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Review

Metalloid cluster compounds of germanium: A novel class of germanium cluster compounds of formulae Ge_nR_m ($n > m$)

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Available online 18 April 2006

Contents

Abstract

Metalloid cluster compounds of germanium of the general formulae Ge_nR_m with $n > m$, where in addition to ligand bound germanium atoms, “naked” germanium atoms are also present, represent a novel class of cluster compounds in germanium chemistry. Due to the fact that the “naked” germanium atoms inside these clusters can be assigned an oxidation state of 0, the average oxidation state of the germanium atoms inside such metalloid cluster compounds is between 0 and 1. Thus these cluster compounds can be seen as on the way to elemental germanium and therefore interesting properties are expected for these compounds which might give impact to nanotechnology.

During the last 3 years, different synthetic strategies have been introduced for the synthesis of such novel cluster compounds featuring unexpected structural and bonding properties. In this article, an account is given to the first developments in this novel field in germanium chemistry in which special attention is given to structural features and bonding properties.

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Keywords: Germanium; Ge_nR_m; Cluster compounds; Bonding properties

1. Introduction

Molecular cluster compounds of germanium have been known for a long time. They were mentioned for the first time by Eduard Zintl in 1933, where he was able to show that germanium as well as lead and tin can form complex polyanions [1]. Later, such polyanions were named Zintl ions.

The first structural characterization of such a Zintl ion was performed in 1976 by Kummer et al., who was able to crystallize the nine atom compound $Sn_9{}^{4-}Na^+{}_4en_7$ (en: ethylendiamin) [2]. The breakthrough in structural characterization of the Zintl ions was achieved by Corbett et al. through the introduction of alkali-metal sequestering cryptant molecules [3]. Following

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doi:10.1016/j.ccr.2006.04.003

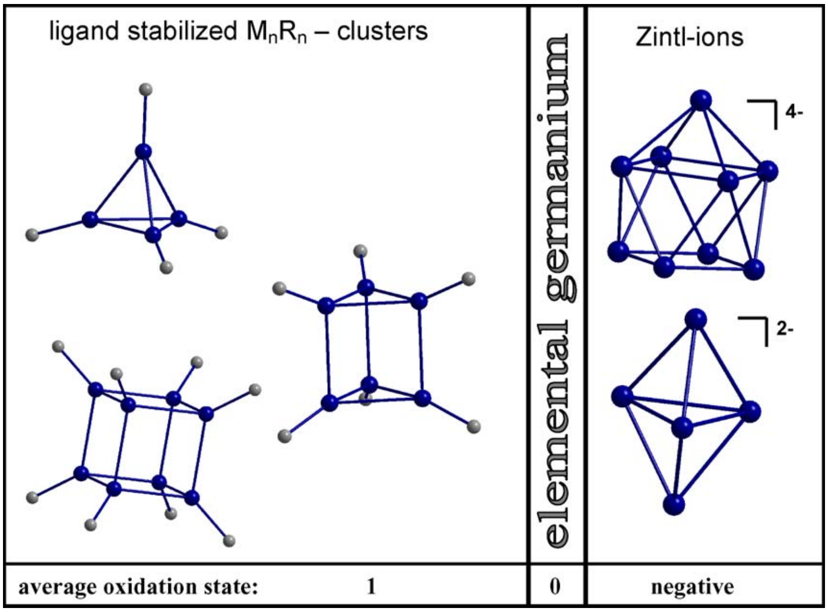


Fig. 1. Selected structures of ligand stabilized clusters of the general formulae $(GeR)_n$ (left) and Zintl ions (right) of germanium.

this approach, many zintl ions of germanium could be synthesized and structurally characterized and have been the topic of many reviews during the last few decades [4]. In all cases, the clusters are formed by reduction of elemental germanium with alkali-metal thus the average oxidation state of the germanium atoms inside the cluster is negative (e.g., −0.4 in $[Ge_5^{2-}]$ [5] and −0.44 in $[Ge_9^{4-}]$ [6]).

After the discovery and structural characterization of the Zintl ions, it could also be shown that it is possible to synthesize ligand stabilized cluster compounds of the general formula $(GeR)_n$ with $n = 4$ [7], $n = 6$ [8], $n = 8$ [9] exhibiting highly symmetric polyhedral structures like tetrahedrane, prismane and cubane, respectively. This new field has been developed rapidly after the first discovery of octasilacubane in 1988 by Matsumoto et al. and has also been the subject of several reviews [10]. The ligand stabilized cluster compounds are usually prepared by reductive dehalogenation of the corresponding halogen precursor, e.g., $n\mathrm{RGeCl_3} + 3n\mathrm{Na} \rightarrow (\mathrm{RGe})_n + 3n\mathrm{NaCl}$. As the germanium atom in the RGe-group can be assigned a formal oxidation state of 1, the average oxidation state in these ligand stabilized cluster compounds of the general formula $(GeR)_n$ is 1.

Therefore, starting from elemental germanium – where the average oxidation state of the germanium atoms is 0 – there exist two broad categories of molecular cluster compounds of germanium as emphasized in Fig. 1. On the one side are the Zintl ions with a negative average oxidation state of the germanium atoms. On the other side are the ligand stabilized cluster compounds, where the average oxidation state of the germanium atoms inside the cluster core is 1 or even higher as in $Ge_8R_8X_2$ ($R = t$-Bu, $X = Cl$ [11], $X = Br$ [12]) [13].

In recent years, a new, third class of cluster compounds of the general formulae Ge_mR_n with $m > n$ could be established [14]. In addition to ligand bearing germanium atoms, these cluster compounds also contain germanium atoms which are only bonded to other germanium atoms and which are referred to as "naked" germanium atoms in the following. Hereby naked does not mean isolated that is interaction-free, but is merely a linguistic simplification to distinguish the different types of metal atoms in these clusters. Alternatively the metal atoms could also be termed ligand free. However, this description is equally inexact since bonded metal atoms can also be classified as ligands. These cluster compounds with naked germanium atoms, which will be called metalloid clusters [15] in the following – due to the primary definition given by Schnöckel et al. – are the subject of this review.

1.1. Germanium nanoparticles

Due to the fact that the naked germanium atoms in metalloid germanium cluster compounds can be assigned a formal oxidation state of 0, the overall oxidation state of the germanium atoms inside these cluster compounds is in-between 0 and 1, a range where most of the germanium nanoparticles are also localized, in which the average oxidation state of the germanium atoms approaches the value of 0 by increasing diameter.

These nanoparticles are of considerable interest for the investigation of quantum size effects [16] and exhibit interesting physical properties. For germanium, e.g., visible photoluminescence (PL) was reported for low dimensional structures involving germanium nanoparticles embedded in a SiO_2 matrix [17]. The germanium nanoparticles are synthesized by a great variety of methods, e.g., germanium nanocrystals embedded in SiO_2 matrix are prepared by co-sputtering of germanium and SiO_2 [17,18], germanium ion implantation [19], atmospheric pressure chemical vapour deposition [20], deposition of germanium on SiO_2 and subsequent high temperature oxidation [21] or H_2 reduction of mixed oxides of the general formulae $Si_{1-x}Ge_xO_2$ [22]. However, these nanoparticles are obtained as a mixture with a certain size distribution and are consequently only poorly structurally characterized. Especially for small particles with diameters less than 2 nm, no experimental information on the structure is available as they exhibit a molecular character instead of nanocrystalline germanium with a diamond lattice [23], although these particles have particularly good photoluminescence properties [22b]. That means that a structural transition from the solid to the molecular state takes place when the size of the germanium nanoparticle decreases under a certain value (ca. 2 nm) [23]. Hence these nanoparticles can no longer be regarded as small pieces of elemental germanium (germanium nanocrystals), they are better described as molecular metalloid cluster compounds with a so far unknown structure. Due to this structural indefiniteness, it is difficult to predict which structural feature of this cluster compounds is responsible for the observed increase of the photoluminescence.

