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Metalloid Cluster Compounds of Germanium: Synthesis – Properties – Subsequent Reactions

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Dedicated to Prof. Hartmut Bärnighausen on the occasion of his 75th birthday

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Metalloid cluster compounds represent ideal model compounds that provide an insight into the area between the molecular and the solid state. This borderland is of particular interest especially for metals or semimetals, as a drastic change of the physical properties takes place from the oxidized species (salt, nonconducting) to the bulk phase (metal, semimetal, conducting, semiconducting). For the heavier group 14 elements, this area is also of great technical interest as the module size in the computer industry approaches the nanometre range. This review describes recent achievements in the synthesis of metalloid cluster compounds of germanium. Besides different ligand systems used in synthesis, first examples of subsequent reactions of such cluster compounds are presented and further applications are discussed.

Introduction

As a result of the miniaturization in industrial applications and the growing field of nanotechnology, the area between the molecular and the solid state moves more and more into the focus of fundamental research investigating how the physical and chemical properties change on the way from a molecule to the bulk phase. Especially for group 14 this area is of particular interest, as for the silicon-based computer industry smaller and smaller structures are realized; for example, the nanometre range was reached by Intel® in 2000, when they started the mass production of microchips with transistor gate lengths of 100 nm and less.[1]

However, this miniaturization will end somewhere in the nanometre range, as quantum size effects will lead to different physical properties.[2] For example, visible photoluminescence (PL) was reported for germanium nanoparticles embedded in a quartz matrix, while elemental germanium shows no comparable PL.[3] Thus, near the nanometre range, a drastic change in physical properties occurs, normally summarized in the term "quantum size effects".[4] Germanium nanoparticles embedded in a quartz matrix are synthesized by a great variety of methods, e.g. co-sputtering of germanium and SiO_2[5] or H_2 reduction of mixed oxides of the general formula $Si_{1-n}Ge_nO_2$.[6] These nanoparticles are thereby obtained as a mixture with a certain size distribution and are therefore structurally only poorly characterized. Especially for small particles with diameters less than 2 nm, no experimental information about the structure is available, although these nanoparticles have the best photoluminescence properties.[7] Such small nanoparticles exhibit a molecular character and can no longer be seen as a small crystalline piece of germanium having a diamond lattice.[8] They are better described as molecular metalloid cluster compounds, featuring the general molecular formula

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Ge_nR_m ($n > m$), where R is any ligand or substituent bound to the surface germanium atoms. In contrast to the ligand-bound germanium atoms at the surface, the internal germanium atoms only form Ge–Ge bonds. Consequently, inside the metalloid germanium cluster compounds, more Ge–Ge bonds are present than germanium–ligand bonds. Structural information about these particles can now come from a bottom-up approach, through chemically synthesized metalloid cluster compounds of germanium, whose structures are well known from crystal structure analysis. The synthesis and structural characterization of these compounds will be an important step into this area between the molecular and the solid state and might lead at the end to an understanding of the relationship between structure and properties in this borderland.[9]

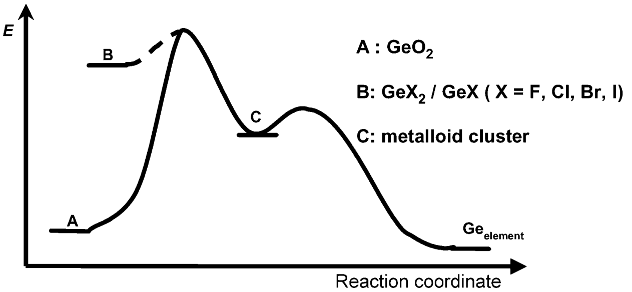
2. Synthesis of Metalloid Germanium Cluster Compounds

2.1. Principles and Experimental Details

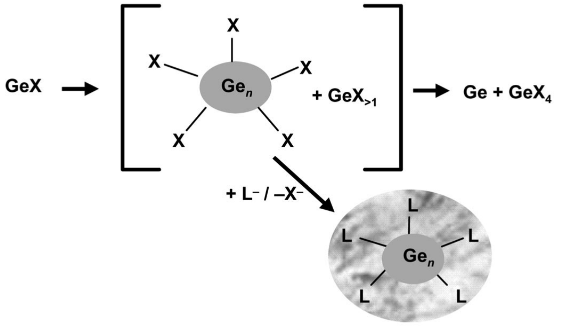
The synthesis of metalloid cluster compounds is in general quite complicated as a great variety of synthetic problems are present, and additionally the synthesis of a metalloid cluster compound of a definite size built from x metal atoms of which y bear a ligand can not yet be planned on a sheet of paper. Only the framework in which metalloid cluster compounds might form can be provided.

For the chemical synthesis of metalloid cluster compounds of germanium, the major problem is that these cluster compounds are metastable intermediates on the way to the bulk phase, as depicted in Scheme 1. This means that kinetic stabilization is necessary for the isolation of these intermediates, and therefore low reaction temperatures are needed for the synthesis. Elemental germanium is normally synthesized from GeO_2 (A), which is reduced to the element with elemental hydrogen at 650 °C. These drastic reaction conditions show that the activation barrier for this synthesis route is high, and during this reaction, an isolation of intermediates on the way to the elemental state (C) in reasonable yield is not possible.

Therefore a different starting material (B), which can be reduced much more easily to the elemental state with a small activation energy at lower reaction temperatures, is necessary. Under such reaction conditions, a kinetic stabilization might be possible, so that intermediates can be isolated as definite species. Subhalides are ideal starting materials, as they are metastable compounds that disproportionate into the thermodynamically stable compounds elemental germanium and germanium(IV) halide. During this disproportionation reaction, metastable metalloid cluster compounds are formed on the way to elemental germanium, as shown in Scheme 2. These intermediates certainly bear halide atoms on their surface, which can be substituted by a ligand in a subsequent metathesis reaction. Through this substitution, the core of germanium atoms is then shielded by a ligand shell and therefore kinetically stabilized, so that these intermediates can be isolated. The kinetic stabilization enables these compounds to be handled at higher temperatures, because no reaction channel having a low reaction barrier is present, as the first step for further reactions is the elimination of a ligand that is normally bonded to the metal core by a covalent 2c2e bond. This synthetic strategy can lead to giant cluster compounds, as it takes advantage of an intrinsic property of a subhalide, whose disproportionation reaction leads at the end to the element itself. For the heavier elements of group 13, aluminium and gallium, this was shown by Schnöckel et al., who were able to synthesize cluster compounds with up to 77 aluminium[10] or 84 gallium[11] atoms in the cluster core. Thus, this strategy can lead to metalloid cluster compounds with diameters in the nanometre range, when the right reaction conditions are known. And exactly this point is the major problem that has to be solved for the synthesis of a metalloid cluster compound, as no definite synthetic protocol is known, and therefore for every reaction system many experiments are necessary until the optimal reaction conditions are established. In other words, the disproportionation reaction definitely leads to metalloid cluster compounds, but finding the reaction conditions under which these compounds are formed and simultaneously stabilized by a ligand shell is very difficult.



Scheme 1. Schematic presentation of the energy distribution during the synthesis of elemental germanium from oxidized starting materials.



Scheme 2. Schematic presentation of the synthesis of a metalloid germanium cluster compound by applying the disproportionation reaction of a germanium subhalide.

