Synthesis and an ab Initio/IGLO/NMR Study of 7-Vertex *nido*-Phosphacarboranes: *nido*-6-R′-3,4-R$_2$-6,3,4-PC$_2$B$_4$H$_4$

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The reactions of $Na^+Li^+[$*nido*-$R_2C_2B_4H_4]^{2-}$ (R = Et, Bz) with $R'PCl_2$ (R′ = Ph, *t*-Bu, Me) have been found to yield new phosphacarboranes **1–6** of the general formula $R'R_2PC_2B_4H_4$. Their observed spectroscopic data and the results of an ab initio/IGLO/NMR study indicate that these compounds have open-cage 7-vertex *nido*-6-R′-3,4-R$_2$-6,3,4-PC$_2$B$_4$H$_4$ geometries, based on a dodecahedron missing one five-connected vertex, with the carbon and phosphorus atoms occupying positions on the open face. The reaction of *nido*-6-Ph-3,4-Et$_2$-6,3,4-PC$_2$B$_4$H$_4$, **1**, with lithium metal or sodium naphthalenide in THF gives quantitative reduction of the phosphacarborane to form *arachno*-PhEt$_2$PC$_2$B$_4$H$_4$$^{2-}$, **1**$^{2-}$. Subsequent reaction of **1**$^{2-}$ with PhPCl$_2$ gives a product that the NMR and mass spectral evidence suggest is the diphosphacarborane *arachno*-Ph$_2$Et$_2$P$_2$C$_2$B$_4$H$_4$. Comparison of the spectral data obtained for *arachno*-PhEt$_2$PC$_2$B$_4$H$_4$$^{2-}$ and *arachno*-Ph$_2$Et$_2$P$_2$C$_2$B$_4$H$_4$ with the results of ab initio/IGLO/NMR calculations support 7-vertex and 8-vertex arachno geometries, respectively, for these cage systems.

Introduction

Hosmane and co-workers recently reported[2] the synthesis of a new phosphacarborane, *closo*-1-[2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]-1-P-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$, from the reaction of $Na^+(THF)$-$Li^+[$*nido*-2,3-$(SiMe_3)_2C_2B_4H_4]^{2-}$ with 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$PCl$_2$ and assigned, on the basis of the spectroscopic data, a closed cage geometry to this compound. In contrast to these results, we report in this paper that the reactions of $Na^+Li^+[$*nido*-$R_2C_2B_4H_4]^{2-}$ (R = Et, Bz) with $R'PCl_2$ (R′ = Ph, *t*-Bu, Me) apparently proceed in a different fashion to yield phosphacarboranes **1–6** of a similar general formula but having spectral data quite different than those of Hosmane's compound. Furthermore, these data and the results of an ab initio/IGLO/NMR study strongly support open-cage 7-vertex *nido*-6-R′-3,4-R$_2$-6,3,4-PC$_2$B$_4$H$_4$ geometries, based on a dodecahedron missing one five-connected vertex.

Experimental Section

All experimental manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.[3]

Materials. Solutions of the lithium–sodium double salt of the carborane dianion *nido*-2,3-R$_2$C$_2$B$_4$H$_4$$^{2-}$ were prepared by a procedure similar to that described by Hosmane.[4] The dichlorophenylphosphine and the 1.6 M solution of *n*-butyllithium (*n*-BuLi) in hexanes were obtained from Aldrich and used as received. NaH (Aldrich) in mineral oil dispersion was washed repeatedly with dry hexane before use. AlCl$_3$ (Aldrich) was sublimed before use. The *tert*-butyldichlorophosphine (used as received) and methyldichlorophosphine (distilled before use) were obtained from Strem Chemicals. Tetrahydrofuran (THF) and pentane were freshly distilled from sodium/benzophenone. Methylene chloride was dried over P$_2$O$_5$ and stored over molecular sieves prior to distillation.

Physical Measurements. ^{11}B NMR spectra at 160.5 MHz, ^{13}C NMR spectra at 125.7 MHz, and ^{1}H NMR spectra at 500 MHz were obtained on a Bruker AM-500 spectrometer equipped with the appropriate decoupling accessories. ^{11}B NMR spectra at 64.2 MHz, ^{13}C NMR spectra at 50.3 MHz, ^{31}P NMR spectra at 81.0 MHz, and ^{1}H NMR spectra at 200 MHz were obtained on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts were referenced to external BF$_3$·O(C$_2$H$_5$)$_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All ^{1}H and ^{13}C chemical shifts were measured relative to the lock solvents (C$_6$D$_6$, CD$_2$Cl$_2$, THF-*d*$_8$) and then referenced to (CH$_3$)$_4$Si (0.0 ppm). All ^{31}P chemical shifts were measured relative to external 85% H$_3$PO$_4$ (0.0 ppm) with a negative sign indicating an upfield shift. NMR data are summarized in Table I.

High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. Elemental analyses were obtained from Galbraith Laboratories Inc., Knoxville, TN.

Reaction of $Li^+Na^+[$*nido*-2,3-$Et_2C_2B_4H_4]^{2-}$ with PhPCl$_2$. To a 100-mL round-bottom two-neck flask equipped with a stirbar, high-vacuum stopcock and a rubber septum was added 0.91 mmol of *n*-BuLi (0.57 mL of a 1.6 M hexane solution). The flask was attached to the vacuum line, and the hexanes were removed at 0 °C. THF (~10 mL) was condensed into the flask at −196 °C, and the contents were then allowed to warm to 0 °C. A solution of $Na^+[$*nido*-2,3-$Et_2C_2B_4H_5]^-$ was prepared by the reaction of *nido*-2,3-Et$_2$C$_2$B$_4$H$_6$ (0.92 mmol, 0.12 g) with excess NaH in ~15 mL of THF. The solution was filtered and then added slowly via syringe to the flask containing the *n*-BuLi solution in THF. After being stirred for 2 h at 0 °C, the solution turned an olive color. At this point, the reaction mixture was cooled at −78 °C and 0.156 g (0.92 mmol, 0.125 mL) of PhPCl$_2$ was syringed into the flask, resulting in a color change to light green. The reaction was warmed slowly to room temperature and stirred for 14 h resulting in a yellow cloudy solution. The flask was attached to the vacuum line, and the volatile components were evaporated at room temperature. Methylene chloride (~40 mL) was condensed into the flask at −196 °C, and the contents were allowed to warm to room temperature. Under an inert atmosphere, the reaction mixture was filtered two times to remove NaCl and LiCl. After the volatile components were vacuum evaporated, distillation at 84 °C under high vacuum yielded 57% (0.118 g, 0.5 mmol) of pure colorless *nido*-6-Ph-3,4-Et$_2$-6,3,4-PC$_2$B$_4$H$_4$, **1**. Data, for **1** are as follows. Mp ~−88 °C. Anal. Calc: C, 60.69; P, 13.04; B, 18.21; H, 8.06. Found: C, 60.87; P, 13.35; B, 16.55; H, 8.00. Exact mass: calc, *m/e* 238.1597; found, *m/e* 238.1580. IR (NaCl): 3070 (w), 3050 (w), 2965 (s), 2930 (s), 2870 (m), 2600 (s, sh), 2560 (s), 1725 (w, br), 1650 (w, br), 1580 (w), 1480 (m), 1450 (m), 1430 (s), 1380 (m), 1330 (w), 1320 (w), 1280 (w), 1260 (w), 1180 (w), 1150 (w), 1130 (w), 1090 (m), 1060 (m), 1025 (m), 1000 (m), 980 (m), 940 (s), 905 (m, br), 840 (m), 820 (w), 800 (w, br), 735 (s), 695 (s, sh), 690 (s) cm^{-1}.

Reaction of $Li^+Na^+[$*nido*-2,3-$Bz_2C_2B_4H_4]^{2-}$ with PhPCl$_2$. A solution of the carborane dianion was prepared in the manner described for **1**, by addition of 1.01 mmol of $Na^+[$*nido*-2,3-$Bz_2C_2B_4H_5]^-$ in 15 mL of THF to 1.01 mmol of *n*-BuLi dissolved in 10 mL of THF. After being stirred for 2 h at 0 °C, the reaction mixture was cooled at −78 °C and 0.13 mL

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

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0020-1669/93/1332-5058$04.00/0

