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The Cation Cluster of Heavier Group 14 Elements: A Free Germyl Cation with Trishomoaromaticity

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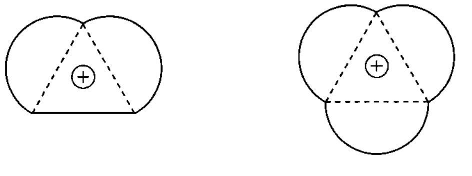
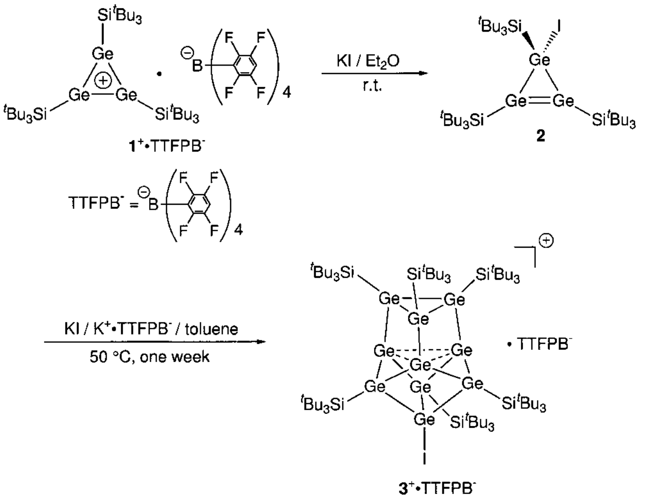
Numerous recent publications[1,2] are concerned with both theoretical and synthetic aspects of three-coordinated cations of heavier group 14 elements, for example, $[Et_3Si(toluene)]^+{\cdot}B(C_6F_5)_4^-$,[3] $^iPr_3Si^+(X_6\text{-}CB_{11}H_6)^-$ [4] and $Mes_3Si^+{\cdot}B(C_6F_5)_4^-$.[5] We have also synthesized and characterized a cyclotrigermenylium ion $[(^tBu_3Si)_3Ge_3]^+$ [6] and a homocyclotrisilenylium ion $[(^tBu_2MeSiSi)_3Si^tBu_2]^+$ [7] as free germyl and silyl cations. Our successful construction of these particular systems suggests that the concept of aromaticity and homoaromaticity is extremely useful for the stabilization of the elusive group 14 element three-coordinated cations. The concept of homoaromaticity in bishomocyclopropenylium and trishomocyclopropenylium ions has also been developed and well-established in the carbon system (Chart 1).[8] Recently, Berndt, Siebert, Schleyer, et al. have also characterized various bis- and tris-homoaromatic boron systems.[9] However, their counterparts, comprising the heavier group 14 elements, are missing, and their stability is still an open question. Here, we report the unexpected formation and structure of the first heavier group 14 element cation cluster compound, $[(^tBu_3Si)_6Ge_{10}I]^+{\cdot}TTFPB^-$ ($\mathbf{3}^+{\cdot}TTFPB^-$; $TTFPB^-$ = tetrakis(2,3,5,6-tetrafluorophenyl)borate), and evidence for its trishomoaromaticity.

Chart 1



Scheme 1



3-Iodo-1,2,3-tris(tri-*tert*-butylsilyl)cyclotrigermene (**2**) was synthesized by the reaction of tris(tri-*tert*-butylsilyl)cyclotrigermenylium TTFPB$^-$ ($\mathbf{1}^+{\cdot}TTFPB^-$) with excess potassium iodide in ether.[10] After the solvent was changed from ether to toluene, the reaction mixture was heated at 50 °C for a week. The dark-red color of **2** slowly disappeared to produce a dark-brown viscous oil. Removal of potassium salts ($K^+{\cdot}TTFPB^-$ and KI) followed by recrystallization in toluene under an inert atmosphere produced the germanium cation cluster, 5-iodo-2,4,6,8,9,10-hexakis(tri-*tert*-butylsilyl)heptacyclo[4.4.0.0^{1,3}.0^{2,5}.0^{3,9}.0^{4,7}.0^{8,10}]decagerman-7-ylium tetrakis(2,3,5,6-tetrafluorophenyl)borate ($\mathbf{3}^+{\cdot}TTFPB^-$), as air- and moisture-sensitive brown crystals in 37% yield (Scheme 1).[11]

The structure of $\mathbf{3}^+{\cdot}TTFPB^-$ was characterized by X-ray crystallography as well as its NMR data,[11] showing the unexpected germanium cation cluster consisting of 10 germanium atoms accompanied by $TTFPB^-$ as a counteranion and one toluene molecule (Figure 1).

