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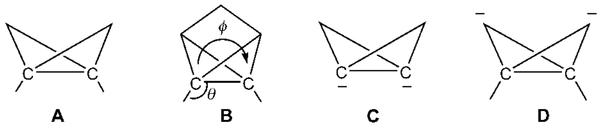
Strained Molecules

The First Bicyclo[1.1.0]butane Dianion of Heavier Group 14 Elements**

Vladimir Ya. Lee, Kazunori Takanashi,
*Masaaki Ichinohe, and Akira Sekiguchi**

The concept of the so-called "non-classical" compounds, which do not follow the generally accepted interpretation of the chemical bonds from the viewpoints of geometry, valency, and hybridization, is a fascinating topic in organic chemistry.[1] Undoubtedly, among such non-classical molecules the highly strained bicyclo[1.1.0]butane and tricyclo[2.1.0.0^{2,5}]pentane, as well as their derivatives, are paramount examples of the most long-standing and attractive challenges for organic chemists (Scheme 1, **A** and **B**, respectively).[2,3] Particularly important is the question of the nature of the bridging bond in both compounds, which has been the subject of theoretical investigations and debates during the last two decades, especially for the derivatives of bicyclo[1.1.0]butane.[2] Experimentally, the chemistry of bicyclo[1.1.0]butane, which has been known since 1959, has been developed, and many representatives of this unusual class of compounds, including their heavy analogues, have been synthesized.[4] However, the stable, charged derivatives (both anionic and cationic) of bicyclo[1.1.0]butanes have remained elusive species until now: neither bridgehead 1,3- (Scheme 1, **C**) nor bridging 2,4-dianions (Scheme 1, **D**) of bicyclo[1.1.0]butane have ever been isolated and characterized.[5] Very recently we have synthesized the $^3\Delta$-1,2,3,4-disiladigermetene **1**,[6] which appeared to be a most promising candidate for reduction to produce the corresponding dianion species. Indeed, by the reaction of **1** with alkali metals, the heavy analogues of the cyclobutadiene dianion were synthesized; their cyclic 6π-



Scheme 1. Highly strained non-classical compounds bicyclo[1.1.0]-butane (**A**) and tricyclo[2.1.0.0^{2,5}]pentane (**B**) and bridgehead 1,3- (**C**) and bridging 2,4-dianions (**D**) of **A**.

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[*] Dr. V. Ya. Lee, Dipl.-Chem. K. Takanashi, Dr. M. Ichinohe,
Prof. Dr. A. Sekiguchi
Department of Chemistry
Graduate School of Pure and Applied Sciences
University of Tsukuba
Tsukuba, Ibaraki 305-8571 (Japan)
Fax: (+81) 298-53-4314
E-mail: sekiguch@staff.chem.tsukuba.ac.jp

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electron system was demonstrated to be non-aromatic.[7] To our surprise, the reduction of **1** with alkaline-earth metals gave a totally different structure with the bicyclo[1.1.0]butane 2,4-dianion skeleton, these compounds were isolated in the form of magnesium, calcium, and strontium salts, whose synthesis and structural characteristics we report herein.

The reduction of **1** with an excess of metallic magnesium or calcium in THF at room temperature resulted in the clean formation of the corresponding magnesium and calcium derivatives of tetrakis(di-*tert*-butylmethylsilyl)-1,3-disila-2,4-digermabicyclo[1.1.0]butane-2,4-diide **2a**,**b** isolated as highly air- and moisture-sensitive, bright orange crystals (Scheme 2). Of note is that both **2a** and **2b** can be prepared alternatively by the reaction of the dipotassium salt **3**[7] with MX_2 (M = Mg, X = Br; M = Ca, X = I) in THF (Scheme 2). Employing this synthetic approach, we were able to synthesize dianion **2** with strontium as the coordinating counterion, compound **2c**.

Reflecting their symmetrical structure, ^{1}H and ^{13}C NMR spectra of **2a–c** have only two sets of signals for the two kinds of $t\mathrm{Bu_2MeSi}$ substituents. The arrangement of the Si atoms at the bridgehead positions of **2** was clearly evident from the ^{29}Si NMR spectra, which show their very diagnostic greatly upfield-shifted signals: −231.9 ppm for **2a**, −220.2 ppm for **2b**, and −225.2 ppm for **2c**.

