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Syntheses and ^1H NMR Spectra of Substituted Zintl Ions $[Ge_9R_n]^{(4-n)-}$: Crystal Structures of $[Ge_9R]^{3-}$ (R = 2,4,6-$Me_3C_6H_2$, $CHCH_2$) and Indication of Tris-Vinylated Clusters

Christian B. Benda,[a] **Jian-Qiang Wang,**[a] **Bernhard Wahl,**[a] **and Thomas F. Fässler***[a]

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The introduction of a mesityl (Mes; 2,4,6-$Me_3C_6H_2$) ligand to a Ge_9 polyanion is accomplished by the reaction of $[Ge_9]^{4-}$ solutions with Ag_4Mes_4. The crystal structure investigation of its [K([2.2.2]crypt)] salt ([2.2.2]crypt: 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) shows that $[Ge_9Mes]^{3-}$ comprises one *exo*-bonded aryl ligand in accordance with the ^1H NMR spectroscopic data. The formation of mono-, bis-, and tris-substituted Zintl Ions $[Ge_9R_n]^{(4-n)-}$ (n = 1, 2, and 3; R = $CHCH_2$) is investigated by ^1H NMR spectroscopy. The mono- and bis-vinylated Ge_9 clusters, $[Ge_9(CHCH_2)]^{3-}$ and $[Ge_9(CHCH_2)_2]^{2-}$, were obtained by the reaction of K_4Ge_9 with $Me_3SiC{\equiv}CSiMe_3$ in ethylenediamine. In the presence of [18]crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and $K(C_5H_5)$ crystals containing both cluster species were isolated and structurally characterized as $[K([18]crown\text{-}6)]_2\{(\eta^5\text{-}C_5H_5)[K([18]crown\text{-}6)]_2\}[Ge_9(CHCH_2)]$ and $[K([18]crown\text{-}6)]\{(\eta^5\text{-}C_5H_5)[K([18]crown\text{-}6)]_2\}[Ge_9(CHCH_2)_2]$, respectively. ^1H NMR experiments hint for the tris-vinylated cluster $[Ge_9(CHCH_2)_3]^-$.

Introduction

Currently, the chemistry of Zintl cluster anions of the type $[E_9]^{4-}$ (E = Si – Pb) is entering a period of prosperity. After the successful crystallization of salts with such anions with the help of sequestering agents and their structural characterization, many reactions in solution have been carried out during the last 20 years.[1–7] The first type of reactions were ligand exchange reactions of transition metal complexes in which $[E_9]^{4-}$ acts as an η^4-ligand that replaces η^6-arene ligands, thereby leading to transition metal complexes of the type $[E_9M(CO)_3]^{4-}$ (E = Sn, Pb; M = Cr, Mo, W).[8–10] More recently, reactions of $[E_9]^{4-}$ with main group fragments, such as $SbPh_3$ and $BiPh_3$, yielded the bis-substituted (dimeric) clusters $[Ph_2Q\text{-}[Ge_9]_n\text{-}QPh_2]^{(2n)-}$ (Q = Sb, Bi; n = 1, 2).[11,12] The synthesis and structural characterization of interconnected deltahedral clusters in the form of dimeric $[Ge_9–Ge_9]^{6-}$ units, a number of linear oligomeric assemblies $[Ge_9]_n{}^{(2n)-}$ (n = 3, 4), and polymeric chains such as $^1_\infty[Ge_9]^{2-}$ revealed the presence of two-center two-electron (2c/2e) Ge–Ge *exo* bonds.[13–20] A second generation of 2c/2e *exo* bonds was achieved with organic ligands with $[PhGe_9\text{-}SbPh_2]^{2-}$ as the first representative.[12] The reaction of K_4Ge_9 and K_4Sn_9 with $Me_3SiC{\equiv}CSiMe_3$ in ethylenediamine (en) yielded the structurally characterized mono-vinylated Sn_9 species and bis-vinylated Ge_9 clusters, respectively.[21–23] Although the hydrogen transfer to the acetylene unit during the formation of the bis-vinylated clusters is under discussion, the synthesis in ethylenediamine has been established for several alkynes.[4,5,21–27] Recently, mono- and bis-vinylated heteroatomic clusters $[(Ge_{9-x}Sn_x)R_{9-x}]^{(x-5)-}$ in which x = 7, 8 and R = $CHCH_2$ have been described,[24] whereas the existence of mono-vinylated Ge_9R clusters has been indicated by mass spectroscopy; a structural characterization exists solely for R = $(CH_3)C{=}CHCH_2CH_3$ and $(CH_3CH_2)CH{=}CHCH_3$, respectively.[22] These organically functionalized Zintl clusters can be considered as bifunctional molecules. The hybrid building blocks might establish regio- and chemoselective reactions both with the inorganic cluster fragment and with its organic groups.

Herein we report the introduction of an *exo*-bonded *aryl* ligand to a Ge_9 cluster using silver mesityl and the structural characterization of this cluster unit in the salt $[K([2.2.2]crypt)]_3[Ge_9Mes]$ (**1**). Furthermore, the first mono-vinylated Ge_9 cluster is structurally characterized in $[K([18]crown\text{-}6)]_2\{(\eta^5\text{-}C_5H_5)[K([18]crown\text{-}6)]_2\}[Ge_9(CHCH_2)]$ (**2**). The unusual co-crystallization of $(C_5H_5)^-$ has also been observed in the bis-vinylated Ge_9 cluster in $[K([18]crown\text{-}6)]\{(\eta^5\text{-}C_5H_5)[K([18]crown\text{-}6)]_2\}$ $[Ge_9(CHCH_2)_2]$ (**3**). ^1H NMR spectroscopic investigations also indicate the existence of tris-vinylated Ge_9 clusters in solution.

Results

Crystal Structures

$[Ge_9Mes]^{3-}$ (**1a**) was formed by the reaction of K_4Ge_9 with Ag_4Mes_4 in ethylenediamine (reaction 1 in Scheme 1).

