order is not observed, the conclusion being that basicity of the entering ligand does not determine the magnitude of the rate constants. Rather, the leaving ligand is of the most importance in this regard.

It was observed that there is a kinetic preference for one optical isomer of CyDTA in attacking the optically active lead–PDTA. This is in partial agreement with recent observations by Pearson, *et al.*,[12] in which different rates for the exchange of *l*-CyDTA with the two isomers of lead–PDTA were reported. The product of this reaction then slowly exchanges with the other isomer to give as final product the racemic mixture of the two CyDTA complexes with lead ion.

The exchange of *d*-PDTA with lead–*l*-PDTA shows the same rate constant when the *d*-PDTA is added as an optically pure reagent and when it is added as the racemic mixture of *d*- and *l*-PDTA. This demonstrates only that the exchange of *l*-PDTA with lead–*l*-PDTA does not remove an appreciable fraction of lead complex as a reaction intermediate at any given time. The concentration of any mixed-ligand intermediate $Pb(PDTA)_2^{6-}$ is less than 1% of the total lead complex concentration.

The structure of the intermediate prior to hydroxide-dependent dissociation of lead–PDTA is visualized to have one nitrogen–lead bond broken and an iminodiacetate segment rotated away from the lead ion. The lead ion then is coordinated to the remaining iminodiacetate group and two hydroxide ions. The analogous intermediate for lead–CyDTA contains only a single hydroxide ion which is sufficient to block the much more rigid ligand from rebonding the lost iminodiacetate group. Both intermediates are subject to rapid loss of the remainder of the original ligand, without help from the substituting ligand.

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[12] K. H. Pearson, W. R. Howell, and P. E. Reinbald, Anachem Conference, Detroit, Mich., Oct 1970.

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The Chemistry of Sodium Bis(borane)dimethylamide(1−)

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In monoglyme solution μ-dimethylaminodiborane and sodium borohydride reversibly form sodium heptahydrodiborate(1−) and sodium bis(borane)dimethylamide(1−), $Na(CH_3)_2N(BH_3)_2$. The latter compound cannot be isolated by solvent removal owing to the volatility of μ-dimethylaminodiborane but may be prepared quantitatively by reaction of sodium hydride with μ-dimethylaminodiborane in monoglyme. Sodium bis(borane)dimethylamide(1−) reacts with diborane to form μ-dimethylaminodiborane and sodium heptahydrodiborate(1−); boron exchange does not occur. Treatment of a monoglyme solution of sodium bis(borane)dimethylamide(1−) with hydrogen chloride results in chlorination and solvent cleavage. Sodium bis(borane)dimethylamide(1−) reacts with ammonium chloride and mono-, di-, and trimethylammonium chloride to form ammonia or amine adducts of μ-dimethylaminodiborane. At lower than ambient temperature the intermediate salt $[(CH_3)_2NH_2][(CH_3)_2N(BH_3)_2]$ can be isolated.

Introduction

Very few examples of compounds with two equivalent borane groups bonded to the same donor atom have been reported. The first to be characterized was the bis-borane adduct of the dihydrogenphosphide(1−) ion, $H_2P(BH_3)_2^-$.[1] Subsequently the sulfur compound $[(C_2H_5)_4N][HS(BH_3)_2]$[2] and another phosphorus complex $Li(CH_3)_2P(BH_3)_2$[3] have been described. Recent studies in this laboratory on the reaction of diborane with $Na(CH_3)_2NBH_3$[4,5] led to the discovery and preliminary description of the first example of a nitrogen complex $Na(CH_3)_2N(BH_3)_2 \cdot 0.5diox$ (I).[6] This paper details the preparation and characterization of I and discusses some of its chemical reactions.

