

1,4,5-Trigermabicyclo[2.1.0]pent-2-en-5-ylum: The Isolable Bishomocyclopropenylium Ion Containing a Heavier Group 14 Element

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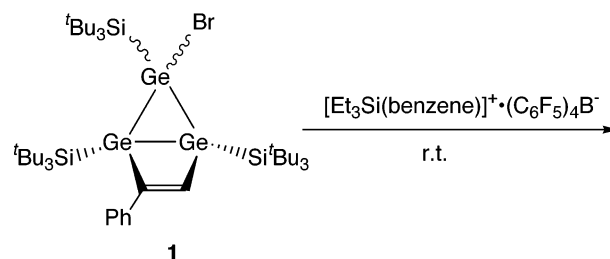
Received May 29, 2003; E-mail: sekiguch@staff.chem.tsukuba.ac.jp

The homoaromaticity concept (pseudoaromaticity) was developed in 1959 by Winstein,¹ and it is well established in carbocation chemistry.² However, homoaromatic compounds containing the heavier Group 14 elements constitute a relatively new field. Very recently, mono- and trishomocyclopropenylium ions consisting of heavier Group 14 elements have been synthesized and characterized in our group.³ Müller et al. reported the formation of bishomocyclopropenylium as a transient species, as deduced from trapping reactions.⁴ On the other hand, the anionic bishomoaromatic boron system was synthesized and characterized by Berndt et al.⁵ However, stable bishomoaromatic cations containing the heavier Group 14 elements were still missing, and their existence remained an open question. Herein, we report the preparation of a new bicyclic compound starting from bromocyclotrigermene and its dehalogenation to form the first isolable bishomocyclopropenylium compound, (2,3,5-*deloc*)-2-phenyl-1,4,5-tris(tri-*tert*-butylsilyl)-1,4,5-trigermabicyclo[2.1.0]pent-2-en-5-ylum TPFPB⁻ (**2**⁺·TPFPB⁻; TPFPB⁻ = tetrakis(pentafluorophenyl)borate).

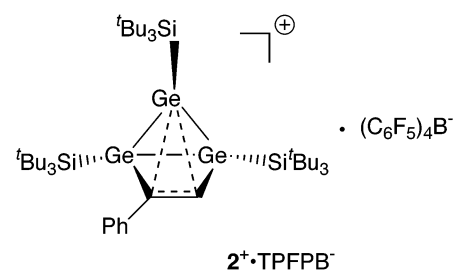
The stable bishomocyclopropenylium compound **2**⁺·TPFPB⁻ was obtained by dehalogenation of 5-bromo-2-phenyl-1,4,5-tris(tri-*tert*-butylsilyl)-1,4,5-trigermabicyclo[2.1.0]pent-2-ene (**1**).⁶ Thus, the reaction of **1** with an equimolar amount of [Et₃Si(C₆H₆)]⁺·TPFPB⁻ in benzene at room temperature immediately produced **2**⁺·TPFPB⁻ as air- and moisture-sensitive pale yellow crystals in 61% yield (Scheme 1).⁸ Compound **2**⁺ is very interesting, since it represents a bishomoaromatic cation stabilized by through-space intramolecular coordination to a C=C double bond.

We determined the actual structure of **2**⁺·TPFPB⁻ by X-ray crystallographic analysis (Figure 1).⁹ The shortest Ge...F distance is ca. 5.4 Å longer than the sum of the van der Waals radii of Ge and F (3.6 Å), that is, **2**⁺ is a free cation in the solid state. The **2**⁺ ions have a highly strained "housene"-type skeleton, which consists of a Ge₃ equilateral triangle and a Ge₂C₂ four-membered ring. The Ge3–C1 (2.415(7) Å) and Ge3–C2 (2.254(7) Å) interatomic distances are very short due to the through-space interaction with the C=C double bond,¹⁰ whereas the C1=C2 bond (1.411(9) Å) is considerably long.¹⁰ These changes in the bond length indicate the effective homoconjugation between the empty 4p-orbital on the Ge atom and the π-orbital of the C=C double bond, resulting in strong bending of the C1C2 unit toward the Ge3 atom, as determined by the dihedral angle of 67° between the Ge1–Ge2–Ge3 plane and the mean plane of Ge1–Ge2–C1–C2. This strong three-center two-electron bonding also leads to a slight pyramidalization of the homoconjugative atoms. The results of a calculation on the trimethylsilyl-substituted model compound **3**⁺ at the B3LYP/DZd level¹¹ well reproduced the experimental bishomocyclopropenylium structure, with bond lengths and angles in good agreement with the X-ray structure. The pyramidalization of the homoconjugative atoms was also found in **3**⁺, which is due to the effective 4p(Ge)–π(C=C) orbitals homoconjugation.