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[a] Department Chemie, Technische Universität München,
Lichtenbergstraße 4, 85747 Garching, Germany
Fax: +49-89-289-13186
E-mail: thomas.faessler@lrz.tum.de

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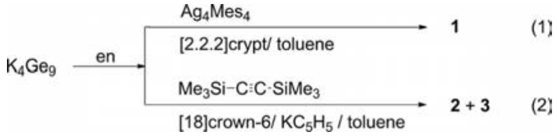
Crystals of **1** were isolated by layering the reaction solution with [2.2.2]crypt dissolved in toluene. The asymmetric unit of **1** consists of three $[K([2.2.2]crypt)]^+$ units and one $[Ge_9Mes]^{3-}$ cluster, **1a**. The –3 charge is typical for mono-functionalized nine-atomic tetrel anions.[23,24] The shape of the cluster is very similar to the known analogous clusters functionalized by one or two main-group organometallic fragments or organic groups.[21,22,24,26,27] The mesityl group in **1a** is connected to Ge1, which is part of the open square of the cluster. The Ge–C distance of 2.03(1) Å is in agreement with the Ge–C bond length of 1.94(1) Å in $[Ph\text{-}Ge_9\text{-}SbPh_2]^{2-}$.[12] For comparison, the Ge–C distance in tetrakis-(pentafluorophenyl)germanium(IV) is 1.956(4) Å.[28]



Scheme 1. Reaction scheme of the syntheses of compounds **1**–**3**.

The Ge1–C1 bond vector is tilted towards the open side of the cluster defined by the atoms Ge1–Ge2–Ge3–Ge4. The out-of-plane angle ω(C1–Ge1–Ge3) of 153° (Figures 1 and 2) leads to a bending of the carbon hexagon of the mesityl group towards the open side. Alternatively, **1a** can be seen as a mono-substituted 2,4,6-trimethylbenzene with the Ge_9 substituent being attached out-of-plane with respect to the planar aromatic mesityl hexagon by ω(Ge1–C1–C4) = 168°, probably as a result of steric repulsion. The angle sum at C1 is equal to $\Sigma\omega$(C1) = ω(Ge1–C1–C6) + ω(Ge1–C1–C2) + ω(C2–C1–C6) = 359°.

As previously observed for other substituted clusters, the mean intra-cluster Ge1–Ge distance of 2.54 Å to atoms Ge2, Ge4, Ge5, and Ge6 is shorter than other intra-cluster Ge–Ge contacts with the mean value, for example, for Ge3–Ge of 2.60 Å (to Ge2, Ge4, Ge7, Ge8), but all distances are still longer than typical covalent 2c/2e bonds, such as in α-Ge (2.45 Å).[29] The cluster framework can be described as a tricapped trigonal prism[1,3] with one elongated prism height h_1 (Ge1–Ge3) of 3.507(2) Å in comparison with the other two heights h_2 (Ge5–Ge8) and h_3 (Ge6–Ge7) of 2.760(2) Å and 2.703(2) Å, respectively. Alternatively, the cluster can be regarded as a distorted C_{4v}-symmetric mono-capped square antiprism in which the distortion is best described by the ratio of the diagonal lengths of the basal plane d_2(Ge2–Ge4): d_1(Ge1–Ge3) of 1.07. Thus, the occurrence of the *exo* bond correlates with the longer diagonal of the open cluster face. The Ge_9 fragment of **1a** can therefore be described as a *nido* cluster with 22 skeleton electrons according the rules of Wade and Mingos.[30–33] Table 1 summarizes the most important structural parameters of **1a**. Generally, the distances within the cluster are very similar to those in other mono-substituted clusters, such as $[Ge_9Sn(CH_3)_3]^{3-}$.[34] The C–C distances within the arene ring of **1a** are in the expected range from 1.34(2) (C1–C2) to 1.44(2) Å (C1–C6). The C_{methyl}–C_{arene} bond lengths range from 1.49(2) (C4–C8) to 1.54(2) Å (C2–C7).

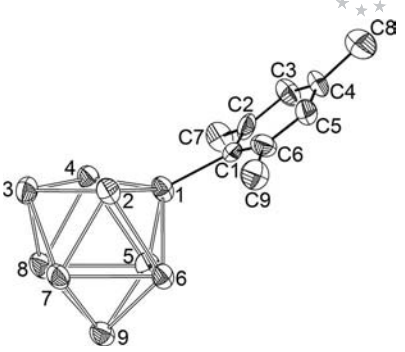


Figure 1. The molecular structure of $[Ge_9Mes]^{3-}$ (**1a**). The displacement ellipsoids of Ge atoms (identified by their number) and C atoms of the mesityl group are shown at 50% probability level. For clarity, hydrogen atoms have been omitted. Selected bond lengths [Å]: Ge1–Ge3 3.507(2), Ge2–Ge4 3.755(2), Ge5–Ge6 2.942(2), Ge7–Ge8 2.927(2), Ge1–C1 2.03(1).

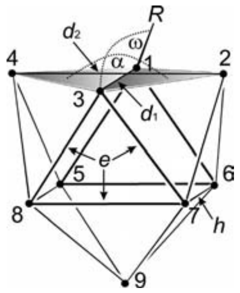


Figure 2. Parameters used for the description of the cluster structures. Values are given in Table 1.[3] d_1 and d_2 reflect the diagonals of the open square. h identifies the height of the trigonal prism. h_1 is equal to d_1. Angle α represents the dihedral angle between the triangular faces 1–3–4 and 1–3–2. Angle ω defines the out-of-plane angle of the *exo*-bonded substituent R with respect to d_1.

Table 1. Selected structural parameters for the anions $[Ge_9Mes]^{3-}$ (**1a**), $[Ge_9(CHCH_2)]^{3-}$ (**2a**), and $[Ge_9(CHCH_2)_2]^{2-}$ (**3a** and **4a**).

