New carboranes and phosphaboranes*

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Abstract: A review is presented on the new routes to the synthesis of the monocarbaboranes [*arachno*-6-CB_9H_{14}]$^-$, *arachno*-4-CB_8H_{14}, and *nido*-1-CB_8H_{12}, that now have become excellent starting materials for the preparation of a family of seven-, eight-, and nine-vertex *closo*-monocarbaborane anions [2-CB_6H_7]$^-$, [1-CB_7H_8]$^-$, and [4-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 phosphacarboranes 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-$PC_2B_8H_{11}$, *nido*-7,8,11-$PC_2B_8H_{11}$, and *nido*-7,8,9,10-$P_3CB_7H_8$, are structural analogs of the corresponding carboranes and are likely to exhibit similar chemical behavior.

INTRODUCTION

Carborane 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 most investigated area of this 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]. We would like to outline some newer aspects of monocarbaborane chemistry that will include recent syntheses of a family of seven-, eight, and nine-vertex *closo*-monocarbaboranes. Together with this chemistry, we shall discuss some new results in the chemistry of phosphacarboranes. These are usually prepared via insertion of phosphorus atoms into open-structured carboranes, as demonstrated for the first time by the pioneering work of Todd et al. [5]. Phosphorus can occupy cluster positions in borane skeletons, in accord with electron counting rules [6] and the isolobal principle [7]. Phosphacarboranes are analogs of the corresponding carboranes, as the bare P-vertex contributes three electrons to the cluster bonding scheme as does the isolobal CH group.

NEW SYNTHESES IN THE AREA OF MONOCARBABORANE CHEMISTRY

One of the best achievements in the area of recent monocarbaborane chemistry has been the new synthesis by Brellochs [8] of the previously reported [9] [*arachno*-6-CB_9H_{14}]$^-$ anion (see Scheme 1). The reaction is based on treatment of $B_{10}H_{14}$ with aqueous NaOH, followed by addition of aqueous CH_2O. The experimental details of this reaction have not been reported, and, therefore, we have examined for

