Heteroborates

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Synthesis and Characterization of Digerma-*closo*-dodecaborate: A Higher Homologue of Icosahedral *ortho*-Carborane**

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Dedicated to Professor Ekkehard Lindner on the occasion of his 75th birthday

When published in 1990, 1,2-dimethyl-1,2-disila-*closo*-dodecaborane[1] was the first higher homologue of the famous icosahedral *ortho*-carbaborane in terms of Group 14 diheteroboranes and borates. *Ortho*-carbaborane had been synthesized 30 years earlier in 1963 from decaborane and acetylene.[2] Because the triple-bond compounds of silicon, germanium, and tin are not available for chemical synthesis, simple adaptation of this method was not possible.[3] The silicon vertices were incorporated into the decaborane skeleton in one step using bis(dimethylamino)methylsilane, $(Me_2N)_2SiHMe$. In 2006, the dianionic distanna-*closo*-dodecaborate was prepared in a two-step synthesis.[4] In a simple one-pot procedure with decaborane, tin(II) chloride, proton sponge, and triethylamine, the dimeric *closo*-cluster 2,2′-bis(1,2-distanna-*closo*-dodecaborate) was isolated as an intermediate. By varying the addition of the reaction partners, the ions $[7\text{-Cl-}7\text{-SnB}_{10}H_{12}]^-$ and $[7,7'\text{-}(SnB_{10}H_{12})_2]^{2-}$ could be isolated as well. Cleavage of the intercluster Sn–Sn bond by $K[HBEt_3]$ in THF gave the desired dianionic compound 1,2-distanna-*closo*-dodecaborate as its potassium salt. After cation exchange with any common ammonium countercation, the cluster was reprecipitated in aqueous solution. We now introduce the missing germanium analogue with an unprecedented product formation that depends on the kind of base used in the first step.

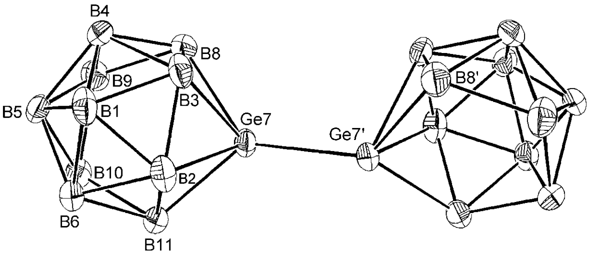
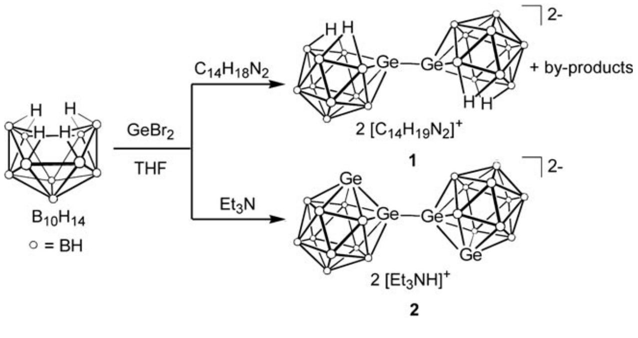


Figure 1. Structure of the dianion of **1** (ORTEP plot, hydrogen atoms omitted, 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ge7–Ge7′ 2.4005(6), B11–Ge7 2.148(3), B8–Ge7 2.142(3), B3–Ge7 2.163(3), B2–Ge7 2.174(3), B8-Ge7-Ge7′ 129.76(9), B3-Ge7-Ge7′ 104.52(9), B11-Ge7-Ge7′ 128.40(9), B8-Ge7-Ge7′-B8′ 23.811(5).

