Synthesis and Structure of Cyclotrigermenium Salts of Tetrakis{3,5-bis(trifluoromethyl)phenyl}borate, Tetrakis(pentafluorophenyl)borate and Tetrakis{4-[*tert*-butyl(dimethyl)silyl]-2,3,5,6-tetrafluorophenyl}borate: A Stable Free Germyl Cation in the Condensed Phase

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The reaction of tetrakis(tri-*tert*-butylsilyl)cyclotrigermene (**1a**) with $Ph_3C^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ ($TFPB^-$), $Ph_3C^+(C_6F_5)_4B^-$ ($TPFPB^-$), and $Ph_3C^+[4\text{-}(t\text{BuMe}_2\text{Si})C_6F_4]_4B^-$ ($TSFPB^-$) in benzene produced the stable free tris(tri-*tert*-butylsilyl)cyclotrigermenium ion (**2a**$^+$) with the corresponding tetraarylborate as the counterion. The crystal structures of **2a**$^+$$TFPB^-$ and **2a**$^+$$TSFPB^-$ reveal a free germyl cation with a two π-electron system. The three-membered ring of germanium atoms constitutes an almost equilateral triangle. The cyclotrigermenium tetraarylborates, **2a**$^+$$TFPB^-$, **2a**$^+$$TPFPB^-$, and **2a**$^+$$TSFPB^-$, are stable in solution. The spectroscopic data show that **2a**$^+$ is a free germyl cation, does not coordinate to either the solvent molecules (dichloromethane, chloroform, toluene, or diethyl ether) or the counter anions ($TFPB^-$, $TPFPB^-$, or $TSFPB^-$). The tris(tri-*tert*-butylgermyl)cyclotrigermenium ion (**2b**$^+$) was also characterized.

Introduction

The chemistry of tricoordinated germyl and silyl cations in the condensed phase has developed rapidly in recent years.[1] Their study is, however, at an early stage compared to that of the carbocations.[2] Over the years, many efforts have been directed towards the synthesis and characterization of free germyl and silyl cations in the condensed phase.[3] In 1997, Lambert and Zhao successfully synthesized the trimesitylsilyl cation, which was a long-sought free silyl cation.[4] Although they did not perform an X-ray study, convincing evidence of its existence was given by its ^{29}Si NMR chemical shift in aromatic solvents.[4,5] The presence of the free silyl cation has been strongly supported by ab initio calculations, demonstrating good agreement between the calculated and experimental ^{29}Si NMR chemical shifts.[6]

In contrast to the silyl cations, very little experimental work has been reported on the germyl cation in the condensed phase.[5,7] Recently, we isolated and characterized $[(t\text{Bu}_3\text{SiGe})_3^+BPh_4^-]$ (**2a**$^+$$TPB^-$, TPB^- = tetraphenylborate) by the reaction of tetrakis(tri-*tert*-butylsilyl)cyclotrigermene with $Ph_3C^+TPB^-$, which was the first example of a free germyl cation with a two π-electron system.[8,9] However, a problem of the TPB anion is its chemical instability.[10] **2a**$^+$$TPB^-$ can survive in a solution of dichloromethane only at temperatures below −78 °C.

$[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ ($TFPB^-$, tetrakis{3,5-bis(trifluoromethyl)phenyl}borate),[11] $(C_6F_5)_4B^-$ ($TPFPB^-$, tetrakis(pentafluorophenyl)borate),[12] and $[4\text{-}(t\text{BuMe}_2\text{Si})C_6F_4]_4B^-$ ($TSFPB^-$, tetrakis{4-[*tert*-butyl(dimethyl)silyl]-2,3,5,6-tetrafluorophenyl}borate)[13] are known to be stable borate anions. These counter anions should increase the stability of the resulting cyclotrigermenium ion. This prompted us to examine the reaction of $t\text{Bu}_3$E- substituted cyclotrigermenes **1a** (E = Si)[14] and **1b** (E = Ge)[14] with $Ph_3C^+TFPB^-$, $Ph_3C^+TPFPB^-$, and $Ph_3C^+TSFPB^-$, producing $[(t\text{Bu}_3\text{EGe})_3^+TFPB^-]$, $[(t\text{Bu}_3\text{EGe})_3^+TPFPB^-]$, and $[(t\text{Bu}_3\text{EGe})_3^+TSFPB^-]$ (E = Si, Ge). These germyl cations can survive for extensive periods without decomposition both in solution and the solid state. We report here spectroscopic and structural evidence that **2**$^+$$TFPB^-$, **2**$^+$$TPFPB^-$, and **2**$^+$$TSFPB^-$ incorporate free germyl cations, which do not coordinate to either the solvent molecules dichloromethane, chloroform, toluene or diethyl ether, or the counter anions $TFPB^-$, $TPFPB^-$, or $TSFPB^-$.