Table I. NMR Data

compd	nucl	δ, ppm (m, assgn, *J*, Hz)
nido-6-Ph-3,4-Et$_2$-6,3,4-PC$_2$B$_4$H$_4$^{a} (**1**)	^{11}B^b	27.2 (d, B2, J_{BH} 172), –5.1 (d, B5,7, J_{BH} 154), –5.9 (d, B1, J_{BH} 130)
	^{1}H^c	7.5–7.35 (m, phenyl), 2.62 (m, CH$_2$), 1.25 (t, CH$_3$, J_{HH} 7.0)
	^{1}H{^{11}B}^{d}	5.38 (s, B2-H), 3.15 (d, B5,7-H, J_{PH} 10), 1.72 (d, B1-H, J_{PH} ~7)
	^{13}C (–82 °C)^e	151.8 (d, cage C, $^2J_{CP}$ 37), 139.5 (d, ipso C, J_{CP} 47), 130.7 (d, phenyl C, J_{CP} 17), 128.4 (s, phenyl C), 127.6 (d, phenyl C, J_{CP} 5), 25.2 (s, *C*H$_2$CH$_3$), 13.6 (s, CH$_2$*C*H$_3$)
	^{31}P^f	63.6
nido-6-Ph-3,4-Bz$_2$-6,3,4-PC$_2$B$_4$H$_4$^{a} (**2**)	^{11}B^b	28.7 (d, B2, J_{BH} 146), –4.1 (d, B5,7, J_{BH} 190), –6.1 (d, B1)^g
	^{1}H^d	7.5–7.3 (m, phenyl, benzyl), 4.0 (m, CH$_2$)
	^{1}H{^{11}B}^{d}	5.47 (s, B2-H), 3.02 (d, B5,7-H, J_{PH} 8), 1.84 (d, B1–H, J_{PH} ~4)
	^{13}C (–80 °C)^e	149.0 (d, cage C, $^2J_{PC}$ 38), 139.5 (d, phenyl ipso C, $^2J_{CP}$ 25), 138.5–124.8 (m, phenyl, benzyl), 38.35 (s, CH$_2$)
	^{31}P^f	71.2
nido-6-*t*-Bu-3,4-Et$_2$-6,3,4-PC$_2$B$_4$H$_4$^{a} (**3**)	^{11}B^h	23.3 (d, B2, J_{BH} 157), –4.8 (d, B5,7 and B1, J_{BH} 153)
	^{1}H^d	2.65–2.3 (m, CH$_2$), 1.22 (d, C(C*H*$_3$)$_3$, J_{HH} 133), 1.19 (t, CH$_2$C*H*$_3$, J_{HH} 7.5)
	^{1}H{^{11}B}^{d}	5.2 (s, B2–H), 2.79 (d, B5,7–H, J_{PH} 11), 1.57 (d, B1–H)^g
	^{13}C (–80 °C)^e	151.0 (d, cage C, $^2J_{CP}$ 32), 34.7 (d, *C*(CH$_3$)$_3$, J_{CP} 38), 30.0 (d, C(*C*H$_3$)$_3$, $^2J_{CP}$ 14), 25.3 (s, *C*H$_2$CH$_3$), 13.6 (s, CH$_2$*C*H$_3$)
	^{31}P^f	110.3
nido-6-*t*-Bu-3,4-Bz$_2$-6,3,4-PC$_2$B$_4$H$_4$^{a} (**4**)	^{11}B^h	24.8 (d, B2, J_{BH} 168), –3.9 (d, B5,7 and B1, J_{BH} 143)
	^{1}H^d	7.5–7.0 (m, benzyl), 3.87 (m, CH$_2$), 1.3 (s, CH$_3$)
	^{1}H{^{11}B}^{d}	5.2 (s, B2–H), 2.7 (d, B5,7–H, J_{PH} 10), 1.7 (d, B1–H)^g
	^{13}C (25 °C)^e	149 (cage C), 129.5–126.0 (m, benzyl), 39.3 (s, CH$_2$), 32.7 (d, *C*(CH$_3$)$_3$, J_{CP} 42), 30.8 (d, (C(*C*H$_3$)$_3$, $^2J_{CP}$ 15)
	^{31}P^f	112.9
nido-6-Me-3,4-Et$_2$-6,3,4-PC$_2$B$_4$H$_4$^{a} (**5**)	^{11}B^h	28.3 (d, B2, J_{BH} 152), –4.7 (d, B5,7 and B1, J_{BH} 158)
	^{31}P^f	16.4
nido-6-Me-3,4-Bz$_2$-6,3,4-PC$_2$B$_4$H$_4$^{a} (**6**)	^{11}B^g	29.5 (d, B2, J_{BH} 154), –3.8 (d, B5,7 and B1, J_{BH} 165)
	^{31}P^f	16.4
(Li$^+$)$_2$PhEt$_2$PC$_2$B$_4$H$_4$$^{2-\,i}$ (**1**$^{2-}$)	^{11}B^h	3.8 (br), –9.5 (br), –27.0 (br), –46.8 (d, J_{BH} 147)
	^{31}P^f	–246.9

^{a} CD$_2$Cl$_2$ solvent. ^{b} 160.5 MHz. ^{c} 500.0 MHz. ^{d} 200.1 MHz. ^{e} 50.3 MHz, ^{1}H spin-decoupled. ^{f} 81.0 MHz. ^{g} Coupling constant could not be accurately measured due to overlapping resonances. ^{h} 64.2 MHz. ^{i} THF-d_8 solvent.

(~0.96 mmol) of PhPCl$_2$ was syringed into the flask causing a color change from deep red to light green. Further reaction (room temperature, 14 h) and workup as described for **1** gave 0.23 g (0.63 mmol, 63% yield) of *nido*-6-Ph-3,4-Bz$_2$-6,3,4-PC$_2$B$_4$H$_4$, **2**. In cases where **2** was contaminated with *nido*-2,3-Bz$_2$C$_2$B$_4$H$_6$ carborane, purification was achieved by addition of NaH to a pentane solution of the products, followed by filtration of the resulting Na$^+$[*nido*-2,3-Bz$_2$C$_2$B$_4$H$_5$]$^-$ salt and removal of the solvent from the filtrate by vacuum evaporation. Alternatively, purification of **2** may be achieved by vacuum distillation. Data for **2** are as follows. Exact mass: calc, *m/e* 362.1910; found, *m/e* 362.1935. IR (NaCl): 3065 (m), 3030 (m), 2960 (s, br), 2875 (s), 2580 (m, br), 2400 (m, br), 2305 (w), 2205 (w), 1950 (w, br), 1885 (w, br), 1810 (w, br), 1755 (w), 1665 (w), 1605 (m), 1495 (w), 1455 (w), 1440 (w), 1420 (w), 1350 (w), 1290 (w, br), 1085 (m), 1035 (w), 975 (m), 920 (w), 810 (w), 735 (m), 720 (m) cm^{-1}.

Reaction of Li$^+$Na$^+$[*nido*-2,3-Et$_2$C$_2$B$_4$H$_4$]$^{2-}$ with *t*-BuPCl$_2$. A solution of the carborane dianion was prepared in the manner described for **1**, by addition of 2.37 mmol of Na$^+$[*nido*-2,3-Et$_2$C$_2$B$_4$H$_5$]$^-$ in 15 mL of THF to 2.40 mmol of *n*-BuLi dissolved in 10 mL of THF. After being stirred for 2 h at 0 °C, the reaction mixture was cooled at –78 °C and a THF solution of excess *tert*-butyldichlorophosphine (4.3 mmol, 0.68 g, in 8 mL of THF) was syringed into the flask. Further reaction (room temperature, 14 h) and workup as described for **1** gave 0.34 g (1.5 mmol, 65% yield) of a pale yellow oil, *nido*-6-*t*-Bu-3,4-Et$_2$-6,3,4-PC$_2$B$_4$H$_4$, **3**. Data for **3** are as follows. Exact mass: calc, *m/e* 218.1910; found, *m/e* 218.1923. IR (NaCl): 2960 (s), 2935 (s), 2900 (s), 2875 (s), 2605 (s, sh), 2565 (s), 2400 (w), 2380 (w), 2360 (w), 1740 (vw, br), 1640 (w), 1460 (s), 1400 (s, sh), 1385 (s, sh), 1367 (s), 1340 (s, br), 1265 (s, br), 1208 (m, sh), 1175 (m), 1155 (m, sh), 1125 (m), 1065 (m), 1030 (m), 945 (s), 910 (m), 850 (m), 815 (m, br), 745 (w), 730 (w, sh), 690 (w, br) cm^{-1}.

Reaction of Li$^+$Na$^+$[*nido*-2,3-Bz$_2$C$_2$B$_4$H$_4$]$^{2-}$ with *t*-BuPCl$_2$. A solution of the carborane dianion was prepared in the manner described for **1**, by addition of 0.98 mmol of Na$^+$[*nido*-2,3-Bz$_2$C$_2$B$_4$H$_5$]$^-$ in 15 mL of THF to 0.99 mmol of *n*-BuLi dissolved in 10 mL of THF. After being stirred for 2 h at 0 °C, the solution turned deep red. At this point, the reaction mixture was cooled at –78 °C and a solution of excess *tert*-butyldichlorophosphine (1.09 mmol, 0.173 g in 5 mL of THF) was syringed into the flask. Further reaction (room temperature, 12 h) and workup as described for **1** gave 0.15 g (0.43 mmol, 44% yield) of a yellow oil, *nido*-6-*t*-Bu-3,4-Bz$_2$-6,3,4-PC$_2$B$_4$H$_4$, **4**. Data for **4** are as follows. Exact mass: calc, *m/e* 342.2223; found, *m/e* 342.2222. IR (NaCl): 3090 (m), 3070 (m), 3030 (s), 2960 (s), 2930 (s), 2900 (s, sh), 2860 (s), 2605 (s, sh), 2570 (s), 2540 (m, sh), 2400 (m, br), 2380 (m), 1945 (w, br), 1880 (w, br), 1805 (w, br), 1730 (w, br), 1605 (s), 1585 (m), 1495 (s), 1475 (m, sh), 1465 (s), 1415 (m, br), 1395 (m, br), 1375 (m), 1310 (m, sh), 1180 (m, br), 1080 (m), 1030 (m), 1025 (m, sh), 985 (m, sh), 910 (w, br), 845 (w), 815 (w, br), 730 (m, br), 700 (s) cm^{-1}.

Reaction of Li$^+$Na$^+$[*nido*-2,3-Et$_2$C$_2$B$_4$H$_4$]$^{2-}$ with MePCl$_2$. A solution of the carborane dianion was prepared in the manner described for **1**, by addition of 0.63 mmol of Na$^+$[*nido*-2,3-Et$_2$C$_2$B$_4$H$_5$]$^-$ in 15 mL of THF to 0.64 mmol of *n*-BuLi dissolved in 10 mL of THF. After being stirred for 2 h at 0 °C, the reaction mixture was cooled at –196 °C and an excess (~2.0 mmol, 0.2 g) of MePCl$_2$ was condensed into the reaction flask. Further reaction (–78 °C, 14 h) and workup as described for **1** gave a yellow, thermally sensitive oil, which, according to the ^{11}B NMR spectrum, was predominantly *nido*-6-Me-3,4-Et$_2$-6,3,4-PC$_2$B$_4$H$_4$, **5**. Accurate yields could not be determined due to decomposition of the product. Data for **5** are as follows. Exact mass: calc, *m/e* 176.1440; found, *m/e* 176.1452.

