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FULL PAPER

Phosphaborane chemistry. Syntheses and calculated molecular structures of mono- and di-chloro derivatives of 1,2-diphospha-*closo*-dodecaborane(10)

Bohumír Grüner,[*a] **Drahomír Hnyk,**[*a] **Ivana Císařová,**[b] **Zbyněk Plzák**[a] **and Bohumil Štíbr**[a]

[a] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic (Research Centre for New Inorganic Compounds and Advanced Materials University of Pardubice), 250 68 Řež, Czech Republic. E-mail: gruner@iic.cas.cz; hnyk@iic.cas.cz*
[b] *Department of Inorganic Chemistry, Faculty of Natural Sciences of the Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic. E-mail: cisarova@natur.cuni.cz*

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The reaction between *nido*-$B_{10}H_{14}$ and PCl_3 in the presence of proton sponge (PS = 1,8-bis(dimethylamino)-naphthalene) in CH_2Cl_2 yielded a mixture of icosahedral diphosphaboranes from which 1,2-*closo*-$P_2B_{10}H_{10}$ (**1a**) and its mono- and di-chloro derivatives 3-Cl-1,2-*closo*-$P_2B_{10}H_9$ (**2a**), 4-Cl-1,2-*closo*-$P_2B_{10}H_9$ (**2b**), 3,6-Cl_2-1,2-*closo*-$P_2B_{10}H_8$ (**3a**), and 3,4-Cl_2-1,2-*closo*-$P_2B_{10}H_8$ (**3b**) were isolated together with 4-$Cl(CH_2)_4O$-1,2-*closo*-$P_2B_{10}H_{10}$ **4** *via* preparative HPLC. Individual compounds were characterized by NMR (^1H, ^{11}B, ^{31}P) spectroscopy and, except for **4**, geometry optimised at the (RMP2(fc)) level with a 6-31G* basis set. The optimisation disclosed considerable distortions of the icosahedral cage as documented by the narrowing of the pentagonal B–P–B angles (*ca.* 93°) and the longer P–P separations (>2.31 Å). In this context, the RMP2(fc)/6-31G* geometries of 1,7-*closo*-$P_2B_{10}H_{10}$ (**1b**) and that of the non-isolated 4,5-Cl_2-1,2-*closo*-$P_2B_{10}H_8$ isomer (**3c**) were also derived. The geometries were used as a basis for GIAO-SCF/II calculations of the ^{11}B NMR chemical shifts which were in good agreement with experimental δ (^{11}B) values. Moreover, the molecular structure of **3a** was determined by an X-ray diffraction analysis to demonstrate satisfactory agreement with the theoretical geometry.

Introduction

The reaction between open-structured boranes or hydroborate anions with phosphorus halides in the presence of dehydrohalogenation agents, resulting in the isolation of the first types of phophaboranes and phosphacarboranes, was developed by Little and Todd several decades ago.[1] Phosphaboranes were reported soon after carboranes and their structural diversity ranks these compounds among the most developed classes of heteroborane species.[2] From the viewpoint of electron count[3] and the isolobal principle,[4] there are two essential types of phosphaboranes. Those containing a bare phosphorus cage vertex possessing an exohehral electron pair are analogues of carboranes as the P-vertex contributes three electrons to the cluster bonding scheme as does the isolobal CH group. In contrast, the second type of phosphaboranes are those in which the P-vertex is attached to an exopolyhedral substituent and thus contributes four skeletal electrons (as do, for example, NH and S groups in aza- and thia-boranes). There is current interest in the chemistry of compounds containing more than one P-atom in the cage and in this area we have isolated *nido* diphospha- and triphospha-carboranes $P_2C_2B_7H_9$ and $P_3CB_7H_8$ or their derivatives.[5,6] The first diphosphaboranes were, however, reported by Hauboldt[7] and Todd[8,9] *et al.* Hauboldt reported on the synthesis of B-perchlorinated *closo* diphosphaboranes 1,2-$P_2B_4Cl_4$ and 1,7-$P_2B_{10}Cl_{10}$ from high-temperature reactions between B_2Cl_4 and PCl_3 and Todd isolated *closo*-1,2-$P_2B_{10}H_{10}$ (**1a**) from the reaction between *nido*-$B_{10}H_{14}$ and PCl_3 in the presence of NEt_3 and $NaBH_4$ in THF. Compound **1a** undergoes thermal rearrangement to give the isomeric 1,7-$P_2B_{10}H_{10}$ (**1b**).[9] Compounds **1a** and **1b** are structural analogues of *o*- and *m*-carborane, respectively. We report here a modification and extension of Todd's reaction[8,9] which, using PS as dehydrohalogenation agent in the absence of $NaBH_4$ and upon more detailed isolation of the reaction products, results in the isolation of mono- and di-chloro derivatives of **1a**, in which chlorine atoms substitute BH positions adjacent to P-vertices.

