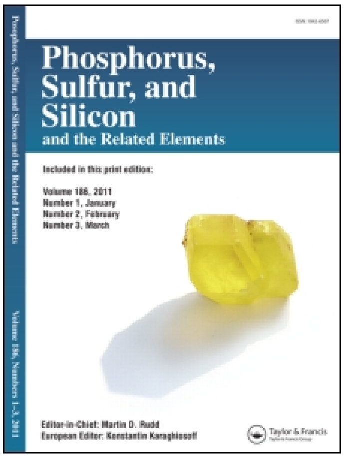

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Cyclotrigermenium Ion by Oxidation of Cyclotrigermene with Trityl Tetrakis {3,5-Bis(Trifluoromethyl)Phenyl}Borate and Trityl Tetrakis(Pentafluoro-Phenyl)Borate. A Stable Free Germyl Cation in the Condensed Phase

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The reaction of tetrakis(tri-*t*-butylsilyl) cyclotrigermene with $Ph_3C^{+}\bullet$ $[3,5\text{-}(CF_3)_2C_6H_3]_4B^{-}$ (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 2π-electron system. The three-membered germanium atoms constitute almost an equilateral triangle, similar to that of **2a**•TPB (TPB = Ph_4B^{-}). In contrast to **2a**•TPB, both **2a**•TFPB and **2a**•TPFPB are thermally stable in solution.

Keywords: germyl cation; electron transfer; oxidation

I. INTRODUCTION

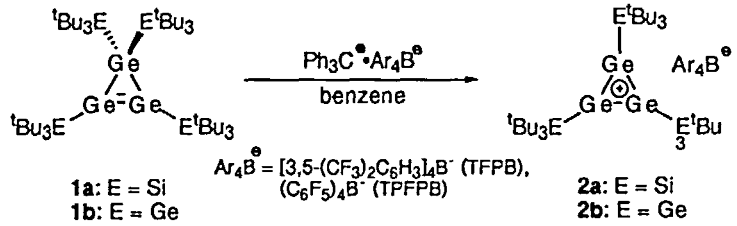
The chemistry of tricoordinate germyl and silyl cations in the condensed phase has developed very rapidly in recent years[1]. Their study is, however, in an early stage compared with that of carbenium ion[2]. Over the years, many efforts have been aimed at synthesizing and characterizing free germyl and silyl cations in the condensed phase[3]. In 1997, Lambert and Zhao successfully synthesized the trimesitylsilyl cation, which is a long sought free silyl cation[4]. Although they did not perform an X-ray study, the convincing evidence was given by its ^{29}Si NMR chemical shift in aromatic solvents. 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[5].

In contrast to the silyl cations, very little experimental work has been reported on the germyl cation in the condensed phase, although the theoretical calculation of $A_3H_3^+$ cations (A = C, Si, Ge, Sn) has been reported[6]. Recently, we isolated and characterized $[(t\text{-}Bu_3SiGe)_3^+ \bullet BPh_4^-]$ (**2a**•TPB, TPB = tetraphenylborate) 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 system[7],[8],[9]. However, the problem of the TPB anion is its chemical stability[10]. The **2a**•TPB can survive in a solution of dichloromethane only at temperatures as low as -78°C.

II. SYNTHESIS OF $[(t\text{-}Bu_3SiGe)_3^+ \bullet Ar_4B^-]$

$[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ (TFPB) (TFPB = tetrakis{3,5-bis(trifluoromethyl)phenyl}borate)[11] and $(C_6F_5)_4B^-$ (TPFPB) (TPFPB = tetrakis(pentafluorophenyl)borate)[12] 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*-Bu_3E-substituted cyclotrigermenes **1a** (E = Si)[13] and **1b** (E = Ge)[13] with Ph_3C^+•TFPB and Ph_3C^+•TPFPB, producing $[(t\text{-}Bu_3EGe)_3{}^+$•TFPB] and $[(t\text{-}Bu_3EGe)_3{}^+$•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 **2**•TFPB and **2**•TPFPB are free germyl cations, which lack any coordination to the solvent molecules of dichloromethane, chloroform or toluene, as well as being counterions.

