Reaction of 1-Disilagermirene with Benzaldehyde:
An Unexpected Combination of Cycloaddition and Insertion Pathways

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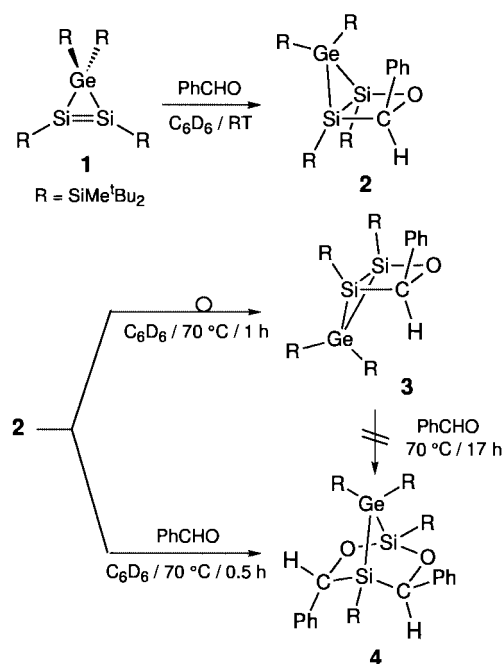*Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571*

New strained bicyclic compounds were formed by the reaction of tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene **1** with benzaldehyde, involving cycloaddition following the rearrangement and insertion pathways. Reaction of **1** with PhCHO gave three different products: two mono-adducts **2**, **3** and one bis-adduct **4**, depending on the ratio of the reagents and the reaction conditions.

Dimetallenes of heavier Group 14 elements, that is, the compounds with metal–metal double bonds, have become a well established and very important class of organometallic compounds. Following the first discovery of tetramesityldisilene by West et al.,[1] the chemistry of dimetallenes has been greatly developed during the past two decades, including their synthesis, structural studies and reactivity aspects.[2] It is well known that the reactions of disilenes with carbonyl compounds proceed via a [2+2] cycloaddition reaction to produce the corresponding disilaoxetanes.[3] Therefore, one could expect the formation of the bicyclic compound, containing the disilaoxetane fragment, in the reaction of 1-disilagermirene **1**, which has a Si=Si double bond in the three-membered ring, with carbonyl compounds.[4,5] Here we report an unusual reaction of tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene **1** with benzaldehyde, which proceeds through a combination of both cycloaddition and insertion reactions, resulting in the formation of new strained bicyclic compounds.

The reaction of **1** with an equivalent amount of benzaldehyde in deuteriobenzene was very quickly accomplished, even at low temperature, to form *cis*-1,4,5,5-tetrakis[di-*tert*-butyl(methyl)-silyl]-3-phenyl-2-oxa-1,4-disila-5-germabicyclo[2.1.0]pentane **2**, which was isolated as yellow crystals in 62% yield (Scheme 1).[6] The formation of **2** is evidently the result of the expected [2+2] cycloaddition reaction, which occurred stereospecifically to produce only one isomer.[7] Compound **2** has a characteristic signal at 79.7 ppm in the ^{13}C NMR spectrum, which is typical for the carbon atom in the four-membered disilaoxetane ring system. However, such an arrangement of the phenyl group is not favorable due to its steric repulsion with silyl substituents on Ge atom. Thus, upon heating at 70 °C for 1 h, the initially formed compound **2** was quantitatively isomerized to a more stable *trans*-isomer **3** (Scheme 1).[8]

The structure of **3** was established by X-ray crystallography, which showed a three- and four-membered fused bicyclic structure having a folded skeleton with a dihedral angle of 107.8° between the mean planes of the three- and four-membered rings (Figure 1).[9] This compound contains disilagermirane fragment on the one hand and disilaoxetane fragment on the other hand. The phenyl group is arranged in a *trans* position to the Ge atom. The Ge–Si bond lengths of 2.4715(5) and 2.4502(5) Å are similar to those of disilagermirane (2.480(3) and 2.458(4) Å)[10] and 1,2-dichlorodisilagermirane (2.467(1) Å).[11] However, the most
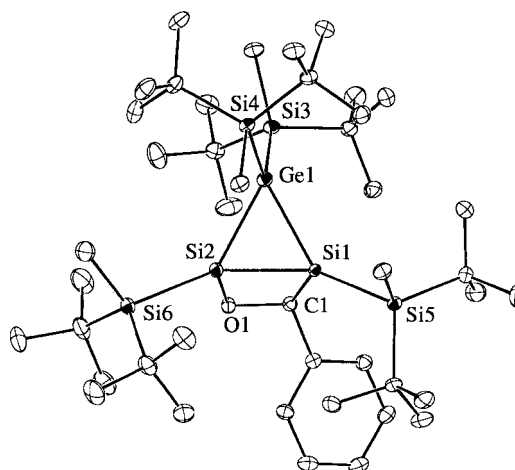

Scheme 1.

