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A Displacement Study and Proton Nuclear Magnetic Resonance Investigation of the Relative Base Strengths of the Dimethylaminophosphines with Triethylborane^{1,2}

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Received March 29, 1963

Pressure-composition studies were conducted on the homogeneous liquid systems of the dimethylaminophosphine triethylborane adducts $(\text{CH}_3)_2\text{PN}(\text{CH}_3)_2 \cdot \text{B}(\text{CH}_2\text{CH}_3)_3$, $\text{CH}_3\text{P}[\text{N}(\text{CH}_3)_2]_2 \cdot \text{B}(\text{CH}_2\text{CH}_3)_3$, $\text{P}[\text{N}(\text{CH}_3)_2]_3 \cdot \text{B}(\text{CH}_2\text{CH}_3)_3$ with trimethylamine. The systems $(\text{CH}_3)_3\text{P}-(\text{CH}_3)_3\text{N} \cdot \text{B}(\text{CH}_2\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{P}-\text{P}[\text{N}(\text{CH}_3)_2]_3 \cdot \text{B}(\text{CH}_2\text{CH}_3)_3$ were also studied. The data were treated in terms of a displacement reaction and allowed the estimation of the relative degree of displacement in each case. These orders of base strength toward $\text{B}(\text{CH}_2\text{CH}_3)_3$ resulted: $(\text{CH}_3)_3\text{P} > (\text{C}_6\text{H}_5)_3\text{N}$ and $(\text{CH}_3)_2\text{PN}(\text{CH}_3)_2 > \text{CH}_3\text{P}-[\text{N}(\text{CH}_3)_2]_2 > \text{P}[\text{N}(\text{CH}_3)_2]_3$. The assumptions involved in relating results of displacement reactions to relative base strengths are discussed. Proton n.m.r. spectra of the aminophosphines and their 1:1 liquid adducts with $\text{B}(\text{CH}_2\text{CH}_3)_3$ in cyclohexane solution were obtained. Interpretation of the spectra supported the order of base strengths determined by the displacement reactions. Proton n.m.r. spectra of the systems used in the displacement studies gave evidence for an exchange process.

Introduction

In compounds containing phosphorus-nitrogen linkages, it is of interest to determine the comparative donor properties of these atoms. It is known, for example, that in the reaction of methyl iodide with compounds such as dimethylaminodimethylphosphine,⁴ $(\text{CH}_3)_2\text{PN}(\text{CH}_3)_2$, and trisdiaminophosphine,⁵ $\text{P}[\text{N}(\text{CH}_3)_2]_3$, the methyl attachment is at the phosphorus atom rather than the "normally" more basic nitrogen atom. It has been suggested⁴ that the nitrogen atom has suffered a decrease in electron density as a result of π -bond formation with phosphorus.

In this paper relative base strengths of a series of aminophosphines are reported. Although earlier studies⁶ have shown that BF_3 , BCl_3 , and $\text{B}(\text{CH}_3)_3$ are unsuitable as reference acids because of complicating secondary reactions, the triethylborane adducts (all of which are liquid) proved to be sufficiently stable against further reaction to allow a study of the comparative base strengths in the series $(\text{CH}_3)_x\text{P}[\text{N}(\text{CH}_3)_2]_{3-x}$. A simple displacement study proved possible in view of the low volatility of all species except trimethylamine, the latter being used as the differentiating base. The condensed phases were homogeneous liquid systems. Proton n.m.r. spectra of the various bases and their triethylborane adducts also were obtained.

Experimental

Apparatus.—The apparatus and techniques employed have been adequately described.^{7,8} All mole fractions reported refer to condensed phase compositions.

(1) Phosphorus Nitrogen Chemistry. IX. Previous paper: R. R. Holmes and R. P. Wagner, *Inorg. Chem.*, **2**, 384 (1963).

(2) This paper represents, in part, part of the work submitted by Richard P. Carter, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

(3) Bell Telephone Laboratories, Inc., Murray Hill, N. J.

(4) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

(5) Unpublished work, P. C. Lauterbur and R. R. Holmes.

(6) R. R. Holmes and R. P. Wagner, *J. Am. Chem. Soc.*, **84**, 357 (1962).

Materials.—Trimethylamine was generated from the hydrochloride as previously described.⁷ The vapor pressure at -78.5° was 6.5 mm. and at 0° , 680 mm.

