Phosphacarborane Chemistry: The 7,8,9,11-, 7,9,8,10- and 7,8,9,10-Isomers of *nido*-$P_2C_2B_7H_9$—Diphosphadicarbaborane Analogues of 7,8,9,10-$C_4B_7H_{11}$

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Abstract: The reaction between the carborane *arachno*-4,6-$C_2B_7H_{13}$ (**1**) and PCl_3 in dichloromethane in the presence of a "proton sponge" (PS = 1,8-dimethylaminonaphthalene) resulted in the isolation of the eleven-vertex *nido*-diphosphadicarbaboranes 7,8,9,11-$P_2C_2B_7H_9$ (**2**) and 3-Cl-7,8,9,11-$P_2C_2B_7H_8$ (3-Cl-**2**) in yields of 54 and 7%, respectively. Replacement of the PS by NEt_3 in the same reaction gave diphosphadicarbaboranes **2** and 3-Cl-**2** together with the isomeric species *nido*-7,9,8,10-$P_2C_2B_7H_9$ (**3**) in yields of 28, 15 and 3%, respectively. The reaction between the isomeric carborane *arachno*-4,5-$C_2B_7H_{13}$ (**4**) and PCl_3 in dichloromethane in the presence of PS gave the asymmetrical isomer, *nido*-7,8,9,10-$P_2C_2B_7H_9$ (**5**), along with the chloro derivatives 4-Cl-7,8,9,10-$P_2C_2B_7H_8$ (4-Cl-**5**) and 11-Cl-7,8,9,10-$P_2C_2B_7H_8$ (11-Cl-**5**) (yields of 21, 1 and 13%, respectively). The structures of the chlorinated derivatives 3-Cl-**2** and 11-Cl-**5** were determined by X-ray diffraction analysis. In addition, the structures of all compounds isolated were geometry-optimised and confirmed by comparison of experimental ^{11}B chemical shifts with those calculated by the GIAO-SCF/II//RMP2(fc)/6-31G* method. The calculations also include the structure and ^{11}B NMR shifts of the isomer *nido*-7,10,8,9-$P_2C_2B_7H_9$ (**6**) which has not yet been isolated.

Keywords: ab initio calculations · carboranes · NMR spectroscopy · phosphacarboranes

Introduction

The reaction of borane-based anions with phosphorus halides in the presence of basic reagents as deprotonation agents, pioneered by Todd and Little several years ago,[1] is known to generate phosphaboranes containing a bare phosphorus centre as a cage vertex. The cluster P atom in these species contributes three electrons and three orbitals into the cluster bonding proper,[1] with two remaining electrons occupying the exoskeletal orbital. The P vertex is thus isolobal with a CH vertex and the phosphaboranes are therefore structural analogues of the corresponding carboranes. The phosphorus insertion reactions led to the isolation of essential representatives of the phosphaborane and phosphacarborane families such as, for example, [*nido*-7-$PB_{10}H_{12}$]$^-$,[2] and to all three isomers of $PCB_{10}H_{11}$,[3] phosphorus analogues of the [*nido*-7-$CB_{10}H_{13}$]$^-$ and $C_2B_{10}H_{12}$ carboranes. The P-insertion reaction can be modified by the use of alkyl- or aryl-substituted RPX_2 (X = halogen) compounds and the reaction then leads to phosphaboranes substituted at the P centre, as exemplified by the *nido* compounds 7-R-7-$PB_{10}H_{12}$ (R = Me and Ph)[4] and 7-R-7,8,9-$PC_2B_8H_{10}$.[5] In a preliminary communication, we have recently reported the synthesis of the parent tricarbollide analogues *nido*-7,8,11-$PC_2B_8H_{11}$ and [*nido*-7,8,11-$PC_2B_8H_{10}$]$^-$ which is based on the reaction between [6,9-$C_2B_8H_{10}$]$^{2-}$ and PCl_3.[6] As a continuation of this search for parent phosphacarboranes, we report here on PCl_3 insertion reactions into the clusters of the two isomeric *arachno* dicarbaboranes 4,6- and 4,5-$C_2B_7H_{13}$. The reactions lead unexpectedly to the incorporation of two P atoms into the cluster area and to the formation of three of the four possible *nido*-$P_2C_2B_7H_9$ isomers of open-face configuration of heteroatoms. The compounds are the first parent (unsubstituted) representatives of the diphosphadicarbaborane family and structural analogues of the previously reported *nido*-7,8,9,10-$C_4B_7H_{11}$ tetracarbaborane.[7] The numbering systems for the nine-vertex *arachno* and eleven-vertex *nido* cages employed in this work are given in general structures **I** and **II**, respectively.

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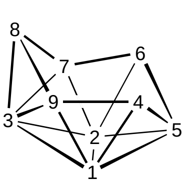

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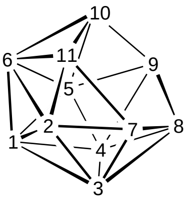


II

Results and Discussion

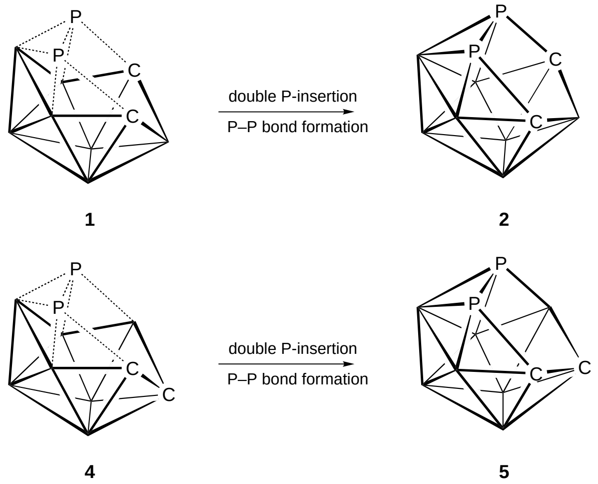
Syntheses: A room-temperature reaction between the carborane *arachno*-4,6-$C_2B_7H_{13}$ (**1**)[8] and PCl_3 in dichloromethane in the presence of "proton sponge" (PS = 1,8-dimethylaminonaphthalene), followed by decomposition of the reaction mixture with water and column chromatography of the products soluble in CH_2Cl_2 on silica gel resulted in the isolation of two main products. These were identified by NMR spectroscopy and mass spectrometry as the eleven-vertex *nido* diphosphadicarbaboranes 7,8,9,11-$P_2C_2B_7H_9$ (**2**) (yield 54 %) and 3-Cl-7,8,9,11-$P_2C_2B_7H_8$ (3-Cl-**2**) (yield 7 %). The structure of compound 3-Cl-**2** was determined by X-ray diffraction analysis. Modification of this reaction by the use of NEt_3 as the deprotonation agent also led to the formation of compounds **2** and 3-Cl-**2** (yields 28 and 15 %, respectively); however, in this case, they were accompanied by the isomeric species 7,9,8,10-$P_2C_2B_7H_9$ (**3**) (yield 3 %). The compound mixture could be readily separated by column chromatography on silica gel.

