

# Metalloid group 14 cluster compounds: An introduction and perspectives to this novel group of cluster compounds†

Andreas Schnepf\*

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Metalloid cluster compounds of group 14 of the general formulae  $E_nR_m$  with  $n > m$  (E = Si, Ge, Sn and Pb, tetrel elements; R = ligand), where “naked” tetrel atoms are present as well as ligand-bound tetrel atoms, represent a novel class of cluster compounds in group 14 chemistry. Since the “naked” tetrel atoms in these clusters exhibit an oxidation state of 0, the average oxidation state of the tetrel atoms in such metalloid group 14 cluster compounds is between 0 and 1. Thus, these cluster compounds may be seen as intermediates on the way to the elemental state. Therefore, interesting properties may be expected for these compounds which might complement results from nanotechnology.

During the last years many different syntheses of such novel cluster compounds have been introduced, leading to several metalloid group 14 cluster compounds which exhibit new and unusual structure and bonding properties. In this *tutorial review* an account is given of the first steps in this novel field of group 14 chemistry. Special attention is focused on structural features and bonding properties.

## 1. Introduction

The appearance of polyhedral group 14 cluster compounds traces back to the observation of Joannis, who found in 1890 that Pb dissolves in the presence of alkali metal in liquid ammonia with the formation of intensely coloured solutions. This was the first observation of a homoatomic cluster

compound, namely an anionic  $Pb_9$  species, as it turned out many years later.<sup>1</sup> These homoatomic cluster compounds are nowadays known as Zintl ions after the German chemist Eduard Zintl, whose work improved the understanding of such polyanions.<sup>2</sup> The Zintl ions are generally formed by reduction of the corresponding element with alkali metals, leading to a negative average oxidation state of the group 14 element.

Nearly 100 years after the first observation of a Zintl ion, the first ligand-stabilized polyhedral cluster compound of the general formulae  $(ER)_n$  (E = Si, Ge, Sn; R = ligand) was synthesized by Matsumoto *et al.* in 1988<sup>3</sup> via the reductive coupling reaction of  $(tBuMe_2Si)SiBr_3$  with sodium, leading to the cubic cluster compound  $Si_8(SitBuMe_2)_8$ . After this synthetic breakthrough this new field developed rapidly, leading to clusters with up to ten tetrel atoms in the cluster core, and it has been the subject of several reviews.<sup>4</sup>

In the last few years a third class of group 14 cluster compounds, the metalloid cluster compounds of the general formulae  $E_nR_m$  with  $n > m$  (E = Si, Ge, Sn, Pb; R = ligand), could be established, in which “naked” metal atoms are present as well as ligand-bound metal atoms and the number of metal–metal bonds exceeds those to the ligands.<sup>5</sup> Here, “naked” does not mean isolated or interaction-free. It is merely a linguistic simplification to distinguish the different kinds of metal atoms in the cluster.

Since the naked metal atoms can be assigned an oxidation state of 0, the average oxidation state of the metal atoms in the cluster core of a metalloid cluster compound is between 0 and 1. Thus, the metalloid cluster compounds can be seen as “being intermediates on the way to the corresponding element”. The most interesting question in this respect is how the physical and chemical properties change while the average oxidation state reaches the value zero, as in the element itself.

Institut für Anorganische Chemie der Universität Karlsruhe (TH), Engesserstr., Geb.30.45, D-76128 Karlsruhe.  
E-mail: schnepf@chemie.uni-karlsruhe.de; Fax: +49 (721) 608 4854; Tel: +49 (721) 608 2951

† The HTML version of this article has been enhanced with colour images.



Andreas Schnepf

Andreas Schnepf received his PhD from the University of Karlsruhe in 2000. From 2000 to 2002 he was postdoctoral fellow at the Institute of Inorganic Chemistry at the University of Karlsruhe where he worked on physical properties of metalloid group 13 cluster compounds. During this period he made some research stays at the German Electron Synchrotron (DESY) at Hamburg and the Paul Scherrer Institute (PSI) at Villingen. He has been work-

ing at the same Institute on his Habilitation since 2002. His current research interests focus on the solution chemistry of metastable high temperature group 14 metal halides and their synthetic employment in the synthesis of metalloid group 14 cluster compounds.

This area is also of great technical interest, as nanoparticles of germanium exhibit interesting physical properties (*e.g.* germanium nanoparticles show good photoluminescence properties).<sup>6</sup> However there is little structural information available for these nanoparticles. For nanoparticles with diameters down to 2–4 nm no structural information is available. They exhibit a molecular character in contrast to that of nanocrystalline germanium with a diamond lattice.<sup>7</sup> Therefore, these nanoparticles with diameters in the range of 2 nm can no longer be regarded as small pieces of germanium; they are better described as molecular metalloid cluster compounds with an unknown structure.<sup>8</sup> Structural information about these nanoparticles could come from chemically synthesized metalloid cluster compounds, whose structures are well known from crystal structure analysis and have the same average oxidation state of the tetrel atoms in the cluster core as the tetrel atoms in a tetrel nanoparticle.

In this review an account is given of the first developments in this new field of group 14 cluster chemistry starting from the smallest metalloid cluster compounds  $E_5R_4$  and ending with the largest structurally characterized metalloid group 14 cluster compound to date,  $Sn_{15}R_6$ .

## 2. Synthesis

For the synthesis of a metalloid group 14 cluster it is necessary to insert naked tetrel atoms into a ligand stabilized tetrel cluster of the general formulae  $(ER)_n$  ( $E$  = tetrel atom;  $R$  = ligand). Various synthetic strategies are known for incorporating naked tetrel atoms into a metalloid group 14 cluster compound.<sup>5b</sup> All strategies use bulky ligands for kinetic stabilization of the metalloid cluster compound:

(a) The reductive elimination of a leaving group  $XY$  can provide naked atoms if the  $X$ - and  $Y$ -bound atoms are further connected only to other atoms of the same kind in the precursor.

(b) The reductive coupling reaction of a  $REX$  or  $REX_3$  precursor with an adequate reducing agent can lead to a metalloid group 14 cluster compound. The naked atoms are inserted by ligand stripping, *i.e.* the elimination of a ligand, or by adding an  $E(II)$  halide (*e.g.*  $SnCl_2$ ), which is completely reduced and inserted into the cluster as naked tetrel atoms.

(c) The disproportionation reaction of a metastable subhalide finally leads to the element and a halide in a higher oxidation state:  $4EX \rightarrow 3E + EX_4$ . During this disproportionation reaction, element rich cluster compounds are formed on the way to the element. These intermediates can be trapped by kinetic stabilization through the substitution of the halide atoms by bulky ligands.

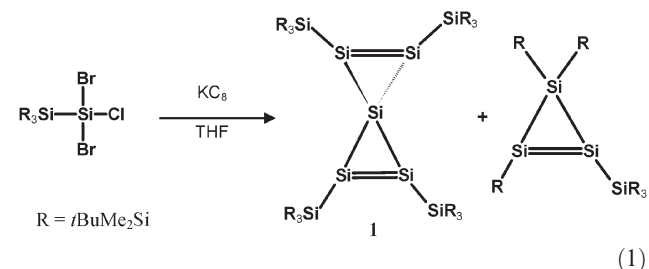
Consequently, different synthetic strategies exist for the synthesis of metalloid cluster compounds of group 14. It should be stressed here that all these synthetic strategies exhibit the same synthetic problem: the reaction pathway leading to metalloid cluster compounds is unknown to date. Therefore no straightforward synthetic strategy exists where the synthesis of a certain cluster compound can be planned on paper. Only the synthetic framework in which the reaction takes place can be controlled.

However, despite these synthetic problems 18 metalloid group 14 cluster compounds have been synthesized in recent years. They will be presented in the following sections.

## 3. Metalloid clusters of formulae $E_5R_4$

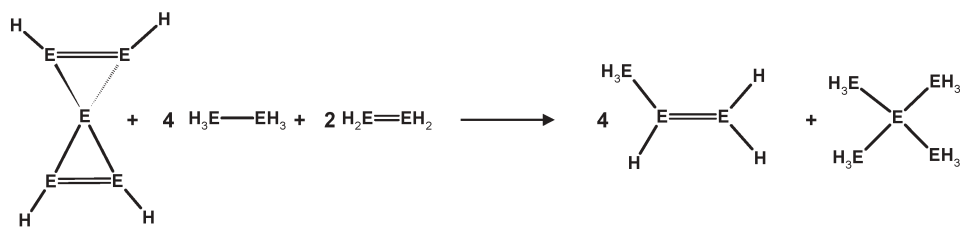
One of the most exciting questions regarding the metalloid cluster compounds that is also of fundamental interest with respect to bonding theory is how the bonding situation changes when a naked metal atom is added to a ligand stabilized cluster compound of formulae  $(ER)_n$ . The smallest model system in this context is the one starting from tetrahedral  $(ER)_4$ , being the smallest possible polyhedral cluster compound, and adding a naked  $E$  atom leading to a cluster compound with the formula  $E_5R_4$ , for which two examples ( $Si_5R_4$  **1**<sup>9</sup> and  $Ge_5R_4$  **2**<sup>10</sup>) are known.

