Zintl Clusters

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Linking Deltahedral Zintl Clusters with Conjugated Organic Building Blocks: Synthesis and Characterization of the Zintl Triad [R-Ge$_9$-CH=CH−CH=CH-Ge$_9$-R]$^{4-}$**

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Dedicated to Professor Hans-Jörg Deiseroth on the occasion of his 70th birthday

Abstract: *The accessibility of triads with deltahedral Zintl clusters in analogy to fullerene–linker–fullerene triads is another example for the close relationship between fullerenes and Zintl clusters. The compound* {[K(2.2.2-crypt)]$_4$[RGe$_9$-CH=CH−CH=CH-Ge$_9$R]}(toluene)$_2$ *(R = (2Z,4E)-7-amino-5-aza-hepta-2,4-dien-2-yl), containing two deltahedral [Ge$_9$] clusters linked by a conjugated (1Z,3Z)-buta-1,3-dien-1,4-diyl bridge, was synthesized through the reaction of 1,4-bis(trimethylsilyl)butadiyne with K$_4$Ge$_9$ in ethylenediamine and crystallized after the addition of 2.2.2-cryptand and toluene. The compound was characterized by single-crystal structure analysis as well asNMR and IR spectroscopy.*

Molecular spintronics and electron spin-based quantum computing have a demand for molecules that can accommodate a variable number of electrons and/or can form stable radicals. Dyads bearing covalently linked electron-donating moieties in close proximity to such molecules offer a valuable approach to novel molecular electronics as well as to artificial photosynthesis. Besides, triads with electroactive spacers are of special interest as the total spin-carrying capacity can be increased, and spins are tunable. Most prominent examples are the fullerenes, and there exists a large variety of C$_{60}$ donor dyads and triads (Figure 1 a) with the C$_{60}$ core being covalently linked to an electron-donating unit, and alternatively, two C$_{60}$ molecules might be connected by organic spacers. Such complex molecules are promising candidates for electron-transfer systems, and the electronic interactions between two C$_{60}$ units has been the subject of different studies.[1,2]

As pointed out earlier, C$_{60}$ molecules show a close relationship to homoatomic deltahedral Zintl ions of Group 14 elements [E$_m$]$^{n-}$ (E = Si, Ge, Sn, Pb; m = 9, 10, 12).[3] Both kinds of basic polyhedral building units feature delocalized electronic systems such as the conjugated π electrons in the former case and an electron-deficient bonding system, according to Wade's rules, which can also be

