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Phosphacarborane Chemistry. Triphosphacarboranes *nido* 4-CH_3-7,8,9,10-$P_3CB_7H_7$ and *nido*-4-CH_3-11-Cl-7,8,9,10-$P_3CB_7H_6$, Analogues of 7,8,9,10-$C_4B_7H_{11}$ and the First Examples of Boron Clusters Containing Three Phosphorus Vertexes

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The reaction of borane-based anions with PCl_3 in the presence of basic reagents as deprotonation agents leading to phosphaboranes/carboranes was pioneered by Todd and Little several years ago.[1,2] There is a current interest in the syntheses of phosphacarboranes, stable structural analogues of carboranes. These may be exemplified by the 11-vertex *nido* compounds 7-R-7,8,9-$PC_2B_8H_{10}$ (R = CH_3 or C_6H_5),[3] 7,8,11-$PC_2B_8H_{11}$, and [7,8,11-$PC_2B_8H_{10}$]$^-$,[4] the last two compounds being analogues of tricarbollides.[5] Just recently,[6] we have developed a route to the three isomers of *nido*-$P_2C_2B_7H_9$ that contain a contiguous string of two P and two C vertexes in the open pentagonal face of the 11-vertex *nido* cage, being thus isostructural with the *nido*-7,8,9,-10-$C_4B_7H_{11}$ tetracarbaborane.[7] As a continuation of this search for new, phosphorus-rich phosphacarborane cages, we report here our preliminary results on an interesting PCl_3-insertion reaction into the cluster of *arachno*-[4,5-$C_2B_7H_{12}$]$^-$ which, via rearrangement, generates triphosphacarborane analogues of *nido*-7,8,9,10-$C_4B_7H_{11}$, the first representatives of boron clusters containing three cage-phosphorus atoms.

Years ago we recognized[8] that prolonged treatment of *arachno*-4,5-$C_2B_7H_{13}$ (**1**)[9] (48 h, RT, DME) (RT, room temperature; DME = 1,2-dimethoxyethane) with excess NaH led ultimately to the disappearance of the *arachno*-[4,5-$C_2B_7H_{12}$]$^-$ anion ($\mathbf{1}^-$) originally formed.[10] Instead, acidification of the reaction mixture with CF_3-COOH resulted in the isolation of an inseparable mixture of two compounds of general formulation $CB_7H_{12}CH_3$ (CH_3-**2**). This was identified by NMR spectroscopy as a mixture of 7-CH_3 and 3-CH_3 substituted isomers (molar ratio ca. 3:1, respectively) of the 8-vertex monocarbaborane *arachno*-CB_7H_{13} (**2**) reported previously.[11] Although no mechanistic investigations have been made, this transformation of anion $\mathbf{1}^-$ seems to be in agreement with an addition of H^- to $\mathbf{1}^-$ with the formation of the two isomeric dianions CH_3-$\mathbf{2}^{2-}$ via extrusion of the 4-CH_2 carbon into exo-skeletal position under the formation of the CH_3 substituent:

$$\underset{\mathbf{1}^{-}}{C_2B_7H_{12}{}^{-}} + H^{-} \rightarrow \underset{CH_3\text{-}\mathbf{2}^{2-}}{CB_7H_{10}CH_3{}^{2-}} \qquad (1)$$

Being still unable to reasonably separate the mixture of the methylated isomers of **2** or their anions, we have made an attempt at in situ incorporation of P-vertexes with the aim of separating the expected phosphacarborane mixture. In a typical experiment, carborane **1** (reaction scale 10 mmol) was treated with excess NaH (48 h, RT, DME), which was followed by the addition of 2 equiv of PS (PS = Proton Sponge = 1,8-dimethylaminonaphthalene) and 3 equiv of PCl_3 and stirring of the mixture for 12 h at RT. Upon adding CH_2Cl_2 and decomposing the mixture with water under cooling to 0 °C, the complex compound mixture contained in the CH_2Cl_2 layer was separated by repeated column chromatography on silica gel in hexane. This procedure led to the separation of three pure fractions, which were evaporated, and the residual solids sublimed at 60−100 °C (bath) to isolate three main products. These were identified by NMR spectroscopy[12] and mass spectrometry as methyl-substituted and methyl- and chloro-substituted derivatives of *nido*-7,8,9,10-$P_3CB_7H_8$ (**3**), namely, compounds 4-CH_3-*nido*-7,8,9,10-$P_3CB_7H_7$ (4-CH_3-**3**) (yield 13%, R_f(hexane) 0.64, mp 183−184 °C, *m/z* 204 [M^+, 59%]. Anal. Calcd for $C_2H_{10}B_7P_3$ (202.8): B, 37.36. Found: B, 36.51) and 4-CH_3-11-Cl-*nido*-7,8,9,10-$P_3CB_7H_6$ (4-CH_3-11-Cl-**3**) (yield 4.0%, R_f 0.25, mp 126−128 °C, *m/z* 240 [M^+, 15%]. Anal. Calcd for $C_2H_9B_7ClP_3$ (237.2): B, 31.93. Found: B, 30.28). The third compound isolated in pure state was the recently reported diphoshadicarbaborane *nido*-7,8,9,10-$P_2C_2B_7H_9$ (yield 3%, R_f 0.39).[6] As evidenced by NMR, also other impure, not yet separable, fractions contained smaller amounts of further methyl and chloro methyl derivatives of **3** which will be characterized in the full paper. The formation of both triphosphamonocarbaboranes is clearly consistent with the CH_2 extrusion from $\mathbf{1}^-$,

