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.

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

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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[19] H. Nöth and H. Beyer, *Chem. Ber.*, **93**, 2251 (1960).

[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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[1] E. Mayer and A. W. Laubengayer, *Monatsh. Chem.*, **101**, 1138 (1970).

[2] R. W. Parry, Amer. Chem. Soc. Annual Conference Sept. 1966

ether at −20° according to eq 3. Above −20° phosphine–borane dissociates considerably into phosphine and diborane. Since both compounds react with *n*-butyllithium, the following side reactions are possible (eq 4–6) which will become dominant with increasing temperature. Only H_2PLi is insoluble in diethyl ether[3] and can therefore be separated by filtration. The lithium salts from reactions 3, 5, and 6 are soluble and a separation is not possible. In order to obtain pure $(H_2P\cdot BH_3)Li$ the reactions 4–6 have to be excluded by carefully controlling the temperature during the reaction.

$$H_3P\cdot BH_3 + n\text{-}C_4H_9Li \longrightarrow (H_2P\cdot BH_3)Li + n\text{-}C_4H_{10} \quad (3)$$

$$PH_3 + n\text{-}C_4H_9Li \longrightarrow PH_2Li + n\text{-}C_4H_{10} \quad (4)$$

$$B_2H_6 + 2n\text{-}C_4H_9Li \longrightarrow 2(H_3B\cdot C_4H_9)Li \quad (5)$$

$$B_2H_6 + 2O(C_2H_5)_2 \longrightarrow 2H_3B\cdot O(C_2H_5)_2 \xrightarrow{2n\text{-}C_4H_9Li} 2(H_3B\cdot O(C_2H_5)(C_2H_4))Li + 2n\text{-}C_4H_{10} \quad (6)$$

The choice of solvent is the second important factor for the preparation of pure $(H_2P\cdot BH_3)Li$. In apolar solvents (*e.g.*, hexane) phosphine–borane is poorly soluble at low temperatures and dissociation occurs *before* reaction with *n*-butyllithium has started. In polar solvents which are stronger donors than diethyl ether a base-displacement reaction will occur (eq 7). Diethyl ether therefore appears to be just the right compromise.

$$H_3P\cdot BH_3 + D \longrightarrow H_3B\cdot D + PH_3 \quad (D = \text{donor}) \quad (7)$$

Third, the stoichiometry of the reaction of *n*-butyllithium with phosphine–borane has to be considered. A nearly pure product is obtained only if equimolar amounts are used. Excess *n*-butyllithium reacts slowly with diethyl ether, ether-soluble products being formed, which cannot be separated, whereas excess phosphine–borane reacts with $(H_2P\cdot BH_3)Li$ according to eq 8 under formation of $(H_2P(BH_3)_2)Li$ which is also soluble in ether.

$$H_3P\cdot BH_3 + (H_2P\cdot BH_3)Li \longrightarrow (H_2P(BH_3)_2)Li + PH_3 \quad (8)$$

$(H_2P\cdot BH_3)Li$ is a white, crystalline solid which is very soluble in aprotic polar solvents such as diethyl ether, dimethoxyethane, and acetonitrile. Since the compound is extremely reactive toward moisture, no conductivity measurements in aqueous solution could be carried out. Although the compound probably exists in the above-mentioned organic solvents of low dielectric constant as the un-ionized unit or as an ion cluster, it appears reasonable to formulate it as the ion $(H_2P\cdot BH_3^-)Li^+$ (a) by analogy with a similar compound $H_2P(BH_3)_2^-Li^+$ which behaves as a strong electrolyte in water[1] and (b) due to the fact that $(H_2P\cdot BH_3)Li$ does not dissolve in apolar solvents such as benzene. In the following the ionic formula $(H_2P\cdot BH_3^-)Li^+$ will be used.

