Synthesis of Halogenated Polyhedral Phosphaboranes. Crystal Structure of *closo*-1,7-$P_2B_{10}Cl_{10}$

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The 12-vertex *closo*-phosphaborane 1,7-$P_2B_{10}Cl_{10}$ (**1**) has been prepared in low yield from the pyrolysis reaction of B_2Cl_4 with PCl_3 at temperatures above 400 °C. A single-crystal X-ray structure determination of **1** (monoclinic space group $P2_1/n$ with $a = 9.239(2)$ Å, $b = 16.786(3)$ Å, $c = 15.739(3)$ Å, $\beta = 93.25(3)°$, and $Z = 4$) confirmed that, consistent with its 26 skeletal electron count, the phosphaborane adopts a distorted icosahedral structure with the phosphorus atoms in the 1,7-positions. Crystals of **1** contain toluene in a 1:1 molar ratio embedded between each P atom of neighboring cluster molecules. Alteration of the pyrolytic conditions resulted in the formation of the phosphaboranes $P_4B_8Cl_6$ (**2**) and $P_2B_8Cl_8$ (**3**), which were characterized spectroscopically. Copyrolysis of B_2Cl_4 with a mixture of PCl_3 and $AsCl_3$ at 450 °C generated the six-vertex arsaphosphaborane $AsPB_4Cl_4$ (**4**) and traces of the icosahedral arsaphosphaborane $AsPB_{10}Cl_{10}$. These compounds are examples of heteroboranes which contain two different group-15 atoms within a single molecule.

Introduction

Since the discovery of the first carboranes in 1962,[1] electron-counting rules[2] and isoelectronic/isolobal principles[3] have guided the syntheses of a wide range of boranes incorporating not only carbon but also other main group elements into their cluster frameworks.[4] Phosphorus-containing polyhedral boranes have been reported in quite a number, and the scope in structural diversity found for these compounds ranks the phosphaboranes among the most extensively developed classes of heteroboranes. Common examples are phosphaboranes[5] and -carboranes[6] in which the cage-inserted phosphorus atoms are attached to an exopolyhedral group and thereby donate four electrons to the cage-bonding. In contrast, *closo*-diphosphaboranes of the general formula $P_2B_nR_n$ are rare in which each phosphorus atom possesses an exopolyhedral lone pair of electrons and thus contributes three skeletal electrons.[7] They are of special interest since they can be seen as the phosphorus analogues of the *closo*-dicarboranes, and, in fact, the majority of the reports covering this type of compound deal with theoretical aspects related to their bonding[8] rather than with their reactivity. Examples include the trigonal bipyramidal type cage compounds $P_2(BNR_2)_3$ with the phosphorus atoms occupying the axial positions.[9] The 12-vertex parent *closo*-diphosphaborane 1,2-$P_2B_{10}H_{10}$ is known[10a] and can be converted by thermal isomerization to the meta isomer, 1,7-$P_2B_{10}H_{10}$[10a] or by degradation reaction to the anion $[7,8\text{-}P_2B_9H_{10}]^-$.[10b] In this laboratory we have synthesized the perhalogenated closo species 1,2-$P_2B_4X_4$ (X = Cl or Br) by copyrolysis of B_2X_4 and PX_3 at 330 °C[11a,b] and have established the structure of the chloro compound by single-crystal X-ray diffraction analysis.[11a] This synthetic approach has also led to the synthesis of new polyhedral boranes with carbon,[12] arsenic,[13a,b] antimony,[13b] sulfur,[13b] or selenium[14] occupying the heterovertices. We now report the extension of this method to the synthesis of several new perchlorinated phosphaboranes and mixed arsaphosphaboranes.

Experimental Section

Instrumentation. ^{11}B NMR (80.25 or 160.46 MHz) and ^{31}P NMR (101.26 or 202.46 MHz) spectra were recorded on a Bruker WM-250 and a Bruker AM 500. All ^{11}B chemical shifts were referenced to external $BF_3{\cdot}O(C_2H_5)_2$, ^{31}P chemical shifts to external 85% H_3PO_4 with

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a negative sign indicating an upfield shift. High- and low-resolution mass spectra were obtained on a Finnigan MAT 8230 (70 eV). GC−MS spectra were obtained on a Hewlett-Packard 5971. Each compound exhibited a strong parent envelope whose intensity pattern was consistent with the calculated spectrum based on natural isotopic abundances.

General Procedures and Materials. All manipulations were conducted using standard high-vacuum or inert atmosphere techniques as described by Shriver.[15] The solvents were reagent grade, dried and purified according to standard procedures. Phosphorus trichloride, arsenic trichloride, and boron trichloride were freshly vacuum-distilled before use. Diboron tetrachloride was prepared by cocondensation of BCl_3 with copper vapor onto cooled walls (−196 °C) of a reactor similar to that described by Timms.[16] After repeated fractionation, B_2Cl_4 exhibited a vapor pressure at 0 °C of 44 Torr.

