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Alkylation of Deltahedral Zintl Clusters: Synthesis of $[R–Ge_9–Ge_9–R]^{4-}$ ($R = {}^tBu, {}^sBu, {}^nBu, {}^tAm$) and Structure of $[{}^tBu–Ge_9–Ge_9–{}^tBu]^{4-}$

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Reactions of nine-atom deltahedral clusters (Zintl ions) of germanium, Ge_9^{n-} ($n = 2, 3, 4$), with alkyl chlorides, RCl ($R = {}^tBu, {}^nBu, {}^sBu, {}^tAm$), yielded the corresponding dialkylated dimers of Ge_9 clusters $[R–Ge_9–Ge_9–R]^{4-}$. The ${}^tBu$ derivative with $[K(2,2,2\text{-crypt})]^+$ countercations was characterized in the solid state by single-crystal X-ray diffraction as $[K(2,2,2\text{-crypt})]_4[{}^tBu–Ge_9–Ge_9–{}^tBu]\cdot 7en$ (monoclinic, $C2/c$, $a = 35.0914(10)$ Å, $b = 24.8161(6)$ Å, and $c = 16.8782(5)$ Å, $\beta = 94.0136(17)°$, $V = 14662.0(7)$ Å^3, and $Z = 4$) and in solution by ^1H and ^{13}C NMR. All species were also characterized in solution by electrospray mass spectrometry in the negative-ion mode. These are the first main group deltahedral clusters functionalized with purely organic substituents.

Introduction

The reactivity of nine-atom deltahedral clusters of group 14, known as deltahedral Zintl anions, has been studied extensively in the past few years.[1] It has been shown that these clusters, specifically those of germanium, can participate in a variety of different reactions such as nucleophilic addition of main group organometallic fragments,[2−4] electrophilic addition of transition-metal organometallic fragments,[5−10] transition-metal atom insertion,[11−19] oligo- and polymerization,[20−30] and face-capping by transition-metal organometallic fragments accompanied by face-opening.[11−19] The list of main group organometallic fragments that have been added to the clusters is relatively short and consists of Ph_2Sb-, Ph_2Bi-, Ph_3Sn-, Ph_3Ge-, and Me_3Sn-.[2−4] Nonetheless, the existence of these compounds showed, for the first time, that these clusters can participate in redox reactions and can be functionalized by groups bonded via normal covalent two-center, two-electron exo-bonds to the clusters. The compounds are synthesized by reacting Ge_9 clusters in ethylenediamine solutions of the intermetallic precursors K_4Ge_9 or Rb_4Ge_9 with the organometallic reagents Ph_3Sb, Ph_3Bi, Ph_4Sn, and Me_4Sn or with the corresponding halides

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Ph_3SnCl, Me_3SnCl, and Ph_3GeCl.[2−4] The resulting derivatized species are mono- or disubstituted clusters such as $[Ph_3Sn-Ge_9]^{3-}$, $[Me_3Sn-Ge_9]^{3-}$, $[Ph_3Ge-Ge_9-GePh_3]^{2-}$, $[Me_3Sn-Ge_9-SnMe_3]^{2-}$, and $[Ph_2Bi-Ge_9-BiPh_2]^{2-}$. In addition to these, the previously characterized dimer of clusters $[Ge_9-Ge_9]^{6-}$ was also functionalized, which produced the disubstituted species $[Ph_2Sb-Ge_9-Ge_9-SbPh_2]^{4-}$ and $[Ph_3Sn-Ge_9-Ge_9-SnPh_3]^{4-}$.[3,4]

