

[Ge₉{Si(SiMe₃)₃]₃{SnPh₃}]₀: A Tetrasubstituted and Neutral Deltahedral Nine-Atom Cluster**

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The chemistry of the well-known Ge₉⁴⁻ deltahedral Zintl ions has been studied fairly extensively in the last decade.^[1] It has been shown that these clusters are capable of participating in a variety of reactions, such as oligomerization,^[2–9] centering and/or capping by d-block metals,^[10–39] and functionalization with main-group organometallic fragments and organic moieties.^[40–46] The latter functionalizations, however, produced only mono- and disubstituted clusters [Ge₉R]³⁻ and [Ge₉R₂]²⁻, respectively, when the reactions were carried out in the traditional ethylenediamine solvent. For long time it seemed that two was the maximum number of substituents that the clusters can add, although the remaining 2– charge suggested possible formation of trisubstituted monoanions [Ge₉R₃]⁻ and tetrasubstituted neutral clusters [Ge₉R₄]. This status quo held until very recently, when we reported the synthesis and structural characterization of the first trisubstituted clusters [Ge₉{Si(SiMe₃)₃]₃⁻ (**1**) made rationally by a reaction of bare Ge₉ clusters with (Me₃Si)₃SiCl in acetonitrile.^[47]

Herein we present the synthesis and characterization of the newest member of this series, namely the first tetrasubstituted neutral cluster [Ge₉{Si(SiMe₃)₃]₃{SnPh₃}]₀ (**2**). It was synthesized by reacting the above trisubstituted species **1** (a benzene suspension of its potassium salt) with triphenyltin chloride, Ph₃SnCl. The dark-red opaque suspension became a transparent solution during the reaction. After filtering out the KCl precipitate and removing the benzene solvent under vacuum, the resulting dark-red solid of **2** was extracted by *n*-hexane. The solution was stored at –20 °C for a week, and large dark-red needle-like single crystals of **2** were obtained. Similarly, the corresponding compounds with Me₃Sn and (*n*Bu)₃Sn as the fourth substituent were synthesized (but not crystallized), demonstrating the versatility of the synthetic approach.

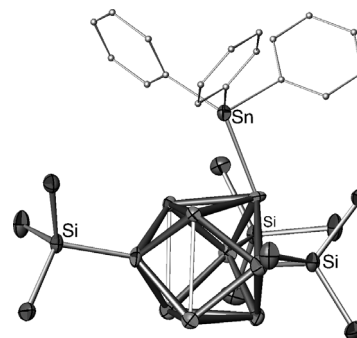


Figure 1. The structure of [Ge₉{Si(SiMe₃)₃]₃{SnPh₃}]₀, in which the Ge₉ core is a tricapped trigonal prism with three (Me₃Si)₃Si groups (methyl groups not shown) bonded to the three capping atoms and the fourth substituent, Ph₃Sn, bonded to one Ge atom (2.686(3) Å) of one of the two equivalent trigonal prismatic bases. This results in uneven vertical trigonal prismatic edges (parallel to the pseudo three-fold axis), namely two short (3.123(1) Å; shown as thin lighter bonds) and one long (3.520(1) Å; not shown as a bond). Ge–Ge distances (Å): 2.705(2) in the bottom triangular base; 2.694(9), 2.710(9), and 2.919(5) in the upper triangular base, where the longest distance is opposite the *exo*-bonded atom; 2.429(3)–2.624(6) at the capping atoms.

