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Arsacarborane chemistry. The 7,8,9,11-, 7,9,8,10- and 7,8,9,10-isomers of *nido*-$As_2C_2B_7H_9$ and some of their halogenated derivatives†

Libor Mikulášek,[a] **Bohumír Grüner,**[a] **Ivana Císařová**[b] **and Bohumil Štíbr** *[a]

[a] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68, Řež, the Czech Republic. E-mail: stibr@iic.cas.cz*

[b] *Faculty of Natural Sciences of Charles University, Hlavova 2030, 128 42, Prague 2*

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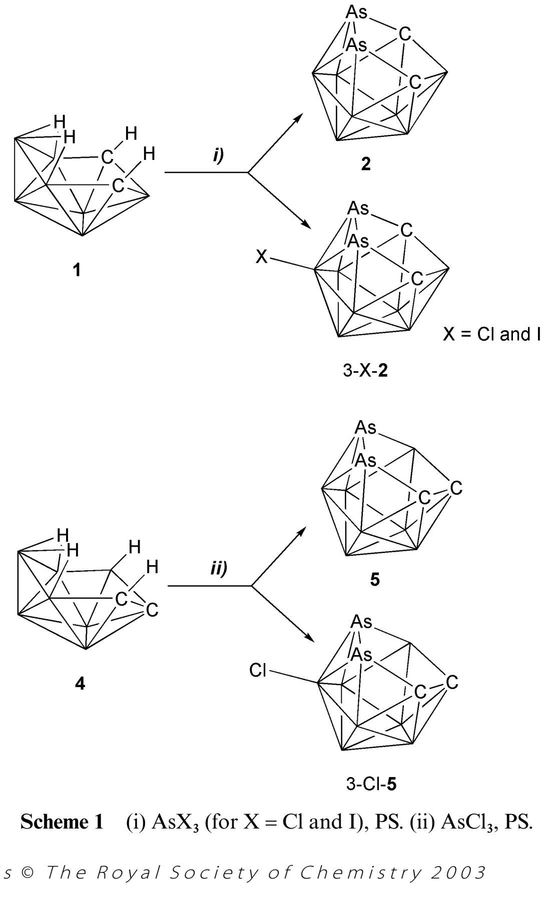
The reaction between *arachno*-4,6-$C_2B_7H_{13}$ (**1**) and $AsCl_3$ or AsI_3 in CH_2Cl_2 in the presence of PS (PS = "proton sponge", 1,8-bis(dimethylamino)naphthalene) resulted in the isolation of the parent, isomeric eleven-vertex *nido* diarsadicarbaboranes 7,8,9,11-$As_2C_2B_7H_9$ (**2**) and 7,9,8,10-$As_2C_2B_7H_9$ (**3**). Isolated were also halogenated derivatives of **2**, 3-Cl-7,8,9,11-$As_2C_2B_7H_8$ (3-Cl-**2**) and 3-I-7,8,9,11-$As_2C_2B_7H_8$ (3-I-**2**). The presence of $Et_3N{\cdot}BH_3$ in the reaction mixture increased the yield of unsubstituted compounds and suppressed the formation of halogenated species. The reaction between the isomeric carborane *arachno*-4,5-$C_2B_7H_{13}$ (**4**) and $AsCl_3$ in CH_2Cl_2 in the presence of PS gave another isomer, *nido*-7,8,9,10-$As_2C_2B_7H_9$ (**5**), which was accompanied by small amounts of its chloroderivative 3-Cl-7,8,9,10-$As_2C_2B_7H_8$ (3-Cl-**5**) and compound **3**. The structure of the iodinated derivative 3-I-**2** was determined by an X-ray diffraction analysis. Moreover, the structures of all parent compounds and chloroderivatives, inclusive of that of the still missing *nido*-7,10,8,9-$As_2C_2B_7H_9$ (**6**) isomer, were geometry-optimised at the DFT-B3LYP/6-31G* level.

Introduction

We have been recently interested in the chemistry of the eleven-vertex open-cage heteroborane compounds containing a larger number of carbon or other heteroatomic vertices than two in the cage. These compounds approach closely a borderline between boron-cluster molecules and classical organic compounds and can be potentially used as new ligands for metal complexation. In the field of main-group heteroboranes, Todd and Little developed two decades ago a reliable synthetic strategy based on reactions between borane or carborane anions and PCl_3 or As(III) halides in the presence of dehydrohalogenation agents (usually Et_3N).[1] These reactions have generated phosphaboranes or arsaboranes containing bare P or As atoms as one of the cage constituents. The cluster As or P atoms in these species contribute three electrons and three orbitals into the cluster bonding proper, with two remaining electrons occupying the exoskeletal orbital. The P or As vertices are thus isolobal with a CH group, and the phosphaboranes and arsaboranes are therefore straightforward structural analogues of the corresponding carboranes. In the area of arsaborane chemistry, these approaches have resulted in the isolation of several essential representatives of the arsaborane and arsacarborane series. These can be exemplified by the [*nido*-7-$AsB_{10}H_{12}$]$^-$ anion, isomers of *closo*-$AsCB_{10}H_{11}$,[2] and by the *closo*-1,2-$As_2B_{10}H_{11}$ diarsaborane,[3] analogues of the corresponding [*nido*-7-$CB_{10}H_{13}$]$^-$ and $C_2B_{10}H_{12}$ carboranes.