The reactions with $SbPh_3$ also produced very small amounts of clusters functionalized with two different groups, Ph_2Sb- and $Ph-$ as in $[Ph_2Sb-Ge_9-Ph]^{2-}$.[3] This was the first example of a cluster with a direct cluster-to-carbon exo-bond and suggested that the clusters could potentially be functionalized with strictly organic substituents. However, all attempts to purposely attach phenyl groups by reacting the clusters with chlorobenzene failed to yield crystalline products. Nonetheless, in analogy with the successful reactions with Me_3SnCl and Ph_3GeCl, we also attempted reactions with the analogous carbon-based halides Me_3CCl and Ph_3CCl. Although the reaction with the latter produced only the stable and inert Ph_3C anion, the reaction with the former was successful and produced the dialkylated dimer of Ge_9 clusters $[Me_3C-Ge_9-Ge_9-CMe_3]^{4-}$. We report here the synthesis, crystal structure, and mass spectroscopy characterization of this species as well as the synthesis and mass spectroscopy characterization of other alkylated clusters with exo-bonds to primary, secondary, and tertiary carbon atoms.

Experimental Section

All manipulations were carried out under argon or nitrogen using standard Schlenk-line and glovebox techniques. Ethylenediamine (Alfa-Aesar, 99%) was distilled over sodium metal and stored in a gastight ampule under nitrogen in the glovebox. The Zintl phase precursor compound K_4Ge_9 was synthesized from stoichiometric mixtures of the elements (K, Strem, +99%; Ge, Alfa-Aesar, 99.999%) heated at 900 °C over 2 days in sealed niobium containers jacketed in evacuated fused silica tubes. 2,2,2-Crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane, Acros, 98%), ^{n}BuCl (1-chlorobutane, Sigma-Aldrich, 99.5%), ^{s}BuCl (2-chlorobutane, Acros, +99%), ^{t}BuCl (2-chloro-2-methylpropane, Acros, 99%), and ^{t}AmCl (2-chloro-2-methylbutane, Avocado, 95%) were used as received. Deuterated pyridine (Cambridge Isotope Labs, 99.9%) was stored over molecular sieves.

Synthesis of $[K(2,2,2\text{-crypt})]_4[{}^tBu-Ge_9-Ge_9-{}^tBu]\cdot 7en$ (1). K_4Ge_9 (92 mg, 0.114 mmol) was weighed out in a test tube in the glovebox and subsequently dissolved in ethylenediamine (1.0 mL) by periodic shaking. ^{t}BuCl (0.0875 mL, 0.786 mmol) was then dissolved in ethylenediamine (1.0 mL) in another test tube, and 0.2 mL of this solution was added dropwise to the germanium solution. 2,2,2-Crypt (95 mg, 0.252 mmol) was dissolved in toluene (2 mL), and the solution was carefully layered onto the top of the previous reaction mixture. Large, black, needlelike crystals suitable for single-crystal X-ray diffraction were obtained after allowing the mixtures to sit undisturbed for several weeks. ^{1}H NMR (pyridine-d_5, 300 K): $\delta = 1.68$ (s, $-CH_3$ in $[{}^tBu-Ge_9-Ge_9-{}^tBu]^{4-}$), $\delta = 1.72$ ($-CH_3$ in $[{}^tBu-Ge_9-{}^tBu]^{2-}$), $\delta = 2.45$, 3.46, 3.53 (2,2,2-crypt), $\delta = 1.48$ (br, $-NH_2$ in en), 2.75 (s, -CH_2 in en). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 300 K): $\delta = 40.00$ (s, CH_3 in $[{}^tBu-Ge_9-Ge_9-{}^tBu]^{4-}$), $\delta = 33.26$ (s, quaternary C in $[{}^tBu-Ge_9-Ge_9-{}^tBu]^{4-}$), $\delta = 39.71$ (CH_3 in $[{}^tBu-Ge_9-{}^tBu]^{2-}$), $\delta = 54.63$, 68.40, 71.18 (2,2,2-crypt), $\delta = 46.46$ (s, en), $\delta = 21.79$, 126.23, 129.13, 129.88 (toluene). ES-MS (DMF, negative-ion mode): $m/z = 710.5$ $[{}^tBu-Ge_9]^{-}$.

