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Systematic Syntheses and Structural Characterizations of Two Isomeric Phosphadicarbaboranes: 6-R-*arachno*-6,8,9-$PC_2B_7H_{11}$ and 6-R-*arachno*-6,5,7-$PC_2B_7H_{11}$. The First 10-Vertex Phosphadicarbaboranes

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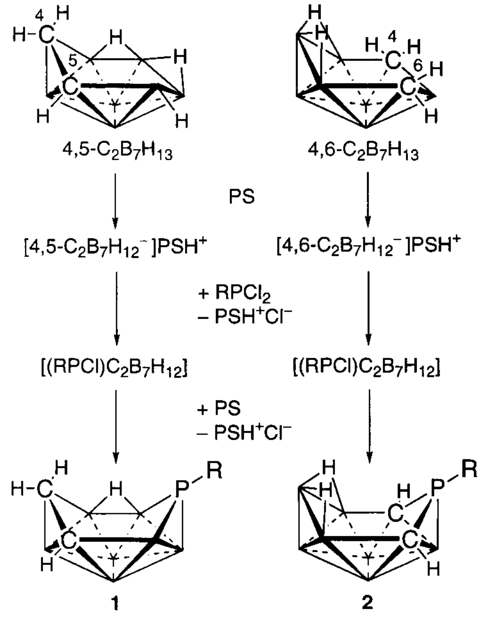
The development of high-yield methods for heteroatom insertion has been the critical step needed to enable the systematic syntheses of heteroatom−polyborane clusters. Recently, we reported a new, efficient method for the syntheses of thia- and phosphapolyborane clusters and applied this method to the synthesis of a range of new 11-vertex thia- and phosphaboranes, thia- and phosphadicarbaboranes, and the first thiaphosphaborane.[1] In this communication, we report the syntheses and structural characterizations of the two isomeric clusters, 6-R-*arachno*-6,8,9-$PC_2B_7H_{11}$ **1** (R = Ph **1a** or Me **1b**) and 6-Me-*arachno*-6,5,7-$PC_2B_7H_{11}$ **2**, which are the first examples of 10-vertex phosphadicarbaboranes.

As outlined in Scheme 1, **1a** and **1b** are synthesized from adjacent-carbon *arachno*-4,5-$C_2B_7H_{13}$,[2] while **2** is derived from the nonadjacent-carbon *arachno*-4,6-$C_2B_7H_{13}$.[3] Both syntheses involve initial deprotonation of the starting dicarbaboranes with Proton Sponge (1,8-bis(dimethylamino)naphthalene), followed by the reaction of the anions with $RPCl_2$ to produce metathesis products. These intermediates were not isolated, but structures in which the RClP groups are substituted at either terminal or bridging sites on the original dicarbaborane frameworks can be reasonably proposed. Further reaction with an additional 1 equiv of Proton Sponge induces dehydrohalogenation and cage insertion of the RP group to yield the final phoshadicarbaborane products which were obtained in 68% (**1a**), 49% (**1b**), and 50% (**2**) isolated yields as air-sensitive oils. Their compositions are established by both elemental analyses and mass spectrometry.

The ^{11}B NMR spectra of **1a** and **2** are presented in Figure 1, and the observed spectral patterns are in agreement with C_1 and C_s cage symmetries, respectively, for the two isomers. The resonances at −12.0 and −19.7 ppm in the spectrum of **1a** both show fine structure characteristic of bridge-hydrogen coupling. The ^1H NMR spectrum of **1a** (and **1b**) shows, in addition to the phenyl (methyl **1b**) and seven terminal BH resonances, an intensity-one bridge-hydrogen resonance and three cage-CH resonances with one of the CH resonances at a high-field shift (−0.72 ppm **1a**, −0.90 ppm **1b**) characteristic of an *endo*-hydrogen of a cage-CH_2 group. The ^1H NMR spectrum of **2** exhibits a methyl resonance and the terminal BH resonances in their expected 1:1:1:2:2 ratios, along with intensity-two bridge-hydrogen and cage-CH resonances. The room temperature $^{13}C\{^1H\}$ NMR spectrum of **2** contains a single resonance with a multiplet structure arising from both boron and phosphorus coupling, but when recorded at temperatures (−83 °C) low enough to thermally decouple ^{11}B coupling,[4] the resonance resolves into a sharp doublet, $J_{^{13}C-^{31}P} = 52$ Hz, consistent with the carbon and phosphorus being in adjacent positions in the cage framework. The proton-coupled ^{13}C NMR spectrum of **1a** (and **1b**) shows the expected two cage-carbon resonances, one of which appears as an apparent triplet and the other as a doublet indicating CH_2 and CH cage units, respectively. In their $^{13}C\{^1H\}$ NMR spectra, the CH_2 resonances of **1a** and **1b** resolve, even at room temperature, into doublets with $J_{^{13}C-^{31}P} = 49$ (**1a**) and 43 Hz (**1b**).

