Synthetic and Structural Studies of Heteroatom−Polyborane Clusters: Simple, High-Yield Syntheses of *nido*-11-Vertex Thia- and Phosphaboranes, Thia- and Phosphadicarbaboranes, and the First Thiaphosphaborane

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A synthetic sequence involving the reaction of a phosphorus or sulfur dihalide with a monoanionic boron cluster followed by an in situ dehydrohalogenation reaction initiated by proton sponge results in the clean insertion of the heteroatom into the cage framework. Using this method, a range of *nido*-11-vertex thia- and phosphaboranes, thia- and phosphadicarbaboranes, and the first thiaphosphaborane has been produced in high yields. Thus, the reaction of decaborane with SCl_2 or $RPCl_2$ and excess proton sponge gave the known anions, *nido*-7-$SB_{10}H_{11}^-$ ($\mathbf{1}^-$) and *nido*-7-$RPB_{10}H_{11}^-$ [$\mathbf{2a}^-$ (R = Me) and $\mathbf{2b}^-$ (R = Ph)], respectively. Acidification of $\mathbf{1}^-$, $\mathbf{2a}^-$, and $\mathbf{2b}^-$ resulted in the isolation of *nido*-7-$SB_{10}H_{12}$ (**1**) and *nido*-7-$RPB_{10}H_{12}$ (**2a** and **2b**), respectively, in near-quantitative yields. Reaction of *nido*-5,6-$C_2B_8H_{12}$ with SCl_2 or $RPCl_2$ in the presence of proton sponge produced the new compounds, *nido*-7,10,11-$SC_2B_8H_{10}$ (**3**) (77%) and *nido*-7,10,11-$RPC_2B_8H_{10}$ [R = Me (97%) **4a**, Ph (83%) **4b**], respectively. Reaction of *arachno*-6-SB_9H_{11} with $PhPCl_2$ and proton sponge resulted in the formation of the new mixed heteroatom cage, *nido*-10-Ph-7,10-SPB_9H_9 (**5**), which is the first example of a thiaphosphaborane cluster. Consistent with their nido skeletal electron counts, all clusters were shown by spectroscopic and DFT/GIAO computational studies to have similar cage frameworks containing a five-membered open face.

Introduction

The development of systematic, high yield synthetic routes for the construction of heteroatom−polyborane clusters, such as the polyhedral thiaboranes and phosphaboranes, has been a formidable challenge. Because of the high reactivity of most polyhedral borane anions, multiple reaction pathways are possible during the heteroatom insertion reaction which can lead to low yields of desired materials.[1] In this paper, a surprisingly simple method for heteroatom insertion is presented that is used to synthesize, in high yields, a range of isoelectronic and isostructural *nido*-11-vertex thia- and phospha-boranes, thia- and phosphadicarbaboranes, and the first thiaphosphaborane cluster.

Experimental Section

All manipulations were carried out using standard high vacuum or inert-atmosphere techniques as described by Shriver.[2]

Materials. Decaborane, $B_{10}H_{14}$, was obtained from laboratory stock and sublimed before use. The carborane *nido*-5,6-$C_2B_8H_{12}$[3] was prepared according to the literature methods. The *arachno*-6-SB_9H_{11} was prepared as previously reported.[4] KH (35 wt % dispersed in mineral oil) and oil-dispersed NaH were rinsed with hexane and then vacuum-dried prior to use. The compounds $RPCl_2$ (R = Me, Ph) and proton sponge (PS, 1,8-bis(dimethylamino)naphthalene) were purchased from Aldrich and used as received. Both S_2Cl_2 and SCl_2 were purchased from Aldrich, and were purified by passing them through a −45 °C trap. Sulfuric acid (99.999%) and 1.0 M $HCl{\cdot}Et_2O$ were purchased from Aldrich and stored under N_2 until used. 1,2-Dimethoxyethane (glyme) and tetrahydrofuran (THF) were dried over sodium benzophenone ketyl and freshly distilled before use. Methylene chloride was dried over P_2O_5, transferred onto activated 4 Å molecular sieves, and stored under vacuum until used. Heptane and hexane were purchased from Fisher and used as received. All other reagents and solvents were reagent grade unless otherwise noted.

Physical Measurements. ^1H NMR spectra at 500.1 MHz, ^{11}B NMR spectra at 160.5 MHz, ^{31}P NMR spectra at 81.0 MHz, and ^{13}C NMR spectra at 125.7 MHz were obtained on a Bruker AM-500 spectrometer. ^1H NMR spectra at 200.1 MHz and ^{11}B NMR spectra at 64.2 MHz were obtained on a Bruker AF-200 spectrometer. Both instruments were equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts are referenced to external $BF_3{\cdot}O(C_2H_5)_2$ (0.00 ppm) with a negative sign indicating an upfield shift. All ^1H and ^{13}C chemical shifts were measured relative to internal residual protons or carbons in the lock solvents and then referenced to Me_4Si (0.00 ppm). All ^{31}P chemical shifts are referenced to external 85% H_3PO_4 (0.0 ppm) with a negative sign indicating an upfield shift. Two-dimensional COSY $^{11}B-^{11}B$ NMR experiments were performed at 160.5 MHz using the procedures described previously.[5] NMR data are presented in Table 1.

High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer using negative ionization techniques. Infrared spectra were obtained on a Perkin-Elmer 7770 Fourier transform spectrometer or a Perkin-Elmer 1430 spectrophotometer. Gas chromatography/mass spectrometry (GC/MS) was performed on a Hewlett-Packard 5890A gas chromatograph (equipped with a cross-linked methylsilicone column) interfaced to a Hewlett-Packard 5970 mass selective detector.

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Table 1. NMR Data for New Compounds