A similar reaction with the isomeric carborane *arachno*-4,5-$C_2B_7H_{13}$ (**4**)[9] in the presence of PS gave the isomeric, parent species *nido*-7,8,9,10-$P_2C_2B_7H_9$ (**5**) (yield 21 %) along with two monochloro derivatives of **5**. These were identified by NMR spectroscopy and mass spectrometry as 4-Cl-7,8,9,10-$P_2C_2B_7H_8$ (4-Cl-**5**) and 11-Cl-7,8,9,10-$P_2C_2B_7H_8$ (11-Cl-**5**) (yields 1 and 13 %, respectively). The structure of the chlorinated compound 11-Cl-**5** was also determined by a single-crystal X-ray diffraction study. It should also be noted that the reactions are stoichiometric only with respect to the formation of the chlorinated derivatives [Eq. (1)].

$$C_2B_7H_{13} + 2\,PCl_3 + 5\,PS \rightarrow P_2C_2B_7H_8Cl + 5\,PSHCl \qquad (1)$$

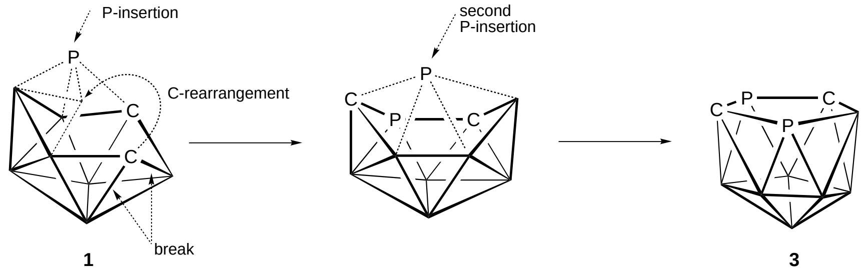
Although there is no direct experimental evidence, it can be surmised that the parent compounds **2**, **3** and **5** are formed by the reduction of the chloro derivatives at some stage in the reaction at the expense of oxidation of the starting compound. Another interesting feature is that the chlorine substituent in all chloro derivatives isolated resides on a boron vertex adjacent to at least one of the cluster P atoms, that is, close to the reaction centre.

As outlined in Scheme 1, the formation of both diphosphadicarbaboranes **2** and **5** and their chlorinated derivatives as well, is consistent with the incorporation of two P vertices into the open hexagonal face of the isomeric $C_2B_7H_{13}$ carboranes **1** and **4** with concomitant formation of a P–P bond. This process generates symmetrical and asymmetrical P-P-C-B-C and P-P-C-C-B pentagonal faces, respectively, within an eleven-vertex *nido* framework without significant movement of the original carbon positions. The formation of compound **3** seems more complex, being consistent with a two-step P insertion associated with a shift of one of the C vertices towards the P centre (Scheme 2).



Scheme 1. Insertion of P into carboranes **1** and **4**.

X-ray diffraction studies: The structures of the chlorinated derivatives 3-Cl-**2** and 11-Cl-**5** were determined unambiguously by an X-ray diffraction analysis (for selected crystallographic parameters see Table 1 and Table 2). As seen from Figure 1, the arrangement of the P and C vertices within the open pentagonal face confirms both reaction paths outlined in Scheme 1. The structure of compound 3-Cl-**2** (Figure 1 top) is consistent with a C_s symmetry plane that bisects the P7–P8 bond and intersects the chlorinated B3 vertex together with the bottom B1 atom. The P–P and two P–C bond lengths of 2.1931(9) and 1.865(3), 1.856(3) Å, respectively, are similar to those found for other phosphaborane and phosphacarborane compounds.[10, 11] The other P–B, C–B, and B–B (Table 2) separations also fall within the usual limits.[1] The structure of compound 11-Cl-**5** (Figure 1 bottom) reveals an asymmetrical disposition of the P and C vertices in the open face and confirms that the Cl substituent lies on the open-face boron. A comparison of intracluster distances in Table 2 with those of



Scheme 2. Formation of compound **3** by a two-step P insertion and shift of one of the C vertices towards the P centre.

Table 1. Crystal data and structure refinement for 3-Cl-**2** and 11-Cl-**5**

	3-Cl-**2**	11-Cl-**5**
empirical formula	$C_2H_8B_7P_2Cl$	$C_2H_8B_7P_2Cl$
M_r	205.14	205.14
crystal system	orthorhombic	monoclinic
space group	$Pna2_1$	$C2/c$
a [Å]	13.648(2)	12.361(3)
b [Å]	7.0560(9)	6.6826(8)
c [Å]	9.5490(9)	23.176(3)
β [°]		98.36(1)
Z	4	8
V [Å^3]	919.6(2)	1894.1(6)
μ [mm^{-1}]	0.684	0.664
ρ_{calcd}, [Mg m^{-3}]	1.482	1.439
λ [Å]	0.71073	0.71073
$F(000)$	408	816
θ range [°]	3–28	3.3–25
scan mode	ϕ and ω	$\Theta-2\theta$
h, k, l collected	$0 \leq h \leq 17, 0 \leq k \leq 9, -12 \leq l \leq 12$	$0 \leq h \leq 14, 0 \leq k \leq 7, -27 \leq l \leq 27$
no. of reflections measured	2443	1725
no. of unique reflections	1463	1659
no. of parameters	140	141
GOF[a, b] all data	1.030	1.137
final R[a, b] indices [$I > 2\sigma(I)$]	$R1$ 0.031, $wR2$ 0.073	$R1$ 0.037, $wR2$ 0.113
R[a] indices (all data)	$R1$ 0.037, $wR2$ 0.077	$R1$ 0.042, $wR2$ 0.122
w_1/w_2	0.028/0.114	0.072/2.077
$\Delta\rho$, max/min [e Å^{-3}]	0.179/ −0.272	0.335/ −0.326

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma/F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2]^{1/2}$, $\mathrm{GOF} = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$.
[b] Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$; $P = [\max(F_o^2,0) + 2F_c^2]/3$

3-Cl-**2** does not disclose any surprising differences and those found can be attributed to the asymmetry of the molecule. As far as intermolecular interactions are concerned, these appear to have purely van der Wals character for both crystals. However, the crystal packing is more efficient for the symmetrical 3-Cl-**2** compound, where the volume fraction of the unit cell per molecule is 229.9 Å^3, whereas that for 11-Cl-**5** amounts to 236.7 Å^3.