We have been currently developing the chemistry of compounds containing four heteroatoms in the eleven-vertex *nido* cage. In this area, we have recently isolated and characterised di- and triphosphacarborane compounds, for example three isomers of $P_2C_2B_7H_9$[4] and the methylated $MeP_3CB_7H_7$ compounds,[5] all of these being structural analogues of *nido*-7,8,9,10-$C_4B_7H_{11}$.[6] In a related area of arsacarborane chemistry, the first and so far a single representative of the eleven-vertex diarsadicarbaborane family, *nido*-7,8,9,11-$As_2C_2B_7H_9$, was synthesized and tentatively characterized by ^{11}B NMR spectroscopy.[7] We report in this paper on the re-investigation of the original reaction of carborane **1** with As(III) halides and extend this type of reaction to the isomeric carborane **4**. We have used slightly modified conditions and applied more detailed isolation and characterization procedures, including the use of separation and high-field NMR methods complemented with an X-ray diffraction analysis and DFT calculations. Unmarked vertices in Scheme 1 stand for cluster BH units, C and As denote cage CH and bare As units.



Scheme 1 (i) AsX_3 (for X = Cl and I), PS. (ii) $AsCl_3$, PS.

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† Electronic supplementary information (ESI) available: selected bond lengths and angles for the crystallographically determined compound 3-I-**2** have been also deposited, together with coordinates for the B3LYP/6-31G* calculated structures for all compounds reported. See http://www.rsc.org/suppdata/dt/b2/b212183b/

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Results and discussion

Syntheses

Reactions between carborane **1** and $AsCl_3$ or AsI_3 in dichloromethane in the presence of PS (dehydrohalogenation agent), followed by decomposition of the reaction mixture with water and column chromatography of the products on silica gel, resulted in the isolation of two main products (see Scheme 1, path (i)). These were identified as the previously reported[7] *nido*-diarsadicarbaborane 7,8,9,11-$As_2C_2B_7H_9$ (**2**) (yield 37%) and a new, isomeric, species 7,9,8,10-$As_2C_2B_7H_9$ (**3**) (yield 4%). Apart from these unsubstituted compounds, two new halogenated derivatives of **2** were also isolated from these reactions, which were identified as 3-Cl-7,8,9,11-$As_2C_2B_7H_8$ (3-Cl-**2**) (yield 25%) and 3-I-7,8,9,11-$As_2C_2B_7H_8$ (3-I-**2**) (yield 16%). It should be noted that, similarly as in the phosphacarborane series,[4] the reactions are stoichiometric only with respect to the formation of the halogenated derivatives [eqn. (1)]:

$$C_2B_7H_{13} + 2\ AsX_3 + 5\ PS \longrightarrow As_2C_2B_7H_8X + 5\ PSHX \qquad (1)$$

Although there is no direct experimental evidence, it can be assumed that the parent compounds **2** and **3** are formed by the reduction of the haloderivatives at some reaction stage at the expense of oxidation of the starting compound.[4] This assumption is supported by observation that their formation is suppressed by adding $Et_3N{\cdot}BH_3$ as a dehydrohalogenation agent. In this modification, the reaction led to the formation of compound **2** in an increased yield of 45%. Moreover, the reaction was accompanied by the formation of compound **3** (yield 1%) and the chloroderivative of **2**, 3-Cl-**2** (yield 8%).

A similar reaction of $AsCl_3$ with carborane **4**, which is isomeric with **1**, in the presence of PS [see Scheme 1, path (ii)] gave two unsubstituted compounds identified as **3** (yield 9%) and the isomeric 7,8,9,10-$As_2C_2B_7H_9$ (**5**) (yield 12%). The main product isolated from this reaction was, however, 3-Cl-7,8,9,10-$As_2C_2B_7H_8$ (3-Cl-**5**) (yield 27%).