Reaction of Li$^+$Na$^+$[*nido*-2,3-Bz$_2$C$_2$B$_4$H$_4$]$^{2-}$ with MePCl$_2$. A solution of the carborane dianion was prepared in the manner described for **1**, by addition of 0.97 mmol of Na$^+$[*nido*-2,3-Bz$_2$C$_2$B$_4$H$_5$]$^-$ in 15 mL of THF to 0.99 mmol of *n*-BuLi dissolved in 10 mL of THF. After being stirred for 2 h at 0 °C, the solution turned deep red. At this point, the reaction mixture was cooled at –196 °C and an excess of MePCl$_2$ (~2.0 mmol, 0.2 g) was condensed into the reaction flask. Further reaction (–78 °C, 14 h) and workup as described for **1** gave a thermally-sensitive yellow oil, which, according to its ^{11}B NMR spectrum, was predominantly *nido*-6-Me-3,4-Bz$_2$-6,3,4-PC$_2$B$_4$H$_4$, **6**. Accurate yields could not be determined due to decomposition of the product. Data for **6** are as follows. Exact mass: calc, *m/e* 300.1753; found, *m/e* 300.1716.

Attempted Reaction of *nido*-6-Ph-3,4-Et$_2$-6,3,4-PC$_2$B$_4$H$_4$, 1, with AlCl$_3$. A 100-mL round-bottom three-neck flask containing a freshly filtered methylene chloride solution of **1** (~0.9 mmol, in 30 mL), prepared as described above, was brought to –78 °C, and an excess of freshly sublimed AlCl$_3$ (1.4 mmol, 0.18 g) then added over 20 min from a charged side arm. The reaction was allowed to warm to room temperature over 2 h. A ^{11}B NMR spectrum taken at this time showed no reaction. The reaction was left stirring at room temperature for 24 h and then heated at reflux for an additional 24 h. ^{11}B NMR spectra taken at these times revealed no evidence of reaction.

Reduction of *nido*-6-Ph-3,4-Et$_2$-6,3,4-PC$_2$B$_4$H$_4$, 1, with Li^0 or Sodium Naphthalenide. To an evacuated 50-mL round-bottom two-neck flask containing clean lithium shavings (3.7 mmol, 0.026 g) and equipped with an air-free filter tube connected to a 3-neck 100-mL round-bottom flask containing a stirbar, high-vacuum stopcock, and a rubber septum was added a 20-mL solution containing 0.162 g (0.68 mmol) of *nido*-6-Ph-3,4-Et_2-6,3,4-$PC_2B_4H_4$, **1**, in THF. The flask was sonicated in a Branson 2200 ultrasonic cleaning bath for 3 h, with the temperature maintained below 40 °C, resulting in a clear orange solution. The reaction mixture was filtered through the side arm into the 100-mL flask to give a solution containing $PhEt_2PC_2B_4H_4^{2-}$, $\mathbf{1}^{2-}$.

Alternatively, a solution of freshly prepared sodium naphthalenide (prepared from 3.36 mmol of naphthalene and ~5 mmol of Na in 30 mL of THF) was added to a stirring solution of *nido*-6-Ph-3,4-Et_2-6,3,4-$PC_2B_4H_4$, **1** (1.684 mmol, 0.4 g, in 20 mL of THF), at −78 °C. The reaction mixture was allowed to warm slowly to room temperature over 2 h, resulting in a yellow solution. A ^{11}B NMR spectrum taken at this time was identical to that obtained from the lithium reduction described above.

Reaction of $\mathbf{1}^{2-}$ with $PhPCl_2$. A flask containing a THF solution of freshly filtered $(Li^+)_2[PhEt_2PC_2B_4H_4^{2-}]$ (~0.6 mmol, in 30 mL) (or $(Na^+)_2[PhEt_2PC_2B_4H_4^{2-}]$), prepared as described above, was brought to −78 °C, and an excess of $PhPCl_2$ (0.68 mmol, 0.19 g) was added by syringe. The reaction was allowed to warm slowly to room temperature over 14 h, resulting in a pale yellow solution. The flask was attached to the vacuum line, and the volatile components were removed at room temperature. Methylene chloride (~40 mL) was then condensed into the flask at −196 °C, and the contents were allowed to warm to room temperature. Under an inert atmosphere, the reaction mixture was filtered two times to remove LiCl or NaCl. Vacuum evaporation of the volatile components left behind a deep yellow oil which contained a mixture of **1** and $Ph_2Et_2P_2C_2B_4H_4$. In addition to resonances attributed to **1**, the ^{11}B NMR spectrum contained three doublets in a 1:2:1 ratio at −38.6, −20.7, and −0.5 ppm, respectively. Exact mass for $Ph_2Et_2P_2C_2B_4H_4$: calc, *m/e* 346.1725; found, *m/e* 346.1744.

Computational Methods. The phosphacarborane cage systems were investigated by employing the combined ab initio[5]/IGLO[6]/NMR method.[7] The geometries were fully optimized within the specified symmetry constraints by employing the GAUSSIAN90 program (using the standard basis sets included) on a Silicon Graphics International IRIS 4D/440VGX computer. A vibrational frequency analysis was carried out on each optimized geometry. A true minimum was found for each structure (i.e. possessing no imaginary frequencies) unless otherwise noted. The NMR chemical shifts were calculated using the IGLO program employing the basis sets in Chart I.

B_2H_6 is the primary reference for the ^{11}B NMR chemical shifts, and the δ values were converted to the $BF_3{\cdot}O(C_2H_5)_2$ scale using the experimental value of $\delta(B_2H_6) = 16.6$ ppm.[8] PH_3 is the primary reference for the ^{31}P NMR chemical shifts, and the δ values were converted to the H_3PO_4 scale using the experimental value of $\delta(PH_3) = -240$ ppm.[9]

Calculations that would include the exopolyhedral substituents (Et, Ph, Bz) on **1**–**6** were not possible, since such calculations would be too large for our available computational resources. Thus, only the all-H substituted molecules and some P- and C-methyl substituted derivatives were employed for the calculations.

Chart I

Basis DZ	C,B	7s3p	contracted to [4111,21]
	P	10s6p	contracted to [511111,3111]
	H	3s	contracted to [21]
Basis II'	C	9s5p1d	contracted to [51111,2111,1] d-exponent 1.0
	B	9s5p1d	contracted to [51111,2111,1] d-exponent 0.5
	P	11s7p2d	contracted to [5111111,211111,11] d-exponents 0.35, 1.4
	H	same as DZ	
Basis II	C	9s5p1d	contracted to [51111,2111,1] d-exponent 1.0
	B	9s5p1d	contracted to [51111,2111,1] d-exponent 0.5
	P	11s7p2d	contracted to [5111111,211111,11] d-exponents 0.35, 1.4
	H	5s1p	contracted to [311,1] p-coefficient 0.65

Results and Discussion

Synthesis and Spectral Characterizations. Both $Li^+Na^+[nido\text{-}Et_2C_2B_4H_4]^{2-}$ and $Li^+Na^+[nido\text{-}Bz_2C_2B_4H_4]^{2-}$ react readily with $R'PCl_2$ reagents to give the new phosphacarboranes indicated in eqs 1 and 2.

$$Li^+Na^+[nido\text{-}Et_2C_2B_4H_4]^{2-} + R'PCl_2 \rightarrow$$
$$nido\text{-}6\text{-}R'\text{-}3,4\text{-}Et_2\text{-}6,3,4\text{-}PC_2B_4H_4 + LiCl + NaCl \quad (1)$$
$$R' = C_6H_5\ (\mathbf{1}),\ t\text{-}Bu\ (\mathbf{3}),\ CH_3\ (\mathbf{5})$$

$$Li^+Na^+[nido\text{-}Bz_2C_2B_4H_4]^{2-} + R'PCl_2 \rightarrow$$
$$nido\text{-}6\text{-}R'\text{-}3,4\text{-}Bz_2\text{-}6,3,4\text{-}PC_2B_4H_4 + LiCl + NaCl \quad (2)$$
$$R' = C_6H_5\ (\mathbf{2}),\ t\text{-}Bu\ (\mathbf{4}),\ CH_3\ (\mathbf{6})$$

Compounds **1**–**4** were isolated as pale-yellow, air-sensitive oily liquids, which are stable in aprotic organic solvents. Such solutions, however, decompose upon exposure to water within several weeks to boric acid. A neat sample of **1** sealed in an evacuated NMR tube neither rearranged nor decomposed upon heating for 5 min at 350 °C. The MeP derivatives, **5** and **6**, are also oils but are thermally unstable at room temperature, and as a result, complete spectroscopic characterizations were not possible. The $R'R_2PC_2B_4H_4$ compositions of **1**–**6** are supported by exact mass measurements and, in the case of **1**, by elemental analysis.

