Rationally Functionalized Deltahedral Zintl Ions: Synthesis and Characterization of $[Ge_9{-}ER_3]^{3-}$, $[R_3E{-}Ge_9{-}ER_3]^{2-}$, and $[R_3E{-}Ge_9{-}Ge_9{-}ER_3]^{4-}$ ($E = Ge$, Sn; $R = Me$, Ph)

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Abstract: Six new derivatized deltahedral Zintl ions have been synthesized by reactions between the known Zintl ions Ge_9^{n-} with the halides R_3EX and/or the corresponding anions R_3E^- for $E = Ge$ or Sn. This rational approach is based on our previous discovery that these derivatization reactions are based on nucleophilic addition to the clusters. All species were structurally characterized as their salts with potassium countercations sequestered in 2,2,2-crypt or [18]crown-6 ether. The tin-containing anions were characterized also in solutions by ^{119}Sn NMR spectroscopy. The reaction types for such substitutions and the structures of the new anions are discussed.

Keywords: cluster compounds · germanium · Zintl anions

Introduction

Despite their more than 100-year history, Zintl ions have remained a remarkably little understood area of inorganic chemistry.[1] These are negatively charged polyatomic clusters of main-group metallic and/or semimetallic elements that can be crystallized from solutions with alkali metal countercations (often sequestered in various crypts or crown ethers). Although they have received more attention recently, the efforts, until a few years ago, involved mostly reproduction and better characterization of the already known or slightly modified species.[2] One of the more recent developments on this front was the discovery that, contrary to the expectations, such Zintl ions exist also in Zintl phases. The latter are polar intermetallic compounds of the heavier main-group p-block elements with alkali or alkaline-earth metals that are electronically balanced (or can be considered as such based on their structures). The Zintl phases can be viewed as salts where the more electropositive element transfers its valence-shell electrons to the more electronegative element and both achieve closed-shell formations. Despite their name, Zintl phases were considered unrelated to Zintl ions until the discovery of the Zintl phases A_4E_9 ($A =$ alkali metal, $E =$ Group 14 element) which contain the known deltahedral Zintl ions E_9^{4-}.[3] The latter were previously characterized in solids crystallized from ethylenediamine or ammonia solutions of the precursors A_xE_y.[2] These nine-atom clusters are cagelike species with the shape of a distorted tricapped trigonal prism (the distortions are elongations along one or more of the prismatic edges parallel to the threefold axis). Bonding in such clusters is achieved by delocalized electrons as in the well known cagelike boranes.

More recent studies revealed that, despite earlier beliefs, such deltahedral E_9^{n-} clusters can bond to each other in different modes and form dimers $[Ge_9{-}Ge_9]^{6-}$,[4] trimers $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$,[5] tetramers $[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$,[6] and infinite chains $_{1\infty}\{[\text{-}Ge_9\text{-}]^{2-}\}$.[7] This indicated that perhaps clusters can bond not only to other clusters but also to other groups. Accordingly, we studied reactions of ethylenediamine solutions of K_4Ge_9 with soft oxidizing agents such as Ph_3Sb and Ph_3Bi and, indeed, these reactions produced the first functionalized Zintl ions $[Ph_2Sb{-}Ge_9{-}SbPh_2]^{2-}$,[8] $[Ph_2Bi{-}Ge_9{-}BiPh_2]^{2-}$,[8] $[Ph{-}Ge_9{-}BiPh_2]^{2-}$,[9] and $[Ph_2Sb{-}Ge_9{-}Ge_9{-}SbPh_2]^{4-}$.[9] However, at this stage it was unclear how the reactions proceeded and what the reacting species might be. More detailed studies were carried out and they suggested that these reactions are in fact nucleophilic additions of the anions Ph_2Sb^- and Ph_2Bi^- to the naked Zintl ions Ge_9^{n-}.[9] The charges of the latter are, most likely, lower than 4−, that is, Ge_9^{2-} and/or the radicals $\cdot Ge_9^{3-}$. These naked clusters are well known: $\cdot Ge_9^{3-}$ has been characterized in a few compounds,[2] while Ge_9^{2-} has been also crystallized from solutions but the structure shows great disorder and was erroneously reported as Ge_{10}^{2-}.[10] (We and others have many times collected single-crystal X-ray diffraction data on compounds containing this cluster, Ge_9^{2-}, but all structure determinations have shown the same disorder, and no additional results have been published.) In ethylenediamine, these Zintl ions of lower charges are most likely in equilibria be-

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tween themselves and with Ge_9^{4-} and free solvated electrons, that is, $Ge_9^{4-} \rightleftharpoons \cdot Ge_9^{3-} + e^- \rightleftharpoons Ge_9^{2-} + 2e^-$ analogous to alkali metals dissolved in ethylenediamine. Both $\cdot Ge_9^{3-}$ and Ge_9^{2-} have a low-lying molecular orbital available for electron donation that is half-filled for the former and empty for the latter. Thus, nucleophiles such as Ph_2Sb^- and Ph_2Bi^- (labeled R_2Pn^-; Pn = pnictogen) donate electrons to this orbital and form bonds to the clusters. We proposed that such reactions should produce the monosubstituted species $[Ge_9{-}PnR_2]^{3-}$, but these were not observed at that time. They, in turn, would be in equilibria with $[\cdot Ge_9{-}PnR_2]^{2-}$, $[Ge_9{-}PnR_2]^-$, and free electrons. Such less-reduced species have similarly a half-filled or empty orbital and can add one more anion PnR_2^- to produce $[R_2Pn{-}Ge_9{-}PnR_2]^{2-}$. They can also react between themselves either as two radicals or as a donor $[Ge_9{-}PnR_2]^{3-}$ and an acceptor of either $[\cdot Ge_9{-}PnR_2]^{2-}$ or $[Ge_9{-}PnR_2]^-$, and produce the observed dimers of $[R_2Pn{-}Ge_9{-}Ge_9{-}PnR_2]^{4-}$. These general ideas were explored further for possible use in more rational synthesis of similar derivatives of deltahedral Zintl ions by addition of other groups. Reported here are the rational syntheses of both mono- and disubstituted germanium clusters by reactions of the clusters with either the organometallic compounds ER_4, their halides ER_3X, or the corresponding anion ER_3^- prepared separately (E = Sn, Ge and R = Me, Ph). The new species are characterized structurally as their $[K\text{-}(2,2,2\text{-crypt})]^+$ or $[K\text{-}([18]\text{crown-6})]^+$ salts in the solid state, and the tin-containing species are also characterized by ^{119}Sn NMR spectroscopy in solution (2,2,2-crypt = 4,7,13,16,21,24-haxaoxa-1,10-diazabicyclo-[8.8.8]-haxacosane).