Synthesis of *closo*-1,7-$P_2B_{10}Cl_{10}$ (1), $P_4B_8Cl_6$ (2), and $P_2B_8Cl_8$ (3). In a typical reaction, 4.9 g (30 mmol) of B_2Cl_4 and 1.03 g (7,5 mmol) of PCl_3 were condensed in vacuo into a 500 mL round-bottomed flask equipped with a seal constriction and a break-seal joint. After sealing, the flask was removed from the vacuum line and heated in an oven at 400 °C for 1 h. The flask was allowed to cool to room temperature over a period of 20 h, resulting in an ochre solid deposited on the walls and partly suspended in colorless liquid. After opening to the vacuum line, all volatile compounds were vacuum-evaporated at 0 °C and the remaining residue was extracted five times with 10 mL of BCl_3 into a separate 50 mL flask. The extractant BCl_3 was evaporated at 0 °C and the residue fractionated by sublimation in vacuo to give at $T_{subl} < 45$ °C 70 mg of $P_2B_4Cl_4$, at T_{subl} 45−85 °C 110 mg of a mixture containing $P_2B_4Cl_4$, $P_4B_8Cl_6$ (**2**), and $P_2B_8Cl_8$ (**3**), and after repeated fractionation at $T_{subl} > 85$ °C 60 mg of pure $P_2B_{10}Cl_{10}$ (**1**), each fraction as white solid. Data for **1** are as follows. Mp > 230 °C; MS, *m/z* (rel int): 524 (100, M^+); 407 (21, $[M - BCl_3]^+$); 290 (26, $[M - 2BCl_3]^+$). Exact mass calcd for $^{31}P_2{}^{11}B_{10}{}^{35}Cl_{10}$: 521.72911. Found: 521.73376. ^{11}B NMR (ppm, $CDCl_3$, 160.46 MHz): 7.6 (B5,12), 1.9 (B4,6,8,11), 0.7 (B9,10), −2.0 (B2,3). ^{31}P NMR (ppm, $CDCl_3$, 101.26 MHz): −123 ppm. Data for **2** are as follows. MS, *m/z* (rel int): 423 (100, M^+); 306 (17, $[M - BCl_3]^+$); 258 (27, $[M - P_2B_3Cl_2]^+$). Exact mass calcd for $^{31}P_4{}^{11}B_8{}^{35}Cl_6$: 421.78261. Found: 421.77611. ^{11}B NMR (ppm, rel int, $CDCl_3$, 160.46 MHz): 24.8 (3B), 15.9 (1B). ^{31}P NMR (ppm, $CDCl_3$, 101.26 MHz): −182 ppm. Data for **3** are as follows. MS, *m/z* (rel int): 432 (100, M^+); 350 (42, $[M - BCl_2]^+$); 315 (76, $[M - BCl_3]^+$). Exact mass calcd for $^{31}P_2{}^{11}B_8{}^{35}Cl_8$: 429.77279. Found: 429.77935. ^{11}B NMR (ppm, $CDCl_3$, 160.46 MHz): 8.7. ^{31}P NMR (ppm, $CDCl_3$, 101.26 MHz): −195 ppm.

Formation of *closo*-1,2-$AsPB_4Cl_4$ (4). B_2Cl_4 (1.11 g, 6.8 mmol) and a mixture of 0.12 g of PCl_3 (0.9 mmol) and 0.16 g (0.9 mmol) of $AsCl_3$ were condensed in vacuo into two separate 200 mL round-bottomed flasks connected by a tube. After sealing, the apparatus was held for 1 h at 450 °C and allowed to cool to room temperature over a period of 20 h. Workup was done as described above and gave a total of 50 mg of raw sublimate. Crystallization in an evacuated, sealed tube at 300 °C afforded, after slow cooling, orange crystals of B_9Cl_9 (15 mg) which could be separated from the amorphous, white solid containing $P_2B_4Cl_4$, $AsPB_4Cl_4$ (**4**), and $As_2B_4Cl_4$. Equal amounts of 15 mg each of $P_2B_4Cl_4$ and **4** could be separated by slow sublimation at 0 °C in vacuo from 5 mg of $As_2B_4Cl_4$ remaining as residue, but $P_2B_4Cl_4$ and **4** could not further be fractionated by sublimation at lower temperatures: −20 °C was too cold for sublimation, and very slow sublimation at −13 °C still afforded only both components in mixture. Appropriate conditions for thermal crystallization yielded crystals of $P_2B_4Cl_4$ and **4**, but the latter were not suitable for X-ray diffraction. Data for **4** are as follows. MS, *m/z* (rel int) 292 (100, M^+); 209 (5, $[M - BCl_2]^+$); 174 (85, $[M - BCl_3]^+$). Exact mass calcd for $^{75}As^{31}P^{11}B_4{}^{35}Cl_4$: 289.80799. Found: 289.81265. ^{11}B NMR (ppm, $CDCl_3$, 160.46 MHz): 24.8 (2B), 7.0 (2B). ^{31}P NMR (ppm, $CDCl_3$, 202.46 MHz): −169 ppm. The NMR data for the new phosphaboranes **1**−**4** are given in Table 1.

