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Small Heteroborane Cluster Systems. 8. Preparation of Phosphaborane Clusters from the Reaction of Polyhedral Boranes with Low-Coordinate Phosphorus Compounds: Reaction Chemistry of Phosphaalkynes with Decaborane(14)[1]

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The room-temperature reaction of equimolar quantities of phosphaalkyne RC≡P (**2a**; R = ^{t}Bu; **2b**, R = adamantyl) with the decaborane(12)−Lewis base adduct $B_{10}H_{12}\cdot 2CH_3CN$ (**3**) resulted in the formation of new phosphaborane compounds (phosphine−methylene ylides), *nido*-RC(H)$PB_{10}H_{13}$ (**4a**, R = ^{t}Bu; **4b**, R = adamantyl), in good yield (approximately 50% each). These slightly air-sensitive compounds were fully characterized by ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR, 2D ^{11}B−^{11}B COSY NMR, FT-IR, and mass spectroscopic analyses. The structures of **4a** and **4b** are proposed to consist of a *nido*-PB_{10} framework formally based upon a 26-skeletal-electron *nido*-$[B_{11}H_{11}]^{-}$ parent compound. Only the phosphorus atom was observed to be incorporated into the polyhedral framework with an exopolyhedral C(H)R group doubly bound to the cage phosphorus atom. Two related mechanisms are proposed to account for the observed products from these reactions.

Introduction

The chemistry of multiply bonded main-group compounds has been an area of intense recent interest.[2,3] For many years such compounds were believed not to be stable enough for isolation, due to the proposed weakness of the pπ−pπ bonding interactions between the elements beyond the second period. These observations gave rise to the well-known "classical double bond rule".[4] In the past decade, however, numerous doubly and triply bonded main-group species have been prepared as stable compounds by either kinetic stabilization (steric blocking) or thermodynamic stabilization (mesomeric π-electron delocalization) techniques.[5] In the former technique, the main-group multiple bond has been found to remain sufficiently reactive to display a wide variety of chemical reactions directed to the unsaturated site, despite the requisite steric blockage.

Phosphaalkenes ($R_2C{=}PR$) and phosphaalkynes (RC≡P) constitute two important types of main-group multiply bonded compounds. Phosphaalkynes have been known since the first report of the formation of HC≡P by Gier in 1961.[6] In this work, HC≡P was prepared by passing phosphine gas (PH_3) through a rotating electric arc discharge and trapping the volatile products under vacuum at low temperature.[6] This phosphaalkyne, however, was stable only under vacuum and at very low temperatures (below −124 °C). The synthetic difficulty and extreme instability of the initially reported phosphaalkynes effectively precluded any significant development of the chemistry of these low-coordinate species. Recently, however, numerous multiply bonded phosphorus compounds, including several phosphaalkynes, have been reported which are rather stable, primarily due to the presence of bulky substituents on the carbon atom (kinetic stabilization).[3,5,7] For example, the sterically protected ^{t}BuC≡P, AdC≡P, and MesC≡P compounds (where Bu = butyl, Ad = adamantyl, and Mes = mesityl) are all air-stable at room temperature and are even stable at elevated temperatures under an inert atmosphere.[8−10] Advances in the understanding of the chemical reactivities of these species have been greatly enhanced by the recent development of several straightforward synthetic procedures for the preparation of relatively large quantities of both phosphaalkenes and phosphaalkynes.[11−13] Thus, the chemistry of the C≡P bond is currently being vigorously investigated, and numerous reviews have been written in the last decade in an attempt to keep pace with this intense activity.[7,11,12,14,15] It is clear from much of this detailed work, however, that phosphaalkynes often react rather similarly to the related organic alkynes in a variety of reactions, despite the presence of the sterically demanding groups.[3−5]

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The reaction of substituted alkynes with polyhedral borane clusters has been shown to readily insert the sp carbons of the alkyne directly into the borane cage framework in good yields, as summarized in Scheme 1.[16−19] This synthetic technique has been employed in the formation of a large variety of exopolyhedrally substituted carborane species. Motivated by some of the striking similarities and apparent differences between unsaturated organic compounds and the related unsaturated phosphorus main-group compounds, two investigations have been reported in which borane cages have been reacted with phosphaalkenes. In the work of Gaines, an inserted *nido*-$R_2C{=}PB_5H_8$ compound was reported from the reaction of $[B_5H_8]^-$ and $R_2C{=}PCl$ (where R = phenyl, $SiMe_3$).[20] In the second report, we described the formation of both bridged $B_5H_8P(H)(CH(OSiMe_3)R)$ and phosphorus-inserted $B_5H_7P{=}C(OSiMe_3)R$ phosphaborane compounds from the reaction of neutral pentaborane(9) with $(Me_3Si){=}CR(OSiMe_3)$ (where R = ^{t}Bu, Ad).[21,22]

Scheme 1. Synthesis of Substituted Carboranes from the Reaction of Alkynes with Borane Clusters[a]

$$RC{\equiv}CR' + nido\text{-}B_{10}H_{12}L_2 \rightarrow closo\text{-}B_{10}H_{10}C_2RR'$$

$$RC{\equiv}CR' + nido\text{-}B_5H_9 \rightarrow nido\text{-}B_4H_6C_2RR'$$

[a] For *nido*-$RR'C_2B_4H_6$:[16−19] R = R′ = H, alkyl, phenyl, benzyl, indenyl, fluorenyl, adamantyl, naphthyl, etc.; R = H, R′ = phenyl, indenyl, fluorenyl, phenethyl, norbornadienyl, etc. For *closo*-$RR'C_2B_{10}$:[16c] R = H, alkyl, phenyl, bromomethyl, etc.; R = H, alkyl, phenyl, bromomethyl, etc.