Experimental Section

General Information.—Conventional high-vacuum and glove bag techniques were used in this investigation. The pure solvents diethyl ether, monoglyme (1,2-dimethoxyethane), diglyme (bis(2-methoxyethyl) ether), and dioxane were stored in evacuated bulbs over lithium aluminum hydride and, when needed, were condensed directly into the reaction vessel. Boron-11 nmr spectra were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz equipped with standard variable-temperature accessories; proton nmr spectra were obtained with Varian HA-100 and A-60 instruments. Boron-11 and proton chemical shifts are reported in ppm relative to diethyl ether–boron trifluoride and tetramethylsilane, respectively. Signals at lower field than the standard have negative chemical shifts. Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers. A KBr matrix was used for solids; a 5- or 10-cm cell with NaCl windows was used for gases.

Boron-10 diborane was prepared by the lithium aluminum hydride reduction of $(C_2H_5)_2O \cdot {}^{10}BF_3$ (96% ^{10}B; $^{10}BF_3$ obtained as $CaF_2 \cdot {}^{10}BF_3$ from Oak Ridge National Laboratory). The μ-dimethylaminodiborane was prepared from the reaction of diborane with $Na(CH_3)_2NBH_3$.[4] Sodium hydride was freed of mineral oil by repeated washing with cyclohexane under a blanket of dry nitrogen. Other reagents used in this work were purchased

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[1] (a) N. R. Thompson, *J. Chem. Soc.*, 6290 (1965); (b) J. W. Gilje, K. W. Morse, and R. W. Parry, *Inorg. Chem.*, **6**, 1761 (1967); (c) R. E. Hester and E. Meyer, *Spectrochim. Acta, Part A*, **23**, 2218 (1967).

[2] P. C. Keller, *Inorg. Chem.*, **8**, 1695 (1969).

[3] L. D. Schwartz and P. C. Keller, *ibid.*, in press.

[4] P. C. Keller, *J. Amer. Chem. Soc.*, **91**, 1231 (1969).

[5] P. C. Keller, *Inorg. Chem.*, **10**, 1528 (1971).

[6] P. C. Keller, *Chem. Commun.*, 1465 (1969).

from commercial sources and were purified by standard methods when necessary.

Reactions monitored by boron-11 nmr were run in nmr reaction vessels fitted with Kontes Teflon high-vacuum O-ring stopcocks for easy addition and recovery of reagents. The internal volume of these vessels was 10–15 ml so that reactions on a 1-mmol scale could be performed conveniently.

Interaction of Sodium Borohydride with μ-Dimethylaminodiborane in Monoglyme Solution.—A solution of 0.031 g (0.82 mmol) of purified sodium borohydride and 0.43 mmol of μ-dimethylaminodiborane in 1 ml of monoglyme was prepared in an nmr reaction vessel. Boron-11 nmr spectra were recorded at sample temperatures of −45, −25, 0, 20, 40, and 60°. The spectra at 0° and below were identical (Figure 1A) and showed a very weak borohydride signal (not due to saturation effects) at 41.6 ppm, a strong quartet with doublet fine structure at 25.3 ppm, characteristic of $B_2H_7^-$,[7] and a second strong quartet of approximately equal intensity at 11.2 ppm. The 20° spectrum (Figure 1B) showed the borohydride signal considerably enhanced at the expense of the other two. Above 20° (Figure 1C and D) a white solid separated from solution, the low-temperature signals disappeared, and a broad featureless resonance at 17 ppm, characteristic of μ-dimethylaminodiborane undergoing rapid hydrogen exchange grew in.[8]

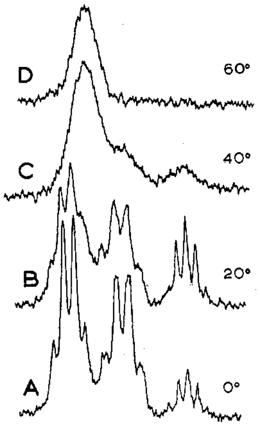

Figure 1.—Boron-11 nmr spectra of sodium borohydride and μ-dimethylaminodiborane (2:1) in monoglyme.

Addition of more μ-dimethylaminodiborane (0.36 mmol) resulted in the appearance of a strong nmr signal characteristic of this compound in the spectra of the system at 20° and below. Separation of volatile materials on the vacuum line produced only μ-dimethylaminodiborane and monoglyme. The boron-11 nmr spectrum of the white solid residue dissolved in fresh monoglyme showed only a borohydride quintet.

