

Borane and Monoiodoborane Derivatives of some Bis(diphenylphosphino)alkanes[†]

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Abstract

A series of borane and monoiodoborane derivatives of bis(diphenylphosphino)alkanes, $(C_6H_5)_2P-(CH_2)_n-P(C_6H_5)_2$ in which n has values of 2 through 4 has been synthesized. Only compounds with the formulae $[(C_6H_5)_2P]_2(CH_2)_n \cdot (BH_3)_2$ and $[(C_6H_5)_2P]_2(CH_2)_n \cdot BH_2I$ were isolable, the latter being boronium iodides. The compounds were characterized by their melting points, elemental analyses, molar conductivities, infrared spectroscopy, and 1H and ^{11}B nuclear magnetic resonance spectroscopy. The relationship between the length of the carbon chain and the ^{11}B NMR chemical shift is discussed.

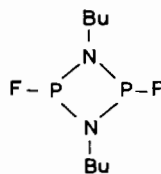
Introduction

In recent years, research in this laboratory has been concerned with studies to elucidate factors affecting a Lewis base–boron bond. Several studies have been completed in which the electron environment around the base atom and the boron atom has been changed by replacement of hydrogen atoms with alkyl, amino, halo and pseudohalo entities. For example, substitution of a bromine atom in borane gives BH_2Br which forms boronium salts as well as adducts with 3- and 4-methylpyridines, quinoline and isoquinoline [1]. Dimethylbromoborane, $B(CH_3)_2Br$, was found to form boronium compounds with pyridine and 4-methylpyridine [2]. Many other examples of boronium compounds have been reported [3].

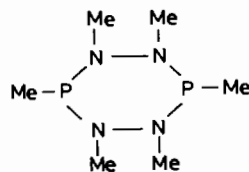
More emphasis has been placed in studying the modifications made in the Lewis base. It was of interest to compare the tendency of the two types of nitrogen atoms in aminopyridines to form adducts with BH_3 . It was found that the pyridyl nitrogen in

2-, 3- and 4-aminopyridines is the donor to borane rather than the amino nitrogen [4]. Also of interest were the donor capabilities of the two nitrogen atoms in pyridazine, pyrimidine and pyrazine and some of its methyl derivatives with respect to BH_3 . Diazinebis(borane) compounds were obtained for all of the diazines and their methyl derivatives except pyrimidine which formed a 1:1 adduct [5]. Pyrazine and some of its methyl derivatives also formed bis(haloborane) adducts. Bis(trifluoro-) and bis(tribromoborane) adducts were formed with pyrazine, 2-methyl-, 2,3-dimethyl-, and 2,6-dimethylpyrazine. A 1:1 adduct could be isolated only with 2,6-dimethylpyrazine and the haloboranes [6].

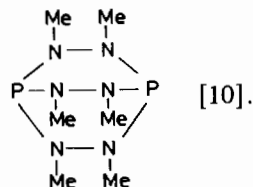
Inasmuch as phosphines are stronger bases than amines toward BH_3 [7] it was of interest to study the behavior of Lewis bases containing two phosphorus atoms. It has been reported that



will add one or two mol of BH_3 depending on the stoichiometry [8]. Similarly,



will add two mol of BH_3 [9] as will

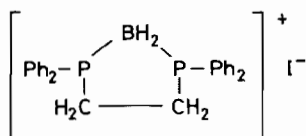


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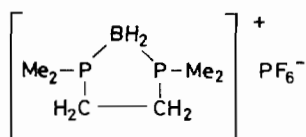
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A number of borane and haloborane adducts of diphosphine ligands (diphos) have been reported. Borane adds to $\text{Me}_2\text{P}-\text{CH}_2-\text{PMe}_2$ to give the bis(borane) adduct, $\text{Me}_2\text{P}-\text{CH}_2-\text{PMe}_2$ [11]. Similarly,

bis(borane) adducts of $\text{Ph}_2\text{P}-\text{CH}_2-\text{PPh}_2$ and $\text{Ph}_2\text{P}-\text{CH}_2-\text{CH}_2-\text{PPh}_2$ have been prepared [12]. It has been found that



results from the reaction of $\text{Ph}_2\text{P}-\text{CH}_2-\text{CH}_2-\text{PPh}_2$ with BH_3I [13]. The analogous cation has been reported [14] as a hexafluorophosphate salt



$\text{Ph}_2\text{P}-\text{CH}_2-\text{PPh}_2$ and $\text{Ph}_2\text{P}-(\text{CH}_2)_2-\text{PPh}_2$ form bis-adducts with BCl_3 and BBr_3 [15]. The latter diphos forms bis-adducts with BI_3 [15] and with CH_3BBr_2 and $(\text{CH}_3)_2\text{BBr}$ [16].

