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The Preparation and Structure of Ammonia and Alkylamine Addition Compounds of Phosphine Diborane, $B_2H_6 \cdot PH_3 \cdot NR_3$

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The compound of empirical composition $B_2H_6 \cdot PH_3 \cdot NH_3$, formed by the reaction of ammonia with H_3BPH_3, has the structure $[NH_4]^+[H_2P(BH_3)_2]^-$. The structure is conclusively supported by chemical evidence, by ^1H, ^{11}B, and ^{31}P nmr spectra, and by infrared spectra. In terms of a useful analogy relating the isoelectronic BH_3 group and an O atom as ligands, the compound $[NH_4][H_2P(BH_3)_2]$ is the BH_3 analog of ammonium hypophosphite, $[NH_4][H_2PO_2]$.

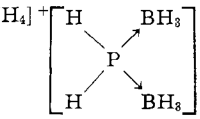
The phosphine adduct of diborane, first reported by Gamble and Gilmont,[1] is now known to have the simple monomeric structure H_3PBH_3.[2,3] On the other hand, the material resulting from the reaction of NH_3 with H_3PBH_3 at −45° or below is *not* the expected base displacement product H_3NBH_3. In the H_3N–H_3PBH_3 reaction about 50% of the original phosphine is displaced to give a compound of empirical composition $B_2H_6 \cdot PH_3 \cdot NH_3$. In terms of the earlier[1,4] representation of phosphine borane as a phosphonium salt, the ammonia reaction could be neatly interpreted by eq 1.

$$NH_3 + [PH_4][H_2P(BH_3)_2] \longrightarrow [NH_4][H_2P(BH_3)_2] + PH_3 \quad (1)$$

However, the recently established fact that phosphine borane exists as the simple monomeric H_3PBH_3 rather than the dimeric phosphonium salt, $[PH_4][H_2P(BH_3)_2]$, complicates the chemical interpretations.

In this paper it will be shown that the compound $B_2H_6 \cdot PH_3 \cdot NH_3$ is properly formulated as $[NH_4][H_2P(BH_3)_2]$. This structure, suggested originally by Gamble and Gilmont[1] and by Burg[4] on the basis of an analogy to the then accepted structure for the diammoniate of diborane, $[NH_4][H_2N(BH_3)_2]$, *is* correct even though the structures of the model compound, $B_2H_6 \cdot 2NH_3$, and of the parent compound, H_3PBH_3, are known to be different from those originally accepted.

Under carefully controlled conditions (see Experimental Section) the following reaction occurs



$$2H_3PBH_3(s) + NH_3(g) \longrightarrow PH_3(g) + [NH_4]^+\left[H_2P(BH_3)_2\right]^- \quad (2)$$

In terms of the oxygen–borane analogy used earlier in this laboratory[5] to interpret the reactions of carbon monoxide borane, etc., the ion $[H_2P(BH_3)_2]^-$ can be considered as the formal borane analog of the hypophosphite anion, $[H_2P(O)_2]^-$.

The dimethylammonium, methylammonium, sodium, and potassium salts of the anion $[H_2P(BH_3)_2]^-$ have been prepared. All salts are air stable, crystalline solids which dissolve in alcohol, acetone, diethylene glycol dimethyl ether, and water. Relatively slow decomposition occurs in water. The salts are insoluble in carbon tetrachloride, diethyl ether, and trichloroethane.

Chemical Evidence for the Structure of $B_2H_6 \cdot PH_3 \cdot NH_3$.—The formula written for the compound $B_2H_6 \cdot PH_3 \cdot NH_3$ is supported by reactions which can be summarized by eq 3–7. Attempts to prepare NaH_2P-

$$[NH_4][H_2P(BH_3)_2] + Na \xrightarrow[-78°]{NH_3(l)} Na[H_2P(BH_3)_2] + {}^1/_2H_2 + NH_3 \quad (3)$$

$$[NH_4](aq)^+ + [H_2P(BH_3)_2](aq)^- + Na(aq)^+ + [B(C_6H_5)_4](aq)^- \xrightarrow[0°]{H_2O} Na(aq)^+ + [H_2P(BH_3)_2](aq)^- + [NH_4][B(C_6H_5)_4](s)\downarrow \quad (4)$$

$$[NH_4](aq)^+ + [H_2P(BH_3)_2(aq)^- + 6H_2O + H(aq)^+ + Cl(aq)^- \longrightarrow H_3P(g)\uparrow + [NH_4](aq)^+ + Cl(aq)^- + 6H_2 + 2B(OH)_3(aq) \quad (5)$$

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[1] E. L. Gamble and P. Gilmont, *J. Am. Chem. Soc.*, **62**, 717 (1940).

