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, Ge₉ⁿ⁺) 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 methylocyclopropyl functionalized clusters, [Ge₉(C₅H₅)]²⁻ and [Ge₉(CH₂CH(CH₃)]²⁻, respectively, were crystallographically characterized in compounds with [K-crypt]⁺ counterions. 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


(16) Ugrinov, A. Holo-Type Binding Sites Ion-Paired Holo-Type Binding Sites Ion-Paired; Sevov, S.; C. C. R. Chimie 2005, 8, 1878.
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 dialkynylated nine-
atom clusters of germanium, \([\text{Ge}_9(CR=CHR')_2]\) and 
\([\text{Ge}_9(CR=CHR')_2]^2-\), respectively, are readily accessible by
reacting \(\text{Ge}_9\) 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 \(\text{Sn}_9\)-clusters as well.\(^{56}\)

We have also shown before that the germanium clusters can be
functionalized with the simplest alkyl group, namely vinyl,
by reacting them with the trimethylsilyl (TMS) disubstituted
acetylene, \(\text{TMS}^-\text{C}==\text{C}^-\text{TM}\), along the following unbalanced
equation:\(^{55}\)

\[
K_2\text{Ge}_9 + 2\text{TMS}^-\text{C}==\text{C}^-\text{TMS} \rightarrow K_2[\text{Ge}_9(\text{CH}==\text{CH})_2]^- \tag{1}
\]

Both mono- and disubstituted species, \([\text{Ge}_9(\text{CH}==\text{CH})_2]^-\)
and \([\text{Ge}_9(\text{CH}==\text{CH})_2]^2-\), 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., \(\text{TMS}^-\text{X} + \text{H}_{12}\text{NR} \rightarrow \text{TMS}^-\text{NR} + \text{HX}
\)
and \(\text{TMS}^-\text{X} + \text{R}^-\text{OH} \rightarrow \text{TMS}^-\text{OR} + \text{HX}.\)\(^{60}\) In the case of ethylendiamine the reaction with \(\text{TMS}^-\text{Cl}\) produces
\(\text{TMS}^-\text{NHCH}_2\text{CH}_2\text{NH}_2:}\)

\[
\text{TMS}^-\text{Cl} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightarrow \[\text{TMS}^-\text{NHCH}_2\text{CH}_2\text{NH}_3^+ + \text{Cl}^- \rightarrow \text{TMS}^-\text{NHCH}_2\text{CH}_2\text{NH}_2 + \text{HCl}
\tag{2}
\]

We carried out this reaction and compared the NMR signal of
the TMS protons of the product \(\text{TMS}^-\text{NHCH}_2\text{CH}_2\text{NH}_2\) with
that in the spectrum of the reaction mixture of an ethylendia-
imine solution of \(K_2\text{Ge}_9\) and \(\text{TMS}^-\text{C}==\text{C}^-\text{TM}\) (Figure S1 in
Supporting Information). The two chemical shifts were identical
and indicated that the cleaved silyl groups end up as
\(\text{TMS}^-\text{NHCH}_2\text{CH}_2\text{NH}_2\). Therefore, eq 1 can be improved by
adding a second product as follows

\[
\]

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ant and (iv) heteroatomic deltahedral Zintl ions.\(^{51,52}\) More
recently a new category has emerged, namely the category of
organos-Zintl clusters.\(^{19,53-56}\) This latest advancement is par-

icularlly promising as it brings Zintl cluster chemistry into
contact with more traditional organic chemistry. The new
organos-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 bond-
ing 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
ions.\(^{60}\) While the reactions of deltahedral Zintl clusters with transi-
tion-metal and main-group organometallic compounds have
been studied before and their pathways are now fairly well
understood,\(^{1,18,30,34,35,66}\) a thorough investigation of the reactions
with organic reagents had not been carried out until now. 

(52) Petrov, I.; Sevov, S. C., MA Thesis.
(57) For a recent review, see: Schnepf, A. Coord. Chem. Rev. 2006, 250, 2758.

