Synthesis and Structure of Cyclotrigermenium Salt of the Tetrakis{3,5-bis(trifluoromethyl)phenyl}borate Anion. A Stable Free Germyl Cation in the Condensed Phase

Masaaki Ichinohe, Norihisa Fukaya, and Akira Sekiguchi*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

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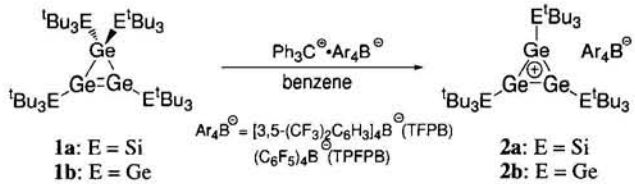
The reaction of tetrakis(tri-t-butylsilyl)cyclotrigermene with $Ph_3C^+\bullet[3,5\text{-}(CF_3)_2C_6H_3]B^-$ (TFPB) and $Ph_3C^+\bullet(C_6F_5)_4B^-$ (TPFPB) in benzene produced the stable free tris(tri-t-butylsilyl)cyclotrigermenium ion (**2a**) with the corresponding tetraarylborate as a counter anion. The crystal structure of **2a**•TFPB reveals a free germyl cation with a 2π-electron system.

The chemistry of tricoordinate germyl and silyl cations in the condensed phase has developed very rapidly in recent years.[1,2] In 1997, Lambert and Zhao successfully synthesized the trimesitylsilyl cation, which is a long sought free silyl cation.[3] Although they did not perform an X-ray study, the presence of the free silyl cation has been strongly supported by *ab initio* calculations, demonstrating a good agreement of the ^{29}Si NMR chemical shift between the calculations and experiments.[4]

In contrast to the silyl cations, very little experimental work has been reported on the germyl cation in the condensed phase.[5] Recently, we isolated and characterized $[(t\text{-}Bu_3SiGe)_3^+\bullet BPh_4^-]$ (**2a**•TPB, TPB = tetraphenyl borate) by the reaction of tetrakis(tri-t-butylsilyl)cyclotrigermene with $Ph_3C^+\bullet$TPB, which was the first example of a free germyl cation with a 2π-electron system.[6,7] However, the problem of the TPB anion is its chemical stability.[8] The **2a**•TPB can survive in a solution of dichloromethane only at temperatures as low as -78 °C.

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB)[9] and tetrakis(pentafluoropenyl)borate (TPFPB)[10] have been recognized as stable borate anions. These counter anions would increase the stability of the resulting cyclotrigermenium ion. This prompted us to examine the reaction of $t\text{-}Bu_3E$ substituted cyclotrigermenes **1a** (E = Si)[11] and **1b** (E = Ge)[11] with $Ph_3C^+\bullet$TFPB and $Ph_3C^+\bullet$TPFPB, producing $(t\text{-}Bu_3EGe)_3^+\bullet$TFPB and $(t\text{-}Bu_3EGe)_3^+\bullet$TPFPB (E = Si, Ge). These germyl cations can survive for a long time without any decomposition both in solution and in the solid state. We report spectroscopic and structural evidence that **2a**•TFPB and **2a**•TPFPB are free germyl cations, which lack any coordination to the solvent molecules of dichloromethane, chloroform or toluene, as well as being counter anions.

The reaction of **1a** (33 mg, 0.03 mmol) with $Ph_3C^+\bullet$TFPB (55 mg, 0.05 mmol) in dry oxygen-free benzene at room temperature led to the immediate formation of a dark-brown substance, which was washed with hexane to give a moisture- and air-sensitive yellow powder of **2a**•TFPB (45 mg) in 91% yield (Scheme 1).



Scheme 1.

The reaction of **1b** with $Ph_3C^+\bullet$TFPB in benzene also proceeded to give **2b**•TFPB. Both **2a**•TFPB and **2b**•TFPB are soluble in dichloromethane, but slightly soluble in toluene.[12] Similar to that of $Ph_3C^+\bullet$TFPB, the reaction of **1a** and **1b** with $Ph_3C^+\bullet$TPFPB produced **2a**•TPFPB and **2b**•TPFPB, respectively.[13] However, several attempts to obtain these crystals failed.