Structural information about these small nanoparticles can possibly be derived from chemically synthesized metalloid cluster compounds of the general formulae Ge_nR_m with $n > m$, which can be seen as intermediates on the way to elemental germanium and whose structures are well known from X-ray structure analysis. These compounds will be discussed in the following, together with the synthetic strategies applied for their synthesis.

2. Synthetic methods

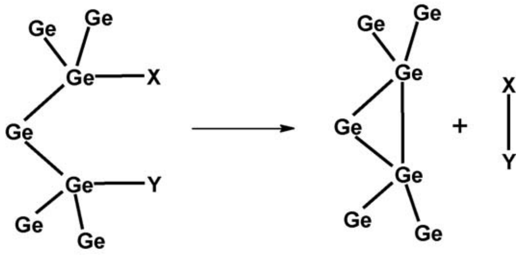
To date three synthetic strategies (method A–C) have been successfully used for the synthesis of metalloid cluster compounds of germanium.

2.1. Method A

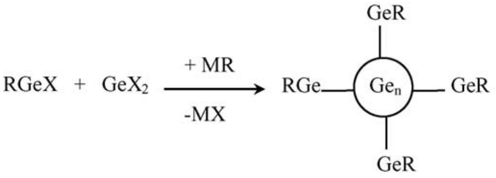
This strategy takes advantage of the reductive elimination of an X–Y group [24] where X and Y were formally bound to germanium atoms (Scheme 1). If the X and Y bound germanium atoms are additionally only connected to other germanium atoms the elimination of XY leads to naked germanium atoms and therefore this can lead to metalloid cluster compounds if the number of germanium atoms exceeds those of the ligands. However, this synthetic route led only once to a metalloid cluster compound (Section 3.1) and therefore it is questionable if this method can be termed a general route to metalloid cluster compounds.

2.2. Method B

A second synthetic strategy can be viewed as an improvement of the reductive coupling reaction which is the synthetic route par excellence for the synthesis of compounds with Ge–Ge bonds including multiple bonded systems like the alkyne analogue $(RGe)_2$ [25] or cluster compounds of the general formulae $(GeR)_n$ with $n = 4, 6, 8$ [10a]. When this reductive coupling reaction of RGeX (X: halogen atom) is performed in the presence of a germanium(II)halide, e.g., $GeCl_2$·Dioxan, naked germanium atoms can be embedded in the cluster leading to metalloid cluster compounds as depicted in Scheme 2 [26,27].



Scheme 1. Schematic presentation of synthetic method A.

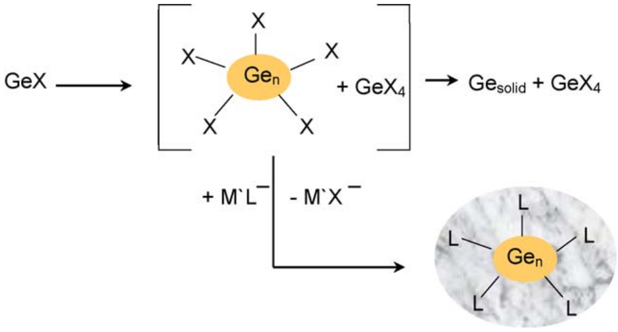


Scheme 2. Schematic presentation of synthetic method B.

2.3. Method C

The third synthetic strategy includes the disproportionation reaction of a metastable subvalent germanium halide (Ge(I) or Ge(II)), which leads at the end to the bulk metal (Ge) and a metal halide in a higher oxidation state (Ge(IV)). During this reaction, metalloid germanium cluster compounds are formed as intermediates on the way to elemental germanium (Scheme 3) [28].

These metastable intermediates certainly bear halide atoms on their surface as shown in Scheme 3, which can be substituted by a ligand in a subsequent reaction. Throughout this substitution the metal core is than shielded by a ligand shell (Scheme 3). Therefore, these intermediates are then kinetically stabilized so that they can be isolated. This method has been successfully applied for the heavier elements of group 13: aluminium and gallium by Schnöckel et al. [29] leading to cluster compounds with up to 77 aluminium [30] or 84 gallium [31] atoms proving that this synthetic route can lead to giant metalloid cluster compounds. Therefore, this strategy might be called the synthetic route par excellence to get to metalloid cluster compounds as it takes advantage of the intrinsic property of metastable subvalent metal halides, whose disproportionation reaction leads at the end to the metal itself. Hence, metalloid cluster compounds with diameters up to a few nanometers are accessible if the right reaction conditions are known.



Scheme 3. Schematic presentation of the synthetic method C.

In the case of germanium, the well known Ge(II)halides are not suitable starting materials since, e.g., Ge(II)Br_2 only disproportionates above 150 °C [32] which is too high in temperature for a kinetic stabilization of intermediates. In contrast Ge(I) bromide, which is available in preparative scale via a co-condensation technique [33], disproportionates already at 90 °C and has been successfully used for the synthesis of metalloid germanium cluster compounds (Section 3.3) [34–36].

Thus three different synthetic strategies – more might emerge in the future – were available for the synthesis of metalloid cluster compounds of germanium in the last 3 years. It should be mentioned here, that all these synthetic strategies exhibit the same synthetic problem, that the reaction mechanism which leads to the cluster compounds is unknown to date and therefore it is difficult to predict which reaction conditions are needed (temperature, stoichiometry, etc.) to get to a definite metalloid cluster species. Regardless these synthetic problems, it was possible to synthesize and structurally characterize seven examples of metalloid cluster compounds of germanium within the last 3 years, which will be discussed in the following.

3. Metalloid cluster compounds of germanium

3.1. $[Ge_{10}(SitBu_3)_6I]^+$ [24]

The synthesis of the cationic Ge_{10} cluster compound $[Ge_{10}(SitBu_3)_6I]^+$ **1** by Sekiguchi et al. [24] started from the cyclotrigermenylium ion $[Ge_3(SitBu)_3]^+$ which is treated with an excess of KI in ether to yield firstly the cyclotrigermen $Ge_3(SitBu_3)_3I$. After replacement of the solvent ether by toluene the reaction mixture was heated to 50 °C for 1 week. During this time, the colour of the reaction mixture changed from red to brown showing that a reaction took place that led to the cationic cluster compound $[Ge_{10}(SitBu_3)_6I]^+$ **1** in 37% yield (Scheme 4).

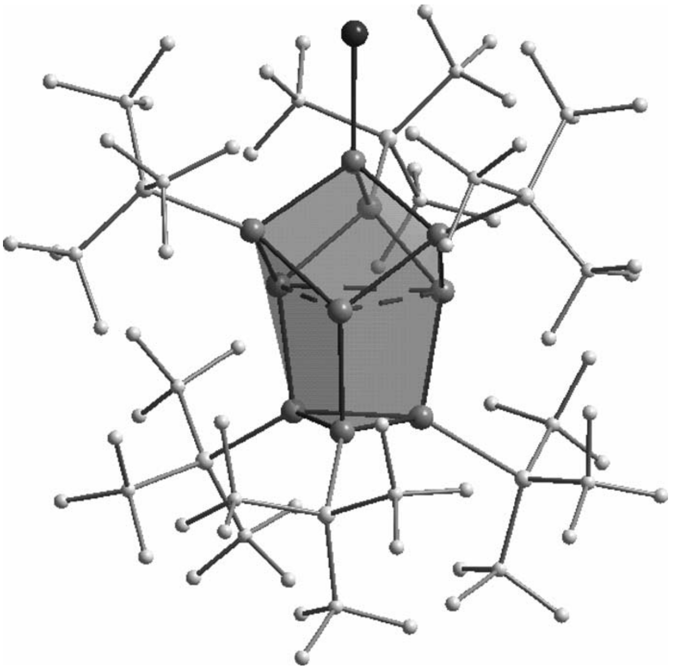
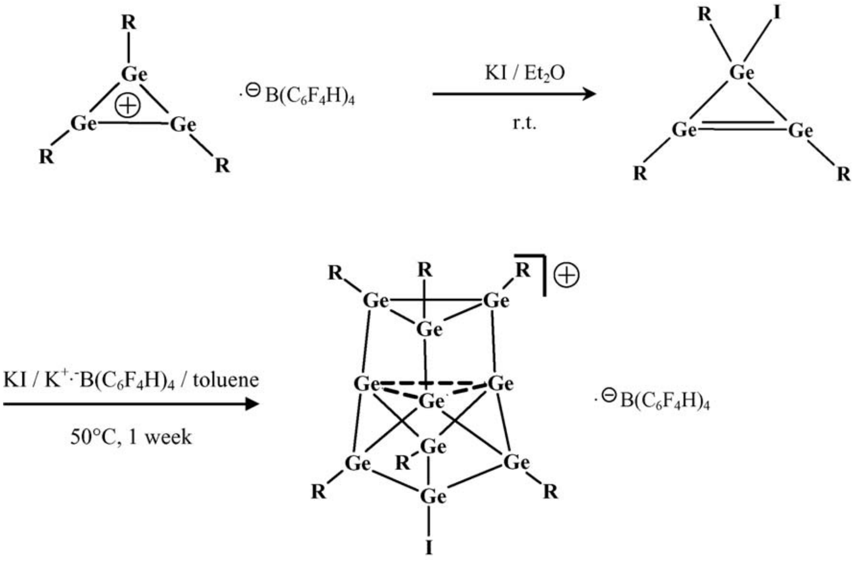