Hydrolysis of $H_2P\cdot BH_3^-$.—$H_2P\cdot BH_3^-$ is hydrolyzed by water or weak acids as acetic acid according to eq 9.

$$H_2P\cdot BH_3^- + 4H_2O \longrightarrow PH_3 + 3H_2 + B(OH)_4 \quad (9)$$

Contrary to $H_2P\cdot BH_3^-$ the ion $H_2P(BH_3)_2^-$ dissolves in water with very little decomposition and can be stored for hours before appreciable evolution of hydrogen starts. These two ions differ in the first place by the coordination number of phosphorus which is 4 in $H_2P(BH_3)_2^-$ and 3 in $H_2P\cdot BH_3^-$. Therefore $H_2P\cdot BH_3^-$ can react as a Brønsted base *and* as a Lewis base, which probably is the reason for its extreme reactivity.

Thermal Stability.—Solid $(H_2P\cdot BH_3)Li$ starts to decompose slowly *in vacuo* at 85°, hydrogen being evolved. Hydrogen evolution ceases after 4 hr of heating at 115°. The pyrolysis can be summarized by eq 10. No diborane and only a trace of phosphine is formed. Further heating between 160 and 240° produces some more hydrogen. The overall stoichiometry is represented by eq 11. Both the stepwise formation of hydrogen and the exact stoichiometries of reactions 10 and 11 suggest that decomposition occurs in two steps with two distinct products being formed. No hydrogen is formed if $(H_2P\cdot BH_3)Li$ dissolved in triglyme is heated up to 180°.

$$3(H_2P\cdot BH_3)Li \longrightarrow 2H_2 + P_3B_3H_{11}Li_3 \quad (10)$$

$$4(H_2P\cdot BH_3)Li \longrightarrow 5H_2 + P_4B_4H_{10}Li_4 \quad (11)$$

Two points are of importance. (a) The course of the reaction is completely different from the decomposition of its conjugate Brønsted acid phosphine–borane which dissociates into phosphine and diborane. No reaction according to eq 12 occurs and no diborane is formed. Thermal decomposition of any possibly formed diborane can be excluded because the reaction was carried out *in vacuo* and diborane would have been removed immediately from the hot reaction zone. (b) Phosphine–borane is much less stable thermally and starts to dissociate already at −30° into its components,[4] while solid $(H_2P\cdot BH_3)Li$ is stable up to 85°. Apparently the boron–phosphorus bond is strengthened in the ion as is reflected in the higher thermal stability, and decomposition involves the boron–hydrogen or phosphorus–hydrogen bonds instead of the boron–phosphorus bond as in phosphine–borane.

$$(H_2P\cdot BH_3)Li \longrightarrow H_2PLi + 0.5B_2H_6 \quad (12)$$

TABLE I
INFRARED AND RAMAN SPECTRA OF $(H_2P\cdot BH_3^-)Li^+$ IN THE SOLID STATE[a]

Ir	Raman	Assignments
2380 sh		A′′ PH_2 str
2350 sh		A′ PH_2 str
2314 vs, sp		
2300 sh		2 A′ and A′′ BH_3 str
2265 vs		
2170 sh		2 × 1093 = 2186
1303 m		2 × 670 = 1340
1220 m		2 × 617 = 1234
1116 m, sh		A′ and A′′ antisym BH_3 def
1093 s	1102 m	A′ sym BH_3 def
1057 s	1067 m	A′ PH_2 def
919 sh		
888 w		A′ PH_2 wag
853 sh		A′′ PH_2 twist
670 m	682 m	A′′ BH_3 wag
645 sh		
629 sh	643 vs	A′ BH_3 wag
617 m	629 s	A′ B–P str?
370 m		
300 m, b		Torsional mode?

[a] All frequencies in cm^{-1}. Key: w, weak; m, medium; s, strong; v, very; sp, sharp; sh, shoulder; b, broad.

Infrared and Raman Spectra.—Table I contains infrared and Raman data of $(H_2P\cdot BH_3)Li$ in the solid state. The ion $H_2P\cdot BH_3^-$ belongs presumably to the

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[3] N. Kreuzkamp, *Chem. Ber.*, **87**, 919 (1954).