BH_3 has been reported to form mono- and bis-adducts with $\text{F}_2\text{P}-(\text{CH}_2)_2-\text{PF}_2$ [17]. The formation of bis-adducts is attributed to localization of charge around each phosphorus atom [18].

In this study, the products of the reactions of borane and monoiodoborane with diphos compounds, having compositions corresponding to $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_n\text{P}(\text{C}_6\text{H}_5)_2$ in which n has values of 2–4, are characterized.

Experimental

All reactions and transfers were performed under an atmosphere of dry nitrogen or in a glass vacuum system. Melting points were measured on samples sealed under nitrogen in capillary tubes.

The proton NMR spectra were recorded on a Varian T-60 or Nicolet NT-200 wide bore spectrometer using tetramethylsilane (TMS) as an internal standard and CDCl_3 or C_6D_6 as a solvent. The ^{11}B NMR spectra were obtained on a Nicolet NT-200 wide bore spectrometer at 64.2 MHz using $(\text{CH}_3\text{O})_3\text{B}$ as an external reference.

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer. The samples were prepared as a Nujol mull and placed between NaCl plates or, as a KBr pellet in a dry nitrogen atmosphere in a glove

box and the spectra taken immediately. A YSI Model 31 conductivity bridge was used to determine conductance. Values reported are for 1.0 mM solutions of phosphine-borane in acetonitrile at 25 °C.

Elemental analyses were determined by Schwartzkopf Microanalytical Laboratories, Inc., Woodside, New York; Galbraith Laboratories, Inc., Knoxville, Tennessee; or in this laboratory using an F and M Model 185 carbon, hydrogen and nitrogen analyzer.

All of the phosphine bases were obtained from Strem Chemicals, Inc., Newburyport, Massachusetts, and were used as received without further purification except for bis(diphenylphosphino)ethane, which was recrystallized from ethanol upon receipt from Arapahoe Chemicals, Inc., Princeton, New Jersey. Sodium borohydride (Fisher Scientific Company, Pittsburgh, Pennsylvania) and $(\text{CH}_3)_2\text{S}\cdot\text{BH}_3$, 10.0 M in BH_3 (Aldrich Chemical Company, Milwaukee, Wisconsin), were used as received. Benzene and ethylene glycol dimethylether (glyme) (Aldrich Chemical Company) were distilled from sodium metal and benzophenone. Hexane was stored over Drierite. Acetonitrile was distilled from P_4O_{10} . All solvents were stored under dry nitrogen.

Preparation of Borane and Monoiodoborane Adducts

The Lewis base adducts with borane and monoiodoborane were prepared using procedures similar to those described previously [1, 4]. All reactions were conducted several times with stoichiometries varying from excess borane to excess base. The reaction product isolated was found not to depend upon the molar stoichiometry.

1,2-Bis(diphenylphosphino)ethane Bis(borane)

In a typical preparation, a solution of 0.63 g (2.5 mmol) of I_2 in 40 ml of glyme was added dropwise with stirring to a solution of 0.38 g (10 mmol) of NaBH_4 and 2.0 g (5 mmol) of bis(diphenylphosphino)ethane in 40 ml of glyme. A white precipitate of sodium iodide formed immediately. Stirring was continued for one hour after which the solvent was removed under vacuum. The resulting solid was suspended in *ca.* 80 ml of benzene and then filtered to remove the NaI. The filtrate was reduced to about 20 ml under vacuum and 200 ml of dry hexane added. The resulting precipitate was collected on a filter and dried overnight under a vacuum.