Phosphaalkynes have been found to react more like alkynes than nitriles in a variety of reactions.[11−13,23a] Since organic alkynes readily participate in insertion reactions with a variety of boranes as described above,[17,18] similar reactions might be expected to occur between phosphaalkynes and boranes. The extension of this synthetic pathway to the formation of heteroborane clusters using triply bound phosphorus species, however, has not been previously explored. In the work reported here, we describe the reactions of several phosphaalkynes with *nido*-decaborane(14) in the preparation of inserted phosphaborane clusters in good yield. The reaction of a phosphaalkyne with the large *nido*-decarborane(14) cluster was initially investigated, since the larger polyhedral phosphaboranes are usually quite stable and are, therefore, often easier to purify and characterize relative to the smaller cage systems.[24−34]

Experimental Section

Physical Measurements. Routine boron (^{11}B) NMR spectra were recorded on either a Bruker WM-360 or a Cryomagnetics CM-250 spectrometer operating at 115.52 and 80.26 MHz, respectively. Spectra were recorded in either 5 or 10 mm (o.d.) tubes in both the coupled and decoupled modes and were externally referenced to BBr_3 at +40.0 ppm (positive chemical shifts indicate downfield resonances). Typical ^{11}B NMR acquisition parameters employed were a relaxation delay of 0.1 s and a 90° pulse of 20 ms for the 80.26 MHz spectra. The 2D ^{11}B−^{11}B {^{1}H} COSY NMR spectra, both the absolute value and pure phase versions, were obtained on either the CM-250 or a GN-500 spectrometer (operating at 160.45 MHz). Typically, a 90° pulse width of 15−25 ms was required on the CM-250, while the GN-500 required approximately twice this value. In most cases, the previously described absolute value mode COSY pulse sequence[35] was used to generate the t_1, t_2 data matrix (relaxation delay $(\pi/2)-t_1-(\pi/2)-t_2$), in which t_1 was incremented by the inverse of the sweep width in the F_1 dimension and t_2 was the usual acquisition time in a 1D experiment. Typically, the t_1, t_2 matrix was collected as 128 × 256 data points, unless otherwise indicated. Data processing involved the application of a dc offset and first point correction, shifted sine bell apodization, zero filling (twice in t_1 and once in t_2), Fourier transformation, and a magnitude calculation to give the 512 × 512 2D ^{11}B−^{11}B COSY NMR spectrum.[36] Carbon (^{13}C) NMR spectra were obtained on a General Electric QE-300 spectrometer operating at 75.48 MHz. The spectrometer was operated in the FT mode while locked on the deuterium resonance of the solvent in 5 mm (o.d.) sample tubes. The reference was set relative to tetramethylsilane from the known chemical shifts of the solvent carbon atoms (either $CDCl_3$ at δ 77.0 ppm or d_8-THF at δ 67.4 ppm). Phosphorus (^{31}P) NMR spectra were obtained in either 5 or 10 mm (o.d.) tubes on either a Bruker WM-360 or a Cryomagnetics CM-250 spectrometer operating at 145.81 and 101.27 MHz, respectively. Chemical shifts were referenced to an external standard of 85% phosphoric acid sealed in a 1 mm capillary tube and held coaxially in the sample tube by a Teflon vortex plug. Both proton broad-band decoupled and coupled

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spectra were routinely observed for each sample with a decoupling power of about 5 W. Proton (^{1}H) NMR spectra were obtained on a General Electric QE-300 spectrometer operating at 300.15 MHz. Spectra were recorded on samples dissolved in $CDCl_3$ in 5 mm (o.d.) tubes with chemical shifts referenced to internal tetramethylsilane, with a positive shift indicating a resonance at an applied field lower than that of the standard. Mass spectra were obtained on a Finnigan 4021 mass spectrometer using an ionization potential of between 11 and 70 eV. Chemical ionization spectra were obtained using methane as the bulk reactant gas. FT-IR spectra in the range of 400−4000 cm^{-1} were measured on either a Mattson Galaxy 2020 spectrometer or an IBM IR/32 spectrometer and were referenced to the 1601.8 cm^{-1} band of polystyrene. All compounds were recorded sandwiched between NaCl plates. HPLC purifications were accomplished on a Waters DeltaPrep-3000 system equipped with both tunable UV−vis absorbance (routinely monitored at 275 nm) and differential refraction detectors. All separations were performed using a 2.5 × 10 cm RCM 15 μm Porasil column and eluting with reagent grade solvents degassed by continuous He sparging.

Materials. All solvents used were reagent grade or better and were distilled from the appropriate drying agents under a dry nitrogen atmosphere prior to use [THF (Na), pentane (Na), acetonitrile (CaH), diethyl ether (Na)]. All solvents, after drying, were first degassed with a stream of dry nitrogen followed by repeated freeze−evacuate−thaw cycles and finally stored *in vacuo* prior to use. Deuterated solvents were used as received and, after degassing cycles, were stored over 4 Å molecular sieves prior to use. Decarborane(14) was purchased from the Callery Chemical Co. and freshly sublimed prior to use. $(Me_3Si)P{=}C(^t\mathrm{Bu})(OSiMe_3)$[13,37] (**1a**) and $(Me_3Si)P{=}C(Ad)(OSiMe_3)$[38] (**1b**) were prepared and purified according to literature methods. The starting material tris(trimethylsilyl)phosphine ($P(SiMe_3)_3$) was prepared by a modification of the procedure previously reported in the literature.[39] The modification employed 10% less than the stoichiometric amount of HMPA, and the product was distilled directly from the reaction precipitate. The following commercially available (Aldrich) anhydrous chemicals were either used as received or purified by the method indicated and, where possible, were stored over 4 Å molecular sieves prior to use: sodium hydroxide (dried at 150 °C under vacuum), hexamethylphosophoric triamide (HMPA), phosphorus trichloride, chlorotrimethylsilane, magnesium metal, bromine, methanol, hexafluoroboric acid, and sodium hydride (the 80% mineral oil dispersion of NaH was washed several times with dry pentane, and the washes were decanted off to remove the mineral oil). Analytical thin-layer chromatography was conducted on 2.5 × 7.5 cm silica gel strips (1B-F, Baker), and conventional column chromatography was conducted using 2.5 × 30 cm columns packed with 230−400 mesh (ASTM) silica gel (EM Science).