If, as found in other phosphaboranes and phosphacarboranes, such as $RPB_{11}H_{11}$ (R = Me,[10] Ph[11]), $RPB_{10}H_{12}$ (R = Me,[10,12] Ph[12]), 7,8- and 7,9-$RPCB_9H_{11}$ (R = Me,[13,14] Bz, Et, *i*-Pr[15]), and $Me_3N{\cdot}CB_{10}H_{10}PR$,[16] the RP unit is a 4-skeletal-electron donor, then a $R'R_2PC_2B_4H_4$ cage would be a nido 18 skeletal-electron system and would be expected, on the basis of simple skeletal electron counting rules,[17] to adopt an open-cage geometry based on a bisdisphenoid (the most spherical dodecahedron) missing one five-connected vertex. On the other hand, as mentioned earlier, Hosmane has proposed[2] that the RP unit in *closo*-1-[2,4,6-$(t\text{-}Bu)_3C_6H_2$]-1-P-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ functions as a two-electron donor with an exopolyhedral lone pair of electrons

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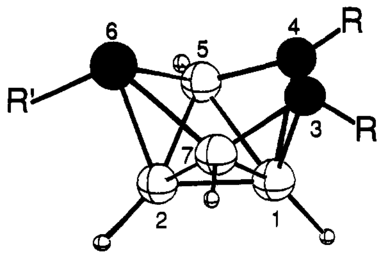

Figure 1. Proposed cage structure for *nido*-6-R'-3,4-R_2-6,3,4-$PC_2B_4H_4$ (R = Et, Bz; R' = Ph, *t*-Bu, Me).

and, as a result, he proposed that the compound adopts a closo configuration. Jutzi[18] has synthesized the phospha and arsa compounds 1-Cl-2,3-Me_2-1-E-2,3-$C_2B_9H_9$ (E = As, P). A structural determination of 1-Cl-2,3-Me_2-1-As-2,3-$C_2B_9H_9$ confirmed a distorted icosahedral cage geometry similar to those found[19] for other 12-vertex nido cage systems (i.e. the ClAs unit functions as a four-electron donor). However, Jutzi has also shown that these compounds react with $AlCl_3$ to form the complexes [1-Cl-2,3-Me_2-1-E-2,3-$C_2B_9H_9$][$AlCl_3$] and proposed that in these adducts the $AlCl_3$ coordinates to an exopolyhedral lone pair of electrons on the arsenic and phosphorus cage atoms, respectively. This suggests the possibility that in these complexes the RE·$AlCl_3$ (E = P, As) unit may then be serving as only a two-electron donor. Likewise, Hawthorne[20] originally proposed that the spectral data for the 3-R-3-As-1,2-$C_2B_9H_{11}$ arsacarboranes support closo rather than nido geometries with an exopolyhedral lone pair on the arsenic atom. In light of the possibility that the RP unit in **1**–**6** could be functioning as either a four- or a two-electron donor, a variety of structures, including two types of nido structures, a closo 7-vertex pentagonal bipyramid, and a "slipped" closo 7-vertex geometry were considered for **1**–**6**.

Until recently, 7-vertex carboranes having a formal nido-skeletal electron count were unknown; however, several such cage systems have now been isolated, including *nido*-3,4-$Et_2C_2B_5H_6^-$,[21] *nido*-6-Al(H)NEt_3-3,4-$Et_2C_2B_4H_4$,[22] *nido*-6-PMe_3CH_2-3,4-Et_2-$C_2B_5H_5$,[23] and *nido*-6-X-3-(Me_3Si)-4-Me-6,3,4-$SiC_2B_4H_5$ (X = H, Cl).[24] Structural studies of *nido*-3,4-$Et_2C_2B_5H_6^-$ and *nido*-6-PMe_3CH_2-3,4-$Et_2C_2B_5H_5$ have now confirmed the open-cage geometry predicted for this cluster class. The structure proposed in Figure 1 for **1**–**6** is based on these confirmed structures and is, in fact, consistent with both the spectroscopic data discussed below and with the ab initio/IGLO/NMR study presented in the next section.

The 160.5-MHz ^{11}B NMR spectra of **1**–**6** are similar, consisting of three resonances (as shown in Figure 2 for **1**) in a 1:2:1 area ratio, indicating C_s cage symmetry. The assignments are based on the ab initio/IGLO calculations discussed in detail in the next section. The shifts of these resonances, as well as the other NMR data (Table I) for **1**–**6**, are quite different from those observed[2] by Hosmane for *closo*-1-[2,4,6-(*t*-Bu)$_3C_6H_2$]-1-P-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ [15.85 (d, 2); 7.68 (d, 1); −16.63 ppm (d, 1)], leading to the conclusion that the latter compound and **1**–**6** must be of different structural types. The chemical shifts of the B2 (27.1 ppm) and B5,7 (−5.1 ppm) resonances for **1** are similar to those observed in the isoelectronic 7-vertex clusters, but the B1 resonance (−5.9 ppm for **1**) is highly deshielded compared to those in *nido*-3,4-$Et_2C_2B_4H_6^-$ (−21.3 ppm), *nido*-6-Al(H)NEt_3-3,4-$Et_2C_2B_4H_4$ (−37.1 ppm), *nido*-6-Me_3PCH_2-3,4-$Et_2C_2B_5H_5$ (−26.0 ppm), and *nido*-6-X-3-(Me_3Si)-4-Me-6,3,4-$SiC_2B_4H_5$ (X = H, −31.0 ppm; X = Cl, −30.1 ppm). However, it is known that phosphorus cage atoms can strongly deshield boron cage atoms, as a comparison of the ^{11}B NMR shifts of 1,2-$P_2B_{10}H_{10}$[25] (17.7, 4.2, −0.3, −2.5 ppm) and the isoelectronic 1,2-$C_2B_{10}H_{12}$[26] (−3.1, −9.6, −13.9, −15.0 ppm) illustrates. The fact that only the B1 resonance, which is the boron farthest from the phosphorus, is shifted significantly suggests the influence of an antipodal effect of the phosphorus cage atom, such as has been observed in *closo*-heteroborane clusters[27] (vide infra).

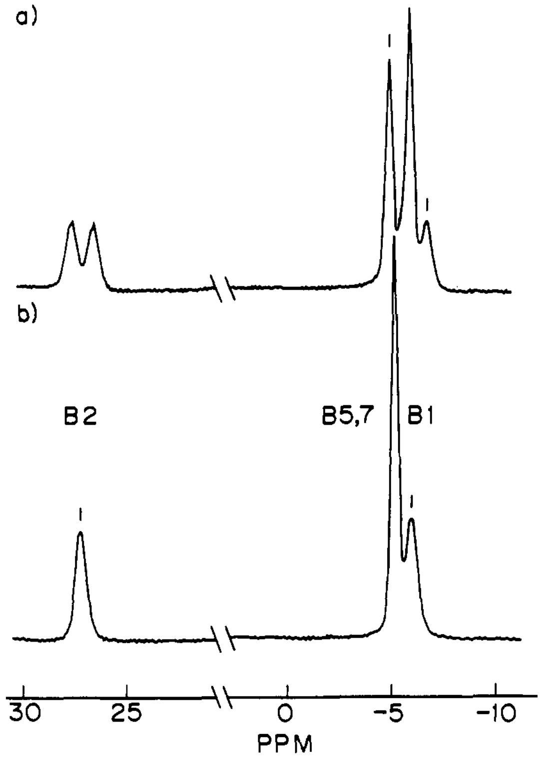

Figure 2. 160.4-MHz ^{11}B NMR spectra of **1**: (a) ^1H coupled; (b) ^1H spin-decoupled.

The 200.1-MHz ^{11}B spin-decoupled ^1H NMR spectrum of **1** is shown in Figure 3a. In addition to the resonances arising from the phenyl and ethyl groups, three B–H resonances are observed in the expected 1:2:1 area ratio. The resonance of intensity-two at 3.15 ppm exhibits doublet fine structure consistent with $^2J_{HP}$ coupling[28,29] and is therefore assigned to the B5,7 protons adjacent to the phosphorus atom. The intensity-one low-field resonance is assigned to B2–H and the resonance at highest field to B1–H, on the basis of selectively proton-decoupled ^{11}B NMR experiments

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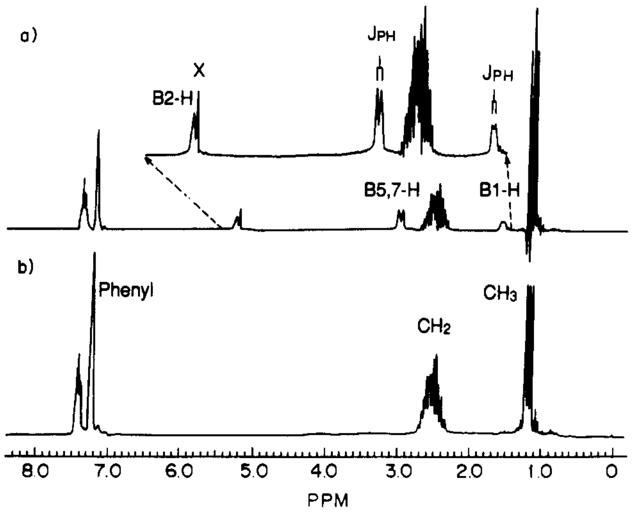

Figure 3. 200.1-MHz ^{1}H NMR spectra of **1**: (a) ^{11}B spin-decoupled; (b) ^{11}B coupled (X indicates solvent resonances).

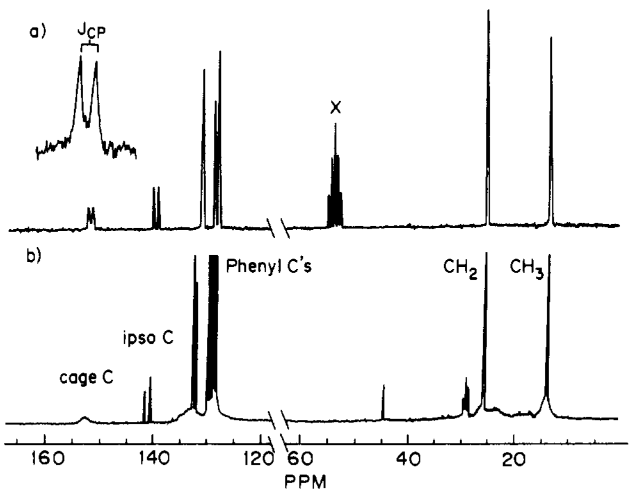

Figure 4. 50.3-MHz $^{13}C\{^{1}H\}$ NMR spectra of **1**: (a) at −82 °C; (b) at room temperature (X indicates solvent resonances).

on **1**. The B1–H resonances in **1** and **2** also show fine structure ($J \sim 4$–7 Hz). Selective proton-decoupled ^{1}H NMR experiments showed that this fine structure is not of ^{1}H–^{1}H origin. Thus, the coupling may be due to a $^{3}J_{HP}$ interaction and could be a consequence of an antipodal interaction between the phosphorus and B1 cage atoms. In this regard, Onak has previously observed[30] long-range coupling interactions between protons substituted on cage atoms located in trans-positions in small *closo*-carboranes. The B2–H resonance at 5.38 ppm exhibits no resolvable P–H coupling, which is surprising given that it is adjacent to the phosphorus atom.