By applying the same synthetic route as used in the synthesis of the 1,2-distanna-*closo*-dodecaborate, the corresponding dimeric *closo*-compound of germanium could not be isolated quantitatively. A product mixture was obtained instead. By layering an acetone solution with hexane, crystals of 7,7′-bis(7-germa-*nido*-undecaborate) (**1**) were obtained in a yield smaller than 5% (Figure 1).[5] Moreover, the ions $[B_{10}H_{13}]^-$, $[7\text{-Cl-}7\text{-GeB}_{10}H_{12}]^-$ (the iodogermaborate is already known from a simple salt elimination reaction of deprotonated decaborane and GeI_2 in THF[8]), and the expected product $[(Ge_2B_{10}H_{10})_2]^{2-}$ could be identified by $^{11}B\{^1H\}$ NMR spectroscopy. Dropwise addition of triethylamine to a mixture of germanium(II) bromide and decaborane in THF at room temperature gave **2** within three hours. After removal of $[Et_3NH]Br$ by filtration, the THF solution of the cluster could be used without further workup. The change of base from proton sponge to triethylamine in THF led to the unprecedented formation of the desired dimeric compound $[(Ge_2B_{10}H_{10})_2]^{2-}$ in good yields (Scheme 1).

This reaction and the formation of the *nido*-product proceed with electron transfer. Germanium withdraws electrons to form the Ge–Ge bonds, and in theory elemental bromine is formed, because no further boron-containing species are observed. The same problem could not be solved in the case of the tin analogue.



Scheme 1. Formation of $[C_{14}H_{19}N_2]_2[(GeB_{10}H_{12})_2]$ (**1**) and $[Et_3NH]_2[(Ge_2B_{10}H_{10})_2]$ (**2**) from the reaction of decaborane and $GeBr_2$ using different bases.

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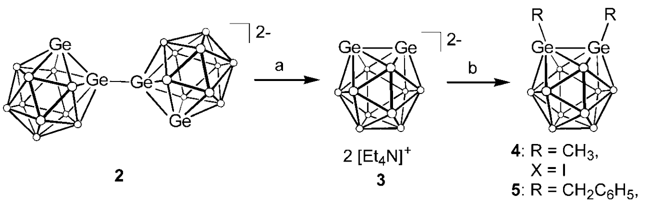
By adding a THF solution of the crude product **2** dropwise to a suspension of sodium hydride in THF, the Ge–Ge bond is reductively cleaved to form $Na_2[Ge_2B_{10}H_{10}]$, and the triethylammonium counterion is deprotonated and evolves hydrogen gas. Filtering off the excess sodium hydride gave a clear, slightly yellowish solution in THF. After removal of the solvent in vacuo and subsequent redissolution of the residue in water, the cluster can be precipitated with any common water-soluble ammonium counterion (Scheme 2). The colorless solids are much less air-sensitive than the tin analogues $[Sn_2B_{10}H_{10}]^{2-}$, which undergo immediate decomposition to $[B_{10}H_{10}]^{2-}$ and tin oxides when exposed to air. Digermaborate **3** can be stored under a moisture-free argon atmosphere for months without any loss of quality. To date, we were not able to isolate crystals of the dianion **3** suitable for single crystal structure analysis.



Scheme 2. a) Cleavage of the Ge–Ge bond with NaH and cation exchange leading to the monomeric 1,2-digerma-*closo*-dodecaborate $[Et_4N]_2[Ge_2B_{10}H_{10}]$; conditions: 1) NaH, THF, 2) $[Et_4N]Br$, H_2O; b) Formation of the disubstituted neutral clusters **4** and **5** with excess methyliodide and benzylbromide, respectively; conditions: RX, benzene.

