

than any previous synthesis. Over a 200 °C temperature range, no evidence for fluctuation on the NMR time scale is observed. Tetraboron tetrachloride, a compound that contains only eight (2n) framework electrons and a compound which in the construct of the graph-theoretical approach is held together by bonds that are neither localized nor delocalized in nature,³ is surprisingly more thermally stable than two *closo*-carboranes of similar size.

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Reactions of Diborane with Some Chelating Bidentate Ligands. A One-Step Synthesis of [(LL)BH₂]₂B₂H₇ Salts

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The reactions of diborane with the chelating ligands 2,2'-bipyridyl (bpy), *N,N,N',N'*-tetramethyl-*o*-phenylenediamine (TMPD), and 1,8-bis(dimethylamino)naphthalene (BDN) have been investigated. bpy reacts with excess diborane to give the ether-insoluble air-stable bis(borane) adduct bpy·2BH₃. TMPD reacts with an equimolar quantity of diborane to form the ether-insoluble air-stable ionic product [(TMPD)BH₂]₂BH₄. Acid hydrolysis of this material gives a solution of the (TMPD)BH₂⁺ cation which has been isolated and characterized as the PF₆⁻ salt. TMPD reacts with excess diborane to yield the air-sensitive ether-insoluble [(TMPD)BH₂]₂B₂H₇. Mild solvolysis with 2-propanol or treatment with (CH₃)₃N converts this to the BH₄⁻ salt. BDN reacts remarkably slowly with excess diborane in diethyl ether to form [(BDN)BH₂]₂B₂H₇. The (BDN)BH₂⁺ cation has been isolated and characterized as the PF₆⁻ salt.

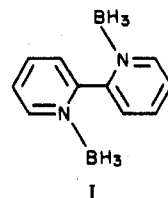
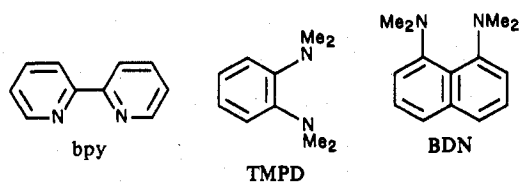
Introduction

While the chemical literature contains many reports on the reactions of monodentate Lewis bases with diborane to give both covalent (symmetrical cleavage) and ionic (unsymmetrical cleavage) products,¹ with a few exceptions^{2,3} studies with polydentate chelating ligands have been neglected in spite of their possible potential for geometrical control of the type of cleavage. This paper is an account of the reactions of diborane with the well-known bidentate donors 2,2'-bipyridyl (bpy), *N,N,N',N'*-tetramethyl-*o*-phenylenediamine (TMPD), and 1,8-bis(dimethylamino)naphthalene (BDN). Normal do-

nor-acceptor reactions occur with these bases, but with others, notably some heteroaromatics like 1,10-phenanthroline, 1,8-naphthyridine, and 8-hydroxyquinoline, hydroboration has been found to occur. The latter results will be detailed elsewhere.

Results and Discussion

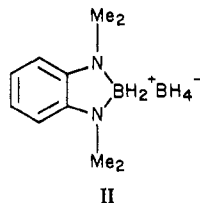
Bipyridine-Diborane. bpy forms an ether-insoluble air-stable product with excess diborane having the composition bpy·B₂H₆. The boron-11 NMR spectrum (acetonitrile) shows a single quartet ($\delta = -13.0$, $J = 95$ Hz), and the IR spectrum contains no bands characteristic of borohydride ion, so the product is the bis(borane) adduct I. The boron-11 NMR parameters



of I are strikingly close to those of pyridine-borane ($\delta = -13.0$, $J = 90$ Hz).⁴

It is interesting that bpy reacts with BF_3 or BCl_3 in toluene to form the ionic product $[(\text{bpy})\text{BX}_2]\text{BX}_4$ under comparable conditions.⁵ Perhaps since bpy exists in solution primarily in a trans conformation,⁶ it may attack diborane like a monodentate ligand and form $\text{bpy}\cdot\text{BH}_3$ as a first step. The bis(borane) complex I may then form preferentially because of the difficulty of nucleophilic displacement of hydride ion from boron.