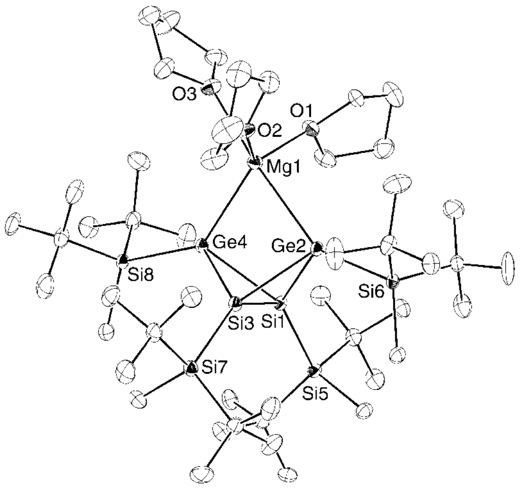
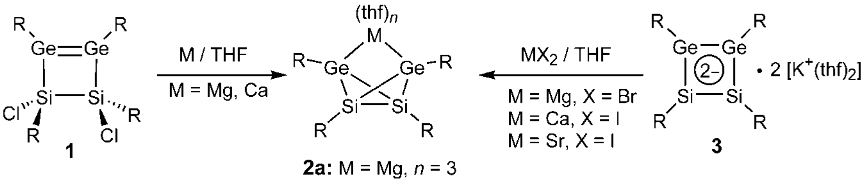


Figure 1. Structure of **2a** (ORTEP plot, thermal ellipsoids set at 30 % probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Si1-Si3 2.3181(15), Si1-Ge2 2.4911(11), Si1-Ge4 2.4480(11), Si3-Ge2 2.4691(12), Si3-Ge4 2.4523(12), Ge2-Mg1 2.7664(15), Ge4-Mg1 2.6259(14); Si3-Si1-Ge2 61.66(4), Si1-Si3-Ge2 62.62(4), Si1-Ge2-Si3 55.72(4), Si1-Si3-Ge4 61.67(4), Si3-Si1-Ge4 61.86(4), Si1-Ge4-Si3 56.46(4), Si3-Si1-Si5 133.65(6), Si1-Si3-Si7 135.75(7), Ge2-Mg1-Ge4 75.59(4).



1

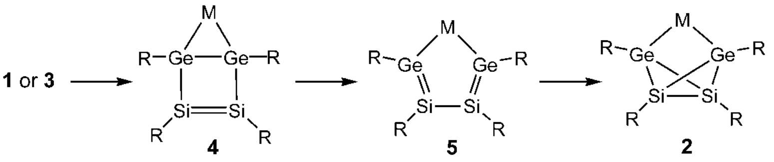
R = SiMe*t*Bu$_2$

2a: M = Mg, *n* = 3
2b: M = Ca, *n* = 4
2c: M = Sr, *n* = 4

3

Scheme 2. Synthesis of 1,3-disila-2,4-digermabicyclol[1.1.0]butane-2,4-diide derivatives **2a–c**. R = SiMe*t*Bu$_2$.

The composition of all of the alkaline-earth-metal derivatives **2a–c** was unambiguously established by X-ray crystallography, as shown in Figure 1 for **2a**.[8] With a capping alkaline-earth metal playing a bridge role, bicyclo[1.1.0]butane dianions **2** actually acquire the properties of tricyclo[2.1.0.0^{2,5}]pentane derivatives (Scheme 1, **B**). This relationship was clearly demonstrated by consideration of the structural characteristics of the $\mathrm{Si_2Ge_2}$ skeleton of **2**: 1) the Si–Si bridging bonds are a little shortened in comparison with the normal Si–Si bond length, 2.3181(15) Å (**2a**), 2.323(2) Å (**2b**), and 2.3304(15) Å (**2c**); 2) the interplanar angles ϕ (see Scheme 1) are acute: 98.90 (**2a**), 102.30 (**2b**), and 104.90 for (**2c**); 3) bond angles θ are wide: 133.65(6) and 135.75(7) (**2a**), 132.76(9) and 132.89(9) (**2b**), and 128.60(8) and 136.42(8) (**2c**). All of these structural features match the properties of tricyclo[2.1.0.0^{2,5}]pentanes (Scheme 1, **B**),[3] in which a small interplanar angle ϕ forces the hybrid orbitals of the bridged atoms towards each other to form short bent C–C bridging bonds. However, such a short Si–Si bridging bond in dianions **2a–c** is in complete contrast to our previously reported tricyclo[2.1.0.0^{2,5}]pentane analogue, which has an extremely long Ge–C bridging bond,[9] owing to its significant biradical character.



4

5

2

Scheme 3. Proposed mechanism of formation of **2**.

The mechanism for the formation of compounds **2** may involve the initial reduction of the starting material **1** with alkaline-earth metals to form **4**, which has a bicyclo[2.1.0]pentene skeleton (Scheme 3). Valence isomerization to release the inherent strain of **4** might be imagined as the next step, to produce the cyclopentadiene-like compound **5**, which finally undergoes intramolecular cross [2+2] cycloaddition to form tricyclo[2.1.0.0^{2,5}]pentane derivatives **2**.[10] Starting from the cyclobutadiene dianion dipotassium salt **3**, the reaction with metal halides MX_2 resulted in the initial formation of **4**, following the isomerization steps described above. Such conclusions are supported by theoretical calculations, which showed that of all the cyclic $\mathrm{R_4Si_2Ge_2Mg}$ isomers **4**, **5**, and **2** ($\mathrm{R = SiH_3}$), the tricyclo[2.1.0.0^{2,5}]pentane **2** is the most stable compound (0 kcal mol^{-1}), compared with the cyclopentadiene **5** (+12.12 kcal mol^{-1}) and the bicyclo[2.1.0]pentene **4** (+12.39 kcal mol^{-1}).[11]