The metalloid cluster compound  $Si_5(SiR_3)_4$  (**1**) ( $R = tBuMe_2Si$ ) was synthesized by a reductive coupling reaction of  $R_3Si-SiBr_2Cl$  with  $KC_8$  in THF and was isolated in 3.5% yield together with cyclotrisilene  $Si_3R_3SiR_3$ , which is the main product of the reaction (eqn (1))



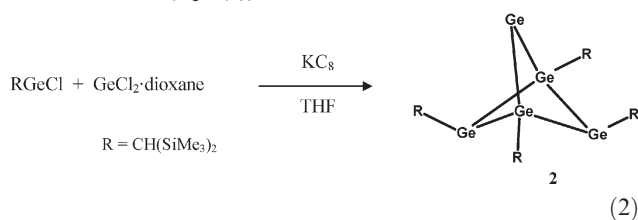
The molecular structure of **1** consists of two  $Si_3$  triangles which are nearly perpendicular to each other (dihedral angle  $78^\circ$ ). The naked silicon atom links the two three-membered rings leading to the observed spiro-pentadiene structure of **1**. The deviation from an ideal perpendicular arrangement is the outcome of steric hindrance as quantum chemical calculations show that the  $D_{2d}$  arrangement is the energetic minimum for the model compound  $Si_5(SiH_3)_4$ , where no steric hindrance is present. The observed deviation leads to an elongation of the  $Si-Si$  double bond and a shortening of the  $Si-Si$  single bonds compared to the corresponding cyclotrisilene. This modification is due to electronic reasons as quantum chemical calculations of the model compound  $Si_5H_4$  **1a** show that there is an effective interaction between the  $\pi$  orbitals of the  $Si-Si$  double bond and the low lying Walsh-type  $\sigma^*$  orbitals of the  $Si-Si$  bonds in the opposite three-membered ring ( $\sigma^*$  aromaticity) by changing the symmetry from  $D_{2d}$  to  $D_2$ .<sup>9</sup>

**1** is thermally very stable and melts between 216 and 218 °C without decomposition. In contrast, the corresponding carbon compound decomposes even below  $-100$  °C and was only identified by NMR spectroscopy. This stability is attributed to a kinetic stabilization of **1** as a result of steric protection by four bulky  $(tBuMe_2Si)_3Si$  groups. Additionally, the small strain energy of the ring systems is important. For **1a** the strain energy for the homodesmotic reaction shown in Scheme 1 was calculated to be  $61.1 \text{ kcal mol}^{-1}$ . For the corresponding carbon compound the calculated strain energy is much larger at  $114.2 \text{ kcal mol}^{-1}$ .



**Scheme 1** Homodesmotic reaction for the calculation of strain energy of an  $E_5H_4$  species ( $E = C, Si$ ).

As the strain energy in polyhedral cluster compounds of group 14 elements decreases in the order carbon  $\rightarrow$  silicon  $\rightarrow$  germanium,<sup>4</sup> a  $Ge_5R_4$  species with the same structure as in **1** might be expected. However the reductive coupling reaction of the germylene  $Ge(Cl)CH(SiMe_3)_2$  in the presence of  $GeCl_2$ -dioxane with magnesium leads to a metalloid cluster compound of the formula  $Ge_5R_4$  **2** ( $R = CH[SiMe_3]_2$ ), which has a totally different arrangement of the germanium atoms in the cluster core (eqn (2)).<sup>10</sup>



The arrangement of the germanium atoms in the cluster core of **2** is best described as a butterfly arrangement of a  $(GeR)_4$  moiety, with a fold angle of  $134^\circ$  which is capped by a naked germanium atom such that two short Ge–Ge distances of 246 pm and two long Ge–Ge distances of 303 pm are formed. Therefore three different kinds of germanium atoms are present in **2**, pointing to a very complex bonding situation, which can be described as follows: the naked germanium atom forms two 2c2e bonds bearing a lone pair of electrons. The two four-coordinated germanium atoms form a classical bonding situation and the three-coordinated germanium atoms form three 2c2e bonds and have additional electron density at one vertex. This description, which is also supported by the results of quantum chemical calculations on the model compound  $Ge_5Me_4$ , leads to the formulation of three resonance forms A, B and C (Scheme 2), in which the zwitterionic forms A and C represent a classical bonding situation having only paired electrons, while form B represents a biradicaloidal form showing that **2** might be a member of this new and growing class of main group compounds.<sup>11</sup>

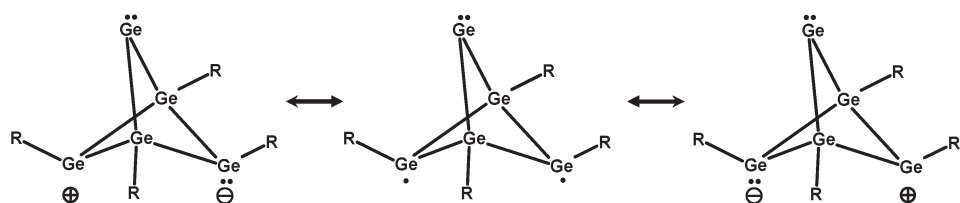
These results for the  $E_5R_4$  species show that there are considerable differences between metalloid silicon and germanium clusters. However, the origin of these differences is

questionable. As both compounds are synthesized *via* a reductive coupling reaction, a similar reaction pathway might be expected. If this is the case, the differences have to be the result of differences in the behaviour of the elements themselves. Here more theoretical work has to be done to get a deeper insight into these differences between metalloid cluster compounds of the same  $E_nR_m$  formulae comprising different E atoms. These differences will become more obvious in the case of the  $E_8R_6$  cluster compounds (section 5), which also show considerable differences between the silicon and germanium compound.

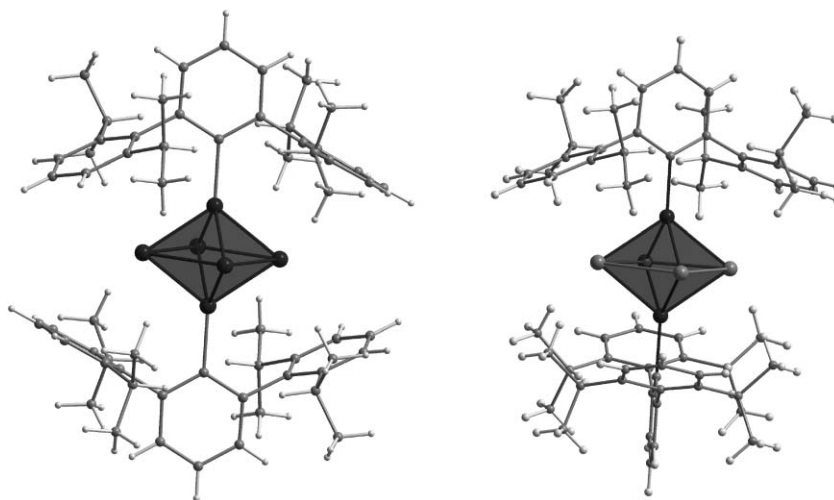
#### 4. $E_6R_2$ species

The metalloid cluster compounds  $Ge_6Ar_2$  (**3**) and the mixed metalloid group 14 cluster compound  $Ge_2Sn_4Ar_2$  (**4**) ( $Ar = C_6H_3-2,6-Dipp_2$ ;  $Dipp = C_6H_3-2,6-iPr_2$ ) are both synthesized *via* the same reaction strategy; *i.e.* the reductive coupling reaction of  $ArGeCl$  in the presence of  $GeCl_2$  or  $SnCl_2$  by  $KC_8$ .<sup>12</sup> The added E(II) halide is completely reduced and the E atoms are then inserted into the cluster compound as naked atoms.  $Ge_6Ar_2$  (**3**) is isolated in the form of orange crystals while  $Ge_2Sn_4Ar_2$  (**4**) forms red crystals. The arrangement of the six tetrel atoms in both cluster compounds is best described as a distorted octahedron as two different sets of bond lengths are found in the cluster cores (Fig. 1). In **3** the Ge–Ge distances between ligand-bound and naked germanium atoms are, with an average distance of 251 pm, shorter than those between naked germanium atoms where an average Ge–Ge distance of 288 pm is found. Thus the germanium atoms with the higher coordination numbers form the shorter Ge–Ge bonds.

This at first glance unusual behaviour can be explained by assuming that the naked germanium atoms bear a lone pair of electrons, thus providing only two electrons for cluster bonding. In the case of the ligand-bound germanium atoms this lone pair of electrons is split and one electron is used for a 2c2e bond to a ligand and the other is used for cluster bonding. Consequently, the ligand-bound germanium atom provides



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



**Fig. 1** Molecular structure of  $\text{Ge}_6\text{Ar}_6$  **3** (left) and  $\text{Ge}_2\text{Sn}_4\text{Ar}_6$  **4** (right) (Ar =  $\text{C}_6\text{H}_3\text{-2,6-Dipp}_2$ ; Dipp =  $\text{C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2$ ). The central octahedral arrangement of the six tetrel atoms is shown by the polyhedra.

three electrons for cluster bonding, leading to shorter Ge–Ge bonds.

This counting leads to a total of 14 bonding electrons, which is the required number for a *closo* type cluster compound ( $2n + 2 = 14$  for  $n = 6$ ) due to Wade's rules.<sup>13</sup> As the octahedron is a *closo* cluster **3** and **4** are in accordance with Wade's rules as is normally the case for Zintl ions. Another similarity to Zintl ions is the fact that the average Ge–Ge distances in **3** of 263 pm are nearly the same as those found in the calculated model Zintl ion  $\text{Ge}_6^{2-}$  for which average Ge–Ge distances of 269 pm are calculated.<sup>14</sup> Such similarities between the Zintl ions and the metalloid cluster compounds will also become obvious in the case of the cluster compounds  $\text{E}_9\text{R}_3$  in section 6. The similarity of **3** to the Zintl ions leads to the suggestion that the bonding electrons in the cluster core might be as highly delocalized as in Zintl ions. This hypothesis could be proven by quantum chemical calculations on the model compound  $\text{Ge}_6\text{H}_2$ , for which three centre bonding components in the triangles of the octahedron with a shared electron number (SEN)<sup>15</sup> of 0.23 are calculated using an Ahlrichs–Heinzmann population analysis.<sup>5</sup> Another interpretation of the bonding situation in the cluster cores of **3** and **4** is that omitting the bonds between the naked germanium or tin atoms leads to a classical bonding situation on the naked atoms, where each atom bears a lone pair and additionally forms two 2c2e bonds. This suggestion is supported by the results of  $^{119}\text{Sn}$  NMR measurements on **4**, where a signal at  $\delta = 1584$  ppm is found, a region most commonly associated with two-coordinated  $\text{Sn}(\text{II})$  species.<sup>12</sup>

In both scenarios lone pairs of electrons can be found on the naked tetrel atoms leading to the suggestion that the formation of a lone pair of electrons on a naked tetrel atom seems to be a common feature in metalloid cluster compounds. However, this is not the case for every metalloid cluster compound as shown in the following sections. Another interesting feature in the case of the metalloid cluster compounds of silicon **3** and **4** is the orientation of the ligands. In the case of the pure germanium compound **3** the ligands have an eclipsed orientation, while they are in a staggered conformation in the case of