Results and Discussion

Synthesis of 2$^+$$TFPB^-$, 2$^+$$TPFPB^-$, and 2$^+$$TSFPB^-$

Synthesis was carried out under an inert atmosphere by standard Schlenk and high-vacuum line techniques. Dry oxygen-free benzene was introduced by vacuum transfer to a mixture of $(t\text{Bu}_3\text{Si})_4\text{Ge}_3$ (**1a**) and $Ph_3C^+TFPB^-$, and the mixture was stirred at room temperature. The solution immediately changed from the dark red color of **1a** to yellow, and a brown powder formed. The solvent was removed under vacuum and the resulting solid was washed with hexane in a glove box to afford **2a**$^+$$TFPB^-$ as a yellow powder in 81% yield (Scheme 1). Despite the large steric congestion, the reaction is very rapid and is complete within 5 min. The reaction is possibly initiated by electron transfer from **1a** to the trityl cation followed by elimination of a $t\text{Bu}_3$Si radical through cleavage of the weak exocyclic Si-Ge bond to produce **2a**$^+$$TFPB^-$.[15] The reaction of **1b** with $Ph_3C^+TFPB^-$

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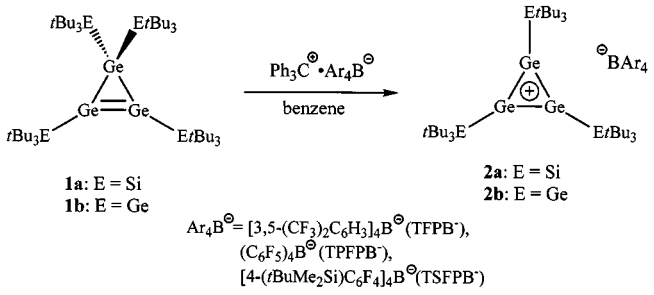

Scheme 1

in benzene also proceeded to give **2b**$^+$TFPB$^-$ in 76% yield. Both **2a**$^+$TFPB$^-$ and **2b**$^+$TFPB$^-$ are soluble in dichloromethane, but only slightly soluble in toluene. Similarly to the reaction with Ph_3C^+TFPB$^-$, the reaction of **1a** and **1b** with Ph_3C^+TPFPB$^-$ in benzene produced **2a**$^+$TPFPB$^-$ (80%) and **2b**$^+$TPFPB$^-$ (80%), respectively. However, several attempts to obtain crystals of these complexes failed. The reaction of **1a** with Ph_3C^+TSFPB$^-$ in benzene produced **2a**$^+$TSFPB$^-$ as orange crystals in 88% yield. The tetraarylborate derivatives of the cyclotrigermenium ion are extremely air- and moisture-sensitive, and the yellow color disappeared immediately when solutions were exposed to the air.

