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# Recent developments in the chemistry of the nine-vertex monocarbaboranes

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## Abstract

A short review is presented on the routes to the synthesis of the nine-vertex monocarbaboranes *arachno*-4-$CB_8H_{14}$ and *nido*-1-$CB_8H_{12}$, which now have become very important starting materials for the preparation of a family of 'smaller-cage' seven-, eight-, and nine-vertex *closo* monocarbaborane anions $[2\text{-}CB_6H_7]^-$, $[1\text{-}CB_7H_8]^-$, and $[4\text{-}CB_8H_9]^-$. These anions exhibit high stability and have a good chance to become new candidates for weakly coordinated anion chemistry. Discussed are also reactions leading new families of phosphamonocarbaboranes that contain one, two, and three phosphorus atoms in the cage. These compounds, namely *closo*-2,1-$PCB_8H_9$, *closo*-6,1-$PCB_8H_9$, *nido*-7,8,9-$P_2CB_8H_{10}$, and *nido*-7,8,9,10-$P_3CB_7H_8$, are structural analogues of the corresponding carboranes and are likely to exhibit similar chemical behavior. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Boron clusters; Carboranes; Monocarbaboranes; Phosphaboranes; Phosphacarboranes

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## 1. Introduction

Due to high stability and relatively good availability of the 12-vertex *closo*-$C_2B_{10}H_{12}$ isomers and other compounds obtainable from these 12-vertex carboranes, borane chemistry is still dominated by dicarbaborane chemistry which is the most investigated area of polyhedral boron-containing cluster chemistry [1]. Monocarbaborane chemistry, by contrast, is much less represented, and the chemistry of many of the fundamental cluster types is much less developed than the corresponding areas of dicarbaborane chemistry. The most investigated area of monocarbaborane chemistry is that of the $[CB_9H_{10}]^-$ and $[CB_{11}H_{12}]^-$ species and their substituted derivatives [2]. These compounds attract much current attention as so-called weakly coordinating anions because of their very low Lewis basicities [3]. Moreover, *closo* monocarbaboranes are studied as starting materials for borane-based liquid crystals [4]. In view of the new method for monocarbon insertion [5], even the open cage nine vertex monocarbarboranes 4-$CB_8H_{14}$ [6] and 1-$CB_8H_{12}$ [6,7], have now become readily available and we would like to outline some newer aspects of their chemistry. These include recent syntheses of a family of 'smaller-cage' *closo* monocarbaboranes and new types of ten- and 11-vertex phosphamonocarbaboranes.

## 2. Syntheses of the nine-vertex monocarbaboranes

A key compound of the open-cage nine-vertex series of monocarbaboranes is *arachno*-4-$CB_8H_{14}$, which was discovered 15 years ago in one of the author's laboratories [6]. As shown in Scheme 1, the original synthesis of this compound is based on a multistep synthesis starting from the commercially available $B_{10}H_{14}$. The key reaction step is the acidification of the [*endo*-6-NC-*arachno*-$B_{10}H_{13}]^{2}$-dianion [8] (path *ii*) leading to a mixture of two *nido*-ligando monocarbaboranes 7-$Me_3N$-7-$CB_{10}H_{12}$ and 6-$Me_3N$-6-$CB_9H_{11}$ [2a,2b] via insertion of the CN carbon into the cage. The 6-$Me_3N$-6-$CB_9H_{11}$ species is then reduced with Na metal to give the parent $[6\text{-}CB_9H_{12}]^-$ anion (path *iii*) [6]