The dimeric germaborate $[(Ge_2B_{10}H_{10})_2]^{2-}$ could be isolated in good yields and fully characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and crystal structure determination. The $^{11}B\{^1H\}$ NMR spectrum shows resonances with an intensity ratio of 1:1:2:2:2:2, consistent with C_{2v} symmetry of the cluster unit. No assignment could be made owing to the short T_1 relaxation times (2.5–5.9 ms) of the boron atoms. In the ESI-MS spectrum, the dimeric cluster with three counterions was detected as a cation in the positive mode and with only one counterion as an anion in the negative mode. Slow evaporation of an acetone solution gave colorless crystals suitable for X-ray crystal structure determination (Figure 2).[9] The cluster shows a rotational disorder around the Ge1–Ge1a bond such that Ge atoms 2a and 2b are approximately 63.7° apart. The disorder only applies to this cage. The refinement gave two orientations in which the two cluster fragments are twisted around the Ge1–Ge1a axis. According to the refinement of the crystal structure, the conformers exist in a 84:16 ratio. An analogous bis(cluster) structure $[(E_2B_{10}H_{10})_2]^{2-}$ is also known for E = C and Sn,[4] whereas the bis(*o*-carbaborane) compound is synthesized as a neutral molecule $(C_2B_{10}H_{12})_2$ from either $B_{10}H_{12}\cdot 2L$ ($L = SEt_2$, CH_3CN) and HC≡C–C≡CH or by a coupling reaction of dilithiocarbaborane and CuCl or $CuCl_2$.[10] The intercage E1–E1a bond of all these compounds is significantly shorter than the intracage E2–E1 bond, and both lengths increase with atom size. They range from 1.530(3) (E1–E1a), 1.690(3) Å (E2–E1) for the carbon analogue to 2.3639, 2.469 and 2.7240(4), 2.795 Å for the germanium and tin compounds, respectively. The same tendency was found in the E–B bond lengths, which increase from 1.724 (average C–B bond length in $C_4B_{20}H_{22}$) to 2.211 (average Ge–B in **2**) and 2.439 Å (average Sn–B in $[Et_3NH]_2[(Sn_2B_{10}H_{10})_2]$). In particular, the unsubstituted heteroatom of the germanium and tin compounds exhibit E–B bonds (E2–B3 and E2–B6) that are much longer than the remaining E–B bonds (by 0.248 Å in **2** and 0.321 Å in $[Et_3NH]_2[(Sn_2B_{10}H_{10})_2]$). The average Ge–B bond length (2.211 Å) in **2** is almost identical with that in the iodogermaborate $[7\text{-}I\text{-}7\text{-}GeB_{10}H_{12}]^-$ (2.214 Å) published by Gaines and co-workers[8] but is slightly greater than in the *nido*-compound **1** (2.157 Å). A further structural change is the E2-E1-E1a bond angle, which increases according to the atom size (C-C-C 116.99(18)°, Ge-Ge-Ge 126.47(4)°, Sn-Sn-Sn 153.57(1)°). The torsional angles of the E-E-E-E unit are 91.816(17)° and 170.286(14)° for the two germanium conformers and 145.12(2)° for the tin analogue. The Ge7–Ge7′ bond in **1** and the Ge2–Ge1 and Ge1a–Ge2a bonds within the cluster **2** are 2.4005(6), 2.4656(8), and 2.4739(11) Å, typical of Ge–Ge single bonds, whereas the intercluster Ge1–Ge1a bond is 2.3639 Å and therefore remarkably shorter.[11]