Crystal Structures of 2a$^+$TFPB$^-$ and 2a$^+$TSFPB$^-$

Recrystallization of **2a**$^+$TFPB$^-$ from toluene yielded yellow-orange crystals suitable for X-ray crystallography; its molecular structure is shown in Figure 1. The three-membered ring consisting of germanium atoms forms an almost equilateral triangle, as determined by the internal bond angles of 59.79(3) to 60.28(3) °. The Ge−Ge distances of the three-membered ring are almost equal, ranging from 2.3284(8) to 2.3398(8) Å (av. 2.3333(8) Å). The Ge−Ge bond lengths observed for **2a**$^+$TFPB$^-$ (Figure 1) 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 **1a**.[14] The three silicon atoms are nearly coplanar with the central three-membered ring. The bond lengths of the Ge−Si bonds (Ge1−Si1, 2.425(1) Å; Ge2−Si2, 2.442(1) Å; Ge3−Si3, 2.444(1) Å) of **2a**$^+$TFPB$^-$ are shorter than those of **1a**[14] (2.629(7) Å for the Ge−Si bond length of sp^3 Ge atom and 2.448(7) Å for the Ge−Si bond length of sp^2 Ge atoms).

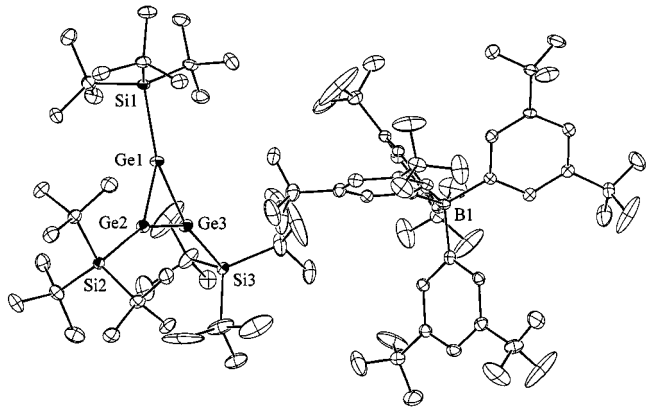

Figure 1. Perspective view of **2a**$^+$TFPB$^-$ in the crystal at the 30% probability level (hydrogen atoms are omitted for the clarity). Selected bond lengths (Å): Ge1−Ge2, 2.3316(9); Ge1−Ge3, 2.3284(8); Ge2−Ge3, 2.3398(8); Ge1−Si1, 2.425(1); Ge2−Si2, 2.442(1); Ge3−Si3, 2.444(1). Selected bond angles (deg): Ge2−Ge1−Ge3, 60.28(3); Ge2−Ge1−Si1, 150.58(5); Ge3−Ge1−Si1, 148.55(5); Ge1−Ge2−Ge3, 59.79(3); Ge1−Ge2−Si2, 145.94(5); Ge3−Ge2−Si2, 152.75(5); Ge1−Ge3−Ge2, 59.93(3); Ge1−Ge3−Si3, 152.36(5); Ge2−Ge3−Si3, 146.70(5).

The perspective view appears to show a weak electrostatic interaction between the germanium and fluorine atoms. The three closest distances range from 3.823 to 5.097 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.[16] Undoubtedly, CF_3 groups of the counter anion are sufficiently remote from the germanium center to preclude any covalent interaction.

We have also obtained X-ray diffraction data for **2a**$^+$TSFPB$^-$, which was obtained by recrystallization from toluene. Due to the steric bulkiness of the *t*BuMe$_2$Si group attached to the *para* positions of the phenyl rings of borate anion, no interaction between the cation moiety and the counter anion can be found (Figure 3). As a consequence, the skeleton of the three-membered framework forms an equilateral triangle; the Ge−Ge bond lengths are 2.3310(8) Å for Ge1−Ge2, 2.3315(7) Å for Ge1−Ge3, and 2.3349(8) Å for Ge2−Ge3, and the Ge−Ge−Ge bond angles are 60.10(2)° for Ge2−Ge1−Ge3, 59.96(2)° for Ge1−Ge2−Ge3, 59.94(2)° for Ge1−Ge3−Ge2. In addition, the silicon atoms of the *t*Bu$_3$Si groups attached to the germanium atoms are in approximately the same plane as the three-membered ring, as determined by the sum of the respective bond angles around the germanium atoms (e.g. 359.99(4)° for Ge1, 359.96(4)° for Ge2, and 359.86(5)° for Ge3).