Table 1. NMR Data for Phosphaboranes **1**−**4**

compd	^{11}B, ppm (assgn or rel areas)	^{31}P, ppm
1,7-$P_2B_{10}Cl_{10}$ (**1**)	7.6 (B5,12), 1.9 (B4,6,8,11), 0.7 (B9,10), −2.0 (B2,3)	−123
$P_4B_8Cl_6$ (**2**)	24.8 (3B), 15.9 (1B)	−182
1,10-$P_2B_8Cl_8$ (**3**)	8.7	−195
1,2-$PAsB_4Cl_4$ (**4**)	24.8 (B4,6), 7.0 (B3,5)	−169

Table 2. Crystallographic Data for *closo*-1,7-$P_2B_{10}Cl_{10}\cdot C_6H_5CH_3$

empirical formula	$C_7H_8B_{10}Cl_{10}P_2$
fw	616.67
cryst size (mm)	0.38, 0.42, 0.20
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	9.239(2)
b, Å	16.786(3)
c, Å	15.739(3)
β, deg	93.25(3)
V, Å^3	2437.0(8)
Z	4
D_{calcd}, g cm^{-3}	1.681
T, °C	20
μ(Mo Kα), cm^{-1}	1.272
λ, Å	0.71073
$2\theta_{max}$, deg	56
no. of indep reflns	5893
no. of obsd reflns ($I > 2\sigma(I)$)	3431
R (obs)[a]	0.0670
R (all)	0.1276
R_w (obs)	0.1567
R_w (all)	0.1812
largest diff peak and hole, e/Å^3	0.12

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

X-ray Structure Determinaton of 1,7-$P_2B_{10}Cl_{10}$ (1). Crystals suitable for X-ray diffraction were obtained from a 30 mg sample of **1**, which initially was dissolved in 2 mL of toluene. After removal of the toluene in vacuo, 2 mL of *n*-pentane was added to the solid, which only scarcely dissolved. By slow evaporation of *n*-pentane at −10 °C under an argon stream, colorless crystals of **1**$\cdot C_6H_5CH_3$ precipitated within several days. Apparently, toluene exhibits specific lattice (electronic and/or steric) affinity toward **1**, leading to an appropriate molecular pattern suitable for crystal packing. The colorless crystals were sealed in thin-wall glass capillaries under an argon atmosphere. The unit cell parameters were acquired by least-squares refinement of the angles 2θ (18−24°) for 27 well-centered reflections collected at 20 °C on a Siemens P4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å; ω scan technique). The Siemens SHELXS-86 and SHELXL-93 software packages were used for solution by direct methods, refinement, and diagrams of the structure. Details of the data collection and structure determination are listed in Table 2.

Results and Discussion

New Phosphaboranes $P_2B_{10}Cl_{10}$, $P_4B_8Cl_6$, and $P_2B_8Cl_8$. Our initial study involved the thermal cage closure reaction of an approximately equimolar mixture of B_2Cl_4 and PCl_3 at 330 °C to the six-vertex phosphaborane $P_2B_4Cl_4$.[11a] The presence of ions in the mass spectrum indicative of $P_2B_5Cl_5$[11a] suggested that this synthetic approach might be applicable to the synthesis of larger phosphaborane cage systems. Following the thermal conversion of neat B_2Cl_4 to the *n*-vertex boron monochlorides B_nCl_n (n = 8−12) in which the size n and the distribution of products has been found to be sensitive to the temperature and time of reaction under thermolytic conditions, we have reexamined the copyrolysis of B_2Cl_4 with PCl_3 in a molar ratio of 5:1 at temperatures above 400 °C, i.e., by employing reaction conditions that should augment the amount of active BCl moieties and thus increase the probability of forming larger

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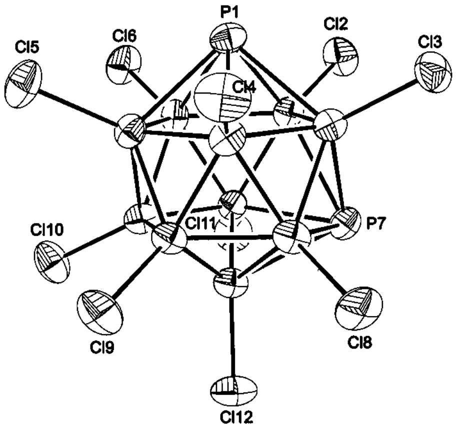