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 Ge₉-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 K₄Ge₉ is partially soluble in acidic additive (in stoichiometric amount with respect to the precursor and (b) either has sufficiently acidic protons, as does ethylenediamine in any solvent that (a) sufficiently dissolves the starting precursor. 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 (CD₃OD) and observed formation of only the completely deuterated product [D₂C≡C–Ge₉–CD=CD₂]⁻. 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 proto analogue (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 alkane and then abstract deuterium from the methanol.

Combining the observations from above, we can now write a balanced equation for the reaction between Ge₉-clusters and TMS–C≡C–TMS in ethylenediamine (shown as H₂NR) as follows

\[ K₄Ge₉ + 2TMS–C≡C–TMS + 6H₂NR → [K]₂[Ge₉(CH=CH₂)]₂ + 4TMS–NHR + 2K–NHR \]  

Vinyl addition can also be achieved by a reaction with the monosilylated acetylene, RSi=C≡C–H, and the reaction yields again the expected vinyl disubstituted cluster:

\[ K₄Ge₉ + 2Et₃Si–C≡C–H + 4H₂NR → [K]₂[Ge₉(CH=CH₂)]₂ + 2Et₃Si–NHR + 2K–NHR \]

Independent of the reaction, the resulting anions [Ge₉(CH=CH₂)]⁻ 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-crown-6)][Ge₉(CH=CH₂)]⁻. Its mass and NMR spectra are in agreement as well.

Since terminal alkynes R–C≡C–H add to the Ge₉-clusters but are also easily deprotonated by strong bases to alkynide anions R–C≡C⁻, we investigated whether the clusters react with these anions. The latter were separately prepared by a reaction of triethylsilylacetylene Et₃Si–C≡C–H with 1 equiv of K–HMDS (K–N(SiMe₃)₂):

\[ Et₃Si–C≡C–H + K–N(TMS)₂ → Et₃Si–C≡C–K + H–N(TMS)₂ \]

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 Ge₉-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 alkylne Et₃Si–C≡C–H begins yielding the disubstituted product within minutes.

To further investigate the mechanism of addition and hydrogenation of the alkyne, we carried out a reaction of germanium clusters with deuterated triethylsilylacetylene Et₃Si–C≡C–D prepared by quenching the available potassium alkynide Et₃Si–C≡CK with deuterated methanol CD₃OD (Figure S2 in Supporting Information). Surprisingly, however, the 'H NMR of the reaction in ethylenediamine showed predominantly the proto-vinyl disubstituted cluster, i.e., [H₂C≡C–Ge₉–CH=CH₂]⁻. (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 Et₃Si–C≡C–D under our specific reaction conditions. Thus, when catalytic amount of K–HMDS is added to ethylenediamine solution of Et₃Si–C≡C–D, the 'H NMR spectrum shows near complete replacement of the deuterium with proto-hydrogen within a few minutes indicating that the enrichment is not sustained in the...
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)$_2$N$^-$. 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$-\text{C(}\text{Br)\text{dCH2}}$ and TMS$-\text{CHdCHBr}$. 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, $[\text{H2C\text{dCH-Ge9-CHdCH2}}]$ 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., [H$_2$C=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

\[
\text{K}_2\text{Ge}_9 + 2\text{Br}(\text{TMS})\text{C=CH}_2 + 2\text{H}_2\text{NR} \rightarrow \text{K}_2\text{[Ge}_9\text{(CH=CH}_2)_2\text{]} + 2\text{KBr} + 2\text{TMS-NHR} \quad (7)
\]

By contrast, vinyltrimethylsilane TMS−CH=CH$_2$ and trimethylysilylcyanide 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$_3$C(Ge$_9$)dCHCH$_2$CH$_3$]$^-$ (1a) and [CH$_3$CH=C(Ge$_9$)CH$_2$−CH$_3$]$^-$ (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 I 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$_2$CH$_3$ and trans CH$_3$CH$_2$−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.
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 CH3(Ge9)C≡CH—CH3CH2 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., CH3(Ge9)C≡CH—CH3CH2, and 7 Hz to the two adjacent methylene protons, i.e., CH2(Ge9)C≡CH—CH2CH3. The strength of the coupling is reversed in CH2CH3(Ge9)C≡CH—CH3, 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:

\[ K_4 Ge_9 + 2 Me—C≡C—Ph + 2H_NR \rightarrow [K_2 Ge_9(C(Me)≡CPh)_2] + 2KNHR \] (8)