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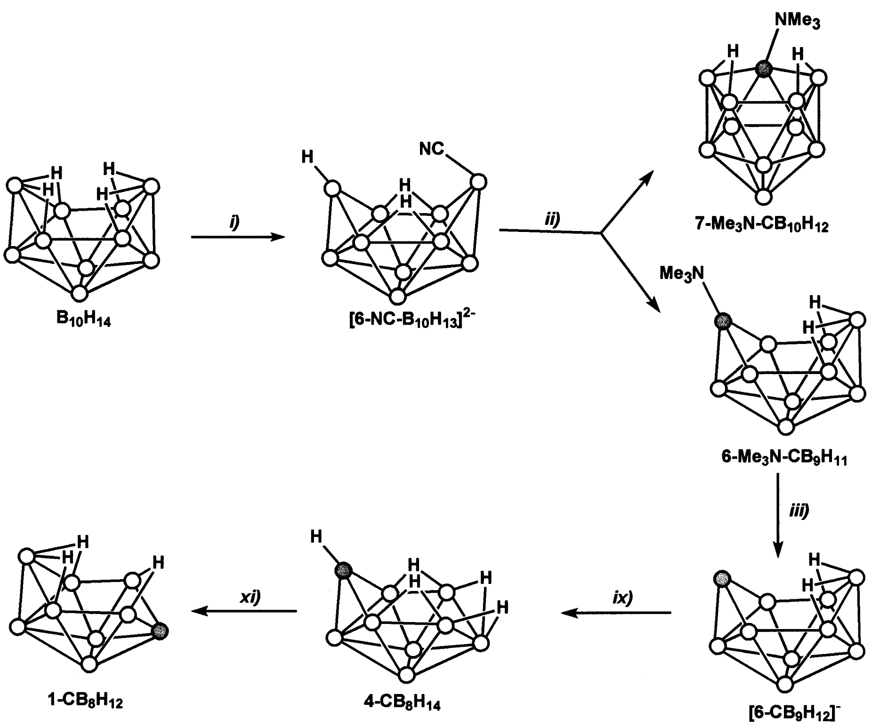
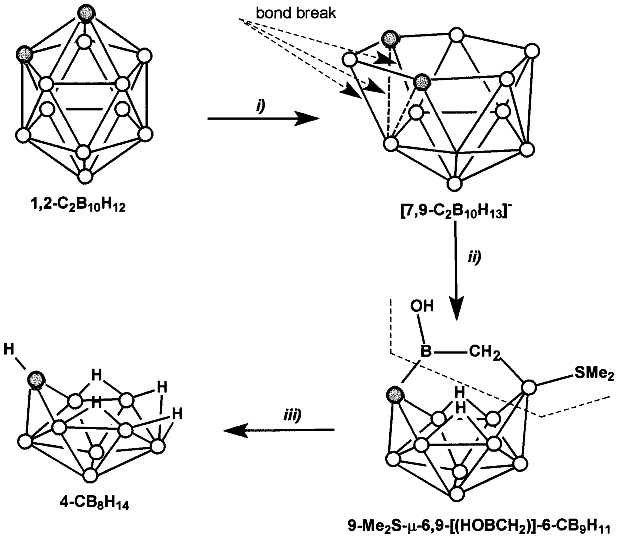


Scheme 1. (*i*) $CN^-$, $H_2O$; (*ii*) 1, dilute HCl 2, *N*-methylation 3, LC or chemical separation; (*iii*) Na, $NH_3$ (1); (*ix*) $Fe^{3+}$, dilute HCl; (*xi*) 350 °C.

which, upon removing the apex B vertex (path *ix*), gives the desired 4-$CB_8H_{14}$ in good yield. Even though the total yield of this multistep synthesis does not exceed 15%, this method was used for many years as the only source of 4-$CB_8H_{14}$. The 4-$CB_8H_{14}$ carborane can be then easily converted (yield 90%) into *nido*-1-$CB_8H_{12}$ by heating at 350 °C [6b,7] and this method remains so far the best access to this compound.