compounds	nucleus	δ (multiplicity, assignment, J (Hz))
nido-7,10,11-$SC_2B_8H_{10}$ (**3**)	$^{11}B^{a,b}$	-0.46 (d, B9, J_{BH} 139, $J_{BB} \sim 38$), -3.5 (d, B4, J_{BH} 145), -6.8 (d, B5, J_{BH} 158), -10.9 (d, B8, J_{BH} 140, $J_{BB} \sim 30$), -12.5 (d, B2, $J_{BH} \sim 200$), -14.0 (d, B6, J_{BH} 190), -15.4 (d, B3, J_{BH} 215), -38.0 (d, B1, J_{BH} 153)
	^{11}B (calc)^{c}	0.13 (B9), -1.5 (B4), -6.2 (B5), -8.8 (B8), -12.9 (B2), -14.5 (B3), -15.1 (B6), -39.5 (B1)
	$^{11}B-^{11}B^{a,b}$	observed crosspeaks: B1−B2,3,4,5,6; B2−B3,6; B3−B4; B4−B5,8,9; B5−B6,9; B8−B9; missing B3−B8
	$^{1}H\{^{11}B\}^{b,d}$	3.29 (s, CH), 3.07 (s, CH), 2.81 (BH), 2.76 (BH), 2.34 (BH), 2.20 (BH), 2.15 (BH), 1.92 (BH), 1.79 (BH), 1.68 (BH)
	$^{13}C^{b,f}$	59.0 (d, J_{CH} 141), 46.5 (d, J_{CH} 189)
nido-7,10,11-$MePC_2B_8H_{10}$ (**4a**)	$^{11}B\{^{1}H\}^{a,b}$	-5.6 (d, B4, J_{BH} 142), -7.3 (d, B9, J_{BH} 131), -14.6 (d, B6, J_{BH} 173), -16.6 (d, B2, J_{BH} 171), -18.8 (d, B8, J_{BH} 156), -21.4 (d, B5, J_{BH} 113), -22.0 (d, B3, J_{BH} 128), -41.7 (d, B1, J_{BH} 148)
	^{11}B (calc)^{c}	-2.1 (B4), -6.0 (B9), -15.0 (B6), -16.0 (B8), -16.9 (B2), -20.8 (B5), -22.7 (B3), -42.4 (B1)
	$^{11}B-^{11}B^{a,b}$	observed crosspeaks: B1−B2,3,4,5,6; B2−B3,6; B3−B4,8; B4−B5,8,9; B5−B6; missing B4,5−B9
	$^{1}H\{^{11}B\}^{b,d}$	2.93 (s, CH), 2.47 (s, CH), 2.30 (1, BH), 2.22 (d, CH_3, J_{HP} 9), 2.20 (1, BH), 2.03 (1, BH), 1.98 (1, BH), 1.65 (1, BH), 1.62 (1, BH), 1.39 (2, BH)
	$^{13}C^{b,f}$	47.91 (m^{e}, CH, J_{CH} 139, $J \sim 28$), 34.29 (d of d, CH, J_{CH} 184, J_{CP} 24), 7.91 (q, CH_3, J_{CH} 139)
	$^{31}P^{b,j}$	-74.40 (s)
nido-7,10,11-$PhPC_2B_8H_{10}$ (**4b**)	$^{11}B^{a,b}$	-6.2 (d, B4, J_{BH} 149), -7.2 (d, B9, J_{BH} 154), -15.0 (d, B6, J_{BH} 174), -16.6 (d, B8, J_{BH} 174), -19.1 (d, B2, J_{BH} 150), -21.1 (d, B5, J_{BH} 156), -22.1 (d, B3, J_{BH} 156), -41.3 (d, B1, J_{BH} 150)
	^{11}B (calc)^{c,h}	-2.1 (B4), -6.0 (B9), -15.0 (B6), -16.0 (B8), -16.9 (B2), -20.8 (B5), -22.7 (B3), -42.4 (B1)
	$^{11}B-^{11}B^{a,b}$	observed crosspeaks: B1−B2,3^{g},4,5,6; B2−B3,6; B3−B4,8^{g}; B4−B5,9; B5−B6; B8−B9; missing B4−B8; B5−B9
	$^{1}H\{^{11}B\}^{b,d}$	7.80−7.54 (m, phenyl), 3.14 (s, CH), 2.59 (s, CH), 2.38 (1, BH), 2.31 (1, BH), 2.14 (1, BH), 2.09(1, BH), 1.91 (1, BH), 1.88 (1, BH), 1.61 (1, BH), 1.53 (1, BH)
	$^{13}C^{b,f}$	134.50−134.48 (d, i-C_6H_5, J_{PC} 2.7), 134.13−134.01 (d, p-C_6H_5, J_{PC} 15), 130.29−130.19 (d, J_{PC} 12.9), 129.12 (s, *o*-C_6H_5), 47.72 (br, CH), 33.68 (d of d, CH, J_{CH} 186, J_{CP} 24)
	$^{31}P^{b,j}$	-68.60 (s)
nido-10-Ph-7,10-SPB_9H_9 (**5**)	$^{11}B^{a,b}$	-5.5 (d, B4, J_{BH} 138), -6.1 (d, B5, $J_{BH} \sim 118$), -7.4 (d, B8, J_{BH} 189), -9.5 (d, B2,6, J_{BH} 168), -14.7 (d, B9,3 J_{BH} broad^{g}), -19.6 (d, B11, J_{BH} 169, J_{BP} 64), -38.5 (d, B1, J_{BH} 155)
	^{11}B (calc)^{c,i}	-2.9 (B4), -5.0 (B8), -6.2 (B5), -7.8 (B2), -9.3 (B6), -13.4 (B3), -13.5 (B9), -17.5 (B11), -41.9 (B1)
	$^{11}B-^{11}B^{a,b}$	observed crosspeaks: B1−B2,3,4,5,6; B2,6^{g}−B3,11; B3−B4; B4-B5,8,9; B5−B9; B8−B9; missing B3−B8, B5−B6
	$^{1}H\{^{11}B\}^{b,d}$	7.99−7.12 (m, phenyl), 2.71 (3, BH), 2.52 (2, BH), 2.43 (1, BH), 2.32 (1, BH), 2.18 (1, BH), 1.65 (1, BH)
	$^{13}C^{b,f}$	134.03−120.58 (m, phenyl)
	$^{31}P^{b,j}$	-48.95 (s)

[a] 160.5 MHz. [b] CD_2Cl_2. [c] DFT B3LYP/6-311G*//B3LYP/6-311G*. [d] 500.1 MHz. [e] Apparent septet. [f] 125.7 MHz. [g] Overlapped. [h] $MePC_2B_8H_{10}$. [i] $MePSB_9H_9$. [j] 81.0 MHz.

Flash column chromatography was performed using silica gel (230−400 mesh, Merck). Elemental analyses were performed at Robertson Microlit, Madison, NJ, or at the University of Pennsylvania microanalysis facility. Melting points were obtained on a standard melting point apparatus and are uncorrected.

***nido*-7-$SB_{10}H_{12}$ (1).** A 0.244 g (2.0 mmol) sample of $B_{10}H_{14}$ was dissolved in 15 mL of glyme under a N_2 atmosphere. To this stirred solution was added 1.28 g (6.0 mmol) of proton sponge. The solution was then chilled in an ice−water bath, and 0.24 mL (3.0 mmol) of S_2Cl_2 was injected slowly by syringe. The contents slowly warmed to room temperature, and after 16 h, the solution was filtered to remove PSH^+Cl^-. The solvent was then vacuum evaporated, and the oily residue was washed with diethyl ether. The remaining residue was dissolved in a minimum of methylene chloride (~2 mL). This solution was then added dropwise to 125 mL of heptane with stirring. The precipitated yellow solid was filtered and then dried in vacuo to yield 0.689 g (1.88 mmol, 94.5%) of PSH^+[*nido*-7-$SB_{10}H_{11}$]$^-$ (**PSH^+1$^-$**) as a yellow solid. The ^{11}B NMR spectrum of the sample was identical to that of an authentic sample.[6]

A methylene chloride solution of 0.689 g of **PSH^+1$^-$** was then chilled with an ice−water bath, and acidified by slow addition of 2 mL of concentrated H_2SO_4. The methylene chloride layer was then extracted, the solvent vacuum evaporated, and the residue sublimed, yielding 0.271 g (1.78 mmol, 91%) of light-yellow *nido*-7-$SB_{10}H_{12}$ (**1**). The ^{11}B NMR spectrum of the product was identical to that of an authentic sample.[6] No other product was detected by GC/MS. HRMS (*m*/*e*) calcd for $^{1}H_{11}{}^{11}B_{10}{}^{32}S$ (P − H): 153.1512. Found: 153.1510.

***nido*-7-$MePB_{10}H_{12}$ (2a).** A 0.240 g (2.0 mmol) sample of $B_{10}H_{14}$ was dissolved in 15 mL of glyme under a N_2 atmosphere. To this stirred solution was added 1.28 g (6.0 mmol) of proton sponge. The flask was chilled in an ice−water bath, and 0.13 mL (3.0 mmol) of

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$MePCl_2$ was injected slowly. The contents gradually warmed to room temperature, and after 16 h the solution was filtered to remove PSH^+Cl^-. The solvent was vacuum evaporated, and the oily residue was copiously washed with diethyl ether. Addition of 1.5 mL of $HCl\cdot Et_2O$ precipitated any excess proton sponge. The contents were then filtered, and the solvent vacuum evaporated to give the crude PSH^+-[*nido*-7-$MePB_{10}H_{11}$]$^-$ as a yellow oil. A chilled methylene chloride solution of **2a**$^-$ was then acidified dropwise with 1 mL of concentrated H_2SO_4. The methylene chloride layer was extracted and reduced to dryness, and sublimation from the yellow oil at 90 °C yielded 0.316 g (1.90 mmol, 95%) of a pale yellow solid that was confirmed to be *nido*-7-$MePB_{10}H_{12}$ (**2a**) by comparison with previously reported spectroscopic data.[7,8] Mp 85−87 °C (lit. 86.5−88.5 °C). No other products were detected by GC/MS.

***nido*-7-$PhPB_{10}H_{12}$ (2b).** A 0.240 g (2.0 mmol) sample of $B_{10}H_{14}$ was dissolved in 15 mL of glyme under a N_2 atmosphere. To this stirred solution was added 1.28 g (6.0 mmol) of proton sponge. The flask was chilled in an ice−water bath, and 0.20 mL (1.5 mmol) of $PhPCl_2$ was injected slowly. The contents gradually warmed to room temperature, and after 16 h the solution was filtered to remove PSH^+Cl^-. The solvent was vacuum evaporated, and the oily residue was washed with diethyl ether. Excess proton sponge was precipitated from the diethyl ether washings using 1 mL of 1.0 M $HCl\cdot Et_2O$. The solution was then filtered, and the solvent was vacuum evaporated from the filtrate to give the resultant crude PSH^+[*nido*-7-$PhPB_{10}H_{11}$]$^-$ as a yellow oil. A chilled methylene chloride solution of **2b**$^-$ was then acidified by dropwise addition of 1 mL of concentrated H_2SO_4. The methylene chloride layer was extracted, reduced to dryness, and sublimation at 90 °C from the yellow oil yielded 0.448 g (1.96 mmol, 98%) of a pale yellow solid which was identified as *nido*-7-$PhPB_{10}H_{12}$ (**2b**) by comparison with previously reported spectroscopic data.[8] Mp 81−83 °C (lit. 82−84 °C). According to GC/MS, no other products were produced.