Fig. 2. Molecular structure of $[Ge_{10}(SitBu_3)_6I]^+$ **1** (hydrogen atoms are omitted for clarity). The arrangement of the 10 germanium atoms of the cluster core is emphasized via a polyhedral presentation.

The reaction pathway leading from the cyclotrigermen $Ge_3(SitBu_3)_3I$ to the metalloid cluster compound **1** is yet unknown but it is assumed that the naked germanium atoms in **1** derive from the elimination of Me_3SiI (method A), which is found as a by-product in the reaction mixture.

The arrangement of the 10 germanium atoms of the cationic cluster $[Ge_{10}(SitBu_3)_6I]^+$ **1** (Fig. 2) is best described as a cubic ensemble of seven germanium atoms, where the eighth corner of a hypothetical cube is replaced by a Ge_3 triangle.

The Ge–Ge distances inside the cubic Ge_7 fragment are in a narrow range with an average value of 248 pm, which is 5 pm shorter than the Ge–Ge distances found in the Ge_3 triangle, where an average value of 253 pm is found. This difference might



Scheme 4. Reaction sequence for the synthesis of the cationic metalloid cluster compound $[Ge_{10}(SitBu_3)_6I]^+$ **1** ($R = SitBu_3$).

be due to a severe steric repulsion of the Si*t*Bu$_3$ groups in the Ge$_3$ triangle. However, as the Ge–Ge distance in the cyclotrigermenylium ion [Ge$_3$(Si*t*Bu)$_3$]$^+$ [37] is with 233 pm substantially shorter than the Ge–Ge distance in the Ge$_3$ triangle of **1** this steric argument seems not to be quite reasonable. A more evident explanation for the elongation of the Ge–Ge distances might be the fact that the Ge$_3$ triangle has to fit the triangle build up by the three naked germanium atoms which show interatomic distances of 326 pm (dashed lines in Fig. 2). This interatomic distance is thus much longer than the other Ge–Ge bond lengths inside the cluster core which are in the range of a Ge–Ge-single bond of 245 pm as found in elemental germanium [38] and therefore it was questionable if there is a bonding interaction between the three naked germanium atoms at all.

However, quantum chemical calculations [24] on the model compound Ge$_{10}$H$_7$$^+$ revealed that there is a bonding interaction which is best described as a three-centre two-electron (3c–2e) bond between the three naked germanium atoms. The existence of a bonding interaction is furthermore supported by a comparison with the fully substituted model compound Ge$_{10}$H$_{10}$ for which an unambiguous nonbonding Ge–Ge distance of 379 pm was calculated.

Furthermore, these calculations show the existence of a homoaromatic system since an aromatic stabilisation energy of −19.2 kJ/mol and a nucleus independent chemical shift (NICS) of −26.4 ppm were calculated. The comparison of the model compounds Ge$_{10}$H$_{10}$ and Ge$_{10}$H$_7$$^+$ also reveals an interesting feature of this compound. In Ge$_{10}$H$_{10}$, all Ge–Ge bonds are best described as 2c2e bonds leading to a classical bonding situation for each germanium atom. Interestingly, the elimination of three ligands leads to the formation of a multicenter bond instead of the formation of a multiple bond which will lead to a shortening of the Ge–Ge distances. This effect of delocalization of bonding electrons inside the cluster core will become more obvious in the following chapters.

3.2. *Ge$_5$[CH(SiMe$_3$)$_2$]$_4$ and Ge$_6$Ar$_2$*

The synthetic method B has been successfully used by Power et al. for the synthesis of the cluster compounds Ge$_5$R$_4$ **2** (R = CH(SiMe$_3$)$_2$) and Ge$_6$Ar$_2$ **3** (Ar = C$_6$H$_3$-2,6-Dipp$_2$; Dipp = C$_6$H$_3$-2,6-*i*Pr$_2$), in which one and four naked germanium atoms are present, respectively.

3.2.1. *Ge$_5$[CH(SiMe$_3$)$_2$]$_4$ [26]*

The cluster compound Ge$_5$R$_4$ **2** (R = CH(SiMe$_3$)$_2$) is synthesized starting from the Ge(II) precursor GeClR which is reductively coupled with magnesium in the presence of half an equivalent of the germanium halide GeCl$_2$·Dioxan. The molecular structure of **2** (Fig. 3) consists of an array of four GeR units that is capped by a naked germanium atom.

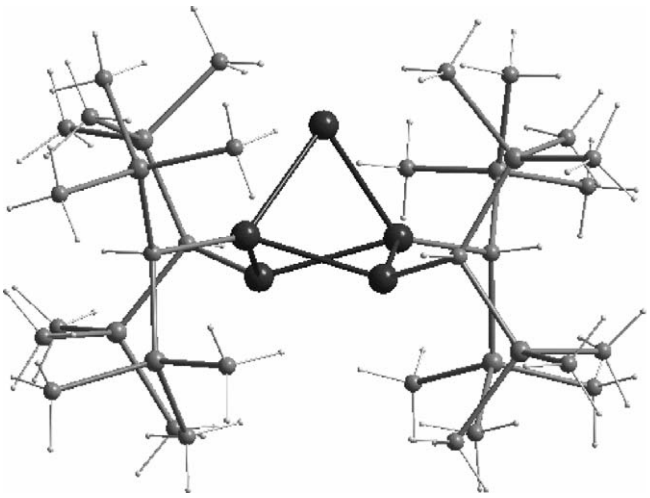


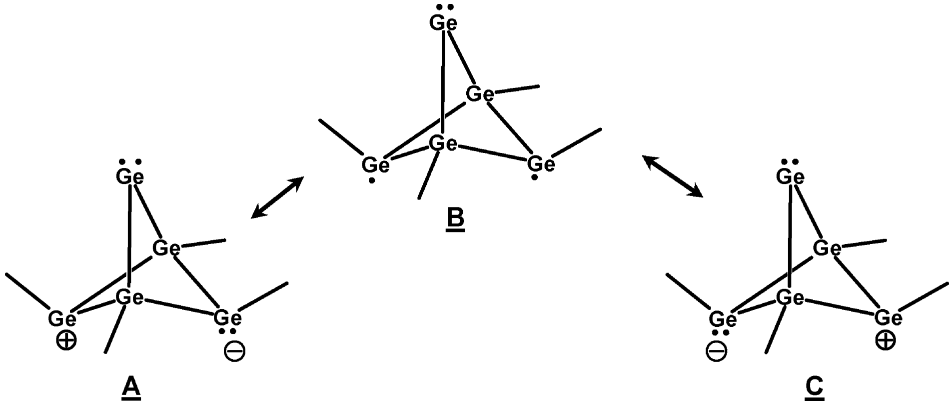
Fig. 3. Molecular structure of Ge$_5$R$_4$ **2** (R = CH(SiMe$_3$)$_2$).