The 50.3-MHz $^{13}C\{^{1}H\}$ NMR spectrum of **1** at room temperature (Figure 4b) shows the expected resonances arising from the ethyl and phenyl groups, but the cage-carbon signal is not observed at this temperature. As shown in Figure 4a, at −82 °C the carbon–boron scalar coupling is quenched[31] and the cage-carbon resonance is clearly observed as a doublet at 151.8 ppm. The magnitude of the coupling ($^{2}J_{CP}$ = 37 Hz) is smaller than that observed for the coupling ($^{1}J_{CP}$ = 47 Hz) of the ipso carbon (at 139.5 ppm) and is in the range observed for other $^{2}J_{CP}$ couplings.[26] It should also be noted that both the shift of the cage carbon (151.8 ppm) and the observed J_{CP} coupling are again very different than those reported[2] by Hosmane for *closo*-1-[2,4,6-$(t\text{-Bu})_3C_6H_2$]-1-P-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (119.25 ppm, J_{CP} = 115 Hz).

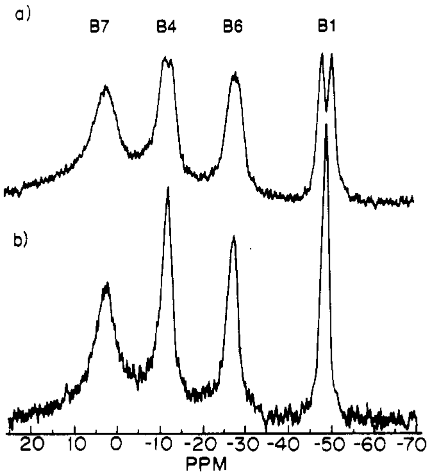

Figure 5. 64.2-MHz ^{11}B NMR spectra of *arachno*-$PhEt_2PC_2B_4H_4^{2-}$ ($\mathbf{1}^{2-}$): (a) ^{1}H coupled; (b) ^{1}H spin-decoupled.

The 81.0-MHz ^{31}P NMR spectrum of **1** consists of one signal which exhibits a line width of 34 Hz when recorded at −71 °C and ∼100 Hz at room temperature. Upon line narrowing, the signal becomes broader, but no J_{BP} or J_{HP} coupling could be resolved. The chemical shifts of the phosphorus resonances in **1**–**6** were highly dependent on the exopolyhedral substituent. Thus, the resonance occurs in the phenyl-substituted compounds at +63.6 (**1**) and +71.2 ppm (**2**), in the *tert*-butyl compounds at +110.3 (**3**) and +112.9 ppm (**4**), and in the methyl compounds at +16.4 (**5**) and +16.4 (**6**) ppm. These shifts are at much lower field than that reported[2] for *closo*-1-[2,4,6-$(t\text{-Bu})_3C_6H_2$]-1-P-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (−129.68 ppm).

Since the spectral data for compounds **2**–**6** (Table I) are analogous to those of **1**, nido-cage geometries similar to that shown in Figure 1 are also proposed for these compounds. The fact that **1** did not react with $AlCl_3$ also suggests that the phosphorus atoms in these compounds do not have an accessible exopolyhedral lone pair of electrons and thus provides additional support for the proposed nido-cage structures of **1**–**6** in which the RP unit is functioning as a 3-orbital, 4-electron donor to the cage.

Preliminary investigations have also shown that **1** can be readily reduced, and the resulting anion can be used to produce cage expanded species. Thus, according to the ^{11}B NMR spectrum, the reaction of *nido*-6-Ph-3,4-Et_2-6,3,4-$PC_2B_4H_4$, **1**, with lithium metal (or sodium naphthalenide) in THF (eq 3) gives quantitative reduction of the phosphacarborane.

$$\textit{nido}\text{-6-Ph-3,4-Et}_2\text{-6,3,4-PC}_2\text{B}_4\text{H}_4 + 2\text{Li}^0 \rightarrow [\textit{arachno}\text{-PhEt}_2\text{PC}_2\text{B}_4\text{H}_4]^{2-}(\text{Li}^+)_2 \quad (3)$$

$$\mathbf{1}^{2-}$$

The ^{11}B NMR spectrum (Figure 5) of $\mathbf{1}^{2-}$ consists of four broad resonances indicating that upon reduction, the anion adopts an asymmetrical structure. Possible 7-vertex arachno structures that are consistent with the observed ^{11}B NMR spectrum and the ab initio/IGLO/NMR calculations are discussed in the next section.

Subsequent reaction of $\mathbf{1}^{2-}$ with 1 equiv of $PhPCl_2$ in THF gave mass spectral and NMR evidence for the formation of the diphosphacarborane *arachno*-$Ph_2Et_2P_2C_2B_4H_4$ in low yields (eq 4).

$$\textit{arachno}\text{-[PhEt}_2\text{PC}_2\text{B}_4\text{H}_4]^{2-}(\text{Li}^+)_2 + \text{PhPCl}_2 \rightarrow \textit{arachno}\text{-Ph}_2\text{Et}_2\text{P}_2\text{C}_2\text{B}_4\text{H}_4 + 2\text{LiCl} \quad (4)$$

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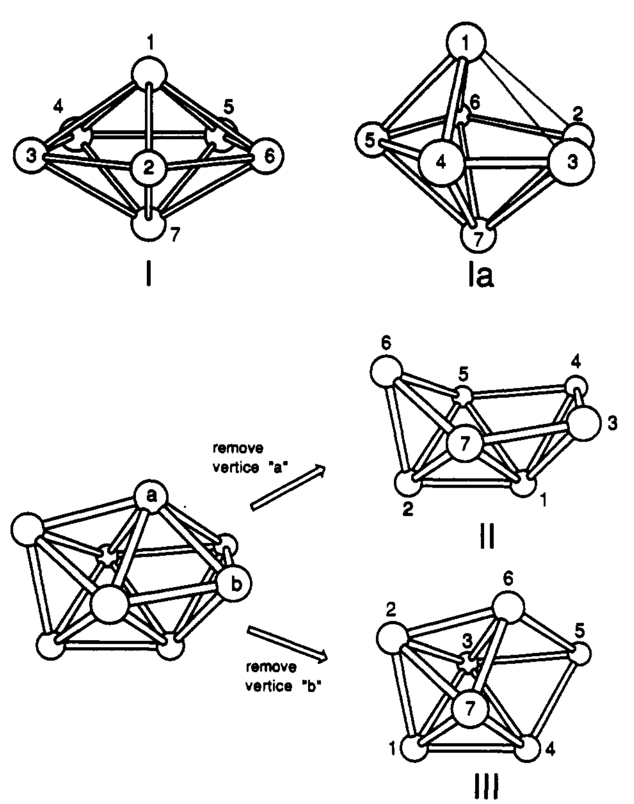

Figure 6. 7-vertex closo framework **I**, "slipped" closo framework **Ia**, and derivation of possible 7-vertex nido geometries **II** and **III**.

The compound could not be isolated in pure form but was always obtained in a mixture with **1**. Therefore, complete characterization of the compound was not possible. However, exact mass measurements confirmed that a compound of the composition $Ph_2Et_2P_2C_2B_4H_4$ was present in this mixture and subtraction of the signals due to *nido*-6-Ph-3,4-Et_2-6,3,4-$PC_2B_4H_4$, **1**, from the ^{11}B NMR spectrum of the mixture gave three new doublets in 1:2:1 ratio, which, on the basis of ab initio/IGLO/NMR calculations discussed below, may be assigned to the new compound.

ab Initio/IGLO/NMR Results. The phosphacarborane cage systems were investigated by employing the combined ab initio[5]/IGLO[6]/NMR method[7] for structural elucidation developed by Schleyer. In this method, the geometries of all potential structures for a given formula are optimized using ab initio theory and then each of these geometries are used as input for an IGLO NMR chemical shift calculation. The geometry for which the calculated IGLO NMR chemical shifts best correlates with the experimental values is deemed the best representation in solution.

The basic cage frameworks considered for the ab initio geometry optimizations of 7-vertex phosphacarboranes included (Figure 6) closo geometry **I**, "slipped" closo geometry **Ia**, and two nido structures **II** and **III**. As shown in Figure 6, depending upon which vertex is removed, two different types of nido structures may be derived from the parent 8-vertex closo bisdisphenoid polyhedron (the most spherical dodecahedron). The structure proposed in Figure 1 is based on geometry **II** of Figure 6 and is derived from a bisdisphenoid by removal of one five-connected vertex, thereby generating a nido 7-vertex framework with a five-membered open face. An alternative nido geometry is also possible, based on a bisdisphenoid with one four-connected vertex removed (as shown by **III** of Figure 6), which results in a nido 7-vertex framework with a four-membered open face.