Preparation of Reaction-Mixture Solutions for Mass Spectrometry. Four test tubes were loaded with K_4Ge_9 (each 75 mg, 0.092 mmol) and ethylenediamine (each 0.75 mL). Added dropwise to each test tube were 0.2 mL ethylenediamine solutions of: (a) ^{t}BuCl (18 mg, 0.156 mmol), (b) the same amount of ^{n}BuCl, (c) the same amount of ^{s}BuCl, and (d) ^{t}AmCl (20.5 mg, 0.154 mmol). The reaction mixtures were then transferred to the mass spectrometer using gastight syringes. ES-MS results for the reactions with BuCl: m/z 710.5 $[Bu-Ge_9]^{-}$, 768.5 $[Bu-Ge_9-Bu]^{-}$, 806.5 $\{(K^+)[Bu-Ge_9-Bu]^{2-}\}^{-}$. ES-MS results for the reaction with ^{t}AmCl: m/z 724.6 $[{}^tAm-Ge_9]^{-}$, 764.5 $\{(K^+)[{}^tAm-Ge_9]^{2-}\}^{-}$, 798.6 $[{}^tAm-Ge_9-{}^tAm]^{-}$, 834.6 $\{(K^+)[{}^tAm-Ge_9-{}^tAm]^{2-}\}^{-}$.

Mass Spectrometry. Electrospray mass spectra (ES-MS) in negative-ion mode were recorded on a Micromass Quattro-LC triple quadropole mass spectrometer (100 °C source temperature, 125 °C desolvation temperature, 2.0−2.8 kV capillary voltage, 25−30 V cone voltage). The samples were introduced by direct infusion with a Harvard syringe pump at 10 μL/min.

NMR Spectroscopy. $^{13}C\{^1H\}$ and ^{1}H NMR spectra were recorded on a Varian UNITYplus 300 MHz spectrometer, locked on the deuterium signal of the deuterated pyridine, and referenced against the farthest downfield peak of the solvent residuals.

Structure Determination. X-ray diffraction data of **1** were collected on a Bruker D8 APEX-II diffractometer equipped with a CCD area detector at 100 K using graphite-monochromated Mo Kα radiation. The single crystal (0.32 mm × 0.28 mm × 0.22 mm, black) was selected under Paratone-N oil, mounted on the fiber, and positioned in the cold stream of the diffractometer. The structure was solved by direct methods and refined on F^2 using the SHELXTL V6.21 package.[31] Crystal data: $[K(2,2,2\text{-crypt})]_4[{}^tBu-Ge_9-Ge_9-{}^tBu]\cdot 7en$, monoclinic, $C2/c$, $a = 35.0914(10)$ Å, $b = 24.8161(6)$ Å, and $c = 16.8782(5)$ Å, $\beta = 94.0136(17)°$, $V = 14662.0(7)$ Å,^{3} $Z = 4$, R1/wR2 = 6.40/16.76% for $I \geq 2\sigma(I)$ and 8.83/18.14% for all data ($2\theta \leq 50°$).

Results and Discussion

Structure. The reaction of an ethylenediamine solution of K_4Ge_9 with ^{t}BuCl produced single crystals of $[K(2,2,2\text{-crypt})]_4[{}^tBu-Ge_9-Ge_9-{}^tBu]\cdot 7en$ (**1**) when layered with a toluene solution of 2,2,2-crypt. An isostructural Rb analogue was also crystallized, but its structure was not fully refined. The structure of the disubstituted dimer of clusters (Figure 1) is virtually identical with that of the analogous dimer of clusters disubstituted with Ph_3Sn, $[Ph_3Sn-Ge_9-Ge_9-SnPh_3]^{4-}$,[4] and is also very similar to the dimer disubstituted with Ph_2Sb, $[Ph_2Sb-Ge_9-Ge_9-SbPh_2]^{4-}$.[3] The two germanium clusters are related by an inversion center and are connected by an intercluster exo-bond of 2.528(1) Å. Although this distance is somewhat longer than that in the tin and antimony analogues, 2.481 and 2.486 Å, respectively, it represents a normal two-center, two-electron Ge−Ge single bond. Similarly related by an inversion center are the clusters of the nonsubstituted dimer $[Ge_9-Ge_9]^{6-}$ with an intercluster distance of 2.488 Å.[20] The nine-atom clusters in $[{}^tBu-Ge_9-Ge_9-{}^tBu]^{4-}$ are tricapped trigonal prisms with one elongated

