

A Stannyl-Decorated Zintl Ion $[\text{Ge}_{18}\text{Pd}_3(\text{Sn}^i\text{Pr}_3)_6]^{2-}$: Twinned Icosahedron with a Common Pd_3 -Face or 18-Vertex *Hypho*-Deltahedron with a Pd_3 -Triangle Inside

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S Supporting Information

ABSTRACT: We report the synthesis and characterization of the title anion which has a germanium/palladium cluster core of $[\text{Ge}_{18}\text{Pd}_3]$ and six tri-isopropyl tin substituents. Its two Ge_9 -halves are the first examples of germanium deltahedra with three nonsilyl substituents, triisopropyl tin in this case. The new cluster is made by a reaction of an acetonitrile suspension of K_4Ge_9 with $^i\text{Pr}_3\text{SnCl}$ that generates primarily trisubstituted 9-atom clusters $[\text{Ge}_9\{\text{Sn}^i\text{Pr}_3\}_3]^-$, followed by addition of $\text{Pd}(\text{PPh}_3)_4$ to the reaction mixture. It was structurally characterized by single-crystal X-ray diffraction in $[\text{K}(222\text{-crypt})]_2[\text{Ge}_{18}\text{Pd}_3\{\text{Sn}^i\text{Pr}_3\}_6]^{2-}\cdot\text{Pr}_2\text{O}$ and was also confirmed in solution by ESI-MS and NMR. The new anion can be viewed both as a dimer of face-fused icosahedra (twinned icosahedron) with a common Pd_3 -face, i.e., $[(^i\text{Pr}_3\text{Sn})_3\text{Ge}_9\text{Pd}_3\text{Ge}_9(\text{Sn}^i\text{Pr}_3)_3]^{2-}$ that resembles but is not isolectronic with the known borane version $\text{B}_{21}\text{H}_{18}^-$ or as a large *hypho*-deltahedron of 18 Ge-atoms with a triangle of Pd_3 inside, i.e., $[\text{Pd}_3@\text{Ge}_{18}(\text{Sn}^i\text{Pr}_3)_6]^{2-}$. DFT calculations show a very large HOMO–LUMO gap of 2.42 eV.

Ligand-stabilized metalloid clusters of groups 13 and 14 have shown to be a very fruitful area of chemistry with species containing both interesting bonding and exotic architectures, e.g., $[\text{Al}_{77}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{2-}$, $[\text{Ga}_{84}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{4-}$, $[\text{Ge}_{18}\{\text{Si}(\text{SiMe}_3)_3\}_6]$, $[\text{Sn}_{15}\{\text{N}(\text{Dipp})\text{SiMe}_3\}_6]$ (Dipp = 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$), etc.¹ Various synthetic approaches have been used for their synthesis including (a) disproportionation of metastable subhalides and entrapment of intermediates with bulky ligands, (b) reductive coupling of main group halides with strong reducing agents, and (c) reductive elimination of smaller main-group reagents with labile leaving groups to generate larger assemblies.² These techniques have produced a large number of metalloid clusters of group 13, but to a much lesser extent of group 14.³ A notable example of the latter is the hypersilylated germanium species $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3]^-$ originally made by reacting the metastable subhalide GeBr with $\text{Li}\{\text{Si}(\text{SiMe}_3)_3\}$.² The same monoanion was later synthesized in better yields by the reaction of acetonitrile suspensions of the Zintl phase K_4Ge_9 with $\text{Si}(\text{SiMe}_3)_3\text{Cl}$.⁴ In this reaction, the preformed Ge_9^{4-} clusters are extracted and trisubstituted, thus providing a fourth synthetic route to generate metalloid clusters. The trihypersilylated clusters have been further derivatized to form species such as $\text{M}[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3]^{2-}$ (n

= 0 for $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$; $n = -1$ for $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$; $n = -2$ for $\text{M} = \text{Pd}$), $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3]\text{Cu}[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3]\text{CuPPh}_3$, $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3\text{M}(\text{CO})_x]^-$ ($x = 3$ for $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $x = 5$ for $\text{M} = \text{Cr}$), $[\text{Ge}_{10}\text{Si}\{\text{Si}(\text{SiMe}_3)_3\}_4\{\text{SiMe}_3\}_2\text{Me}]^-$, $[\text{Ge}_{18}\{\text{Si}(\text{SiMe}_3)_3\}_6]$, and $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3(\text{R})]$ ($\text{R} = \text{Et}, \text{SnPh}_3, \text{Tl}$), $[(\text{Ph}_3\text{P})\text{PdGe}_9\{\text{Si}(\text{SiMe}_3)_3\}_3\text{Et}]^{1d,5,6}$.