Preparation of Sodium Bis(borane)dimethylamide(1−).—In a high-vacuum filter apparatus 3.83 mmol of μ-dimethylaminodiborane was allowed to react with a well-stirred monoglyme suspension of mineral oil free sodium hydride (threefold excess). After 1 hr at room temperature, the mixture was filtered and the monoglyme was stripped off under vacuum leaving a clear colorless oil. Dissolving the oil in 4–5 ml of dioxane and evaporating the solvent produced a white crystalline solid. The last traces of free solvent were removed by pumping on the product for 12 hr. The collected solid weighed 0.513 g, 96% based upon $Na(CH_3)_2N(BH_3)_2 \cdot 0.5C_4H_8O_2$.

For hydrogen, boron, and nitrogen analyses, a sample of the solid was hydrolyzed in 1 *N* sulfuric acid in a closed evacuated bulb. Hydrolytic hydrogen was collected and measured using a Toepler pump–gas buret assembly, boric acid was determined by titration of the D-mannitol complex with standard base, and dimethylamine was estimated by a Kjeldahl-type procedure. Dioxane of crystallization was recovered quantitatively by mild pyrolysis of the solid at 80° in the vacuum line. The purity of the dioxane was confirmed by its gas-phase infrared spectrum.

Anal. Calcd for $Na(CH_3)_2N(BH_3)_2 \cdot 0.5C_4H_8O_2$ (in mmol/g): H_2, 43.3; $B(OH)_3$, 14.4; $(CH_3)_2NH$, 7.22; dioxane, 3.61. Found: H_2, 41.8; $B(OH)_3$, 14.3; $(CH_3)_2NH$, 6.87; dioxane, 3.50.

The infrared spectrum of I showed the following bands (in cm^{-1}): 2990 (w, sh), 2965 (m), 2925 (w), 2900 (w, sh), 2875 (w), 2865 (w), 2830 (vw), 2350 (m, sh), 2295 (vs), 2235 (s), 2070 (w, sh), 1465 (m), 1440 (w), 1420 (w), 1390 (vw), 1365 (w), 1295 (w), 1255 (m), 1230 (w, sh), 1200 (s, sh), 1190 (s), 1165 (vs), 1135 (s), 1110 (s), 1080 (m), 1040 (w, sh), 1025 (s), 1010 (m), 940 (w), 920 (w), 900 (vw), 885 (m), 875 (s), 805 (w).

The infrared spectrum of I after removal of dioxane by vacuum pyrolysis at 80° contained the following bands: 2990 (w), 2965 (m), 2930 (w), 2875 (w), 2830 (vw), 2350 (m, sh), 2295 (vs), 2235 (s), 2070 (w, sh), 1465 (m), 1440 (w), 1420 (w), 1390 (vw), 1250 (w, sh), 1225 (m, sh), 1195 (s, sh), 1170 (vs), 1025 (s), 935 (w), 905 (vw), 810 (w).

The boron-11 nmr spectrum of a monoglyme solution of I consisted of a well-resolved quartet centered at 11.2 ppm with a coupling constant of 90 ± 1 Hz. The proton nmr spectrum of a D_2O solution of I showed, in addition to a dioxane singlet, a sharp singlet at −2.28 ppm, assigned to the CH_3 protons, and a 1:1:1:1 quartet centered at −1.50 ppm with coupling constant 89 Hz, assigned to the protons bound to boron-11. After 1 month at room temperature the boron-11 nmr spectrum of this solution indicated only 10% hydrolysis.

Reaction with Diborane.—Equal quantities of diborane and I were brought together in diglyme solution in an nmr reaction vessel. The boron-11 nmr spectrum of the clear colorless solution at −10° showed broadened equal-intensity signals characteristic of μ-dimethylaminodiborane and sodium heptahydrodiborate(1−). Further cooling reduced the line broadening, but the doublet fine structure of the signals could not be resolved. Separation of the products on the vacuum line resulted in isolation of μ-dimethylaminodiborane in 80% yield.

