A Free Cyclotrigermenium Cation with a 2π-Electron System

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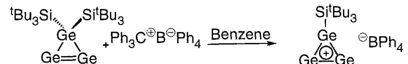
The reaction of tetrakis(tri-*tert*-butylsilyl)cyclotrigermene with trityl tetraphenylborate in benzene produces tris(tri-*tert*-butylsilyl)cyclotrigermenium tetraphenylborate [(*tert*-Bu$_3$SiGe)$_3$$^+BPh_4$$^-$], which can be isolated as a yellow solid that is stable in the absence of air. The crystal structure of the cyclotrigermenium ion reveals a free germyl cation with a 2π-electron system. The three germanium atoms form an equilateral triangle similar to the carbon analog, the cyclopropenium ion.

Silyl and germyl cations, and more recently also silicon and germanium compounds with double bonds, have been known for some time in the gas phase (*1*, *2*), but their characterization in the condensed phase has been considerably more difficult. The synthesis of several compounds with double bonds involving silicon or germanium has recently been accomplished, after the discovery of Mes$_2$Si=SiMes$_2$ (Mes = 2,4,6-trimethylphenyl) and (Me$_3$Si)$_2$Si=C(OSiMe$_3$)Ad (Ad = 1-adamantyl) (*3*, *4*). However, tricoordinate free silyl and germyl cations, the analogs of the carbenium ion (R$_3$C$^+$, R = alkyl), have yet to be characterized unambiguously in the condensed phase (*5*). The closest approach structurally to the silyl cation to date has been achieved in Et$_3$Si(toluene)$^+$B(C$_6$F$_5$)$_4$$^-$ and *i*-Pr$_3$Si$^+$ CB$_{11}$H$_6$Br$_6$$^-$ (*6*, *7*). In contrast to the carbenium ion, the cyclopropenium ion (C$_3$R$_3$$^+$), which represents the simplest Hückel-type aromatic system, is relatively stable despite the large ring strain (*8*). Recent theoretical calculations of cyclic A$_3$H$_3$$^+$ cations (A = C, Si, Ge, Sn, and Pb) suggest new possibilities for the experimental observation of free cations of the group 14 elements heavier than carbon (*9*).

We report the isolation and characterization of tris(tri-*tert*-butylsilyl)cyclotrigermenium tetraphenylborate **2** [(^{t}Bu$_3$SiGe)$_3$ $^+$BPh$_4$$^-$], which incorporates a free germyl cation with a 2π-electron system. Treatment of tetrakis(tri-*tert*-butylsilyl)cyclotrigermene **1** with trityl tetraphenylborate in dry benzene produces a dark-brown viscous oil from which the cyclotrigermenium tetraphenylborate **2** can be isolated as air- and moisture-sensitive yellow crystals in 90% yield (Eq. 1) (*10*, *11*). Despite the steric congestion, the reaction proceeds rapidly and is complete within 1 min. The reaction may involve electron transfer from **1** to trityl tetraphenylborate to produce the cyclotrigermenium ion **2** and a ^{t}Bu$_3$Si radical following cleavage of the weak Si–Ge bond in **1** (*12*).



(1)

Compound **2** was purified by recrystallization from toluene. The physical and spectroscopic properties of **2** are consistent with the assigned structure (*13*), which was subsequently confirmed by single-crystal x-ray crystallographic analysis (Fig. 1) (*14*). The three Ge atoms form a nearly equilateral triangle [Ge–Ge bond lengths: 2.321(4) to 2.333(4) Å, average 2.326(4) Å; Ge–Ge–Ge bond angles: 59.8(1)° to 60.3(1)°, average 60.0(1)°; numbers in parentheses are the standard errors in the last digit]. The Ge–Ge bond lengths observed for **2** are intermediate between the Ge=Ge double bond [2.239(4) Å] and the Ge–Ge single bond [2.522(4) Å] of the precursor **1** (*10*). Thus, the positive charge is delocalized over the three Ge atoms to produce a structure similar to that of the cyclopropenium ion of carbon (*8*). In addition, the Si atoms of the ^{t}Bu$_3$Si substituents are in the approximately same plane as the three-membered germanium ring; the angles between the Ge1–Ge2–Ge3 plane and the Si–Ge bonds are 1.7° to 3.2°. The sum of the bond angles around the Ge atoms (for example, ∠Si1–Ge1–Ge2 + ∠Si1–Ge1–Ge3 + ∠Ge2–Ge1–Ge3 for Ge1) are 359.9(2)° for Ge1, 359.7(2)° for Ge2, and 359.7(2)° for Ge3.