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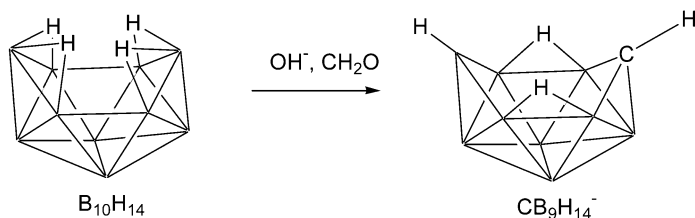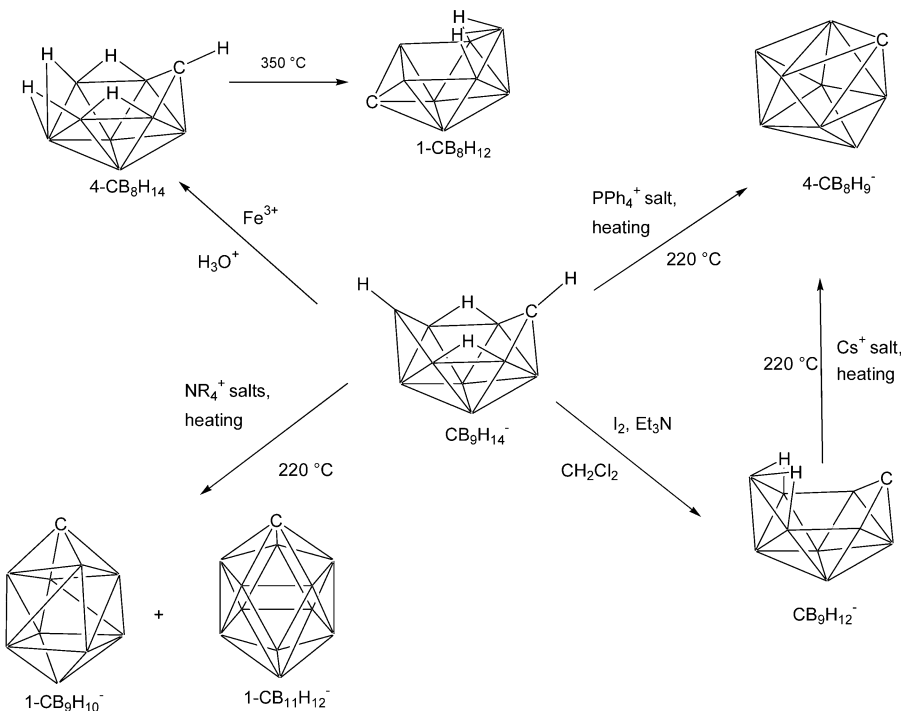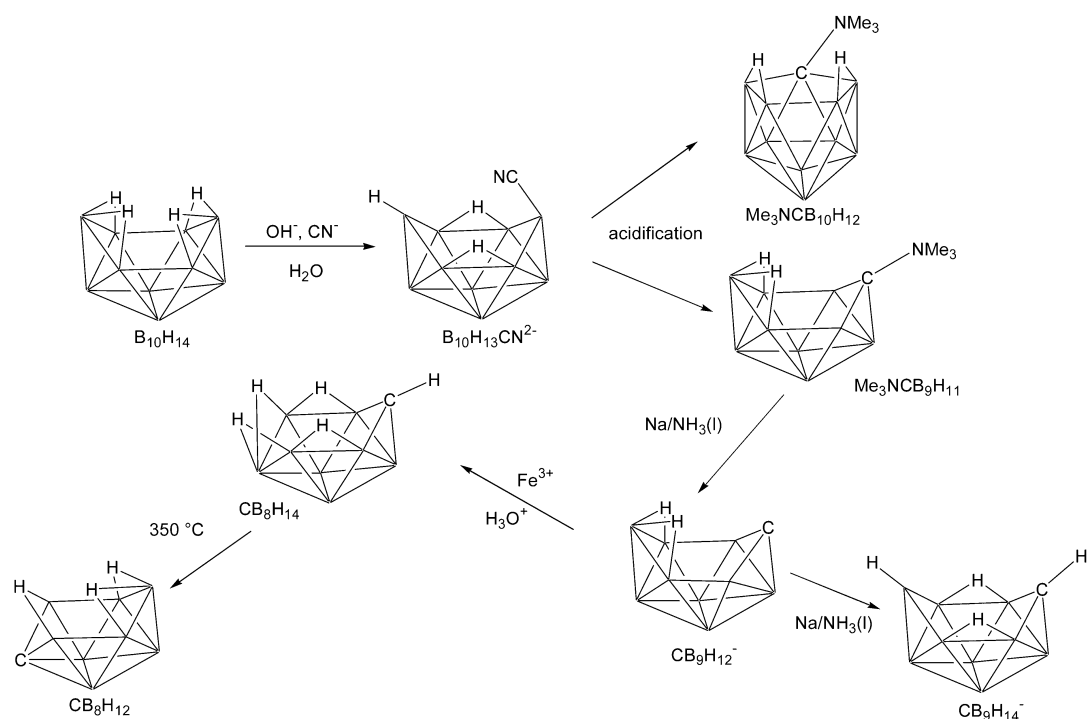
Scheme 1

optimum conditions in our laboratories [10]. The synthesis is carried out at room temperature with a $B_{10}H_{14}/CH_2O$ molar ratio 1:4.5, and the product can be isolated in 48 % yield as a NEt_4^+ salt.