Inside the (GeR)$_4$ moiety the Ge–Ge distances are in a narrow range with an average value of 242 pm. The (GeR)$_4$ unit has a butterfly structure with a fold angle of 134° leading to transannular separations of 323 and 333 pm. The naked germanium atom is localized above this (GeR)$_4$ moiety in a way that two short Ge–Ge distances of 246 pm and two long Ge–Ge distances of 303 pm are realized. Therefore, three differently coordinated germanium atoms are present in the cluster compound Ge$_5$R$_4$ **2**: the naked germanium atom has the coordination number 2 and in the (GeR)$_4$ unit two germanium atoms have the coordination number 3 and two are four coordinated, indicating a very complex bonding situation.

At first glance, the cluster may be described as a nido cluster according to Wade's rules [39]. In this case, the four GeR units provide three bonding electrons and the naked germanium atom, bearing a lone pair provides two electrons for cluster bonding to afford a total number of 14 electrons for cluster bonding which is exactly the required number of bonding electrons for a five vertex nido cluster ($14 = 2n + 4$ with $n = 5$). This description seems to fit but it is surely overlooked as the arrangement of the five germanium atoms can hardly be described as a square pyramidal arrangement since the Ge–Ge distances from the basal (GeR)$_4$ unit to the naked apex germanium atom differ by 57 pm.

A better description of the bonding situation which is also supported by first results of quantum chemical calculations on the model compound Ge$_5$Me$_4$ [26] takes into account that the naked germanium atom bears a lone pair and the two remaining electrons form two 2c2e bonds to two germanium atoms of the (GeR)$_4$ unit. The two four coordinated germanium atoms resemble the classical bonding situation for germanium having four 2c2e bonds. The remaining three coordinated germanium atoms form three 2c2e bonds and have additional electron density at one vertex. This description of the bonding situation leads to a formulation of three resonance forms A, B and C as shown in Scheme 5. Hereby the zwitterionic form A and C represent the simplest description having only paired electrons, whereas form B represents a biradicaloid form showing that **2** might be a member of the class of singlet biradicaloid compounds which is a growing class of main group compounds [40].

More theoretical calculations have to be carried out to understand the unusual bonding situation in **2**, which seems to be a favourable arrangement of a molecule of the general formula Ge$_5$R$_4$ as with Ge$_5$Ar$_4$ **2a** (Ar = C$_6$H$_3$-2,6-Mes$_2$; Mes = C$_6$H$_2$-2,4,6-Me$_3$) a second example is known where aryl ligands are



Scheme 5. Possible resonance forms for the presentation of the bonding situation in Ge_5R_4 **2** (R = $CH(SiMe_3)_2$).

bound to the germanium atoms [26]. Throughout these calculations the most interesting question that has to be answered is why the three coordinated germanium atoms do not form a 2c2e bond leading to a tetrahedral arrangement of the $(GeR)_4$ unit with one edge of the tetrahedra bridged by the naked germanium atom.

This question leads to the gedanken experiment where **2** or **2a** is formed, starting from a tetrahedral $(GeR)_4$ unit and a naked germanium atom. The germanium atom approaches the tetrahedra hereby from one edge, breaking the RGe–GeR bond to form two new Ge–GeR bonds. Now the exiting question arises whether this structure is a stable product of our gedanken experiment or will the Ge–Ge bond which is at the opposite side of the tetrahedra break, leading to a structure as in **2** and **2a**. In this case, the addition of one naked germanium atom has led to a strong reorientation of bonding electrons inside the whole cluster compound, an effect which will also become apparent in the Ge_8R_6 cluster compounds **4** and **5** in Section 3.3.1.

In the case of **2**, this interesting question has to be answered by future theoretical calculations which will show if the structure in **2** is electronically favoured or if the Ge–Ge bond breached due to sterical repulsion of the ligands in the $(GeR)_4$ unit.

3.2.2. Ge_6Ar_2 (Ar = C_6H_3-2,6-$Dipp_2$; Dipp = C_6H_3-2,6-iPr_2) [27]

The metalloid cluster compound Ge_6Ar_2 **3** (Ar = C_6H_3-2,6-$Dipp_2$; Dipp = C_6H_3-2,6-*i*Pr_2) is synthesized by the same synthetic method as **2** starting from ArGeX. That means that ArGeCl is reductively coupled by C_8K in the presence of one equivalent of $GeCl_2$·Dioxan leading to Ge_6Ar_2 **3** in about 40% yield which is quite high if one takes into account the complex reaction course taking place during the formation of **3** from monomeric units. The molecular structure of **3** is depicted in Fig. 4 and is best described as a distorted octahedral arrangement of six germanium atoms. Inside the cluster two different Ge–Ge distances are present. The Ge–Ge distance inside the square of four naked germanium atoms is 286 pm while the Ge–Ge distance to the ligand bearing germanium atoms is much shorter with an average value of 250 pm.

The distorted octahedral arrangement of the six germanium atoms is in good agreement with Wade's rules which predict a closo structure since $2n+2$ electrons are available for cluster bonding (n = number of vertices). Thus each naked germanium atom bearing a lone pair provides two electrons and each ligand bearing germanium atom provides three electrons to afford a total number of 14 electrons for cluster bonding. This method of electron counting also explains the fact that the ligand bound germanium atoms form the shorter Ge–Ge bonds although the coordination number is higher as here more electron density is available for bonding interactions.

The description of **3** as a closo cluster is also supported by the results of quantum chemical calculations on the model compound Ge_6H_2 for which a similar structure as in **3** was calculated [41]. An analysis of the calculated energies of the individual molecular orbitals show a significant leap of 1.8 eV in the orbital energy between the HOMO-6 and the HOMO-7 which supports the presence of 14 bonding electrons. Furthermore, the results of the quantum chemical calculations show that the bonding electrons in the cluster core of Ge_6H_2 are highly delocalized as it is the case for the Zintl ions, e.g., in accordance with an Ahlrichs Heinzmann population analysis the three center shared electron

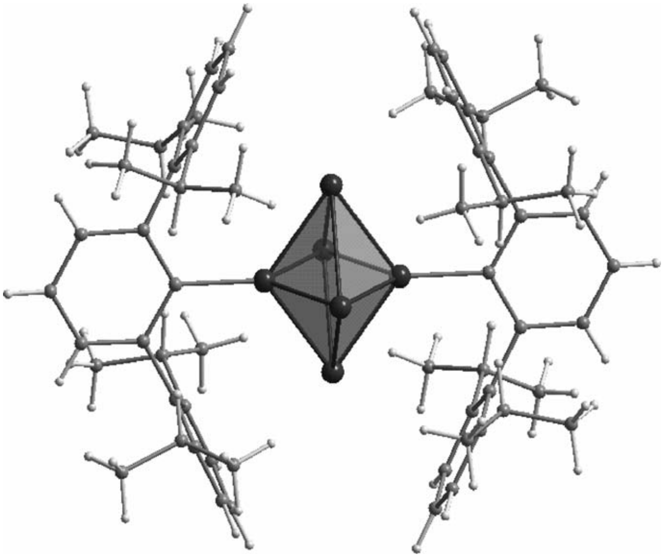


Fig. 4. Molecular structure of Ge_6Ar_2 **3** (Ar = C_6H_3-2,6-$Dipp_2$; Dipp = C_6H_3-2,6-*i*Pr_2). The central Ge_6 octahedral arrangement is emphasized via a polyhedral presentation.