Results and discussion

Synthesis

Diphosphorus PCl_3-insertion reactions into the *nido*-$B_{10}H_{14}$ cage in the presence of PS are stoichiometric only on condition that mono- and di-chloro derivatives are formed as in eqns. (1) and (2).

$$B_{10}H_{14} + 2PCl_3 + 5PS \longrightarrow P_2B_{10}H_9Cl + 5PS{\cdot}HCl \quad (1)$$

$$B_{10}H_{14} + 2PCl_3 + 4PS \longrightarrow P_2B_{10}H_8Cl_2 + 4PS{\cdot}HCl \quad (2)$$

Although there is no direct experimental evidence, parent compound **1a** can be formed only at the expense of the reduction of the starting borane reactant. In this work, we are interested in a more detailed study of other twelve-vertex reaction products, especially chloro derivatives of **1a** that should be formed in accord with reactions (1) and (2). The PS chosen as deprotonation agent allowed for using CH_2Cl_2 solvent. The reaction carried out under such conditions over prolonged refluxing time seems to provide higher yields of the *closo* diphosphaboranes **1**–**3** with substantial amounts of chlorinated species. The yields of the products in the reaction mixtures obtained under these conditions decreased approximately in the order $\mathbf{1a} \geq \mathbf{2a} > \mathbf{2b} \gg \mathbf{3a} > \mathbf{3b}$, which points to predominant participation of reaction (1). All species were isolated in pure forms using LC and HPLC techniques. Noteworthy is the unexpected elution order in chromatography on silica gel,

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where the dipole moments of the compounds apparently play a decisive role. Thus, the symmetrically substituted 3,6-Cl_2-derivative **3a** elutes before the 3-monochloro derivative **2a**, which is followed by the 4-Cl-monochloro derivative **2b** and the 3,4-disubstituted species **3b**. According to GC/MS evidence, minor quantities of other two dichloro derivatives (<2% of all *closo*-products) were also formed, one of them being probably the last member of the **3**-series, *i.e.* 4,5-Cl_2-1,2-*closo*-$P_2B_{10}H_8$ (**3c**).

When the same reaction was carried out in THF instead of CH_2Cl_2, another derivative could be isolated as the second most abundant product. Based on NMR and MS evidence, this semi-solid compound was characterised as 4-$Cl(CH_2)_4O$-1,2-*closo*-$P_2B_{10}H_9$ (**4**). This species may originate from *in situ* addition of the solvent molecule to the 9-position of the eleven vertex intermediate [*nido*-7-$PB_{10}H_{12}$]$^-$ to produce the zwitterionic 9-THF-*nido*-7-$PB_{10}H_{11}$ with a positive charge on the oxonium oxygen atom. This reaction is analogous to the reported[11] B(10) substitution of the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ cage THF or dioxane. Upon subsequent insertion of the second P atom into the compound and cage closure, the heterocycle ring is then cleaved by Cl^- attack at the oxonium oxygen[10,11] to form a $Cl(CH_2)_4O$ chloroalkyoxo chain attached to the cage *via* an oxygen atom. When THF is used as solvent, this mechanism apparently predominates over halogenation of the cage boron atoms. The mechanism can be supported by the fact that only the B(4) substituted isomer **4** was formed.

NMR studies

All compounds were characterised by GC/MS spectrometry and multinuclear (^{11}B, ^1H, and ^{31}P) NMR spectroscopy, and [^{11}B–^{11}B]-COSY measurements[12] combined with $^1H\{^{11}B$-(selective)$\}$ experiments[13] led to complete assignments of all resonances to individual BH cluster units. The last method was substantially helpful in assigning the signals as the singlet $^1H\{^{11}B\}$ resonances of the BH vertices adjoining one P atom are split into a doublet due to distinct $^2J_{PH}$ coupling. Moreover, the resonances of the unsubstituted BH vertices in positions 3 and 6 adjacent to two P atoms exhibit triplets in the corresponding $^1H\{^{11}B\}$ spectra.

The ^{11}B NMR spectra of the C_{2v}-symmetry compounds **1a** and **3a** consist of one intensity 4 and three intensity 2 (of which one is a singlet for **3a**) resonances, while the spectrum of the C_s-symmetry **2a** exhibits 2 : 1 : 2 : 2 : 1 : 1 patterns of doublets and one B(3) singlet due to Cl substitution. The asymmetrical 4-substituted derivatives **2b** and **4** display eight resonances (with some coincidental overlaps), of which one is a singlet due to Cl and $Cl(CH_2)_4O$ substitution. The presence of four non-equivalent CH_2 groups in the $O(CH_2)_4Cl$ chain can be clearly seen from the ^1H NMR spectrum of **4**. The Cl substitution in the chlorinated derivatives results in the usual deshielding at the substituted site (α) (range of $\Delta\sigma(^{11}B)_\alpha = -11.8$–$-14.0$ ppm) and the deshielding in the $Cl(CH_2)_4O$ substituted compound **4** amounts to -19.7 ppm. The ^{31}P NMR spectra of the symmetrically substituted compounds **2a** and **3a** consist of one broad singlet resonance, while two different signals were observed for **2b**, **3b**, and **4** in agreement with the asymmetry. Due to the high sensitivity of the ^{31}P NMR spectra in comparison to ^{11}B NMR, the β-shielding effects by the vicinal 3- and 3,6-Cl_2-substitution are quite pronounced, amounting to a range of $\Delta\sigma(^{31}P)_\beta = +8.1$–$+15.2$ ppm, while the β-effect of the vicinal 4-Cl substitution results in $\Delta\sigma(^{31}P)_\beta = -8.1$ ppm. An even more enhanced β-deshielding effect is at $\Delta\sigma(^{31}P)_\beta = -29.0$ ppm exerted by the 4-$O(CH_2)_4Cl$ substituent in **4**. Mass spectra of all compounds of types **2**, **3** and **4** show theoretical cut-offs in their molecular-ion envelopes. The spectrum of **4** contains lower-mass fragmentation peaks at *m/z* 91 ($[(^{12}C^1H_2)_4$-$^{35}Cl]^+$) and 55 ($[(^{12}C^1H_2)_2{}^{37}Cl]^+$), which are significant for alkyl chains with a terminal chlorine atom.