Figure 1. Molecular structure of 1,7-$P_2B_{10}Cl_{10}$ (**1**) showing the atom-numbering scheme. The numbering of the boron atoms has been omitted for clarity. Selected bond distances (Å) and bond angles (deg) are as follows (estimated standard deviations in parentheses): P(1)−B(2) 2.060(6), B(2)−B(3) 1.926(7), B(10)−B(12) 1.775(9), B(11)−B(12) 1.854(8), $B-P_{average}$ 2.0601 (total 10), $B-B_{average}$ 1.8214 (total 20), $B-Cl_{average}$ 1.7622 (total 10), $C-C(cycl)_{average}$ 1.373 (total 6), C(1)−C(7) 1.521(10), P(1)−P(7) 3.538, B(2)−B(9) 3.497, Cl(2)−Cl′(10′) 3.508; B(2)−P(1)−B(6) 53.2(2), B(2)−P(1)−B(3) 55.8(2), B(10)−B(11)−B(12) 58.1(3), B(4)−B(3)−B(8) 58.3(3), P(1)−B(2)−B(3) 62.0(3), B(4)−B(9)−B(5) 62.3(3), B(4)−P(1)−B(6) 93.3(2), B(2)−P(1)−B(4) 94.7(2), B(6)−B(10)−B(9) 109.1(4), P(1)−B(6)−B(10) 113.9(3), B(4)−B(8)−B(7) 115.2(4), P(1)−B(2)−P(7) 119.0(3).

phosphaborane cages. In agreement with our initial report, this reaction again yielded $P_2B_4Cl_4$ as the major product. However, we were also able to isolate the 12-vertex *closo*-phosphaborane $P_2B_{10}Cl_{10}$ (**1**) and prepare phosphaboranes with the molecular formula $P_4B_8Cl_6$ (**2**) and $P_2B_8Cl_8$ (**3**), as suggested in eqs 1−3.

$$2PCl_3 + 13B_2Cl_4 \rightarrow P_2B_{10}Cl_{10} + 16BCl_3 \quad (1)$$

$$4PCl_3 + 15B_2Cl_4 \rightarrow P_4B_8Cl_6 + 22BCl_3 \quad (2)$$

$$2PCl_3 + 11B_2Cl_4 \rightarrow P_2B_8Cl_8 + 14BCl_3 \quad (3)$$

After repeated fractional sublimation, *closo*-1,7-$P_2B_{10}Cl_{10}$ (**1**) (Figure 1) could be obtained in pure form, and it represents the first structurally characterized icosahedral *closo*-diheteroborane with the heteroatoms in nonadjacent positions. Compounds **2** and **3** were always obtained in a mixture with $P_2B_4Cl_4$. High-resolution mass determinations confirmed the molecular formula, and analysis of the NMR signals for each compound led to clear assignments and elucidation of the structures of these compounds: boron−boron linked *conjuncto*-3,3′-(1,2-$P_2B_4Cl_3)_2$ geometry for **2** (Figure 3) and a 10-vertex *closo*-1,10-$P_2B_8Cl_8$ geometry for **3** (Figure 4) with the P atoms in 1,10-positions.

Based on the idealized eq 1, the yield of **1** was approximately 5%. **1** does not melt until 230 °C in a sealed capillary. The new phosphaboranes are air-sensitive but thermally stable, not decomposing or rearranging until temperatures above 500 °C in an evacuated glass tube. They are soluble in common aprotic solvents as, e.g., benzene, toluene, chloroform, and methylene chloride and slightly soluble in pentane.

New Mixed 6- and 12-Vertex Arsaphosphaboranes $AsPB_4Cl_4$ and $AsPB_{10}Cl_{10}$. Parallel to the present study, first attempts to prepare arsaboranes by the same type of reaction in a single flask reactor failed. Thereby, $AsCl_3$ is reduced almost quantitatively by B_2Cl_4 to elemental arsenic and BCl_3, as shown in eq 4. This redox reaction is suppressed by condensing B_2Cl_4 and $AsCl_3$ separately into the two flasks of a two-flask reactor, and copyrolysis at 330 °C produces the six-vertex diarsaborane *closo*-1,2-$As_2B_4Cl_4$.[13a] Elevating the temperature to 450 °C results in the formation of the icosahedral diarsaborane 1,2-$As_2B_{10}Cl_{10}$ and a molecule with elemental composition $As_4B_8Cl_6$.[13b] The formulation of this compound is postulated as the *conjuncto*-arsaborane $(As_2B_4Cl_3)_2$.[13b]

$$2AsCl_3 + 3B_2Cl_4 \rightarrow 2As + 6BCl_3 \quad (4)$$

By adopting similar conditions to a copyrolysis of B_2Cl_4 with a mixture of $AsCl_3$ and PCl_3 we have now obtained the new mixed 6-vertex arsaphosphaboranes $AsPB_4Cl_4$ (**4**) and—only in traces—the 12-vertex $AsPB_{10}Cl_{10}$. Based on the idealized eq 5, the yield of **4** was approximately 5%.

$$AsCl_3 + PCl_3 + 7B_2Cl_4 \rightarrow AsPB_4Cl_4 + 10BCl_3 \quad (5)$$

The elemental composition of **4** was confirmed by exact-mass determination, and the 1,2-positions of the heteroelements could be clearly assigned by ^{11}B NMR spectroscopy.