To date, the acetonitrile suspension reaction described above has been successful only for the addition of silyl-based substituents, primarily $\text{Si}(\text{SiMe}_3)_3$ and, to a lesser extent, $\text{Si}(\text{SiMe}_3)_2(\text{SiPh}_3)$.⁷ We have now succeeded in attaching the first stannyl-based substituents by the same approach, specifically $^i\text{Pr}_3\text{Sn}$ -groups. The resulting species $[\text{Ge}_9\{\text{Sn}^i\text{Pr}_3\}_3]^-$ (confirmed by ESI-MS; Figure S1) were reacted further with $\text{Pd}(\text{PPh}_3)_4$. This led to cluster aggregation wherein a palladium triangle became incorporated into the resulting aggregate.

The new hexa-substituted cluster $[\text{Ge}_{18}\text{Pd}_3\{\text{Sn}^i\text{Pr}_3\}_6]^{2-}$ (**1**) was structurally characterized by single-crystal X-ray diffraction in $[\text{K}(222\text{-crypt})]_2(\text{1})\cdot\text{Pr}_2\text{O}$ (Figure 1) which was crystallized from its acetonitrile solution after layering with isopropyl ether (Pr_2O (details in SI)). The corresponding hepta-substituted species $[\text{Ge}_{18}\text{Pd}_3\{\text{Sn}^i\text{Pr}_3\}_7]^-$ (**2**) was also isolated (ESI-MS, Figure S8), but in minute yield, and was structurally characterized as well (Figure S9 and CIF). Its existence indirectly suggests the existence of the neutral tetra-substituted species $[\text{Ge}_9\{\text{Sn}^i\text{Pr}_3\}_4]^0$ in the reaction mixture; however, we cannot rule out the possibility of **1** reacting with excess $^i\text{Pr}_3\text{SnCl}$. The presence of **1** in solution was confirmed by ESI-MS (Figure S2) with major peaks corresponding to $[\text{Ge}_{18}\text{Pd}_3\{\text{Sn}^i\text{Pr}_3\}_6]^{2-}$ ($m/z = 1556$) and $[\text{K}(222\text{-crypt})][\text{Ge}_{18}\text{Pd}_3\{\text{Sn}^i\text{Pr}_3\}_6]^-$ ($m/z = 3529$).

1 has a 21-atom cluster core of $\text{Ge}_{18}\text{Pd}_3$ (Figure 1) and six Sn^iPr_3 -substituents exobonded to six of the 18 Ge-atoms (atoms 4, 5, 6, 7', 8', 9'). The core can be described as a prolated spheroid with pseudo- D_{3h} symmetry that consists of two trisubstituted $[\text{Ge}_9\{\text{Sn}^i\text{Pr}_3\}_3]^-$ units that have “trapped” a Pd_3 -triangle in the center between them. Noble-metal triangular moieties have been observed before in the ligand-free Zintl cluster anions $[\text{Ge}_{18}\text{Au}_3]^{5-}$, $[\text{Ge}_{45}\text{Au}_3]^{9-}$, and $[\text{Pd}_3\text{Sn}_8\text{Bi}_6]^{4-}$ as well as in the anionic transition-metal clusters $[\text{Os}_{18}\text{C}_2(\text{CO})_{42}\text{Hg}_3]^{2-}$ and $[\text{Os}_{18}\text{C}_2(\text{CO})_{40}\text{Pd}_3]^{2-}$.⁸ A number of ligand-stabilized triangles with Pd^{2+} are also known and have been well documented by Mingos et al.⁹ Reported recently was

