

Addition of Alkenes to Deltahedral Zintl Clusters by Reaction with Alkynes: Synthesis and Structure of $[\text{Fc}-\text{CH}=\text{CH}-\text{Ge}_9-\text{CH}=\text{CH}-\text{Fc}]^{2-}$, an Organo-Zintl–Organometallic Anion**

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The chemistry of nine-atom deltahedral Zintl anions of germanium has made huge strides in recent years. The early expectations for low or no chemical reactivity have now been proven wrong as these clusters have been shown to be capable of undergoing a variety of reactions, such as oligomerization, addition of various main-group and transition-metal organometallic fragments, centering by transition-metal atoms, cage expansion, and so on.^[1] Particularly exciting among these are the redox reactions based on the ability of the clusters to carry different charges, to coexist in equilibria with solvated electrons (in ethylenediamine) such as $\text{Ge}_9^{4-} \rightleftharpoons \text{Ge}_9^{3-} + e^- \rightleftharpoons \text{Ge}_9^{2-} + 2e^-$, and to easily interconvert.^[1] The most remarkable among these reactions is the recently reported alkylation of Ge_9 clusters in a simple reaction with alkyl halides (RX).^[2] The resulting species $[\text{Ge}_9-\text{R}]^{3-}$, $[\text{R}-\text{Ge}_9-\text{R}]^{2-}$, and $[\text{R}-\text{Ge}_9-\text{Ge}_9-\text{R}]^{4-}$, together with the very first cluster with an organic substituent, namely $[\text{Ph}-\text{Ge}_9-\text{SbPh}_2]^{2-}$,^[3,4] have direct cluster–carbon bonds and warrant the name organo-Zintl compounds. These species, which can be made by modifying already assembled Zintl ions, nicely complement the growing class of germanium metallloid clusters assembled from organogermanium fragments containing low-valent and low-coordination germanium.^[5]

The discovery that deltahedral clusters can be derivatized by simple reactions with organic halides is an important method for adding organic functionality to the Zintl ions and ensures the diversity of the new organo-Zintl class of compounds. We have now made another significant breakthrough in this new area of chemistry and report herein that Ge_9 clusters also react with alkynes, which bond to the clusters as alkenes after undergoing hydrogenation. We demonstrate the new method by reactions with $\text{FcC}\equiv\text{CH}$ (Fc = ferrocenyl), $[\text{FcC}\equiv\text{C}]\text{K}$, $\text{PhC}\equiv\text{CH}$, $t\text{BuC}\equiv\text{CH}$, $\text{PhC}\equiv\text{CPh}$, and 4-MeO- $\text{PhC}\equiv\text{CH}$, and report the structure of the organo-Zintl–

organometallic anion $[\text{Fc}-\text{CH}=\text{CH}-\text{Ge}_9-\text{CH}=\text{CH}-\text{Fc}]^{2-}$ (**1**), which is formed by a reaction between K_4Ge_9 and $\text{FcC}\equiv\text{CH}$ in an ethylenediamine solution.

Crystals of **1** were obtained with both 2,2,2-crypt and [18]crown-6 ([18]c-6) as cation-sequestering agents, but the structures showed extensive disorder and could not be refined to publication quality. However, after recrystallization of the crystalline compound with 2,2,2-crypt from pyridine we obtained the compound reported here, $[\text{K}(2,2,2\text{-crypt})]_2\mathbf{1}\cdot 1.5\text{py}\cdot 0.5\text{en}$, with a more well-behaved structure. The anion, which is a disubstituted Ge_9 cluster, has two slightly different orientations with occupancies of 73% and 27% (see the Supporting Information).

The Ge_9 cluster in **1** (Figure 1), as in all other disubstituted species, is a tricapped trigonal prism (triangular bases of atoms 1-2-3 and 4-5-6; atoms 7, 8, and 9 are capping) with one elongated prismatic edge at the ends of which the two substituents are bonded (the dashed edge 1-4 in Figure 1 is 3.091(1) Å while the edges 2-5 and 3-6 are 2.6131(12) and 2.7054(11) Å, respectively). All three prismatic edges, however, are shorter than in the naked Ge_9^{4-} anionic cluster in