The nmr experiment was repeated using $^{10}B_2H_6$. In this case the spectrum showed only a signal diagnostic of μ-dimethylaminodiborane. After several hours at room temperature the spectrum was unchanged, indicating no detectable exchange of boron isotopes.

Reaction with Hydrogen Chloride.—A 1.18-mmol sample of hydrogen chloride was condensed into a liquid nitrogen cooled reaction bulb containing 0.061 g (0.44 mmol) of I and 3 ml of diglyme. Vigorous evolution of hydrogen commenced when the diglyme melted and ceased 2–3 min after the solution reached room temperature. The hydrogen produced amounted to 1.17 mmol. After addition of more hydrogen chloride (5 mmol), brisk hydrogen evolution resumed for a few minutes and gradually slowed. After 18 hr a grand total of 2.06 mmol of hydrogen had evolved. Separation of volatile products resulted in the isolation of 1.41 mmol of methyl chloride (identified by vapor pressure and infrared spectrum). No volatile boron-containing material was found.

Reaction with Amine Hydrochlorides.—In separate experiments monoglyme solutions of I were allowed to react with ammonium and mono-, di-, and trimethylammonium chloride. Typically for the first three compounds, a solution of 0.21 g (1.5 mmol) of I in 3 ml of monoglyme was stirred in an evacuated reaction bulb with 2.5 mmol of the ammonium salt. No reaction occurred at room temperature but when the mixture was warmed to 50–60°, hydrogen evolved smoothly over 2–3 hr. The vessel was then immersed in an ice–water bath and the solvent was evaporated on the vacuum line. The collected white solid residue sublimed quickly to a 0° cold finger when warmed to 70–80°. The sublimates were identified as μ-dimethylaminodiborane adducts of the appropriate amine by comparison of their infrared spectra with literature data.[9] Separation of the solvent fraction produced some free amine, usually 20–30% based on I, indicating a chlorination side reaction.

With trimethylammonium chloride, reaction occurred at room temperature. Since the product was similar to monoglyme in volatility and could not be isolated by vacuum line fractionation, identification was achieved by comparing the boron-11 nmr spectrum of the monoglyme solution with that reported for the trimethylamine adduct of μ-dimethylaminodiborane.[9]

To determine whether I would react with tetramethylammonium chloride, an intimate mixture of the two solids was heated to 185° on the vacuum line. The only volatile product detected was a stoichiometric quantity of dioxane. The infrared spectrum of the heat-treated mixture was a superposition of the spectra of tetramethylammonium chloride and dioxane-free sodium bis(borane)dimethylamide(1−).

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[7] D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).

[8] D. F. Gaines and R. Schaeffer, *J. Amer. Chem. Soc.*, **86**, 1505 (1963).

[9] G. A. Hahn and R. Schaeffer, *ibid.*, **86**, 1503 (1964).

Preparation of Crude $[(CH_3)_2NH_2][(CH_3)_2N(BH_3)_2]$.—An absolute ethanol solution of 0.210 g (1.51 mmol) of I and 0.122 g (1.51 mmol) of dimethylammonium chloride was stirred at 0° for 70 min in a vacuum filtration apparatus. During this time a precipitate of sodium chloride slowly formed and a trace of noncondensable gas appeared. The mixture was filtered quickly and the ethanol was removed under vacuum while the filtrate was immersed in an ice–water bath. The infrared spectrum of the solid residue showed only bands characteristic of dimethylammonium and bis(borane)dimethylamide(1−) ions. The remaining solid was slowly warmed in a reaction vessel on the vacuum line. At about 50° hydrogen began to form and a volatile solid slowly condensed on the cool upper walls of the vessel. The temperature was maintained at 60–70° until 80% of the hydrogen expected for eq 1 had evolved. The infrared spectrum

$$[(CH_3)_2NH_2][(CH_3)_2N(BH_3)_2] \longrightarrow H_2 + (CH_3)_2NHBH_2N(CH_3)_2BH_3 \quad (1)$$

of the sublimed solid established its identity as the dimethylamine adduct of μ-dimethylaminodiborane. The small amount of involatile solid residue in the reaction vessel was identified as dimethylammonium chloride by its infrared spectrum.