***nido*-7,10,11-$SC_2B_8H_{10}$ (3).** A 0.245 g (2.0 mmol) sample of *nido*-5,6-$C_2B_8H_{12}$ was dissolved in 15 mL of glyme under a N_2 atmosphere. To this stirred solution at 0 °C was added 0.047 g (2.0 mmol) of NaH. After gas evolution ceased, 0.162 mL (3.0 mmol) of S_2Cl_2 was injected slowly. At this point, 0.214 g (1.0 mmol) of proton sponge was quickly added. The contents were allowed to gradually warm to room temperature, and after 16 h the solution was filtered to remove PSH^+Cl^-. The solvent was then vacuum evaporated. The oily residue was extracted three times with 30 mL of diethyl ether. Excess proton sponge was precipitated from the diethyl ether washings using 1 mL of 1.0 M $HCl\cdot Et_2O$. The solution was filtered, and the solvent was vacuum evaporated to give 0.236 g (1.55 mmol, 77%) of *nido*-7,8,9-$SC_2B_8H_{10}$ (**3**). According to GC/MS no other product was formed. For **3**: yellow solid, mp 135−137 °C. IR (KBr, cm^{-1}), 3221 (s), 3051 (m), 2567 (s), 2361 (w), 2256 (w), 1457 (s), 1251 (m), 1197 (m), 1071 (w), 1007 (m), 938 (m), 883 (m), 832 (w), 744 (m), 649 (w), 545 (w). HRMS (*m*/*e*) cald for $^{12}C_2{}^1H_{10}{}^{11}B_8{}^{32}S$ 154.1428. Found: 154.1242. Anal. Calcd for $C_2H_{10}B_8S$: C, 15.74; H, 6.60. Found: C, 15.59; H, 6.43.

***nido*-7,10,11-$MePC_2B_8H_{10}$ (4a).** A 0.245 g (2.0 mmol) sample of *nido*-5,6-$C_2B_8H_{12}$ was dissolved in 15 mL of glyme under a N_2 atmosphere. To this stirred solution was added 0.642 g (3.0 mmol) of proton sponge; 0.26 mL (3.0 mmol) of $MePCl_2$ was then injected into the flask. After 17 h the solution was filtered to remove PSH^+Cl^-. The solvent was vacuum evaporated, and the orange oily residue was extracted three times with 50 mL aliquots of diethyl ether. Excess proton sponge was then precipitated from the diethyl ether using 2 mL of 1.0 M $HCl\cdot Et_2O$. The solution was filtered, and the diethyl ether was vacuum evaporated. The resulting solid was dried under vacuum to give 0.323 g (1.94 mmol, 97%) of **4a**. GC/MS detected no other products. For **4a**: pale yellow solid, mp 138 °C(dec). IR (KBr, cm^{-1}): 3214 (s), 3043 (w), 2562 (m), 2359 (m), 2260 (w), 1471 (s), 1452 (s), 1437 (s), 1419 (s), 1395 (s), 1309 (m), 1194 (m), 1100 (w), 1010 (w), 928 (w), 831 (w), 771 (w), 738 (w), 681 (w), 647 (w), 548 (m), 484 (m). HRMS (*m*/*e*) calcd for $^{12}C_2{}^1H_{10}{}^{11}B_8{}^{31}P$ (P − CH_3): 153.1564. Found: 153.1290. Anal. Calcd for $C_3H_{13}B_8P$: C, 21.63; H, 7.87. Found C, 21.21; H, 7.29.

***nido*-7,10,11-$PhPC_2B_8H_{10}$ (4b).** The phenyl analogue was prepared and isolated in an analogous manner as **4a**. A 0.245 g (2.0 mmol) sample of *nido*-5,6-$C_2B_8H_{12}$ was reacted with proton sponge (0.642 g, 3.0 mmol) and $PhPCl_2$ (0.26 mL, 3 mmol) to yield 0.379 g of *nido*-7,10,11-$PhPC_2B_8H_{10}$ (**4b**) (1.66 mmol, 83% yield). No other products were detected by GC/MS. For **4b**: pale yellow solid, mp 73−74 °C. IR (KBr, cm^{-1}): 3044 (s), 2991 (w), 2564 (s), 2198 (w), 1966 (w), 1897 (w), 1814 (w), 1582 (m), 1573 (m), 1480 (m), 1438 (s), 1335 (m), 1276 (w), 1245 (w), 1184 (m), 1162 (w), 1101 (s), 1069 (m), 1026 (m), 1007 (m), 997 (m), 940 (m), 862 (m), 739 (s), 683 (m), 655 (w), 608 (m), 543 (m), 512 (s), 485 (s), 464 (m). HRMS (*m*/*e*) calcd for $^{12}C_8{}^1H_{15}{}^{11}B_8{}^{31}P$: 230.1656. Found: 230.1654.

***nido*-10-Ph-7,10-SPB_9H_9 (5).** A 0.421 g (3.0 mmol) sample of *arachno*-6-SB_9H_{11} was dissolved in 15 mL of glyme under a N_2 atmosphere. To this stirred solution was added 1.93 g (9.0 mmol) of proton sponge. A 0.60 mL (4.5 mmol) aliquot of $PhPCl_2$ was injected slowly. After the contents were allowed to react for 16 h, the solution was filtered to remove PSH^+Cl^-. The solvent was then vacuum evaporated from the filtrate. The oily residue was then extracted with diethyl ether. Excess proton sponge was precipitated upon the addition of 2 mL of $HCl\cdot Et_2O$. The solution was filtered, and the solvent was vacuum evaporated. The pale yellow solid was dried under vacuum, affording 0.732 g (2.97 mmol, 99%) of **5**. No other products were detected by GC/MS. For **5**: pale yellow solid, mp 110 °C (dec). IR (KBr, cm^{-1}): 3214 (s), 3099 (w), 2562 (m), 2364 (w), 2259 (w), 1457 (s), 1438 (s), 1195 (s), 1128 (w), 1000 (w), 975 (m), 795 (w), 748 (m), 692 (m), 649 (w), 547 (m), 470 (w), 418 (w). HRMS (*m*/*e*) calcd for $^{12}C_6{}^1H_{14}{}^{11}B_9{}^{31}P_1{}^{32}S_1$: 248.1391. Found: 248.1388. Anal. Calcd for $C_6H_{14}B_9P_1S_1$: C, 29.24; H, 5.72. Found: C, 30.34; H, 5.19.

Computational Methods. The DFT/GIAO/NMR method,[9] using the GAUSSIAN94[10] program, was used in a manner similar to that previously described.[11−13] The geometries were fully optimized at the DFT B3LYP/6-311G* level within the specified symmetry constraints (using the standard basis sets included) on a (2)-processor Origin 2000 computer running IRIX 6.4. Calculations that would include the phenyl exopolyhedral substituent were not possible, since such calculations would be too large for our available computational resources. Thus, only methyl- or hydrogen-substituted derivatives were employed for the calculations. Cartesian coordinates for each calculated structure are listed in Tables 1−10 of the Supporting Information. Selected calculated intramolecular bond distances are listed and compared when possible to crystallographically determined distances in Tables 11−20 of the Supporting Information. The electronic energy (kcal/mol) of each optimized structure is listed in Table 21 of the Supporting Information. A vibrational frequency analysis was carried out on each optimized geometry at the DFT B3LYP/6-311G* level with a true minimum found for each structure (i.e. possessing no imaginary frequencies). The NMR chemical shifts were calculated using the GIAO option within GAUSSIAN94. GIAO NMR calculations were carried out at the B3LYP/6-311G*//B3LYP/6-311G* level. ^{11}B NMR GIAO chemical shifts are referenced to $BF_3\cdot O(C_2H_5)_2$ using an absolute shielding constant of 102.24 ppm.[13,14] ^{13}C NMR GIAO chemical shifts

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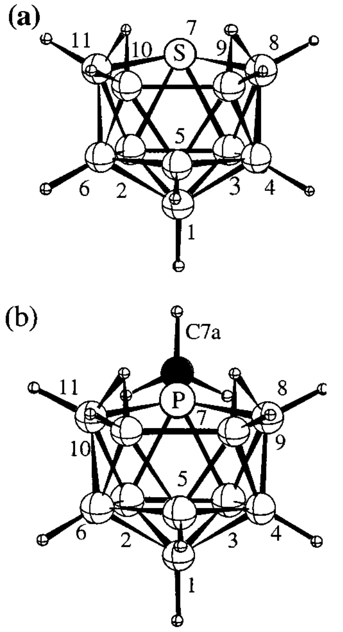

