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A Chemical Trick: How To Make a Digermene from a Disilene, Formation of $^3\Delta$ -1,2,3,4-Disiladigermetene

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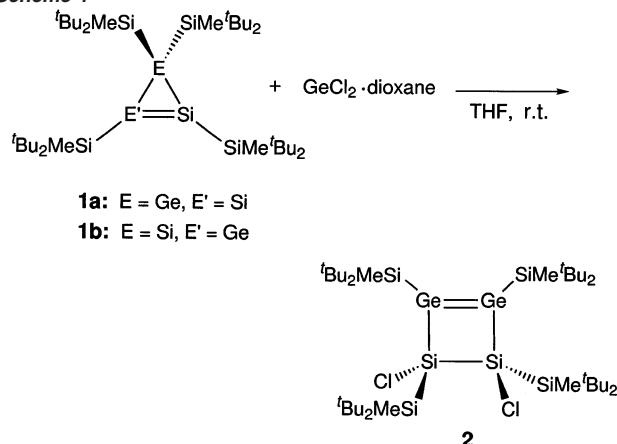
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The chemistry of doubly bonded compounds of heavier group 14 elements is one of the most fascinating topics discovered over the past two decades.¹ The chemistry of such compounds has been greatly developed following the pioneering work of Brook and West on the synthesis of the first stable silene, $>\text{Si}=\text{C}<$,² and disilene, $>\text{Si}=\text{Si}<$,³ respectively, and many new representatives have now been synthesized.¹ In contrast, the cyclic version of such compounds incorporating an $>\text{E}=\text{E}'<$ (E, E' = heavier group 14 elements) double bond in the ring has become accessible only quite recently.^{4,5} Thus, in 2000, we reported the synthesis of the heavy cyclopropene analogues of different group 14 elements, 1- and 2-disilagermirenes,⁶ which exhibited very interesting chemistry.⁷ We report here on a rather unusual, new type of reaction of these compounds with $\text{GeCl}_2\cdot\text{dioxane}$ and $\text{SnCl}_2\cdot\text{dioxane}$, which give fast and effective access to new unsaturated four-membered ring systems of heavier group 14 elements.

We have examined the possibility of the $[2 + 1]$ cycloaddition reaction of disilagermirenes **1** with $\text{GeCl}_2\cdot\text{dioxane}$. Surprisingly, the reaction course was completely different from the expected one. Thus, the reaction of equimolar amounts of **1a** and $\text{GeCl}_2\cdot\text{dioxane}$ in THF proceeds extremely quickly and cleanly, even at low temperature, to form exclusively one product, *trans*-1,2-dichloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]- $^3\Delta$ -1,2,3,4-disiladigermetene, **2**, in quantitative yield (Scheme 1). Compound **2** was isolated as highly air- and moisture-sensitive bright-orange hexagonal crystals, whose constitution was determined by spectral data.⁸

Scheme 1



The crystal structure of **2** was determined by X-ray crystallography to show a four-membered ring skeleton composed of two Si and two Ge atoms in the sequence Si–Ge–Ge (Figure 1).⁹ This Si_2Ge_2 ring represents a nearly regular trapeze, although the four-membered ring is not planar but folded with a folding angle of 28° . The geometry of the Si substituents connected to sp^2 -Ge atoms is *trans*-bent with a torsional angle Si3–Ge1–Ge2–Si4 of $55.22(7)^\circ$.