Theoretical Calculations. The MNDO (Modified Neglect of Differential Overlap) calculations employed in this work were performed with either version 4.01 or 5.02 of MOPAC[40] on either a Hewlett-Packard Series 800 computer system in the Center for Molecular Electronics at Syracuse University or a VAX 8820 system of the Syracuse University Academic Computing Services, respectively. Parameterizations used for the atoms were those reported in the literature.[41] All calculations were freely varied and were run with the PRECISE[42] option employed. The procedure used to find the MNDO-optimized minimum energy geometries on the potential energy surface for the phosphaborane clusters followed the procedure previously reported.[43]

$(^t\mathrm{Bu})C{\equiv}P$ (2a). Phosphaalkyne **2a** was prepared by using a literature synthesis[44] modified according to a private communication from Prof. J. F. Nixon and summarized here. In a typical preparation employed in our work, the phosphaalkene $(Me_3Si)P{=}C(^t\mathrm{Bu})(OSiMe_3)$ (**1a**; 5.0 g, 19 mmol) was syringed into a dry nitrogen-filled dropping funnel which was attached to a flask containing approximately 0.5 g of dry NaOH ground into small pieces. This flask was then connected to a vacuum line equipped with cold traps which were maintained at 0, −78, and −196 °C (10^{-3} mmHg vacuum). The NaOH in the flask was then heated to 150−160 °C under vacuum, at which point the phosphaalkene was added slowly dropwise to the hot NaOH. The $(MeSi)_2O$ and $(^t\mathrm{Bu})C{\equiv}P$ products were formed immediately and were collected together in the −78 °C trap. The 0 °C trap contained small amounts of phosphaalkene that distilled over along with small amounts of other impurities. From this reaction, 1.5 g of $(^t\mathrm{Bu})C{\equiv}P$ (75% yield) was collected with $(Me_3Si)_2O$ and used without further purification. The product gave spectroscopic data consistent with those previously reported.[44]

$(Ad)C{\equiv}P$ (2b). Phosphaalkyne **2b** was prepared in a fashion similar to that employed for the synthesis of compound **2a** described above. In a typical preparation, the starting phosphaalkene $(Me_3Si)P{=}C(Ad)(OSiMe_3)$ (**1b**; 5.0 g, 15 mmol) was added to a dry nitrogen-filled dropping funnel and slowly dropped in 1 mL portions onto approximately 0.5 g of ground pieces of NaOH which had been previously heated to 180 °C under vacuum. The $(Me_3Si)_2O$ and $(Ad)C{\equiv}P$ (**2b**) that formed were collected in the −196 and 0 °C cold traps, respectively. $(Ad)C{\equiv}P$ was then dissolved in pentane, and this solution was passed down a 7.5 cm × 2.5 cm column of silica gel which was eluted with pentane; the eluate was resublimed under vacuum to give pure $(Ad)C{\equiv}P$. Typically, 1.3 g of pure product was obtained (50% yield) which gave spectroscopic data consistent with those previously reported.[44] Compound **2a** was then used without further purification.

***nido*-$B_{10}H_{12}(CH_3CN)_2$ (3).** Compound **3** was prepared according to a literature procedure by refluxing freshly sublimed *nido*-$B_{10}H_{14}$ in dry, degassed CH_3CN.[45] After 5 h, the refluxing solution was found to contain a white precipitate. The reaction mixture was then cooled to room temperature and the solvent removed under vacuum. The resultant off-white compound gave spectroscopic data which were consistent with those previously reported and was used without further purification.

***nido*-$(^t\mathrm{Bu})C(H)PB_{10}H_{13}$ (4a).** In a typical reaction, 0.81 g (4.0 mmol) of $B_{10}H_{12}(CH_3CN)_2$ (**3**) was added to 15 mL of dry, degassed THF in a 50 mL round-bottom flask under dry nitrogen. One equivalent (0.40 g, 4.0 mmol) of $(^t\mathrm{Bu})C{\equiv}P$ (**2a**), in about 1 mL of $(Me_3Si)_2O$, was added to the reaction flask, and the mixture was stirred under nitrogen. The solution slowly turned bright orange, and the solvent was removed under vacuum after 12 h, leaving an orange-yellow solid residue. The residue was then dissolved in a small quantity of ethyl acetate and this solution passed down a 15 cm × 2.5 cm silica gel column to give the product as a slightly air-sensitive, off-white oil in 50.4% yield. The product was found to contain a small amount of THF which could not be removed from the oily product. The difficulty in removing all traces of THF presumably stems from the oily and very viscous nature

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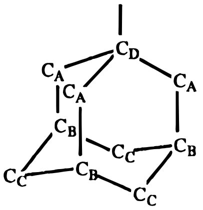
Table 1. NMR Data (ppm) for RCP and RC(H)$PB_{10}H_{13}$ Compounds (Where R = ^{t}Bu, Ad)

compd	^{11}B[a]	^1H[b]	$^{13}C\{^1H\}$[c,d]	^{31}P[e]	ref
2a		1.08 (d, 9H, $J_{PH} = 1.2$ Hz)	31.36 (d, $C(CH_3)_3$, $J_{CP} = 6.0$ Hz), 36.39 (d, $C(CH_3)_3$, $J_C3P = 18.0$ Hz), 184.64 (d, PC, $J_{CP} = 37.6$ Hz)	−71.8	this work[f]
2b		1.6−2.1 (m, 15H, $C_{10}H_{15}$)	27.8 (s, C_B), 35.7 (s, C_C), 38.5 (d, C_D, $J_{CP} = 18.0$ Hz), 42.9 (d, C_A, $J_{CP} = 6.0$ Hz), 184.7 (d, PC, $J_{CP} = 39.0$ Hz)	−66.8	this work[g]
4a	4.3 (d, B(5), $J_{BH} = 172$ Hz), −18.0 (d, B(8,9,10,11), $J_{BH} = 163$ Hz), −19.3 (d, B(2,3), $J_{BH} = 163$ Hz), −39.3 (d, B(1,4,6), $J_{BH} = 176$ Hz)	−3.54 (br, 3H, bridging H), 1.64 (s, 9H, $C(CH_3)_3$), 2.66 (d, 1H, PCH, $J_{HP} = 1.5$ Hz)	30.31 (s, $C(CH_3)_3$), 37.21 (d, $C(CH_3)_3$, $J_{CP} = 13.0$ Hz), 125.51 (s, PC)	−45.0	this work
4b	4.4 (d, B(5), $J_{BH} = 168$ Hz), −17.8 (d, B(8,9,10,11), $J_{BH} = 160$ Hz), −19.2 (d, B(2,3), $J_{BH} = 163$ Hz), −39.4 (d, B(1,4,6), $J_{BH} = 168$ Hz)	−3.63 (br, 3H, bridging H), 1.5−2.1 (m, 15H, $C_{10}H_{15}$), 2.36 (d, 1H, PCH, $J_{HP} = 1.8$ Hz)	25.15 (s, $C_{10}H_{15}$), 27.86 (s, $C_{10}H_{15}$), 36.07 (s, $C_{10}H_{15}$), 43.17 (d, $C_{10}H_{15}$, $J_{CP} = 6.0$ Hz), 80.38 (s, PC)	−71.0	this work