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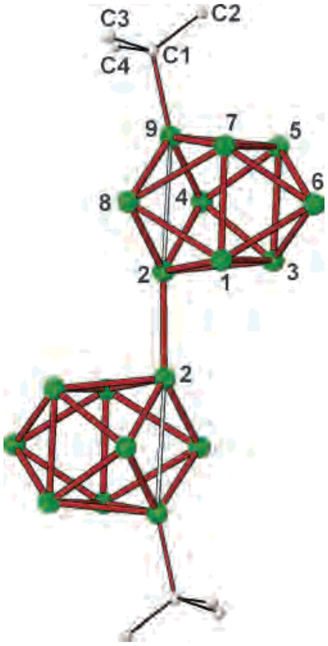

Figure 1. The dialkylated dimer [^{t}Bu−Ge_9−Ge_9−^{t}Bu]$^{4-}$ with the germanium atoms numbered (the two halves are related by an inversion center). There are two positions for the ^{t}Bu groups, but only one is shown. Each Ge_9 cluster is a tricapped trigonal prism (atoms 4, 6, and 8 are capping) with one elongated prismatic edge (shown in white) along which the exo-bonding occurs.

prismatic edge each, as often observed.[1] The two triangular bases of the prism are formed of atoms 1, 2, and 3 and 5, 7, and 9 whereas atoms 4, 6, and 8 cap the rectangular faces (Figure 1). The elongated edge, shown in white in Figure 1, is between atoms 2 and 9 and measures 3.213(1) Å whereas the other two edges of the prism, between atoms 1−7 and 3−5, are much shorter, 2.684(1) and 2.691(1) Å, respectively. As in all other cases of functionalized Ge_9 clusters, the exo-bonding occurs at the ends of the elongated edge and the exo-bonds are nearly collinear with that edge.[1] The remaining distances in the cluster are in the range of 2.570−2.904 Å, which is typical for such clusters.

If naked, a cluster with this geometry is typically a *nido*-species with a charge of −4, i.e., Ge_9^{4-}, and carries 22 cluster-bonding and 18 lone-pair electrons (one lone pair per Ge-atom).[1] When coupled with another cluster, the lone pairs on the two germanium atoms involved in the intercluster bond are replaced with one bonding pair and the charge of the dimer is reduced to −6, i.e., −3 per cluster. When an additional substituent is exo-bonded to each cluster, one more lone pair of electrons per cluster is replaced with a bonding pair and the charge is reduced further by one per cluster because one of the electrons of the bonding pair is provided by the external group. This makes the dialkylated dimer acquire a charge of −4. Thus, although the overall charge is −2 per half dimer, the Ge_9 cluster itself is still a *nido*-species with $2n + 4 = 22$ cluster-bonding electrons. The original charge of −4 is reduced because of the two exo-bonds per cluster and not because of the reduction of the number of cluster-bonding electrons. This is the same charge and electron count observed in the previous cases of disubstituted dimers of Ge_9 clusters.

Although the two Ge_9 clusters are related by an inversion center at the midpoint of the intercluster bond (the four cryptated potassium cations and the seven solvent molecules in the structure are also related by this inversion center), apparently this is not the case for the two exo-bonded ^{t}Bu groups. This causes the appearance of two positions for each butyl group. They were refined with partial occupancies that add up to one alkyl group per cluster (Figure S1 in Supporting Information). The corresponding Ge−C distances, 2.002(5) and 2.012(5) Å, are slightly longer than the statistical mean distance of 1.965 Å on the basis of 552 distances between sp^3 hybridized Ge and C found in the Cambridge Structural Database.[32] Nonetheless, the range of such distances is quite broad, from 1.715 to 2.242 Å, and the two distances reported here compare very well with other Ge−^{t}Bu distances such as those observed in tetrakis(*tert*-butyl-germanium-sesquichlorosulfide), 2.003 Å, 4,8-dibromo-octa-*tert*-butyl-tetracyclo-(3.3.0.02,7.03,6) octagermane, 2.020 Å, 1,3-dibromohexa-*tert*-butyltrigermane, 2.017 Å, and tetrakis(tri-*tert*-butylgermy1)cyclotrigermene, 2.011 Å.[33] Similar minor elongations are observed for the exo-bonds in the other disubstituted dimers [Ph_3Sn−Ge_9−Ge_9−$SnPh_3$]$^{4-}$ and [Ph_2Sb−Ge_9−Ge_9−$SbPh_2$]$^{4-}$.

