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Functionalization of Nine-Atom Deltahedral Zintl Ions with Organic Substituents: Detailed Studies of the Reactions

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Abstract: Presented are the results of a systematic investigation of the reactions of nine-atom deltahedral clusters of germanium (Zintl ions, Ge_9^{n-}) with alkynes and alkyl halides that result in alkenylation and alkylation of the clusters, respectively. The reaction pathways have been probed in depth using various, appropriately substituted alkynes and organic halides, including some typical mechanistic probes and radical clocks. The regioselectivity and stereoselectivity of the reaction with alkynes was examined by systematically varying the steric and electronic nature of the substituents. The studies showed that the Zintl clusters act as strong, anionic nucleophiles toward the alkynes and primary and secondary alkyl halides but, most likely, as electron donors in reactions with tertiary alkyl halides and halogenated olefins. The pentenyl and methylcyclopropyl functionalized clusters, $[Ge_9(C_5H_9)]^{3-}$ and $[Ge_9(CH_2CH(CH_2)_2)]^{2-}$, respectively, were crystallographically characterized in compounds with $[K\text{-crypt}]^+$ countercations. All compounds were also analyzed by NMR and electrospray mass spectrometry.

Introduction

The chemistry of deltahedral Zintl ions has continued to expand at an impressive rate over the past decade.[1] Compared to the beginning, when the original Zintl ions were made by dissolving a main-group metal in reducing liquid ammonia/alkali-metal solutions,[2−9] the current synthetic, structural, and compositional diversity of species with deltahedral Zintl ions is enormous. Broadly speaking, these species can be categorized as: (i) oligomers of clusters including dimers,[10−12] trimers,[13] tetramers,[14] and polymers;[15−17] (ii) clusters functionalized with main-group organometallic fragments based on Group 14 and Group 15 elements;[18−20] (iii) clusters centered and/or functionalized with d-block metals or organometallic fragments including early transition metals,[21−26] iron and cobalt species,[27,28] precious metals,[29−43] coinage metals,[44,45] and post-transition metals;[46−50]

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anti and (iv) heteroatomic deltahedral Zintl ions.[51,52] More recently a new category has emerged, namely the category of organo-Zintl clusters.[19,53−56] This latest advancement is particularly promising as it brings Zintl cluster chemistry into contact with more traditional organic chemistry. The new organo-Zintl species complement nicely the already existing body of germanium-based metalloid clusters.[57−59] In terms of bonding modes, these various sectors of germanium chemistry span from "normal" 2-center-2-electron bonding in the common organogermanium species, to low-valent-low-coordination bonding in the germanium metalloid clusters, and to electron-deficient, delocalized bonding modes in the deltahedral Zintl ions.

Although deltahedral Zintl ions have been known for a very long time, their chemistry and reactivity toward other reagents have been studied very little. The reasons for this are that (a) taken alone, the naked Zintl clusters of Group 14 are too reducing and, thus, "incompatible" with many organic substrates, i.e., the clusters are often oxidized to the corresponding neutral element, and (b) they can be handled only in a limited number of very specific solvents such as liquid ammonia, ethylenediamine, and occasionally dimethylformamide and crown ethers, i.e., solvents that are not common for typical chemical reactions. However, we have shown that the reducing strength of the clusters is lowered significantly when functionalized with organic groups via reactions with alkynes or alkyl halides.[53−56] Thus, while naked Ge_9^{4-} clusters readily reduce tetra-alkyl ammonium cations R'_4N^+, the corresponding disubstituted species $[R\text{-}Ge_9\text{-}R]^{2-}$ do not. This allows for ion exchange of the original alkali-metal countercations for such quaternary ammonium cations, some with long chain alkyl groups, to form $[R'_4N]_2[R\text{-}Ge_9\text{-}R]$. The latter compounds are soluble in many common and less polar solvents—some as nonpolar as toluene.[55]

While the reactions of deltahedral Zintl clusters with transition-metal and main-group organometallic compounds have been studied before and their pathways are now fairly well understood,[1,18,30,34,35,46] a thorough investigation of the reactions with organic reagents had not been carried out until now. Herein we delineate the reaction paths of such reactions between nine-atom germanium Zintl clusters and alkynes, both with terminal and internal triple bonds, and the results are compared with the reactivity of the clusters toward organic halides.

Results

We have already shown that mono- and dialkenylated nine-atom clusters of germanium, $[Ge_9(CR{=}CHR')]^{3-}$ and $[Ge_9(CR{=}CHR')_2]^{2-}$, respectively, are readily accessible by reacting Ge_9-clusters with the corresponding alkynes. The addition of the alkyne is accompanied by hydrogenation of the triple bond to a double bond, and the cluster ends up in a *cis*-geometry with respect to the other alkene substituent, i.e., the R′ group.[54−56] The same nine-atom clusters can also be alkylated and alkenylated by reactions with the corresponding alkyl or alkenyl halides RX where the halide can be at a primary, secondary, or tertiary carbon atom.[53,54,56] Furthermore, these reactions are not specific only for germanium clusters but proceed similarly for Sn_9-clusters as well.[56]

We have also shown before that the germanium clusters can be functionalized with the simplest alkenyl group, namely vinyl, by reacting them with the trimethylsilyl (TMS) disubstituted acetylene, TMS−C≡C−TMS, along the following unbalanced equation:[55]

$$K_4Ge_9 + 2TMS{-}C{\equiv}C{-}TMS \rightarrow K_2[Ge_9(CH{=}CH_2)_2] \quad (1)$$

Both mono- and disubstituted species, $[Ge_9{-}CH{=}CH_2]^{3-}$ and $[Ge_9(CH{=}CH_2)_2]^{2-}$, can be synthesized by controlling the ratio of the reagents. A number of questions related to the reaction path were not answered at the time of the initial report, and eq 1 above could not be balanced. For example, it was not clear where the hydrogen for the hydrogenation of the triple bond and for replacing the trimethylsilyl groups came from. Similarly unknown was the fate of the trimethylsilyl groups and the type of reaction for their substitution. We have now addressed these and similar questions about reactions of cluster functionalization with organic groups.

First, we investigated the fate of the silyl groups at the end of the above reaction. Silyl groups are known to be nitro- and oxo-philic,[60] and the reactions between silylhalides and amines or alcohols are known to proceed cleanly to the corresponding silyl-substituted compounds, i.e., $TMS{-}X + H_2NR \rightarrow TMS{-}NHR + HX$ and $TMS{-}X + R{-}OH \rightarrow TMS{-}OR + HX$.[60] In the case of ethylenediamine the reaction with TMS−Cl produces $TMS{-}NHCH_2CH_2NH_2$:

$$TMS{-}Cl + H_2NCH_2CH_2NH_2 \rightarrow [TMS{-}NH_2CH_2CH_2NH_2]^+ + Cl^- \rightarrow TMS{-}NHCH_2CH_2NH_2 + HC1 \quad (2)$$

We carried out this reaction and compared the NMR signal of the TMS protons of the product $TMS{-}NHCH_2CH_2NH_2$ with that in the spectrum of the reaction mixture of an ethylenediamine solution of K_4Ge_9 and TMS−C≡C−TMS (Figure S1 in Supporting Information). The two chemical shifts were identical and indicated that the cleaved silyl groups end up as $TMS{-}NHCH_2CH_2NH_2$. Therefore, eq 1 can be improved by adding a second product as follows

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$$K_4Ge_9 + 2TMS{-}C{\equiv}C{-}TMS + 4H_2NR \rightarrow K_2[Ge_9(CH{=}CH_2)_2] + 4TMS{-}NHR \quad (3)$$

Equation 2 is still not balanced; however, because the hydrogen for hydrogenation of the triple bond of the alkyne is not included. It has been reasonably postulated that the source for this hydrogen is the ethylenediamine solvent. We have now carried out an isotope labeling study in order to learn more about this hydrogenation process. It turns out that the reaction between Ge_9-clusters and TMS−C≡C−TMS can be successfully carried out in any solvent that (a) sufficiently dissolves the starting precursor and (b) either has sufficiently acidic protons, as does ethylenediamine for example, or is combined with a sufficiently acidic additive (in stoichiometric amount with respect to the clusters). Thus, the precursor K_4Ge_9 is partially soluble in pyridine (in the presence of sequestering agents such as 2,2,2-crypt). We have shown that the clusters can be alkylated in this solvent by reactions with alkyl halides, including primary, secondary, and tertiary halides because these reactions do not need external protons. On the other hand, the reaction with TMS−C≡C−TMS does not proceed in pyridine because the solvent does not have acidic enough protons. (It produces only trace amounts of substituted clusters, where the protons perhaps come from minor impurities). However, when a small amount of methanol is added to the pyridine solution, the analogous vinyl-functionalized clusters are synthesized. We carried out the reaction with TMS−C≡C−TMS in pyridine with deuterated methanol (CD_3OD) and observed formation of only the completely deuterated product $[D_2C{=}CD{-}Ge_9{-}CD{=}CD_2]^{2-}$. The latter was confirmed by electrospray mass spectrometry (ES-MS) where the mass of the anion is higher by six atomic mass units relative to the mass of the protio version (Figure 1). It should be pointed out that the major reaction of the clusters with methanol and TMS−C≡C−TMS in pyridine is the reduction by the clusters of the methanol's protons to deuterium gas. Nonetheless, some of the clusters undergo the secondary reaction with the available alkyne and then abstract deuterium from the methanol.

Combining the observations from above, we can now write a balanced equation for the reaction between Ge_9-clusters and TMS−C≡C−TMS in ethylenediamine (shown as H_2NR) as follows

$$K_4Ge_9 + 2TMS{-}C{\equiv}C{-}TMS + 6H_2NR \rightarrow [K]_2[Ge_9{-}(CH{=}CH_2)_2] + 4TMS{-}NHR + 2K{-}NHR \quad (4)$$

Vinyl addition can also be achieved by a reaction with the monosilylated acetylene, $R_3Si{-}C{\equiv}C{-}H$, and the reaction yields again the expected vinyl disubstituted cluster:

$$K_4Ge_9 + 2Et_3Si{-}C{\equiv}C{-}H + 4H_2NR \rightarrow [K]_2[Ge_9(CH{=}CH_2)_2] + 2Et_3Si{-}NHR + 2K{-}NHR \quad (5)$$

Independent of the reaction, the resulting anions $[Ge_9(CH{=}CH_2)_2]^{2-}$ can be crystallized with 18-crown-6 as a cation-sequestering agent, and the structure is identical with the already reported one for $[K{-}(18\text{-crown-}6)]_2[Ge_9(CH{=}CH_2)_2]$.[55] Its mass and NMR spectra are in agreement as well.

