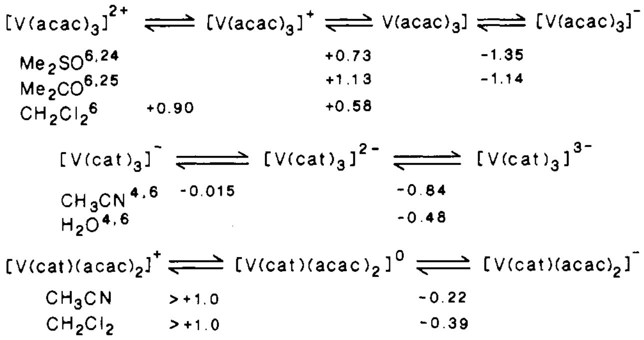
lution's color changed from dark blue or purple to almost colorless, a current flowed in the direction that would reduce the complex, and the subsequent CV (after the current became almost zero) was changed irreversibly with the introduction of several new peaks.[23]

For $[V(acac)_3]^{+,0}$ and $[V(bzac)_3]^{+,0}$ the potentials are identical,[6] whereas the potential for $[V(dtbc)_3]^{2-,3-}$ is 0.35 V more negative than that for $[V(cat)_3]^{2-,3-}$ due to the electron-releasing alkyl groups.[4] For the mixed-chelate complexes studied here, a change from 2,4-pentanedionate to 1-phenyl-1,3-butanedionate has little effect on the potentials for the vanadium(IV)–vanadium(III) couples, but the alkyl groups' electron-releasing property in the dtbc complex again causes the potential to become more negative by 0.14–0.19 V.

No evidence was obtained for reduction of the mixed-chelate vanadium(III) complexes to vanadium(II). A cyclic voltammetric study of the oxidation of the vanadium(IV) complexes to vanadium(V) is complicated by the oxidation of the catechol ligand in the potential range expected for the metal oxidation. Catechol and 3,5-di-*tert*-butylcatechol in acetonitrile give peaks at 1.26 and 1.14 V (NHE), respectively. $[V(cat)(acac)_2]$ and $[V(dtbc)(bzac)_2]$ give oxidation peaks at 1.1 and 1.0 V, respectively, in acetonitrile with similar behavior in dichloromethane.

The potentials (V vs NHE) for the tris chelate and mixed-chelate complexes are as follows:



For the tris(2,4-pentanedionato)vanadium system, the III state is the most stable. The IV state is relatively stable to oxidation but is easily reduced to the III state, which is stable to further reduction. Nevertheless, the IV state is stable to disproportionation. For the catecholato system, the V state is the most stable. The III state is easily oxidized to the IV state, which, although stable to disproportionation, in turn requires a relatively weak oxidizing agent to go to the V state. In contrast to these two tris chelate systems, the mixed-chelate complexes have the IV state as the most stable: $[V(cat)(acac)_2]$ and its related complexes are stable to disproportionation and relatively stable to oxidation and reduction.

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(23) Attempts to isolate the V(III) species by controlled-potential reduction of the V(IV) complexes were unsuccessful. The deep blue or purple color of the V(IV) complexes changed during the electrolysis to give a much lower intensity red-brown and finally green color.

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Synthesis of Polyhedral Phosphaboranes. Crystal Structure of $6\text{-}(C_2H_5)_3N\cdot 2\text{-}PB_9H_8$

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The diphosphaborane $1,2\text{-}P_2B_{10}H_{10}$ has been prepared in low yield from $B_{10}H_{14}$ by using PCl_3 as the source of phosphorus. This reaction gives a complex mixture of products, one of which is the *closo*-phosphaborane, $6\text{-}(C_2H_5)_3N\cdot 2\text{-}PB_9H_8$, which has been fully characterized, including a single-crystal X-ray structure determination (space group $P2_1/c$, a = 13.589 (3) Å, b = 11.758 (3) Å, c = 18.224 (5) Å, β = 99.57 (1)°, Z = 8). The thermal conversion of $1,2\text{-}P_2B_{10}H_{10}$ to $1,7\text{-}P_2B_{10}H_{10}$ occurred at 560–590 °C in a sealed tube. Aqueous base rapidly removed one phosphorus atom from $1,2\text{-}P_2B_{10}H_{10}$ to form the $7\text{-}PB_{10}H_{12}^-$ ion.

Introduction

There exist a rather extensive number of known borane and carborane derivatives containing group 15 atoms, the synthesis and properties of which are summarized in reviews.[1] Recently, we reported improved methods for the synthesis of $7\text{-}B_{10}H_{12}As^-$ and $1,2\text{-}B_{10}H_{10}As_2$.[2] These results have led us to again study improved methods for the synthesis of phosphaboranes.