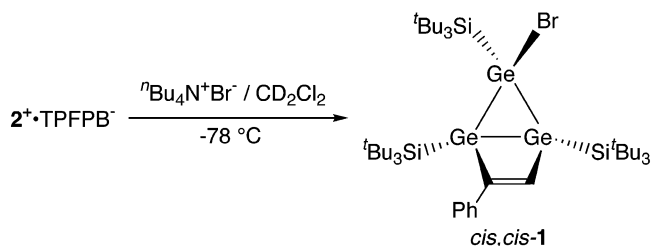
Scheme 1



(1:1 mixture of *cis,trans* and *cis,cis*)



Scheme 2



The characteristic deshielded ²⁹Si NMR signals of **2**⁺ were observed at 56.1 and 67.2 ppm in a ratio of 1:2 in C₆D₆ (the two signals of the silicon atoms attached to bridgehead germanium atoms occasionally overlap). One of the most important features of **2**⁺ is the considerably shielded ¹³C NMR chemical shifts of the endocyclic atoms, phenyl (C1) or hydrogen (C2) substituted carbon atoms and ¹H NMR chemical shift for the olefinic proton attached to atom C2, relative to those of the neutral precursor **1** (compared with *cis,trans*-**1**). Despite the partial delocalization of the positive charge over Ge3, C1, and C2, dramatic upfield shifts ($\Delta\delta_{^{13}\text{C}}(\text{C1}) = -29.8$, $\Delta\delta_{^{13}\text{C}}(\text{C2}) = -54.5$, $\Delta\delta_{^1\text{H}}(\text{H2}) = -1.17$) are observed due to the partial rehybridization of C1 and C2 atoms from sp²- to sp³-type that are similar to the carbon congeners.¹² The relatively large ¹J_{C–H} coupling constant of 165.9 Hz for **2**⁺ is also typical for a bishomoaromatic cation.¹²

In accordance with the homoconjugative structure, NBO analysis¹³ of **3**⁺ clearly shows the electron deficiency of the π(C=C) orbital (1.28 e) and an appreciable occupation of the empty 4p(Ge3) orbital (0.42 e). The bond orders (WBI) of Ge3–C1, Ge3–