Structural studies

The molecular geometries of all compounds of types **2** and **3** were derived on the basis of *ab initio*[14] optimisations at a correlated level of theory (MP2) and were verified in terms of the GIAO-SCF/II ^{11}B NMR calculations applied to the corresponding RMP2(fc)/6-31G* geometries. This approach has been successfully applied in the area of phosphaboranes[5,15] and other heteroboranes.[6,16] The molecular structure of **3a** was also determined by single-crystal X-ray diffraction in order to compare the icosahedral distortion brought about by the Cl and P atoms in the solid state with the parameters computed for free **3a**. Although the structures of the parent compounds **1a** and **1b** have already been computed at the SCF level (6-31G*),[17] their geometries were re-optimised at the same level as for **2** and **3** in order to get a consistent set of molecular structures of all species of types **1**, **2**, and **3**. Moreover, the MP2 bond lengths computed for boron clusters proved to be superior to those calculated at the SCF level.[18] Finally, the shielding tensors for **1a** and **1b** were computed in the same manner as for types **2** and **3** in order to verify the structures of **1a** and **1b**.

As already pointed out by Jemmis *et al.*,[17] the presence of the two P vertices in **1a** and **1b** brings about a considerable distortion of the icosahedral $[B_{12}H_{12}]^{2-}$ skeleton. For instance, the B(3)–P(2)–B(6) and B(8)–P(7)–B(11) angles are reduced from ideal 108.0° to 93.0° and 93.5°, respectively, as calculated now at the RMP2(fc)/6-31G* level. This originates from the P atoms in **1a** and **1b** being pushed away from the centre of the cluster. Interestingly, all B–P–B pentagonal angles in **2** and **3** are not too much affected by Cl substitution (see Table 1). Whereas the P–P nearest-neighbour separation is practically unaffected by the Cl substitution, the P(1)–B(X) separations in **2** and **3**, where X = 3,4,5,6, are slightly lengthened in relation to the corresponding P(1)–B(X) bond lengths in **1a** (see Table 1). This observation is also reflected by smaller WBI and NAO values for these bonds in **2** and **3** than for those in **1a** (see Table 2). However, the overall RMP2(fc)/6-31G* geometries of the substituted compounds **2** and **3** do not differ appreciably from that calculated for **1a** as shown in Table 1. The B–Cl bond lengths are longer than that in BCl_3 (1.738 Å) but considerably shorter than in BCl_4^- (1.857 Å)[19] as calculated at the same level as for **2** and **3**. Moreover, the structure of **3a** was determined by a single-crystal X-ray diffraction study (see Fig. 1a and Tables 3 and 4) and this experimental structure revealed the same features as the calculated structure (*cf.* Tables 1 and 3), *e.g.* the narrowing of the calculated pentagonal B–P–B angles compares well to the experimental mean, $\angle(B–P–B)_{mean} = 93.5°$, a value slightly smaller than that reported for the crystal structure of the decachloro derivative of **1b**, *closo*-1,7-$P_2B_{10}Cl_{10}$.[7c] Fig. 1(b) shows the RMP2(fc)/6-31G* structure of **3a** as a representation of the calculated structures. The drawings of other calculated structures are more or less similar and are available on request. The theoretically derived structures of compounds of types **1**, **2**, and **3** were used as a basis for GIAO-SCF/II calculations (see Experimental) of the underlying ^{11}B shifts and the comparison between experimental and calculated values reveals an excellent agreement (maximum differences < 2 ppm). This serves as compelling evidence that the calculated RMP2(fc)/6-31G* structures may be deemed very good representations of their solution-state structures.

Experimental

General procedures

All reactions were carried out with using standard vacuum or inert-atmosphere techniques as described by Shriver and Drezdon,[20] although some operations, such as preparative LC, were carried out in air. The starting *nido*-$B_{10}H_{14}$ was sublimed