As seen from Scheme 1, the mode of incorporation of two As centres into the cluster area in **1** and **4** is essentially the same as that reported for the formation of the corresponding *nido*-$P_2C_2B_7H_9$ compounds.[4] Very similar is also the formation of the halogenated derivatives of **2** and **5**, in which the halogen substituent resides exclusively on the boron vertex B(3) adjacent to both cluster As-atoms. In contrast to the diphosphadicarbaborane series,[4] no compounds substituted on the open-face boron have been isolated.

NMR spectroscopy

Entirely consistent with the X-ray diffraction and DFT-B3LYP/6-31G* calculations presented below are the NMR characteristics of all isomeric $As_2C_2B_7$ compounds isolated in this work (see Table 1). In accord with the C_s symmetry, the ^{11}B NMR spectrum of **2** consists of 1 : 2 : 2 : 1 : 1 patterns of doublets, as reported previously.[4] In the spectrum of 3-I-**2** the highest-field doublet of intensity 1 collapses to a singlet and is shifted upfield by about 5 ppm. The ^{11}B NMR spectra of the asymmetrical parent compounds **3** and **5** show seven doublets of equal intensities, two of them being coincidentally overlapped. The spectrum of 3-Cl-**5** displays six doublets and one singlet, all of equal intensities. Application of the [^{11}B–^{11}B]-COSY[8] and $^1H\{^{11}B\text{-selective}\}$ spectroscopy[9] allowed for complete assignments of all resonances to individual BH vertices. The comparison of the ^{11}B chemical shifts shows that the diarsadicarbaboranes of types **2**, **3**, and **5** are analogues of the previously reported compounds of the *nido* $C_4B_7H_{11}$[5] and $P_2C_2B_7H_9$[4] series. This similarity is reflected by a similar range of ~32–35 ppm in the ^{11}B spectra, but the comparison reveals that the isolobal substitution of two CH vertices for P or As produces systematic deshielding in the order CH < P < As for all BH positions. The ^1H NMR spectra of **2** and 3-I-**2** display one signal of intensity two assigned to CH(9,11), while those of compounds **5** and 3-Cl-**5** show two different CH(8) and CH(10) resonances. The $^1H\{^{11}B\}$ NMR patterns for all compounds of types **2**, **3**, and **5** are consistent with those found for the corresponding compounds of the $P_2C_2B_7H_9$ series previously reported,[4] however, all peaks are singlets.

Structural studies

The structure of the halogenated derivative 3-I-**2** was determined unambiguously by an X-ray diffraction analysis. The structure of two symmetrically independent molecules 3-I-**2** (see Fig. 1) is consistent with a C_s symmetry plane bisecting the As–As bond and intersecting the iodinated B(3) vertex and the bottom B(1) atom (both molecules are in special position on the mirror of the space group *Pbam*). Selected crystal data and structure refinement parameters are in Table 2, and selected bond distances and angles are in Fig. 1. The average As–As distance in 3-I-**2** (2.413 Å) is comparable to As–As separations found for the *closo* compounds 9,12-I_2-$As_2B_{10}H_8$ (2.435 (2) Å) and 8,12- I_2-$As_2B_{10}H_8$ (2.421 (2) Å)[10] and to that found for the *closo* metalladiarsaboranes [3,3-$(Me_2PPh)_2$-3,1,2-$PtAs_2B_9H_9$] (2.497 (3) Å), [3-Cl-3,3-$(PPh_3)_2$-3,1,2-$PdAs_2B_9H_8$] (2.477 (3) Å),[11] [3,3-$(Et_3P)_2$-3,1,2-$PtAs_2B_9H_9$] (2.4594 (15) Å),[12] [1,1-$(Me_2PPh)_2$-1,2,3-$PdAs_2B_9H_9$] (2.4885 (15) Å), [1,6-Cl2-1,5-$(Me_2PPh)_2$-1,2,3-$PdAs_2B_9H_7$] (2.517 (5) Å),[13] [5-CN-1,1-$(Me_2PPh)_2$-1,2,3-$PdAs_2B_9H_9$] (2.4911 (13) Å), and [1-^{t}BuNC-5-CN-1-$(Me_2PPh)_2$-1,2,3-$PdAs_2B_9H_8$] (2.5410 (9) Å)[14] previously reported.