Figure 1. Optimized cage geometries for (a) *nido*-7-$SB_{10}H_{12}$, experimental (**1**) and DFT/GIAO calculated chemical shifts (**I**) and assignments {exp(assgn) [calc(assgn)]}, 16.3(B5) [19.2(B5)], −1.7(B2,3) [0.31(B2,3)], −3.9(B8,11) [−4.2(B8,11)], −10.9(B9,10) [−11.3(B9,10)], −17.8(B1) [−18.5(B1)], −25.2(B4,6) [−26.8(B4,6)]; (b) *nido*-7-$CH_3PB_{10}H_{12}$, experimental (**2a**) and DFT/GIAO calculated chemical shifts (**IIa**) and assignments {exp(assgn) [calc(assgn)]}, 1.9(B5) [5.1(B5)], −8.5(B2,3) [−8.0(B2,3)], −13.0(B8,11) [−13.5(B8,11)], −18.4(B9,10) [−18.1(B9,10)], −26.0(B1,4,6) [−25.3(B1), −26.4(B4,6)].

are referenced to TMS using an absolute shielding constant of 184.38 ppm and are corrected according to the method described by Schleyer.[15] ^{31}P NMR GIAO δ values were first referenced to PH_3 using an absolute shielding constant of 557.2396 ppm and then converted to the H_3PO_4 reference scale using the experimental value of $\delta(PH_3) = -240$ ppm.

Results

Improved Syntheses of the *nido*-7-$SB_{10}H_{12}$ Thiaborane and the *nido*-7-$RPB_{10}H_{12}$ Phosphaboranes. Two previous synthetic routes to *nido*-7-$SB_{10}H_{12}$ have been reported. One method involves the initial synthesis of *arachno*-6-$SB_9H_{12}^-$ from decaborane and ammonium polysulfide. Pyrolytic disproportionation of the cesium salt of the *arachno*-6-$SB_9H_{12}^-$ anion then gives *nido*-7-$SB_{10}H_{11}^-$. Protonation produces the neutral *nido*-7-$SB_{10}H_{12}$ in a 37% yield, with an overall 33% yield from $B_{10}H_{14}$.[6] More recently it was found that when *nido*-6-SB_9H_{11}, which can be synthesized in 86.5% yield by iodine oxidation of *arachno*-6-$SB_9H_{12}^-$,[4,16] was refluxed with $NaBH_4$, the *nido*-7-$SB_{10}H_{11}^-$ anion is produced.[5] This anion can then be acidified using aqueous HCl in methylene chloride to give *nido*-7-$SB_{10}H_{12}$ in ~60% yield based on consumed *nido*-6-SB_9H_{11}. The overall yield of *nido*-7-$SB_{10}H_{12}$ from $B_{10}H_{14}$ using this procedure is 46.7%. Unfortunately, both of the above procedures require the initial cage degradation of $B_{10}H_{14}$ to form $SB_9H_{12}^-$, followed by a second cage insertion reaction to form $SB_{10}H_{12}$. Thus, at the outset of this work there was no efficient synthetic route to the *nido*-7-$SB_{10}H_{12}$ cluster.

As described in the Experimental Section, it has now been found that the reaction of decaborane with S_2Cl_2 (or SCl_2) and proton sponge (PS), at room temperature in DME or THF, followed by acidification of the resulting anion **1**$^-$, using a two-phase methylene chloride/aqueous H_2SO_4 system, results in the formation of *nido*-7-$SB_{10}H_{12}$ (**1**) in a typical yield of 91% (eqs 1 and 2). The acidification of the proton sponge salt can only

$$B_{10}H_{14} + 3PS + SCl_2 \rightarrow \underset{\mathbf{1}^-}{PSH^+[\textit{nido}\text{-}7\text{-}SB_{10}H_{11}]^-} + 2PSH^+Cl^- \quad (1)$$

$$2PSH^+[\textit{nido}\text{-}7\text{-}SB_{10}H_{11}]^- + H_2SO_4 \rightarrow 2\underset{\mathbf{1}}{\textit{nido}\text{-}7\text{-}SB_{10}H_{12}} + (PSH^+)_2SO_4^{2-} \quad (2)$$

be accomplished by a strong acid system such as aqueous H_2SO_4. Thus, prior to acidification with H_2SO_4, the reaction mixture containing **1**$^-$ can be treated with HCl•Et_2O to easily remove any excess proton sponge as $(PSH^+)_2SO_4^{2-}$, without producing *nido*-7-$SB_{10}H_{12}$.

Compound **1** was sublimed and isolated as an air-sensitive, yellow solid in 91% yield. Comparison of both its ^{11}B and ^1H NMR spectra with those of literature values[5,6] clearly confirm its identity. As shown in Figure 1a, the proposed structure and experimentally observed chemical shifts and assignments were also found to be in excellent agreement with DFT/GIAO/NMR calculations at the DFT B3LYP/6-311G*//B3LYP/6-311G* level.[9]

Isoelectronic with *nido*-7-$SB_{10}H_{12}$ (**1**) are the known 11-vertex *nido*-7-$RPB_{10}H_{12}$ phosphaboranes, where R = Me, Ph (**2a** and **2b**). A crystallographic determination[7] of the methyl compound has confirmed a cage geometry consistent with that proposed for the *nido*-7-$SB_{10}H_{12}$ cluster. The *nido*-7-$RPB_{10}H_{12}$ (R = Me, Ph) compounds were first synthesized by the reaction of the decaborane dianion with a phosphorus dihalide in a 33% yield.[8] Shore[7] later prepared *nido*-7-$MePB_{10}H_{12}$ in a 12% yield by reaction of $K_2^+[B_{11}H_{13}]^{2-}$ with $MePCl_2$ over 7 days at room temperature.

When a method similar to that used for the synthesis of *nido*-7-$SB_{10}H_{12}$, was used, it was found that the overnight reaction of decaborane with $RPCl_2$ (R = Me, Ph) and excess proton sponge at room temperature produced the anions *nido*-7-$MePB_{10}H_{11}^-$ (**2a**$^-$) and *nido*-7-$PhPB_{10}H_{11}^-$ (**2b**$^-$) in almost quantitative yields. The reaction mixture was treated with HCl•Et_2O to precipitate any unreacted proton sponge, followed by acidification of the phosphaborane anions (**2a**$^-$ or **2b**$^-$) again using the two-phase CH_2Cl_2/aqueous H_2SO_4 system, to give *nido*-7-$MePB_{10}H_{12}$ (**2a**) and *nido*-7-$PhPB_{10}H_{12}$ (**2b**) in almost quantitative yields (eqs 3−4).

$$B_{10}H_{14} + 3PS + RPCl_2 \rightarrow PSH^+[\textit{nido}\text{-}7\text{-}RPB_{10}H_{11}]^- + 2PSH^+Cl^- \quad (3)$$

$$2PSH^+[\textit{nido}\text{-}7\text{-}RPB_{10}H_{11}]^- + H_2SO_4 \rightarrow 2\textit{nido}\text{-}7\text{-}RPB_{10}H_{12} + (PSH^+)_2SO_4^{2-} \quad (4)$$

2a, R = Me, 95% yield
2b, R = Ph, 98% yield

Compounds **2a** and **2b** were sublimed and isolated as air-sensitive, yellow solids. Comparisons of the ^{11}B and ^1H NMR spectra of **2a** and **2b** with those in the literature[7,8] confirm their identity. GC/MS showed the presence of no other compounds.

Density functional theory calculations at the B3LYP/6-311G* level performed on compound **2a** produced the optimized geometry **II** (Figure 1b). A comparison (Supporting Information) of calculated bond lengths with those determined crystal-

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(15) Maerker, C.; Schleyer, P. v. R.; Salahub, D. R.; Malkina, O. L.; Malkin, V. G., submitted.

(16) Pretzer, W. R.; Rudolph, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1441−1447.

