A Direct Route to Halogenated Arsaborane Clusters: Crystal Structure of 3,4,5,6-Tetrachloro-1,2-diarsa-*closo*-hexaborane(4)☆

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Copyrolysis of B_2Cl_4 and $AsCl_3$ at 330 °C leads to the formation of *closo*-1,2-$As_2B_4Cl_4$ (**1**) and further products the mass spectral evidence of which suggests that they are perchlorinated arsaboranes $As_2B_5Cl_5$, $As_4B_8Cl_6$, and $As_2B_{10}Cl_{10}$. The pyrolysis temperature and the molar ratio of the reactants exert an essential influence on the type and distribution of the products. At temperatures above 400 °C and higher $B_2Cl_4/AsCl_3$ ratios the formation of $As_2B_{10}Cl_{10}$ is preferred to that of smaller arsaboranes. A single-crystal X-ray study of **1** confirmed that, consistent with its 14-skeletal electron count, the arsaborane adopts a slightly distorted octahedral structure with the arsenic atoms in adjacent *cis* positions.

There are only very few boranes known so far containing two arsenic atoms in the polyhedral framework. They were synthesized by a reaction involving two arsenic insertions into decaborane in the presence of a base to yield *closo*-1,2-$As_2B_{10}H_{10}$[1,2]. Derived thereof are *closo*-1,2-$As_2B_{10}H_8I_2$[3] and *nido*-7,8-$As_2B_9H_{10}^-$[1]. However, aside from 11- or 12-vertex arsaboranes there are no examples where arsenic atoms are part of frameworks deriving from smaller boron compounds.

In this paper we report on the first direct method of combining arsenic and boron species starting from molecules with 2-center 2-electron bonds to yield several previously unknown small- and medium-sized polyhedral diarsaboranes with chlorine ligands attached to the boron atoms.

Results and Discussion

Recently, we have reported on the thermal disproportionation of tetrahalodiboranes(4) B_2X_4 in the presence of the coreactants PX_3, CX_4, or C_2X_4 (X = Cl, Br). Stable polyhedral heteroboranes such as *closo*-1,2-$P_2B_4Cl_4$[4] (**2**), *closo*-1,2-$P_2B_4Br_4$[5], and $C_2B_nX_{n+2}$ (n = 5−8)[6] could be obtained in case the reaction took place in the vapor phase. In order to apply this method to the preparation of heteroboranes aside from phospha- and carbaboranes we studied the copyrolyses of B_2Cl_4 with various other volatile main group halides.

Preliminary attempts to prepare arsaboranes via copyrolysis of B_2Cl_4 with $AsCl_3$ under corresponding conditions in a single-flask reactor failed. Thereby trichloroarsane is reduced almost quantitatively by tetrachlorodiborane(4) to elemental arsenic and trichloroborane (eq. 1). This redox reaction already occurs in the mixture at room temperature.

$$2\,\mathrm{AsCl_3} + 3\,\mathrm{B_2Cl_4} \longrightarrow 2\,\mathrm{As} + 6\,\mathrm{BCl_3} \qquad (1)$$

$$2\,\mathrm{AsCl_3} + 7\,\mathrm{B_2Cl_4} \longrightarrow \underset{\mathbf{1}}{\mathrm{As_2B_4Cl_4}} + 10\,\mathrm{BCl_3} \qquad (2)$$

However, if B_2Cl_4 and $AsCl_3$ are condensed into two separate flasks which are connected by a tube, and the reactants are transferred into a preheated oven immediately after sealing, simultaneous vaporization and pyrolysis partly suppress the redox reaction to give new arsaborane clusters. The reaction mixture can be sublimed fractionally. The components were identified by mass spectrometry as $As_2B_4Cl_4$ (**1**), B_9Cl_9, $As_4B_8Cl_6$, and − only in traces − as $As_2B_5Cl_5$. The remaining low-volatile residue contains $As_2B_{10}Cl_{10}$ and elemental arsenic.

The formation of $As_2B_{10}Cl_{10}$ is favored compared to smaller arsaboranes when the pyrolysis is performed at higher temperatures. By increasing both the molar ratio $B_2Cl_4/AsCl_3$ to 3:1 and the temperature to 450 °C $As_2B_{10}Cl_{10}$ was the only detectable arsaborane after work-up as described above and subsequent extraction of the low-volatile residue with chloroform.