Previously, the most readily available derivatives were $7\text{-}B_{10}H_{12}PR$ (R = Me, Et, Pr, Ph) and their metal complexes, $(\eta^5\text{-}C_5H_5)Co(B_{10}H_{10}PR)$.[3] The *nido*-phosphaboranes were prepared by reacting $B_{10}H_{14}$ and $RPCl_2$ in the presence of NaH or triethylamine. Early attempts[4] to obtain $7\text{-}B_{10}H_{12}P^-$ from the reaction of PCl_3, $B_{10}H_{14}$, and a base in diethyl ether gave a mixture containing this anion. Its presence in the mixture was proven by full characterization of the σ-bonded complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2PB_{10}H_{12}$.[5]

We have studied in more detail the synthesis of phosphaboranes from $B_{10}H_{14}$, PCl_3, and a base. Reported here are our initial results on this very complex, but extremely interesting, set of reactions.

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. Broad-band ^1H decoupling (3 W) was continuously used. A general description for two-dimensional (^{11}B–^{11}B) NMR technique has been previously discussed.[16] Typically, the 2-D t_1, t_2 matrix was collected as

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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 spectra were referenced to the proteo solvent impurity, and the ^{31}P NMR spectra 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 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} mmHg. All other commercially available reagents were used as received.

Preparation of $1,2\text{-}P_2B_{10}H_{10}$ (1). To a 1-L three-necked flask flushed with nitrogen and fitted with an overhead stirrer and two pressure-equalized dropping funnels were added 3.8 g of $NaBH_4$ (100 mmol), 200 mL of THF, and 70 mL of triethylamine. A solution of 6.1 g of $B_{10}H_{14}$ (50 mmol) in 25 mL of THF was placed in one of the dropping funnels, and a solution of 18 mL of PCl_3 (204 mmol) in 25 mL of THF was placed in the other dropping funnel.

The solutions were added alternately with stirring at room temperature over 1 h, first 20 drops of the $B_{10}H_{14}$ solution and then 30 drops of the PCl_3 solution. The remaining PCl_3 solution was added over 15 min, and stirring was continued for 2 h. The reaction mixture was filtered, and the copious solids were washed with several 30–40-mL portions of THF. The combined filtrate and washings were rotary-evaporated onto 100 g of 100–200-mesh silica gel, and the moist solids were placed in an evaporating dish in a hood overnight.

A 1.5 cm o.d. × 50 cm length chromatography column was made up with hexane and 400 g of 100–200-mesh silica gel. The silica gel containing the product mixture was ground in a mortar and slurried in hexane, and the slurry was placed atop the column. Elution with hexane gave 1.05 g of $1,2\text{-}P_2B_{10}H_{10}$ (**1**). Elution with 1:1 hexane–toluene gave a mixture of **1** and a liquid phosphaborane of unknown structure, which was rechromatographed on 50 g of silica gel with hexane to give a further 0.08 g of **1**: total yield 1.13 g (12.4% based on $B_{10}H_{14}$).

Sublimation of **1** at 80 °C and 10^{-2} mmHg produced slightly purer material: mp 397–399 °C; MS *m/e* 182 (M^+); exact mass calcd for $^{11}B_{10}{}^1H_{10}{}^{31}P_2$ 182.1188, found 182.1186; ^{31}P NMR ($CDCl_3$) δ −19.3; ^1H NMR ($CDCl_3$, ^{11}B decoupled) δ (J_{PH}, Hz) 3.56, 3.21, 2.72 (16), 2.52 (19) (area ratio 2:2:4:2, respectively); IR (KBr) 2575 (vs), 1003 (m), 910 (w), 893 (m), 745 (w), 721 (s), 625 (m), 507 (w), 458 (m), 415 (w), 371 (m) cm^{-1}.

Preparation of $6\text{-}(C_2H_5)_3N\cdot2\text{-}PB_9H_8$ (2). After the chromatography column described above was eluted with 1:1 hexane–toluene to remove **1**, elution was carried out with toluene to remove most of a liquid phosphaborane of unknown structure. Subsequent elution with chloroform gave 108 mg of a mixture of the unknown liquid and solid $6\text{-}(C_2H_5)_3N\cdot2\text{-}PB_9H_8$. Recrystallization three times by slow rotary evaporation of a $CHCl_3$–heptane solution afforded needle crystals of **2**: 56 mg, 0.5% yield; mp 145–147 °C; MS *m/e* 239 (M^+); exact mass calcd for $^{11}B_9{}^1H_{23}{}^{12}C_6{}^{31}P^{14}N$ 239.2406, found 239.2405; ^{31}P NMR ($CDCl_3$) δ −233; ^1H NMR ($CDCl_3$) δ 3.16 (m, CH_2CH_3), 1.19 (t, J = 7.25 Hz, CH_2CH_3); IR (KBr) 3010 (w), 2984 (w), 2933 (s), 2540 (vs), 1743 (s), 1462 (m), 1184 (w), 1141 (s), 1090 (w), 1002 (s), 943 (s), 879 (w), 612 (s), 770 (m), 735 (w), 667 (w), 648 (w), 445 (w), 410 (w) cm^{-1}.