[4] L. Gamble and P. Gilmont, *J. Amer. Chem. Soc.*, **62**, 717 (1940).

point group C_s. The same symmetry has been assumed for methylamine,[5] methylphosphine,[6] and methylarsine[7] which are its structural analogs. Of the 15 fundamental vibrations, 9 belong to the A′ and 6 to the A″ species which are all active in the infrared and Raman spectra. The assignments listed in Table I result from comparisons with the spectra of similar compounds, such as $H_3P \cdot BH_3$ and $H_3B \cdot PF_3$,[8] $H_2P(BH_3)_2^-$,[9] and $H_3B \cdot CO$[10] and from intensity considerations in the Raman spectrum.

PH stretching modes normally occur at higher wave numbers than BH stretching modes.[8,9] Therefore the bands at 2380 and 2350 cm^{-1} are assigned to the PH_2 stretching modes. These absorptions are still lower in frequency than PH stretching absorptions in similar compounds with tetracoordinated phosphorus. For example in $H_3P \cdot BH_3$ PH stretching modes occur at 2426, 2422, and 2399 cm^{-1} [8] and in $H_2P(BH_3)_2^-$ at 2400 and 2380 cm^{-1}.[9] This decrease in PH stretching frequencies is generally found in compounds with tricoordinated phosphorus and has been explained as bond weakening due to change of hybridization of the phosphorus bonding orbitals from sp^3 to mainly p^3.[11] Surprisingly no lines have been found in the BH and PH stretching regions of the Raman spectrum.

The B–P stretching mode certainly has to be assigned to one of the four absorptions between 617 and 670 cm^{-1} in the infrared spectrum and should be of considerable intensity in the Raman spectrum. The 682-cm^{-1} line in the Raman spectrum appears to be too high because in $H_3B \cdot PH_3$ B–P stretching occurs at 564 cm^{-1}. The Raman line at 629 cm^{-1} is therefore tentatively assigned as the B–P stretching mode. A study of the deuterated compound, which is currently under way, should provide further evidence.

Proton Nmr Spectrum.—In the ^1H nmr spectrum of $(H_2P \cdot BH_3)Li$ in CD_3CN two distinct types of proton signals were observed (Figure 1). A 1:1:1:1 quartet is found centered 0.32 ppm downfield from TMS which results from coupling of the protons in the BH_3 group with ^{11}B ($I = {}^3/_2$). The J_{B-H} coupling constant of 88 Hz and the chemical shift are comparable with the values for $H_2P(BH_3)_2^-$ (93 Hz, 0.43 ppm).[9]

A doublet is found at 0.78 ppm downfield from TMS which is assigned to the protons on phosphorus split by ^{31}P ($I = {}^1/_2$). Each component of the doublet is split further into a 1:3:3:1 quartet due to coupling of the protons of the PH_2' group with the three magnetically equivalent BH_3 protons ($J_{H-H'} = 7$ Hz). The $J_{P-H'}$ coupling constant of 175 Hz is quite different from the value found in $H_2P(BH_3)_2^-$ ($J_{P-H} = 320$ Hz) or in $H_3P \cdot BH_3$ ($J_{P-H} = 372$ Hz)[12] and is within the range expected for compounds with tricoordinated phosphorus.[13]

Exact peak intensities could not be determined because both components of the PH_2 doublet superimpose a signal of the BH_3 quartet.

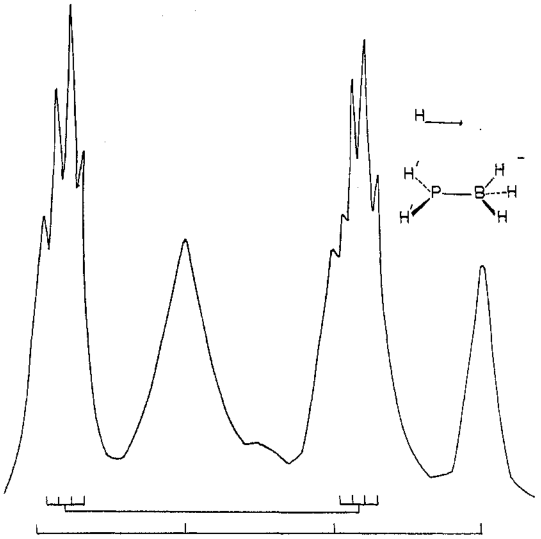

Figure 1.—The ^1H nmr spectrum of $(H_2P \cdot BH_3)Li$. $J_{B-H} = 88$ Hz, $J_{P-H'} = 175$ Hz, and $J_{H-H'} = 7$ Hz.