[2] E. L. McGandy, *Dissertation Abstr.*, **22**, 754 (1961). Laboratory of Professor K. Eriks, Boston University.

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

[4] (a) A. B. Burg, *Record Chem. Progr.*, **15**, 159 (1954); (b) H. J. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 1 (1942).

[5] (a) J. C. Carter and R. W. Parry, *J. Am. Chem. Soc.*, **87**, 2354 (1965); (b) L. J. Malone and R. W. Parry, *Inorg. Chem.*, **6**, 817 (1967); (c) G. Kodama and R. W. Parry, *J. Inorg. Nucl. Chem.*, **17**, 125 (1961).

$$[NH_4][H_2P(BH_3)_2](s) + (CH_3)_2NH(l) \xrightarrow[25°]{-196\text{ to}} [(CH_3)_2NH_2][H_2P(BH_3)_2] + NH_3 \quad (6)$$

$$[(CH_3)_2NH_2][H_2P(BH_3)_2] + NaNH_2 \xrightarrow[\text{or without solvent}]{\text{formamide}} NH_3(g) + (CH_3)_2NH(g) + Na[H_2P(BH_3)_2](s) \quad (7)$$

$(BH_3)_2$ by the direct reaction of NaH_2P and B_2H_6 were not successful in our hands, perhaps because of solubility problems. The sodium salt, $Na[H_2P(BH_3)_2]$, prepared in reaction 3 was identical with that prepared in reactions 4 and 7; samples prepared in all these processes were used for the proton nmr studies discussed in the next section. When the dimethylammonium salt was substituted for the ammonium salt in reaction 4, the sodium salt obtained as a product was identical with that prepared from the ammonium salt. When the potassium salt was hydrolyzed by acid (reaction 5), the stoichiometry was identical with that given in reaction 5 except that KCl remained as a product in solution instead of NH_4Cl. Clearly, the anion is sufficiently stable to maintain its identity through metathesis reactions carried out in neutral aqueous solutions, in liquid ammonia, and in formamide solutions.

The Nuclear Magnetic Resonance Spectra of the $H_2P(BH_3)_2^-$ Anion. The Proton Nmr Spectrum (60 Mc).—The proton spectrum of $NaH_2P(BH_3)_2$ was taken at 0° in D_2O using a Varian HA 60 instrument. The expected quartet arising from the six hydrogens of the BH_3 groups (J_{BH} = 91 cps, δ 0.49 ppm downfield from TMS) and the expected doublet arising from the two hydrogens attached to phosphorus (J_{PH} = 350 cps, δ 3.17 ppm downfield from TMS) are clearly apparent. In this study the ammonium salt gave the spectrum of highest resolution, which is shown in Figure 1. It is seen that *each member of the P–H doublet* is split into a 1:5.8:15:20:15:6.3:1.5 septet with J_{HPBH} equal to 7.1 cps. The peak heights correspond to splitting by six equivalent protons of the two BH_3 groups (theory: 1:6:15:20:15:6:1), rather than to splitting by the two attached boron atoms of spin $^3/_2$. That the protons rather than the borons are responsible for the splitting was shown unequivocally by examining the spectrum of $H_2P(BD_3)_2^-$. The signal due to the two hydrogens attached to the phosphorus was split into a broad doublet but no further splitting could be observed. Coupling constants and chemical shift data for the ammonium, methylammonium, dimethylammonium, and sodium salts of $H_2P(BH_3)_2^-$ are shown in Table I. The values for J_{BH} and J_{PH} of 90 and 321 cps, respectively, are roughly consistent with values of 90 and 350 cps obtained by Shoolery[6] in an early study of the related compound $(CH_3)_2PHBH_3$. Our reexamination[7] of this same compound, $(CH_3)_2PHBH_3$, using better instrumentation, gives a value of 97.6 cps for J_{BH} and 365 cps for J_{PH}.

The peak heights for the two members of the P–H doublet are not equal in the spectra of any of the $H_2P(BH_3)_2^-$ salts. In $NaH_2P(BH_3)_2$ the high-field member is about 0.8 of the height of the low-field member, but the ratio of high-field peak area to low-field peak area is about 0.95.