Scheme 1. Reaction Sequences Leading to the Formation of **1** and **2**



According to cluster electron counting methods,[5] **1** and **2** have 26 skeletal electrons and should adopt 10-vertex *arachno* geometries based on an icosahedron missing two vertices, but a number of isomeric structures are possible based on this framework. Since the compounds are oils, crystallographic determinations have not been possible. However, the structures of both isomers have been firmly established using DFT/GIAO/NMR calculations (Gaussian 94) in conjunction with two-dimensional COSY $^{11}B-^{11}B$ NMR studies.[6] Density functional theory (DFT) was first used to obtain optimized molecular geometries and

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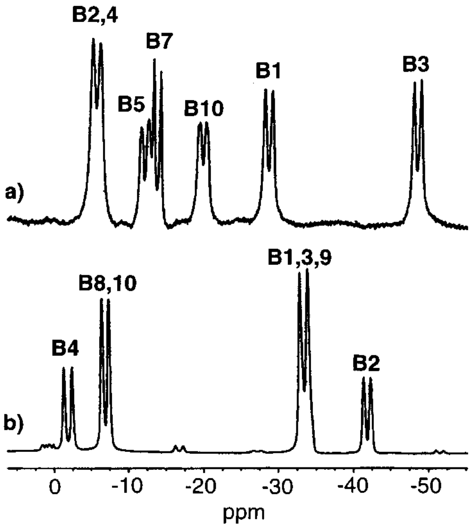


Figure 1. ^{11}B NMR spectra (160.5 MHz) of (a) **1a** and (b) **2**.

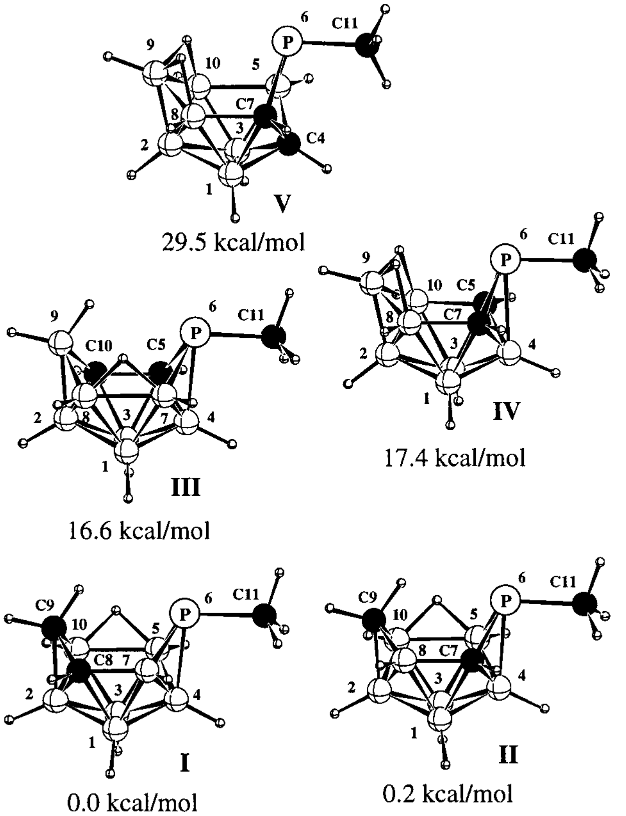
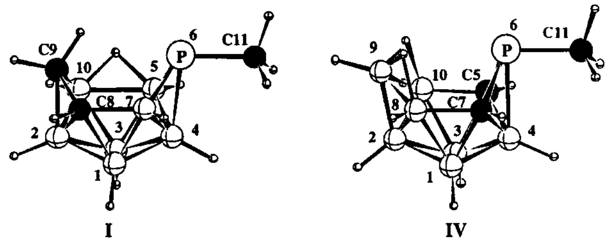


Figure 2. DFT calculated optimized geometries and relative energies (B3LYP/6-311G*//B3LYP/6-311G*) for isomeric *arachno*-RPC$_2$B$_7$H$_{11}$ structures.