These structural features for **2a**$^+$TFPB$^-$ and **2a**$^+$TSFPB$^-$ are practically the same as those of **2a**$^+$TPB$^-$,[8a] i.e. the counter anion does not affect the framework of the cyclotrigermenium ion. Thus, the crystal structure of the cyclotrigermenium ion reveals a free germyl cation with a two π-electron system. The three germanium atoms form an equilateral triangle similar to its carbon analog, the cyclopropenium ion.[17]

The structures of **2a**$^+$TFPB$^-$ and **2a**$^+$TSFPB$^-$ presented here are very close to those predicted by a calculation on the corresponding D_{3h} $(HGe)_3^+$ isomer.[7d] The observed average Ge−Ge distances for **2a**$^+$TFPB$^-$ and **2a**$^+$TSFPB$^-$ are 2.3333(8) Å and 2.3325(8) Å, compared with the calculated value of 2.361 Å for a $(HGe)_3^+$ ion with D_{3h} symmetry. The theoretical calculations also predict a hydrogen-bridged nonplanar structure with C_{3v} symmetry that has a lower energy than that of a planar one with D_{3h} symmetry.[7d] However, the more stable hydrogen-bridged $(HGe)_3^+$ isomer cannot be expected when the hydrogens are replaced by other groups. Due to the steric hindrance and electronic properties of the *t*Bu$_3$Si group,[18] the cyclotrigermenium ion favors a planar structure similar to that of the cyclopropenium ion. A cyclotrigallane dianion, Na_2[(2,6-$Mes_2C_6H_3$)Ga]$_3$ (Mes = 2,4,6-trimethylphenyl), has been

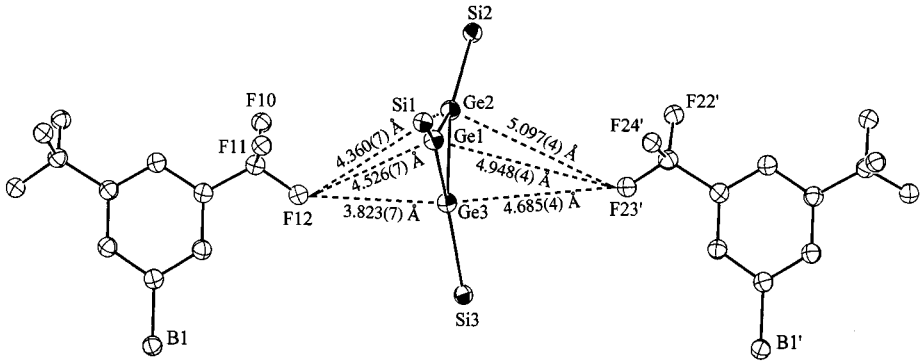

Figure 2. Section from the structure of $\mathbf{2a}^{+}$TFPB^{-} with the closest atomic distances between Ge and F.