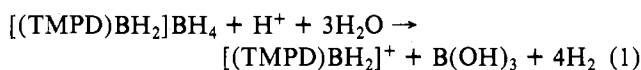
***N,N,N',N'*-Tetramethyl-*o*-phenylenediamine-Diborane.** Equimolar quantities of diborane and TMPD react rapidly in ether solution to precipitate $[(\text{TMPD})\text{BH}_2]\text{BH}_4$ (II). Evi-



dently, the nearly fixed geometry of the TMPD ligand is ideal for the formation of the ionic unsymmetrical cleavage product.

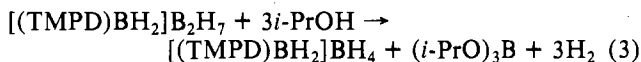
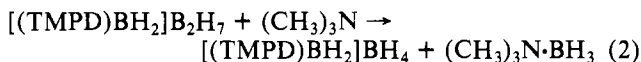
The salt is a colorless air-stable crystalline solid which is insoluble in ethers and acetone but dissolves readily in chloroform, methylene chloride, and hot 2-propanol. It dissolves and slowly solvolyzes in water, methanol, and ethanol. The infrared spectrum contains the BH bands characteristic of ionic borohydride in addition to those of the cation (see below); the proton NMR is fully consistent with this structure.

Typical of bis(amine)boronium salts, the cation is inert to attack by aqueous acid,⁷ so that hydrolysis of II produces only 4 of the possible 6 mol of hydrogen according to reaction 1.

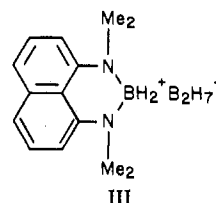


The cation may be precipitated as the hexafluorophosphate and recrystallized from water. The infrared spectrum contains the slightly unsymmetrical BH stretching doublet in the 2450–2500- cm^{-1} region observed for other L_2BH_2^+ salts.⁷

Treatment of an ether solution of TMPD with excess diborane results in the precipitation of a colorless air- and moisture-sensitive solid of composition $\text{TMPD}\cdot\text{B}_3\text{H}_9$ which is the heptahydrodiborate salt $[(\text{TMPD})\text{BH}_2]\text{B}_2\text{H}_7$. The cation is, evidently, large enough to stabilize B_2H_7^- in the solid state,⁸ so this reaction represents a simple one-step synthesis of both $(\text{TMPD})\text{BH}_2^+$ and B_2H_7^- . The infrared bands in the 2000–2500- cm^{-1} region correspond closely to those reported for $[(\text{C}_4\text{H}_9)_4\text{N}]\text{B}_2\text{H}_7$ and $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]\text{B}_2\text{H}_7$ by Shore and co-workers.⁹ The salt is soluble in chloroform and methylene chloride but not in diethyl ether, monoglyme, tetrahydrofuran, or benzene. The salt may be converted to the borohydride II by reaction with excess trimethylamine or by solvolysis in 2-propanol according to reactions 2 and 3, respectively.



1,8-Bis(dimethylamino)naphthalene-Diborane. Although there are very few reported reactions of this hindered base with acceptors other than the proton, examination of space filling models shows there is significant room in its bidentate "bite" to accommodate a small double acceptor group like BH_2^+ . Accordingly, excess diborane reacts *slowly* with a diethyl ether solution of BDN to precipitate $[(\text{BDN})\text{BH}_2]\text{B}_2\text{H}_7$ (III). The infrared spectrum of III shows BH absorptions characteristic of B_2H_7^- and the cation (see below). The boron-11 NMR spectrum (monoglyme) shows a broad unresolved signal at



approximately 0 ppm (intensity 1) assigned to the cation and a quartet ($\delta = -25.8$, $J = 105$ Hz, intensity 2) typical of B_2H_7^- .¹⁰ The cation is not susceptible to acid hydrolysis and may be precipitated from aqueous solution as the air-stable hexafluorophosphate salt.

A peculiar feature of the BDN-diborane reaction is its slowness for a donor-acceptor process involving diborane. Depending on the diborane pressure, times of from 1 to 14 days are required for complete precipitation at room temperature. When the reaction in diethyl ether is monitored by boron-11 NMR at ambient or low temperature, only a signal with chemical shift and line shape characteristic of diborane *alone* in this solvent¹⁰ can be detected. On the basis of this information the slowness of the reaction can only be ascribed to the unusual hindered conformation of the BDN molecule.¹¹ Conceivably, this base could be employed in synthesis as a moderately strong proton acceptor in the presence of diborane, if overall reaction times were kept short.