Table 1 Salient geometrical parameters at the RMP2(fc)/6-31G* level

	1a (C_{2v})	**1b** (C_{2v})	**2a** (C_s)	**2b** (C_1)	**3a** (C_{2v})	**3b** (C_1)	**3c** (C_s)
Distances/Å							
1–2[a]	2.317	2.022	2.319	2.313	2.321	2.315	2.309
1–3	2.094	2.022	2.117	2.095	2.116	2.120	2.089
1–4	2.015	2.037	2.017	2.039	2.015	2.043	2.045
1–5	2.015	2.037	2.013	2.015	2.015	2.017	2.045
1–6	2.094	2.037	2.091	2.089	2.116	2.088	2.089
2–3	2.094	1.906	2.117	2.097	2.116	2.121	2.099
2–6	2.094	1.813	2.091	2.097	2.116	2.093	2.099
3–4	1.823	1.814	1.824	1.831	1.825	1.840	1.831
4–5	1.834	1.832	1.834	1.839	1.834	1.839	1.851
5–6	1.823	1.832	1.823	1.822	1.825	1.822	1.831
2–7	2.015	2.022	2.017	2.016	2.015	2.020	2.013
2–11	2.015	1.813	2.013	2.011	2.015	2.010	2.013
3–7	1.823	2.022	1.824	1.824	1.825	1.826	1.823
3–8	1.761	1.813	1.757	1.761	1.756	1.759	1.760
4–8	1.771	1.759	1.773	1.770	1.773	1.773	1.771
4–9	1.773	1.774	1.775	1.770	1.775	1.772	1.774
5–9	1.773	1.768	1.772	1.775	1.775	1.775	1.775
5–10	1.771	1.768	1.771	1.772	1.773	1.771	1.771
6–10	1.761	1.774	1.759	1.759	1.756	1.757	1.760
6–11	1.823	1.759	1.823	1.820	1.825	1.821	1.823
$(B–B)_{mean}$[b]	1.789	1.778[d]	1.789	1.788	1.788	1.787	1.787
$(B–B)_{mean}$[c]	1.778	1.800[e]	1.777	1.777	1.777	1.776	1.777
$(B–H)_{mean}$	1.190	1.190	1.190	1.190	1.190	1.190	1.190
B–Cl			1.777	1.783	1.775	1.775[f]	1.777
Angles/°							
3–2–6	93.0	107.0	93.1	92.7	93.4	93.1	92.6
2–3–4	114.2	107.0	113.2	114.5	113.2	113.4	114.8
2–6–5	114.2	108.8	114.3	114.2	113.2	114.4	114.8
4–5–6	109.2	108.2	109.2	109.6	110.0	109.8	108.9
3–4–5	109.2	108.8	109.9	108.6	110.0	109.2	108.9
7–2–11	54.2	63.9	54.1	54.2	54.1	54.1	54.2
7–8–9	108.5	113.5	108.7	108.6	108.9	108.7	108.6
8–7–11	107.4	93.5	107.2	107.4	107.2	107.2	107.3
9–10–11	108.5	109.5	108.5	108.5	108.7	108.5	108.6

[a] For numbering schemes, see Fig. 1. [b] Lower pentagon. [c] B(12)–B. [d] P(7)–B(8,11) = 2.037 Å. [e] P(7)–B(12) = 2.037. B(12)–B(8,11) = 1.832 Å. B(12)–B(9,10) = 1.768 Å. [f] Mean value.

Table 2 Wiberg bond indices (natural atomic bond orders) for selected bonds in the pentagonal pyramids P(1)P(2)B(3)B(4)B(5)B(6) of **1a**, **2a**, **2b**, **3a**, **3b**, and **3c**

Compound[a]	Bond				
	P(1)–P(2)	P(1)–B(3)	P(1)–B(4)	P(1)–B(5)	P(1)–B(6)
1a	0.4828 (0.4915)	0.5451 (0.6079)	0.5609 (0.6457)	0.5609 (0.6457)	0.5451 (0.6079)
2a	0.4778 (0.4891)	0.5260 (0.6043)	0.5553 (0.6415)	0.5597 (0.6471)	0.5450 (0.6097)
2b	0.4841 (0.4948)	0.5419 (0.6066)	0.5418 (0.6363)	0.5542 (0.6404)	0.5471 (0.6112)
3a	0.4745 (0.4883)	0.5251 (0.6050)	0.5543 (0.6430)	0.5543 (0.6430)	0.5251 (0.6050)
3b	0.4804 (0.4936)	0.5233 (0.6027)	0.5351 (0.6305)	0.5537 (0.6423)	0.5463 (0.6124)
3c	0.4844 (0.4974)	0.5457 (0.6115)	0.5343 (0.6298)	0.5343 (0.6298)	0.5457 (0.6115)

[a] For numbering schemes, see Fig. 1(b).

in vacuo before use. THF (Aldrich) and hexane were freshly distilled from sodium diphenylketyl, and CH_2Cl_2 from P_2O_5 prior to use. Other chemicals were reagent or analytical grade and were used as purchased. Column chromatography was carried out using silica gel (Aldrich, 130–270 mesh) as the stationary phase. Analytical TLC was carried out using silica gel TLC plates coated with Silufol (Kavalier Votice, Czech Rep., silica gel on aluminium foil; starch as binder detection in diiodine vapour followed by 2% aqueous $AgNO_3$ spray).

Physical measurements

Low-resolution mass spectra were obtained using a Finnigan MATMAGNUM ion-trap quadrupole mass spectrometer equipped with a GC-MS inlet or with a heated inlet option, as developed by Spectronex AG, Basle, Switzerland (70 eV, EI ionisation). Proton (^1H), boron (^{11}B), and phosphorus (^{31}P) NMR spectroscopy was performed at 11.75 Tesla on a Varian UNITY-500 instrument. The [^{11}B–^{11}B]-COSY[12] and ^1H-{^{11}B(selective)}[13] NMR experiments were essentially as described in other related papers from our laboratories.[21] Chemical shifts ($CDCl_3$, 293 K) are given in ppm to high-frequency (low field) of Ξ = 32.083971 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ± 0.5 ppm), Ξ = 40.4805 MHz (H_3PO_3) for ^{31}P (quoted ± 0.5 ppm), and Ξ = 100 MHz ($SiMe_4$) for ^1H (quoted ± 0.05 ppm), Ξ being defined as in ref. 22. Residual solvent ^1H resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B–^1H)$ are taken from resolution-enhanced ^{11}B spectra with a digital resolution of 8 Hz and are given in Hz. All theoretical [^{11}B–^{11}B]-COSY crosspeaks were observed for all compounds.