Geometry optimisation: According to Gimarc's topological charge stabilisation rule,[12] elements more electronegative than boron, namely C, S, N and P (although the electronegativity of P does not differ too much from that of B), prefer cluster sites of the highest negativity. The systems under study are formally derived from the hypothetical parent [*nido*-$B_{11}H_{11}$]$^{4-}$ ion (derived from *closo*-[$B_{12}H_{12}$]$^{2-}$ by removal of one [BH]$^{2-}$ vertex; the solid-state structure of [*nido*-$B_{11}H_{14}$]$^-$ is known[13]) in which the charge distribution in the open pentagonal face is uniform (RMP2(fc)/6-31G* natural population analysis (NPA) charge −0.334, in contrast to −0.170 associated with the B_5 pentagonal belt capped by B1; NPA for B1 = −0.250)[14]. Consequently, an 11-vertex *nido* heteroborane of a [*nido*-$B_{11}H_{11}$]$^{4-}$-type deltahedral shape will prefer its heteroatoms to occupy the open-face sites.[15] The presence of more than one heteroatom, for example three, in such a structural arrangement leads to a number of positional isomers.[6, 15b] Herein, we extend such studies and examine the possibility of accommodating two pairs of two kinds of heteroatoms, namely C and P, both experimentally and computationally. This evidently results in four positional isomers with contiguous open-face {C-P-P-C}, {P-P-C-C}, {P-C-P-C} and {P-C-C-P} configurations corresponding to isomers **2**, **5**, **3** and **6**. Since the charge distribution in the open-face of [*nido*-$B_{11}H_{11}$]$^{4-}$ is uniform, there does not seem to be a special preference as for the individual accommodations of two Ps and two Cs (N.B. the electronegativity of P is quite close to that of B!) from the energetical point of view. Indeed, the four possible positional isomers of *nido*-$P_2C_2B_7H_9$ are computed to differ in their energies only slightly, as revealed in Table 3. The fact that the symmetrical compound **6** is highest in energy may account for the experimental unavailability of this cluster to date. The chloro derivatives differ also in their energies marginally (see Table 3). The fit between the computed and experimental shifts was found to be consistently good (see Table 4), the maximum deviation was ≈4 ppm. As anticipated, the chlorine substitutions do not affect the NMR patterns too much with respect to the corresponding parent compounds, with the exception of the substituted boron atom.[16]

The RMP2(fc)/6-31G*-optimised geometries of the parent diphosphadicarbaboranes **2**, **3**, **5** and **6** are shown in Figure 2, and those of the chlorinated species 3-Cl-**2**, 4-Cl-**5** and 11-Cl-**5** are depicted in Figure 3. The most striking features of the computed molecular structures of these systems are the considerable deformations of the open-pentagonal belts. Thus, the X-P-X angles (X = C,B,P) lie in the narrow interval 94.5–97.4°; these values are very close to 96.6° computed for the B-S-B angle in 7,8,10-$C_2SB_8H_{10}$ at the same level.[15a] Interestingly, the P-P-P angles in the two newly prepared *nido*-$P_3CB_7H_8$ deviate from a regular pentagonal angle of 108° by only ≈7°.[17] This may be the consequence of the similar electronegativities of B and P, whereas in the $P_2C_2B_7H_9$ derivatives the electronegativity of C, which affects the X-P-X angles, differs considerably from that of B and P. These pentagons are far from being planar, as demonstrated by the dihedral angles given in Table 5. The P–P and B–P separations determined for all seven compounds span narrow intervals of 2.21–2.23 Å and 2.03–2.09 Å, respectively. The relatively high electron densities between the paired atoms that constitute the open-face rings were revealed by the WBI and NBO values (Table 6).

NMR studies: Entirely consistent with the X-ray diffraction studies are the NMR characteristics of the compounds isolated (Table 4). In accord with the C_s symmetry, the ^{11}B NMR spectrum of **2** consists of 1:2:2:1:1 patterns of doublets while in the spectrum of 3-Cl-**2** one of the doublets with an intensity of 1 collapses to a singlet. The ^{11}B NMR spectrum of

Table 2. Selected bond lengths [Å] and angles [°] for 3-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (3-Cl-**2**) and 11-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$ (11-Cl-**5**)

Compound 3-Cl-**2**			
B1–B2	1.774(4)	B1–B3	1.768(5)
B1–B4	1.764(4)	B1–B5	1.797(5)
B1–B6	1.798(5)	B2–B3	1.840(5)
B2–B6	1.785(5)	B2–P7	2.048(3)
B2–C11	1.730(5)	B3–B4	1.839(5)
B3–P7	2.110(3)	B3–P8	2.118(4)
B4–B5	1.779(5)	B4–P8	2.048(3)
B4–C9	1.728(5)	B5–B6	1.737(5)
B5–C9	1.709(4)	B5–B10	1.805(5)
B6–B10	1.804(5)	B6–C11	1.716(4)
P7–P8	2.1931(9)	P7–C11	1.856(3)
P8–C9	1.865(3)	C9–B10	1.615(5)
B10–C11	1.617(5)	B2-P7-B3	52.50(13)
B2-P7-P8	100.54(8)	B3-P7-P8	58.91(10)
B3-P8-P7	58.59(9)	B4-P8-B3	52.37(13)
B4-P8-P7	100.16(9)	C9-P8-B3	90.61(13)
C9-P8-B4	52.15(15)	C9-P8-P7	97.61(10)
C9-B10-C11	111.8(3)	C11-P7-B2	52.34(16)
C11-P7-B3	90.62(13)	C11-P7-P8	97.30(10)
B10-C9-P8	114.6(2)	B10-C11-P7	115.2(2)
Compound 11-Cl-**5**			
B1–B2	1.778(4)	B1–B3	1.759(4)
B1–B4	1.754(4)	B1–B5	1.774(4)
B1–B6	1.777(4)	B2–B3	1.824(4)
B2–B6	1.742(4)	B2–P7	2.053(3)
B2–B11	1.833(4)	B3–B4	1.815(4)
B3–P7	2.088(3)	B3–P8	2.107(3)
B4–B5	1.776(4)	B4–P8	2.026(3)
B4–C9	1.749(4)	B5–B6	1.758(4)
B5–C9	1.711(4)	B5–C10	1.725(4)
B6–C10	1.728(4)	B6–B11	1.783(4)
P7–P8	2.2029(10)	P7–B11	1.957(3)
P8–C9	1.843(3)	C9–C10	1.535(4)
C10–B11	1.599(4)	B2-P7-B3	52.26(12)
B2-P7-P8	99.15(9)	B3-P8-P7	57.91(9)
B3-P7-P8	58.75(9)	B4-P8-B3	52.06(12)
B4-P8-P7	100.77(9)	C9-P8-B3	90.21(12)
C9-P8-B4	53.53(12)	C9-P8-P7	98.07(9)
C9-C10-B11	115.2(2)	C10-C9-P8	117.43(18)
C10-B11-P7	113.60(17)	B11-P7-B2	54.33(11)
B11-P7-B3	92.10(12)	B11-P7-P8	95.22(9)

the parent compounds **3** and **5** show seven doublets of intensity 1 and the spectra of the 4-chloro and 11-chloro derivatives of **5** display six doublets and one singlet of equal intensities. Application of the [^{11}B,^{11}B]-COSY[18] spectroscopy together with ^{1}H{^{11}B-selective)} spectroscopy,[19] assigned all resonances to individual BH vertices. The comparison of the ^{11}B chemical shifts shows that the diphosphadicarbaboranes of types **2**, **3** and **5** are analogues of the previously reported[7] *nido* tetracarbaborane 7,8,9,10-$C_4B_7H_{11}$. This similarity is also demonstrated by similar trends in ^{11}B chemical shifts (spectral range $\delta \approx 32-35$); however, a comparison reveals that the isolobal substitution of two CH vertices for P produces systematic deshielding (average $\delta \approx 10$) of all BH positions. The geometry optimisation of all compounds isolated was used as a basis for GIAO-SCF/II calculations[20] of the underlying ^{11}B shifts and the comparison between experimental and calculated values (see Table 4) reveals satisfactory agreement (maximum differences are in the range of 4.0 ppm).