The 1H 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. For example, the methyl group couples to the olefinic proton at 1.5 Hz in Ph—C≡C(GeMe3)CH2, while the methylene group couples to the olefinic proton at 6.0 Hz in (C2H5)CH2—C≡C(GeEt3).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≡C—CH2=C. 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 1H 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:

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., \( \text{Ge}_9(\text{CH}_2\text{CH}(\text{CH}_2)_2) \), 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, \( \text{Ge}_9(\text{CH}_2\text{C}(\text{CH}_2)_2) \), 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, \( \text{H}_2\text{C}(\text{CH}_2\text{C}(\text{CH}_2)_2) \).

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 \( \text{Cl}-\text{CH}_2\text{CH}(\text{CH}_2)_2 \). Analogous to the cyclopropylvinyl radical, the cyclopropylmethyl radical rapidly rearranges to the open-ring isomer, i.e., \( \text{CH}_2\text{CH}(\text{CH}_2)_2 \rightarrow \text{CH}_2\text{C}(\text{CH}_2)_2 \). In our case however, according to both \(^1\text{H} \) NMR and single-crystal X-ray diffraction studies, the organic fragment attaches to the cluster without ring-opening:

\[
\text{K}_4\text{Ge}_9 + \text{H}-\text{C}=\text{C}-\text{CH}_2\text{CH}_2 + 2\text{H}_2\text{NR} \rightarrow \\
\text{K}_4[\text{Ge}_9(\text{CH}=\text{C}-\text{CH}_2\text{CH}_2)_2] + 2\text{KNHR}
\]

\[
\text{K}_4\text{Ge}_9 + \text{Cl}-\text{CH}_2-\text{CH}(\text{CH}_2)_2 \rightarrow \\
\text{K}_4[\text{Ge}_9(\text{CH}_2\text{CH}(\text{CH}_2)_2)_2] + 2\text{KCl}
\]

There were no olefinic signals in the \(^1\text{H} \) 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, \( \text{Ge}_9-\text{CH}_2-\text{CH}(\text{CH}_2)_2 \), 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 \( [\text{Ge}_9(\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2)_2)_2]^2^- \) 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 \( \text{Ge}-\text{C} \) 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 \( \text{Ge}-\text{C} \) in the Cambridge Structural Database, but are well in the observed range 1.72–2.24 Å and are virtually identical to those in the \(^t\text{Bu}\)-functionalized \( \text{Ge}_9\)-dimer \( [\text{tBu}-\text{Ge}_9-\text{Ge}_9-\text{tBu}]^4^- \).

**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, transition-metal organometallics, and with organic halides and alkynes. The latter reactions,
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 Ge9-clusters with cyclopropylacetylene, (CH₂)₂CH=C=CH₂, and ethynylferrocene, Fe=C=CH₂, where the clusters add to the terminal alkene 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 Sn₉-clusters in their reaction with phenylacetylene to form cis-[Sn₉=CH=CH=Ph]⁺.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 Ge₉-clusters with ethynylferrocene54 and cyclopropylacetylene as well as those of Sn₉-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 Ge₉-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)(=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 Ge₉⁺⁺ cluster to the π* orbital of the radical cluster, Ge₉⁻, and the same radical anion [R–(C)(=C)=R]⁻. Then, while in close proximity, the two radicals could recombine to form [R–C(=C–Ge₉⁻)][(C)=R]⁺. 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)=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 (pKₐ ≈ 35) with respect to the generated intermediate vinyl anions (pKₐ ≈ 44).83 The reaction, on the other hand, does not proceed in pure pyridine because of its low acidity (also pKₐ ≈ 45), but it does after addition of small amounts of methanol (pKₐ ≈ 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.