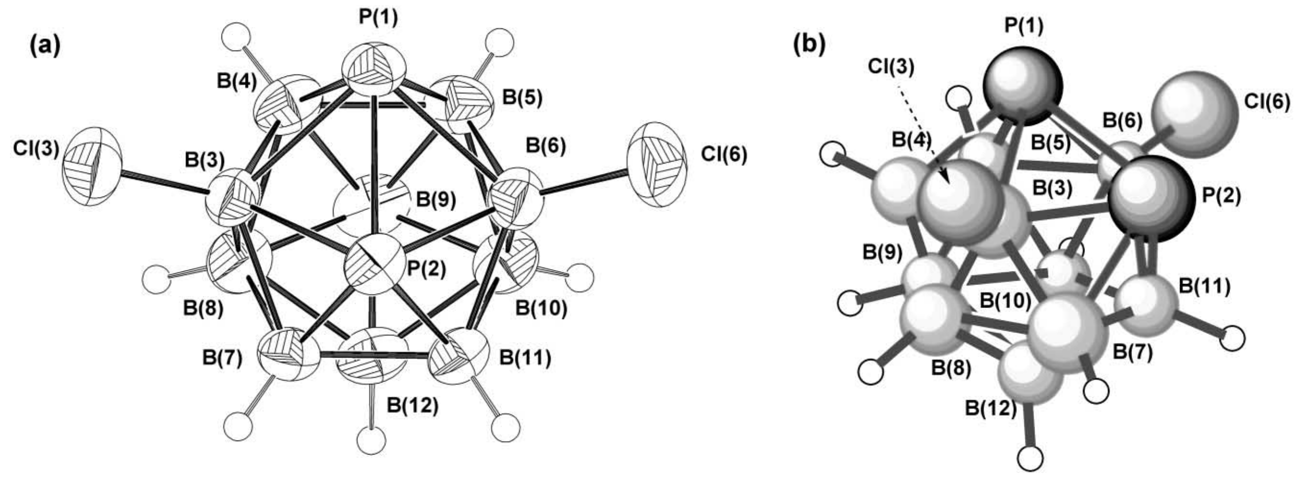

Fig. 1 (a) PLATON[32] representation of the crystallographically determined molecular structure of 3,6-Cl_2-1,2-$P_2B_{10}H_8$ (**3a**) with thermal ellipsoids drawn at the 50% probability level. (b) RMP2(fc)/6-31G* optimised structure of **3a**.

Table 3 Selected bond lengths (Å) and bond angles (°) for 3,6-Cl_2-1,2-*closo*-$P_2B_{10}H_8$ (**3a**)

P(1)–B(4)[a]	2.014(3)	P(1)–B(5)	2.039(4)
P(1)–B(3)	2.102(3)	P(1)–B(6)	2.117(3)
P(1)–P(2)	2.2936(10)	P(2)–B(7)	2.020(3)
P(2)–B(11)	2.022(3)	P(2)–B(6)	2.103(3)
P(2)–B(3)	2.106(3)	Cl(3)–B(3)	1.782(3)
Cl(6)–B(6)	1.777(3)	B(3)–B(8)	1.757(5)
B(3)–B(7)	1.827(4)	B(3)–B(4)	1.829(5)
B(4)–B(9)	1.782(5)	B(4)–B(8)	1.785(5)
B(4)–B(5)	1.848(5)	B(5)–B(9)	1.780(5)
B(5)–B(10)	1.793(5)	B(5)–B(6)	1.852(5)
B(6)–B(10)	1.772(5)	B(6)–B(11)	1.835(4)
B(7)–B(12)	1.772(5)	B(7)–B(8)	1.776(5)
B(7)–B(11)	1.838(5)	B(8)–B(9)	1.773(6)
B(8)–B(12)	1.782(5)	B(9)–B(12)	1.766(5)
B(9)–B(10)	1.773(5)	B(10)–B(12)	1.776(5)
B(10)–B(11)	1.794(5)	B(11)–B(12)	1.782(5)
B(4)–P(1)–B(5)	54.24(15)	B(4)–P(1)–B(3)	52.70(14)
B(5)–P(1)–B(3)	93.50(14)	B(4)–P(1)–B(6)	93.40(13)
B(5)–P(1)–B(6)	52.89(14)	B(3)–P(1)–B(6)	93.64(12)
B(4)–P(1)–P(2)	99.35(10)	B(5)–P(1)–P(2)	99.43(10)
B(3)–P(1)–P(2)	57.06(9)	B(6)–P(1)–P(2)	56.80(9)
B(7)–P(2)–B(11)	54.09(13)	B(7)–P(2)–B(6)	93.17(13)
B(11)–P(2)–B(6)	52.79(12)	B(7)–P(2)–B(3)	52.53(12)
B(11)–P(2)–B(3)	93.48(13)	B(6)–P(2)–B(3)	93.91(12)
B(7)–P(2)–P(1)	99.02(9)	B(11)–P(2)–P(1)	99.67(10)

[a] For numbering see Fig. 1(a).