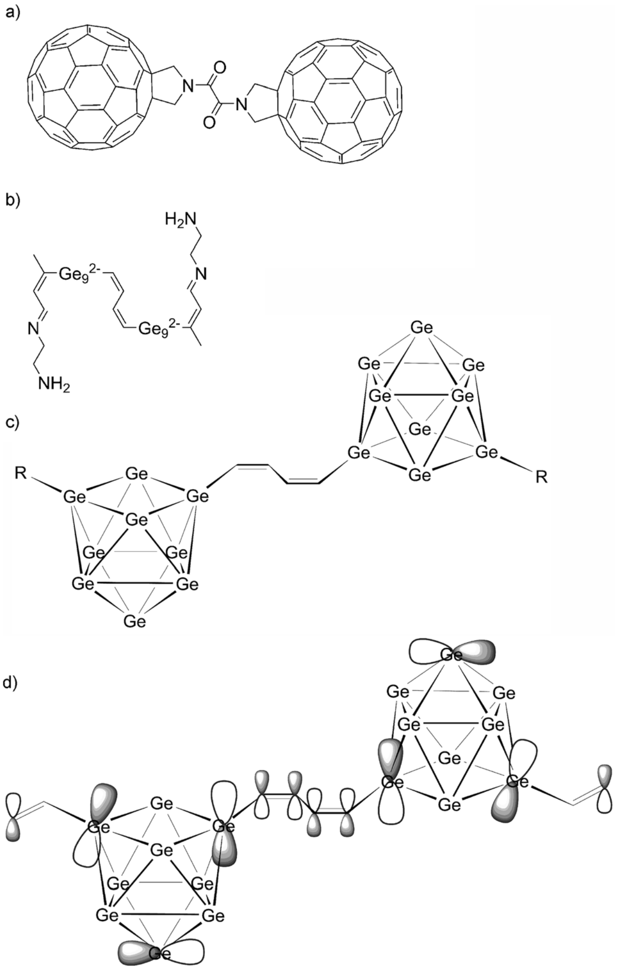

Figure 1. a) A fullerene-linker-fullerene triad. b), c) The organo Zintl triad [R-Ge$_9$-CH=CH−CH=CH-Ge$_9$-R]$^{4-}$, R = (2Z,4E)-7-amino-5-aza-hepta-2,4-dien-2-yl comprising a conjugated C$_4$ linkage between two [Ge$_9$] Zintl clusters. d) View of the HOMO of **1**. The corresponding wave functions of the HOMO and LUMO as well as that of HOMO−25 reflecting π-type interactions within the C$_4$ chain are shown in the Supporting Information.

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considered as resonance-delocalized σ bonds (spherical aromaticity),[4] in the latter. Furthermore, both polyhedral molecules can adopt different charges (C_{60}^{n-} for $n=0$–6 and E_9^{n-} for $n=2$–4). As a further parallel, both clusters form endohedral species with a heteroatom trapped inside the fullerene or Zintl cage, respectively.[5,6b]

Deltahedral Zintl cluster ions $[E_9]^{4-}$ (E = Si, Ge, Sn, Pb) are conveniently accessible as binary alkali metal phases A_4E_9 (A = Na–Cs) obtained from solid-state reactions of the respective elements. Using sequestering agents like cryptands or crown ethers, such phases can be dissolved in a fairly limited selection of organic solvents to investigate the reactivity of these Zintl ions in solution.[6]

The solution chemistry of such homoatomic clusters is well-developed for E = Ge. $[Ge_9\text{-}Ge_9]^{6-}$ dimers,[7] $[Ge_9]_n^{(2n)-}$ ($n=3$, 4) oligomers[8] and ${}^{1}_{\infty}[Ge_9]^{2-}$ polymers[9] occur with classical (2c/2e) as well as non-classical Ge−Ge *exo* bonds. These examples are manifestations of a rational assembly of molecular structures with valuable electronic and optical properties.[10] Besides directly coupled clusters, a few examples are known in which *exo*-bonded main-group element fragments have been attached.[11–13] $[Ph\text{-}Ge_9\text{-}SbPh_2]^{2-}$ was the first $[E_9]$ Zintl anion containing a covalent 2c/2e cluster–carbon bond.[12] Later, alkylated species $[E_9\text{-}R]^{3-}$ and $[R\text{-}(E_9)_2\text{-}R]^{4-}$ have been obtained by the reaction of $[E_9]^{4-}$ (E = Ge, Sn) with alkyl halides RX.[14,15] Furthermore, $[E_9]^{4-}$ (E = Ge, Sn) was found to readily react with alkynes $R^1\text{-}C{\equiv}C\text{-}R^2$ leading to alkenylated Zintl anions, $[E_9(R^{1/2}CH{=}CR^{1/2})_n]^{(4-n)-}$ ($n=1$–2; R = H, organic residue; a list of known compounds is given in the Supporting Information).[15–19]

Whereas many of these products are only available in rather low yields, the vinylation of $[Ge_9]^{4-}$ by bis(trimethylsilyl)acetylene in ethylenediamine leads to good quantities of the bis-vinylated clusters $[Ge_9\text{-}(CH{=}CH_2)_2]^{2-}$[17] besides minor amounts of mono- and, in that case, even tris-vinylated species, $[Ge_9\text{-}(CH{=}CH_2)]^{3-}$ and $[Ge_9\text{-}(CH{=}CH_2)_3]^{-}$, respectively.[15,16] Although it is obvious to link such $[Ge_9\text{-}(CR{=}CHR)_n]^{(4-n)-}$ ($n=1$–2) species via their olefinic substituents,[20] as successfully applied for fullerenes,[1] such reactions have not been reported to date.