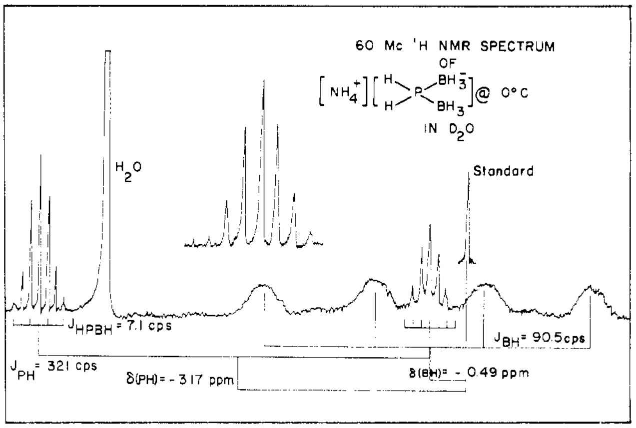


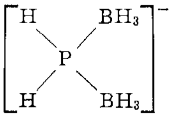
Figure 1.—Proton nmr spectrum of ammonium bisboranohypophosphite.

If the ^{11}B creating the quartet is present with its normal abundance of 80%, the ratio of the area under one of the four B–H peaks to the area under one of the two P–H peaks should be 1.2:1.0. Experimentally, the ratio is approximately 1.1:1 0.[8]

The ^{11}B Nmr Spectrum (32.1 Mc).—The ^{11}B spectrum of $[NH_4][H_2P(BH_3)_2]$ measured in H_2O consists of a 1:3:3:1 quartet centered at 59.8 ppm upfield from $B(OCH_3)_3$ (J_{BH} = 91.2 cps) (Figure 2). Each member of the quartet is split into a doublet (J_{BP} = 60 cps) [see Table I]. For the related $(CH_3)_2PHBH_3$ the comparable value of J_{BP} = 54.3 cps.[7]

The ^{31}P Nmr Spectrum (40.4 Cps).—The ^{31}P spectrum for $[NH_4][H_2P(BH_3)_2]$, measured in saturated aqueous solution, showed a 1:2:1 triplet with a J_{PH} of 320 ± 10 cps (δ 117 ± 10 ppm upfield from 85% H_3PO_4). Because of low signal strength the separation of noise from spectral details was troublesome and no further assignments were attempted.

The three nmr spectra indicate without question the validity of the structure



The Infrared Spectrum.—The symmetry of the $H_2P(BH_3)_2^-$ anion may be classified as C_{2v}.[9] The expected $3N - 6$ fundamental vibrations should include

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(6) J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).

(7) K. W. Morse, Ph.D. Dissertation, University of Michigan, 1966.

(8) The ^{10}B septet overlaps the two central members of the boron quartet and one member of the phosphorus doublet. For this reason, the area under one of the nonoverlapping (outer) ^{11}B–H peaks was compared to the area under one of the nonoverlapping P–H peaks. The precision of the area measurement was not high and the 1.1 measured ratio constitutes satisfactory agreement with the expected 1.2 value.

(9) C_{2v} symmetry has also been assumed by Herzberg for the propane molecule (G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Princeton, N. J., 1945, p 359), which is a structural analog of the $H_2P(BH_3)_2^-$ anion. As noted by Herzberg, completely free rotation is not assumed to occur in propane and preferred conformations such as one requiring one hydrogen of each terminal methyl group in the symmetry plane containing the three carbons is required for a strict C_{2v} designation.

TABLE I

NMR DATA FOR VARIOUS $H_2P(BH_3)_2^-$ SALTS

		J_{PH}, cps	J_{BH}, cps	J_{BP}, cps	J_{HPBH}, cps	δ(BH),[a] ppm	δ(PH),[a] ppm	δ(CH),[a] ppm
$[NH_4][H_2P(BH_3)_2]$	$^1H^a$	321	90.5	...	7.1	−0.49	−3.17	
	$^{11}B^b$	...	91.2	60	...	+59.8	...	
	$^{31}P^c$	320 ± 10	...	...	...	...	117 ± 10	
$NaH_2P(BH_3)_2$	$^1H^a$	322	90.5	...	7.1	−0.48	−3.16	
$[(CH_3)_2NH_2][H_2P(BH_3)_2]$	$^1H^a$	319	91.5	...	6.9	−0.46	−3.11	−2.7
	$^{11}B^b$	...	92.6	61	...	57.3	...	...
$[CH_3NH_2][H_2P(BH_3)_2]$	$^1H^a$	322	92	...	7.2	−0.43	−3.16	−1.3