Solution Studies. Electrospray mass spectra in negative-ion mode were taken of crystals of [K(2,2,2-crypt)]$_4$[^{t}Bu−Ge_9−Ge_9−^{t}Bu]·7en dissolved in DMF as well as of all reaction mixtures (before layering with toluene/2,2,2-crypt solutions). The specific isotope pattern of the nine germanium atoms per cluster provides very distinct mass envelopes that make the ion identification unequivocal. A drawback of the electrospray methodology is the tendency of redox active species, Zintl anions in this case, to fragment electrochemically during the ionization process.[34] In the negative-ion mode, this process for highly charged Zintl anions is expressed in the lowering of high negative charges by the loss of electrons that were possibly needed for bonding. Thus, as is often the case, observed in the spectra are only anions that can withstand reduction of the charge to −1. Anions with higher charges are sometimes found coupled with cations into complex monoanions. In the case of **1** dissolved in DMF the negative-ion spectrum showed a very strong peak for the monoanion [^{t}Bu−Ge_9]$^-$ which represents half of the dialkylated dimer (Figure 2). The whole dialkylated dimer itself was not observed in any of the spectra. The fragmentation is most likely due to the loss of two electrons caused by the relatively high cone voltage of 25−30 V used for the ES-MS experiment. Lower voltages that could potentially preserve higher-charged anions produced very noisy spectra that could not be interpreted.

The most likely reason for the observation in the mass spectra of a monoanion of the monoalkylated monomer

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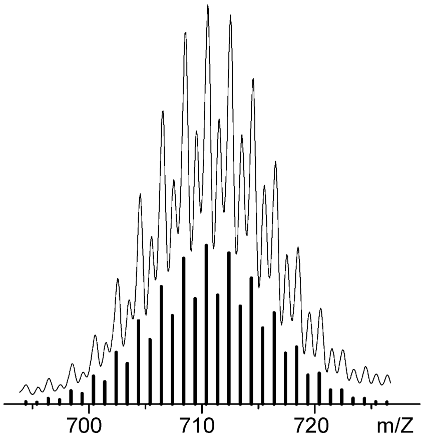

Figure 2. [^{t}Bu$-$Ge$_9$]$^-$ observed in the ES-MS (negative-ion mode) of a DMF solution of **1**. Shown under the peak is the theoretical isotope distribution for the anion.

instead of a monoanion of the dialkylated dimer is the following. As already mentioned, monosubstitution of a *nido*-Ge$_9$$^{4-}$ results in species with a charge of -3 as the observed [Me$_3$Sn$-$Ge$_9$]$^{3-}$ and [Ph$_3$Sn$-$Ge$_9$]$^{3-}$. We have shown before that in ethylenediamine solutions these Ge$_9$$^{4-}$ clusters are in equilibria with the less-reduced clusters Ge$_9$$^{3-}$ and Ge$_9$$^{2-}$ and solvated electrons. It is reasonable to speculate that, similar to Ge$_9$$^{4-}$, the latter two clusters can be monosubstituted to form [R$-$Ge$_9$]$^{2-}$ and [R$-$Ge$_9$]$^-$, respectively. The latter represents an alkylated *closo*-Ge$_9$$^{2-}$ cluster that is expected to be relatively stable and sufficiently long-lived for observation in the electrospray mass spectra.