Experimental Section

General Procedure. Standard vacuum-line and inert-atmosphere techniques were used in this work.¹² The bases 2,2'-bipyridyl (Aldrich) and *N,N,N',N'*-tetramethyl-*o*-phenylenediamine (Eastman) were used as received. The 1,8-bis(dimethylamino)naphthalene (Aldrich) was purified by vacuum sublimation and stored in a desiccator. Diborane was prepared by the reaction of sodium borohydride with warm polyphosphoric acid. Trimethylamine (Matheson Gas Co.) was passed through a -78°C trap before use. Potassium hexafluorophosphate was purchased from Alfa Inorganics. Diethyl ether and monoglyme (1,2-dimethoxyethane) were stored over LiAlH_4 and vacuum transferred into reaction vessels when needed. Other solvents were reagent grade and were used as received.

Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer; Nujol absorption bands are omitted from the spectral data. Boron-11 NMR spectra were obtained at 32.1 MHz by using a Varian HA-100 spectrometer with standard accessories. Chemical shifts are relative to $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$ (0.0 ppm) and downfield shifts are positive. Proton NMR spectra were obtained by using a Varian T-60 spectrometer. Analyses for C, H, and N were performed by Huffman Laboratories, Inc. Hydrolytic hydrogen was collected and measured with a Toepler pump-calibrated gas buret assembly.

Synthesis of $\text{bpy}\cdot 2\text{BH}_3$. A 1.62-mmol sample of diborane was condensed into a vessel containing a solution of 0.098 g (0.63 mmol) of bpy in 5 mL of monoglyme. On warming of the solution to room temperature, a colorless precipitate formed as soon as the solvent melted and no further change was observed. After 1 day, volatile materials were evaporated and separated (-95°C slush) on the vacuum line; 1.00 mmol of diborane was recovered, indicating the consumption of 0.62 mmol (B_2H_6 :bpy ratio 0.98). The colorless solid residue was soluble in dimethyl sulfoxide and dimethylformamide, slightly soluble in acetone and acetonitrile, and insoluble in other common solvents. The solid had no sharp melting point and began to darken at ca. 124°C .

Infrared spectrum (Nujol) of $\text{bpy}\cdot 2\text{BH}_3$, in cm^{-1} (relative intensity): 2375 (s), 2350 (s, sh), 2270 (m, sh), 1605 (w), 1595 (m), 1555 (w), 1430 (m), 1420 (m), 1300 (w), 1255 (vw), 1190 (s), 1170 (m), 1145 (vw), 1125 (w), 1105 (m), 1080 (w), 1060 (vw), 1040 (w), 950 (w, sh), 940 (m), 795 (s), 765 (w), 570 (w). Samples exposed to the atmosphere for several days had the same spectrum.

Synthesis of $[(\text{TMPD})\text{BH}_2]\text{BH}_4$. A 5.75-mmol sample of B_2H_6 was condensed into a stopcock-adaptor-equipped 200-mL vessel containing a solution of 0.960 g (5.85 mmol) of TMPD in 20 mL of $(\text{C}_2\text{H}_5)_2\text{O}$. A precipitate formed as soon as the solvent melted and the mixture was stirred magnetically at room temperature for 24 h. A few milliliters of 2-propanol was admitted through the stopcock and the slurry was stirred for a few seconds to destroy any unreacted

diborane. No reaction was detected. The vessel was opened to the air and the solid was collected by filtration, washed several times with $(C_2H_5)_2O$, dried in air, and recrystallized from 2-propanol; yield 0.695 g (66%).

A 0.0676-g (0.352 mmol) sample of $[(TMPD)BH_2]BH_4$ in an evacuated 100-mL reaction vessel was dissolved in 15 mL of ethanol and then treated with 15 mL of 10% hydrochloric acid. After 15 min the vessel was cooled to $-196^\circ C$ and the hydrogen collected: calculated (on the basis of eq 1) 1.41 mmol; found 1.42 mmol.

The proton NMR spectrum ($CDCl_3$) of $[(TMPD)BH_2]BH_4$ showed a symmetrical multiplet at τ 1.47 (aromatic protons), a sharp singlet at τ 5.28 (CH_3), and the usual pattern of sharp peaks characteristic of BH_4^- .