Preparation of $1,7\text{-}P_2B_{10}H_{10}$ (3). Compound **1** (300 mg) was sealed in an evacuated thick-walled glass tube and heated to 560–590 °C for 1.5 h. Sublimation of the reaction mixture at 70 °C and 10^{-2} mmHg gave 56 mg that was 10% **1** and 90% **3** by ^{11}B NMR spectroscopy. The sublimate was shaken for 10 min with 10% NaOH solution to remove unreacted **1** and the remaining solid sublimed at 60 °C and 10^{-2} mmHg to afford 30 mg of pure **3**: mp 378–380 °C; MS *m/e* 182 (M^+); exact mass calcd for $^{11}B_{10}{}^1H_{10}{}^{31}P_2{}^+$ 182.1188, found 182.1190; ^1H NMR ($CDCl_3$, ^{11}B decoupled) δ 3.11, 2.94, 2.87, 2.79 (area ratio 2:2:4:2, respectively); ^{31}P NMR ($CDCl_3$) δ −20.2; IR (KBr) 2580 (vs), 1015 (m), 1002 (w), 914 (w), 745 (s), 706 (w), 675 (w), 652 (w), 623 (m), 543 (m), 446 (s) cm^{-1}.

Preparation of $(CH_3)_4N[7\text{-}PB_{10}H_{12}]$ (4). Sublimed **1** (200 mg) was powdered and stirred at room temperature in 5% NaOH solution for 10 min. Acidification with dilute HCl to pH 2 gave 31 mg of white solid, which was shown to be starting material by ^{11}B NMR spectroscopy. The filtrate was precipitated with $(CH_3)_4NCl$ solution, and the solid was separated by filtration, washed with water, and crystallized from acetone-methanol. Recrystallization from acetone–methanol gave 100 mg of analytically pure **4**: 27% yield; ^{31}P NMR (acetone-d_6) δ −103; ^1H NMR (acetone-d_6) δ 3.42 (12 H), −4.33 (2 H); IR 3114 (w), 2510 (vs), 1480 (s), 1110 (w), 1026 (s), 997 (m), 951 (s), 876 (w), 774 (w), 722 (w), 606 (w) cm^{-1}. Anal. Calcd for $B_{10}H_{24}C_4NP$: C, 21.30; H, 10.74. Found: C, 21.46; H, 10.26.

Table I. Summary of Crystal Data and Intensity Information for $6\text{-}(C_2H_5)_3N\cdot2\text{-}PB_9H_8$

empirical formula	$B_9H_{23}C_6PN$
color	colorless
crystal dimens	0.25 mm on a side
space group	$P2_1/c$
cell dimens (at −155 °C, 36 reflcns)	
a	13.589 (3) Å
b	11.758 (3) Å
c	18.224 (5) Å
β	99.57 (1)°
Z (molecules/cell)	8
vol	2871.13 $Å^3$
d_{calcd}	1.099 g cm^{-3}
wavelength	0.71069 Å
M_r	237.52
linear abs coeff	1.553
detector-to-sample dist	22.5 cm
sample-to-source dist	23.5 cm
takeoff angle	2.0°
av ω scan width at half-height	0.25°
scan speed	5.0°/min
scan width	1.8° + dispersion
single bkgd time at extremes of scan	6 s
aperture size	3.0 × 4.0 mm
limits of data collection	
min 2(θ)	6°
max 2(θ)	45°
total no. of reflcns collcd	4076
no. of unique intensities	3772
no. with $F > 0.0$	3181
no. with $F < 2.33\sigma(F)$	2716
final results	
$R(F)$	0.0792
$R_w(F)$ (*w* based on counting statistics)	0.0727
goodness of fit for last cycle	1.289
max Δ/σ for last cycle	0.35

Preparation of $7\text{-}CH_3\text{-}7\text{-}PB_{10}H_{12}$. Compound **4** (85 mg) was placed in a 15-mL two-necked flask fitted with a reflux condenser and dissolved in 7 mL of THF with stirring. Methyl iodide (2.5 mL) was added, and stirring was continued at room temperature for 28 h. THF was removed in vacuo, and the reaction residues were sublimed at 105 °C and 10^{-2} mmHg to obtain 10 mg (16% yield) of $7\text{-}CH_3\text{-}7\text{-}PB_{10}H_{12}$. ^{11}B NMR and IR spectra were identical with those of the authentic material.[3]

X-ray Structure Determination for $6\text{-}(C_2H_5)_3N\cdot2\text{-}PB_9H_8$. A colorless crystal of dimensions 0.25 mm on a side was grown by slow evaporation of a chloroform–heptane solution. The crystal was mounted on a previously described goniostat[11] and cooled to −155 °C. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least-squares techniques. Lattice parameters were determined from a least-squares fit of angular data from 36 reflections and centered by using automated top/bottom and left/right slit assemblies. A summary of crystal data and intensity information is given in Table I.

