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Germanium/phosphorus cage compounds with germanium in three different oxidation states†‡

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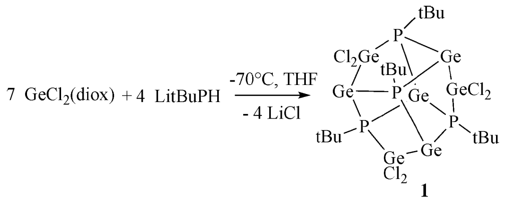
Novel germanium/phosphorus cage compounds with new structural motifs have been synthesized containing germanium in three different oxidation states. The key to obtain this new class of compounds is the use of monolithiated primary phosphine LiHP*t*Bu in the reaction with GeX_2.

Mixed valence is the basis of essential physicochemical properties of compounds such as colour, electron transfer. By analyzing the nature of the bonding of the components the electronic properties of the materials can be better understood and influenced.[1] This phenomenon has been known for a long time and broadly used in transition metal chemistry, however for main group compounds it has been explored less. Here, for example the large metalloidal clusters of group 13 elements[2] and those of group 14 elements[3] are known for homoatomic cage systems. For heteroatomic arrangements, 13/15 compounds[4] have been intensively investigated due to the important role for semiconducting materials.[5] These compounds and also the rarely studied group 14/15 compounds are usually electron precise.[6] For the latter, there are only known a few compounds with tin atoms in two different formal oxidation states, *e.g.* $[Sn_8(PSi\textit{i}Pr_3)_6Cl_2]$.[7] The only two Ge/P systems known in the literature are the cage compound $[(R_2Ge)_6P_4]$ (R = CH_3, C_2H_5), which was synthesized by thermal condensation of $R_2Ge(PH_2)_2$,[8] and the hexagonal prismatic $[Ge_6(PSi\textit{i}Pr_3)_6]$ obtained from the reaction of $GeCl_2(diox)_2$ with $Li_2PSi\textit{i}Pr_3$.[7] To the best of our knowledge, there is no Ge/P cage compound with the germanium atom in different oxidation states. The polymeric 14/16 compound $\{[Ge_5Te_{10}]^{4-}\}_n$ is the only example with three different oxidation states of germanium being observed in a single compound.[9] Herein we report the synthesis and characterization of novel 14/15 cage compounds with new structural motifs and with germanium atoms in three different formal oxidation states. In contrast to published synthetic procedures involving reactions between RPH_2 or LiHPR with, for example, $Sn(NMe_2)_2$,[10] or LiCl elimination reactions using the doubly lithiated species $RPLi_2$ and dihalides of group 14 elements,[7] we focused on the monolithiated species Li*t*BuPH in reactions with $GeCl_2$, which seem to be the key to obtain unprecedented mixed-valence cage compounds.

Initial attempts resulted in the successful synthesis and structural characterization of the germanium phosphorus compound $[Ge_7(P\textit{t}Bu)_4Cl_6]$ (**1**), which features different Ge oxidation states, by the reaction of $GeCl_2(diox)$ with Li*t*BuPH in THF (eqn (1)). Flat rods of the product are formed during a period of three days at −28 °C. Variations of the stoichiometry always resulted in the formation of **1** but the best yield was achieved by using the molar ratio of 7 : 4, as found in the product.



1 (1)

Compound **1** crystallizes in the trigonal space group $P\bar{3}$. The central structural motif of the Ge_7P_4 core is formed by six five-membered rings which can be derived from a cubane through bridging of three edges (Fig. 1). The structure is reminiscent of

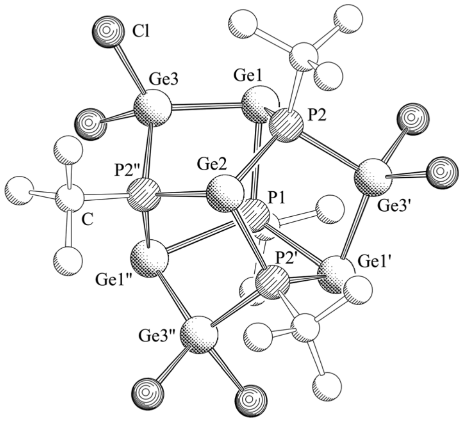


Fig. 1 Molecular structure of **1** (ball-and-stick model). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: Ge1–P1 2.500(5), Ge2–P2 2.432(2), Ge1–P2 2.425(1), Ge3–P2 2.355(2), Ge1–Ge3 2.486(8), Ge–Cl 2.185(2)–2.187(6); Ge1–P1–Ge1 115.31(5), P2–Ge2–P2 93.24(7), Ge1–P2–Ge3 91.17(5), P2–Ge3–Ge1 105.22(6), Ge3–Ge1–P2 87.72(6).