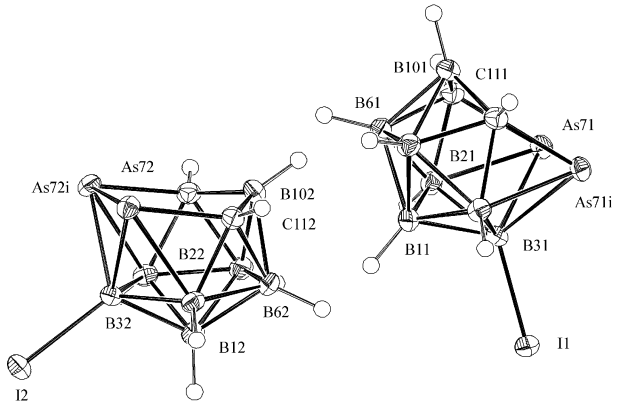


Fig. 1 PLATON representation of the crystallographically determined molecular structure of 3-I-*nido*-7,8,9,11-$As_2C_2B_7H_8$ (3-I-**2**) (crystallographic numbering) with thermal elipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): As(71)–As(71)i 2.4111(6), As(71)–C(111) 2.007(3), B(101)–C(111) 1.608(4), C(111)–As(71)–As(71)i 94.36(8), and C(112)–B(102)–C(112)ii 114.4(3).

The remaining bonding distances in 3-I-**2** are unaffected as the As–B and B–B separations differ only within a range of standard deviations when compared to other compounds with the As–As bond mentioned above.[10–14] The same situation repeats when we compare the distances in the $\{As_2C_2B_7\}$ moiety in 3-I-**2** with those found for the $P_2C_2B_7$ series,[4] where the only significant differences are in parameters involving As or P atoms. As expected, bond lengths associated with the As atom are longer than the corresponding distances to the P centre (As–As 2.413 Å, P–P 2.193 Å; average As–C 2.005 Å, P–C 1.861 Å; As–B 2.193 Å, P–B 2.081 Å). Consequently, the open face in 3-I-**2** is highly distorted, the most deviated atom from the least-squares As_2C_2B plane being the B(10) vertex (atom–plane distances for B101 −0.156(3) Å and B102 −0.161(3) Å).

In addition to the crystallographic work, also optimised geometries for all four $As_2C_2B_7H_9$ isomers **2**, **3**, **5**, and **6** of the open-face heteroatom configurations were calculated (see Fig. 2) together with those for the two chloro derivatives obtained from the synthesis. Selected geometrical parameters obtained at the DFT-B3LYP/6-31G* level are summarized in Table 3. For

Table 1 NMR data for the $As_2C_2B_7H_9$ compounds and their halogenated derivatives ($CDCl_3$, 293 K)

Compound	Nucleus	δ (ppm) [multiplicity, assignment, $^1J(^{11}B–^1H)$/Hz]
nido-7,8,9,11-$As_2C_2B_7H_9$ (**2**)	^{11}B	−2.60 [d, B10, 142], −3.32 [s, B(5,6), 154], −5.55 [s, B(2,3), 165], −15.12 [s, B(3), 169], −33.55 [s, B(1), 154]
	$^{11}B–^{11}B$	B1–B2,4(s), B1–B3(s), B1–B5,6(s), B2,4–B5,6(m), B2,4–B3(s), B5,6–B10(w)
	^1H	3.14 [s, H(2,4)], 3.09 [s, H(5,6)], 2.92 [s, H(10)], 2.56 [s, CH(9,11)], 2.51 [s, H(1)], 2.34 [s, H(3)]
nido-7,9,8,10-$As_2C_2B_7H_9$ (**3**)	^{11}B	−2.98 [d, B(3, 6), 150], −3.60 [d, B(11), 112], −7.25 [d, B(5), 162], −8.19 [d, B(2), 150], −13.54 [d, B(4), 169], −36.26 [d, B(1), 154]
	$^{11}B–^{11}B$	B1–B2(w), B1–B3,6(s), B1–B4(s), B1–B5(s), B2–B3,6(s), B2–B11(s), B3,6–B11(s), B3,6–B4(w), B3,6–B5(w), B4–B5(m)
	^1H	3.16 [s, H(3)], 3.10 [s,H(5)], 2.95 [s, H(11)], 2.66 [s, H(6)], 2.60 [s, H(2)], 2.51 [s, H(4)], 2.38 [s, CH(10)], 2.27 [s, H(1)], 1.90 [s, CH(8)]
nido-3-Cl-7,8,9,11-$As_2C_2B_7H_8$ (3-Cl-**2**)	^{11}B	2.492 [s, B(3)], −3.17 [d, B(2,4,5,6), 165], −6.41 [d, B(10), 146], −30.76 [d, B(1), 158]
	$^{11}B–^{11}B$	B1–B2,4,5,6(s), B1–B3(m), B2,4,5,6–B3(s), B2,4,5,6–B10(w)
	^1H	3.73 [s, H(2,4)], 3.13 [s, H(5,6)], 2.91 [s, CH(9,11)], 2.76 [s, H10], 2.56 [s, H(1)]
nido-3-I-7,8,9,11-$As_2C_2B_7H_8$ (3-I-**2**)	^{11}B	−1.54 [d, B(5,6), 162], −3.32 [d, B(2,4), 165], −3.82 [d, B(10), 146], −27.62 [s, B(3)], −28.44 [d, B(1), ≈196]
	$^{11}B–^{11}B$	B1–B2,4(s), B1–B3(w), B1–B5,6(m), B2,4–B5,6(w), B2,4–B3(w), B5,6–B10(w)
	^1H	3.74 [s, H(2,4)], 3.26 [s, H(10)], 3.17 [s, H(5,6)], 2.93 [s, CH(9,11)], 2.80 [s, H(1)]
nido-7,8,9,10-$As_2C_2B_7H_9$ (**5**)	^{11}B	1.34 [d, B(5), 162], −1.37 [d, B(6,11), 150], −4.56 [d, B4, (165)], −5.04 [d, B(2), 146], −10.80 [d, B(3), 165], −34.60 [d, B(1), 154]
	$^{11}B–^{11}B$	B1–B2,4(m), B1–B3(s), B1–B5(m), B1–B6,11(s), B2,4–B3(s), B2,4–B5(s), B2,4–B6,11(w), B5–B6,11(m)
	^1H	3.53 [s, H(5)], 3.46 [s, H(6)], 3.28 [s, CH[a]], 3.21 [s, CH[a]], 3.11 [s, H(3,11)], 2.84 [s, H(4)], 2.70 [s, H(2)], 2.46 [s, H(1)]
nido-3-Cl-7,8,9,10-$As_2C_2B_7$H8 (3-Cl-**5**)	^{11}B	10.29 [s, B(3)], 1.17 [d, B(6), ≈196], −0.03 [d, B(11), ≈150], −2.48 [d, B(5), ≈169], −3.39 [d, B(2), ≈142], −10.03 [d, B(4), 169], −32.04 [d, B(1), 158]
	$^{11}B–^{11}B$	B1–B2(m), B1–B3(s), B1–B4(s), B1–B5(s), B1–B6(s), B2–B3(w), B2–B6(s), B2–B11(w), B3–B4(s), B4–B5(m), B5–B6(m), B6–B11(m)
	^1H	3.53 [s, (H(6),CH(9))], 3.48 [s, H(4)], 3.39 [s, H(5)], 3.22 [s, H(11)], 3.14 [s, H(2)], 3.07 [s, CH(10)], 2.57 [s, H(1)]

