PHOSPHORUS INSERTION INTO BORANE CLUSTERS. A REVIEW

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday for his pioneering work in the area of boron-cluster chemistry.

A review is presented on the methods of incorporation of phosphorus vertices into borane, carborane and heteroborane clusters. The structural diversity of boron cluster compounds allows for the synthesis of various types of phosphaboranes, phosphacarboranes and phosphaheteroboranes of structurally different cluster shapes, sizes, and positional isomerism. The phosphaborane compounds outlined in this work are direct analogues of corresponding carboranes. This analogy is the main reason for recent interest and developments in this area. A review with 45 references.

Keywords: Boron; Boranes; NMR spectroscopy; Phosphaboranes; Phosphacarboranes; Heteroboranes.

1. INTRODUCTION

By the discovery of carboranes in 1962 [1] it was demonstrated that other elements than boron can also occupy cluster positions in borane skeletons, in accord with electron counting rules[2] and the isolobal principle[3], both formulated later. Quite a number of phosphaboranes were reported soon after carboranes and the scope in structural diversity ranks these compounds among the most developed classes of heteroborane species[4]. From the viewpoint of electron count there are two essential types of phosphaboranes. Those containing a bare phosphorus cage vertex and therefore possessing a formally exohedral 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 thiaboranes). The aim of this short review is to outline general methods for the synthesis of phosphaboranes, phosphacarboranes, and phosphaheteroboranes, inclusive of recent developments in this area. Theoretical aspects of phosphaborane chemistry related to bonding and stability (see, *e.g.*, refs[5–8]) will be discussed only in connection with experimental work. Included are also selected experimental data for comparison with corresponding parameters of other compounds in related areas of boron cluster chemistry. For the sake of clarity, the structures of individual compounds are presented in a simplified manner: the unlabelled vertices of individual polyhedra denote cluster BH groups and C stands for a cage CH unit.

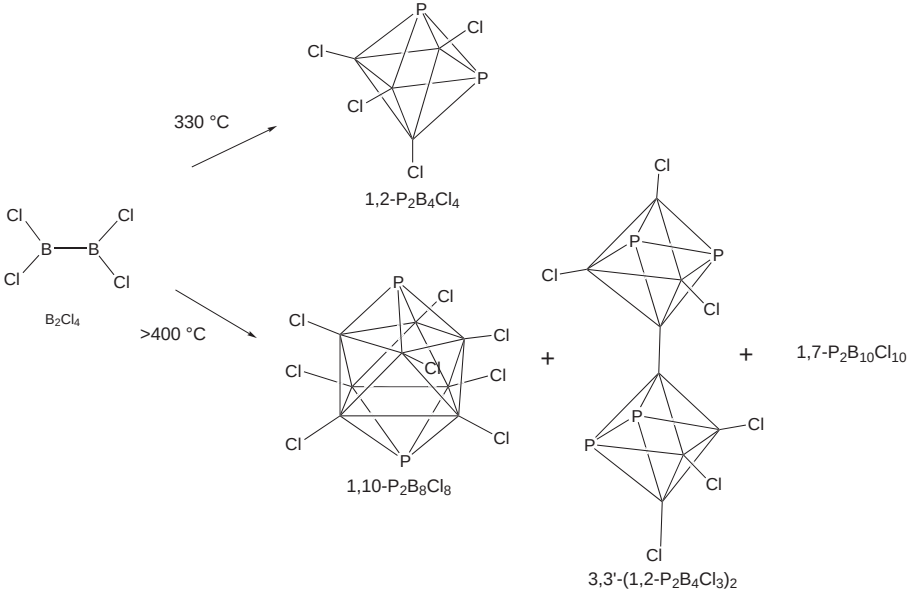
2. PHOSPHORUS INSERTION REACTIONS

2.1. Insertion Into Small Borane Cages

Although there is a good potential of phosphorus insertion reactions into smaller borane cages, such as those of $[B_3H_8]^-$ and B_4H_{10}, for example, no reactions of this kind have so far been reported. Nevertheless, one of the first phosphaborane compounds have been obtained from B_2Cl_4. Haubold *et al.*[9] have isolated *closo* diphosphahexaborane 1,2-$P_2B_4Cl_4$ from the co-pyrolysis of a mixture of B_2Cl_4 and PCl_3 at 330 °C (Scheme 1).

$$7\ B_2Cl_4 + 2\ PCl_3 \longrightarrow P_2B_4Cl_4 + 10\ BCl_3 \qquad (1)$$

The octahedral arrangement distorted from regular with two adjacent phosphorus positions (P–P bond length 222.3 pm) was proved by an X-ray diffraction study. In a white-hot flow pyrolysis tube (T > 1 370 K), 1,2-$P_2B_4Cl_4$ extrudes a P_2 moiety rather than rearranges to the 1,6-isomer[10]. This decomposition pathway has been simulated by theoretical calculation for the unknown parent 1,2-$P_2B_4H_4$ in order to rationalize the experimentally observed decomposition of the Cl_4 derivative[11]. The electronic structure and the stability of the unknown 1,6-$P_2B_4H_4$ isomer have been calculated by *ab initio* MO methods[12].



SCHEME 1

The tetrabromodiborane(4) adduct $B_2Br_4 \cdot 2PBr_3$ was found to react at 350 °C to give the analogous tetrabromo derivative, *closo*-1,2-$P_2B_4Br_4$, in 25% yield[13]. This compound also neither rearranges to the 1,6-isomer nor decomposes to an appreciable extent upon heating to 650 °C.

At higher temperatures (>400 °C, see Scheme 1), the same reaction as in Eq. (*1*) generated the 12-vertex diphosphaborane *closo*-1,7-$P_2B_{10}Cl_{10}$ in low yield together with a mixture of the *closo* phosphaboranes (3,3′-1,2-$P_2B_4Cl_3)_2$ and 1,10-$P_2B_8Cl_8$. The mixture of the last two compounds was characterized spectroscopically. A single-crystal X-ray structure was determined on the *closo*-1,7-$P_2B_{10}Cl_{10} \cdot C_6H_5CH_3$ solvate, in which the cluster part adopts an icosahedral structure distorted from regular with the phosphorus

atoms in meta positions. Copyrolysis of B_2Cl_4 with a mixture of PCl_3 and $AsCl_3$ at 450 °C generated the six-vertex arsaphosphaborane 1,2-$AsPB_4Cl_4$ and traces of the icosahedral arsaphosphaborane $AsPB_{10}Cl_{10}$. These compounds are examples of heteroboranes which contain two different group-15 atoms within a single molecule[14].

Subsequently, selective homonuclear $^{11}B\{^{11}B\}$ decoupling experiments[15] on the *closo* diheteroboranes 1,2-$P_2B_4Cl_4$, 1,2-$P_2B_4Br_4$ and 1,2-$AsPB_4Cl_4$ and on the icosahedral *closo* species 1,7-$P_2B_{10}Cl_{10}$ and 1,7-$P_2B_{10}Br_{10}$ confirmed previous signal assignments and improved the resolution of ^{11}B NMR spectra (by simplifying the complex spin systems). These experiments allowed the determination of coupling constants $^1J_{PB}$ of the order of 27–39 Hz, which are significantly smaller than those for known non-halogenated parent compounds.

High-resolution vibrational spectra of the tetrahalo-*closo*-1,2-diphosphahexaboranes $P_2B_4X_4$ (for X = Cl and Br) were measured at low temperatures (20–60 K)[16]. The boron–halogen stretching vibrations were observed below 370 cm^{-1} while the P–P valence vibrations were found at 414 (Cl) and 372 cm^{-1} (Br). Due to the presence of the boron isotopes ^{10}B and ^{11}B, the P–P stretching vibrations and the cage modes in the region of 550 to 1 200 cm^{-1} are split. Based on the crystallographic data of $P_2B_4Cl_4$, normal coordinate analyses were performed to achieve a good agreement between observed and calculated frequencies.

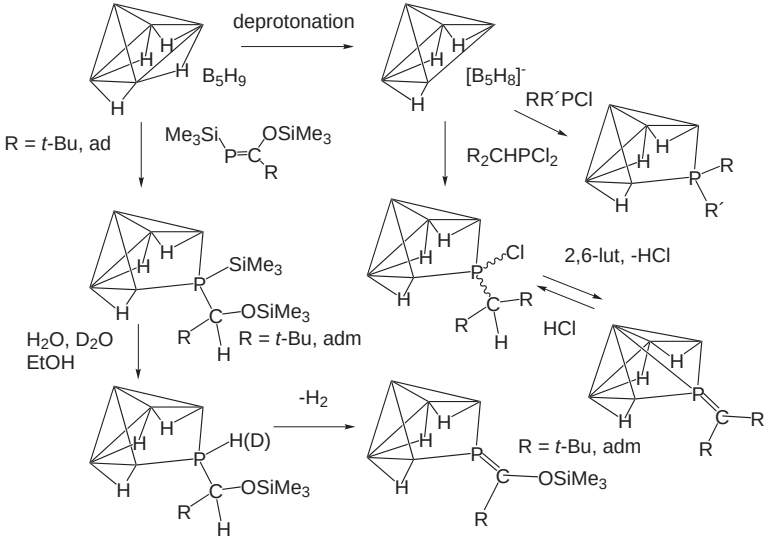
2.2. Insertion Into 5-Vertex Cages

An extensive area of phosphaborane chemistry is that of the compounds derived from reactions with the [*nido*-B_5H_8]$^-$ anion. Surprisingly, no reactions with PCl_3 and $RPCl_2$ compounds (where R = alkyl or aryl) that should lead to a more intimate incorporation of phosphorus vertices into cluster positions have not been reported to date. Nevertheless, a lot of attention have been paid to reactions with RR′PCl compounds.

$$RR'PCl + [B_5H_8]^- \longrightarrow 2,3\text{-}\mu\text{-}RR'P\text{-}B_5H_8 \qquad (2)$$

As demonstrated in Scheme 2, phosphine derivatives of the RR′PCl (where R, R′ = Me, Me; Me, CF_3 [17]; Me, Cl [18,19]; Et, Cl; Ph_2CH, Cl; $(Me_3Si)_2CH$, Cl [19]; Ph, Ph [18,20]) type generally react with $[B_5H_9]^-$ in ethers to form P-bridged derivatives of general formulation 2,3-μ-RR′P-B_5H_8 in which the P

atom is not fully incorporated into the cluster area. The 2,3-μ-Me$(CF_3)_{ax}$P-B_5H_8 derivative rearranges irreversibly to 2,3-μ-Me$(CF_3)_{eq}$P-B_5H_8 and the terminally substituted 1-$(F_3C)_2$P-B_5H_8 [17]. The reactions between $RPCl_2$ (for R = Me, Et, Ph_2CH, and $(Me_3Si)_2CH$) and $[B_5H_8]^-$ result in mixtures of the 2,3-μ-RCl_{ax}P-B_5H_8 and 2,3-μ-RCl_{eq}P-B_5H_8 isomers, which were not separated further[19]. The 2,3-μ-Ph_2P-B_5H_8 derivative has been deprotonated with NaH *via* removal of the 4,5-μ-H proton to give the $Na^+[2,3\text{-}\mu\text{-}RR'P\text{-}B_5H_7]^-$ salt[20].



SCHEME 2

Another approach to the 2,3-μ-P-bridging derivatives consists in the reaction of $(Me_3Si)P{=}C(R)(OSiMe_3)$ (where R = *t*-Bu or adm (adamantyl)) with one equivalent of neutral B_5H_9 which, under mild conditions, produces the synthetically versatile, small bridge phosphaboranes 2,3-μ-[$R(Me_3SiO)HCP(SiMe_3)$]-B_5H_8 in excellent yields[21]. Two possible mechanisms for the formation of these compounds by this reaction are supported by both experimental and semiempirical MNDO data. These compounds are relatively thermally and air-stable, and are also stable with respect to the elimination of $Me_3SiOSiMe_3$. They are, however, quantitatively converted to μ-[$R(Me_3SiO)CHPX$]-B_5H_8 (where X = H and D) by nucleophilic substitution reactions with water, D_2O, or alcohol. 2,3-μ-[*t*-$Bu(Me_3SiO)HCP(SiMe_3)$]-B_5H_8 is readily bridge-deprotonated by the action of NaH to produce the corresponding anion, {2,3-μ-[*t*-$Bu(Me_3SiO)CHP(SiMe_3)$]-B_5H_7}$^-$, while the adm derivative is unreactive under similar conditions. The 2,3-μ-[*t*-$Bu(Me_3SiO)CHPH$]-B_5H_8 slowly loses H_2 on standing at room temperature to form the bridged P=C

system, μ-[*t*-Bu(Me_3SiO)C=P]-B_5H_8. Compound 2,3-μ-[*t*-Bu(Me_3SiO)CHPH]-B_5H_8 is readily cage-deprotonated to form the corresponding anion, {2,3-μ-[*t*-Bu(Me_3SiO)CHPH]-B_5H_7}$^-$, which, when allowed to react with metal halides, forms metallaphosphaborane complexes. Data from MNDO calculations for all P-bridging compounds show linear relationships between the calculated charge on the bridgehead basal boron bond and the centroid-P–C bond angle[21].