Samples of the dimethylaminomethylphosphines which were prepared previously⁶ were used. In each case the aminophosphine sample was refractionated just prior to its use since small increases in pressure were noted with time. Similarly the triethylborane (Callery) was purified and used according to the previous description⁶ and refractionated just prior to a determination. Representative vapor pressures are: $\text{P}[\text{N}(\text{CH}_3)_2]_3$, 2.2 mm. at 20.0° (lit.⁴ 2.8 mm. at 20°); $\text{CH}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$, 1.2 mm. at 0.0° ; $(\text{CH}_3)_2\text{PN}(\text{CH}_3)_2$, 12.7 mm. at 0.0° (lit.⁴ 12.53 mm. at 0.0°); $\text{B}(\text{CH}_2\text{CH}_3)_3$, 12.2 mm. at 0.0° (lit.⁹ 12.4 mm. at 0.0°).

Trimethylphosphine was taken from a sample used in previous work¹⁰ whose purification is therein described; vapor pressure at 0° , 159.0 mm. Cyclohexane (Spectroanalyzed Fisher Certified Reagent) used as a solvent in the n.m.r. investigation was dried over calcium hydride.

Results

The System $(\text{CH}_3)_3\text{N}-\text{CH}_3\text{P}[\text{N}(\text{CH}_3)_2]_2 \cdot \text{B}(\text{CH}_2\text{CH}_3)_3$.—Equimolar amounts (1.356 mmoles) of $\text{CH}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and $\text{B}(\text{CH}_2\text{CH}_3)_3$ were condensed together in the "reaction" section.⁷ The 1:1 liquid adduct that formed had a vapor pressure of 0.2 mm. at 0° , in agreement with a previous description.⁶

The pressure-composition diagram was determined at 0° (Fig. 1). The data represented in Table I show the total pressure, the mole fraction of $(\text{CH}_3)_3\text{N}$ in the condensed phase, the partial pressure of $(\text{CH}_3)_3\text{N}$, and the estimated equilibrium constants resulting from the following interpretation.

The curve (Fig. 1) shows that the solubility of $(\text{CH}_3)_3\text{N}$ is much greater than that expected for ideal behavior. It seems reasonable to assume that $(\text{CH}_3)_3\text{N}$ is displacing $\text{CH}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ from its adduct with $\text{B}(\text{CH}_2\text{CH}_3)_3$, giving rise to the equilibrium $(\text{CH}_3)_3\text{N}(\text{soln.}) + (\text{CH}_3)\text{P}[\text{N}(\text{CH}_3)_2]_2 \cdot \text{B}(\text{CH}_2\text{CH}_3)_3(\text{soln.}) =$

(7) R. R. Holmes, *J. Phys. Chem.*, **64**, 1295 (1960).

(8) R. R. Holmes, *J. Am. Chem. Soc.*, **82**, 5285 (1960).

(9) H. C. Brown, *ibid.*, **67**, 374 (1945).

(10) R. R. Holmes and E. F. Bertaut, *ibid.*, **80**, 2980 (1958).

TABLE I
EQUILIBRIUM DATA FOR THE TRIMETHYLAMINE-BIS-
(DIMETHYLAMINO)-METHYLPHOSPHINE TRIETHYLBORANE
SYSTEM AT 0°

Mole fraction ^a (CH ₃) ₃ N	Total pressure, mm.	(CH ₃) ₃ N pressure, mm.	K
0.0	0.2	0.0	
.135	2.0	1.6	10.2 ^b
.257	9.3	8.6	9.5
.333	19.7	18.9	9.3
.350	23.4	22.6	9.2
.396	34.3	33.5	9.5
.394	34.5	33.6	9.2
.438	49.8	48.9	9.6
.465	64.6	63.7	8.9
.514	99.5	98.6	8.4
.552	127.3	126.4	8.8
.579	154.0	153.1	8.7

^a Mole fraction, (CH₃)₃N, equals $N_1/N_1 + N_0$. ^b Value was not used in calculating the average.

(CH₃)₃N · B(CH₂CH₃)₃(soln.) + (CH₃)₂P[N(CH₃)₂]₂(soln.), particularly since it has been established^{8,9} that both bases involved form 1:1 liquid adducts with B(CH₂CH₃)₃ and no others.