Two independent molecules are present in the asymmetric unit; a disorder is present in the position of the phosphorus atom in each of the molecules. In one of the molecules, there is 53% P in position PB(2) and 47% P in position BP(3) (see Figure 1). In the other molecule, the disorder is 83% P in PB(2) and 17% P in BP(3).

Results and Discussion

Reaction of $B_{10}H_{14}$ with PCl_3 and Base. Several years ago, J.L.L.[4] attempted to synthesize $1,2\text{-}B_{10}H_{10}P_2$ (**1**) by the method

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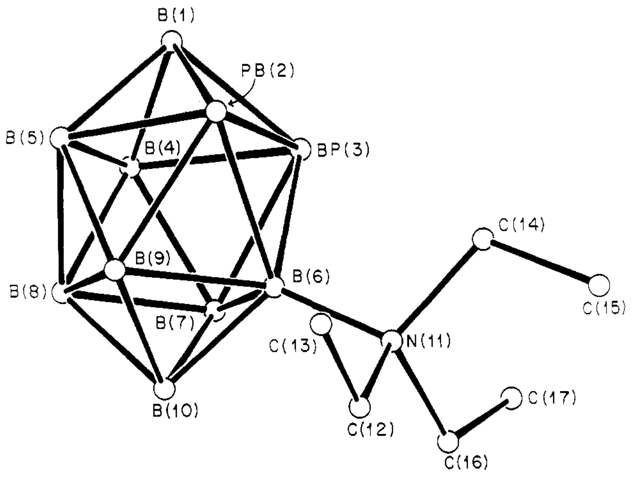

Figure 1. Structure of 6-$(C_2H_5)_3N{\cdot}2{-}PB_9H_8$.

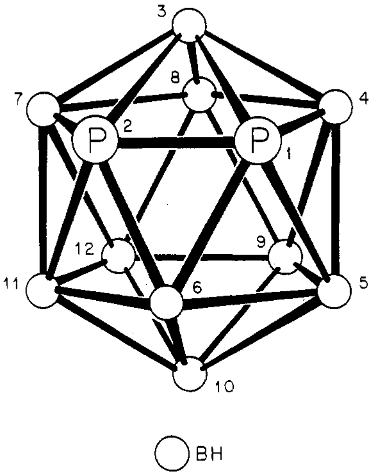

Figure 2. Numbering system for 1,2-$P_2B_{10}H_{10}$.

used to produce the analogous arsaborane[2,6] and stibaborane.[7] This method involved the slow addition of a THF solution of $AsCl_3$ or $SbCl_3$ to a THF solution of decaborane(14), triethylamine, and a reducing agent. However, when PCl_3 was substituted in this procedure, a very low (<1%), erratic yield of **1** was obtained.

We have now found that placing the reducing agent ($NaBH_4$), triethylamine, and THF in a flask and then adding alternately THF solutions of $B_{10}H_{14}$ and PCl_3 from dropping funnels will give consistent yields of **1** in the range 12–13%. The product mixture from this reaction is very complex, and in addition, it should be noted that PCl_3 is known to form an adduct of the type 3 $R_3N{\cdot}PCl_3$ with triethylamine.[12] In spite of these diffficulties, we have isolated some new phosphaborane compounds from the mixture that point to certain types of side reactions that occur in this process.

Compound **1** is high melting, as is 1,2-$B_{10}H_{10}Sb_2$,[7] and it has a sweet odor reminiscent of 1,2-$B_{10}H_{10}CHP$.[8] The exact mass determination of the parent ion peak in the high-resolution mass spectrum verified the molecular formula of **1** as $P_2B_{10}H_{10}$. Compound **1** exhibited a ^{11}B NMR spectrum containing four doublets in a 2:2:4:2 ratio, which is consistent with the C_{2v} symmetry of this icosahedral molecule. The ^{11}B NMR data are given in Table IV.

Two-dimensional (^{11}B–^{11}B) NMR spectroscopy was used in an attempt to assign boron nuclei to specific resonances. The resonances at 4.2 and −0.3 ppm are the only ones that show cross peaks in the 2-D ^{11}B NMR contour plot with all other resonances. This suggests that the resonance at 4.2 ppm is due to B(8,10) and, by its intensity, the signal at −0.3 ppm is due to B(4,5,7,11) (see Figure 2 for the numbering of 1,2-$P_2B_{10}H_{10}$). There is no possibility of using 2-D NMR to determine the assignments of the resonances at 17.7 and −2.5 ppm, since both signals show cross peaks in the 2-D contour plot with B(8,10) and B(4,5,7,11). If the ^{11}B NMR spectrum of **1** is analogous to that of 1,2-$C_2H_2B_{10}H_{10}$, then the resonance at −2.5 ppm would be assigned to B(3,6) and the resonance at 17.7 ppm to B(9,12).[13]

Table II. Interatomic Distances for 6-$(C_2H_5)_3N{\cdot}2{-}PB_9H_8$[a]