As shown in Scheme 2, the $[6\text{-}CB_9H_{14}]^-$ anion has become an excellent reagent for the synthesis of a variety of essential monocarbaborane compounds. Oxidation of its Na^+ salt with an acidic solution of $FeCl_3\cdot 6\ H_2O$ in an aqueous solution gives an almost quantitative yield of *arachno*-4-CB_8H_{14}. A great advantage of this synthesis is that it can be performed in one pot directly from $B_{10}H_{14}$, without isolating the $[6\text{-}CB_9H_{14}]^-$ 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 in Scheme 2), have now become some of the most readily available monocarbaboranes [10].
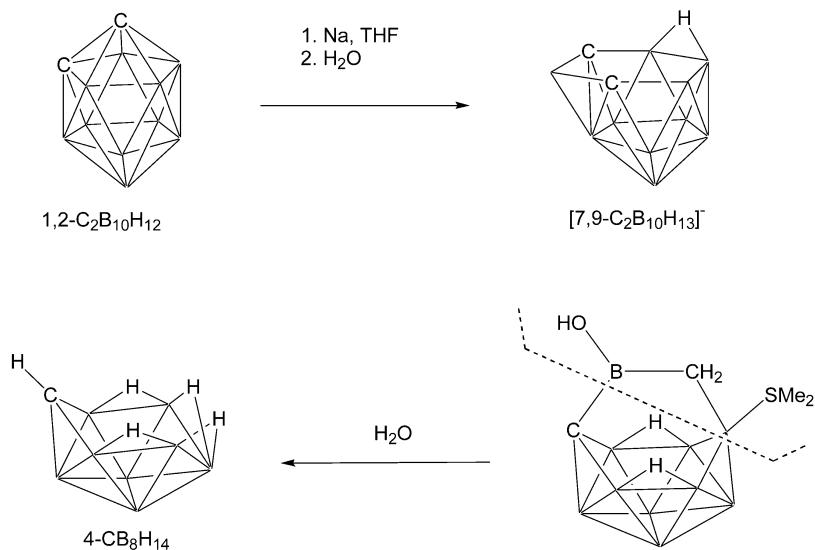

Scheme 2

The 4-CB_8H_{14} monocarbaborane was discovered more than 20 years ago in our laboratories [11], and, as shown in Scheme 3, the original synthesis of this compound was based on a multistep sequence from $B_{10}H_{14}$. The reaction consisted in the acidification of the [*endo*-6-NC-*arachno*-$B_{10}H_{13}]^{2-}$ dianion [12], which resulted in the formation of a mixture of two *nido*-monocarbaborane ligand adducts, 7-Me_3N-7-$CB_{10}H_{12}$ and 6-Me_3N-6-CB_9H_{11} [13], via insertion of the CN carbon into the cage. The 6-Me_3N-6-CB_9H_{11} species was then reduced with Na metal to give the parent [*nido*-6-$CB_9H_{12}]^-$ anion [11] that, upon removing the apex B vertex, gives the desired 4-CB_8H_{14} in a good

Scheme 3

yield [11]. Although the total yield of this multistep synthesis did not exceed 15 %, this method was used for many years as the only source of 4-CB$_8$H$_{14}$. The 4-CB$_8$H$_{14}$ carborane can be then easily converted (yield 90 %) into *nido*-1-CB$_8$H$_{12}$ by heating at 350 °C [11,14], and this method has remained so far the best access to this compound. Scheme 3 also shows the previous, inconvenient, access to the [6-CB$_9$H$_{14}$]$^-$ anion. A considerable improvement of the 4-CB$_8$H$_{14}$ synthesis [15] is shown in Scheme 4. Cluster opening of *o*-carborane via reaction with Na metal, followed by in situ reaction of the in-
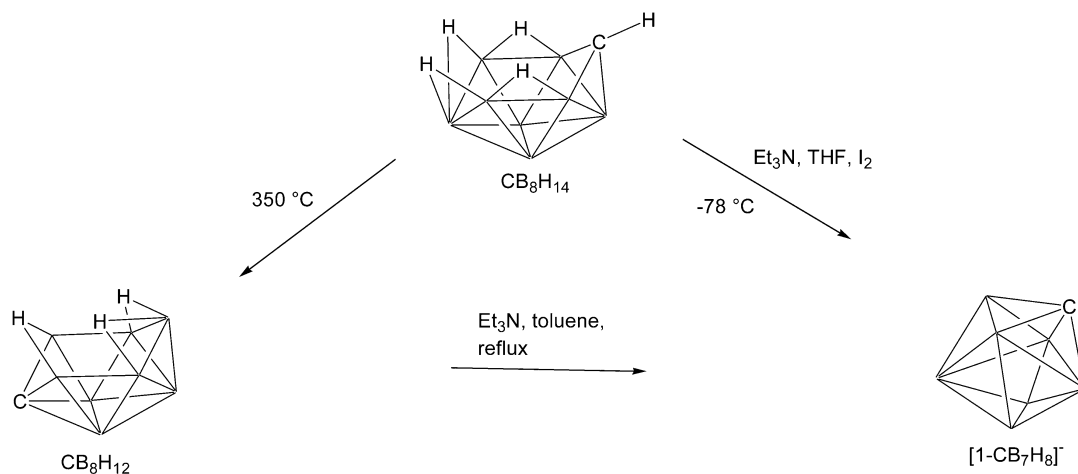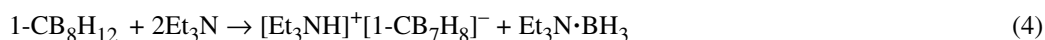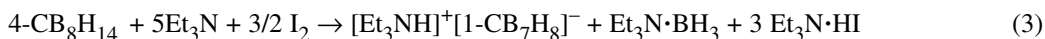