Results and Discussion

Formation and Characterization of I.—The Lewis acidity of μ-dimethylaminodiborane has been studied by several workers. Burg and Randolph described the formation of ammonia and trimethylamine complexes[10] and Hahn and Schaeffer prepared and characterized adducts with ammonia and mono-, di-, and trimethylamine;[9] the structures of the complexes were established as N–B–N–B chains by boron-11 and proton nmr.[9] Prior to this work, however, the ability of μ-dimethylaminodiborane to function as a hydride ion acceptor had not been investigated.

In glyme ethers μ-dimethylaminodiborane rapidly and reversibly accepts a hydride ion from sodium borohydride (eq 2). The μ-dimethylaminodiborane

$$\mu\text{-}(CH_3)_2NB_2H_5 + 2NaBH_4 \rightleftharpoons Na(CH_3)_2N(BH_3)_2 + NaB_2H_7 \quad (2)$$

will not react further with sodium heptahydrodiborate(1−), since diborane is a much stronger Lewis acid than μ-dimethylaminodiborane[11] and successfully competes for the remaining available hydride ion. The equilibrium lies to the right below room temperature but, upon warming, shifts to the left by virtue of the insolubility of sodium borohydride in monoglyme at elevated temperatures.[12] The equilibrium also shifts to the left if the solution is evaporated owing to the volatility of μ-dimethylaminodiborane. Because of the labile nature of this system, sodium bis(borane)dimethylamide(1−) cannot be prepared conveniently if sodium borohydride is used as a hydride ion source.

Sodium bis(borane)dimethylamide(1−) may be prepared easily and quantitatively by the direct reaction of excess sodium hydride with μ-dimethylaminodiborane in monoglyme (eq 3). Filtration and evapora-

$$NaH + \mu\text{-}(CH_3)_2NB_2H_5 \longrightarrow Na(CH_3)_2N(BH_3)_2 \quad (3)$$

tion produces an oil; treatment with dioxane and reevaporation yields the crystalline dioxane solvate $Na(CH_3)_2N(BH_3)_2 \cdot 0.5C_4H_8O_2$ (I). The dioxane may be quantitatively removed to give an unsolvated salt by gentle pyrolysis at 80° under vacuum. If eq 3 is attempted in dioxane, separation of I from unreacted sodium hydride requires many extractions owing to low solubility.

In thermal stability and resistance to hydrolysis I compares favorably with the other known group V bis-borane complexes, $NaH_2P(BH_3)_2$[1] and $Li(CH_3)_2P(BH_3)_2$.[3] The compound is stable in air, although hygroscopic, and dissolves without reaction in glyme ethers, alcohols, and neutral water. Acidification of an aqueous solution of I generates the expected hydrolysis products, hydrogen, boric acid, and dimethylammonium ion.

Four infrared bands occur in the B–H stretching region at 2350, 2295, 2235, and 2070 cm^{-1}. The first is probably an overtone of a BH_3 deformation mode at 1170 cm^{-1}. The second and third may be assigned to the asymmetric and symmetric B–H stretching vibrations, respectively, while the last is likely to be a combination band. Assignments in the 1250–800-cm^{-1} region can only be guesswork without more data. Detailed spectral studies of the related compounds trimethylamine–borane,[13] μ-dimethylaminodiborane,[14] and sodium bis(borane)dihydrogenphosphide(1−)[15] indicate considerable variation in the frequencies of the expected bands in this region.