The distances between cationic germanium atoms (Ge5, Ge6, Ge7) and the fluorines of $TTFPB^-$ or toluene are beyond the range of any significant interaction (greater than 6.4 Å). Therefore, $\mathbf{3}^+$ is a free germyl cation in the solid state. The Ge_{10} core of $\mathbf{3}^+$ shows an approximately C_{3v} symmetry, which is consistent with ^1H, ^{13}C, and ^{29}Si NMR data in solution.[11] Surprisingly, six germanium atoms (Ge2, Ge3, Ge4, Ge8, Ge9, Ge10) carry $^tBu_3Si$ groups, and one germanium atom (Ge1) has an iodo substituent. The remaining three atoms (Ge5, Ge6, Ge7) are "naked", which is thought to be derived via elimination of $^tBu_3SiI$ from **2**, because $^tBu_3SiI$ was found in the reaction mixture.

The interatomic distances between the "naked" germanium atoms are almost the same (Ge5−Ge6; 3.2642(15) Å, Ge6−Ge7; 3.2622(17) Å, Ge5−Ge7; 3.2542(15) Å), which are much longer than the Ge−Ge single bond lengths in $\mathbf{3}^+$ but are in the range of the metallic Ge−Ge bond length found in the Zintl anion (Ge_9^{3-}).[12] What is the nature of bonding between the three "naked" Ge atoms that are forced to adopt inverted tetrahedral geometries? A DFT calculation on the model compound $Ge_{10}H_7^+$ ($\mathbf{4}^+$) with C_{3v} symmetry at the B3LYP/6-31G(d) level represents the same cluster skeleton of $\mathbf{3}^+$ as a global minimum structure. The molecular orbitals of $\mathbf{4}^+$ calculated at MP2/6-31G(d)//B3LYP/6-31G(d) level presented in Figure 2 show a nondegenerate HOMO and doubly degenerate LUMOs. The picture of the HOMO for $\mathbf{4}^+$ reveals the presence of a bonding interaction between the three "naked" germanium atoms (Ge5, Ge6, Ge7). The positive charge is evenly distributed over these germanium atoms. This indicates that a three-center two-electron (3c−2e) bond is formed by charge delocalization inside the conjunctive central core, giving rise to the trishomocyclotrigermenylium system. Indeed, the trishomoconjugative distance in $\mathbf{4}^+$ is 3.423 Å, which is 0.353 Å (ca. 9%) shorter than those in the saturated system $Ge_{10}H_{10}$ (C_{3v}). To characterize the nature of the bonding in $\mathbf{4}^+$, a natural bond orbital (NBO)

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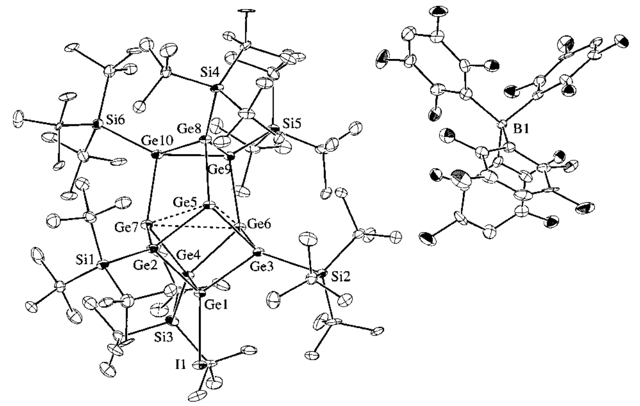