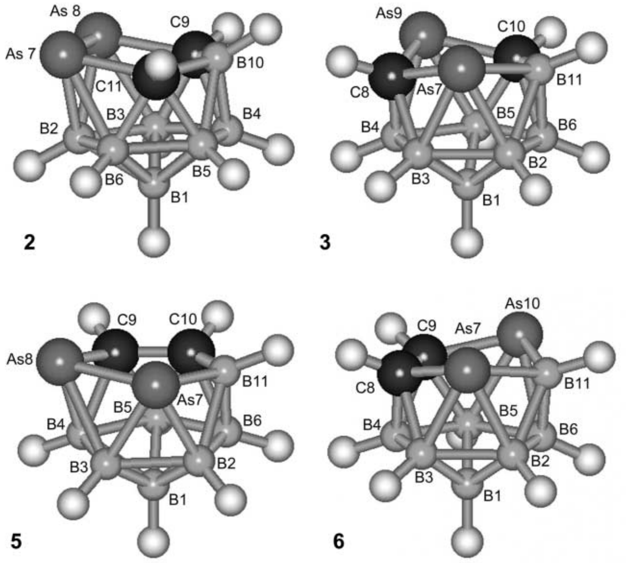
[a] Impossible to assign unambiguously the CH signals.

Table 2 Crystal data and structure refinement for 3-I-**2**

Empirical formula	$C_2H_8As_2B_7I$
M	384.49
Crystal system	Orthorhombic
Space group	*Pbam*
a/Å	10.0670(2)
b/Å	19.8700(1)
c/Å	9.9910(3)
Z	8
V/Å^3	1998.51(7)
μ/mm^{-1}	9.705
No. of reflections measured	36133
No. of unique reflections (R_{int})	2413 (0.068)
No. of parameters	136
Final R[a] indices [$I > 2\sigma(I)$]	$R_1 = 0.022$, $wR_2 = 0.053$
R[a] indices (all data)	$R_1 = 0.024$, $wR_2 = 0.054$

[a] Definitions: $R(F) = \Sigma\, ||F_o| - |F_c|| / \Sigma\, |F_o|$, $wR_2 = [\Sigma\, (w(F_o^2 - F_c^2)^2)/\Sigma\, (w(F_o^2)^2]^{½}$, GOF $= [\Sigma\, (w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{½}$; weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$; $P = [\max(F_o^2,0)+2F_c^2]/3$.