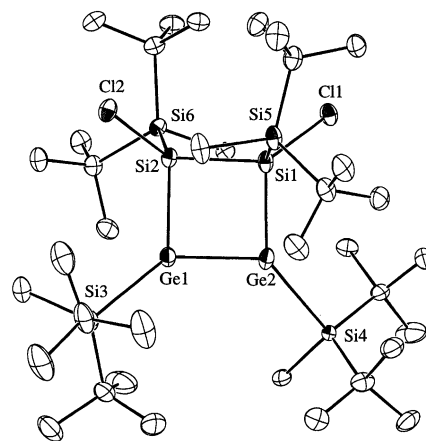
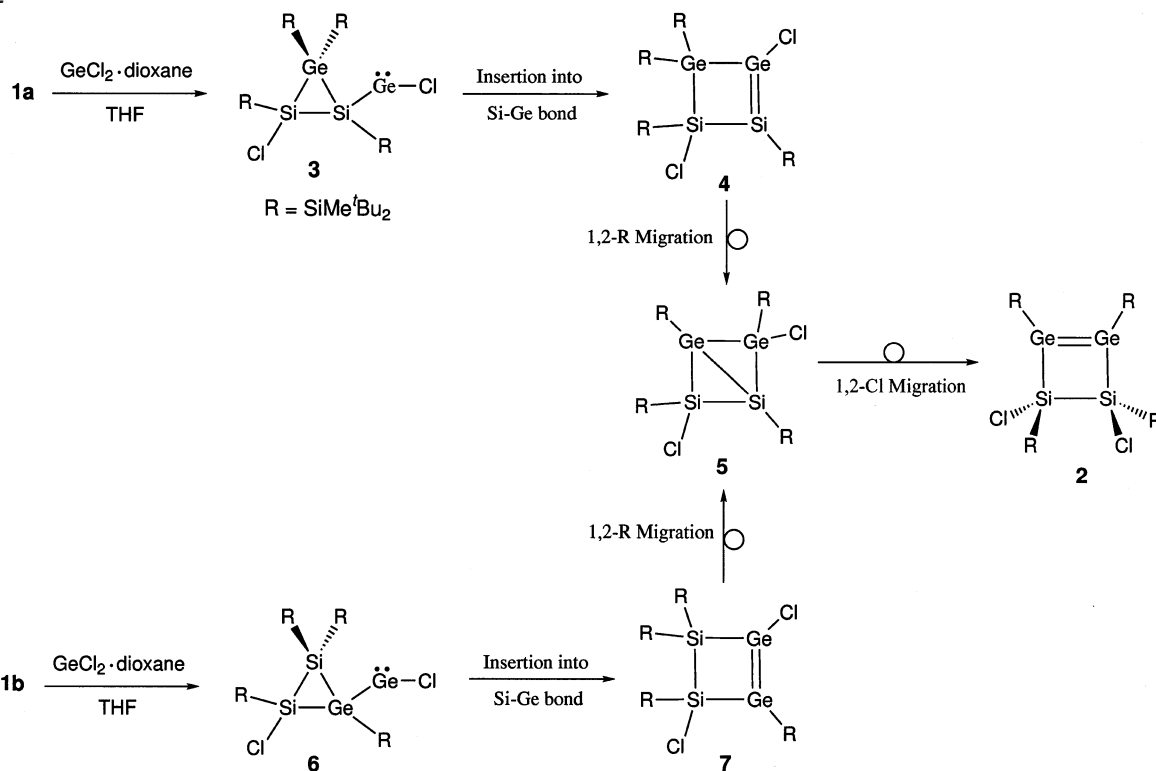


Figure 1. ORTEP drawing of **2**. The $^t\text{Bu}_2\text{MeSi}$ group on the Ge2 atom is orientationally disordered, and the major configuration (57% occupancy) is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge1–Ge2 = 2.2911(4), Si1–Si2 = 2.3722(10), Si2–Ge1 = 2.3585(9), Si1–Ge2 = 2.3576(10), Si1–Cl1 = 2.1345(10), Si2–Cl2 = 2.1325(10). Selected bond angles (deg): Si2–Ge1–Ge2 = 89.63(2), Si1–Ge2–Ge1 = 88.75(2), Si2–Si1–Ge2 = 87.72(3), Si1–Si2–Ge1 = 86.84(3). Selected torsional angle (deg): Si3–Ge1–Ge2–Si4 = 55.22(7).

The Ge=Ge double bond length of 2.2911(4) Å lies inside the range of 2.213–2.460 Å reported for other digermenes;¹⁶ however, it is evidently stretched, being the longest bond length among all known cyclic digermenes (2.239–2.274 Å).¹⁰ In contrast, the endocyclic Si–Ge bonds in **2** are greatly shortened (2.3576(10) and 2.3585(9) Å),¹¹ being even shorter than the endocyclic Si–Si bond (2.3722(10) Å).¹² Accordingly, the Si–Cl bonds are elongated, 2.1325(10) and 2.1345(10) Å, lying at the top of the range for Si–Cl bond lengths (av 2.050 Å).¹³ Such phenomena (lengthening of the endocyclic Ge=Ge bond and exocyclic Si–Cl bonds, as well as shortening of endocyclic Si–Ge bonds) can be definitely ascribed to the appreciable delocalization of the π -electrons of the high-lying orbitals of the Ge=Ge double bond through conjugation with low-lying σ^* -orbitals of the Si–Cl bonds.¹³ It is known that highly electronegative substituents, for example, Cl, significantly increase the degree of such π – σ^* conjugation.¹³

