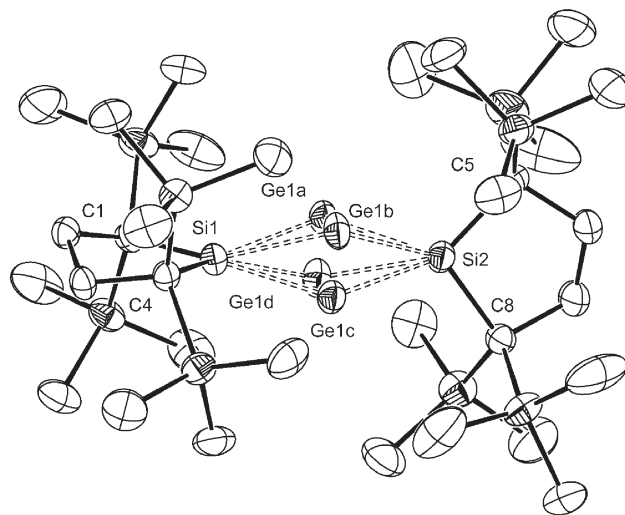


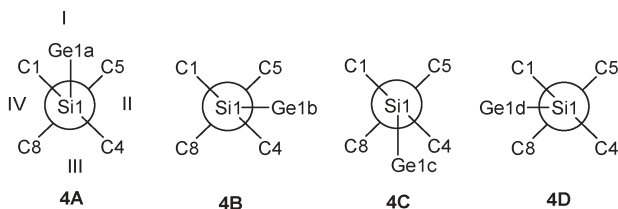
Fig. 1 Molecular structure of 2-germadisilaallene **4** at –50 °C. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

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† Electronic supplementary information (ESI) available: Tables giving the details of the X-ray structure determination, and UV-vis and NMR spectra of **4**, plots of $\ln[\text{4X}]/[\text{4A}]$ vs. $1/T$, relative enthalpies and entropies among **4A–4D**, details of the reaction of **2** with germanium tetrachloride, and details of theoretical study. See <http://dx.doi.org/10.1039/b509878e>



Scheme 1 Schematic representation of rotational isomers **4A–4D** using a projection along the axis through the Si1 and Si2 atoms. The germanium atoms labelled Ge1a to Ge1d are found in four quadrants divided by the C1–Si1–C4 and C5–Si2–C8 planes, respectively. The dihedral angles defining quadrants I to IV (-50.0°), \angle C1–Si1 \cdots Si2–C5, \angle C4–Si1 \cdots Si2–C5, \angle C4–Si1 \cdots Si2–C8, and \angle C1–Si1 \cdots Si2–C8, are 79.6 , 93.2 , 94.4 , and 92.9° , respectively.

Table 1 Site Occupancy Factors (SOF) of Germanium Atom (Ge1) of **4**

| Temp/ $^\circ$ C | Crystal | SOF | | | |
|------------------|----------------|----------|----------|----------|----------|
| | | Ge1a | Ge1b | Ge1c | Ge1d |
| -50 | A | 0.612(2) | 0.170(2) | 0.049(2) | 0.168(2) |
| 0 | B ^a | 0.533(2) | 0.202(2) | 0.078(1) | 0.187(1) |
| -50 | B ^a | 0.614(2) | 0.169(2) | 0.049(1) | 0.168(1) |
| -100 | B ^a | 0.726(1) | 0.136(2) | 0.020(1) | 0.117(1) |
| -150 | B ^a | 0.878(1) | 0.076(1) | — | 0.046(1) |
| -50 | C ^b | 0.621(2) | 0.168(1) | 0.047(1) | 0.164(1) |
| -180 | C ^b | 0.950(1) | 0.038(1) | — | 0.012(1) |

^a Data were collected at -50 , -100 , 0 , and then -150°C . ^b Data were collected at -50 and then -180°C .

suggesting the difference in the environments of the four quadrants in **4** is larger than in **1**. Consistently, the dihedral angles defining the quadrants I–IV are 79.2 , 93.2 , 94.5 , and 93.1° for **4** (Scheme 1), while the corresponding angles are 82.6 , 92.6 , 92.7 , and 92.1° for **1**. While the largest difference in the angles in **4** ($\Delta\theta = 14.8^\circ$) is slightly larger than that in **1** ($\Delta\theta = 10.1^\circ$), the $\Delta\theta$ values in **1** are much smaller than those of **2** ($\Delta\theta = 37.8^\circ$) and **3** ($\Delta\theta = 46.7^\circ$) that show no dynamic disorder.⁷ The sums of the bond angles around the Si1 and Si2 atoms of **4** (354.0° and 353.9°) are only slightly smaller than the corresponding values in **1** (354.1 and 354.9°),⁶ but are significantly larger than those in **2** (348.5 and 348.6°) and **3** (349.30°).⁷ As we pointed out in a previous paper,⁷ the smaller difference in the environments among the four quadrants of **4** as well as **1** compared to those in **2** and **3** is ascribed to the smaller pyramidalization at the terminal silicon atoms in **1** and **4**.

