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Main-Group Chemistry

$[Ge_{12}\{FeCp(CO)_2\}_8\{FeCp(CO)\}_2]$: A Ge_{12} Core Resembles the Arrangement of the High-Pressure Modification Germanium (II)**

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Metalloid cluster compounds[1] of the general formula M_nR_m ($n > m$; R = ligand such as $Si(SiMe_3)_3$ or $N(SiMe_3)_2$) are ideal model compounds for molecular entities in the gray area between molecules and the solid state.[2] This borderland is of particular interest especially for metals or semi-metals, as drastic changes in the physical properties take place during the reduction from salt-like oxidized compounds (e.g. oxides, halides: non-conducting) to the elemental bulk phase (metal: conducting; semi-metal: semiconducting).[3] As the dimensions of metalloid clusters are in the nanometer range, the synthesis of metalloid clusters also opens the possibility of obtaining structural information on small nanoparticles, an important prerequisite for structure–property relations in this expanding area.[4]

In the case of germanium, several different synthetic routes have been introduced in recent years, leading to a number of metalloid clusters, which exhibit new and unusual structures as well as exceptional bonding properties. Hence, by a reductive elimination reaction $[Ge_{10}(SitBu_3)_6I]^+$ is obtained,[5] whereas the metalloid clusters $[Ge_5\{CH(SiMe_3)_2\}_4]$[6] and $[Ge_6(C_6H_3Dipp_2)_2]$ (Dipp = 2,6-$i$$Pr_2C_6H_3$)[7] have been synthesized by reductive coupling reactions. The most fruitful route to metalloid germanium clusters to date uses the disproportionation reaction of dissolved metastable Ge^I halides, which thus allows the synthesis of clusters with eight $[Ge_8\{N(SiMe_3)_2\}_6]$,[8] $[Ge_8\{(OtBu)_2C_6H_3\}_6]$,[9] nine $[Ge_9\{Si(SiMe_3)_3\}_3]^-$,[10] ten $[Ge_{10}Si\{Si(SiMe_3)_3\}_4(SiMe_3)_2Me]^-$,[11] $[Ge_{10}\{Fe(CO)_4\}_8\{Na(thf)_3\}_6]$,[12] and up to fourteen $[Ge_{14}\{E(SiMe_3)_3\}_5\{Li(thf)_2\}_3]$ (E = Si, Ge)[13,14] germanium atoms in the cluster core.

Among metalloid main-group clusters in general $[Ge_{10}\{Fe(CO)_4\}_8\{Na(thf)_3\}_6]$ is an exceptional example as it is the only metalloid cluster which is exclusively stabilized by transition-metal-based ligands. This shows that the influence of transition-metal ligands on metalloid clusters is nearly unexplored. Furthermore, such metalloid clusters stabilized with transition-metal-based ligands might open an access to new metastable binary materials.[15] However, transition-metal reagents have already been used in the chemistry of germanium clusters; either as ligands in direct synthesis to gain fully substituted clusters, such as $[Ge_6\{Cr(CO)_5\}_6]^{2-}$,[16] or in various subsequent reactions with Zintl ions[17] to give large clusters, such as $[Pt@Pb_{12}]^{2-}$,[18] $[Au_3Ge_{45}]^{9-}$,[19] $[Ni_3Ge_{18}]^{4-}$.[20] Such subsequent reactions have been recently carried out successfully with the metalloid germanium cluster $[Ge_9\{Si(SiMe_3)_3\}_3]^-$, which yielded the ten-atom cluster cores in $[M(CO)_3Ge_9\{Si(SiMe_3)_3\}_3]^-$ (M = Cr, Mo, W)[21,22] and in the transition-metal linked nineteen-atom cluster cores within $[MGe_{18}\{Si(SiMe_3)_3\}_6]^X$ compounds ($X = -1$: M = Cu, Ag, Au;[23,24] $X = 0$: M = Zn, Cd, Hg[25]).