Since terminal alkynes R−C≡C−H add to the Ge_9-clusters but are also easily deprotonated by strong bases to alkynide anions $R{-}C{\equiv}C^-$, we investigated whether the clusters react with these anions. The latter were separately prepared by a reaction of triethylsilylacetylene $Et_3Si{-}C{\equiv}C{-}H$ with 1 equiv of K−HMDS ($K{-}N(SiMe_3)_2$):

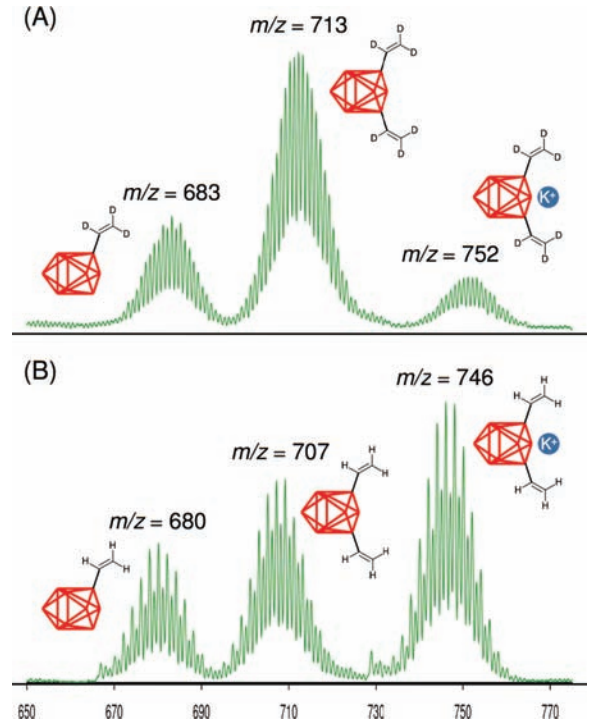

Figure 1. Electrospray mass spectra (negative-ion mode) showing (A) $[Ge_9{-}CD{=}CD_2]^-$, $[Ge_9{-}(CD{=}CD_2)_2]^-$, and $\{[K^+][Ge_9{-}(CD{=}CD_2)_2]^{2-}\}^-$ and (B) $[Ge_9{-}CH{=}CH_2]^-$, $[Ge_9{-}(CH{=}CH_2)_2]^-$, and $\{[K^+][Ge_9{-}(CH{=}CH_2)_2]^{2-}\}^-$).

$$Et_3Si{-}C{\equiv}C{-}H + K{-}N(TMS)_2 \rightarrow Et_3Si{-}C{\equiv}C{-}K + H{-}N(TMS)_2 \quad (6)$$

The NMR of the product confirmed the complete deprotonation of the alkyne by the disappearance of the alkyne proton signal and the appearance of a signal from the amine protons (Figure S2 in Supporting Information). When this anion is added to an ethylenediamine solution of Ge_9-clusters, there seems to be no noticeable reaction for over 2 h according to both NMR and mass spectrometry. However, after that period the corresponding vinyl-substituted cluster slowly begins to form and becomes detectable by NMR. By contrast, the reaction with the corresponding alkyne $Et_3Si{-}C{\equiv}C{-}H$ begins yielding the disubstituted product within minutes.

To further investigate the mechanism of addition and hydrogenation of the alkynes, we carried out a reaction of germanium clusters with deuterated triethylsilylacetylene $Et_3Si{-}C{\equiv}C{-}D$ prepared by quenching the available potassium alkynide $Et_3Si{-}C{\equiv}CK$ with deuterated methanol CD_3OD (Figure S2 in Supporting Information). Surprisingly, however, the ^1H NMR of the reaction in ethylenediamine showed predominantly the protio-vinyl disubstituted cluster, i.e., $[H_2C{=}CH{-}Ge_9{-}CH{=}CH_2]^{2-}$. (The anion was later crystallized with 18-crown-6, yielding the already reported structure.[55]) This unexpected result led to subsequent investigation of the degree of retention of the isotope enrichment of $Et_3Si{-}C{\equiv}C{-}D$ under our specific reaction conditions. Thus, when catalytic amount of K−HMDS is added to ethylenediamine solution of $Et_3Si{-}C{\equiv}C{-}D$, the ^1H NMR spectrum shows near complete replacement of the deuterium with protio-hydrogen within a few minutes indicating that the enrichment is not sustained in the

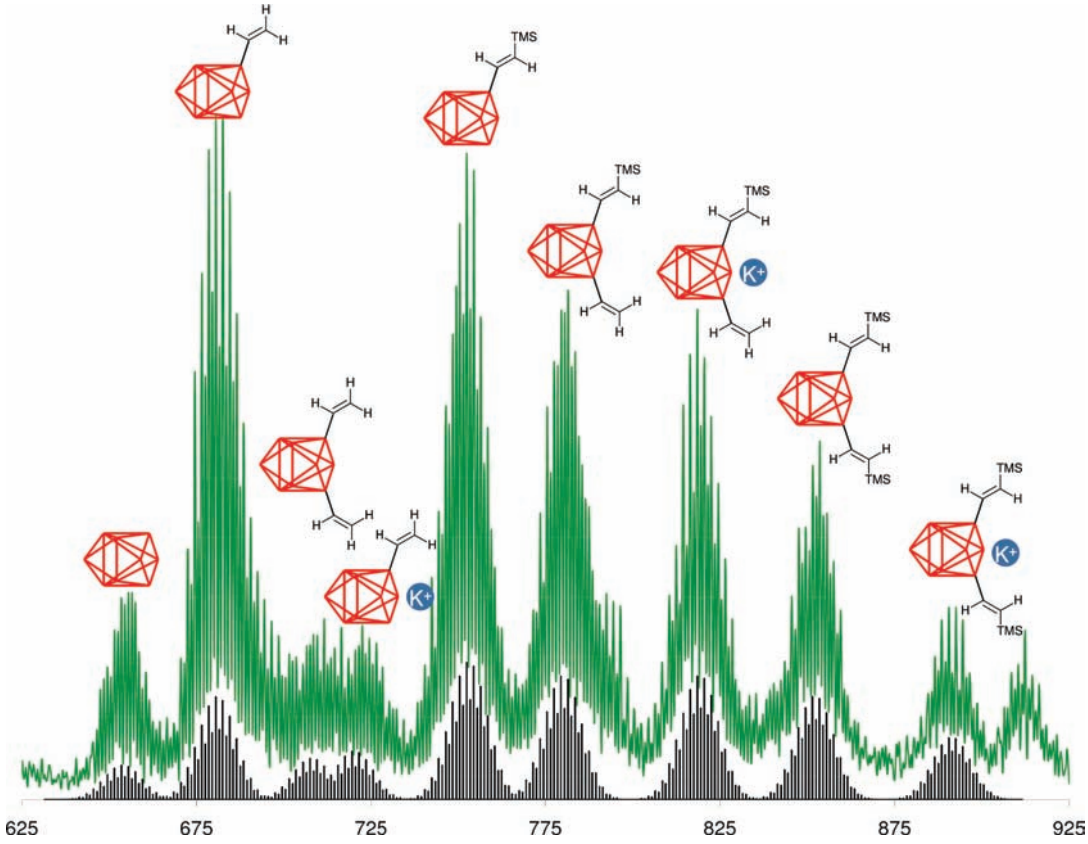

Figure 2. Electrospray mass spectrum (negative-ion mode) of the reaction of Ge_9^{4-} with 2-bromovinyltrimethylsilane taken a few minutes after mixing the reagents, showing mono- and disubstituted clusters with vinyl substituents still bearing the trimethylsilyl group. (Green spectrum, experimental; black bars, theoretical).

presence of strong bases (Figure S2 in Supporting Information). The deuterium is replaced quickly by protons from the ethylenediamine in a process obviously catalyzed by the available amide anions $(TMS)_2N^-$.

By analogy with the previously reported reactions of clusters with alkyl and alkenyl halides we carried out similar reactions with TMS-substituted alkenyl halides, namely TMS−C(Br)═CH_2 and TMS−CH═CHBr. These two halides were selected in order to check whether or not they add simple vinyl groups to the clusters as in the reactions with TMS-substituted alkynes. The two reactions proceeded identically and the final product was indeed the same vinyl disubstituted cluster, $[H_2C{=}CH{-}Ge_9{-}CH{=}CH_2]^{2-}$, confirmed by both mass spectrometry and single-crystal X-ray diffraction of the crystallized compound with 18-crown-6 cation-sequestering agent.[55] However, the mass spectra taken within a few minutes after mixing the reagents showed clusters predominantly functionalized with TMS-substituted vinyl groups, i.e., [CH_2═CH−Ge_9−CH═CH−TMS] and [TMS−CH═CH−Ge_9−CH═CH−TMS] (Figure 2 and Figure S3 in Supporting Information). After ∼4 h almost all clusters become disubstituted with TMS-free vinyl substituents. The net reaction can be written as the following

$$K_4Ge_9 + 2Br(TMS)C{=}CH_2 + 2H_2NR \rightarrow K_2[Ge_9(CH{=}CH_2)_2] + 2KBr + 2TMS{-}NHR \quad (7)$$

By contrast, vinyltrimethylsilane TMS−CH═CH_2 and trimethylsilylcyanide TMS−C≡N do not add to the clusters.