NMR Studies. The ^{11}B NMR spectrum of compound **1** consists of four resonances in a 2:4:2:2 pattern. This is consistent with the C_{2v} symmetry of an icosahedral molecule with two equivalent heteroatoms. $^{11}B-^{11}B$ COSY NMR spectroscopy was applied in order to assign ^{11}B resonances to specific boron nuclei but also to differentiate between positional isomers. In contrast to the 1,2-isomer, the 1,7-isomer (see Figure 1 for the numbering) has a boron environment (2,3) that is adjacent to only one other boron type (4,6,8,11). The signal at −2.0 ppm which exhibits a cross peak only with the unique area 4 resonance at 1.9 ppm can therefore be assigned to B(2,3) and the latter, also indicative from its integration, to B(4,6,8,11). The remaining resonances at 7.6 and 0.7 ppm must come from either B(5,12) or B(9,10). Both positions exhibit the same interboron linkages, and therefore $^{11}B-^{11}B$ COSY NMR spectroscopy does not allow one to assign these ^{11}B resonances unequivocally. On the other hand, the boron−phosphorus connectivities are not equal at these positions and several diagnostics, such as selective B−P coupling,[10] broadening of the corresponding line width,[11b] or weakening of $^{11}B-^{11}B$ correlations by neighboring heteroatoms,[18] have been used to distinguish such signals unambiguously. However, none of these features are found applicable for **1**, and therefore both equivocal signals are tentatively assigned as follows: Comparison with the data of the previously reported parent phosphaborane 1,7-$P_2B_{10}H_{10}$,[10a] where the lowest field signal could be reliably assigned to B(5,12) due to its splitting into a doublet, suggests that the resonance at 7.6 ppm, which appears at the lowest field in **1**, should correspond also to boron atoms B(5,12), and consequently the signal at 0.7 ppm will correspond to B(9,10). These assignments are also similar to those[19] determined for 1,7-$C_2B_{10}H_{10}$ and give further evidence for the influence of an antipodal deshielding effect of heteroatoms to cross-cage boron atoms which has been observed in the ^{11}B spectra of a series of heteroborane clusters.[20]

The ^{31}P NMR spectrum of **1** shows one resonance at −123 ppm which is remarkably upfield when compared to the ^{31}P

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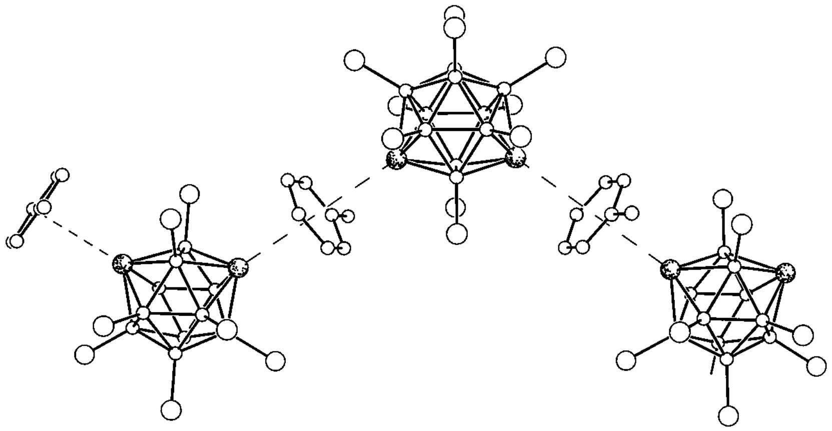

Figure 2. Perspective view of crystal packing at 1,7-$P_2B_{10}Cl_{10}\cdot C_6H_5CH_3$.

NMR signal of the reported[10a] all-hydrogen phosphaborane, the ortho-isomeric 1,2-$P_2B_{10}H_{10}$ (−19.3 ppm). Apparently, unlike the antipodal deshielding effect caused by heteroatoms, chlorine as a +M-type substituent exhibits a shielding influence from positions B 5, 12 to the opposite P 1, 7. Antipodal shielding toward P, C, and B nuclei has also been observed in substituted icosahedral boranes such as 9,12-Br_2-1,2-$CHPB_{10}H_8$ and 1-$ClB_{12}H_{11}^{2-}$.[19,21]