Figure 1. ORTEP drawing of **3**. Selected bond lengths (Å): Ge(1)-Si(1) 2.4715(5), Ge(1)-Si(2) 2.4502(5), Si(1)-Si(2) 2.3269(6), Si(1)-C(1) 2.005(2), Si(2)-O(1) 1.700(1), C(1)-O(1) 1.455(2). Selected bond angles (°): Si(2)-Ge(1)-Si(1) 56.4(0), Si(2)-Si(1)-Ge(1) 61.3(0), Ge(1)-Si(2)-Si(1) 62.3(0), Si(1)-Si(2)-O(1) 82.9(1), Si(2)-Si(1)-C(1) 70.1(1), Si(2)-O(1)-C(1) 104.6(0), Si(1)-C(1)-O(1) 101.8(0).

important feature is the length of the endocyclic Si–Si bond, which is only 2.3269(6) Å, compared with 2.418(5) Å for Watanabe's disilagermirane.[10] Such a significant shortening of the Si–Si bond is caused by the rigidly fused skeleton of **3**, which makes the bridgehead Si–Si bond highly strained. The same highly strained Si–Si bond is, apparently, also characteristic of the isomeric compound **2**.

And indeed, when we performed the reaction of **1** with an excess of benzaldehyde, first the bicyclic compound **2** was formed, which after short heating (C_6D_6, 70 °C, 0.5 h) was converted to the new bicyclic compound: 1,4,7,7-tetrakis[di-*tert*-butyl(methyl)silyl]-3,5-diphenyl-2,6-dioxa-1,4-disila-7-germa-bicyclo[2.2.1]heptane **4** in 58% yield (Scheme 1).[12] The formation of compound **4** can be considered as the result of an insertion reaction of the C=O group of a second molecule of benzaldehyde into the strained bridgehead Si–Si bond of **2**. Compound **4** cannot be formed from compound **3**, even upon prolonged heating at 70 °C for 17 h with excess benzaldehyde. From the crystal structure data of **4**, it is evident that insertion of the C=O group of benzaldehyde into the Si–Si bond occurs both regiospecifically and stereospecifically to form exclusively only one isomer, in which the two oxygen atoms are connected with the same silicon atom and the two phenyl groups are arranged in *endo* and *exo* positions to each other (Figure 2).[13] Thus, the reaction of **1** with benzaldehyde represents a quite unusual example of the combination of [2+2] cycloaddition followed by an insertion pathway in one reaction.
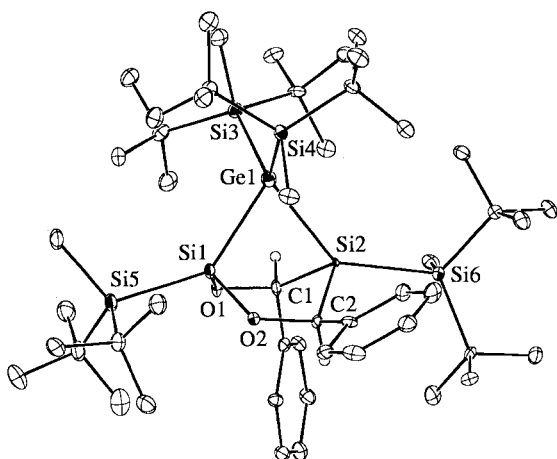

Figure 2. ORTEP drawing of **4**. Selected bond lengths (Å): Ge(1)-Si(1) 2.467 (2), Ge(1)-Si(2) 2.513(1), Si(2)-C(1) 2.017 (5), Si(2)-C(2) 1.968(5), Si(1)-O(1) 1.664(4), Si(1)-O(2) 1.666(4), C(1)-O(1) 1.463(6), C(2)-O(2) 1.454 (6). Selected bond angles (°): Si(1)-Ge(1)-Si(2) 73.0(1), Si(2)-C(2)-O(2) 108.2 (3), Si(1)-O(2)-C(2) 121.0(3), Si(2)-C(1)-O(1) 109.5 (3), Si(1)-O(1)-C(1) 118.5(3).