Table 4 Crystal data and structure refinement for **3a**

Empirical formula	$B_{10}Cl_2H_8P_2$
M_r	249
Crystal system	Orthorhombic
Space group	*Pbca* (no. 61)
a/Å	13.2830(5)
b/Å	12.3110(3)
c/Å	13.7860(6)
Z	8
V/Å^3	2254.38(14)
μ/mm^{-1}	0.797
D_c/Mg m^{-3}	1.467
Wavelength/Å	0.71073
$F(000)$	976
Scan mode	ϕ and ω
No. of reflections measured	16748
No. of unique reflections	2566 ($R_{int} = 0.024$)
No. of observed reflections [$I > 2\sigma(I)$]	2030
No. of parameters	159
GOF[a] all data	1.068
Final R[a] indices [$I > 2\sigma(I)$]	$R1 = 0.046$, $wR2 = 0.117$
R[a] indices (all data)	$R1 = 0.064$, $wR2 = 0.135$
w_1/w_2[b]	0.0608/1.9683

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

Synthesis of 1,2-*closo*-$P_2B_{10}H_{10}$ (1a), 3-Cl-1,2-*closo*-$P_2B_{10}H_9$ (2a), 4-Cl-1,2-*closo*-$P_2B_{10}H_9$ (2b), 3,6-Cl_2-1,2-*closo*-$P_2B_{10}H_8$ (3a), 3,4-Cl_2-1,2-*closo*-$P_2B_{10}H_8$ (3b), and 4-Cl(CH_2)$_4$-1,2-*closo*-$P_2B_{10}H_9$ (4)

Decaborane (1.0 g, 8.2 mmol) was dissolved in CH_2Cl_2 (30 ml) and a solution of PS (8.7 g, 41 mmol) in dichloromethane (30 ml) was added. The dark solution was stirred for 1 h and PCl_3 (2.8 ml, 32 mmol) was added dropwise over 1 h. The reaction mixture was stirred for 2 h at ambient temperature and refluxed for 16 h. After cooling down to −33 °C, water (50 ml) was added carefully to the red slurry with stirring and the solution warmed up to ambient temperature. The solid materials were filtered off, the organic layer separated, and then evaporated with 20 g of silica gel. The silica gel was placed onto the top of a silica gel column (2.5 × 25cm) and eluted with pentane. The first fraction contained almost pure **1a** (220 mg, 15%) which was re-purified by LC and crystallised by slow evaporation of a hexane solution. Subsequent elution with pentane gave a mixture of the chloro derivatives **3a** and **2a** (195 mg, mol. ratio *ca.* 1 : 5, according to HPLC), after evaporation. The third pentane LC fraction contained a mixture of **2b** and **3b** (85 mg, mol. ratio *ca.* 4 : 1 according to HPLC). Elution with CH_2Cl_2 gave after evaporation of the solvent slightly impure $PSH^+[7\text{-}P\text{-}PB_{10}H_{12}]$ (240 mg) which was identified by NMR spectroscopy as previously reported.[8,9] The fraction containing mixtures of the chloro derivatives **2a**–**3b** was separated by preparative HPLC.

The same reaction carried out in THF at ambient temperature over a period of 16 h gave, after a similar work-up of the reaction mixture and repeated LC purification in pentane, 158 mg (11%) of **1a** together with negligible amounts of the chlorinated products. Elution with hexane–CH_2Cl_2 (1 : 1, v/v) gave pure **4** (37 mg, 2.5%) and subsequent elution with CH_2Cl_2 during the first LC purification gave $PSH^+[7\text{-}P\text{-}B_{10}H_{12}]^-$ (190 mg).

For **1a**: ^{11}B NMR: $\delta = 17.0$ (d, $^1J_{BH} = 150$ Hz, B9,12), 3.5 (d, $^1J_{BH} = 154$ Hz, B8,10), −1.0 (d, $^1J_{BH} = 162$ Hz, B4,5,7,11), −3.2 (d, $^1J_{BH} = 170$ Hz, B3,6). ^{11}B NMR (calcd, GIAO-SCF/II//RMP2(fc)/6-31G*): $\delta = 17.3$ (B9,12), 3.0 (B8,10), −1.0 (B4,5,7,11), −2.7 (B3,6). $^1H\{^{11}B\}B$ NMR: $\delta = 3.57$ (s, H9,12), 3.22 (s, H8,10), 2.74 (t, $^2J_{PH} = 14$ Hz, H4,5,7,11), 2.54 (t, $^2J_{PH} = 18$ Hz, H3,6). $^{31}P\{^1H\}$ NMR: $\delta = -19.3$ (br s, P1,2).

For **1b**: ^{11}B NMR (calcd, GIAO-SCF/II//RMP2(fc)/6-31G*): $\delta = 11.4$ (B5,12), 2.0 (B9,10), −1.9 (B4,6,8,11), −4.4 (B2,3).

For **2a**: R_F 0.38 (hexane), mp 268–270 °C (subl.), ^{11}B NMR: $\delta = 15.8$ (d, $^1J_{BH} = 154$ Hz, B9,12), 10.7 (s, B3), 4.0 (d,

$^1J_{BH}$ = 154 Hz, B8), 0.1 (d, $^1J_{BH}$ = 162 Hz, B4,7), −1.0 (d, $^1J_{BH}$ = 165 Hz, B5,11), −3.5 (d, $^1J_{BH}$ = 173 Hz, B6), −5.2 (d, $^1J_{BH}$ = 158 Hz, B10). ^{11}B NMR (calcd, GIAO-SCF/II//RMP2(fc)/6-31G*): δ = 16.2 (B9,12), 11.6 (B3), 4.1 (B8), 0.4 (B4,7), −1.0 (B5,11), −3.0 (B6), −3.7 (B10). ^{1}H{^{11}B} NMR: δ = 3.51 (s, H9,12), 3.45 (s, H8), 3.0 (d, H4), 3.1(d, H7), 2.77 (m, H5,11), 2.55 (t, $^2J_{PH}$ = 19 Hz, H6), 3.01(s, H10). ^{31}P{^{1}H} NMR: δ = −11.2 (br s, P1,2). MS (70 eV): *m*/*z* (%): 219 [M$^+$ + 1] (9%), 214 (100%).