An entirely new approach to the synthesis of 4-$CB_8H_{14}$ is shown in Scheme 2 [9]. This three-step synthesis is based on a polyhedral expansion of *o*-carborane via reaction with Na metal, followed by in situ reaction of the intermediate [*nido*-7,9-$C_2B_{10}H_{13}$]$^-$ anion (path *i*)[10] with $Me_2S$ and hydrochloric acid to isolate a structurally unique 9-$Me_2S$-μ-6,9-[($HOBCH_2$)]-*arachno*-6-$CB_9H_{11}$ compound (path *ii*). Hydrolytical removal of the -B(OH)$CH_2$B(apex)- section from this compound leads in turn to 4-$CB_8H_{14}$ (path *iii*). The overall yield of the synthesis of Scheme 2 is 45%, which was a remarkable improvement in comparison with the previous method.

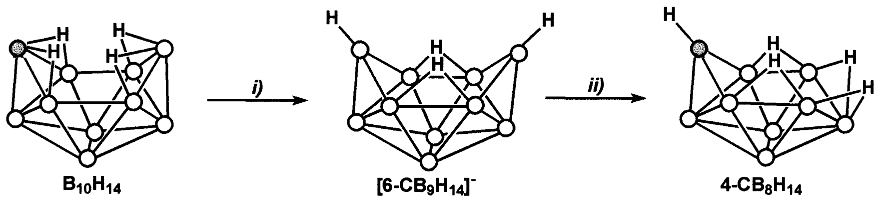


Scheme 2. (*i*) 1, Na, THF; 2, $NMe_4Cl$, $H_2O$; (*ii*) $Me_2S$, concd. HCl; (*iii*) hydrolysis.

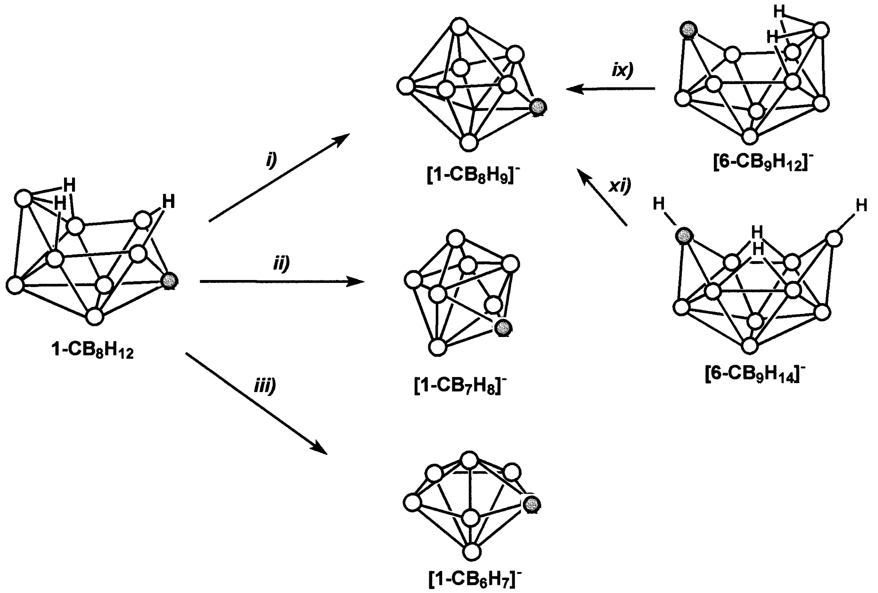
The best route for the preparation of 4-$CB_8H_{14}$ is, however, that based on the recent ingenious synthesis by Brellochs [5] of the previously reported [11] [*arachno*-6-$CB_9H_{14}$]$^-$ anion (path *i* in Scheme 3). As we have reported just recently [12], the anion can be oxidized by $Fe^{3+}$ in an acidic medium to give an almost quantitative yield of 4-$CB_8H_{14}$ (path *ii* in Scheme 3). The great advantage of the synthesis outlined in Scheme 3 is that it can be performed in one pot, without isolating the [6-$CB_9H_{14}$]$^-$ anion, and the total yield of 4-$CB_8H_{14}$ falls into the range of 45–48%. Thanks to this synthesis, 4-$CB_8H_{14}$, and, therefore, also 1-$CB_8H_{12}$ (see dehydrogenation path *xi* in Scheme 1), have now become ones of the most readily available monocarbaboranes.