Results and Discussion

Synthesis: The reaction path for addition of functional groups to the Ge_9 clusters that was proposed before (above) can be described in more details by the following reactions:[9]

Equilibria 1:

$$Ge_9^{4-} \rightleftharpoons \cdot Ge_9^{3-} + e^- \rightleftharpoons Ge_9^{2-} + 2\,e^- \tag{1}$$

Reaction steps 1:

$$\begin{aligned}
&Ge_9^{2-} + SbPh_2^- \rightarrow [Ge_9{-}SbPh_2]^{3-}\ \text{(intermediate) and/or}\\
&\cdot Ge_9^{3-} + SbPh_2^- \rightarrow [\cdot Ge_9{-}SbPh_2]^{4-}\\
&\rightarrow [Ge_9{-}SbPh_2]^{3-}\ \text{(intermediate)} + e^-
\end{aligned} \tag{1a}$$

Side reactions of Ge_9^{n-}:

$$\begin{aligned}
&\cdot Ge_9^{3-} + \cdot Ge_9^{3-} \rightarrow [Ge_9{-}Ge_9]^{6-}\ \text{and/or}\\
&Ge_9^{2-} + Ge_9^{4-} \rightarrow [Ge_9{-}Ge_9]^{6-}\ \text{and/or}\\
&\cdot Ge_9^{3-} + Ge_9^{4-} \rightarrow [Ge_9{-}Ge_9]^{6-} + e^-
\end{aligned} \tag{1b}$$

Equilibria 2:

$$\begin{aligned}
&[Ge_9{-}SbPh_2]^{3-} \rightleftharpoons [\cdot Ge_9{-}SbPh_2]^{2-}\\
&+ e^- \rightleftharpoons [Ge_9{-}SbPh_2]^- + 2e^-
\end{aligned} \tag{2}$$

Reaction steps 2:

$$\begin{aligned}
&[Ge_9{-}SbPh_2]^- + SbPh_2^- \rightarrow [Ph_2Sb{-}Ge_9{-}SbPh_2]^{2-}\ \text{and/or}\\
&[\cdot Ge_9{-}SbPh_2]^{2-} + SbPh_2^- \rightarrow [\cdot Ph_2Sb{-}Ge_9{-}SbPh_2]^{3-}\\
&\rightarrow [Ph_2Sb{-}Ge_9{-}SbPh_2]^{2-} + e^-
\end{aligned} \tag{2a}$$

Side reactions of $[Ge_9\text{-}SbPh_2]^{n-}$:

$$\begin{aligned}
&[\cdot Ge_9{-}SbPh_2]^{2-} + [\cdot Ge_9{-}SbPh_2]^{2-}\\
&\rightarrow [Ph_2Sb{-}Ge_9{-}Ge_9{-}SbPh_2]^{4-}\ \text{and/or}\\
&[Ge_9{-}SbPh_2]^- + [Ge_9{-}SbPh_2]^{3-}\\
&\rightarrow [Ph_2Sb{-}Ge_9{-}Ge_9{-}SbPh_2]^{4-}\ \text{and/or}\\
&[\cdot Ge_9{-}SbPh_2]^{2-} + [Ge_9{-}SbPh_2]^{3-}\\
&\rightarrow [Ph_2Sb{-}Ge_9{-}Ge_9{-}SbPh_2]^{4-} + e^-
\end{aligned} \tag{2b}$$

Based on this, we expected relatively stable monosubstituted *intermediates* $[Ge_9{-}SbPh_2]^{3-}$ that, perhaps, might be susceptible for crystallization under appropriate conditions. However, all attempts to crystallize such species from solution were unsuccessful. Also, it was impossible to prove their existence in solution because neither Ge or Sb are good nuclei for NMR spectroscopy, and therefore their existence, and ultimately the reaction path, could not be unequivocally established. This led to shifting our attention to tin-based substituents for which the corresponding reactions can be monitored in solutions by ^{119}Sn NMR spectroscopy. Furthermore, it is relatively easy to prepare simple R_3E^- ions (rather than various aggregates) of the carbon group by reduction of the corresponding halide with alkali metal. Although this reaction can proceed along different pathways with different intermediates, its final product with a small excess of alkali metal is always the anion R_3E^-.[11]