[a] Chemical shifts for protons based on tetramethylsilane as a standard. [b] Chemical shifts for ^{11}B based on trimethyl borate. For temperatures below −29° trimethylboron was used [$\delta B(OCH_3)_3 - \delta B(CH_3)_3 = 68$ ppm; determined at −30 and −60°]. [c] Chemical shifts for ^{31}P based on 85% H_3PO_4.

TABLE II

INFRARED SPECTRA OF $M[H_2P(BH_3)_2]$ SALTS AND RELATED COMPOUNDS

$[NH_4][H_2P(BH_3)_2]$	$Na[H_2P(BH_3)_2]$	NH_4Cl	$[(CH_3)_2NH_2]Cl$	$[(CH_3)_2NH_2][H_2P(BH_3)_2]$	$[(CH_3)NH_2][H_2P(BD_3)_2]$	$K[H_2P(BH_3)_2]$	$K[H_2P(BD_3)_2]$	$[H_2PO_2^-]$
3200 cm^{-1} vs,		3200 cm^{-1}		3145 cm^{-1} vs	3170 cm^{-1} vs			
vbr ν_{NH}		3138		3110 vs	3120 vs			
		3044		3020 m	3020 ms			
		2810		2960 mw	2960 m			
				2785 mw	2820 mw			
			2600 - 3150 cm^{-1}	2660 mw	2680 w			
2376 vs ν_{as} PH_2	2385 cm^{-1}		2440 s	2445 vs	2430 mw			
	vs ν_{as} PH_2		2410 s	2420 vs				
2359 s ν_s PH_2	2335 vs			2375 vs	2360 sh	2380 cm^{-1} vs ν_{as} PH_2	2370 cm^{-1} ms	2345 ν_{as} PH
2336 vs ν_{as} B-H	ν_s PH_2			2350 s	2340 m	2345 vs $\nu_{as}BH$ ν_sPH_2	2345 m	2320 ν_{sym} PH
	ν_{as} B-H			2300 ms	2290 w	2295 vs ν_{sBH}		
2296 vs ν_s B-H	2290 vs ν_{sBH}		2280 sh	2275 ms				
		2000 vbr,			1850 ms			
		vw			1770 s		1770 s	
		1762 br, vw			1740 sh		1725 w	
1611 w, br								
			1475 s	1466 s	1460 vs			
				1446 m	1440 (sh)			
1406 ν_{N-H}		1403 s,	1430 ms	1435 m	1420 ms			
		sharp	1410 ms	1415 m				
				1352 ms	1335 s	1350 w?	1355 ms	
	1340 - 60 (br) ms			1330 sh	1267 mw			
			1265 ms	1234 w	1235 w			
1184 δ_{as} BH_3	1190 m δ_{as} BH_3		1238 m	1187 vs	1193 w	1190 m $\delta_{as}BH_3$		1194 P-C ν_a
				1158 m	1151 mw	1174 ms δ_{sPH_2}		1172 scissor H_2P
δ_s PH_2	1171 ms δ_{sPH_2}			1146 sh	1125 mw			
	1158 sh			1103 mw	1090 sh		1095 ms	
1070 vs δ_{sBH_3}	1065 s δ_{sBH_3} or		1085 mw	1062 - 67 s	1070 ms	1067 vs δ_{sBH} or ρ_{H_2P}		
1032 m ρ_{H_2P}	ρ_{H_2P}		1044 w	1032 m	1025 s		1025 ms	
			1026 s	1017 m				
884 s ρ_{BH_3}?				996 m	975 w			
				918 s	945		923 ms	
882 mv ρ_{H_2P}	878 ms ρ_{BH_3}?		878 ms	896 s	905 w			
	820 mw ρ_{H_2P}		868 ms	874 s		878 s ρ_{BH_3}?		
				810 w	818 ms	808 vw ρ_{H_2P}	810 ms	812 ρ_{H_2P}
642 ms	641 w				790 sh		782 w	
620 m ν_{P-B}	618 w ν_{P-B}				760 w			
	571 w				690 w	640 w	692 m	
566				629 m		608 w ν_{P-B}	594 w	
405 w - m				559 w		562 w		474 scissor PO_2
386								
293								
250 - 270								