References

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 $R_3C\equiv CH$. 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 ($pK_a \approx 25$) and are readily reduced to hydrogen by the solvated electrons. The reaction stops with the formation of an alkynide anion:

$$R_3C\equiv CH + e^{-}_{solv} \rightarrow R_3C\equiv C^- + H^+ \text{ (as H}_2)$$

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:

$$R_3C\equiv CH + Ge_9^+ + RNH_2 \rightarrow [R-C\equiv CH=Ge_9]^3^- + RNH^-$$

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 $R_3C\equiv C^-$ ($K^-$) 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 alkynyl anion that is generated in very small amounts from the finite equilibrium with the alkynide in the presence of amines (Figure S2):

$$R_3C\equiv CH + K + H_2NR \leftrightarrow R_3C\equiv C^- + H + K^-NH$$

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 $\pi$ electron density of the triple bond. In such reactions a polar $H^+X^-$ molecule ($X$ = halogen, hydroxide, alkoxide, etc.) is attracted by the $\pi$ 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 vinylc anion 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 $\pi^*$ 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 $\pi^*$ orbitals of the triple bond. A number of strong anionic nucleophiles such as $R_3Ge^-$, $R_3Sn^-$, $RS^-$, $RTe^-$, $R_2P^-$, etc. are known to attack the $\pi^*$ orbitals and add to various alkynes. $^{84-87}$ The resulting vinylc 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 gemanyl and stannyl anions add to the terminal carbon of phenylacetylene and to the methyl end of methylphenylacetylene. $^{84,86}$

$$Et_3GeLi + H^-C\equiv C^-Ph (+H_2O) \rightarrow \text{cis-Et}_3GeCH=CH^-Ph + LiOH \quad (14)$$

$$Et_3SnLi + Me^-C\equiv C^-Ph (+H_2O) \rightarrow \text{Et}_3SnC(Me)CH=CH^-Ph + LiOH \quad (15)$$

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 $\pi^*$ orbitals of the alkynes. While the empty alkynyl $\pi^*$ 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 $E_9^+$ are made predominantly of the $p_f$ 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 $p_f$ orbitals at the two atoms.

![Figure 7](image-url)
forming the elongated edge of the tricapped trigonal prismatic cluster which is the shape most often observed for E94−.

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-antibonding between them (Figure 7A), while the HOMO-1 is exactly the opposite: it is π-antibonding 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 E94− 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 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 vinyl 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,RE− (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 Ge9-clusters with cyclopentadienylene, HCC•−CH2H2, provides a good handle on one of the steps in the process of addition. Cyclopentadienyl 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 cyclopentadienyl-vinyl radical, H2C≡C(CH2)2, is known to readily rearrange into the open-chain allene radical H2C≡C(CH2)2. By contrast, the ring in the corresponding cyclopentadienyl-vinyl anion, H2C≡C(CH2)2, is stable and does not open.67–72 Instead, it gets protonated. The 1H NMR of the reaction of Ge9-clusters with cyclopentadienylene 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 Ge9−CH≡C(CH2)2− and that no electron transfer and radical formation occur. This is consistent with the already discussed nucleophilic attack by the Ge9-clusters at the terminal carbon atom.

The reaction of Ge9-clusters with bis(trimethylsilylacetylene, TMS−C≡C−TMS, can also be understood as initial nucleophilic addition and formation of [Ge9−C(TMS)=CH−TMS]3−. This step is then followed by a desilylation step in which, according to the 1H NMR results, the TMS group replaces a proton in an ethylenediamine molecule to form TMS−NHCH2CH2NH2 (see Figure S11). One piece of evidence that the desilylation is a secondary process is the lack of reaction between clusters and CH2=CH−TMS, the compound that would be generated after single desilylation of TMS−C≡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 alkynyl groups, i.e., Ge9−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 CH2=CH−Ge9−CH=CH2 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 S2 substitution reactions by strong nucleophiles.60 There are two possible nucleophiles in our particular case that would result in formation of TMS−NCH2CH2NH2, namely the ethylenediamine solvent and its amide anion H2NCH2CH2NH− formed after deprotonation of an ethylenediamine molecule by the vinyl anion in the first step of the reaction, i.e.,

\[
\text{Ge}_9^{\text{4+}} + \text{Me}_3\text{Si−C≡C−SiMe}_3 + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{[Ge}_9−\text{C(SiMe)}_3\text{=CH−SiMe}_3]^{3−} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}^{-}
\] (16)