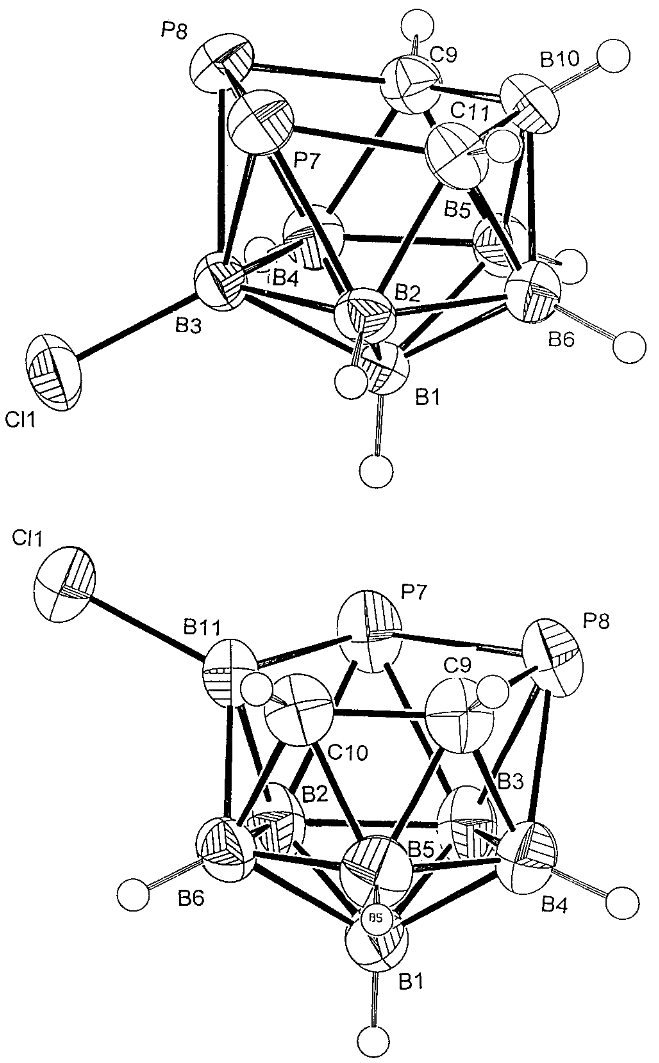


Figure 1. ORTEP representation of the crystallographically determined molecular structures of 3-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (3-Cl-**2**; top) and 11-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$ (11-Cl-**5**; bottom).

Table 3. Energy data for positional isomers of *nido*-$P_2C_2B_7H_9$ and its chloro derivatives.

Isomer	Symmetry	ZPE[a] [kcal mol^{-1}]	RMP2/6-31G*[b] [Hartree]	Relative energies[c] [kcal mol^{-1}]
$P_2C_2B_7H_9$				
2	C_s	90.337(0)	– 936.388998	0.000
5	C_1	90.559(0)	– 936.388054	0.817
3	C_1	90.287(0)	– 936.386866	1.294
6	C_s	90.579(0)	– 936.386390	1.851
Cl-$P_2C_2B_7H_8$				
11-Cl-**5**	C_1	85.380(0)	– 395.464404	0.000[d]
4-Cl-**5**	C_1	83.961(0)	– 395.462471	1.211[d]
3-Cl-**2**	C_s	85.062(0)	– 395.462138	1.422[d]

[a] Zero point energies calculated at the RHF/6-31G* level. The number of imaginary frequencies NIMAG is given in parentheses. [b] Total energies at the RMP2/6-31G*level. [c] Relative energies with ZPEs corrections scaled by 0.89. [d] Relative energies without ZPE corrections; upon inclusion of the ZPEs, scaled by 0.89, 11-Cl-**5** is destabilised by 0.052 kcal mol^{-1}.

Table 4. NMR data of the compounds ($CDCl_3$, 293 K).