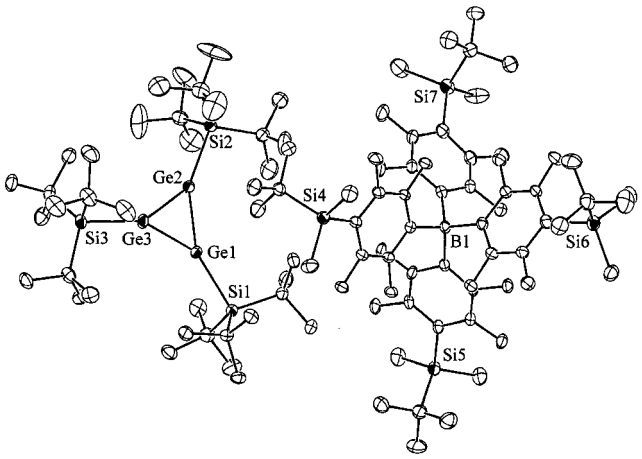

Figure 3. Perspective view of $\mathbf{2a}^{+}$TSFPB^{-} in the crystal at the 30% probability level (hydrogen atoms are omitted for the clarity). Selected bond lengths (Å): Ge1−Ge2, 2.3310(8); Ge1−Ge3, 2.3315(7); Ge2−Ge3, 2.3349(8); Ge1−Si1, 2.420(1); Ge2−Si2, 2.460 (1); Ge3−Si3, 2.434(1). Selected bond angles (deg): Ge2−Ge1−Ge3, 60.10(2); Ge2−Ge1−Si1, 151.17(4); Ge3−Ge1−Si1, 148.72 (4); Ge1−Ge2−Ge3, 59.96(2); Ge1−Ge2−Si2, 150.86(4); Ge3−Ge2−Si2, 149.14(4); Ge1−Ge3−Ge2, 59.94(2); Ge1−Ge3−Si3, 151.94(5); Ge2−Ge3−Si3, 147.98(5).

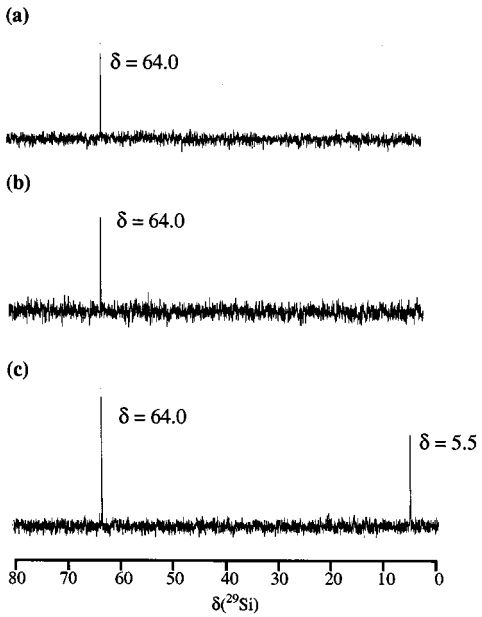

Figure 4. ^{29}Si NMR spectra of $\mathbf{2a}^{+}$TFPB^{-} (a), $\mathbf{2a}^{+}$TPFPB^{-} (b), $\mathbf{2a}^{+}$TSFPB^{-} (c) in CD_2Cl_2 at 298 K.

synthesized as a metallic ring system possessing aromatic character.[19]

Free Cyclotrigermenium Ion in Solution

The evidence for the free cyclotrigermenium ion is supported by the NMR spectroscopic data. The ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts for the cyclotrigermenium moiety of $\mathbf{2a}^{+}$TFPB^{-}, $\mathbf{2a}^{+}$TPFPB^{-}, and $\mathbf{2a}^{+}$TSFPB^{-} in CD_2Cl_2 are practically the same (see the Experimental Section). For example, ^{29}Si NMR chemical shifts of $\mathbf{2a}^{+}$TFPB^{-}, $\mathbf{2a}^{+}$TPFPB^{-}, and $\mathbf{2a}^{+}$TSFPB^{-}, as shown in Figure 4, are independent of the counter anion. The ^{29}Si NMR chemical shift of $\mathbf{2a}^{+}$TFPB^{-} is also essentially the same in the different solvents, appearing at $\delta = 64.0$ in CD_2Cl_2, $\delta = 64.2$ in $CDCl_3$, $\delta = 64.4$ in [D_8]toluene, and $\delta = 64.5$ in Et_2O. This independence from the both counter anion and solvent clearly indicates that $\mathbf{2a}^{+}$ is a free germyl cation in solution.

The large downfield shift of the ^{29}Si NMR resonance of $\mathbf{2a}^{+}$, relative to that of **1** ($\delta = 37.2$ for tBu$_3$Si attached to the saturated Ge atom and 50.1 for tBu$_3$Si attached to the Ge=Ge double bond), is due to the positive charge on the cyclotrigermenium ion. The positive charge is not localized on the germanium atoms, but is significantly transferred to the silicon centers. According to the Mulliken charges, most of the positive charge is distributed on the silicon atoms of the substituents rather than on the ring germanium atoms. It has been reported that the positive charge on the ring carbon atoms of cyclopropenium cations $(RC)_3^{+}$ decreases with decreasing electronegativity of the substituent: +0.200 (R = CH_3), +0.026 (R = H), −0.243 (R = SiH_3).[20] The atomic (Mulliken) charges on $(H_3SiGe)_3^{+}$, according to the HF/6−31G* level calculations, indicate a similar delocalization of the positive charge: −0.07 for the ring germanium

atoms, +0.64 for the silicon atoms of the SiH_3 substituents.[21]