B(1)–PB(2)[a]	1.899 (7)	B(6)–B(7)	1.826 (8)
B(1)–BP(3)[a]	1.780 (9)	B(6)–B(9)	1.935 (9)
B(1)–B(4)	1.677 (10)	B(6)–B(10)	1.686 (9)
B(1)–B(5)	1.730 (10)	B(6)–N(11)	1.593 (7)
PB(2)–BP(3)	2.148 (5)	B(7)–B(8)	1.814 (9)
PB(2)–B(5)	2.099 (7)	B(7)–B(10)	1.698 (9)
PB(2)–B(6)	2.100 (6)	B(8)–B(9)	1.818 (9)
PB(2)–B(9)	2.069 (7)	B(8)–B(10)	1.695 (10)
BP(3)–B(4)	1.907 (8)	B(9)–B(10)	1.698 (9)
BP(3)–B(6)	1.927 (8)	N(11)–C(12)	1.525 (7)
BP(3)–B(7)	1.921 (8)	N(11)–C(14)	1.525 (7)
B(4)–B(5)	1.820 (10)	N(11)–C(16)	1.538 (7)
B(4)–B(7)	1.805 (9)	C(12)–C(13)	1.516 (8)
B(4)–B(8)	1.826 (10)	C(14)–C(15)	1.512 (8)
B(5)–B(8)	1.797 (10)	C(16)–C(17)	1.510 (8)
B(5)–B(9)	1.855 (9)		

[a] Molecule B; contains 17% phosphorus in BP(3) and 83% phosphorus in PB(2).

Upon line narrowing, the resonance at −0.3 ppm was split into a doublet ($J_{^{11}B-^{31}P}$ = 60 Hz) and the resonance at −2.5 ppm was split into a four-line pattern (the coupling between the inner two lines was 26 Hz, and the coupling between the inner and outer lines was 40 Hz). The four-line pattern was simulated by using PANIC (Bruker AM-500 software) with $J_{^{11}B(3,6)-^{11}B(8,10)}$ = 15 Hz, $J_{^{11}B-^{31}P}$ = 60 Hz, and a line width of 45 Hz. Single-frequency ^{11}B decoupling of the resonance at 4.2 ppm (4 W) resulted in a collapse of the −2.5 ppm resonance into a triplet, suggesting coupling to two equivalent phosphorus nuclei ($J_{^{11}B-^{31}P}$ = 61 Hz). Single-frequency ^{11}B decoupling of the resonance at −0.3 ppm only resulted in a broadening of the resonance at −2.5 ppm. This could be due to the proximity of the decoupler frequency to the observed resonance (difference of ~245 Hz). These data strengthen our assignments for B(3,6) and B(9,12) as shown in Table IV. The ^{31}P NMR spectrum of **1** shows a singlet at −19.3 ppm. Upon line narrowing, this signal becomes a broad multiplet, probably due to unresolvable coupling to boron. The decoupled proton NMR spectrum showed a 2:2:4:2 pattern similar to the ^{11}B NMR spectrum. The area 2 signal at 2.52 ppm is a triplet due to ^{31}P coupling to two equivalent phosphorus atoms. This resonance can be assigned to the hydrogens on B(3,6). Thus, the two highest field signals in the ^{1}H NMR spectrum of **1** show the expected parallel with the ^{11}B nuclear shieldings that have been observed in several previous studies.[14]

After removal of **1** from the silica gel chromatograph column with 50% toluene–hexane, a liquid phosphaborane of unknown structure was eluted with toluene. Further elution with chloroform gave a solid product (compound **2**), which was crystallized from chloroform–heptane. The exact mass determination of the parent ion peak in the mass spectrum verified the molecular formula of **2** as $C_6H_{23}B_9NP$ (i.e., $Et_3N{\cdot}B_9H_8P$).

The ^{11}B NMR spectrum of **2** exhibited nine resonances, all of area 1, indicating a total lack of symmetry in this molecule. The structure of **2** was determined by a single-crystal X-ray structure study. Table I is a summary of crystal data and intensity information for **2**, and Tables II and III give the interatomic distances, atomic coordinates, and isotropic thermal parameters for this molecule. A drawing of one enantiomer is shown in Figure 1. The results are complicated by the fact that two different molecules are present in the asymmetric unit, each of which exists