Initially, solutions of K_4Ge_9 were allowed to react with $GePh_4$ and $SnPh_4$ to find out whether these react in a similar way to $SbPh_3$ and $BiPh_3$. The tin reaction was successful and disubstituted $[Ph_3Sn{-}Ge_9{-}SnPh_3]^{2-}$ (**1**) was obtained and characterized as its $[K\text{-}(2,2,2\text{-crypt})]^+$ salt. The reaction with $GePh_4$, on the other hand, produced only $\cdot Ge_9^{3-}$ and dimers of $[Ge_9{-}Ge_9]^{6-}$ as crystalline products (depending on the amount of 2,2,2-crypt used).[4,12] We have shown before, however, that these same products can be obtained directly from solutions of K_4Ge_9, that is, without reacting them with $GePh_4$.[9] This indicates, therefore, that the Ge_9 clusters do not react with $GePh_4$, most likely because of the stronger Ph–Ge bond that prevents generation of Ph_3Ge^- ions in the solution. Next, we tested reactions with the much more ionic Ph_3GeCl (as well as Ph_3SnCl and Me_3SnCl) which can be reduced very easily to Ph_3Ge^- and Cl^-. As expected, the reaction was very vigorous and produced plenty of gray-black precipitation of elemental germanium. This particular experiment was performed with excess of Ph_3GeCl, and clearly the following reaction must have occurred: $2\,Ph_3GeCl + K_4Ge_9 \rightarrow 2\,KCl + 2\,K^+ + 2\,Ph_3Ge^- + 9\,Ge^0$. Therefore, Ph_3Ge^- ions were generated for the expense of all the available Ge_9^{4-} clusters which became fully oxidized to Ge^0 and precipitated. If excess of clusters were used the additional amount would have been able to react with the generated Ph_3Ge^- ions. This was tested and, indeed, reactions with excess of K_4Ge_9 with respect to R_3EX produced various R_3E-substituted clusters including a disubstituted dimer of germanium clusters $[Ph_3Sn{-}Ge_9{-}Ge_9{-}SnPh_3]^{4-}$ (**6**). This confirmed again that the corresponding anions of the substituents are needed for successful addition. The direct reactions between the clusters and the halides are somewhat difficult to control and also involve the "sacrifice" of a fraction of the clusters for the reduction of the halide. For these reasons it was decided to generate the R_3E^- ions separately by reduction of the halides with alkali metals. Thus, reactions of R_3EX with potassium in ethylenediamine were used for this purpose. The resulting solutions were then allowed to react with solutions of K_4Ge_9 and, depending on the molar ratios, the following substituted species were crystallized with $[K\text{-}(2,2,2\text{-crypt})]^+$ as countercations (see Figure 1): $[Ph_3Sn{-}Ge_9{-}SnPh_3]^{2-}$ (**1**), $[Me_3Sn{-}Ge_9{-}SnMe_3]^{2-}$ (**2**), $[Ph_3Ge{-}Ge_9{-}GePh_3]^{2-}$ (**3**), $[Ge_9{-}SnPh_3]^{3-}$ (**4**), and $[Ge_9{-}SnMe_3]^{3-}$ (**5**) (**1** and **5** were also characterized with $[K\text{-}([18]\text{crown-6 ether})]^+$ as countercations). The rational synthesis of these species by this approach proves that the reaction is based on the nucleophilic addition of R_3E^- to the germanium clusters. One more advantage of using pre-formed anions is that the reaction is independent of the strengths of the E–R and E–X bonds. The successful synthesis of Ph_3Ge-substituted clusters using this approach confirms this. Furthermore, the use of the anions allows better control of the reaction, and this made possible the synthesis of the monosubstituted species **4** and **5** when smaller amounts of R_3Sn^- were used ($R_3E^-:K_4Ge_9 = 1{:}2$ or less). Their synthesis and characterization prove the proposed reaction path described above.

In addition to the structural characterization, the tin-containing anions **1**, **2**, **4**, and **5** were characterized also in solution by ^{119}Sn NMR spectroscopy. Crystals of $[K\text{-}(2,2,2\text{-crypt})]_2\mathbf{1}$, $[K\text{-}([18]\text{crown-6})]_2\mathbf{1}\cdot 0.25([18]\text{crown-6})\cdot 2\,\text{en}$, $[K\text{-}(2,2,2\text{-crypt})]_2\mathbf{2}\cdot 3.5\,\text{tol}$, $[K\text{-}(2,2,2\text{-crypt})]_3\mathbf{4}\cdot\text{en}$, $[K\text{-}(2,2,2\text{-crypt})]_3\mathbf{5}$, and $[(K\text{-}([18]\text{crown-6})]_3\mathbf{5}\cdot\text{THF}\cdot 2\,\text{en}$ were dissolved in pyridine and their spectra showed peaks with chemical shifts (with respect to Me_4Sn in $CDCl_3$ as external standard) at $\delta = 15.1$, 14.9, 21.9, 260.0, 130.3, 116.2 ppm, respectively. For comparison, solutions of Ph_3Sn^- and Me_3Sn^- prepared by reduction of the corresponding chlorides with excess potassium in ethylenediamine showed chemical shifts of $\delta = -113.0$ and -176.9 ppm, respectively. It should be pointed out that traces of Ph_3Sn^- were observed in the spectra of **1** and **4** (in pyridine) at $\delta = -108.1$ and -109.8 ppm, respectively, but no Me_3Sn^- was observed in the solutions of **2** and **5**. It may be that Ph_3Sn^- is more stable in pyridine, most likely because of better solvation by the aromatic solvent.

Structure: The six new species **1**–**6** are shown in Figure 1. Those of type **1** in the (K-([18]crown-6) salt and **2** have two crystallographically different geometries each, **A** and **B**, that are otherwise very similar. The cores of all these species are the well-known deltahedral Zintl ions Ge_9^{n-} that can exist on their own, that is, without substituents. As already discussed, they have been characterized both as Zintl ions in numerous compounds crystallized from solutions as well as in Zintl phases.[2,3] These clusters are quite flexible in shape and charge. Overall, they resemble tricapped trigonal prisms with variously elongated one, two, or three trigonal prismatic edges parallel to the threefold axis and can carry charges of 2−, 3−, and 4−. Referring to the numbering of the Ge atoms shown in Figure 1 a, the trigonal prism is made of the triangular bases 4–5–9 and 2–3–7 (the threefold axis is vertical), while the capping atoms are 1, 5, and 6. It should be mentioned that tricapped trigonal prisms with one elongated edge can be viewed also as monocapped (atom 1) square antiprisms (squares 2–3–4–5 and 6–7–8–9). The same type distortions are observed in the core clusters of the substituted species **1**–**6**. Thus, the edges 7–9 are elongated in all of them, while also elongated in **4** is the edge 3–4 (Figure 1 and Table 1). As observed before, the elongations in such substituted species are related to the positioning of the substituents. It can be seen in Figure 1 that the *exo*-bonds are always to atoms of these elongated edges, that is, atoms 7 and 9 for **1**–**3**, atom 7 in **5**, and atoms 3 and 7 in **4**. Furthermore, with the exception of **4**, the *exo*-bonds are almost parallel to the elongated edges and look like their outward extensions. The subsituent in **4** bonds to two atoms, and it is geometrically impossible for the two *exo*-bonds to be parallel to these edges. The closest to such a position is for the subsituent to be within the plane defined by these two edges, and this is exactly where Ph_3Sn is located in this structure.