Ethylenediamine, however, does not react with Me3Si−C≡C−SiMe3 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:

\[
\text{[Ge}_9−\text{C(SiMe)}_3\text{=CH−SiMe}_3]^{3−} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}^{-} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{[Ge}_9−\text{CH=CH−SiMe}_3]^{3−} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}^−
\] (17)

The lack of generated amide anions in the reaction of Ge9-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, Ge9−+ Br−→CH=CH−TMS → [Ge9−+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≡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.
Lastly, the observed absence of deuterated product in the reaction with Et₃Si─C≡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 Et₃Si─C≡C─D with proto-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. Structurally characterized were the products of the reactions of Ge₉⁺ and Sn₉⁺ with BuCl, the disubstituted dimer [Bu⁻Ge₉⁻Ge₉⁻Bu⁺]⁺ and the monosubstituted monomer [Sn₉⁻Bu⁻Bu⁺], respectively. 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 BuCl but also primary and secondary halides such as Cl─CH₂CH₂CH₂CH₃ ("BuCl) and CH₃CH(CH₃)Cl/CH₂CH₃ ("BuCl) can attach to the clusters to form similarly mono- and disubstituted species, [E⁻R⁻]⁺ and [R⁻E⁻]⁺, respectively (where E = Ge, Sn). Finally, alkyl halides also undergo such reactions and form the corresponding alkenylated clusters, for example [Ge₉⁻CH₃=C=CH₂⁻]⁺ from a reaction with PhCH₂=CHBr, and reported here [Ge₉⁻CH=CH₃]⁺ from the reaction with Br⁻CH=CH₂-TMS.

Clearly, the reactions with tertiary halides can not possibly be a S₈2 nucleophilic substitution type reaction because of the sterically inaccessible carbon center protected by three substituents, methyl groups in the case of BuCl. Similarly impossible is such a reaction mechanism for the reactions with halogenated olefins, RCH=CHR and RXCHR₂ in our case, because sp² carbon atoms can not be directly attacked by nucleophiles in a S₈2 mechanism either. S₈1 substitution is also impossible because ethylenediamine is not polar enough for the ionization of these halides. It should be mentioned here that BuCl does not react with the solvent ethylenediamine to form [Bu⁻NH₂CH₂CH₂NH₂]⁺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 alkyl halides. One remaining but unproven scenario is electron transfer in very close proximity from the Ge₉⁺ cluster to the tertiary or alkyl halide to form an organic radical, a halide anion, and a cluster radical Ge₉⁻ (the cluster Ge₉⁻ has an odd number of electrons, 39, and is a radical). This would be quickly followed by radical recombination to form [Ge₉⁻Bu⁻]⁺ and [RCH=CH⁻Ge₉⁻]⁺, respectively. In a way, the reactions can be viewed as a variation of the known radical nucleophilic substitution of S₈1 type.