[a] In $CDCl_3$ relative to BBr_3 (40.0 ppm). [b] In $CDCl_3$ relative to TMS (0.0 ppm). [c] In $CDCl_3$ relative to TMS. [d] Adamantyl numbering scheme:



[e] In $CDCl_3$ relative to 85% H_3PO_4. [f] ^{13}C, ^1H, and ^{31}P data for this compound were originally reported in ref 37. The data shown here for comparison are our data, which are comparable with those reported earlier. [g] ^{13}C, ^1H, and ^{31}P data for this compound were originally reported in ref 38. The data shown here for comparison are our data, which are comparable with those reported earlier.

Table 2. Infrared Data for RCP and RC(H)$PB_{10}H_{13}$ Compounds (Where R = ^{t}Bu, Ad)

compd	IR (cm^{-1})[a]	ref
2a	2968 (vs), 2922 (vs), 2898 (sh), 2862 (vs), 2363 (vw), 2858 (vw), 1533 (vs), 1462 (sh), 1451 (s), 1361 (vs), 1252 (vw), 1198 (vs), 1175 (sh), 1049 (sh), 1022 (m), 925 (vw), 845 (sh), 835 (m), 531 (vs), 463 (w), 355 (w)	this work[b]
2b	1528 (vs, ν_{CP})	33[c]
4a	2990 (m, ν_{CH}), 2955 (m, ν_{CH}), 2896 (w, ν_{CH}), 2555 (s, br, ν_{BH}), 2420 (sh, ν_{BH}), 1660 (w), 1613 (sh), 1594 (w), 1578 (w), 1539 (sh), 1520 (sh), 1502 (sh), 1488 (m), 1467 (m), 1425 (m), 1389 (w), 1278 (m), 1212 (m), 1171 (w), 1114 (m), 1026 (m), 995 (sh), 970 (w), 850 (w), 808 (m), 686 (w)	this work
4b	2955 (m, ν_{CH}), 2892 (s, ν_{CH}), 2840 (s, ν_{CH}), 2522 (m, br, ν_{BH}), 2418 (sh, ν_{BH}), 1521 (m), 1446 (m), 1400 (w), 1337 (w), 1296 (w), 1255 (m), 1094 (m), 1065 (m), 1006 (s), 909 (w), 793 (s), 680 (w)	this work

[a] NaCl or CsI plates. Abbreviations: vs = very strong; s = strong; m = medium; w = weak, sh = shoulder; br = broad. [b] IR data for this compound were originally reported in ref 38. The data shown here for comparison are our data, which are comparable with those reported earlier. [c] IR/Raman data for solid film.

of the product compound, and no evidence has been found supporting the formation of a complex between **4a** and THF. Negative ion mass spectroscopy for **4a** (the reported percent relative intensity values are normalized to the largest peak in the spectrum (at m/e 147 from the $PB_{10}H_{10}$ envelope)): m/e 224 (0.31%; P^+ envelope), 223 (1.51%; $P^+ - 1H$ envelope), 175 (7.93%, $C_2PB_{10}H_{10}$ envelope), 174 (12.75%; $C_2PB_{10}H_{10}$ envelope), 173 (12.35%; $C_2PB_{10}H_{10}$ envelope), 172 (7.93%; $C_2PB_{10}H_{10}$ envelope), 171 (5.22%; $C_2PB_{10}H_{10}$ envelope), 151 (32.93%; $PB_{10}H_{10}$ envelope), 150 (44.08%; $PB_{10}H_{10}$ envelope), 149 (76.20%; $PB_{10}H_{10}$ envelope), 148 (96.59%; $PB_{10}H_{10}$ envelope), 147 (100%; $PB_{10}H_{10}$ envelope), 146 (83.84%; $PB_{10}H_{10}$ envelope), 145 (64.76%; $PB_{10}H_{10}$ envelope), 144 (39.66%; $PB_{10}H_{10}$ envelope), 143 (23.29%; $PB_{10}H_{10}$ envelope), 142 (15.46%; $PB_{10}H_{10}$ envelope), 141 (9.34%; $PB_{10}H_{10}$ envelope), 69 (21.39%; C_5H_9), 57 (70.68%; $^{12}C_4H_9$). The ^1H, ^{11}B, ^{13}C, and ^{31}P NMR data are given in Table 1, and FT-IR data are given in Table 2.