Estimates of the equilibrium constant at 0° for the displacement process were made using a modified treatment⁷ based on Dolezalek's method¹¹ in which it is assumed that the unreacted components and products formed in solution obey Raoult's law. Recently a test of the latter assumption in the associating system⁷ PCl₃-(CH₃)₃N was made and found to be a good approximation in this case. Using the symbols

N_1 = moles of (CH₃)₃N in condensed phase
 N_0 = moles of aminophosphine-B(CH₂CH₃)₃ complex
 N_2 = moles of each of the products formed
 P_t = total vapor pressure
 p_1 = partial vapor pressure of (CH₃)₃N
 p_1^0 = vapor pressure of pure (CH₃)₃N
 a_1 = activity of (CH₃)₃N
 K = equilibrium constant

the following equations result

$$a_1 = p_1/p_1^0 = N_1 - N_2/N_1 + N_0$$

$$N_2 = N_1 - p_1/p_1^0(N_1 + N_0)$$

$$K = (N_2)^2/(N_1 - N_2)(N_0 - N_2)$$

To perform the calculations a method of successive approximations was used. First it was assumed that the pressure observed was due entirely to (CH₃)₃N and that the vapor behaved ideally. Values of N_2 were calculated as a function of concentration at each temperature.

The resulting values of N_2 allowed approximate amounts of the various components to be determined. Assuming all components in the displacement to behave ideally, their contribution to the total pressure at each point was evaluated. The value of the vapor pressure of pure (CH₃)₃N · B(CH₂CH₃)₃⁹ is 1.4 mm. at 0°. The value for CH₃P[N(CH₃)₂]₂ determined previously⁶ is 1.2 mm. at 0°, while the volatility of the B(CH₂CH₃)₃ adduct of CH₃P[N(CH₃)₂]₂ is sufficiently

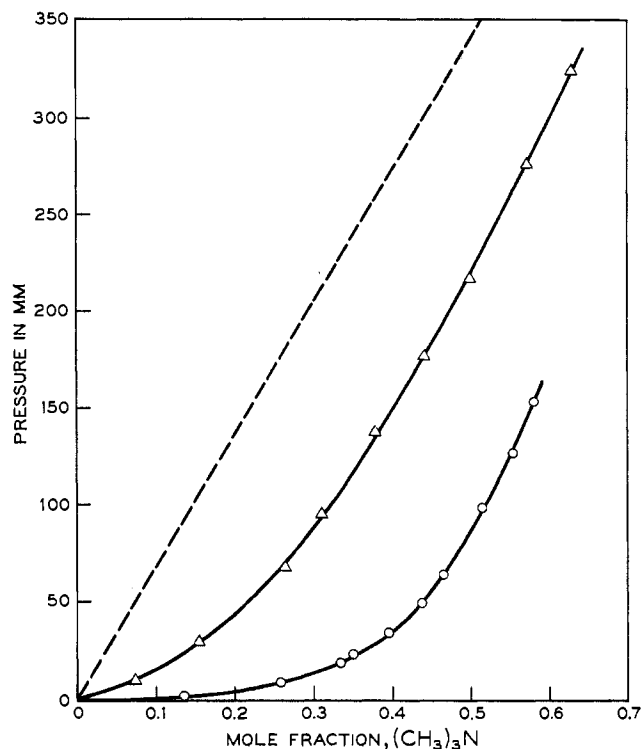


Fig. 1.—The (CH₃)₃N-CH₂P[N(CH₃)₂]₂ · B(CH₂CH₃)₃ system at 0°, O; the (CH₃)₃N-(CH₃)₂PN(CH₃)₂ · B(CH₂CH₃)₃ system at 0°, Δ; Raoult's law line, ---.

low that it need not be considered. Column 3 of Table I shows the pressure attributed to (CH₃)₃N. With corrected values of p_1 , the calculations were repeated to obtain values of K .

Considering the nature of the assumptions, the variation in the value of the equilibrium constant as a function of concentration is not extraordinary. The average value is 9.90 ± 0.32 , showing that the displacement toward (CH₃)₃N · B(CH₂CH₃)₃ is strongly favored. For example, at an amine mole fraction of 0.465 the estimated displacement is 80% complete based on (CH₃)₃N.