For germanium, the well known germanium(II) halides are not suitable starting materials for the synthesis of metalloid germanium cluster compounds by the disproportionation reaction, as, for example, $GeBr_2$ only begins to disproportionate at 150 °C,[12] which is too high a temperature for kinetic stabilization of the metalloid cluster compounds (C, Scheme 1) on the way to elemental germanium. Consequently, one has to go a step further toward the elemental state to the corresponding monohalides GeX (X = F, Cl, Br, I), which are less stable and disproportionate at lower temperatures as shown in the following discussion.

Germanium monohalides are stable compounds in the gas phase at high temperatures and low pressures, as shown by thermodynamic calculations based on quantum chemically computed thermodynamic data (Figure 1).[13] Here, the contribution of the partial pressure of the different gaseous compounds of the reaction of germanium with HBr is calculated by using all independent equilibrium reactions. The calculations reveal that GeBr is the major gaseous compound in the reaction of germanium with HBr at a reaction temperature of 1900 K and a total reaction pressure of 10^{-2} mbar as shown in Figure 1.

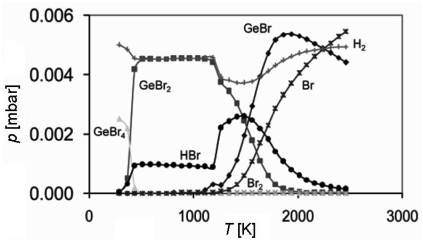


Figure 1. Distribution of the partial pressures of gaseous compounds in the reaction of HBr and Ge at a starting HBr pressure of 10^{-2} mbar.

However, the calculations only show that GeBr can be synthesized under these drastic reaction conditions, but obviously as a gas phase species it can not be used for the synthesis of metalloid cluster compounds in solution. Therefore the monohalide has to be transferred into a reasonable phase, and to achieve this, the preparative matrix isolation technique can be used, which is useful to trap reactive species in an inert matrix.[14] Thus, the high-temperature molecule GeBr is trapped at low temperatures and is hereby brought to conditions in which it is no longer the stable form but represents a metastable compound. The co-condensation reaction is performed in a homemade apparatus shown in Figure 2, where the high-temperature reaction between HBr and elemental germanium takes place inside a graphite reactor (A in Figure 2), which is heated inductively to 1900 K. During the co-condensation reaction, the apparatus is evacuated to 10^{-5} mbar, so the gaseous reaction products effuse from the graphite reactor, where a higher reaction pressure of ca. 10^{-2} mbar is present.

The reaction pressure inside the graphite reactor is controlled by the stream of the hydrogen halide gas (HX) during the reaction, which normally flows at 0.2 mmol min^{-1}.

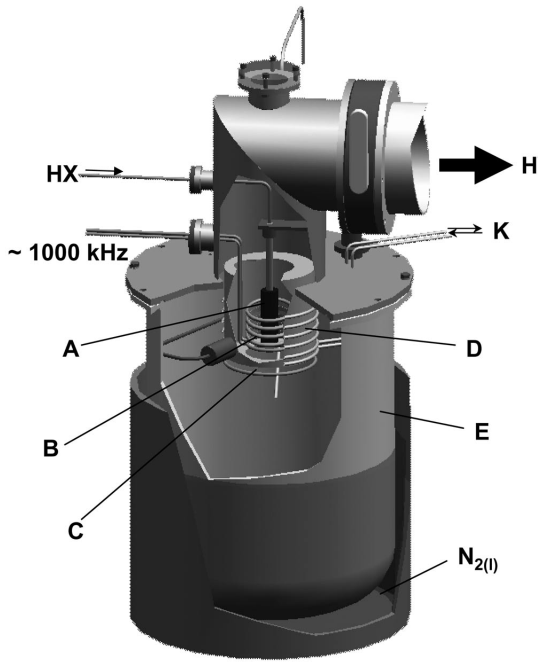


Figure 2. Scheme of the co-condensation apparatus for the synthesis of germanium(I) halides: A: graphite reactor; B: induction coil; C: solvent inlet; D: copper cooling shield; E: stainless steel vessel (30 L); K: cooling water; HX: hydrogen halide gas; HV: high vacuum.

The gas particles resulting from the high-temperature reaction are then condensed together with a solvent at a surface at –196 °C in a solid matrix, without further collision in the gas phase. Inside the matrix, the GeBr molecules are separated from each other by solvent molecules. When the matrix is warmed, the solvent melts and the GeBr molecules are free to move.

When only toluene is used as solvent, GeBr is isolated in the form of an orange-red solid, which begins to disproportionate into Ge and $GeBr_4$ at 90 °C. Thus, GeBr seems to be a better starting material for the synthesis of metalloid germanium cluster compounds, as the temperature at which it begins to disproportionate is 60 K lower than that of the corresponding $Ge^{II}Br_2$. Additionally, the colour of GeBr is unusual, as all other bromides of germanium are pale yellow or colourless solids or liquids.[15] The higher reactivity of the monohalide also becomes obvious from the reaction of GeBr with acetone. Here Ge^{I} is oxidized to Ge^{IV}, and acetone is reductively coupled to 1,1-dimethyl-3-oxobutan-1-yl.[16] Such a redox reaction is not known from germanium(II) halides. However, as the solid GeBr is insoluble in inert solvents, it can not be used for the synthesis of distinct molecular cluster compounds in solution. Nevertheless, when the co-condensation reaction is performed with a toluene/NnPr$_3$ mixture, an emulsion is obtained in which GeBr is a dark red oil. In this form, GeBr can be used for the synthesis of metalloid cluster compounds of germanium as discussed in the following section.

The synthetic route by the disproportionation reaction is not the only possible way to access metalloid cluster compounds. Additionally, the more classical way through the reductive coupling reaction of a RGeX or $RGeX_3$ precursor with an adequate reducing agent can lead to metalloid germanium cluster compounds.[17] Here the naked atoms are inserted by ligand stripping, i.e. the elimination of a ligand, or by adding an E^{II} halide (e.g. $GeCl_2$), which is completely reduced and inserted into the cluster as naked germanium atoms.[18] Similar to all the synthetic strategies is the use of bulky ligands for the protection of the germanium cluster core (kinetic stabilization). Normally organic ligands like aryl or amide are used for the protection of the cluster core, but inorganic ligands can also be used. As the group of organic-ligand-shielded metalloid clusters is by far larger, it will be discussed first.

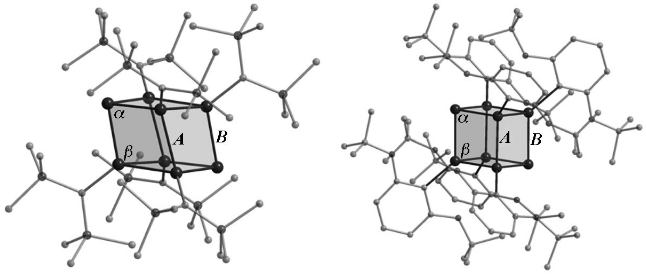


Figure 3. Molecular structure of the metalloid cluster compounds $Ge_8[N(SiMe_3)_2]_6$ (**1**) (left) and $Ge_8[C_6H_3(OtBu)_2]_6$ (**2**) (right) without hydrogen atoms. The central Ge_8 core is emphasized by a polyhedral presentation. **1**: A = 267 pm, B = 250 pm, α = 82°, β = 101°; **2**: A = 251 pm, B = 249 pm, α = 87°, β = 92°.