A 68.2% yield of a white solid (m.p. 156–158° dec (uncorrected); 162–167.5 °C dec [12]) was obtained. The compound was characterized by elemental analyses and proton and B-11 NMR data and agreed with those data previously reported [12]. The IR spectrum follows: 2420(w), 2395(m), 2340(w), 1435(w), 1416(m), 1178(m), 1160(w), 1105(m), 1055(s), 1025(m), 995(m), 730(s), 690(s), 670(s), 595 cm^{-1} .

1,3-Bis(diphenylphosphino)propane Bis(borane)

A 50.4% yield of greenish-white crystals (m.p. 146–149° dec) of 1,3-bis(diphenylphosphino)propane bis(borane) was obtained using a procedure similar to that used to prepare 1,2-bis(diphenylphosphino)ethane bis(borane). *Anal.*, $[H_3BP(C_6H_5)_2]_2(CH_2)_3$; Calc.: C, 73.68; H, 7.33; P, 14.08%. Found: C, 73.43; H, 7.24; P, 13.92%. IR Spectrum: 2400(w), 2380(m), 2330(w), 1435(s), 1405(w), 1305(m), 1130(m), 1110(m), 1055(m, doub.), 1022(w), 995(w, doub.), 960(m), 812(w), 760(m), 732(s), 695(m), 685(m), 620(m), 608(m), 590(m) cm^{-1} (doub: doublet).

1,4-Bis(diphenylphosphino)butane Bis(borane)

A solution of 0.55 g (2.2 mmol) of I_2 in 40 ml glyme was added to a solution of 1.0 g (2.3 mmol) 1,4-bis(diphenylphosphino)butane and 0.80 g (21.1 mmol) of $NaBH_4$ in about 40 ml glyme, following a procedure similar to that used for the synthesis of 1,2-bis(diphenylphosphino)ethane bis(borane). A 52.5% yield of greenish-white crystals (m.p. 186.5–189° dec) was obtained. *Anal.*, $[H_3BP(C_6H_5)_2]_2(CH_2)_4$; Calc.: C, 74.05; H, 7.55; P, 14.64%. Found: C, 73.83; H, 7.83; P, 13.52%. IR Spectrum: 2400(s), 2378(s), 2350(s), 2280(w), 2260(w), 1432(s), 1410(w), 1335(w), 1308(w), 1180(m), 1160(m), 1142(m), 1132(w), 1105(s), 1058(s), 1025(w), 995(w), 850(w, doub.), 778(w), 748(w), 732(s), 708(w), 690(s, doub.), 613(s), 595(s) cm^{-1} .

1,2-Bis(diphenylphosphino)ethaneboronium Iodide

In a typical preparation, a solution of 1.0 ml (10 mmol) of $(CH_3)_2S \cdot BH_3$ and 1.27 g (5 mmol) I_2 in 30 ml benzene was stirred overnight at room temperature. To this was added 1.99 g (10 mmol) of 1,2-bis(diphenylphosphino)ethane in 30 ml benzene. A precipitate formed immediately. After stirring overnight, the solid was collected on a filter, washed with benzene, and dried under vacuum to yield 2.69 g (84.4% yield) of a light yellow solid (m.p. 228–231° dec.). *Anal.*, $\{[(C_6H_5)_2P]_2(CH_2)_2BH_2\}^+I^-$; Calc.: C, 58.03; H, 4.87; P, 11.51%. Found: C, 57.90; H, 5.00; P, 11.67%. IR Spectrum: 2475(m), 2430(m), 1435(s), 1411(m), 1315(w), 1108(s), 995(m), 825(m), 758(m), 720(s), 710(s), 690(sh), 685(s), 615(s), 608(m) cm^{-1} .