One attempt to optimize to a closo or a slip-distorted closo geometry (**I** or **Ia**, Figure 6) for $PC_2B_4H_7$, such as that proposed by Hosmane for *closo*-1-[2,4,6-(*t*-Bu)$_3$$C_6H_2$]-1-P-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$, used the HF/3-21G optimized geometry[32] for *closo*-2,3-$C_2B_5H_7$ with one apex BH unit replaced by a PH as the initial input. However, at the HF/STO-3G level of theory this structure optimized to a nido geometry with a five-membered open face. The HF/STO-3G optimized geometry was then used as input for higher level calculations, and at all levels of theory employed, the resulting optimized geometry is a nido structure with a five-membered open face (see Figure 7, **IIa**, for the HF/6-31G* optimized geometry). A second attempt to optimize to a closo or "slipped" closo structure used as a model the slip-distorted cages in *commo*-2,2′-$(Me_3Si)_2$-3,3′-$(CH_3)_2$-1,1′-Si(1,2,3-Si-$C_2B_4H_4$)$_2$ with one 2-(Me_3Si)-3-(CH_3)-1,2,3-$SiC_2B_4H_4$ cage replaced by a PH group (and the 2-Me_3Si and 3-Me groups replaced by H) as the initial input.[24] However, at the HF/STO-3G level of theory, the nido-structure **IIa** was again obtained after geometry optimization. Other attempts at higher levels of theory and/or modified input geometries never yielded a closo or "slipped" closo structure for the $PC_2B_4H_7$ cage after geometry optimization. The fact that a closo or "slipped" closo structure could not be obtained would apparently argue against Hosmane's assignment of a closo geometry to *closo*-1-[2,4,6-(*t*-Bu)$_3$$C_6H_2$]-1-P-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$. However, it should be recognized that, due to the complexity of the trimethylsilyl and supermesityl groups substituted at the cage carbon and phosphorus atoms, it is not possible to treat this molecule computationally. Thus, it is not possible to evaluate the steric and/or electronic effects that these substituents may have on the cage structure and, as a result, no definitive conclusions concerning the structure of this compound are possible. However, the fact that the ^{11}B NMR spectra of **1**–**6** and *closo*-1-[2,4,6-(*t*-Bu)$_3$$C_6H_2$]-1-P-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ are very different does suggest that the compounds are of different structural types.

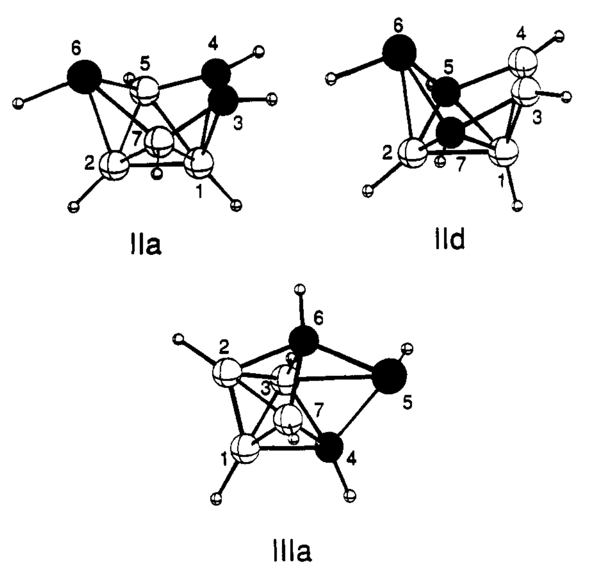

Figure 7. HF/6-31G* optimized cage geometries for 7-vertex *nido*-phosphacarboranes: *nido*-6,3,4-$PC_2B_4H_7$ (**IIa**); *nido*-6,5,7-$PC_2B_4H_7$ (**IId**); *nido*-5,4,6-$PC_2B_4H_7$ (**IIIa**).

Isomeric nido 7-vertex cage geometries of C_s symmetry with five-membered open faces were also considered (Figure 6): *nido*-1,3,4-$PC_2B_4H_7$ (**IIb**), *nido*-2,3,4-$PC_2B_4H_7$ (**IIc**), *nido*-6,5,7-$PC_2B_4H_7$ (**IId**), and *nido*-1,5,7-$PC_2B_4H_7$ (**IIe**). However, using ab initio theory, no structures corresponding to geometries **IIb,c,e** were found. A structure corresponding to isomer **IId** (see Figure 7 for the HF/6-31G* optimized structure), the carbons-apart isomer of **IIa**, was located using ab initio theory but is considerably less stable than **IIa**, >50 kcal/mol at the HF/6-31G* level of theory (Table II).

Two nido 7-vertex cage structures of C_s symmetry with four-membered open faces were also considered (Figure 6): *nido*-5,4,6-$PC_2B_4H_7$ (**IIIa**) and *nido*-5,1,2-$PC_2B_4H_7$ (**IIIb**). Optimized

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[32] Bausch, J. W.; Prakash, G. K. S.; Williams, R. E. Unpublished results.

Table II. Absolute (–au) and Relative Energies of ab Initio Optimized Phosphacarborane Systems

calculated structure	E_{abs}	E_{rel}
nido-6,3,4-$PC_2B_4H_7$ (**IIa**)	519.233 93	0
nido-6,5,7-$PC_2B_4H_7$ (**IId**)	519.153 55	50.4
nido-5,4,6-$PC_2B_4H_7$ (**IIIa**)	519.179 71	34.0
nido-3,4-Me_2-6,3,4-$PC_2B_4H_5$ (**IIf**)	594.241 52	
nido-6,3,4-Me_3-6,3,4-$PC_2B_4H_4$ (**IIg**)	633.069 68	
nido-6-Me-6,3,4-$PC_2B_4H_6$ (**IIh**)	558.272 84	
arachno-5,2,3-$PC_2B_4H_7^{2-}$ (**IVa**)	519.080 65	0
arachno-5,3,4-$PC_2B_4H_7^{2-}$ (**IVb**)	519.031 33	30.9
arachno-7,8,4,5-$P_2C_2B_4H_8$ (V)	860.535 91	

geometries were found for **IIIa,b**, although a frequency calculation indicated one imaginary frequency for **IIIb** at all levels of theory employed (see Figure 7 for the HF/6-31G* optimized structure for **IIIa**). Energetically, **IIIa** is more stable than **IId** by ~16 kcal/mol at HF/6-31G* but is less stable than **IIa** by ~35 kcal/mol (Table II).

Thus, on the basis of the energy calculations of the 7-vertex structures discussed above, **IIa** is strongly favored. A detailed inspection of the cage structural parameters for **IIa** clearly indicates that it has the expected nido-geometry **II** similar to that which has been observed in all of the previously structurally characterized isoelectronic 7-vertex carboranes.[21,23] In the HF/6-31G* optimized structure **IIa**, the P6–C3(4) distance is a nonbonding 2.75 Å (the sum of the covalent radii[33] for phosphorus and carbon is 1.87 Å) and the dihedral angle between the B5–C4–C3–B7 and B5–B2–B7 planes is 150.2°. In an idealized nido 7-vertex structure **II** (which may be generated by removing a high-coordination vertex from *closo*-$B_8H_8^{2-}$ [34]), the distance between B6–B3 and B6–B4 is 2.81 Å and the dihedral angle between B5–B4–B3–B7 and B5–B2–B7 planes is 140°. Other structurally characterized nido 7-vertex clusters have similar distances and angles. For example, the B6–C3,4 distances in *nido*-3,4-$Et_2C_2B_5H_6^-$ (2.686(6) and 2.695(7) Å) and *nido*-6-Me_3PCH_2-3,4-$Et_2C_2B_5H_5$ (2.69(2) and 2.71(2) Å) are nonbonding (the sum of the covalent radii for a boron and carbon is 1.65 Å) and the dihedral angles between the B5–C3–C4–B7 and B5–B2–B7 planes are 156.2(6)° and 158.3(9)°, respectively. Kennedy has used similar geometric relationships to show that [2,2,2-$(CO)(PPh_3)_2$-7,7-$Cl(PMe_2Ph)$-2,7-$OsPtB_5H_8$] has a nido 7-vertex framework, **II**.[35] In the typical "slipped" closo structure (**1a** of Figure 6) that has been observed for many 7-vertex clusters having both a formal closo skeletal electron count and an uncomplexed heteroatom, the elongated distances (1–2 and 1–3) between the apical heteroatom (1 position) and the ring atoms (2 and 3) are usually only slightly longer (~0.3–0.4 Å) than the sum of the covalent radii, and the five atoms of the 2–3–4–5–6 ring are nearly planar with the B4 boron being only slightly (~0.05 Å) displaced out of the plane. For example, in Hosmane's structurally characterized "slipped" closo cluster[4b] 2,2′-$(Me_3Si)_2$-3,3′-$(CH_3)_2$-1,1′-Si(1,2,3-$SiC_2B_4H_4$)$_2$ the cage Si–C distances are 2.236(6) and 2.228(7) Å (the sum of the covalent radii for silicon and carbon is 1.95 Å) and the dihedral angle between the B5–C3–C4–B7 and B5–B2–B7 planes is 178.6°.[36]

The IGLO method was then used to calculate the NMR chemical shifts of isomers **IIa,d** and **IIIa** using the ab initio optimized geometries as input. The IGLO results at the highest level of theory employed for each structure are summarized in Tables III and IV.

The large differences between the ^{11}B and ^{13}C NMR shifts observed for **1–6** and the IGLO calculated shifts (Table III) for structures **IId** and **IIIa** allow these structures to be ruled out. It should be noted, however, that the IGLO calculated ^{11}B NMR shifts for isomer **IIIa** are reasonably close to those of the phosphacarborane reported by Hosmane, but the calculated ^{13}C shift (15.2 ppm) of the cage carbon is very different from the reported value (119.2 ppm).[2]

Cage-geometry **IIa** gave reasonably good correlation of the IGLO calculated ^{11}B NMR values (II//6-31G*) with the experimental data for compounds **1–6** (Table I), although the chemical shift of B2 in this all-H-substituted model is calculated (40.7 ppm) at lower field than the observed shift (27.2 ppm in **1**). However, IGLO calculations (DZ//3-21G*) on two methylated derivatives of **IIa**, *nido*-3,4-$(CH_3)_2$-6,3,4-$PC_2B_4H_5$ (**IIf**) and *nido*-6,3,4-$(CH_3)_3$-6,3,4-$PC_2B_4H_4$ (**IIg**) (see Figure 7 for the HF/3-21G* optimized geometries), gave chemical shifts for B2 which approach the experimental values (Table III). Molecules **IIf,g** are too large for our available computational resources to permit higher level calculations, but the DZ//3-21G* level gives reasonably accurate ^{11}B chemical shifts.