3. Metalloid Germanium Clusters

3.1 Metalloid Germanium Clusters with Organic Ligands

The reaction of the GeBr emulsion, described before, with $LiN(SiMe_3)_2$ leads to the metalloid cluster compound $Ge_8[N(SiMe_3)_2]_6$ (**1**),[19] where six ligand-bound and two naked germanium atoms are present in the cluster core. The eight germanium atoms in **1** are arranged in the form of a distorted cube, as two different Ge–Ge distances of 250 and 267 pm are found inside the cluster core (Figure 3). The Ge–Ge distances are longer than those for a normal single bond, which is unusual, as due to the naked germanium atoms two extra electrons are now available for bonding inside the cluster core, and shorter Ge–Ge bonds might therefore be expected. However, quantum chemical calculations on the model compound $Ge_8(NH_2)_6$ reveal that a delocalization of bonding electrons inside the cluster core has taken place, as three-centre bonding components with a shared electron number (SEN)[20] of 0.13 have been calculated. As the bonding electrons inside the fully substituted cubic cluster compound Ge_8R_8 (R = $C_6H_3Et_2$;[21] 1,1,2-trimethylpropyl[22]) are completely localized, the presence of the naked germanium atoms has led to a delocalization of bonding electrons inside the cluster core and not to the formation of multiple bonds. The formation of multiple bonds would rather lead to a shortening of the Ge–Ge bonds as in the series germane (244 pm in Ge_2Ph_6)[23] – germene (230 pm in $Ge_2Ar'_4$; Ar′ = C_6H_3-2,6-$i$$Pr_2$)[24] – germyne (228 pm in Ge_2Ar_2; Ar = C_6H_3-2,6-$Dipp_2$, Dipp = C_6H_3-2,6-$i$$Pr_2$).[25] However, the degree of delocalization depends strongly on the ligand used, which becomes obvious when another Ge_8R_6 compound, $Ge_8[C_6H_3(OtBu)_2]_6$ (**2**), which is also synthesized from GeBr by using the lithium salt Li[2,6-$(OtBu)_2C_6H_3$],[26] is taken into account.

In the case of the metalloid cluster compound **2** the eight germanium atoms are arranged in a nearly perfect cube, as the Ge–Ge–Ge angles inside the cluster core are 90 ± 3° and the Ge–Ge distances vary in a narrow range from 249 to 251 pm (Figure 3).

Additionally the SENs of the three-centre bonding components inside the cluster core of the model compound Ge_8Ph_6 are only 0.06.[26] Therefore a different bonding situation seems to be present in **1** and **2** although both compounds exhibit the same molecular formula, Ge_8R_6. This different bonding situation also has a great influence on the physical properties of the compounds: crystals of **1** are nearly black, while crystals of **2** are orange-red. This finding shows, that the ligand used is not only necessary for the protection of the cluster core against the exterior, it also has a strong influence on the bonding situation and the structural and physical properties of a metalloid cluster compound.

Another factor that strongly influences the bonding situation in a metalloid cluster compound is the average oxidation state of the germanium atoms inside the cluster core. This area was first addressed by the metalloid cluster compounds Ge_6Ar_2 (**3**) (Ar = $C_6H_3Dipp_2$; Dipp = C_6H_3-2,6-$i$$Pr_2$)[17b] and $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**)[27] (Figure 4), in which four and six naked germanium atoms are present, respectively, leading to an average oxidation state of the germanium atoms of 0.33 in **3** and 0.22 in **4**. The two metalloid cluster compounds **3** and **4** are obtained by different synthetic strategies. Ge_6Ar_2 (**3**) was synthesized by a reductive coupling reaction of ArGeCl with C_8K in the presence of $GeCl_2$, while the anionic compound $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**) was synthesized from GeBr by using $LiSi(SiMe_3)_3$ as the ligand source. Both compounds exhibit highly symmetric arrangements of the germanium atoms inside the cluster core. The six germanium atoms in **3** are arranged octahedrally, and the nine germanium atoms of **4** are arranged in the form of a tricapped trigonal prism (Figure 4).

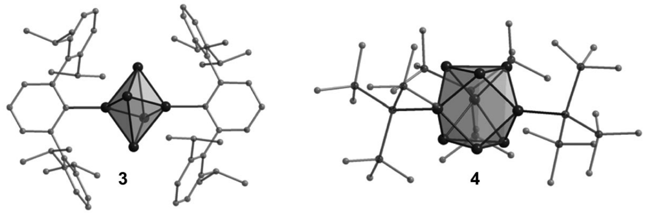


Figure 4. Molecular structure of the metalloid germanium cluster compounds Ge_6Ar_2 (**3**) (Ar = $C_6H_3Dipp_2$; Dipp = C_6H_3-2,6-$i$$Pr_2$) and $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**) without hydrogen atoms.

In both compounds, two different Ge–Ge distances are found, following the same trend. The Ge–Ge distance between ligand-bound and naked germanium atoms is 250 pm in **3** and 252 pm in **4**. In contrast to this, the Ge–Ge distances between naked germanium atoms are substantially longer: 286 pm in **3** and 267 pm in **4**. Thus the germanium atoms with the higher coordination number form the shorter Ge–Ge bonds. Quantum chemical calculations on the model compounds Ge_6H_2 (**3′**) and $Ge_9H_3^-$ (**4′**) reveal that in both compounds highly delocalized bonding electrons are present as the maximum SENs of the three-centre bonding components are 0.23 and 0.32 for **3′** and **4′**, respectively.[28]

Hence, the bonding situation inside the two metalloid cluster compounds **3** and **4** give an interesting hint to a correlation between the metalloid cluster compounds on the one hand and the Zintl anions on the other hand, as in both classes of compounds highly delocalized bonding electrons are present. Additionally, the bonding situation in **3**, **4** and the Zintl anions can be described primarily according to Wade's rules.[29] The octahedral shape of **3** can be traced back to a *closo* cluster bonding situation, as 2*n*+2 bonding electrons are present inside the cluster core. However, for **4** a *nido* structure is to be expected, as 2*n*+4 bonding electrons are present in the cluster core. In the case of **4** the *closo* structure of a tricapped trigonal prism seems to be energetically more favourable, leading to a large edge/high value of 1.27 for the trigonal prism as expected for a *closo* cluster of nine atoms with 2*n*+4 skeletal electrons.[30] As the structures of the Zintl anions are also mainly described according to Wade's rules,[31] a similarity between the two groups of clusters is obvious. However, in the case of the Zintl anions, the average oxidation state of the germanium atoms is negative, while the average oxidation state of the germanium atoms in the metalloid cluster compounds is positive. Therefore, starting from the element, the oxidation leading to metalloid cluster compounds as well as the reduction leading to Zintl anions seems to end at cluster compounds with comparable bonding situations. However, one major structural difference is the fact that, in the case of the Zintl anions, the germanium atoms with the higher coordination number form the longer Ge–Ge bonds, which is exactly the other way around in the case of the metalloid cluster compounds **3** and **4**, as described before. This difference shows that the presence of a ligand has a strong influence on the bonding situation inside the cluster core. The unusual similarities between the metalloid cluster compounds and the Zintl anions have to be elucidated by further experimental results and theoretical calculations. Nevertheless, the delocalization of bonding electrons inside the cluster core leads to another interesting correlation within the metalloid cluster compounds.

