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Syntheses of Some 10-, 11-, and 12-Atom Phosphaboranes. Crystal Structure of 2-(trimethylamine)-1-$PB_{11}H_{10}$

John L. Little, Michael A. Whitesell, Robert W. Chapman, John G. Kester, John C. Huffman, and Lee J. Todd*

Department of Chemistry and the Molecular Structure Center, Indiana University,
Bloomington, Indiana 47405

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The heteroboranes 1,2-$PAsB_{10}H_{10}$ and 1,2-$PSbB_{10}H_{10}$ were prepared in low yield by reaction of $B_{10}H_{14}$ with triethylamine and mixtures of PCl_3 and $AsCl_3$ or PCl_3 and SbI_3, respectively. From the product mixture in the related synthesis of 1,2-$P_2B_{10}H_{10}$, the phosphaborane anion 2-$PB_9H_9^-$ has been isolated. Treatment of 1,2-$P_2B_{10}H_{10}$ with excess piperidine formed the 7,8-$P_2B_9H_{10}^-$ ion in good yield. Treatment of $Me_3NH[B_{11}H_{14}]$ with excess *n*-butyllithium and PCl_3 formed both $B_{11}H_{11}P^-$ and 2-NMe_3-1-$PB_{11}H_{10}$ in moderate yield. The compound 2-NMe_3-1-$PB_{11}H_{10}$ has been characterized by a single-crystal X-ray structure determination (space group $P2_1/m$, a = 6.910(1) Å, b = 10.603(1) Å, c = 8.821(1) Å, β = 108.27(1)°, Z = 2).

Introduction

There are quite a number of known borane and carborane derivatives containing one or more group 15 atoms. The syntheses and properties of these compounds have been summarized in earlier reviews.[1] Recently, there has been renewed interest in polyhedral phosphaboranes. Thus, reaction of B_2Cl_4 with PCl_3 at 300 °C formed *closo*-1,2-$P_2B_4Cl_4$ in low yield.[2] This is the first example of a six-vertex *closo* phosphaborane. A low yield of the air-sensitive *closo*-$B_{11}H_{11}PMe$ was obtained by reaction of $B_{11}H_{13}^{2-}$ with $MePCl_2$ in tetrahydrofuran.[3] The phenyl-substituted derivative, *closo*-$B_{11}H_{11}PPh$ had been prepared years ago.[4] Some new 12-vertex metallaphosphaboranes have been reported as well. Reaction of $NEt_4[B_{10}H_{12}PPh]$ with $PtCl_2(PMe_2Ph)_2$ or $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ formed 2-Ph-1,1-$(PMe_2Ph)_2$-*closo*-1,2-$PtPB_{10}H_{10}$ and 1-Ph-2,3-(η^5-C_5Me_5)-*closo*-2,3,1-$Rh_2PB_9H_9$, respectively.[5]

Recently, we reported the synthesis of 1,2-$P_2B_{10}H_{10}$ by the reaction of decaborane with triethylamine, sodium borohydride, and PCl_3.[6] This reaction gave a number of other products, in addition to 1,2-$P_2B_{10}H_{10}$, such as 6-(triethylamine)-2-PB_9H_8. This triethylamine derivative was fully characterized in our previous report, including a single-crystal X-ray structure determination.[6]

We have continued our synthetic investigations of polyhedral phosphaboranes and wish to report the syntheses and characterization of a number of new 10-, 11-, and 12-vertex phosphaboranes.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 115.8 MHz with a Nicolet NT-360 spectrometer and were externally referenced to $BF_3 \cdot O(C_2H_5)_2$ (positive values downfield). Two-dimensional NMR (^{11}B–^{11}B) spectra were obtained on the same instrument. Broadband ^1H NMR decoupling (3W) was continuously used. A general description for the two-dimensional (^{11}B–^{11}B) NMR technique has been previously reported.[7] Typically, the 2-D t_1, t_2 matrix was collected as 128 × 256 (real, plus imaginary) data points. The matrix was zero-filled once in both dimensions after apodization with an exponential function and a sine function. The F_1, F_2 matrix was symmetrized before projecting the contour plot. Proton (^1H) and phosphorus (^{31}P) NMR spectra were obtained at 361.1 and 146.2 MHz, respectively, on the same instrument. The proton NMR were referenced to the proteo solvent impurity and the ^{31}P NMR were externally referenced to 85% H_3PO_4 (positive values downfield). Infrared spectra were determined by using KBr disks with a Perkin-Elmer 283 spectrometer. Mass spectral data were collected on a Kratos 80 spectrometer. Melting points were obtained in sealed, evacuated melting point capillaries and are uncorrected. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Triethylamine was distilled from sodium hydroxide. Phosphorous trichloride was freshly distilled and degassed before use. Decaborane(14) was sublimed at 60 °C and 10^{-2} mm Hg. $(CH_3)_3NHB_{11}H_{14}$ was prepared from $NaBH_4$ and $BF_3 \cdot OEt_2$.[8] All other commercially-available reagents were used as received.