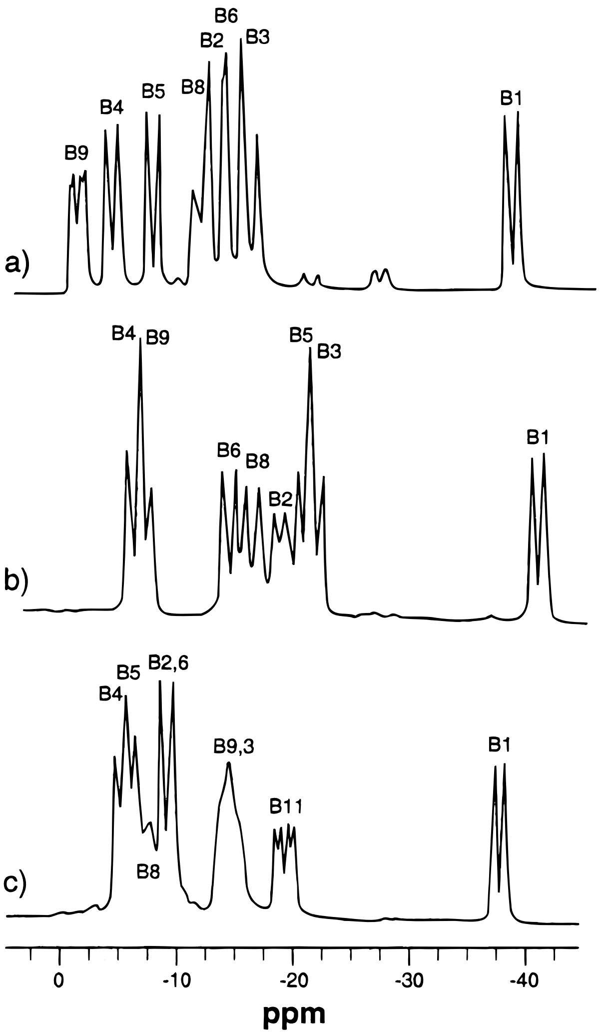


Figure 2. 160.5 MHz ^{11}B NMR spectra for (a) *nido*-7,10,11-$SC_2B_8H_{10}$ (**3**) (b) *nido*-7,10,11-$PhPC_2B_8H_{10}$ (**4b**), and (c) *nido*-10-Ph-7,10-SPB_9H_9 (**5**).

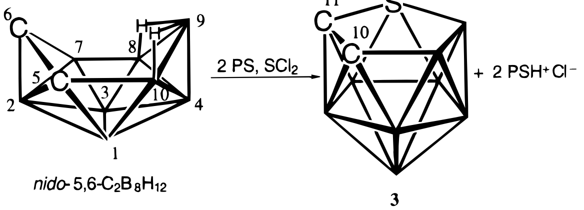
lographically[7] shows good agreement. Similarly, a comparison of the experimentally determined ^{11}B NMR shifts[7,8] and assignments for **2a** and **2b** with those for the calculated structure **II** show good agreement, with the difference in shifts being only 0.1−3.2 ppm.

Syntheses of the New 7,10,11-$SC_2B_8H_{10}$ Thiadicarbaborane and the 7,10,11-$MePC_2B_8H_{10}$ and 7,10,11-$PhPC_2B_8H_{10}$ Phosphadicarbaboranes. Isoelectronic with the 11-vertex thiaborane and phosphaborane clusters **1** and **2** are the thia- and phosphadicarbaboranes of the general formula $EC_2B_8H_{10}$ (E = S, RP). While no previous phosphadicarbaborane has been reported, one thiadicarbaborane, *nido*-7,9,10-$SC_2B_8H_{10}$, has been previously synthesized in a 30% yield from the reaction of aqueous bisulfate with $K^+C_2B_9H_{12}^-$.[17] The structure of this compound has been confirmed by both electron diffraction and ab initio/NMR calculations.[18,19]

When the proton sponge initiated in situ dehydrohalogenation method was used, it was found that the reaction of *nido*-5,6-$C_2B_8H_{12}$ with proton sponge and SCl_2 (or S_2Cl_2) in DME at 0 °C gave the new *nido*-thiadicarbaborane *nido*-7,10,11-$SC_2B_8H_{10}$ (**3**) in 77% yield as a yellow solid (eq 5).

$$\textit{nido}\text{-5,6-}C_2B_8H_{12} + 2PS + SCl_2 \rightarrow \underset{\mathbf{3}}{\textit{nido}\text{-7,10,11-}SC_2B_8H_{10}} + 2PSH^+Cl^- \quad (5)$$

The reported[17,18] ^{11}B NMR spectrum for *nido*-7,9,10-$SC_2B_8H_{10}$ shows five resonances in 1:2:2:2:1 ratios in agreement with its established C_s symmetry.[18,19] The 160.5 MHz ^{11}B NMR spectrum of the new isomer **3** consists of eight resonances, indicative of C_1 symmetry (Figure 2a). Likewise, the 125.7 MHz ^{13}C NMR spectrum for **3** reveals two different cage CH resonances observed as doublets at 46.5 and 59.0 ppm. A more detailed investigation of the ^{11}B NMR spectrum using a 2D ^{11}B−^{11}B COSY experiment (Table 1) led to the preliminary assignment of the structure shown in eq 6 in which the sulfur and carbon atoms occupy adjacent positions on the five-membered open face. Such a structure can be generated from *nido*-5,6-$C_2B_8H_{12}$ in a straightforward manner, with the initial insertion of a −SCl unit onto the C5−C6−B9−B10 edge followed by dehydrohalogenation, to create the new five-membered open face containing the original S−C5−C6−B9−B10 atoms.



(6)

DFT/GIAO/NMR calculations were employed to confirm the structure of **3**. Two isomeric structures having C_1 symmetry, as well as the symmetric C_s isomer were examined: *nido*-7,10,11-$SC_2B_8H_{10}$ (**III.a**), *nido*-7,9,11-$SC_2B_8H_{10}$ (**III.b**), and *nido*-7,9,10-$SC_2B_8H_{10}$ (**III.c**). The optimized geometries for the three structures are presented in Figure 3.

Although best agreement is found for **III.a**, the ^{11}B and ^{13}C NMR chemical shifts calculated for both of the two C_1 symmetry isomers (**III.a** and **III.b**) fall in the range of the experimental NMR shifts of **3** (Figure 4). However, only the boron resonance assignments of **III.a** are in agreement with the assignments determined experimentally by 2D ^{11}B−^{11}B NMR for **3** (Table 1). For example, the experimental 2D ^{11}B−^{11}B NMR spectra of **3** show that the resonances at −3.4 and −6.8 ppm are 5- and 4-coordinate, respectively. This agrees with the calculations on the 7,10,11-isomer (**III.a**), but disagrees with the calculations on the 7,9,11-isomer (**III.b**) that predict the two resonances in this region (i.e., −1.8 and −3.8 ppm) are 4- and 2-coordinate, respectively. Likewise, the resonances at −0.46 and −10.9 ppm in the boron NMR spectrum of **3** show evidence of J_{BB} coupling (~30−40 Hz), consistent with their assignment in the calculations on **IIIa** as the adjacent B8 and B9 borons.

Structure **III.c** (*nido*-7,9,10-$SC_2B_8H_{10}$) corresponds to the structure proposed for the known isomer, and the GIAO calculated ^{11}B chemical shifts are in agreement both with those that were experimentally determined[17] (Figure 4 caption) and with earlier ab initio/IGLO calculations.[18] The *nido*-7,9,10-$SC_2B_8H_{10}$ would be expected to be the most stable isomer since electron-rich heteroatoms, such as carbon, phosphorus, and sulfur, are known to favor both low-coordinate cage positions on the open faces of polyhedral frameworks and arrangements

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(17) Brattsev, V. A.; Knyazev, S. P.; Danilova, G. N.; Stanko, V. I. *Zh. Obshch. Khim.* **1975**, *45*, 1393−1394.

(18) Hynk, D.; Hofmann, M.; Schleyer, P. v. R.; Bühl, M.; Rankin, D. W. H. *J. Phys. Chem.* **1996**, *100*, 3435−3440.

(19) Vondrak, T.; Heřmánek, S.; Plešek, J. *Polyhedron* **1993**, *12*, 1301−1310.