We now present a second example of a metalloid main-group cluster exclusively stabilized by transition-metal-based ligands, showing a unique arrangement of the tetrel atoms in the cluster core. After work up of a reaction mixture of a metastable GeBr solution (CH_3CN, THF, nBu_3N (2:2:1); 0.28 M) with solid $K[FeCp(CO)_2]$ (Cp = cyclopentadienyl) we obtained black crystals of the metalloid germanium cluster $[Ge_{12}\{FeCp(CO)_2\}_8\{FeCp(CO)\}_2]$ (**1**). The molecular structure of **1**, as shown in Figure 1, was determined with the aid of synchrotron radiation (ANKA Karlsruhe, Germany). The application of synchrotron radiation was necessary as all larger crystals of **1** were twinned, showing the characteristic feature of a dovetail twin. Only the smallest crystals were single crystals which could be used for structure determination. Nevertheless, by applying synchrotron radiation we obtained a data set with which the structure of **1** could be accurately solved.[26]

The metalloid cluster **1** crystallizes in the triclinic crystal system in space group $P\bar{1}$ with the inversion center in the middle of the bond between the two "naked" germanium atoms Ge6 and Ge6a, that is, **1** has C_i symmetry. The Ge–Ge bonds within the cluster core of **1** are in a narrow range (249–260 pm) and the germanium atoms Ge1 to Ge5 and their symmetry equivalents are each bound to four other atoms in a slightly distorted tetrahedral arrangement. The two naked germanium atoms Ge6 and Ge6a, which have a long Ge–Ge bond of 275 pm, both form five bonds to atoms which are all located in only one half of the coordination sphere around the

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Supporting information for this article (synthetic procedure, mass spectrometric investigations, and results of theoretical calculations) is available on the WWW under http://dx.doi.org/10.1002/anie.201207224.

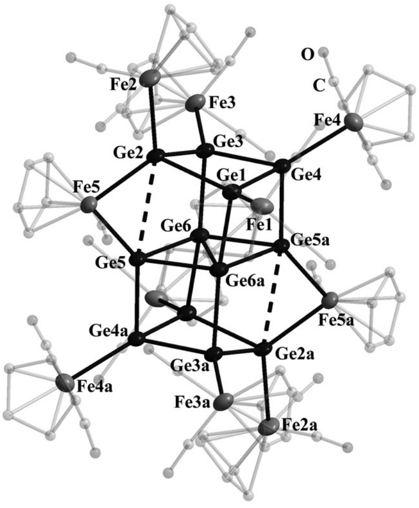

Figure 1. Molecular structure of the metalloid cluster **1** without hydrogen atoms (vibrational ellipsoids for Fe and Ge at 50% probability). The CO and Cp groups are transparent for clarity. Selected bond lengths [pm] and angles [°]: Ge1–Ge2 260.41(15), Ge1–Ge4 253.33(13), Ge1–Ge6 255.34(15), Ge1–Fe1 243.52(17), Ge2–Ge3 257.35(13), Ge2–Fe2 249.3(2), Ge2–Fe5 240.59(17), Ge3–Ge6a 254.38(14), Ge3–Fe3 241.14(16), Ge4–Ge5 249.05(15), Ge4–Fe4 243.73(17), Ge5–Ge6 256.05(13), Ge5–Ge6a 251.37(16), Ge5–Fe5 230.80(17), Ge6–Ge6a 275.28(18); Ge1-Ge4-Ge3 83.113(47), Ge1-Ge2-Ge3 80.933(46), Ge1-Ge4-Ge5 89.875(45), Ge5-Ge6-Ge5a 114.298(53), Ge6-Ge5-Ge6a 65.702(43), Ge2-Fe5-Ge5a 86.055(59).

germanium atom. Such an arrangement is also observed for the naked silicon atoms in $Si_8(SitBu_3)_6$[27] or the naked germanium atoms in $[Ge_{14}\{E(SiMe_3)_3\}_5\{Li(thf)_2\}_3](E{=}Si, Ge)$,[13,14] in which a comparable Ge–Ge bond length of 286 pm is found. This result indicates that such a so called "inverse tetrahedral" arrangement[27] seems to be a central structural motive in metalloid cluster compounds of Group 14.

The arrangement of the twelve germanium atoms in the cluster core of **1** can be described as two distorted face-sharing cubes, connected by the central four-membered ring Ge6-Ge5-Ge6a-Ge5a. This is a novel structural motive for molecular compounds in germanium chemistry. However, a comparable arrangement of germanium atoms is found in the high-pressure modification of germanium (II) [Ge(*tI*4)],[28] where Ge_{12} units are also present, and which can be described in the same manner (Figure 2).