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Table III. Atomic Coordinates and Isotropic Thermal Parameters[a]

atom	*x*	*y*	*z*	B_{iso},[b] Å^2
B(1A)	2932 (5)	1046 (6)	9974 (4)	29
PB(2A)	2497 (2)	1607 (2)	9007 (1)	22
BP(3A)	3935 (2)	711 (3)	9424 (2)	30
B(4A)	4007 (5)	1772 (7)	10304 (4)	30
B(5A)	2847 (5)	2511 (6)	9964 (4)	27
B(6A)	3872 (4)	2069 (5)	8729 (3)	17
B(7A)	4777 (5)	2131 (6)	9605 (4)	26
B(8A)	4024 (5)	3212 (6)	9965 (4)	27
B(9A)	3110 (5)	3198 (6)	9115 (4)	25
B(10A)	4355 (5)	3295 (6)	9109 (4)	29
N(11A)	4022 (3)	1795 (4)	7902 (2)	21
C(12A)	3604 (4)	2757 (5)	7374 (3)	26
C(13A)	2491 (5)	2842 (6)	7211 (4)	39
C(14A)	3529 (4)	676 (5)	7615 (3)	25
C(15A)	3655 (4)	367 (5)	6824 (3)	33
C(16A)	5140 (4)	1765 (5)	7869 (3)	27
C(17A)	5715 (4)	753 (6)	8213 (4)	36
B(1B)	693 (6)	6434 (6)	6502 (4)	32
PB(2B)	55 (1)	6700 (1)	7337 (1)	19
BP(3B)	1610 (3)	6392 (5)	7322 (3)	34
B(4B)	1576 (5)	7434 (6)	6517 (4)	29
B(5B)	273 (5)	7824 (6)	6485 (4)	27
B(6B)	1258 (4)	7481 (5)	8025 (3)	18
B(7B)	2153 (5)	7902 (6)	7430 (3)	22
B(8B)	1235 (5)	8805 (6)	6873 (4)	28
B(9B)	281 (5)	8438 (6)	7424 (4)	24
B(10B)	1448 (5)	8852 (5)	7816 (4)	21
N(11B)	1436 (3)	7138 (4)	8883 (2)	19
C(12B)	1155 (4)	5901 (5)	8993 (3)	24
C(13B)	1314 (4)	5496 (5)	9793 (3)	30
C(14B)	861 (4)	7931 (5)	9322 (3)	23
C(15B)	−259 (4)	7777 (5)	9179 (3)	32
C(16B)	2540 (4)	7321 (5)	9217 (3)	22
C(17B)	3271 (4)	6481 (5)	8987 (3)	26

[a] Fractional coordinates are ×10^4. B_{iso} values are ×10. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

as an enantiomeric pair. The enantiomers cause the PB(2) and BP(3) positions to be disordered. Because of the complexities of this structure, all P–B bond distances should be considered as approximate values.

The B–B bond distances are normal for this type of closo cage. The B–N distance in **1** of 1.588 (7) Å is quite similar to the B–N single bond distances of $H_3B{\cdot}NH_3$[9] and $N_3H{\cdot}B_3H_7$,[15] which are 1.56 (4) and 1.58 Å, respectively.

We are continuing to study other compounds formed in the reaction of $B_{10}H_{14}$ with PCl_3 and base. The PCl_3 appears to act as a hydride acceptor, converting the anionic derivative $2\text{-}PB_9H_9^-$ to compound **2** in the presence of triethylamine. Other examples of this type of reaction will be reported later.

Thermal Isomerization of $1,2\text{-}P_2B_{10}H_{10}$. Heating of **1** in a sealed tube at 560–590 °C formed $1,7\text{-}P_2B_{10}H_{10}$ (compound **3**) in low yield. The molecular composition of **3** was confirmed by the high-resolution mass spectrum of the parent ion. The ^{11}B NMR spectrum of **3** contained the 2:2:4:2 pattern of resonances expected for this icosahedral molecule. The ^{11}B NMR data are presented in Table IV. The 2-D ^{11}B–^{11}B COSY spectrum of **3** suggested that the resonance at −3.3 ppm should be assigned to B(2,3) (see Figure 3 for numbering), since it shows a cross peak only with the area 4 resonance at −0.4 ppm, which is due to B(4,6,8,11). The 2-D COSY spectrum will not allow specific assignments for the remaining two resonances at 3.4 and 11.2 ppm. Upon line narrowing, the ^{11}B NMR resonance at 11.2 ppm split into a doublet ($J_{^{11}B-^{31}P}$ = 59 Hz), while the resonance at 3.4 ppm remained unchanged. This suggests that the 11.2 ppm resonance should be assigned to B(5,12), which has one nearest-neighbor phosphorus atom in the cage. In addition, line narrowing showed that the resonance at −3.3 ppm (assigned to B(2,3)) split into a 1:2:1 triplet ($J_{^{11}B-^{31}P}$ = 82 Hz) and the area 4 signal at −0.4 ppm exhibited unresolved multiplet character. The assignments of the resonances of **3** are similar to those determined previously for $1,7\text{-}B_{10}C_2H_{12}$.[13]