Molecular Structure of $As_2B_4Cl_4$ (1)

According to Wade's rules[7] **1** should adopt an octahedral geometry based on its skeletal electron count n = 14. This prediction was confirmed by the spectroscopic and X-ray crystal data. As a consequence of the large covalent radius of arsenic there is a stronger distortion of the octahedron compared to the homologous phosphaborane *closo*-1,2-$P_2B_4Cl_4$ (**2**)[4]. The As−As distance (244.2 pm) is approximately equivalent to a single-bond length defined by Pauling (242 pm[8]) while the opposite (antipodal) B2−B4 edge (169.2 pm) is remarkably shorter compared not only to the other B−B distances (173.6−175.1 pm) in the cluster but also to regular octahedral *closo*-hexaborates $B_6Cl_6^{2-}$ (171.3−171.9 pm[9]) or $B_6H_6^{2-}$ (172.3 pm[10]). Analogously, such a cross-cage effect of heteroatoms on antipodal cluster-boron atoms was also observed with the diphosphahexaborane **2**[4].

Likewise, the heteroatoms of **1** as of **2** and almost all known heteroboranes containing two group 15 atoms are in adjacent cis position in the clusters. In contrast to 1,2-$P_2B_{10}H_{10}$ which isomerizes to 1,7-$P_2B_{10}H_{10}$ upon heating at 590 °C[11], no 1,6-diarsahexaborane was detected. For the homologous diphospha-*closo*-hexaboranes $P_2B_4X_4$ (X = H, Cl) ab initio studies support the higher stability of the 1,2- compared with the 1,6-position of the P

[+] Single-crystal X-ray structure determination.

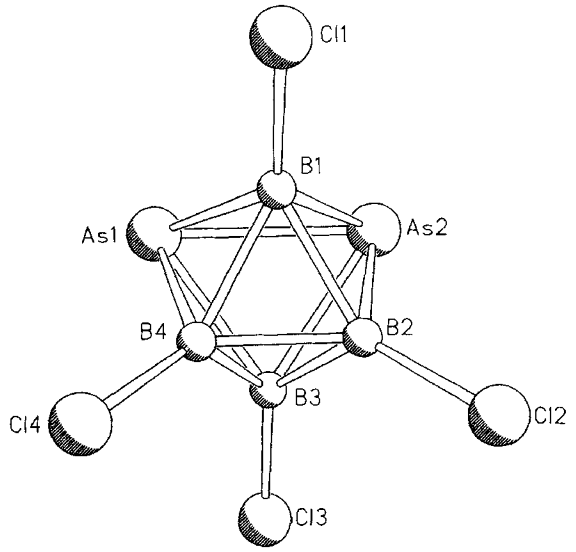

Figure 1. Molecular structure of **1**

Selected bond lengths [pm] and angles [°]: As1–As2 244.2(1), As1–B1 215.3(7), As1–B3 214.2(4), As1–B4 211.4(4), As2–B1 214.8(6), As2–B2 210.0(5), As2–B3 216.4(6), B1–B2 174.6(6), B1–B4 175.1(9), B2–B3 174.6(9), B2–B4 169.2(9), B3–B4 173.6(8), B–Cl 175.4(6)–176.7(6); As1–As2–B2 79.8(2), As2–As1–B4 79.7(2), As1–B4–B2 99.8(3), As2–B2–B4 100.7(3), B1–As1–B3 72.7(2); B1–As2–B3 72.4(2), B1–B2–B3 93.6(4), B1–B4–B3 93.8(4).

atoms (approximately 2 kcal/mol for X = H and 9 kcal/mol for X = Cl)[12].

Further New Arsaboranes

Specific conditions during the copyrolysis of B_2Cl_4 and $AsCl_3$ resulted in the formation of compounds which gave mass spectral evidence for arsaboranes with formulas $As_4B_8Cl_6$ and $As_2B_{10}Cl_{10}$ along with traces of $As_2B_5Cl_5$.

$As_4B_8Cl_6$ can be interpreted as a *conjuncto*-borane $(As_2B_4Cl_3)_2$ with two boron-boron-linked As_2B_4 octahedrons, while $As_2B_{10}Cl_{10}$ should have an icosahedral structure analogous to 1,2-$As_2B_{10}H_8I_2$[3] and 1,2-$As_2B_{10}H_{10}$[1,2].