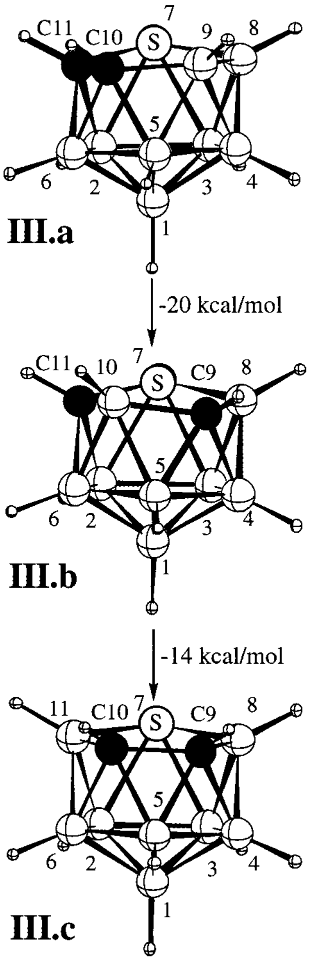
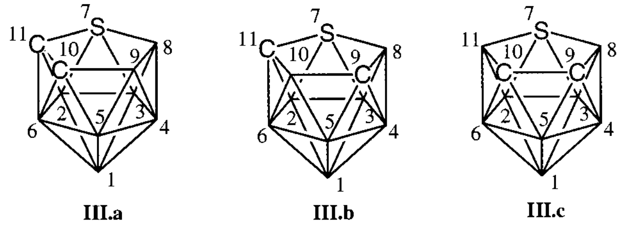


Figure 3. Optimized geometries and relative energies for *nido*-7,10,11-$SC_2B_8H_{10}$ (**III.a**), *nido*-7,9,11-$SC_2B_8H_{10}$ (**III.b**), and *nido*-7,9,10-$SC_2B_8H_{10}$ (**III.c**).



nido-7,10,11-$SC_2B_8H_{10}$ (**3**) experimental	*nido*-7,10,11-$SC_2B_8H_{10}$ (**III.a**) calculated	*nido*-7,9,11-$SC_2B_8H_{10}$ (**III.b**) calculated	*nido*-7,9,10-$SC_2B_8H_{10}$ (**III.c**) calculated
^{11}B NMR:			
-0.46(B9)	0.13(B9)	-0.2(B2)	-2.0(B5)
-3.5(B4)	-1.5(B4)	-1.8(B5)	-5.1(B2,3)
-6.8(B5)	-6.2(B5)	-3.8(B10)	-11.8(B8,11)
-10.9(B8)	-8.8(B8)	-8.2(B8)	-13.6(B4,6)
-12.5(B2)	-12.9(B2)	-8.8(B4)	-42.6(B1)
-14.0(B6)	-14.5(B3)	-18.3(B6)	
-15.4(B3)	-15.1(B6)	-20.0(B3)	
-38.0(B1)	-39.5(B1)	-37.5(B1)	
^{13}C NMR:			
46.5	50.81(C11)	44.63(C11)	53.50(C9,10)
59.0	56.60(C10)	53.73(C9)	

Figure 4. Comparison of the experimental chemical shifts and assignments for **3** with those DFT/GIAO calculated values for *nido*-7,10,11-$SC_2B_8H_{10}$ (**III.a**), *nido*-7,9,11-$SC_2B_8H_{10}$ (**III.b**), and *nido*-7,9,10-$SC_2B_8H_{10}$ (**III.c**). Experimentally observed ^{11}B NMR shifts for *nido*-7,9,10-$SC_2B_8H_{10}$: −2.8(B5), −7.4(B2,3), −13.0(B8,11), −13.8(B4,6), −41.5(B1).[17,18]

that allow the maximum separation of the heteroatoms.[12,20] The DFT calculations confirm that the symmetrical 7,9,10-isomer (**III.c**) should be the most stable. Thus, the 7,9,10-isomer (**III.c**) is 34 kcal/mol lower in energy than **III.a**, and **III.b** is 20 kcal/mol lower than **III.a** (Figure 3). The exclusive synthesis of the 7,10,11-isomer, (**III.a**), the least stable of the three possible isomers, clearly shows that the mild conditions of the dehydrohalogenation heteroatom insertion reaction allows the isolation of kinetic rather than thermodynamic products. Attempts to isomerize **3** to the other isomers were made by heating a sealed sample for 40 min at 110 °C. There was extensive decomposition, but two peaks corresponding to two other $SC_2B_8H_{10}$ isomers were detected by GC/MS.

The new phosphadicarbaboranes, *nido*-7,10,11-$RPC_2B_8H_{10}$ [R = Me (**4a**), Ph (**4b**)], were synthesized as pale yellow, air-sensitive solids in 83% (**4a**) and 97% (**4b**) yields in a manner similar to **3** by reaction of *nido*-5,6-$C_2B_8H_{12}$ with proton sponge and methyl- or phenyl-substituted $RPCl_2$ (eq 7).

$$\textit{nido}\text{-5,6-}C_2B_8H_{12} + 2PS + RPCl_2 \rightarrow \textit{nido}\text{-7,10,11-}RPC_2B_8H_{10} + 2PSH^+Cl^- \quad (7)$$
$$R = \text{Me } (\mathbf{4a}),\ \text{Ph } (\mathbf{4b})$$

The 160.5 MHz ^{11}B NMR spectra for **4a** and **b** are somewhat similar to that of the isoelectronic cluster **3**, consisting of eight resonances, again suggesting C_1 symmetry and a 7,10,11-configuration (Figure 2b). DFT/GIAO/NMR calculations at the B3LYP/6-311G*//B3LYP/6-311G* level were employed to examine several possible structures: *nido*-7,10,11-$MePC_2B_8H_{10}$ (**IV.a**), *nido*-7,9,11-$MePC_2B_8H_{10}$ (**IV.b**), and *nido*-7,9,10-$MePC_2B_8H_{10}$ (**IV.c**). The optimized geometries for the three isomers are presented in Figure 5. Comparison of the ^{11}B NMR shifts of the three calculated structures with the experimental ^{11}B NMR shifts of **4a** (Figure 6) indicate that while the calculated shifts of both **IV.a** (7,10,11-isomer) and **IV.b** (7,9,11-isomer) fall in the range of the experimentally determined shifts for **4a** and **4b**, only the assignments of **IV.a** (7,10,11-isomer) are consistent with the experimental data. For example, the experimental 2D $^{11}B-^{11}B$ NMR spectra show that the resonances at −5.6 and −14.6 ppm are 5- and 3-coordinate, respectively. This is correctly predicted by the calculations on the 7,10,11-isomer (**IV.a**) but does not agree with the calculations on the 7,9,11-isomer (**IV.b**), where it is predicted that the two resonances in this region (i.e., −5.0 and −8.1 ppm) are 3- and 4-coordinate, respectively.

Consistent with the proposed structure, the 125.7 MHz $^{13}C\{^1H\}$ NMR spectra of **4a** and **4b** each show two cage-CH resonances. The CH resonance near 48 ppm is broad, while the CH resonance near 34 ppm for both compounds **4a** and **4b** is a sharp doublet, clearly showing phosphorus coupling ($^1J_{CP}$ = 24 Hz), thereby allowing the assignment of the two resonances to the C10 and C11 carbons, respectively. These assignments are consistent with the relative ^{13}C NMR shifts

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(20) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67−142.

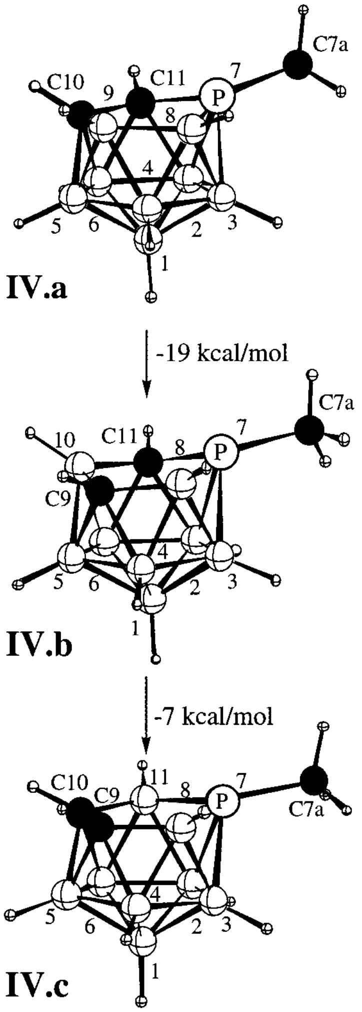


Figure 5. Optimized geometries and relative energies for *nido*-7,10,11-$MePC_2B_8H_{10}$ (**IV.a**), *nido*-7,9,11-$MePC_2B_8H_{10}$ (**IV.b**), and *nido*-7,9,10-$MePC_2B_8H_{10}$ (**IV.c**).

calculated for **IV.a** (7,10,11-isomer) (Figure 6). Likewise, the observed chemical shift of the phosphorus resonance in the 81.0 MHz ^{31}P NMR spectrum of **4a** (−74.4 ppm) is in good agreement with that calculated for structure **IV.a** (−82.0 ppm).

As was the case for the $SC_2B_8H_{10}$ cage, energy calculations on the phosphadicarbaboranes reveal that the symmetrical 7,9,10-$RPC_2B_8H_{10}$ cluster (**IV.c**) is the most stable. **IV.c** is approximately 26 kcal/mol more stable than **IV.a**, and **IV.b** is more stable than **IV.a** by ∼19 kcal/mol (Figure 5). Preliminary investigations by GC/MS reveal that, although significant decomposition is observed upon heating **4a** for 20 min at 110 °C, a mixture containing two new isomers is produced.