Purification of $(CH_3)_4N[2\text{-}PB_9H_9]$ (1). The complex product mixture derived from reaction of $B_{10}H_{14}$ with PCl_3 and triethylamine was separated by column chromatography on silica gel. Elution with hexanes gave 1,2-$P_2B_{10}H_{10}$, and subsequent elution with toluene and then chloroform yielded two more phosphaborane products. Finally, the column was eluted first with methylene chloride and then 20% acetone/methylene chloride to give a yellow band. The solvent was removed from this fraction and the oily product extracted several times with toluene. The residual oil was dissolved in 20 mL of 10% NaOH solution, and the solution was filtered to remove insoluble solids and precipitated with tetramethylammonium chloride solution. The precipitate was dissolved in acetone and the solution filtered to remove insoluble solids. The filtrate was boiled down and some methyl alcohol added. Upon cooling, crystalline material was obtained. The crude crystals were recrystallized three more times from acetone/methanol to obtain 33 mg of $(CH_3)_4NB_9H_9P$ (0.3% yield). Anal. Calcd for $B_9H_{21}C_4NP$: C, 22.72; H, 10.01. Found: C, 21.65; H, 9.79. ^{31}P NMR (acetone-d_6): δ −224 ppm. ^1H NMR (acetone-d_6): δ 3.41 ppm. IR: 3042 (w), 2540 (vs), 1490 (s), 990 (m), 985 (s), 886 (w), 676 (w), 480 (w), 442 (m), 396 (w), 384 (w) cm^{-1}.

Preparation of $(CH_3)_4N[7,8\text{-}P_2B_9H_{10}]$ (2). A 50-mL, two-necked flask was equipped with a gas inlet and a rubber septum. The system was then evacuated and filled with nitrogen. 1,2-$B_{10}H_{10}P_2$ (0.202 g, 1.12 mmol) was added and dissolved in 15 mL of chloroform. Piperidine (2 mL, 20.2 mmol) was added via syringe and the solution was allowed to stir at room

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temperature for 4 h. After this time, the chloroform and excess piperidine were pumped off under high vacuum and nitrogen was added to the flask. The residue was extracted with several 10–15-mL aliquots of acetone, and solids were removed by filtration. To the filtrate was added excess $(CH_3)_4NCl$ solution, and dilution with water formed a yellow precipitate, which was isolated by filtration. Crystallization was accomplished with an acetone–methanol solution which gave 205 mg (0.85 mmol) of pure white crystals of $(CH_3)_4N[7,8\text{-}P_2B_9H_{10}]$ (75.5% yield). Anal. Calcd for $C_4H_{22}NB_9P_2$: C, 19.73; H, 9.11. Found: C, 19.83; H, 9.22. ^1H NMR (acetone-d_6): δ 3.44. ^{31}P NMR (acetone): δ –55.9 ppm. IR: 2520 (vs), 1480 (s), 1390 (w), 1285 (w), 1010 (s), 950 (s), 875 (m), 775 (m), 730 (m), 690 (w), 615 (w), 540 (w), 460 (w), 410 (m), 345 (w) cm^{-1}.

Preparation of 2-(trimethylamine)-1-$PB_{11}H_{10}$ (3). A 100-mL flask was fitted with two pressure-equalized dropping funnels and a nitrogen inlet was charged with 3.0 g (16 mmol) $(CH_3)NHB_{11}H_{14}$ and 40 mL of THF. After the flask was cooled in an ice bath, 26 mL (2.5 M) of *n*-butyllithium in hexane was added slowly from one of the dropping funnels. To the other dropping funnel was added 2.7 mL (32 mmol) of PCl_3 and 7.0 mL of THF, which was added over 15 min.