## 3. Reactions of 4-$CB_8H_{14}$ and 1-$CB_8H_{12}$

The syntheses of metallacarbaboranes from 4-$CB_8H_{14}$ have been mostly reviewed [13]. These included, e.g. the



Scheme 3. (*i*) 1, NaOH, $H_2O$; 2, aq. $CH_2O$; 3, $Et_2O$ extraction, $H_2O$; (*ii*) $Fe^{3+}$, dilute HCl.



Scheme 4. (*i*) 1, $Et_3N$; 2, $I_2$, THF, −78 °C; (*ii*) Ar atmosphere, $Et_3N$, toluene, reflux 24 h; (*iii*) 1, $N_2$–$O_2$ atmosphere, $Et_3N$, toluene, reflux 24 h, evaporation; 2, $H_2O$, crystallization; 3, precipitation of mother liquors with $PPh_4Cl$;4, TLC separation; (*ix*) 220 °C; (*xi*) 220 °C.

formation and structural aspects of the ten-vertex complexes $[9,9\text{-}(PPh_3)_2\text{-}arachno\text{-}9,6\text{-}PtCB_8H_{12}]$ [14], $[2\text{-}(\eta^5\text{-}C_5H_5)\text{-}closo\text{-}2,1\text{-}CoCB_8H_9]^-$ [15], $[10\text{-}(\eta^5\text{-}C_5H_5)\text{-}closo\text{-}10,1\text{-}NiCB_8H_9]$ [15,16], $[6,7\text{-}(\eta^5\text{-}C_5H_5)\text{-}closo\text{-}6,7,1\text{-}Ni_2CB_7H_8]$ [15], and the complex $[asym\text{-}9\text{-}(CO)\text{-}9,9\text{-}(PPh_3)_2\text{-}9\text{-}H\text{-}arachno\text{-}9,6\text{-}IrCB_8H_{12}]$ was prepared later [17]. The only metallacarborane synthesized from $1\text{-}CB_8H_{12}$ has so far been the nine-vertex $[6,6\text{-}(PPh_3)_2\text{-}arachno\text{-}6,4\text{-}PtCB_7H_{11}]$ [18], a structural analogue of $4\text{-}CB_8H_{14}$. This very short list of reactions suggests that metallacarborane chemistry of $4\text{-}CB_8H_{14}$, and $1\text{-}CB_8H_{12}$ has still been almost untouched area of boron chemistry.

Just recently we have found that also $1\text{-}CB_8H_{12}$ is a very useful reagent for the synthesis of a series of novel compounds in the area of monocarbaborane chemistry. As shown in Scheme 4 (path *i*), oxidation of *nido*-$1\text{-}CB_8H_{12}$ with $I_2$ in THF at −78 °C in the presence of $NEt_3$ gives the first nine-vertex *closo* monocarbaborane, the stable $[closo\text{-}4\text{-}CB_8H_9]^-$ anion, in a yield of 75% [12]. Alternatively, $[4\text{-}CB_8H_9]^-$ can be also prepared by the pyrolysis of the anions $[6\text{-}CB_9H_{14}]^-$ and $[6\text{-}CB_9H_{12}]^-$ at 220 °C in yields 56 and 61%, respectively [12] (paths *ix* and *xi* in Scheme 4).

Under strictly anaerobic conditions, the reaction between $1\text{-}CB_8H_{12}$ (path *ii* in Scheme 4) and $Et_3N$ in