2,3-μ-R_2CHClP-B_5H_8 compounds (for R = Ph and Me_3 Si) undergo dehydrochlorination[19] by the action of 2,6-lutidine (2,6-lut) to produce the derivatives of 2-phosphahexaborane of structure 2-R_2C=PB_5H_8, in which the phosphorus atom is fully incorporated into the cluster area (see Scheme 2).

$$2,3\text{-}\mu\text{-}R_2CHClP\text{-}B_5H_8 + 2,6\text{-lut} \longrightarrow 2\text{-}R_2C{=}PB_5H_8 + 2,6\text{-lut}\cdot HCl \quad (3)$$

The 2-(Me_3 Si)$_2$C=PB_5H_8 can also be prepared *via* treatment of $[B_5H_8]^-$ with (Me_3Si)$_2$C=PCl and the reaction (*3*) can be reversed, as demonstrated by the reaction of 2-(Me_3Si)$_2$C=PB_5H_8 with anhydrous HCl[19].

$$2\text{-}(Me_3Si)_2C{=}PB_5H_8 + HCl \longrightarrow 2,3\text{-}\mu\text{-}(Me_3Si)_2CHClP\text{-}B_5H_8 \quad (4)$$

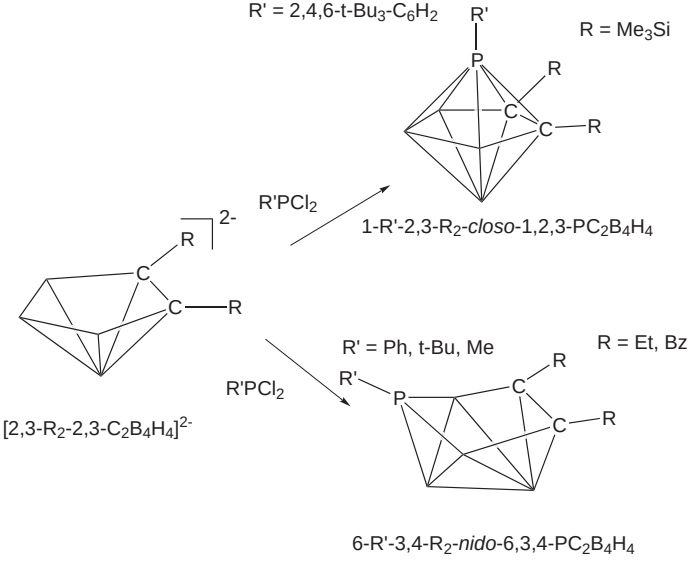
isomer B

Isomer B then slowly converts on standing at 25 °C to isomer A. Isomers A and B differ in mutual Cl-to-cluster orientations, but absolute configurations of both isomers are unknown. Using the semiempirical MNDO-SCF method, the relationship between the P-bridged and P-inserted (phosphahexaborane) structures has been related to the variation in MO energies as a function of the (P-bridged B-atom plane)–(basal B-plane) dihedral angle[5].

2.3. Insertion Into 6-Vertex Cages

No report on phosphorus insertion into the hexaborane *nido*-B_6H_{10} or its derivatives has appeared so far. However, two initial and a little bit controversial studies, leading to monophosphorus insertion, have been made with the relatively well available salts derived from the 6-vertex *nido*-$C_2B_4H_6$ dicarbaborane. As demonstrated in Scheme 3, the reaction between the $Na^+(THF)Li^+[2,3\text{-}(Me_3Si)_2\text{-}nido\text{-}C_2B_4H_4]^{2-}$ double salt and 2,4,6-*t*-Bu_3-$C_6H_2PCl_2$ in a molar ratio of 1 : 1 in THF at 0 °C for two hours produces a

compound which has been characterized as 1-(2,4,6-*t*-Bu_3-C_6H_2)-2,3-(Me_3Si)$_2$-*closo*-1,2,3-$PC_2B_4H_4$. This white, air-sensitive compound has been supposed to contain 16 cage electrons[22]. This exceptional electron count, however, can be achieved only on the condition that the phosphorus centre would donate only two electrons into cluster bonding scheme, with additional two electrons residing in an exopolyhedral orbital.

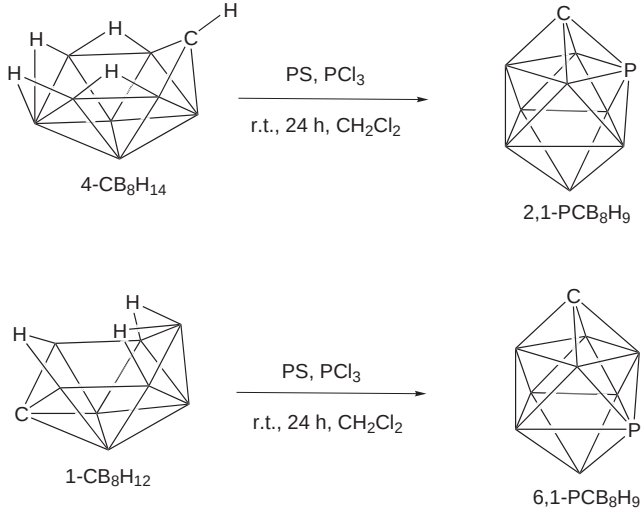


SCHEME 3

In contrast to the reaction discussed in the preceding paragraph[22], similar reactions of Na^+Li^+[*nido*-$R_2C_2B_4H_4$]$^{2-}$ (R = Et and Bz) with R′PCl_2 (R′ = Ph, *t*-Bu, and Me) have been found to yield 7-vertex phosphadicarbaboranes of the general formula 6-R′-3,4-R_2 -*nido*-6,3,4-$PC_2B_4H_4$ (see Scheme 3, bottom part). The structures have been proposed on the basis of spectroscopic data and the results of an *ab initio*/IGLO/NMR study. These compounds are regular 18-electron *nido* systems, as expected by theory[2]. The reaction of *nido*-6-Ph-3,4-Et_2-6,3,4-$PC_2B_4H_6$, with lithium metal or sodium naphthalenide in THF gives quantitative reduction of the phosphacarborane to form the [*arachno*-$PhEt_2PC_2B_4H_4$]$^{2-}$ dianion. Subsequent reaction of this dianion with $PhPCl_2$ gives an impure product that, according to NMR and mass spectrometric evidence, is the diphosphacarborane *arachno*-$Ph_2Et_2P_2C_2B_4H_4$. Comparison of the spectroscopic data obtained for [*arachno*-$PhEt_2PC_2B_4H_4$]$^{2-}$ and *arachno*-$Ph_2Et_2P_2C_2B_4H_4$ with the results of *ab initio*/IGLO/NMR calculations support 7- and 8-vertex *arachno* geometries, respectively, for these cage systems[23].

2.4. Insertion Into 9-Vertex Cages

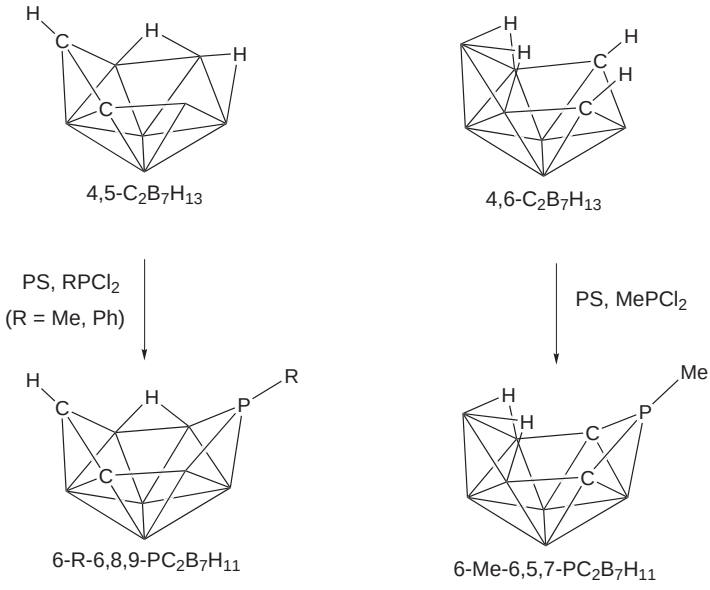
Because of the low availability of the 7- and 8-vertex cage compounds, no phosphorus insertion reactions have so far been attempted in this area. The opposite is true for the 9-vertex compounds as these are well represented, particularly by mono- and dicarbaborane compounds. Thus, the reaction between *arachno*-4-CB_8H_{14} and PCl_3 in the presence of PS (proton sponge = 1,8-bis(dimethylamino)naphthalene) in CH_2Cl_2 at room temperature for 24 h produced the neutral phosphacarborane *closo*-2,1-PCB_8H_9 (yield 35%), while a similar reaction of *nido*-1-CB_8H_{12} gives the isomeric compound *closo*-6,1-PCB_8H_9 (yield 27%) (see Scheme 4). The structures of both compounds have been derived on the basis of the combined *ab initio*/GIAO/NMR (^1H, ^{11}B, ^{13}C) approach. The optimized structures at a correlated level of theory (MP2) with 6-31G* basis set were used as a basis for calculations of the ^{11}B and ^{13}C chemical shifts at GIAO-SCF/II and GIAO-MP2/II levels which showed excellent agreement with experimental data[24]. Both reactions in Scheme 4 thus result in monophosphorus insertion.



SCHEME 4

Another monophosphorus insertion process is outlined in Scheme 5. The dicarbaborane *arachno*-4,5-$C_2B_7H_{13}$ was found to react with $RPCl_2$ (R = Me and Ph) in the presence of two equivalents of PS to produce the phosphadicarbaboranes 6-R-*arachno*-6,8,9-$PC_2B_7H_{11}$ in 49 and 68% yields, respectively. A similar reaction of the isomeric species *arachno*-4,6-$C_2B_7H_{13}$ with $MePCl_2$ yielded the isomeric compound 6-R-*arachno*-6,5,7-$PC_2B_7H_{11}$ in a

yield of 50%. Both compounds were isolated as the first 10-vertex phosphadicarbaboranes and their formation discussed in terms of sequential dehalogenation and cage insertion. The structures were established using comparisons between experimental NMR data and DFT/GIAO/NMR calculations. An order of relative stabilities for individual 6-Me-*arachno*-$PC_2B_7H_{11}$ cage isomers was established using the DFT calculations: 6,8,9- > 6,5,9- > 6,5,10- > 6,5,7- > 6,4,7- [25].

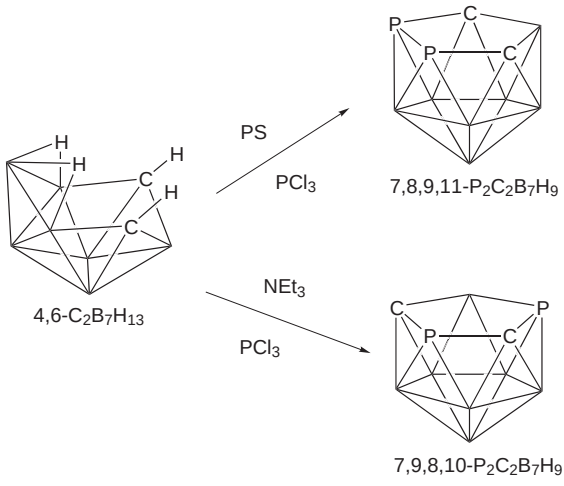


SCHEME 5

In contrast to their reactions with $RPCl_2$, reactions of the mutually isomeric 4,5- and 4,6-*arachno*-$C_2B_7H_{13}$ dicarbaboranes with PCl_3 proceed exclusively with a diphosphorus insertion, with the formation of the corresponding isomeric 11-vertex *nido*-$P_2C_2B_7H_9$ compounds[26]. Thus, treatment of 4,6-*arachno*-$C_2B_7H_{13}$ with PCl_3 in the presence of PS in CH_2Cl_2 results in the formation of *nido*-7,8,9,11-$P_2C_2B_7H_9$ and 3-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ in yields 54 and 7%, respectively.

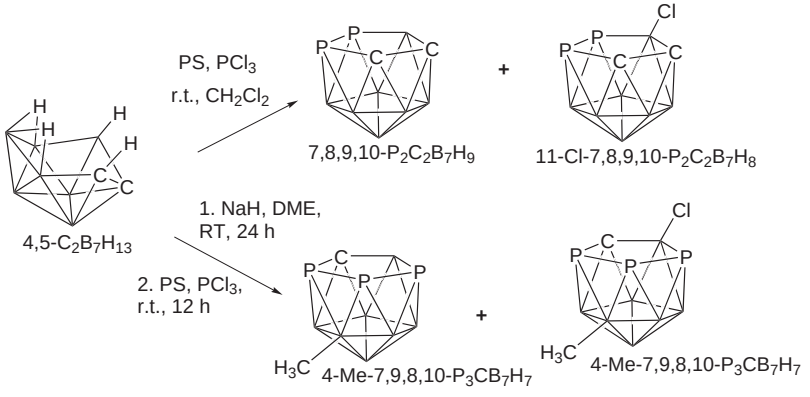
The same compounds have been isolated, together with another 11-vertex isomer *nido*-7,9,8,10-$P_2C_2B_7H_9$, in yields of 28, 15, and 3%, respectively, when NEt_3 was employed as a dehydrohalogenation agent (see Scheme 6).