The shapes of the Ge_9 clusters and the positioning of the substituents are directly related to the cluster's electronic structure. This relationship has been already discussed in some detail based on molecular orbital calculations for Ph_3Sb-substituted clusters.[9] The main points are that the HOMO for Ge_9^{4-} is made of p_z orbitals (z along the threefold axis of the prism) and is within a relatively large energy gap, that is, there are comparable gaps below and above it. This same orbital is half-filled for Ge_9^{3-} and is empty and the LUMO for Ge_9^{2-}. Its energy depends very strongly on the elongation of the prismatic edges: greater elongation and more elongated edges lower the orbital's energy due to relief of antibonding interactions between the two triangular bases of the prism. Thus, Ge_9^{4-} clusters (*nido*-species according to Wade's rules; 22 cluster-bonding electrons) typically have one or more elongated edges and, correspondingly, this orbital is at relatively low energy and is occupied. For example, the lengths of such edges are approximately in the ranges 3.61–3.70, 3.15–3.54, and 3.03–3.19 Å for clusters with one, two, and three elongated edges, respectively. It should be pointed out that, as these number show, the elongation is less pronounced when more edges are elongated. Although the structure of Ge_9^{2-} (*closo*-species, 20 cluster-bonding electrons) has not been determined well, it is clear that none of