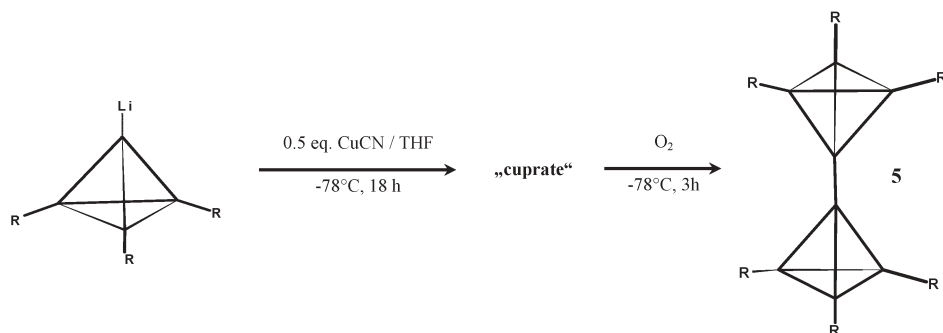
the mixed compound **4**. This different orientation might be due to packing effects inside the crystal. Another plausible explanation for the staggered conformation is the existence of  $n-\pi^*$  interactions between the lone pair of the tin atom and the  $\pi^*$  orbitals of the aromatic ring as Sn–C distances (360–380 pm) exist that are in the range of the sum of their van der Waals radii of 385 pm.

## 5. $\text{E}_8\text{R}_6$ clusters: from carbon to tin and a $\text{Sn}_8\text{R}_4$ cluster

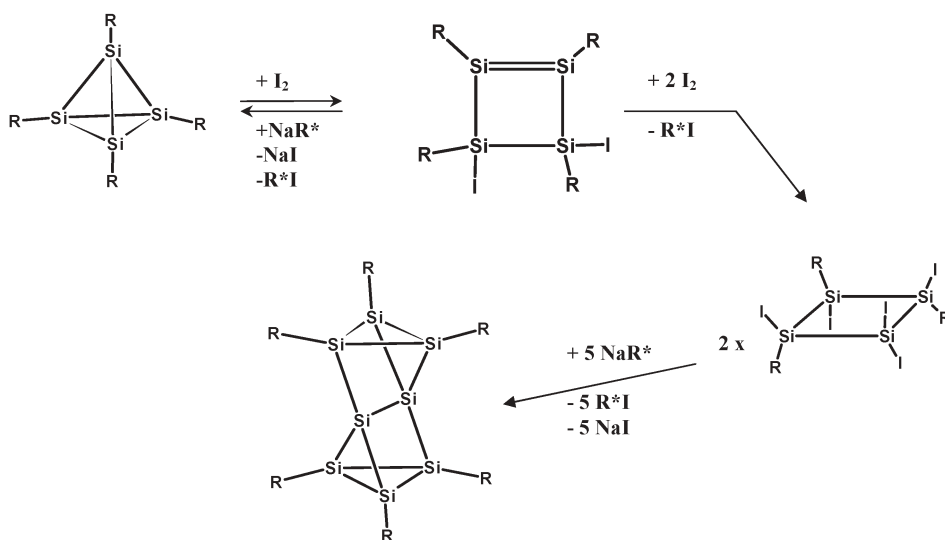
Group 14 cluster compounds of the general formulae  $\text{E}_8\text{R}_6$  are known for nearly all tetrel atoms, only the lead compound is missing. Therefore one can take a look at the different bonding behaviour when descending group 14 from C to Sn. Here the carbon compound is included as it completes the row, surprisingly being the only one to resemble the perhaps most expected structure for a tetrel  $\text{E}_8\text{R}_6$  cluster compound as shown in Scheme 3. However, as carbon is a non-metal, the cluster compound cannot be named metalloid as no metal atoms are involved.

The carbon compound  $\text{C}_8(\text{SiMe}_3)_6$  (**5**)<sup>16</sup> is synthesized starting from the fully substituted tetrahedrane  $\text{C}_4(\text{SiMe}_3)_4$ , which is reduced with MeLi leading to the anionic compound  $\text{LiC}_4(\text{SiMe}_3)_3$ . This lithium salt is then transformed into the corresponding cuprate complex by reaction with CuCN at  $-78^\circ\text{C}$ . Finally the oxidation of the cuprate complex with oxygen leads to the cluster compound  $\text{C}_8(\text{SiMe}_3)_6$  (**5**) in 3% yield (Scheme 3). Structurally, **5** can be described as two tetrahedral  $\text{C}_4(\text{SiMe}_3)_3$  fragments that are bound to each other by a direct C–C bond of the ligand free carbon atoms. The most striking feature of **5** is that the linking C–C  $\sigma$ -bond (144 pm) is very short for a carbon atom with a coordination number of four, which is thought to be the result of the high s-character of the bonding orbitals. This interpretation is supported by the results of quantum chemical calculations which show that the linking C–C bond is formed by  $sp^{1.53}$  orbitals.

As this synthesis works quite well in the case of carbon, representing a straightforward synthesis of a group 14 cluster



**Scheme 3** Synthetic route for the synthesis of  $C_8R_6$  **5** ( $R = SiMe_3$ ).

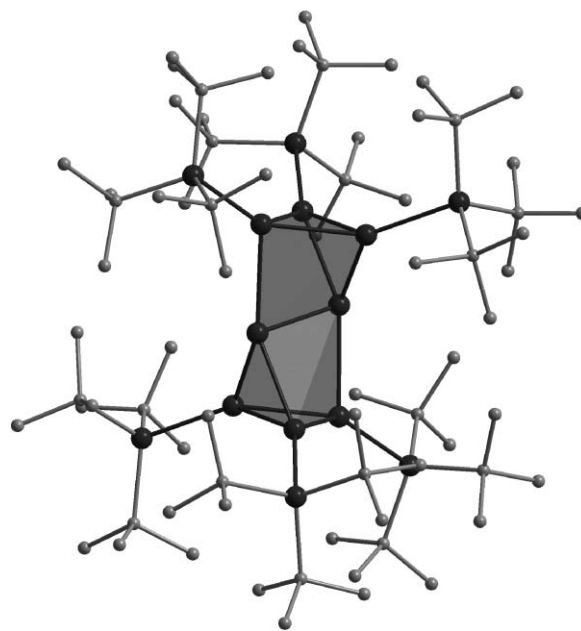


**Scheme 4** Reaction pathway from tetrahedrane  $Si_4R_4$  to the metalloid cluster compound  $Si_8R_6$  **6** ( $R = Si-tBu_3$ ).

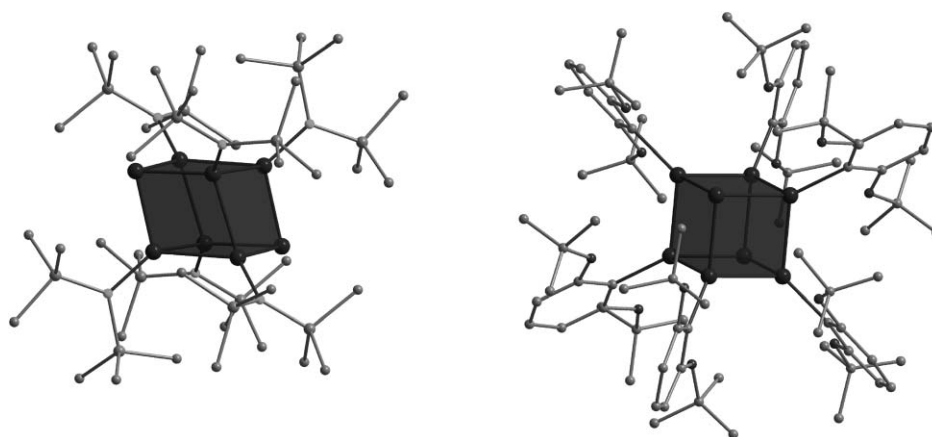
compound with naked atoms, it was expected that this synthesis might also work, and perhaps work even better, in the case of silicon or germanium, as in these cases the tetrahedral core is less strained<sup>4</sup> and therefore energetically more favoured. Additionally, the *s*-*p* separation in silicon and germanium is much larger than in carbon and therefore the formation of the linking bond with a high *s*-character should also be favoured. However, despite all these vantages no synthesis of an  $E_8R_6$  cluster of silicon or germanium with the same structure as **5** is known,<sup>17</sup> although a similar starting material  $Si_4R_3^-$  ( $R = Si(Dis_2Me)$ ;  $Dis = CH(SiMe_3)_2$ ) has been synthesized.<sup>18</sup>

Only very recently has another synthetic route, starting from the fully substituted silicon cluster compound  $Si_4(Si-tBu_3)_4$  (Scheme 4), led to a silicon cluster compound of the formula  $Si_8R_6$  ( $R = Si-tBu_3$ ) (**6**), which has a totally different molecular structure.<sup>19</sup>

The molecular structure of **6** depicted in Fig. 2 exhibits two  $Si_3R_3$  three-membered rings in *anti* configuration. The Si–Si bond lengths in the three-membered rings are 240 pm, being in the normal region for single bonds in polyhedral cluster compounds. Between the two three-membered rings a  $Si_2$  dumbbell of two naked silicon atoms is localized, featuring a quite short Si–Si bond of 229 pm. The silicon atoms of the



**Fig. 2** Molecular structure of  $Si_8(Si-tBu_3)_6$  **6**, the hydrogen atoms are omitted for clarity and the central  $Si_8$  unit is emphasized by the polyhedra.



**Fig. 3** Molecular structure of  $\text{Ge}_8[\text{N}(\text{SiMe}_3)_2]_6$  **7** (left) and  $\text{Ge}_8[\text{C}_6\text{H}_3\text{-}2,6\text{-(OtBu)}_2]_6$  **8** (right); hydrogen atoms are omitted for clarity. The central cubic arrangement of both clusters is emphasized by the polyhedra.

central dumbbell additionally form three further Si–Si bonds: two Si–Si bonds of 233 pm to two silicon atoms of one three-membered ring and one long Si–Si bond of 275 pm to one silicon atom of the opposite three-membered ring.