The System (CH₃)₃N-(CH₃)₂PN(CH₃)₂ · B(CH₂CH₃)₃.—Equivalent amounts (0.994 mmole) of (CH₃)₂PN(CH₃)₂ and B(CH₂CH₃)₃ were condensed together. The resulting 1:1 liquid adduct had a vapor pressure of 0.4 mm. at 0° and 2.2 mm. at 26.8°, in agreement with a previous description.⁶ The system was studied in a manner analogous to that used for the related CH₃P[N(CH₃)₂]₂ system described above. The data are summarized in Table II and shown in Fig. 1. It is seen (Fig. 1) that (CH₃)₃N is less soluble in this system compared to the CH₃P[N(CH₃)₂]₂ system, which indicates that the displacement does not proceed as far. Correspondingly, the value of the equilibrium constant calculated in this case (average, 0.35 ± 0.06 at 0°) is smaller.

In making the calculations of the contribution of the other components to the total vapor pressures, a vapor pressure of 12.5 mm.⁴ at 0° for (CH₃)₂PN(CH₃)₂ was used; the contribution of the B(CH₂CH₃)₃ adduct proved negligible. The resulting calculated vapor pressures of (CH₃)₃N are shown in column 3 of Table II.

The System (CH₃)₃N-P[N(CH₃)₂]₃ · B(CH₂CH₃)₃.—

(11) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 176.

TABLE II
EQUILIBRIUM DATA FOR THE TRIMETHYLAMINE-
DIMETHYLAMINODIMETHYLPHOSPHINE TRIETHYLBORANE
SYSTEM AT 0°

Mole fraction (CH ₃) ₂ N	Total pressure, mm.	(CH ₃) ₃ N pressure, mm.	K
0.0	0.4		
.0711	10.0	8.9	0.29
.152	30.2	28.4	.39
.264	69.2	66.7	.50
.309	96.0	93.4	.42
.379	138.4	135.6	.37
.380	137.7	134.9	.38
.442	178.1	175.3	.36
.445	177.3	174.5	.38
.499	218.0	215.2	.33
.571	277.0	274.4	.27
.628	324.7	322.3	.24

Equivalent amounts (0.427 mmole) of B(CH₂CH₃)₃ and P[N(CH₃)₂]₃ were condensed together. A sample of (CH₃)₃N was added to the adduct in the "reaction" section and stirred at 0°. The pressure equilibrated at 25.5 mm. after 2 hr. The mole fraction of (CH₃)₃N in the condensed phase, 0.465, was used to compute the equilibrium constant. The value obtained was 48.3, which corresponds to a displacement of P[N(CH₃)₂]₃ by (CH₃)₃N of 92% at this mole fraction. In making the latter calculation it was not necessary to consider the contribution of P[N(CH₃)₂]₃ because of its low volatility. The partial pressure of (CH₃)₃N · B(CH₂CH₃)₃ was calculated to be 0.6 mm. The contribution of P[N(CH₃)₂]₃ · B(CH₂CH₃)₃ proved small due to the high degree of displacement.

The System (CH₃)₃P-B(CH₂CH₃)₃ at 0°.—Additions of (CH₃)₃P to 1.052 mmoles of B(CH₂CH₃)₃ at 0° produced a white solid having a 1:1 composition shown by the rise in pressure near 1:1 in Table III. The complex

TABLE III
THE TRIMETHYLPHOSPHINE-TRIETHYLBORANE SYSTEM AT 0°

Mole fraction (CH ₃) ₃ P	Pressure, mm.	Observation
0.140	11.9	
.305	8.7	Liquid
.402	7.2	
.456	5.3	Solid-liquid
.479	5.0	
.487	21.2	Solid
.514	36.6	Solid-liquid
.553	37.3	Nearly all liquid
.573	46.3	Liquid
.596	56.4	
.616	65.2	
.644	76.3	
.659	82.4	

is very soluble in either excess (CH₃)₃P or excess B(CH₂CH₃)₃ as seen by the small range of the solid-liquid plateaus at 5 and 37 mm. The latter was confirmed by visual observation (column 3).

The System (CH₃)₃P-(CH₃)₃N · B(CH₂CH₃)₃.—The liquid adduct, (CH₃)₃N · B(CH₂CH₃)₃, 1.063 mmoles, was formed in the lower section of a double bulb ar-

angement attached to the "reaction" section. The lower bulb (volume about 10 ml.) was separated by a stopcock from the upper portion (volume about 500 ml.).

After introducing 1.161 mmoles of (CH₃)₃P and warming to 0°, a homogeneous liquid system was present. With the valve opened the system was allowed to come to equilibrium. The pressure rose slowly; solid started to separate out at 17 mm. The pressure rise continued to 35.0 mm. and thereafter remained constant. The gas phase was transferred out with the valve closed so as not to disturb the equilibrium. The gas proved to be substantially (CH₃)₃N; vapor pressure at -78.5°, 6.0 mm.; mol. wt. (vapor density) 57.3 (calcd. 59.1).