This structural similarity accordingly indicates that the arrangement of the 12 germanium atoms within the cluster core of **1** can be seen as a structural approximation of the β-tin like solid-state structure of germanium (II), which is only stable at a pressure of 10.8 GPa. Such a structural resemblance to a high-pressure modification is also realized in $[Sn_{15}\{NDippSiMe_3\}_6]$ (Dipp = 2,6-iPr$_2$C$_6$H$_3$,), where the arrangement of the 15 tin atoms can be seen as a cut-out of the bcc packing,[29] found for elemental tin at a pressure of (45 ± 5) GPa.[30] Consequently **1** is the second example where the arrangement of tetrel atoms within a metalloid cluster shows a structural resemblance to a high-pressure modification, this arrangement seems to be induced by the dense packing of the ligands in the cluster shell.[31]

In the case of **1** the Ge_{12} cluster core is shielded by two different kinds of ligands, that is, eight [FeCp(CO)$_2$] ligands are bound terminally with quite long Ge–Fe single bonds (240.7 to 249.4 pm).[32] Two [FeCp(CO)] ligands are bound in an unsymmetrical bridging position, they have much shorter Ge–Fe bond of 231 pm (Ge5–Fe5) and 239 pm (Ge2–Fe5). These short Ge–Fe distances to the bridging [FeCp(CO)] unit additionally lead to a Ge–Ge contact of the bridged Ge atoms (Ge2, Ge5) of 322 pm, which is significantly smaller than the sum of the van der Waals radii of 422 pm.[33] The strongly interlocked arrangement of the ligands thereby leads to a densely packed ligand shell as is evident from the space-filling model (Figure S2 in the Supporting Information). This dense packing of the ligand shell in **1** seems to be the reason for the structural approach to the high-pressure solid-state structure of germanium (II), which is only possible by the loss of two of the CO molecules of the [FeCp(CO)$_2$] ligands, enabling Fe10 and Fe10a to move to a bridged position.

To gain a deeper insight into the bonding of **1**, DFT calculations on the full molecule of **1** have been carried out including an Ahlrichs–Heinzmann population analysis (see the Supporting Information for details).[34] According to the population analysis all terminally bound iron atoms of the [FeCp(CO)$_2$] units have a charge of −1.1 making them usual 18 valence electron (18 VE) complexes. Despite this, both of the bridging iron atoms of the [FeCp(CO)] units are charged −0.3, and have two shorter germanium interactions of 239 and

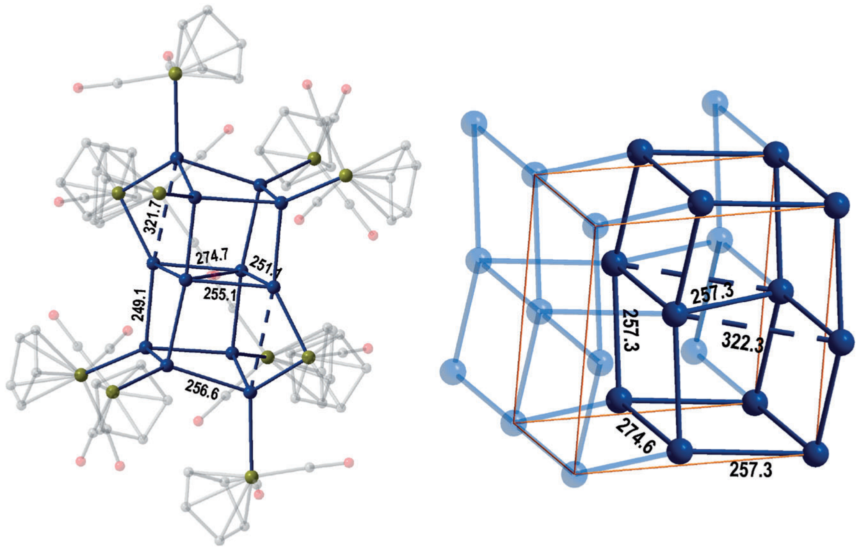

Figure 2. Comparison of the arrangement of the germanium atoms within **1** (left) and the solid-state structure of germanium (II) [Ge(*tI*4)] (right).

231 pm. This situation indicates a substantial degree of backbonding from the iron atoms to the germanium atoms which might decrease their negative charge. The naked Ge6 atoms are slightly negatively charged with −0.2 and the remaining ligand-bound germanium atoms are neutral or up to +0.2 charged. All outer Ge−Ge edges of the cluster core framework of **1** reveal slightly elongated Ge−Ge single bonds with 249 to 260 pm. In contrast the inner bond between the two naked Ge6 atoms is clearly longer at 275 pm. This trend is in line with the calculated two-center (2c) SEN (shared electron number)[35] in which the long Ge6−Ge6a bond has a lower 2c-SEN value of 0.9 while the shorter outer Ge−Ge bonds show higher 2c-SENs from 1 to 1.16. These are normal values for localized two center bonds. Additionally, a weak bonding interaction is present between the two germanium atoms (Ge2, Ge5) connected by the bridging [FeCp(CO)] unit as shown by the calculated 2c-SEN of 0.2. The sigma bonds of the normal two center single bonds can be seen in the illustration of the calculated MO picture of the HOMO of **1** (Figure 3).