Gas evolution was observed and the reaction mixture turned deep orange. Removal of the THF *in vacuo* gave an orange solid, which was soluble in acetone. The acetone solution was rotary evaporated onto 5 g of 230–400 mesh silica gel. The solids were slurried in hexane and placed atop a 32 × 250 mm column of 230–400 mesh silica gel. After the column (flash chromatography) was eluted with hexanes and chloroform to remove organics, compound **3** was removed with dichloromethane. Recrystallization from 10:1 dichloromethane/acetone gave 1.0 g of pure **3**, mp 391–393 °C (29% yield).

Anal. Calcd for $C_{11}H_{19}C_3NP$: C, 16.44; H, 8.74. Found: C, 16.40; H, 8.68. ^1H NMR (acetone-d_6), δ 2.86 (br s). ^{31}P NMR (acetone-d_6): δ –83.7. IR: 3015 (w), 2956 (w), 1472 (s), 1461 (s), 1412 (m), 1229 (w), 1115 (w), 1024 (m), 983 (m), 970 (m), 959 (s), 883 (m), 747 (w), 883 (m), 730 (m), 628 (w), 457 (m) cm^{-1}.

Preparation of $(CH_3)_4N[B_{11}H_{11}P]$ (4). A solution of 500 mg of $(CH_3)_3NHB_{11}H_{14}$ (2.6 mmol) in 10 mL of THF was cooled in an ice bath and treated with 2.0 mL of 2.5 M *n*-butyllithium in hexane. After the mixture was stirred for 5 min, the ice bath was removed and the THF evaporated *in vacuo*. Nitrogen was let in the system and 10 mL of THF added and the flask cooled in an ice bath. After addition of 3 mL of 2.5 M *n*-butyllithium in hexane, 0.5 mL (2.85 mmol) of PCl_3 in 5 mL of THF was slowly added from a dropping funnel.

The solution was stirred overnight and the THF removed *in vacuo*. The solids were extracted with water and the solution clarified by filtration. Precipitation with $(CH_3)_4NCl$ solution gave a mixture of product and starting material. Starting material was hydrolyzed by reaction with several milliliters of concentrated aqueous HCl. The remaining solid product was purified by crystallization from acetone/water. Yield: 87 mg (14%). Anal. Calcd for $B_{11}H_{23}C_4PN$: C, 20.43; H, 9.86. Found: C, 20.56; H, 9.66. ^1H NMR (acetone-d_6): δ 3.43. ^{31}P NMR (acetone-d_6): δ –94.5. IR: 2535 (vs), 1482 (s), 1426 (w), 1037 (m), 955 (m), 733 (m), 632 (w), 619 (w), 606 (w), 458 (w) cm^{-1}.

Preparation of 1,2-$PAsB_{10}H_{10}$ (5). Method A. A 100-mL, two-necked flask was equipped with a gas inlet and a pressure-equalized dropping funnel. To the flask was added 0.51 g of $(CH_3)_3NHB_{10}H_{12}As$ (2.0 mmol) dissolved in 30 mL of THF, and then 3.0 mL triethylamine was added via syringe. A solution of 0.70 mL of PCl_3 (4.0 mmol) in 10 mL of THF was added from the dropping funnel over a 1-h period. The solution was allowed to stir overnight and was filtered, and the solids were washed three to four times with 15-mL aliquots of THF. The combined filtrate and washings were rotary evaporated onto 6.0 g of 100–200 mesh silica gel and slurried atop a column of 50.0 g of 100–200 mesh silica gel using hexane. Compound **5** was eluted with a 1:1 mixture of hexane/toluene. The crude product (42 mg) was sublimed at 90 °C to give 18.5 mg of pure 1,2-$PAsB_{10}H_{10}$, mp 442–445 °C (4.1% yield). *Caution*! The sublimate is sometimes pyrophoric due to small amounts of P_4 byproduct, which may be removed by fractional sublimation.