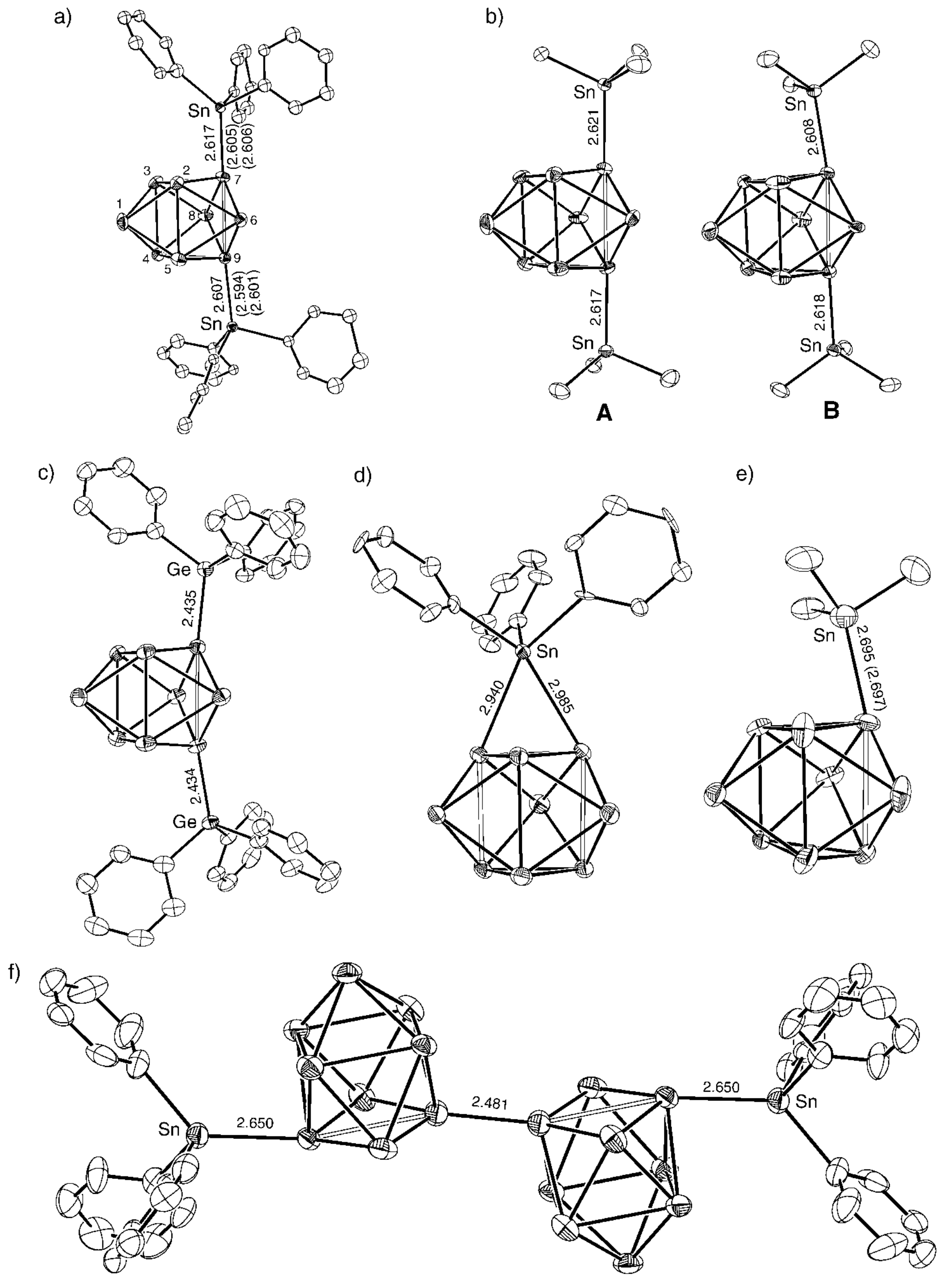

Figure 1. Structures of **1**–**6** (ORTEP drawings; 50% thermal ellipsoids): a) **1** in [K-(2,2,2-crypt)]$_2$[Ph$_3$Sn–Ge$_9$–SnPh$_3$] (and in [K-([18]crown-6)]$_2$[Ph$_3$Sn–Ge$_9$–SnPh$_3$]·0.25([18]crown-6)·2en); b) **2** in [K-(2,2,2-crypt)]$_2$[Ph$_3$Sn–Ge$_9$–SnPh$_3$]·3.5tol; c) **3** in [K-(2,2,2-crypt)]$_2$[Ph$_3$Sn–Ge$_9$–SnPh$_3$]·tol·0.5en; d) **4** in [K-(2,2,2-crypt)]$_3$[Ge$_9$–SnPh$_3$]·en; e) **5** in [K-(2,2,2-crypt)]$_3$[Ge$_9$–SnMe$_3$] (and in [K-([18]crown-6)]$_3$[Ge$_9$–SnMe$_3$]·THF·2en); and f) **6** in [K-(2,2,2-crypt)]$_4$[Ph$_3$Sn–Ge$_9$–Ge$_9$–SnPh$_3$]·2en. Anion **1** in [K-([18]crown-6)]$_2$[Ph$_3$Sn–Ge$_9$–SnPh$_3$]·0.25([18]crown-6)·2en) and anion **2** are represented by two crystallographically slightly different geometries in the corresponding structures, **A** and **B**. The Ge–Sn distances are shown (the distances in parentheses in a) and e) are for [K-([18]crown-6)]$_2$**1**·0.25([18]crown-6)·2en and [K-([18]crown-6)]$_3$**5**·THF·2en, respectively) while the Ge–Ge distances are listed in Table 1. Open bonds indicate elongated edges. The numbering of the germanium atoms of the clusters is shown in a) and is the same for all clusters.

the edges is elongated.[10] This makes the molecular orbital in question more antibonding and empty. The situation with Ge$_9^{3-}$ is somewhat in the middle, that is, the elongation of the edges is not as pronounced as in Ge$_9^{4-}$. The lengths of the elongated edges fall in the ranges 3.21–3.55 and 3.02–3.33 Å for the known examples of such clusters with one and two elongated edges, respectively.

The structures of the new species **1**–**6** show that the antibonding character of the same molecular orbital can be alleviated not only by edge elongations but also by the addition of substituents along the general direction of the p$_z$ orbitals at the atoms of the trigonal prism. Thus, although the Ge$_9$ cluster cores in the new species carry the same number of cluster-bonding electrons, 22, as the naked Ge$_9^{4-}$ cluster, their single elongated edges are notably shorter: 2.997–3.107 Å in the disubstituted **1**, **2**, **3**, and **6**, and 3.212 Å in the monosubstituted **5** (3.218 Å with [K-([18]crown-6)]). The latter is somewhat longer than the former but is shorter than in non-substituted species. The trend is observed also for the clusters in the dimer [Ge$_9$–Ge$_9$]$^{6-}$ with one *exo*-bond per cluster and the chain $_{1\infty}$\{[-Ge$_9$-]$^{2-}$\} with two such bonds per cluster where the lengths of the single-elongated edges are 3.433 and 3.194 Å, respectively.[4,7] The same is true for clusters with two elongated edges, that is, the elongation is more pronounced in naked clusters and less so in *exo*-bonded ones. Thus, these two edges in the monosubstituted **4** with bridging Ph$_3$Sn, 2.949 and 2.985 Å, are much shorter than in the corresponding naked clusters (above).

The *exo*-bond lengths in **1** and **2** (2.594–2.617 Å) and in **3** (2.434 and 2.435 Å) correspond to single-bond Ge–Sn and Ge–Ge lengths, respectively. The same is true for the intercluster distance of 2.481 Å in **6**. They compare well with 2.599 Å for Ge–Sn in Me$_3$GeSnPh$_3$ and with 2.438 and 2.441 Å for Ge–Ge in [Ph$_3$Ge–Ge(Ph)$_2$–GePh$_3$].[13,14] The effect of the bridging in **4** and the associated three-center–two-electron interaction are clearly manifested in the longer Sn–Ge distances of 2.940 and 2.985 Å. Although the trimethyltin substituent in **5** is not exactly bridging, it is noticeably bent towards the threefold axis of the prism and brings the tin atom close to the other two germanium atoms of the triangular base Ge2 and Ge3

Table 1. Ge–Ge distances [Å] in the Ge_9 clusters of the new species **1**–**6** (**1′** and **1″** are the anions in [K-(2,2,2-crypt)]$_2$**1** and [K-([18]crown-6)]$_2$**1**·0.25([18]crown-6)·2en, respectively; **5′** and **5″** are the anions in [K-(2,2,2-crypt)]$_3$**5** and [K-([18]crown-6)]$_3$**5**·THF·2en, respectively).[a]