Compound	Nucleus	δ
nido-7,8,9,11-$P_2C_2B_7H_9$ (**2**)	^{11}B[a, b]	−0.5 [d, B10, 150], −2.5 [d, B(5,6), 162], −4.8 [d, B(2,4), 169], −17.5 [d, B3, 170], −34.5 [d, B1, 154]
	^{11}B(calcd)[c]	−1.7 [B10], −0.8 [B5,6], −1.4 [B2,4], −17.2 [B3], −35.1 [B1]
	^{11}B,^{11}B[a]	all theoretical cross-peaks observed
	^{1}H{^{11}B}[d, e]	3.02 [s, H10], 2.91 [br s, H(2,4)], 2.52 [s, H(5,6)], 2.21 [br s, H(9,11)], 2.16 [t (asym.) H3, 35/20], 2.07 [s, H1]
	^{31}P{^{1}H}[f, g]	−43.4 [s, P(7,8)]
3-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (3-Cl-**2**)	^{11}B[a, b]	−0.8 [s, B3, −], −2.1 [d, B(2,4), ≈165], −2.1 [d, B(5,6), ≈165], −4.7 [d, B10, 150], −32.2 [d, B1, 150],
	^{11}B(calcd)[c]	−1.2 [B3], 0.7 [B(2,4)], −0.6 [B(5,6)], −5.1 [B10], −31.1 [B1],
	^{11}B,^{11}B[a]	all theoretical cross-peaks observed
	^{1}H{^{11}B}[d, e]	3.37 [s, H(2,4)], 2.77 [d, H(9,11), 20], 2.73 [s, H10], 2.48 [s, 2H, H(5,6)], 1.98 [s, 1H, H1]
	^{31}P{^{1}H}[f, g]	−25.2 [s, P(7,8)].
nido-7,9,8,10-$P_2C_2B_7H_9$ (**3**)	^{11}B[a, b]	−1.2 [d, B6, ≈177], −2.4 [d, B3, ≈180], −4.2 [d, B11, 146], −7.5 [d, B5, ≈162], −8.4 [d, B2, ≈142], −13.3 [d, B4, 173], −36.3 [d, B1, 150]
	^{11}B(calcd)[c]	1.6 [B6], 1.6 [B3], −5.0 [B11], −5.9 [B5], −6.5 [B2], −12.1 [B4], −36.9 [B1]
	^{11}B,^{11}B[a]	all theoretical cross-peaks observed
	^{1}H{^{11}B}[d, e]	3.06 [d, H3, 10], 2.70 [s, H6], 2.55 [d, H11, 45], 2.55 [d, H5, 15], ≈2.55 [d, H4, ≈15], 2.33 [d, H10, 35], 2.10 [d, H2, 20], 2.01 [s, H1], 1.73 [t (asym.), H8, ≈35/25]
	^{31}P{^{1}H}[f, g]	−38.8 [s, P(7 or 9)], −41.3 [s, P(7 or9)]
nido-7,8,9,10-$P_2C_2B_7H_9$ (**5**)	^{11}B[a, b]	−0.1 [d, B5, ≈170], −0.1 [d, B6, ≈170], −2.9 [d, B11, 150], −4.7 [d, B2, ≈176], −5.9 [d, B3, ≈177], −12.0 [d, B4, 170], −34.6 [d, 1B, B1, 158]
	^{11}B(calcd)[c]	1.1 [B5], 1.9 [B6], −4.3 [B11], −1.6 [B2], −2.6 [B3], −10.3 [B4], −35.5 [B1]
	^{11}B,^{11}B[a]	all theoretical cross-peaks observed
	^{1}H{^{11}B}[d, e]	3.23 [s, H10], 2.90 [s, H5], 2.87 [d, H9, 32], 2.86 [d, H4, 22], 2.79 [s, H6], 2.72 [d, H11, 37], 2.62 [t (asym.), H3, 15/20], 2.41 [d, H2, 22], 2.07 [s, H1]
	^{31}P{^{1}H}[f, g]	−49.2 [d (asym.), P8, 240], −58.2 [d (asym.), P7, 240].
4-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$ (4-Cl-**5**)	^{11}B[a, b]	1.0 [d, B5, ≈170], 0.5 [s, B4], −0.6 [d, B6, ≈165], −3.8 [d, B2, ≈150], 3.8 [d, B3, ≈150], −7.8 [d, B11, 150], −34.3 [d, B1, 157]
	^{11}B(calcd)[c]	2.2 [B5, ≈170], 2.7 [B4], 1.1 [B6], −0.7 [B2], −1.2 [B3], −8.1 [B11], −34.6 [B1]
	^{11}B,^{11}B[a]	all theoretical cross-peaks observed
	^{1}H{^{11}B}[d, e]	3.56 [s, H10], 3.25 [s, H5], 3.22 [t, H3, ≈20], 3.21 [d, H9, 34], 2.79 [s, H6], 2.66 [d, H11, 38], 2.40 [d, H2, 20], 2.13 [s, H1]
	^{31}P{^{1}H}[f, g]	−30.6 [d (asym.), P8, 244], −60.8 [d (asym.), P7, 244]
11-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$ (11-Cl-**5**)	^{11}B[a, b]	7.6 [s, B11], 2.0/4.0 [d, B6], −1.9 [d, B5, ≈180], −3.1 [d, B2, ≈190], −7.7 [d, B3, 170], −18.0 [d, B4, 173], −34.9 [d, B1, 158]
	^{11}B(calcd)[c]	7.3 [B11], 4.0 [B6], −0.7 [B5], 0.6 [B2], −4.6 [B3], −14.7 [B4], −35.9 [B1]
	^{11}B,^{11}B[a]	all theoretical cross-peaks observed
	^{1}H{^{11}B}[d, e]	3.57 [s, H10], 2.84 [s, H5], 2.83 [d, H2, 26], 2.83 [d, H4, ≈15], 2.82[d, H9, 32] 2.51 [t (asym.), H3, ≈20/15], 2.39 [s, 1H, H6], 2.04 [s, H(1)]
	^{31}P{^{1}H}[f, g]	−66.6 [d (asym.), P8, 238], −73.7 [d (asym.), P7, 238]
nido-7,10,8,9-$P_2C_2B_7H_9$ (**6**)	^{11}B(calcd)[c]	−1.2 [B6], −2,4 [B3], −4.2 [B11], −7.5 [B5], −8.4 [B2], −13.3 [B4], −36.3 [B1]

[a] 160.4 MHz. [b] δ(^{11}B) [multiplicity, assignment, ^{1}J(B,H) in Hz]. [c] GIAO-SCF/II//RMP2(fc)/6−31G*. [d] 500 MHz. [e] δ(^{1}H){^{11}B} [multiplicity, assignment, ^{2}J(P,H) in Hz (if applicable)]. [f] 202.4 MHz. [g] δ(^{31}P){^{1}H} [multiplicity, assignment, ^{1}J(P,P) in Hz (if applicable)].

The ^{1}H NMR spectra of **2** and 3-Cl-**2** display one intensity with two CH(9,11) signals which exhibits doublet splitting as a result of ^{1}H−^{31}P coupling. The ^{1}H NMR spectrum of the parent compound **3** exhibits two different CH resonances, CH(8) (asym. t) and CH(10) (d), the asymmetrical triplet splitting of the former resonance arises from interaction with two non-equivalent ^{31}P nuclei. The corresponding spectra of **5**, 4-Cl-**5** and 11-Cl-**5** contain two CH(9) and CH(10) resonances, the former being split into a doublet by ^{1}H−^{31}P coupling. In all cases, the ^{1}H{^{11}B} resonances of the BH vertices adjacent to the P sites exhibit clear doublet splittings and those of BH connected to two P vertices are split into triplets, which helps the unambiguous assignment of all the proton resonances. The ^{31}P NMR spectra of the symmetrical compounds **2** and 3-Cl-**2** consist of one singlet resonance, while that of **3** contains two different singlets. As a consequence of the P−P bond between the magnetically non-equivalent P vertices, the corresponding spectra of compounds **5**, 4-Cl-**5** and 11-Cl-**5** consist of two asymmetrical doublets.

Conclusions

Even though there is a mention in the literature of the isolation of a mixture that contains *nido*-$Ph_2Et_2P_2C_2B_4H_4$ as one of the components,[21] the compounds described in this work are first parent representatives of the diphosphadicarbaborane series isolated in a pure state and their synthesis further demonstrates the viability of the PCl_3-mediated insertion reactions into borane clusters.[1] A very interesting aspect of the reactions described is the explicit trend for the incorporation of a maximum number of the P vertices under the formation of very stable eleven-vertex *nido*-phosphacarborane cages. These readily available compounds are structural analogues of the previously reported tetracarbaborane 7,8,9,10-$C_4B_7H_{11}$;[7] however, in the present case, it should be also noted how much the presence of the two P centres increases the number of isomeric structures. The molecules of the phosphacarboranes, that contain a contiguous electron-rich heteroatomic string in the open pentagonal face, thus