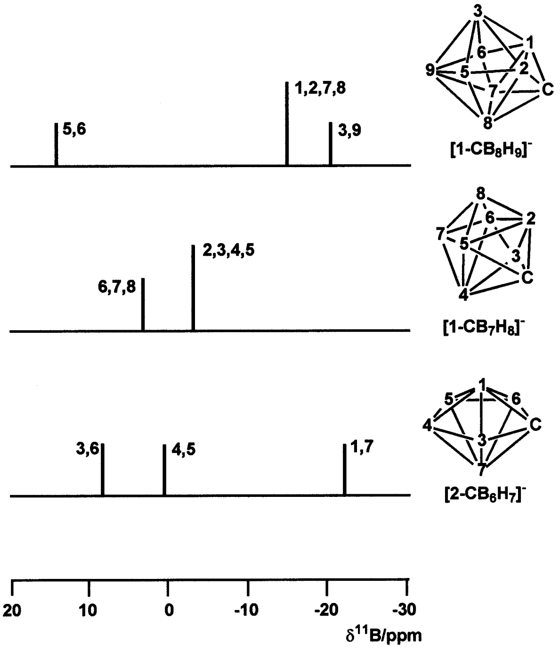


Fig. 1. Stick representation of the intercomparison of the $^{11}B$ chemical shifts for the *closo* monocarbaborane anions $[2\text{-}CB_6H_7]^-$ $[1\text{-}CB_7H_8]^-$, and $[4\text{-}CB_8H_9]^-$. Data from references [12,20].

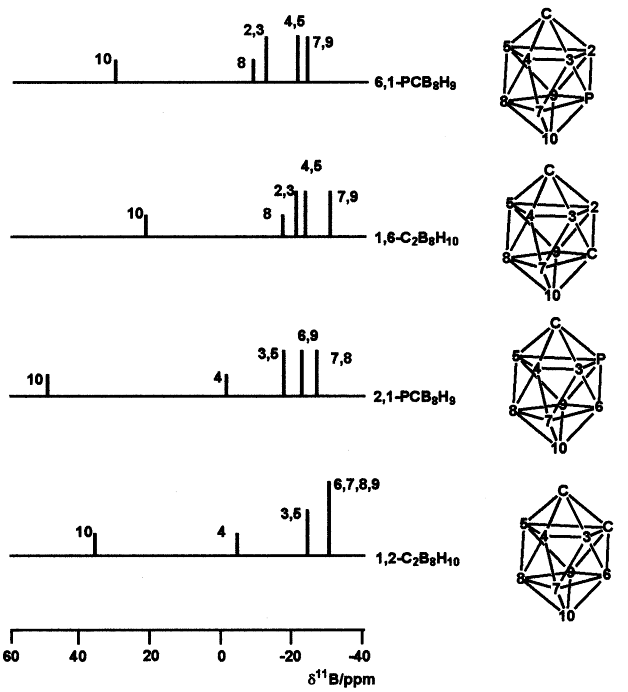


Fig. 2. Stick representation of the intercomparison of the $^{11}$B chemical shifts for the ten-vertex *closo* phosphamonocarboranes with the corresponding isostructural *closo* dicarbaboranes. Data from references [21,25,26].