The new compound **2** crystallizes in the rhombohedral crystal system (space group *R*3̄) with the molecules positioned at the three-fold axis. The Ge₉ core is a tricapped trigonal prism (Figure 1) where the three capping Ge atoms are *exo*-bonded to the three silyl substituents, exactly as in the trisubstituted precursor [Ge₉{Si(SiMe₃)₃]₃⁻ (**1**).^[47, 48] The tin atom of the fourth substituent is found bonded to one of the three equivalent Ge atoms at one of the two triangular bases of the prism. It is slightly off the threefold axis and generates three positions, each with 1/3 occupancy. Initially, the tin atom was refined positioned exactly at the axis as capping the germanium triangular base, but the resulting large lens-like thermal ellipsoid strongly suggested an off-axis position (Supporting Information, Figure S1). Furthermore, the germanium atoms forming the capped triangular base exhibited thermal ellipsoids elongated tangentially towards the Sn atom. They were later refined as split atoms with one of the positions (refined at 33% occupancy) closer to and the other (67% occupancy) further from the tin atom. This means that the Sn atom is bonded to one Ge atom at a time with a distance of 2.686(3) Å. This distance compares well with the observed range of single-bond Ge–Sn distances, 2.601–2.675 Å, for organotin fragments in mono- and difunctionalized Ge₉ clusters, [Ge₉SnR₃]³⁻ and [R₃SnGe₉–SnR₃]²⁻,^[40] respectively. The other two Ge atoms of the triangular face in **2** are significantly further from the tin atom, with Ge–Sn

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distances of 3.391(3) and 3.409(3) Å. Having one short and two long Sn–Ge distances affects the lengths of the three prismatic edges parallel to the threefold axis, resulting in one longer (3.520(1) Å) and two shorter distances (3.123(1) Å each). This is very similar to the previously reported anion $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3\text{Cr}(\text{CO})_5]^-$ in which **1** is found coordinated as a ligand to $\text{Cr}(\text{CO})_5$ by one bare Ge vertex. There, the longer edge (at the coordinated Ge atom) is 3.812 Å, while the two shorter edges are 3.014 and 3.089 Å.^[50] Furthermore, similar positioning of the Sn atom as *exo*-bonded to one vertex but also tilted towards the trigonal base has been observed before in the monosubstituted Ge_9 and Sn_9 clusters $[\text{Ge}_9\text{SnPh}_3]^{3-}$ and $[\text{Sn}_9\text{SnCy}_3]^{3-}$.^[40,51] In those cases, however, it is found closer to only one of the other two atoms in the base, and thus can be viewed as close to bridging a trigonal prismatic edge.

Although the crystal structure of **2** in the solid state indicates very low symmetry, that is, only a pseudo mirror plane, in solutions it behaves as if with C_{3v} symmetry. Thus, the room-temperature ^1H , ^{13}C , and ^{29}Si NMR spectra of **2** as well as of the analogous compounds with Me_3Sn and $(n\text{Bu})_3\text{Sn}$ groups showed signals consistent with the three-fold symmetry (Supporting Information, Figures S2–S8). Furthermore, even at a low temperature of -80°C , the ^1H and ^{29}Si NMR spectra of **2** did not indicate significant peak broadening or splitting (Supporting Information, Figure S9 and S10). This suggests that the Sn atom hops from one germanium atom to another faster than the NMR timescale even at low temperature, indicating a fairly low energy barrier for the process. Upon crystallization, on the other hand, the tin atom freezes at one of its three possible positions as bonded to one of the three Ge atoms, and the structure is the average image of these three different positions.

DFT calculations were carried out to study the bonding in **2**, and specifically the interactions of the Ph_3Sn fragment with the already-known trisubstituted anion **1**. The most significant interaction involves the HOMO of the latter (Supporting Information, Figure S11), an orbital that is bonding within the two trigonal prismatic bases of **1** but antibonding between them. Exactly the same orbital is found in the bare nine-atom clusters, and furthermore has been perhaps the most often-discussed orbital for the latter species. Its occupation defines the charge of the bare clusters, namely Ge_9^{2-} where it is empty and the LUMO, Ge_9^{3-} where it is occupied by one electron and the HOMO, and Ge_9^{4-} where it is fully occupied. As it is mainly positioned at the six germanium atoms forming the trigonal prism, it remains virtually unchanged upon addition of the three substituents *exo*-bonded to the three capping Ge atoms in **1**. The interaction with the Ph_3Sn frontier orbital results in a filled bonding combination and an empty antibonding orbital. This directly affects the distances between the triangular bases of the trigonal prism; that is, the vertical edges in Figure 1. Thus, the bonding Ge–Sn combination is antibonding along the prismatic Ge–Ge edge involving that same Ge atom. As it is occupied, that antibonding interaction leads to longer edge as observed. At the same time, the antibonding Ge–Sn combination is also antibonding along the remaining two prismatic edges. However, as it is empty, that antibonding character has no effect on