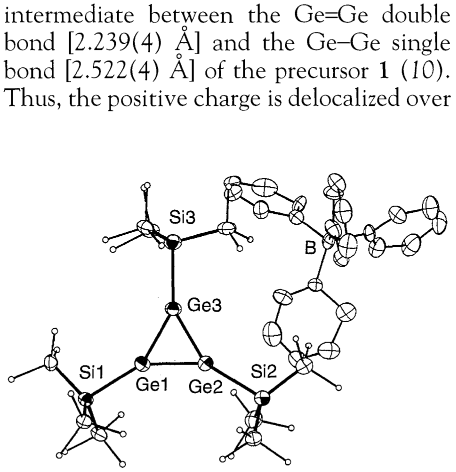


Fig. 1. Molecular structure of tris(tri-*tert*-butylsilyl) cyclotrigermenium tetraphenylborate [(^{t}Bu$_3$SiGe)$_3$$^+$ BPh$_4$$^-$] **2** (30% probability ellipsoids for Ge, Si, and C). Methyl carbon atoms of ^{t}Bu are shown isotropically and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge1–Ge2 2.325(4), Ge1–Ge3 2.321(4), Ge2–Ge3 2.333(4), Ge1–Si1 2.444(8), Ge2–Si2 2.439(9), Ge3–Si3 2.447(9). Selected bond angles (in degrees): Ge2–Ge1–Ge3 60.3(1), Ge2–Ge1–Si1 148.0(2), Ge3–Ge1–Si1 151.6(2), Ge1–Ge2–Ge3 59.8(1), Ge1–Ge2–Si2 147.5(2), Ge3–Ge2–Si2 152.4(2), Ge1–Ge3–Ge2 59.9(1), Ge1–Ge3–Si3 150.4(2), Ge2–Ge3–Si3 149.4(2). Estimated standard deviations are in parentheses.

The crystal structure can be described as (^{t}Bu$_3$SiGe)$_3$$^+$ and BPh$_4$$^-$ ions alternating along the *c* axis to form a sheetlike layer parallel to the plane formed by the *a* and *b* axis (Fig. 2). The distances between the Ge and B atoms range from 6.941(3) to 9.695(3) Å. The closest distance between Ge and phenyl C atoms is >4 Å, well beyond the range of any significant interaction. These structural features indicate that **2** is a cyclotrigermenium ion and that it is a free germyl cation with a 2π-electron system (*15*). The stabilization of the cyclotrigermenium ion and the charge delocalization explain the observed lack of any close interaction with the counterion (*16*).

The structure of **2** presented here is similar to that predicted in a recent calculation of the corresponding D_{3h} Ge$_3$H$_3$$^+$ isomer (*9*). The observed average Ge-Ge distance for **2** is 2.326(4) Å, compared to the calculated value of 2.361 Å for the Ge$_3$H$_3$$^+$ ion with D_{3h} symmetry. The calculations also predicted a hydrogen-bridged nonplanar structure with C_{3v} symmetry to be lower in energy than the D_{3h} minimum. However, bridging cannot be expected when the hydrogens are replaced by other groups. As a result of steric hindrance and the electronic properties of the ^{t}Bu$_3$Si groups, the cyclotrigermenium ion **2** favors the planar structure similar to the cyclopropenium ion (*17*).