22 vibrations which are infrared active and 5 vibrations which are Raman active only. The spectra for $M[H_2P(BH_3)_2]$ salts (where M = NH_4^+, Na^+, K^+, and $[(CH_3)_2NH_2]^+$), for $[(CH_3)_2NH_2][H_2P(BD_3)_2]$ and $K_2[H_2P(BD_3)_2]$, for NH_4Cl, for $[(CH_3)_2NH_2]Cl$, and for $H_2PO_2^-$ are shown in Table II. The data reveal clearly that the same anion is being considered in the four salts and that the spectrum of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ is a superposition of the spectra of $[(CH_3)_2NH_2]Cl$ and $K[H_2P(BH_3)_2]$. Tentative assignments listed in the table result from comparisons with the spectra of previously studied compounds, some of which are included in Table II.

The spectrum of the ammonium salt is clearly resolved into four peaks in the region 2250 to 2400 cm^{-1}. The highest peak at 2376 cm^{-1} can be assigned to the P–H asymmetric stretch and the lowest peak at 2296 cm^{-1} to the symmetric B–H stretch. Assignments are made on the basis of the constancy of the 2376-cm^{-1} band and the shift in the 2296-cm^{-1} band in the deuterated species, $H_2P(BD_3)_2^-$ (Table II). On the other hand, it has been impossible, at least until the present time, to assign the vibrations at 2359 and 2336 cm^{-1} unequivocally. One of these is the asymmetric B–H stretch while the second is the symmetric P–H stretch; unfortunately the bands are so close together and the

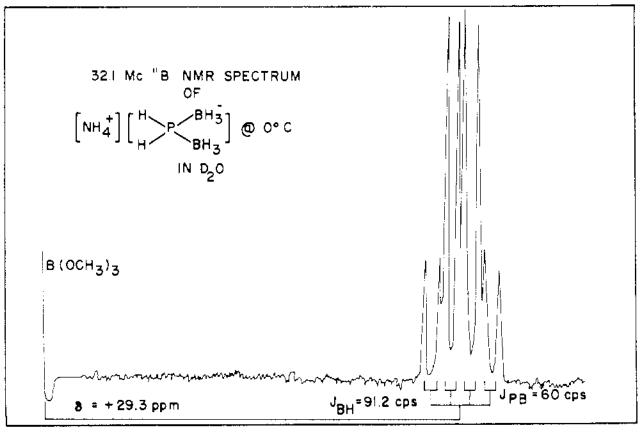

Figure 2.—Boron-11, 32.1-Mc nmr spectrum of ammonium bisboranohypophosphite.

peaks in $KH_2P(BD_3)_2$ and $KH_2P(BH_3)_2$ are so broad that we cannot tell which is which.

Upon deuteration the two B–D stretching modes appear as expected[10] at 1770 cm^{-1} (ν_{as}) and 1740–1725 cm^{-1} (ν_s).

Experimental Section

(1) **General Procedures and Reagents.**—Standard high vacuum techniques were used throughout except as specifically noted. All reagents were checked for purity by examination of vapor pressure and infrared data.

(2) **Preparation of $[NH_4^+][H_2P(BH_3)_2^-]$.**—In a representative run 8.43 mmoles of PH_3[11a] and 3.76 mmoles of B_2H_6[11b] were frozen into a reaction tube at −196°. The system was allowed to warm from −196 to −112° over a 4-hr period; then volatile components were removed. After further increase of the temperature from −112 to −78°, the remaining volatile components were removed. Since the combined amount of volatiles (H_3P and B_2H_6) removed corresponded to 6.99 mmoles, the amount of H_3PBH_3 remaining in the tube corresponded to 3.47 mmoles. An 8.45-mmole sample of NH_3 was frozen into the tube; then the system was held at −78° for 2 hr and at −45° for 22 hr. During this period 50.4% of the phosphine in H_3PBH_3 was liberated; ammonia was then distilled from the system over a 6-day period. During the first 3 days, the sample was warmed from −45 to −30°; during the fourth and fifth days the temperature was held at −30° then raised slowly to 25° during the sixth day. Less than 0.10 mmole of H_2 was evolved over-all. A white solid remained in the reaction tube. *Anal.* Calcd for $[NH_4][H_2P(BH_3)_2]$: total H, 15.27; N, 17.81; H$^-$, 7.64 mmoles/g; B, 27.5. Found: total H, 15.10; N, 17.70; H$^-$, 7.56 mmoles/g; B, 28.7. The X-ray diffraction powder gave *d* values as follows (A): 5.717 (m), 4.270 (mw), 4.040 (s, broad), 3.867 (w), 3.770 (vs), 3.648 (vvw), 3.028 (s), 2.849 (vvw), 2.706 (vvw), 2.462 (m), 2.417 (mw), 2.332 (w), 2.298 (mw), 2.156 (w), 2.127 (vvw), 2.076 (vvw), 2.049 (vvw), 2.010 (w), 1.969 (mw), 1.929 (w), 1.888 (m), 1.870 (m). This pattern could not be indexed in either the cubic or tetragonal system. The product was converted to the dimethylammonium salt as noted below; the molecular weight of the dimethylammonium salt was determined as reported in the next section. Spectroscopic characterization has been described in Tables I and II. The ammonium salt decomposed slowly when heated to give B_2H_6, PH_3, H_2, and an unidentified white solid.