Method B. A 200-mL, three-necked flask was equipped with a gas inlet and two pressure-equalized dropping funnels. The system was evacuated and filled with nitrogen. Sodium borohydride (1.00 g; 26.4 mmol) was dissolved in 50 mL of THF and then 20 mL of triethylamine was added. To one dropping funnel was added 1.2 g of decaborane (10 mmol) dissolved in 20 mL of THF. In the other dropping funnel, a solution of 1.75 mL of PCl_3 (20 mmol), 1.00 mL of $AsCl_3$ (11.8 mmol), and 20 mL of THF was made up. The solutions in the dropping funnels were alternately added dropwise, beginning with decaborane, over a 1-h period. Stirring was continued, the solids were removed by filtration, and then the solids were washed three to four times with 15-mL aliquots of THF. The combined filtrate and washings were rotary evaporated onto 6 g of 100–200 mesh silica gel which was placed atop a column of 30 g of 100–200 mesh silica gel using hexane. Hexane eluted 100 mg of 1,2-$PAsB_{10}H_{20}$, and a 50% hexane–toluene solution eluted 75 mg of a 1:9 mixture of 1,2-$PAsB_{10}H_{10}$:1,2-$As_2B_{10}H_{10}$, respectively. Crude compound **5** was sublimed at 90 °C to yield 51 mg (0.23 mmol, 2.3% yield) of pure 1,2-$PAsB_{10}H_{10}$. MS: *m/e* 224 (M^+). Exact mass of $^{11}B_{10}{}^1H_{10}{}^{75}As^{31}P$: calcd, 224.0744; found, 224.0738. ^{31}P NMR ($CDCl_3$): δ –9.7. IR: 2560 (vs), 1000 (s), 930 (w), 910 (m), 890 (m), 860 (w), 760 (m), 725 (s), 685 (w), 615 (w), 540 (w), 475 (w), 445 (s), 410 (w), 370 (m), 350 (m), 315 (s) cm^{-1}.

Table I. Summary of Crystal Data and Intensity Information for 2-(trimethylamine)-1-$PB_{11}H_{10}$

empirical formula: $B_{11}H_{19}C_3PN$
color: colorless
crystal dimens: 0.25 mm on a side
space group: $P2_1/m$
cell dimens (at –155 °C, 36 refcns)
  $a = 6.910(1)$ Å
  $b = 10.603(1)$ Å
  $c = 8.821(1)$ Å
  $\beta = 108.27(1)°$
Z (molecules/cell) = 2
volume = 613.70 Å^3
$d_{calcd} = 1.186$
wavelength = 0.710 69 Å
$M_r = 219.07$
linear abs coeff = 1.744
detector-to-sample dist = 22.5 cm
sample-to-source dist = 23.5 cm

take-off angle = 2.0°
av w scan width at half-height = 0.25°
scan speed = 10.0°/min
scan width = 1.8° + dispersion
single bkgd time at extremes of scan = 4 s
aperture size = 3.0 × 4.0 mm
limits of data collcn
  min $2(\theta) = 6°$
  max $2(\theta) = 45°$
tot no. of reflns. collcd 1130
  no. of unique intens 852
  no. with $F > 0.0$ 840
  no. with $F > 2.33(\sigma)(F)$ 816
final results
  $R(F) = 0.0303$
  $R_w(F)$ (*w* based on counting statistics) = 0.0399
goodness of fit for last cycle = 1.709
max Δ/σ for last cycle = 0.01