Since some solid, presumably (CH₃)₃P · B(CH₂CH₃)₃, separated out by the time equilibrium was reached, the determination was repeated at 0° confining the vapor phase to the smaller volume initially. The valve was opened and the pressure allowed to increase to 15 mm. The condensed phase was liquid. After closing the valve, the gas was analyzed as before. Similar results were obtained (vapor pressure 6.0 mm. at -78.5°, mol. wt. 62.0), allowing one to conclude that (CH₃)₃N was displaced nearly completely by (CH₃)₃P.

The System (CH₃)₃P-P[N(CH₃)₂]₃ · B(CH₂CH₃)₃.—To substantiate the low basicity of P[N(CH₃)₂]₃ shown by the data in the (CH₂)₃N-P[N(CH₃)₂]₃ · B(CH₂CH₃)₃ system, the corresponding system with (CH₃)₃P was studied at 0°. On adding (CH₃)₃P to P[N(CH₃)₂]₃ · B(CH₂CH₃)₃, the pressure remained low until approximately 1:1 was reached which qualitatively indicates that the introduction of the volatile component, (CH₃)₃P (vapor pressure at 0°, 159.0 mm.), caused almost complete displacement of P[N(CH₃)₂]₃. After 1:1 further additions of (CH₃)₃P caused the pressure to rise rapidly.

Proton N.m.r. Measurements.—Proton n.m.r. spectra were obtained at 60 Mc. with a Varian Associates HR-60 spectrometer. The spectra were recorded at room temperature and calibrated by the audio side-band technique.

Samples of the separate pure aminophosphines, their 1:1 liquid adducts with B(CH₂CH₃)₃, and related compounds were prepared in cyclohexane solvent (serving as an internal reference) using the vacuum line. The components were measured as gases or liquids, transferred to n.m.r. tubes along with measured amounts of cyclohexane solvent, and sealed under vacuum. The concentration of the samples was about 10% by volume. The n.m.r. spectrum of pure cyclohexane showed only one peak. The effect of change of concentration on the chemical shift was checked with (CH₃)₃N and (CH₃)₃N · B(CH₂CH₃)₃. No appreciable variation was found in the concentration range 5 to 30%.

The chemical shifts relative to cyclohexane and coupling constants reported in Table IV are average values of at least three determinations for which no noticeable variation in sweep rate per run was detected. The uncertainty associated with the N-CH₃ and P-CH₃

TABLE IV
PROTON CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS (J) OF AMINOPHOSPHINES
AND RELATED COMPOUNDS IN CYCLOHEXANE SOLUTION AT 25°

Compound	Chemical shift, p.p.m. ^a			Coupling constant, c.p.s.	
	δ_{N-CH_3}	δ_{P-CH_3}	$\delta_{B-CH_2CH_3}$	J_{HCNP}	J_{HCP}
$B(CH_2CH_3)_3$			0.41		
$(CH_3)_3P$		0.50			2.9
$(CH_3)_3P \cdot B(CH_2CH_3)_3$.30	.76		9.1
$(CH_3)_3N$	-0.66				
$(CH_3)_3N \cdot B(CH_2CH_3)_3$ ^b	-.86		.70		
$(CH_3)_2PN(CH_3)_2$	-1.03	.47		9.8	5.9
$(CH_3)_2PN(CH_3)_2 \cdot B(CH_2CH_3)_3$	-1.11	.28	.72	9.6	5.7
$CH_3P[N(CH_3)_2]_2$	-1.20	.27		9.0	7.4
$CH_3P[N(CH_3)_2]_2 \cdot B(CH_2CH_3)_3$	-1.16	.19	.62	8.4	3.8
$P[N(CH_3)_2]_3$	-1.08			8.6	
$P[N(CH_3)_2]_3 \cdot B(CH_2CH_3)_3$	-1.06		.52	8.8	

^a Relative to cyclohexane, internal reference. $\delta = (H - H_i/H_i) \times 10^6$. ^b See ref. 13.

chemical shifts is about ± 0.03 p.p.m. and ± 0.35 c.p.s. for that associated with the coupling constants. In all cases only spectra expected for the presence of the aminophosphines and their simple 1:1 adducts were observed, showing the absence of possible further reaction that might be expected analogous to that observed with aminophosphines and trimethylborane.⁶ Spectra of the samples recorded about a year later showed no change. The $\delta_{B-CH_2CH_3}$ listed in Table IV represent average values determined by the moment method.¹² The values also were estimated simply by measuring areas with a planimeter. The two procedures gave values which agreed to ± 0.04 p.p.m.