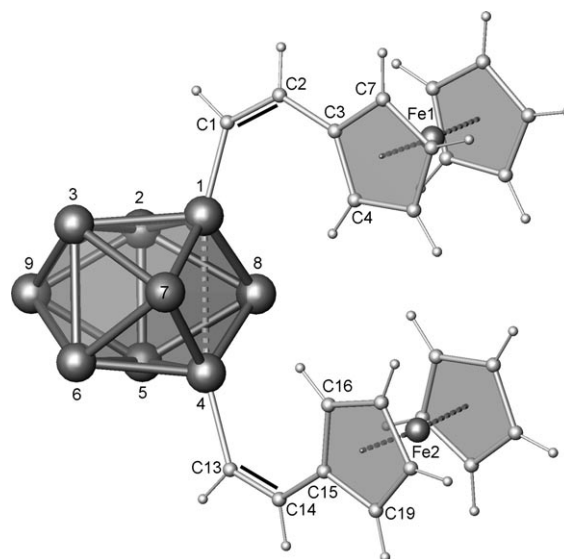


Figure 1. The new anion $[\text{Fc}-\text{CH}=\text{CH}-\text{Ge}_9-\text{CH}=\text{CH}-\text{Fc}]^{2-}$ (**1**). The two substituents are *exo* bonded as extensions of the elongated edge of the Ge_9 cluster (broken line), which has the shape of a distorted tricapped trigonal prism. The ferrocene groups and the cluster are in a *cis* geometry at the double bonds. Atoms C1, Ge1, Ge4, and C13 are almost coplanar, with this plane being nearly perpendicular to the cluster's open face (Ge1-Ge7-Ge4-Ge8) and both Fe atoms on the same side of the plane (*syn* conformation).

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

$\text{Rb}_4\text{Ge}_9\text{en}$ crystallized from ethylenediamine solution (the average distances of the two shorter and one longer edges are 2.93 and 3.65 Å, respectively).^[6] Although both clusters can also be viewed as monocapped square antiprisms, the latter resembles this geometry more.

The Ge–C bond lengths of 1.967(4) and 1.927(8) Å for Ge1–C1 and Ge4–C13, respectively, compare well with the $\text{Ge}_9\text{–C}(\text{sp}^2)$ bond length of 1.94(1) Å to the phenyl ring in the $[\text{Ph–Ge}_9\text{–SbPh}_2]^{2-}$ anion,^[4] and are somewhat shorter than the $\text{Ge}_9\text{–C}(\text{sp}^3)$ distances to the *t*Bu groups in the $[\text{tBu–Ge}_9\text{–Ge}_9\text{–tBu}]^{4-}$ anion (2.002(5) and 2.012(5) Å).^[2] They are very close to the statistical mean distance of 1.961 Å based on 241 distances between Ge and an sp^2 -hybridized carbon atoms (range of 1.91–2.04 Å) found in the Cambridge Structural Database.^[7] The lengths of the double bonds C1–C2 and C13–C14 (1.325(7) and 1.325(10) Å, respectively) and the adjacent single bonds C2–C3 and C14–C15 (1.456(8) and 1.458(7) Å, respectively) are typical for such bonds between sp^2 -hybridized C atoms.

The cluster and the ferrocene moieties are in a *cis* geometry at the double bonds, with the latter lying only slightly off the approximate plane defined by the two *exo* bonds of the cluster (Ge1–C1 and Ge4–C13). This arrangement is somewhat surprising because it puts the two ferrocene groups very close to each other, so close in fact that in order to avoid overlapping the two substituents twist slightly around the Ge–C bonds in opposite directions. This makes the cyclopentadienyl planes slightly offset from each other (space-filling figure available in the Supporting Information). While the two ferrocene groups in **1** are on the same side of the C1–Ge1–Ge4–C13 plane (*syn* conformation), they are in an *anti* geometry in the two partially refined structures crystallized from ethylenediamine solutions with 2,2,2-crypt and [18]c-6 (see above). This means that one of the ferrocene groups in these structures is rotated 180° around the *exo* C–C bond of the cyclopentadienyl ring, that is, around C2–C3 (see the Supporting Information). The existence of both *syn* and *anti* geometries suggests that the ferrocene groups rotate in solution. This was confirmed by the ¹H NMR spectrum, which shows that the hydrogen atoms at C4, C7, C16, and C19 are equivalent.

The presence of **1** in solution was confirmed by electrospray mass spectrometry (ES-MS) and ¹H NMR spectroscopy. The mass spectrum of the crystalline compound with $[\text{K}([18]\text{c-6})^+]$ counteranions shows **1** as an isolated monoanion as well as a dianion ion-paired with K^+ or with $[\text{K}([18]\text{c-6})^+]$ (Figure 2). The spectra of ethylenediamine reaction mixtures (prior to crystallization and without sequestering agents) also show the presence of the monosubstituted anionic species $[\text{Fc–CH=CH–Ge}_9]^{3-}$.