Most unusual in this compound are the “inverse tetrahedrally” coordinated silicon atoms of the central dumbbell. This unusual arrangement leads to the question why the central  $\text{Si}_2$  unit is not oriented in a way that lays it perpendicularly to the three-membered  $\text{Si}_3\text{R}_3$  rings, thus leading to an ideal tetrahedral environment for each silicon atom as is the case in the carbon compound **5**. Steric reasons cannot be responsible for the observed structure as in the directly linked tetrahedral structure steric hindrance would be reduced. Thus electronic reasons have to be responsible for the observed structure, which will have to be elucidated by future theoretical calculations. At the moment it is only obvious that the  $\text{Si}_2$  unit seems to be very stable as the oxidation of **6** with  $\text{CCl}_4$  leads to the cyclotrisilane  $\text{Si}_3\text{R}_3\text{Cl}_3$  and possibly  $\text{Si}_2\text{Cl}_6$  and not to a cubic cluster compound  $\text{Si}_8\text{R}_6\text{Cl}_2$  or two tetrahedral compounds  $\text{Si}_4\text{R}_3\text{Cl}$ .<sup>19</sup>

$\text{E}_8\text{R}_6$  cluster compounds of germanium are synthesized *via* a different synthetic route, using the disproportionation reaction of the Ge(I) halide  $\text{GeBr}$ . To date two germanium cluster compounds of formulae  $\text{Ge}_8\text{R}_6$  ( $\text{Ge}_8[\text{N}(\text{SiMe}_3)_2]_6$  **7**,<sup>20</sup>  $\text{Ge}_8[\text{C}_6\text{H}_3\text{-}2,6\text{-(OtBu)}_2]_6$  **8**<sup>21</sup>) are known, whose structures are shown in Fig. 3. Both structures can be described as a cubic arrangement of eight germanium atoms where two germanium atoms are naked and the remaining six bear a ligand. The naked germanium atoms are localized on opposite sides of the cube.

A closer look at the arrangement of the germanium atoms in the cluster cores shows significant differences between both

**Table 1** Comparison of distances and angles in the cluster compounds  $\text{Ge}_8[\text{N}(\text{SiMe}_3)_2]_6$  **7** and  $\text{Ge}_8[\text{C}_6\text{H}_3\text{-}2,6\text{-(OtBu)}_2]_6$  **8**

	$\text{Ge}_8[\text{N}(\text{SiMe}_3)_2]_6$ <b>7</b>	$\text{Ge}_8[\text{C}_6\text{H}_3\text{-}2,6\text{-(OtBu)}_2]_6$ <b>8</b>
$d(\text{GeR}-\text{Ge})/\text{pm}$	249.9–250.3	250.3–252.9
$d(\text{GeR}-\text{GeR})/\text{pm}$	266.1–267.2	249.1–249.5
$\text{GeR}-\text{GeR}-\text{GeR}/^\circ$	74.4–75.7	87.7–90.0
$\text{Ge}-\text{GeR}-\text{GeR}/^\circ$	101.2–101.6	90.5–92.5
$\text{GeR}-\text{Ge}-\text{GeR}/^\circ$	81.3–81.8	86.9–88.7

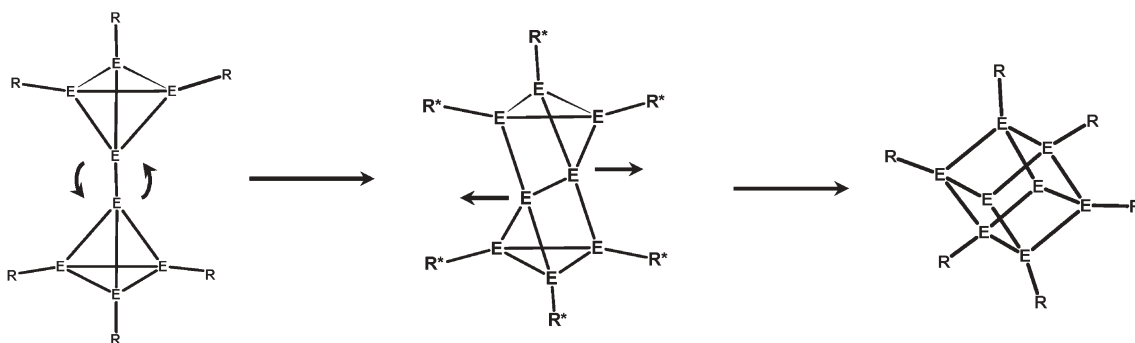
cluster compounds (Table 1). In the case of the aryl substituted compound **8**, the arrangement is nearly perfectly cubic, which means the bond lengths in the cluster core differ only by 2 pm and the Ge–Ge–Ge angles in the cluster amount to  $90 \pm 1^\circ$ . In contrast to this, the cubic arrangement in **7** is strongly distorted as two different Ge–Ge distances (250 and 267 pm) are found in the cluster core and the Ge–Ge–Ge angles vary from 74 to  $102^\circ$ .

The observed differences are therefore the result of different bonding situations in the cluster core, which are induced by the different kind of ligands attached to the cluster core. This was shown by quantum chemical calculations on the model compounds  $\text{Ge}_8\text{R}_6$  ( $\text{R} = \text{PH}_2, \text{NH}_2, \text{CH}_3, \text{C}_6\text{H}_5$ ). The results of the quantum chemical calculations (Table 2)<sup>21</sup> reveal that a ligand possessing a free pair of electrons on the hetero atom directly bound to the germanium atom leads to a higher degree of delocalization of bonding electrons in the cluster core. On the other hand, a ligand with no free electron pair at the hetero atom bound to germanium results in more localized bonding electrons in the cluster core.

The results for the  $\text{Ge}_8\text{R}_6$  clusters **7** and **8** show that the ligand thought to be necessary only for the protection of the cluster core against the exterior influences the bonding situation within the cluster leading to different arrangements, bonding situations and thus to different physical properties of the metalloid cluster compounds. The different physical properties can be seen as the crystal colour of **7** and **8** is different. While crystalline **8** is nearly black, crystals of **7** are orange red. These differences might also be of importance for nanotechnology where little is known about the influence of ligands (environment) on the physical properties of a group 14 nanoparticle.

**Table 2** Results of quantum chemical calculations for the model compounds  $\text{Ge}_8\text{R}_6$

Ligand (R)	$\text{PH}_2$	$\text{NH}_2$	$\text{CH}_3$	$\text{C}_6\text{H}_5$
$d(\text{Ge}-\text{GeR})/\text{pm}$	257.8	254.8	259.7	259.0
$d(\text{GeR}-\text{GeR})/\text{pm}$	265.5	266.3	251.0	251.8
SEN (Ge–GeR)	1.03	1.10	0.93	0.97
SEN (GeR–GeR)	0.16	0.13	0.06	0.06



**Scheme 5** Graphical representation of the structural transition from an  $E_8R_6$  cluster like  $C_8(SiMe_3)_6$  (**5**) to a cluster like  $Ge_8[C_6H_3-2,6-(OtBu)_2]_6$  (**8**, E = tetrel atom).

The results for the germanium cluster compounds **7** and **8** also seem to be valid for the corresponding Sn compounds, as the cluster compound  $Sn_8(Si^tBu_3)_6$  (**9**),<sup>22</sup> for which only a preliminary structure is known, shows a nearly undistorted cubic arrangement of the eight Sn atoms inside the cluster core. As the ligand ( $Si^tBu_3$ ) does not bear a free pair of electrons on the directly bound hetero atom (Si), an undistorted cubic arrangement similar to that of  $Ge_8Ar_6$  (**7**) is to be expected. The main difference between germanium and tin is that for germanium the neutral compound is energetically favoured while for tin the diaionic compound is favoured, as shown by quantum chemical calculations.<sup>20</sup>

Comparing the structures of all group 14  $E_8R_6$  cluster compounds leads to a scenario starting from two directly bound tetrahedral  $E_4R_3$  groups and ending with a cubic arrangement with two ligands missing at opposite sites (Scheme 5)

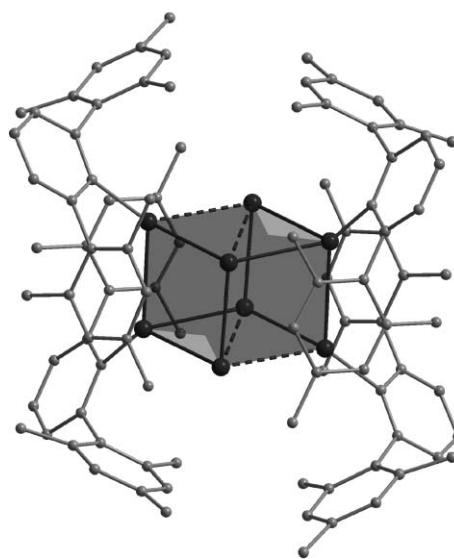
From carbon to silicon the central linking  $E_2$  unit is rotated in such a way that after the rotation it lies nearly parallel to the two three-membered  $E_3R_3$  rings. Descending group 14 further, from silicon to germanium, the direct bond between the two naked E atoms breaks, leading to a structure with a cubic arrangement with two naked germanium atoms located opposite to each other. On descending further from germanium to tin only slight changes in geometry are observed. Therefore, as to be expected, strong differences exist between carbon and silicon. However, the results also show that there are significant differences between silicon and germanium as was the case for the  $E_5R_4$  species **1** and **2** and only slight differences between germanium and tin are present.

These findings are different to those found for the class of alkyne congeners of the heavier group 14 elements, for which theoretical calculations show that the bonding in the silicon and the germanium compounds are very similar and the main differences are found between germanium and tin—the lead compound is then comparable to the corresponding tin species.<sup>23</sup> Such calculations are missing for the  $E_8R_6$  species, where the most interesting question to be answered is that of the energetic behaviour of an  $E_8R_6$  compound when the geometry changes from linked tetrahedra to a cubic arrangement as is depicted in Scheme 5.