$As_2B_{10}Cl_{10}$ represents the first example of a heteroborane containing group 15 atoms where the molecule can exist both with *all*-hydrogen or *all*-chlorine ligands. The stability of these two dodecaboranes $As_2B_{10}X_{10}$ shows that electronegativity and binding orbitals of the ligands X are not the only determining factor for the stability of these clusters.

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Experimental

All experiments were carried out by using standard high-vacuum or inert-gas techniques as described by Shriver[13]. Trichloroborane was purified by vacuum fractionation. Tetrachlorodiborane(4) was prepared by the method described by Timms[14]. $AsCl_3$ was freshly distilled before use. All solvents were of reagent grade, dried, and purified by literature methods.

^{11}B NMR: Bruker WM-250 at 80.253 MHz with external $BF_3 \cdot OEt_2$ ($\delta = 0.0$) as standard in $CDCl_3$. – MS: Varian-MAT 311 A (70 eV).

X-ray structure determination[15]: **1**: $As_2B_4Cl_4$, $M = 334.9$, colorless needles, $0.1 \times 0.2 \times 0.25$ mm^3, triclinic, space group $P\bar{1}$, $T = 153$ K, $a = 6.862(1)$, $b = 7.134(1)$, $c = 10.692(2)$ Å, $V = 437.3(2)$ Å^3, $\alpha = 99.42(3)$, $\beta = 99.44(3)$, $\gamma = 118.19(3)°$, $Z = 2$, $d_{calc.} = 2.543$ g cm^{-3}, $\mu(MoK_\alpha) = 8.772$ mm^{-1}; $\lambda = 0.71073$ Å, Siemens R3m/V diffractometer, graphite monochromator, ω-scan, 2θ range = 7.0–45.0°, 2121 independent reflections, 1868 reflections were observed [$F > 3.0\,\sigma(F)$], structure solved by direct methods, semiempirical absorption correction, maximal transmission 0.925, minimal transmission 0.470, 91 parameters refined, $R = 0.0299$, $Rw = 0.0334$, largest difference peak 0.74 eÅ^{-3}, program: SHELXTL PLUS (PC version).

3,4,5,6-Tetrachloro-1,2-diarsa-closo-hexaborane(4) (**1**): $AsCl_3$ (300 mg, 1.65 mmol) was condensed into a 250-ml round-bottom flask which was equipped with a seal constriction and a break-seal joint and which was connected via a tube with a 100-ml flask. B_2Cl_4 (940 mg, 5.75 mmol) was condensed into this second flask. After sealing the whole apparatus was heated in an oven at 330°C for 1 h and subsequently allowed to cool to room temp. over a period of 20 h resulting in a brown amorphous powder besides colorless and orange-red crystals. After evaporation of the volatile components at room temp. fractional sublimation of these crystals at approximately 100°C yielded $As_2B_4Cl_4$ (**1**), B_9Cl_9, $As_4B_8Cl_6$, and only traces of $As_2B_5Cl_5$. The remaining low-volatile residue contained $As_2B_{10}Cl_{10}$ and elemental arsenic. After repeated fractional sublimation 10–20 mg of **1** could be obtained as colorless crystalline needles. Based on idealized eq. (2), the yield for **1** was approximately 5%. – ^{11}B NMR ($CDCl_3$, 295 K): $\delta = 26.6$ ($h_{1/2} = 105$ Hz), 10.6 ($h_{1/2} = 108$ Hz) (Int. 1:1); – MS (70 eV); *m/z* (%): 336 [$^{75}As_2{}^{11}B_4{}^{35}Cl_3{}^{37}Cl$] (80), 253 [$^{75}As_2{}^{11}B_3{}^{35}Cl_2$] (6), 218 [$^{75}As_2{}^{11}B_3{}^{35}Cl$] (100) (calculated and found $^{10}B/^{11}B/^{35}Cl/^{37}Cl$-isotopic patterns are in good agreement). – **1** sublimes at approximately 40°C/0.001 Torr.

☆ Dedicated to Professor *Peter Paetzold* on the occasion of his 60th birthday.

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[15] Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-59003, the names of the authors, and the journal citation.

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