$H_2P \cdot BH_3^-$ as a Lewis Base.—The Lewis base character of $H_2P \cdot BH_3^-$ is demonstrated by its reaction with diborane to form $H_2P(BH_3)_2^-$ (eq 13). Another Lewis

$$H_2P \cdot BH_3^- + 0.5B_2H_6 \longrightarrow H_2P(BH_3)_2^- \qquad (13)$$

base reaction is the formation of $H_2P(BH_3)_2^-$ as a by-product of the $(H_2P \cdot BH_3)Li$ preparation, which most probably proceeds *via* eq 8 as a base displacement. These reactions of $H_2P \cdot BH_3^-$ are in agreement with a mechanism for the formation of $(NH_4^+)(H_2P(BH_3)_2^-)$ from phosphine–borane and ammonia which was presented by Parry[2] (eq 14 and 15).

$$H_3P \cdot BH_3 + NH_3 \longrightarrow H_2P \cdot BH_3^- + NH_4^+ \qquad (14)$$

$$H_2P \cdot BH_3^- + H_3P \cdot BH_3 \longrightarrow H_2P(BH_3)_2^- + PH_3 \qquad (15)$$

Exchange of PH_2 Hydrogens in CD_3CN.—The proton nmr spectrum of $(H_2P \cdot BH_3)Li$ in CD_3CN changes drastically within a few hours after dissolving the solid in CD_3CN. After 3 hr at room temperature the intensity of the PH_2 signals decreases noticeably, and the intensity of the signals due to the small amount of partially protonated acetonitrile increases. After 6 hr the intensity of the PH_2 proton signal has gone to zero while the formation of protonated acetonitrile is shown by a strong signal. No change in intensity occurs on the BH_3 proton signals. The exchange of hydrogen for deuterium probably proceeds *via* a series of acid–base reactions such as

$$H_2P \cdot BH_3^- + CD_3CN \longrightarrow H_2DP \cdot BH_3 + CD_2CN^- \qquad (16)$$

$$H_2DP \cdot BH_3 + CD_3CN \longrightarrow HDP \cdot BH_3^- + CD_3CNH^+ \qquad (17)$$

The ion $H_2P(BH_3)_2^-$, however, does *not* exchange with CD_3CN even at 80° or with D_2O at room temperature. Apparently exchange is kinetically possible only if phosphorus is tricoordinated as in $H_2P \cdot BH_3^-$.

These results compare quite well with exchange studies on hypophosphorous acid and its anion. A comparison of these systems is especially interesting because it has been found that various oxy acids or anions and their isoelectronic analogs with BH_3 groups instead of oxygen behave chemically very similarly.[14] Jenkins and Yost[15] have shown that the kinetics of

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(5) A. P. Gray and R. C. Lord, *J. Chem. Phys.*, **26**, 690 (1957).

(6) J. A. Lannon and E. R. Nixon, *Spectrochim. Acta, Part A*, **23**, 2713 (1967).

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(8) W. Sawodny and J. Goubeau, *Z. Anorg. Allg. Chem.*, **356**, 289 (1968).

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(10) R. C. Taylor, *J. Chem. Phys.*, **26**, 1131 (1957).

(11) A. B. Burg, *Inorg. Chem.*, **3**, 1325 (1964).

(12) R. W. Rudolph, R. W. Parry, and C. F. Farran, *ibid.*, **5**, 723 (1966).

(13) L. C. D. Groenweghe, L. Maier, and K. Moedritzer, *J. Phys. Chem.*, **66**, 901 (1962).

(14) J. L. Malone and R. W. Parry, *Inorg. Chem.*, **6**, 817 (1967).