0947-6539/01/0707-1550 $ 17.50+.50/0

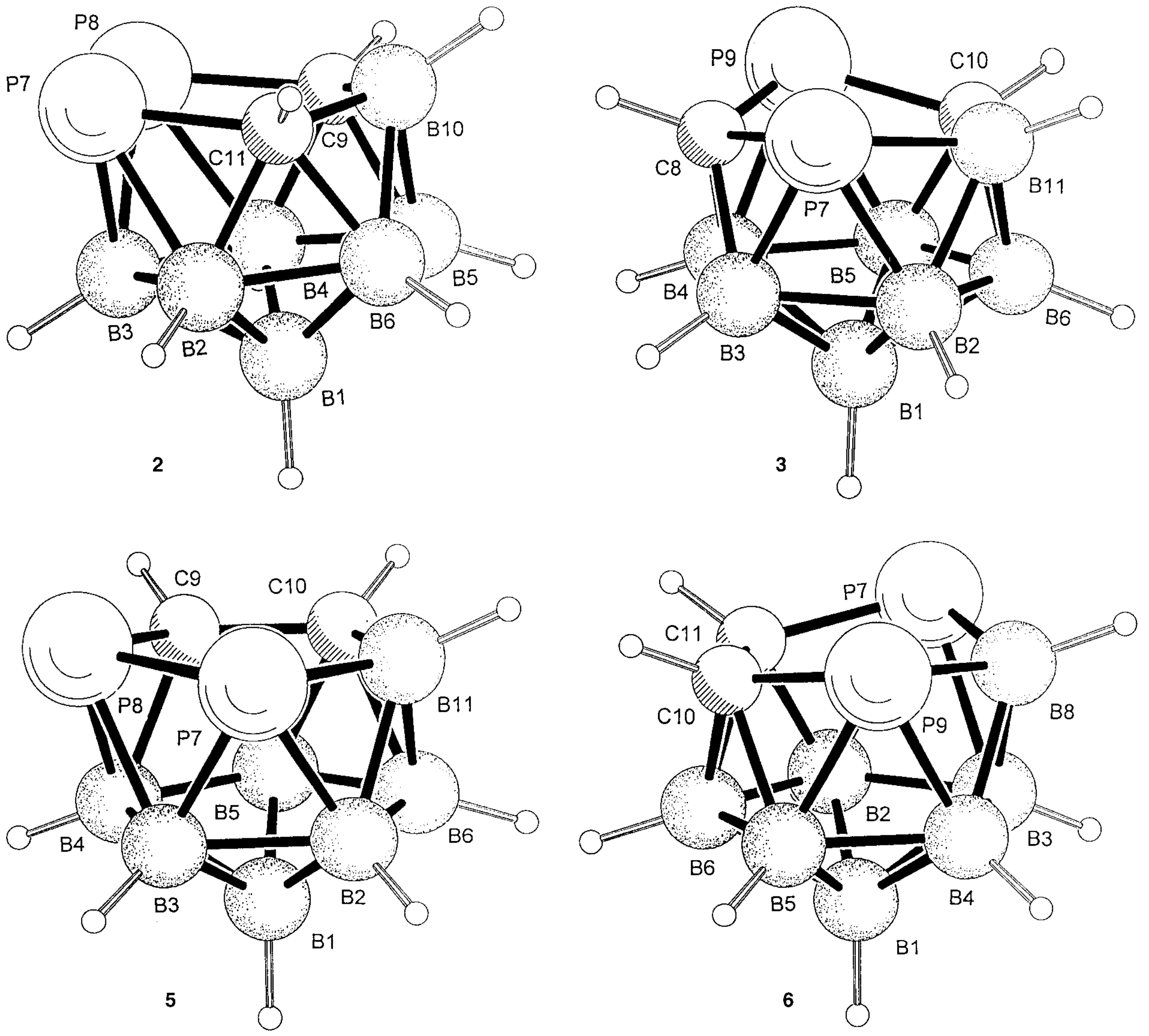


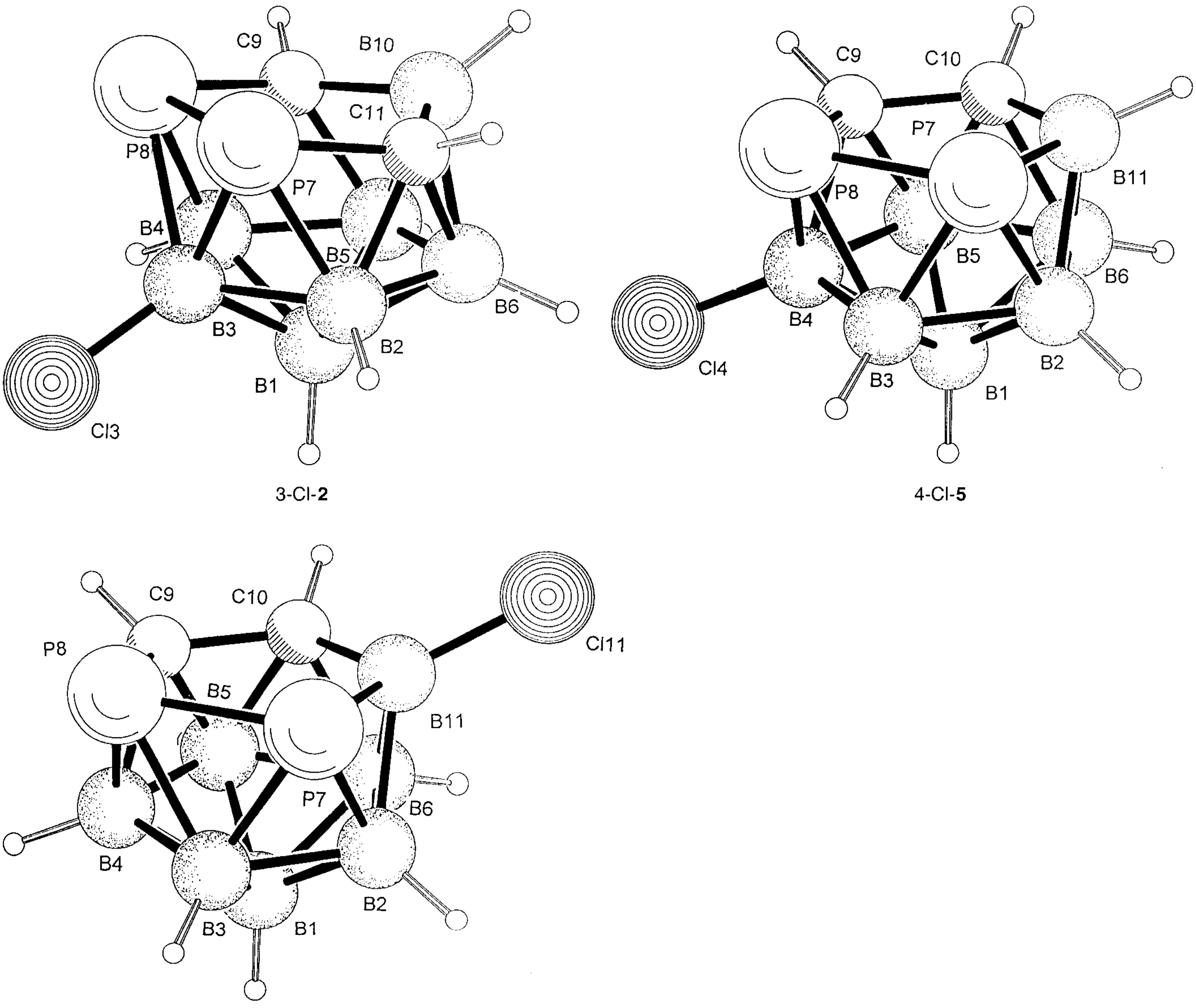
Figure 2. RMP2(fc)/6-31G* energy/geometry-optimised structures of the parent *nido* diphosphadicarbaboranes 7,8,9,11-$P_2C_2B_7H_9$ (**2**), 7,9,8,10-$P_2C_2B_7H_9$ (**3**), 7,8,9,11-$P_2C_2B_7H_9$ (**5**) and 7,10,8,9,-$P_2C_2B_7H_9$ (**6**).

constitute new chemical systems. These can be employed for further developments in the general area of heteroborane chemistry. For instance, metal complexation and boron-degradation reactions are expected to generate novel metallaheteroborane and heteroborane compounds and to extend considerably the area of boron-cluster chemistry. We are currently developing this chemistry and relevant experiments in this interesting area are in progress in our laboratories.