the distances, and the two edges are shorter. DFT calculations were also performed on the optimized structures during the migration of the Sn atom from one Ge vertex to another via the intermediate edge-bridging position. Such mode of migration is in agreement with the previously reported simultaneous interactions with two atoms at a time in $[\text{Ge}_9\text{SnPh}_3]^{3-}$ and $[\text{Sn}_9\text{SnCy}_3]^{3-}$.^[40,51] The calculated energy barrier is fairly high (10.54 kcal mol⁻¹; Supporting Information, Figure S12). More detailed studies of the dynamics and energetics of the cluster with variety of possible intermediate structures are currently being carried out.

The overall electron count and charge of **2** can be easily understood and rationalized as a tetrasubstituted *nido* cluster that requires $2n + 4 = 22$ cluster bonding electrons for $n = 9$. These 22 electrons are available from the five bare and four *exo*-bonded Ge atoms as follows: $5 \times 2 + 4 \times 3 = 22$.^[49]

The ability of **1** to add a fourth substituent and form **2** as reported herein supplements some prior results using the same species as ligands to transition metals. Typically, it uses one of its open triangular faces to act as η^3 and even η^5 ligands. In the latter mode, the transition metal opens up the triangular face and interacts in addition with two of the three *exo*-bonded Ge atoms. This is typical for very electrophilic fragments, such as $\text{M}(\text{CO})_3$, where $\text{M} = \text{Cr}, \text{Mo},$ and W .^[50,52] In the η^3 mode, the transition metal is found coordinated to two clusters to form anionic or neutral dimers $[\mathbf{1-M-1}]^-$ and $[\mathbf{1-M-1}]$, respectively, where $\text{M} = \text{Cu}, \text{Ag},$ and Au for the anionic dimers,^[53,54] and $\text{M} = \text{Zn}, \text{Cd},$ and Hg for the neutral dimers.^[55] Clearly, in all of these compounds, the **M-1** interactions are of the donor–acceptor type signified by the equidistant positioning of the transition-metal atom from the Ge atoms. In **2**, on the other hand, the Sn–**1** interaction is much more covalent as it clearly exhibits a two-center–two-electron Sn–Ge bond. Finally, as an interesting side note, we point out that **2** contains all but one of the elements of one group, namely C, Si, Ge, and Sn of Group 14, with only Pb missing.

Experimental Section

All manipulations were carried out under nitrogen using a glove box. The Zintl precursor, K_4Ge_9 , was synthesized from stoichiometric mixtures of the elements (K: Strem, 99 + %; Ge: Alfa-Aesar, 99.999 %) heated at 950°C over two days in sealed niobium containers jacketed in evacuated fused silica tubes. *n*-Hexane (Alfa-Aesar, 98.5 + %) was dried by passage over copper-based catalyst and 4 Å molecular sieve and was stored in a gas-tight ampule under nitrogen. Acetonitrile (Acros, anhydrous, 99.9 %) was stored over molecular sieves. Benzene (Alfa-Aesar, anhydrous, 99.8 + %) was stored over molecular sieves in a gas-tight ampule under nitrogen. $(\text{Me}_3\text{Si})_3\text{SiCl}$ (TCl, 95 + %), Me_3SnCl (Aldrich, 97 %), $n\text{Bu}_3\text{SnCl}$ (Alfa-Aesar, 96 %), and Ph_3SnCl (Alfa-Aesar, 97 + %) were used as received.

NMR spectroscopy: Deuterated dichloromethane (Cambridge Isotope Laboratories, 99.9 %), deuterated benzene (Cambridge Isotope Laboratories, 99.9 %), and deuterated toluene (Cambridge Isotope Laboratories, 99.9 %) were used as received and stored in an N_2 -filled glove box. ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer, locked on the deuterium signal of the deuterated dichloromethane, benzene, or toluene, and referenced against Me_4Si (Sigma-Aldrich, ACS).