What happens when two more ligands are eliminated from an  $E_8R_6$  cluster compound can be seen in the metalloidal cluster compound  $Sn_8Ar_4$  (**10**) ( $Ar = 2,6-Mes_2C_6H_3$ ;

$Mes = 2,4,6-Me_3C_6H_2$ ),<sup>24</sup> which was synthesized *via* a reductive coupling reaction of  $[(RSn(\mu-Cl))_2]$  with potassium. The structure of this compound, shown in Fig. 4, can be described as a strongly distorted cubic arrangement, since the Sn–Sn distances in the cluster core vary from 285 to 302 pm. The distortion of the cubic core leads additionally to Sn–Sn contacts along the diagonal of the four-membered rings (dashed lines in Fig. 4) of 311 pm.

Consequently, the elimination of two more ligands leads to a distortion of the cubic arrangement in such a way that additional Sn–Sn contacts are formed. The distortion also leads to very different Sn–Sn bonds in the cluster core. Thus two naked tin atoms form two long (311 and 302 pm) and two short (285 and 288 pm) Sn–Sn bonds. The other two naked tin atoms form three short Sn–Sn bonds (285, 287 and 289 pm) and one long Sn–Sn contact of 311 pm. Assuming that the two tin atoms that only form two short Sn–Sn bonds bear a lone pair shows that the bonding situation in **10** is very complex. Nevertheless the appearance of three different kinds of Sn atoms in **10** can only be realized when the bonding electrons



**Fig. 4** Molecular structure of  $Sn_8Ar_4$  **10** ( $Ar = 2,6-Mes_2C_6H_3$ ;  $Mes = 2,4,6-Me_3C_6H_2$ ); hydrogen atoms are omitted for clarity. The central strongly distorted  $Sn_8$  cube is emphasized by the polyhedron. All Sn–Sn bonds longer than 300 pm are presented by dashed lines.

are strongly delocalized within the cluster core. Such a delocalization will become more obvious in the  $E_9R_3$  cluster compounds described in the next section.

## 6. $E_9R_3$ clusters: radicals and anions and a metalloid cation with ten atoms

Metalloid cluster compounds with nine tetrel atoms in the cluster core are known for germanium and tin, having the same formulae  $E_9R_3$ . The germanium compound is an anion that is isolated in the form of orange crystals with  $Li(THF)_4^+$  as the counter ion. The tin compound is neutral, being a radical and isolated as dark red, almost black, crystals. Both cluster compounds are synthesized *via* different synthetic routes: the anionic germanium compound  $\{Ge_9[Si(SiMe_3)_3]_3\}^-$  (**11**) is isolated from the reaction of  $GeBr$  with  $LiSi(SiMe_3)_3$ .<sup>25</sup> The neutral tin compound  $Sn_9Ar_3$  ( $Ar = 2,6-Trip_2-C_6H_3$ ;  $Trip = 2,4,6-iPr_3-C_6H_2$ ) (**12**) is synthesized by thermolysis of the hydride precursor  $[ArSn(\mu-H)]_2$  in hot toluene.<sup>26</sup>

Despite these differences the arrangement of the nine tetrel atoms in the cluster cores is similar and is best described as a tricapped trigonal prismatic arrangement, where each capping tetrel atom bears a ligand (Fig. 5).<sup>27</sup> Inside the cluster core two different sets of bond distances are found, showing similar behaviours, as the distances between ligand-bound and naked tetrel atoms are shorter than those between naked atoms. This is similar to the behaviour found in the octahedral  $E_6Ar_2$  cluster compounds **3** and **4**, leading to the similar suggestion that the naked tetrel atoms provide only two electrons for cluster bonding, bearing a lone pair of electrons, and the ligand-bound tetrel atoms provide three electrons for cluster bonding, additionally forming a  $2c2e$  bond to a ligand. This way of electron counting results in a total number of 22 skeletal electrons for the germanium compound **11** and 21 for the tin compound **12**.

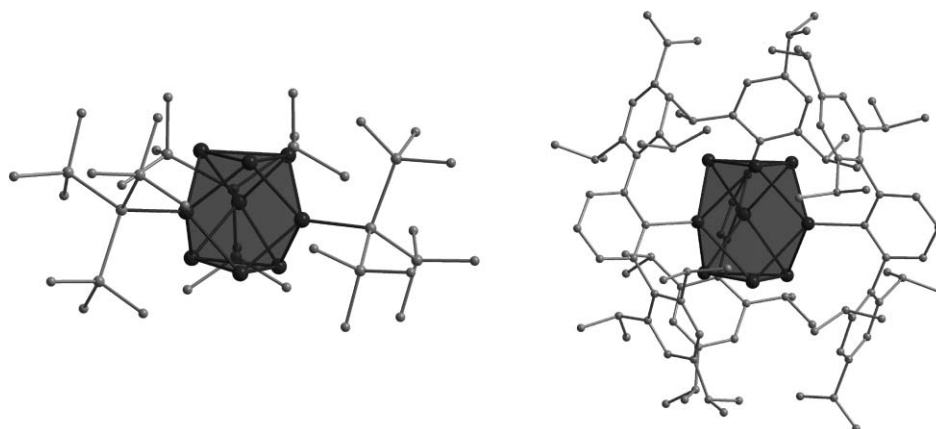
As 22 bonding electrons are required for a *nido* cluster according to Wade's rules<sup>13</sup> a monocapped square antiprismatic arrangement of the nine atoms is expected. For the two metalloid clusters **11** and **12** this structure is energetically unfavourable as the structure of a tricapped trigonal prism is formed, different from the Zintl ions where a rather distorted

monocapped square antiprismatic structure is observed for  $Ge_9^{4-}$  and  $Sn_9^{4-}$ .<sup>2</sup>

The most prominent structural feature of a tricapped trigonal prismatic structure is the height to edge ratio ( $h : a$ ) of the trigonal prism, which is 1 in the ideal structure. In the case of **11** and **12** large  $h : a$  ratios of 1.27 and 1.37 are found, respectively. This large  $h : a$  ratio is to be expected as a  $D_{3h}$  symmetric nine atom cluster with 20 skeletal electrons (*i.e.* for a *closo* compound) possesses a lowest unoccupied molecular orbital (LUMO) which is bonding along the edges and antibonding along the height.<sup>28</sup> In **11** and **12** this LUMO is now occupied with one or two electrons, leading to the observed distortion towards large  $h : a$  ratios.<sup>29</sup>

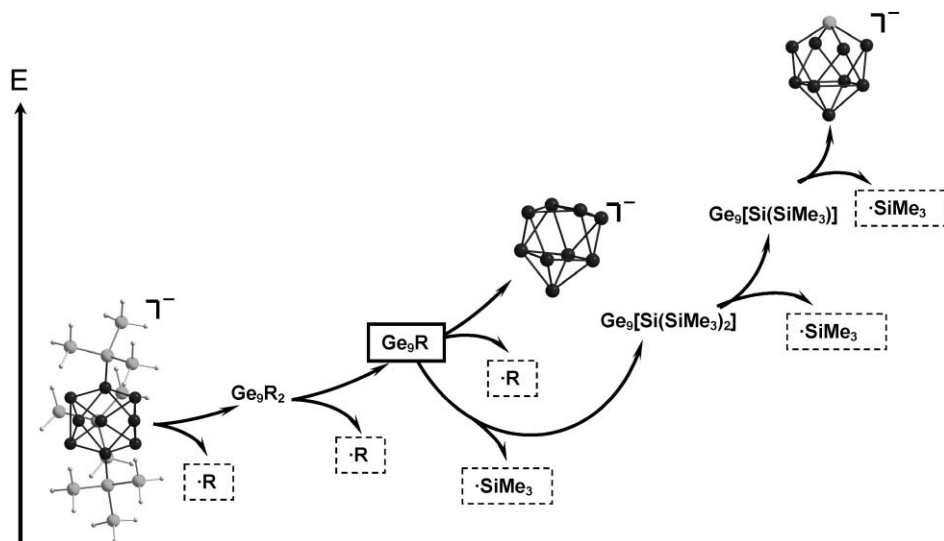
This result on the  $E_9R_3$  clusters **11** and **12** shows that the bonding to a ligand leads to considerable differences between the metalloid cluster compounds and Zintl ions. Another difference between these two groups of tetrel clusters is the different solution behaviour. As Zintl ions are normally insoluble in organic solvents, **11** and **12** are easily dissolved in THF or toluene, opening the way for subsequent solution-based chemistry. First results in this respect are the gas phase measurements on the anionic germanium compound **11** that is easily transferred intact into the gas phase *via* the electrospray ionisation (ESI) technique.<sup>30</sup> Collision experiments (sustained off resonance irradiation collision activated dissociation, SORI-CAD) in the gas phase lead to cluster dissociation as shown in Scheme 6.

First of all, two  $\cdot Si(SiMe_3)_3$  ligands leave the cluster, leading to the anionic compounds  $\{Ge_9[Si(SiMe_3)_3]_2\}^-$  and  $\{Ge_9[Si(SiMe_3)_3]\}^-$ , respectively. Afterwards, the situation changes as now two dissociation pathways open, leading to the cluster compounds  $Ge_9^-$  and  $Ge_9Si^-$ . As the cluster compound  $Ge_9^-$  is also available in the gas phase, starting from the Zintl ion  $Ge_9^{4-}$  *via* an oxidation process, the anion  $Ge_9^-$  links the group of the metalloid cluster compounds with the group of Zintl ions. Secondly, the gas phase experiments show that the weakest bonds of the metalloid cluster **11** are those to the ligands, thus first of all a Ge–Si bond breaks rather than a Ge–Ge bond within the cluster (step 1 and 2). Additionally, the formation of the mixed anionic cluster compound  $Ge_9Si^-$  gives the first hints as to how a metalloid



**Fig. 5** Molecular structure of  $\{Ge_9[Si(SiMe_3)_3]_3\}^-$  **11** (left) and  $Sn_9Ar_3$  ( $Ar = 2,6-Trip_2-C_6H_3$ ;  $Trip = 2,4,6-iPr_3-C_6H_2$ ) **12** (right). All hydrogen atoms are omitted for clarity and the central  $E_9$  units are emphasized by the polyhedra.