A reaction of Ge_9-clusters with 2-pentyne was carried out in order to confirm that not only terminal alkynes but also alkynes with internal triple bonds add to the clusters and also to test the stereo- and regiochemistry of the addition. The reaction produced the expected pentenyl-substituted Ge_9-clusters, and the electrospray mass spectra of the reaction mixture showed both mono- and disubstituted species (Figure S4 in Supporting Information). An equimolar reaction produced exclusively single crystals of the monosubstituted species (**1**) crystallized with potassium countercations sequestered by 2,2,2-crypt, and their structure was determined by single-crystal X-ray diffraction. It revealed the coexistence of the two possible regioisomers, $[CH_3C(Ge_9){=}CHCH_2CH_3]^{3-}$ (**1a**) and $[CH_3CH{=}C(Ge_9)CH_2{-}CH_3]^{3-}$ (**1b**), which differ only in the point of attachment of the Zintl cluster to the alkene, either at the second or the third carbon atoms (Figure 3). However, in both structures the alkyl groups are *trans* to each other and, therefore, the cluster is again in a *cis* geometry. The shape of the cluster, as in all naked and substituted clusters, can be described as a distorted tricapped trigonal prism with one elongated trigonal prismatic edge parallel to the pseudo-3-fold axis. The pentenyl group in **1** is bonded to one of the two germanium atoms forming that elongated edge, Ge1 (Figure 4). The observed disorder in the pentenyl group is due to superposition of *trans* $CH_3{-}C{=}CH{-}CH_2CH_3$ and *trans* $CH_3CH_2{-}C{=}CH{-}CH_3$ (the italicized carbon atom is bonded to the cluster) in about a 75:25 ratio. The two different modes of bonding affect slightly the positioning of the cluster in the structure and it is also refined in two slightly different orientations in a 75:25 ratio. Although the anion is partially disordered, the bond geometric parameters are within the range of what would be expected for a monosubstituted cluster. The elongated edge Ge1−Ge4 of the major fragment is significantly longer, 3.349(2) Å, than the other two prismatic vertical edges

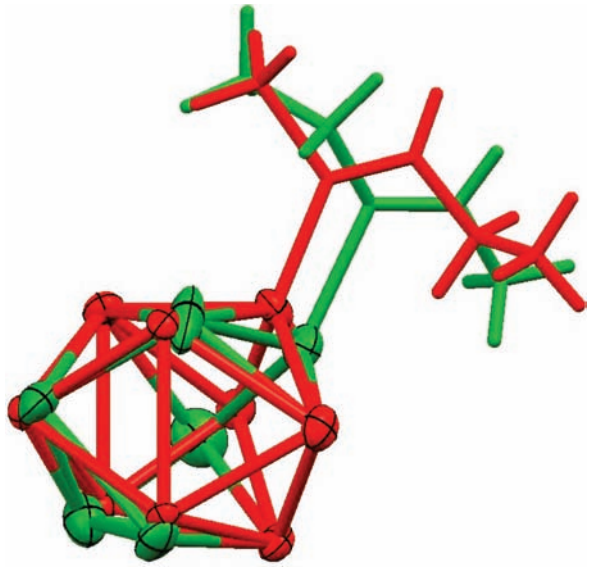

Figure 3. ORTEP drawing showing the two independently refined clusters substituted to the pentenyl fragment at the C2 (red) and C3 (green) positions.

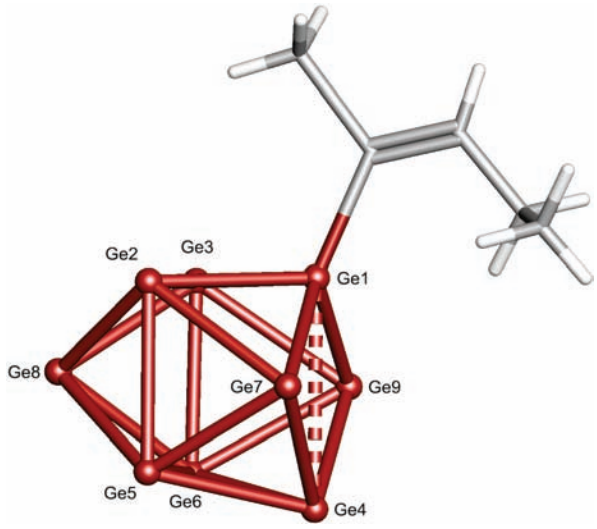

Figure 4. $[Ge_9{-}C(CH_3){=}CH{-}CH_2CH_3]^{3-}$ showing the distorted tricapped trigonal prismatic structure with one elongated edge (Ge1−Ge4).

Ge3−Ge6, 2.778(3) Å, and Ge2−Ge5, 2.752(6) Å (Figure 4). Overall, the distances within the cluster are very similar to the known monosubstituted clusters such as $[Ge_9{-}Ge_9]^{6-}$, $[Ge_9{-}SnMe_3]^{3-}$, and $[Ge_9{-}SnMe_3]^{3-}$.[10,18] The Ge−C distance in the main residue $[Ge_9{-}C(Me){=}CH{-}CH_2CH_3]^{3-}$ is 2.04(1) Å. Although the precision of this distance is lower due to the disorder, this is within the range for a Ge−C(sp^2) bond distance (1.82−2.05 Å) according to the Cambridge Structural Database.[62]

^{1}H NMR of redissolved crystals of **1** in pyridine-d_5 (Figure 5) showed the two regioisomers **1a** and **1b** in equal amounts (49:51 by NMR integration) indicating that the ratio of regioisomers varies from crystal to crystal but the overall sample shows a statistical mixture. Stereochemically however, both **1a** and **1b** exhibit *trans* geometry for the methyl and ethyl groups which means that the cluster is always in a *cis* position. The observed splitting pattern and strength of coupling for the single olefinic proton are distinct for each specific regio- and stereochemistry. Thus, the NMR signal of this proton in $CH_3(Ge_9)C{=}C\mathit{H}{-}CH_2CH_3$ is split into a triplet of quartets, reflecting coupling to both the methyl and the methylene protons on either side of the double bond. The strength of the coupling is 1 Hz to the three methyl protons, i.e., $C\mathit{H}_3(Ge_9)C{=}C\mathit{H}{-}CH_2CH_3$, and 7 Hz to the two adjacent methylene protons, i.e., $CH_3(Ge_9)C{=}C\mathit{H}{-}C\mathit{H}_2CH_3$. The strength of the coupling is reversed in $CH_3CH_2(Ge_9)C{=}C\mathit{H}{-}CH_3$, i.e., it is 1 Hz to the two methylene protons and 7 Hz to the three methyl protons. This results in a quartet of triplets instead. A similar analysis can be performed for the remaining protons of the two isomers, and they all are in agreement with an equimolar mixture of the two regioisomers with *trans* alkyl groups (Figure 5).

Next we investigated a reaction of clusters with an alkyne with two very sterically and electronically different substituents, namely phenyl and methyl groups in Ph−C≡C−Me. This resulted in the cluster bonded exclusively to the methyl side of the corresponding alkene:

$$K_4Ge_9 + 2Me{-}C{\equiv}C{-}Ph + 2H_2NR \rightarrow [K]_2[Ge_9(C(Me){=}CHPh)_2] + 2KNHR \quad (8)$$

The ^{1}H NMR shows the olefinic proton split into a quartet with a coupling constant of 2 Hz which is a signature for an allyl proton coupled to three methyl protons in a four-bond coupling. Correspondingly, the methyl group protons are split into a doublet with the same 2 Hz coupling constant reflecting their coupling to the single olefinic proton (Figures S5 and S6 in Supporting Information). If instead the attachment were at the carbon adjacent to the phenyl group, the olefinic proton would have been on the carbon closest to the methyl group and coupled to the methyl group at 6−8 Hz—the significant difference of a 3-bond versus 4-bond coupling.[63] For example, the methyl group couples to the olefinic proton at 1.5 Hz in $Ph{-}C\mathit{H}{=}C(GeMe_3)C\mathit{H}_3$,[64] while the methylene group couples to the olefinic proton at 6.0 Hz in $(C_5H_{11})C\mathit{H}_2{-}C\mathit{H}{=}CHGeEt_3$.[65,66] The 3-bond/6 Hz coupling was not observed, indicating a single regioisomer.

A reaction of clusters was also carried out with cyclopropyl-substituted acetylene, $H{-}C{\equiv}C{-}CH(CH_2)_2$. The reason was to establish whether the reaction proceeds via formation of a vinyl radical that is known to cause opening of the cyclopropyl ring or via a vinyl anion which keeps the ring intact.[67−72] According to the ^{1}H NMR of the reaction mixture, the cluster adds to the terminal alkynyl carbon as expected, a hydrogen atom is added *trans* to the cluster, and the cyclopropyl ring stays intact:

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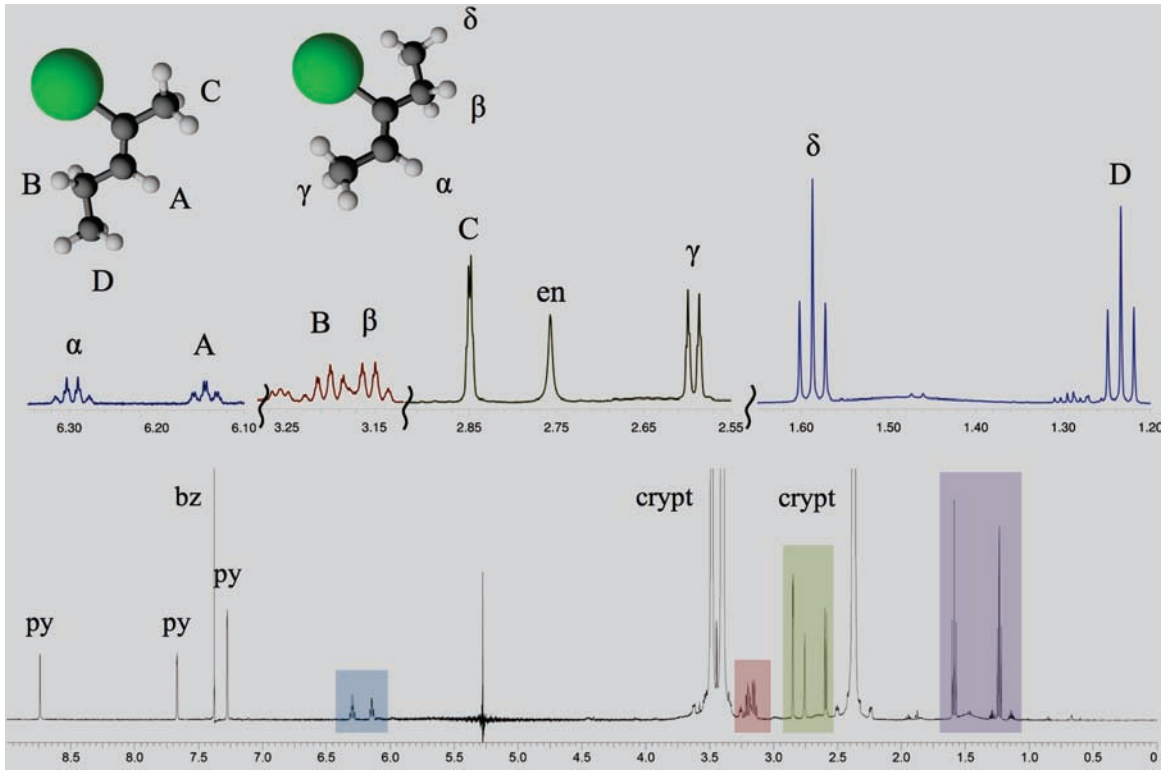