Although **1** is the only crystallographically characterized species from reactions with alkynes so far, the mass spectra of ethylenediamine reaction mixtures of K_4Ge_9 with other alkynes provide very strong evidence for similarly functionalized Ge_9 clusters and similar hydrogenation of the alkyne to alkene. Thus, the spectra of reactions with $\text{PhC}\equiv\text{CH}$, *t*BuC≡CH, and the methoxy-functionalized phenylacetylene 4-MeOPhC≡CH clearly show the corresponding mono- and disubstituted anionic species $[\text{Ge}_9\text{–CH=CH–R}]^{3-}$ and $[\text{R–}$

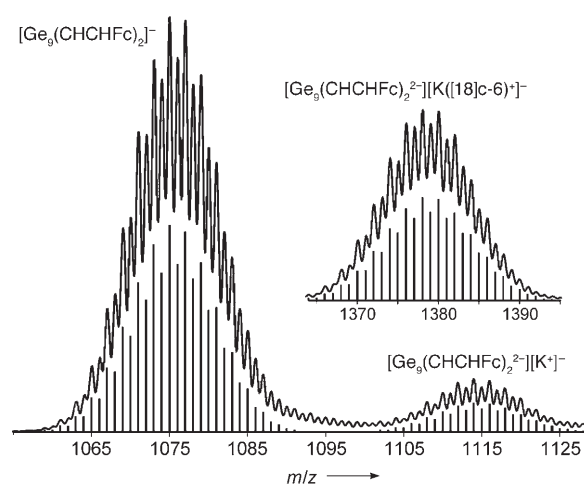


Figure 2. Two portions of the electrospray mass spectrum of **1** crystallized with $[\text{K}([18]\text{c-6})^+]$ (negative-ion mode, dissolved in DMF) showing **1** as a monoanion, a dianion coupled with K^+ , and a dianion coupled with $[\text{K}([18]\text{c-6})^+]$. The theoretical isotope distributions are shown under each peak. No other peaks corresponding to cluster species are observed in the spectrum.

$\text{CH=CH–Ge}_9\text{–CH=CH–R}]^{2-}$ (see the Supporting Information).

Internal triple bonds can also apparently react with the clusters. Thus, the ES mass spectrum of a sample taken from the reaction mixture with $\text{Ph–C}\equiv\text{C–Ph}$ exhibits clusters functionalized with $\text{–C}(\text{Ph})=\text{CH–Ph}$ groups (see the Supporting Information). With the aim of shedding more light on the mechanism of these functionalizations and the associated hydrogenation of the triple bonds, we also carried out reactions with some alkene halides such as PhCH=CHX and PhCX=CH_2 , as well as with the potassium salt of ethynylferrocene $[\text{Fc–C}\equiv\text{C}]\text{K}$. According to the ES mass spectra of the reaction mixtures, the clusters were functionalized in all cases to form $[\text{Ge}_9\text{–CH=CH–Ph}]^{3-}$, $[\text{Ge}_9\text{–C}(\text{Ph})=\text{CH}_2]^{3-}$, $[\text{Ge}_9\text{–CH=CH–Fc}]^{3-}$, and the corresponding disubstituted analogs (see the Supporting Information).

Although it is not very clear how the formation of **1** proceeds, it can be reasonably described by individual steps analogous to known organic reactions. It is well known that hydrogenation of an internal triple bond with an alkali metal in amines results in a *trans* alkene,^[8] and it is also known that terminal triple bonds resist hydrogenation under such conditions because the alkyne undergoes deprotonation and the resulting negative charge prevents additional uptake of an electron for further reduction. The formation of **1**, therefore, most likely starts with the formation of the anion $[\text{Fc–C}\equiv\text{C}]^-$, either simply from the potassium salt or generated from $\text{Fc–C}\equiv\text{CH}$ by reduction with solvated electrons from the dissolved precursor. This anion is a nucleophile and bonds to the Ge_9^{2-} moiety using the cluster's low-lying LUMO exactly as observed previously for the main-group anionic nucleophiles R_3Sn^- , R_3Ge^- , R_2Sb^- , and R_2Bi^- .^[1,3,4,9] The species thus formed, namely $[\text{Fc–C}\equiv\text{C–Ge}_9]^{3-}$, then undergoes normal hydrogenation with the difference that the product is a *cis* isomer. The geometry of the hydrogenated product is usually determined at the stage when one or two electrons occupy a

π^* -orbital of the alkyne and, in the case of neutral R groups, the resulting occupied but nonbonding sp^2 orbitals as well as the two R groups take *trans* positions in order to minimize orbital and/or steric repulsion. However, it is possible that when one of the R groups is very negatively charged, as is the Ge_9^{3-} cluster anion in this case, the more important repulsion to be minimized is that between the cluster and the occupied nonbonding sp^2 orbital at the other carbon atom. This would place the cluster and the ferrocene on the same side of the double bond and lead to a *cis* isomer for the resulting olefin.