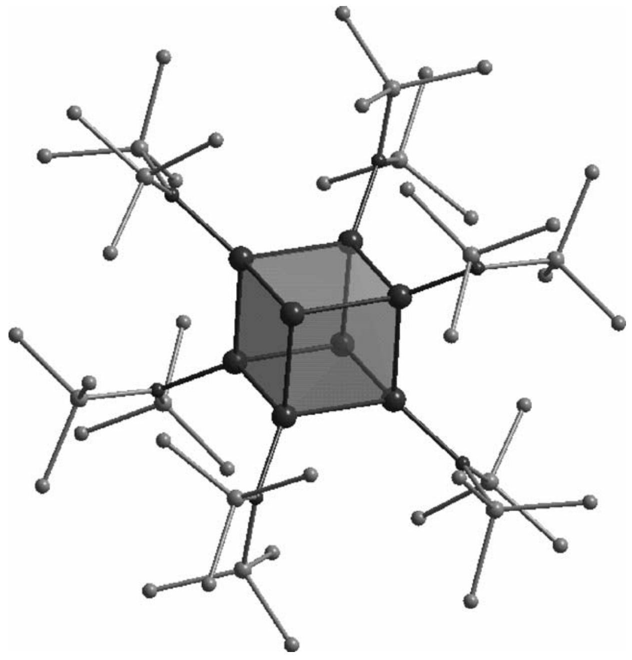


Fig. 5. Molecular structure of $Ge_8[N(SiMe_3)_2]_6$ **4** (hydrogen atoms are omitted for clarity). The geometry of the central eight germanium atoms is highlighted via a polyhedral arrangement.

number (SEN) [42] in the triangle faces of the octahedra is 0.23. This resemblance to the Zintl ions can also be seen by a comparison with the theoretical regular octahedral Zintl ion Ge_6^{2-} for which a Ge–Ge distance of 269 pm is calculated [43] which is in good agreement to the average Ge–Ge distance of 263 pm for the twelve Ge–Ge bonds in **3**. Such similarities to the Zintl ions will become also obvious in the discussion of the metalloid cluster compound $Ge_9R_3^-$ **6** (Section 3.3.2).

3.3. $Ge_8[N(SiMe_3)_2]_6$, $Ge_8[2,6\text{-}(tBuO)_2C_6H_3]_6$ and $\{Ge_9[Si(SiMe_3)_3]_3\}^-$

The metalloid cluster compounds $Ge_8[N(SiMe_3)_2]_6$ **4**, $Ge_8[2,6\text{-}(tBuO)_2C_6H_3]_6$ **5** and $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **6** have been synthesized using the synthetic method C. Thus a metastable solution of Ge(I) bromide, which is synthesized via a preparative co-condensation technique is treated with a solution of the lithium salt of a ligand source LiR (R = $N(SiMe_3)_2$; $Si(SiMe_3)_3$; $2,6\text{-}(tBuO)_2C_6H_3$) at −78 °C. The reaction mixture is then warmed to room temperature leading to a dark red almost black coloured solution. After different workup procedures the cluster compounds **4**, **5** and **6** are isolated as dark red, orange red or orange coloured crystals, respectively. Especially the different colours of the two cluster compounds **4** and **5** should be stressed out here, which is due to a different bonding situation in both cluster compounds which will be discussed in detail in the following.

3.3.1. $Ge_8[N(SiMe_3)_2]_6$ and $Ge_8[2,6\text{-}(tBuO)_2C_6H_3]_6$ [34,35]

The molecular structure of $Ge_8[N(SiMe_3)_2]_6$ **4** (Fig. 5) consists of a cubane like Ge_8 cluster in which six ligand bearing and two naked germanium atoms are present. The two different germanium sites inside the cluster core lead as expected to two different Ge–Ge distances. The Ge–Ge distance between ligand bound germanium atoms is 267 pm and the Ge–Ge distance between ligand bound and naked germanium atom is 251 pm.

Comparing these Ge–Ge distances with those found in the fully substituted cubic Ge_8R_8 clusters (R = 2,6-diethylphenyl [9a], 1,1,2-trimethylpropyl [9b]) where Ge–Ge distances in the range of 250 ± 1 pm are found, shows, that the Ge–Ge distances between naked and ligand bound germanium atoms are in the same region while the Ge–Ge distances between ligand bound germanium atoms are longer. This is quite unusual as one would expect that the Ge–Ge distances inside the cluster core decrease considering the two extra electrons from the naked germanium atoms that are available for cluster bonding.

To understand this unexpected elongation quantum chemical calculations [34] on the model compound $Ge_8(NH_2)_6$ **4a** were performed in which a similar distortion of the cubane structure as in **4** was calculated ($d(Ge\text{–}Ge(NH_2)) = 255$ pm; $d(Ge(NH_2)\text{-}Ge(NH_2)) = 266$ pm), showing that steric reasons are not responsible for the different bond distances. Thus electronic reasons must be responsible for the observed structure.

An inspection of the electronic structure of **4a** with the aid of an Ahlrichs Heinzmann population analyses which leads to shared electron numbers [42] shows that the two-center SEN reflect the trend in the bond length quite well because the two-center SEN between ligand bound germanium atoms (0.87) is smaller than those between ligand bound and naked germanium atom (1.1). Additionally to these two-center SEN's three center bonding components are found in the three membered ring of ligand bound germanium atoms with a SEN of 0.13. This result shows that the presence of naked germanium atoms in a ligand stabilized germanium cluster compound leads to a delocalization of bonding electrons inside the whole cluster core which might also be the case in Ge_5R_4 **2** and **2a** as mentioned above [44]. In the case of **4**, the delocalisation of the bonding electrons results in the observed unusual elongation of the bond distance between ligand bound germanium atoms, demonstrating that the two additional electrons from the naked germanium atoms give rise to a novel bonding situation inside the cluster core.

Additionally, the quantum chemical calculations reveal that in case of the Ge_8R_6 cluster compound a strong dependency between the bonding situation inside the cluster core and the ligand attached to the germanium atoms exists. This correlation becomes most obvious when the calculated structural features and SEN's of the model compounds $Ge_8(NH_2)_6$ **4a** and Ge_8Me_6 **5a** are compared (Table 1). Hereby the Ge–Ge distance between ligand bound germanium atoms differs by 15 pm that is due to the fact that in Ge_8Me_6 **5a** the bonding electrons are more localized as the three center SEN decreases from 0.13 in the case of $Ge_8(NH_2)_6$ **4a** to 0.06 in the case of Ge_8Me_6 **5a**.

These theoretical predictions were proved experimentally as with Ge_8Ar_6 **5** (Ar = $2,6\text{-}(tBuO)_2C_6H_3$) a second example of a metalloid cluster compound of the general formulae Ge_8R_6 could be isolated where now aryl ligands are attached to the germanium atoms (Fig. 6) [35].

Table 1
Results of quantum chemical calculations [34] on the model compounds **4a** and **5a** (distances are given in pm, SEN cf. [42])

	$Ge_8(NH_2)_6$ ($R = NH_2$) **4a**	Ge_8Me_6 ($R = Me$) **5a**
d(GeR–Ge)	254.8	259.7
d(GeR–GeR)	266.3	251.0
SEN (Ge–GeR)	1.10	0.93
SEN (GeR–GeR)	0.88	1.04
SEN (GeR–GeR–GeR)	0.13	0.06

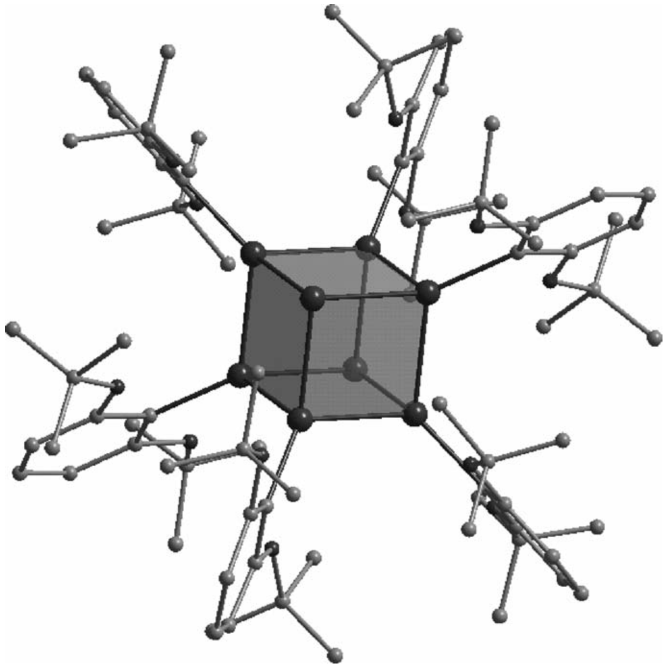


Fig. 6. Molecular structure of Ge_8Ar_6 **5** ($Ar = 2,6\text{-}(tBuO)_2C_6H_3$) (hydrogen atoms are omitted for clarity). The cubic ensemble of the eight germanium atoms inside the cluster core is emphasized via a polyhedral presentation.