Figure 5. ^{1}H NMR spectrum of [K-crypt]$_3$[Ge$_9$−C(CH$_3$)═CH−CH$_2$CH$_3$]$_{0.5}$[Ge$_9$−C(CH$_2$CH$_3$)═CH−CH$_3$]$_{0.5}$ in pyridine-d_5.

$$K_4Ge_9 + H{-}C{\equiv}C{-}CH(CH_2)_2 + 2H_2NR \rightarrow K_2[Ge_9(CH{=}CH{-}CH(CH_2)_2)_2] + 2KNHR \quad (9)$$

$$K_4Ge_9 + Cl{-}CH_2{-}CH(CH_2)_2 \rightarrow K_2[Ge_9(CH_2CH(CH_2)_2)_2] + 2KCl \quad (10)$$

Thus, the NMR spectrum showed one doublet and one doublet of doublets (Figures S7 and S8 in Supporting Information). The former is attributed to the proton of the terminal olefinic carbon, i.e., Ge$_9$(C*H*═CH−CH(CH$_2$)$_2$)$_2$, and the observed coupling constant of 12 Hz reflects its *cis* positioning with respect to the second olefinic hydrogen. The doublet of doublets is due to the second vinyl proton, Ge$_9$(CH═C*H*−CH(CH$_2$)$_2$)$_2$, reflecting coupling to both the terminal proton across the double bond at 12 Hz, as well as the methine proton of the adjacent cyclopropyl ring at 9 Hz. The latter constant is similar to the observed coupling of 8 Hz for regular vinylcyclopropane, H$_2$C═CH−CH(CH$_2$)$_2$.[73] The protons on the cyclopropyl ring show the complex coupling associated with asymmetry of the two faces of the ring. The most significant observation was the absence of signals corresponding to ring-opening.

A similar test reaction was carried out with the corresponding cyclopropyl halide Cl−CH$_2$CH(CH$_2$)$_2$. Analogous to the cyclopropylvinyl radical, the cylcopropylmethyl radical rapidly rearranges to the open-ring isomer, i.e., $^{\bullet}$CH$_2$CH(CH$_2$)$_2$ → CH$_2$═CHCH$_2$CH$_2^{\bullet}$.[74−80] In our case however, according to both ^{1}H NMR and single-crystal X-ray diffraction studies, the organic fragment attaches to the cluster without ring-opening:

There were no olefinic signals in the ^{1}H NMR spectrum of the reaction mixture, indicative of the absence of olefin-functionalized cluster or a free olefin (Figures S9 and S10 in Supporting Information). At the same time, the spectrum showed all the signals of the intact cyclopropyl ring. Thus, the methylene protons of the cluster-bonded carbon atom, Ge$_9$−C*H*$_2$−CH(CH$_2$)$_2$, were split into a doublet with a coupling constant of 7 Hz due to the methine proton of the cyclopropyl ring. The methylene protons of the ring again showed the expected complex coupling associated with the asymmetry of the two faces of the ring. The disubstituted cluster [Ge$_9$(CH$_2$CH(CH$_2$)$_2$)$_2$]$^{2-}$ was crystallized with the help of 2,2,2-crypt as the sequestering agent for the potassium cations, and the structure clearly showed intact cyclopropyl rings (Figure 6). Again, the cluster is a distorted tricapped trigonal prism with one elongated edge (3.1128(4) vs 2.7102(4) and 2.6862(4) Å), and the two atoms of the elongated edge are exo-bonded to the two methylcyclopropyl substituents. The Ge−C bond distances, 2.004(3) and 2.007(3) Å, are again slightly longer than the statistical mean of 1.965 Å based on 552 reported distances for Ge−C(sp^3) in the Cambridge Structural Database,[62] but are well in the observed range 1.72−2.24 Å and are virtually identical to those in the ^{t}Bu-functionalized Ge$_9$-dimer [^{t}Bu-Ge$_9$−Ge$_9$−^{t}Bu]$^{4-}$.[53]

Discussion

The nine-atom deltahedral Zintl ions of Group 14 have proven to be very diverse in their reactivity. They react with a variety of very different compounds such as main-group organometallics and their halides,[18−20] transition-metal organometallics,[21−50] and with organic halides and alkynes.[52−56] The latter reactions,

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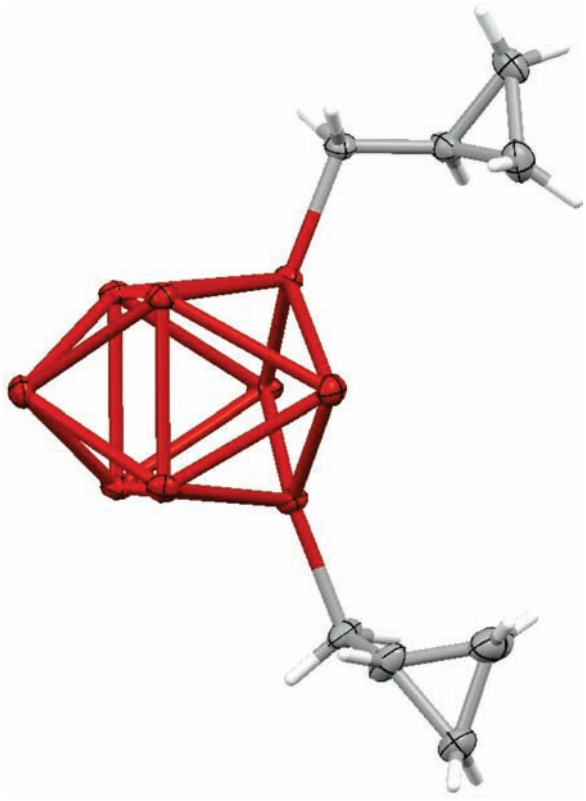

Figure 6. ORTEP drawing of $[Ge_9\text{-}(CH_2\text{-}CH(CH_2)_2)_2]^{2-}$ showing the cyclopropyl ring still intact after attachment.

especially with alkynes, are particularly useful because of the ease of attaching a variety of organic fragments to the clusters and the possibility for subsequent manipulation of the organic functionalities. Therefore, it was important to learn more about these reactions of addition and specifically, more about their reaction paths.

1. Reactions with Alkynes. A number of significant observations emerge from the results described above. One of them is that the reaction of clusters with alkynes always results in *trans* addition of the cluster and a hydrogen atom across the triple bond.[54−56] The *trans* geometry is obvious from both crystal structures and NMR spectra. Thus, although two regioisomers are formed in the reaction with 2-pentyne, the stereochemistry is always the same (*anti* addition) with regards to the addition of the cluster and hydrogen. The lack of regioselectivity in this case is not surprising because the methyl and ethyl groups are essentially identical sterically and electronically. *Anti* addition of clusters and hydrogen is also observed in the reaction of Ge_9-clusters with cyclopropylacetylene, $(CH_2)_2CH-C{\equiv}CH$, and ethynylferrocene, $Fc-C{\equiv}CH$,[54] where the clusters add to the terminal alkyne carbon with the hydrogen *trans* to the cluster. As already mentioned, it appears that the reaction is not specific to germanium clusters because it has been observed for Sn_9-clusters in their reaction with phenylacetylene to form *cis*-$[Sn_9-CH{=}CH-Ph]^{3-}$.[56] This stereoselectivity is an important feature of the reactivity of Zintl clusters toward alkynes and, as discussed later, is reflective of the reaction pathway.

Second, the reactions with alkynes exhibit regioselectivity when the substituents are sufficiently different sterically and electronically. Thus, in the case of terminal alkynes the clusters always add to the terminal carbon. For example, this is the case in the reactions of Ge_9-clusters with ethynylferrocene[54] and cyclopropylacetylene as well as those of Sn_9-clusters with phenylacetylene.[56] The consistency is not surprising given the dramatic steric and electronic differences between a hydrogen substituent on the alkyne carbon and all other possible substituents. The picture is slightly more complicated for internal alkynes. Only one regioisomer is formed from the reaction of Ge_9-clusters with methylphenylacetylene: the cluster adds exclusively to the carbon closest to the methyl group. This regioselectivity is consistent with the substantive steric and electronic differences between the methyl and phenyl groups. At the same time, the lack of regioselectivity in the case of 2-pentyne is understandable and is consistent with there being virtually no steric and electronic differences between the methyl and ethyl substituents.