Recrystallization of **2a**•TFPB from toluene yields yellow-orange crystals suitable for X-ray crystallography; its molecular structure is shown in Figure 1.[14] The three-membered ring of germanium atoms is almost an equilateral triangle, as determined by the internal bond angles of 59.8(1) to 60.3(1)°. The Ge-Ge distances of the three-membered ring are almost equal, ranging from 2.329(2) to 2.343(2) Å (av. 2.335(2) Å). The three silicon atoms are nearly coplanar with the central three-membered ring. The bond lengths of the Ge-Si bonds (Ge1-Si1, 2.428(3); Ge2-Si2, 2.439(3); Ge3-Si3, 2.447(3) Å) of **2a**•TFPB are shortened compared with those of **1a**[11] (2.629(7) Å for the exo bond and 2.448(7) Å for the bond attached to Ge=Ge). These structural features for **2a**•TFPB are practically the same as those of **2a**•TPB.[6] Thus, the counterion does not affect the framework of the cyclotrigermenium ion.

The perspective view appears to show a weak electorostatic interaction between the germanium and fluorine atoms. The closest distances ranging from 3.840 to 4.562 Å are longer than the sum of the van der Waals radii for germanium and fluorine atoms (3.57 Å). Undoubtedly, CF_3 groups of the counter anion are sufficiently remote from the germanium center to preclude any covalent interaction.

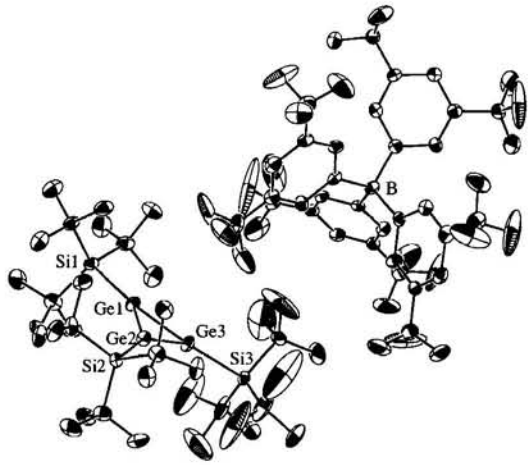


Figure 1. Molecular structure of **2a**•TFPB (hydrogen atoms are omitted for the clarity).

The evidence for the free cyclotrigermenium ion is supported by the NMR spectroscopic data. The ^1H,^{13}C, and ^{29}Si NMR chemical shifts for the cyclotrigermenium moiety of **2a**•TFPB and **2a**•TPFPB in CD_2Cl_2 are practically the same as each

other.[12,13] In addition, **2a**•TFPB and **2a**•TPFPB have an identical chemical shift of the ^{29}Si NMR signal, appearing at δ = 64.0 in CD_2Cl_2, δ = 64.2 in $CDCl_3$ and δ = 64.4 in toluene-d_8. The independence of both counter anions and solvents clearly indicates that **2a** is a free germyl cation in dichloromethane, chloroform, and aromatic solvents.

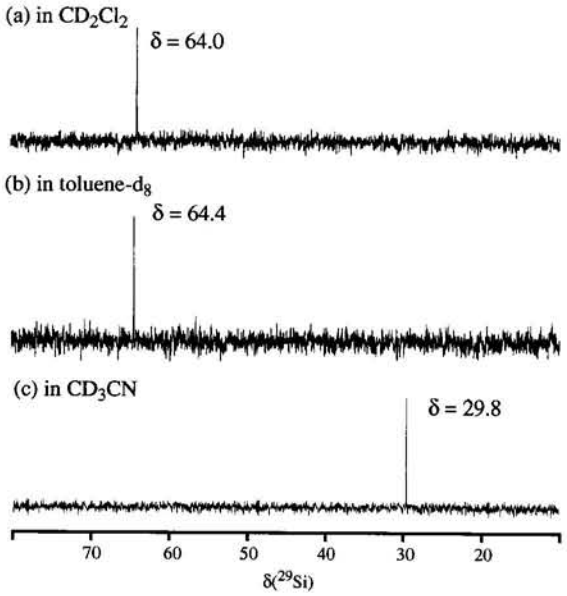


Figure 2. ^{29}Si NMR spectra of **2a**•TFPB in (a) CD_2Cl_2, (b) toluene-d_8, (c) CD_3CN (298 K).