The reactions with primary and secondary halides, however, may proceed along the S₈2 mechanism because the halogenated carbon atom is sufficiently exposed for nucleophilic attack by the cluster. The reaction with chloromethylcyclopropane, Cl─CH₂CH₂CH₃, 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 BuCl case or b) direct nucleophilic attack at the α carbon by the cluster. The former pathway will generate the radicals Ge₉⁻ and 'CH₃CH(CH₃)₂⁺ as well as chloride anions. The methycyclopropyl radical, however, rearranges very fast with opening of the ring and formation of a double bond to form CH₃=CH(CH₂)CH₃. The rate of the rearrangement is around 9.4 × 10⁷ s⁻¹ and approaches the diffusion limit of the molecules. The absence of any observable amounts of the corresponding substituted cluster [Ge₉⁻CH₃CH(CH₂)CH₃]⁺ 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., [Ge₉⁻CH₃CH(CH₂)]⁺, and this is exactly what was observed. Therefore, we can state that the reactions between Ge₉⁻ clusters and primary halides (and most likely secondary halides) do not involve electron transfer and radical formation but are of the S₈2 type instead. Different reaction pathways for sp carbon centers, tertiary sp³ 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⁻NH₂CH₂CH₂NH₂]⁺X⁻ and [RCH⁻NH₂CH₂CH₂NH₂]⁺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 Ge₉⁻ clusters. However, the fact that the reactions with BuCl and 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 [‘Bu⁻NC(H₃)₂⁺Cl⁻] and [‘Bu⁻NC(H₃)₂⁺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 triciped 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., E₀⁺, E₀⁻, and E₀⁻. The change of oxidation state from the most reduced E₀⁻ to the least reduced E₀⁻ 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 bonding with two electrons in E₀⁻ to nonbonding with one electron in E₀⁻, and to antibonding with zero electrons in E₀⁻. 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 Ph₂Sn, Ph₂SnCl, and Ph₂GeCl 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 Me₃SnCl for example. Clearly, this is by far the preferred reaction with primary halides as shown in the reaction with chloromethylcyclopropane.
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 $S_2$ 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$_3$Sn$^-$ 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 Et$_3$Si$^+$, 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 deltaedral 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. Ethylendediamine (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$_4$Ge$_9$ was synthesized by heating a TMS container jacketed in evacuated fused-silica ampules according to previously reported synthetic procedures. TMS containers were made of 99.999% K and Et$_3$Si (Acros, 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$_3$OD, Cambridge Isotope Laboratories, 99.8%), and benzene (Sigma-Aldrich, 99.8%) were all used as received.

Et$_3$SiCl$_2$ (0.089 g, 0.44 mmol) was dissolved in benzene (2.0 mL) in a Schlenk tube. Et$_3$Si–C≡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$_3$Si–C≡C–K product. A portion of the alkynide was used for reactions with K$_4$Ge$_9$. The remaining Et$_3$Si–C≡C–K was redissolved in benzene (1.0 mL) and CD$_3$OD (0.016 g, 0.40 mmol) was added to form Et$_3$Si–C≡C–D.

**Synthesis of [K–crypt][Ge$_9$–(CD)$_2$–D$_2$]: Method I.** K$_4$Ge$_9$ (0.086 g, 0.11 mmol) was dissolved in 2 mL of ethylendediamine (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(trimethylsilylacetylene. Synthesis of [K–crown][Ge$_9$–(CH–CH$_2$)$_2$] using Et$_3$Si–C≡C–D followed this same procedure and yielded the same result.

**Synthesis of [K–crown][Ge$_9$–(CH–CH$_2$)$_2$]: Method II.** K$_4$Ge$_9$ (0.082 g, 0.10 mmol) was dissolved in 2 mL of ethylendediamine (red solution) in a test tube inside a glovebox. Triethylsilylacetylene (0.053, 0.36 mmol) was added dropwise, and the reaction mixture was stirred for 24 h. The solution was centrifuged, 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 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(trimethylsilylacetylene. Synthesis of [K–crown][Ge$_9$–(CH–CH$_2$)$_2$] using Et$_3$Si–C≡C–D followed this same procedure and yielded the same result.

**Synthesis of [K–crypt][Ge$_9$–(CD)$_2$–D$_2$]: Method II.** K$_4$Ge$_9$ (0.082 g, 0.10 mmol) was dissolved in 2 mL of ethylendediamine (red solution) in a test tube inside a glovebox. Triethylsilylacetylene (0.053, 0.36 mmol) was added dropwise, and the reaction mixture was stirred for 24 h. The solution was centrifuged, 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 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(trimethylsilylacetylene. Synthesis of [K–crown][Ge$_9$–(CH–CH$_2$)$_2$] using Et$_3$Si–C≡C–D followed this same procedure and yielded the same result.