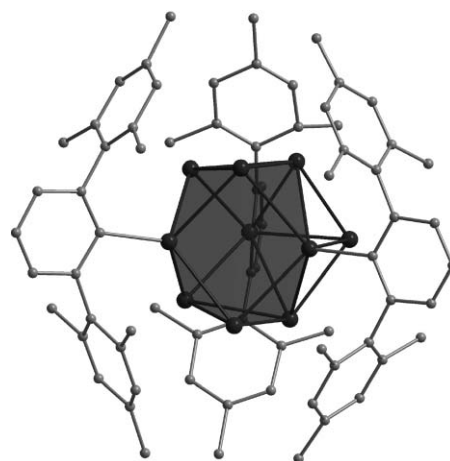
**Scheme 6** Schematic drawing of the experimentally found reaction pathways for the dissociation of  $\text{Ge}_9\text{R}_3^-$  **11** in the gas phase. The energies of the model compounds with  $\text{R} = \text{Si}(\text{SiH}_3)_3$  derived from quantum chemical calculations are emphasized schematically by the height in the Scheme.

cluster can be enlarged by one more atom. Such a scenario also seems possible in the metalloid cluster compound  $\{\text{Ge}_{10}\text{Si}[\text{Si}(\text{SiMe}_3)_3]_4(\text{SiMe}_3)_2\text{Me}\}^-$  **15** which will be discussed in section 8.

The gas phase experiments on the anionic cluster **11** are currently the only ones that have been performed on a metalloid group 14 cluster compound, leading to a first experimental insight into the bonding situation of a metalloid group 14 cluster compound. Unfortunately, corresponding experiments on the tin compound **12** have not been described, which might be due to the fact that **12** is a neutral compound and has to be charged before gas phase measurements can be performed. In the case of the tin compound it would be of great interest if the weakest bonds are again those to the ligands. This is uncertain as here a Sn–C bond has to break before a Sn–Sn bond and thus it is questionable if  $\text{Sn}_9\text{Ar}_3^-$  (**12'**) would involve the same dissociation pathway as  $\text{Ge}_9\text{R}_3^-$  (**11**).

However, in the case of the tin compound another interesting question could be answered; *i.e.* the possibility of cluster enlargement, as the cluster compound  $\text{Sn}_{10}\text{Ar}_3^+$  **13** ( $\text{R} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$ ;  $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) could also be synthesized by a reductive coupling reaction of  $\text{ArSnCl}$  with  $\text{KC}_8$  in the presence of  $\text{AlCl}_3$ .<sup>26</sup> The molecular structure of **13** can be described as a  $\text{Sn}_9\text{Ar}_3$  moiety as in **12**, where an additional tin atom is capping one of the heights of the central trigonal prism (Fig. 6). The addition of the tin atom leads to strong distortions of the  $\text{Sn}_9$  moiety such that the two three-membered rings of naked tin atoms are no longer parallel to each other. Thus the relatively uniform height in **12** of approximately 400 pm splits into distances of 382, 394 and 451 pm. The longest distance of 451 pm is the one capped by the additional tin atom.

This result can be interpreted as showing that further addition of tin atoms to a  $\text{Sn}_9\text{R}_3$  cluster leads to larger clusters where the capping edge is elongated. Further capping of the remaining two heights would therefore lead to a cluster with 12 tin atoms ( $\text{Sn}_{12}\text{R}_3$ ) comprising a nearly icosahedral shape.



**Fig. 6** Molecular structure of the cationic compound  $\text{Sn}_{10}\text{Ar}_3^+$  **13** ( $\text{R} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$ ;  $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ); hydrogen atoms are omitted. The central  $\text{Sn}_9$  unit is shown as a polyhedron, in which the capping Sn atom (on the right) is not included.

As an icosahedron is structurally incommensurable to elemental tin, the question arises of when a structural transition onto the elemental structure will occur.

## 7. Approaching the elemental structure?

As metalloid cluster compounds can be seen as intermediates on the way to the element due to the average oxidation state of the tetrel atoms in the cluster core, the arrangement of the tetrel atoms as well as the bonding situation in the cluster should develop in such a way that it will reach the situation realized in the element when the average oxidation state reaches the value zero. In the case of germanium an increase in the delocalization of the bonding electrons in the cluster core can be seen when decreasing the average oxidation state, when the cluster compounds with six, eight and nine atoms are taken into account (Table 3).

**Table 3** SEN and average oxidation states for the germanium compounds

	Ge <sub>8</sub> (NH <sub>2</sub> ) <sub>6</sub>	Ge <sub>6</sub> H <sub>2</sub>	Ge <sub>9</sub> H <sub>3</sub> <sup>-</sup>
SEN <sup>15</sup> (three-centre bonding component)	0.13	0.23	0.32
Average oxidation state	0.75	0.33	0.22

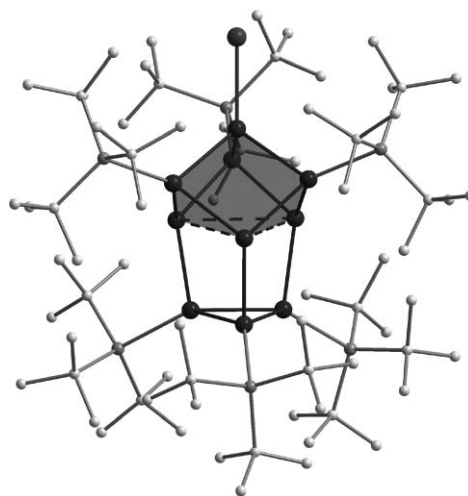
If this trend continues, it will end with elemental germanium with an average oxidation state of zero with highly delocalized bonding electrons, *i.e.* a metallic state, which is quite unusual for elemental germanium. Therefore it is more likely that at a certain cluster size this trend of delocalization will invert, finally leading to an elemental state with localized bonding electrons, as found in  $\alpha$ -germanium. This critical size seems to be in the range of ten germanium atoms as described in the following section.

## 8. Metalloid group 14 clusters with ten and more tetrel atoms in the core

To date three metalloid cluster compounds of germanium with ten germanium atoms in the cluster core are known, which are synthesized *via* very different synthetic routes.

The cationic cluster compound [Ge<sub>10</sub>(Si*t*Bu<sub>3</sub>)<sub>6</sub>I]<sup>+</sup> (**14**) is synthesized from germacyclopriene Ge<sub>3</sub>(Si*t*Bu<sub>3</sub>)<sub>3</sub>I, which is reacted for one week with a mixture of the potassium salts KI/KB(C<sub>6</sub>F<sub>4</sub>H)<sub>4</sub> in toluene at 50 °C (eqn (3)).<sup>31</sup> The reaction pathway that leads to the metalloid cluster compound **14** is unknown, but it is thought that the naked germanium atoms derive from a reductive elimination of *t*Bu<sub>3</sub>SiI, which is found as a by-product in the reaction mixture.

The arrangement of the ten germanium atoms in the cluster core was described by Sekiguchi *et al.* as a cubic arrangement of seven germanium atoms, where the eighth corner of the hypothetical cube is occupied by a Ge<sub>3</sub> triangle (Fig. 7).<sup>31</sup> The Ge–Ge distances for the Ge<sub>3</sub> triangle (253 pm) are 5 pm longer than the other Ge–Ge bonds in the cubic Ge<sub>7</sub> fragment, where Ge–Ge distances of 248 pm are found. This elongation can be traced back to the fact that the Ge<sub>3</sub> triangle of ligand bound germanium ions has to fit the triangle of naked germanium atoms, where interatomic distances of 326 pm are present (dashed lines in Fig. 7). These interatomic distances are much longer than a normal Ge–Ge single bond of 245 pm and it was questionable whether there was a bonding interaction between the naked germanium atoms. However, quantum chemical calculations on the model compound Ge<sub>10</sub>H<sub>7</sub><sup>+</sup> reveal that there is a bonding interaction, which is best described as a 3c2e (3 centre 2 electron) bond between the naked germanium atoms. Furthermore, the calculations reveal that

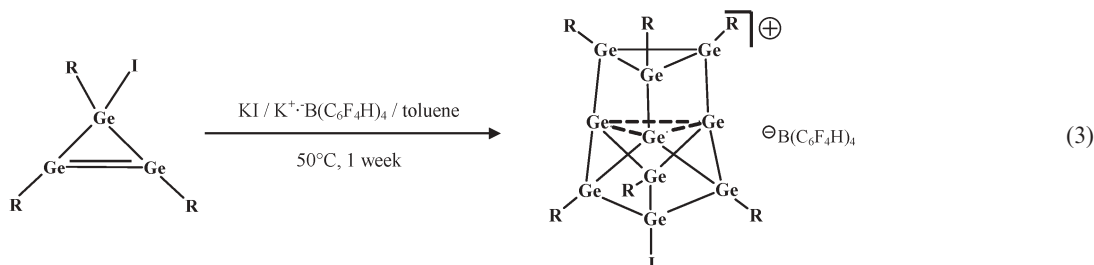


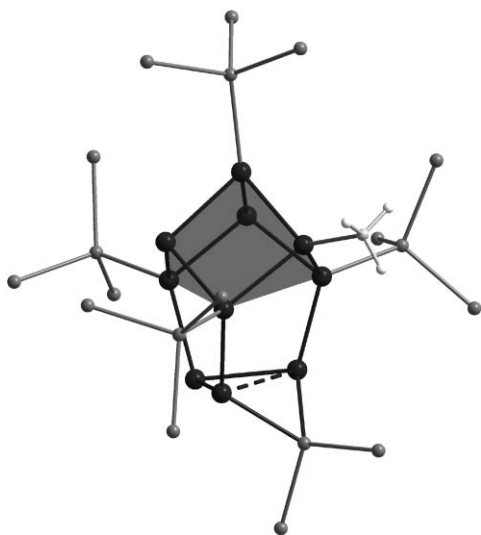
**Fig. 7** Molecular structure of [Ge<sub>10</sub>(Si*t*Bu<sub>3</sub>)<sub>6</sub>I]<sup>+</sup> **14** with the hydrogen atoms omitted. The upper cubic Ge<sub>7</sub> part of the cluster is emphasized by the polyhedra.

a homoaromatic system is present since an aromatic stabilization energy of  $-19.2$  kcal mol<sup>-1</sup> and a nucleus independent chemical shift (NICS) of  $-26.4$  ppm were calculated.