Herein we present the synthesis and the structure of the first deltahedral Zintl cluster anions that are covalently linked by a conjugated C_4 unit. The anion $[RGe_9\text{-}CH{=}CH\text{-}CH{=}CH\text{-}Ge_9R]^{4-}$ (R = (2*Z*,4*E*)-7-amino-5-aza-hepta-2,4-dien-2-yl) (**1**) is also interesting because it features side chains with an imine functionality, which further enlarge the delocalized π-electron system (Figure 1b).

The anion **1** (Figure 1b) was obtained by adding K_4Ge_9 to a mixture of 1,4-bis(trimethylsilyl)butadiyne (**2**) with ethylenediamine and crystallized in presence of the sequestering agent 2.2.2-cryptand and toluene as {[K(2.2.2-crypt)]$_4$**1**}(toluene)$_2$. The new compound was characterized by single-crystal X-ray analysis and NMR and IR spectroscopy.

The crystal structure of {[K(2.2.2-crypt)]$_4$**1**}(toluene)$_2$ contains four $[K(2.2.2)\text{-crypt}]^+$ complexes, the title anion **1**, and two disordered toluene molecules. The anion **1** consists of two Ge_9 clusters, which are linked by a zigzag chain of four carbon atoms, and each cluster carries an eight-atom side chain (Figure 1b and Figure 2).

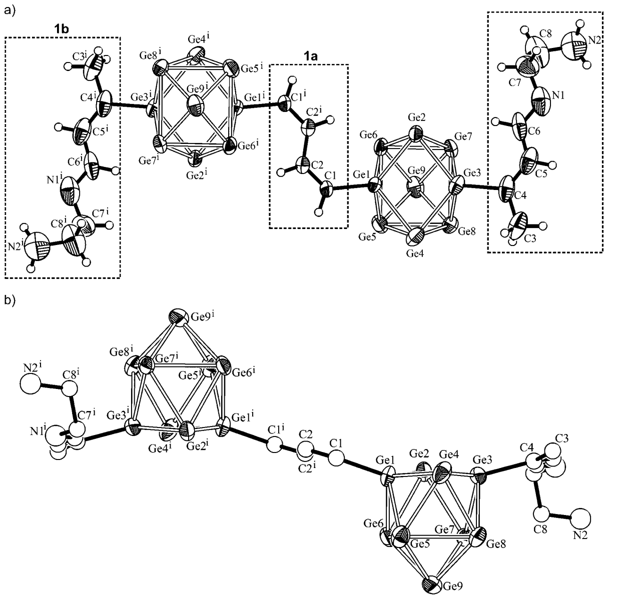


Figure 2. Two views of the molecular structure of the anion **1**, viewed a) perpendicular and b) parallel to the plane of the connecting C_4 unit. a) Cluster bridge (**1a**) and side chains (**1b**) are emphasized with a dashed frame. For reasons of clarity hydrogen atoms are omitted; in (b), C and N atoms are shown as empty spheres. Ellipsoids are set at 50% probability. Symmetry code: (*i*) $-x$, $-y$, $1-z$.

The molecular anion is located around a crystallographic inversion center, which lies in the middle of the $C2{-}C2^i$ bond. The Ge1−C1 distance of 1.950(7) Å is indicative of a covalent $Ge{-}C(sp^2)$ single bond and is in the range of other observed $Ge_9{-}C$ bonds.[16] Bond lengths of 1.47(2) Å for the central $C2{-}C2^i$ bond and of 1.33(1) Å for the C1−C2 bond clearly indicate single and double bonds, respectively.[21] Consequently all C atoms of the C_4 chain and the atoms Ge1 and $Ge1^i$ are in plane (Figure 2b, maximum deviation of all atoms of 0.0146 Å from an idealized plane through the atoms Ge1, C1, C2, $C2^i$, $C1^i$, and $Ge1^i$). Both double bonds of the C_4 chain are in *Z* configuration, giving a (1*Z*,3*Z*)-buta-1,3-dien-1,4-diyl (**1a**) cluster linkage.