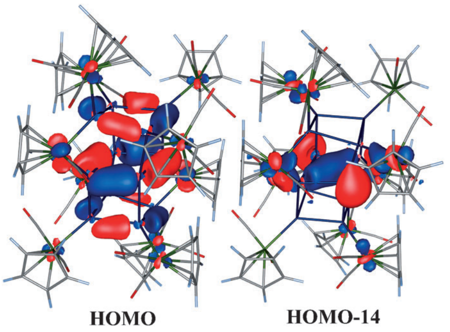

Figure 3. Illustration of selected calculated molecular orbitals of **1**.

In addition to the two center interactions the population analysis point out strong multi-center bonding interactions in the central Ge_4 ring (Ge6-Ge5-Ge6a-Ge5) with a high three-center (3c) SEN of 0.34 in both triangles (Ge6-Ge6a-Ge5 and Ge6-Ge6a-Ge5a), which can be linked to HOMO−14 (Figure 3). Moreover within the two outer Ge_4 rings (Ge1-Ge2-Ge3-Ge4 and Ge1a-Ge2a-Ge3a-Ge4a) 3c-SEN of 0.12 (Ge1-Ge2-Ge3) and 0.10 (Ge1-Ge2-Ge4) are calculated. Thus **1** apparently contains three four-membered rings, exhibiting delocalized bonding electrons, which are connected by localized 2c2e Ge−Ge bonds (Ge1−Ge6, Ge3−Ge6, and Ge4−Ge5).[36]

The presence in **1** of Ge_4 rings, with delocalized bonding electrons, connected by localized 2c2e bonds is comparable to the arrangement in the core of the metalloid germanium cluster $[Ge_{14}\{E(SiMe_3)_3\}_5\{Li(thf)_2\}_3]$ (**2**; E = Si, Ge).[13,14] In **2**, three four-membered Ge_4 rings with delocalized bonds are present, the rings are connected to each other by strongly localized 2c2e Ge−Ge bonds. The bonding within the Ge_4 units in the Ge_{14} clusters **2** can be described as singlet biradicaloid according to comprehensive DFT calculations. Additionally **2** has a high reactivity towards the C−H bonds of solvent molecules.[13] This indication of a possible radicaloid character of **1** and the calculated HOMO–LUMO gap of **1** of only 0.8 eV[37] are a reasonable explanation for the high reactivity of **1**, whose crystals are unfortunately very unstable. However, the occurrence of Ge_4 units raises the fundamental question if such four-membered germanium rings are important intermediates and building blocks for the assembly and growth of metalloid clusters and thus intermediates on the way to the bulk phase.

To address this aspect we performed further quantum chemical calculations, which first of all show that the formation of an annular $[Ge_4\{FeCp(CO)_2\}_4]$ molecule from $[Ge\{FeCp(CO)_2\}]^{\bullet}$ radicals is exothermic with $\Delta G = -483\ \mathrm{kJ\,mol^{-1}}$. Subsequent reaction steps of the cluster growth become more and more complicated and must be regarded as relatively speculative.[38] The consecutive formation of the metalloid germanium cluster $[Ge_{12}\{FeCp(CO)_2\}_8\{FeCp(CO)\}_2]$(**1**) from three $[Ge_4\{FeCp(CO)_2\}_4]$ units is thereby mildly exothermic with $\Delta G = -61\ \mathrm{kJ\,mol^{-1}}$ (Figure 4).

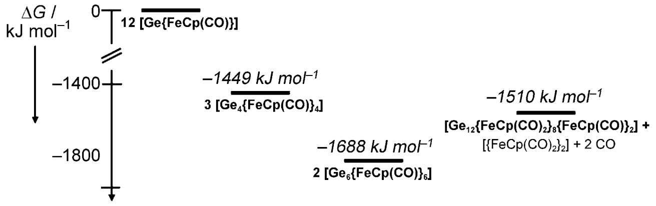

Figure 4. Calculated energies for the formation of **1** from monomeric $[Ge\{FeCp(CO)_2\}]$ units. All the energies are relative to twelve monomeric $[Ge\{FeCp(CO)_2\}]$ units.[39]