Scheme 4

termediate [*nido*-7,9-C$_2$B$_{10}$H$_{13}$]$^-$ anion [16] with Me$_2$S and hydrochloric acid produces the structurally unique 9-Me$_2$S-μ-6,9-[(HOBCH$_2$)]-*arachno*-6-CB$_9$H$_{11}$ compound. Hydrolytical removal of the—B(OH)CH$_2$B(apex)—section from this compound leads in turn to 4-CB$_8$H$_{14}$ in an overall yield of 45 %. As shown in Scheme 2, the [*nido*-6-CB$_9$H$_{12}$]$^-$ anion can be newly prepared in a quantitative yield by the oxidation of [*arachno*-6-CB$_9$H$_{14}$]$^-$ with elemental iodine in the presence of triethylamine, the reaction being an example of a clean arachno to nido conversion [17] (see also eq. 1). Heating of the Cs$^+$[6-CB$_9$H$_{14}$]$^-$ or Cs$^+$[6-CB$_9$H$_{12}$]$^-$ salts at 220 °C for 3 h has resulted in the formation of the first representative of the closo nine-vertex monocarbaborane family, the [4-CB$_8$H$_9$]$^-$ anion in approximately 60 % yields [10]. This pyrolysis is rather sensitive to the type of the countercation, as a similar heating of the NR$_4^+$[6-CB$_9$H$_{14}$]$^-$ salts leads also to a side formation mixture of the [*closo*-1-CB$_9$H$_{10}$]$^-$ [*nido*-1-CB$_{10}$H$_{13}$]$^-$, and [*closo*-1-CB$_{11}$H$_{12}$]$^-$ anions, while the heating of the PPh$_4^+$ salt leads cleanly to PPh$_4^+$[4-CB$_8$H$_9$]$^-$ in 96 % yield [18]:

$$[6\text{-CB}_9\text{H}_{14}]^- + \text{I}_2 + 2\text{NEt}_3 \rightarrow [6\text{-CB}_9\text{H}_{12}]^- + 2\text{NEt}_3\cdot\text{HI} \tag{1}$$