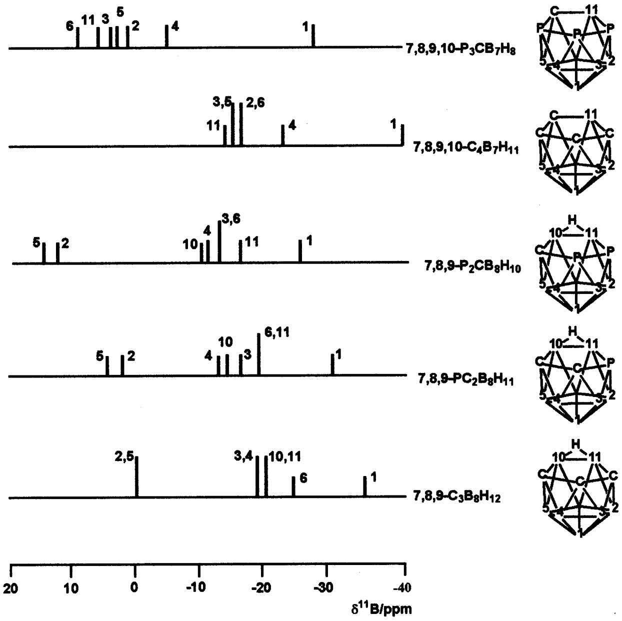
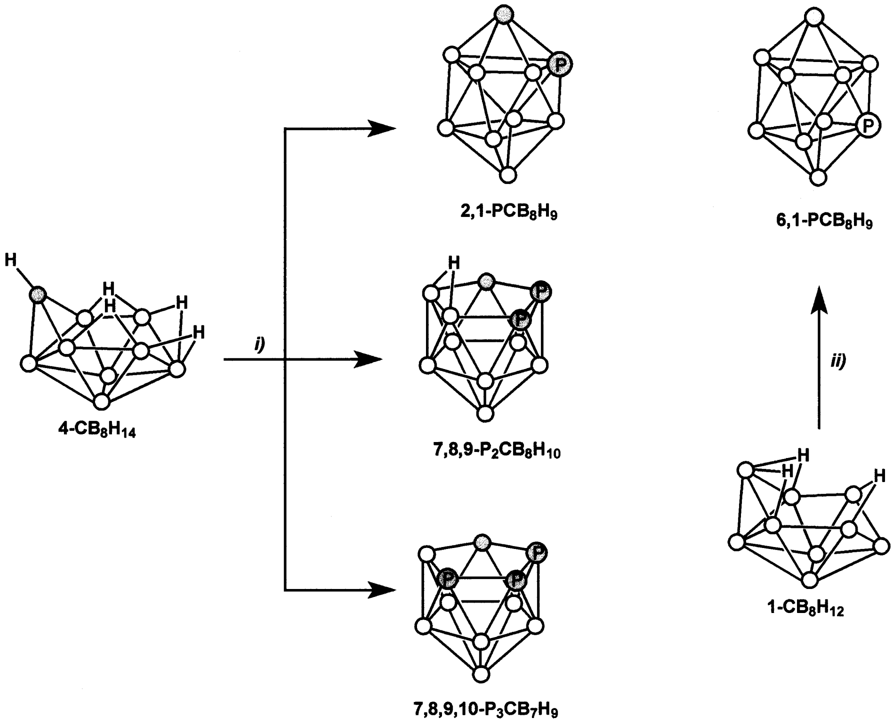


Fig. 3. Stick representation of the intercomparison of the $^{11}$B chemical shifts for the eleven-vertex *nido* phosphamonocarboranes with the corresponding isostructural *nido* tri- and tetracarbaboranes. Data from references [21,27,28].

dry toluene at reflux resulted in the isolation of the previously reported [10b,19] anion [*closo*-1-$CB_7H_8$]$^-$ in 75% yield [20]. The reaction products are, however, entirely different when the same reaction is carried out in the atmosphere of 5% $O_2$–$N_2$ (see Scheme 4 path *iii*). Under these conditions, the reaction led to the formation of a mixture of the anions [1-$CB_7H_8$]$^-$ and [4-$CB_8H_9$]$^-$ (yields 35 and 49%, respectively) and precipitation of the mother liquors by $PPh_4Cl$ resulted finally in the isolation of [$PPh_4$]$^+$[*closo*-2-$CB_6H_7$]$^-$ in



Scheme 5. (*i*) and (*ii*) 1, proton sponge, $PCl_3$, $CH_2Cl_2$, 24 h; 2, LC separation.

6% yield [20]. The formation of all these new *closo* anions is consistent with stoichiometries as in equations (1–4):

$$1\text{-}CB_8H_{12} + 3NEt_3 + I_2 \rightarrow 2Et_3N \cdot HI + [Et_3NH]^+[4-CB_8H_9]^- \quad (1)$$

$$1\text{-}CB_8H_{12} + 2Et_3N \rightarrow [Et_3NH]^+[1-CB_7H_8]^- + Et_3N \cdot BH_3 \quad (2)$$

$$1\text{-}CB_8H_{12} + Et_3N + O_2 \rightarrow [Et_3NH]^+[4-CB_8H_9]^- + H_2O \quad (3)$$

$$1\text{-}CB_8H_{12} + 2Et_3N + O_2 + H_2O \rightarrow [Et_3NH]^+[2-CB_6H_7]^- + Et_3N \cdot BH_3 + B(OH)_3 \quad (4)$$