The molecular structure of **5** consists like **4** of a Ge_8 cubane framework in which six of the eight germanium atoms bear a ligand. In case of **5** the cubane geometry is nearly undistorted as the Ge–Ge distance between ligand bound germanium atoms is with 249 pm only 2 pm shorter than those between naked and ligand bound germanium atoms where a Ge–Ge distance of 251 pm is found. Furthermore, the Ge–Ge–Ge angles inside the cluster core differ only marginally from the ideal value of 90°. A comparison of the bond distances and angles of the structurally characterized cluster compounds **4** and **5** is given in Table 2. The most obvious difference between both structures can be seen in the Ge–Ge distances between ligand bound germanium atoms which differ by 17 pm.

Table 2
Comparison of the structural features (distances [pm] and angles [°]) of the cluster compounds **4** and **5**

	$Ge_8[2,6\text{-}(tBuO)_2C_6H_3]_6$ **5**	$Ge_8[N(SiMe_3)_2]_6$ **4**
d(GeR–Ge)	252	250
d(GeR–GeR)	250	267
GeR–GeR–GeR	89.9	75.3
GeR–Ge–GeR	90.5	81.3
GeR–GeR–Ge	90.8	101.8

Table 3
Results of quantum chemical calculations [35] for the model compounds Ge_8R_6 (distances in pm, SEN cf. [42])

Ligand (R)	SiH_3	CH_3	C_6H_5	OH	PH_2	NH_2
d(Ge–GeR)	256.6	259.7	259.0	256.7	257.8	254.8
d(GeR–GeR)	252.6	251.0	251.8	266.6	265.5	266.3
SEN (Ge–GeR)	1.04	0.93	0.97	1.14	1.03	1.10
SEN (GeR–GeR)	0.05	0.06	0.06	0.14	0.16	0.13

This behaviour verifies exactly what was predicted by quantum chemical calculations, showing that the ligand attached to the cluster compound clearly modifies the bonding situation inside the cluster core leading in the case of the Ge_8R_6 cluster compounds **4** and **5** to the observed strong differences.

The decisive factor of the ligand that is responsible for the different bonding situation was identified to be the free electron pair on the hetero atom directly bound to the germanium atom what becomes obvious by comparing the bond distances and SEN's of the model compounds listed in Table 3. Hereby a ligand with a free electron pair on the hetero atom directly bound to the germanium atom ($R = NH_2$, OH, PH_2) leads to a higher degree of delocalization of bonding electrons inside the cluster core. In contrast ligands with no free electron pair at the hetero atom bound to germanium ($R = CH_3$, Ph, SiH_3) lead to more localized bonding electrons inside the cluster core [45].

This means in the case of the Ge_8R_6 cluster compounds the ligand attached to the cluster core is not only necessary for protecting the cluster core against the exterior but also modifies the bonding situation inside the cluster core which could now be verified experimentally for the first time. The differences in the bonding situation can also be visualized by an inspection of the orbital picture of the HOMO of the model compounds **4a** and **5a** which are substantially different as shown in Fig. 7.

In the case of $Ge_8(NH_2)_6$ **4a** the HOMO consists of nonbonding electron density at the naked germanium atom and additionally delocalized electron density in the belt of ligand bound germanium atoms which correlates with the delocalized bonding situation in the three membered ring of ligand bound germanium atoms. In contrast to this the electron density of the HOMO of Ge_8Me_6 **5a** is mainly localized between two germanium atoms and correlates therefore mostly with 2c2e bonds between the germanium atoms in accordance to more localized bonding electrons.

In summary, the results on the Ge_8R_6 cluster compounds **4** and **5** can be interpreted in that way that the bonding situation inside the cluster core can be influenced by changing the ligand. This different bonding situation in **4** and **5** will lead to different physical properties of the compounds and the most obvious difference between both compounds is their colour as mentioned before. While crystalline **4** is almost black, crystalline **5** is orange-red (Fig. 8).

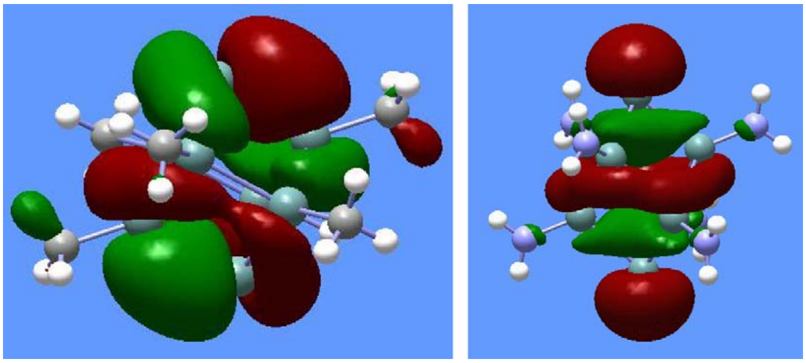


Fig. 7. Orbital pictures of the HOMO of Ge_8Me_6 **5a** (left) and $Ge_8(NH_2)_6$ **4a** (right).

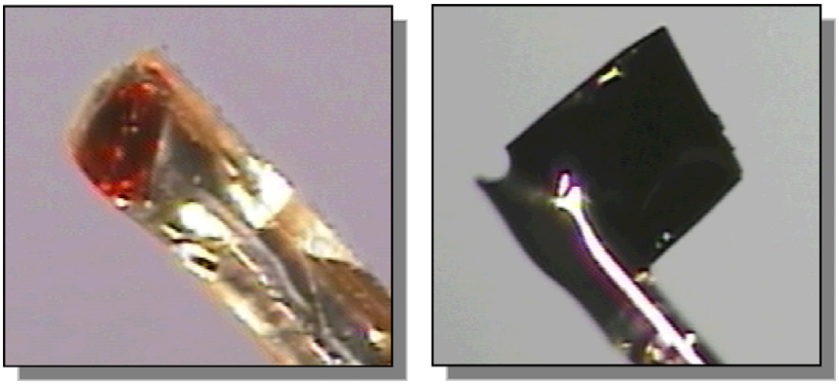


Fig. 8. Photo of crystals of the cluster compounds $Ge_8[2,6\text{-}(tBuO)_2C_6H_3]_6$ **5** (left) and $Ge_8[N(SiMe_3)_2]_6$ **4** (right).

3.3.2. $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ [36]

The anionic cluster compound $Ge_9R_3^-$ ($R = Si(SiMe_3)_3$) **6**, which can be isolated together with $Li(THF)_4^+$ as counter ion in form of orange coloured crystals from the reaction of Ge(I)Br with $LiSi(SiMe_3)_3$ (method C) shows a highly symmetric arrangement of the nine germanium atoms in the cluster core as shown in Fig. 9. The number of nine germanium atoms reminds hereby of the Zintl ions where many examples of nine atom clusters ($Ge_9^{n-}, n = 3, 4$) [4d] are known and it will become obvious in the following that there exist both, similarities as well as differences between **6** and the Zintl ions.