The Ge_9 unit adopts almost perfect C_{2v} point symmetry and contains two planes including the atoms Ge1 to Ge4 and Ge5 to Ge8, with maximum torsion angles of each set of 4 atoms of 7.5° and 0.01°, respectively. The Ge−Ge bond lengths in the cluster are in the narrow range from 2.519(1) to 2.691(1) Å, except for two distances which are significantly longer (d(Ge5−Ge6) = 2.966(1) Å and d(Ge7−Ge8) = 2.932(1) Å). The shortest bonds are observed in the Ge1/Ge2/Ge3/Ge4 plane, forming a rhombus with one significantly shortened diagonal (3.15 Å compared to 3.95 Å) between the atoms Ge1 and Ge3 that are covalently bonded to C atoms.[22] Consequently, a distinct deviation of the cluster shape from a monocapped square antiprism with C_{4v} symmetry, as expected for a 22 skeletal electron cluster, is shown by the ratio of 1.26 between the diagonal lengths of the uncapped Ge1/Ge2/Ge3/Ge4 plane. The deviation from a tricapped trigonal prism with D_{3h} symmetry is indicated by the ratio of the three heights of the central trigonal prism of 1:1.01:1.18 for Ge6−Ge7, Ge5−Ge8, and Ge2−Ge4, respectively. The observed shape and distances correspond well to other Ge$_9$ clusters with 22 skeletal electrons and covalently bonded organic groups.[16–19]

The second organic side chain (atoms C3 to N2, **1b**) form a conjugated electron system with C4=C5 and C6=N1 double bonds.[23] Consequently, the atoms C3 to C7 and Ge3 are in plane with a maximum deviation of 0.074 Å. In summary each cluster is bisubstituted, at Ge1 by the conjugated C$_4$ linkage and at Ge3 by (2*Z*,4*E*)-7-amino-5-aza-hepta-2,4-dien-2-yl side chains (**1b**).[23]

The structure of **1** is confirmed by the ^{1}H NMR spectrum of {[K(2.2.2-crypt)]$_4$**1**} in [D$_3$]acetonitrile (Figure 3 and Experimental Section). The signals of the linking unit **1a** are observed as doublets of doublets 1aα$^{(\prime)}$ and 1aβ$^{(\prime)}$, with a major coupling constant of 8.3 Hz typical of *cis*-orientated olefinic hydrogen atoms. For the signals 1aα$^{(\prime)}$ and 1aβ$^{(\prime)}$ a characteristic fine structure is visible, which can be attributed to the magnetically non-equivalent protons 1aα/1aα′ and 1aβ/1aβ′, respectively, analogous to other 1,4-disubstituted *cis*,*cis*-buta-1,3-dienes.[24] The imine functionality of the dangling unit **1b** appears as a strongly down-field shifted signal 1bδ, which corresponds to other reported ^{1}H chemical shift values of imines.[24,25] Furthermore, crystals of {[K(2.2.2-crypt)]$_4$**1**}-(toluene)$_2$ were analyzed by ATR-FTIR spectroscopy. Apart from bands in the spectral range 2729–2949 cm^{-1} indicative of ν(C-H) stretching modes, ν_s(N-H) and ν_{as}(N-H) stretching modes, which are typical of primary amines R-NH$_2$, are observed at 3347 and 3269 cm^{-1}, respectively. Furthermore, the presence of amine and imine functionalities in **1** is indicated by a strong band at 1609 cm^{-1} and a weaker band at 1582 cm^{-1}.[24,25]