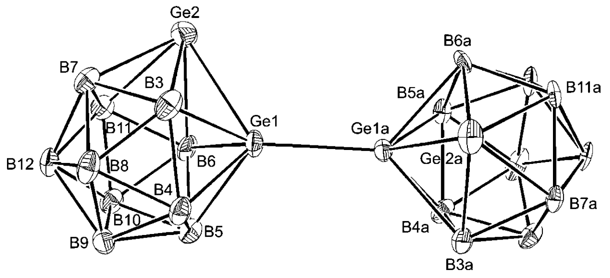


Figure 2. Structure of the dianion of **2** (ORTEP plot, hydrogen atoms omitted, 50% probability ellipsoids). Only the conformer with 84% existence is shown, the second structure exists to 16% and was refined isotropically except for the germanium atoms. Selected bond lengths [Å] and angles [°]: Ge1–Ge1a 2.3639, Ge2–Ge1 2.4656(8), Ge2a–Ge1a 2.4739(11), Ge2–B3 2.3914(17), Ge2–B7 2.1867(16), Ge2–B11 2.1822(17), Ge2–B6 2.4028(17), Ge1–B3 2.1371(16), Ge1–B6 2.1651(16), Ge1–B5 2.1164(17), Ge1–B4 2.1066(16), Ge2a–B3a 2.4094, Ge2a–B7a 2.1891 Ge2a–B11a 2.1948, Ge2a–B6a 2.3971, Ge1a–B3a 2.1752, Ge1a–B6a 2.1473, Ge1a–B5a 2.1149, Ge1a–B4a 2.1311, Ge2-Ge1-Ge1a 126.47(4), Ge1-Ge1a-Ge2a 129.4, Ge2-Ge1-Ge1a-Ge2a 91.6.

According to the C_{2v} symmetry, the monomeric cluster $[Ge_2B_{10}H_{10}]^{2-}$ exhibits four signals in the $^{11}B\{^1H\}$ NMR spectrum. Using ^{11}B–^{11}B COSY NMR spectroscopy, six of the ten boron atoms could be unambiguously assigned. In the ESI MS spectrum the cluster associated with three counterions was detected as a cation in the positive mode, and without any counterion as monoanion in the negative mode.

It is known that the monoheteroborates $[EB_{11}H_{11}]^{2-}$ (E = Ge, Sn) can be easily methylated in acetonitrile using methyliodide to form the heteroatom-substituted monoanion.[12] Applying this approach to the diheteroborates, a neutral disubstituted cluster similar to $[Me_2Si_2B_{10}H_{10}]$ would be expected. Adding excess alkylating agent to a suspension of **3** in benzene led to a benzene-soluble product (Scheme 2).

Filtering off the ammonium halide precipitate as well as degradation products and removing all volatile materials in vacuo gave the dialkylated cluster **4** and **5** as colorless solids. The compounds are air-stable as solids and even in solution.

The $^{11}B\{^1H\}$ NMR spectrum of **4** shows three signals with an intensity ratio of 4:4:2. Compared to the spectrum of the dianion, these signals are shifted to upfield. On the basis of the molecular symmetry, four signals (2:2:2:4) would be expected. A ^{11}B–^{11}B COSY NMR experiment allows a definite assignment of the ten boron atoms to the three observed signals at $\delta = -11.4$, -14.7, and -16.3 ppm in the $^{11}B\{^1H\}$ NMR spectrum. The boron-decoupled $^1H\{^{11}B\}$ NMR spectrum exhibits the ten cluster protons in the desired 2:2:4:2 fashion. By an $^{11}B\{^1H\}$–^1H HETCOR NMR spectroscopy experiment, the boron signals could be correlated to the proton signals at $\delta = 3.5$, 2.8, 2.3, and 2.1 ppm. The remaining difficulty is that the four boron atoms (B3, B6, B9, B12) which correspond to the signal at $\delta = -11.4$ in the $^{11}B\{^1H\}$ NMR spectrum are not identical and therefore exhibit cross peaks to two different proton signals at $\delta = 3.5$ and 2.1 ppm. As they couple to all other boron atoms in the cluster, no assignment of the proton signals can be made on the basis of this spectral information. A ^1H–^1H NOESY NMR experiment allows an assignment, because the methyl protons correlate to the protons at B3 and B6 rather than to the protons at B9 and B12 on the antipodal position. This experiment, together with the assumption that heteroatom bridged B–B contacts show weak cross peaks in the ^{11}B–^{11}B COSY NMR spectrum, argues for the following assignment: BH9, BH12: $^{11}B\{^1H\}$ NMR $\delta = -11.3$ ppm, $^1H\{^{11}B\}$ NMR $\delta = 2.1$ ppm; BH3, BH6: $^{11}B\{^1H\}$ NMR $\delta = -11.6$ ppm, $^1H\{^{11}B\}$ NMR $\delta = 3.5$ ppm. The methyl group resonance was observed at $\delta = 0.5$ ppm in the ^1H NMR spectrum and at $\delta = -4.6$ ppm in the ^{13}C NMR spectrum.