The spectra of the reaction mixtures of germanium clusters with Cl$-$CH$_2$CH$_2$CH$_2$CH$_3$ (^{n}BuCl), CH$_3$CH(Cl)CH$_2$CH$_3$ (^{s}BuCl), and (CH$_3$)$_2$C(Cl)CH$_2$CH$_3$ (^{t}AmCl) showed the same half of a dialkylated dimer [R$-$Ge$_9$]$^-$ as a major peak in the spectra (Figure 3). The reaction with ^{t}Am also shows the dianion [R$-$Ge$_9$]$^{2-}$ paired with K$^+$ in the monoanion {(K$^+$)-[^{t}Am$-$Ge$_9$]$^{2-}$}$^-$. The existence of all of these species shows that cluster functionalization with organic halides is not unique for tertiary carbon atoms but also occurs with primary and secondary halides. Another very important observation from the mass spectra of the reaction mixtures is that these reactions also produce the dialkylated monomeric clusters of [R$-$Ge$_9$$-$R]$^{2-}$ (Figure 3). Thus, peaks corresponding to [R$-$Ge$_9$$-$R]$^-$ and {(K$^+$)[R$-$Ge$_9$$-$R]$^{2-}$}$^-$ are observed in all of the spectra. As already discussed, such disubstituted clusters have been structurally characterized before, with pairs of substituents such as Me$_3$Sn$-$, Ph$_3$Sn$-$, Ph$_3$Ge$-$, Ph$_2$-Sb$-$, and Ph$_2$Bi$-$ bonded along the elongated prismatic edges of the clusters. Although none of the dialkylated monomers were crystallized, it is quite likely that their structures are analogous to the corresponding monomers with two organometallic substituents. Their crystallization may be possible with appropriate countercations and different combinations of solvents and layering agents. The significance of these results is that simple reactions with organic halides can attach organic substituents to the clusters or, viewed conversely, clusters can be attached to organic molecules with sp^3 hybridized carbon atoms.

In addition to the mass spectrometry, the dialkylated dimers of [^{t}Bu$-$Ge$_9$$-Ge_9$$-$^{t}Bu]$^{4-}$ were studied by ^{13}C{^{1}H} and ^{1}H NMR spectroscopy (spectra in Supporting Information). The ^{13}C spectrum of **1** dissolved in pyridine-d_5 shows a very strong signal from the methyl carbon atoms of the