On the other hands, in tetrahydrofuran, ^{29}Si NMR signal of **2a**•TFPB has slightly shifted to high field, appearing at δ = 60.4. In the strong coordinating solvent such as acetonitrile, the ^{29}Si NMR signal has largely shifted to higher fields; the ^{29}Si NMR signal of **2a**•TFPB has been observed at δ = 29.8 in CD_3CN (Figure 2). Thus, the acetonitrile molecule is small enough to complex the cyclotrigermenium ion **2a**. These NMR data must be interpreted as an indication that cyclotrigermenium ion **2a** forms Lewis base complexes with coordinatable solvents such as THF and acetonitrile.

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12 **2a**•TFPB: ^1H NMR (CD_2Cl_2, 298 K, δ) 1.40 (s, 81 H), 7.56 (s, 4 H), 7.73 (s, 8 H); ^{13}C NMR (CD_2Cl_2, 298 K, δ) 27.2, 31.8, 117.8, 125.0 (q, $^1J^{13}C\text{-}^{19}F$ = 270 Hz), 129.5 (m), 135.2, 162.2 (q, $^1J^{13}C\text{-}^{11}B$ = 50 Hz); ^{29}Si NMR (CD_2Cl_2, 298 K, δ) 64.0. **2b**•TFPB: ^1H NMR (CD_2Cl_2, 298 K, δ) 1.48 (s, 81 H), 7.56 (s, 4 H), 7.73 (s, 8 H); ^{13}C NMR (CD_2Cl_2, 298 K, δ) 32.4, 37.1, 117.8, 125.0 (q, $^1J^{13}C\text{-}^{19}F$ = 270 Hz), 129.5 (m), 135.2, 162.2 (q, $^1J^{13}C\text{-}^{11}B$ = 50 Hz).

13 **2a**•TPFPB: ^1H NMR (CD_2Cl_2, 298 K, δ) 1.40 (s, 81 H); ^{13}C NMR (CD_2Cl_2, 298 K, δ) 27.2, 31.8, 123.5–126.5 (m), 136.7 (d, $^1J^{13}C\text{-}^{19}F$ = 240 Hz), 138.6 (d, $^1J^{13}C\text{-}^{19}F$ = 240 Hz), 148.5 (d, $^1J^{13}C\text{-}^{19}F$ = 240 Hz); ^{29}Si NMR (CD_2Cl_2, 298 K, δ) 64.0. **2b**•TPFPB: ^1H NMR (CD_2Cl_2, 298 K, δ) 1.48(s, 81 H); ^{13}C NMR (CD_2Cl_2, 298 K, δ) 32.4, 37.1, 123.5–126.5 (m), 136.7 (d, $^1J^{13}C\text{-}^{19}F$ = 240 Hz), 138.6 (d, $^1J^{13}C\text{-}^{19}F$ = 240 Hz), 148.5 (d, $^1J^{13}C\text{-}^{19}F$ = 240 Hz).

14 Crystal data for **2a**•TFPB at 120 K: MF = $C_{68}H_{93}BF_{24}Ge_3Si_3$, MW = 1679.34, monoclinic, a = 16.912(1) Å, b = 20.919(1) Å, c = 23.399(1) Å, ß = 108.147(4)°, V = 7866.4(2) Å^3, space group = $P2_1/n$, Z = 4, Dcalcd = 1.372 g/cm^3. The final R factor was 0.060 (Rw = 0.058) for 9039 reflections with Io > 3σ(Io).