Our initial attempts to rationalize the stereoselectivity of the addition were focused on analogies with hydrogenation of internal triple bonds by alkali metals dissolved in liquid ammonia or amines. It is well known that such hydrogenation of internal alkynes to alkenes adds the two hydrogen atoms *trans* to each other and, therefore, the two substituents in the resulting alkene also end up in a *trans* geometry—just like in the reactions with clusters. Such hydrogenation reactions start with the addition of a solvated electron (available from the dissolved alkali metal) to the π^* molecular orbital of the triple bond. This results in the formation of a radical anion, $[R-(C^{\bullet}){=}(C^{-})-R]$, which assumes a *trans* conformation in order to diminish electronic repulsion.[81,82] We envisioned that in the clusters case, such an electron transfer could occur from the Ge_9^{4-} cluster to the π^* orbital to form the radical cluster, Ge_9^{3-}, and the same radical anion $[R-(C^{\bullet}){=}(C^{-})-R]$. Then, while in close proximity, the two radicals could recombine to form $[R-C(Ge_9^{3-}){=}(C^{-})-R]^{4-}$. The negatively charged cluster and the lone pair of electrons of the carbon anion would assume a *trans* conformation due to electrostatic repulsion. After proton abstraction from the ethylenediamine solvent, the two organic substituents in the final alkene end up *trans* to each other. Furthermore, this model explained the regioselectivity observed for the reaction with methylphenylacetylene where the cluster adds to the methyl end of the triple bond because of the greater stability of the resulting anion $Ph-(C^{-}){=}(C^{\bullet})-Me$ due to the better charge delocalization over the phenyl ring. The proton in all these reactions comes from the ethylenediamine solvent which is sufficiently acidic ($pK_a \approx 35$) with respect to the generated intermediate vinyl anions ($pK_a \approx 44$).[83] The reaction, on the other hand, does not proceed in pure pyridine because of its low acidity (also $pK_a \approx 45$), but it does after addition of small amounts of methanol ($pK_a \approx 16$).[83] The isotope labeling studies of the latter reaction with deuterated methanol demonstrated that the proton comes from the most acidic source, the methanol.

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Although the above analogy between reactions of clusters with alkynes and hydrogenation of alkynes with alkali metals in amines works very well for alkynes with internal triple bonds, it fails completely for terminal alkynes, i.e., for R−C≡CH. It is well known that such alkynes can not be hydrogenated by ammonia solutions of alkali metals simply because their terminal protons are too acidic ($pK_a \approx 25$)[83] and are readily reduced to hydrogen by the solvated electrons. The reaction stops with the formation of an alkynide anion:

$$R-C\equiv CH + e^-_{(solv)} \rightarrow R-C\equiv C^- + H^\bullet \text{ (as } H_2) \quad (11)$$

The reactions of clusters with terminal alkynes, on the other hand, proceed to completion with addition of the cluster as in the reactions with internal triple bonds:

$$R-C\equiv CH + Ge_9^{4-} + RNH_2 \rightarrow [R-CH=CH-Ge_9]^{3-} + RNH^- \quad (12)$$

Furthermore, it is clear from our results that the reaction with clusters does not involve alkynide anions as intermediates. We have shown that alkynide salts such as $R-C\equiv C^-(K^+)$ react with clusters by an order of magnitude slower (more than two hours before a detectable amount of product) than the corresponding alkynes (complete within a few minutes). The slow reaction is rationalized as actually proceeding via the corresponding alkyne that is generated in very small amounts from the finite equilibrium with the alkynide in the presence of amines (Figure S2):

$$R-C\equiv C-K + H_2NR \leftrightarrow R-C\equiv C-H + K-NHR \quad (13)$$

Therefore, the inconsistency between reactions of terminal alkynes with amine solutions of alkali metals and with clusters suggested looking into other possible analogies for reactions with alkynes.

The most common reactions of alkynes are those of electrophilic addition, and this is not surprising given the high concentration and accessibility of the π electron density of the triple bond. In such reactions a polar H^+X^- molecule (X = halogen, hydroxide, alkoxide, etc.) is attracted by the π electrons of the triple bond with its electrophilic end, i.e., the proton in HX. Once the proton is added, the anionic X^- adds to the resulting vinylic cation to form the final olefin. Due to the diversity and wide range of electrophilic additions to alkynes, often overlooked and much less known is another type of addition reactions, namely nucleophilic addition. In these reactions, a strong nucleophile is attracted by the empty, relatively low-lying, and spatially accessible π^* orbitals of the triple bond. Hydrogenation of alkynes with alkali metals dissolved in amines is one special case of nucleophilic addition in which the solvated electron is the nucleophile attracted to the π^* orbitals of the triple bond. A number of strong anionic nucleophiles such as R_3Ge^-, R_3Sn^-, RSe^-, RTe^-, R_2P^-, etc. are known to attack the π^* orbitals and add to various alkynes.[84−87] The resulting vinylic anions are then protonated stereoselectively *trans* to the added nucleophile (i.e., *anti* addition). Furthermore, the nucleophilic addition is regioselective and proceeds with terminal alkynes as well. For example, it has been shown that germanyl and stannyl anions add to the terminal carbon of phenylacetylene and to the methyl end of methylphenylacetylene:[84,86]

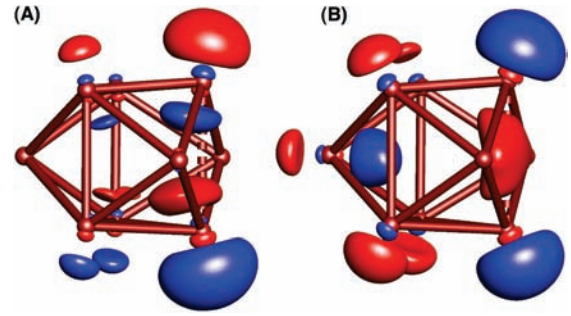

Figure 7. HOMO (A) and HOMO-1 (B) of Ge_9^{4-}.

$$Et_3GeLi + H-C\equiv C-Ph\ (+H_2O) \rightarrow \textit{cis}\text{-}Et_3Ge-CH=CH-Ph + LiOH \quad (14)$$

$$Et_3SnLi + Me-C\equiv C\text{-}Ph\ (+H_2O) \rightarrow Et_3Sn-C(Me)=CH-Ph + LiOH \quad (15)$$

These reactions are significant in a number of ways: (i) They show that alkynes, including those with terminal triple bonds, can be attacked by nucleophilic anions; (ii) the addition of the nucleophile occurs at the most electropositive carbon of the triple bond (the hydrogen end for terminal alkynes); (iii) the addition of the nucleophile is accompanied by (predominately) *anti* addition of hydrogen across the triple bond; and (iv) the reaction with terminal alkynes does not proceed via the alkynide anion but along the same mechanism as for internal alkynes. All these observations are also valid for the reactions between E_9-clusters (E = Ge and Sn) and alkynes, namely the clusters add to alkynes by attacking the most electropositive carbon center and the addition is accompanied by *trans* addition of hydrogen across the triple bond. Therefore, it can be concluded that the clusters add to alkynes as nucleophiles by interacting with the available and electron-accepting empty π^* orbitals of the alkynes.

While the empty alkyne π^* orbitals are good electron acceptors, the occupied frontier orbitals of the anionic cluster are excellent electron donors and are perfectly positioned sterically for nucleophilic addition. It has been discussed in previous publications that the HOMO and HOMO-1 of E_9^{4-} are made predominantly of the p_z orbitals of the atoms forming the two triangular bases of the trigonal prism of the tricapped trigonal prismatic cluster (Figure 7).[1,14,19,88−95] Furthermore, as can be seen in Figure 7, the largest contribution to these molecular orbitals comes from the p_z orbitals at the two atoms

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forming the elongated edge of the tricapped trigonal prismatic cluster which is the shape most often observed for E_9^{4-}. Naturally, these same two atoms are the ones involved in forming exo bonds to substituents. The HOMO of the cluster is π-bonding within the trigonal bases of the prism but σ-*anti*bonding between them (Figure 7A), while the HOMO-1 is exactly the opposite: it is π-*anti*bonding within the bases but σ-bonding between them (Figure 7B). The negative charge of the cluster and the outward spatial distribution of these two frontier orbitals make the E_9^{4-} clusters very good nucleophiles. The orbitals are very well positioned, both energetically and sterically, to attack and overlap with the empty π^* orbital of the triple bonds. The resulting exo bonds to the cluster are then naturally parallel to the pseudo-3-fold axis exactly as are the p_z atomic orbitals of the exo-bonded atoms.

It has been shown that the stereochemistry of the nucleophilic addition to alkynes is determined by the approach of the nucleophile. According to Houk et al.,[96−98] the nucleophiles approach alkynes at an angle of ~120° with respect to the triple bond which is the direction of the overall space distribution of the π^* orbitals. An anionic nucleophile then donates two electrons to the π^* LUMO and effectively "breaks" one of the π bonds in the triple bond. The substituents bend *trans* to each other, and the molecule loses linearity. The resulting vinylic anion is very basic and readily abstracts a proton or other electrophile. The net result is an *anti* addition across the alkyne. It should be pointed out that although to date we have observed only *anti* addition of clusters to alkynes, we do not rule out syn addition under some—yet unknown—conditions. Such addition has been shown to partially occur in reactions involving the anionic nucleophiles R_3E^- (E = Ge, Sn),[84−87] especially when the barrier to isomerization of the vinyl anion is low and/or the rate of protonation of the vinyl anion is particularly slow. Apparently, such conditions exist when the substituent at the β-carbon are phenyl or alkoxy groups that can stabilize the vinyl anion.[96,97] In general, Houk and Perrin expect this to be the case for alkynes with electron withdrawing substituents. In these cases, the nucleophile initially adds *anti*, but the vinyl anion can then invert before undergoing protonation, resulting in the syn addition product.[96,97]

The reaction of Ge_9-clusters with cyclopropylacetylene, $HC{\equiv}C{-}CH(CH_2)_2$, provides a good handle on one of the steps in the process of addition. Cyclopropyl rings are often used in mechanistic investigations as "radical clocks" in which the radical-triggered ring-opening and rearrangement are very fast and the known rate of opening can be compared with other reaction rates. The cyclopropyl-vinyl radical, $H_2C{=}(C^{\bullet}){-}CH(CH_2)_2$, is known to readily rearrange into the open-chain allene radical $H_2C{=}C{=}CHCH_2(C^{\bullet})H_2$. By contrast, the ring in the corresponding cyclopropyl-vinyl anion, $H_2C{=}(C^-){-}CH(CH_2)_2$, is stable and does not open.[67−72] Instead, it gets protonated. The ^{1}H NMR of the reaction of Ge_9-clusters with cyclopropylacetylene showed only protons from intact rings with no signs of ring-opening. This, therefore, proves that the cluster addition proceeds along an anionic route, i.e. via the formation of the anion $Ge_9{-}CH{=}(C^-){-}CH(CH_2)_2$, and that no electron transfer and radical formation occur. This is consistent with the already discussed nucleophilic attack by the Ge_9-clusters at the terminal carbon atom.