$$[6\text{-CB}_9\text{H}_{14}]^- \rightarrow [4\text{-CB}_8\text{H}_9]^- + \tfrac{1}{2}\text{B}_2\text{H}_6 \tag{2}$$
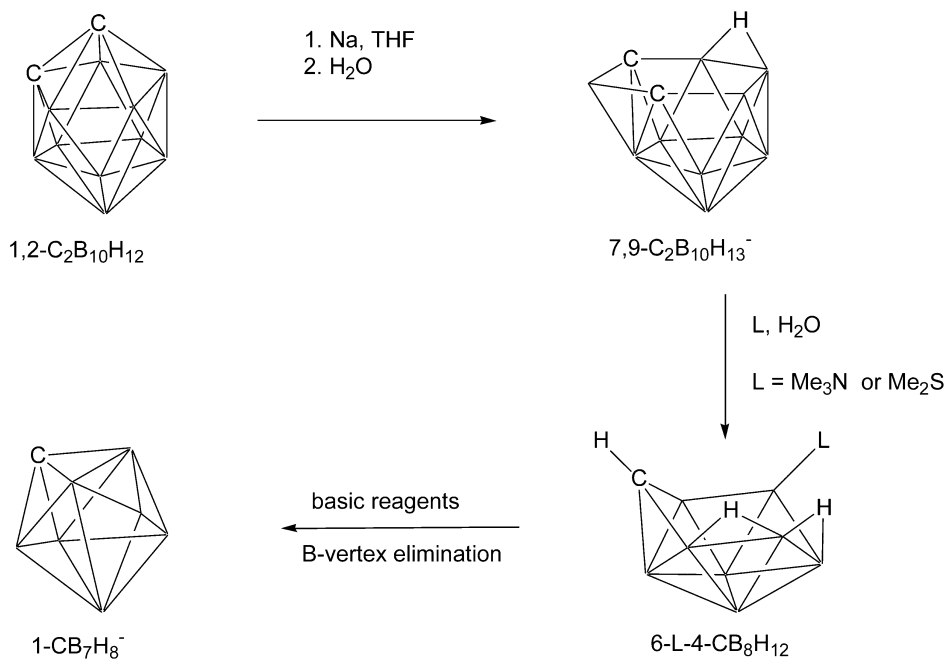
Scheme 5 shows the two new ways developed recently for the synthesis of the eight-vertex anion [*closo*-1-CB$_7$H$_8$]$^-$ [17,19]. Treatment of 4-CB$_8$H$_{14}$ with triethylamine and iodine in tetrahydrofuran (THF) at –78 °C leads to the formation of NEt$_3$H$^+$[1-CB$_7$H$_8$]$^-$ in 70 % yield and elimination of one boron vertex as NEt$_3$·BH$_3$ [17] (see eq. 3). Under strictly anaerobic conditions, also the reaction between 1-CB$_8$H$_{12}$ and Et$_3$N in dry toluene at reflux resulted in the isolation of NEt$_3$H$^+$[1-CB$_7$H$_8$]$^-$ in 75 % yield (see eq. 4) [19]:

$$4\text{-CB}_8\text{H}_{14} + 5\text{Et}_3\text{N} + 3/2\,\text{I}_2 \rightarrow [\text{Et}_3\text{NH}]^+[1\text{-CB}_7\text{H}_8]^- + \text{Et}_3\text{N}\cdot\text{BH}_3 + 3\,\text{Et}_3\text{N}\cdot\text{HI} \tag{3}$$

$$1\text{-CB}_8\text{H}_{12} + 2\text{Et}_3\text{N} \rightarrow [\text{Et}_3\text{NH}]^+[1\text{-CB}_7\text{H}_8]^- + \text{Et}_3\text{N}\cdot\text{BH}_3 \tag{4}$$
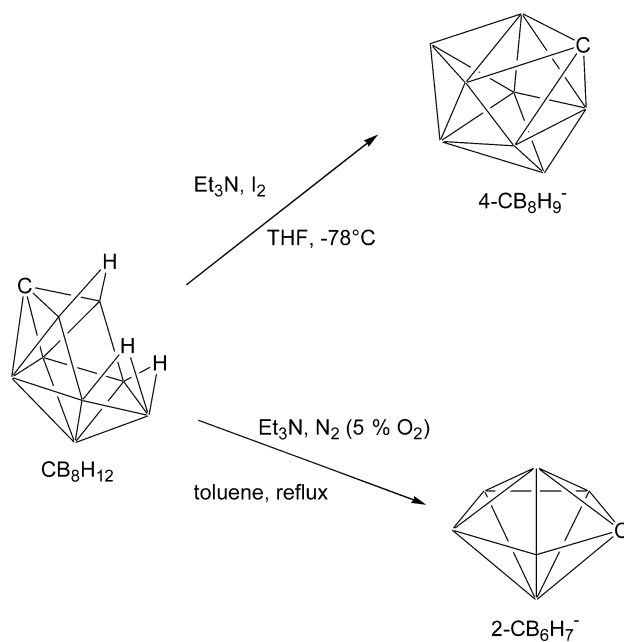

Scheme 5

The [1-CB$_7$H$_8$]$^-$ anion was previously isolated [20] as a product of a dismantling of the *o*-carborane cage, as outlined in Scheme 6. The key reaction step is the reaction between 6-L-CB$_8$H$_{12}$ (L = Me$_3$N and Me$_2$S) and basic reagents (NaH or OH$^-$), which results in the elimination of the L-substituted vertex, followed by cage closure upon formation [1-CB$_7$H$_8$]$^-$.