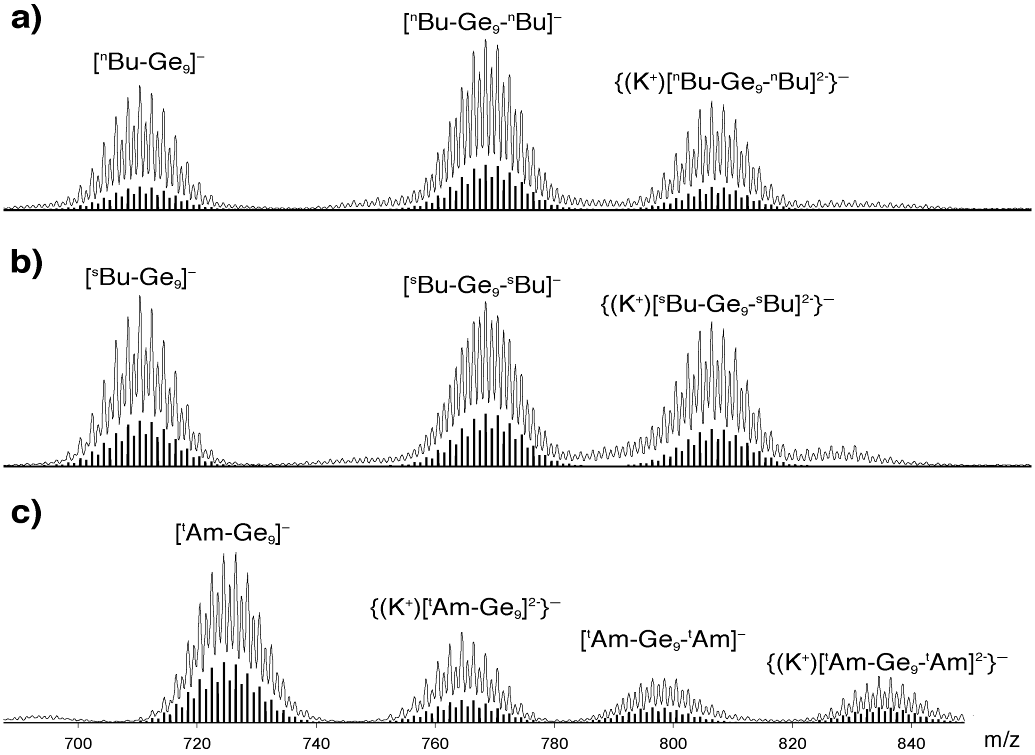

Figure 3. Electrospray mass spectra (negative-ion mode) of the reaction mixtures of ethylenediamine solutions of K$_4$Ge$_9$ reacted with: (a) ^{n}BuCl, (b) ^{s}BuCl, and (c) ^{t}AmCl. Shown under each peak is the calculated isotope distribution for the corresponding ion. The spectrum of the reaction with ^{t}BuCl (in Supporting Information) is virtually identical with those seen in a and b.

^{t}Bu substituents at 40.00 ppm and a much weaker peak for the corresponding tertiary carbon atom at 33.26 ppm. A weak resonance at 39.71 ppm is likely from the methyl carbon atoms of the dialkylated monomer $[^t\mathrm{Bu{-}Ge_9{-}}^t\mathrm{Bu}]^{2-}$. As already discussed, the mass spectra of the reaction mixtures (before crystallization) always show large amounts of the latter anion. It is reasonable to assume that a small amount of it is present in one form or another in the solid product dissolved in pyridine for these measurements. (This hypothesis is further confirmed by the ^{1}H NMR discussed below.) Also visible in the spectrum are some residual toluene signals left from the crystallization, 2,2,2-crypt, and ethylenediamine solvent captured in the crystal structure.

All species identified from the ^{13}C spectrum are nicely confirmed by the ^{1}H NMR. A very sharp peak at 1.68 ppm corresponds to the ^{t}Bu groups of $[^t\mathrm{Bu{-}Ge_9{-}Ge_9{-}}^t\mathrm{Bu}]^{4-}$, and another very sharp but much smaller peak at 1.72 ppm corresponds most likely to the disubstituted dimer $[^t\mathrm{Bu{-}Ge_9{-}}^t\mathrm{Bu}]^{2-}$. Also present are three peaks for the 2,2,2-crypt and one for the CH_2 groups of ethylenediamine. The integrated area under the two ^{t}Bu peaks corresponds to 0.11 of the area under the three 2,2,2-crypt peaks and is virtually identical with the predicted ratio of 0.12 generated on the basis of the formula of the compound, $[\mathrm{K(2,2,2\text{-}crypt)}]_4$-$[^t\mathrm{Bu{-}Ge_9{-}Ge_9{-}}^t\mathrm{Bu}]$•7en. The NH_2 protons of the ethylenediamine solvent molecules in the structure show a broad peak at 1.48 ppm, whereas a second broad peak at 5.02 ppm can be attributed to the corresponding amide. Amide formation is typical for ethylenediamine in the presence of highly reduced clusters which can provide electrons for its slow reduction and deprotonation. When the sample is cooled to −30 °C, the two broad peaks narrow substantially (and shift slightly) due to slower exchange of protons between the amine and the amide, but nothing else changes in the spectrum.