Atoms[b]	**1′**	**1″(A)**	**1″(B)**	**2(A)**	**2(B)**	**3**	**4**	**5′**[c]	**5″**	**6**
1–2	2.588(1)	2.560(2)	2.565(2)	2.579(1)	2.611(1)	2.579(1)	2.552(2)	2.435	2.562(1)	2.560(2)
1–3	2.573(1)	2.573(1)	2.573(1)	2.597(1)	2.597(1)	2.595(1)	2.527(2)	2.533	2.538(1)	2.556(2)
1–4	2.587(1)	2.573(2)	2.562(2)	2.583(1)	2.590(1)	2.575(1)	2.618(2)	2.608	2.619(1)	2.583(2)
1–5	2.576(1)	2.571(2)	2.585(1)	2.590(1)	2.599(1)	2.577(1)	2.591(2)	2.504	2.603(1)	2.586(2)
2–3	2.823(1)	2.805(1)	2.821(1)	2.819(1)	2.866(1)	2.862(1)	2.756(2)	2.811	2.813(1)	2.868(2)
2–5	2.735(1)	2.713(1)	2.734(1)	2.744(1)	2.800(1)	2.719(1)	2.850(2)	2.899	2.855(1)	2.729(2)
2–6	2.636(1)	2.637(1)	2.605(1)	2.647(1)	2.676(1)	2.621(1)	2.574(2)	2.651	2.609(1)	2.588(2)
2–7	2.617(1)	2.612(1)	2.636(2)	2.646(1)	2.667(1)	2.612(1)	2.734(2)	2.723	2.660(1)	2.652(2)
3–4	2.717(1)	2.739(1)	2.729(1)	2.752(1)	2.752(1)	2.687(1)	*2.949(2)*	2.791	2.864(1)	2.737(2)
3–7	2.628(1)	2.593(1)	2.636(1)	2.660(1)	2.669(1)	2.587(1)	2.687(2)	2.694	2.657(1)	2.670(2)
3–8	2.613(1)	2.636(1)	2.603(1)	2.671(1)	2.639(1)	2.655(1)	2.537(2)	2.622	2.594(1)	2.574(2)
4–5	2.827(1)	2.852(1)	2.815(1)	2.865(1)	2.855(1)	2.887(1)	2.659(2)	2.817	2.794(1)	2.796(2)
4–8	2.625(1)	2.598(2)	2.634(1)	2.637(1)	2.661(1)	2.633(1)	2.627(2)	2.619	2.618(1)	2.623(2)
4–9	2.622(1)	2.642(2)	2.606(1)	2.634(1)	2.612(1)	2.609(1)	2.613(2)	2.615	2.657(1)	2.623(2)
5–6	2.615(1)	2.596(1)	2.628(1)	2.645(1)	2.682(1)	2.647(1)	2.582(2)	2.584	2.616(1)	2.675(2)
5–9	2.620(1)	2.644(1)	2.591(1)	2.643(1)	2.635(1)	2.600(1)	2.659(2)	2.596	2.637(1)	2.606(2)
6–7	2.559(1)	2.566(1)	2.560(1)	2.571(1)	2.638(1)	2.564(1)	2.560(2)	2.525	2.511(1)	2.553(2)
6–9	2.544(1)	2.559(1)	2.555(1)	2.587(1)	2.621(1)	2.566(1)	2.595(2)	2.609	2.666(1)	2.540(2)
7–8	2.578(1)	2.550(1)	2.575(1)	2.595(1)	2.568(1)	2.553(1)	2.551(2)	2.505	2.503(1)	2.579(2)
7–9	*3.035(1)*	*3.018(1)*	*2.997(1)*	*3.096(1)*	*3.107(1)*	*3.089(1)*	*2.985(2)*	*3.212*	*3.218(1)*	*3.077(2)*
8–9	2.586(1)	2.561(1)	2.560(1)	2.602(1)	2.565(1)	2.548(1)	2.626(2)	2.609	2.661(1)	2.570(2)

[a] The distances in italics are the elongated prismatic edges of the Ge_9 clusters shown as open bonds in Figure 1. [b] The numbering of the atoms is shown in Figure 1a. [c] This cluster is disordered among two positions and the reported distances are averages.

(3.3–3.9 Å). The weak interactions with these two germanium atoms results in a somewhat longer Ge–Sn bond length of 2.695 Å (2.697 Å for the [K-([18]crown-6)] salt) that is somewhat longer than in **1** and **2** but shorter than in **4**.

Conclusions

Deltahedral Zintl ions functionalized with various organic derivatives of elements of Groups 14 and 15, R_3E- and R_2E-, respectively, can be synthesized by design. The rationality of the approach is based on the understanding that the substituents are added as anions to the clusters. The reaction is based on nucleophilic addition to an empty or half-filled cluster orbital. This knowledge opens doors for further exploration of many other nucleophiles as potential substituents in such clusters.

Experimental Section

Materials and techniques: All manipulations were performed in a nitrogen-filled glove box with a moisture level below 1 ppm. A precursor of nominal composition K_4Ge_9 was synthesized by heating (900 °C, 2 days) a stoichiometric mixture of the elements (K: 99+ %, Strem; Ge: 99.999 %, Alfa-Aesar) in sealed niobium containers (arc-welded in argon at low pressure) that were in turn sealed in quartz ampoules under vacuum. The reactions were performed in ethylenediamine (99.5+ %, Aldrich) or pyridine (extra dry, Acros). The reagents 2,2,2-crypt (98 %, Acros), Ph_4Sn (95 %, Acros), Ph_3SnCl (95 %, Strem), Me_3SnCl (99 %, Acros), Ph_4Ge (97 %, Aldrich), and Ph_3GeCl (99 %, Strem) were used after careful drying under vacuum.

^{119}Sn NMR spectra were taken in ethylenediamine or pyridine on a Bruker 400 MHz spectrometer. Sealed capillaries with C_6D_{12} were used as deprotonated solvent while Me_4Sn in $CDCl_3$ was used as an external reference.

Synthesis of [K-(2,2,2-crypt)]$_2$1: K_4Ge_9 (133 mg, 0.16 mmol) and 2,2,2-crypt (247 mg, 0.65 mmol) were dissolved in ethylenediamine (1 mL) and the solution was treated with $SnPh_4$ (118 mg, 0.28 mmol) while stirring at 50 °C for 24 h. The resulting red-brown solution was filtered, carefully layered with toluene, and left undisturbed for a few days. After decanting the mother liquor, yellow-orange plates of [K-(2,2,2-crypt)]$_2$**1** were recovered (~45 % yield based on the precursor). The same reaction performed in pyridine instead of ethylenediamine gave exactly the same result. (It should be pointed out that the yields in all the reactions have very large uncertainties due to the uncertainty of the purity and the degree of decomposition of the precursors.)

The compound was also prepared by treating the precursor with a solution containing Ph_3Sn^-. The latter was made by reduction of Ph_3SnCl (100 mg, 0.23 mmol) dissolved in ethylenediamine (1 mL) with elemental K (18 mg, 0.46 mmol). This solution was stirred until all potassium was dissolved and then the resulting pale orange suspension was centrifuged and the solid KCl was filtered out. ^{119}Sn NMR: $\delta = -113.0$ ppm (s, $SnPh_3^-$). The solution was treated with K_4Ge_9 (95 mg, 0.117 mmol) and stirred for 24 h at 50 °C. After filtration, 2,2,2-crypt (264 mg, 0.7 mmol) was added and the solution was carefully layered with toluene. After a few days the mother liquor was decanted and crystals of [K-(2,2,2-crypt)]$_2$**1** (~20 % yield) were collected. ^{119}Sn NMR of crystals dissolved in pyridine: $\delta = 15.1$ (s, $[Ph_3Sn{-}Ge_9{-}SnPh_3]^{2-}$), -108.1 ppm (s, $SnPh_3^-$).