***nido*-(Ad)C(H)=$PB_{10}H_{13}$ (4b).** In a typical reaction, 1.0 g (5.6 mmol) of (Ad)C≡P (**2b**) and 1.1 g (5.6 mmol) of *nido*-$B_{10}H_{12}(CH_3CN)_2$ (**3**) were added under inert conditions to a 100 mL round-bottom flask containing 40 mL of dry, degassed THF. The initially cloudy, colorless solution was stirred for 2.5 h at room temperature to give a clear, light orange solution. The solution was concentrated *in vacuo*, dissolved in a minimum of dry ethyl acetate, and chromatographed on a 15 cm × 2.5 cm silica gel column eluted with ethyl acetate. The product was obtained as a slightly air-sensitive, off-white oil in 50% yield (based on ^{11}B NMR). As with compound **4a**, the **4b** product was found to contain a small amount of THF which could not be removed from the oily product. Negative ion mass spectroscopy for **4b** (the reported percent relative intensity values are normalized to the base peak in the spectrum): m/e 295−302 ($C_{11}H_{29}B_{10}P^+$ parent envelope, observable but relatively low in intensity), 151 (4.4%; $PB_{10}H_{10}$ envelope), 150 (4.4%; $PB_{10}H_{10}$ envelope), 149 (22.2%; $PB_{10}H_{10}$ envelope), 148 (7.4%; $PB_{10}H_{10}$ envelope), 147 (7.5%; $PB_{10}H_{10}$ envelope), 146 (4.8%; $PB_{10}H_{10}$ envelope), 145 (4.7%; $PB_{10}H_{10}$ envelope), 144 (2.3%; $PB_{10}H_{10}$ envelope), 136 (11.3%; $^{12}C_9{}^{13}C_1H_{15}$), 135 (61.0%; $^{12}C_{10}H_{15}$). The ^1H, ^{11}B, ^{13}C, and ^{31}P NMR data are given in Table 1, and FT-IR data are given in Table 2.

Results and Discussion

The reaction of several phosphaalkynes with a decaborane bis-adduct compound under relatively mild experimental conditions has been explored. In the room-temperature reaction of equimolar quantities of phosphaalkyne RC≡P (**2a**, R = ^{t}Bu; **2b**, R = adamantyl) with the decarborane(12)−Lewis base adduct $B_{10}H_{12}$·$2CH_3CN$ (**3**), two new phosphaborane compounds (compounds **4a** and **4b**) were isolated in rather good yield (each obtained in approximately 50% yield). These slightly air-sensitive phosphine−methylene ylide compounds have been fully characterized by ^1H, ^{11}B, ^{13}C, and ^{31}P NMR, 2D $^{11}B-^{11}B$ COSY NMR, FT-IR, and mass spectroscopic analyses. The synthetic pathways employed in the preparation of **4a** and **4b** are summarized in Scheme 2. The structure of these closely related compounds is proposed to be based on an *nido* 11-vertex, phosphorus cage inserted compound on the basis of the data presented below.

From precedent established in previous reactions of unsaturated compounds, including organic alkynes and

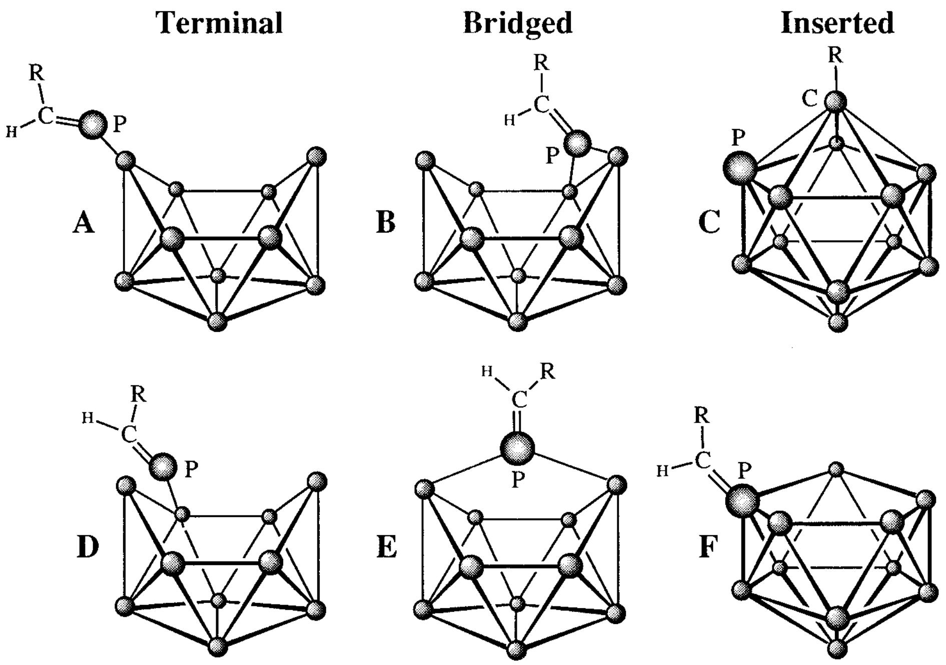
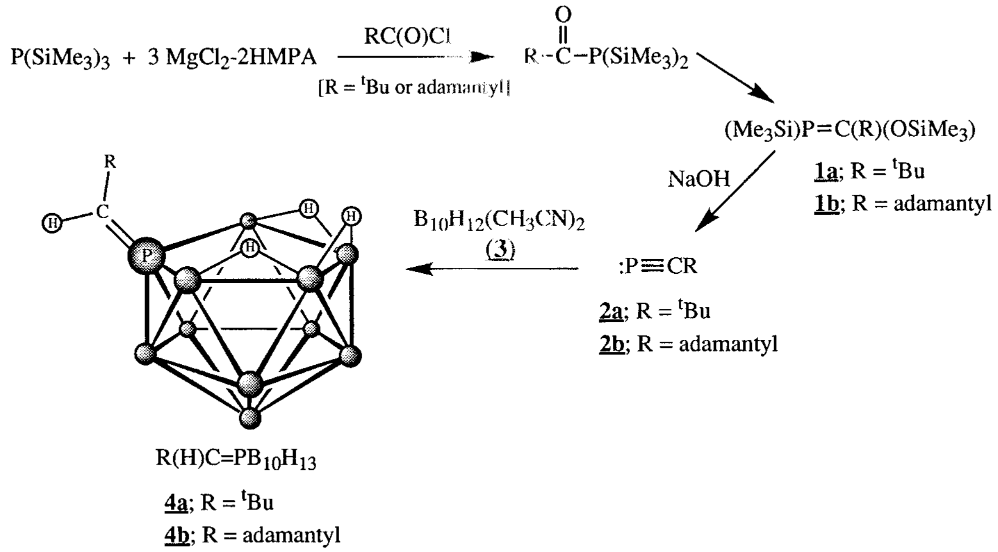


Figure 1. Possible structural types for compound **4** (all cage hydrogens have been omitted for clarity).