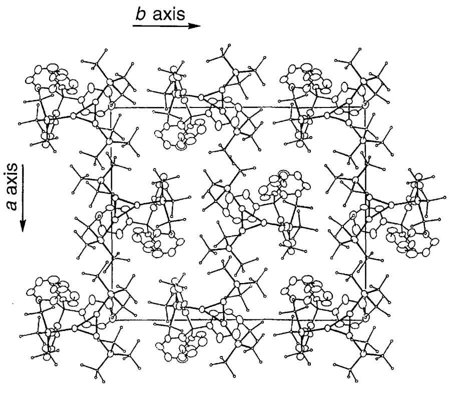


Fig. 2. Perspective view of the orthorhombic cell of **2** down the *c* axis.

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7. While our work was in progress, we learned that Lambert and Zhao have synthesized the trimesitylsilylium cation with a ^{29}Si chemical shift at δ = 225.5. We thank them for sending us a preprint (J. B. Lambert and Y. Zhao, *Angew. Chem.*, in press).
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10. The cyclotrigermene **1** was prepared by reaction of GeCl$_2$-dioxane with ^{t}Bu$_3$SiNa [A. Sekiguchi, H. Yamazaki, C. Kabuto, H. Sakurai, S. Nagase, *J. Am. Chem. Soc.* **117**, 8025 (1995)].
11. Crystals of **1** (20 mg, 0.02 mmol) and trityl tetraphenylborate (20 mg, 0.036 mmol) were put in a glass tube and degassed. Dry oxygen-free benzene was introduced by vacuum transfer and the solution was stirred at room temperature. The solution turned from dark red due to **1** to yellow within 1 min; and the dark brown viscous oil containing **2** separated from the solution. The oily substance was washed with benzene and subsequently with hexane in a glove box to afford air- and moisture-sensitive yellow powders of **2**.
12. The electron transfer reaction followed by cleavage of a Si-Ge bond in **1** may produce the cyclotrigermenium ion **2**, a ^{t}Bu$_3$Si radical, and a Ph$_3$C radical. However, the details of this reaction are not clear at this moment.
13. Nuclear magnetic resonance (NMR) of **2** ([D$_2$]dichloromethane solution, 240 K, ^{1}H) δ values (parts per million): 1.34 (singlet, 81H), ^{t}Bu protons; 6.87 (triplet, 4H, spin-spin coupling constant J = 7.2 Hz), aromatic *p*-protons; 7.02 (triplet, 8H, J = 7.2 Hz), aromatic *m*-protons; 7.24 − 7.30 (multiplet, 8H), aromatic *o*-protons; NMR of **2** (^{13}C) δ values: 26.6, 31.2, 121.6, 125.7, 135.5, 163.7 (quartet, $^1J_{13C\text{-}11B}$ = 49 Hz); NMR of **2** (^{29}Si) δ values: +62.4. The large downfield shift of the ^{29}Si resonances of **2**, relative to those of **1** (δ = 37.2 and 50.1), results from the positive charge of the cyclotrigermenium ion. Ultraviolet spectrum (in dichloromethane solution): λ_{max} (wavelength, maximum of absorption) 276 nm, 350 nm.
14. A yellow-orange crystal (approximate dimensions: 0.30 mm by 0.30 mm by 0.40 mm) of **2** was sealed in a glass capillary and used for x-ray diffraction data collection on a Rigaku Denki AFC-5R diffractometer using a rotating anode (45 kV, 200 mA) with graphite monochromatized Mo K_α radiation (λ = 0.71069 Å). Cell constants and an orientation matrix for data collection corresponded to the orthorhombic space group $P2_12_12_1$, with a = 19.10(3) Å, b = 22.84(1) Å, c = 14.84(1) Å, and V= 6475(13) Å^3, there are four molecules, (^{t}Bu$_3$SiGe)$_3$$^+BPh_4$$^-$, per unit cell ($Z$ = 4), giving a formula weight of 1135.25, and a calculated density of 1.165 g cm^{-3}. Data were collected at 13° C using the ω-θ scan mode to a maximum 2θ value of 53.0°. From 5154 observed reflections, the structure was solved by direct methods using the applied library program UNICS III system and the RANTAN 81 direct-method program. The structure was refined with all non-hydrogen atoms modelled anisotropically. The H atoms were included in the calculated crystal structure factor F_c, but not refined. The final block-diagonal least squares refinement converged with the unweighted and weighted agreement factors equal to R = 0.0959 and R_w = 0.1027 for 2797 reflections, with the observed crystal structure factor $F_o > 4\sigma(F_o)$. The large thermal motions of methyl carbon atoms of the ^{t}Bu groups are the main contributing factor to the relatively high R factors. Coordinates will be deposited in the Cambridge Crystallographic Database.
15. A cyclotrigallane dianion, Na$_2$[(MesC$_6$H$_3$)Ga]$_3$ (Mes = 2,4,6-trimethylphenyl), has recently been synthesized and shown to be a metallic ring system possessing aromatic character [X.-W. Li, W. T. Pennington, G. H. Robinson, *J. Am. Chem. Soc.* **117**, 7578 (1995); Y. Xie, P. R. Schreiner, H. F. Schaefer III, X.-W. Li, G. H. Robinson, *ibid.* **118**, 10635 (1996)].
16. Aromatic stabilization energies of the D_{3h} A$_3$H$_3$$^+$ cation are calculated to be 58.7 (A = C), 35.6 (A = Si), 31.9 (A = Ge), 26.4 (A = Sn), and 24.1 (A = Pb) kcal · mol^{-1} (*9*).
17. Electropositive substituents such as silyl groups generally lead to planar Ge=Ge double bonds rather than *trans*-bent structures (*10*). In addition, such electropositive substituents are predicted to reduce the strain within three-membered rings formed by group 14 elements considerably [S. Nagase, *Pure Appl. Chem.* **65**, 675 (1993)].