example, the table readily suggests that the calculated distances for compounds **2** and 3-Cl-**2** are very similar to those found crystallographically for 3-I-**2** (see ESI †). Similarly as calculated for the $P_2C_2B_7H_9$ series,[4] the next-nearest As-to-As separations deform the open pentagonal arrangement in a similar manner. As expected, the final distortion is greater than that in the corresponding phosphorus series. The deformations may be best demonstrated by closing the X_1–As–X_2 ($X_{1,2}$ = C, As, B) angles (calculated values range 93.6–94.6°). The angles significantly differ from the ideal value of 108° expected for a regular pentagon. As a consequence, the pentagonal face of the molecules is not planar, but severely distorted, even more than in the $P_2C_2B_7H_9$ series.[4]



2 **3** **5** **6**

Fig. 2 Drawings of the DFT-B3LYP/6-31G* geometry-optimised molecules for all four *nido*-$As_2C_2B_7H_9$ isomers of the open-face configurations of heteroatoms.

Conclusions

The work has led to appreciable extension and continuation of the chemistry of the *nido*-$As_2C_2B_7H_9$ family of diarsadicarbaboranes. The structure originally proposed[3] for compound **2** was confirmed and two new isomeric unsubstituted species **3** and **5** have been isolated together with some of their halogenated derivatives. The molecular structure of 3-I-**2** was determined crystallographically and the structures of all four possible *nido*-$As_2C_2B_7H_9$ isomers have been geometry-optimized. It should be pointed out that the reactions of the AsX_3 compounds (X = Cl and I) with the nine vertex *arachno* carboranes **1** and **4** proceed exclusively with the insertion of two As atoms into the cluster; no sign of the formation of a transient ten-vertex AsC_2B_7 have been observed. In this and other structural aspects, this chemistry is very similar to that reported for

Table 3 Selected bond lengths (Å), bond angles (°) and dihedral angles (°) calculated at the DFT B3LYP/6-31G* level

	2	3-Cl-**2**	**3**	**5**	3-Cl-**5**	**6**
B1–B2	1.761	1.764	1.794	1.782	1.786	1.784
B1–B3	1.767	1.770	1.770	1.766	1.770	1.776
B2–B3	1.873	1.873	1.843	1.856	1.854	1.839
B2–B6	1.772	1.777	1.749	1.774	1.746	1.776
B3–B4	1.873	1.873	1.803	1.859	1.864	1.779
B4–B5	1.772	1.777	1.856	1.778	1.781	1.839
B5–B6	1.724	1.724	1.779	1.755	1.754	1.839
B2–B11	–	–	1.864	1.878	1.883	1.819
B6–B10	1.826	1.821	–	–	–	–
B6–B11	–	–	1.782	1.778	1.780	1.819
As–As	2.401	2.406	–	2.416	2.420	–
C–C	–	–	–	1.526	1.526	1.517
B11(10)–H	(1.191)	(1.191)	1.191	1.190	1.190	1.190
(B[1–6]–H) mean	1.187	1.186	1.187	1.186	1.186	1.187
(C–H) mean	1.086	1.087	1.086	1.086	1.086	1.085
B–Cl	–	1.799	–	–	1.798	–
2–1–3	64.1	64.0	62.3	63.1	62.9	62.2
2–7–3	50.9	50.6	50.7	50.3	50.0	50.6
7–8–9	94.6	94.5	112.1	94.5	94.4	117.2
7–11–10	115.6	115.9	113.6	114.2	114.5	109.1
8–7–11	94.6	94.5	93.7	93.7	93.6	94.3
8–9–10	115.6	115.9	94.1	117.7	118.1	117.2
9–10–11	114.9	114.5	115.7	119.2	118.8	94.3
7–8–9–10	12.7	12.6	−33.0	8.1	8.1	0.0
9–10–11–7	24.0	23.6	−8.5	5.0	4.6	26.4

nido-$P_2C_2B_7H_9$ compounds.[4] We are currently extending the strategies of Main Group 5-element insertion reactions to other borane and carborane compounds with the aim of generating new types of chemically versatile heteroborane cages. General aspects of cluster contraction and metal insertion in this field of chemistry are also being developed.