Experimental Section

General procedures: All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver,[22] although some operations, such as preparative TLC, were carried out in air. The starting carboranes **1** and **4** were prepared according to the literature.[8, 9] Hexane, benzene and dichloromethane (Fluka) were dried over CaH_2 and freshly distilled before use. Other chemicals were reagent or 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 aluminum foil; detection by diiodine vapor, followed by 2% aqueous $AgNO_3$ spray). Melting points were measured in sealed capillaries under nitrogen and are uncorrected. Low-resolution mass spectra were obtained with a Finnigan MAT MAGNUM ion-trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basle (Switzerland) (70 eV, EI ionisation). Proton (^1H) and boron (^{11}B) NMR spectroscopy was performed at 11.75 Tesla on a Varian XL-500 instrument. The [^{11}B,^{11}B]-COSY[18] and $^1H\{^{11}B$-selective$\}$[19] NMR experiments were essentially as described in other related papers from our laboratories.[23] Chemical shifts are given in ppm to high-frequency (low field) of $\Xi = 32.083971$ MHz (nominally $F_3B \cdot OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm) and $\Xi = 100$ MHz ($SiMe_4$) for ^1H (quoted ±0.05 ppm), Ξ being defined as in ref. [24]. Solvent resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B,^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in Hz. IR spectra were obtained on a EU 9512 Pye-Unicam Fourier transform spectrometer.

Synthesis of *nido*-7,8,9,11-$P_2C_2B_7H_9$ (2) and 3-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (3-Cl-2): A solution of *arachno*-4,6-$C_2B_7H_{13}$ (**1**, 510 mg, 4.5 mmol) in dichloromethane (25 mL) was treated with PS (3.0 g, 14 mmol). PCl_3 (3.14 g, 23 mmol) was added under stirring and cooling to 0 °C. The stirring was continued at room temperature for 24 h and the mixture was then cooled to 0 °C and decomposed by the addition of water (50 mL, dropwise). The dichloromethane layer was separated and evaporated with silica gel (5 g). The solids were mounted onto a silica gel column (2.5 × 30 cm) and



11-Cl-**5**

Figure 3. RMP2(fc)/6-31G* energy/geometry-optimised structures of the chlorinated *nido* diphosphadicarbaboranes 3-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (3-Cl-**2**), 4-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$ (4-Cl-**5**) and 11-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$ (11-Cl-**5**).

the column was eluted gradually with hexane. The purity of individual fractions was checked by analytical TLC. The chromatography led to the separation of two main fractions of $R_f = 0.33$ and 0.16, which were evaporated to dryness. The solids thus obtained were purified by vacuum sublimation at 70–100 °C (bath) and identified by NMR spectroscopy and mass spectrometry as compounds **2** and 3-Cl-**2**, respectively.

2: M.p. 295 °C; IR (KBr): $\tilde{\nu} = 2920$, 2852 (C–H), 2576 (B–H) cm^{-1}; MS (70 eV, EI): *m/z* (%): 172 (45) $[M]^+$, 170 (100) $[M-2H]^+$; elemental analysis calcd (%) for $C_2H_9B_7P_2$ (170.8): C 14.07, H 5.31; found: C 14.22, H 5.20.

3-Cl-**2**: M.p. 232 °C; IR (KBr): $\tilde{\nu} = 3020$ (C–H), 2576(sh), 2540 (B–H) cm^{-1}; MS (70 eV, EI): *m/z* (%): 208 (12) $[M]^+$, 204 (100) $[M-4H]^+$; elemental analysis calcd (%) for $C_2H_8B_7P_2Cl$ (205.2): C 11.70, H 3.93; found: C 11.90, H 3.76.

Synthesis of *nido*-7,9,8,10-$P_2C_2B_7H_9$ (3) and alternative synthesis of *nido*-7,8,9,11-$P_2C_2B_7H_9$ (2) and 3-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (3-Cl-2): A solution of *arachno*-4,6-$C_2B_7H_{13}$ (**1**, 2.0 g, 17.2 mmol) in dichloromethane (50 mL) was treated with NEt_3 (2.2 g, 22 mmol). PCl_3 (15.7 g, 120 mmol) was added under stirring and cooling to 0 °C. The stirring was continued and room temperature for 24 h and the mixture was then cooled again to 0 °C and decomposed by the addition of water (50 mL, dropwise). The dichloromethane layer was then worked up as in the preceding experiment. Chromatography led to the separation of three main fractions of $R_f =$ (hexane) 0.33, 0.25 and 0.16, which were evaporated to dryness. The solids thus obtained were purified by vacuum sublimation at 70–100 °C (bath) and identified by NMR spectroscopy and mass spectrometry as compounds **2**, **3** and 3-Cl-**2**, respectively (yields 28, 3 and 15 %).

3: M.p. 165 °C; IR (KBr): $\tilde{\nu} = 2920$, 2852 (C–H), 2576 (B–H) cm^{-1}; MS (70 eV, EI): *m/z* (%): 172 (45) $[M]^+$, 170 (100) $[M-2H]^+$; elemental analysis calcd (%) for $C_2H_9B_7P_2$ (170.8): C 14.07, H 5.31; found: C 14.22, H 5.20.

Synthesis of *nido*-7,8,9,10-$P_2C_2B_7H_9$ (5), 4-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$ (4-Cl-5) and 11-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$ (11-Cl-5): A solution of *arachno*-4,5-$C_2B_7H_{13}$ (**4**, 1.1 g, 9.6 mmol) in dichloromethane (100 mL) was cooled to 0 °C and PS (5.5 g, 25.7 mmol) was added together with PCl_3 (4.0 g, 29.1 mmol) (dropwise) under stirring. After the initial exothermic reaction had ceased, the mixture was stirred at room temperature for additional 12 h. The mixture was then cooled to 0 °C and decomposed by the addition of water (20 mL, dropwise). The dichloromethane layer was separated and evaporated with silica gel (5 g). The solids were mounted onto a silica gel column (2.5 × 30 cm) and the column was eluted with chloroform to collect a fraction of $R_f = 0.75$. This was evaporated to dryness and re-chromato-

Table 5. Selected geometrical parameters at the RMP2(fc)/6-31G* level.

