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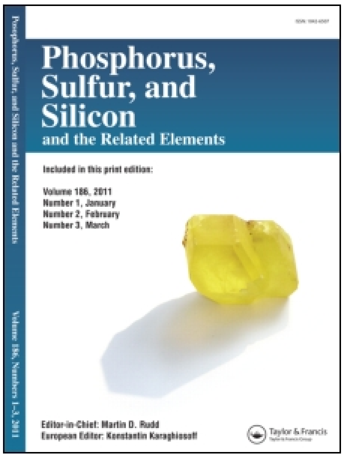

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Ge(I) BROMIDE: A NEW SOURCE FOR GERMANIUM CLUSTER COMPOUNDS

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Ge(I) BROMIDE: A NEW SOURCE FOR GERMANIUM CLUSTER COMPOUNDS

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Ge(I)Br represents a good starting material for the synthesis of Ge cluster compounds which feature in addition to ligand bound Ge atoms also naked Ge atoms. The synthetic concept, the structures, and bond properties of a Ge_8 *and a* Ge_9 *cluster compound are reported.*

The synthesis of metal cluster compounds with an average oxidation state of the metal atoms inside the cluster core between 0 and 1 is of great interest, as those clusters are on the borderline between the molecular and solid state and therefore interesting physical properties are expected for these compounds.[1]

The disproportionation reaction of subvalent metal halides is a promising route to get access to such clusters. Herein the synthetic concept and first results in germanium chemistry will be reported.

RESULTS AND DISCUSSION

The disproportionation reaction of subvalent metal halides leads at the end to the bulk metal and a metal halide in a higher oxidation state. During this reaction metal cluster compounds can be regarded as intermediates on the way to the bulk metal (Scheme 1). This implies that the disproportionation reaction of subvalent metal halides opens up a pathway to cluster compounds, where the average oxidation state of the metal atoms inside the cluster is between 0 and 1.[2]

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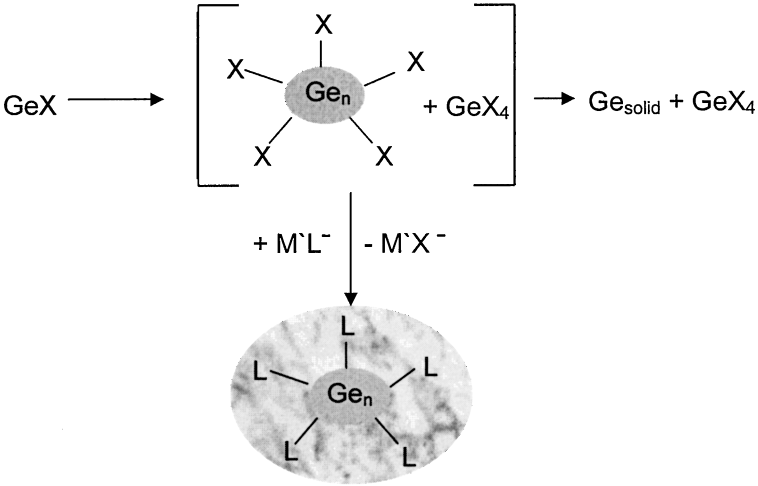


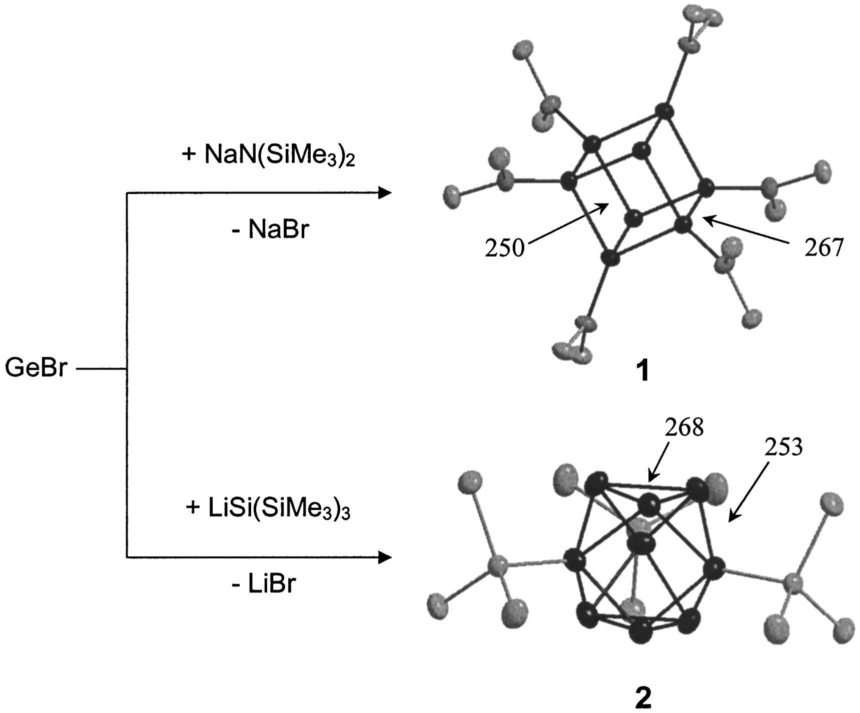
SCHEME 1 Schematic presentation of the synthesis of Ge cluster compounds with an average oxidation state of the Ge atoms inside the cluster between 0 and 1 via the disproportionation reaction of the subvalent Ge(I) halide GeX (X = halide, M′ = alkaline or alkaline earth metal, L = ligand).