Proton spectra also were obtained on samples of the bases and their 1:1 adducts in pure liquid form (benzene capillaries were used as a means of external referencing). The spectral patterns were identical with those obtained in cyclohexane solution and coupling constants were similar to those reported in Table IV. The relative values of the chemical shifts were not the same as those obtained for the determinations performed in dilute cyclohexane solution, presumably due to differences in bulk diamagnetic susceptibility from sample to sample. In general, though, similar trends in the chemical shift data were seen in the pure liquid samples as were seen in the data obtained from samples dissolved in cyclohexane solution.

Representative spectra obtained in the absence of cyclohexane solvent are shown in Fig. 2a-c. Choosing the spectrum of $CH_3P[N(CH_3)_2]_2 \cdot B(CH_2CH_3)_3$ as typical, one sees, as a function of increasing field, a sharp doublet attributed to $N-CH_3$ protons split by phosphorus, another sharp doublet of one-fourth the area (shown by integrating the intensities) attributed to $P-CH_3$ protons again split by phosphorus, and partially resolved ethyl groups of $B(CH_2CH_3)_3$.

Proton n.m.r. measurements also were made at room

(12) W. Anderson and H. M. McConnell *J. Chem. Phys.*, **26**, 1496 (1957).

(13) O. Ohashi, Y. Kurita, T. Totani, H. Watanabe, T. Nakagawa, and M. Kubo, *Bull. Chem. Soc. Japan*, **35**, 1317 (1962), report the proton spectrum of $(CH_3)_3N \cdot B(CH_2CH_3)_3$ determined in the pure liquid state and list a $N-CH_3$ shift of -0.77 p.p.m. (relative to cyclohexane). Also a proton shift of -0.77 p.p.m. for $(CH_3)_3N$ is listed, reported to have been taken from an article by B. P. Dailey and J. N. Shooley, *J. Am. Chem. Soc.*, **77**, 3977 (1955). However, no such value was found in the latter reference. Since the shifts for $(CH_3)_3N \cdot B(CH_2CH_3)_3$ are in the pure liquid and not corrected for bulk diamagnetic susceptibility changes in going to cyclohexane solution, our results are not comparable.

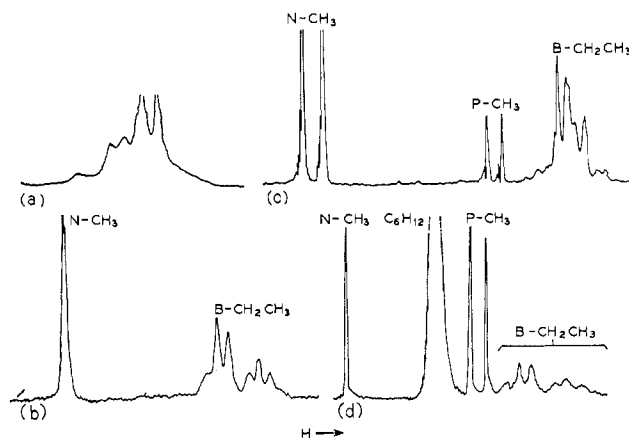


Fig. 2.—Proton n.m.r. spectra of pure liquid samples of (a) $B(CH_2CH_3)_3$, (b) $(CH_3)_3N \cdot B(CH_2CH_3)_3$, (c) $CH_3P[N(CH_3)_2]_2 \cdot B(CH_2CH_3)_3$, and (d) the system $(CH_3)_3N-(CH_3)_3P-B(CH_2CH_3)_3$, in cyclohexane solution.

temperature on cyclohexane solutions of the systems used in the displacement studies. Since these mixtures consisted of two bases competing for bonding with $B(CH_2CH_3)_3$, it might be expected that the proton spectrum would show the presence of the bases in both the uncoordinated and coordinated forms. In all spectra examined, however, in addition to the $B(CH_2CH_3)_3$ peaks, peaks appeared corresponding to the presence of only one form of each base.