As pointed out earlier, the B1 resonance in **1–6** is shifted downfield compared to the analogous boron atoms in the isoelectronic cage systems *nido*-3,4-$Et_2C_2B_5H_6^-$, *nido*-6-Al(H)-NEt_3-3,4-$C_2B_4H_4$, *nido*-6-Me_3PCH_2-3,4-$Et_2C_2B_5H_5$, and *nido*-6-X-3-(Me_3Si)-4-Me-6,3,4-$SiC_2B_4H_5$ (X = H, Cl). A comparison of the bond distances and angles about B1 in the optimized geometry **IIa**, with those found in the crystallographically determined structures for *nido*-3,4-$Et_2C_2B_5H_6^-$ and *nido*-6-Me_3PCH_2-3,4-$Et_2C_2B_5H_5$, revealed no significant structural differences that could account for the large change in the chemical shift of B1. Thus, the deshielded B1 shift may be due to an antipodal effect of the phosphorus on the trans B1 boron. It is significant that the IGLO method predicts this shift, and indeed, Bühl et al. have recently used[27] the IGLO method to correctly predict the boron chemical shifts in *closo*-heteroboranes in which an antipodal effect is observed and have discussed the origin of this phenomenon.

The IGLO calculated (II//6-31G*) ^{13}C chemical shift of the cage carbon of the all-H-substituted **IIa** is 136.0 ppm, to be compared to the experimental value of 151.8 ppm for **1**. The methylated derivatives **IIf,g** gave IGLO calculated (DZ//3-21G*) ^{13}C shifts of 150.8 ppm and 150.2 ppm, respectively, in good agreement with the experimental value for **1**.[37]

Although there are many problems associated with the theoretical calculation of ^1H NMR chemical shifts, the IGLO calculated ^1H chemical shifts (II′//MP2/6-31G*) of the terminal hydrogens in a variety of boranes and borane anions are relatively close to the experimental values, with the ordering of resonances usually reproduced correctly.[38] The IGLO calculated (II//6-

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(33) Gordon, J. A.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972; pp 82–87.

(34) Guggenberger, L. J. *Inorg. Chem.* **1969**, *8*, 2771–2774.

(35) Kennedy, J. D. *Main Group Met. Chem.* **1989**, *12*, 149–154.

(36) For other examples of 7-vertex "slip-distorted" clusters see the following and references therein: (a) Hosmane, N. S.; Barreto, R. D.; Tolle, M. A.; Alexander, J. J.; Quintana, W.; Siriwardane, U.; Shore, S. G.; Williams, R. E. *Inorg. Chem.* **1990**, *29*, 2698–2701. (b) Hosmane, N. S.; Lu, K. J.; Zhang, H.; Jia, L.; Cowley, A. H.; Mardones, M. A. *Organometallics* **1991**, *10*, 963–970. (c) Hosmane, N. S.; Lu, K. J.; Zhu, H.; Siriwardane, U.; Shet, M. S.; Maguire, J. A. *Organometallics* **1990**, *9*, 808–815. (d) Hosmane, N. S.; Lu, K. J.; Zhang, H.; Cowley, A. H.; Mardones, M. A. *Organometallics* **1991**, *10*, 392–393 and references therein.

(37) Schleyer and co-workers[7a] have shown a basis set dependence (i.e., from basis DZ to II′) of the IGLO calculated ^{13}C chemical shifts on some carboranes. However, in the phosphacarborane systems reported here and other carboranes studied in our laboratories, we have found only small changes in the calculated ^{13}C chemical shifts upon going from IGLO basis set DZ to II′ (or II). For example, the DZ//6-31G* ^{13}C shift of **IIa** is 138.4 ppm, to be compared with the II//6-31G* value of 136.0 ppm. Therefore, the DZ//3-21G* calculated values for **IIf** and **IIg** should not change significantly at II//3-21G*. Of course, it could be argued that the HF/3-21G* level of ab initio theory does not give a sufficiently accurate geometry, but our experience on a variety of cage systems has been that the DZ//3-21G* level of theory gives reliable ^{13}C chemical shifts.

(38) Schleyer, P. v. R. *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp 113–142.

Table III. IGLO ^{11}B, ^{13}C, and ^{31}P NMR Chemical Shifts for 7-Vertex *nido*-Phosphacarboranes

compd	level of theory	^{11}B, ppm[a] (assgn)			^{13}C, ppm[b] (assgn)	^{31}P, ppm[c] (assgn)
		Experimental Results				
nido-6-Ph-3,4-Et_2-6,3,4-$PC_2B_4H_4$ (**1**)		−5.9	−5.1	27.2	151.8	63.6
nido-6-Me-3,4-Et_2-6,3,4-$PC_2B_4H_4$ (**5**)		−4.7	−4.7	28.3		16.4
		Calculated Structures Based on Geometry II				
adjacent carbons isomers						
nido-6,3,4-$PC_2B_4H_7$ (**IIa**)	II//6-31G*	−8.3 (B1)	−4.2 (B4,5)	40.7 (B2)	136.0 (C3,4)	−16.8 (P6)
nido-3,4-Me_2-6,3,4-$PC_2B_4H_5$ (**IIf**)	DZ//3-21G*	3.3 (B1)	0.1 (B4,5)	31.7 (B2)	150.8 (C3,4)	−64.6 (P6)
nido-6,3,4-Me_3-6,3,4-$PC_2B_4H_4$ (**IIg**)	DZ//3-21G*	1.4 (B1)	2.4 (B4,5)	31.6 (B2)	150.2 (C3,4)	−2.8 (P6)
nido-6-Me-6,3,4-$PC_2B_4H_6$ (**IIh**)	II′//6-31G*	−9.2 (B1)	−0.9 (B4,5)	39.2 (B2)	135.7 (C3,4)	55.4 (P6)
carbon apart isomer						
nido-6,5,7-$PC_2B_4H_7$ (**IId**)	II//6-31G*	13.9 (B1)	29.9 (B3,4)	24.9 (B2)	42.4 (C5,7)	−55.3 (P6)
		Calculated Structure Based on Geometry III				
nido-5,4,6-$PC_2B_4H_7$ (**IIIa**)	DZ//6-31G*	−2.4 (B7)	10.4 (B1,2)	9.6 (B3)	15.2 (C4,6)	−240.8 (P5)

[a] Referenced to $BF_3{\cdot}OEt_2$ (0.0 ppm). [b] Referenced to TMS (0.0 ppm). [c] Referenced to 85% H_3PO_4 (0.0 ppm).

Table IV. IGLO ^{11}B, ^{13}C, and ^{31}P NMR Chemical Shifts for 7-Vertex *arachno*-Phosphacarborane Dianions and 8-Vertex *arachno*-Diphosphacarborane

compd	level of theory	^{11}B, ppm[a] (assgn)				^{13}C, ppm[b] (assgn)	^{31}P, ppm[c] (assgn)
		Experimental Results					
1^{2-}		−46.8	−27.0	−9.5	3.8		−246.7
		arachno 7-Vertex Dianions					
5,2,3-$PC_2B_4H_7^{2-}$ (**IVa**)	II′//6-31G*	−61.8 (B1)	−31.5 (B6)	−18.2 (B4)	6.2 (B7)	101.7 (C2), 35.9 (C3)	−412.9 (P5)
5,3,4-$PC_2B_4H_7^{2-}$ (**IVb**)	II′//6-31G*	−47.7 (B1)	−19.3 (B6)	−12.5 (B7)	22.5 (B2)	37.2 (C3), 14.0 (C4)	−370.9 (P5)

compound	level of theory	^{11}B, ppm[a] (assgn)			^{13}C, ppm[b] (assgn)	^{31}P, ppm[c] (assgn)
		Experimental Results				
$Ph_2Et_2P_2C_2B_4H_4$		−38.6	−20.7	−0.5		
		arachno 8-Vertex diphosphacarborane				
7,8,4,5-$P_2C_2B_4H_8$ (V)	II′//6-31G*	−48.6 (B1)	−18.3 (B3,6)	2.7 (B2)	126.0	−339.2

[a] Referenced to $BF_3{\cdot}OEt_2$ (0.0 ppm). [b] Referenced to TMS (0.0 ppm). [c] Referenced to 85% H_3PO_4 (0.0 ppm).

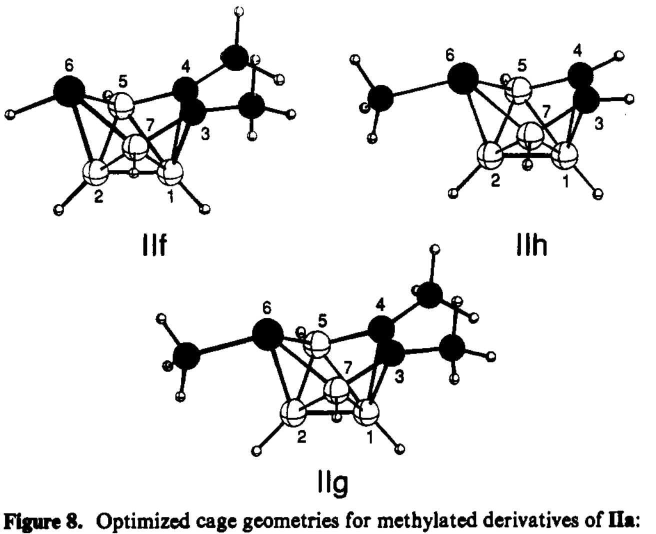

Figure 8. Optimized cage geometries for methylated derivatives of **IIa**: *nido*-3,4-$(CH_3)_2$-6,3,4-$PC_2B_4H_5$ (**IIf**); *nido*-6,3,4-$(CH_3)_3$-$PC_2B_4H_4$ (**IIg**); *nido*-6-CH_3-$PC_2B_4H_6$ (**IIh**).