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† Dedicated to Prof. R. Kirmse on the occasion of his 65th birthday

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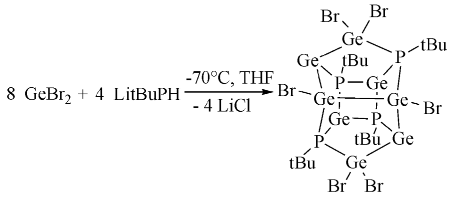
the tris-homocubane-like cage "ufosane" of P_{11}^{3-} in Na_3P_{11}.[11] Compound **1** possesses molecular C_3 symmetry. The P1 atom lies on a three-fold axis and forms bonds to the Ge1 atoms of 2.501(1) Å, which are slightly longer than the bonds connecting the symmetry-related P2 atoms to neighbouring Ge atoms (d(P2–Ge1) = 2.425(1) Å; d(P2–Ge3) = 2.355(2) Å). The remaining three symmetry-equivalent bonds between Ge2 and P2 have a length of 2.432(2) Å. In comparison to $[Ge_6(PSi\textit{i}Pr_3)_6]$[7] ($d$(Ge–P) = 2.416(2)–2.487(2) Å) the Ge–P distances in **1** are slightly shorter. The Ge–Ge bond length of 2.487(1) Å (Ge1–Ge3) is slightly longer than in the compound $[(\textit{t}BuP)_2(GePh)_2]$[12] with a Ge_2P_2 four-membered ring (d[Ge–Ge] = 2.421(1) Å). All phosphorus atoms carry a *t*Bu group and are connected to three different types of germanium atoms. Compound **1** was further characterized by mass spectrometry, which revealed the molecular ion peak, and by elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum shows one quartet for the P1 atom at δ 4 ppm (^2J(P,P) 22 Hz) and a doublet at δ 85 ppm (^2J(P,P) 22 Hz) for the three P2 atoms (*cf.* Fig. 1). These signals can also be detected very weakly in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, in addition to three other singlets of unknown compounds.

The reaction of $GeBr_2$ with Li*t*BuPH in the molar ratio 2 : 1 leads to the formation of $[Ge_8(P\textit{t}Bu)_4Br_6]$ (**2**) which can be isolated as orange crystals. Compound **2** is insoluble in common solvents. Variations of the stoichiometry of the starting materials resulted always in the formation of **2**. The best yield was achieved by using the molar ratio pre-determined by the product. Due to the insolubility of the product it was not found in the ^{31}P NMR spectrum of the reaction mixture. Compound **2** could be characterised by its molecular ion peak in the EI-MS spectrum, elemental analysis and X-ray crystallography.



2

(2)

Compound **2** crystallizes in the orthorhombic space group *Pbcn* (Fig. 2). The molecule contains a two-fold axis which connects the middle of the Ge3–Ge3′ bond and the middle of the P1/Ge1/P1′/Ge1′ four-membered ring. The Ge_8P_4 cage consists of six five-membered rings and one four-membered ring. The Ge–P bond lengths fall over a narrow range of 2.349(1) (Ge3–P2) to 2.440(1) Å (Ge1–P1). The Ge–Ge distances (average: 2.499(9) Å) are slightly longer than those in compound **1**. As in **1** all phosphorus atoms have distorted tetrahedral environments, coordinated by three germanium atoms and one *t*Bu fragment. In **2** four different germanium atoms are found, the Ge1 and Ge1′ connected to three phosphorus atoms, the Ge2 and Ge2′ connected to two germanium and one phosphorus atoms, the Ge3 and Ge3′ connected to two germanium and one bromine atoms and finally, the Ge4 and Ge4′ connected to one germanium, one phosphorus and two bromine atoms. The ^{31}P MAS NMR spectrum of **2** shows two signals for the two different P1 and P2 atoms at −92 and +58 ppm.

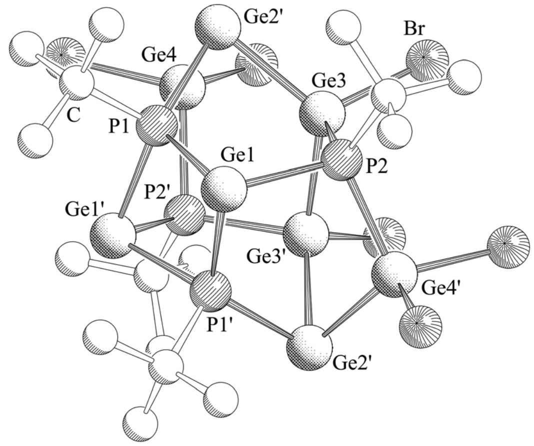


Fig. 2 Molecular structure of **2** (ball-and-stick model). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: Ge1–P1 2.427(1)–2.440(3), Ge1–P2 2.381(8), Ge2–P1 2.420(3), Ge3–P2 2.349(4), Ge4–P2 2.368(8), Ge–Ge 2.496(9)–2.501(9), Ge–Br 2.331(6)–2.340(7); Ge–P–Ge (four-membered ring) 94.88(6), Ge–P–Ge (five-membered ring) 101.51(7)–124.72(7), P–Ge–P (four-membered ring) 82.53(6), P–Ge–P (five-membered ring) 92.58(6)–95.49(6).