One very important feature of both the ^{13}C and ^{1}H NMR spectra is that the peaks of the attached ^{t}Bu groups are very sharp and, therefore, arise from diamagnetic species. This fact combined with the single predominant ^{t}Bu peak in both spectra suggests that the dialkylated dimer species is intact in solution. Eventual fragmentation to monoalkylated monomers would generate either the paramagnetic $[\mathrm{R{-}Ge_9}]^{2-}$ species (ruled out by the spectra) or the disproportionation products $[\mathrm{R{-}Ge_9}]^{-}$ and $[\mathrm{R{-}Ge_9}]^{3-}$. The latter two should produce two different but nearly equal sets of peaks in the ^{13}C and ^{1}H NMR spectra, but this is not what is observed in the spectra.

Discussion. We have shown before that the functionalization of Ge_9 clusters with main group organometallic halides can proceed via initial generation of an anion of the organometallic fragment by two-electron reduction of the reagent with solvated electrons from the equilibria $Ge_9^{4-} \leftrightarrows Ge_9^{3-} + e^- \leftrightarrows Ge_9^{2-} + 2e^-$. The organometallic anions are very nucleophilic and interact with the LUMO of Ge_9^{2-}, which happens to be very low lying and spatially accessible.[4] This reaction path, however, does not discard possible functionalization with radical fragments generated by one-electron reduction of the reagent to the corresponding organometallic radical and a halide anion. It is very likely that, depending on the relative stabilities of the radical and the anion as well as the nucleophilicity of the latter, the reaction can proceed along both paths or predominantly along one of them. In the case of the alkyl halides, it is quite unlikely that the reactions proceed via alkyl anions because of their very high basicity. Such an alkyl anion would very easily abstract a proton from the ethylenediamine solution to form the corresponding alkane and an amide anion. A similar process was observed in the reactions of Ge_9 clusters with Ph_3Sb and Ph_4Sn where the generated phenyl anions abstracted protons to form benzene, which was subsequently observed in the NMR spectra. The organic radicals, on the other hand, have enough lifetime in ethylenediamine to bond to the clusters and it is very likely that the reactions with alkyl halides proceed along this radical pathway instead. It is unlikely for the radicals to bond to the fully reduced cluster Ge_9^{4-} because of the very antibonding character and very high energy of its LUMO. On the other hand, the LUMO of Ge_9^{2-} and the half-filled HOMO of Ge_9^{3-} are relatively low and accessible, and the alkyl radical can bond to these clusters to form $[\mathrm{R{-}Ge_9}]^{2-}$ radicals and $[\mathrm{R{-}Ge_9}]^{3-}$, respectively. The radicals can pair to form the dialkylated dimers whereas both $[\mathrm{R{-}Ge_9}]^{2-}$ and $[\mathrm{R{-}Ge_9}]^{3-}$ can undergo additional alkylation to form $[\mathrm{R{-}Ge_9{-}R}]^{2-}$.

The fact that deltahedral Zintl ions can be functionalized by reactions with common primary, secondary, and tertiary organic halides may have great implications in this and other areas of chemistry. Furthermore, although substituted derivatives of the Ge_9^{2-} clusters have not yet been structurally characterized, it is encouraging that the monosubstituted species $[\mathrm{R{-}Ge_9}]^{-}$ are stable enough to be seen in the electrospray mass spectra. Even more importantly, the corresponding disubstituted clusters of the parent Ge_9^{2-} will be neutral, $[\mathrm{R{-}Ge_9{-}R}]^0$, and will not need accompanying countercations.

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Supporting Information Available: X-ray crystallographic file in CIF format; ORTEP drawing of $[^t\mathrm{Bu{-}Ge_9{-}Ge_9{-}}^t\mathrm{Bu}]$ with anisotropic displacement ellipsoids showing the two orientations of the ^{t}Bu groups; mass spectrum of the reaction mixture of ethylenediamine solution of K_4Ge_9 with ^{t}BuCl, ^{13}C{^{1}H}, and ^{1}H NMR spectra of $[\mathrm{K(2,2,2\text{-}crypt)}]_4[^t\mathrm{Bu{-}Ge_9{-}Ge_9{-}}^t\mathrm{Bu}]$•7en dissolved in pyridine-d_5. This material is available free of charge via the Internet at http://pubs.acs.org.

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