The boron-11 chemical shift of I in monoglyme (11.2 ppm) fits among those of the closely related compounds $Na(CH_3)_2NBH_3$ (14.7 ppm),[4] $(CH_3)_2NH \cdot BH_3$ (13.5 ppm),[4] and $(CH_3)_3N \cdot BH_3$ (8.1 ppm).[8] The chemical shift of the boron nucleus in $(CH_3)_2N \cdot BH_3^-$ is decreased by groups bound to nitrogen in the order of effectiveness $CH_3^+ > BH_3 > H^+$. The greater effect of BH_3 compared to H^+ is seen also in comparing the boron-11 chemical shifts of $H_3P \cdot BH_3$ (42.7 ppm)[16] and $H_2P(BH_3)_2^-$ (41.7 ppm).[17]

Chemical Reactions of I.—In discussing chemical behavior it is interesting to compare I with the isoelectronic trimethylamine–borane and, where possible, with the closely related lithium bis(borane)dimethylphosphide(1−). In glyme ethers diborane reacts with I to produce μ-dimethylaminodiborane and sodium heptahydrodiborate(1−). The temperature-dependent line broadening of the boron-11 nmr spectrum and

$$Na(CH_3)_2N(BH_3)_2 + B_2H_6 \rightleftharpoons \mu\text{-}(CH_3)_2NB_2H_5 + NaB_2H_7 \quad (4)$$

the absence of rapid boron isotope exchange suggest a hydride ion exchange equilibrium shifted well to the right owing to the greater Lewis acidity of diborane.[11] At low temperature neutral and less hydridic trimethylamine–borane reversibly forms a very weak single hydrogen bridge complex with BH_3 (eq 5).[18] In this

$$(CH_3)_3NBH_3 + 0.5B_2H_6 \rightleftharpoons (CH_3)_3NBH_2\text{–}H \cdots BH_3 \quad (5)$$

system hydride ion transfer probably does not occur owing to the very high Lewis acidity of a species like $(CH_3)_3NBH_2^+$. Lithium bis(borane)dimethylphosphide(1−) exchanges hydrogen with diborane, possibly through an equilibrium like eq 4, but only the starting

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(10) A. B. Burg and C. L. Randolph, Jr., *J. Amer. Chem. Soc.*, **71**, 3451 (1949).

(11) A. B. Burg and J. Sandhu, *Inorg. Chem.*, **4**, 1467 (1965).

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(14) D. E. Mann, *J. Chem. Phys.*, **22**, 70 (1954).

(15) E. Meyer and R. E. Hester, *Spectrochim. Acta, Part A*, **25**, 237 (1969).

(16) R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg. Chem.*, **5**, 723 (1966).

(17) Reference 1. The value 41.7 is for the NH_4^+ salt. An even lower value of 39.2 ppm was found for the $(CH_3)_2NH_2^+$ salt.

(18) S. G. Shore and C. L. Hall, *J. Amer. Chem. Soc.*, **88**, 5346 (1966).

materials can be detected by boron-11 nmr and isolated from solution.[3]

Sodium bis(borane)dimethylamide(1−) is also more reactive toward proton acids than its isoelectronic counterpart trimethylamine–borane, which reacts rapidly with hydrogen chloride below room temperature to produce a monochloroborane adduct[19] but requires a temperature of 100° before a second hydrogen is replaced. In contrast at least five of the six BH hydrogens of I react with hydrogen chloride in diglyme at room temperature within a few hours. The chlorinated products react with the solvent as evidenced by the recovery of a substantial quantity of methyl chloride. A similar reaction was found for lithium bis(borane)dimethylphosphide(1−).[3]

Trimethylamine–borane and I differ in their behavior toward the more weakly acidic ammonium chloride and its methyl derivatives. Miller and Muetterties found that amine–boranes react with amine hydrochlorides at elevated temperatures (100–180°) to generate amine–monochloroboranes.[20] Ammonium chloride and mono-, di-, and trimethylammonium chloride react with I to give the corresponding amine adduct of μ-dimethylaminodiborane (eq 6) as the principal product. Recovery of some free amine indicates chlorination is a secondary process.

$$Na(CH_3)_2N(BH_3)_2 + (CH_3)_nNH_{4-n}Cl \longrightarrow (CH_3)_nNH_{3-n}BH_2N(CH_3)_2BH_3 + H_2 + NaCl \quad (n = 0\text{–}3) \qquad (6)$$