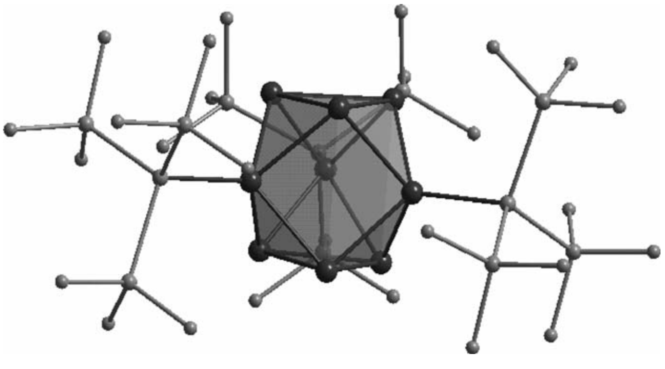


Fig. 9. Molecular structure of $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **6** (hydrogen atoms are omitted for clarity). The central tricapped trigonal prismatic arrangement of the nine germanium atoms is emphasized via a polyhedral presentation.

The arrangement of the nine germanium atoms in **6** is best described as a tricapped trigonal prismatic arrangement of nine germanium atoms where each capping germanium atom bears a ligand. The Ge–Ge distances in the three membered ring of naked germanium atoms are in a narrow range with an average value of 267 pm whereas the Ge–Ge distance between ligand bound and naked germanium atoms has an average value of 253 pm. This means the germanium atoms with the higher coordination number form the shorter Ge–Ge bonds what is exactly the opposite to the Zintl ions where the germanium atoms with the higher coordination number form the longer Ge–Ge bonds. This difference can be explained in the way that the ligand bound germanium atom provides three electrons for cluster bonding as the naked germanium atoms only provide two electrons for cluster bonding, bearing a lone pair of electrons. Thus, although the germanium atom forms a 2c2e bond to the ligand it provides more electrons for cluster bonding than those who are naked because the naked germanium atoms bear a lone pair of electrons as it is the case for all the germanium atoms in the Zintl ions. Thus the formation of a 2c2e bond to the ligand splits the lone pair in the way that one electron is used for the formation of a 2c2e bond to the ligand while the second electron is used for cluster bonding [46].

This way of electron counting – the naked germanium atoms provide two electrons and the ligand bound germanium atoms provide three electrons for cluster bonding – results in a total number of 22 skeletal electrons ($2n + 4$; $n = 9$), which is the required number of electrons for a nido cluster according to Wade's rules. Thus a monocapped square antiprismatic structure is expected. For **6** this structure is energetically unfavourable as the structure of a tricapped trigonal prism is formed in difference to the Zintl ions where a rather distorted monocapped square antiprismatic structure is observed for a Ge_9^{4-} Zintl ion with 22 skeletal electrons [6b,47]. As **6** adopts a closo structure which is expected for a nine atom cluster with 20 skeletal electrons a distortion of the ideal trigonal prismatic arrangement towards a larger a:h ratio should occur [4d]. This distortion is expected as a D_{3h} symmetric nine atom cluster with 20 skeletal electrons (e.g., *closo*-$B_9H_9^{2-}$ [48]) possesses a LUMO which is bonding along the edges and antibonding along the heights of the trigonal prism [49]. As **6** features 22 skeletal electrons this LUMO is now occupied (becoming the HOMO) and leads to a distortion towards a larger a:h value in comparison to an ideal polyhedron with equal edge lengths (a:h = 1). In **6**, the a:h value is 1.27, exactly what is expected for a nine atom cluster in D_{3h} symmetry with more than 20 skeletal electrons [4d].

The presence of 22 skeletal electrons becomes also evident by an analysis of the results of quantum chemical calculations on the model compound $Ge_9H_3^-$ **6a** for which a similar arrangement of the nine germanium atoms was calculated [36]. Analysing the energies of the individual molecular orbitals show a significant leap of 2.2 eV in the orbital energy between HOMO-10 and HOMO-11 supporting the presence of 22 skeletal electrons. The calculations also show in accordance to the Zintl ions highly delocalized bonding electrons inside the cluster core as for example the SEN for the three center bonding component in the three membered ring of naked germanium atoms is 0.32. Another similarity of **6** to the Zintl ions is the high reactivity against moisture and air, e.g., crystals of **6** ignite spontaneously when exposed to air. This high reactivity can be traced back to the poor shielding of the cluster core by the three ligands what becomes obvious when the space filling model of **6** is observed along the three-fold axis (Fig. 10).

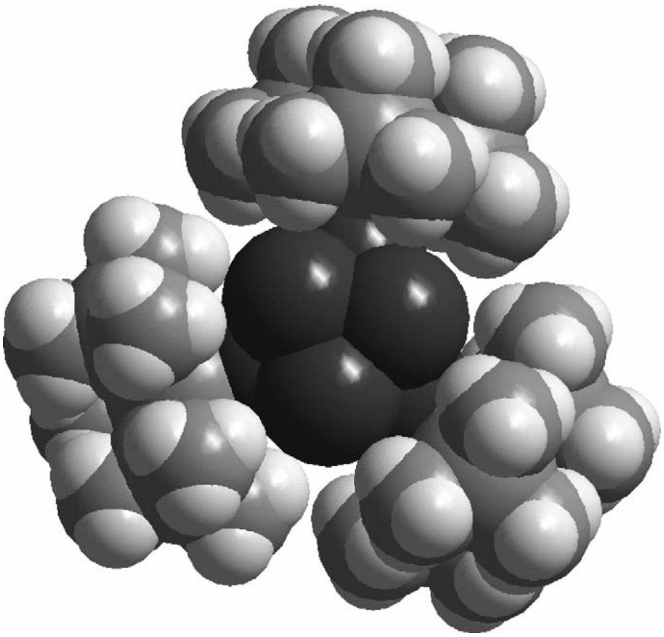
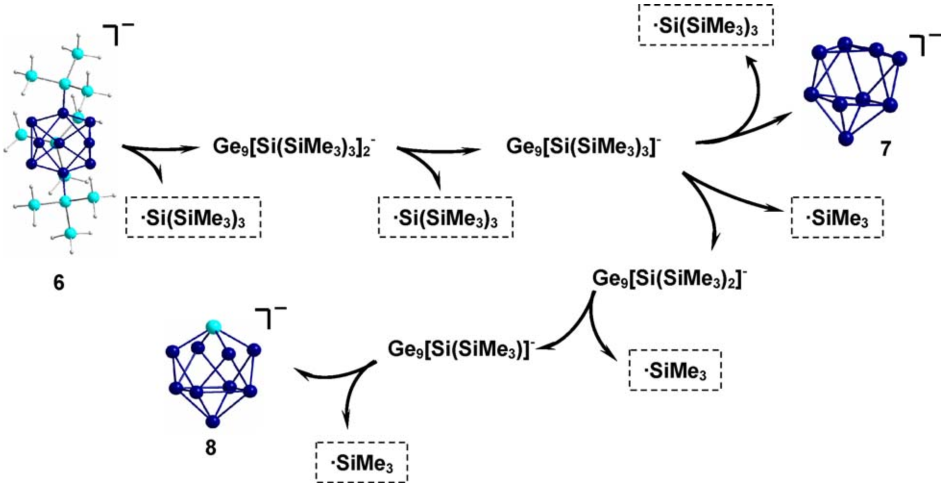


Fig. 10. Space filling model of $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **6**. View along the three-fold axis.

However, the three ligands lead to a high solubility of **6** in organic solvents as THF with respect to the Zintl ions which are insoluble in THF. From this THF solution **6** can be transferred intact into the gas phase by electro spray experiments (ESI) giving access to gas phase reactions [50]. Throughout these experiments the dissociation pathway of the molecule after a collision with an inert gas is observed. This technique allows the weakest bond to break first and therefore such collision experiments (SORI CAD: sustained off resonance irradiation collision activated dissociation) are a perfect experimental test on the bonding situation in the cluster compound. In case of **6** the dissociation pathway may be described as in Scheme 6.

First of all two $^\bullet Si(SiMe_3)_3$ fragments (all leaving fragments are radicals) leave the cluster leading to $Ge_9R_2^-$ and Ge_9R^-,



Scheme 6. Schematic presentation of the dissociation pathways for the dissociation of $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **6** in the gas phase (the leaving groups, $^\bullet Si(SiMe_3)$ and $^\bullet SiMe_3$ are presented in dashed boxes). The calculated molecular structures of the cluster compounds Ge_9^- **7** and Ge_9Si^- **8** are shown.

respectively, showing that the weakest bonds inside the cluster are those to the ligands [51].