Experimental

General

All reactions were carried out with use of standard vacuum or inert atmosphere techniques, although some operations, such as chromatographic separations, were carried out in air. The starting *arachno* dicarbaboranes **1** and **4** were prepared according to the literature.[15,16] Hexane and dichloromethane were dried over P_2O_5 and freshly distilled before use. Other chemicals were reagent of analytical grade and were used as purchased. Column chromatography was carried out on silica gel (Aldrich, 130–270 mesh) as the stationary phase. The purity of individual chromatographic fractions was checked by analytical TLC on Silufol (silica gel on aluminium foil, detection by I_2 vapours, followed by aqueous 2% $AgNO_3$ spray). Melting points were measured in sealed capillaries under nitrogen and are uncorrected. Low-resolution mass spectra were obtained with a Finnigan MATMAG-NUM ion-trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basle (Switzerland) (70 eV, EI ionisation). Proton (^{1}H) and boron (^{11}B) NMR spectroscopy was performed at 11.75 Tesla on a Varian UNITY 500 instrument. The [^{11}B,^{11}B]-COSY[8] and ^{1}H{^{11}B-selective}[9] NMR experiments were essentially as described in other related papers from our laboratories.[17] Chemical shifts are given in ppm to high-frequency (low field) of Ξ = 160.379 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.01 ppm) and Ξ = 499.876 MHz ($SiMe_4$) for ^{1}H (quoted ±0.005 ppm), Ξ was defined as in ref. 18. Solvent resonances were used as internal secondary standards. Coupling constants $^1J_{BH}$ are taken from resolution-enhanced ^{11}B spectra with digital resolution ±2 Hz and are given in Hz. IR spectra were obtained on a EU9512 Pye Unicam Fourier transform spectrometer.

Reaction of *arachno*-4,6-$C_2B_7H_{13}$ (1) with $AsCl_3$

(a) A solution of compound **1** (500 mg, 4.4 mmol) in CH_2Cl_2 (25 cm^3) was treated with PS (3.8 g, 17.7 mmol) and then by $AsCl_3$ (0.8 cm^3, 9 mmol) under stirring and cooling to 0 °C. The stirring was continued at room temperature for 6 h and the mixture was then decomposed by the addition of water (50 cm^3, dropwise). The CH_2Cl_2 layer was separated and evaporated with silica gel (10 g) and the resulting solids were mounted onto a silica gel column (2.5 × 30 cm) which was eluted gradually with hexane. The chromatography led to the separation of three main fractions of R_f(hexane) 0.20, 0.15 and 0.06, which were evaporated to dryness. The solids thus obtained were identified by NMR spectroscopy and mass spectrometry as compounds **2** (yields 420 mg, 37%), **3** (40 mg, 4%), and 3-Cl-**2** (320 mg, 25%), respectively. For **2**: mp ~250 °C (decomp.); IR (KBr): ν_{max}= 3412 (s), 3220 (m), 2564 (s), 1624 (w), 1406 (m), 1154 (m), 1062 (s), 962 (s), 904 (m), 832 (m), 722 (m), 630 (w), 450 (w), 350 (m); MS (70 eV, EI), *m*/*z* (%): 261 (2) [M]$^+$, 258 (100) [M − 3 H]$^+$; elemental analysis calcd. (%) for $C_2H_9B_7As_2$ (258.62): C 9.29, H 3.51; found: C 9.25, H 3.20. For **3**: mp ~270 °C (decomp.); IR (KBr): ν_{max} = 3788 (w), 3580 (w), 3324 (w), 2568 (s), 1640 (w), 1382 (w), 1136 (w), 964 (s), 924 (s), 760 (w) 690 (s) 566 (w), 344 (m); MS (70 eV, EI), *m*/*z* (%): 261 (2) [M]$^+$, 257 (100) [M − 4 H]$^+$; elemental analysis calcd. (%) for $C_2H_9B_7As_2$ (258.62): C 9.29, H 3.51; found: C 9.34, H 3.68. For 3-Cl-**2**: mp ~270 °C (decomp.); IR (KBr): ν_{max} = 3468 (w), 3245 (w), 3020 (w), 2520 (s), 1644 (w), 1158 (m), 1122 (w), 950 (s), 912 (s), 822 (s), 758 (m), 684 (w), 626 (w), 586 (w), 456 (s), 374(s), 290 (m); MS (70 eV, EI), *m*/*z* (%): 296 (11) [M]$^+$, 292 (100) [M − 4 H]$^+$; elemental analysis calcd. (%) for $C_2H_8B_7As_2Cl$ (293.06): C 8.20, H 2.76; found: C 8.26, H 2.63. (b) The reaction procedure was carried out by a similar manner as in the preceding experiment (a) except that two equivalents of $Et_3N{\cdot}BH_3$ (1.0 g, 8.8 mmol) were added after adding the $AsCl_3$. This modification led to the isolation of compounds **2** (511 mg, 45%), **3** (10 mg, 1%), and 3-Cl-**2** (yield 91 mg, 8%).