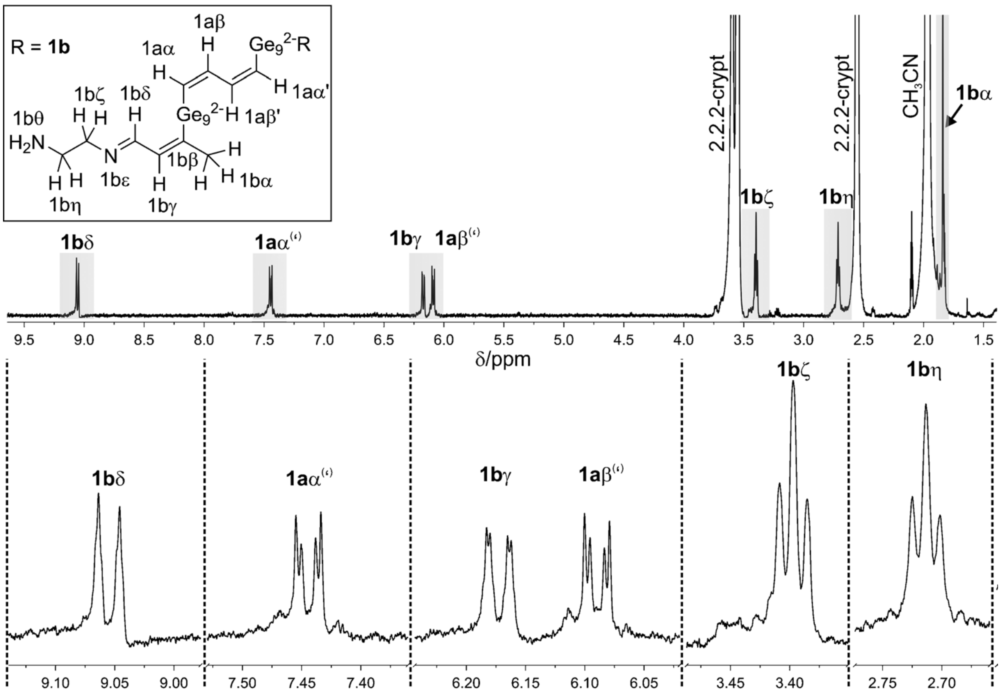
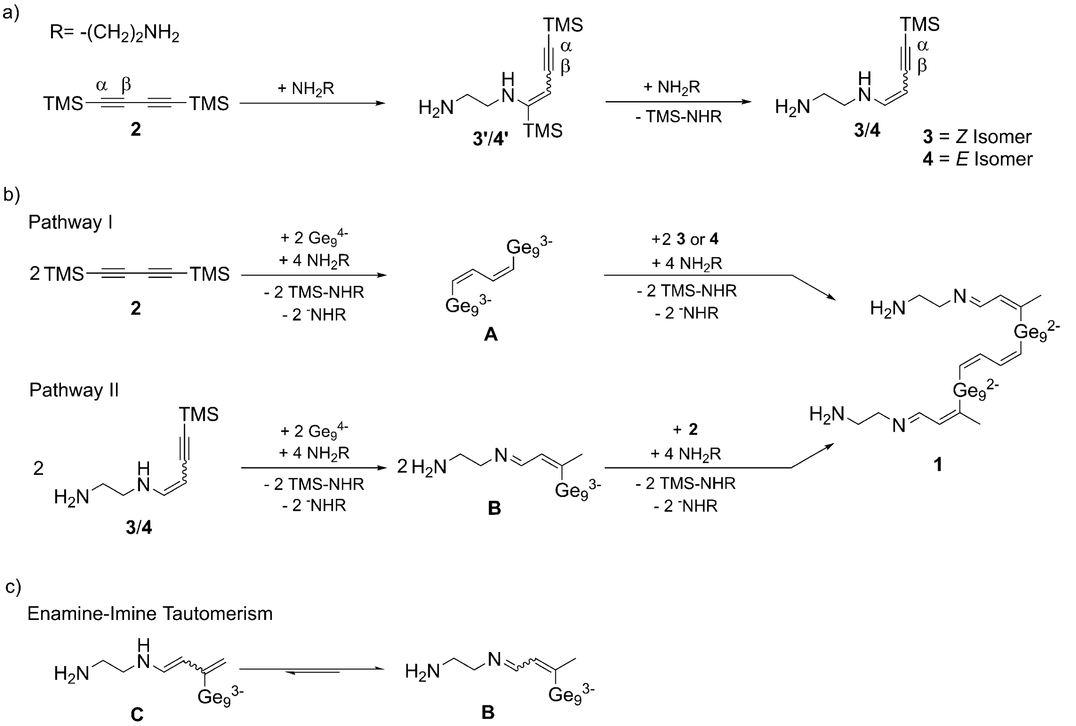


Figure 3. ^{1}H NMR resonances of the anion **1** in [D$_3$]acetonitrile. Crystals of {[K(2.2.2-crypt)]$_4$**1**}(toluene)$_2$ were recrystallized from [D$_5$]pyridine in a vacuum and redissolved in [D$_3$]acetonitrile. Thus the ^{1}H NMR spectrum in [D$_3$]acetontrile does not show signals of toluene, whereas the ^{1}H NMR spectrum of {[K(2.2.2-crypt)]$_4$**1**}-(toluene)$_2$ in [D$_5$]pyridine displays the signals of toluene (see the Supporting Information). Resonances originating from **1** are highlighted in gray and magnified below. Assignments are given in the Experimental Section.