	1a	**2a**	**3a**	**4a**[21]
h_2 [Å]	2.703(2)	2.772(1)	2.685(1)	2.6746(3)
h_1/h_2	1.30	1.22	1.17	1.16
h_3/h_2	1.02	1.00	1.00	1.01
d_2/d_1	1.07	1.15	1.28	1.29
α[a] [°]	172.23(8)	176.17(3)	173.61(4)	174.89(1)
ω[b] [°]	153	167, 153	169, 159	162, 160
$d_{Ge\text{-}C}$ [Å]	2.03(1)	1.95(1), 2.05(1)	1.969(4), 1.954(4)	1.950(2), 1.961(2)
$d_{C=C}$ [Å]	1.34–1.44	1.30(1)	1.288(5), 1.263(5)	1.316(2), 1.318(2)

[a] Dihedral angle at the open basal plane. [b] Out-of-plane angle: two values due to disordering in **2a** or two vinyl groups in **3a** and **4a**.

Red crystals of compound **2** containing $[Ge_9(CHCH_2)]^{3-}$ (**2a**) were obtained as shown by Reaction 2 (Scheme 1), along with orange crystals of **3**, which contain the bis-substituted anion $[Ge_9(CHCH_2)_2]^{2-}$ (**3a**). The ratio of the amounts of **2** and **3** can be adjusted by varying the concentration of $Me_3SiC{\equiv}CSiMe_3$. Interestingly, the mono-vinylated cluster **2a** always cocrystallizes with KC_5H_5 to give compound **2**, whereas the bis-vinylated cluster **3a** crystallizes with and without KC_5H_5 to form either compound **3** or the previously described compound $[K([18]crown\text{-}6)]_2 [Ge_9(CHCH_2)_2]\cdot(en)$ (**4**).[21]

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with seven $[K([18]crown\text{-}6)]^+$ units, one cyclopentadienyl anion, and two $[Ge_9(CHCH_2)]^{3-}$ clusters per unit cell (Figure 3, a). The Ge–Ge bond lengths in **2a** range from 2.485(1) Å (Ge1 to Ge2) to 2.879(1) Å (Ge7 to Ge8) and, as observed for **1a**, the Ge1–Ge distances (Ge1–Ge2, Ge4, Ge5, Ge6) with a mean value of 2.53 Å are shorter than other intracluster Ge–Ge contacts (Ge3 to Ge2, Ge4, Ge7, Ge8 with an average value of 2.64 Å). The vinyl ligand is disordered and was refined by a splitting model. Only one vinyl group is depicted in Figure 3 (a). The Ge1–C1A and Ge1–C1B distances of 2.05(1) and 1.95(1) Å are slightly different with out-of-plane angles of ω_A = 167° and ω_B = 153°, respectively.

The C–C distances in each disordered vinyl group are equal to 1.30(1) Å (C1A–C2A and C1B–C2B) (Figure 3, a). The open face in **2a**, defined by Ge1–Ge2–Ge3–Ge4, can be described as rhombic with a dihedral angle of α_1 = 176.17(3)° and d_2(Ge2–Ge4)/d_1(Ge1–Ge3) = 1.15. The heights of the prism are h_1 (Ge1–Ge3) = 3.394(1) Å, h_2 (Ge5–Ge8) = 2.772(1) Å, and h_3 (Ge6–Ge7) = 2.775(1) Å [c.f. **1a**: h_1 = 3.507(2) Å, h_2 = 2.760(2) Å, and h_3 = 2.703(2) Å]. The symmetry of **2a** is reduced from C_{4v} to C_S as a consequence of one *exo* substituent.

The cation K1 caps the triangular face Ge5–Ge6–Ge9 at an average distance of 3.60 Å, and K2 caps the Ge2–Ge3–Ge4 face with the shortest contact of 3.39 Å between K2 and Ge3 and the longest distance of 3.89 Å between K2 and Ge2 (average 3.66 Å). There are no K contacts to Ge1, which binds to the C1 atom, and the particularly short distance between K2 and Ge3 indicates a significant localization of the electronic charge at Ge3 in **2a**. Due to the potassium–cluster interactions all sequestered K atoms are shifted out of the plane of the O atoms of the coordinating [18]crown-6 molecules. The K–O distances within the $[K([18]crown\text{-}6)]^+$ unit are around 2.9 Å. The $C_5H_5^-$ unit

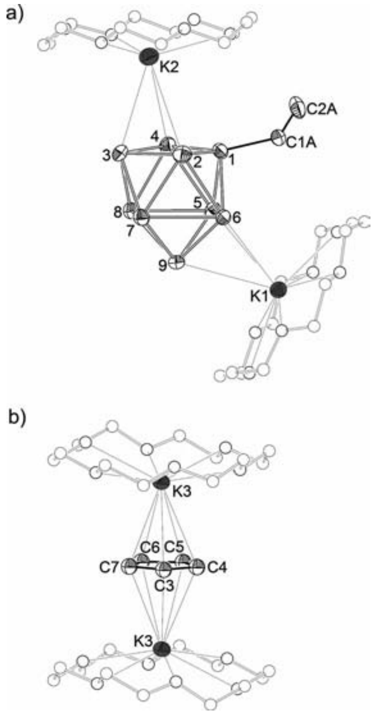


Figure 3. The molecular structure of $[Ge_9(CHCH_2)]^{3-}$ (**2a**) with its coordinating $[K([18]crown\text{-}6)]^+$ units (a) and the $\{(\eta^5\text{-}C_5H_5)\text{-}[K([18]crown\text{-}6)]_2\}^+$ unit (b) in the crystals of **2**. Germanium atoms (identified by their atom number), potassium, and carbon atoms of one disordered vinyl group are shown anisotropically with 50% occupation probability. For clarity, hydrogen atoms have been omitted, and the atoms of the [18]crown-6 molecules are shown as empty spheres. Selected bond length [Å]: Ge1–Ge3 3.394(1), Ge2–Ge4 3.911(1), Ge5–Ge6 2.868(1), Ge7–Ge8 2.879(1), Ge1–C1A 2.05(1), Ge1–C1B 1.95(1), C1A–C2A 1.30(2), C1B–C2B 1.29(2), Ge2–K2 3.888(1), Ge3–K2 3.385(1), Ge4–K2 3.715(1), Ge5–K1 3.584(1), Ge6–K1 3.615(1), Ge9–K1 3.586(1), C3–K3 3.111(5), C6–K3 3.043(6), C4–C5 1.40(1), C5–C6 1.41(1).