Synthesis of [K-([18]crown-6)]$_2$1·0.25([18]crown-6)·2en: K_4Ge_9 (43.5 mg, 0.05 mmol) was dissolved in ethylenediamine (0.5 mL) to form an intensely colored red-brown solution. Mixed in a separate test tube were Ph_3SnCl (20 mg, 0.05 mmol) and ethylenediamine (1 mL), and this solution was added slowly to the precursor solution. [18]crown-6 ether (105 mg, 0.39 mmol, molar ratio of 2:1 with respect to potassium) was added to the resulting very dark red-brown solution and this was stirred for 15 min. After filtration the solution was layered with toluene and was left undisturbed until crystals of good size formed. Yellow-orange to orange-red crystals of [K-([18]crown-6)]$_2$**1**·0.25([18]crown-6)·2en were obtained (~40–50 % yield). ^{119}Sn NMR of crystals dissolved in pyridine: $\delta = 14.9$ ppm (s, $[Ph_3Sn{-}Ge_9{-}SnPh_3]^{2-}$).

Synthesis of [K-(2,2,2-crypt)]$_2$2·3.5 tol: Me_3SnCl (88 mg, 0.44 mmol) and K (35 mg, 0.88 mmol) were added to ethylenediamine (1 mL) and the solution was stirred until all K dissolved. The solution was centrifuged and filtered. ^{119}Sn NMR: $\delta = -176.9$ ppm (s, Me_3Sn^-). K_4Ge_9 (44 mg, 0.05 mmol) and 2,2,2-crypt (250 mg, 0.65 mmol) were added and the solution was stirred for 24 h at 50 °C. The resulting very dark red-brown solution was filtered (^{119}Sn NMR: $\delta = -9.2$ ppm (s, $[Me_3Sn{-}Ge_9{-}SnMe_3]^{2-}$))

and layered with toluene. It was left undisturbed, and when crystals of good size were visible, the mother liquor was decanted and the yellow-orange plates of [K-(2,2,2-crypt)]$_2$**2**·3.5 tol (ca. 10 % yield) were collected. ^{119}Sn NMR of crystals dissolved in pyridine: $\delta = 21.9$ ppm (s, $[Me_3Sn{-}Ge_9{-}SnMe_3]^{2-}$).

Synthesis of [K-(2,2,2-crypt)]$_2$3·tol·0.5 en: Ph_3GeCl (71 mg, 0.21 mmol) in ethylenediamine (1 mL) was treated with K (16 mg, 0.42 mmol), and the mixture was stirred until everything was dissolved. The yellow-orange solution was centrifuged and filtered. K_4Ge_9 (55 mg, 0.07 mmol) and 2,2,2-crypt (160 mg, 0.42 mmol) were added to the solution and stirred for 24 h at 50 °C. The resulting very dark brown-red solution was filtered and carefully layered with toluene. After a few days the mother liquor was decanted and orange-red crystals of [K-(2,2,2-crypt)]$_2$**2**·3.5 tol were recovered (ca. 50 % yield).

Synthesis of [K-(2,2,2-crypt)]$_3$4·en: Ph_3SnCl (20 mg, 0.05 mmol) in ethylenediamine (1 mL) was treated with K (3.8 mg, 0.1 mmol), and the mixture was stirred until everything dissolved. The resulting pale orange solution was separated from the KCl precipitation and was treated with K_4Ge_9 (105 mg, 0.13 mmol) and 2,2,2-crypt (233 mg, 0.62 mmol) while stirring for 1 h at 50 °C. After filtration the orange-red solution was layered with toluene, and after a few days orange-red plates of [K-(2,2,2-crypt)]$_3$**4**·en were recovered (ca. 20 % yield). ^{119}Sn NMR of crystals dissolved in pyridine: $\delta = 260.0$ (s, $(Ph_3Sn{-}Ge_9)^{3-}$), -109.8 ppm (s, $SnPh_3^{-}$).

Synthesis of [K-(2,2,2-crypt)]$_3$5: Me_3SnCl (10 mg, 0.05 mmol) in ethylenediamine (1 mL) was treated with K (3.8 mg, 0.1 mmol), and the mixture was stirred until everything dissolved. Added to this solution were K_4Ge_9 (90 mg, 0.11 mmol) and 2,2,2-crypt (203 mg, 0.54 mmol) and the mixture was stirred for 1 h at 50 °C. After filtration the red-brown solution was layered with toluene and left undisturbed for a few days. Large red-orange crystals of [K-(2,2,2-crypt)]$_3$**5** were recovered (ca. 55 % yield). ^{119}Sn NMR of crystals dissolved in pyridine: $\delta = 130.3$ ppm (s, $(Me_3Sn{-}Ge_9)^{3-}$). The solution in pyridine was then layered with toluene and **5** was recrystallized in [K-(2,2,2-crypt)]$_3$**5**·2 tol·py with a different unit cell due to the extra solvent molecules.

Synthesis of [(K-([18]crown-6)]$_3$5·thf·2 en: Following the same procedure as for [K-(2,2,2-crypt)]$_3$**5** used was [18]crown-6 ether (143 mg, 0.54 mmol) instead of 2,2,2-crypt. The resulting solution was divided in two reaction tubes and one was layered with toluene and the other with THF. Red crystals of (K-18-crown-6)$_3$**5**·THF·2en were recovered from the latter (ca. 30–40 %). ^{119}Sn NMR of crystals dissolved in pyridine: $\delta = 116.2$ ppm (s, $(Me_3Sn{-}Ge_9)^{3-}$).

Synthesis of (K-(2,2,2-crypt)$_3$6·2 en: K_4Ge_9 (43.5 mg, 0.05 mmol) was dissolved in ethylenediamine (0.5 mL) and formed intensely colored red-brown solution. Separately, Ph_3SnCl (40 mg, 0.1 mmol) was dissolved in ethylenediamine (1 mL), and 0.2 mL of this solution (0.02 mmol Ph_3SnCl) were added to the solution of the precursor. The red color became darker and after stirring the solution for 15 min it was layered with 2 mL of a solution of 2,2,2-crypt (83 mg, 0.22 mmol) in toluene. After a few days crystals of two phases were recovered: orange plates of (K-crypt)$_2$**1** and orange plates of (K-crypt)$_4$**6**·2 en.