The structure of **1** and its electronic structure were quantum chemically investigated on a PBE0/def2-TZVPP/PCM level of theory by using the bis-vinylated derivative [H$_2$C=CH-Ge$_9$-CH=CH−CH=CH-Ge$_9$-H$_2$C=CH]$^{4-}$ as a model structure. All Ge−Ge distances are in the range of the experimental values (2.54–2.95 Å). The central C$_4$ unit (**1a**) reveals two shorter bonds (1.37 Å, cp. exp.1.33 Å) and a longer bond (1.44 Å cp. exp.1.47 Å.), reflecting double and single bonds, respectively. The HOMO–LUMO gap of 3.43 eV confirms the high stability of **1**. The HOMO reflects that the main orbital contributions bear the typical electronic structure for a conjugated π-system extending over the whole molecule (Figure 1 d). Similarly the LUMO shows for all four C atoms of **1a** contribution of the p-orbitals perpendicular to the plane of the C atoms with an additional nodal plane and neglecting contributions of the Ge atoms (see isosurfaces of the wave functions in the Supporting Information).

From the applied synthetic procedure, it would be expected at a first glance that there is a simple connection of two clusters via the bridge **1a**; however, the imine side chain **1b** is also formed, which was unforeseen. Formally the formation of the organic bridge **1a** can be rationalized by an addition of two [Ge$_9$]$^{4-}$ or [Ge$_9$R]$^{3-}$ at **2** on its terminal 1,4-positions (Scheme 1). The overall *cis* configuration of **1a** is consistent with observations of Sevov that the alkenylation of [E$_9$]$^{4-}$ with alkynes selectively proceeds via an *anti*-addition of a cluster unit and a proton to the alkyne triple bond.[18] The role of ethylenediamine as proton source for the hydrogenation of the triple bond has been emphasized before; however, without confirmation of the direct transfer of the proton from ethylenediamine and the formation of the respective anion K[NHR].[18] According to NMR experiments on reaction mixtures involving **2**, ethylenediamine and K$_4$Ge$_9$, the formation of the side chain **1b** entails a reaction of the solvent ethylendiamine with **2**.



Scheme 1. a) Reaction of 1,4-bis(trimethylsilyl)butadiyne with ethylenediamine leading to (3*Z*)- and (3*E*)-7-amino-5-aza-hepta-3-en-1-yne (**3/4**) intermediates, which seem to play a key role in the formation of **1** and its side chain **1b**. b) Possible reaction pathways leading to anion **1**. c) Supposed enamine–imine tautomerizm involved in the formation of side chain **1b**.

The reaction of **2** with ethylenediamine in the absence of clusters forms both (3*Z*)- and (3*E*)-7-amino-5-aza-hepta-3-en-1-yne (**3/4**) in an approximate isomer ratio of $Z/E = 30{:}70$ and $(TMS)NH(CH_2)_2NH_2$ according to NMR spectra. In ethylenediamine, owing to a fast exchange of TMS^+ and H^+, **3′/4′** were not observed.[26] Such hydroamination reactions that occur by nucleophilic addition of amines to alkynes or alkenes via their amino functionality are well-known.[28] Given that **2** undergoes fast reaction with ethylenediamine, pre-mixing of **2** and ethylenediamine has a crucial influence on the entire reaction. Owing to their alkyne functionality, the resulting enamines **3** and **4** are also reactants towards the clusters with a preferred cluster addition at the more positively polarized β position.[29]