Preparation of 1,2-$PSbB_{10}H_{10}$ (6). The same apparatus was used as in the preparation of **5** (method B). Sodium borohydride (1.0 g, 26.4 mmol) was dissolved in 50 mL of THF and then 15.0 mL of triethylamine was added. To one dropping funnel was added 1.2 g of decaborane (10 mmol) dissolved in 20 mL of THF. The other dropping funnel contained 1.75 mL of PCl_3 (20 mmol) and 2.51 g of SbI_3 (5 mmol) slurried in 20 mL of THF. The solutions in the dropping funnels were alternately added dropwise, beginning with decaborane, over a 45-min period. Workup of the reaction mix was the same as for **5**, method B, except that the chromatography column was built with 75 g of 100–200 mesh silica gel. Toluene was used to elute 1,2-$B_{10}H_{10}Sb_2$, and a solution of 1:1 toluene–chloroform eluted 1,2-$B_{10}H_{10}PSb$. The crude 1,2-$B_{10}H_{10}PSb$ (109 mg) was sublimed at 100–115 °C for several hours, which afforded 75.1 mg (0.28 mmol) of pure 1,2-$B_{10}H_{10}PSb$ (2.83% yield), mp >450. MS: *m/e* 272 (M^+). Exact mass of $^{11}B_{10}{}^1H_{10}{}^{31}P^{121}Sb$: calcd, 272.0489; found, 272.0483. ^{31}P NMR (acetone-d_6): –31.9. IR: 2540 (vs), 1390 (w), 1260 (m), 1100 (m), 1000 (s), 910 (m), 890 (m), 805 (m), 765 (s), 615 (w), 470 (w), 435 (m), 362 (m) cm^{-1}.

X-ray Structure Determination of 2-(trimethylamine)-1-$PB_{11}H_{10}$. A small, colorless crystal was grown from a 10:1 mixture of dichloromethane–acetone. The crystal was mounted on the end of a glass fiber on a goniometer head using silicone grease, and transferred to the goniostat where it was cooled to –155 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences ($0k0 = 2n + 1$) corresponding to a monoclinic space group with only a screw axis. Subsequent solution and refinement of the structure confirmed the centrosymmetric $P2_1/m$. Data were collected in the usual manner using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. A final difference Fourier was featureless, with the largest peak being 0.15 e/Å^3. No absorption correction was performed. A summary of crystal data and intensity information is given in Table I. Interatomic distances and atomic coordinates and isotropic thermal parameters are shown in Tables II and III, respectively.

Table II. Interatomic Distances (Å) for 2-(trimethylamine)-1-$PB_{11}H_{10}$

P(1)–B(2)	2.042(3)	B(6)–B(7)	1.7914(27)
P(1)–B(3)	2.0488(21)	B(6)–B(8)	1.7803(27)
P(1)–B(4)	2.0287(20)	B(7)–B(7)	1.804(4)
N(9)–C(10)	1.507(3)	B(7)–B(8)	1.785(3)
N(9)–C(11)	1.5019(23)	C(10)–H(7)	0.895(19)
N(9)–B(2)	1.593(3)	C(10)–H(8)	0.91(3)
B(2)–B(3)	1.8464(25)	C(11)–H(9)	0.892(21)
B(2)–B(7)	1.777(3)	C(11)–H(10)	0.910(20)
B(3)–B(4)	1.8433(28)	C(11)–H(11)	0.892(21)
B(3)–B(6)	1.7766(28)	B(3)–H(1)	1.049(19)
B(3)–B(7)	1.7849(28)	B(4)–H(2)	1.116(19)
B(4)–B(4)	1.849(4)	B(5)–H(3)	1.06(3)
B(4)–B(5)	1.777(3)	B(6)–H(4)	1.059(20)
B(4)–B(6)	1.782(3)	B(7)–H(5)	1.012(20)
B(5)–B(6)	1.7809 (26)	B(8)–H(6)	1.00(3)
B(5)–B(8)	1.776(4)		

Table III. Fractional Coordinates and Isotropic Thermal Parameters for 2-(trimethylamine)-1-$PB_{11}H_{10}$[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
P(1)	4665(1)	2500*	8975(1)	14
B(2)	7772(4)	2500*	−141(3)	11
B(3)	6567(3)	3916(2)	8739(2)	12
B(4)	4603(3)	3372(2)	6913(2)	14
B(5)	5885(5)	2500*	−4204(3)	14
B(6)	7054(3)	3864(2)	6878(2)	13
B(7)	8966(3)	3351(2)	−1340(2)	11
B(8)	8541(4)	2500*	−3162(3)	14
N(9)	8671(3)	2500*	1757(2)	12
C(10)	10968(4)	2500*	2304(3)	18
C(11)	8007(3)	3648(2)	2460(2)	16
H(1)	645(3)	476(2)	933(2)	15(4)
H(2)	314(3)	388(2)	636(2)	18(4)
H(3)	527(5)	250*	−547(4)	28(6)
H(4)	724(3)	474(2)	−365(2)	21(4)
H(5)	26(3)	384(2)	918(2)	17(4)
H(6)	958(5)	250*	−374(4)	28(6)
H(7)	1143(3)	320(2)	197(2)	15(4)
H(8)	1147(4)	250*	339(4)	17(6)
H(9)	843(3)	434(2)	209(2)	11(4)
H(10)	854(3)	360(2)	354(3)	13(4)
H(11)	665(3)	366(2)	218(2)	17(4)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609. Parameters marked by an asterisk were not varied.