1,2-$C_2B_{10}H_{12}$ → (1. Na, THF 2. H_2O) → 7,9-$C_2B_{10}H_{13}^-$

L, H_2O

L = Me_3N or Me_2S

6-L-4-CB_8H_{12}

basic reagents
B-vertex elimination

1-$CB_7H_8^-$

Scheme 6

Scheme 7 illustrates further usefulness of 1-CB_8H_{12} for the synthesis of new compounds in the area of monocarbaborane chemistry. Just recently, we have found that the oxidation of 1-CB_8H_{12} with I_2 in THF at –78 °C in the presence of NEt_3 gives the [*closo*-4-CB_8H_9]$^-$ anion in a yield of 75 % (see eq. 5) [10]. The reaction products from the reaction between 1-CB_8H_{12} and NEt_3 (for anaerobic conditions, see Scheme 5 and eq. 4) are, however, entirely different when the same reaction is carried out in


CB_8H_{12}

Et_3N, I_2
THF, -78°C → 4-$CB_8H_9^-$

Et_3N, N_2 (5 % O_2)
toluene, reflux → 2-$CB_6H_7^-$

Scheme 7

the atmosphere of 5 % O_2/N_2 (see Scheme 7). Under these conditions, the reaction leads to the formation of a mixture of the anions $[1\text{-}CB_7H_8]^-$ and $[4\text{-}CB_8H_9]^-$ (yields 35 and 49 %, respectively), and precipitation of the mother liquors by PPh_4Cl resulted finally in the isolation of $[PPh_4]^+[closo\text{-}2\text{-}CB_6H_7]^-$ in 6 % yield [19].

$$1\text{-}CB_8H_{12} + 3NEt_3 + I_2 \rightarrow 2Et_3N\cdot HI + [Et_3NH]^+[4\text{-}CB_8H_9]^- \qquad (5)$$

The *closo*-monocarbaborane 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 coordinated 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 [20] and that of the parent $[4\text{-}CB_8H_9]^-$ anion has been reported just recently [10]. The structure determination of the seven-vertex anion $[2\text{-}CB_6H_7]^-$ resulted in a disorder, but it has been determined on its diiodo derivative [19].

SYNTHESES OF NEW PHOSPHACARBORANES

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 phoshacarborane *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 8). The structures of both compounds have been derived on the basis of the combined ab initio/GIAO/NMR (^{1}H, ^{11}B, ^{13}C) approach [21].
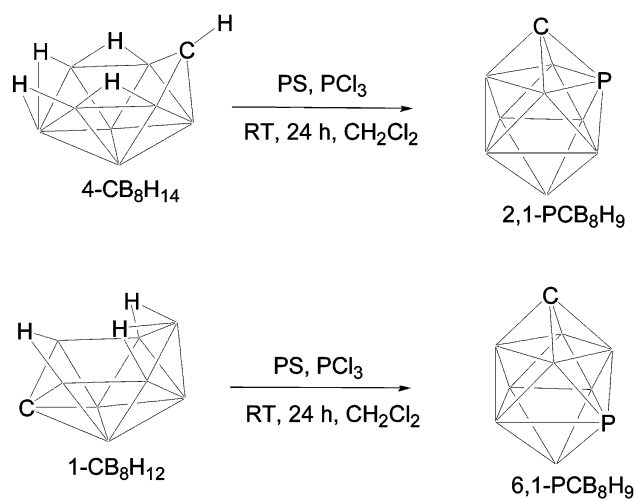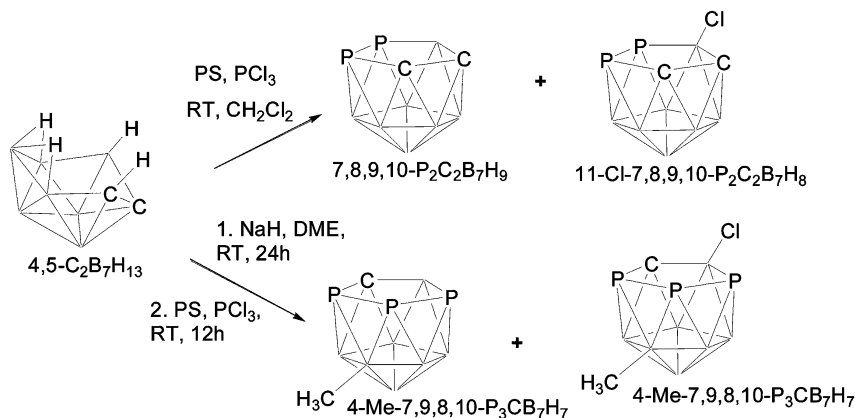