(3) **Preparation of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$.**—The direct reaction of $(CH_3)_2NH$ and other amines with $H_{3-x}R_xPBH_3$ will be discussed in a subsequent paper. The dimethylammonium salt of boranohypophosphite can, however, be prepared by the base displacement reaction represented by the equation

$$[NH_4][H_2P(BH_3)_2] + (CH_3)_2NH \longrightarrow [(CH_3)_2NH_2][H_2P(BH_3)_2] + NH_3$$

A measured quantity of $(CH_3)_2NH$ (0.633 mmole) (Matheson Co.) was frozen (−196°) into a vacuum line reaction tube containing 0.332 mmole of $[NH_4][H_2P(BH_3)_2]$. Liberation of ammonia from the solid proceeded as the temperature rose to 25°. After about 12 hr a mixture of NH_3 and $(CH_3)_2NH$, identified by infrared and amounting to a total of 0.580 mmole, was removed at room temperature. The oil which remained was dissolved in D_2O. Its ^1H nmr and infrared spectra were those of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$. Solid $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ melted sharply at 65–66°; its molecular weight, determined by freezing point depression in formamide [K_f = 3.80] at a concentration range of 0.083 to 0.045 *m*, was 106 ± 3. Theory for $[(CH_3)_2NH_2][P(BH_3)_2]$ is 107.

Preparation of $K[H_2P(BH_3)_2]$.—The dimethylammonium salt indicated above could be converted to the potassium salt by use of the potassium form of an ion-exchange resin. A 0.1-g sample of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ was dissolved in 0.5 ml of H_2O and placed on an ion-exchange column containing 3 ml (volume) of 50–100 mesh Dowex 50 X 8 (K^+ form). The column was eluted with water until no more K^+ was detectable in a drop of the eluent using $NaB(C_6H_5)_4$. Evaporation of the water from the eluent under vacuum gave a white solid whose analysis and infrared and nmr spectra indicated $K[H_2P(BH_3)_2]$. *Anal.* Calcd for $K[H_2P(BH_3)_2]$: K, 39.1; B, 21.7; H, 8.0; H$^-$, 6.0. Found: K, 38.8; B, 21.7; H, 7.4; H$^-$, 5.8.

The X-ray powder pattern for $KH_2P(BH_3)_2$ can be represented as (A): 4.98 (ms), 4.60 (s), 3.86 (m), 2.73 (m), 2.51 (mw).

In some cases decomposition of the boranohypophosphite was evidenced by release of bubbles from the water solution during ion exchange. In such a case $KH_2P(BH_3)_2$ could be extracted in relatively pure form from the impure salt mixture using 1 or 2 ml of acetone. The salt could be recovered unchanged from acetone.

Reactions of $K[H_2P(BH_3)_2]$. (a) **Pyrolysis.**—A sample (0.103 mmole) of $KH_2P(BH_3)_2$ could be heated to 350° for 15 min in an evacuated tube with no evidence of gas evolution. When the salt was heated with a torch in an evacuated quartz tube to temperatures estimated at 500 to 700°, 90 to 100% of the theoretical hydrogen present originally as H$^-$ was evolved. More detailed pyrolysis studies are in progress.