The EI mass spectra show the mass peaks of **4** and **5** as well as the fragments with only one or no R group, having the correct isotope pattern. Single crystals of **4** and **5** were grown by slow evaporation of benzene solutions (Figure 3).[13] The digermaborane **4** crystallizes with one benzene molecule between the C1-Ge1-Ge2-C2 units of two clusters. The bond lengths and angles of **4** and **5** are similar, therefore only the structure of the methylated cluster is discussed (the crystal structure and experimental data of **5** is given in the Supporting Information). The Ge–Ge bond length (2.3974(8) Å) and the average Ge–B bond length (2.159 Å) are slightly smaller than in the dimeric compound **2** (Ge–Ge 2.469, Ge–B 2.216 Å). The Ge–C bond (1.924(6) Å is in a typical range for Ge–C single bonds.[11b,c] The C1-Ge1-Ge2 angle (132.14(19)°) is similar to the Ge2-Ge1-Ge1a angle in **2** (126.47(4)°). This neutral disubstituted cluster geometry is also known for the carbon and silicon analogues. The bonds between the heteroelements E are similar to typical single bonds. The individual bond lengths are 1.566(12) (C–C in 1,2-Me_2-1,2-$C_2B_{10}H_{10}$),[14] 2.308(2) (Si–Si in 1,2-Me_2-1,2-$Si_2B_{10}H_{10}$) and 2.3974(8) Å in the corresponding germanium compound **4**. Moreover, the E–B bond lengths increase from the carbaborane (1.669 Å) to the sila- (2.087 Å) and germaborane (2.159 Å). The more the sizes of the atoms in the cluster differ, the more distorted is the icosahedral structure, influencing in particular the distinct E–B distances.

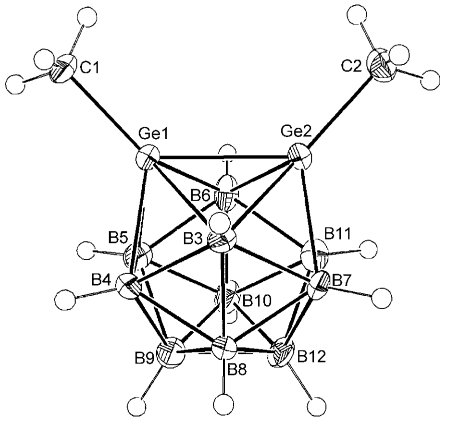


Figure 3. Structure of the neutral cluster **4** (ORTEP plot, 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ge1–Ge2 2.3974(8), Ge1–C1 1.924(6), Ge1–B3 2.219(6), Ge1–B4 2.091(6), Ge1–B5 2.098(7), Ge1–B6 2.226(7), C1-Ge1-Ge2 132.14(19).

Theoretical work on *nido*- and *closo*-germaboranes and borates has been done by Hofmann and Kiani, indicating that, amongst others, the *ortho*-$Ge_2B_{10}H_{12}$ is preferred by 2.4 kcal mol^{-1} compared to the *para* isomer.[15] In agreement with these results, no isomerization of **4** in toluene at reflux was observed.

The series of the Group 14 diheteroboranes and borates could now be extended to the germanium compound. It exists as a dianion, in analogy to the tin cluster, and is synthesized from the corresponding reaction intermediate, the dimeric $[(E_2B_{10}H_{10})_2]^{2-}$ ion. Furthermore, it can be disubstituted to a neutral monomeric cluster similar to the existing carbon and silicon analogues. Similarities in reactivity, chemistry, and application, as well as the comparison of our results with the theoretical outcomes, are now under investigation.

Experimental Section

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were purified by established methods and stored under argon. The ESI mass spectrometry measurements were recorded in positive- and negative-ion mode using a Bruker esquire 3000^{plus} spectrometer equipped with an ESI interface. The EI mass spectrometry measurements were done using a Finnigan MAT TSQ 70 spectrometer. NMR spectra were recorded using a Bruker DRX250 and a Bruker Avance II + 500 NMR spectrometer. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Tübingen using a Vario EL analyzer.