Scheme 8

The reactions of the isomeric 4,5- and 4,6-*arachno*-$C_2B_7H_{13}$ dicarbaboranes with PCl_3 proceed exclusively with diphosphorus insertion and formation of the corresponding isomeric 11-vertex *nido*-$P_2C_2B_7H_9$ compounds [22]. 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 9).

The reaction between the 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 [22]. In contrast to this reaction, aging of the
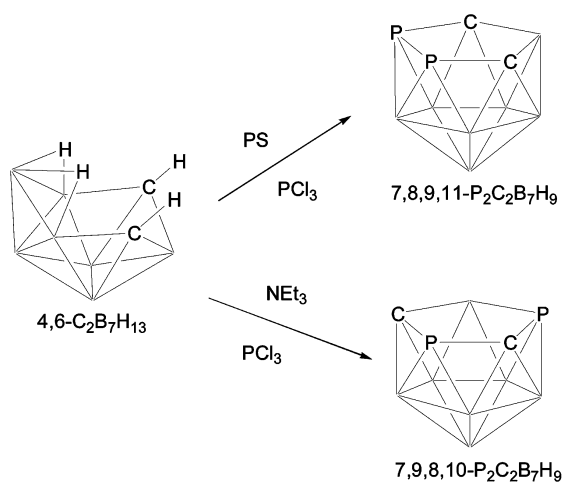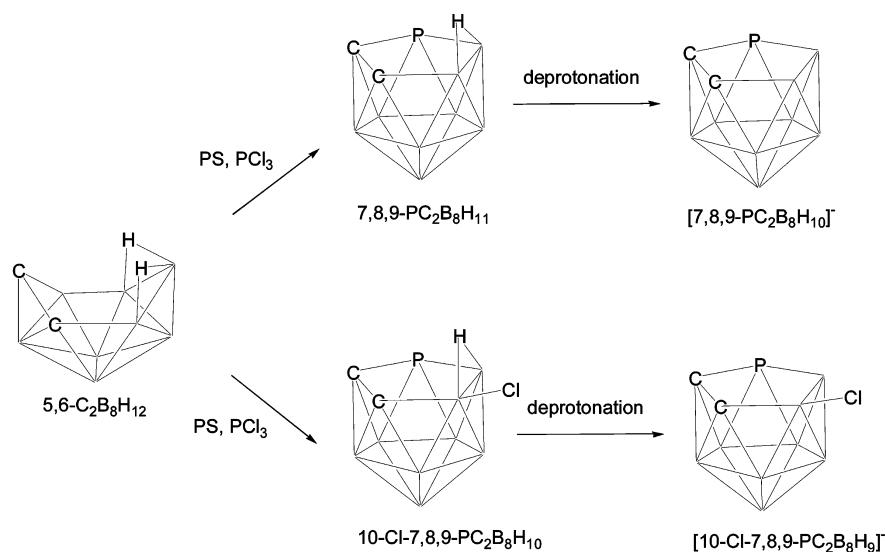
Scheme 9