Since reaction 6 required warming to 50–60° in all cases except that of trimethylammonium chloride, it proved possible to prepare the crude dimethylammonium salt of $(CH_3)_2N(BH_3)_2^-$ by a simple metathesis reaction carried out at 0° in ethanol. The infrared spectrum of the product was in agreement with its formulation and showed no bands characteristic of the dimethylamine adduct of μ-dimethylaminodiborane. The salt decomposed at 50° in accord with eq 6. This salt is an isomer of $[((CH_3)_2NH)_2BH_2][BH_4]$ and is also the *N,N,N′,N′*-tetramethyl derivative of the unknown compound $[NH_4][H_2N(BH_3)_2]$.[21–23] The existence of $[(CH_3)_2NH_2][(CH_3)_2N(BH_3)_2]$ and the moderate thermal stability of $[NH_4][H_2P(BH_3)_2]$[1b] suggest that it may be possible to prepare $[NH_4][H_2N(BH_3)_2]$. If this is so, it is intriguing to consider the possibility that this compound may be one of the yet uncharacterized products of the ammonia–diborane reaction.

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[20] N. E. Miller and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 1033 (1964).

[21] This compound was originally thought to be the main product of the reaction of ammonia with diborane, the "diammoniate of diborane."[22] However, it was conclusively demonstrated some years later that the ammonia–diborane product was really $[(NH_3)_2BH_2][BH_4]$.[23]

[22] H. I. Schlesinger and A. B. Burg, *J. Amer. Chem. Soc.*, **60**, 290 (1938).

[23] D. R. Schultz and R. W. Parry, *ibid.*, **80**, 4 (1958).

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Phosphinotrihydroborate(1−), $H_2P \cdot BH_3^-$, the Conjugate Brønsted Base of Phosphine–Borane. Synthesis, Reactions, and Stability of the Lithium Salt

BY ERWIN MAYER

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Phosphine–borane reacts with *n*-butyllithium to form $(H_2P \cdot BH_3)Li$. This compound is soluble in aprotic solvents and is extremely reactive toward moisture. Proton nmr, infrared, and Raman data are presented and analyzed in terms of C_s symmetry for the anion. The thermal stability points to an increase in B–P bond strength compared with the B–P bond in $H_3P \cdot BH_3$. $(H_2P \cdot BH_3)Li$ behaves as a Lewis base and reacts with diborane to form $(H_2P(BH_3)_2)Li$. $(H_2P \cdot BH_3)Li$ dissolved in CD_3CN exchanges its PH_2 protons for deuterium, whereas no exchange occurs in $(H_2P(BH_3)_2)Li$–CD_3CN solutions. This is analogous to the kinetics of exchange in hypophosphorous acid and in phosphoric acid where a conversion into a tautomeric form with tricoordinated phosphorus has been postulated as the rate-determining step.

Introduction

The bis(borane)dihydrogenphosphide(1−) ion ($H_3B \cdot PH_2 \cdot BH_3^-$) is prepared by the reaction of phospine–borane with $NaBH_4$.[1] A possible mechanism for this reaction is

$$H_3P \cdot BH_3 + BH_4^- \longrightarrow H_2P \cdot BH_3^- + H_2 + 0.5B_2H_6 \qquad (1)$$

$$H_2P \cdot BH_3^- + 0.5B_2H_6 \longrightarrow H_3B \cdot PH_2 \cdot BH_3^- \qquad (2)$$

The intermediate $H_2P \cdot BH_3^-$, a conjugate Brønsted base of phosphine–borane, has not been isolated so far, but it has been postulated as an intermediate by Parry for the reaction of phosphine–borane with ammonia.[2] For an interpretation of the mechanism of these simple hydride-transfer reactions a knowledge of reactions and stability of the possible intermediates would be very helpful. Therefore preparation and properties of the lithium salt of $H_2P \cdot BH_3^-$ will be reported in this paper.

Results and Discussion

Preparation of $(H_2P \cdot BH_3^-)Li^+$.—Phosphine–borane reacts quantitatively with *n*-butyllithium in diethyl

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