Conclusion

Treatment of tetrakis(tri-*tert*-butylsilyl)cyclotrigermene (**1a**) with the trityl cation in benzene produces the stable free tris(tri-*tert*-butylsilyl)cyclotrigermenium ion (**2a**$^+$) with three different counter anions. The crystal structures and the spectroscopic data show that **2a**$^+$ is a free germyl cation, which does not coordinate to either the counter anions or the solvent molecules.

Experimental Section

All manipulations were carried out under an inert atmosphere in a MBRAUN MB 150B-G gas-replacement type glove box or by standard Schlenk and high-vacuum line techniques. – ^{1}H NMR spectra were recorded at 300.1 MHz on a Bruker AC-300 FT NMR spectrometer. ^{13}C and ^{29}Si NMR spectra were collected on a Bruker AC-300 at 75.5, 59.6 MHz, respectively. – All solvents were dried and degassed over potassium mirror in vacuo prior to use in the preparation of cyclotrigermenium ion. The cyclotrigermenes **1a**,[14] **1b**,[14] and trityl cations Ph_3C^+ [3,5-$(CF_3)_2C_6H_3]_4B^-$ (TFPB$^-$),[11] $Ph_3C^+(C_6F_5)_4B^-$ (TPFPB$^-$),[12] and Ph_3C^+[4-(*t*Bu-Me_2Si) $C_6F_4]_4B^-$ (TSFPB$^-$)[13] were prepared according to literature procedures. On account of the inclusion of solvent molecules, no satisfactory elemental analyses data for the cyclotrigermenium salts could be obtained.

Tris(tri-*tert*-butylsilyl)cyclotrigermenium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (2a$^+$TFPB$^-$): Dry oxygen-free benzene was introduced by vacuum transfer to a mixture of **1a** (60 mg, 0.06 mmol) and Ph_3C^+TFPB$^-$ (65 mg, 0.06 mmol), and the mixture was stirred at room temperature for 10 min. The dark red solution of **1a** became yellow, and brown powder was formed. The solvent was removed under vacuum and the resulting solid was washed with hexane in a glove box to afford a yellow powder of **2a**$^+$TFPB$^-$ (80 mg, 81%). M.p. 132–134 °C (dec). – ^{1}H NMR (CD_2Cl_2): δ = 1.40 (s, 81 H), 7.56 (s, 4 H), 7.73 (s, 8 H). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 27.2, 31.8, 117.8, 125.0 [q, $^1J(^{13}C\text{-}^{19}F)$ = 270 Hz], 129.1–129.9 (m), 135.2, 162.2 [q, $^1J(^{13}C\text{-}^{11}B)$ = 50 Hz]. – ^{29}Si{^{1}H} NMR (CD_2Cl_2): δ = 64.0.

Tris(tri-*tert*-butylsilyl)cyclotrigermenium Tetrakis(pentafluorophenyl)borate (2a$^+$TPFPB$^-$): By the procedure described above, the reaction of **1a** (60 mg, 0.06 mmol) and Ph_3C^+TPFPB$^-$ (55 mg, 0.06 mmol) provided **2a**$^+$TPFPB$^-$ (ca. 80%) as a yellow waxy solid. – ^{1}H NMR (CD_2Cl_2): δ = 1.40 (s, 81 H). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 27.2, 31.8, 124.0–125.5 (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{^{1}H} NMR (CD_2Cl_2): δ = 64.0.