[*arachno*-4,5-$C_2B_7H_{12}$]$^-$ anion in 1,2-dimethoxy ethane (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 10) [23]. The reaction is associated with the extrusion of one of the skeletal carbons into an exoskeletal position (see Scheme 10). 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-optimized 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 [22,23].
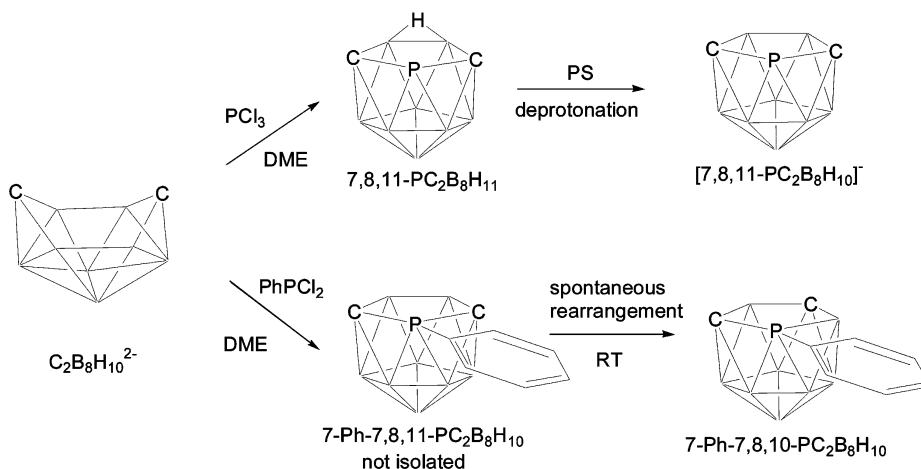

Scheme 10

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 phosphadicarboranes 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-$PC_2B_8H_{10}$]$^-$ and [10-Cl-7,8,9-$PC_2B_8H_9$]$^-$ (Scheme 11). The molecular geometries of all these compounds have been optimized ab initio at a correlated 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

Scheme 11

structure of $[10\text{-}Cl\text{-}7,8,9\text{-}PC_2B_8H_9]^-$ has been determined by an X-ray diffraction analysis. The anionic compounds $[7,8,9\text{-}PC_2B_8H_{10}]^-$ and $[10\text{-}Cl\text{-}7,8,9\text{-}PC_2B_8H_9]^-$ are analogs of the cyclopentadienyl anion as they are monoanionic and contain a pentagonal open face [24].

As shown in Scheme 12, treatment of $Na_2[nido\text{-}6,9\text{-}C_2B_8H_{10}]$ with PCl_3 in DME at room temperature for 24 h, followed by hydrolysis of the reaction mixture, produces the neutral 11-vertex phoshadicarbaborane $nido\text{-}7,8,11\text{-}PC_2B_8H_{11}$ (yield 35 %). The compound is isomeric with $7,8,9\text{-}PC_2B_8H_{11}$ discussed in the preceding paragraph and can be quantitatively deprotonated by PS to give the corresponding $[nido\text{-}7,8,11\text{-}PC_2B_8H_{10}]^-$ anion. A similar reaction using $PhPCl_2$ as the source of phosphorus yields $7\text{-}Ph\text{-}7,8,10\text{-}nido\text{-}PC_2B_8H_{10}$ (yield 64 %), which has a different configuration of heteroatoms in the open face. A side product, $nido\text{-}7,8,11\text{-}PC_2B_8H_{11}$ (yield 14 %), apparently results from an accompanying dephenylation process. The formation of $7\text{-}Ph\text{-}7,8,10\text{-}nido\text{-}PC_2B_8H_{10}$ has been supposed to proceed via a room-temperature cage rearrangement of $7\text{-}Ph\text{-}7,8,11\text{-}nido\text{-}PC_2B_8H_{10}$ [25]. The DFT-GIAO//B3LYP/6/31G* calculations were used to show that conformation changes about the

Scheme 12

exo-cluster C(cage)-Ph bond in 7-Ph-*nido*-7,8,10-PC$_2$B$_8$H$_{10}$ have significant differential effects of up to ca. 6 ppm on the nuclear shieldings of adjacent boron atoms within the cluster [26].

ACKNOWLEDGMENTS

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