The formation of **2** is very unusual and unexpected, meriting a discussion about its possible mechanism. In the first step, it is reasonable to assume that $\text{GeCl}_2\cdot\text{dioxane}$ undergoes oxidative addition across the $\text{Si}=\text{Si}$ double bond to produce chlorogermylene **3** (Scheme 2). The resulting **3** then may quickly undergo intramolecular insertion into the Si–Ge bond to form compound **4** with a $\text{Si}=\text{Ge}$ bond. The latter then possibly rearranges to bicyclo[1.1.0]butane **5**: the driving force for such an isomerization may be the presence of the highly electronegative and π -donating Cl substituent on the sp^2 -Ge atom in **4**, which is known to be a destabilizing factor for $\text{E}=\text{E}'$ bonds.¹⁶ Final 1,2-Cl migration from Ge to Si atom would complete this reaction sequence, resulting in the isomerization to form the final disiladigermetene **2**.¹⁴ As the overall result of such

Scheme 2

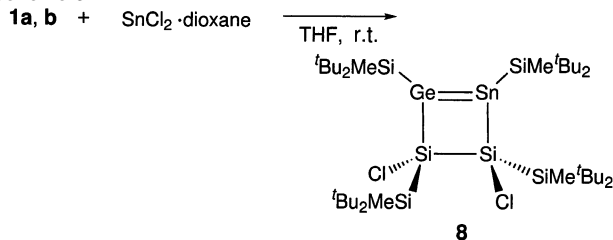


transformations, the unusual four-membered ring compound **2** with a Ge=Ge double bond was formed, starting from the three-membered ring compound **1** with a Si=Si double bond.

It is interesting that when we performed the similar reaction of GeCl₂·dioxane with 2-disilagermirene **1b**, we obtained quantitatively exactly the same disiladigermetene **2** (Schemes 1 and 2). This result provides evidence for the existence of the same immediate precursor of **2** (compound **5** formed through **6** and **7**) starting from either **1a** or **1b**.

The generality of the reaction mode of cyclotrimetallenes with heavy dichlorocarbene analogues was unequivocally demonstrated by the reaction of both **1a** and **1b** with SnCl₂·dioxane, which quantitatively produced the same product, *trans*-1,2-dichloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-³Δ-1,2,3,4-disilagermantanetene, **8**, as dark-orange crystals (Scheme 3).⁸ The formation

Scheme 3



of **8** is in complete agreement with the proposed mechanism (Scheme 2).

Note Added after ASAP. This Communication was inadvertently published before the corrections were made. The version posted 04/21/2003 and the print version are correct.

Supporting Information Available: Experimental procedures and spectral data of **2** and **8**, tables of crystallographic data including atomic positional and thermal parameters for **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) For the experimental procedures and spectral data of **2** and **8**, see the Supporting Information.
- (9) Crystal data for **2** at 120 K: MF = C₃₆H₈₄Cl₂Ge₂Si₆, MW = 901.65, monoclinic, C2/c, *a* = 41.1840(14), *b* = 15.5870(5), *c* = 17.2300(5) Å, β = 112.973(2)°, *V* = 10183.3(6) Å³, *Z* = 8, *D*_{calcd} = 1.176 g·cm⁻³. The final *R* factor was 0.0457 for 9041 reflections with *I* > 2σ(*I*) (*R*_w = 0.1262 for all data, 12 165 reflections), GOF = 1.024.
- (10) See: (a) ref 4 and (b) Sekiguchi, A.; Ishida, Y.; Fukaya, N.; Ichinohe, M.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2002**, *124*, 1158.
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- (14) In accordance with a proposed mechanism (Scheme 2), the theoretical calculations at B3LYP/6-31G(d) level on the model compounds **2**–**5** (*R* = SiH₃) showed the successive increase in the stability on going from **3** to **2** (in kcal/mol): **3** (+7.3), **4** (+4.9), **5** (+2.7), **2** (0).

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