When two $^{\bullet}Si(SiMe_3)_3$ fragments have left the cluster the situation changes significantly as now two dissociation pathways are accessible, leading to the naked cluster compounds Ge_9^- **7** and Ge_9Si^- **8** (Scheme 6). As the average oxidation state of the germanium atoms in the clusters **7** (−0.11) and **8** (−0.1) is now negative we have here a direct connection in the gas phase between the metalloid cluster compounds, where the average oxidation state in the cluster core is in-between 0 and 1 and the Zintl ions, where the germanium atoms are negatively charged. The similarity of the naked anionic cluster compounds Ge_9^- **7** and Ge_9Si^- **8** to the Zintl ions becomes also obvious by an analysis of the calculated bond distances inside the clusters as the metal atoms with the higher coordination number form the longer metal–metal bonds as it is the case in the Zintl ions [50]. An additional feature that underlines the connecting character of the Ge_9^- cluster **7** is the fact, that this cluster compound is also observed in the mass spectra of the Zintl phase K_4Ge_9 after laser desorption [52].

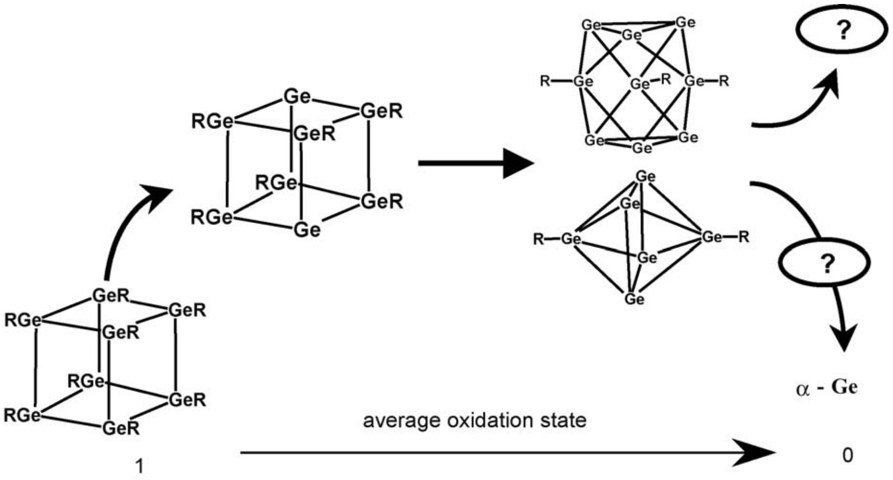
These gas phase investigations thus show that a cluster compound consisting of nine germanium atoms is a favourable unit with a high stability. Therefore, the metalloid cluster compound $Ge_9R_3^-$ **6** might be a good precursor in order to generate definite Ge_9 species maybe on ordered surfaces due to its solubility.

4. Concluding remarks and outlook

As shown in this review a new class of metalloid cluster compounds of germanium with the general formulae Ge_nR_m with $n > m$ is now established as a third group of molecular cluster compounds of germanium. In these metalloid cluster compounds a novel bonding situation for ligand stabilized cluster compounds is observed, where the bonding electrons are highly delocalized. Interestingly in the metalloid cluster compounds known so far, the delocalization of the bonding electrons in the cluster core increases with decreasing average oxidation state of the germanium atoms:

	Ge_8Me_6	$Ge_8(NH_2)_6$	Ge_6H_2	$Ge_9H_3^-$
SEN (three-center bonding component)	0.06	0.13	0.23	0.32
Average oxidation state	0.75	0.75	0.33	0.22

If this trend goes further it will end with elemental germanium with an average oxidation state of 0 with highly delocalized bonding electrons what can be interpreted as a metallic state known for metals like aluminium or copper but not for germanium. This means starting from the metalloid cluster compounds it might be possible to get access to a metallic state of elemental germanium [53] what seems unlikely but not impossible. However, as the bonding electrons in elemental α germanium are localized in 2c2e bonds it is most likely that the process of delocalization of bonding electrons will invert at a certain size of the cluster leading at the end to a completely localized bonding situation as found in α germanium. These two possible pathways are emphasized in the following scheme:



What influence this interplay between localized and delocalized bonding electrons will have on the physical properties has to be explored by future experiments. This means for the future that the synthesis has to be extended to prepare larger cluster systems [54] with more naked germanium atoms to obtain more experimental data on the fascinating behaviour of the bonding situation inside the new class of metalloid germanium cluster compounds.

Another fact that has to be clarified in the future is the fascinating similarity between the Zintl ions on the one hand and the metalloid clusters on the other hand, what becomes most obvious in the case of the Ge_9 system (Section 3.3.2). This similarity is amazing as the average oxidation state of the germanium atoms in the cluster cores of both types of clusters have different algebraic signs (Zintl ions: negative; metalloid clusters: positive). Therefore, starting from elemental germanium the oxidation as well as the reduction, two totally different chemical manipulations, lead to the same kind of cluster. This relationship is quite unusual and the reason for this behaviour has to be clarified by future experiments and theoretical calculations leading hopefully to a coherent picture of the bonding situation in germanium cluster compounds.

Acknowledgements

The author thanks the DFG and the Fonds der Chemischen Industrie for financial support. Prof. H. Schnöckel and Dr. H.-J. Himmel are acknowledged for fruitful discussions and suggestions.

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[44] Another similarity of 4 and 2 is the fact that both can be described as a singlet biradicaloid even though the Ge—Ge distance between naked germanium atoms of 518 pm in 4 is substantially longer than that in 2 where the Ge—Ge distance between the three coordinated germanium atoms is 332 pm. However, the description of 4 as a singlet biradicaloid species is

supported by the energy difference of 96.5 kJ mol^{-1} between singlet and triplet state for 4a which is in the same order of magnitude as those found in the 1.1.1-propellanes which are known members of the family of singlet biradicaloid compounds [40]. Three biradicaloid neutral tin clusters are known;
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C. Drost, M. Hildenbrandt, P. Lonnecke, Main Group Met. Chem. 25 (2002) 93.

[45] This influence of the ligand on the bonding situation inside the cluster core is further supported by the results of a preliminary crystal structure analysis of the metalloid tin compound Sn_8R_6 (R = SitBu$_3$) for which an almost undistorted cubic arrangement of the eight tin atoms is found and again the hetero atom directly bound to the tin atoms (Si) has no free electron pair;
N. Wiberg, H.-W. Lerner, S. Wagner, H. Nöth, T. Seifert, Z. Naturforsch. 54B (1999) 877.

[46] This behaviour is different to that found in the EPh$_2$-functionalized Ge$_9$ cluster $[Ge_9(EPh_2)]^{2-}$ (E = Sb, Bi), in which no significant change in the Ge$_9$ core is observed, compared to the Zintl ions, emphasizing the special role of the ligand in **6**;
A. Ugrinov, S.C. Sevov, J. Am. Chem. Soc. 124 (2002) 2442.

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(b) A.M. Mebel, P. v Rague Schleyer, K. Najafian, O.P. Charkin, Inorg. Chem. 37 (1998) 1693.

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[50] K. Koch, A. Schnepf, H. Schnöckel, Z. Anorg. Allg. Chem., in press.

[51] This behaviour is totally different to the only other structurally characterized metalloid cluster compound $Ga_{19}R_6^-$ (R = C(SiMe$_3$)$_3$) for which such gas phase investigations are performed, in which the weakest bonds is between the metal atoms;
(a) K. Weiss, H. Schnöckel, Z. Anorg. Allg. Chem. 629 (2003) 1175;
(b) K. Weiss, R. Köppe, H. Schnöckel, Int. J. Mass Spectrom. 214 (2002) 383.

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[54] Another plausible route to get to larger cluster compounds is a coupling of individual clusters to larger aggregates which has already led to interesting compounds with the Zintl ions [4c].