(15) W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, **11**, 297 (1959).

P–H exchange *and* of oxidation to phosphorous acid follow the same rate law. As the rate-determining step the conversion of $H_2PO(OH)$ with tetracoordinated phosphorus into its tautomeric form $HP(OH)_2$ with tricoordinated phosphorus has been postulated. A clear test naturally is impossible because $HP(OH)_2$ is present only in an extremely small amount and cannot be isolated. However the analogous behavior of the tri- and tetracoordinated boron–phosphorus anions supports this mechanism.

Experimental Section

General Information.—Standard high-vacuum techniques were used throughout except as specifically noted. Nonvolatile air-sensitive substances were handled in a nitrogen-filled glove box. All reagents were checked for purity by examination of vapor pressure and infrared data.

Phosphine, diborane, and phosphine–borane were prepared as described previously.[1] Diethyl ether, triglyme, and *n*-hexane were vacuum distilled from $LiAlH_4$ into the reaction vessel.

Infrared spectra were obtained for Nujol and Halocarbon oil mulls of solid $(H_2P \cdot BH_3)Li$. The mulls were prepared in a glove box and the CsI plates were taped together to exclude air. The spectra were measured from 4000 to 250 cm^{-1} using a Perkin-Elmer Model 457 spectrometer. For the Nujol mull a drastic loss of ir transmission occurred below 400 cm^{-1} which probably is due to strong reflection losses at the solid–liquid interface. The absorptions below 400 cm^{-1} therefore were taken from the Halocarbon oil mull spectrum.

The Raman spectrum of solid $(H_2P \cdot BH_3)Li$ was recorded with a Coderg PH 1 instrument.

Proton nmr spectra were obtained for approximately 1 *M* CD_3CN solutions of the compounds, using a Jeol C-60-HL spectrometer (operating at 60 Mc). As the internal standard TMS was used. The spectrum of the $(H_2P \cdot BH_3)Li$ solution was recorded immediately after adding the solvent to the solid. The solvation is a strongly exothermic process. The nmr tube therefore has been cooled during dissolving the substance in order to slow down exchange reactions. Exchange in $(H_2P(BH_3)_2)Li$–CD_3CN solutions has been studied in a sealed nmr tube. No exchange occurred during 1 week at room temperature and during 6 hr at 85°.

Preparation of $(H_2P \cdot BH_3)Li$. (a) In Diethyl Ether.—Diethyl ether (30 ml) was condensed onto $H_3P \cdot BH_3$ (19.5 mmol) and the adduct was dissolved at the lowest possible temperature (about $-20°$). At temperatures above $-20°$ considerable dissociation occurs. The solution was frozen down to $-196°$ and an exactly equimolar amount of *n*-butyllithium dissolved in *n*-hexane was added with a syringe. The system was allowed to warm slowly from -196 to $-20°$ and was kept at $-20°$ for 2 hr with continuous stirring. Afterward the colorless clear solution was warmed to room temperature and all volatile materials were pumped off. During removal of the solvent two liquid layers formed, one apparently containing the solvated $Li(H_2P \cdot BH_3)$ and the other, pure solvent. The volatile products were fractionated and a small amount of phosphine (0.24 mmol), but no diborane, was found. The nonvolatile residue was extracted with diethyl ether and the ether was pumped off *in vacuo*. In the absence of oxygen, white $(H_2P \cdot BH_3)Li$ crystallized; oxygen impurities gave a yellow product. The yield was 1.002 g (=95.5%, based on originally taken $H_3P \cdot BH_3$). The compound did not react with carefully dried oxygen in the absence of solvent. *Anal.* Calcd for LiH_2PBH_3: H, 9.38; B, 20.1; P, 57.6; H^-, 5.62 (calcd according to eq 9); C, 0.00. Found: H, 9.51; B, 19.9; P, 57.00; H^-, 5.54; C, 0.31.