Table IV. Boron NMR Data of Some of the New Phosphaborane Compounds

compd	$\delta_{^{11}B}$ (rel intens)[a]
$Me_4N[2\text{-}PB_9H_9]$ (1)	12.2 (1), 1.3 (1), −16.3 (1), −26.9 (2), −29.4 (2), −31.8 (2)
$Me_4N[7,8\text{-}P_2B_9H_{10}]$ (2)	−0.1 (2), −0.7 (2), −9.5 (3), −17.5 (1), −36.0 (1)
2-Me_3N-1-$PB_{11}H_{10}$ (3)	6.8 (1),[b] 5.0 (1), −6.2 (2), −6.7 (2), −9.6 (3), −11.4 (2)
$Me_4N[PB_{11}H_{11}]$ (4)	6.3 (1), −5.4 (5), −10.0 (5)

[a] Acetone solvent. [b] Singlet resonance.

Results and Discussion

Reaction of $B_{10}H_{14}$ with PCl_3 and Triethylamine—Further Progress. An earlier report described the isolation and characterization of 1,2-$P_2B_{10}H_{10}$ and 6-(trimethylamine)-2-PB_9H_8 from the complex product mixture derived from the reaction of $B_{10}H_{14}$ with PCl_3 and triethylamine.[6] Another phosphaborane product was isolated by silica gel chromatography when the polar eluent mixture 20% acetone/methylene chloride was used. This was an anionic product (compound **1**), which was precipitated from aqueous solution with the tetramethylammonium counterion. The ^{11}B NMR of **1** (see Table IV) exhibited a 1:1:1:2:2:2 pattern of doublets consistent with a *closo*-2-$PB_9H_9^-$ structure for the anion. The charge compensated derivative, 6-(triethylamine)-2-PB_9H_8, had been fully characterized earlier, including a single-crystal X-ray structure determination.[6] This neutral phosphaborane compound is probably derived from *closo*-2-$PB_9H_9^-$ by hydride abstraction by PCl_3 and subsequent attack by triethylamine. Thus, prior characterization of the neutral derivative assists in the characterization of **1**.

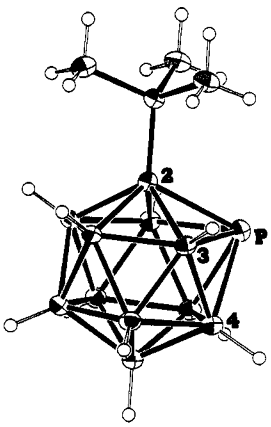

Figure 1. ORTEP drawing of 2-Me_3N-1-$PB_{11}H_{10}$.

Boron Atom Abstraction from 1,2-$P_2B_{10}H_{10}$. Previously, we had observed that 1,2-$P_2B_{10}H_{10}$ reacted rapidly at room temperature with 5% aqueous sodium hydroxide to abstract a phosphorus atom and generate 7-$PB_{10}H_{12}^-$ in moderate yield.[6] In an anhydrous oxygen-free environment, 1,2-$P_2B_{10}H_{10}$ reacted with piperidine in chloroform solution to give 7,8-$P_2B_9H_{10}^-$ in good yield. We suggest that **2** has the *nido* 11-vertex icosahedral fragment structure resulting from abstraction of a boron atom adjacent to both phosphorus atoms of 1,2-$P_2B_{10}H_{10}$. The 2:2:3:1:1 pattern of doublets of the ^{11}B NMR spectrum of **2** (see Table IV) would be consistent with a *nido* structure with the two phosphorus atoms in adjacent positions in the open face if one assumes that the area 3 peak is due to accidental overlap of an area 2 and an area 1 signal. The isoelectronic 7,8-$As_2B_9H_{10}^-$ ion was obtained previously from 1,2-$As_2B_{10}H_{10}$ by the same type of reaction.[9] The ^{11}B NMR spectrum of this diarsaborane anion is quite similar to that of **2** and in this case, the 2:2:1:2:1:1 doublet pattern expected of the 7,8-$As_2B_9H_{10}^-$ ion was observed.[10] The heteroatom placement in 7,8-$As_2B_9H_{10}^-$ was determined from recent X-ray studies of platinum complexes of this anion.[11]