References and Notes
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6   Mp 195–196 °C (dec) ^{1}H NMR (C_6D_6, δ) 0.14 (s, 3 H), 0.406 (s, 3 H), 0.408 (s, 3 H), 0.43 (s, 3 H), 0.95 (s, 9 H), 1.07 (s, 9 H), 1.23 (s, 9 H), 1.27 (s, 9 H), 1.28 (s, 9 H), 1.32 (s, 9 H), 1.33 (s, 9 H), 1.39 (s, 9 H), 6.26 (s, 1 H), 6.99 (t, J = 7.4 Hz, 1 H), 7.13–7.18 (m, 2 H), 7.64 (d, J = 8.2 Hz, 2 H); ^{13}C NMR (C_6D_6, δ) −4.5, −3.2, −1.3, −1.2, 22.3, 22.4, 22.5, 22.7, 22.8, 23.00, 23.03, 23.1, 30.0, 30.5, 30.6, 30.86, 30.94, 31.1, 31.5, 32.1, 79.7, 125.6, 126.8, 127.3, 145.2; ^{29}Si NMR (C_6D_6, δ) −47.7, 16.8, 21.0, 27.4, 30.6, 41.4; Anal. Calcd for $C_{43}H_{90}GeOSi_6$: C, 59.76; H, 10.50%. Found: C, 59.46; H, 10.11%.
7   The reaction mechanism to form only one isomer **2** is not clear at this moment. However, it is likely that the transition state to form **2** may be stabilized by the through-space attractive interaction of the electron-rich phenyl group and the empty σ*-orbital of the exocyclic Ge–Si bond.
8   Mp 206–208 °C (dec.); ^{1}H NMR (C_6D_6, δ) 0.05 (s, 3 H), 0.11 (s, 3 H), 0.46 (s, 3 H), 0.64 (s, 3 H), 0.96 (s, 9 H), 1.10 (s, 9 H), 1.22 (s, 9 H), 1.26 (s, 9 H), 1.317 (s, 9 H), 1.32 (s, 9 H), 1.39 (s, 9 H), 1.40 (s, 9 H), 6.01 (s, 1 H), 6.99 (t, J = 7.3 Hz, 1 H), 7.21 (t, J = 7.3 Hz, 2 H), 7.60 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (C_6D_6, δ) −4.30, −4.27, −0.7, −0.4, 21.8, 21.9, 22.0, 22.1, 22.5, 22.7, 23.1, 24.8, 30.16, 30.19, 30.3, 30.5, 30.8, 31.2, 32.3, 84.6, 126.3, 126.5, 128.6, 147.0; ^{29}Si NMR (C_6D_6, δ) −32.5, 16.2, 23.5, 25.9, 28.6, 37.2; Anal. Calcd for $C_{43}H_{90}GeOSi_6$: C, 59.76; H, 10.50%. Found: C, 59.46; H, 10.10%.
9   Crystal data for **3** at 120 K: $C_{43}H_{90}GeOSi_6$, fw = 864.28, triclinic, space group $P\bar{1}$, a = 11.2180(3), b = 12.5600(4), c = 21.3540(7) Å, α = 75.825(2), β = 84.506(2), γ = 64.206(2)°, V = 2626.28(14) Å³, Z = 2, d_{calc} = 1.093 g·cm⁻³. The final R factor was 0.0372 (Rw = 0.1078 for all data) for 10703 reflections with $I > 2σ(I)$. GOF = 1.03.
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11   V. Ya. Lee, T. Matsuno, M. Ichinohe, and A. Sekiguchi, *Heteroatom. Chem.*, **12**, 223 (2001).
12   Mp 223–224 °C (dec.); ^{1}H NMR (C_6D_6, δ) −0.06 (s, 3 H), 0.29 (s, 3 H), 0.40 (s, 3 H), 0.47 (s, 9 H), 0.63 (s, 3 H), 1.19 (s, 9 H), 1.22 (s, 9 H), 1.257 (s, 9 H), 1.262 (s, 9 H), 1.29 (s, 9 H), 1.34 (s, 9 H), 1.42 (s, 9 H), 5.52 (s, 1 H), 6.08 (s, 1 H), 6.99 (t, J = 7.3 Hz, 1 H), 7.06 –7.20 (m, 5 H), 7.69 (d, J = 7.3 Hz, 2 H), 7.77 (d, J = 7.2 Hz, 2 H); ^{29}Si NMR (C_6D_6, δ) −2.2, 7.4, 18.3, 30.0, 30.5, 31.6; Anal. Calcd for $C_{50}H_{96}GeO_2Si_6$: C, 61.89; H, 9.97%. Found: C, 61.60; H, 9.67%.
13   Crystal data for **4** at 120 K: $C_{50}H_{96}GeO_2Si_6$, fw = 970.40, monoclinic, space group $P2_1/c$, a = 23.7500(16), b = 11.5900(7), c = 23.3570(18) Å, β = 116.977(4)°, V = 5729.7(7) Å³, Z = 4, d_{calc} = 1.125 g·cm⁻³. The final R factor was 0.0821 (Rw = 0.2220 for all data) for 7311 reflections with $I > 2σ(I)$. GOF = 1.03.