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(12) Compound 4-CH_3-**3**: $\delta(^{11}B)/\delta(^{11}B)$(calcd) (160.4 MHz, $CDCl_3$, 293 K) [multiplicity, intensity, assignment, $^1J_{BH}$ in Hz] 8.8/10.0 [d, 1 B, B(6), ∼160], 8.2/6.3 [s, 1 B, B(4), —], 5.5/9.1 [d, 1 B, B(3), ∼160], 4.4/5.8 [d, 1 B, B(5), ∼180], 2.3/3.8 [d, 1 B, B(2), ∼165], 1.2/−0.5 [d, 1 B, B(11), ∼150], −27.5/−29.7 [d, 1 B, B(1), 154], all theoretical $^{11}B-^{11}B$ cross peaks observed; $\delta(^1H)\{^{11}B\}$ (500 MHz, $CDCl_3$, 293 K) [multiplicity, intensity, assignment, $^2J_{PH}$ in Hz (if applicable)] 3.65 [t (asym), 1 H, H(3), 16/17], 3.53 [d, 1 H, H(5), 17], 3.21 [s, 1 H, H(6), —], 3.05 [s (broad), 1 H, H(11), —], 2.94 [d, H(10), 34], 2.89 [d, H(2), 20], 2.58 [s, 1 H, H(1), —], 0.90 [m, 3 H, CH_3, ∼5]; $\delta(^{31}P)\{^1H\}$ (202.4 MHz, $CDCl_3$, 293 K) [multiplicity, intensity, assignment, $^1J_{PP}$ in Hz] 37.9 [d (asym), 1 P, P(7) or P(9), 243], 0.7 [d (asym), 1 P, P(7) or P(9), 232], −13.6 [t (asym), 1 P, P(8), 251/257]. Compound 4-CH_3-11-Cl-**3**: $\delta(^{11}B)/\delta(^{11}B)$-(calcd) 12.5/11.4 [s, 1 B, B(11), —], 10.1/11.5 [d, 1 B, B(6), 162], 4.0/6.2 [d, 1 B, B(2), ∼169], 4.0/7.0 [d, 1 B, B(3), ∼169], 2.4/2.1 [s, 1 B, B(4), —], 2.4/3.8 [d, 1 B, B(5), ∼150], −27.4/−29.7 [d, 1 B, B(1), 154], all theoretical $^{11}B-^{11}B$ cross peaks observed; $\delta(^1H)\{^{11}B\}$ 3.54 [t (asym), 1 H, H(3), 17/16], 3.47 [d, 1 H, H(5), 15], 3.33 [s, 1 H, H(1), —], 3.28 [d, 1 H, H(2), 15],], 3.28 [d, 1 H, H(10), 33],], 0.89 [m, 3 H, CH_3, ∼5]; $\delta(^{31}P)\{^1H\}$ 25.3 [d (asym), 1 P, P(7) or P(9), 252], −18.0 [d (asym), 1 P, P(7) or P(9), 243], −32.7 [t (asym), 1 P, P(8), 232/251].

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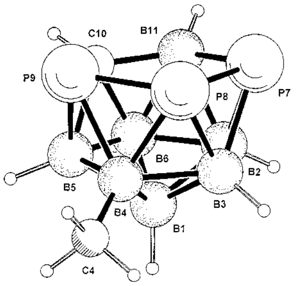


Figure 1. RMP2(fc)/6-31G* optimized geometry for 4-CH_3-**3**. Selected calculated bond distances and angles: mean B(1)−B 1.769 Å, mean B−B(lower pentagon) 1.803 Å, mean P−B(lower pentagon) 2.071 Å, P(7)−P(8) 2.241 Å, P(8)−P(9) 2.218 Å; ∠P(7)−P(8)−P(9) 101.1°, ∠P(8)−P(9)−P(10) 101.1°, τ[P(9)−P(8)−P(7)−B(11)] −6.9°, τ[P(8)−P(7)−B(11)−C(10)] −0.1°.