1,3-Bis(diphenylphosphino)propaneboronium Iodide

To a solution of 1 ml (10 mmol) of $(CH_3)_2S \cdot BH_3$ and 1.27 g (5 mmol) of I_2 in 30 ml benzene was added 2.06 g (5 mmol) of 1,3-bis(diphenylphosphino)propane in 30 ml benzene. After stirring overnight, the solvent was removed under vacuum. The resulting yellow solid was suspended in benzene, collected on a filter, and washed with benzene to yield

2.22 g (80.4% yield) of 1,3-bis(diphenylphosphino)propaneboronium iodide (m.p. 216–218° dec.). *Anal.*, $\{[(C_6H_5)_2P]_2(CH_2)_3BH_2\}^+I^-$; Calc.: C, 58.73; H, 5.11; B, 1.92%. Found: C, 52.01; H, 5.19; B, 0.81%. IR Spectrum: 2470(m), 2410(m), 1585(w), 1432(s), 1345(w), 1318(w), 1190(m), 1155(w, doub.), 1108(s), 1025(w), 998(w), 970(s), 932(s), 840(w), 790(m), 752(m), 745(s), 718(s), 690(s), 640(w), 635(sh), 595(m) cm^{-1} .

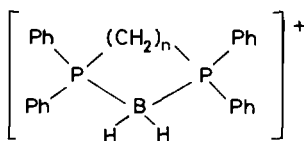
1,4-Bis(diphenylphosphino)butaneboronium Iodide

A procedure similar to that used to prepare 1,3-bis(diphenylphosphino)propaneboronium iodide was used to synthesize 1,4-bis(diphenylphosphino)butaneboronium iodide. The off-white solid (m.p. 172–175° dec) was collected in 73.8% yield (2.09 g). *Anal.*, $\{[(C_6H_5)_2P]_2(CH_2)_4BH_2\}^+I^-$; Calc.: C, 59.40; H, 5.34%. Found: C, 60.63; H, 5.77%. IR Spectrum: 2485(m), 2465(w), 2430(m), 1583(m), 1490(m), 1447(s), 1190(w), 1180(w), 1108(s), 995(w), 950(s), 855(w), 835(m), 755(s), 743(s), 720(s), 690(s), 615(w, doub.) cm^{-1} .

Results and Discussion

The reaction of borane with $\{[(C_6H_5)_2P]_2(CH_2)_n\}$ ($n = 2-4$), produces the bis(borane) adduct. When varying stoichiometries from excess base to excess borane, only the bis adduct could be isolated. The infrared spectra for the borane adducts show three characteristic bands due to B–H symmetric and asymmetric stretching at 2330–2420 cm^{-1} . In addition, a band at 590–595 cm^{-1} resulting from B–P stretching is also observed.

The reaction of monoiodoborane with $\{[(C_6H_5)_2P]_2(CH_2)_n\}$ ($n = 2-4$) produces the boronium iodide salt. For $n = 2-4$, the boronium cation can easily form the cyclic structure



in which a 5, 6, or 7 membered ring forms. The infrared spectra of the monoiodoborane adducts show two bands at 2415–2430 cm^{-1} and 2470–2495 cm^{-1} , which are characteristic for a BH_2 group, corresponding to the symmetric and asymmetric H–B–H stretching [19]. In addition, the relative complexity of the spectra between 2000–2500 cm^{-1} is characteristic of the presence of an ionic rather than neutral species.

The formation of the boronium iodide upon reaction of the phosphine with monoiodoborane is further confirmed by the molar conductivity in an

acetonitrile solution (Table I). The diphenylphosphinobis(borane) derivatives have small molar conductivities, whereas the adducts with monoiodoborane have molar conductivities of 0.0130–0.0140 $\Omega^{-1} \text{ mol}^{-1} \text{ m}^2$. These values are in good agreement with the previously reported 0.0144 $\Omega^{-1} \text{ mol}^{-1} \text{ m}^2$ for $[\text{H}_2\text{B}\cdot\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]^+\text{PF}_6^-$ [13] and are indicative of the presence of two ions in solution.

The ^1H -NMR spectra of the phosphine boronium iodide salts show aliphatic proton resonances shifted downfield from the resonances for the corresponding borane adducts (Table II). The effect of constraining the phosphine–borane adduct into a ring deshields the protons, with the largest chemical shift difference occurring in the five-membered ring formed when $n = 2$. The chemical shifts of the aromatic protons show little to no difference between the borane and boronium iodide complexes because the phenyl rings do not participate in the bonding or become constrained upon ring formation.