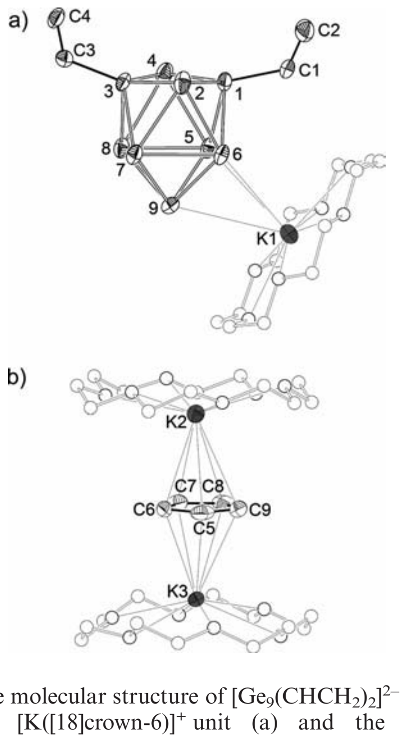


Figure 4. The molecular structure of $[Ge_9(CHCH_2)_2]^{2-}$ (**3a**) with its coordinating $[K([18]crown\text{-}6)]^+$ unit (a) and the $\{(\eta^5\text{-}C_5H_5)\text{-}[K([18]crown\text{-}6)]_2\}^+$ unit (b). Germanium atoms (identified by their atom number), potassium, and the carbon atoms of the vinyl and cyclopentadienyl groups are shown anisotropically with 50% occupation probability. For clarity, hydrogen atoms have been omitted, and the atoms of the [18]crown-6 molecules are shown as empty spheres. Selected distances [Å]: Ge1–Ge3 3.127(1), Ge2–Ge4 3.991(2), Ge5–Ge6 2.9323(7), Ge7–Ge8 2.9138(7), Ge1–C1 1.969(4), Ge3–C3 1.954(4), C1–C2 1.288(5), C3–C4 1.263(5), Ge5–K1 3.741(1), Ge6–K1 3.707(1), Ge9–K1 3.771(1), C7–K2 3.027(6), C9–K2 3.185(6), C7–K3 3.017(6), C9–K3 3.153(5).

coordinates to two K3 atoms, which are located above and below the plane of the cyclopentadienide anion with mean K3–C distances of 3.1 Å as shown in Figure 3b. The coordination sphere of each K3 is completed by a crown ether molecule.

Compound **3** crystallizes in the monoclinic space group $P2_1/c$. The unit cell comprises three $[K([18]crown-6)]^+$ units and one cyclopentadienyl moiety per $[Ge_9(CHCH_2)_2]$ cluster, and thus the electronic charge of the cluster is –2. The intra-cluster distances in **3a** range from 2.527(1) Å (Ge3 to Ge4) to 2.932(1) Å (Ge5 to Ge6). Neglecting the symmetry of the *exo*-ligands, the symmetry of **3a** can be described as C_S (Figure 4, a).

Structural parameters of **3a** are summarized in Table 1. The two *exo*-bonded vinyl groups are located at the Ge1 and Ge3 atoms with similar bond lengths of 1.969(4) Å (Ge1 to C1) and 1.954(4) Å (Ge3 to C3), but different out-of-plane angles of ω of 169° and 159°, respectively. It is worth mentioning that the values of ω in compounds **1**, **2**, and **3** increase with decreasing cluster symmetry (C_{4v} to C_s) and an increasing number of *exo* bonds (Table 1).

The C–C distances of the two vinyl groups in **3** are slightly different with values of 1.288(5) Å (C1–C2) and 1.263(5) Å (C3–C4), and the *exo* ligands are again pointing away from the open face of the cluster. K1 caps the triangle Ge5–Ge6–Ge9 at an average distance of 3.74 Å. These