**Synthesis of [K–crown][Ge$_9$–(CH–CH$_2$)$_2$]: Method III.** K$_4$Ge$_9$ (0.082 g, 0.10 mmol) was dissolved in 2 mL of ethylendediamine (red solution) in a test tube inside a glovebox. Triethylsilylacetylene (0.053, 0.36 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 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(trimethylsilylacetylene. Synthesis of [K–crown][Ge$_9$–(CH–CH$_2$)$_2$] using Et$_3$Si–C≡C–D followed this same procedure and yielded the same result.
Functionalization of Nine-Atom DeltaHedral Zintl Ions

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Supporting Information Available: NMR and electrospray mass spectrometry (ES-MS) spectra for [K−crypt][Ge9-(C(Me)=CH−Ph)] (n = 1, 2), [K-crown][Ge9-(CH=CH−CH(CH2)2)], [K−crypt][Ge9-(CH=CH−CH(CH2)2)]·3en, NMR spectra of TMS−NHCH2CH2NH2, Et3Si−C≡C−K, Et3Si−C≡C−D, and Et3Si−C≡C−H, and ES-MS spectrum of the reaction of Ge9− with (1-bromovinyl)trimethylsilane and 2-pentene, as well as an X-ray crystallographic file of [K−crypt][Ge9-(CH=CH−CH(CH2)2)]·3en in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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... 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-crypt/toluene solution (0.162 g crypt, 0.43 mmol, 8 mL toluene). Deep red plate-like crystals formed after about 10 days: triclinic, P1, a = 14.2449(4) Å, b = 14.3354(4) Å, and c = 20.8288(6) Å, α = 94.688(2) °, β = 94.819(2) °, and γ = 102.300(2) °. 1H NMR (pyridine-d5): δ 1.23 (t, 7 Hz, [Ge9−(C(CH3)2)=CH−CH(CH2)2])2, 1.59 (v, 7 Hz, [Ge9−(C(CH3)2)=CH−CH(CH2)2])2, 3.37 (t, crypt), 2.59 (d, 7 Hz, [Ge9−(C(CH3)2)=CH−CH(CH2)2])2, 2.85 (d, 1 Hz, [Ge9−(C(CH3)2)=CH−CH(CH2)2])2, 3.16 (qd, 7 Hz, 1 Hz, [Ge9−(C(CH3)2)=CH−CH(CH2)2])2, 3.20 (dq, 7 Hz, 6 Hz, [Ge9−(C(CH3)2)=CH−CH(CH2)2])2, 3.40 (t, crypt), 3.49 (s, crypt) 6.15 (qt, 7 Hz, 1 Hz, [Ge9−(C(CH3)2)=CH−CH(CH2)2])2, 6.30 (s, benzene). ES-MS: m/z 722 [Ge9−(C(CH3)2)]2, 761 ([K+] [Ge9−(C(CH3)2)]2), 791 [Ge9−(C(CH3)2)]2, 1135 ([K−crypt][Ge9−(C(CH3)2)])2, 1204 ([K−crypt][Ge9−(C(CH3)2)])2.

Synthesis of [K−crypt][Ge9−(C(Me)=CH−Ph)]n (n = 1, 2). K3Ge9 (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. 1H NMR (pyridine-d5): δ 2.50 (d, 7 Hz, [Ge9−(C(CH3)2)=CH−Ph])2, 2.52 (d, 2 Hz, [Ge9−(C(CH3)2)=CH−Ph])2, 3.59 (s, 18-crown-6), 8.00 (q, 2 Hz, [Ge9−(C(CH3)2)=CH−Ph])2), 8.02 (q, 2 Hz, [Ge9−(C(CH3)2)=CH−Ph])2), 3.16 (t, crypt), 2.59 (d, 7 Hz, [Ge9−(C(CH3)2)=CH−Ph])2, 2.85 (d, 1 Hz, [Ge9−(C(CH3)2)=CH−Ph])2, 3.16 (qd, 7 Hz, 1 Hz, [Ge9−(C(CH3)2)=CH−Ph])2, 3.20 (dq, 7 Hz, 6 Hz, [Ge9−(C(CH3)2)=CH−Ph])2, 3.40 (t, crypt), 3.49 (s, crypt) 6.15 (qt, 7 Hz, 1 Hz, [Ge9−(C(CH3)2)=CH−Ph])2, 6.30 (s, benzene). ES-MS: m/z 770 [Ge9−(C(CH3)2)=CH−Ph]2, 887 [Ge9−(C(CH3)2)=CH−Ph]2, 926 ([K−crypt][Ge9−(C(CH3)2)=CH−Ph])2.

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