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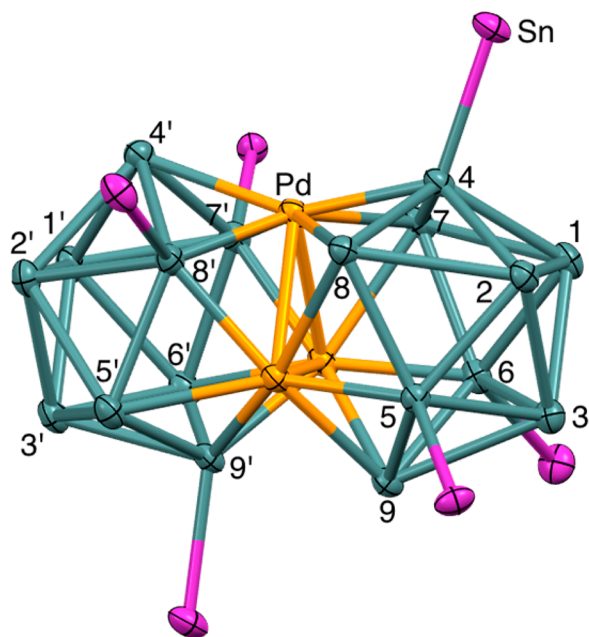


Figure 1. “Twinned icosahedron” structure of the title anion with numbered Ge-atoms. Sn and Pd are shown in purple and gold, respectively. The relatively short intericosahedral distances 7–7′, 8–8′, and 9–9′ are not shown.

also a Pd₃-triangle with a three-center–two-electron bond in [Pd₃(μ₂-SC₇H₇)₃(P(C₆H₄F)₃)₃]⁺.¹⁰

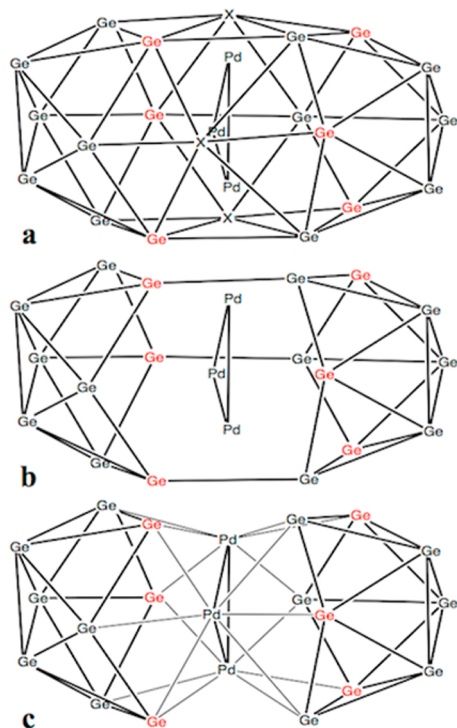
Each Ge₉-subunit of **1** can be viewed as a tricapped trigonal prism with one wide-open triangular base (7–8–9 and 7′–8′–9′ in the right- and left-hand halves, respectively; the other two bases are 1–2–3 and 1′–2′–3′, respectively). The Sn-substituents in the right-hand half are bonded to the capping atoms (atoms 4, 5, 6) as expected for a “normal” trisubstituted 9-atom cluster.^{4–6} However, in the left-hand side they are bonded to its open-triangular prismatic base (atoms 7′, 8′, 9′). The different positioning of the substituents is corroborated by ¹H, ¹³C, and ¹¹⁹Sn NMR spectroscopy showing two different environments for the SnⁱPr₃ groups (Figures S3–S7). It can be concluded that the “abnormal” positioning of the substituents in the left half means that they have moved from their “normal” positions in [Ge₉{SnⁱPr₃}₃][−], most likely during the cluster aggregation. Such dynamics for tin-based substituents is not unusual and has been observed before in [Ge₉{Si(SiMe₃)₃{SnR₃}₃] (R= ⁿBu, Ph).^{6a,b} It can be speculated that it is this ability of the SnⁱPr₃-substituents to readily move, and their smaller size compared to the less labile and much larger silicon-based Si(SiMe₃)₃-substituents that make possible the assembly of **1**.

The Ge–Ge distances within the two halves are in a fairly normal range of 2.5656(10)–2.8903(10) Å with the longest three being the prismatic heights in the right-hand half (1–7, 2–8, 3–9). Such elongation is seen in all hypersilyl trisubstituted species.^{2,4–6} What is interesting in such face-fused icosahedra, as pointed by Burdett and Canadell a quarter century ago, is that three pairs of atoms from different icosahedra are brought very close to each other.¹¹ Thus, the intericosahedral distances 7–7′, 8–8′, and 9–9′ (Figure 1; bonds not drawn) are in the range 2.939–2.988 Å and are comparable with the upper end of the intracuster distances. The Pd–Pd contacts, 2.8712(7)–2.8925(7) Å, are longer than in other compounds wherein very weak to no Pd–Pd

interaction have been suggested, i.e., [Pd@Pd₂Pb₁₀Bi₆]^{4−}, [Pd₃Sn₈Bi₆]^{4−}, and [Pd₂@Ge₁₈]^{4−} averaging to 2.762, 2.765, and 2.831 Å, respectively.^{8c,12} Lastly, the Ge–Sn distances, 2.5963(8)–2.6290(8) Å, compare well with those in [Ge₉{SnMe₃}₃]^{3−}, [Ge₉{SnPh₃}₂]^{2−}, [Ge₉{SnPh₃}₂]^{4−}, and Ge₉(Si(SiMe₃)₃(SnR₃)) with R = Ph and ⁿBu.^{6a,b,13}