Attempts to separate the compounds $P_4B_8Cl_6$ (**2**) and $P_2B_8Cl_8$ (**3**) by fractionation or crystallization processes from their mixtures with 1,2-$P_2B_4Cl_4$ failed. However, the assignment of the NMR signals to compounds **2** and **3** was possible by comparison of NMR and GC/mass spectral data of different fractions containing different amounts of either compound. Two ^{11}B NMR signals at 24.8 and 15.9 ppm which show cross-peak correlation in $^{11}B-^{11}B$ COSY NMR spectroscopy are present in a ratio of 3:1 in all mixtures containing **2**, **3**, and 1,2-$P_2B_4Cl_4$ and could be clearly assigned to $P_4B_8Cl_6$ (**2**). The corresponding signal at ^{31}P NMR consists of one resonance at −182 ppm, not much different from that of the previously reported *closo*-1,2-$P_2B_4Cl_4$ at −187 ppm.[11a] Exact mass measurements on the parent ion support the formulation of the compound **2** as $P_4B_8Cl_6$, and application of Wade's rules suggests that two $P_2B_4Cl_3$ units are symmetrically boron−boron linked to the phosphaborane $(P_2B_4Cl_3)_2$, where three ^{11}B NMR signals in a ratio of 2:1:1 are expected. However, only two ^{11}B NMR signals are observed in **2**, which suggests that the area 3 resonance is due to accidental overlap of an area 2 and an area 1 signal. Similar superposition of ^{11}B signals has been observed for the coupled-cage carborane 2,2′-$(1,6\text{-}C_2B_4H_5)_2$, where the chemical shifts of the linked boron atoms B(2,2′) and the adjacent B(3,3′,5,5′) differ only by 0.3 ppm.[22] Since **2** shows only one signal in the ^{31}P NMR spectrum, the isomer with the P atoms on positions having different boron environments P(1,1′,4,4′) is excluded. On this basis, the remaining possible structures for **2** are 3,3′-$(1,2\text{-}P_2B_4Cl_3)_2$ and 2,2′-$[1,6\text{-}P_2B_4Cl_3]_2$. The NMR data tend to favor the former isomer, shown in Figure 3, due to the small difference in ^{31}P NMR chemical shifts between **2** and the *cis*-diphosphaborane *closo*-1,2-$P_2B_4Cl_4$.

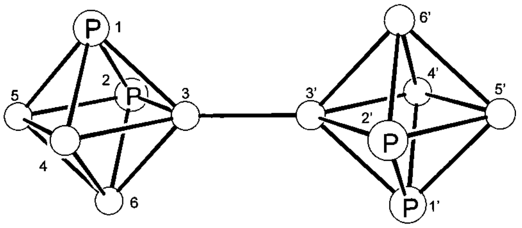

Figure 3. Proposed structure for $P_4B_8Cl_6$ (**2**).

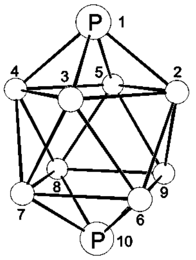

Figure 4. Proposed structure for $P_2B_8Cl_8$ (**3**).

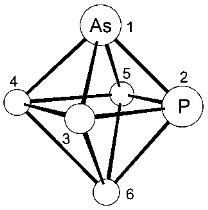

Figure 5. Proposed structure for $AsPB_4Cl_4$ (**4**).

The ^{11}B NMR and the ^{31}P NMR spectra of $P_2B_8Cl_8$ (**3**) consist of one signal each, at 8.7 ppm and −195 ppm, respectively, indicating equivalent boron and phosphorus sites in this molecule, which fits only for a bicapped square antiprism with the P atoms in apical 1,10-positions, as represented in Figure 4. Resolution enhancement of the ^{11}B NMR spectrum resulted in a splitting of the resonance at 8.7 ppm into a pseudo-triplet with a splitting of the outer lines corresponding to $\Sigma[{}^{1}J({}^{31}P,{}^{11}B) + {}^{1}J({}^{11}B,{}^{11}B) + {}^{3}J({}^{31}P,{}^{11}B)] = 42.6$ Hz.

The ^{11}B NMR spectrum of 1,2-$AsPB_4Cl_4$ (**4**) consists of two signals of equal intensities at 24.8 and 7.0 ppm, indicating a structure analogous to those of 1,2-$P_2B_4Cl_4$ and 1,2-$As_2B_4Cl_4$ with adjacent heteroatoms as given in Figure 5. Surprisingly, unlike other previously reported mixed diheteroboranes as 1,2-$PEB_{10}H_{10}$ (E = As, Sb),[10b] where the signal of the boron atoms B(9,12) is split due to the unsymmetrical substitution, in **4** no splitting of the ^{11}B NMR signal at 24.8 ppm, which derives from the boron positions B(4,6) lying opposite to the heteroatoms P and As, could be observed. The ^{31}P NMR spectrum

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shows one signal at −169 ppm which is downfield when compared to the signal for 1,2-$P_2B_4Cl_4$, found at −187 ppm. This downfield trend of the ^{11}B and ^{31}P chemical shifts in compounds in which one phosphorus atom is substituted by arsenic is in agreement with the NMR data reported for the 12-vertex diheteroboranes 1,2-$P_2B_{10}H_{10}$ and 1,2-$PAsB_{10}H_{10}$.[10]

The signal assignments of **1**, **4**, and other halogenated heteroboranes have been further confirmed using homonuclear 1D $^{11}B\{^{11}B\}$ decoupling experiments which are discussed in a separate paper.[23] These studies also provide insights into $^1J(^{31}P,^{11}B)$, $^1J(^{31}P,^{31}P)$, and $^1J(^{11}B,^{11}B)$ and allow comparisons with previously reported values.