The reaction of Ge_9-clusters with bis(trimethylsilyl)acetylene, $TMS{-}C{\equiv}C{-}TMS$, can also be understood as initial nucleophilic addition and formation of $[Ge_9{-}C(TMS){=}CH{-}TMS]^{3-}$. This step is then followed by a desilylation step in which, according to the ^{1}H NMR results, the TMS group replaces a proton in an ethylenediamine molecule to form $TMS{-}NHCH_2CH_2NH_2$ (see Figure SI1). One piece of evidence that the desilylation is a secondary process is the lack of reaction between clusters and $CH_2{=}CH{-}TMS$, the compound that would be generated after single desilylation of $TMS{-}C{\equiv}C{-}TMS$. Furthermore, the ES-MS spectrum taken early in the course of the reaction with $TMS{-}CH{=}CH{-}Br$ shows the presence of clusters substituted with silyl-terminated alkenyl groups, i.e., $Ge_9{-}CH{=}CH{-}TMS$ (Figures 2 and S3). As the reaction proceeds further, the silyl groups are cleaved and replaced by protons until the final product of $[CH_2{=}CH{-}Ge_9{-}CH{=}CH_2]^{2-}$ is achieved. The importance of this observation is that the TMS-substituted vinyl groups are desilylated after being attached to the clusters. The silicon atom in a TMS group is electrophilic and accessible for S_N2 substitution reactions by strong nucleophiles.[60] There are two possible nucleophiles in our particular case that would result in formation of $TMS{-}NHCH_2CH_2NH_2$, namely the ethylenediamine solvent and its amide anion $H_2NCH_2CH_2NH^-$ formed after deprotonation of an ethylenediamine molecule by the vinyl anion in the first step of the reaction, i.e.,

$$Ge_9^{4-} + Me_3Si{-}C{\equiv}C{-}SiMe_3 + H_2NCH_2CH_2NH_2 \rightarrow [Ge_9{-}C(SiMe){=}CH{-}SiMe_3]^{3-} + H_2NCH_2CH_2NH^- \quad (16)$$

Ethylenediamine, however, does not react with $Me_3Si{-}C{\equiv}C{-}SiMe_3$ while, at the same time, it is well known that the silicon atom is readily attacked by amides in a variety of organosilicon compounds.[60] The desilylation with the amide produces a vinyl anion which then deprotonates another molecule of ethylenediamine, and this reaction keeps going until all TMS groups are replaced by protons:

$$[Ge_9{-}C(SiMe_3){=}CH{-}SiMe_3]^{3-} + H_2NCH_2NH^- + H_2NCH_2CH_2NH_2 \rightarrow [Ge_9{-}CH{=}CH{-}SiMe_3]^{3-} + H_2NCH_2CH_2NH_2{-}SiMe_3 + H_2NCH_2CH_2NH^- \quad (17)$$

The lack of generated amide anions in the reaction of Ge_9-clusters with $TMS{-}CH{=}CH{-}Br$, on the other hand, delays the completion of the desilylation. This, in turn, made possible the observation by ES-MS of the intermediate species of clusters functionalized with TMS-substituted vinyl groups (Figures 2 and S3). The initial reaction here, $Ge_9^{4-} + Br{-}CH{=}CH{-}TMS \rightarrow [Ge_9{-}CH{=}CH{-}TMS]^{3-} + Br^-$, generates only halide anions. At the same time, a small amount of amide anions are always available from the slow reduction of ethylenediamine by the clusters themselves and/or by unreacted alkali metal in the intermetallic precursor.

In light of the discussion of nucleophilic attack upon the alkyne by the cluster, it is not surprising that alkynides anions, $RC{\equiv}C^-$, do not undergo the same reactions. Although the π^*-orbitals of the triple bond are still the LUMO of the alkynide (analogous to the alkynes), they are pushed up in energy by the overall negative charge and are no longer low-lying or electrophilic enough to be available for nucleophilic attack.

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Lastly, the observed absence of deuterated product in the reaction with $Et_3Si-C\equiv C-D$ is due to the effective scrambling of the deuterium in exchange for protons from the ethylenediamine in the presence of a relatively strong base (e.g., $R-NH^-$, see Figure S2). This was confirmed by the complete replacement of the deuterium in $Et_3Si-C\equiv C-D$ with protio-hydrogen in ethylenediamine solutions in the presence of catalytic amounts of $KN(TMS)_2$.

2. Reactions with Organic Halides. We have already reported that nine-atom deltahedral clusters can be alkylated by reactions with alkyl halides.[52−56] Structurally characterized were the products of the reactions of Ge_9^{4-} and Sn_9^{4-} with ^{t}BuCl, the disubstituted dimer $[^t Bu-Ge_9-Ge_9-{}^t Bu]^{4-}$ and the monosubstituted monomer $[Sn_9-{}^t Bu]^{3-}$, respectively.[53,56] The substitution with a large variety of R−X substrates was also confirmed by ES-MS where various mono- and dialkylated cluster anions and their ion pairs with potassium cations were observed. Subsequent experiments and ES-MS studies showed that not only tertiary halides such as ^{t}BuCl but also primary and secondary halides such as $Cl-CH_2CH_2CH_2CH_3$ (^{n}BuCl) and $CH_3CH(Cl)CH_2CH_3$ (^{s}BuCl) can attach to the clusters to form similarly mono- and disubstituted species, $[E_9-R]^{3-}$ and $[R-E_9-R]^{2-}$, respectively (where E = Ge, Sn).[53,56] Finally, alkenyl halides also undergo such reactions and form the corresponding alkenylated clusters, for example $[Ge_9-CH_2{=}CHPh]^{3-}$ from a reaction with PhCH=CHBr,[54] and reported here $[Ge_9-CH{=}CH_2]^{3-}$ from the reaction with Br−CH=CH−TMS.

Clearly, the reactions with tertiary halides can not possibly be a S_N2 nucleophilic substitution type reaction because of the sterically inaccessible carbon center protected by three substituents, methyl groups in the case of ^{t}BuCl. Similarly impossible is such a reaction mechanism for the reactions with halogenated olefins, RCH=CHX and $RXC{=}CH_2$ in our case, because sp^2 carbon atoms can not be directly attacked by nucleophiles in a S_N2 mechanism either. S_N1 substitution is also impossible because ethylenediamine is not polar enough for the ionization of these halides. It should be mentioned here that ^{t}BuCl does not react with the solvent ethylenediamine to form $[^t Bu-NH_2CH_2CH_2NH_2]^+Cl^-$ because the amine nucleophile can not attack the tertiary carbon atom for the same steric reasons as described above. Therefore, such ionic species can not be involved in the reaction mechanism. The same is true for the alkenyl halides. One remaining but unproven scenario is electron transfer in very close proximity from the Ge_9^{4-} cluster to the tertiary or alkenyl halide to form an organic radical, a halide anion, and a cluster radical $^{\bullet}Ge_9^{3-}$ (the cluster Ge_9^{3-} has an odd number of electrons, 39, and is a radical). This would be quickly followed by radical recombination to form $[Ge_9-{}^t Bu]^{3-}$ and $[RCH{=}CH-Ge_9]^{3-}$, respectively. In a way, the reactions can be viewed as a variation of the known radical nucleophilic substitution of $S_{RN}1$ type.

The reactions with primary and secondary halides, however, may proceed along the S_N2 mechanism because the halogenated carbon atom is sufficiently exposed for nucleophilic attack by the cluster. The reaction with chloromethylcyclopropane, $Cl-CH_2CH(CH_2)_2$, was carried out in order to test for this reaction path. The two possible mechanisms for the reaction are to proceed via: a) electron transfer and radical formation as in the ^{t}BuCl case or b) direct nucleophilic attack at the α carbon by the cluster. The former pathway will generate the radicals $^{\bullet}Ge_9^{3-}$ and $^{\bullet}CH_2CH(CH_2)_2$, as well as chloride anions. The methylcyclopropyl radical, however, rearranges very fast with opening of the ring and formation of a double bond to form $CH_2{=}CH-CH_2-CH_2^{\bullet}$. The rate of the rearrangement is around $9.4 \times 10^7\ s^{-1}$ and approaches the diffusion limit of the molecules.[74−80] The absence of any observable amounts of the corresponding substituted cluster $[Ge_9-CH_2CH_2CH{=}CH_2]^{3-}$ or ring-opened olefin product at all clearly indicates that the reaction does not proceed along the radical path. Direct nucleophilic attack on the other hand, will result in an intact cyclopropyl ring and clusters functionalized with the original organic fragments, i.e., $[Ge_9-CH_2CH(CH_2)_2]^{3-}$, and this is exactly what was observed. Therefore, we can state that the reactions between Ge_9-clusters and primary halides (and most likely secondary halides) do not involve electron transfer and radical formation but are of the S_N2 type instead. Different reaction pathways for sp^2 carbon centers, tertiary sp^3 carbon centers, and primary and secondary carbon centers is a very common phenomenon for a variety of organic reactions, and it should not be surprising that different behavior is observed in their reactions with deltahedral clusters too.

It can be argued that primary and secondary halides may form the corresponding secondary ammonium salts with ethylenediamine, $[RCH_2-NH_2CH_2CH_2NH_2]^+X^-$ and $[R_2CH-NH_2CH_2CH_2NH_2]^+X^-$, respectively, because the carbon centers would be open for nucleophilic attack by the nucleophilic amine, and then these salts would react somehow with the Ge_9-clusters. However, the fact that the reactions with ^{n}BuCl and ^{s}BuCl produced the corresponding substituted clusters when carried out in pyridine clearly speaks against this being the major reaction because the corresponding butyl-pyridinium salts $[^n Bu-NC_5H_5]^+Cl^-$ and $[^s Bu-NC_5H_5]^+Cl^-$ do not form. Thus, although some amounts of salt may form for primary and secondary halides in ethylenediamine, the primary reaction path in the presence of deltahedral nine-atom clusters seems to be the direct nucleophilic substitution of the halide with the cluster.