Taking a closer look into the amount of delocalization of bonding electrons inside a metalloid cluster compound, as shown in Table 1 reveals that the level of delocalization – indicated by the magnitude of the SEN of the multicentre bonding component – increases when the average oxidation state of the germanium atoms decreases. If this trend would continue, it would lead to elemental germanium, with zero oxidation state and highly delocalized bonding electrons, representing a metallic state. Thus here an access to a metallic form of germanium seems possible, and for the heavier element tin, the synthesis of a $Sn_{15}R_6$ compound (R = NSiMe$_3$Dipp; Dipp = C_6H_3-2,6-*i*Pr$_2$)[32] shows that a metallic arrangement can be realized within the metalloid group 14 cluster compounds. Inside the Sn_{15} compound the tin atoms are arranged in the form of a bcc structure leading to an 8+6 coordination number for the central tin atom.

Table 1. Comparison of the average oxidation state of the germanium atoms inside a metalloid cluster compound with the degree of delocalization of bonding electrons inside the cluster core.

	$Ge_8(C_6H_5)_6$	$Ge_8(NH_2)_6$	Ge_6H_2	$Ge_9H_3^-$
Average oxidation state	0.75	0.75	0.33	0.22
Highest SEN (three-centre bonding components)	0.06	0.13	0.23	0.32

However, a metallic state is quite unusual for the semimetal germanium having a bandgap of 0.6 eV. Hence, one would expect that at a larger size, the trend of delocalization will invert, leading to an elemental state with localized 2c2e bonds, which exhibits a diamond lattice. Recent results indicate that such a transition might already occur at a size of ten germanium atoms in the cluster core as demonstrated in the following discussion. Here the molecular structures of two Ge_{10} cluster compounds $[Ge_{10}(Si\mathit{t}Bu_3)_6I]^+$ (**5**)[17a] and $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ (**6**)[33] have to be taken into account. The arrangement of the ten germanium atoms in the two cluster compounds is quite similar, as shown in Figure 5. This similarity is unusual, however, as there are significant differences between the two compounds.

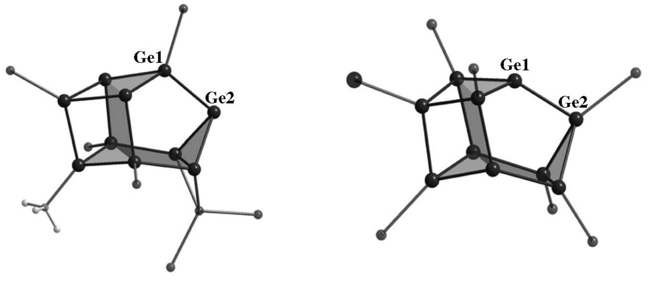


Figure 5. Molecular structure of $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ (**6**) (left) and $[Ge_{10}(Si\mathit{t}Bu_3)_6I]^+$ (**5**) (right) without $SiMe_3$ and *t*Bu groups. The adamantine-like arrangement of the germanium atoms inside the cluster core is emphasized by a polyhedral presentation.

First of all, the average oxidation state of the germanium atoms inside the cluster core is 0.8 in cation **5** and 0.4 in anion **6**. Secondly, one compound is a cation while the other is an anion. Third and most important is the fact that the substitution pattern is different, which means that the ligands in the two cluster compounds are bound to different germanium atoms. For example, as shown in Figure 5, in the anionic compound **6**, Ge1 is bound to a ligand while Ge2 is naked, and in cation **5** Ge1 is naked and Ge2 binds a ligand. Thus in the case of Ge1 and Ge2 the ligand-bound and naked germanium atoms have switched. The fact that, beside all these differences, the germanium atoms inside the two compounds are arranged in a similar way shows that this arrangement is favourable for a metalloid cluster compound with ten germanium atoms in the cluster core. A reason for this behaviour can be seen in the fact that in both compounds **5** and **6** an adamantine-like arrangement of the ten germanium atoms is present, as shown in Figure 5 by a polyhedral presentation. Hence, here exists for the first time a topological approach to the structure of elemental germanium, which is much more pronounced in the case of the anionic compound **6**, as the average oxidation state of the germanium atoms is 0.4 here, which is much closer to the value 0 for the element. The structural features of **5** and **6** were additionally observed in the cluster anion $Au_3Ge_{45}^{9-}$, which was synthesized from the Zintl anion Ge_9^{4-},[34] showing that this arrangement of germanium atoms is important in the borderland between the molecular and the solid state. However, other arrangements are also possible when ten germanium atoms are present in the cluster core of a metalloid cluster compound, as discussed in the following chapter.

3.2 Metalloid Germanium Clusters with Inorganic Ligands

All metalloid cluster compounds discussed so far exhibit organic ligands shielding the germanium core against the exterior. However, transition-metal compounds such as $CpFe(CO)_2$ ($Cp = C_5H_5$), $Co(CO)_4$, $Cr(CO)_5$, etc. might also be used as ligands for the stabilization of a polyhedral cluster core. The first result in this respect was published by Huttner et al., who synthesized the octahedral anionic cluster compound $\{Ge_6[Cr(CO)_5]_6\}^{2-}$ (**7**),[35] in which each germanium atom is bound to a $Cr(CO)_5$ ligand. The octahedral shape of this cluster compound was attributed to a *closo* cluster bonding situation by reference to Wade's rules. Hence, the bonding situation inside the anionic compound **7** is comparable to that found in the Zintl anions or in the metalloid cluster compounds **3** and **4** depending on whether the transition-metal ligand is counted as a neutral $Cr(CO)_5$ or as a dianionic $[Cr(CO)_5]^{2-}$ ligand. Nevertheless, this first result reveals that transition-metal ligands can be used for the synthesis of germanium cluster compounds, and very recently the first metalloid cluster compound of germanium, $(thf)_{18}Na_6Ge_{10}[Fe(CO)_4]_8$ (**8**), was synthesized by the reaction of a GeBr solution with Collmann's reagent, $Na_2Fe(CO)_4$.[36]

The arrangement of the ten germanium atoms in the cluster core of **8** is totally different from that of the two other Ge_{10} compounds, **5** and **6**, showing that an adamantine-like arrangement must not necessarily occur when ten germanium atoms are present in the cluster core of a metalloid cluster compound. In the case of the metalloid cluster **8**, the ten germanium atoms are arranged in a unique fashion. The polyhedron formed by the ten germanium atoms exhibits two different sites and is built up of a cubic part on the one side and an icosahedral part on the other side as depicted in Figure 6. In accordance with the description of the Centaur in Greek mythology (half human half horse), a polyhedron built from two different polyhedrons (here: half cube half icosahedron) was named a centaur polyhedron, and therefore the polyhedron built from the ten germanium atoms in **8** can be named a centaur polyhedron.

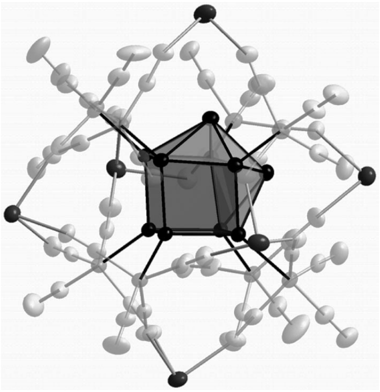


Figure 6. Molecular structure of $(thf)_{18}Na_6Ge_{10}[Fe(CO)_4]_8$ (**8**) without coordinating thf molecules. The central germanium atoms and the surrounding sodium atoms are dark coloured. The different parts of the centaur polyhedron of the central Ge_{10} unit are distinguished by a polyhedral presentation in which the cubic part is dark coloured and the icosahedral part is light coloured.