Chemical Shifts of Halogenated Icosahedral Heteroboranes. In recent years, there have been several reports on factors describing characteristic ^{11}B NMR chemical shift changes caused by skeletal heteroatom or ligand substitution in parent boranes.[20] Thus, replacement of an icosahedral cage-boron vertex BH^- by an isolobal heterovertex E = CH < P < As < Sb < S^+ results in a progressive deshielding of the skeletal boron atoms which is most significant at the boron atom opposite the heteroatom even though it is the farthest away. This observation has been labeled the *antipodal effect or A-effect*.

Substitution of hydrogen ligands by halogen atoms has been found to result in a superposition of several, partly counteracting effects. Primarily, halogen ligands cause an antipodal effect which is reverse in sign compared to the antipodal effect caused by heteroatoms. In addition, due to both the inductive attraction and the π-donation exhibited by electronegative substituents bearing free electron pairs, there is a progressive −I type deshielding mainly of the substituted α-boron atoms in the order Br < Cl < F and, in turn, a +M type shielding of all neighboring β-, γ-, and δ-skeletal atoms which again is the most effective at the cross-cage positions. The order of the described effects depends on the nature of the substituents and cluster geometry. Experience has shown that heteroatoms (except Al, Si) exhibit a stronger antipodal effect than do +M substituents at the same positions. In halogenated heteroboranes it is therefore difficult to assess the NMR spectra as substitution increases. The most common examples for the exo-cage substituent effects are partial halogenation, either mono- or dihalogenated carboranes. However, until recently there was a lack of experimental NMR data on fully halogenated heteroboranes with the exception of *B*-perchloro-*o*-carborane.[24] Supplementation with the present NMR data and that of the previously reported perchloroarsa- and thiaboranes[13b] (Table 3) gives a number of such compounds which still is quite small, but allows one to qualitatively assess some shielding trends in perchlorinated icosahedral *closo*-heteroboranes and also helps to quantify the changes in ^{11}B NMR chemical shifts introduced by the substitution of heterovertices and chlorine ligands.

As can be observed in Table 3, perchlorination of *closo*-$B_{12}H_{12}^{2-}$ shifts the ^{11}B NMR signal 2.4 ppm to the lower field, indicating that the −I-type electron attraction of chlorine in *closo*-$B_{12}Cl_{12}^{2-}$ exceeds its electron donation brought by +M type shielding, which leads to a net deshielding of the substituted boron atoms. In analogy, compared to the unsubstituted compounds, the boron atoms of the chlorinated carborane are deshielded at all positions and those of the heteroboranes $E_2B_{10}Cl_{10}$ (E = P, As) and $SB_{11}Cl_{11}$ at most positions, but not at those antipodal to the heteroatoms. Obviously, the antipodal *deshielding* effect of heteroatoms is gradually diminished by chlorine ligands, which may mainly result from the antipodal *shielding* of chlorine ligands bound to boron atoms cross-cage to the heteroatoms. The strongest diminution of the antipodal deshielding is found at $SB_{11}Cl_{11}$ with an increment of 5.1 ppm on position B(12). In 1,7-$P_2B_{10}Cl_{10}$ (**1**) not only the "antipodal" boron atoms B(5,12) but also B(9,10) are deshielded compared to the all-hydrogen compound which gives rise to a conversion of the 2:2:4:2 signal ratio into 2:4:2:2.

Table 3. ^{11}B Chemical Shifts for Icosahedral Boranes

compd	δ ppm				ref
$B_{12}H_{12}^{2-}$	−15.3	−15.3	−15.3	−15.3	20a
$B_{12}Cl_{12}^{2-}$	−12.9	−12.9	−12.9	−12.9	17
E(1,7)	B(5,12)	B(9,10)	B(4,6,8,11)	B(2,3)	
$P_2B_{10}H_{10}$	11.2	3.4	−0.4	−3.3	10a
$P_2B_{10}Cl_{10}$	7.6	0.7	1.9	−2.0	this work
E(1,2)	B(9,12)	B(3,6)	B(4,5,7,11)	B(8,10)	
$As_2B_{10}H_{10}$	15.5	3.8	0.9	−0.8	25
$As_2B_{10}Cl_{10}$	12.9	6.0	3.6	0.3	13b
$(CH)_2B_{10}H_{10}$	−1.2	−14.3	−12.9	−8.2	26
$(CH)_2B_{10}Cl_{10}$	1.2	−13.0	−10.3	−7.3	24
E(1)	B(12)	B(7−11)	B(2−6)		
$SB_{11}H_{11}$	18.4	−4.2	−6.7		27
$SB_{11}Cl_{11}$	13.3	1.0	−3.7		13b