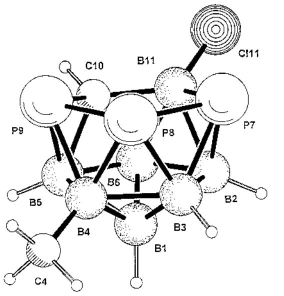
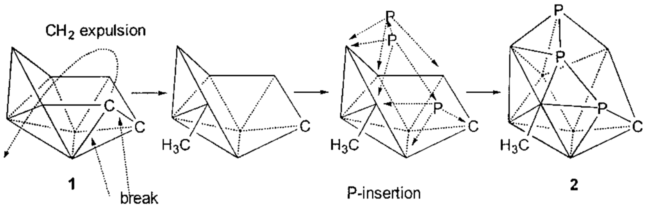


Figure 2. RMP2(fc)/6-31G* optimized geometry for 4-CH_3-11-Cl-**3**. Selected calculated bond distances and angles: mean B(1)−B 1.768 Å, mean B−B(lower pentagon) 1.801 Å, mean P−B(lower pentagon) 2.070 Å, P(7)−P(8) 2.243 Å, P(8)−P(9) 2.219 Å, B(11)−Cl 1.795 Å; ∠P(7)−P(8)−P(9) 101.3°, ∠P(8)−P(9)−P(10) 101.3°, τ[P(9)−P(8)−P(7)−B(11)] −6.9°, τ[P(8)−P(7)−B(11)−C(10)] −0.3°.

Scheme 1



followed by triple P-insertion into the 7-CH_3-$\mathbf{2}^{2-}$ intermediate thus formed, as outlined in Scheme 1 (extra hydrogens omitted for clarity; the vertexes of individual polyhedra denote BH units).

The X-ray diffraction studies on both substituted derivatives of **3**, 4-CH_3-**3** and 4-CH_3-11-Cl-**3**, led unfortunately to extensive disorder of the phosphorus positions. Nevertheless, in both cases, the structure can be unambiguously suggested on the basis of ^{11}B, ^{1}H, and ^{31}P NMR spectra.[12] The interpretation of [^{11}B−^{11}B]-COSY[13] correlation spectra and the results of $^{1}H\{^{11}B(selective)\}$ NMR spectroscopy[14] led to complete assignments of all ^{11}B and ^{1}H resonances to individual BH cluster vertexes. The $^{31}P\{^{1}H\}$ NMR spectra of 4-CH_3-**3** and 4-CH_3-11-Cl-**3** consist of two asymmetrical doublets and one asymmetrical triplet, which undoubtedly reveals the presence of three nonequivalent P-vertexes. Moreover, the geometries of the of 4-CH_3-**3** and 4-CH_3-11-Cl-**3** molecules were optimized at the RMP2(fc)/6-31G* level (see Figures 1 and 2), and the results of this optimization were used for GIAO-SCF/II//RMP2(fc)/6-31G* (level of theory// geometry) calculations of ^{11}B chemical shifts. All calculations used the Gaussian94 program package,[15] and the geometries were fully optimized first at the RHF/6-31G* level within the C_1 symmetry. According to second derivative analysis, carried out at the same level, both structures showed minima (NIMAG = 0). Final optimizations at RMP2(fc)/6-31G* included also the effect of electron correlation. The chemical shieldings were calculated at the SCF level, using the GIAO (gauge-invariant atomic orbital) method incorporated in the Gaussian94 and employed a II Huzinaga basis set[16] well-designed for the calculations of magnetic properties.[17] The calculations led in turn to good agreement between theoretical and experimental values,[12] which can be taken as additional proof of the structures proposed. The most striking features of both structures are the more or less planar open pentagonal belts (for some dihedral angles τ, see Figures 1 and 2) and the relatively modest deformations around the P-vertexes with respect to the strictly pentagonal angle of 108°, as demonstrated by the computed P−P−P bond angle of ca. 101° (cf. smaller X−P−X (X = P, C, B) angles (ca. 95°) found for the isostructural isomers of *nido*-$P_2C_2B_7H_9$).[6]

In conclusion, it should be noted that the synthesis of the triphosphamonocarbaboranes 4-CH_3-**3** and 4-CH_3-11-Cl-**3** outlined above provides smooth access to boron clusters that contain three identical other-than-carbon main-group elements in cluster positions. Moreover, the compounds are very stable analogues of tetracarbaboranes, namely, of *nido*-7,8,9,10-$C_4B_7H_{11}$, and of additional interest is the straightforward generation of a contiguous P−P−P−C string of heteroatoms in the open face of the borane skeleton. Also striking is the explicit trend for facile formation of P−P bonds and for incorporation of a maximum number of P-vertexes into the cluster area. Also of interest is the formation of the methylated $CH_3CB_7H_{12}$ monocarbaborane intermediate via unusual extrusion of the original cage CH_2 vertex into the exo-skeletal position. There is no doubt that the strategy of multiple phosphorus insertion demonstrated in this paper will be applicable even to other carborane and borane cages. The polyphosphacarboranes/boranes thus formed are expected to undergo further transformations, such as polyhedral contraction or metal insertion reactions, to generate varieties of structurally interesting skeletons containing a high number of other-than-carbon heteroatoms in the cage. We have been currently investigating these possibilities with the aim of extending the scope of cluster heteroborane chemistry.

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Supporting Information Available: Coordinates for the RMP2(fc)/6-31G* calculated structures of 4-CH_3-*nido*-7,8,9,10-$P_3CB_7H_7$ (4-CH_3-**3**) and 4-CH_3-11-Cl-*nido*-7,8,9,10-$P_3CB_7H_6$ (4-CH_3-11-Cl-**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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