The centaur polyhedron is well known in solid state chemistry, as it represents one possibility for the coordination number ten.[37] However, **8** is the first empty centaur polyhedron, as no atom is localized inside the Ge_{10} polyhedron. Eight of the ten germanium atoms inside the cluster core of **8** are bound to one $Fe(CO)_4$ ligand each and the $Fe(CO)_4$ ligands are bound through the CO molecules to six sodium cations, which surround the cluster in a pseudo-octahedral fashion. The sodium cations are coordinatively saturated by three thf molecules each, leading to the neutral compound $(thf)_{18}Na_6Ge_{10}[Fe(CO)_4]_8$ (**8**), which can be dissolved and recrystallized from thf. A closer look into the bonding situation inside the cluster core was taken with the aid of quantum chemical calculations on the model compound $\{Ge_{10}[Fe(CO)_4]_8\}^{6-}$ (**8′**), which revealed that inside the different sides of the centaur polyhedra different bonding situations are also present (Figure 7). On the cubic side, three-centre bonding components with SENs of 0.058 to 0.086 were calculated, while the SENs in the icosahedral part are in the range of 0.278 to 0.284. Thus the bonding situation inside **8′** changes from localized in the cubic part to delocalized in the icosahedral part of the centaur polyhedron, as depicted in Figure 7. Such a bonding situation is unique in the field of metalloid cluster compounds as, for example, in the large multishell group 13 metalloid cluster compounds, the bonding situation changes from the inner to the outer side but not from one side to the other.[38]

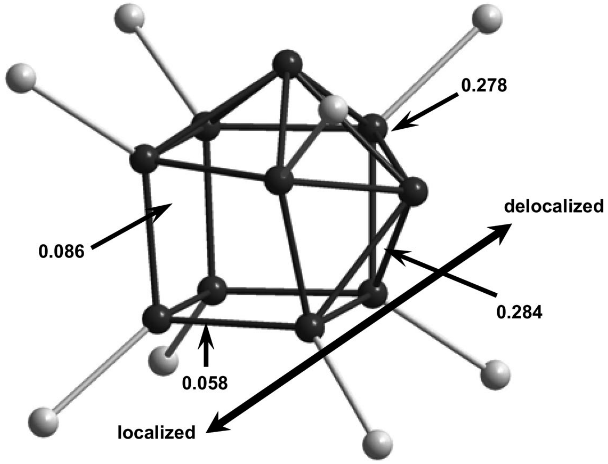


Figure 7. $Ge_{10}Fe_8$ core of the calculated model compound $\{Ge_{10}[Fe(CO)_4]_8\}^{6-}$ (**8′**). The calculated SENs of the three-centre bonding components are shown.

Thus, all metalloid cluster compounds of germanium discussed so far show that the bonding situation and the physical properties associated with it change drastically with size, average oxidation state and ligand used. In this respect one important question is what happens when the size of the metalloid cluster increases, leading to cluster compounds with more than ten germanium atoms inside the cluster core. To access larger cluster compounds, the established synthetic routes have to be extended. In this respect, the synthetic route through the disproportionation reaction is the most fruitful, as it takes advantage of the intrinsic property of metastable subhalides to reach the elemental state under mild conditions, as mentioned above. However, another possibility to access larger metalloid cluster compounds can be seen in subsequent reactions of the synthesized and isolated metalloid cluster compounds. Thus, a coupling of individual metalloid cluster compounds can lead to larger compounds or aggregates. Such a synthetic route has already led to larger compounds with the Zintl anions; for example, the reaction of the Zintl anion Ge_9^{4-} with Ni, Pd or Au reagents yields anionic cluster compounds with 13 $[Ge_{13}Ni_6(CO)_5^{4-}]$,[39] 18 $(Ge_{18}Pd_2^{4-})$[40] and 45 $(Au_3Ge_{45}^{9-})$[34] germanium atoms in the cluster core. To perform subsequent reactions with metalloid germanium cluster compounds, the shielding of the cluster core by the ligand shell, necessary for the synthesis and isolation, is counterproductive as the naked germanium atoms are not available for reagents such as transition-metal compounds (Figure 8). However some metalloid clusters are less shielded by the ligand shell and might be potential starting materials for subsequent reactions, and first results of such reactions are discussed in the following chapter.

3.3 Subsequent Reactions of Metalloid Germanium Clusters

Taking a look at the space-filling models of the metalloid cluster compounds $Ge_8[N(SiMe_3)_2]_6$ (**1**), Ge_6Ar_2 (**3**) (Ar = $C_6H_3Dipp_2$; Dipp = C_6H_3-2,6-*i*Pr_2), $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**) and $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ (**6**), as shown in Figure 8 reveals that the naked germanium atoms are well shielded by the ligand shell in nearly all cases. However, in the anionic compound $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**), the three $Si(SiMe_3)_3$ ligands shield the cluster core only incompletely against the exterior, and the three-membered rings of naked germanium atoms are not protected by the ligand shell. Therefore, these germanium atoms are readily available for possible attacking reagents, and in fact, the reaction

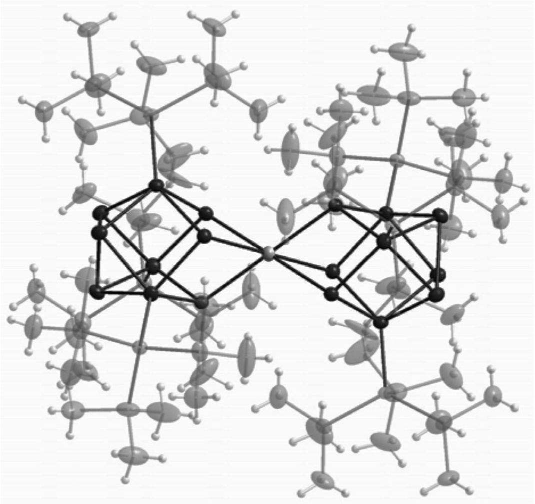


Figure 9. Molecular structure of $\{Ge_{18}Au[Si(SiMe_3)_3]_6\}^-$ (**9**). The germanium atoms are dark coloured and the $Si(SiMe_3)_3$ ligands and the central gold atom are light coloured.