To isolate such metal cluster compounds, the generally metastable intermediates have to be kinetically stabilized, for example with the aid of bulky ligands attached to the cluster surface (Scheme 1).[2]

In the case of germanium, the well known Ge(II) halides are not suitable as a starting material since, for example, germanium(II) bromide only begins to disproportionate at 150°C,[3] which is too high in temperature for a kinetic stabilization. On the other hand Ge(I)Br disproportionates already above 90°C giving elemental germanium and germanium tetrabromide. Thus Ge(I)Br is anticipated to be a better starting material.[4]

The high temperature molecule Ge(I) bromide can be synthesized from the reaction of germanium with HBr at 1600°C and a pressure of 10^{-2} mbar, where it is the dominating gaseous compound. Using a cocondensation technique it can be isolated in preparative scale (30 mmol) in the form of a dark red coloured amorphous solid, when only toluene is used as the solvent during the cocondensation.[4] Due to the insoluability of Ge(I)Br in inert solvents subsequent reactions are difficult. Fortunately Ge(I)Br can be transferred into a soluable form using $N^{n}Pr_3$ as a donor molecule during the cocondensation reaction and in this form Ge(I)Br can be used for subsequent reactions.

Initial reactions with the metastable soluable form of this new binary compound (GeBr) show that the above mentionend pathway to cluster compounds works, since the reaction of Ge(I)Br with $NaN(SiMe_3)_2$ or $LiSi(SiMe_3)_3$ yields a $Ge_8[N(SiMe_3)_2]_6$ **1**[5] or a $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **2**[6] cluster compound respectively (Scheme 2), where the average oxidation state of the Ge-atoms inside the cluster is 0.75 (**1**) and 0.22 (**2**).[7*]



SCHEME 2 Reaction scheme for the synthesis of $Ge_8[N(SiMe_3)_2]_6$ **1** and $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **2**. Molecular structures of **1** and **2** are shown without methyl groups for clarity. The different Ge—Ge distances [pm] inside the cluster cores are marked by arrows.

Inside the cluster core of **1** Ge—Ge bond distances of 250 (Ge—GeR) and 267 pm (GeR-GeR) are found (Scheme 2). A comparison of these bond distances to those found in the completely substituted Ge cluster compounds Ge_nR_n ($n = 4$,[8] 6,[9] 8,[10]), where Ge—Ge bond distances of

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[*] Beside the approach via the disproportionation reaction other pathways to get to Ge cluster compounds with an average oxidation state of the Ge atoms inside the cluster core between 0 and 1 ($[Ge_{10}R_6]^+$,[7a] Ge_6R_2[7b]) are possible.

244–258 pm are found, shows that the bond distance between the ligand bound Ge-atoms has increased, while the Ge—Ge distance between the naked and the ligand bound Ge-atom is in the same order of magnitude as those found in the fully substituted clusters Ge_nR_n.

This trend in the Ge—Ge distances in **1** is reproduced by the shared electron numbers (SENs) from an Ahlrichs Heinzmann population analysis calculated on the model compound $Ge_8(NH_2)_6$ **1′**.[5] Additionally three-centered bonding components in the three membered ring (GeR—GeR—GeR) with a SEN of 0.13 are found. Consequently the two additional electrons from the naked Ge-atoms lead to a delocalization of the bonding electrons inside the cluster core, which represents a bonding situation that has not previously been observed in ligand stabilized cluster compounds.

A similar bonding situation is found in **2**, while here three-centered bonding components with a SEN of 0.32 are found inside the three membered ring of naked Ge-atoms. Future work will now concentrate on extending the synthetic concept to prepare larger cluster compounds in which more Ge atoms, especially more naked, non ligand bearing Ge atoms are present.

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