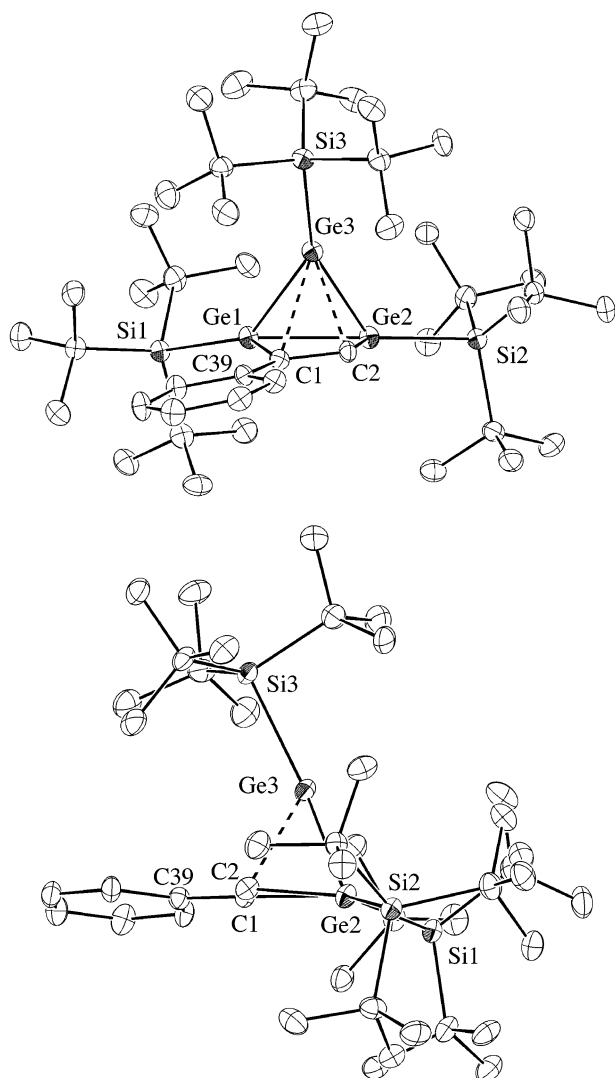


Figure 1. ORTEP drawing of $2^+\cdot\text{TPFPB}^-$. There are two crystallographically independent molecules in the unit cell, and both structures are identical except for the orientation of the tBu_3Si group on the Ge1 atom; one of these molecular structures is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA): Ge1–Ge2 = 2.4765(10), Ge1–Ge3 = 2.4671(10), Ge2–Ge3 = 2.4740(10), Ge3–C1 = 2.415(7), Ge3–C2 = 2.254(7), C1–C2 = 1.411(9). Selected bond angles (deg): Ge1–Ge2–Ge3 = 59.78(3), Ge2–Ge3–Ge1 = 60.16(3), Ge3–Ge1–Ge2 = 60.06(3). Selected torsion angles (deg): C1–Ge1–Ge2–Ge3 = $-69.3(2)$, Ge3–Ge1–Ge2–C2 = 64.5(2), C39–C1–C2–Ge2 = 176.2(6), Ge2–Ge1–Ge3–Si3 = $-171.65(10)$.

C2, and C1–C2 in 3^+ are 0.37, 0.46, and 1.39, respectively, which agrees with the formation of three-center two-electron bonding mode. Further support for the bishomoaromaticity was provided by the calculation of NICS¹⁴ at 1 \AA above the center of the triangle

composed of the homoconjugative atoms (Ge3,C1,C2) (NICS(1)). This NICS value is negative (NICS(1) = -11.0) indicating the presence of diatropic ring current in 3^+ .¹⁵

The reaction of $2^+\cdot\text{TPFPB}^-$ with tetrabutylammonium bromide in CH_2Cl_2 at -78°C gave the brominated compound **1** as the single *cis,cis*-isomer (Scheme 2). Because of the steric shielding by the bulky tBu_3Si group, Br^- attacked the Ge^+ center from the side of the homoconjugative ring giving selectively only one isomer.

Supporting Information Available: The experimental procedures of **1** and $2^+\cdot\text{TPFPB}^-$, table of crystallographic data including atomic positional and thermal parameters for $2^+\cdot\text{TPFPB}^-$, calculated energy and geometry for 3^+ . X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) Compound **1** as a mixture of two stereoisomers (1:1) was prepared by the reaction of 3-bromo-1,2,3-tris(tri-*tert*-butylsilyl)cyclotrigermene with phenylacetylene. For halogen-substituted cyclotrigermenes, see: Sekiguchi, A.; Ishida, Y.; Fukaya, N.; Ichinohe, M.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2002**, *124*, 1158.
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- (8) For the experimental procedure and spectral data of $2^+\cdot\text{TPFPB}^-$, see the Supporting Information.
- (9) Crystal data for $2^+\cdot\text{TPFPB}^-$ at 120 K: MF = $\text{C}_{68}\text{H}_{87}\text{BF}_{20}\text{Ge}_3\text{Si}_3$, MW 1597.23, triclinic, $P1$, $a = 14.2100(9)$, $b = 14.4170(11)$, $c = 36.2190(21)$ \AA , $\alpha = 88.679(4)$, $\beta = 83.103(4)$, $\gamma = 90.055(4)^\circ$, $V = 7364.3(8)$ \AA^3 , $Z = 4$, $D_{\text{calcd}} = 1.441$ g cm^{-3} . The final R factor was 0.0802 with $I_0 > 2\sigma(I_0)$ ($R_w = 0.2235$ for all data, 31382 reflections), GOF = 1.034.
- (10) The $\text{Ge}\cdots\text{C}$ interatomic distance in 5-mesityl-2-phenyl-1,4,5-tris(tri-*tert*-butylsilyl)-1,4,5-trigermabicyclo[2.1.0]pent-2-ene, which has a $\text{C}=\text{C}$ double bond length of 1.357(4) \AA , is ca. 3.2 \AA , see: Fukaya, N.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3881.
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JA030327A