All protons in **1** are clearly visible in the 1H NMR spectrum (see the Supporting Information). Those at the double bonds, H1/H2 and H13/H14, show two doublets resulting from coupling within each pair. The coupling constant of 13 Hz indicates that the double bonds retain the *cis* geometry observed in the solid state in solution. Furthermore, the reaction mixture before isolation of the crystalline products shows exactly the same pair of doublets in addition to a weaker second pair of doublets with exactly the same coupling constant, which can be assigned to the monosubstituted anion *cis*-[Fc-CH=CH- Ge_9] $^{3-}$. Importantly, neither spectrum indicates the presence of a *trans* isomer, which demonstrates that the reaction generates only *cis* isomers.

One of the most exciting features of this new functionalized cluster is the presence of redox active ferrocene groups. Furthermore, these groups are attached to the cluster by double bonds and, together with the cyclopentadienyl rings, form π -delocalized conjugated systems. This may allow for eventual electronic "communication" between the ferrocene groups and the cluster, and the latter may provide a communication link between the two substituents if, of course, one or both ferrocene groups can be oxidized without oxidizing the cluster first. Preliminary cyclic voltammetry studies, however, suggest that the cluster decomposes upon oxidation, which is in line with the observation by Fässler et al. of irreversible oxidation of naked germanium clusters.^[10] More detailed and extensive electrochemical and computational studies are needed in order to find out if these functionalized clusters are capable of any intramolecular electron transfer.

The results presented here expand further the emerging class of organo-Zintl compounds. They show that a variety of alkenes can be attached to Ge_9 clusters by reaction with the corresponding alkynes, which should open the door to many new opportunities in the chemistry of deltahedral clusters, such as further reactions at the double bonds attached to the clusters, the attachment of organic fragments with functional groups that can undergo other reactions, the use of these organic fragments to assemble the clusters or attach them to surfaces, and so on. Together with the alkylated clusters, these alkenyl-Zintl ions can be placed in the broader context of metalloid and intermetalloid clusters, the numbers of which have been growing seemingly exponentially in recent years.^[5,11,12] All these clusters can be considered as structurally characterized models of the much larger organically functionalized main-group nanoparticles with inaccessible atomic structures and, as such, can be used to gain a better understanding of the properties of these nanoformations.

Experimental Section

All manipulations were carried out under argon or nitrogen using standard Schlenk-line and glovebox techniques. Ethylenediamine (Alfa-Aesar, 99 %) was distilled from over sodium metal and stored in a gas-tight ampoule under nitrogen. K_2Ge_9 was synthesized from a stoichiometric mixture of the elements (K: Strem, 99 + %; Ge: Alfa-Aesar, 99.999 %), which was heated at 900 °C for two days in sealed niobium containers jacketed with evacuated fused-silica tubes. 2,2,2-Crypt (Acros, 98 %), ethynylferrocene (Acros, 97 %), phenylacetylene (Acros, 98 %), diphenylacetylene (Acros, 99 %), α -bromostyrene (Acros, 95 %), β -bromostyrene (Acros, 97 %), 3,3-dimethyl-1-butene (Acros, 98 %), 1-ethynyl-4-methoxybenzene (Aldrich, 97 %), and pyridine (Acros, 99 %) were used as received. Deuterated pyridine (Cambridge Isotope Labs, 99.9 %) was stored over molecular sieves.

Electrospray mass spectra in negative-ion mode were recorded with a Micromass Quattro-LC triple quadrupole mass spectrometer (100 °C source temperature, 125 °C desolvation temperature, 2.5 kV capillary voltage, 30 V cone voltage). The samples were introduced by direct infusion with a Harvard syringe pump at 20 $\mu L min^{-1}$.

1H NMR spectra were recorded with a Varian INOVA 500 MHz spectrometer, locked on the deuterium signal of the deuterated pyridine, and referenced against the farthest downfield peak of the residual protonated solvent.

Single-crystal X-ray diffraction data were collected with a Bruker X8 APEX-II diffractometer equipped with a CCD area detector at 100 K with $Mo_{K\alpha}$ radiation. All crystals were selected under Paratone-N oil, mounted on fibers, and positioned in the cold stream of the diffractometer. The structures were solved and refined (on F^2) with the aid of the SHELXTL V6.2 package.^[13]

Cyclic voltammetry studies were performed with a BAS Epsilon-EC potentiostat using a Pt working electrode, Pt-plate auxiliary electrode, and a 0.1M $Ag/AgBF_4$ reference electrode. Sodium tetraphenylborate (Acros, 0.1M) was used as a supporting electrolyte. Cyclic voltammograms were recorded at a scan rate of 100 $mV s^{-1}$ at room temperature under nitrogen in a glovebox.