The reaction of **1a** with Ph_3C^+•TFPB 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; ^1H NMR (CD_2Cl_2, 298 K, δ) 1.40 (s, 81 H), 7.56(s, 4 H), 7.73 (s, 8H); ^{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. The reaction of **1b** with Ph_3C^+•TFPB in benzene also proceeded to give **2b**•TFPB; ^1H NMR (CD_2Cl_2, 298 K, δ) 1.48 (s, 81 H), 7.56(s, 4 H), 7.73 (s, 8H); ^{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



Ar_4B^{-} = $[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ (TFPB), $(C_6F_5)_4B^-$ (TPFPB)

1a: E = Si
1b: E = Ge

2a: E = Si
2b: E = Ge

(m), 135.2, 162.2 (q, $^1J_{^{13}C-^{11}B} = 50$ Hz). Both **2a**•TFPB and **2b**•TFPB are soluble in dichloromethane, but slightly soluble in toluene. Similar to that of Ph_3C^+•TFPB, the reaction of **1a** and **1b** with Ph_3C^+•TPFPB in benzene produced **2a**•TPFPB and **2b**•TPFPB, respectively[14]. However, several attempts to obtain these crystals failed.

III. SOLID STRUCTURE OF $[(t\text{-}Bu_3SiGe)_3^+\cdot Ar_4B^-]$

Recrystallization of **2a**•TFPB from toluene yields yellow-orange crystals suitable for X-ray crystallography; its molecular structure is shown in Figure 1. 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 = $P2_1/n$, $Z = 4$, $D_{calcd} = 1.372$ g/cm^3. The final R factor was 0.060 (Rw = 0.058) for 9039 reflections with $I_o > 3\sigma(I_o)$.

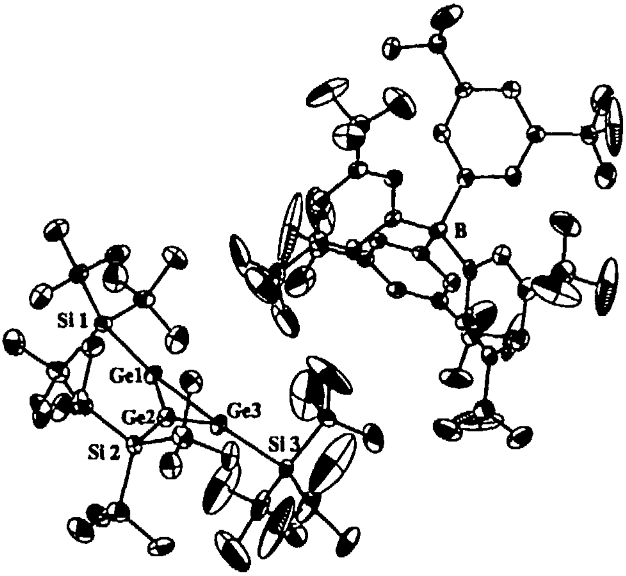


FIGURE 1 Molecular structure of 2a•TFPB.

Selected Bond Lengths (Å)	
Ge1-Ge2	2.333(2)
Ge1-Ge3	2.329(2)
Ge2-Ge3	2.343(2)
Ge1-Si1	2.428(3)
Ge2-Si2	2.439(3)
Ge3-Si3	2.447(3)

Selected Bond Angles (°)	
Ge2-Ge1-Ge3	60.3(1)
Ge2-Ge1-Si1	150.5(1)
Ge3-Ge1-Si1	148.5(1)
Ge1-Ge2-Ge3	59.8(1)
Ge1-Ge2-Si2	146.0(1)
Ge3-Ge2-Si2	152.8(1)
Ge1-Ge3-Ge2	59.9(1)
Ge1-Ge3-Si3	152.4(1)
Ge2-Ge3-Si3	146.6(1)

The structure of the TFPB anion is tetrahedral at boron, and shows no disorder in the CF_3 group at 120 K. 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**[13] (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[7]. *Thus, the counterion does not affect the framework of the cyclotrigermenium ion.*

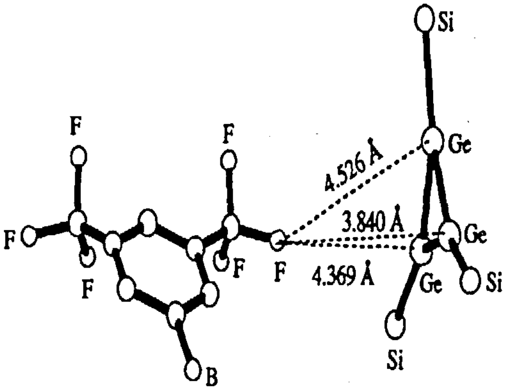


FIGURE 2 Section from the structure of **2a**•TFPB with the closest atomic distances between Ge and F.