Crystal Structure Analysis of 1. As expected, the single-crystal X-ray analysis confirms the general structural features proposed for **1** based upon spectral data. The structure consists of a distorted icosahedron of 10 boron atoms and two phosphorus atoms in the 1,7-positions whereby the symmetry is reduced from I_h to C_{2v}. Within the limits of error there are two mirror planes passing through atoms B(2,3,9,10) and through B(5,12),P(1,7). An ORTEP drawing with atom labeling, selected bond lengths, and bond angles is given in Figure 1. Deviations from regular bond distances and angles of the ideal icosahedral structure are obviously a consequence of the substitution of the larger-sized phosphorus atoms. Within the pentagonal belt defined by P1−B2−P7−B8−B4 the bond angles of P1−B2−P7 and B4−B8−B7 have been increased to 119.0(3)° and 115.2(4)° compared with the ideal pentagonal angle of 108° while the bond angle of B2−P1−B4 has been reduced to 94.7(2)°. Similar, but less distinct, trends have been observed at the icosahedral monophosphorus phosphaborane $CH_3PB_{11}H_{11}$, in which the average pentagonal B−B−B and B−P−B bond angles have been found to be 110.2° and 101.5°, respectively.[5] The boron−boron distance between the equivalent B2 and B3 atoms, adjacent to both phosphorus atoms, is 1.926(7) Å while the average boron−boron distance is 1.827 Å, which is slightly longer than those found in $B_{12}H_{12}^{2-}$ (1.77 Å).[28] The shortest boron−boron distances (average 1.786 Å) are located between B(5,12) and B(9,10), which are the boron atoms opposite and farthest from the phosphorus atoms. The average B−P distance of **1** (2.060 Å) compares well with the B−P bond lengths reported for other icosahedral phosphaboranes (2.038−1.953 Å).[5,10b] The intramolecular P−P distance is 3.538 Å while that of the cross-cage boron atoms B5−B12 is markedly shorter (2.910 Å). The intermolecular Cl−Cl contacts are 3.508 Å or longer.

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Crystals of $P_2B_{10}Cl_{10}$ contain toluene in a 1:1 molar ratio as illustrated in Figure 2. The toluene rings are exactly perpendicular to the P atoms of two neighboring icosahedrons at a distance between 3.04 and 3.08 Å with a mean P−C distance of ∼3.1 Å, which is well below the sum of the van der Waals radii of ∼3.5 Å. The proximity and the linear orientation of toluene between two cluster molecules suggest a significant electronic interaction between the lone pairs of the P atoms and the aromate and cannot be compared with the bonding in metallaborane sandwiches where the aromatic ligands function as isoelectronic and isolobal electron donors to the metal.

Cluster Size and Isomer Preferences. The preferred formation of phosphaborane clusters of sizes 6, 10, and 12 by a thermodynamically controlled synthetic route is in agreement with recent computional studies dealing with the relative stability and "three-dimensional aromaticity" of *closo*-borane dianions $B_nH_n^{2-}$, *closo*-monocarborane anions $CB_{n-1}H_n^{-}$, and *closo*-dicarboranes $C_2B_{n-2}H_n$.[29] It was found that on the basis of average BH-bond energies for each member's most stable positional isomer, the 12- and 6-vertex polyhedra are more stable than the other members of their families, followed by the 10- and 7-vertex systems.

The sites of the heteroatom placements in the new phosphaboranes follow closely trends already observed in *closo*-dicarba- and parent phosphaboranes. Analogous to the 10-vertex $C_2B_8H_{10}$ carboranes with 1,10-$C_2B_8H_{10}$ as the thermodynamically most stable positional isomer,[30] the phosphorus atoms in $P_2B_8Cl_8$ (**3**) obviously prefer the apical position, i.e., where the connectivity is the lowest and the charge density is the largest[29a,30] within the reference compound $B_{10}H_{10}^{2-}$. In contrast, the coordination number of the cluster vertices at **1** and **2** is equal for all positions. Calculation[8g] of the relative stabilities of icosahedral diphosphaboranes $P_2B_{10}H_{10}$ suggests that the isomer stability should follow the order 1,12 > 1,7 > 1,2, which is confirmed in part by the previously described thermal conversion of 1,2-$P_2B_{10}H_{10}$ to the 1,7-isomer at 560 °C[10a] and the present synthesis of 1,7-$P_2B_{10}Cl_{10}$ (**1**) via pyrolytic conditions at temperatures above 400 °C. The para isomer is not yet amenable to synthesis, which suggests that the formation of this compound may require temperatures beyond its thermal stability.

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Supporting Information Available: Interatomic distances, selected bond angles, and selected dihedral angles between least-squares planes. X-ray crystallographic files for the structure determination of **1**·toluene, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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