2: Triethylamine (0.75 mL, $\rho = 0.726$ g cm^{-3}, 5.381 mmol) was added dropwise to a solution of decaborane (154.5 mg, 1.264 mmol) and germanium(II) bromide (590.4 mg, 2.540 mmol) in THF (40 mL). After stirring for 24 h, the solvent was evaporated in vacuo. The residue was dissolved in acetone and filtered. Slow evaporation of the solvent yields colorless plates of $[NHEt_3]_2[(Ge_2B_{10}H_{10})_2]$ (73.2 mg, 16%). $^{11}B\{^1H\}$ NMR (80 MHz, [D$_6$]acetone): $\delta = -1.7$ (1B), -2.4 (1B), -5.2 (2B), -8.0 (2B), -8.7 (2B), -11.6 ppm (2B); MS (ESI, CH_3CN): *m/z*: 833.4 $\{[NHEt_3]_3[(Ge_2B_{10}H_{10})_2]\}^+$, 528.0 $\{[NHEt_3][(Ge_2B_{10}H_{10})_2]\}^-$; elemental analysis (%) calcd for $C_{12}H_{52}B_{20}Ge_4N_2$: C 19.71, H 7.17, N 3.83; found: C 20.08, H 7.16, N 3.83.

3: A THF solution (40 mL) of the raw product **2** (starting from 154.5 mg decaborane) was added dropwise to a suspension of sodium hydride (242.7 mg, 10.11 mmol) in THF (10 mL). The mixture turned dark brown and the evolving hydrogen gas was allowed to escape through a bubbler. The mixture was filtered through Celite and washed with THF (3 × 5 mL), and solvent was removed from the filtrate in vacuo. The light yellow residue was dissolved in water (20 mL) and added to a solution of [Et$_4$N]Br (slight excess) in water (5 mL). The colorless precipitate was collected by filtration, washed with diethyl ether, and dried in vacuo to give **3** as a colorless powder (384.2 mg, 58 % based on $B_{10}H_{14}$). $^{11}B\{^1H\}$ NMR (80 MHz, [D$_7$]DMF): $\delta = 1.4$ (2B), -0.3 (2B), -3.8 (4B; B4, B5, B7, B11), -8.8 ppm (2B; B8, B10); $^1H\{^{11}B\}$ NMR (250 MHz, [D$_7$]DMF): $\delta = 3.4$ (q, $J = 7.3$ Hz, 16H; NCH_2), 3.1 (s, 2H; BH), 2.1 (s, 4H; BH), 1.3 (t, $J = 7.3$ Hz, 24H; NCH_2CH_3), 1.2 ppm (2H; BH); $^{13}C\{^1H\}$ NMR (63 MHz, [D$_7$]DMF): $\delta = 52.4$ (NCH_2), 7.4 ppm (NCH_2CH_3); MS (ESI, CH_3CN): m/z: 363.6 $\{[Ge_2B_{10}H_{10}]\}^-$, 654.4 $\{[NEt_4]_3[Ge_2B_{10}H_{10}]\}^+$; elemental analysis (%) calcd for $C_{14}H_{36}B_{10}Ge_2N_2$: C 33.91, H 9.35, N 5.65; found: C 32.35, H 9.15, N 4.44. Even after a series of elemental analyses from samples with different ammonium countercations, no better correspondence was achieved.