Figure 1. ORTEP drawing of $\mathbf{3}^+\cdot$TTFPB$^-$ (C_7H_8). Hydrogen atoms and toluene are omitted for clarity. Selected bond lengths (Å): Ge1−Ge2 2.4890(16), Ge1−Ge3 2.4915(16), Ge1−Ge4 2.4783(14), Ge2−Ge5 2.4711(17), Ge3−Ge5 2.4784(17), Ge3−Ge6 2.4831(15), Ge4−Ge7 2.4836(17), Ge2−Ge7 2.4861(14), Ge8−Ge9 2.5449(15), Ge9−Ge10 2.5208(17) Ge8−Ge10 2.5381(15), Ge5−Ge8 2.5112(16), Ge6−Ge9 2.5309(16), Ge7−Ge10 2.5171(16), Ge1−I1 2.5703(13).

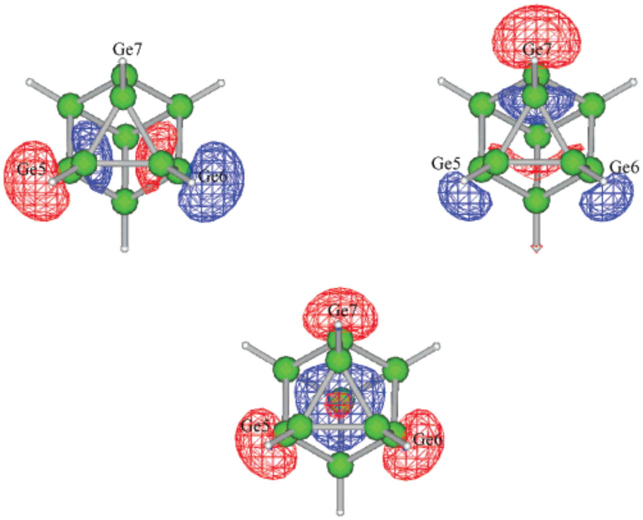

Figure 2. HOMO (below) and two degenerate LUMOs (upper) for $Ge_{10}H_7{}^+$ ($\mathbf{4}^+$) at MP2/6-31G(d)// B3LYP/6-31G(d).

analysis was employed.[13] The Wiberg bond index (WBI) (0.288) and the over-weighted natural atomic orbital (NAO) bond order (0.183) for the trishomoconjugative bond suggest the formation of a 3c−2e bond.

The trishomoaromatic conjugation is supported and quantified by evaluation of the aromatic stabilization energy (ASE)[14] value and by the nucleus-independent chemical shift (NICS)[15] value for $\mathbf{4}^+$.[16] The ASE value is quite exothermic (−19.2 kcal mol^{-1}), which predicts a large homoaromatic stabilization. Furthermore, $\mathbf{4}^+$ also has a strongly diatropic NICS value at the center of the triangle composed of trishomoconjugative atoms (−26.4). These results of the quantitative evaluation of the energetic and magnetic properties of $\mathbf{4}^+$ confirm the trishomoaromatic character of $\mathbf{3}^+$. To the best of our knowledge, no analogous carbon system has been reported.[17]

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Supporting Information Available: Experimental procedure, spectral data, tables of crystallographic data including atomic positional and thermal parameters for $\mathbf{3}^+\cdot$TTFPB$^-$, isodesmic reaction, calculated energies for calculation of ASE and NICS analysis for $\mathbf{4}^+$ (PDF). These materials are available free of charge via the Internet at http://pubs.acs.org.

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(14) The zero-point energies (ZPEs) were calculated at the B3LYP/6-31G-(d)//B3LYP/6-31G(d) level of theory. Final energies were calculated at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) + ZPE level.

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(16) For details of isodesmic reaction and calculated energies for the calculation of ASE and NICS analysis for $\mathbf{4}^+$, see the Supporting Information.

(17) A DFT calculation on the compound $C_{10}H_7{}^+$ with C_{3v} at the B3LYP/6-31G(d) level also reveals the similar structure as a global minimum. The trishomoaromaticity for $C_{10}H_7{}^+$ is also shown (WBI = 0.368, ASE = −24.1, NICS = −33.4).

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