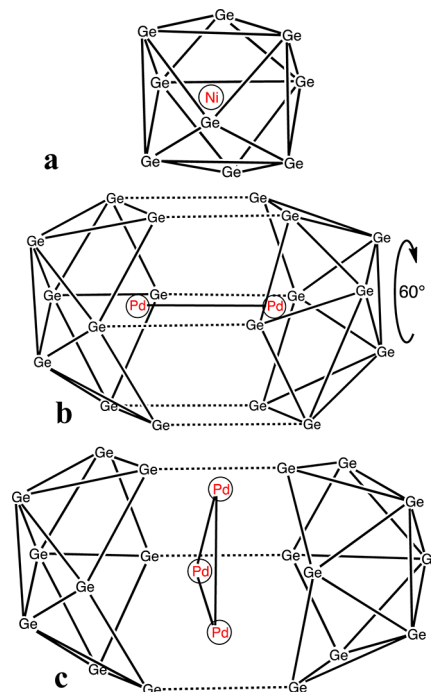
There are two ways to describe the core of **1**: (A) as a “twinned icosahedron” made of two Ge₉Pd₃ icosahedra fused via the Pd₃ triangular face and (B) as a single-cage *hypho*-deltahedron of Ge₁₈ (derived from 21-atom *closo*-deltahedron after removal of three vertices) “stuffed” with a Pd₃-triangle. Burdett and Canadell used description (A) to discuss the electronic structure of the isostructural B₂₁H₁₈[−].¹¹ Following their approach, we can view **1** as assembled of two [Ge₉{SnⁱPr₃}₃][−] *hypho*-clusters, i.e., clusters derived from icosahedral Ge₁₂ after removal of a triangular face and a Pd₃ triangle. A similar *hypho*-Ge₉ core was recently found linked to a *nido*-Ge₉ cluster in [Ge₁₈{Si(SiMe₃)₃}₆].¹⁴ When the two *hypho*-units are brought close to each other as in **1**, they interact along the 7–7′, 8–8′, and 9–9′ contacts. The resulting formation requires 22 cluster-bonding orbitals as discussed by Burdett and Canadell for B₁₈H₁₈ (see Figure 1c in ref 11 and Figure S11). When the B₃ triangle is inserted inside the latter to form B₂₁H₁₈[−], one of the triangle’s bonding orbital is added to this number to become 23 required orbitals with 46 electrons (see Figure 1d in ref 11). Those electrons come from 18 B–H units (2 electrons each), the B₃ triangle (3 × 3 = 9 electrons), and the charge of 1− (totals 36 + 9 + 1 = 46). When applied to our case, we find that again 22 cluster-bonding orbitals are required for the dimer [Ge₉{SnⁱPr₃}₃]₂^{2−} (Figure S11). However, the 5s/5p-based Pd₃ molecular orbitals are very high in energy compared to the dimer’s filled MOs that no additional bonding MO is added.¹⁴ Thus, [Ge₁₈Pd₃{SnⁱPr₃}₆]^{2−} requires only 44 cluster-bonding electrons (plus the additional 3 × 10 Pd-4d electrons) which come from 6 exobonded Ge-atoms (3 electrons each), 12 naked Ge-atoms (2 electrons each), and the charge of 2− (totals 18 + 24 + 2 = 44). In order to prove that the high energy of the palladium 5s/5p levels is the reason for this different count, we calculated a hypothetical cluster with a central Ga₃ instead of Pd₃ triangle, i.e., [Ge₁₈Ga₃][−] (Figure S16). Clearly, the species is stable with 46 cluster-bonding electrons, i.e., [Ge₁₈Ga₃][−] which is exactly isoelectronic with [B₂₁H₁₈][−].