For the synthesis of **1**, a suspension of **2** in ethylenediamine is mixed with K_4Ge_9, thus **3/4** and **2** are both potential reactants for $[Ge_9]^{4-}$. To follow this synthesis by NMR spectroscopy, we added a solution of **3/4** to a mixture of K_4Ge_9 and **2**, so that **2** and **3/4** were present in a stoichiometric ratio with respect to **1**. The ^{1}H NMR spectrum (see the Supporting Information) of the mixture does not show signals of **3/4**, but resonances assignable to the organic fragments **1a** and **1b** (Figure 3).[30]

In conclusion, we can derive two possible pathways leading to **1** (Scheme 1): Pathway I involves first an addition of $[Ge_9]^{4-}$ at **2** giving intermediate **A**, and a subsequent reaction of **A** with **3** or **4** to the final product **1**. Alternatively, pathway II is in the reverse order and starts with the addition of $[Ge_9]^{4-}$ to **3** or **4**, forming intermediate **B**. The subsequent reaction of **B** with **2** gives rise to **1**. Thereby, further intermediates on the way to **1** are conceivable.[31]

We have shown the synthesis of {[E_9]-linker-[E_9]} triads comprising two deltahedral Zintl clusters and a conjugated organic linker, which are analogous to {fullerene-linker-fullerene} triads. As the (1*Z*,3*Z*)-buta-1,3-dien-1,4-diyl cluster linkage and the (2*Z*,4*E*)-7-amino-5-aza-hepta-2,4-dien-2-yl side chains in the anion **1** are π-delocalized conjugated systems, intramolecular cluster-to-cluster electron transfer processes are conceivable. Thus, a further characterization of **1** concerning its physical and chemical properties is needed, including its redox behavior and optical properties. Preliminary cyclic voltametric measurements in acetonitrile show an irreversible oxidation at approximately 1 V.

An appropriate adjustment of the reaction conditions should also allow for the synthesis of oligomers and polymers with alternating Ge_9 and conjugated (1*Z*,3*Z*)-buta-1,3-dien-1,4-diyl subunits.

Experimental Section

All manipulations were carried out under a purified argon atmosphere using a glove box and standard Schlenk techniques. The Zintl compound of the nominal composition K_4Ge_9 was synthesized by heating a stoichiometric mixture of the elements K and Ge.[6d]

Synthesis of {$[K(2.2.2\text{-crypt})]_4$**1**}$(toluene)_2$: In a glove box, 1,4-bis(trimethylsilyl)butadiyne (Alfa Aesar, 98 %, 93.3 mg, 0.48 mmol) was filled into a Schlenk tube and suspended in ethylenediamine (2 mL), whereby within 30 min a pale yellow solution with undissolved bis(trimethylsilyl)butadiyne was obtained. The mixture was dropped onto solid K_4Ge_9 (97.2 mg, 0.12 mmol) under vigorous stirring. The reaction mixture was further stirred for 3 h at room temperature, resulting in a deep-red solution. After careful layering the filtrate with a solution of 2.2.2-crypt (180.7 mg, 0.48 mmol) in toluene (8 mL), red plates of {[K(2.2.2-crypt)]$_4$**1**}(toluene)$_2$ suitable for single-crystal X-ray diffraction were obtained after two weeks (yield 30%, based on K_4Ge_9) beside reddish-black blocks of {[K(2.2.2-crypt)]$_2$[Ge$_9$]} (yield ca. 10%).[32] Crystals of {[K(2.2.2-crypt)]$_4$**1**}(toluene)$_2$ were separated from side products by hand and washed with toluene and dried at ambient pressure.

Crystal data: $M_r = 3243.38$, triclinic space group $P\bar{1}$, $a = 11.8949(4)$, $b = 12.8395(4)$, $c = 24.5578(7)$ Å, $\alpha = 104.112(2)$, $\beta = 92.007(2)$, $\gamma = 109.831(2)°$, $V = 3393.1(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.59\ g\,cm^{-3}$, $\mu = 4.1\ mm^{-1}$; 45570 measured and 11865 independent reflections, $R_{int} = 0.064$; $R_1 = 0.065$ and $wR_2 = 0.186$ for $I > 2\sigma(I)$, $R_1 = 0.099$ and $wR_2 = 0.201$ for all data. Min/max residual electron density: $-0.96/2.66\ e\,Å^{-3}$. The positions of the hydrogen atoms were calculated and refined using a riding model. All non-hydrogen atoms were treated with anisotropic displacement parameters. Disordered solvent molecules were treated with the SQUEEZE option in PLATON.[33,34] CCDC 1025862 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.