Table IV. Boron-11 NMR Data for Phosphaboranes **1–4**

compd	rel area	δ_B, ppm ($J_{^{11}B-^{1}H}$, Hz)	assgnt
$1,2\text{-}P_2B_{10}H_{10}$ (**1**)[a]	2	17.7 (151)	B(9,12)
	2	4.2 (155)	B(8,10)
	4	−0.3 (159)	B(4,5,7,11)
	2	−2.5 (172)	B(3,6)
$1,7\text{-}P_2B_{10}H_{10}$ (**3**)[a]	2	11.2 (155)	B(5,12)
	2	3.4 (154)	B(9,10)
	4	−0.4 (160)	B(4,6,8,11)
	2	−3.3 (166)	B(2,3)
$6\text{-}N(C_2H_5)_3{\cdot}2\text{-}PB_9H_8$ (**2**)[a]	1	7.0 (158)	B(3)
	1	1.4 (173)	B(9) or B(7)
	1	−2.8	B(6)
	1	−10.6 (146)	B(8)
	1	−18.8 (154)	B(1)
	1	−22.9 (154)	B(5) or B(4)
	1	−27.7 (158)	B(7) or B(9)
	1	−29.7 (155)	B(10)
	1	−31.9 (150)	B(4) or B(5)
$N(CH_3)_4[7\text{-}B_{10}H_{12}P]$ (**4**)[b]	1	7.0 (135)	B(5)
	2	−7.4 (150)	B(2,3)
	2	−9.5 (140)	B(8,11)
	2	−15.6 (130)	B(9,10)
	1	−21.5 (187)	B(1)
	2	−23.2 (150)	B(4,6)

[a] $CDCl_3$ solvent. [b] Acetone-d_6 solvent.

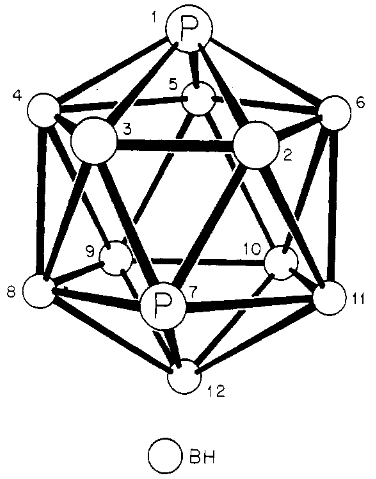

Figure 3. Numbering system for $1,7\text{-}P_2B_{10}H_{10}$.

This is the first completely characterized heteroborane of the type $1,7\text{-}M_2B_{10}H_{10}$ (where M = P, As, Sb, Bi). Attempts to isomerize $1,2\text{-}As_2B_{10}H_{10}$ at 585 °C in a sealed tube formed a very low yield of volatile products.[6,10] Boron-11 NMR analysis of the products suggested the presence of 1,2-, 1,7-, and $1,12\text{-}As_2B_{10}H_{10}$ in the mixture. Complete characterization of the 1,7- and 1,12-isomers of $As_2B_{10}H_{10}$ must await a better synthetic route for their production.

Further Chemistry of Phosphaboranes. Aqueous base reacted with **1** rapidly at room temperature to give a clear aqueous solution. Addition of a saturated solution of tetramethylammonium chloride precipitated $(CH_3)_4N[7\text{-}B_{10}H_{12}P]$ (compound **4**). Repeated crystallization of the precipitate from acetone–methanol gave analytically pure **4** in moderate yield. We suggest that **4** has the nido 11-atom icosahedral fragment structure resulting from abstraction of one phosphorus atom from $1,2\text{-}P_2B_{10}H_{10}$ (see Figure 2). The 1:2:2:2:1:2 pattern of the ^{11}B NMR spectrum of **4** is consistent with this suggested structure (see Table IV). Treatment of **4** with methyl iodide formed $7\text{-}CH_3\text{-}7\text{-}PB_{10}H_{12}$. This neutral

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phosphaborane was prepared previously by reaction of $B_{10}H_{14}$ and CH_3PCl_2 in the presence of a base.[3] The ^{11}B NMR and IR spectra of the methylation product were identical with those of the previously prepared compound.

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Supplementary Material Available: Tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and intramolecular angles (15 pages). Ordering information is given on any current masthead page.

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Steric Effects in Polypyrazolylborate Ligands. Poly(3-isopropylpyrazolyl)borates: Ligands of Intermediate Steric Requirements