(b) **Attempted Reaction with Ethylene.**—The solid salt will not react with ethylene in a stainless steel bomb at 7 atm pressure and a temperature of 45° for 4 days.

The Reaction of $[NH_4][H_2P(BH_3)_2]$ and $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ with Sodium Metal in Liquid Ammonia.—A sample amounting to about 0.5 mmole of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ or $[NH_4][H_2P(BH_3)_2]$ in a vacuum line reaction tube was allowed to react at −45° for 2 hr with about 0.3 g of Na[12] in 2 ml of liquid NH_3. A sample of H_2 (identified by its molecular weight of 2.8) amounting to 0.5 mmole of H_2/mmole of $[NH_4][H_2P(BH_3)_2]$ was removed by means of a Toepler pump. Excess Na metal was removed by adding several drops of mercury to the ammonia solution. The mercury and excess sodium were removed by filtration using the vacuum line filtration assembly. The condensable gases which were removed contained 1 mmole of $(CH_3)_2NH$/mmole of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$. The white solid which remained was identified as $Na[H_2P(BH_3)_2]$ by its infrared and nmr spectra.

The Reaction of $[NH_4][H_2P(BH_3)_2]$ and $[(CH_3)_2NH_2][H_2P$-

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[10] If one uses the simplified relationship $\nu_{X-H} = \nu_{X-D}\sqrt{M_D/M_H} = 1.41\nu_{X-D}$, the expected values would be somewhat lower than observed. On the other hand, the observed ratio of ν_{B-H}/ν_{B-D} is equal to 1.33, a ratio which is identical with that observed using Burg's data for $(CH_3)_2HPBH_3$ and $(CH_3)_2HPBD_3$: A. B. Burg and R. J. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

[11] (a) Prepared by pyrolysis of phosphorous acid at 200–250°: D. Gokhole and W. L. Jolly, *Inorg. Syn.*, to be published. (b) Obtained from Callery Chem. Co., Callery, Pa., and fractionated in a vacuum system.

[12] The weighed quantity of sodium was contained in a sealed bulb which was broken in the reaction system.

$(BH_3)_2]$ with $NaB(C_6H_5)_4$ in Water.—An approximately 0.6-mmole sample of the appropriate salt in 3 ml of H_2O at 0° was treated with an equimolar quantity of $NaB(C_6H_5)_4$ contained in 15 ml of ice water. The white precipitate which formed was filtered off in about 3 min, washed with ice water, and dried at 100°. The theoretical amount of $[R_2NH_2][B(C_6H_5)_4]$, R = H or CH_3, was obtained from the filter (X-ray powder pattern identification). $NaH_2P(BH_3)_2$ was identified in the filtrate by nmr.

The Hydrolysis of $[NH_4][H_2P(BH_3)_2]$.—A 0.500-mmole sample of $[NH_4][H_2P(BH_3)_2]$ was placed in a reaction tube; the tube was evacuated, then 3–4 ml of 6 *N* HCl was frozen in. After sealing the tube and allowing it to warm to +85° overnight, the contents were cooled to −196° and the tube opened to the vacuum line. The noncondensable gas recovered corresponded to 3.01 mmoles of H_2; the remaining volatile products were distilled through traps held at −78, −112, and −196°. A 0.332-mmole sample of PH_3 was recovered in the −196° trap (when necessary the PH_3 was separated from HCl by forming an azeotrope with H_2O and distilling off the free PH_3). The solid remaining contained NH_4Cl and $B(OH)_3$ (X-ray powder pattern). Boron present in the products was determined by titration in the presence of mannitol as described elsewhere:[13] experimental, 27.5%; theoretical based on equation, 28.7%. The equation which is consistent with all of the observation is

$$M[H_2P(BH_3)_2] + 6H_2O + HCl \longrightarrow H_3P + MCl + 6H_2 + 2B(OH)_3$$

The Reaction of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ with $NaNH_2$.—A 1.07-mmole sample of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ was mixed in a vacuum line reaction tube with a 1.74-mmole sample of $NaNH_2$[14] in a drybox. Immediate evolution of ammonia required rapid transfer of the tube to the vacuum line and freezing of the contents to −196°. After evacuation of the air, the system was allowed to warm to 25°, held for 30 min, and then raised to 100° for 45 min. Gaseous products which were evolved were fractionated and identified by vapor pressure measurements as NH_3 and $(CH_3)_2NH$. The white solid which remained was identified by infrared spectroscopy as $Na[H_2P(BH_3)_2]$.