For **2b**: R_F 0.29 (hexane), mp > 280 °C. ^{11}B NMR: δ = 17.2 (d, $^1J_{BH}$ = 150 Hz, B 9), 15.3 (d, $^1J_{BH}$ = 150 Hz, B12), 11.2 (s, B4), 3.2 (d, $^1J_{BH}$ = 154 Hz, B8,10), 0.2 (d, $^1J_{BH}$ = 173 Hz, B5), −2.0 (d, $^1J_{BH}$ = 158 Hz, B3,7), −4.9 (d, $^1J_{BH}$ = 162 Hz, B6), −9.5 (d, $^1J_{BH}$ = 165 Hz, B11). ^{11}B NMR (calcd, GIAO-SCF/II//RMP2(fc)/6-31G*): δ = 18.0 (B9), 15.6 (B12), 12.0 (B4), 3.1 (B8), 2.5 (B10), 0.7 (B5), −1.3 (B3), −1.8 (B7), −4.2 (B6), −7.6 (B11). ^{1}H{^{11}B} NMR: δ = 3.80 (s, H9), 3.50 (s, H12), 3.37 (s, H8 or H10), 3.22 (s, H8 or H10), 3.11 (d, H5), 2.95 (t, $^2J_{PH}$ = 19 Hz, H3), 2.70, (d, $^2J_{PH}$ = 29 Hz, H7), 2.42 (t, $^2J_{PH}$ = 18 Hz, H6), 2.62 (d, $^2J_{PH}$ = 30 Hz, H11). ^{31}P{^{1}H} NMR: δ = −24.3 (br s, P2), −28.4 (br s, P1). MS (70 eV): *m*/*z* (%): 218 [M$^+$] (6%), 214 (100%).

For **3a**: R_F 0.39(hexane), mp 148–150 °C. ^{11}B NMR: δ = 14.5 (d, $^1J_{BH}$ = 154 Hz, B9,12), 10.9 (s, B3,6), 0.1 (d, $^1J_{BH}$ = 162 Hz, B4,5,7,11), −4.7 (d, $^1J_{BH}$ = 158 Hz, B8,10). ^{11}B NMR (calcd, GIAO-SCF/II//RMP2(fc)/6-31G*): δ = 15.1 (B9,12), 11.7 (B3,6), −2.7 (B8,10), −4.0 (B4,5,7,11). ^{1}H{^{11}B} NMR: δ = 3.45 (s, H9,12), 3.10 (t, $^2J_{PH}$ = 14 Hz, H4,5,7,11), 3.21 (s, H8,10). ^{31}P{^{1}H} NMR: δ = −4.10 (br s, P1, P2). MS (70 eV): *m*/*z* (%): 254 [M$^+$] (3%), 250 (100%).

For **3b**: R_F 0.23 (hexane), mp > 280 °C. ^{11}B NMR: δ = 15.9 (d, $^1J_{BH}$ = 154 Hz, B9), 13.3 (d, $^1J_{BH}$ = 158 Hz, B12), 10.8 (s, B3,4), 3.6 (d, $^1J_{BH}$ = 154 Hz, B8), 0.3 (d, $^1J_{BH}$ = 173 Hz, B5), −1.0 (d, $^1J_{BH}$ = 168 Hz, B7), −4.7 (d, $^1J_{BH}$ = 162 Hz, B10), −6.5 (d, $^1J_{BH}$ = 173 Hz, B6), −8.5 (d, $^1J_{BH}$ = 154 Hz, B11). ^{11}B NMR (calcd, GIAO-SCF/II//RMP2(fc)/6-31G*): δ = 16.8 (B9), 13.9 (B12), 11.7 (B3,4), 3.9 (B8), 0.7 (B5), −0.6 (B7), −3.7 (B10), −5.5 (B6), −7.0 (B11). ^{1}H{^{11}B} NMR: δ = 3.74 (s, H9), 3.41 (s, H12), 3.42 (s, H8), 3.12 (d, $^2J_{PH}$ = 38 Hz, H5), 2.96 (d, $^2J_{PH}$ = 28 Hz, H7), 3.05 (s, H10), 2.38 (t, $^2J_{PH}$ = 18 Hz, H6), 2.65 (d, $^2J_{PH}$ = 31 Hz, H11). ^{31}P{^{1}H} NMR: δ = −15.9, −19.1 (br s, P1, P2). MS (70 eV): *m*/*z* (%): 254 [M$^+$] (2%), 248 (100%).

For **3c**: ^{11}B NMR (calcd, GIAO-SCF/II//RMP2(fc)/6-31G*): δ = 18.4 (B9), 13.2 (B12), 12.3 (B4,5), 2.7 (B8,10), −2.7 (B3,6), −7.9 (B7).