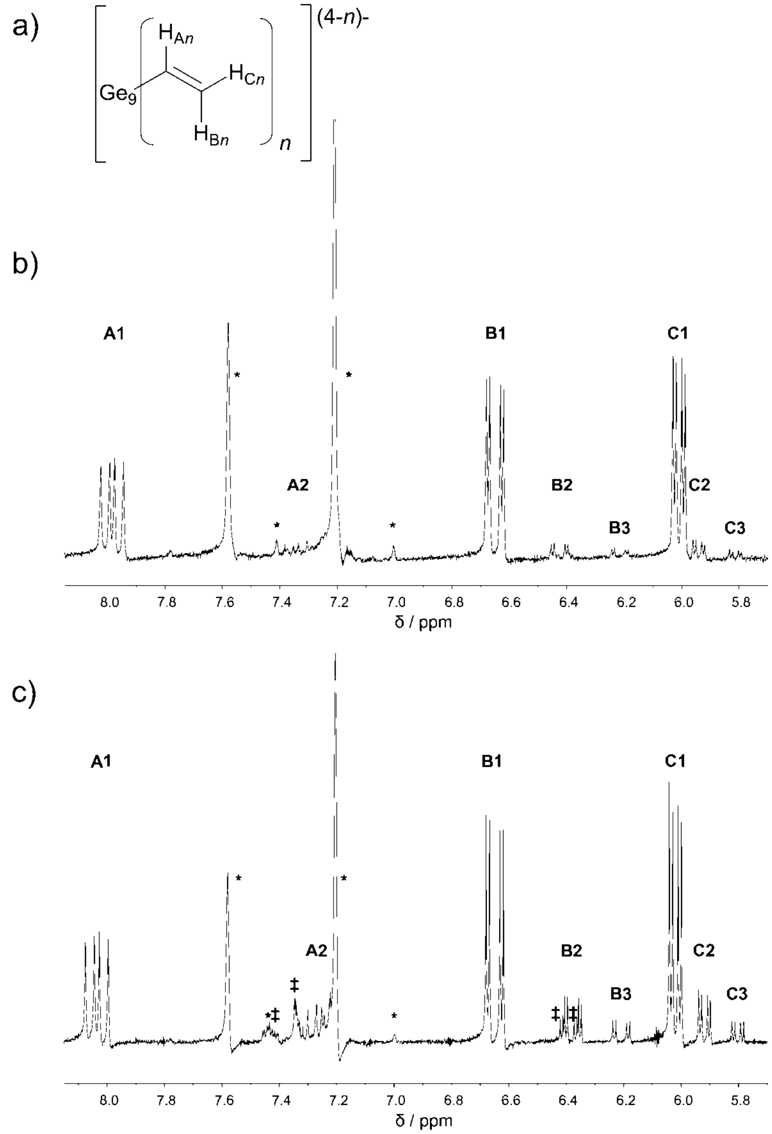


Figure 5. Vinylated Ge_9 cluster with proton assignment (a); region of the vinyl protons of the ^1H NMR spectrum obtained from ethylenediamine solutions containing K_4Ge_9 and 0.9 equiv. of $Me_3SiC{\equiv}CSiMe_3$ (b) and 2.8 equiv. of $Me_3SiC{\equiv}CSiMe_3$ (c). Signals attributed to mono-vinylated $[Ge_9(CHCH_2)]^{3-}$ are labeled A1, B1, and C1; bis-vinylated $[Ge_9(CHCH_2)_2]^{2-}$ are labeled A2, B2, and C2. The two signal groups B3 and C3 are attributed to tris-vinylated $[Ge_9(CHCH_2)_3]^{-}$. Signals labeled with * mark solvent peaks ([D5]pyridine), and resonances that are not assignable are marked with ‡.

longer (0.3 Å) Ge–K distances in **3** compared with those in **2** can be interpreted as a consequence of the weaker Coulomb interactions between the potassium ions and the lower cluster charge of –2 in **3** instead of –3 in **2**. In contrast to **2** and **4**, **3a** is capped by only one [K([18]crown-6)]$^+$ unit.

^{1}H NMR Spectroscopic Investigations

From a series of ^{1}H NMR spectra recorded from reaction mixtures of K_4Ge_9 and $Me_3SiC{\equiv}CSiMe_3$ in ethylenediamine with different $K_4Ge_9/Me_3SiC{\equiv}CSiMe_3$ ratios, the coexistence of mono-, bis-, and probably also tris-vinylated Ge_9 clusters $[Ge_9(CHCH_2)_n]^{(4-n)-}$ (n = 1, 2, 3) can be derived. As shown in Figure 5, the reaction solutions show three sets of signals in the typical shift region of vinylic protons.[21,25]

The three doublets of doublets, labeled as A1, B1, and C1 in Figure 5, originate from the protons H_{A1}, H_{B1}, and H_{C1} (Figure 5, a) of the mono-vinylated Ge_9 (MVG) cluster $[Ge_9(CHCH_2)]^{3-}$ (**2a**) as concluded from the identical chemical shifts and coupling constants observed in the ^{1}H NMR spectrum of a solution of a pure sample of compound **2**. The signals A2, B2, C2 arise from the vinyl protons H_{A2}, H_{B2}, and H_{C2} of the bis-vinylated Ge_9 cluster (BVG) $[Ge_9(CHCH_2)_2]^{2-}$ (**3a**), as can be deduced from the ^{1}H NMR spectrum of a solution of pure **3** and from the spectrum of the previously reported compound [K[18]-crown-6]$_2$[$Ge_9(CHCH_2)_2$]·en.[21] The ^{1}H NMR spectra of solutions of pure samples of **2** and **3** are shown in Figure S2 in the Supporting Information and the chemical shift values and coupling constants serve as reference values for mono- and bis-vinylated Ge_9 clusters.

In the spectrum of the MVG/BVG clusters, each pair of signals A1/A2, B1/B2, and C1/C2 show identical coupling constants of 19/12, 19/4, and 12/4 Hz, respectively. These values are in agreement with those previously published for the bis-vinylated Ge_9 cluster[21] and confirm the MVG structure reported here.

The charges Λ of –2 and –3 of the bis- and mono-vinylated Ge_9 clusters, respectively, correlate with the downfield chemical shifts of the vinyl protons. With increasing cluster charge and thus a decreasing degree of vinylation, the resonances of the vinyl protons are shifted to lower magnetic field ($\Lambda \approx 1/\delta$) and for $\Delta\Lambda = 1$ the following relative shifts are observed: $\Delta\delta(H_A) >> \Delta\delta(H_B) > \Delta\delta(H_C)$. Notice, also the resonances of the vinyl protons of vinyl cyanide are high-field shifted owing to the electron-withdrawing effect of the CN group.[21] The equivalence of the signals of both vinyl groups reveal that the C_{2v} symmetry of the cluster framework of **3a** as it is observed in crystals of **3** is retained in solution or that a fast rearrangement of the framework-Ge atoms arises in only one set of signals as it is observed for the MVG cluster.

The only structurally characterized Ge_9 cluster with three R substituents has been isolated as the $[Ge_9\{Si(SiMe_3)_3\}_3]^-$ salt. The crystal structure determination accounts for a tricapped trigonal prismatic Ge_9 cluster framework with D_{3h} symmetry and with the $Si(SiMe_3)_3$ groups attached to the three capping Ge atoms. As a consequence of the D_{3h} symmetry, or due to a fast ligand exchange mechanism on the NMR spectroscopic time scale, only one group of signals has been observed for the methyl protons for $[Ge_9\{Si(SiMe_3)_3\}_3]^-$.[35] Therefore, only one set of signals of the three vinyl protons is expected for the tris-vinylated Ge_9 cluster. Furthermore, the signals of the vinyl protons of the tris-vinylated Ge_9 cluster are expected to appear at higher magnetic fields than those of the bis-vinylated clusters (A2, B2, and C2). Two signals from the expected set of TVG signals are observed and labeled as B3 and C3 in Figures 5 (b,c) and 6 (b).