The anionic cluster compound {Ge<sub>10</sub>Si[Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>Me}<sup>-</sup> (**15**) is synthesized together with the metalloid Ge<sub>9</sub> species {Ge<sub>9</sub>[Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>3</sub>}<sup>-</sup> (**11**) by a reaction of GeCl with LiSi(SiMe<sub>3</sub>)<sub>3</sub>.<sup>32</sup> In this reaction, **15** is built from an as yet unknown precursor *via* rearrangement of a Si(SiMe<sub>3</sub>)<sub>3</sub> ligand. During this rearrangement, the ligand is decomposed in such a way that the central silicon atom is integrated into the cluster core. Additionally, a methyl group of the ligand is directly bound to a germanium atom. Such a reaction behaviour of cluster enlargement *via* dismantling of a ligand was also observed in the gas phase measurements of the anionic cluster {Ge<sub>9</sub>[Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>3</sub>}<sup>-</sup> (**11**, see section 6). As the same ligand is present, such a reaction behaviour is not unusual for the Si(SiMe<sub>3</sub>)<sub>3</sub>-ligand.

Structurally **15** can be described, like **14**, as a distorted cubic arrangement of seven germanium atoms, where the eighth corner of the cube is substituted by a Ge<sub>3</sub> triangle. The Ge–Ge distances in the cluster vary in a narrow range between 245 and 253 pm. Only the Ge–Ge distance that is capped by the Si(SiMe<sub>3</sub>)<sub>2</sub> group (274 pm) is significantly different (dashed line in Fig. 8). This is also the weakest Ge–Ge bond in the cluster core as the SEN for the two centre bonding component on the model compound Ge<sub>10</sub>SiH<sub>7</sub><sup>-</sup> amounts to 0.75. For the other Ge–Ge bonds two centre bonding components with SENs between 1.06 and 1.18 are calculated. As well as two





**Fig. 8** Molecular structure of  $\{\text{Ge}_{10}\text{Si}[\text{Si}(\text{SiMe}_3)_3]_4(\text{SiMe}_3)_2\text{Me}\}^-$  **15**. The Me groups of the  $\text{SiMe}_3$  groups are omitted for clarity. Only the methyl group directly bound to a germanium atom is shown. The upper cubic  $\text{Ge}_7$  part of the cluster is emphasized by the polyhedron.

centre bonding components, three centre bonding components with SENs from 0.23 to 0.25 are found in the cluster core, *e.g.* the SEN of the three centre bonding component in the three-membered ring consisting of two germanium atoms and the silicon atom of the bridging  $\text{Si}(\text{SiMe}_3)_2$  unit amounts to 0.23. The appearance of a three centre bonding component in the  $\text{Ge}_2\text{Si}$  triangle reveals that the silicon atom belongs to the cluster core. Thus, **15** represents the first mixed metalloid Ge–Si cluster.

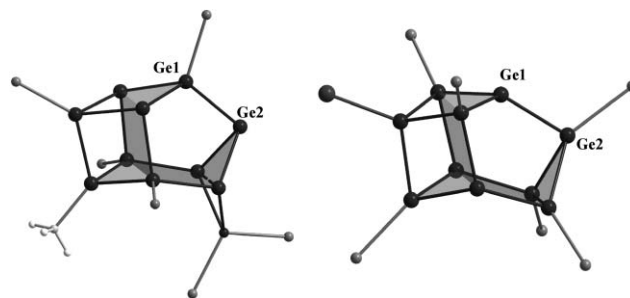
The structural similarity of **14** and **15** is quite unlikely as there are significant differences between both compounds:

(a) The average oxidation state of the germanium atoms in the cluster core differs. In the case of **14** the average oxidation state of the germanium atoms in the cluster core is 0.8. In the case of **15** it is 0.6 or 0.4, depending on whether the germanium atoms in the  $\text{Ge}_2\text{Si}$  triangle are considered as +1 or 0.

(b) The substitution pattern is different, that means the ligands are bound to different germanium atoms (see Fig. 9: *e.g.*, in **15** Ge1 is ligand-bound and Ge2 is naked, in **14** the situation is totally different as here Ge1 is naked and Ge2 bears a ligand).

(c) **14** is a cationic metalloid cluster compound while **15** is an anionic one.

However, the similar arrangement of the germanium atoms in **14** and **15** indicates that this arrangement is favourable for a metalloid germanium cluster compound with ten germanium atoms. The reason for this preference might be that this arrangement can be seen as a structural approach to the structure of  $\alpha$ -germanium as demonstrated in Fig. 9, where the characteristic arrangement of the diamond lattice, six-membered rings in a chair conformation, is emphasized *via* a polyhedral representation. This is the first example of a topological transition to the solid state structure of  $\alpha$ -germanium, and it is much more pronounced in the case of **15**, as the average oxidation state of the germanium atoms in this case is closer to the element value of 0.

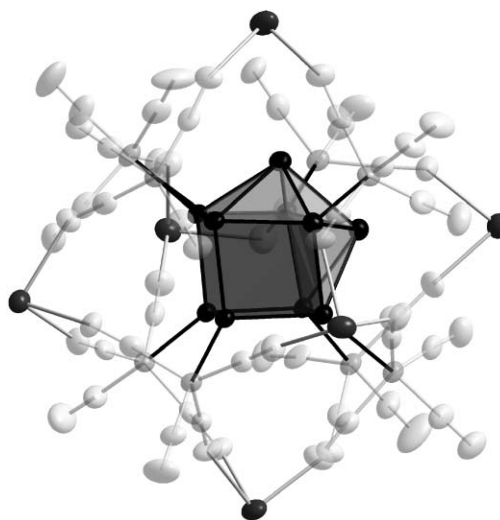


**Fig. 9** Arrangement of the central ten germanium atoms of  $\{\text{Ge}_{10}\text{Si}[\text{Si}(\text{SiMe}_3)_3]_4(\text{SiMe}_3)_2\text{Me}\}^-$  **15** (left) and  $[\text{Ge}_{10}(\text{Si}t\text{Bu}_3)_6\text{I}]^+$  **14** (right). The adamantine-like arrangement is emphasized by the polyhedra.

Consequently, the results for the  $\text{Ge}_{10}$  clusters **14** and **15** clearly indicate that a structural transition to the arrangement of the germanium atoms in elemental germanium can occur in the range of 10 germanium atoms.

Such a transition may not necessarily occur when ten germanium atoms are localized within the cluster core. This becomes obvious when another metalloid cluster compound of germanium  $\text{Na}_6\text{Ge}_{10}[\text{Fe}(\text{CO})_4]_8 \cdot 18\text{THF}$  (**16**) is taken into account. In this compound transition metal fragments are bound to the cluster core as ligands.<sup>33</sup> This cluster compound, whose molecular structure is presented in Fig. 10, is synthesized by a reaction of  $\text{GeBr}$  with  $\text{Na}_2\text{Fe}(\text{CO})_4$  and is isolated in the form of dark, nearly black, coloured crystals.

Inside the cluster core eight germanium atoms bear a ligand and two germanium atoms are naked. The ligand-bound germanium atoms are arranged in the form of a distorted cube, where two of the six cubic faces are capped by a naked germanium atom. This arrangement shows no resemblance to the diamond lattice but it exhibits an interesting similarity to



**Fig. 10** Molecular structure of  $\text{Na}_6\text{Ge}_{10}[\text{Fe}(\text{CO})_4]_8 \cdot 18\text{THF}$  **16**. The coordinating THF molecules are not shown. The Na atoms at the exterior are shown in black, and the  $\text{Fe}(\text{CO})_4$  units are light coloured. The two different areas of the central  $\text{Ge}_{10}$  centaur polyhedra are highlighted by different colours (dark grey: cubic part; light grey: icosahedral part).

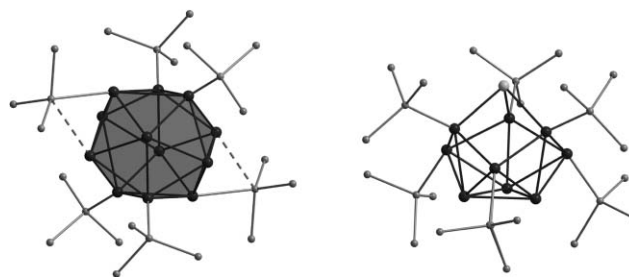
another well known polyhedral arrangement. The arrangement of the 10 germanium atoms can be called a centaur polyhedron as it is constructed from two different polyhedra (cube and icosahedron) that interpenetrate, as emphasized in Fig. 10. This type of polyhedron is well known in solid state chemistry, representing a textbook example of a compound with a coordination number of 10. However, in group 14 cluster chemistry it is a new structural motif.

The bonding situation in **16** can be described in different ways. On one hand the cluster fulfils Wade's rules by having 26 electrons for cluster bonding ( $2n + 6$ ;  $n = 10$ ), the expected number for an *arachno*-type structure, and the structure of **16** can indeed be described as a distorted *arachno* structure. The addition of two more germanium atoms leads to the *closo* structure of an icosahedron. As **16** can be described by Wade's rules, delocalized bonding electrons are expected inside the cluster core. However, quantum chemical calculations on the model compound  $\{\text{Ge}_{10}[\text{Fe}(\text{CO})_4]_8\}^{6-}$  reveal that a delocalized bonding situation is present only in the icosahedral part, while in the cubic part the bonding electrons are more localized. Therefore **16** consists of two kinds of polyhedra (icosahedra and cube), in which different bonding situations are realized. Thus the bonding situation in the cluster core changes from "localized" in the cubic part to "delocalized" in the icosahedral part, representing a completely new bonding situation in metalloid group 14 cluster compounds.