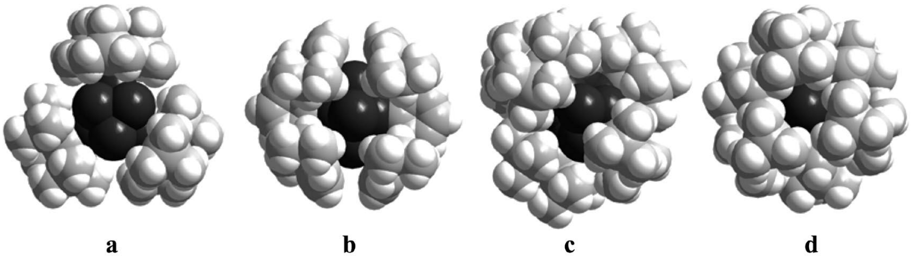
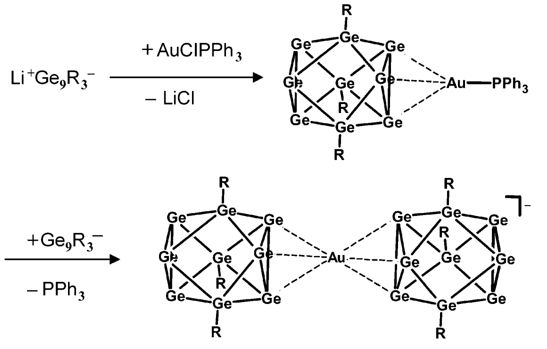


Figure 8. Space-filling model of metalloid cluster compounds of germanium; view along the most open side of the ligand shell: (a) $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**); (b) Ge_6Ar_2 (**3**) (Ar = $C_6H_3Dipp_2$; Dipp = C_6H_3-2,6-*i*Pr_2); (c) $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ (**6**); (d) $Ge_8[N(SiMe_3)_2]_6$ (**1**).

of **4** with the Au^I reagent $AuClPPh_3$ leads to an anionic cluster compound, $\{Ge_{18}Au[Si(SiMe_3)_3]_6\}^-$ (**9**), whose molecular structure is shown in Figure 9. The subsequent reaction is thought to proceed by a metathesis leading to the neutral product, $[Si(SiMe_3)_3]_3Ge_9Au–PPh_3$, in which the gold atom is bound to a three-membered ring of germanium atoms of **4** and additionally to the PPh_3 ligand. In a second step, the PPh_3 ligand is then substituted by another $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ unit leading to the anionic product $\{Ge_{18}Au[Si(SiMe_3)_3]_6\}^-$ (**9**) as shown in Scheme 3.



Scheme 3. Possible reaction sequence for the formation of $\{Ge_{18}Au[Si(SiMe_3)_3]_6\}^-$ (**9**).

The molecular structure of **9** (Figure 9) can be described as two $Ge_9[Si(SiMe_3)_3]_3$ units that are linked by a central gold atom. The two $Ge_9[Si(SiMe_3)_3]_3$ units are oriented in such a way that the sterically demanding $Si(SiMe_3)_3$ ligands are arranged in a staggered fashion, leading to C_{3i} symmetry for the whole cluster compound; the central $Ge_{18}Au$ unit possesses D_{3d} symmetry.

The bonding of the gold atom to the Ge_9 unit leads to a strong distortion of the arrangement of the germanium atoms as compared to the arrangement in the metalloid cluster $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**). Thus the Ge–Ge distance between the gold-bound germanium atoms in **9** is 296 pm, which is 29 pm longer than the Ge–Ge distance of 267 pm between the naked germanium atoms in **3**. This indicates that a strong electronic interaction between the gold atom and the $Ge_9[Si(SiMe_3)_3]_3$ unit is present. Quantum chemical calculations for the model compound $Ge_{18}AuH_6$ (Figure 10) show that the bonding electrons in **9** are highly delocalized over the whole cluster core as three-centre bonding components with SENs up to 0.33 are calculated for the model compound $AuGe_{18}H_6^-$ (Figure 10).

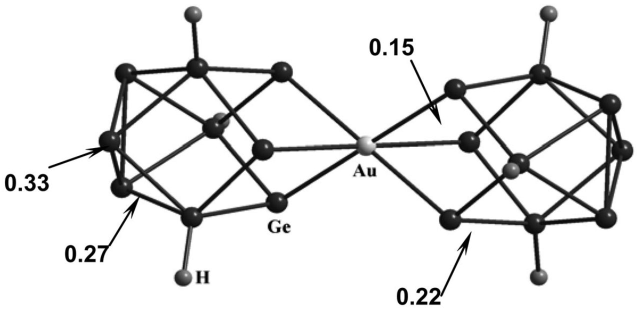


Figure 10. Calculated structure of $Ge_{18}AuH_6^-$. The calculated SENs of multicentre bonding components are indicated by arrows.

Additionally a four-centre bonding component in the trigonal pyramid built from three germanium atoms and the gold atom is calculated with a SEN of 0.15. The appearance of the four-centre bonding component shows that the central gold atom is an integral part of the cluster system. Consequently, the description of **9** as two $Ge_9[Si(SiMe_3)_3]_3$ units linked by a central gold atom is only valid from a geometrical point of view. The electronic situation shows that **9** is better described as an anionic $Ge_{18}Au$ cluster compound in which six germanium atoms are bound to one $Si(SiMe_3)_3$ ligand each. Additionally, gas-phase investigations demonstrate that the whole cluster compound remains intact as it is transferred into the gas phase as shown in Figure 11. Collision experiments in the gas phase show that the weakest bonds inside **9** are those to the central gold atom. In the SORI-CAD (sustained off resonance irradiation collision activated dissociation) experiments, the parent ion **9** dissociates to give the fragment ion $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**). The relative abundance of the fragment ion **4** depends on the translation energy of the parent ion **9** prior to fragmentation as shown in Figure 11. Low energy gives fewer fragment ions than does higher energy. Increasing the translation energy further should lead to the known fragmentation of $Ge_9[Si(SiMe_3)_3]_3^-$ in the gas phase.[41]

A comparison of $\{Ge_{18}Au[Si(SiMe_3)_3]_6\}^-$ (**9**) with the gold–germanium cluster $[Au_3Ge_{18}]^{5-}$ (**10**), which is also synthesized from a reaction of $AuClPPh_3$, this time with the Zintl anion Ge_9^{4-}, reveals significant differences. The main difference is the effect of the bonding of the gold atom to the bonding situation inside the Ge_9 unit. In the case of the metalloid cluster species $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**), the bonding to the gold atom has led to a strong distortion of the arrangement of the nine germanium atoms in the cluster core as discussed before. In contrast to this, only slight differences in the Ge_9 units in **10** are observed (Figure 12) relative to Ge_9^{4-}. This different behaviour indicates that a different bonding situation is to be expected. The observed elongation in the three-membered Ge_3 ring in **9** is rather comparable to the situation found in $[Ni_3Ge_{18}]^{4-}$, where an additional transition-metal atom (Ni) is present inside the Ge_9 unit.[42] Another significant difference between **9** and **10** is the calculated charge on the central gold atom. For **9** a negative partial charge is calculated for the gold atom, while the gold atoms in $[Au_3Ge_{18}]^{5-}$ are positively charged as estimated by theoretical calculations.[46] Thus again significant differences between the metalloid cluster compounds and the Zintl anions are obvious. Another difference, important for subsequent reactions, can be seen in the fact that in the case of the metalloid cluster compound **4**, the cluster compound is stable in solution while in the case of the Zintl anions, a dynamic system is present when the Zintl phase (K_4Ge_9) is dissolved in ethylenediamine (en).[43] This becomes obvious when the second cluster compound $[Au_3Ge_{45}]^{9-}$ (**11**) (Figure 12), which is also isolated from the reaction of $AuClPPh_3$ with a solution of Ge_9^{4-},[34] is taken into account.