This reaction was also run in formamide; a sample (0.88 mmole) of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$, 1.00 mmole of $NaNH_2$, and 2 ml of formamide were mixed. The $NaNH_2$ was added to a frozen solution of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ by rapidly removing the nitrogen-filled reaction tube from the line, adding solid $NaNH_2$, then rapidly replacing the reaction tube and evacuating the system. A sample (0.92 mmole) of gas was identified as NH_3 and a 0.84-mmole sample of gas was identified as $(CH_3)_2NH$. Formamide could not, however, be removed from the solid product.

Attempted Preparation of $Na[H_2P(BH_3)_2]$ by the Reaction of $NaPH_2$ and B_2H_6.—A solution of $NaPH_2$ in liquid NH_3, prepared by the reaction of Na with PH_3 in NH_3,[15] was filtered in the vacuum filtration apparatus. The volatiles were then removed at −78° (12 hr); then the N_2-filled, stoppered tube was transferred to the drybox where a sample (0.238 mmole) of $NaPH_2$ was weighed into a vacuum line reaction tube. After evacuation of the tube on the vacuum line, a 1.36-mmole sample of B_2H_6 was distilled into the system. The B_2H_6 was allowed to melt and held in contact with the solid phase for about 1 hr; the system was then warmed to room temperature and held for 12 hr. All but 0.07 mmole of B_2H_6 was recovered from the system. No evidence for $NaH_2P(BH_3)_2$ was found in the solid.

Attempts to dissolve $NaPH_2$ in diethyl ether and diglyme were unsuccessful. When NH_3 was used as a solvent, only $[(H_3N)_2BH_2]BH_4$ was detectable as a solid product [nmr in liquid NH_3 at −45°].

Physical Measurements.—Infrared spectra were obtained using a Beckman IR-12. Nmr spectra for ^{11}B and ^{31}P were obtained with a Varian Associates H-R 100 instrument operating at 94.1 and 40.4 Mc, respectively. Chemical shifts were determined by tube interchange. Proton nmr spectra were obtained with a Varian Associates HA-60 instrument.

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(13) F. J. Foote, *Ind. Eng. Chem., Ind. Ed.*, **4**, 39 (1932); T. C. Bissot, Doctoral Dissertation, University of Michigan, 1955.

(14) W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960, p 153.

(15) R. I. Wagner and A. B. Burg, *J. Am. Chem. Soc.*, **75**, 1369 (1953).

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Studies in the Synthesis and Chloramination of Some Hydrazinophosphines

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The new hydrazino phosphine derivatives $P[N(CH_3)N(CH_3)_2]_3$ and $C_6H_5P[N(CH_3)N(CH_3)_2]_3$ were prepared. The chloraminations of $C_6H_5P[N(CH_3)N(CH_3)_2]_2$, $[(C_6H_5)_2P]_2NN(CH_3)_2$, and $[(C_6H_5)_2P]_2NN[P(C_6H_5)_2](CH_3)$ were carried out in both the presence and absence of ammonia. As found in previous studies of P–N compounds, the phosphorus atoms are the sites of the chloramination reaction. In the absence of ammonia no dehydrochlorination occurs and multiply charged complex aminophosphonium ions are obtained from the chloramination of the bis- and trisphosphinohydrazines.

Recent work has shown that hydrazinophosphines can be prepared by allowing chlorophosphines to react, in the presence of an HCl acceptor, with hydrazines containing an N–H group.[1] We have used this method to prepare tris(1,2-trimethylhydrazino)phosphine and bis(1,2,2-trimethylhydrazino)phenylphosphine.

The reactions of chloramine with hydrazinophosphines and aminophosphines have indicated that the hydrazino or amino nitrogens apparently are inert to attack by chloramine;[2-5] it is rather the phosphorus

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(1) R. P. Nielsen and H. H. Sisler, *Inorg. Chem.*, **2**, 753 (1963).

(2) R. P. Nielsen, J. P. Vincent, and H. H. Sisler, *ibid.*, **2**, 760 (1963).

(3) H. H. Sisler and J. Weiss, *ibid.*, **4**, 1514 (1965).

(4) W. A. Hart and H. H. Sisler, *ibid.*, **3**, 617 (1964).

(5) D. F. Clemens and H. H. Sisler, *ibid.*, **4**, 1222 (1965).