The ^{11}B -NMR spectral data, Table III, show similar chemical shifts for the phosphine–borane adducts. This result demonstrates that there is little change in the B–P bonding upon increasing the number of carbon atoms between the phosphorus atoms. For the boronium iodide salts, the ^{11}B resonances are all downfield from those for the corresponding

TABLE I. Molar Conductivity of 1 mM Acetonitrile Solutions of Borane and Monoiodoborane–phosphine Adducts.

Formula	Λ ($\Omega^{-1} \text{ mol}^{-1} \text{ m}^2$)
$[\text{H}_3\text{B}\cdot\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{CH}_2)_2$	– (dec.)
$[\text{H}_3\text{B}\cdot\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{CH}_2)_3$	0.0004
$[\text{H}_3\text{B}\cdot\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{CH}_2)_4$	0.0008
$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{CH}_2)_2\text{BH}_2\}^+ \text{I}^-$	0.0130
$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{CH}_2)_3\text{BH}_2\}^+ \text{I}^-$	0.0137
$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{CH}_2)_4\text{BH}_2\}^+ \text{I}^-$	0.0140

TABLE II. Proton NMR Chemical Shift Data.

Formula	^1H NMR Chemical Shift ppm (mult) ^a
$[(\text{C}_6\text{H}_5)_2\text{P}\cdot\text{BH}_3]_2(\text{CH}_2)_2$	2.38(d, J = 1 Hz) 7.46(m), 7.66(m)
$[(\text{C}_6\text{H}_5)_2\text{P}\cdot\text{BH}_3]_2(\text{CH}_2)_3$	1.81(m), 2.60(m) 7.41(m), 7.61(m)
$[(\text{C}_6\text{H}_5)_2\text{P}\cdot\text{BH}_3]_2(\text{CH}_2)_4$	1.60(m), 2.19(m) 7.39(m), 7.61(m)
$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{CH}_2)_2\text{BH}_2\}^+ \text{I}^-$	3.37(d, J = 9 Hz) 7.57(m), 7.77(m)
$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{CH}_2)_3\text{BH}_2\}^+ \text{I}^-$	1.65(m), 2.95(br, m) 7.45(m), 7.7(br, m)
$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{CH}_2)_4\text{BH}_2\}^+ \text{I}^-$	1.68(br, m), 2.43(br, m) 7.43(m), 7.78(m)

^a Reference: TMS in CDCl_3 or C_6D_6 ; mult = multiplicity, d = doublet, m = multiplet, br = broad.

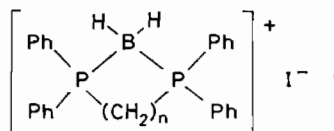
TABLE III. ^{11}B NMR Chemical Shift Data.

Formula	B-11 NMR Chemical Shift (ppm) ^a
$[(\text{C}_6\text{H}_5)_2\text{P}\cdot\text{BH}_3]_2(\text{CH}_2)_2$	–58.63
$[(\text{C}_6\text{H}_5)_2\text{P}\cdot\text{BH}_3]_2(\text{CH}_2)_3$	–58.11
$[(\text{C}_6\text{H}_5)_2\text{P}\cdot\text{BH}_3]_2(\text{CH}_2)_4$	–58.46
$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{CH}_2)_2\text{BH}_2\}^+ \text{I}^-$	–52.60
$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{CH}_2)_3\text{BH}_2\}^+ \text{I}^-$	–54.63
$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{CH}_2)_4\text{BH}_2\}^+ \text{I}^-$	–55 \pm 0.7 ^b

^a Reference: $\text{B}(\text{OCH}_3)_3$. ^b Signal with low signal/noise ratio and broad width.

borane adducts due to the lesser electron density on the four-coordinate boronium cation. In this case, however, changing the number of methylene groups between the phosphorus atoms does alter the chemical shift. This is probably the result of changes in the ring strain and in the P–B–P orbital overlap as the ring size increases from five to seven members.

In conclusion, increasing the length of the carbon chain does not alter appreciably the B–P bond for borane adducts of bis(diphenylphosphino)alkanes. The length of the chain becomes important when monoiodoborane reacts with the bis(diphenylphosphino)alkanes because it determines the size of the ring in the resulting cyclic boronium cations



Acknowledgement

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