On the basis of the electronegativity of P and Ge, a formal charge of −2 can be assigned to each of the four P*t*Bu fragments of **1**. The six chlorine atoms contribute one negative charge each resulting in a total formal negative charge of −14 to be compensated by charges at the Ge atoms. Due to the neutrality of the overall molecule the three Ge1 atoms can be assigned to oxidation state +1, the Ge2 atom to +2 and the three Ge3 atoms to +3. Therefore the compound can be described as electron precise. NBO analysis on the DFT optimized structure of **1** at the BP86/TZVP level are in accordance with the different oxidation states of the germanium atoms as well as the electron precise nature of **1**.‡ Additionally, the NBO analysis reveals that the Ge1 and Ge2 atoms possess a lone pair of electrons, hence arising from a divalent Ge whereas the remaining Ge3 atoms substituted by chloride ligands result from tetravalent Ge (see Fig. 3). Furthermore, the electron precise nature of **1** is also supported by the shared electron numbers, which shows no significant electron sharing over three or four bonds. The natural charge distribution given by NBO analysis (Ge1: 0.26, Ge2: 0.34 and Ge3: 0.67; for labeling *cf.* Fig. 4) shows a relatively high positive charge on the Ge3 atoms (oxidation state +3) whereas the Ge1 and Ge2 atoms are less charged indicating the rather polar nature of **1**.

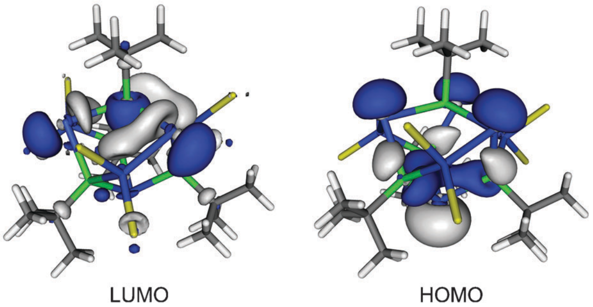
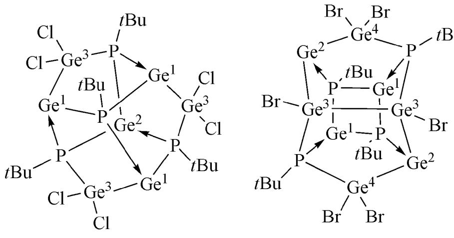


Fig. 3 Isosurfaces of the lowest unoccupied (representing a combination of the σ*–Ge–P bonds) as well as highest occupied (representing mainly a combination of the lone pair of electrons of the Ge atoms derived from divalent Ge) molecular orbital in **1**.



1 **2**

Fig. 4 Representation of compounds **1** and **2** with dative bonds.

As in **1**, the total formal negative charges to be compensated for the electron precise compound **2** amount to −14. Due to the neutrality of the overall cage the two Ge1 as well as the two Ge3 atoms can be assigned to oxidation state +2, the Ge2 atoms to 0 and the two Ge4 atoms to +3 (see Fig. 4). The NBO analysis also reveals that in **2** the Ge1 and Ge2 atoms possess a lone pair of electrons and arise from a divalent Ge whereas the Ge3 and Ge4 atoms carrying halide substituents result from a tetravalent Ge (see ESI‡). Furthermore, the natural charge distribution in **2** shows a positive charge accumulation on the four different types of Ge atoms (Ge1: 0.23, Ge2: 0.17, Ge3: 0.33 and Ge4: 0.49) whereas the phosphorus atoms are neutral or slightly negatively charged (0 as well as −0.13).

In summary we have shown that by using the monolithiated phosphine LiHP*t*Bu a novel synthetic approach to new mixed-valence germanium/phosphorus cage compounds was obtained. In contrast to previously employed procedures in group 14/15 element cluster chemistry, here incomplete halide exchange leads to cage compounds in which the germanium atoms reveal three different oxidation states. The low solubility of the products is probably the driving force for their formation. The previously used synthetic approach employed *i*Pr$_3$Si as substituents at the phosphines which led to the formation of soluble products in high yields. In contrast, the use of the smaller *t*Bu group at phosphorus in the present case is responsible for the formation on one side of a mixture of products, but on the other side—due to their low solubility—of the observed, structurally unprecedented mixed-valence products.

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