31G*) ^1H shifts of the terminal hydrogens of **IIa** are 5.74 (B2–H), 1.69 (B5,7–H), and 0.58 (B1–H) ppm, which are in reasonable agreement with the experimental values for **1** of 5.38, 3.15, and 1.72 ppm.

It has been shown[6c] that to obtain reliable ^{31}P NMR chemical shifts using the IGLO method requires a triple-ζ basis set (II or II′). Furthermore, the NMR chemical shift of the phosphorus nuclei is very sensitive to electronic and steric factors. Thus, a *P*-methyl derivative of **IIa**, *nido*-6-CH_3-6,3,4-$PC_2B_4H_6$ (**IIh**, Figure 8), was chosen as the model for the calculation since it was the largest P-alkylated system that could be calculated by employing a triple-ζ basis set using the available computational resources. The geometry of **IIh** was optimized up to the HF/6-31G* level of ab initio theory. The IGLO calculated (II//6-31G*) ^{31}P chemical shift for **IIh** is 55.4 ppm, to be compared with the experimental value of 16.4 ppm for *nido*-6-Me-3,4-Et_2-6,3,4-$PC_2B_4H_4$ (**5**), which is a reasonable correlation, considering the approximations made.

As discussed above, **1** reacts with lithium metal or sodium naphthalenide (eq 3) to produce the four-line ^{11}B NMR spectrum shown in Figure 5. The expected geometry resulting from a two-electron reduction of a 7-vertex nido cage system would be a 7-vertex arachno structure based on a tricapped trigonal prism missing two vertices. Such a geometry has been confirmed for Shore's[39] $B_7H_{12}^-$, which was structurally characterized as an $Fe(CO)_4$ adduct, and is proposed on the basis of ab initio/IGLO/NMR calculations for Onak's[40] *arachno*-$C_2B_5H_{10}^-$. Using ab initio calculations, two optimized geometries of C_1 symmetry (**IVa,b**, Figure 9) were found for *arachno*-$PC_2B_4H_7^{2-}$ in agreement with the predicted skeletal framework. Isomer **IVa** is ~31 kcal/mol more stable than **IVb** at the HF/6-31G* level of theory (Table II). The IGLO calculated (II′//6-31G*) ^{11}B NMR chemical shifts for **IVa** (Table IV) correlate fairly well with the experimental values for the phosphacarborane dianion **1**$^{2-}$. The resonance for the high-coordinated B1 boron calculates at much higher field (~15 ppm), but this is probably due to the use of the all-H-substituted model. The energetically unfavorable isomer **IVb** also gives fairly good correlation of the IGLO calculated ^{11}B NMR chemical shifts (II′//6-31G*) with the experimental values, although B2 is shifted ~19 ppm upfield from the experimental

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(39) (a) Johnson, H. D., II; Shore, S. G. *J. Am. Chem. Soc.* **1971**, *93*, 3798–3799. (b) Remmel, R. J.; Johnson, H. D.; Jaworiwsky, I. S.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 5395–5403. (c) Mangion, M.; Clayton, W. R.; Hollander, O.; Shore, S. G. *Inorg. Chem.* **1977**, *16*, 2110–2114.

(40) Onak, T. P. Presented at the Eighth International Meeting on Boron Chemistry, Knoxville, TN, July, 1993, paper no. SA-8.

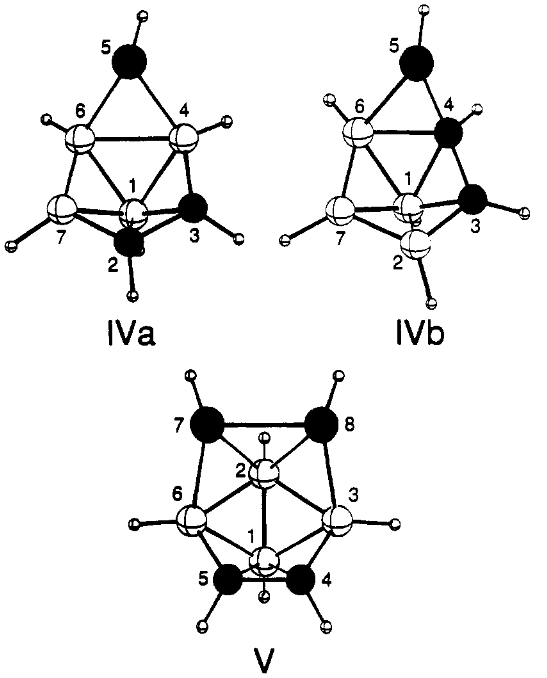

Figure 9. HF/6-31G* optimized cage geometries found for *arachno*-5,2,3-$PC_2B_4H_7^{2-}$ (**IVa**), *arachno*-5,3,4-$PC_2B_4H_7^{2-}$ (**IVb**), and *arachno*-7,8,4,5-$P_2C_2B_4H_8$ (**V**).

value (Table IV). Thus, while the experimentally observed ^{11}B chemical shifts for $\mathbf{1}^{2-}$ are in the ranges of the IGLO calculated shifts for either **IVa** or **IVb**, the energy calculations clearly favor **IVa**.[41] The conversion from the nido 7-vertex structure **IIa** to the 7-vertex arachno-structure **IVa** upon two-electron reduction can be seen to occur in a straightforward manner. Thus, in **IIa** (Figure 7) the phosphorus is connected to the B2, B5, and B7 cage atoms, but upon reduction the P–B7 bond is broken and the phosphorus atom migrates toward the B5–B2 edge (B4–B6 edge in **IVa**). The *arachno*-$C_2B_5H_{10}^-$ ion is proposed to adopt a similar structure with a CH_2 group bridging a $CB_5H_8^-$ cage.[40]

The experimental ^{31}P NMR chemical shift for $\mathbf{1}^{2-}$ is −246.9 ppm, which is a ~300 ppm shift upfield from the precursor phosphacarborane **1**. Due to the lack of symmetry of the arachno 7-vertex system, the calculation of a P-alkylated derivative of **IVa** to serve as a model for $\mathbf{1}^{2-}$ exceeds the limits of our computational facilities. However, the IGLO calculated (II′//6-31G*) ^{31}P NMR chemical shift of **IVa** is −412.9 ppm, which at least qualitatively agrees with the tremendous upfield shift from the shift observed in **1**.

Although the product obtained from the reaction of $\mathbf{1}^{2-}$ with $PhPCl_2$ could not be completely characterized, the NMR data are consistent with the structural predictions for an *arachno*-$Ph_2Et_2P_2C_2B_4H_4$ cage system. The expected geometry for an 8-vertex arachno-cage system would be a symmetrically bicapped square antiprism missing two vertices. Previously isolated examples of 8-vertex arachno clusters include the spectroscopically characterized *arachno*-B_8H_{14},[42] *arachno*-$C_2B_6H_{11}^-$,[43] and *arachno*-$C_2B_6H_{12}$.[44] Both *arachno*-B_8H_{14} and *arachno*-$C_2B_6H_{11}^-$ have the expected six-membered open-face arachno geometry, while *arachno*-$C_2B_6H_{12}$ is proposed to have a seven-membered open-face structure. Structure **V** (Figure 9) having C_s symmetry was found using ab initio theory and has the expected 8-vertex arachno geometry. The IGLO calculated (II′//6-31G*) ^{11}B NMR chemical shifts of the all-H-substituted structure **V** (Table IV) correlate well with the experimental values for $Ph_2Et_2P_2C_2B_4H_4$. Other cage isomers of C_s symmetry were also considered, but no optimized structures corresponding to these geometries could be found. Again, the conversion of the structure in **IVa** to **V** can be envisioned as occurring in a straightforward manner by the insertion of the second phosphorus atom at the B6–B7 edge in **IVa**.

In summary, the results reported here have demonstrated the synthesis of a new series of phosphacarboranes **1–6** of the formula *nido*-6-R′-3,4-R_2-6,3,4-$PC_2B_4H_4$ (R = Et, Bz; R′ = Ph, *t*-Bu, Me). These compounds exhibit spectral data very different from that reported[2] by Hosmane for *closo*-1-[2,4,6-(*t*-Bu)$_3$$C_6H_2$]-1-P-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ suggesting that the latter compound and **1–6** are in different structural classes. The spectroscopic and ab initio/IGLO/NMR studies of **1–6** strongly indicate that these clusters adopt the normal 7-vertex nido geometry that has previously confirmed for the isoelectronic 7-vertex *nido*-carboranes.

Acknowledgment. We thank the National Science Foundation for the support of this research. We would also like to thank Prof. W. Kutzelnigg of the Bochum group for a copy of the IGLO program and Dr. J. Yates at University of Pennsylvania for implementation of the program. Dr. Robert E. Williams is also thanked for helpful comments.

Supplementary Material Available: Tables of Cartesian coordinates of each calculated structure, energies, and IGLO calculated chemical shifts, at other levels of theory (9 pages). Ordering information is given on any current masthead page.

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(41) The fact that the IGLO calculations do not strongly favor **IVa** over **IVb** may be the result of using an all H-substituted model. Also, a higher level of ab initio theory may be needed to treat these anions.

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