The system $(CH_3)_3N-(CH_3)_3P-B(CH_2CH_3)_3$ is taken as representative (Fig. 2d). The components were present in the mole ratio (excluding cyclohexane) of amine to phosphine to $B(CH_2CH_3)_3$ of 0.9:1.3:1. Relative to the internal reference, cyclohexane, the peaks appeared as follows: $N-CH_3$, -0.68 p.p.m.; $P-CH_3$, $+0.33$ p.p.m.; $B-CH_2CH_3$, $+0.82$ p.p.m. Comparison of these data with the chemical shift data for the free bases and 1:1 adducts in Table IV indicates that the system may be regarded as a mixture of $(CH_3)_3P \cdot B(CH_2CH_3)_3$, $(CH_3)_3N$, and excess $(CH_3)_3P$. Thus the n.m.r. data on the system provide further support for the interpretation given the displacement study where it was concluded that $(CH_3)_3P$ displaced $(CH_3)_3N$ almost quantitatively from its $B(CH_2CH_3)_3$ adduct.

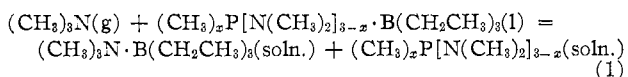
The fact that the $B(CH_2CH_3)_3$ shift is slightly higher upfield ($+0.82$ p.p.m. compared to $+0.76$ p.p.m. (Table IV) for the $(CH_3)_3P \cdot B(CH_2CH_3)_3$ adduct) most likely

means that the presence of excess base shifts the equilibrium more toward the adduct form. However, as Fig. 2d shows, only one P-CH₃ environment is indicated even though excess (CH₃)₃P is present. Hence it seems reasonable to conclude that the equilibrium involves rapid exchange of (CH₃)₃P between coordinated and uncoordinated forms.

Exchange is further supported by examining the n.m.r. spectrum of the system (CH₃)₃P-B(CH₂CH₃)₃, present in a mole ratio of phosphine to B(CH₂CH₃)₃ of 2.3:1. Again, only one (CH₃)₃P environment is seen in the n.m.r. spectrum. The position of the P-CH₃ doublet signal, +0.43 p.p.m., is moved further toward free (CH₃)₃P, +0.50 p.p.m., as it should with a greater excess of (CH₃)₃P than used in the (CH₃)₃N-(CH₃)₃P-B(CH₂CH₃)₃ system. The B-CH₂CH₃ shift was +0.80 p.p.m.

Discussion

The data obtained in the displacement studies show that the solubility of (CH₃)₃N at 0° as measured by the equilibrium pressure above the liquid aminophosphine-triethylborane systems increases along the series: (CH₃)₂PN(CH₃)₂ < CH₃P[N(CH₃)₂]₂ < P[N(CH₃)₂]₃. Since previous work has shown that the various bases involved⁶ including (CH₃)₃N⁹ form liquid 1:1 adducts with no evidence for any others, the presence of the equilibrium displacement is assumed



Furthermore, interpretation of the n.m.r. spectra of the liquid systems used in the displacement studies, as discussed above, conformed to the presence of such an equilibrium.

Accordingly, the variation in solubility of (CH₃)₃N is taken to reflect the degree of displacement in the different systems. Assuming that the degree of displacement parallels base strength the order toward B(CH₂CH₃)₃ is obtained: (CH₃)₂PN(CH₃)₂ > CH₃P[N(CH₃)₂]₂ > P[N(CH₃)₂]₃. Furthermore the displacement (CH₃)₃P(g) + (CH₃)₃N · B(CH₂CH₃)₃(l) = (CH₃)₃P · B(CH₂CH₃)₃(soln.) + (CH₃)₃N(g) was shown to proceed nearly quantitatively to the right by the demonstrated presence of essentially pure (CH₃)₃N above the solution. Thus the base strength of (CH₃)₃P is predicted to be greater than (CH₃)₃N toward B(CH₂CH₃)₃ on this basis.

Treatment of the pressure-composition data for the various aminophosphine systems in terms of a displacement process in solution yielded estimates of the "equilibrium constants." The constants are summarized in Table V and show the same ordering as that obtained on the basis of simple solubility considerations.