4: Methyliodide (0.178 mL, $\rho = 2.27\ \mathrm{g\,cm^{-3}}$, 2.863 mmol) was added in one portion to a suspension of **3** (150 mg, 0.286 mmol) in benzene (20 mL). The mixture was stirred for 11 h and filtered, and the solvent as well as the excess alkylating agent were removed from the filtrate in vacuo (123 mg, 82 %). Colorless crystals suitable for X-ray analysis were obtained by slow evaporation of a benzene solution. $^{11}B\{^1H\}$ NMR (160 MHz, [D$_6$]benzene): $\delta = -11.4$ (4B; B3, B6, B9, B12), -14.7 (2B; B8, B10), -16.3 ppm (4B; B4, B5, B7, B11); $^1H\{^{11}B\}$ NMR (500 MHz, [D$_6$]benzene): $\delta = 3.5$ (s, 2H; BH3, BH6 or BH9, BH12), 2.8 (s, 2H; BH8, BH10), 2.3 (s, 4H; BH4, BH5, BH7, BH11), 2.1 (s, 2H; BH3, BH6 or BH9, BH12), 0.5 ppm (s, 6H; CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, [D$_6$]benzene): $\delta = -4.6$ ppm (CH_3); MS (EI): m/z: 293.1 $\{(CH_3)_2Ge_2B_{10}H_{10}\}^+$; elemental analysis (%) calcd for $C_2H_{16}B_{10}Ge_2$: C 8.19, H 5.50; found: C 10.09, H 5.98. Despite the fact that the samples were dried in vacuo for days, the benzene molecule which crystallizes within the cluster structure could not be removed completely.

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Keywords: boranes · cluster compounds · germanium · heteroborates · structure elucidation

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[5] For all structure determinations: crystals were studied at 173(2) K using a STOE IPDS 2T diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Crystal data for **1**: $C_{28}H_{62}B_{20}Ge_2N_4$, $M_r = 816.20$, monoclinic, space group $C2/c$ (no. 15); $a = 27.0248(17)$, $b = 10.2329(6)$, $c = 17.3238(13)$ Å, $\beta = 113.420(5)°$, $V = 4396.1(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.233\ \mathrm{g\,cm^{-3}}$, $\mu(Mo_{K\alpha}) = 1.395\ \mathrm{mm^{-1}}$, $F(000) = 1687.5$; 15909 reflections with $11.4 < 2\theta < 52.8°$, 4261 independent reflections in structure solution and refinement of 268 parameters;[6] $R_1 = 0.056$, $wR_2 = 0.089$; numerical absorption correction based on an optimized crystal shape;[7] all hydrogen atoms were either placed in calculated positions or found and isotropically refined. CCDC 736392 (**1**), 736393 (**2**), 736394 (**4**) and 736395 (**5**) contain 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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[9] Crystal data for **2**: $C_{12}H_{52}B_{20}Ge_4N_2$, $M_r = 731.12$, triclinic, space group $P\bar{1}$ (no. 2); $a = 8.8217(13)$, $b = 13.9030(19)$, $c = 14.846(2)$ Å, $\alpha = 66.553(10)$, $\beta = 83.605(12)$, $\gamma = 87.445(11)°$, $V = 1660.1(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.463\ \mathrm{g\,cm^{-3}}$, $\mu(Mo_{K\alpha}) = 3.597\ \mathrm{mm^{-1}}$, $F(000) = 732$; 30992 reflections with $6.4 < 2\theta < 58.6°$, 8949 independent reflections in structure solution and refinement of 329 parameters and 92 restraints (comments on the disorder and its refinement are given in the cif file); $R_1 = 0.0701$, $wR_2 = 0.1066$.

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[13] Crystal data for **4**: $C_5H_{19}B_{10}Ge_2$, $M_r = 332.48$, monoclinic, space group $P2_1/c$ (no. 14); $a = 7.0490(7)$, $b = 14.3378(16)$, $c = 14.0978(16)$ Å, $\beta = 94.741(9)°$, $V = 1419.9(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.555\ \mathrm{g\,cm^{-3}}$, $\mu(Mo_{K\alpha}) = 4.193\ \mathrm{mm^{-1}}$, $F(000) = 575.7$; 17979 reflections with $11.4 < 2\theta < 52.8°$, 2814 independent reflections in structure solution and refinement of 139 parameters and 2 restraints; $R_1 = 0.071$, $wR_2 = 0.111$.

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