The reaction between the other isomeric carborane, *arachno*-4,5-$C_2B_7H_{13}$, and PCl_3 in the presence of PS in CH_2Cl_2 gives another 11-vertex isomer, *nido*-7,8,9,10-$P_2C_2B_7H_9$, along with its 4-Cl and 11-Cl derivatives, in yields 21, 1, and 13%, respectively[26]. In contrast to this reaction, ageing of the



SCHEME 6

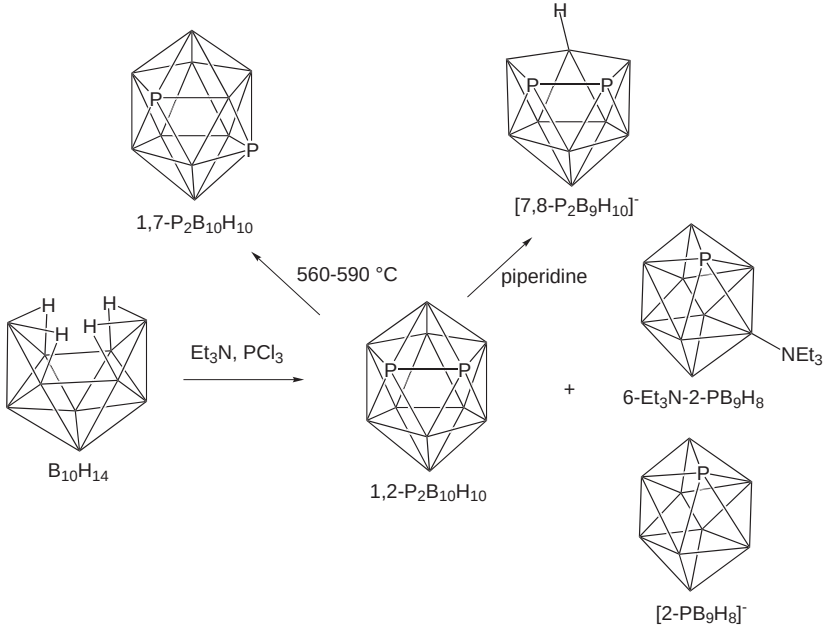
[*arachno*-4,5-$C_2B_7H_{12}$]$^-$ anion in 1,2-dimethoxyethane (DME), followed by the addition of equivalent amounts of PS and PCl_3, results in the formation of the first compounds of the triphosphacarborane type, the 11-vertex *nido* compounds 4-CH_3-7,8,9,10-$P_3CB_7H_6$ and 4-CH_3-11-Cl-7,8,9,10-$P_3CB_7H_6$ (yields 13 and 4%, respectively, see Scheme 7)[27]. The reaction is associated with the extrusion of one of the skeletal carbons into an exoskeletal position (see Scheme 7). The structures of 3-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ and 11-Cl-*nido*-7,8,9,10-$P_2C_2B_7H_8$ have been established by X-ray diffraction analyses, and all $P_2C_2B_7$ and P_3CB_7 compounds have been geometry-optimised at the RMP2(fc)/6-31G* level, and the geometries used for GIAO-SCF/II calculations of the ^{11}B NMR shifts and their comparison with experimental values[26,27].



SCHEME 7

2.5. Insertion Into 10-Vertex Cages

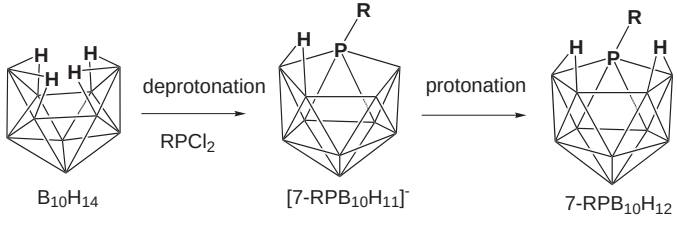
The relatively well available 10-vertex borane and dicarbaborane compounds have been widely used for phosphorus insertion reactions.The diphosphaborane *closo*-1,2-$P_2B_{10}H_{10}$, an analogue of *o*-carborane, has been isolated in 12% yield from the reaction between $B_{10}H_{14}$ and PCl_3 in the presence of NEt_3 and $NaBH_4$ in THF, followed by chromatographic separation of the products. The reaction is obviously consistent with the cage insertion of two phosphorus atoms[28]. The reaction is accompanied by the formation of the 10-vertex [*closo*-2-PB_9H_9]$^-$ anion (yield 0.3%)[29] and 6-Et_3N-*closo*-2-PB_9H_8 (yield 0.5%, see Scheme 8)[28]. The structure of this last ligand derivative has been determined by an X-ray diffraction study[28]. The 1,2-$P_2B_{10}H_{10}$ undergoes thermal rearrangement on heating at 560–590 °C for 1.5 h to give the 1,7-$P_2B_{10}H_{10}$ isomer (see Scheme 8). Aqueous NaOH was found to remove one of the P-vertices from 1,2-$P_2B_{10}H_{10}$ to produce the parent 11-vertex anion [7-$PB_{10}H_{12}$]$^-$, which can be methylated with MeI in THF to afford the neutral species 7-Me-7-$PB_{10}H_{12}$ [28]. Treatment of *closo*-1,2-$P_2B_{10}H_{10}$ with excess piperidine forms the [*nido*-7,8-$P_2B_9H_{10}$]$^-$ anion in 76% yield (see Scheme 8)[29]. The mixed-heteroatom heteroborane 1,2-$PAsB_{10}H_{10}$ has been prepared in low yield by reaction of $B_{10}H_{14}$ with



SCHEME 8

triethylamine and a mixture of PCl_3 and $AsCl_3$, respectively[29]. 1,2-$PSbB_{10}H_{10}$ has been prepared similarly using PCl_3 and SbI_3 [29]. *Ab initio* studies were employed[30] to calculate total and relative energies for all the three isomers of $P_2B_{10}H_{10}$.

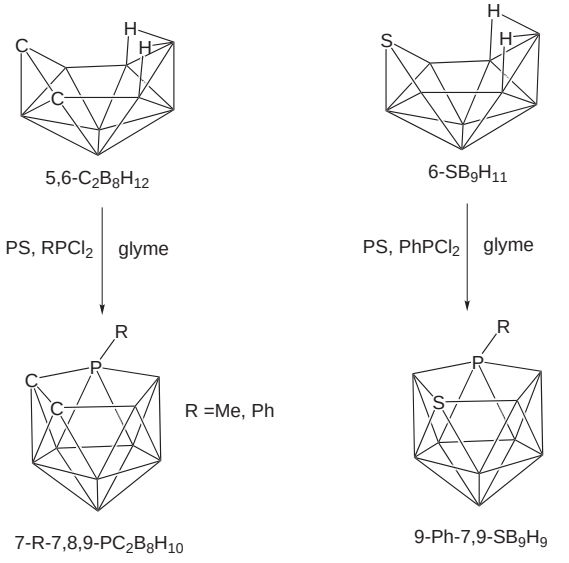
The reaction of $B_{10}H_{14}$ with $RPCl_2$ (R = Me, Et, Pr, and Ph) in the presence of four equivalents of NaH in Et_2O leads to monophosphorus insertion and the *nido*-phosphaundecaborane anions $[7\text{-}RPB_{10}H_{11}]^-$ have been isolated in 15–35% yields (Scheme 9)[31,32]. This method was subsequently improved by using PS as the dehydrohalogenation agent[33] to isolate two of these anions (where R = Me and Ph) in near-quantitative yields. The anions can be easily protonated (concentrated HCl or H_2SO_4) to give the neutral 7-R-*nido*-$7\text{-}PB_{10}H_{12}$ compounds. The 7-Me derivative has also been obtained in 12% yield from the reaction of $K_2B_{11}H_{13}$ with $MePCl_2$ in Et_2O, and its structure determined by X-ray diffraction[34].



SCHEME 9

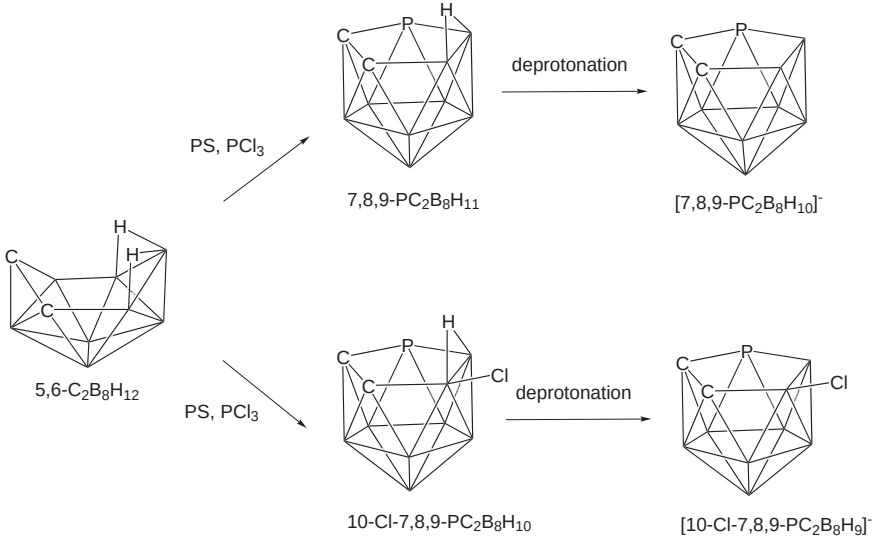
Reaction of *nido*-5,6-$C_2B_8H_{12}$ with $RPCl_2$ (R = Me and Ph) in DME in the presence of PS has produced the *nido* phosphadicarbaboranes 7-R-7,8,9-$PC_2B_8H_{10}$ in high yields (97 and 83%, respectively) and a similar reaction with *nido*-$6\text{-}SB_9H_{11}$ with $PhPCl_2$ and PS has resulted in the formation of the new mixed heteroatom cage, *nido*-9-Ph-7,9-SPB_8H_9 (see Scheme 10). The last compound was the first example of a thiaphosphaborane cluster. Consistent with their *nido* skeletal electron counts, all clusters were shown by spectroscopic and DFT/GIAO computational studies to have similar cage frameworks containing a five-membered open face[33].

Reactions between the carborane *nido*-5,6-$C_2B_8H_{12}$ and PCl_3 in the presence of PS in dichloromethane, followed by hydrolysis of the reaction mixture, has resulted in the formation of the 11-vertex *nido* phosphadicarbaboranes 7,8,9-$PC_2B_8H_{11}$ and 10-Cl-7,8,9-$PC_2B_8H_{10}$, depending on the ratio of reactants (isolated in yields 38 and 30%, respectively). Both of these compounds can be deprotonated by PS to give the *nido* anions $[7,8,9\text{-}PC_2B_8H_{10}]^-$ and $[10\text{-}Cl\text{-}7,8,9\text{-}PC_2B_8H_9]^-$ (Scheme 11). The molecular geometries of all these compounds have been optimized *ab initio* at a corre-



SCHEME 10

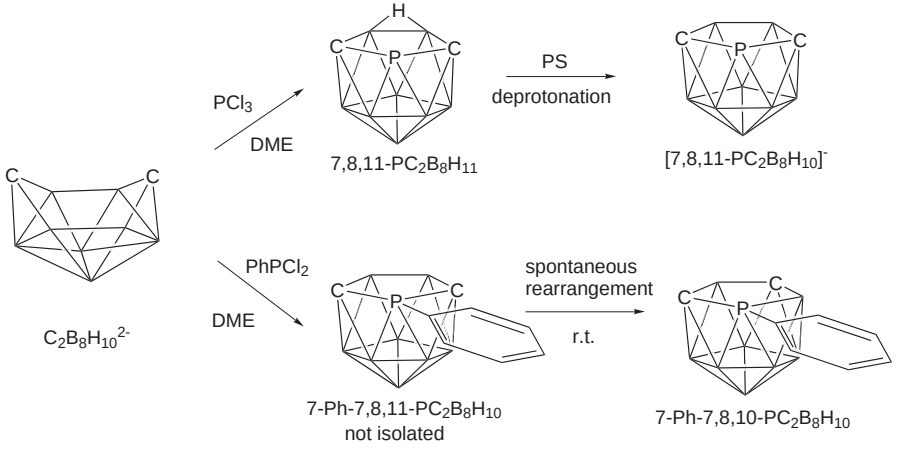
lated level of theory (RMP2(fc)) using 6-31G* basis set and their correctness assessed by comparison of experimental ^{11}B chemical shifts with those calculated by the GIAO-SCF/II//RMP2(fc)/6-31G* method. The structure of [10-Cl-7,8,9-$PC_2B_8H_9$]$^-$ has been determined by an X-ray diffraction analysis. The anionic compounds [7,8,9-$PC_2B_8H_{10}$]$^-$ and [10-Cl-7,8,9-$PC_2B_8H_9$]$^-$



SCHEME 11

are, in contrast to compounds discussed in the preceding paragraph, analogs of the cyclopentadienyl anion[35] as they are monoanionic and contain a pentagonal open face.

As shown in Scheme 12, treatment of Na_2[*nido*-6,9-$C_2B_8H_{10}$] with PCl_3 in DME at room temperature for 24 h, followed by hydrolysis of the reaction mixture, produces the neutral 11-vertex phoshadicarbaborane *nido*-7,8,11-$PC_2B_8H_{11}$ (yield 35%). The compound is isomeric with 7,8,9-$PC_2B_8H_{11}$ discussed in the preceding paragraph and can be quantitatively deprotonated by PS to give the corresponding [*nido*-7,8,11-$PC_2B_8H_{10}$]$^-$ anion. A similar reaction using $PhPCl_2$ as the source of phosphorus yields 7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$ (yield 64%), which has a different configuration of heteroatoms in the open face. A side product, *nido*-7,8,11-$PC_2B_8H_{11}$ (yield 14%), apparently results from an accompanying dephenylation process. The formation of 7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$ has been supposed to proceed *via* a room-temperature cage rearrangement of 7-Ph-7,8,11-*nido*-$PC_2B_8H_{10}$ [36]. The DFT-GIAO//B3LYP/6/31G* calculations were used to show that conformation changes about the *exo*-cluster C(cage)–Ph bond in 7-Ph-*nido*-7,8,10-$PC_2B_8H_{10}$ have significant differential effects of up to *ca* 6 ppm on the nuclear shieldings of adjacent boron atoms within the cluster[37].