Synthesis of the *nido*-10-Ph-7,10-SPB_9H_9 Thiaphosphaborane. Isoelectronic with the thiadicarbaboranes and phosphadicarbaboranes discussed above are mixed phosphathiaborane [(R)PSB_9H_9] clusters. However, no previous examples of this class of mixed heteroborane have been reported.

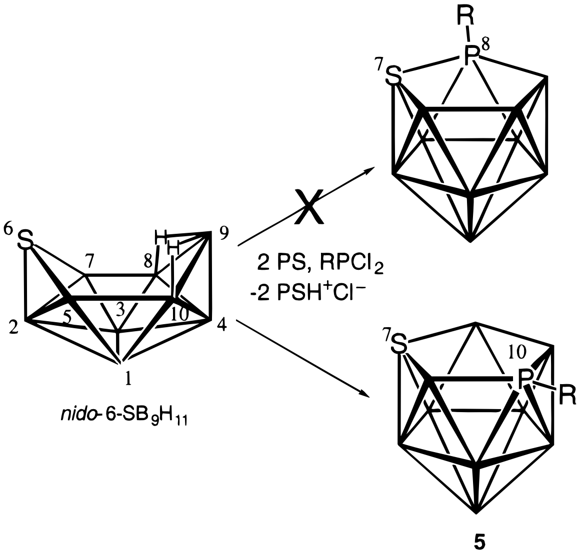
Again using the proton sponge initiated in situ dehydrohalogenation method, the new phosphathiaborane, *nido*-10-Ph-7,10-SPB_9H_9, (**5**) was synthesized in a 98% yield, and isolated as a pale yellow, air-sensitive solid (eq 8).

$$\textit{nido}\text{-6-}SB_9H_{11} + 2PS + PhPCl_2 \rightarrow \underset{\mathbf{5}}{\textit{nido}\text{-10-Ph-7,10-}PSB_9H_9} + 2PSH^+Cl^- \quad (8)$$

The experimental 160.5 MHz $^{11}B\{^1H\}$ NMR spectrum for **5** reveals seven resonances, in ratios of 1:1:1:2:2:1:1, in the same ranges found for the other 11-vertex heteroboranes, *nido*-7,10,11-$RPC_2B_8H_{10}$ (**4a,b**) and *nido*-7,10,11-$SC_2B_8H_{10}$ (**3**) (Figure 2c).

If the formation of **5** was achieved by a heteroatom insertion process similar to that discussed earlier for **3** and **4**, involving an initial addition of a -P(R)Cl unit to the S6−B7−B8−B9 edge of *nido*-6-SB_9H_{11}, then the 7,8-structure shown below should be produced. This would have the phosphorus and sulfur atoms in adjacent positions.

The spectral and computational characterizations of **5** revealed, however, that it has the 7,10-configuration shown in eq 9. DFT/GIAO/NMR calculations were employed to examine



(9)

both cage geometries: *nido*-8-Me-7,8-SPB_9H_9 (**V.a**) and *nido*-10-Me-7,10-SPB_9H_9 (**V.b**). The optimized geometries and relative energies of these two structures are shown in Figure 7. As can be seen in Figure 8, a comparison of the experimental NMR shifts and 2D $^{11}B-^{11}B$ determined assignments of **5** with those calculated for *nido*-8-Me-7,8-SPB_9H_9 (**V.a**) and *nido*-10-Me-7,10-SPB_9H_9 (**V.b**) clearly favors the *nido*-10-Me-7,10-SPB_9H_9 (**V.b**) structure for **5**. For example, only the calculations on **V.b** correctly predict that the resonance at −19.6 ppm of **5**, which exhibits doublet J_{BP} coupling (J = 64 Hz) in the $^{11}B\{^1H\}$ NMR spectrum, should be due to the boron (B11) that is adjacent to the phosphorus atom. The ^{31}P NMR spectrum of **5** consists of one resonance at −48.95 ppm which is in excellent agreement with the calculated shift of −55.37 ppm for **V.b**.

Calculations on the relative energies of the two methyl substituted isomers (**V.a** and **V.b**) reveal that the 7,10-isomer (**V.b**) is 40 kcal/mol more stable than the 7,8-isomer (Figure 7). Thus, unlike in **3** and **4**, in compound **5** maximum separation of the heteroatoms on the open face is achieved.

Discussion

A seemingly straightforward route to a phospha- or thiaborane or carborane could involve the reaction of SCl_2 or $RPCl_2$ with a polyhedral borane *nido*-dianion. However, there are problems with this approach.[21] One method of forming dianions requires

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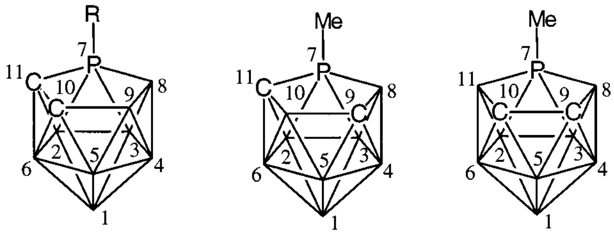
(21) For general methods used for the formation of polyborane dianions, see: Grimes, R. N. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 1, pp 459−542 and references therein.



IV.a **IV.b** **IV.c**

nido-7,10,11-$MePC_2B_8H_{10}$ (**4a**) experimental	*nido*-7,10,11-$MePC_2B_8H_{10}$ (**IV.a**) calculated	*nido*-7,9,11-$MePC_2B_8H_{10}$ (**IV.b**) calculated	*nido*-7,9,10-$MePC_2B_8H_{10}$ (**IV.c**) calculated
^{11}B NMR:			
-5.6(B4)	-2.1(B4)	-5.0(B2)	-11.3(B2,3)
-7.3(B9)	-6.0(B9)	-6.5(B10)	-16.2(B4,6)
-14.6(B6)	-15.0(B6)	-8.1(B4)	-16.7(B5)
-16.6(B2)	-16.0(B8)	-10.2(B8)	-19.6(B8,11)
-18.8(B8)	-16.9(B2)	-15.7(B6)	-45.4(B1)
-21.4(B5)	-20.8(B5)	-15.8(B5)	
-22.0(B3)	-22.7(B3)	-26.7(B3)	
-41.7(B1)	-42.4(B1)	-39.5(B1)	
^{13}C NMR:			
47.91(C10)	53.38(C10)	49.97(C9)	49.88(C9,10)
34.29(C11)	38.80(C11)	39.08(C11)	
7.91(C7a)	12.39(C7a)	14.13(C7a)	9.20(C7a)
^{31}P NMR:			
-74.40	-82.00	-102.52	-89.10

Figure 6. Comparisons of the experimental chemical shifts and assignments for **4** with those DFT/GIAO calculated values for *nido*-7,10,11-$MePC_2B_8H_{10}$ (**IV.a**), *nido*-7,9,11-$MePC_2B_8H_{10}$ (**IV.b**), and *nido*-7,9,10-$MePC_2B_8H_{10}$ (**IV.c**).

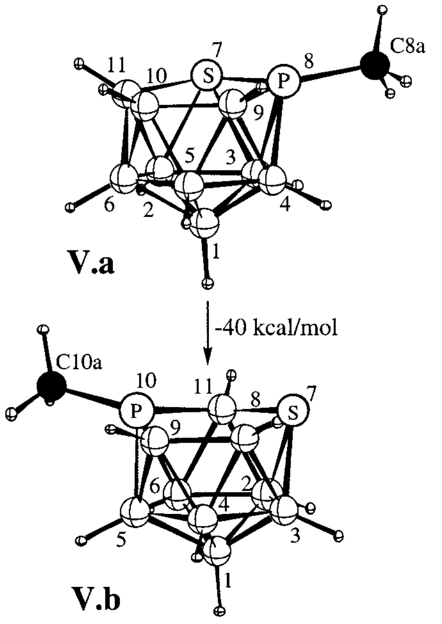
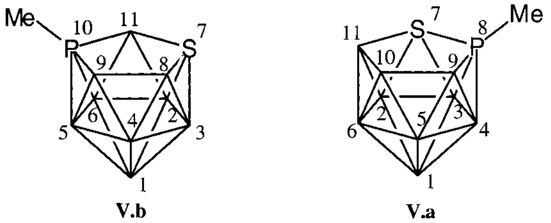


Figure 7. Optimized geometries and relative energies for *nido*-8-Me-7,8-SPB_9H_9 (**V.a**) and *nido*-10-Me-7,10-SPB_9H_9 (**V.b**).