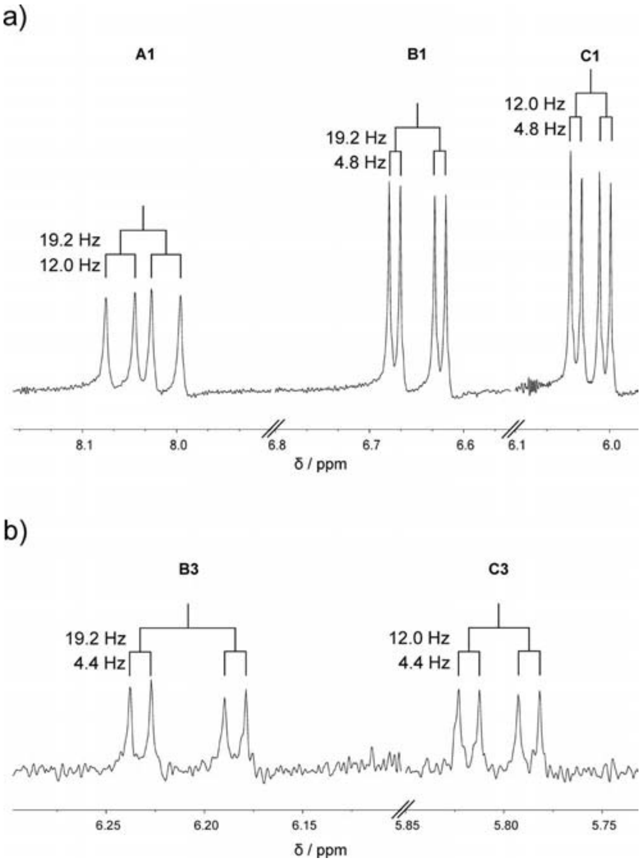


Figure 6. Enlarged sections of part c in Figure 5. Signals A1, B1, and C1 of the mono-vinylated $[Ge_9(CHCH_2)_3]^-$ with corresponding coupling constants (a), and signals B3 and C3 and coupling constants attributed to the tris-vinylated $[Ge_9(CHCH_2)_3]^-$ (b).

The coupling constants of the doublet of doublets B3 and C3 (19 Hz/ 4 Hz and 12 Hz/4 Hz, respectively) again agree with those of B1/C1 and B2/C2 (Figure 6 and Figure S3, Supporting Information). The missing doublet of doublets A3 (analogous to A1 and A2) is expected in the range of 6.2–7.2 ppm (Figure S4, Supporting Information) with low intensity. Indeed a doublet of doublets with expected low intensity and as shown in Figure 5 (c) and Figure S3 (marked with ‡) can be recognized in the region of the B2 signal at approximately 6.4 ppm, however, it could also overlap with other signal groups, for example, B1.

In summary, these observations probably hint for a low concentration of tris-vinylated Ge_9 clusters in ethylenediamine solutions. As mentioned above, the existence of a tris-functionalized Ge_9 cluster has been proven by the isolation and characterization of the cluster compound $[Ge_9R_3]^-$ in which R = $Si(SiMe_3)_3$; a cluster, however, obtained by a completely different synthetic approach.[35]

Discussion and Conclusion

We presented the transfer of a mesityl group from the transition metal complex Ag_4Mes_4 to a Ge_9 cluster. The structurally characterized compound $[K([2.2.2]crypt)]_3$-$[Ge_9Mes]$ contains the first Ge_9 cluster with only *one exo*-bonded aryl ligand. Interestingly, the corresponding reaction of K_4Sn_9 with Ag_4Mes_4 in ethylenediamine led to an oxidative coupling of the $[Sn_9]^{4-}$ units and the formation of an $[Ag(Sn_9–Sn_9)]^{5-}$ cluster.[36] Thus, depending on the anion $[E_9]^{4-}$ (E = Ge, Sn), Ag_4Mes_4 can act either as a mesityl group or a silver ion donor, which is roughly in agreement with the hard/hard and soft/soft acid/base concept by Pearson and Klopman.[37–40] In the related reaction of $K_6Rb_6Si_{17}$ with CuMes in liquid ammonia, the CuMes unit binds as a neutral molecule to the tetrahedral silicon cluster $[Si_4]^{4-}$ with the formation of $[(MesCu)_2Si_4]^{4-}$.[41]

In the course of our investigations, we were also able to provide the as yet missing structure of a mono-vinylated Ge_9 cluster in the series of both homo- and heteroatomic deltahedral Zintl ions $[Ge_{9-x}Sn_xR_n]^{(4-n)-}$ in which $x = 0, 7, 8$; $n = 1, 2$ and R = $(CHCH_2)$, (CHCH–Ph), (CHCH–CPr), (CHCH–Fc).[24] It turned out that the mono-vinylated cluster $[K([18]crown-6)]_2\{(\eta^5-C_5H_5)[K([18]crown-6)]_2\}[Ge_9(CHCH_2)]$ forms crystals exclusively with co-crystallized KC_5H_5. Furthermore, we demonstrated that the bis-vinylated Ge_9 cluster can also co-crystallize with KC_5H_5 to give $[K([18]crown-6)]\{(\eta^5-C_5H_5)[K([18]crown-6)]_2\}$ $[Ge_9(CHCH_2)_2]$.

Based on a series of ^1H NMR spectroscopic measurements we have shown that ethylenediamine solutions of K_4Ge_9 and $Me_3SiC{\equiv}CSiMe_3$ contain the mono-, bis-, and probably also traces of the tris-vinylated Ge_9 cluster.