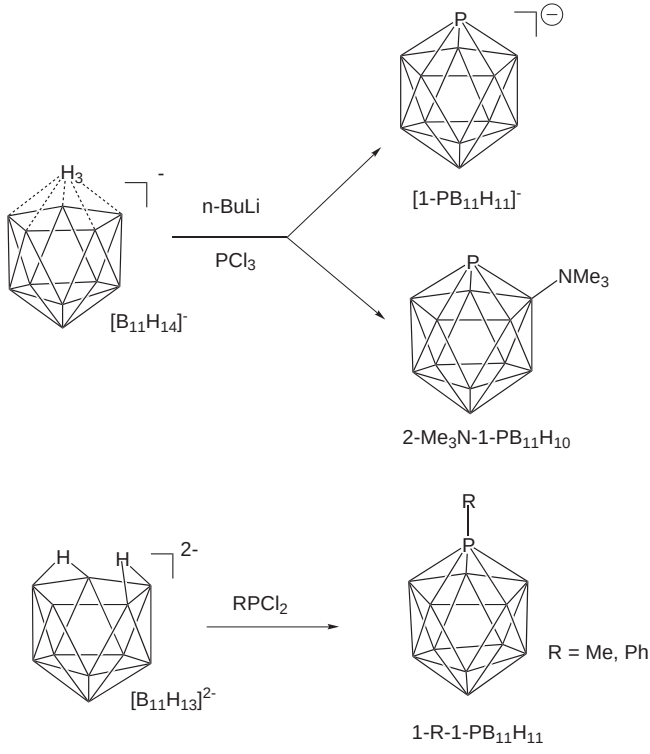


SCHEME 12

2.6. Insertion Into 11-Vertex Cages

Several 11-vertex *nido* boranes have been found suitable as starting materials for the insertion phosphorus atoms into cluster positions. As shown in Scheme 13, treatment of [Me_3NH]$^+$[$B_{11}H_{14}$]$^-$ with excess BuLi and PCl_3 forms both [*closo*-1-$PB_{11}H_{11}$]$^-$ and zwitterionic 2-Me_3N-*closo*-1-$PB_{11}H_{10}$ in

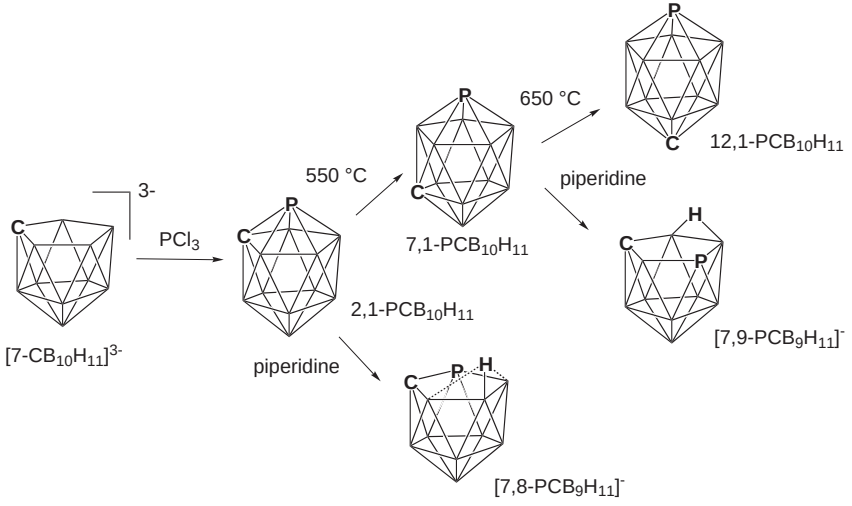
moderate yield. The compound 2-NMe_3-1-$PB_{11}H_{10}$ has been characterized by a single-crystal X-ray structure analysis[29]. Reactions of $[B_{11}H_{13}]^{2-}$ with $RPCl_2$ (R = Me and Ph) have given, after repeated sublimation of the reaction products, stable, but air-sensitive, compounds 1-R-*closo*-$PB_{11}H_{11}$ in low yields[34,38]. The structure of the Me derivative was determined by an X-ray diffraction analysis[34].



SCHEME 13

Todd *et al.*[38,39] have demonstrated that the treatment of a slurry of $Na_3[CB_{10}H_{11}]\cdot 2THF$ with PCl_3 in solvents such as petroleum ether, benzene or toluene produces *closo*-1,2-$PCB_{10}H_{11}$ in 40–50% yield. This air-stable compound is an analogue of 1,2-$C_2B_{10}H_{12}$ and is formed *via* insertion of a phosphorus vertex into the open pentagonal face of [*nido*-7-$CB_{10}H_{11}]^{3-}$ (see Scheme 14). The 2,1-isomer undergoes thermal rearrangement (550 °C, 8 h) to form the 1,7-isomer (yield 60–65%), while at higher temperatures (650 °C, 19 h) significant amounts of the 1,12-isomer are formed. $AlCl_3$ catalyzed bromination of 1,2-$PCB_{10}H_{11}$ in CS_2 gives mono-, di-, and, with excess Br_2, ultimately a B-substituted tribromo derivative[39]. The same reaction with

1,7-$PCB_{10}H_{11}$ gives only mono- and dibromo derivatives. The structure of $PCB_{10}H_9Cl_2$ has been determined by an X-ray diffraction study[40]. Treatment of 1,7-$PCB_{10}H_{11}$ with BuLi, followed by reaction with MeI gives 7-Me-1,7-$PCB_{10}H_{10}$ [38]. Reactions of 1,2- and 1,7-$PCB_{10}H_{11}$ with piperidine[39] result in the elimination of one B-vertex and formation of two isomeric ions 7,8- and [*nido*-7,9-$PCB_9H_{11}]^-$, which were isolated as piperidinium ($C_4H_8N_2H_3^+$) salts (yields 80 and 90%, respectively) and also converted into $[NMe_4]^+$ salts. The salts should contain one extra hydrogen atom on the open face of the 11-vertex cage (see Scheme 14), but this was not detected by NMR spectroscopy in the original work[39]. Passage of [7,9-$PCB_9H_{11}]^-$

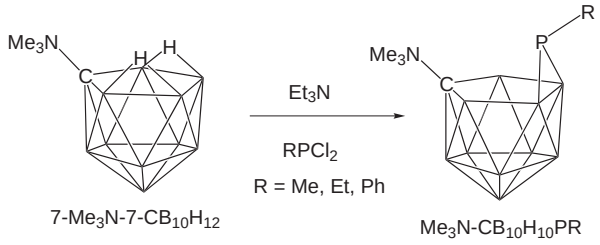


SCHEME 14

through an acid ion-exchange column gives neutral *nido*-7,9-$HPCB_9H_{11}$ as a sublimable hygroscopic solid in 91% yield[39]. Alkylation of [7,8-$PCB_9H_{11}]^-$ with MeI or $PhCH_2Br$ in THF or MeCN produces the neutral *nido* alkyl derivatives 7-R-7,8-PCB_9H_{11} (yields 40 and 30%, respectively). Similar reactions of RBr (R = $PhCH_2$–, CH_2=$CHCH_2$–, and PhCH=$CHCH_2$–) and RI (R = Me, Et) with [7,9-$PCB_{10}H_{11}]^-$ in MeCN yield the corresponding 7-R-7,9-PCB_9H_{11} compounds (yields 52–94%)[39,41,42]. All the alkyl derivatives have been assumed to adopt the same structure as the original ions, but with the alkyl substituent residing exclusively on the cage phosphorus atom.

Reactions of the zwitterionic 7-(Me_3N)-*nido*-7-$CB_{10}H_{12}$ compound[43] with Et_3N and then $RPCl_2$ (R = Me, Et, and Ph) in THF afford a series of the 12-vertex *nido*-(Me_3N)$CB_{10}H_{10}$PR compounds in yields 85, 88, and 83%, respectively (see Scheme 15). The compounds are obviously phospha-

carborane analogues of one of the two known isomers of the [*nido*-$C_2B_{10}H_{13}]^-$ anion[31,44]. The structure of the $Me_3NCB_{10}H_{10}PPh$ derivative has been determined crystallographically[43].



SCHEME 15

3. CONCLUSIONS

Reactions of PCl_3 or its organyl-substituted derivatives have become an established synthetic route to boron-cluster compounds containing one or more phosphorus vertices as constituents of the cage. The reactions can be, in principle, modified and the phosphorus atom can, in many cases, occupy a bridging position. As demonstrated in this review, phosphorus insertion reactions lead to a large variety of phosphaborane and phosphacarborane compounds, the area of phosphaheteroborane chemistry being still almost completely untouched. As demonstrated by some examples (see refs[21,31,32,45]), open-structured phosphaborane compounds can be effectively employed for the synthesis of structurally diverse metallaphosphaborane/carborane complexes, the field of chemistry that still awaits rapid development. Another reason for the current enhanced interest in this area is the relative stability of the most phosphaborane and, particularly, phosphacarborane compounds. The whole area of phosphaborane chemistry is open to derivatisation on boron, carbon, and phosphorus vertices in order to synthesise structurally designed compounds for various uses, *e.g.*, in medicine. We can expect rapid development of this area in the nearest future and this review should help those interested in this field of cluster chemistry.

4. APPENDIX

4.1. Selected Experimental Data for 5-Vertex Phosphaboranes

nido compounds

2,3-μ-*Me_2P-B_5H_8*: [17] m.p. 17 °C; b.p. (est) 191 °C; δ(^{11}B): –1.1 (d, $^1J_{BH}$ = 156, B4,5), –23.3 (dd, $^1J_{BH}$ = 117, B2,3), –46.8 (d, $^1J_{BH}$ = 154, B1); δ(^{31}P): –85.

2,3-μ-*Me(CF_3)$_{ax}$P-B_5H_8*: [17] m.p. 14 °C; b.p. (est) 191 °C; δ(^{11}B): –1.8 (d, $^1J_{BH}$ = 160, B4,5), –24.1 (dd, $^1J_{BH}$ = 105, B2,3), –45.7 (d, $^1J_{BH}$ = 163, B1); δ(^{31}P): –33.5.

2,3-μ-*Me(CF$_3$)$_{eq}$P-B$_5$H$_8$*: [17] m.p. –28 °C; b.p. (est) 137 °C; δ(^{11}B): –0.6 (d, $^1J_{BH}$ = 164, B4,5), –23.1 (dd, $^1J_{BH}$ = 112, B2,3), –46.2 (d, $^1J_{BH}$ = 163, B1); δ(^{31}P): –47.

2,3-μ-*MeClP-B$_5$H$_8$* (isomer A): [19] δ(^{11}B): –1.0 (d, B4,5), –242 (dd, $^1J_{BP}$ = 88, B2,3), –45.4 (d, B1).

2,3-μ-*MeClP-B$_5$H$_8$* (isomer B): [19] δ(^{11}B): 0.2 (d, B4,5), –8.7 (dd, $^1J_{BP}$ = 88, B2,3), –46.0 (d, B1).

2,3-μ-*PhClP-B$_5$H$_8$* (isomer A): [19] δ(^{11}B): –0.1 (d, B4,5), –21.7 (dd, $^1J_{BP}$ = 93, B2,3), –43.7 (d, B1).

2,3-μ-*PhClP-B$_5$H$_8$* (isomer B): [19] δ(^{11}B): –0.1 (d, B4,5), –9.9 (dd, $^1J_{BP}$ = 93, B2,3), –45.5 (d, B1).

2,3-μ-*Ph$_2$CHClP-B$_5$H$_8$* (isomer A): [19] δ(^{11}B): –0.5 (d, B4,5), –21.8 (dd, $^1J_{BP}$ = 88, B2,3), –44.8 (d, B1).

2,3-μ-*Ph$_2$CHClP-B$_5$H$_8$* (isomer B): [19] δ(^{11}B): –0.5 (d, B4,5), –10.0 (dd, $^1J_{BP}$ = 88, B2,3), –45.8 (d, B1).

2,3-μ-*(Me$_3$Si)$_2$CHClP-B$_5$H$_8$* (isomer A): [19] δ(^{11}B): –0.1 (d, B4,5), –17.4 (dd, $^1J_{BP}$ = 88, B2,3), –44.5 (d, B1).

2,3-μ-*(Me$_3$Si)$_2$CHClP-B$_5$H$_8$* (isomer B): [19] δ(^{11}B): –0.1 (d, B4,5), –8.8 (dd, $^1J_{BP}$ = 96, B2,3), –46.4 (d, B1).

2,3-μ-*Ph$_2$P-B$_5$H$_8$*: [20] δ(^{11}B) ($CDCl_3$): –0.5 (d, $^1J_{BH}$ = 164, B4,5), –22.7 (dd, $^1J_{BH}$ = 110, $^1J_{BP}$ = 94, B2,3), –45.6 (d, $^1J_{BH}$ = 153, B1); δ(^{31}P) ($CDCl_3$): –52.3 (br s).

Na[2,3-μ-*Ph$_2$P-B$_5$H$_7$]*: [20] δ(^{11}B) (THF-d_8): –3.0 (d, $^1J_{BH}$ = 185, B4,5), –23.5 (dd, $^1J_{BH}$ = 134, $^1J_{BP}$ = 60, B2,3), –48.0 (d, $^1J_{BH}$ = 172, B1); δ(^{31}P) (THF-d_8): –38.9 (br s).

2,3-μ-*t-Bu(OSiMe$_3$)CH(Me$_3$Si)P-B$_5$H$_8$*: [21] m/z_{max}: 329; δ(^{11}B) ($CDCl_3$): –2.2 (s, B4,5), –19.6 (s, B2,3), –48.6 (d, $^1J_{BH}$ = 152, B1); δ(^{1}H) ($CDCl_3$): –0.37 (q, 1 H, H1), –1.75 (s, 3 H, μH); δ(^{31}P) ($CDCl_3$): –124.5 (s); ν (NaCl): 2 580, 2 533 sh, 2 519, 2 365 (BH) cm^{-1}.