Reaction of *arachno*-4,6-$C_2B_7H_{13}$ (1) with AsI_3

PS (4.94 g, 23 mmol) was added to a solution of compound **1** (650 mg, 5.8 mmol) in CH_2Cl_2 (25 cm^3), followed by addition of AsI_3 (5.25 g, 11 mmol) under continuous stirring at 0 °C. The stirring was then continued over a period of 6 h at room temperature. The mixture was then cooled to *ca.* 10 °C and decomposed by adding water (50 cm^3, dropwise). The CH_2Cl_2 layer was separated and evaporated with silica gel (6 g). The solid materials were placed onto a silica gel column, which was eluted with hexane to collect three main fractions of R_f(hexane) 0.22, 0.16, and 0.05. These were evaporated and the solids identified by NMR spectroscopy as compounds **2** (yield 180 mg, 12%), **3** (yield 50 mg, 3%), and 3-I-**2** (yield 360 mg, 17%), respectively. For 3-I-**2**: mp 195–196°C; IR (KBr): ν_{max}= 3436 (s), 3024 (w), 2567 (s), 2528 (s), 1640 (w), 1154 (m), 1112 (w), 1058 (m), 966 (m), 886 (m), 776 (s), 662 (m), 622 (w), 580 (w), 454 (m), 362 (w); MS (70 eV, EI), *m*/*z* (%): 387 (1) $[M]^+$, 285 (100) $[M - 2\ H]^+$; elemental analysis calcd. (%) for $C_2H_9B_7As_2I$ (384.51): C 6.25, H 2.10; found: C 6.15, H 2.18.

Reaction of *arachno*-4,5-$C_2B_7H_{13}$ (4) with $AsCl_3$

A solution of compound **4** (1.1 g, 10 mmol) in CH_2Cl_2 (50 cm^3) was cooled to 0 °C under stirring and then PS (8,6 g, 40 mmol) was added, followed by $AsCl_3$ (1.6 cm^3, 20 mmol, dropwise). The mixture was stirred at room temperature for additional 10 h, cooled to 0 °C, and decomposed by water (75 cm^3, dropwise). The CH_2Cl_2 layer was separated and evaporated with silica gel (10 g). The solids were mounted onto a silica gel column and the column was eluted with hexane to collect fractions of R_f 0.22, 0.15, and 0.09. These were evaporated to give compounds **5** (yield 290 mg, 11%), **3** (yield 230 mg, 9%), and 3-Cl-**5** (yield 490 mg, 17%), respectively. For **5**: mp ~260 °C (decomp.); IR (KBr): ν_{max}= 3436 (s), 2564 (s), 1256 (m), 1066 (m), 1008 (s), 900 (s), 738 (s), 664 (m), 346 (s); MS (70 eV, EI), *m*/*z* (%): 261 (2) $[M]^+$, 257 (100) $[M - 4\ H]^+$; elemental analysis calcd. (%) for $C_2H_9B_7As_2$ (258.62): C 9.29, H 3.51; found: C 9.17, H 3.43. For 3-Cl-**5**: mp 304 °C (decomp.); IR (KBr): ν_{max} = 3436 (s), 3020 (w), 2576 (s), 1632 (w), 1382 (w), 1252 (m), 1064 (m), 948 (s), 880 (s), 858 (s), 736 (m) 666 (w), 582 (m), 482 (w), 368 (w); MS (70 eV, EI), *m*/*z* (%): 296 (14) $[M]^+$, 292 (100) $[M - 4\ H]^+$; elemental analysis calcd. (%) for $C_2H_9B_7As_2Cl$ (293.06): C 8.20, H 2.76; found: C 8.12, H 2.63.

X-ray crystallography

The colourless crystal of compound 3-I-**2** of dimensions 0.175 × 0.1 × 0.075 mm was mounted onto a glass fiber with glue and measured on a four-circle diffractometer Nonius Kappa CCD equipped with area detector at 150 K with (graphite monochromated) MoKα radiation. The crystallographic details are summarized in Table 2. The structure was solved by the direct method (SIR92)[19] and refined by a full matrix least squares procedure based on F^2 (SHELXL97).[20] The absorption correction was carried out using a multi-scan method.[21] The hydrogen atoms were found on a difference map and those of the open $As_2C_2BH_3$ face were refined isotropically, the others were put into calculated positions riding during refinement on the respective pivot atom (136 parameters) with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom. Scattering factors were those implemented in the SHELX programs. For further details see Table 2.

CCDC reference number 198853.

See http://www.rsc.org/suppdata/dt/b2/b212183b/ for crystallographic data in CIF or other electronic format.

Computational details

All calculations were carried out using the program package Gaussian 98[22] and performed on the cluster of 90 Pentium II/440 MHz and Pentium III/800 MHz processors running under Linux OS at the J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic. The structures proposed on the basis of ^{11}B and ^{1}H experiments were optimized by the Becke functional B3LYP/6-31G* method.[23] The figures of standard output orientation were captured using Hyperchem Profesional, release 7.

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