Scheme 2. Synthetic Pathways for the Formation of *nido*-RC(H)PB$_{10}$H$_{13}$ Compounds (4a, R = ^{t}Bu; 4b, R = Ad) from the Reaction of Phosphaalkynes 2a and 2b with B$_{10}$H$_{12}$·2CH$_3$CN (3)



phosphaalkenes, with borane clusters and from a more general consideration of other potential structural modifications, four types of structures are possible for compounds **4a** and **4b** which incorporate both a B$_{10}$ framework and the components of the phosphaalkyne reactant (on the basis of the molecular formula established from mass spectral data). These structural types include phosphorus-bridged structures, phosphorus terminally substituted compounds, structures in which both the carbon and the phosphorus atoms are inserted into the cage framework, and the compound which results from the insertion of only the phosphorus atom into the cluster. These possible structural modifications are shown in Figure 1. Literature examples for each of these structural types are known in boron cluster chemistry, albeit with different cage sizes and phosphorus substituents.

^{11}B and ^{1}H NMR data provide a great deal of information on the structure of compounds **4a** and **4b**. Figure 2 shows both the proton-coupled and -decoupled ^{11}B NMR spectra of compound **4a**. The spectrum for compound **4b** was essentially identical with that observed for **4a**. Both spectra consist of four resonances in a 1:4:2:3 relative intensity pattern. In the spectra, each resonance was observed to be split into B–H-coupled doublets and no phosphorus–boron couplings were observed for any of the resonances. The ^{1}H NMR data show, besides peaks clearly assignable to the R substituents on carbon (either the ^{t}Bu or adamantyl group), resonances arising from bridging B–H–B protons (at −3.54 and −3.63 ppm for compounds **4a** and **4b**, respectively). In addition, the spectra show a peak for a proton on carbon which is clearly coupled to phosphorus (2.66 ppm with $^2J_{PH}$ = 1.5 and 1.8 ppm for compounds **4a** and **4b**, respectively).

In consideration of the observed ^{11}B and ^{1}H NMR data, most of the structures shown in Figure 1 may be readily eliminated from consideration. Structures **A**

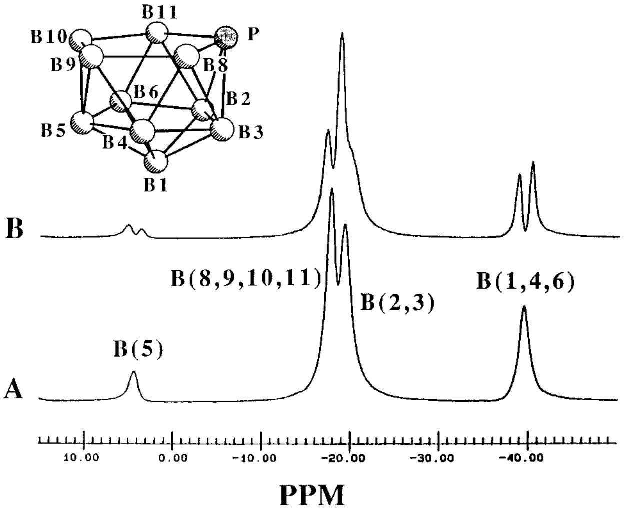
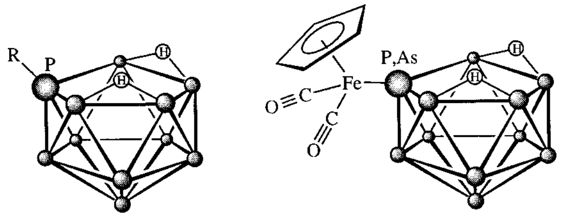


Figure 2. Proton coupled (upper plot) and decoupled (lower plot) ^{11}B NMR spectra for compound **4a**.

and **D** (Figure 1) display a terminal phosphorus cage substitution pattern. Structure **A** contains seven sets of inequivalent boron atoms, while in structure **D** all the boron atoms are chemically inequivalent. Fortuitous overlap of peaks, however, could simplify the spectra of **A** and **D** considerably. The ^{11}B NMR data, however, unambiguously eliminate the terminally substituted phosphorus structures, since all the boron resonances clearly display B−H terminal coupling. It is possible to obtain a phosphorus terminal substitution pattern in which a cage boron atom has both a proton and a terminal phosphino linkage. This substitution pattern can also be eliminated, however, since P−B coupling would be expected for this pattern and such coupling was not observed for any of the ^{11}B NMR resonances. From precdent well established in the literature for terminal B−P systems, terminal P−B−H substitution patterns should result in large P−B couplings (ca. 100 Hz), which were clearly not observed.[341] The bridging structures **B** and **E** can be similarly eliminated due to the absence of any observed P−B coupling in the ^{11}B NMR spectra. In the 5,6-bridged structure **B**, all the boron atoms are chemically inequivalent. The known 5,6-bridged compound $[B_{10}H_{13}$-5,6-μ-$(PPh_2)]$ (**5**) shows all 10 resonances in the ^{11}B NMR spectrum.[10] The 6,9-bridged structure **E** contains four types of boron atoms in a 1:2:1:1 ratio. The ^{11}B NMR spectrum of the closely related deprotonated 6,9-bridged compound $[B_{10}H_{13}$-6,9-μ-$(PPh_2)]^-$ (**6**) clearly shows this four-peak pattern with phosphorus coupling observed.[10] Finally, the *closo* structure C can also be eliminated, since resonances due to B−H−B bridging protons were clearly observed in the ^1H NMR spectra of **4a** and **4b**.