2,3-μ-*adm(OSiMe$_3$)CH(Me$_3$Si)P-B$_5$H$_8$*: [21] m/z_{max}: 407; δ(^{11}B) ($CDCl_3$): –2.7 (s, B4,5), –19.4 (s, B2,3), –48.2 (d, $^1J_{BH}$ = 147, B1); δ(^{1}H) ($CDCl_3$): –0.40 (q, 1 H, H1), –1.70 (s, 3 H, μH); δ(^{31}P) ($CDCl_3$): –127.9 (s); ν (NaCl): 2 577, 2 531 sh, 2 513, 2 426 sh, 2 381 (BH) cm^{-1}.

2,3-μ-*t-Bu(OSiMe$_3$)CHPH-B$_5$H$_8$*: [21] m/z_{max}: 256; δ(^{11}B) ($CDCl_3$): –1.6 (d, $^1J_{BH}$ = 156, B4,5), –22.0 (t, $^1J_{BH}$ = 80, $^1J_{BP}$ = 82, B2,3), –47.5 (d, $^1J_{BH}$ = 152, B1); δ(^{1}H) ($CDCl_3$): 5.27 (d, $^1J_{PH}$ = 410, 1 H, PH), –0.04 (q, 1 H, H1), –1.40 (s, 1 H, μH), –1.80 (s, 2 H, μH); δ(^{31}P) ($CDCl_3$): –97.5 (d, $^1J_{PH}$ = 410); ν (NaCl): 2 587, 2 541 (BH), 2 400 (PH) cm^{-1}.

2,3-μ-*adm(OSiMe$_3$)CHPH-B$_5$H$_8$*: [21] m/z_{max}: 334; δ(^{11}B) ($CDCl_3$): –1.1 (d, $^1J_{BH}$ = 153, B4,5), –21.6 (t, $^1J_{BH}$ = 99, $^1J_{BP}$ = 77, B2,3), –46.5 (d, $^1J_{BH}$ = 155, B1); δ(^{1}H) ($CDCl_3$): 5.32 (d, $^1J_{PH}$ = 406, 1 H, PH), –0.12 (q, 1 H, H1), –1.40 (s, 1 H, μH), –1.80 (s, 2 H, μH); δ(^{31}P) ($CDCl_3$): –101.0 (d, $^1J_{PH}$ = 406); ν (NaCl): 2 587, 2 541 (BH), 2 400 (PH) cm^{-1}.

2,3-μ-*t-Bu(OSiMe$_3$)C=P-B$_5$H$_8$*: [21] m/z_{max}: 254; δ(^{11}B) ($CDCl_3$): –1.0 (d, $^1J_{BH}$ = 143, B4,5), –9.9 (t, $^1J_{BH}$ = 152, $^1J_{BP}$ = 111, B2,3), –12.3 (t, $^1J_{BH}$ = 147, $^1J_{BP}$ = 97, B2,3), –47.5 (d, $^1J_{BH}$ = 159, B1); δ(^{1}H) ($CDCl_3$): –0.34 (q, 1 H, H1), –1.70 (s, 3 H, μH); δ(^{31}P) ($CDCl_3$): 26.1.

Na[2,3-μ-*t-Bu(OSiMe$_3$)CH(Me$_3$Si)P-B$_5$H$_7$]*: [21] δ(^{11}B) ($CDCl_3$): –1.9 (s, B4,5), –18.7 (s, B2,3), –48.4 (d, $^1J_{BH}$ = 157, B1); δ(^{1}H) ($CDCl_3$): –0.68 (q, 1 H, H1), –1.72 (s, 2 H, μH); δ(^{31}P) ($CDCl_3$): –124.3 (s); ν (NaCl): 2 535, 2 442, 2 394 (BH) cm^{-1}.

4.2. Selected Experimental Data for 6-Vertex Phosphaboranes and Phosphacarboranes

closo compounds

1,2-P$_2$B$_4$Cl$_4$: [9] δ(^{11}B) (C_6D_6): 22.1 (s, B4,6), 2.2 (s, B3,5); δ(^{31}P) (C_6D_6): –187.0 (P1,2); X-ray diffraction.

3,3′-(1,2-P$_2$B$_4$Cl$_3$)$_2$: [14] m/z_{max}: 421.77611; δ(^{11}B) ($CDCl_3$): 24.8 (s, 3 B), 15.9 (s, 1 B); δ(^{31}P) ($CDCl_3$): –182.0 (P1,2).

1,2-$P_2B_4Br_4$: [13] m.p. 104–107 °C; δ(^{11}B) (C_6D_6): 19.0 (s, B4,6), 0.0 (s, B3,5); δ(^{31}P) (C_6D_6): –145.0 (P1,2).

1,2-$PAsB_4Cl_4$: [14] m/z_{max}: 289.81265; δ(^{11}B) ($CDCl_3$): 24.8 (s, B4,6), 7.0 (s, B3,5).

nido compounds

2-H_2C=PB_5H_8: [19] δ(^{11}B) (Et_2O): 26.6 (d, $^1J_{BH}$ = 164, B4,5), 8.3 (d, $^1J_{BH}$ = 141, B3,6), –36.9 (d, $^1J_{BH}$ = 152, B1).

2-Ph_2C=PB_5H_8: [19] δ(^{11}B) (Et_2O): 26.6 (d, $^1J_{BH}$ = 161, B4,5), 8.9 (d, $^1J_{BH}$ = 146, B3,6), –35.3 (d, $^1J_{BH}$ = 161, B1).

2-$(Me_3Si)_2C$=PB_5H_8: [19] δ(^{11}B) (Et_2O): 23.3 (d, $^1J_{BH}$ = 156, B4,5), 6.9 (d, $^1J_{BH}$ = 142, B3,6), –39.9 (d, $^1J_{BH}$ = 161, B1); δ(^{31}P): 209 (br s, P2).

4.3. Selected Experimental Data for 7-Vertex Phosphaboranes and Phosphacarboranes

closo compounds

1-(2,4,6-t-Bu_3-C_6H_2)-2,3-$(Me_3Si)_2$-1,2,3-$PC_2B_4H_4$: [22] m.p. 147–148 °C; δ(^{11}B) (C_6D_6): 15.85 (d, $^1J_{BH}$ = 166, B4,6), 7.7 (d, $^1J_{BH}$ = 165, B5), –16.6 (d, $^1J_{BH}$ = 174, B7); δ(^{13}C) (C_6D_6): 119.3 (br d, $^1J_{CP}$ = 154, C2,3); δ(^{31}P) (C_6D_6): –129.7 (br s, P1); ν (C_6D_6): 2 600 (BH) cm^{-1}.

nido compounds

6-Ph-3,4-Et_2-6,3,4-$PC_2B_4H_4$: [23] m.p. ≈ –88 °C; m/z_{max}: 238.1580; δ(^{11}B) (CD_2Cl_2): 27.2 (d, $^1J_{BH}$ = 172, B2), –5.1 (d, $^1J_{BH}$ = 154, B5,7), –5.9 (d, $^1J_{BH}$ = 130, B1); δ(^{1}H){^{11}B} (CD_2Cl_2): 5.38 (s, H2), 3.15 (d, $^2J_{PH}$ = 10, H5,7), 1.72 (d, $^2J_{PH}$ ≈ 7, H1); δ(^{13}C) (CD_2Cl_2, –82 °C): 151.8 (d, $^1J_{PC}$ = 37, C3,4); δ(^{31}P) (CD_2Cl_2): 63.6 (s, P6); ν (NaCl): 2 600 sh, 2 560 (BH) cm^{-1}.

6-Ph-3,4-Bz_2-6,3,4-$PC_2B_4H_4$: [23] m/z_{max}: 362.1935; δ(^{11}B) (CD_2Cl_2): 28.7 (d, $^1J_{BH}$ = 146, B2), –4.1 (d, $^1J_{BH}$ = 190, B5,7), –6.1 (d, B1); δ(^{1}H){^{11}B} (CD_2Cl_2): 5.47 (s, H2), 3.02 (d, $^2J_{PH}$ = 8, H5,7), 1.84 (d, $^2J_{PH}$ ≈ 4, H1); δ(^{13}C) (CD_2Cl_2, –80 °C): 149.0 (d, $^1J_{PC}$ = 38, C3,4); δ(^{31}P) (CD_2Cl_2): 71.2 (s, P6); ν (NaCl): 2 580 (BH) cm^{-1}.

6-t-Bu-3,4-Et_2-6,3,4-$PC_2B_4H_4$: [23] m/z_{max}: 218.1910; δ(^{11}B) (CD_2Cl_2): 23.3 (d, $^1J_{BH}$ = 157, B2), –4.8 (d, $^1J_{BH}$ = 153, B1,5,7); δ(^{1}H){^{11}B} (CD_2Cl_2): 5.20 (s, H2), 2.79 (d, $^2J_{PH}$ = 11, H5,7), 1.57 (d, H1); δ(^{13}C) (CD_2Cl_2, –80 °C): 151.0 (d, $^1J_{PC}$ = 32, C3,4); δ(^{31}P) (CD_2Cl_2): 110.3 (s, P6); ν (NaCl): 2 565 (BH) cm^{-1}.

6-t-Bu-3,4-Bz_2-6,3,4-$PC_2B_4H_4$: [23] m/z_{max}: 342.2222; δ(^{11}B) (CD_2Cl_2): 24.8 (d, $^1J_{BH}$ = 168, B2), –3.9 (d, $^1J_{BH}$ = 143, B1,5,7); δ(^{1}H){^{11}B} (CD_2Cl_2): 5.20 (s, H2), 2.70 (d, $^2J_{PH}$ = 10, H5,7), 1.70 (d, H1); δ(^{13}C) (CD_2Cl_2, 25 °C): 149.0 (C3,4); δ(^{31}P) (CD_2Cl_2): 112.9 (s, P6); ν (NaCl): 2 570, 2 540 sh (BH) cm^{-1}.

6-Me-3,4-Et_2-6,3,4-$PC_2B_4H_4$: [23] m/z_{max}: 176.1452; δ(^{11}B) (CD_2Cl_2): 28.3 (d, $^1J_{BH}$ = 152, B2), –4.7 (d, $^1J_{BH}$ = 158, B1,5,7); δ(^{31}P) (CD_2Cl_2): 16.4 (s, P6).

arachno compounds

$(Li^+)_2[PhEt_2PC_2B_4H_4]^{2-}$: [23] δ(^{11}B) (THF-$d_8$): 3.8 (br), –9.5 (br), –46.8 (d, $^1J_{BH}$ = 147); δ(^{31}P) (CD_2Cl_2): –246.9 (s, 1 P).

4.4. Selected Experimental Data for 10-Vertex Phosphacarboranes

closo compounds

$NMe_4^+[2\text{-}PB_9H_9]^-$: [29] δ(^{11}B) (acetone-d_6): 12.2 (d, 1 B), 1.3 (d, 1 B), –16.3 (d, 1 B), –26.9 (d, 2 B), –29.4 (d, 2 B), –31.8 (d, 2 B); δ(^{31}P) (acetone-d_6): –224.0 (P2); ν: 2 540 (BH) cm^{-1}.

6-Et$_3$N-2-PB$_9$H$_8$: [28] m.p. 145–147 °C; *m/z*$_{max}$: 239.2405; δ(^{11}B) (acetone-*d*$_6$): 7.0 (d, $^1J_{BH}$ = 158, B3), 1.4 (d, $^1J_{BH}$ = 173, B9 or 7), –2.8 (d, B6), –10.6 (d, B8), –18.8 (d, $^1J_{BH}$ = 154, B5 or 4), –27.7 (d, $^1J_{BH}$ = 158, B7 or 9), –29.7 (d, $^1J_{BH}$ = 155, B10), –31.9 (d, $^1J_{BH}$ = 150, B4 or 5); δ(^{31}P) (acetone-*d*$_6$): –233.0 (P2); ν: 2 540 (BH) cm^{-1}; X-ray diffraction.

2,1-PCB$_8$H$_9$: [35] m.p. > 350 °C, *m/z*$_{max}$: 140; δ(^{11}B) (CDCl$_3$): 50.2 (d, $^1J_{BH}$ = 173, B10), –5.0 (d, $^1J_{BH}$ = 169, B4), –17.5 (d, $^1J_{BH}$ = 173, B3,5), –24.4 (br d, $^1J_{BH}$ = 165, B6,9), –26.6 (d, $^1J_{BH}$ = 150, B7,8); δ(^{1}H){^{11}B} (CDCl$_3$): 6.94 (s, H10), 6.22 (d, $^2J_{PH}$ = 15.5, H1), 2.88 (s, H4), 1.71 (d, $^2J_{PH}$ = 14.5, H3,5), 1.31 (s, H7,8), 1.28 (d, $^2J_{PH}$ = 15.5, H6,9); δ(^{13}C) (CDCl$_3$): 54.4 (d, $^1J_{CH}$ = 191, C1): δ(^{31}P) (CDCl$_3$): –129.9 (s, P2); ν: 2 576 (BH) cm^{-1}.