Beside this, the formation of a trigonal prismatic fully substituted $[Ge_6\{FeCp(CO)_2\}_6]$ cluster **3**[40] is strongly exothermic with $\Delta G = -239\ \mathrm{kJ\,mol^{-1}}$. Hence the formation of **1** is disfavored with respect to the formation of the fully substituted Ge_6 cluster **3**. Evidence for **3** can be found in the FT-ICR mass spectrum of the reaction solution, in which the anionic species $[Ge_6\{FeCp(CO)_2\}_6\{FeCp(CO)\}]^-$ (**3a**) corresponds to the dominant signal.[41] The addition of a further $[FeCp(CO)_2]$ ligand to **3** to give **3a** is in line with the reaction conditions in which the ligand is used in 7% excess.[42]

In summary, we presented the synthesis and structural characterization of the metalloid germanium cluster $[Ge_{12}\{FeCp(CO)_2\}_8\{FeCp(CO)\}_2]$ (**1**), which is formed within an extremely complicated reaction system, with a highly competitive side reaction towards $[Ge_6\{FeCp(CO)_2\}_6]$ (**3**). The unique arrangement of the 12 germanium atoms within the cluster core of **1** can be seen as a structural approach to the high-pressure modification of germanium (II), and seems to be induced by the tightly closed-packed ligand shell, indicating that structural motives from high-pressure modifications are also present within metalloid germanium clusters giving further insight into the nano-regime on the way to elemental germanium.

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[26] Crystal structure data for **1**: $[Ge_{12}\{FeCp(CO)_2\}_8\{FeCp(CO)\}_2]\cdot 0.5\,C_6H_6$, $Ge_{12}Fe_{10}O_{18}C_{74}H_{56}$, $M_r = 2662.77\,g\,mol^{-1}$, crystal dimensions $0.1\times 0.02\times 0.01\,mm^3$, triclinic, space group $P\bar{1}$, $a = 12.1426(9)$, $b = 12.4854(9)$, $c = 15.2993(10)$ Å, $\alpha = 70.124(5)$, $\beta = 75.123(5)$, $\gamma = 67.488(5)°$, $V = 1993.6(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.218\,g\,cm^{-3}$, $\mu_{Mo} = 6.267\,mm^{-1}$, $2\theta_{max} = 56°$, 12011 measured, 6184 independent reflections ($R_{int} = 0.0922$), absorptions correction: numerical (min./max. transmission 0.4011/0.8808), $R_1 = 0.0537$, $wR_2 = 0.1212$, STOE IPDS II diffractometer (synchrotron radiation ($\lambda = 0.8$ Å), 150 K). The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs used: SHELXS and SHELXL (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122). CCDC 896198 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[32] The Ge–Fe bond lengths are in between those found in $[GeClMe_2\{FeCp^*(CO)_2\}]$ (233.9 pm),[32a] $[GeCl_2\{FeCp(CO)_2\}_2]$ (235.7 pm)[32b] and $[LGe\{FeCp(CO)_2\}]$ (249.6 pm)[32c] [L = CH-$\{CMe(NAr)\}_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$]; a) H. Tobita, K. Ishiyama, Y. Kawano, S. Inomata, H. Ogino, *Organometallics* **1998**, *17*, 789–794; b) M. A. Bush, P. Woodward, *J. Chem. Soc. A* **1967**, 1833–1838; c) S. Inoue, M. Driess, *Organometallics* **2009**, *28*, 5032–5035.

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[36] The arrangement of the three four-membered rings, exhibiting delocalized bonding is reminiscent of the layers of graphite, a solid-state structure motive which is unknown for the Group 14 element germanium.

[37] The HOMO–LUMO gaps of other metalloid germanium clusters with conventional ligands (e.g. tBu, SiMe$_3$, or N(SiMe$_3$)$_2$) are usually above 2 eV calculated with the same DFT method.

[38] See the Supporting Information for details; energy, HOMO–LUMO gap, atom coordinates, and pictures of the calculated structures.

[39] An extended scheme, showing all the calculated compounds can be found in the Supporting Information Figure S7.

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[42] Theoretical calculations show that the addition of another [$FeCp(CO)_2$] ligand to [$Ge_6\{FeCp(CO)_2\}_6$] (**3**) to give [$Ge_6\{FeCp(CO)_2\}_6\{FeCp(CO)\}$]$^-$ (**3a**) is exothermic:

$$\mathbf{3} + \{FeCp(CO)_2\}^- \rightarrow \mathbf{3a} + CO;\ \Delta G = -25\ \text{kJ mol}^{-1}$$