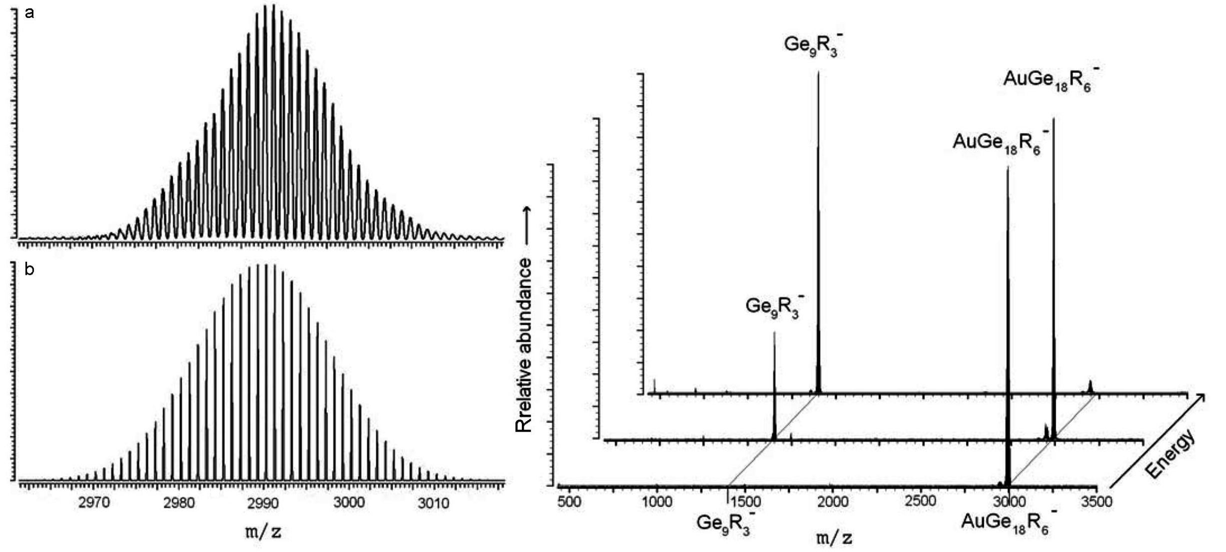


Figure 11. Comparison of the measured (a) and simulated (b) FT/ICR mass spectra of $\{Ge_{18}Au[Si(SiMe_3)_3]_6\}^-$ (**9**) in thf after electrospray ionization. (left). The dissociation experiments (SORI-CAD, right) show that the metalloid cluster **9** fragments giving the fragment ion $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**). The abundance of the fragment ions depends on the translational energy of the parent ion **9** prior to fragmentation.

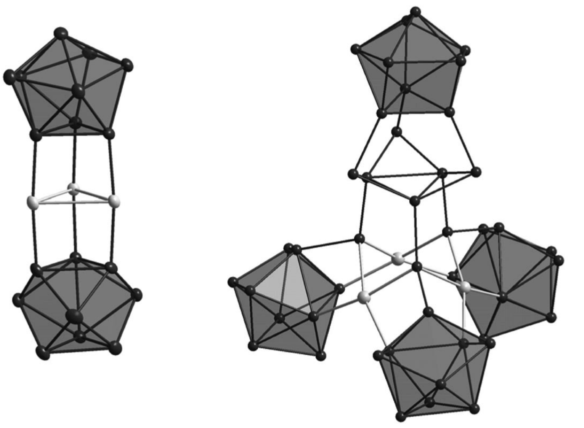


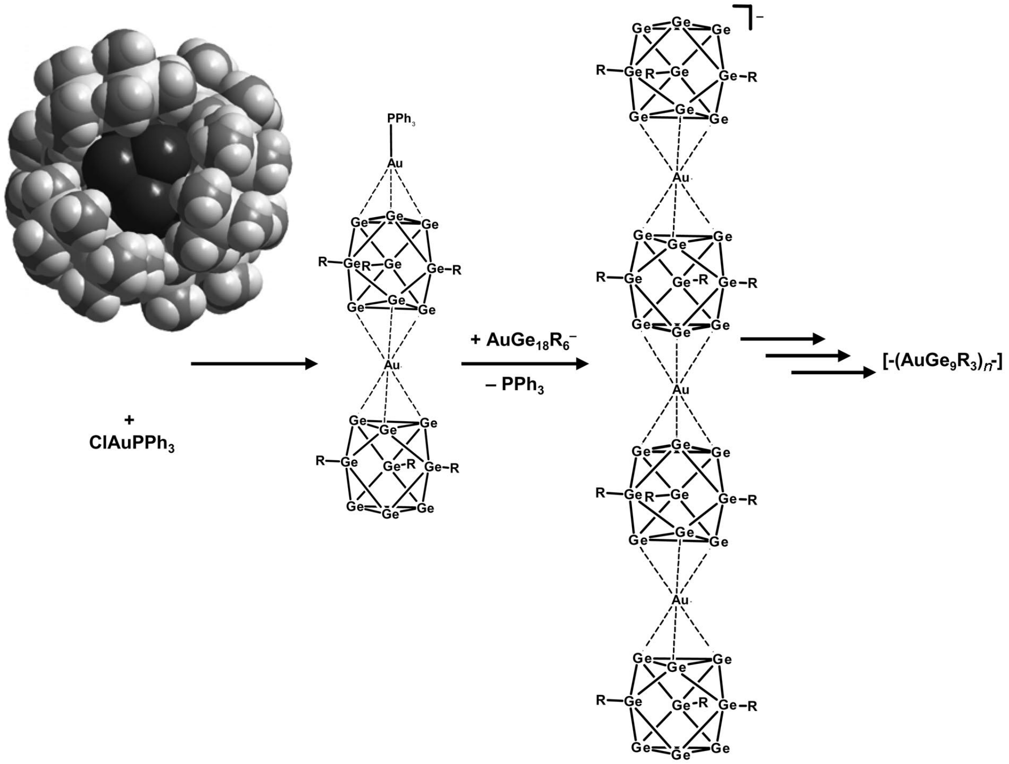
Figure 12. Molecular structure of the gold-bound Zintl anions $[Ge_{18}Au_3]^{5-}$ (**10**) (left) and $[Ge_{45}Au_3]^{9-}$ (**11**) (right). The Ge$_9$ units are emphasized by a polyhedral presentation.

In the case of **11**, besides relatively unchanged Ge$_9$ units (emphasized by a polyhedral presentation in Figure 12) one completely different Ge$_9$ unit is present, in which the germanium atoms are arranged in a similar manner to the arrangement found in the metalloid Ge$_{10}$ compounds $[Ge_{10}(Si\mathit{t}Bu_3)_6I]^+$ (**5**) and $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ (**6**). These findings show that, in the case of subsequent reactions, the metalloid cluster compounds can be seen as stable synthons, while the Zintl anions behave as a dynamic system from which different products can be isolated by changing the reagent and the reaction conditions used.