The C content can be used to make sure that only a minor side reaction according to eq 5 and 6 occurs. If the reaction with *n*-butyllithium is carried out at 0° instead of $-20°$, the C value increases to about 7%. Likewise infrared absorptions in the C–H stretching region are very weak, if the reaction is carried out at $-20°$, and are strong, if higher temperatures are used. In all preparations a minor amount of $H_2P(BH_3)_2Li$ was formed which could be detected by its proton nmr spectrum. If equimolar amounts of reactants were used, the $H_2P(BH_3)_2Li$ impurity amounted to less than 5% whereas with excess phosphine–borane the band intensity of the impurity increased considerably.

(b) In *n*-Hexane.—$H_3P \cdot BH_3$ (14.60 mmol) did not dissolve in 30 ml of *n*-hexane even at room temperature, but strong gassing due to dissociation started. After addition of an equimolar amount of *n*-butyllithium at $-196°$ reaction started only at room temperature and was over after 0.5 hr. The volatile substances were fractionated and 1.07 mmol of phosphine (=7.3%, based on originally taken $H_3P \cdot BH_3$), but no diborane, was collected. The infrared spectrum of the nonvolatile ether-soluble residue showed strong absorptions in the C–H stretching region. Both the unreacted phosphine and the C–H absorption are indicative of the reaction of dissociated diborane with *n*-butyllithium according to eq 5.

Hydrolysis of $(H_2P \cdot BH_3)Li$.—A 1.40-mmol sample of $(H_2P \cdot BH_3)Li$ was dissolved in 10 ml of ether and a glacial acetic acid–water (1:1) mixture was added at $-196°$. Vigorous reaction started at low temperature. H_2 evolution ceased after stirring for 0.5 hr at room temperature. Addition of dilute HCl produced some more H_2. The solution was fractionated and the H_2 yield was determined with a Toepler pump. A 1.22-mmol amount of phosphine (=87.2%) and 4.14 mmol of hydrogen (=98.5%) were produced, but no diborane. If the hydrolysis was carried out slowly, a clear colorless solution was obtained, whereas some black insoluble material was formed if the reaction was too vigorous. In this case the B–H hydrogens were hydrolyzed only partially and the yield was too low.

Thermal Decomposition of $(H_2P \cdot BH_3)Li$. (a) In the Solid State.—A 4.20-mmol sample of $(H_2P \cdot BH_3)Li$ was pyrolyzed *in vacuo* (10^{-2} Torr) and all volatile products were pumped off continuously. H_2 evolution started slowly at 85°. The temperature was raised gradually to 115° and 2.78 mmol of H_2 was evolved over a period of 4 hr. Prolonged heating produced no further hydrogen. A small amount of phosphine (0.28 mmol), but no trace of diborane, was formed. Further heating to about 160° was necessary to start H_2 evolution again. Between 160 and 240° 2.47 mmol more of H_2 was formed during 4 hr, but no phosphine or diborane. A total of 5.25 mmol of H_2 was formed therefore which corresponds exactly to a formation of 5.00 mmol of H_2 from 4.00 mmol of $(H_2P \cdot BH_3)Li$. The dark nonvolatile residue still reacts with water, phosphine being formed.

(b) In Solution.—$(H_2P \cdot BH_3)Li$ (1.95 mmol) was dissolved in 20 ml of triglyme and the solution was gradually heated *in vacuo* in a closed system to 180°. No hydrogen and only a trace of phosphine (0.5 ml) were formed. No attempt was made to recover and identify the unreacted starting material because even the much more volatile monoglyme can be pumped off *in vacuo* only with great difficulty.

Reaction of $(H_2P \cdot BH_3)Li$ with Diborane.—A sample of 1.36 mmol of $(H_2P \cdot BH_3)Li$ was dissolved in 20 ml of diethyl ether and 0.68 mmol of diborane was condensed at $-196°$ into the reaction tube. After warming up to room temperature the volatile products were fractionated and 0.24 mmol of hydrogen and 0.06 mmol of diborane were collected. The nonvolatile residue was extracted with diethyl ether. After removal of the solvent 0.080 g of $H_2P(BH_3)_2Li$ (=87%, based on $(H_2P \cdot BH_3)Li$) was collected. The salt was characterized by its proton nmr spectrum.

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