DFT calculations were performed with Gaussian09 program package[35] using the exchange correlation hybrid functional after Perdew, Burke, and Ernzerhof (PBE0)[36] and a def2-TZVPP basis set for C, H, and Ge.[37] For the compensation of the negative charge, a solvation model (polarizable continuum model, PCM) was estimated.[38] The structure of the compound was optimized under preservation of the C_i point symmetry (keyword symm = loose). Harmonic frequencies were calculated numerically to confirm the nature of the stationary point on the potential-energy surface as a true minimum. As starting input structure, the experimentally determined atom positions were used keeping point group symmetry C_i.

For additional illustrations and a list of known alkenyl functionalities attached to [Ge$_9$] Zintl-clusters, a detailed experimental section and crystallographic data including selected bond lengths and angles, NMR data and the ATR-FTIR data of {[K(2.2.2-crypt)]$_4$**1**}(toluene)$_2$, and in situ NMR spectroscopy data on reaction solutions involving **2**, ethylenediamine, and K_4Ge_9, see the Supporting Information.

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[23] Selected bond lengths in Å: Ge1–C1 1.950(7), C1–C2 1.33(1), C2–C2^i 1.47(2), Ge3–C4 1.99(1), C4–C3 1.53(2), C4–C5 1.37(2), C5–C6 1.40(2), C6–N1 1.28(1), N1–C7 1.45(2), C7–C8 1.56(2), C8–N2 1.43(2), Ge1–Ge2 2.519(1), Ge2–Ge3 2.520(1), Ge3–Ge4 2.544 (2), Ge4–Ge1 2.537(1), Ge1–Ge5 2.563(1), Ge1–Ge6 2.595(1), Ge2–Ge6 2.668(1), Ge2–Ge7 2.678(1), Ge3–Ge7 2.584(1), Ge3–Ge8 2.593(1), Ge4–Ge8 2.633(1), Ge4–Ge5 2.652(2), Ge5–Ge6 2.966(1), Ge6–Ge7 2.676(1), Ge7–Ge8 2932(1), Ge8–Ge5 2.691(1), Ge5–Ge9 2.590(1), Ge6–Ge9 2.589(1), Ge7–Ge9 2.580(1), Ge8–Ge9 2.595 (2).

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[26] The TMS cleavage for the formation of **3**/**4** occurs most probably through intermediates **3′**/**4′**, still bearing TMS groups, in analogy to the reaction of bis(trimethylsilyl)acetylene with [Ge$_9$]$^{4-}$ in

ethylenediamine. It was found that TMS-substituted alkenes are able to quickly undergo a TMS^+/H^+ exchange reaction with ethylenediamine under formation of $(TMS)NH(CH_2)_2NH_2$. The ^1H NMR spectrum of the solution containing **3/4** shows an intense singlet around 0.1 ppm, which can be attributed to the TMS groups of both **2** and/or $(TMS)NH(CH_2)_2NH_2$. According to ^{13}C NMR spectra, **2** is not present in the solution (for NMR data, see the Supporting Information).[18,27]

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[29] In the ^{13}C NMR spectrum, stronger downfield shifts of the β-C atoms of **3/4** when compared to those of the α-C atoms indicate that the β-C atoms are more positively polarized and therefore easier accessible for nucleophiles.

[30] It is not yet fully established whether the resonances of the fragments **1a** and **1b** found in this reaction mixture belong to the same molecule or arise from independent species. Furthermore it is possible that the signals assigned to fragment **1b** arise from a cluster bearing two side chain **1b**. Investigations concerning these questions are still ongoing.

[31] The addition of $[Ge_9]^{4-}$ to **3/4** should involve also enamine intermediate **C**, which might tautomerize to the corresponding imine (Scheme 1). Furthermore it is unclear at this point whether there is a preference of clusters to react either with **3** or **4.** Currently we also investigating which parameters determine the configuration of the double bonds in the side chain **1b**.

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