Conclusion

The nine-atom deltahedral Zintl ions of Group 14 are clearly very diverse species. Their flexible geometry—a tricapped trigonal prism that can easily distort in various ways along the 3-fold axis—allows for a flexible electronic structure that, in turn, leads to different electron counts. The net result is that the nine-atom clusters have multiple oxidation states that are readily accessible and relatively stable, i.e., E_9^{4-}, E_9^{3-}, and E_9^{2-}. The change of oxidation state from the most reduced E_9^{4-} to the least reduced E_9^{2-} is accompanied by contraction of one or more of the three trigonal prismatic edges parallel to the pseudo-3-fold axis. This oxidation/contraction takes one molecular orbital (Figure 7a) from being bonding with two electrons in E_9^{4-}, to nonbonding with one electron in E_9^{3-}, and to *anti*bonding with zero electrons in E_9^{2-}. It may be possible that the clusters in their most negative oxidation act as electron donors in reactions involving electron-transfer to the sterically protected carbon atoms in tertiary and olefinic halides. The electron transfer would lead to halide anion elimination and addition of the organic residue to the cluster. This is possibly the type of reaction that also occurs with the heavily protected main-group organometallic reagents Ph_4Sn, Ph_3SnCl, and Ph_3GeCl that have already been reported. At the same time, the clusters behave as classical anionic nucleophiles when an exposed electrophilic target is available as in primary and secondary halides, alkynes, and, most likely, main-group organometallic reagents with a large metal atom and relatively small ligands, as in Me_3SnCl for example. Clearly, this is by far the preferred reaction with primary halides as shown in the reaction with chloromethylcy-

clopropane: the reaction shows only product with the ring intact even though the compound is capable of reacting by either an electron-transfer (ring-opened product) or a S_N2 mechanism (ring-intact product). Finally—demonstrating the breadth of reactivity—the clusters also seem to be able to play the role of an electrophile in some reactions. Thus, we have shown before that reactions of clusters with strong anionic nucleophiles such as Ph_3Sn^- lead to the corresponding substituted species. The most likely scenario of this reaction is the one where the clusters participate in their least reduced state, i.e., as E_9^{2-}, and the available low-lying and empty molecular orbital (Figure 7a) is the acceptor of the pair of electrons from the nucleophile. Combined, these insights into the available reaction paths for deltahedral Zintl ions allow for creative design of other chemical transformations and the potential is wide open for many novel cluster-based species.

Experimental Section

General Methods. All operations were carried out under an inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. Ethylenediamine (Alfa-Aesar, 99%) was distilled over sodium metal and stored in a gas-tight ampule under nitrogen. 18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, Acros, 99%) was dried over sodium in ether, recrystallized, and further purified by pumping under vacuum. K_4Ge_9 was synthesized by heating a stoichiometric mixture of the elements (K, 99+%, Strem; Ge, 99.999%, Alfa Aesar) at 950 °C for 2 days in sealed niobium containers jacketed in evacuated fused-silica ampules according to previously reported synthetic procedures. TMS−Cl (trimethylsilylchloride, Acros, 98%), 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane, Acros, 98%), deuterated methanol (CD_3OD, Cambridge Isotope Laboratories, 99.8%), $Me_3Si-C\equiv C-SiMe_3$ (bis(trimethylsilyl)acetylene, Acros, 99%), $Et_3Si-C\equiv C-H$ (triethylsilylacetylene, Alfa-Aesar, 97%), 1-bromovinyltrimethylsilane (Aldrich, 97%), 2-bromovinyltrimethylsilane (predominantly *trans*, Aldrich, 98%), TMS−C≡N (trimethylsilylcyanide, Alfa-Aesar, 97%), $TMS-CH=CH_2$ (vinyltrimethylsilane, Acros, 97%), 2-pentyne (Acros, 98%), Me−C≡C-Ph (1-phenyl-1-propyne, Aldrich, 99%), $H-C\equiv C-CH(CH_2)_2$ (cyclopropylacetylene, 97%, Aldrich), $Cl-CH_2-CH(CH_2)_2$ (chloromethylcyclopropane, Alfa-Aesar, 98%), K−HMDS (potassium hexamethyldisilylazide, Aldrich, 95%), DMF (dimethylformamide, anhydrous, Acros, 99.8%), and benzene (Sigma-Aldrich, 99.8%) were all used as received.

Mass Spectrometry. Electrospray mass spectra were recorded from ethylenediamine solutions (0.03−0.4 M) on a Micromass Quattro-LC triple quadropole mass spectrometer (125 °C source temperature, 150 °C desolvation temperature, 2.8 kV capillary voltage, and a 35 V cone voltage). The samples were introduced by direct infusion with a Harvard syringe pump at 20 μL/min. Spectra were taken in the negative-ion mode.

NMR Spectroscopy. Deuterated pyridine (Cambridge Isotope Laboratories, 99.9%) was stored over molecular sieves. ^{1}H NMR spectra were recorded on a Varian Unity*Plus* 300 MHz spectrometer, locked on the deuterium signal of the deuterated pyridine, and referenced against the farthest downfield peak of the solvent residuals.

Synthesis of $Me_3Si-NHCH_2CH_2NH$. Ethylenediamine (0.6 mL) was combined with benzene-d_6 (0.15 mL) in a 3 mL NMR tube. To this solution was added trimethylsilylchloride (0.099 g). The NMR was capped, the solution shook, and the spectrum collected. ^{1}H NMR (in situ, benzene-d_6 lock): δ 2.70 (s, $H_2NCH_2CH_2NH-Si(CH_3)_3$), 2.44 (s, $H_2NCH_2CH_2NH-Si(CH_3)_3$), 1.32 (s, br, $H_2NCH_2CH_2NH-Si(CH_3)_3$), −0.11 (s, $H_2NCH_2CH_2NH-Si(CH_3)_3$).

Synthesis of $Et_3Si-C\equiv C-K$ and $Et_3Si-C\equiv C-D$. K−HMDS ($K-N(TMS)_2$, 0.089 g, 0.44 mmol) was dissolved in benzene (2.0 mL) in a Schlenk tube. $Et_3Si-C\equiv C-H$ (0.053 g, 0.39 mmol) was added and allowed to react with the K-HMDS. The entire sample was then pumped down on a Schlenk line to remove the benzene and resultant H−HMDS to isolate the $Et_3Si-C\equiv C-K$ product. A portion of the alkynide was used for reactions with K_4Ge_9. The remaining $Et_3Si-C\equiv C-K$ was redissolved in benzene (1.0 mL) and CD_3OD (0.016 g, 0.40 mmol) was added to form $Et_3Si-C\equiv C-D$.

Synthesis of $[K-crypt]_2[Ge_9-(CD=CD_2)_2]$. 2,2,2-Crypt (0.148 g, 0.39 mmol) and bis(trimethylsilyl)acetylene (0.052 g, 0.31 mmol) were dissolved in pyridine (1.0 mL) along with methanol-d_4 (CD_3OD, 0.051 g, 1.42 mmol). K_4Ge_9 (0.084 g, 0.10 mmol) was added to this solution and stirred for ~2 h. The resulting mixture was centrifuged, filtered through a packed glass wool plug, and layered with toluene (8 mL). The system was left undisturbed for 2 weeks, after which small block-like, orange crystals were isolated. ES-MS: *m*/*z* 683 $[Ge_9-CD=CD_2]^-$, 713 $[Ge_9-(CD=CD_2)_2]^-$, 752 $\{[K][Ge_9-(CD=CD_2)_2]^{2-}\}^-$, 1128 $\{[K\text{-crypt}][Ge_9-(CD=CD_2)_2]\}^-$.

Synthesis of $[K-crown]_2[Ge_9-(CH=CH_2)_2]$: Method I. K_4Ge_9 (0.086 g, 0.11 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. Triethylsilylacetylene (0.050, 0.36 mmol) was added dropwise, and the reaction mixture was stirred for 4 h. The resulting orange solution was filtered and layered with a solution of 18-crown-6 (0.124 g, 0.47 mmol) dissolved in 8 mL toluene. It yielded well-formed orange needle-like crystals of the compound after 3 days. The unit cell determined by X-ray crystallography was identical to that reported for the synthesis by reaction with bis(trimethylsilyl)acetylene. Synthesis of $[K-crown][Ge_9-(CH=CH_2)_2]$ using $Et_3Si-C\equiv C-D$ followed this same procedure and yielded the same result.

Synthesis of $[K-crown]_2[Ge_9-(CH=CH_2)_2]$: Method II. K_4Ge_9 (0.082 g, 0.10 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. 2-Bromovinyltrimethylsilane (0.039, 0.22 mmol) was added dropwise, and the reaction mixture was stirred for 20 min. The solution was centrifuged and filtered, and an aliquot taken for mass spectrometry. The solution was then allowed to further react for 4 h, centrifuged, and filtered again. The resulting solution was layered with a solution of 18-crown-6 (0.190 g, 0.72 mmol) dissolved in 8 mL of toluene. It yielded well-formed orange needle-like crystals of the compound after 3 days. The unit cell determined by X-ray crystallography was identical to that reported for the synthesis by reaction with bis(trimethylsilyl)acetylene. ES-MS: *m*/*z* 680 $[Ge_9-CH=CH_2]$, 707 $[Ge_9-(CH=CH_2)_2]$, 719 $\{[K][Ge_9-CH=CH_2]^{2-}\}$, 752 $[Ge_9-CH=CH-TMS]$, 779 $[(CH_2=CH)-Ge_9-(CH=CH-TMS)]$, 818 $\{[K][(CH_2=CH)-Ge_9-(CH=CH-TMS)]^{2-}\}$,851$[Ge_9-(CH=CH-TMS)_2]$, 890 $\{[K][Ge_9-(CH=CH-TMS)_2]^{2-}\}$. [Note: The position of the TMS group is not known; both regioisomers are potentially present.]