Single-crystal X-ray diffraction data were collected on a Bruker X8 APEX-II diffractometer equipped with a CCD area detector at 120 K using graphite-monochromated Mo-K α radiation. The crystal was selected under Paratone-N oil, mounted on a Mitegen micro-mount loop, and positioned in the cold stream of the diffractometer. The structure was solved by direct methods and refined on F^2 against all reflections using the SHELXTL V6.21 package.^[56] Crystal data: rhombohedral, $R\bar{3}$, $a = 23.963(3)$ and $c = 22.707(3)$ Å, $V = 11293(3)$ Å³, $Z = 6$, $R1/wR2 = 0.0587/0.1229$ for the observed data and $0.0732/0.1266$ for all data. CCDC 873770 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculations were carried out using the ADF 2010.01 code^[57] employing triple- ζ Slater basis set plus double polarization (STO-TZ2P) basis set in conjunction with the nonlocal Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).^[58] Relativistic effects were taken into account by ZORA formalism using two-component wavefunctions.^[59]

Synthesis of $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3\text{SnPh}_3]$ (**2**): K_4Ge_9 (85 mg, 0.105 mmol) was weighed out in a test tube in the N_2 -filled glove box. An acetonitrile (3.0 mL) solution of $(\text{Me}_3\text{Si})_3\text{SiCl}$ (102 mg, 0.359 mmol) was added to the test tube. The reaction mixture was stirred for three hours, filtered, and the solvent was removed under vacuum. A benzene (3.0 mL) solution of Ph_3SnCl (42 mg, 0.109 mmol) was added to extract the red solid residue, and a dark red suspension initially formed. The reaction mixture was stirred for two hours. During this period, the reaction mixture turned darker and a white precipitate of KCl formed. The solution was filtered and the benzene solvent was removed under vacuum. Hexane was added to redissolve the dark-red solid and it formed a clear red solution. After concentration under vacuum, the solution was stored at -20°C for crystallization. Large, dark-reddish, needle-like single crystals suitable for X-ray crystallography were obtained after one week (ca. 60% yield). ^1H NMR (CD_2Cl_2): $\delta = 7.732$ (m, phenyl), 7.263 (m, phenyl), 0.199 ppm (s, CH_3). ^{13}C NMR (CD_2Cl_2): $\delta = 145.771$ (phenyl), 137.519 (phenyl), 128.655 (phenyl), 128.534 (phenyl), 2.406 ppm (CH_3). ^{29}Si NMR (CD_2Cl_2): $\delta = -8.663$ (SiMe_3), -99.984 ppm (Si).

Synthesis of $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3\text{SnMe}_3]$ and $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3\text{Sn}(\text{nBu})_3]$: Reactions similar to the one described above were carried out in a benzene suspension of $\text{KGe}_9\{\text{Si}(\text{SiMe}_3)_3\}$ with Me_3SnCl and $(\text{nBu})_3\text{SnCl}$. The reaction mixtures were stirred at room temperature for two hours. The solvent was removed under vacuum and the dark-red residues were washed with acetonitrile. Deuterated benzene or toluene was added to redissolve the remaining solids. After filtration, the filtrates were transferred into gas-tight screw-cap NMR tubes and introduced into the NMR spectrometer directly. NMR spectroscopy data of $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3\text{SnMe}_3]$: ^1H NMR ($[\text{D}_8]$ toluene): $\delta = 0.809$ (t, SnMe_3), 0.388 ppm (s, SiMe_3). ^{13}C NMR ($[\text{D}_8]$ toluene): $\delta = 5.483$ (SnMe_3), 2.406 ppm (SiMe_3); NMR spectroscopy data for $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3\text{Sn}(\text{nBu})_3]$: ^1H NMR ($[\text{D}_8]$ toluene): $\delta = 1.854$ (m, Bu), 1.582 (m, Bu), 1.510 (m, Bu), 1.056 (t, Bu), 0.430 ppm (s, SiMe_3). ^{13}C NMR ($[\text{D}_8]$ toluene): $\delta = 31.326$ (Bu), 28.449 (Bu), 22.547 (m, Bu), 14.632 (t, Bu), 3.381 ppm (SiMe_3).

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