The remaining structure in Figure 1, **F**, consists of a *nido*-PB_{10} framework. This structure is formally based upon a 26-skeletal-electron *nido*-$[B_{11}H_{11}]^-$ parent compound.[46] The PB_{10} cage contains boron atoms in six different chemical environments in a 2:2:2:1:2:1 ratio. A number of heteroborane clusters are known which display structures similarly based upon the *nido*-EB_{10} framework. These closely related compounds include *nido*-$RPB_{10}H_{12}$ (**7**, where R = CH_3, C_2H_5),[32] *nido*-(Fe(η^5-C_5H_5)(CO)$_2$)$PB_{10}H_{12}$ (**8**),[33] and *nido*-(Fe(η^5-C_5H_5)(CO)$_2$)$AsB_{10}H_{12}$ (**9**),[33] as shown in Figure 3. As described previously, compounds **4a** and **4b** show four ^{11}B NMR resonances in a 1:4:2:3 ratio. The ^{11}B NMR data for the previously reported *nido*-EB_{10} heteroboranes **7**−**9** often show a single resonance for boron atoms B(1), B(4), and B(6) (numbering scheme shown in Figure 4). In addition, boron atoms B(8), B(9), B(10), and B(11) may also be observed as a single ^{11}B resonance, as has been reported for compound **9**.[33] The ^{11}B NMR for compounds **4a** and **4b** would, therefore, be expected to exhibit the observed four resonances in a 1:4:2:3 ratio, as reported for the closely related cluster **9**. The chemical shifts and distributions of peak intensities observed for the resonances of **4a** and **4b** are also very similar to those found for the other known *nido*-EB_{10} heteroboranes, with the resonance of intensity 1 at lowest field strength and the resonance of intensity 3 at highest field strength.



7

8 (P)
9 (As)

Figure 3. Structures of *nido*-$RPB_{10}H_{12}$ (**7**; R = CH_3, C_2H_5),[32] *nido*-(Fe(η^5-C_5H_5)(CO)$_2$)$PB_{10}H_{12}$ (**8**),[33] and *nido*-(Fe-(η^5-C_5H_5)(CO)$_2$)$AsB_{10}H_{12}$ (**9**)[33] (terminal cage hydrogen atoms have been omitted for clarity).

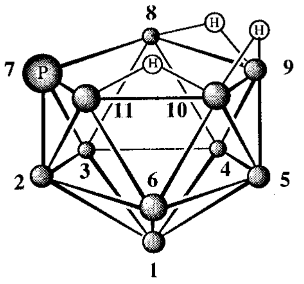


Figure 4. Numbering scheme for compounds **4a** and **4b**.

The ^{11}B−^{11}B COSY NMR spectrum of compound **4** provides support for the structural assignment presented above. In the 2D spectrum, cross-peaks were only observed between adjacent equivalent sets of cage boron atoms, as expected on the basis of previous 2D experiments.[47,48] Recently, the 2D ^{11}B−^{11}B COSY NMR and X-ray crystal structure of compound **7**, *nido*-(CH_3 or C_2H_5)$PB_{10}H_{12}$, was reported by Shore.[32] The spectroscopic assignments reported for **7**, on the basis of the crystallographic structure, are fully consistent with our spectral and structural assignments. All attempts to prepare a crystalline sample of either compound **4a** and **4b** for X-ray analysis, however, have been unsuccessful.

Further support for the proposed structures of compounds **4a** and **4b** may be obtained from other spectro-

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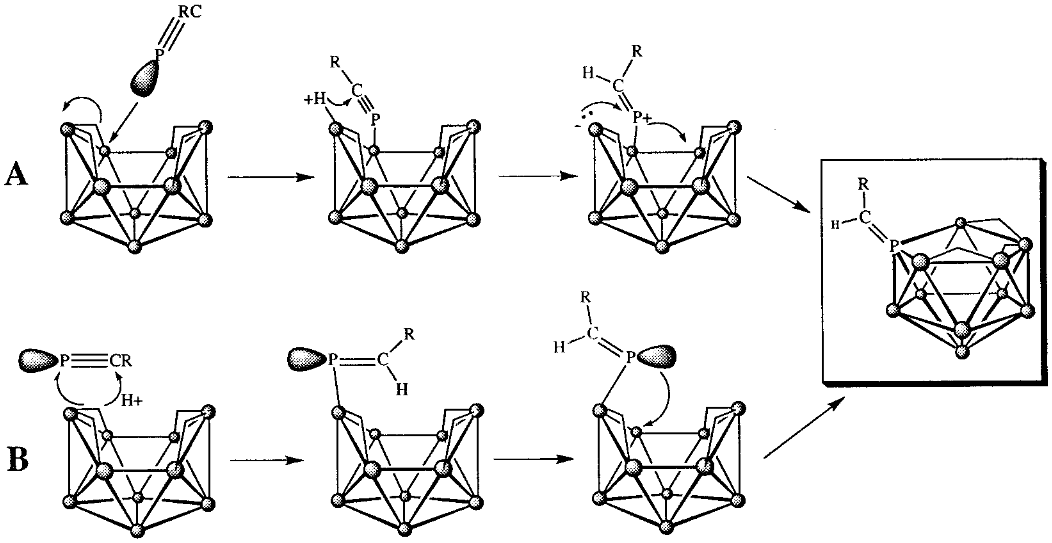
Scheme 3. Possible Mechanistic Steps in the Formation of *nido*-RC(H)$PB_{10}H_{13}$ from the Reaction of $B_{10}H_{12}L_2$ with Phosphaalkynes[a]



[a] Terminal hydrogen atoms of the cage have been omitted for clarity.

scopic data. Both compounds clearly show phosphorus-coupled doublets (**4a**, $^{2}J_{PH} = 1.5$ Hz; **4b**, $^{2}J_{PH} = 1.8$ Hz) at 2.66 ppm in the ^{1}H NMR data which arise from a single proton on the doubly bound, exopolyhedral carbon attached to the cage phosphorus. The ^{31}P NMR data show a single resonance for compounds **4a** and **4b** at −45 and −71 ppm, respectively. These chemical shifts are comparable to the ^{31}P NMR data for the other previously reported *nido*-EB_{10} heteroborane compounds. The $^{13}C\{^{1}H\}$ NMR data show the resonances expected for the exopolyhedral R group (either ^{t}Bu or Ad) along with a resonance at lower field. This ^{13}C resonance was assigned to the P=C unit and occurs, for example, in **4a** (125.5 ppm) approximately equidistantly between the ^{13}C resonance for the phosphaalkyne starting material **1** (184.8 ppm)[8] and that observed for P—C single-bonded ^{13}C resonances in phosphinopentaborane compounds (near 80 ppm).[22] This P=C resonance is also quite similar to the ^{13}C resonances reported for exopolyhedral P=C units in other phosphaborane cluster systems (148.5 ppm for [μ-((^{t}Bu)(Me_3SiO)C=P)B_5H_8]).[22] Finally, as presented above, the mass spectra for compounds **4a** and **4b** displayed parent envelopes for R(H)C=$PB_{10}H_{13}$ as the highest mass peaks.[49] Also observed in the mass spectra were components from cage and exopolyhedral organic unit fragmentation along with the PB_{10} fragment envelope, which contained the largest intensity peaks (the base peak for **4a**).