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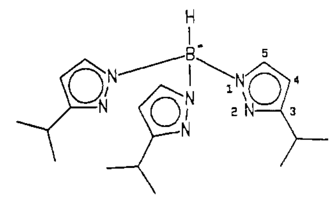
The synthesis, structures, and coordination chemistry of a series of polypyrazolylborate ligands, $[H_nB(3\text{-isopropylpyrazol-1-yl})_{4-n}]^-$ and $[HB(3\text{-isopropyl-4-bromopyrazol-1-yl})_3]^-$, are presented. These ligands are made by the reaction of tetrahydroborate ion with the appropriate pyrazole. A series of metal complexes was prepared and characterized by analytical and spectroscopic data. In addition, four complexes were characterized by means of X-ray diffraction techniques. The complex $Co(HB(3\text{-isopropyl-4-bromopyrazol-1-yl})_3)(NCS)$ crystallizes in the tetragonal space group $P\bar{4}2_1m$ with four molecules per unit cell of dimensions a = 17.450 (3) Å and c = 9.025 (1) Å at −70 °C. Least-squares refinement of 160 variables led to a value of the conventional R index (on F) of 0.042 and of R_w of 0.033 for 879 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to three pyrazolyl nitrogen atoms and the nitrogen atom of the thiocyanate group, is tetrahedral. The isopropyl group and the bromine atom are in the 3- and 4-positions of the pyrazolyl ring, respectively. The complex $Co(B(3\text{-isopropylpyrazol-1-yl})_4)_2$ crystallizes in the monoclinic space group $C2/c$ with four molecules in a unit cell of dimensions a = 15.276 (3) Å, b = 19.856 (5) Å, c = 19.274 (3) Å, and β = 109.37 (1)° at −70 °C. Least-squares refinement of 309 variables led to a value of the conventional R index of 0.057 and of R_w of 0.050 for 2800 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to four pyrazolyl nitrogen atoms from two ligands, is tetrahedral. The isopropyl group is in the 3-position of each pyrazolyl ring. The complex $Co(HB(3\text{-isopropylpyrazol-1-yl})_2(5\text{-isopropylpyrazol-1-yl}))_2$ crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell of dimensions a = 9.076 (2) Å, b = 10.784 (2) Å, c = 11.079 (1) Å, α = 108.66 (1)°, β = 93.35 (1)°, and γ = 100.12 (1)° at −70 °C. Least-squares refinement of 232 parameters led to a value of the conventional R index of 0.037 and of R_w of 0.045 for 3581 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to six pyrazolyl nitrogen atoms from two ligands, is octahedral. The isopropyl group is in the 3-position for two rings, whereas for the third, this group is in the 5-position. The complex $Co(HB(3\text{-isopropyl-4-bromopyrazol-1-yl})_2(5\text{-isopropyl-4-bromopyrazol-1-yl}))_2$ crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell of dimensions a = 10.164 (1) Å, b = 10.236 (2) Å, c = 12.938 (2) Å, α = 111.08 (1)°, β = 99.26 (1)°, and γ = 106.28 (1)° at −70 °C. Least-squares refinement of 259 variables led to a value of the conventional R index of 0.037 and of R_w of 0.032 for 2950 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion and ring substitution patterns are the same as those for the octahedral complex described above, with the addition of a bromine atom in the 4-position of each ring. These last two structural studies reveal a unique feature of these new ligands: rearrangement of the mode of coordination by a pyrazolyl group in octahedral complexes to relieve steric crowding. The results presented here indicated that these ligands have properties that are unique and transitional from those of the previously reported, relatively unhindered ligands such as $[H_nB(\text{pyrazolyl-1-yl})_{4-n}]^-$ to the sterically bulky ligands $[H_nB(3\text{-R-pyrazol-1-yl})_{4-n}]^-$, where R = *tert*-butyl and phenyl groups.

Introduction

In this contribution, we present the synthesis and coordination chemistry of a new generation of polypyrazolylborate ligands that have properties lying between those of the parent $[H_{4-n}B(pz)_n]^-$ ligands[1] (pz = pyrazolyl) and those of the more recently reported derivatives $[H_{4-n}B(3\text{-Rpz})_n]^-$, where R = *tert*-butyl and phenyl groups.[2,3] The parent ligands, in particular the derivatives with $n = 3$, have been extensively used in inorganic and bioinorganic chemistry. However, the chemistry is severely limited because of the tendency of the first-row transition-metal ions to form the bisligand complex (i.e., $M(HB(pz)_3)_2$). On the other hand, the bulky groups of the 3-R derivatives[2,3] prevent formation of this type of complex. The 3-*tert*-butyl ligand allows no further access to the metal ion and is a "tetrahedral enforcer", whereas the 3-phenyl derivative accommodates five-coordination with a trigonal-bipyramidal geometry. Although bisligand complex formation is prevented, the metal ion is not readily accessible to other molecules because of the steric bulk of the 3-substituents. The new ligands reported here, with a 3-isopropyl group (**1**), show characteristics of both of these ligands: limited formation of the $M(HB(3\text{-Rpz})_3)_2$ complexes and accessibility of the metal ion. In addition the synthesis and coordination chemistry of another new derivative, $[HB(3\text{-}i\text{-Pr-4-Br-pz})_3]^-$, with a bromine atom in the 4-position of the pyrazolyl ring, are presented. The importance of electronic effects in the coordination chemistry of this growing family of ligands is demonstrated for the first time.



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Experimental Section

General Methods. All chemicals were reagent grade and were used as received. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. ^1H NMR spectra were obtained with a Nicolet NT360WB spectrometer. Diamagnetic compounds were studied with typical conditions of 16K data points, a spectral width of 3000–4000 Hz, 90° pulse angles, and a recycle time of 4–5 s. Paramagnetic compounds were studied with 64K data points, a

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