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Compressibility, Phase Transitions, and Oxygen Migration in Zirconium Tungstate, ZrW$_2$O$_8$

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In situ neutron diffraction experiments show that at pressures above 2 kilobars, cubic zirconium tungstate (ZrW$_2$O$_8$) undergoes a quenchable phase transition to an orthorhombic phase, the structure of which has been solved from powder diffraction data. This phase transition can be reversed by heating at 393 kelvin and 1 atmosphere and involves the migration of oxygen atoms in the lattice. The high-pressure phase shows negative thermal expansion from 20 to 300 kelvin. The relative thermal expansion and compressibilities of the cubic and orthorhombic forms can be explained in terms of the "cross-bracing" between polyhedra that occurs as a result of the phase transition.

Materials with a negative coefficient of thermal expansion (either as pure phases or as constituents of composite materials designed to achieve a desired overall coefficient) may become useful in a variety of electronics applications and as substrates for high-precision optical mirrors, components of high-precision thermometers, and catalyst supports. Cubic ZrW$_2$O$_8$ was recently shown to exhibit isotropic negative thermal expansion from 0.3 to 1050 K (*1*, *2*). The coefficient of this thermal contraction ($\alpha = -8.8 \times 10^{-6}$ K^{-1}) (*2*) is of the same order of magnitude as that of a so-called high-expansion normal ceramic such as Al$_2$O$_3$ ($\alpha = +9 \times 10^{-6}$ K^{-1}) (*3*). The material remains cubic over the entire temperature range, and the contraction is therefore isotropic. In contrast, the low thermal expansion materials currently in use generally expand anisotropically, which can lead to severe problems such as microcracking in ceramics. Further insights into the mechanisms leading to the negative thermal expansion in ZrW$_2$O$_8$ may therefore be important both to gain fundamental insight and to design materials.

The structure of ZrW$_2$O$_8$ consists of a framework of corner-sharing ZrO$_6$ octahe-

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