The anions $[2\text{-}CB_6H_7]^-$, $[1\text{-}CB_7H_8]^-$, and $[4\text{-}CB_8H_9]$ exhibit considerably high stability in air and thus have a good chance to become new candidates for substitution and weakly co-ordinated anion chemistry [3] to complement $[CB_9H_{10}]^-$, $[CB_{11}H_{12}]^-$ and their derivatives.

The structure of $[1\text{-}CB_7H_8]^-$ was already determined by an X-ray diffraction study on its mono- and diiododerivatives [19] and that of the parent $[4\text{-}CB_8H_9]^-$ anion has been reported just recently [12]. The structure determination of the seven-vertex anion $[2\text{-}CB_6H_7]^-$ resulted in a disorder between boron and carbon positions, but was confirmed by excellent agreement between theoretical and experimental $^{11}B$ chemical shifts [20]. The graphical intercomparison of the $^{11}B$-NMR spectra of this family of *closo* monocarbaborane anions is given in Fig. 1.

The open-structured carboranes $4\text{-}CB_8H_{14}$, and $1\text{-}CB_8H_{12}$ are designed for the insertion of main-group element atoms into their structures. As the first approach to this type of chemistry, their reactions with $PCl_3$, in the presence of proton sponge as the deprotonation agent, were examined [21]. As shown in Scheme 5 (path *i*), there are several modes of P-insertion into the hexagonal open face in $4\text{-}CB_8H_{14}$. The main product of the reaction is the ten-vertex phosphacarborane *closo*-$2,1\text{-}PCB_8H_9$ as a result of monophosphorus insertion; other two products being the 11-vertex *nido* species $7,8,9\text{-}P_2CB_8H_{10}$ and $7,8,9,10\text{-}P_3CB_7H_8$ arising from multiple P-insertion. Under the same reaction conditions, the only phosphacarborane product from a similar reaction with $1\text{-}CB_8H_{12}$ was *closo*-$6,1\text{-}PCB_8H_9$ (path *ii*). It should be noted that $7,8,9\text{-}P_2CB_8H_{10}$ is structurally similar to the recently reported [22] $7,8,11\text{-}PC_2B_8H_{11}$ and $7,8,9,10\text{-}P_3CB_7H_8$ is an analogue of the isomeric diphosphadicarbaboranes $P_2C_2B_7H_9$ [23]. Moreover, methyl- and chloromethyl derivatives of $7,8,9,10\text{-}P_3CB_7H_8$ were prepared from $4,5\text{-}C_2B_7H_{13}$ via reaction with NaH and $PCl_3$ [24].

All the phosphamonocarbaboranes isolated as outlined above contain bare P atoms in their cage positions and are hence isoelectronic and isostructural with the corresponding *n*-vertex carboranes. These relationships are demonstrated in Fig. 2 Fig. 3 by similar $^{11}B$-NMR behaviour of individual isostructural pairs (triples) $1,2\text{-}C_2B_8H_{10}$–$2,1\text{-}PCB_8H_9$,$1,6\text{-}C_2B_8H_{10}$–$6,1\text{-}PCB_8H_9$,$7,8,9\text{-}C_3B_8H_{12}$–$7,8,9\text{-}PC_2B_8H_{11}$–$7,8,9\text{-}P_2CB_8H_{10}$, and $7,8,9,10\text{-}C_4B_7H_{11}$–$7,8,9,10\text{-}P_3CB_7H_8$. No doubt that the new ten- and 11 vertex phophacarboranes, the analogues of the corresponding carboranes, will be used in near future as starting compounds for substitution and, namely, metallaphoshacarborane chemistry.

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