The above compounds have a high potential for the bottom-up synthesis of nano-sized materials with a well-defined ratio of its composites. Such clusters may be linked through their functional groups or fixed at surfaces either through their vinyl groups by classical organic reactions (e.g., polymerization, metatheses, cycloaddition reactions). More complex assemblies may arise via the inorganic cluster moiety by the reaction with transition metal compounds as it has been shown for $[Ni_3Ge_{18}]^{4-}$, $[Si(SiMe_3)_3]_6Ge_{18}M$ (M = Cu, Ag, Au), $[Cu(\eta^4-Ge_9)(\eta^1-Ge_9)]^{7-}$, $[Sn_9AgSn_9]^{5-}$, $[Au_3Ge_{18}]^{5-}$, $[Au_3Ge_{45}]^{9-}$, ${}^1_\infty[HgGe_9]^{2-}$, $[Hg_3(Ge_9)_4]^{10-}$, $[E_9Ir(cod)]^{3-}$ (E = Sn, Pb), and $[Sn_9HgSn_9]^{6-}$.[36,42–53]

Furthermore, the organo-functionalized Zintl clusters are less negatively charged due to the *exo* bonds. Hence these clusters are much more stable towards oxidizing agents than the naked Zintl clusters $[E_9]^{4-}$. As mentioned previously, these functionalized clusters are prone to dissolve in less-polar organic solvents, such as toluene, in particular using phase-transfer catalysts.[21] This fact may open up new perspectives for subsequent reactions of organo-functionalized Zintl clusters in less-polar non-nucleophilic organic solvents.

Experimental Section

Syntheses: All manipulations and reactions were performed under a purified argon atmosphere by using standard Schlenk line and glove box techniques. The Zintl compound of the nominal composition K_4Ge_9 was synthesized by heating a stoichiometric mixture of the elements K and Ge at 650 °C for 20 h in a stainless steel tube. Ethylenediamine (Merck) was distilled from calcium hydride and used immediately after collection. [2.2.2]crypt (Merck) was dried under vacuum for eight hours. [18]crown-6 (Merck) was sublimed under vacuum at 80 °C. $Me_3SiC{\equiv}CSiMe_3$ (Merck) was used as received. Ag_4Mes_4 was synthesized according to the literature.[54] Deuterated pyridine and acetonitrile were dried with an activated molecular sieves (4 Å) for several days and stored in a glove box.

$[K([2.2.2]crypt)]_3[Ge_9Mes]$ (1): A dark-green solution of K_4Ge_9 (0.11 mmol) in ethylenediamine (2 mL) was added to solid Ag_4Mes_4 (25 µmol). The resulting dark-red solution was stirred for 3 h at r.t., separated from the residue by filtration and carefully layered with a solution of [2.2.2]crypt (400 µmol) in toluene (5 mL). After one week, dark-red crystals of **1** appeared at the bottom of the flask (yield 30 mol-%). ^1H NMR (CD_3CN, 400 MHz, 25 °C): δ = 6.51, (m, 2 H, C_6H_2), 3.56 (s, [2.2.2]crypt), 3.52 (t, $^3J(^1H,^1H)$ = 4.8 Hz, [2.2.2]crypt), 2.52 (t, $^3J(^1H,^1H)$ = 4.8 Hz, [2.2.2]crypt), 2.31 (s, 6 H, *o*-CH_3), 2.05 (s, 3 H, *p*-CH_3) ppm.

$[K([18]crown-6)]_2\{(\eta^5-C_5H_5)[K([18]crown-6)]_2\}[Ge_9(CHCH_2)]$ (2): Originally, **2** was obtained by the reaction of $[Ge_9]^{4-}$, $Me_3SiC{\equiv}CSiMe_3$, ferrocene and K in ethylenediamine/toluene solution. Since CpFe was not found in the characterized products we repeated the reaction using KCp for the crystallization.

$[K([18]crown-6)]_2\{(\eta^5-C_5H_5)[K([18]crown-6)]_2\}[Ge_9(CHCH_2)]$ (2) and $[K([18]crown-6)]\{(\eta^5-C_5H_5)[K([18]crown-6)]_2\}[Ge_9(CHCH_2)_2]$ (3): Clusters **2** and **3** were obtained from the reaction of K_4Ge_9 (0.12 mmol) and $Me_3SiC{\equiv}CSiMe_3$ (0.11 mmol) in ethylenediamine (2 mL) at room temp. After stirring for 2 h, the dark-brown solution was filtered and layered with a solution of KC_5H_5 (0.12 mmol) and [18]crown-6 (0.56 mmol) dissolved in toluene (4 mL). After one week, dark-red crystals of **2** along with orange crystals of **3** were obtained on the glass wall of the reaction flask (yield of **2** and **3** 60 mol-%). The yield of **3** can be increased by using an excess of $Me_3SiC{\equiv}CSiMe_3$ (0.34 mmol). After one week, dark-orange crystals of **3** appeared on the glass wall of the reaction flask (yield 60 mol-%).

^1H NMR of crystals of **2** (C_5D_5N, 400 MHz, 298(2) K): δ = 7.93 (dd, $^3J(^1H,^1H)$ = 12.4 and 19.2 Hz, H_A), 6.55 (dd, $^3J(^1H,^1H)$ = 4.8 and 19.2 Hz, H_B), 6.49 (s, C_5H_5), 6.02 [dd, $^3J(^1H,^1H)$ = 4.8 and 12.4 Hz, H_C], 3.49 (s, [18]crown-6), 2.74 (s, en, CH_2), 1.46 (br s, en, NH_2) ppm.

^1H NMR of crystals of **3** [C_5D_5N, 400 MHz, 298(2) K]: δ = 7.35 [dd, $^3J(^1H,^1H)$ = 12.2 and 19.3 Hz, H_A], 6.49 (s, C_5H_5), 6.44 [dd, $^3J(^1H,^1H)$ = 3.9 and 19.3 Hz, H_B], 5.94 [dd, $^3J(^1H,^1H)$ = 3.9 and 12.2 Hz, H_C], 3.49 (s, [18]crown-6), 2.74 (s, en, CH_2), 1.46 (br s, en, NH_2) ppm.

Table 2. Crystallographic data for $[K([2.2.2]crypt)]_3[Ge_9Mes]$ (**1**), $[K([18]crown\text{-}6)]_2\{(\eta^5\text{-}C_5H_5)[K([18]crown\text{-}6)]_2\}[Ge_9(CHCH_2)]$ (**2**), and $[K([18]crown\text{-}6)]\{(\eta^5\text{-}C_5H_5)[K([18]crown\text{-}6)]_2\}[Ge_9(CHCH_2)_2]$ (**3**).