[K(2,2,2-crypt)] $_2$ ·1.5py·0.5en: K_2Ge_9 (88 mg, 0.109 mmol) and 2,2,2-crypt (142 mg, 0.377 mmol) were dissolved in ethylenediamine (2.0 mL) by stirring. FcCCH (45 mg, 0.214 mmol) was then added and the mixture stirred for five minutes. The reaction mixture was filtered into a test tube, layered with excess toluene, and left for crystallization. Crystals were selected after a week and diffraction data collected from a few of them. The structure (monoclinic, $P2_1$, $a = 11.429(3)$, $b = 24.569(7)$, $c = 27.791(8)$ Å, $\beta = 101.610(5)^\circ$) showed very extensive disorder of the cluster and the 2,2,2-crypt moiety and could not be refined to completeness. Thus, all the crystalline material was isolated from the ethylenediamine/toluene solution, redissolved in pyridine, and layered again with toluene. Large, red-orange, block and needle-like crystals (45 % yield), many of which were suitable for single-crystal X-ray diffraction, were obtained after a week. Crystal data: triclinic, $P\bar{1}$, $a = 11.6388(10)$, $b = 12.7411(11)$, $c = 28.218(2)$ Å, $\alpha = 95.782(4)^\circ$, $\beta = 94.892(4)^\circ$, $\gamma = 91.872(4)^\circ$, $V = 4144.4(6)$ Å 3 , $Z = 2$, $R1/wR2 = 0.0423/0.0833$ for the observed data and 0.0741/0.1023 for all data.

CCDC-644631 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1H NMR ($[D_5]$ pyridine): $\delta = 7.27$ (d, $J = 13$ Hz, 2H; $Ge_9-CH=CH$), 7.07 (d, $J = 13$ Hz, 2H; $CH=CH-Fc$), 6.01 (s; Fc), 4.55 (s; Fc), 4.33 (s; Fc), 3.44 (s; 2,2,2-crypt), 3.39 (s; 2,2,2-crypt), 2.38 ppm (s; 2,2,2-crypt).

Anion **1** was also synthesized with $[K([18]c-6)^+]$ counteranions following the procedure described above but replacing 2,2,2-crypt with $[18]c-6$. Layering with toluene produced nice single crystals, a few of which were used to collect X-ray diffraction data sets. However, the structure again showed great disorder, this time predominantly at the crown ether, and the refinement was unsat-

isfactory (monoclinic, $P2_1/n$, $a = 10.9435(8)$, $b = 14.1547(9)$, $c = 49.603(3)$, $\beta = 95.818^\circ$). ES-MS (DMF): m/z 1075 $[\text{Ge}_9^-(\text{CH}=\text{CH}-\text{Fc})_2]^-$, 1114 $[[\text{K}^+][\text{Ge}_9^-(\text{CH}=\text{CH}-\text{Fc})_2]^-]$, 1378 $[[\text{K}([18\text{-c-6})][\text{Ge}_9^-(\text{CH}=\text{CH}-\text{Fc})_2]^{2-}]^-]$.

Preparation of reaction mixtures for ES mass spectrometry: Reactions similar to the one described above but without sequestering agents were carried out between ethylenediamine solutions of K_2Ge_9 and each of the following compounds (amounts): $\text{PhC}\equiv\text{CH}$ (1.5 equiv), $t\text{BuC}\equiv\text{CH}$ (less than 1 equiv), 4-MeOPhC $\equiv\text{CH}$ (more than 2 equiv), $\text{PhC}=\text{CPh}$ (less than 1 equiv), $\text{PhCH}=\text{CHBr}$ (1.3 equiv), and $\text{PhCBr}=\text{CH}_2$ (1.5 equiv). Samples of the resulting reaction mixtures were introduced directly into the mass spectrometer. The spectra, along with the anions identified, are provided in the Supporting Information. The mass and ^1H NMR spectra of similar reactions with less than 1.5 equivalents of $\text{FcC}\equiv\text{CH}$ or $[\text{FcC}\equiv\text{C}]\text{K}$ confirmed the presence of both $[\text{FcCH}=\text{CHGe}_9]^{3-}$ and $[(\text{FcCH}=\text{CH})_2\text{Ge}_9]^{2-}$.

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