6,1-PCB$_8$H$_9$: [35] m.p. > 350 °C, *m/z*$_{max}$: 140; δ(^{11}B) (CDCl$_3$): 34.9 (d, $^1J_{BH}$ = 181, B10), –11.6 (d, $^1J_{BH}$ = 154, B8), –13.6 (dd, $^1J_{BH}$ = 172, $^1J_{BP}$ = 32, B2,3), –22.2 (d, $^1J_{BH}$ = 169, B4,5), –23.9 (br d, $^1J_{BH}$ = 162, B7,9); δ(^{1}H){^{11}B} (CDCl$_3$): 6.44 (s, H10), 6.05 (s, H1), 2.53 (d, $^2J_{PH}$ = 21.5, H2,3), 2.34 (s, H8), 1.76 (s, H4,5), 1.00 (d, $^2J_{PH}$ = 21.5, H7,9); δ(^{13}C){^{1}H} (CDCl$_3$): 69.9 (s, C1); δ(^{31}P) (CDCl$_3$): –191.2 (s, P6); ν: 2 582 (BH) cm^{-1}.

1,10-P$_2$B$_8$Cl$_8$: [14] *m/z*$_{max}$: 429.77935; δ(^{11}B) (CDCl$_3$): 8.7 (s); δ(^{31}P) (CDCl$_3$): –195.0.

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6-Ph-6,8,9-PC$_2$B$_7$H$_{11}$: [25] δ(^{11}B): –5.5 (d, B2,4), –12.0 (d, B5), –13.6 (d, B7), –19.7 (d, B10), –25.8 (d, B1), –48.4 (d, B3); δ(^{1}H): –0.72 (*endo*-H9); δ(^{13}C): 13.2 (C9), 25.2 (C8); δ(^{31}P): –162.3 (P6).

6-Me-6,8,9-PC$_2$B$_7$H$_{11}$: [25] δ(^{11}B): –6.0 (d, B2), –6.7 (d, B4), –11.1 (d, B5), –12.2 (d, B7), –19.9 (d, B10), –28.7 (d, B1), –48.8 (d, B3); δ(^{1}H): –0.90 (*endo*-H9); δ(^{13}C): 12.8 (C9), 25.5 (C8); δ(^{31}P): –184.3 (P6).

6-Me-6,5,7-PC$_2$B$_7$H$_{11}$: [25] δ(^{11}B): –1.9 (d, B4), –6.9 (d, B8,10), –33.5 (d, B1,3,9), –41.9 (d, B2); δ(^{13}C): 3.0 (C5,7); δ(^{31}P): –65.2 (P6).

4.5. Selected Experimental Data for 11-Vertex Phosphaboranes and Phosphacarboranes

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NMe$_4^+$[7-PB$_{10}$H$_{12}$]$^-$: [28] δ(^{11}B) (acetone-*d*$_6$): 7.0 (d, $^1J_{BH}$ = 135, B5), –7.4 (d, $^1J_{BH}$ = 150, B2,3), –9.5 (d, $^1J_{BH}$ = 140, B8,11), –15.6 (d, $^1J_{BH}$ = 130, B9,10), –21.5 (d, $^1J_{BH}$ = 187, B1), –23.2 (d, $^1J_{BH}$ = 150, B4,6); δ(^{1}H) (acetone-*d*$_6$): –4.33 (μH); δ(^{31}P) (acetone-*d*$_6$): –103.0 (P7); ν (KBr): 2 510 (BH) cm^{-1}.

7-Me-7-PB$_{10}$H$_{12}$: [32,34] m.p. 88–89 °C; *m/z*$_{max}$: 168; δ(^{11}B) (CD$_3$CN): 3.3 (d, $^1J_{BH}$ = 145, 1 B), –7.2 (d, $^1J_{BH}$ = 160, 2 B), –11.7 (d, $^1J_{BH}$ = 161, 2 B), –16.9 (d, $^1J_{BH}$ = 149, 2 B), –24.5 (d, $^1J_{BH}$ = 148, 3 B); δ(^{1}H){^{11}B} (CD$_3$CN): 2.61, 2.30, 1.72, 1.59 (br), 1.14 (terminal H), –4.04 (μH); δ(^{31}P){^{11}B} (CD$_3$CN): –85.6 (s br, P7); ν: 2 560 (BH) cm^{-1}.

7-Et-7-PB$_{10}$H$_{12}$: [32] m.p. 82–83 °C; *m/z*$_{max}$: 182; δ(^{11}B) (CDCl$_3$): 2.9 (d, $^1J_{BH}$ = 139, 1 B), –9.3 (d, $^1J_{BH}$ = 169, 2 B), –12.6 (d, $^1J_{BH}$ ≈ 165, 2 B), –17.2 (d, $^1J_{BH}$ = 146, 2 B), –25.6 (d, $^1J_{BH}$ = 129, 3 B) ; ν: 2 560 (BH) cm^{-1}.

7-Pr-7-PB$_{10}$H$_{12}$: [32] m.p. 50–51 °C; *m/z*$_{max}$: 196; δ(^{11}B) (CDCl$_3$): 2.9 (d, $^1J_{BH}$ = 147, 1 B), –9.2 (d, $^1J_{BH}$ = 167, 2 B), –12.7 (d, $^1J_{BH}$ = 166, 2 B), –17.3 (d, $^1J_{BH}$ = 148, 2 B), ≈ –24.6 (d, $^1J_{BH}$ ≈ 140, 1 B), –25.6 (d, $^1J_{BH}$ = 151, 2 B); ν: 2 555 (BH) cm^{-1}.

7-Ph-7-PB$_{10}$H$_{12}$: [32] m.p. 82–84 °C; *m/z*$_{max}$: 230; δ(^{11}B) (CDCl$_3$): 3.0 (d, $^1J_{BH}$ = 146, 1 B), –8.3 (d, $^1J_{BH}$ = 162, 2 B), –12.5 (d, $^1J_{BH}$ = 163, 2 B), –17.2 (d, $^1J_{BH}$ = 149, 2 B), ≈ –24.3 (d, $^1J_{BH}$ ≈ 145, 1 B), –25.8 (d, $^1J_{BH}$ = 143, 2 B); ν: 2 560 (BH) cm^{-1}.

$NMe_4^+[7\text{-}Me\text{-}7\text{-}PB_{10}H_{11}]^-$: [2] $\delta(^{11}B)$ (acetone): –11.2 (d, $^1J_{BH}$ = 146, 2 B), –21.1 (d, $^1J_{BH}$ = 135, 6 B), –28.2 (d, $^1J_{BH}$ = 136, 1 B), –36.7 (d, $^1J_{BH}$ = 142, 1 B); ν: 2 510 (BH) cm^{-1}.

$NMe_4^+[7\text{-}Et\text{-}7\text{-}PB_{10}H_{11}]^-$: [32] $\delta(^{11}B)$ (acetone): –11.6 (d, $^1J_{BH}$ = 146, 2 B), ≈ –21.5 (d, $^1J_{BH}$ ≈ 130, 4 B), ≈ –22.5 (d, $^1J_{BH}$ ≈ 150, 2 B), –28.3 (d, $^1J_{BH}$ = 137, 1 B), –37.2 (d, $^1J_{BH}$ = 139, 1 B); ν: 2 510 (BH) cm^{-1}.

$NMe_4^+[7\text{-}Pr\text{-}7\text{-}PB_{10}H_{11}]^-$: [32] $\delta(^{11}B)$ (acetone): –11.4 (d, $^1J_{BH}$ = 136, 2 B), –21.2 (d, $^1J_{BH}$ ≈ 140, 4 B), –22.2 (d, $^1J_{BH}$ ≈ 140, 2 B), –28.1 (d, $^1J_{BH}$ = 146, 1 B), –37.0 (d, $^1J_{BH}$ = 140, 1 B); ν: 2 505 (BH) cm^{-1}.

$NMe_4^+[7\text{-}Ph\text{-}7\text{-}PB_{10}H_{11}]^-$: [32] $\delta(^{11}B)$ (acetone): –11.5 (d, $^1J_{BH}$ = 137, 2 B), –20.8 (d, $^1J_{BH}$ ≈ 130, 4 B), –22.6 (d, $^1J_{BH}$ ≈ 130, 2 B), –27.5 (d, $^1J_{BH}$ = 137, 1 B), –36.4 (d, $^1J_{BH}$ = 138, 1 B); ν: 2 510 (BH) cm^{-1}.

$NMe_4^+[7,8\text{-}P_2B_9H_{10}]^-$: [29] $\delta(^{11}B)$ (acetone): –0.1 (d, 2 B), –0.7 (d, 2 B), –9.5 (d, 3 B), –17.5 (d, 1 B) –36.0 (d, 1 B); $\delta(^{31}P)$ (acetone): –55.9 (s, P7,8); ν (KBr): 2 520 (BH) cm^{-1}.

$NMe_4^+[7,8\text{-}PCB_9H_{11}]^-$: [39] $\delta(^1H)$ (acetone-d_6): 1.14 (d, $^2J_{PH}$ = 26, H8).

7-Me-7,8-PCB_9H_{11}: [9] m.p. 108–109 °C; *m/z*$_{max}$: 168; $\delta(^1H)$ ($CDCl_3$): 2.25 (d, $^2J_{PH}$ = 11, 3 H, CH_3), 2.10 (br s, H8); ν ($CHCl_3$): 2 560 (BH) cm^{-1}.

7-Bz-7,8-PCB_9H_{11}: [42] $\delta(^1H)$: 1.90 (br s, H8).

$[C_4H_8N_2H_3]^+[7,9\text{-}PCB_9H_{11}]^-$: [39] m.p. 296–297 °C.

$NMe_4^+[7,9\text{-}PCB_9H_{11}]^-$: [39] $\delta(^1H)$ (acetone-d_6): 1.90 (s, H9); ν: 2 540 (BH) cm^{-1}.

7,9-$HPCB_9H_{11}$: [39] m.p. 206–210 °C; *m/z*$_{max}$: 154; ν (CS_2): 2 595 (BH), 2 400 (PH) cm^{-1}.

9-Me-7,9-PCB_9H_{11}: [39] m.p. 112–113 °C; *m/z*$_{max}$: 168; $\delta(^1H)$ ($CDCl_3$): 2.40 (br s, H9), 1.97 (d, $^2J_{PH}$ = 12, 3 H, CH_3); ν (CS_2): 2 552 (BH) cm^{-1}.

9-R-7,9-PCB_9H_{11} (R = Bz, CH_2=$CHCH_2$, PhCH=$CHCH_2$): [42] $\delta(^1H)$: 2.40 (br s, H9).

7,8,9-$PC_2B_8H_{11}$: [35] m.p. 260 °C; *m/z*$_{max}$: 154; $\delta(^{11}B)$ ($CDCl_3$): 5.7 (d, $^1J_{BH}$ = 162, B5), 2.2 (d, $^1J_{BH}$ = 158, B2), –12.8 (d, B4), –13.6 (d, $^1J_{B\text{-}\mu H}$ = 42, B10), –17.2 (d, B3), ≈ –18.0 (d, B6), –18.3 (d, B11), –30.9 (d, $^1J_{BH}$ = 158, B1); $\delta(^1H)\{^{11}B\}$ ($CDCl_3$): 3.22 (s, H9), 3.02 (d, $^2J_{PH}$ = 17, H8), 2.96 (s, H5), 2.68 (d, $^2J_{PH}$ = 23, H2), 2.35 (d, $^2J_{PH}$ = 23, H3), 2.34 (s, H4), 2.29 (s, H10), 1.88 (s, H1), 1.73 (s, H11), 1.72 (s, H6), –2.73 (q, $^2J_{HH}$ = 12, 1 H, μH10,11); $\delta(^{13}C)\{^1H\}$ ($CDCl_3$): 63.3 (d, $^1J_{PC}$ = 72, C8), 53.4 (s, C9); $\delta(^{31}P)\{^1H\}$ ($CDCl_3$): –60.1 (s, P7); ν: 2 926 (CH), 2 576 (BH) cm^{-1}.

10-Cl-7,8,9-$PC_2B_8H_{11}$: [35] m.p. 150 °C; *m/z*$_{max}$: 189; $\delta(^{11}B)$ ($CDCl_3$): 7.8 (d, $^1J_{BH}$ = 165, B5), –0.4 (d, $^1J_{BH}$ = 154, B2), –2.2 (s, B10), –13.1 (d, $^1J_{B\text{-}\mu H}$ = 177, B4), –16.9 (d, $^1J_{BH}$ = 154, B6), ≈ –19.9 (d, $^1J_{BH}$ = 158, B11), –22.8 (d, $^1J_{BH}$ = 173, B3), –31.2 (d, $^1J_{BH}$ = 154, B1); $\delta(^1H)\{^{11}B\}$ ($CDCl_3$): 3.48 (s, H9), 3.35 (s, H5), 2.96 (d, $^2J_{PH}$ = 28, H8), 2.61 (d, $^2J_{PH}$ = 21, H2), 2.39 (s, H4), 2.20 (d, $^2J_{PH}$ = 14, H3), 1.98 (s, H6), 1.85 (d, $^2J_{PH}$ = 55, H11), 1.80 (s, H1), –1.12 (q, $^2J_{HH}$ = 9, μH10,11); $\delta(^{13}C)\{^1H\}$ ($CDCl_3$): 61.5 (d, $^1J_{PC}$ = 72, 1 C, C8), 54.6 (q, $^1J_{CB}$ ≈ 33, 1C, C9); $\delta(^{31}P)\{^1H\}$ ($CDCl_3$): –67.7 (s, P7); ν: 2 932 (CH), 2 581 (BH) cm^{-1}.