For **4**: R_F 0.35 (hexane–CH_2Cl_2, 1 : 1). ^{11}B NMR : δ = 18.8 (s, B4), 14.4 (d, $^1J_{BH}$ = 146 Hz, B9), 12.6 (d, $^1J_{BH}$ = 150 Hz, B12), 0.6 (d, $^1J_{BH}$ = 173 Hz, B8), −0.7 (d, $^1J_{BH}$ = 147 Hz, B10), −2.3 (d, $^1J_{BH}$ = 173 Hz, B5), −4.9 (d, $^1J_{BH}$ = 154 Hz, B3,7), −7.6 (d, $^1J_{BH}$ = 169 Hz, B6), −14.2 (d, $^1J_{BH}$ = 165 Hz, B11). ^{1}H{^{11}B} NMR : δ = 3.75 (t, 2H, CH_2–O), 3.63 (s, H9), 3.57 (m, 2H, CH_2–Cl), 3.32 (s, H12), 3.11 (s, H10), 2.99 (s, H8), 2.86 (d, $^2J_{PH}$ = 33 Hz, H5), 2.68 (t, $^2J_{PH}$ = 19 Hz, H3), 2.42 (d, $^2J_{PH}$ = 27 Hz, H7), 2.19 (t, $^2J_{PH}$ = 15 Hz, H6), 2.37 (d, $^2J_{PH}$ = 32 Hz, H11), 1.87 (m, 2H, CH_2–CH_2–O), 1.77 (m, 2H, CH_2–CH_2–Cl). MS (70 eV): *m*/*z* (%): 290 [M$^+$] (2%), 251 [$C_4H_{17}B_{10}P_2O$] (9%), 209 (100%), 196 [$H_9B_{10}P_2O$] (11%), 179 (30%) [$H_9B_{10}P$], 163 (13%), 149 (8%), 91 [C_4H_9Cl] (17%), 55 (64%), 49 (20%).

HPLC separations

The mixture of the four chloroderivatives **2a**, **2b** and **3a**, **3b** was separated by conventional preparative HPLC on a silica gel support,[23] using dry hexane as the mobile phase. Analytical system: Merck-Hitachi, 6200 Intelligent pump, D-6000 Interface, Rheodyne 7125 injection valve with 20 µl sample loop, L 7450 Diode Array detector with D-7000 HPLC System Manager Software (Hitachi, Japan, 1995). Preparative system: Micropump LCP 3001 with the preparative option, Rheodyne 7010 injection valve with 2 ml sample loop, UV-Vis variable wavelength detector LCD 2040 with a preparative cell, TZ 4200 line recorder (ECOM Prague). Chromatographic conditions: Analytical separation; a 4 × 250 mm I.D. steel column (Lichrosorb SI 60, Merck Darmstadt, packed by Labio Ltd., Prague) (10 µm), hexane as mobile phase, flow rate 1.0 ml min^{-1}, detection by Diode Array, 200–300 nm, sensitivity range 0–2.0 A.U.F.S. Chromatographic data: Capacity factors (k'), selectivity (α) and resolution values (*Rs*) for analytical separations were: **3a**: k_2' = 2.11; **2a**: k_3' = 2.44, α = 1.16, *Rs* = 1,47; **2b**: k_4' = 3.53, α = 1.44, *Rs* = 3.87; **3b**: k_5' = 4.16, α = 1.18, *Rs* = 2,22; **4**: k_6' = 16.5. (the k' values for diphenyl and terphenyl used as the reference under identical chromatographic conditions were 0.93 and 1.37, respectively). Preparative separation; stainless steel column (250 × 25 mm) packed by Labio Ltd., Prague with Lichrosorb SI 60, Merck (10 µm) (more than 20000 theoretical plates per m for all isomers), hexane as mobile phase, flow rate: 27 ml min^{-1}, detection UV 230 nm, sensitivity 0.16 A.U.F.S.; sample amount *ca*. 50 mg per single injection dissolved in 4 ml of the mobile phase. Despite a low retention and a relatively small resolution value (*Rs* = 0.95), for peaks of **2a** and **3a**, both derivative isomers were obtained in more than 98% purity (analytical HPLC and GC-MS monitoring) collecting the eluent from the front part of the first peak (**3a**) and the descending part of the second one (**2a**). Effluent from the baseline resolved peaks of **2b** and **3b** was taken from the 10% peak height at the start up to 10% height at the end.

X-Ray crystallography

The colourless crystal of compound **3a** of dimensions 0.25 × 0.15 × 0.1 mm was mounted on glass fibers with glue and measured on a four-circle Kappa CCD diffractometer with a CCD area detector at room temperature with graphite monochromated Mo-Kα radiation. The crystallographic details are summarized in Table 4. The structures were solved direct methods (SIR92)[24] and refined by a full matrix least squares procedure based on F^2 (SHELXL 97).[25] The absorption was neglected. The hydrogen atoms were found on a difference map and refined isotropically. Scattering factors were those implemented in the SHELX programs. For selected bond lengths see Table 3.

CCDC reference number 173484.

See http://www.rsc.org/suppdata/dt/b2/b201086k/ for crystallographic data in CIF or other electronic format.

Computational details

All calculations were carried out with the GAUSSIAN 94 program package[26] and were performed on the Power Challenge XL computer of the Supercomputing Center of the Charles University in Prague. The structures proposed on the basis of experimental ^{11}B and ^{1}H NMR spectroscopy were optimized first at RHF/6-31G* within the given symmetry restriction. Frequency calculations, carried out at the same level, determined the nature of the stationery points and gave the zero point energies (ZPE).[27] Minima were characterized with zero imaginary frequency (NIMAG = 0). Further optimisations at RMP2(fc)/6-31G* included the effect of electron correlation and gave the relative energies. Selected geometry parameters are given in Table 1. The natural population analysis (NPA)[28] obtained at the RMP2(fc)/6-31G* level is discussed. The Wiberg bond indices (WBI)[29] and the overlap-weighted natural atomic orbital (NAO) bond orders[28] were also computed (see Table 2). The chemical shieldings were calculated at a SCF level using the GIAO (gauge-invariant atomic orbital) method incorporated in GAUSSIAN 94 and employed a II Huzinaga basis set,[30] well-designed for magnetic properties calculations.[31]

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