	1	**2**	**3**
Empirical formula	$C_{63}H_{119}Ge_9K_3N_6O_{18}$	$C_{93}H_{179}Ge_{18}K_7O_{42}$	$C_{47}H_{91}Ge_9K_3O_{18}N_2$
Formula weight [g mol $^{-1}$]	2019.25	3549.68	1742.83
T [K]	150(2)	150(2)	150(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	17.5249(5)	14.3580(2)	14.5373(3)
b [Å]	22.4902(9)	16.2427(3)	18.0229(3)
c [Å]	21.2684(9)	20.0168(3)	26.5519(5)
α [°]	90	84.685(1)	90
β [°]	96.39(3)	69.124(2)	90.334(2)
γ [°]	90	65.181(2)	90
V [Å^3]	8330.6(5)	3949.9(1)	6956.6(2)
Z	4	1	4
$D_{calcd.}$ [g cm^{-3}]	1.61	1.49	1.66
Absorption coefficient [m^{-1}]	3.4	3.6	4.0
F(000)	4112	1782	3504
Crystal size [mm^3]	$0.30 \times 0.18 \times 0.15$	$0.50 \times 0.15 \times 0.15$	$0.20 \times 0.15 \times 0.15$
Crystal color	red	red	orange
θ_{max}	26.37	26.02	32.87
Goodness-of-fit on F^2	1.136	1.011	0.740
Data [$I > 2\sigma(I)$]	9153	10684	9575
R_1 [$I > 2\sigma(I)$]	0.0917	0.0365	0.0450
wR_2 [$I > 2\sigma(I)$]	0.1847	0.0910	0.0647
$R_{int.}$	0.0671	0.0367	0.1109
R_1 (all data)	0.1432	0.0552	0.1571
wR_2 (all data)	0.1948	0.0937	0.0793
Residual map [e Å^{-3}]	1.22/–0.96	1.84/–0.81	0.94/–0.90
Twin matrix	–	–	–100 010 001
Volume fraction	–	–	0.284(1)

Structure Determination: Crystals of compounds **1**, **2**, and **3** were selected under perfluoropoly(alkyl ether) inside a glove box. All compounds are sensitive to air and moisture. Since a silver compound was used for the synthesis, preparation was carried out under dim conditions and the data collection was carried out in the dark. For the crystal structure analysis, single crystals of the compounds were fixed on glass capillaries and positioned in a cold N_2 stream. The data sets of compound **1**, **2**, and **3** were collected with an Oxford Diffraction Xcalibur3 Diffractometer, Mo-K_α radiation (λ = 0.71073 Å) at 150(2) K. The structures were solved by direct methods and were refined by full-matrix least-squares calculations against F^2 using the SHELXTL v6.1 package.[55] All non-hydrogen atoms were set anisotropic with exceptions mentioned below. The hydrogen atoms were refined using a riding model. The contribution of the highly disordered solvent molecules to the structure factors was modeled with the PLATON-SQUEEZE routine.[56] The parameters of data collection, structure solution, and refinement of the parameters for compounds **1**, **2**, and **3** are given in Table 2.

Structure Determination of 1: The atoms of [2.2.2]crypt, which are sequestering K2 and K3, were found to be disordered and were refined by split positions with occupancy of 50%. Atoms of [2.2.2]crypt sequestering K1 are set anisotropic.

Structure Determination of 2: The cyclopentadienyl ring and K4 are disordered along the inversion center with occupancy of 50%. The *exo* bonded vinyl group connected at Ge1 is disordered (C1A/B and C2A/B) and was refined using a splitting model. The center of the cyclopentadienyl anion is an inversion center. Therefore, the η^5-anion was described as a cyclodecanyl ring with 50% occupancy for each carbon atom. Atoms of [18]crown-6 capping K2 and K3 were refined in split positions with a site-occupation factor of 0.5 for each atom.

Structure Determination of 3: Several crystals of **3** showed a splitting of the reflexion spots at high scattering angles. The structure of compound **3** was refined using the twin matrix –100 010 001. The volume fraction of the twin was determined to 0.284(1).

CCDC-815135 (for **1**), -815137 (for **2**), and -815136 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

^{1}H NMR Measurement: Crystals of compound **1**, **2**, and **3** were cleaned from solvents using perfluoropoly(alkyl ether) and were collected inside a glove box using a microscope and transferred into a glass NMR tube, dissolved in 0.5 mL deuterated acetonitrile (99.5%, Merck) and sealed with a ground-in glass stopper with additional Parafilm®. Crystals of compound **2** and **3** were separated due to their different colors (crystals of compound **2** were dark red, crystals of compound **3** were orange) under a microscope, transferred in the same manner into a NMR tube and were dissolved in 0.5 mL of deuterated pyridine (99.0%, Deuterio GmbH). The ^{1}H NMR spectra of the reaction solutions were recorded after a reaction time of two hours with subsequent removing of all volatiles and extracting the residue in presence of 10 mg of [18]crown-6 with deuterated pyridine. The extract was filtered through glass wool into a NMR tube inside a glove box.

All spectra of the single crystals of compound **2** and **3**, as well as the NMR series of the reaction solutions were recorded with a JEOL JNM-GX400 Spectrometer with a JEOL JNM-LA400 FT-System at 400 MHz with 256 scans at 298(2) K. Single crystals of compound **1** were recorded with a BRUKER Ultrashield400 Spectrometer and a BRUKER AvanceIII400 FT-System [400 MHz, 256 scans, 298(2) K].

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra of compound **1** (Figure S1) and compounds **2** and **3** (Figure S2), enlarged section of part c in Figure 5 of the bis-vinylated Ge_9 (A2, B2, C2 signals) (Figure S3) as well as chemical shifts of vinyl protons in dependence of cluster charge (Figure S4).

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