The Si–Ge–Si bond angle of the most populated isomer **4A** at -180°C [$132.38(2)^\circ$] is smaller than the corresponding angle of **1** [$136.49(6)^\circ$] but larger than those of **2** [$122.61(6)^\circ$] and **3** [$125.71(7)^\circ$]. The Si1 \cdots Si2 distance of **4** is 4.093 \AA , which is in the range of the corresponding distances in **1–3**. The distances will be kept constant to avoid steric repulsion between trimethylsilyl substituents. The Si1–Ge1a and Si2–Ge1a distances of **4** ($2.2366(7)$ and $2.2373(7)\text{ \AA}$) are slightly shorter than those of **3** ($2.2694(8)\text{ \AA}$)⁷ and a disilagermacyclopentadiene ($2.250(1)\text{ \AA}$).¹⁰

Similarly to trimetallaallenes **1–3**, **4** shows highly symmetric ^1H , ^{13}C , and ^{29}Si NMR spectral patterns in solution; 2 unsaturated silicon nuclei, 8 trimethylsilyl and 4 methylene groups, and 4 methine carbon nuclei are equivalent in **4** even at -80°C . The ^{29}Si

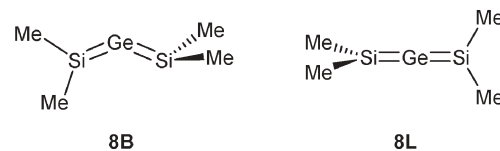


Chart 1 Model 2-germadisilaallene, **8B** (bent allenic) and **8L** (linear).¹¹

resonance for the unsaturated silicon nuclei of **4** (219.4 ppm) is close to the calculated value for tetramethyl-2-germasilaallene **8B** whose skeletal structure is fixed to that of **4** observed in the solid state (231.3 ppm at the GIAO/B3LYP/6-311 + G(2df,p)//B3LYP/6-31 + G(d,p) level) but very far from that of linear **8L** ($+98.4\text{ ppm}$ at the same level) (Chart 1).[†] The highly-symmetric spectral pattern and the ^{29}Si resonance indicate that **4** adopts a bent and fluxional allenic structure in solution.

The UV-vis spectrum of **4** shows two distinct absorption maxima (ϵ) at 409 ($22\,000$) and 599 nm (1130) in hexane at room temperature.[†] The spectral pattern is similar to those of **1–3**, indicating significant conjugation between two Si=Ge double bonds in **4**. The longest wavelength absorption band of **4** (599 nm) is red-shifted from that of **1** (584 nm) but significantly blue-shifted from those of **2** (630 nm) and **3** (612 nm).

Further work on the reactivity of **4** is currently in progress.

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Notes and references

[†] Synthesis of 2-germadisilaallene **4**. All operations were carried out under an argon atmosphere. A suspension of dialkylsilylene **5** (120 mg , 0.32 mmol), GeCl_2 -dioxane complex (**6**, 40 mg , 0.17 mmol) and KC_8 (60 mg , 0.44 mmol) in THF (10 mL) was stirred at -40°C for 2 days. After removal of the solvent *in vacuo*, dry hexane was introduced into the mixture and then the resulting salt and graphite were filtered off. Recrystallization from hexane at -30°C gave pure **4** (84 mg , 0.10 mmol) in 63% yield as air-sensitive dark green crystals. **4**: mp 200°C ; δ_{H} (C_6D_6 , 400 MHz) 0.38 (s, 2H), 2.01 (s, 8H), δ_{C} (C_6D_6 , 100 MHz) 3.4 (SiMe_3), 30.0 (C), 34.5 (CH_2), δ_{Si} (C_6D_6 , 79 MHz) 0.8 (SiMe_3), 219.4 ($\text{Si}=\text{Ge}=\text{Si}$); UV-vis (hexane) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 599 (1130), 409 (22000). Crystal data (-180°C). $\text{C}_{32}\text{H}_{80}\text{GeSi}_{10}$, $M = 818.45$, triclinic, $a = 11.683(3)$, $b = 12.214(3)$, $c = 18.607(4)\text{ \AA}$, $\alpha = 73.588(7)^\circ$, $\beta = 87.156(8)^\circ$, $\gamma = 71.628(7)^\circ$, $V = 2414.8(9)\text{ \AA}^3$, $T = 93\text{ K}$, space group $P\bar{1}$ (no. 2), $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.903\text{ mm}^{-1}$, 37880 reflections measured, 10992 unique ($R_{\text{int}} = 0.0546$) which were used in all calculations. The final $wR(F^2)$ was 0.0838 (all data). The variable temperature crystal data for three different crystals are reported in the electronic supplementary information (ESI) section.[†] CCDC 279203–279209. See <http://dx.doi.org/10.1039/b509878e> for crystallographic data in CIF or other electronic format.

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