Thus the metalloid cluster compound $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **4** might be seen as a stable ligand in coordination chemistry. However, **4** is very sensitive against moisture and oxygen, and crystals of **4**·Li(thf)$_4$ ignite spontaneously when exposed to air, thus redox-labile reagents are unfavourable. As the gold–germanium cluster compound, $\{Ge_{18}Au[Si(SiMe_3)_3]_6\}^-$ (**9**), is also stable in solution, further reactions seem possible. When the space-filling model of **9** is observed along the threefold axis (Scheme 4 top left) one can see that the three naked germanium atoms of the three-membered Ge$_3$ ring are again poorly shielded by the Si(SiMe$_3$)$_3$ ligands, as was the case for $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**). Therefore, a subsequent reaction of **9** with AuClPPh$_3$ seems possible, leading to a cluster compound built from three gold atoms and four Ge$_9$R$_3$ units as depicted in Scheme 4. At this point, the reaction must not end, as the hypothetical anionic $Au_3Ge_{36}R_{12}^-$ unit again exhibits three-membered rings of naked germanium atoms. Consequently, further reactions will yield the cluster compounds $Au_7Ge_{72}R_{24}^-$, $Au_{15}Ge_{144}R_{48}^-$, etc. that will lead at the end to a linear chain with the composition $[Ge_9R_3\text{-}(AuGe_9R_3)_n\text{-}]^-$.

Quantum chemical calculations on the model compound $Ge_{36}Au_3R_{12}$ [R = H **12a**, Si(SiMe$_3$)$_3$ **12b**][44] show, as a first approximation, that the formation of the oligomer is exothermic by ca. 100 kJ mol^{-1} and not sterically hindered by the large Si(SiMe$_3$)$_3$ ligands. A population analysis of the bonding electrons inside **12a** additionally shows that here again strongly delocalized bonding electrons are present in the Ge$_{36}$Au$_3$ cluster core; therefore, this linear chain can be considered as a "one-dimensional conductor". However, delocalized bonding electrons alone are not sufficient for a conductor as empty orbitals with a level spacing less than the thermal energy are also needed.

To answer this question, one possibility is to take a look into the contribution of the HOMO–LUMO gap of calculated model compounds as shown in Figure 13. Hereby it



Scheme 4. Schematic presentation for the formation of a $(AuGe_9R_3)_n$ – wire from $AuGe_{18}R_6^-$ units [R = $Si(SiMe_3)_3$].

becomes obvious that the HOMO–LUMO gap steadily decreases as the length of the chain increases; e.g. the HOMO–LUMO gap for the model compound $Ge_{18}AuH_6^-$ is 1.91 eV, and a gap of 1.37 eV is calculated for the model compound $Au_3Ge_{36}H_{12}^-$. Further extrapolation of this behaviour shows that the HOMO–LUMO gap reaches a thermal energy of about 2.5 kJ at a length of about 50 Ge_9Au units. Thus, for the species $Au_{50}Ge_{459}[Si(SiMe_3)]_{153}^-$, a metallic state is to be expected. This compound will then have a length of 39 nm and a diameter of 1.5 nm, leading to a length to diameter ratio of 26. But the point of the transition to the metallic state might be reduced by an oxidation or reduction of the cluster compound, leading to single occupied orbitals. This conducting–nonconducting transition is now one of the most fascinating features within the subsequent reactions of the metalloid cluster species **4**. However, the question whether such larger aggregates can be synthesized has to be clarified by future experiments; but the nearly black colour of the reaction solution of the reaction of $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ (**4**) with $AuClPPh_3$ hints that larger aggregates might be present in solution.

The linear $-(AuGe_9R_3)_n-$ arrangement exhibits another interesting feature: the $Au_{n-1}(Ge_9)_n$ core is totally shielded by $3n$ $Si(SiMe_3)_3$ ligands. Hence, such an arrangement can be seen as a molecular cable, where the metal core is isolated by a plastic mantle as sketched in Figure 14.[45] Comparing the physical properties of such a nanocable with those of a normal cable is thereby quite challenging, as quantum effects will play an important role.

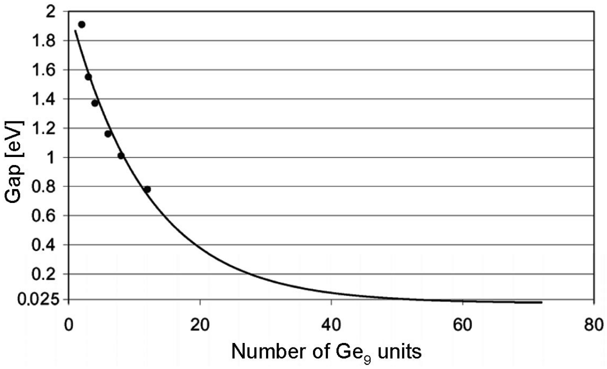


Figure 13. Calculated HOMO–LUMO gap of model compounds $(Au_n)[Ge_9H_3]_{n+1}^-$. Calculated points are fitted by an exponential function (solid line).

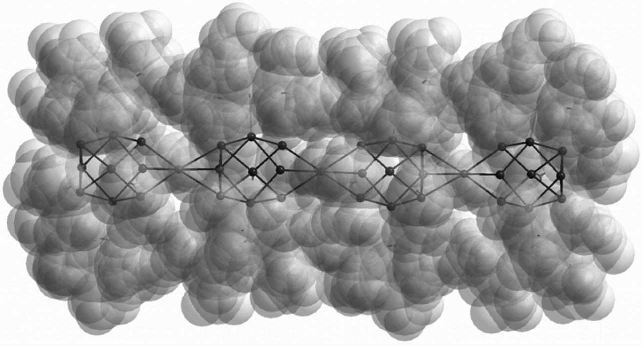


Figure 14. Calculated molecular structure of the model compound $Ge_{36}Au_3[Si(SiMe_3)_3]_{12}^-$ (**12b**). The $Si(SiMe_3)_3$ groups are presented as a space-filling model.

4 Conclusions and Outlook

During the last years, the novel group of metalloid cluster compounds of germanium could be established as a new group of cluster compounds in germanium chemistry, and a couple of members of this group have been synthesized, isolated and structurally characterized. As the average oxidation state of the germanium atoms inside a metalloid cluster compound is between 0 and 1, these compounds are localized between the molecular and the solid state. Thus, they are ideal model compounds for the observation of the change of physical and chemical properties in this borderland on the way to elemental germanium. First results show that the bonding electrons inside a metalloid cluster compound get more and more delocalized as the average oxidation state approaches the value 0 for the bulk phase. Thus the synthetic routes leading to metalloid cluster compounds might open the way to a metallic form of elemental germanium. However, already at a size of ten germanium atoms inside the cluster core, the structure can approach that of elemental germanium. Therefore, in this borderland between the molecular and the solid state, a highly dynamic behaviour is present, and more experimental results, especially the isolation of larger cluster compounds, are necessary to shed more light onto this fascinating area. Besides the synthesis of more and maybe larger metalloid cluster compounds, it is necessary to perform measurements on the physical properties of these cluster compounds to find a relationship between the structure, the bonding and the physical properties of such cluster compounds. Such measurements are not trivial, because of the sometimes high reactivity of the compounds, but they might lead to an understanding of the physical properties of the photoluminescence of germanium nanoparticles on a molecular scale, which is the most exciting and definitely the most difficult question to be answered in the future.

The possibility of subsequent reactions with the metalloid cluster compounds additionally opens the field of new and unusual materials, e.g. molecular wires. As the metalloid cluster compounds can be seen as stable building blocks, the formation of the $AuGe_{18}$ compound **9** can be seen as the first step into a supramolecular chemistry with metalloid cluster compounds as building blocks. This chemistry is just at the beginning stage and exhibits great potential for further applications, as metalloid cluster compounds are building blocks with interesting electronic situations that might be distributed over the whole framework. Thus, an exciting and fruitful future in this area can be expected.

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