$PSH^+[7,8,9\text{-}PC_2B_8H_{10}]^-$: [35] m.p. 230 °C; $\delta(^{11}B)$ ($CDCl_3$): –8.0 (d, B6), –8.3 (d, B10), –13.6 (d, B11), –14.4 (d, $^1J_{BH}$ ≈ 150, B10), –15.5 (d, $^1J_{BH}$ ≈ 165, B4), –19.0 (d, $^1J_{BH}$ = 143, B2), –20.9 (d, $^1J_{BH}$ = 158, B3), –41.1 (d, $^1J_{BH}$ = 142, B1); $\delta(^1H)\{^{11}B\}$ (CD_3CN): 2.16 (d, $^2J_{PH}$ = 10, H3), 2.15 (s, H6), 2.13 (s, H4), 2.03 (s, H9), 1.81 (s, H5), 1.80 (s, H10), 1.46 (d, $^2J_{PH}$ = 30, H8), 1.18 (d, $^2J_{PH}$ = 40, H11), 1.18 (d, $^2J_{PH}$ = 20, H2), 1.02 (s, H1); $\delta(^{13}C)\{^1H\}$ (CD_3CN): 44.1 (s, C9), 35.4 (d, $^1J_{CP}$ = 55, C8); $\delta(^{31}P)\{^1H\}$ (CD_3CN): –91.0 (s, P7); ν: 2 574 (BH) cm^{-1}.

$PSH^+[10\text{-}Cl\text{-}7,8,9\text{-}PC_2B_8H_9]^-$: [35] m.p. 155 °C; $\delta(^{11}B)$ ($CDCl_3$): 3.0 (s, B_{10}), –7.3 (d, $^1J_{BH}$ = 138, B6), –11.8 (d, $^1J_{BH}$ = 147, B5), –16.4 (d, B11), –17.2 (d, $^1J_{BH}$ ≈ 165, B4), –20.8 (d, $^1J_{BH}$ = 142, B2), –25.6 (d, $^1J_{BH}$ = 154, B3), –42.2 (d, $^1J_{BH}$ = 139, B1); $\delta(^1H)\{^{11}B\}$ (CD_3CN): 1.91 (s, H6), 1.84 (s, H4), 1.69 (s, H9), 1.64 (s, H5), 1.54 (d, $^2J_{PH}$ = 32, H11), 1.80 (s, H10), 1.14 (d,

$^2J_{PH}$ = 32, H8), 0.78 (d, $^2J_{PH}$ = 40, H2), 0.60 (d, $^2J_{PH}$ = 20, H3), 0.44 (s, H1); δ(^{13}C){^{11}B} (CD_3CN): 44.8 (d, $^1J_{CH}$ = 163, C9), 33.0 (dd, $^1J_{CH}$ = 170, $^1J_{CP}$ = 56, C8); δ(^{31}P){^{1}H} (CD_3CN): –91.0 (s, P7); ν: 2 579 (BH) cm^{-1}.

7-Me-7,8,9-PC$_2$B$_8$H$_{10}$: [33] m.p. 138 °C (dec.); *m/z*$_{max}$: 153.1564 (M – CH_3)$^+$; δ(^{11}B) (CD_2Cl_2): –5.6 (d, $^1J_{BH}$ = 142, B6), –7.3 (d, $^1J_{BH}$ = 131, B10), –14.6 (d, $^1J_{BH}$ = 173, B4), –16.6 (d, $^1J_{BH}$ = 171, B3), –18.8 (d, $^1J_{BH}$ = 156, B11), –21.4 (d, $^1J_{BH}$ = 113, B5), –22.0 (d, $^1J_{BH}$ = 128, B2), –41.7 (d, $^1J_{BH}$ = 148, B1); δ(^{1}H){^{11}B} (CD_2Cl_2): 2.93, 2.47 (s, H8,9), 2.2, 2.03, 1.98, 1.65, 1.62, 1.39 (s, terminal H); δ(^{13}C) (CD_2Cl_2): 47.9 (m br, $^1J_{CH}$ = 139, $^1J_{CP}$ ≈ 28, C9), 34.3 (dd, $^1J_{CH}$ = 184, $^1J_{CP}$ = 24, C8); δ(^{31}P) (CD_2Cl_2): –74.4 (s, P7); ν (KBr): 2 562 (BH) cm^{-1}.

7-Ph-7,8,9-PC$_2$B$_8$H$_{10}$: [33] m.p. 73–74 °C; *m/z*$_{max}$: 230.1654; δ(^{11}B) (CD_2Cl_2): –6.2 (d, $^1J_{BH}$ = 149, B6), –7.2 (d, $^1J_{BH}$ = 154, B10), –15.0 (d, $^1J_{BH}$ = 174, B4), –16.6 (d, $^1J_{BH}$ = 174, B11), –19.1 (d, $^1J_{BH}$ = 150, B3), –21.1 (d, $^1J_{BH}$ = 156, B5), –22.1 (d, $^1J_{BH}$ = 156, B2), –41.3 (d, $^1J_{BH}$ = 150, B1); δ(^{1}H){^{11}B} (CD_2Cl_2): 3.14, 2.59 (s, H8,9), 2.38, 2.31, 2.14, 2.09, 1.91, 1.88, 1.61, 1.53 (s, terminal H); δ(^{13}C) (CD_2Cl_2): 47.7 (m br, C9), 33.4 (dd, $^1J_{CH}$ = 186, $^1J_{CP}$ = 24, C8); δ(^{31}P) (CD_2Cl_2): –68.6 (s, P7); ν (KBr): 2 564 (BH) cm^{-1}.

7,8,11-PC$_2$B$_8$H$_{11}$: [36] *m/z*$_{max}$: 151; δ(^{11}B) ($CDCl_3$): 9.1 (d, $^1J_{BH}$ = 161, B4,6), –18.0 (d, $^1J_{BH}$ = 160, B9,10), –18.5 (d, $^1J_{BH}$ = 160, B2,3), –22.7 (d, $^1J_{BH}$ = 150, B5), –32.8 (d, $^1J_{BH}$ = 150, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 3.30 (s, H4,6), 2.49 (br s, $^1J_{PH}$ = 34, H8,11), 2.17 (br s, H9,10), 1.85 (s, H2,3), 1.39 (s, H5), 1.76 (s, H1), 2.07 (s, H1); δ(^{31}P){^{1}H} ($CDCl_3$): –22.7 (s, P7).

PSH$^+$[7,8,11-PC$_2$B$_8$H$_{10}$]$^-$: [36] δ(^{11}B) (CD_3CN): –8.2 (d, $^1J_{BH}$ = 127, B5,9,10), –14.5 (d, $^1J_{BH}$ = 146, B4,6), –21.5 (d, $^1J_{BH}$ = 157, B2,3), –42.6 (d, $^1J_{BH}$ = 134, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 2.11 (br s, H8,11), 1.69 (s, H9,10), 1.69 (d, $^1J_{PH}$ = 20, H2,3), 1.46 (s, H4,6), 1.43 (s, H5), 0.70 (s, H1); δ(^{31}P){^{1}H} ($CDCl_3$): –104.0 (s, P7).

7-Ph-7,8,10-PC$_2$B$_8$H$_{10}$: [36] *m/z*$_{max}$: 230; δ(^{11}B) ($CDCl_3$): –7.6(d, $^1J_{BH}$ = 154, B3), –8.0 (d, $^1J_{BH}$ = 154, B3), –8.7 (d, $^1J_{BH}$ = 160, B6), –13.8 (d, $^1J_{BH}$ = 160, $^1J_{BP}$ = 62, B11), –16.2 (d, –, B4), –16.2 (d, –, B5), –25.3 (d, $^1J_{BH}$ = 150, B1), –39.7 (d, $^1J_{BH}$ = 150, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 2.39 (s, H9), 2.68 (s, H3), 2.17 (br s, H9,10), 2.30 (s, H6), 2.72 (s, H11), 2.07(s, H4), 1.79 (s, H5), 1.61(s, H2), 1.21(s, H1); δ(^{31}P){^{1}H} ($CDCl_3$): –84.7 (s, P7).

9-Ph-7,9-SPB$_9$H$_9$: [33] m.p. 110 °C; *m/z*$_{max}$: 248.1388; δ(^{11}B) (CD_2Cl_2): –6.1 (d, $^1J_{BH}$ ≈ 118, B5), –7.4 (d, $^1J_{BH}$ = 189, B11), –9.5 (d, $^1J_{BH}$ = 168, B3,4), –14.7 (d, B2,10), –19.6 (d, $^1J_{BH}$ = 169, $^1J_{BP}$ = 64, B8), –38.5 (d, $^1J_{BH}$ = 155, B1); δ(^{1}H){^{11}B} (CD_2Cl_2): 2.71 (3 H), 2.52 (2 H), 2.43, 2.09, 1.91, 1.88, 1.61, 1.53 (all 1 H) (terminal H); δ(^{31}P) (CD_2Cl_2): –48.95 (s, P7); ν (KBr): 2 562 (BH) cm^{-1}.

7,8,9,11-P$_2$C$_2$B$_7$H$_9$: [26] m.p. 295 °C; *m/z*$_{max}$: 172; δ(^{11}B) ($CDCl_3$): –0.5 (d, $^1J_{BH}$ = 150, B10), –2.5 (d, $^1J_{BH}$ = 162, B5,6), –4.8 (d, $^1J_{BH}$ = 169, B2,4), –17.5 (d, $^1J_{BH}$ = 170, B3), –34.5 (d, $^1J_{BH}$ = 154, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 3.02 (s, H10), 2.91 (br s, H2,4), 2.52 (s, H5,6), 2.21 (br s, H9,11), 2.16 (asym. t, $^2J_{PH}$ = 35/20, H3), 2.07 (s, H1); δ(^{31}P) ($CDCl_3$): –43.4 (s, P7,8); ν (KBr): 2 920, 2 852 (CH), 2 576 (BH) cm^{-1}.

3-Cl-7,8,9,11-P$_2$C$_2$B$_7$H$_8$: [26] m.p. 232 °C; *m/z*$_{max}$: 208; δ(^{11}B) ($CDCl_3$): –0.8 (s, B3), –2.1 (d, $^1J_{BH}$ ≈ 165, B2,4,5,6), –4.7 (d, $^1J_{BH}$ = 150, B10), –32.2 (d, $^1J_{BH}$ = 150, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 3.37 (s, H2,4), 2.77 (d, $^2J_{PH}$ = 20, H9,11), 2.73 (s, H10), 2.48 (s, H5,6), 1.98 (s, H1); δ(^{31}P) ($CDCl_3$): –25.2 (s, P7,8); ν (KBr): 3 020 (CH), 2 576 sh, 2 540 (BH) cm^{-1}.

7,8,9,10-P$_2$C$_2$B$_7$H$_9$: [26] m.p. 165 °C; *m/z*$_{max}$: 172; δ(^{11}B) ($CDCl_3$): –1.2 (d, $^1J_{BH}$ ≈ 177, B6), –2.4 (d, $^1J_{BH}$ ≈ 180, B3), –4.2 (d, $^1J_{BH}$ = 146, B11), –7.5 (d, $^1J_{BH}$ ≈ 162, B5), –8.4 (d, $^1J_{BH}$ ≈ 142, B2), –13.3 (d, $^1J_{BH}$ = 173, B4), –36.3 (d, $^1J_{BH}$ = 150, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 3.06 (d, H3,10), 2.70 (s, H6), 2.55 (d, $^2J_{PH}$ = 15, H5), ≈ 2.55 (d, $^2J_{PH}$ ≈ 15, H4), 2.33 (d, $^2J_{PH}$ = 35, H10), 2.10

(d, $^2J_{PH}$ = 20, H2), 2.01 (s, H1), 1.73 (asym. t, $^2J_{PH}$ ≈ 35/25, H8); δ(^{31}P) ($CDCl_3$): –38.8 (s, P7 or 9), –41.3 (s, P7 or 9); ν (KBr): 2 920, 2 852 (CH), 2 576 (BH) cm^{-1}.

7,8,9,10-$P_2C_2B_7H_9$: [26] m.p. 312–313 °C; *m/z*$_{max}$: 172; δ(^{11}B) ($CDCl_3$): –0.1 (d, $^1J_{BH}$ ≈ 170, B5,6), –2.9 (d, $^1J_{BH}$ = 150, B11), –4.7 (d, $^1J_{BH}$ ≈ 176, B2), –5.9 (d, $^1J_{BH}$ ≈ 177, B3), –12.0 (d, $^1J_{BH}$ = 170, B4), –34.6 (d, $^1J_{BH}$ = 158, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 3.23 (s, H10), 2.90 (s, H5), 2.87 (d, $^2J_{PH}$ = 32, H9), 2.86 (d, $^2J_{PH}$ = 22, H4), 2.79 (s, H6), 2.72 (d, $^2J_{PH}$ = 37, H11), 2.62 (asym. t, $^2J_{PH}$ = 15/20, H3), 2.41 (d, $^2J_{PH}$ = 22, H2), 2.07 (s, H1); δ(^{31}P) ($CDCl_3$): –49.2 (asym. d, $^1J_{PP}$ = 240, P8), –58.2 (asym. d, $^1J_{PP}$ = 240, P7); ν (KBr): 3 016, 2 916 (CH), 2 584 (BH) cm^{-1}.

4-Cl-7,8,9,10-$P_2C_2B_7H_8$: [26] m.p. 201–202 °C; *m/z*$_{max}$: 208; δ(^{11}B) ($CDCl_3$): 1.0 (d, $^1J_{BH}$ ≈ 170, B5), 0.5 (s, B4), –0.6 (d, $^1J_{BH}$ ≈ 165, B6), –3.8 (d, $^1J_{BH}$ ≈ 150, B2,3), –7.8 (d, $^1J_{BH}$ = 150, B11), –34.3 (d, $^1J_{BH}$ = 157, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 3.56 (s, H10), 3.25 (s, H5), 3.22 (t, $^2J_{PH}$ ≈ 20, H3), 3.21 (d, $^2J_{PH}$ = 34, H9), 2.79 (s, H6), 2.66 (d, $^2J_{PH}$ = 38, H11), 2.40 (d, $^2J_{PH}$ = 20, H2), 2.13 (s, H1); δ(^{31}P) ($CDCl_3$): –30.6 (asym. d, $^1J_{PP}$ = 244, P8), –60.8 (asym. d, $^1J_{PP}$ = 244, P7); ν (KBr): 3 016, 2 916 (CH), 2 604 sh, 2 584 (BH) cm^{-1}.