New 12-Vertex Monophosphaboranes. Freshly prepared $Me_3NH[B_{11}H_{14}]$ was reacted in THF with 4 equiv of *n*-butyl lithium. This was followed by reaction with an excess of PCl_3 in THF solution. The product mixture was separated by silica gel chromatography and subsequent crystallization to give, as the major product, 2-Me_3N-1-$PB_{11}H_{10}$ (compound **3**) in 29% yield. The ^{11}B NMR spectrum of **3** contains six resonances of relative area 1:1:2:2:3:2. The lowest field resonance (area 1) is a singlet and is attributed to the trimethylamine-substituted cage boron atom. It is assumed that the area 3 resonance is due to accidental overlap of an area 2 and an area 1 signal. The ^{11}B NMR data is consistent with an icosahedral phosphaborane having a Me_3N substituent at either B(2) or B(7).

A single-crystal X-ray study of **3** clearly showed that the trimethylamine is attached to B(2) as illustrated in Figure 1. As expected, the phosphorus atom causes a local distortion of the icosahedron. The average P–B distance of $MePB_{11}H_{11}$ (1.953 Å)[3] is very similar to the average P–B distance of **3** (2.038 Å) (see Table II). As expected, the phosphorus atom causes a local distortion of the icosahedron such that the boron–boron distances

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Table V. ^{11}B NMR Data and Assignments of 1,2-$PEB_{10}H_{10}$ Derivatives (E = P, As, Sb, Bi)

	^{11}B chem shift, ppm[a]					
compd	B(12)	B(9)	B(3,6)	B(4,5)	B(7,11)	B(8,10)
1,2-$P_2B_{10}H_{10}$	17.7	17.7	−2.5	−0.3	−0.3	4.2
1,2-$PAsB_{10}H_{10}$	15.5	19.7	−0.5	−2.7	2.0	2.0
1,2-$PSbB_{10}H_{10}$	13.6	15.9	0.3	−3.6	2.2	−0.2
1,2-$PBiB_{10}H_{10}$	~12.0	~12.6	2.7	−7.1	6.1	−1.2

[a] Acetone solvent.

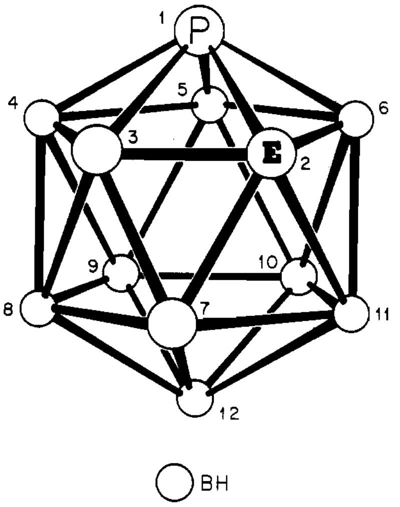

Figure 2. Numbering scheme for 1,2-$PEB_{10}H_{10}$.

between the five boron atoms adjacent to the phosphorus atom are 1.85 and 1.84 Å for $MePB_{11}H_{11}$ and **3**, respectively. The other boron–boron distances of these two icosahedra are approximately 1.77 Å, which is similar to the value for $B_{12}H_{12}^{-2}$.[12]

A second compound was isolated from this reaction but was not fully characterized. The ^{11}B NMR spectrum of this new compound (acetone solvent) contained resonances at δ 4.8 (1B), 2.9 (1B, singlet), −4.7 (2B), −5.7 (2B), −8.3 (2B), −10.7 (2B), and −12.0 (1B). We suspect that this new compound is the isomeric 7-Me_3N-1-$PB_{11}H_{10}$.