Consequently, the results for the metalloid cluster compounds **14**, **15** and **16** show that a structural transition to the structure of the elemental state can, but may not necessarily, occur when 10 germanium atoms are present in the cluster core.

Another possible arrangement of a metalloid group 14 cluster compound with ten tetrel atoms in the cluster core is found in the metalloid lead cluster  $\text{Pb}_{10}[\text{Si}(\text{SiMe}_3)_3]_6$  (**17**),<sup>34</sup> which is isolated from a reaction of  $\text{Pb}[\text{Si}(\text{SiMe}_3)_3]_2$  with  $\text{CuH}$ . The reaction pathway is very complicated and little understood to date, but it is thought that a reductive elimination of  $\text{HSi}(\text{SiMe}_3)_3$  is an important step during the reaction. In a similar reaction, where  $\text{PH}_3$  is used as the hydride source, another lead cluster with 12 lead atoms inside the cluster core,  $\text{Pb}_{12}[\text{Si}(\text{SiMe}_3)_3]_6$  (**18**), could be synthesized in low yield.<sup>34</sup> As elemental lead is one of the products in both reactions, **17** and **18** can be thought of as intermediates on the way to the element as is generally thought for metalloid cluster compounds. Consequently, the appearance of two different metalloid lead cluster compounds **17** and **18** indicates that a mixture of metalloid lead clusters is formed during the reaction of  $\text{Pb}[\text{Si}(\text{SiMe}_3)_3]_2$  with a hydride source, and only the least soluble are isolated on the way to elemental lead.

The molecular structures of compounds **17** and **18** are shown in Fig. 11. These compounds bear six ligands each and the lead atoms are arranged in a similar way in the cluster cores. In the core of the  $\text{Pb}_{12}$  compound **18** the twelve lead atoms are arranged in the form of a distorted icosahedron. The six naked lead atoms are arranged in the form of a six-membered ring in a chair conformation. The six ligand-bound lead atoms form two three-membered rings above and below the central six-membered ring of naked lead atoms. The Pb–Pb distances in the cluster core vary in a wide range from 306 to



**Fig. 11** Molecular structure of  $\text{Pb}_{12}[\text{Si}(\text{SiMe}_3)_3]_6$  **18** (left) and  $\text{Pb}_{10}[\text{Si}(\text{SiMe}_3)_3]_6$  **17** (right), methyl groups are omitted for clarity. The icosahedral arrangement of the twelve lead atoms in **18** is emphasized by the polyhedron. In the case of **17** the single lead atom is highlighted by a different colour.

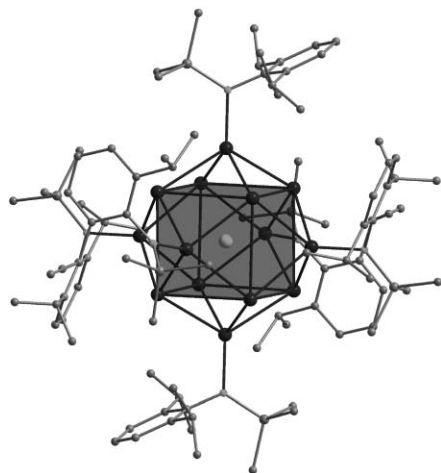
339 pm, meaning that a strongly distorted icosahedron is present. Interestingly, only four of the six ligands in **18** are bound end on while two ligands are located in a semi-bridging position (Si–Pb distances: 270 and 309 pm; dashed lines in Fig. 11) leading to the shortest Pb–Pb distances in the cluster core of 306 pm.

The metalloid lead cluster  $\text{Pb}_{10}[\text{Si}(\text{SiMe}_3)_3]_6$  **17** is structurally very similar to the  $\text{Pb}_{12}$  cluster **18** as its structure can be derived from **18** when a  $\text{Pb}_3$  unit in the icosahedral cluster is substituted by a single lead atom (highlighted in Fig. 11). The Pb–Pb distances to this lead atom are within the narrow range of 299.8–300.6 pm, and are shorter than the other Pb–Pb distances in the cluster core, which vary from 312–321 pm. These differences in the Pb–Pb distances led to the assumption that **17** is built of a  $\text{Pb}_9\text{R}_6^{2-}$  fragment coordinated to a  $\text{Pb}^{2+}$  cation. This interpretation would be in line with Wade's rules since the  $\text{Pb}_9\text{R}_6^{2-}$  fragment would have 26 bonding electrons ( $2n + 6$ ,  $n = 9$ ) and could be interpreted as a *hypho* fragment.

However, as a zwitterionic form would be energetically unfavourable, this interpretation is questionable. Additionally, **17** is very dynamic in solution as only one  $^1\text{H}$  NMR signal is observed for the ligands at room temperature. This signal splits into two signals at 243–248 K leading to an activation barrier for the dynamic process of  $50 \text{ kJ mol}^{-1}$ .<sup>34</sup> In the solid state, the ligands are bound to the lead atoms of the central  $\text{Pb}_6$  ring of the icosahedral-like core structure. The opposite is found in the  $\text{Pb}_{12}$  species **18**, as here the six lead atoms of the central  $\text{Pb}_6$ -ring are naked, leading to the assumption that an icosahedral arrangement of lead atoms is favourable for a metalloid lead cluster compound.

As the  $\text{Ge}_{10}$  species **16** also shows structural features of an icosahedron, an icosahedral arrangement appears to be favourable for larger metalloid group 14 cluster compounds that show no structural transition towards the element.

When the structures and therefore the numbers of the tetrel atoms inside the cluster core increase, a cluster size is reached where metalloid cluster compounds with more than one sphere form. To date, only two examples of such a metalloid cluster compound are known: the  $\text{Sn}_{15}$  species  $\text{Sn}_{15}\text{R}_6$  ( $\text{R} = \text{NAr}(\text{SiMe}_3)$  **19**;  $\text{NAr}(\text{SiMe}_2\text{Ph})$  **19a**,  $\text{Ar} = \text{C}_6\text{H}_3$ , 2,6-*i*Pr<sub>2</sub>).<sup>35</sup> The clusters are synthesized *via* different synthetic routes. While **19** is synthesized *via* a reductive coupling reaction, **19a** is synthesized *via* thermolysis of a suitable precursor.



**Fig. 12** Molecular structure of  $\text{Sn}_{15}\text{R}_6$  ( $\text{R} = \text{NArSiMe}_3$ ;  $\text{Ar} = \text{C}_6\text{H}_3$ , 2,6-*i*Pr<sub>2</sub>) **19**, hydrogen atoms are omitted for clarity. The central atom is light grey and the cube of naked atoms is highlighted by the polyhedron.

The molecular structures of both clusters are essentially the same as in both structures the arrangement of the tin atoms (Fig. 12) can be described as a body centred arrangement of 15 tin atoms, being the first metalloids group 14 cluster compounds with a central tetrel atom. The naked tin atoms form a body centred distorted cube, where each of the six faces of the cube is capped by a ligand-bound tin atom.

Interestingly this arrangement cannot be compared with the structure of elemental tin (neither grey nor white). It is only similar to the arrangement in a high pressure modification found at  $45 \pm 5$  GPa.<sup>36</sup> Such a relation between the arrangement of the metal atoms inside a metalloids cluster compound and a high pressure modification of the corresponding element seems to be a common feature for metalloids cluster compounds and has also been observed in the case of group 13 elements.<sup>37</sup>

The  $\text{Sn}_{15}$  clusters **19** and **19a** are the first examples of group 14 cluster compounds that show such a relation, and it will be of great interest to see what happens for the other heavier group 14 elements Si, Ge and Pb when the clusters become as large as **19** and **19a**. When the metalloids cluster compound  $\text{SiAl}_4\text{Cp}^*_6$ <sup>38</sup> is taken into account, it becomes apparent that high coordination numbers are possible even for the lightest element silicon, as it is structurally very similar to the  $\text{Sn}_{15}$  compounds. In the case of the mixed Si–Al compound the central Si atom has also the coordination number 8 + 6 as is the case for the central tin atom in **19** and **19a**.

## Summary and outlook

Metalloids cluster compounds of the heavier group 14 elements of the general formulae  $\text{E}_n\text{R}_m$  ( $\text{E} = \text{Si}, \text{Ge}, \text{Sn}$  and  $\text{Pb}$ ) with  $n > m$  represent a new class of group 14 cluster compounds. As the average oxidation state of the tetrel atoms in a metalloids cluster is between 0 and 1, the metalloids clusters can be seen as intermediates on the way to the element. Therefore, the most interesting question to be answered is: How does the bonding

situation change as the average oxidation state reaches the elemental state value of 0?

The results available to date, summarized in this review, show that a delocalization of bonding electrons inside the cluster compound occurs even in the smallest possible compound  $\text{E}_5\text{R}_4$ . The results for the  $\text{E}_8\text{R}_6$  species ( $\text{E} = \text{C}, \text{Si}, \text{Ge}$  and  $\text{Sn}$ ) also show significant differences between different elements and a significant dependence of the bonding situation in the cluster core on the ligand attached. A preference in larger polyhedral clusters towards the formation of icosahedrally shaped clusters can also be seen for the different elements. Further increases in the cluster size lead to more delocalized bonding electrons that will finally lead to an elemental state with highly delocalized bonding electrons, *i.e.* a metallic state. As this is quite unusual for silicon as well as for germanium, the trend of delocalization seems to invert at a size of 10 tetrel atoms, as here structures are observed that resemble the atomic arrangement of elemental silicon and germanium. Nevertheless, this inversion may not necessarily occur, as in the  $\text{Sn}_{15}$  compound a metallic arrangement (coordination number 8 + 6) is observed.

In future experiments it will be necessary to synthesize more and hopefully larger metalloids group 14 cluster compounds to shed more light onto this new area of group 14 cluster chemistry, leading to a deeper understanding of the development of the bonding situation on the way to the metallic state. Additionally, it will be necessary to perform measurements on the physical properties of such metalloids cluster compounds to find the relationship between the structure, bonding and physical properties of such cluster compounds. This might lead to an understanding of the physical properties of the photoluminescence of germanium nanoparticles on a molecular scale, being the most exciting and definitely the most difficult question to be answered.

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