1a *exp*	1b *exp*	I *cal*	2 *exp*	IV *cal*
^{11}B NMR			*^{11}B NMR*	
-5.5 (B2,4)	-6.0 (B2)	-4.8 (B2)	-1.9 (B4)	-3.8 (B4)
	-6.7 (B4)	-6.6 (B4)	-6.9 (B8,10)	-8.9 (B8,10)
-12.0 (B5)	-11.1 (B5)	-10.7 (B5)		
-13.6 (B7)	-12.2 (B7)	-11.0 (B7)	-33.5 (B1,3,9)	-34.6 (B1,3)
-19.7 (B10)	-19.9 (B10)	-22.1 (B10)		-36.5 (B9)
-28.5 (B1)	-28.7 (B1)	-30.3 (B1)		
-48.4 (B3)	-48.8 (B3)	-50.4 (B3)	-41.9 (B2)	-46.0 (B2)
^{13}C NMR			*^{13}C NMR*	
	7.3 (C11)	11.4 (C11)	3.0 (C5,7)	8.0 (C5,7)
13.2 (C9)	12.8 (C9)	14.4 (C9)	18.3 (C11)	22.8 (C11)
25.2 (C8)	25.5 (C8)	31.5 (C8)		
^{31}P NMR			*^{31}P NMR*	
-162.3	-184.3	-169.5	-65.2	-55.0

Figure 3. Comparisons of the experimental NMR shifts (ppm) and assignments for compounds **1** and **2** (160.5 MHz ^{11}B NMR; 125.8 MHz ^{13}C NMR, 25 °C; and 145.8 MHz ^{31}P NMR) with the DFT/GIAO calculated values (B3LYP/6-311G*//B3LYP/6-311G*) for structures **I** and **IV**.

relative energies for the possible isomers shown in Figure 2 that could result from phosphorus insertion at the different positions on the open face of the two dicarbaboranes. Gauge independent atomic orbital (GIAO) NMR shift calculations were then used to predict the chemical shifts and assignments for each structure. As shown in Figure 3, the calculated values at the B3LYP/6-311G*//B3LYP/6-311G* level for the 6-Me-*arachno*-6,8,9-PC$_2$B$_7$H$_{11}$ (**I**) and 6-Me-*arachno*-6,5,7-PC$_2$B$_7$H$_{11}$ (**IV**) structures are in excellent agreement with the experimentally determined ^{11}B, ^{13}C, and ^{31}P chemical shifts and the ^{11}B assignments (from 2D ^{11}B−^{11}B COSY experiments) for isomers **1** and **2**. One unanticipated result of the spectroscopic and structural analyses is the fact that the CH$_2$ carbon (C9) of compound **1** exhibits strong coupling to the phosphorus, even though these two atoms are not in adjacent cage positions.[7]

A comparison of the relative energies of the isomers in Figure 2 reveals that **I** is thermodynamically favored, with **IV** at considerably higher energy. This difference in energy is in agreement with the well-known tendency for electron-rich elements to favor lower coordinate vertices on the open faces of polyhedral clusters.[8] Thus, in **I** (and **1**) the phosphorus and one carbon are situated in the low-coordinate 6,9 cage positions, whereas in **IV** (and **2**) one of these sites is occupied by a boron. The fact that a higher energy isomer such as **2** can be synthesized using the Proton Sponge initiated in situ dehydrohalogenation method again illustrates the advantages of this mild reaction method for achieving kinetic products.

We will report in future publications our explorations of the chemical properties of these phosphadicarbaboranes, including their use for the syntheses of new families of both smaller-cage phosphadicarbaboranes and metallaphosphadicarbaborane complexes.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: Characterization data and descriptions of the syntheses of compounds **1a**, **1b**, and **2**. Tables listing Cartesian coordinates and bond distances for the optimized geometries at the B3LYP/6-311G* level for **I**−**V**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) We also previously reported a long-range coupling between phosphorus and carbon cage atoms in 6-R′-3,4-R$_2$-6,3,4-*nido*-PC$_2$B$_4$H$_4$; see: Keller, W.; Barnum, B. A.; Bausch, J. W.; Sneddon, L. G. *Inorg. Chem.* **1993**, *32*, 5058−5066.

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