The perspective view appears to show a weak electrostatic interaction between the germanium and fluorine atoms. Three different, closest distances range from 3.840 to 4.526 Å, as depicted in Figure 2. However, these distances are longer than the sum (3.57 Å) of the van der Waals radii for germanium and fluorine atoms. Undoubtedly, CF_3 groups of the counter anion are sufficiently remote from the germanium center to preclude any covalent interaction.

IV. STRUCTURE OF $[(t\text{-}Bu_3SiGe)_3{}^+ \cdot Ar_4B^-]$ IN SOLUTION

The evidence for the free cyclotrigermenium ion is supported by the

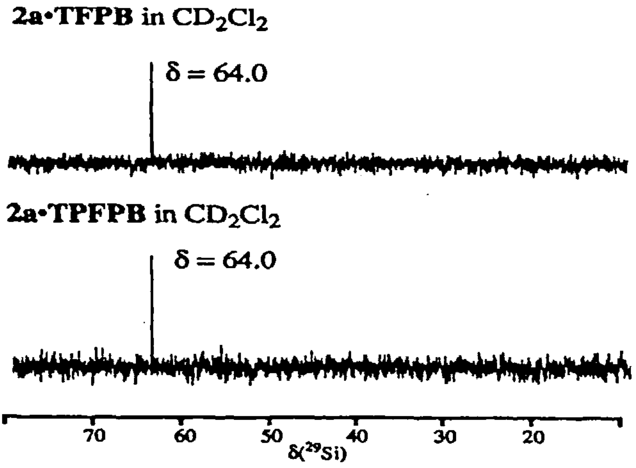


FIGURE 3 ^{29}Si NMR spectra of 2a•TFPB and 2a•TPFPB in CD_2Cl_2.

NMR spectroscopic data. The ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts for the cyclotrigermeium moiety of **2a**•TFPB and **2a**•TPFPB in CD_2Cl_2 are practically the same as each other (Figure 3). Both **2a**•TFPB and **2a**•TPFPB have an identical chemical shift of the ^{29}Si NMR signal, appearing at $\delta = 64.0$ in CD_2Cl_2, $\delta = 64.2$ in $CDCl_3$, and $\delta = 64.4$ in toluene-d_8. *The independence of counteranions and solvents clearly indicates that **2a** is a free germyl cation in solution.* The observed ^{29}Si NMR shift to a relatively low field compared to **1a** ($\delta = 37.2$, 50.1) shows that the positive charge is not localized on the germanium atoms, but is significantly transferred to the silicon center. It is precedent that the positive charge in the three-membered ring carbon atoms of cyclopropenium cations ($R_3C_3^+$) decreases with decreasing electronegativity of the substituent; +0.200 (R = CH_3), +0.026 (R = H), -0.243 (R = SiH_3)[15]. The atomic charge of $Ge_3(SiH_3)_3^+$ at HF/6-31G* level indicates the similar delocalization of the positive charge; -0.07 for the ring germanium atoms; +0.64 for the silicon atoms of SiH_3 substituent as shown in Figure 4. According to Mulliken charge, most of the positive charge is distributed on the silicon atoms of the substituents rather than at the ring germanium.

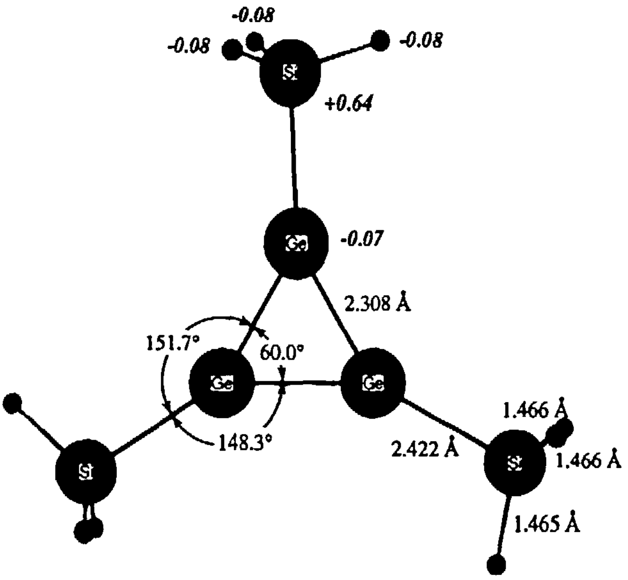


FIGURE 4 Optimized structure and Mulliken charge of $Ge_3(SiH_3)_3^+$ at HF/6-31G* level.

Acknowledgments

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