	2	3-Cl-**2**	**5**	4-Cl-**5**	11-Cl-**5**	**3**	**6**
Bond lengths [Å]							
1–2[a]	1.762	1.762	1.779	1.774	1.782	1.783	1.772
1–3	1.762	1.764	1.765	1.768	1.766	1.768	1.778
1–4	1.762	1.762	1.755	1.757	1.756	1.757	1.778
1–5	1.792	1.786	1.772	1.772	1.773	1.769	1.772
1–6	1.792	1.786	1.787	1.785	1.782	1.783	1.755
3–7	2.088	2.104	2.087	2.094	2.081	2.047	2.056
3–8	2.088	2.104	2.095	2.090	2.094	1.723	1.800
2–7	2.036	2.039	2.035	2.040	2.044	2.051	2.043
4–8	2.036	2.039	2.031	2.048	2.028	1.722	1.800
2–11	1.722	1.724	1.834	1.834	1.836	1.830	1.743
4–9	1.722	1.724	1.743	1.748	1.744	2.046	2.056
6–11	1.696	1.699	1.775	1.772	1.781	1.775	1.709
5–11	1.696	1.699					
5–9			1.712	1.714	1.712	2.048	2.043
5–10	1.803	1.799	1.714	1.712	1.713	1.722	1.743
6–10	1.803	1.799	1.718	1.723	1.722	1.699	1.709
7–8	2.206	2.210	2.231	2.224	2.232	1.900	1.958
7–11	1.880	1.875	1.962	1.960	1.969	1.951	1.882
9–8	1.880	1.875	1.868	1.871	1.868	1.857	1.958
9–10	1.617	1.618	1.526	1.525	1.525	1.860	1.882
10–11	1.617	1.618	1.613	1.615	1.611	1.628	1.517
(B–H)mean	1.189	1.189	1.189	1.189	1.188	1.189	1.189
(C–H)mean	1.089	1.090	1.089	1.090	1.090	1.091	1.089
B-Cl		1.779		1.777	1.794		
Bond angles [°]							
9–10–11	111.7	111.4	116.1	116.2	115.9	115.3	116.9
8–9–10	115.2	115.5	117.7	117.3	117.8	95.6	95.2
11–7–8	97.2	97.1	95.7	95.8	95.4	94.5	95.2
9–8–7	97.2	97.1	97.1	97.4	97.3	115.1	110.8
7–11–10	115.2	115.5	113.0	113.0	113.3	112.2	116.9
Dihedral angles [°]							
7-11-10-9	– 20.3	– 20.1	– 2.9	– 3.3	– 2.7	8.1	0.0
7-8-9-10	– 11.3	– 11.3	– 6.8	– 6.9	– 6.7	27.9	21.3

[a] For numbering schemes, see Figures 2 and 3.

Table 6. Wiberg bond indices (natural atomic bond orders) for individual bonds in the open-pentagonal faces of the four positional isomers of *nido*-$P_2C_2B_7H_9$.

Compound	Bond 7–8	8–9	9–10	10–11	7–11
2	0.877 (0.685)	0.775 (0.682)	0.783 (0.804)	0.783 (0.804)	0.775 (0.682)
5	0.814 (0.652)	0.801 (0.707)	0.955 (0.824)	0.791 (0.997)	0.864 (0.607)
3	0.728 (0.652)	0.795 (0.709)	0.797 (0.708)	0.770 (0.786)	0.886 (0.817)
6	0.856 (0.798)	0.856 (0.798)	0.767 (0.686)	0.966 (0.841)	0.767 (0.686)

[a] For the atom numbering scheme, see Figures 2 and 3.

graphed with hexane as the liquid phase. This separation led to the isolation of three main fractions ($R_f = 0.39$, 0.21 and 0.10), the purity of which was checked by analytical TLC. Individual fractions were evaporated to dryness and the white, crystalline solids thus obtained were purified by vacuum sublimation at 70–100 °C (bath) and identified by NMR spectroscopy and mass spectrometry as compounds **5** (yield 350 mg, 21 %), 4-Cl-**5**, (yield 25mg, 1 %) and 11-Cl-**5** (yield 250 mg, 13 %), respectively.

5: M.p. 312–313 °C; IR (KBr): $\tilde{\nu} = 3016$, 2916 (C–H), 2584 (B–H) cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 172 (45) $[M]^+$, 170 (100) $[M-2H]^+$; elemental analysis calcd (%) for $C_2H_9B_7P_2$ (170.8): C 14.07, H 5.31; found: C 14.36, H 5.27.

4-Cl-5: M.p. 201–202 °C; IR (KBr): $\tilde{\nu} = 3016$, 2916 (C–H), 2604(sh), 2584 (B–H) cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 208 (12) $[M]^+$, 204 (100) $[M-4H]^+$; elemental analysis calcd (%) for $C_2H_9B_7P_2$ (205.2): C 11.70, H 3.93; found: C 11.94, H 3.68.

11-Cl-5: M.p. 196 °C; IR (KBr): $\tilde{\nu} = 3024$ (C–H), 2612(sh), 2588, 2552 (B–H) cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 208 (15) $[M]^+$, 205 (100) $[M-3H]^+$; elemental analysis calcd (%) for $C_2H_9B_7P_2$ (205.2): C 11.70, H 3.93; found: C 11.87, H 3.71.

X-ray crystallography: A colourless crystal of the compound 3-Cl-**2** of dimensions 0.3 × 0.3 × 0.2 mm was mounted on glass fibers with epoxy cement and measured on four-circle diffractometer Kappa CCD with a CCD area detector at 293(2) K with $Mo_{K\alpha}$ radiation. Similar measurements on a colourless crystal of 11-Cl-**5** (dimensions 0.9 × 0.6 × 0.2 mm) were carried out on a four-circle diffractometer CAD4-MACHIII at 293(2) K with $Mo_{K\alpha}$ radiation. The crystallographic details are summarised in Table 1. The structures were solved by the direct method (SIR 97)[25] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL 97).[26] The absorption was neglected. Hydrogen atoms were localised on a difference Fourier map and refined isotropically. The final difference map had no peaks of chemical significance. Scattering factors were those implemented in the SHELX programs.

Computational details: All calculations used the Gaussian 94 program package[27] and were performed on the Power Challenge XL computer of the Supercomputing Centre of the Charles University in Prague (Czech Republic). The structures proposed on the basis of experimental ^{11}B and ^{1}H NMR spectroscopy were optimised first at RHF/6-31G* within the given symmetry restriction. Frequency calculations, carried out at the same level, determined the nature of the stationary points and gave the zero point energies (ZPE).[28] Minima were characterised with zero imaginary frequency (NIMAG = 0). Further optimisations at RMP2(fc)/6-31G* included the effect of electron correlation and gave the relative energies (see Table 3). Selected geometry parameters are given in Table 5. The natural population analysis (NPA)[14] obtained at the RMP2(fc)/6-31G* level for the hypothetical $[nido\text{-}B_{11}H_{11}]^{4-}$ fragment, from which all seven molecules examined are formally derived, is discussed. The Wiberg bond indices (WBI)[29] and the overlap-weighted natural atomic orbital (NAO) bond orders[14] are also included. The chemical shieldings were calculated at a SCF level with the GIAO (gauge-invariant atomic orbital) method incorporated in the Gaussian 94 package and employed a II Huzinaga basis set[20] well-designed for the calculations of magnetic properties.[30]

Full crystallographic data for the structures of 3-Cl-**2** and 11-Cl-**5** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148121 and CCDC-148122, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Coordinates for the RMP2(fc)/6-31G* calculated structures for all compounds reported in this paper are available from the authors on request (e-mail: hnyk@iic.cas.cz)

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