The insertion of only the phosphorus atom and not the carbon atom of the phosphaalkyne unit into the cage framework was initially somewhat surprising. Phosphaalkynes have been found to react more similarly to alkynes than to nitriles in a variety of reactions.[15,32,33,49,50] The lower electronegativity of phosphorus most likely significantly contributes to this reactivity by inducing a reversal of the polarity in phosphaalkynes relative to nitriles. Thus, in phosphaalkynes, the phosphorus has a small partial positive charge, while in nitriles the nitrogen has a much larger and negative partial charge.[13,50] A directly analogous reaction for the phosphaalkynes to alkynes would have resulted in the insertion of both the phosphorus and the carbon into the cluster framework, forming a *closo*-cage system. The mechanism for the formation of compound **4** from a phosphaalkyne and $B_{10}H_{12}L_2$ may be considered to be similar to that proposed for the reaction of phosphaalkenes with pentaborane(9). Several mechanisms, of which only two are summarized in Scheme 3, may be proposed to account for the observed reactivity patterns. In the first mechanism (A in Scheme 3), the lone pair of electrons on the phosphorus center is proposed to initially attack at a boron position of the decaborane cage system. This nucleophilic attack presumably occurs at the open face of the cage at one of the B(5,7,8,-10) atoms, since these are among the most electropositive and sterically free sites in the cage.[51] This results in the formation of a phosphorus—boron bond and a hydride shift from an adjacent bridging position to a terminal position on the neighboring boron. This shift may then be followed by the transfer of a terminal proton from this boron unit to the carbon center of the phosphaalkyne, resulting in the hydroboration of the phosphaalkyne bond. As a result of this rearrangement, a basic boron center is generated adjacent to the phosphorus—boron linkage. The close proximity of the relatively electropositive phosphorus center to this basic site allows the cage insertion reaction to occur. A very similar mechanism, shown in Scheme 4, from the work of Gaines[20] is believed to occur, which results in the insertion of only a phosphorus atom into a pentaborane cage to form the observed inserted *nido*-B_5H_8P=CR_2 compound.

In a second mechanistic pathway, the first step may involve a proton shift from the cage to the carbon center of the incoming phosphaalkyne concurrent with the formation of a phosphorus—boron bond. The lone pair of electrons on the phosphorus may then attack at an

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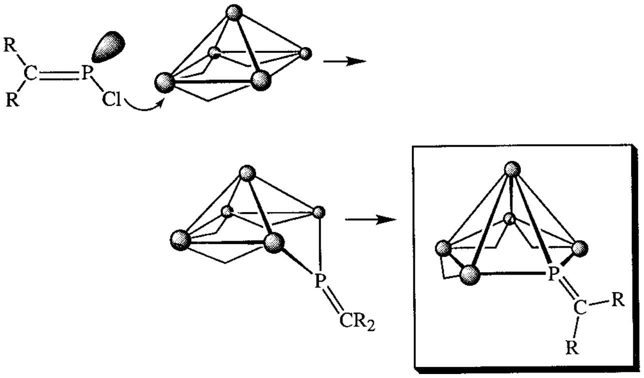
Scheme 4. Possible Mechanistic Steps in the Formation of *nido*-$R_2C{=}PB_5H_8$ from the Reaction of Pentaborane(8) with a Chlorophosphaalkene[a]



[a] Terminal hydrogen atoms of the pentaborane cage have been omitted for clarity.

adjacent borane cage site to accomplish the insertion reaction to produce the observed product. This mechanistic pathway can be related to that reported previously by Sneddon[52] for the incorporation of a cyanide unit into a borane cluster from the reaction of *arachno*-$S_2B_7H_8^-$ anion with nitriles. In the *arachno*-$S_2B_7H_8^-$ mechanism, the first step was proposed to involve the nucleophilic attack of a thiaborane anion on the relatively electropositive carbon atom of the polarized nitrile, followed by a hydroboration of the nitrile bond. As a consequence of this interaction, the lone pair of electrons on the pendant imino group becomes strongly nucleophilic and attacks at the most electropositive center of the thiaborane cage. This lone-pair interaction forces a cage rearrangement and closes the cage ring system to produce the observed cluster.

The final step in each of the mechanisms presented above in the formation of the final product, however, raises significant concern. In these steps, the two Lewis base ligands are lost from the cage and a net of two hydrogens are added. The loss of the Lewis base ligands from $B_{10}H_{12}L_2$ has, however, been observed to readily occur in the formation of carboranes, such as $R_2C_2B_{10}H_{10}$, from the reaction of $B_{10}H_{12}L_2$ with alkynes.[16−19] The final net addition of two hydrogens to the cage is much less straightforward. It may be that, since no starting decaborane complex was isolated from the reaction mixture and the maximum yield observed for the reaction was near 50%, that some of the $B_{10}H_{12}L_2$ itself may have served as the hydrogen source through an intermolecular process. These two questions have not been adequately resolved, and further detailed mechanistic studies are required to elucidate the reaction pathway in greater depth.

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Supporting Information Available: A table of MNDO calculated bond indices for [^{t}BuC(H)$PB_{10}H_{13}$] (**4a**) and figures giving ^{1}H, ^{11}B, and 2D $^{11}B-^{11}B$ COSY NMR spectra for **4a**,**b** and ^{13}C NMR and FT-IR spectra for **4b** (9 pages). Ordering information is given on any current masthead page.

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