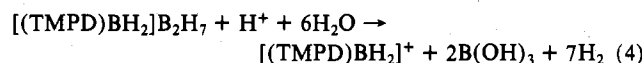
Infrared spectrum (KBr pellet) of $[(TMPD)BH_2]BH_4$ in cm^{-1} (relative intensity): 3030 (vw), 2995 (w), 2975 (w), 2475 (m), 2445 (m), 2365 (vw), 2280 (vs), 2200 (s), 2120 (w), 1475 (m), 1450 (m), 1310 (vw), 1255 (w), 1200 (m), 1170 (m), 1155 (s), 1135 (m), 1125 (s), 1075 (m, br), 1025 (w), 1010 (m), 930 (m), 825 (w, br), 785 (s), 525 (w). The spectrum of a fresh sample of $[(TMPD)BH_2]BH_4$ that had not been exposed to air or 2-propanol was virtually identical with the above.

Synthesis of $[(TMPD)BH_2]PF_6$. A sample of $[(TMPD)BH_2]BH_4$ was hydrolyzed in a small volume of dilute hydrochloric acid and the resulting solution treated with a saturated aqueous solution of KPF_6 until no more precipitate formed. After filtration, the colorless solid was recrystallized from water containing a little KPF_6 .

Anal. Calcd for $C_{10}H_{18}N_2BPF_6$: C, 37.3; H, 5.59; N, 8.70. Found: C, 37.12; H, 5.53; N, 8.69.

Infrared spectrum of $[(TMPD)BH_2]PF_6$ (Nujol), in cm^{-1} (relative intensity): 2495 (m), 2460 (m), 2375 (vw), 1480 (m), 1405 (w), 1265 (w), 1205 (w), 1185 (m), 1175 (m), 1160 (w), 1140 (w), 1120 (vw), 1085 (vw), 1030 (w), 1010 (m), 955 (vw), 925 (w), 885 (s), 840 (vs), 770 (s), 755 (vw), 720 (w), 555 (s), 525 (w).

Synthesis of $[(TMPD)BH_2]B_2H_7$. A 4.72-mmol sample of diborane was condensed into a vessel containing a solution of 0.412 g (2.51 mmol) of TMPD in 10 mL of monoglyme. On warming of the mixture to room temperature a colorless precipitate formed shortly after the solvent melted and no further change was observed. After 1 h at room temperature, the volatiles were removed and fractionated ($-126^\circ C$ slush) to give 0.93 mmol of diborane recovered showing a consumption of 3.79 mmol (B_2H_6 :TMPD ratio 1.51). Acid hydrolysis of a sample of the colorless solid gave hydrogen in reasonable agreement with eq 4: calculated H_2 33.9 mmol/g, found H_2 32.6 mmol/g (96%).

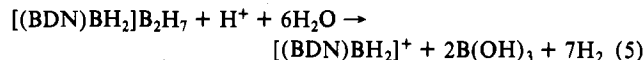


Infrared spectrum of $[(TMPD)BH_2]B_2H_7$ (Nujol), cm^{-1} (relative intensity): 2495 (m), 2460 (m), 2400 (s), 2360 (m, sh), 2300 (w), 2040 (m), 1480 (m), 1265 (w), 1210 (w), 1175 (m), 1170 (m), 1150 (w), 1040 (s), 1035 (s), 1010 (m), 935 (m), 820 (w), 800 (w), 780 (m), 725 (w), 530 (w). The infrared spectrum of a sample exposed to air for 1 h was substantially different from the above.

Reaction of $[(TMPD)BH_2]B_2H_7$ with 2-Propanol. A 100-mL reaction flask equipped with a stopcock adapter was charged with 0.079 g (0.383 mmol) of $[(TMPD)BH_2]B_2H_7$ in a dry nitrogen atmosphere. The apparatus was evacuated and 10 mL of 2-propanol was admitted through the stopcock. There was a moderate evolution of gas and the reaction mixture was kept at room temperature for 1.5 h after which hydrogen was collected: calculated (on the basis of eq 3) 1.15 mmol, found 1.17 mmol. The infrared spectrum of the solid remaining after vacuum evaporation of volatile products was identical with that of $[(TMPD)BH_2]BH_4$.