Structure determination: Single-crystal X-ray diffraction data sets were collected at 100 K on a Bruker APEX diffractometer with a CCD area detector (graphite-monochromated $Mo_{K\alpha}$ radiation, crystals protected with Parathone-N oil). The structures were solved by direct methods and refined on F^2 using the SHELXTL V5.1 package (after absorption corrections with SADABS). Details of the data collections and refinements are given in Table 2. CCDC–230728–230735 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Some disorder was observed in **5** in both its [K-(2,2,2-crypt)] and the [K-([18]crown-6)] salts. Each germanium atom in the former has an image, that is, the Ge_9 core has two positions. The disorder in the latter is at the tin atom with two close positions. This makes somewhat less certain the distances in these species. However, such a disorder is quite understandable in light of the very weak interactions between cluster and sequestering agents, and has been observed quite often before.

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Table 2. Crystallographic data for [K-(2,2,2-crypt)]$_2$**1**,[a] [K-([18]crown-6)]$_2$**1**·0.25([18]crown-6)·2en, [K-(2,2,2-crypt)]$_2$**2**·3.5tol, [K-(2,2,2-crypt)]$_2$**3**·tol·en, [K-(2,2,2-crypt)]$_3$**4**·en,[a] [K-(2,2,2-crypt)]$_3$**5**, [K-([18]crown-6)]$_3$**5**·2 en·THF, and [K-(2,2,2-crypt)]$_4$**6**·2 en.

Formula	(K-crypt)$_2$**1**	(K-18C6)$_2$**1**·0.25(18c6)·2 en	(K-crypt)$_2$**2**·3.5 tol	(K-crypt)$_2$**3**·tol·0.5 en	(K-crypt)$_3$**4**·en	(K-crypt)$_3$**5**	(K-18C6)$_3$**5**·2 en·THF	(K-crypt)$_4$**6**·2 en
fw	2184.47	2142.47	2042.40	2214.46	2310.17	2063.87	1909.57	3789.16
space group, Z	$P\bar{1}$, 2	$P\bar{1}$, 4	Cc, 8	$P2_1/c$, 4	$P2_1/c$, 4	$P2_1/c$, 4	$P2_1/c$, 4	$P\bar{1}$, 1
a [Å]	15.714(1)	16.056(1)	13.732(1)	16.768(1)	27.192(2)	16.834(1)	14.378(1)	12.618(3)
b [Å]	16.693(1)	16.850(1)	24.0378(1)	17.949(1)	20.457(2)	20.904(1)	30.157(2)	14.961(3)
c [Å]	17.361(2)	32.336(3)	47.707(3)	30.423(2)	17.151(2)	23.587(1)	17.541(1)	21.589(4)
α [°]	106.347(2)	78.280(3)						90.097(4)
β [°]	98.984(2)	82.054(2)	97.392(1)	93.259(2)	93.560(2)	94.837(1)	95.492(1)	102.601(3)
γ [°]	99.595(2)	75.809(10)						111.103(3)
V [Å^3	4208.4(6)	8268.8(11)	16135.7(2)	9141.9(1)	9524.0(1)	8270.6(7)	7571.1(9)	3694.9(13)
ρ_{calcd} [g cm^{-3}]	1.724	1.721	1.681	1.606	1.611	1.658	1.675	1.703
no. of measured refl.	45190	49422	88978	76833	78720	48770	44778	21422
no. of indep. refl.	20749	28557	39202	16085	16783	14439	13278	12622
no. of used refl.	16248	20759	34835	14402	12703	13661	10282	7102
μ [cm^{-1}]	3.902	3971	4.064	3.708	3.249	3.729	4.057	4.105
$2\theta_{max}$ [°]	56	50	56	50	50	50	50	50
$R1/wR2$ ($I \geq 2\sigma_I$)[b] [%]	3.58/7.68	5.92/13.71	4.10/8.86	3.31/8.56	9.19/18.41	7.45/19.69	4.82/11.25	7.70/18.93
$R1/wR2$ (all data) [%]	5.16/8.27	8.67/15.14	4.88/9.18	3.83/8.88	11.92/19.32	7.71/19.84	6.65/12.24	14.38/23.01

[a] **1** and **4** were structurally characterized also in (Rb-crypt)$_2$**1**·en (Pn, $a = 17.433(1)$, $b = 15.667(1)$, and $c = 37.709(3)$ Å, $\beta = 95.031(2)$°, $V = 10259(1)$ Å^3, $Z = 4$) and (Rb-crypt)$_3$**4**·en·tol ($P\bar{1}$, a = 15.164(6), b = 23.286(8), and c = 29.74(1) Å, $\alpha = 77.557(9)$, $\beta = 89.341(9)$, and $\gamma = 89.802(9)$°, V = 10253(6) Å^3, Z = 4), respectively, but the quality of the refinements was poor. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{[\Sigma[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$, $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$ where $P = [(F_o)^2 + 2(F_c)^2]/3$; A (B) = 0.0347 (0.000) for (K-crypt)$_2$**1**, A (B) = 0.0599 (58.2235) for (K-18c6)$_3$**1**·0.25(18c6)·2en, A (B) = 0.0325 (12.5834) for (K-crypt)$_2$**2**·3.5 tol, A (B) = 0.0394 (19.6685) for (K-crypt)$_2$**3**·tol·0.5 en, A (B) = 0.0495 (115.9095) for (K-crypt)$_3$**4**·en, A (B) = 0.0688 (135.2153) for (K-crypt)$_3$**5**, A(B) = 0.0501 (33.4451) for (K-18c6)$_3$**5**·2en·THF, and A(B) = 0.1208 (0.0) for (K-crypt)$_4$**6**·2en.

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