Synthesis of $[K-crown]_2[Ge_9-(CH=CH_2)_2]$: Method III. K_4Ge_9 (0.082 g, 0.10 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. 2-Bromovinyltrimethylsilane (0.036, 0.20 mmol) was added dropwise, and the reaction mixture was stirred for 20 min. The solution was centrifuged and filtered, and an aliquot taken for mass spectrometry. The solution was then allowed to further react for 4 h, centrifuged, and filtered again. The resulting solution was layered with a solution of 18-crown-6 (0.163 g, 0.61 mmol) dissolved in 8 mL of toluene. It yielded well-formed orange needle-like crystals of the compound after 3 days. The unit cell determined by X-ray crystallography was identical to that reported for the synthesis by reaction with bis(trimethylsilyl)acetylene. ES-MS: *m*/*z* 680 $[Ge_9-CH=CH_2]$, 707 $[Ge_9-(CH=CH_2)_2]$, 719 $\{[K][Ge_9-CH=CH_2]^{2-}\}$, 752 $[Ge_9-CH=CH-TMS]$, 779 $[(CH_2=CH)-Ge_9-(CH=CH-TMS)]$, 818 $\{[K][(CH_2=CH)-Ge_9-(CH=CH-TMS)]^{2-}\}$, 851 $[Ge_9-(CH=CH-TMS)_2]$, 890 $\{[K][Ge_9-(CH=CH-TMS)_2]^{2-}\}$. [Note: The position of the TMS group is not known; both regioisomers are potentially present.]

Synthesis of $[K-crypt]_3[Ge_9-((CH_3)C=CH-CH_2CH_3)]_{0.5}$-$[Ge_9-((CH_3CH_2)CH=CH-CH_3)]_{0.5}\cdot bz$. K_4Ge_9 (0.086 g, 0.11 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in

a test tube inside a glovebox. 2-Pentyne (0.037 g, 0.54 mmol) was added dropwise slowly, and the reaction mixture was stirred for 3 h. The solution was centrifuged, filtered, and layered with a 2,2,2-krypt/toluene solution (0.162 g crypt, 0.43 mmol; 8 mL toluene). Deep red plate-like crystals formed after about 10 days: triclinic, $P\bar{1}$, $a = 14.2449(4)$ Å, $b = 14.3354(4)$ Å, and $c = 20.8288(6)$ Å, $\alpha = 94.688(2)°$, $\beta = 94.819(2)°$, and $\gamma = 102.300(2)°$, $V = 4119.3(2)$ Å^3, $Z = 2$. ^{1}H NMR (pyridine-d_5): δ 1.23 (t, 7 Hz, [Ge_9−C(CH_3)=CH−CH_2CH_3]$^{3-}$), 1.59 (t, 7 Hz, [Ge_9−C(CH_2CH_3)=CH−CH_3]$^{3-}$), 3.37 (t, crypt), 2.59 (d, 7 Hz, [Ge_9−C(CH_2CH_3)=CHCH_3]$^{3-}$), 2.85 (d, 1 Hz, [Ge_9−C(CH_3)=CH−CH_2CH_3]$^{3-}$), 3.16 (qd, 7 Hz, 1 Hz, [Ge_9−C(C$H_2$$CH_3$)=CH−$CH_3$]$^{3-}$), 3.20 (dq, 7 Hz, 6 Hz, [Ge_9−C(CH_3)=CH−C$H_2$$CH_3$]$^{3-}$), 3.40 (t, crypt), 3.49 (s, crypt) 6.15 (tq, 7 Hz, 1 Hz, [Ge_9−C(CH_3)=CH−CH_2CH_3]$^{3-}$), 6.30 (qt, 7 Hz, 1 Hz, [Ge_9−C(CH_2CH_3)=CH−CH_3]$^{3-}$), 7.38 (s, benzene). ES-MS: *m*/*z* 722 [Ge_9−(C_5H_9)], 761 {[K+][Ge_9−(C_5H_9)]$^{2-}$}, 791 [Ge_9−(C_5H_9)$_2$], 1135 {[K−crypt]$^+$[Ge_9−(C_5H_9)]$^{2-}$}, 1204 {[K−crypt]$^+$[Ge_9−(C_5H_9)$_2$]$^{2-}$}.

Synthesis of [K−crown]$_{4-n}$[Ge_9−(C(Me)=CH−Ph)$_n$] (*n* = 1, 2). K_4Ge_9 (0.085 g, 0.10 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. 1-Phenyl-1-propyne (0.055 g, 0.47 mmol) was added dropwise slowly, and the reaction mixture was stirred for 4 h. The solution was centrifuged, filtered, and layered with an 18-crown-6/toluene solution (0.118 g 18-crown-6, 0.45 mmol, 8 mL toluene). The solution was left undisturbed for 2 weeks to allow the two phases to diffuse. A dark red oil formed at the bottom of the test tube after diffusion with the toluene phase. The supernate was decanted and the red oil (cluster phase) washed with hexanes and dried under vacuum. The resulting residue was analyzed by mass spectrometry and NMR spectroscopy. ^{1}H NMR (pyridine-d_5): δ 2.50 (d, 2 Hz, [Ge_9−(C(CH_3)=CH−Ph)]$^{3-}$), 2.52 (d, 2 Hz, [Ge_9−(C(CH_3)=CH−Ph)$_2$]$^{2-}$), 3.59 (s, 18-crown-6), 8.00 (q, 2 Hz, [Ge_9−(C(CH_3)=CH−Ph)]$^{3-}$), 8.02 (q, 2 Hz, [Ge_9−(C(CH_3)=CH−Ph)$_2$]$^{2-}$). ES-MS: *m*/*z* 770 [Ge_9−(C(CH_3)=CH−Ph)], 887 [Ge_9−(C(CH_3)=CH−Ph)$_2$], 926 {[K$^+$][Ge_9−(C(CH_3)=CH−Ph)$_2$]$^{2-}$}.

Synthesis of [K−crown]$_2$[Ge_9−(CH=CH−CH(CH_2)$_2$)$_2$]. K_4Ge_9 (0.080 g, 0.10 mmol) was dissolved in 1.5 mL of ethylenediamine (red solution) in a test tube inside the glovebox. Cyclopropylacetylene (0.056 g, 0.85 mmol) was added dropwise slowly, and the reaction mixture was stirred for 4 h. The solution was centrifuged, filtered, and 18-crown-6 added (0.096 g, 0.36 mmol). The solution was layered with toluene and left undisturbed for a week. After diffusion a dark red-brown residue formed on the bottom of the test tube. The supernate was decanted, and the residue dissolved in pyridine-d_5 for NMR analysis. ^{1}H NMR (pyridine-d_5): δ 0.55−0.80 (m, [Ge_9−(CH=CH−CH(CH_2)$_2$]$^{2-}$), 1.49 (m, [Ge_9−(CH=CH−CH(CH_2)$_2$]$^{2-}$), 3.62 (s, 18-crown-6), 5.58 (dd, [Ge_9−(CH=CH−CH(CH_2)$_2$]$^{2-}$), 6.68 (d, [Ge_9−(CH=CH−CH(CH_2)$_2$]$^{2-}$). ES-MS: *m*/*z* 720 [Ge_9−(CH=CH−CH(CH_2)], 787 [Ge_9−(CH=CH−CH(CH_2)$_2$], 826 {[K$^+$][Ge_9−(CH=CH−CH(CH_2)$_2$]$^{2-}$}.

Synthesis of [K−crypt]$_2$[Ge_9−(CH_2−CH(CH_2)$_2$)$_2$]·3en. K_4Ge_9 (0.080 g, 0.10 mmol) was dissolved in 1.5 mL of ethylenediamine (red solution) in a test tube inside the glovebox. A solution of chloromethylcyclopropane (0.022 g, 0.24 mmol) dissolved in ethylenediamine (0.22 mL) was added dropwise slowly, and the reaction was stirred for 3 h. The solution was centrifuged, filtered, and layered with a 2,2,2-crypt/toluene solution (0.146 g crypt, 0.39 mmol, 8 mL toluene). The solution was left undisturbed to allow for crystallization. Small, orange block-like crystals formed after about 2 weeks: monoclinic, $P2(1)/n$, $a = 14.9391(3)$ Å, $b = 25.7127(5)$ Å, and $c = 19.0906(4)$ Å, $\alpha = 90°$, $\beta = 93.8900(10)°$, and $\gamma = 90°$, $V = 7316.3(3)$ Å^3, $Z = 4$. ^{1}H NMR (pyridine-d_5): δ 0.37, 0.48 (m, [Ge_9−(CH_2−CH(CH_2)$_2$)$_2$]$^{2-}$), 1.15 (m, [Ge_9−(CH_2−CH(CH_2)$_2$)$_2$]$^{2-}$), 1.72 (d, [Ge_9−(CH_2−CH(CH_2)$_2$)$_2$]$^{2-}$), 2.23 (s, toluene), 2.40 (s, crypt), 2.75 (s, ethylenediamine), 3.42 (s, crypt), 3.48 (s, crypt). ES-MS: *m*/*z* 708 [Ge_9−(CH_2−CH(CH_2)$_2$)], 763 [Ge_9−(CH_2−CH(CH_2)$_2$)$_2$], 802 {[K$^+$][Ge_9−(CH_2−CH(CH_2)$_2$)]$^{2-}$}.

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Supporting Information Available: NMR and electrospray mass spectrometry (ES-MS) spectra for [K−crown]$_{4-n}$[Ge_9−(C(Me)=CH−Ph)$_n$] (*n* = 1, 2), [K-crown]$_2$[Ge_9−(CH=CH−CH(CH_2)$_2$], [K−crypt]$_2$[Ge_9−(CH_2−CH(CH_2)$_2$)$_2$]·3en, NMR spectra of TMS−$NHCH_2CH_2NH_2$, Et_3Si−C≡C−K, Et_3Si−C≡C−D, and Et_3Si−C≡C−H, and ES-MS spectrum of the reaction of Ge_9^{n-} with (1-bromovinyl)trimethylsilane and 2-pentyne, as well as an X-ray crystallographic file of [K−crypt]$_3$[Ge_9−((CH_3)-C=CH−CH_2CH_3)]$_{0.5}$[Ge_9−((CH_3CH_2)CH=CH−CH_3)]$_{0.5}$·bz and [K−crypt]$_2$[Ge_9−(CH_2−CH(CH_2)$_2$)$_2$]·3en in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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