Reaction of $[(TMPD)BH_2]B_2H_7$ with Trimethylamine. A slurry of 0.128 g (0.622 mmol) of $[(TMPD)BH_2]B_2H_7$ in 10 mL of monoglyme was allowed to react with 1.76 mmol of trimethylamine for 1 day at room temperature. Fractionation of volatiles through $-95^\circ C$ led to the recovery of 1.14 mmol of trimethylamine showing the consumption of 0.62 mmol (Me_3N : $[(TMPD)BH_2]B_2H_7$ ratio 1.0). Fractionation of the material stopping at $-95^\circ C$ through $-22^\circ C$ yielded a volatile solid identified as trimethylamine-borane by its infrared spectrum. The infrared spectrum of the involatile solid residue was identical with that of $[(TMPD)BH_2]BH_4$.

Synthesis of $[(BDN)BH_2]B_2H_7$. A vessel of approximately 20 mL volume was charged with 0.330 g (1.54 mmol) of BDN, 5 mL of diethyl ether and 3.15 mmol of diborane were condensed in, and the vessel was sealed and warmed to room temperature. A clear colorless solution resulted from which a colorless solid precipitated over a period of 3 days. In a similar experiment using about half the above quantities of reactants in a 150-mL vessel, complete precipitation required 14 days. Fractionation of volatiles from the first reaction ($-126^\circ C$ slush) resulted in the recovery of 0.74 mmol of diborane demonstrating the consumption of 2.41 mmol (B_2H_6 :BDN ratio 1.56). Acid hydrolysis of the colorless involatile solid residue produced hydrogen in reasonable agreement with eq 5: calculated H_2 27.3 mmol/g, found H_2 26.1 mmol/g (96%). The $[(BDN)BH_2]B_2H_7$ is soluble in monoglyme.



Infrared spectrum of $[(BDN)BH_2]B_2H_7$ (KBr pellet), in cm^{-1} (relative intensity): 3000 (w), 2950 (w, sh), 2450 (m, sh), 2380 (vs), 2300 (m, sh), 2200 (w, sh), 2030 (s), 1630 (w), 1605 (m), 1580 (w), 1510 (vw), 1475 (m), 1450 (s), 1415 (m), 1405 (w), 1380 (s), 1300 (w), 1275 (m), 1260 (w, sh), 1215 (s, br), 1165 (w), 1150 (m), 1130 (w), 1070 (w), 1025 (s, br), 995 (m), 905 (m), 895 (s), 880 (m), 835 (s), 770 (s), 640 (w), 630 (w), 575 (w).

Synthesis of $[(BDN)BH_2]PF_6$. The solution resulting from the acid hydrolysis of a sample of $[(BDN)BH_2]B_2H_7$ was mixed with excess saturated aqueous KPF_6 . The resulting colorless precipitate was isolated by filtration and recrystallized from water containing a little KPF_6 .

Anal. Calcd for $C_{14}H_{20}N_2BPF_6$: C, 45.2; H, 5.37; N, 7.54. Found: C, 46.01; H, 6.05; N, 7.67.

Infrared spectrum of $[(BDN)BH_2]PF_6$ (Nujol), in cm^{-1} (relative intensity): 3060 (vw, sh), 3045 (vw, sh), 3020 (w), 2945 (vs), 2910 (vs), 2850 (vs), 2490 (m), 2450 (m), 2400 (w, sh), 2345 (vw), 2325 (vw), 1945 (vw), 1805 (vw), 1710 (vw), 1620 (w), 1605 (m), 1570 (w), 1455 (s), 1405 (m), 1380 (m), 1275 (m), 1260 (w), 1230 (s), 1205 (s), 1160 (m), 1140 (m), 1110 (m), 1075 (m), 1015 (s), 1000 (s), 985 (w), 925 (s), 885 (s), 840 (vs, br), 775 (m, sh), 765 (s), 740 (m), 630 (w), 620 (w), 555 (s), 490 (w).

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Registry No. bpy-2 BH_3 , 24442-12-4; $[(TMPD)BH_2]BH_4$, 71393-35-6; $[(TMPD)BH_2]PF_6$, 19584-75-9; $[(TMPD)BH_2]B_2H_7$, 71393-36-7; $[(BDN)BH_2]B_2H_7$, 71393-37-8; $[(BDN)BH_2]PF_6$, 71393-38-9; B_2H_6 , 19287-45-7; bpy, 366-18-7; TMPD, 704-01-8; BDN, 20734-58-1.

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