V.b **V.a**

nido-10-Ph-7,10-SPB_9H_9 (**5**) experimental	*nido*-10-Me-7,10-SPB_9H_9 (**V.b**) calculated	*nido*-8-Me-7,8-SPB_9H_9 (**V.a**) calculated
^{11}B NMR:		
-5.5(B4)	-2.9(B4)	19.9(B10)
-6.1(B5)	-5.0(B8)	13.7(B5)
-7.4(B8)	-6.2(B5)	3.6(B9)
-9.5(B2,6)	-7.8(B2)	-0.9(B11)
	-9.3(B6)	-1.2(B3)
-14.7(B9,3)	-13.4(B3)	-5.5(B2)
	-13.5(B9)	-9.6(B6)
-19.6(B11)	-17.5(B11)	-21.6(B4)
-38.5(B1)	-41.9(B1)	-30.9(B1)
^{31}P NMR:		
-48.95	-55.37	-24.32

Figure 8. Comparisons of the experimental chemical shifts and assignments for **5** with those DFT/GIAO calculated values for *nido*-8-Me-7,8-SPB_9H_9 (**V.a**) and *nido*-10-Me-7,10-SPB_9H_9 (**V.b**).

the removal of two protons from a *nido*-cage structure containing two bridge-hydrogens. The removal of the second proton is often difficult and typically requires either strong bases, such as MeLi, or extended reaction times. Such conditions can cause cage degradation, leading to the generation of side products and lower yields. Alternatively, dianions can be generated from *closo*-clusters by reduction with agents such as sodium naphthalide. Because sodium naphthalide is a strong reducing agent, cage degradation leading to the generation of numerous side products is also usually an important drawback of this method. Thus, regardless of which procedure is used, the conditions required to generate dianions are generally harsh and can result in low yields and selectivities due to cage fragmentation.

The synthetic method presented in this paper avoids the formation of the reactive polyborane dianions. Instead, the pathway involves the reaction of a phosphorus or sulfur dihalide with a *monoanionic* boron cluster, followed by a proton sponge initiated in situ dehydrohalogenation reaction. Although the reaction is a one-pot method, the actual reaction sequence must proceed via a multistep process. A reasonable series of steps is illustrated in Figure 9 for the reaction of $B_{10}H_{14}$ with SCl_2 or $RPCl_2$. Initial deprotonation by proton sponge would generate the $B_{10}H_{13}^-$ monoanion. Because of the cluster's negative charge, the second bridge hydrogen has decreased acidity and is not removed by proton sponge. However, following the metathesis reaction in which the -X(R)Cl unit is inserted into the vacant bridge site, the negative charge is balanced and the acidity of the bridge hydrogen is restored. Another equivalent of proton sponge can then abstract this hydrogen to generate a species such as $PSH^+[B_{10}H_{12}{\cdot}X(R)Cl]^-$. Such a species was

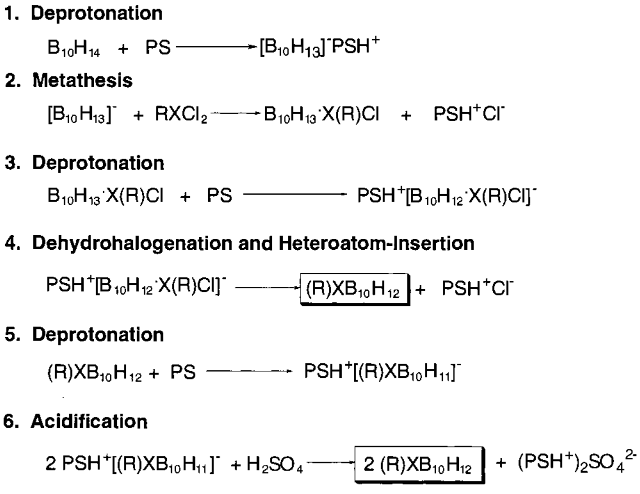


Figure 9. Multistep schematic of dehydrohalogenation heteroatom insertion reaction.

not observed by ^{11}B NMR, but would be expected to be unstable and readily undergo dehydrohalogenation with elimination of the remaining chloride on the -X(R)Cl group as PSH^+Cl^-. This last step then allows the incorporation of the -X(R) group into the cage. A similar sequence for the insertion reactions with *nido*-5,6-$C_2B_8H_{12}$ correctly predicts the formation of the observed 7,10,11-isomers, i.e., *nido*-7,10,11-$SC_2B_8H_{10}$ (**3**) and *nido*-7,10,11-$RPC_2B_8H_{10}$ (**4a** and **4b**), rather than the 7,9,11- or 7,9,10-isomers of these cage systems, even though DFT calculations clearly show the 7,10,11-isomers are higher in energy.

The key feature in this synthetic sequence is that proton sponge acts as both a deprotonating agent and a halogen scavenger. Other less expensive reagents such as NaH or KH can be used as the initial deprotonating agent; however, the use of only proton sponge allows the sequence to be carried out as a one-pot reaction.

In cases where the products have acidic hydrogens, such as *nido*-7-$SB_{10}H_{12}$ (**1**) and *nido*-7-$RPB_{10}H_{12}$, (**2a** and **2b**), they are also deprotonated by proton sponge to produce their corresponding monoanions, PSH^+[*nido*-7-$SB_{10}H_{12}$] (PSH^+**1**$^-$) and PSH^+[*nido*-7-$RPB_{10}H_{12}$], (PSH^+**2a**$^-$ and PSH^+**2b**$^-$). Thus, to avoid making a mixture of neutral and anionic products, it is convenient in these reactions to employ an excess of proton sponge to convert all of the product to its anion (step 5, Figure 9). The excess proton sponge can be easily removed from the reaction mixture by addition of $HCl{\cdot}Et_2O$, followed by filtration of the insoluble PSH^+Cl^-. The neutral cluster products are then regenerated by acidification using a two-phase aqueous H_2SO_4/methylene chloride system (step 6, Figure 9).

The routes to *nido*-7-$SB_{10}H_{12}$ (**1**) and *nido*-7-$RPB_{10}H_{12}$, (**2a** and **2b**) along with their respective anions are a significant improvement over the previous literature methods outlined earlier,[5−8] in terms of both convenience and yields. The syntheses of the new phospha- and thiacarbaboranes, *nido*-7,10,11-$SC_2B_8H_{10}$ (**3**), *nido*-7,10,11-$RPC_2B_8H_{10}$ (**4a,b**), and the mixed phosphathiaborane, *nido*-10-Ph-7,10-SPB_9H_9 (**5**), illustrate the potential importance of this method for generating new types of heteroatom−polyboranes derived from other cage systems. These methods should also be applicable to the incorporation of a wide range of heteroatoms. Studies of these possibilities are presently ongoing and will be reported in future publications.[22]

Finally, it should also be noted that since each of the 11-vertex *nido*-clusters (**1**−**5**) has a five-membered open face that is similar to both the cyclopentadienyl ($C_5H_5^-$) and dicarbollide ($C_2B_9H_{11}^{2-}$) anions, these heteroatom−polyboranes are of special interest because of their potential metal coordination chemistry. Thus, the *nido*-$SB_{10}H_{10}^{2-}$ and *nido*-$RPB_{10}H_{10}^{2-}$ dianions are analogues of dicarbollide anion, while the neutral compounds, *nido*-7,10,11-$SC_2B_8H_{10}$ (**3**), *nido*-7,10,11-$RPC_2B_8H_{10}$ (**4a** and **4b**), and *nido*-10-Ph-7,10-SPB_9H_9 (**5**) could be considered η^5- 6-π electron-donor analogues of π-arenes and are expected to form similar types of sandwich complexes. Thus, by controlling the elemental composition of these 11-vertex *nido*-heteroatom−polyboranes, it is possible to both control their formal charges and further tune the bonding properties of these cage systems. This should then allow the production of extensive series of sandwich complexes derived from these ligands, that, although isoelectronic and isostructural, will each exhibit unique properties which are a function of the individual bonding abilities of the particular metal-coordinated cage. The fact that compounds **1**−**5** can now be readily synthesized in large scales should enable extensive explorations of such coordination complexes.

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Supporting Information Available: Tables containing the Cartesian coordinates for each optimized geometry, selected calculated intramolecular bond distances, and a listing of the electronic energy (kcal/mol) of each structure (22 pages). Ordering information is given on any current masthead.

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[22] Shedlow, A. M.; Sneddon, L. G., manuscripts in preparation.