Tris(tri-*tert*-butylgermyl)cyclotrigermenium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (2b$^+$TFPB$^-$): By the procedure described above, the reaction of **2b** (30 mg, 0.03 mmol) and Ph_3C^+TFPB$^-$ (30 mg, 0.03 mmol) provided **2b**$^+$TPFPB$^-$ (34 mg, 76%) as yellow crystals. M.p. 112–114 °C (dec). – ^{1}H NMR (CD_2Cl_2): δ = 1.48 (s, 81 H), 7.56 (s, 4 H), 7.73 (s, 8 H). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 32.4, 37.1, 117.8, 125.0 [q, $^1J(^{13}C\text{-}^{19}F)$ = 270 Hz], 129.1–129.9 (m), 135.2, 162.2 [q, $^1J(^{13}C\text{-}^{11}B)$ = 50 Hz].

Tris(tri-*tert*-butylgermyl)cyclotrigermenium Tetrakis(pentafluorophenyl)borate (2b$^+$TPFPB$^-$): By the procedure described above, the reaction of **2b** (30 mg, 0.03 mmol) and Ph_3C^+TPFPB$^-$ (25 mg, 0.03 mmol) provided **2b**$^+$TPFPB$^-$ (ca. 80%) as a yellow waxy solid. – ^{1}H NMR (CD_2Cl_2): δ = 1.48 (s, 81 H). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 32.4, 37.1, 124.0–125.5 (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].

Tris(tri-*tert*-butylsilyl)cyclotrigermenium Tetrakis{4-[*tert*-butyl(dimethyl)silyl]-2,3,5,6-tetrafluorophenyl}borate) (2a$^+$TSFPB$^-$): By the procedure described above, the reaction of **2a** (200 mg, 0.20 mmol) and Ph_3C^+TSFPB$^-$ (258 mg, 0.20 mmol) provided **2a**$^+$TSFPB$^-$ (326 mg, 88%) as orange crystals. M.p. 154–156 °C (dec). – ^{1}H NMR (CD_2Cl_2): δ = 0.33 (s, 24 H), 0.90 (s, 36 H), 1.41 (s, 81 H). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = –3.2, 18.3, 27.0, 27.7, 32.3, 108.8 [t, $^2J(^{13}C\text{-}^{19}F)$ = 33 Hz], 134.3–135.8 (m), 149.2 [d, $^1J(^{13}C\text{-}^{19}F)$ = 262 Hz]. – ^{29}Si{^{1}H} NMR (CD_2Cl_2): δ = 5.47, 64.0.

X-ray Crystal Structure Determination of 2a$^+$TFPB$^-$ and 2a$^+$TSFPB$^-$: Single crystals of **2a**$^+$TFPB$^-$ and **2a**$^+$TSFPB$^-$ suitable for X-ray diffraction were grown from toluene solutions. The X-ray crystallographic experiments were performed on a MacScience DIP2020 or DIP2030 image plate diffractometer equipped with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). Crystal data for **2a**$^+$TFPB$^-$ at 120 K: $M_F = C_{68}H_{93}BF_{24}Ge_3Si_3$, Mr = 1679.27, monoclinic, a = 16.912(1) Å, b = 20.919(1) Å, c = 23.399(1) Å, β = 108.147(4)°, V = 7866.4(7) Å^3, space group = $P2_1/n$, Z = 4, $D_{calcd.}$ = 1.418 g/cm^3, R = 0.0849 (R_w = 0.2153 for all data). Crystal data for **2a**$^+$TSFPB$^-(C_7H_8)_2$ at 120 K: $M_F = C_{98}H_{157}BF_{16}Ge_3Si_7$, Mr = 2064.54, orthorhombic, a = 13.3320(5) Å, b = 20.5110(3) Å, c = 40.638(1) Å, V = 11112.6(5)Å^3, space group = $Pc2_1n$, Z = 4, $D_{calcd.}$ = 1.234 g/cm^3, R = 0.0523 (R_w = 0.1512 for all data). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137540 and 137541. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223)336–033; E-mail:deposit@ccdc.cam.ac.uk].

Computational Details: Calculations at the Hartree–Fock (HF) level were performed by using the Gaussian 94 computer program.[21] The 6–31G* basis set was used for all geometry optimizations.

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