Description (B) starts with a hypothetical 21-atom *closo*-cluster which is calculated to have the shape shown in Scheme 1a. This geometry was originally predicted by Lipscomb et al. in a theoretical studies of various large-cage boranes.¹⁵ The ellipsoid-shaped cluster requires $n + 2 = 23$ bonding orbitals (n tangential + 2 radial) instead of the typical $n + 1$ because of its two focal centers that allow for two radial bonding MOs pointing at them (Figure S12).^{12b} Removal of three of the 6-connected atoms (marked with X in Scheme 1a and positioned radially away and very close from each Pd-atom) generates the *hypho*-cage shown in Scheme 1b. It is well-known that removal of one or two atoms and generating the corresponding *nido*- and *arachno*-species does not change the number of required bonding MOs of a deltahedron (Figure S14).¹⁶ However, removal of three atoms reduces those MOs by a number that depends on the location of the removed atoms, e.g., by three MOs when a triangular face is removed and by one if the atoms are not neighbors (see Figures 1 and 6 in ref 11). Thus, in our case the number of required MOs is lowered by one to become 22 with 44 bonding electrons (Figure S14).

Scheme 1. Construction of **1**^a

^a(a) A hypothetical *closo*-21-atom cluster with a central Pd₃-triangle. (b) The three 6-connected vertices marked with X are then removed to generate the *hypko*-cluster. (c) Connecting the Pd-triangle with the two halves generates **1** as shown in Figure 1 (exo-bonded atoms are shown in red).

Description (B) is also useful to place the new species in the context of similar endohedral clusters that contain one or more atoms of the d¹⁰-group. Thus, a single Ni-atom can be inserted inside a 9-atom cluster by a reaction of Ge₉⁴⁻ with Ni(COD)₂ (Scheme 2a) to form [Ni@Ge₉]³⁻ (COD acts as a mild oxidant for the cluster and thus the charge of 3- instead of the original 4-; [Ni@Sn₉]⁴⁻ can be extracted from tertiary precursor with nominal composition K₄Sn₉Ni).¹⁷ The 3d¹⁰ central atom behaves as a closed-shell atom and does not bring new bonding orbitals nor electrons. Its empty 4s/4p orbitals only further stabilize the existing cluster-bonding molecular orbitals. The bonding picture in [Pd₂@Ge₁₈]⁴⁻ where a palladium dimer is captured inside a single-cage 18-atom cluster (Scheme 2b) is exactly the same, i.e., the two Pd-atoms only contribute to the cluster bonding with their 5s/5p empty orbitals.^{12b} The 18-atom cage of the latter is made of two 9-atom clusters, each with the shape of a tricapped trigonal prism with one open trigonal prismatic base exactly as in **1**. Unlike **1**, however, the two 9-atom clusters are staggered with respect to each other, and six intercluster interactions are generated. Their distances are again comparable with those within each cluster. A rotation of 60° of one of the clusters in [Pd₂@Ge₁₈]⁴⁻ leads to their eclipsed conformation as found in **1** (Scheme 2b,c) This geometry provides space for a triangle of Pd-atoms to be captured inside. Electronically, however, the three Pd-atoms behave exactly the same as in the previous two cases, i.e., they bring only additional stabilization to the existing cluster-bonding molecular orbitals without providing additional bonding orbitals and electrons.^{12b,18,19}

Scheme 2. The Relationship between Endohedral Clusters Containing (a) One, (b) Two, and (c) Three Central Atoms Represented by [Ni@Ge₉]³⁻, [Pd₂@Ge₁₈]⁴⁻, and **1**, Respectively^a

^aBoth (b) and (c) are made of two 9-atom halves that are staggered with respect to each other in (b) and are eclipsed (60° rotation of a half) in (c).

In conclusion, we can answer the title question whether **1** is a twinned icosahedron with a common Pd₃-face or an 18-vertex *hypko*-deltahedron with a Pd₃-triangle inside with both yes and yes. The two views are both geometrically and electronically accurate. Perhaps the most valuable lesson to be learned from the existence of **1** and its overall difference from the hypersilyl-substituted species is that substituents with different bulkiness and lability could provide other novel species in the future.

■ ASSOCIATED CONTENT

📄 Supporting Information

X-ray crystallographic data for compounds **1** and **2** (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06545.

General procedures; synthetic, crystallographic, spectroscopic, and computational details and data (PDF) (PDF)
 Crystallographic data for **1** (CIF)
 Crystallographic data for **2** (CIF)

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Notes

The authors declare no competing financial interest.

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