Experimental Section

2a: The mixture of **1** (96 mg, 0.106 mmol) and excess magnesium (35 mg, 1.44 mmol) in dry oxygen-free THF (2 mL) was stirred for two days at room temperature, during which time the color of the reaction mixture turned from yellow to dark brown. After filtration and evaporation of solvent from the filtrate, recrystallization from hexane–THF gave **2a** as bright-orange crystals (83 mg, 73 %). M.p. 205 °C (dec.). ^{1}H NMR (400 MHz, [D$_8$]THF, TMS): $\delta = 0.16$ (s, 6H, Me), 0.30 (s, 6H, Me), 1.16 (s, 36H, *t*Bu), 1.19 ppm (s, 36H, *t*Bu); ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF, TMS): $\delta = -2.6, -1.6, 22.4, 22.7, 31.4, 31.5$ ppm; ^{29}Si{^{1}H} NMR (79 MHz, [D$_8$]THF, TMS): $\delta = -231.9$ (bridgehead Si), 22.5 and 34.5 ppm (substituent Si).

2c: The mixture of **3** (127 mg, 0.106 mmol) and excess $\mathrm{SrI_2}$ (60 mg, 0.176 mmol) in dry oxygen-free THF (2 mL) was stirred for 2 h at room temperature, during which time the color of the reaction mixture turned from dark green to orange. After filtration and evaporation of solvent from the filtrate, recrystallization from THF gave **2c** as bright-orange crystals (95 mg, 74 %). M.p. 137 °C (dec.). ^{1}H NMR (400 MHz, [D$_8$]THF, TMS): $\delta = 0.14$ (s, 6H, Me), 0.22 (s, 6H, Me), 1.16 (s, 36H, *t*Bu), 1.21 ppm (s, 36H, *t*Bu); ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF, TMS): $\delta = -1.9, -1.7, 22.6, 22.9, 32.1, 32.3$ ppm; ^{29}Si{^{1}H} NMR (79 MHz, [D$_8$]THF, TMS): $\delta = -225.2$ (bridgehead Si), 21.1 and 33.6 ppm (substituent Si).

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[8] Crystal structure analysis of **2a**, **2b**, and **2c**: The single crystals for X-ray analysis were grown from the THF/hexane solution for **2a** and THF solutions for **2b** and **2c**. Diffraction data were collected at 120 K on a MacScience DIP2030 K Image Plate Diffractometer employing graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71070$ Å). Crystal data for **2a**: $(t\mathrm{Bu_2MeSi})_4\mathrm{Si_2Ge_2Mg(thf)_3}$, $\mathrm{C_{48}H_{108}Ge_2MgO_3Si_6}$, $M_r = 1071.37$, orthorhombic, space group $= Pna2_1$, $a = 13.1680(5)$, $b = 21.5230(3)$, $c = 21.5320(7)$ Å, $V = 6102.5(3)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.166\ \mathrm{g\,cm^{-3}}$, GOF = 1.042. The final R factor was 0.0369 ($R_w = 0.0990$ for all data) for 6569 reflections with $I_0 > 2\sigma(I_0)$. Crystal data for **2b**: $(t\mathrm{Bu_2MeSi})_4\mathrm{Si_2Ge_2Ca(thf)_4}$, $\mathrm{C_{52}H_{116}CaGe_2O_4Si_6}$, $M_r = 1159.25$, triclinic, space group $= P\bar{1}$, $a = 13.7440(6)$, $b = 13.7440(6)$, $c = 21.4360(9)$ Å, $\alpha = 71.755(2)$, $\beta = 71.749(2)$, $\gamma = 60.250(2)°$, $V = 3277.1(2)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.175\ \mathrm{g\,cm^{-3}}$, GOF = 1.241. The final R factor was 0.0795 ($R_w = 0.1888$ for all data) for 12054 reflections with $I_0 > 2\sigma(I_0)$. Crystal data for **2c**: $(t\mathrm{Bu_2MeSi})_4\mathrm{Si_2Ge_2Sr(thf)_4}$, $\mathrm{C_{52}H_{116}Ge_2O_4Si_6Sr}$, $M_r = 1206.79$, monoclinic, space group $= Cc$, $a = 23.7800(11)$, $b = 13.9470(3)$, $c = 21.4460(10)$ Å, $\beta = 110.935(2)°$, $V = 6643.2(5)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.207\ \mathrm{g\,cm^{-3}}$, GOF = 0.953. The final R factor was 0.0383 ($R_w = 0.0990$ for all data) for 7000 reflections with $I_0 > 2\sigma(I_0)$. All structures were solved by the direct method and refined by the full matrix Least-squares method using SHELXL-97 program. CCDC-246460 (**2a**), CCDC-246461 (**2b**), CCDC-246462 (**2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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