In a separate experiment, $Me_3NH[B_{11}H_{14}]$ was first treated with 2 equiv of *n*-butyllithium in THF and then the mixture was evaporated to dryness to remove trimethylamine. An additional 3 equiv (a slight excess) of *n*-butyllithium in THF was added to the mixture, followed by a THF solution of PCl_3. Aqueous workup gave $Me_4N[PB_{11}H_{11}]$ (compound **4**) in low yield. The ^{11}B NMR spectrum of **4** had the 1:5:5 pattern of doublet resonances expected for this icosahedral ion.

Boron-11 NMR Study of Some of the 12-Vertex Phosphaborane Derivatives. The assignment of individual boron atoms in 1,2-$PEB_{10}H_{10}$ (E = As, Sb or Bi) to specific resonances in the corresponding ^{11}B NMR spectra was accomplished by the use of two-dimensional ^{11}B–^{11}B COSY NMR and the observation of ^{31}P–^{11}B coupling to adjacent boron atoms. The results of this study are given in Table V. The B(3,6) resonance (see Figure 2) is assigned due to its lack of cross peaks in the 2D ^{11}B NMR with the area 1 peaks which are due to B(9) and B(12). The B(8,10) resonance can be uniquely assigned because it shows cross peaks with every other resonance. Phosphorus-31 coupling to the B(3,6) and B(4,5) resonances was observed upon line narrowing the appropriate ^{11}B NMR spectrum. The resonance associated with B(9) was then assigned by its cross peaks to B(4,5), and finally B(12) was assigned by its cross peaks to B(7,11).

Table VI. Antipodal ^{11}B Chemical Shift Values of $B_{11}H_{11}E^-$ Anions

element	N	P	As	Sb	Bi
antipodal $\delta_{^{11}B}$, ppm	−1	6.3	8.0	9.4	12.3
ref	18	this report	9	25	26

The cross cage (antipodal) substituent effects were reported in the ^{11}B NMR spectra of *closo* boranes and heteroboranes many years ago.[13,14,15] This subject has been reviewed recently.[16] For an icosahedral cage of the form $EB_{11}H_{11}^{n-}$, the antipodal ^{11}B signal moves progressively to lower field as E is changed from BH^{2-} to CH^- to NH (with antipodal shift values of −15.5, −7,[17] and 2.7[18] ppm, respectively). This same trend is observed as one moves from left to right in other sections of the periodic table as well and with other size *closo* cages (e.g., 10-vertex cage). In these cases, it is believed that the shift of the antipodal signal to lower field is related to decreasing electron density on vertices E and also decreasing electron density on the antipodal boron atoms as well. Recently, several groups have applied molecular orbital methods to calculate chemical shift values for these antipodal ^{11}B nuclei.[19,20,21]

Icosahedral cages of the type $B_{11}H_{11}E^-$, where the heteroatom is only a group-15 element, exhibit an upfield trend of the ^{11}B chemical shift of the antipodal boron atom with decreasing heteroatom size or increasing electronegativity of the heteroatom (see Table VI). Similar antipodal trends are observed for $B_{11}H_{11}E^{2-}$ cages containing group-14 elements (Ge, −5 ppm; Sn, −3.8 ppm; Pb, −2.9 ppm)[22] as well as $B_{11}H_{11}E$ cages containing group-16 elements (S, 18.7 ppm,[23] Se, 22.9 ppm).[24] However, calculated antipodal ^{11}B NMR chemical shift values employing the IGLO method (for 10-vertex heteroboranes) predict an opposite trend[21] (i.e., 1-$B_9H_9E^-$, N, 45.8 ppm; P, 40.7 ppm).

In contrast, 12-vertex heteroboranes of types 1,2-$E_2B_{10}H_{10}$ and 1,2-$EE'B_{10}H_{10}$ (E and E′ = P, As, Sb or Bi) exhibit, in general, a downfield trend of the ^{11}B chemical shift of the antipodal boron atom with decreasing heteroatom size or increasing electronegativity of the heteroatoms (see Table V). These antipodal boron chemical shift trends will give a further challenge to those who apply molecular orbital methods to calculate ^{11}B chemical shift values.

Supplementary Material Available: Tables crystal data, anisotropic thermal parameters, bond distances, and intramolecular angles (10 pages). Ordering information is given on any current masthead page.

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