11-Cl-7,8,9,10-$P_2C_2B_7H_8$: [26] m.p. 196 °C; *m/z*$_{max}$: 208; δ(^{11}B) ($CDCl_3$): 7.6 (s, B11), 2.0 (d, B6), –1.9 (d, $^1J_{BH}$ ≈ 180, B5), –3.1 (d, $^1J_{BH}$ ≈ 190, B2), –7.7 (d, $^1J_{BH}$ = 170, B3), –18.0 (d, $^1J_{BH}$ = 173, B4), –34.9 (d, $^1J_{BH}$ = 158, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 3.56 (s, H10), 3.25 (s, H5), 3.22 (t, $^2J_{PH}$ ≈ 20, H3), 3.21 (d, $^2J_{PH}$ = 34, H9), 2.79 (s, H6), 2.66 (d, $^2J_{PH}$ = 38, H11), 2.40 (d, $^2J_{PH}$ = 20, H2), 2.13 (s, H1); δ(^{31}P) ($CDCl_3$): –66.6 (asym. d, $^1J_{PP}$ = 238, P8), –73.7 (asym. d, $^1J_{PP}$ = 238, P7); ν (KBr): 3 024(CH), 2 612 sh, 2 588, 2 552 (BH) cm^{-1}.

4-Me-7,8,9,10-$P_3CB_7H_7$: [27] m.p. 183–184 °C; *m/z*$_{max}$: 204; δ(^{11}B) ($CDCl_3$): 8.8 (d, $^1J_{BH}$ ≈ 160, B6), 8.2 (d, B4), 5.5 (d, $^1J_{BH}$ ≈ 160, B3), 4.4 (d, $^1J_{BH}$ ≈ 180, B5), 2.3 (d, $^1J_{BH}$ ≈ 165, B2), 1.2 (d, $^1J_{BH}$ ≈ 150, B11), –27.5 (d, $^1J_{BH}$ = 154, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 3.65 (t, $^2J_{PH}$ = 16/17, H3), 3.53 (s, H5), 3.22 (t, $^2J_{PH}$ ≈ 20, H3), 3.21 (s, H6), 3.05 (br s, H11), 2.94 (d, $^2J_{PH}$ = 34, H10), 2.89 (d, $^2J_{PH}$ = 20, H2), 2.58 (s, H1), 0.90 (m, $^2J_{PH}$ ≈ 5, CH_3); δ(^{31}P) ($CDCl_3$): 37.9 (asym. d, $^1J_{PP}$ = 243, P7 or P9), 0.7 (asym. d, $^1J_{PP}$ = 232, P7 or P9), –13.6 (asym. t, $^1J_{PP}$ = 251/257, P8).

4-Me-11-Cl-7,8,9,10-$P_3CB_7H_6$: [27] m.p. 183–184 °C; *m/z*$_{max}$: 204; δ(^{11}B) ($CDCl_3$): 8.8 (d, $^1J_{BH}$ ≈ 160, B6), 8.2 (d, B4), 5.5 (d, $^1J_{BH}$ ≈ 160, B3), 4.4 (d, $^1J_{BH}$ ≈ 180, B5), 2.3 (d, $^1J_{BH}$ ≈ 165, B2), 1.2 (d, $^1J_{BH}$ ≈ 150, B11), –27.5 (d, $^1J_{BH}$ = 154, B1); δ(^{1}H){^{11}B} ($CDCl_3$): 3.65 (t, $^2J_{PH}$ = 16/17, H3), 3.53 (s, H5), 3.22 (t, $^2J_{PH}$ ≈ 20, H3), 3.21 (s, H6), 3.05 (br s, H11), 2.94 (d, $^2J_{PH}$ = 34, H10), 2.89 (d, $^2J_{PH}$ = 20, H2), 2.58 (s, H1), 0.90 (m, $^2J_{PH}$ ≈ 5, CH_3); δ(^{31}P) ($CDCl_3$): 37.9 (asym. d, $^1J_{PP}$ = 243, P7 or P9), 0.7 (asym. d, $^1J_{PP}$ = 232, P7 or P9), –13.6 (asym. t, $^1J_{PP}$ = 251/257, P8).

4.6. Selected Experimental Data for 12-Vertex Phosphaboranes and Phosphacarboranes

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$NMe_4^+[1\text{-}PB_{11}H_{11}]^-$: [29] δ(^{11}B) (acetone-d_6): 6.3 (d, 1 B), –5.4 (d, 5 B), –10.0 (d, 5 B); δ(^{31}P) (acetone-d_6): –94.5 (P1); ν (KBr): 2 535 (BH) cm^{-1}.

2-NMe_3-1-$PB_{11}H_{10}$: [29] m.p. 391–393 °C; δ(^{11}B) (acetone-d_6): 6.8 (s, B2), 5.0 (d, 1 B), –6.2 (d, 2 B), –6.7 (d, 2 B), –9.6 (d, 3 B), –11.4 (d, 2 B); δ(^{31}P) (acetone-d_6): –83.7 (P1); X-ray diffraction.

1-Me-$PB_{11}H_{11}$: [34] δ(^{11}B) (CD_2Cl_2): –1.1 (d, $^1J_{BH}$ = 150, B12), –6.72 (d, $^1J_{BH}$ = 150, B7-11), –14.4 (d, $^1J_{BH}$ = 164, B2-6); ν (Nujol): 2 581, 2 563, 2 544 (BH) cm^{-1}; X-ray diffraction.

1-Ph-$PB_{11}H_{11}$: [38] m.p. 157–159 °C; *m/z*$_{max}$: 241; δ(^{11}B): –3.0 (d, 1 B), –8.4 (d, 5 B), –15.0 (d, 5 B).

1,2-PCB$_{10}$H$_{11}$: [39] m.p. 353.5–354.5 °C; *m/z*$_{max}$: 164.1530; δ(^{11}B) (C_6H_6): 6 unresolved 1 : 1 : 2 : 2 : 2 : 2 doublets (9.6–14.4); δ(^{1}H): 2.15 (d, $^2J_{PH}$ = 14, H2); δ(^{31}P): 57.0 (s, P1); ν (CCl_4): 2 592 (BH) cm^{-1}; λ$_{max}$ (ε) (MeCN): 253 (400), 198 (4150) nm.

1,2-PCB$_{10}$H$_{10}$Br: [39] m.p. 244.5–245.5 °C; *m/z*$_{max}$: 244; δ(^{1}H) (acetone-d_6): 4.25 (broad, H2); ν (CS_2): 2 590 (BH) cm^{-1}.

1,2-PCB$_{10}$H$_9$Br$_2$: [39] m.p. 255–256 °C; *m/z*$_{max}$: 324; δ(^{1}H) (acetone-d_6): 4.22 (broad d, H2); ν (CS_2): 2 605 (BH) cm^{-1}.

1,2-PCB$_{10}$H$_8$Br$_3$: [39] m.p. 352–353 °C; *m/z*$_{max}$: 404; δ(^{1}H) (acetone-d_6): 4.4 (broad d, H2); ν: 2 600 (BH) cm^{-1}.

1,7-PCB$_{10}$H$_{11}$: m.p. 325–327 °C; *m/z*$_{max}$: 164.1531; δ(^{11}B) (C_6H_6): 6 unresolved 1 : 1 : 2 : 2 : 2 : 2 doublets (since 3.9); δ(^{1}H): 2.48 (s, H7); δ(^{31}P): 71.0 (s, P1); ν (CCl_4): 2 595 (BH) cm^{-1}; λ$_{max}$ (ε) (MeCN): 245 (265) nm.

1,7-PCB$_{10}$H$_{10}$Br: [39] m.p. 226–227.5 °C; *m/z*$_{max}$: 244.0613; ν: 2 590 (BH) cm^{-1}.

1,7-PCB$_{10}$H$_9$Br$_2$: [39] m.p. 234–235 °C; *m/z*$_{max}$: 324; ν: 2 600 (BH) cm^{-1}.

1,12-PCB$_{10}$H$_{11}$: [39] m.p. 314–315.5 °C; *m/z*$_{max}$: 164.1531; δ(^{11}B): –9.8 (d, $^1J_{BH}$ = 167, 10 B); δ(^{1}H): 2.7 (s, H12); ν (CCl_4): 2 580 (BH) cm^{-1}.

1,2-P$_2$B$_{10}$H$_{10}$: [28] m.p. 397–399 °C; *m/z*$_{max}$: 182.1186; δ(^{11}B) ($CDCl_3$): 17.7 (d, $^1J_{BH}$ = 151, B9,12), 4.2 (d, $^1J_{BH}$ = 155, B8,10), –0.3 (d, $^1J_{BH}$ = 159, B4,5,7,11), –2.5 (d, $^1J_{BH}$ = 172, B3,6); δ(^{1}H){^{11}B} ($CDCl_3$): 3.56 (s, 2 H), 3.21 (s, 2 H), 2.72 (d, $^2J_{PH}$ = 16, 4 H), 2.52 (d, $^2J_{PH}$ = 16, 2 H); δ(^{31}P) ($CDCl_3$): –19.3 (s, P1,2); ν (KBr): 2 575 (BH) cm^{-1}.

1,7-P$_2$B$_{10}$H$_{10}$: [28] m.p. 378–380 °C; *m/z*$_{max}$: 182.1188; δ(^{11}B) ($CDCl_3$): 11.2 (d, $^1J_{BH}$ = 155, B5,12), 3.4 (d, $^1J_{BH}$ = 154, B9,10), –0.4 (d, $^1J_{BH}$ = 160, B4,6,8,11), –3.3 (d, $^1J_{BH}$ = 166, B2,3); δ(^{1}H){^{11}B} ($CDCl_3$): 3.11 (s, 2 H), 2.94 (s, 2 H), 2.87 (d, 4 H), 2.79 (d, 2 H); δ(^{31}P) ($CDCl_3$): –20.2 (s, P1,7); ν (KBr): 2 580 (BH) cm^{-1}.

1,7-P$_2$B$_{10}$Cl$_{10}$: [14] m.p. > 230 °C; *m/z*$_{max}$: 524; δ(^{11}B) ($CDCl_3$): 7.6 (s, B5,12), 1.9 (s, B4,6,8,11), 0.7 (s, B9,10), –2.0 (s, B2,3); δ(^{31}P) ($CDCl_3$): –123.0 (s, P1,7).

1,2-PAsB$_{10}$H$_{10}$: [29] m.p. 442–448 °C; *m/z*$_{max}$: 224.0738; δ(^{11}B) (acetone): 19.7 (d, B9), 15.5 (d, B12), 2.0 (d, B7,8,10,11), –0.5 (d, B3,6), –2.7 (d, B4,5); δ(^{31}P) ($CDCl_3$): –9.7 (P1); ν (KBr): 2 560 (BH) cm^{-1}.

1,2-PSbB$_{10}$H$_{10}$: [29] m.p. > 450 °C; *m/z*$_{max}$: 272.0483; δ(^{11}B) (acetone): 15.9 (d, B9), 13.6 (d, B12), 2.2 (d, B7,11), 0.3 (d, B3,6), –0.2 (d, B8,10), –3.6 (d, B4,5); δ(^{31}P) ($CDCl_3$): –31.9 (P1); ν (KBr): 2 540 (BH) cm^{-1}.

1,2-PBiB$_{10}$H$_{10}$: [29] δ(^{11}B) (acetone): 12.6 (d, B9), 12.0 (d, B12), 6.1 (d, B7,11), 2.7 (d, B3,6), –1.2 (d, B8,10), –7.1 (d, B4,5).

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Me$_3$NCB$_{10}$H$_{10}$PMe: [44] δ(^{11}B) (acetone-d_6): 0.9 (d, $^1J_{BH}$ = 146, 3 B), –3.9 (d, $^1J_{BH}$ = 139, 1 B), –8.1 (d, $^1J_{BH}$ = 154, 2 B), –11.9 (d, $^1J_{BH}$ = 142, 2 B), –21.9 (d, $^1J_{BH}$ = 146, 2 B); ν (KBr): 2 585, 2 535 (BH) cm^{-1}.

Me$_3$NCB$_{10}$H$_{10}$PEt: [44] δ(^{11}B) (acetone-d_6): 0.8 (d, $^1J_{BH}$ = 149, 3 B), –3.9 (d, $^1J_{BH}$ = 134, 1 B), –8.1 (d, $^1J_{BH}$ = 147, 2 B), –13.1 (d, $^1J_{BH}$ = 142, 2 B), –22.3 (d, $^1J_{BH}$ = 142, 2 B); ν (KBr): 2 580, 2 530 (BH) cm^{-1}.

Me$_3$NCB$_{10}$H$_{10}$PPh: [44] m.p. 295–296 °C; δ(^{11}B) (acetone-d_6): 1.5 (d, 3 B), –4.1 (d, $^1J_{BH}$ = 142, 1 B), –8.4 (d, $^1J_{BH}$ = 159, 2 B), –13.4 (d, $^1J_{BH}$ = 142, 2 B), –20.2 (d, $^1J_{BH}$ = 144, 2 B); ν (KBr): 2 570, 2 520 (BH) cm^{-1}; X-ray diffraction.

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