In either case, free energy considerations are involved and the assumed parallelism between equilibrium data and base strength implies that the entropy terms are similar from system to system.¹⁴ The latter

TABLE V
EQUILIBRIUM DATA IN THE TRIMETHYLAMINE-AMINOPHOSPHINE
TRIETHYLBORANE SYSTEMS AT 0°

	<i>K</i>	% displacement ^a <i>N</i> ₂ / <i>N</i> ₁
(CH ₃) ₃ N + (CH ₃) ₂ PN(CH ₃) ₂ · B(CH ₂ CH ₃) ₃	0.35	40
(CH ₃) ₃ N + CH ₃ P[N(CH ₃) ₂] ₂ · B(CH ₂ CH ₃) ₃	9.09	80
(CH ₃) ₃ N + P[N(CH ₃) ₂] ₃ · B(CH ₂ CH ₃) ₃	48.3	92

^a At an amine mole fraction of 0.465.

implication is reasonable for the systems in Table V since the aminophosphines are closely related in structure. The values of *K* (Table V), however, have significance only relative to each other since the entropy term for (CH₃)₃N may vary appreciably from that of the aminophosphines and even then may only be regarded as a crude approximation.

Ideally, one would like the gas phase values of the heat of dissociation of the aminophosphine · B(CH₂CH₃)₃ complexes. Comparison with the process actually investigated here (eq. 1) shows that aside from entropy considerations, two additional assumptions are involved in ordering the basicity of the aminophosphines *relative* to each other. They are

$$\Delta H_v B + \Delta H_v \Delta B_1 = \Delta H_v B_1 + \Delta H_v \Delta B$$

and

$$\Delta H_s B(\text{l}) = \Delta H_s B_1(\text{l})$$

where B and B₁ refer to two different liquid aminophosphines, A is B(CH₂CH₃)₃, Δ*H*_v is the heat of vaporization, and Δ*H*_s is the heat of solution in the equilibrium mixture. Both of these assumptions are reasonable when the bases B and B₁ are closely related in structure.

In the aminophosphine series reported here, the fact that the solubility of (CH₃)₃N or the estimated values of *K* vary considerably from system to system allows for appreciable violation of the assumptions without changing the order of basicity.

The literature¹⁴ shows in general that orders of stability determined by displacement reactions agree uniformly with the results of gas phase dissociation measurements where such measurements have been made; thus it is implied that the assumptions involved hold fairly well. In many of the studies where solids are present it must be further assumed that variations in crystal lattice energy along a series are relatively small. The latter assumption is not needed in the present investigation.

Table VI summarizes the changes in chemical shifts upon adduct formation for the compounds listed in Table IV. Assuming an upfield shift reflects an increase in electron density an order of base strengths may be derived from the proton n.m.r. data. As expected the average position of the B-CH₂CH₃ protons shifts upfield upon coordination with a basic center. The magnitude of the upfield shift is greatest with (CH₃)₃P and least with P[N(CH₃)₂]₃. The order of base strength toward B(CH₂CH₃)₃ arrived at in this man-

TABLE VI
CHANGE IN CHEMICAL SHIFTS ($\Delta\delta$) ON ADDUCT FORMATION WITH
TRIETHYLBORANE FOR AMINOPHOSPHINES AND RELATED
COMPOUNDS IN CYCLOHEXANE SOLUTION AT 25°

Compound	Change in chemical shift, p.p.m. ^a		
	$\Delta\delta_{N-CH_3}$	$\Delta\delta_{P-CH_3}$	$\Delta\delta_{B-CH_2CH_3}$
(CH ₃) ₃ P		-0.20	+0.35
(CH ₃) ₂ PN(CH ₃) ₂	-0.08	- .19	+ .31
(CH ₃) ₃ N	- .20		+ .29
CH ₃ P[N(CH ₃) ₂] ₂	+ .04	- .08	+ .21
P[N(CH ₃) ₂] ₃	+ .02		+ .11

^a A positive change indicates an upfield shift.

ner is (CH₃)₃P > (CH₃)₃N ~ (CH₃)₂PN(CH₃)₂ > CH₃-P[N(CH₃)₂]₂ > P[N(CH₃)₂]₃.

This agrees with the greater basicity of (CH₃)₃P over (CH₃)₃N and the ordering of base strength in the aminophosphine series toward B(CH₂CH₃)₃ obtained from the displacement study. In fact it is interesting to note that on the basis of the "equilibrium constant" (Table V), (CH₃)₃N is estimated to approximate (CH₃)₂PN(CH₃)₂ in base strength. Thus the correspondence in ordering obtained by the two methods strengthens the support for the interpretation. In agreement with the above consideration the P-CH₃ protons shift downfield on adduct formation with B(CH₂CH₃)₃, reflecting an expected decrease in electron density.

Previously, chemical shifts of methyl protons in adducts of methyl-substituted bases and chemical shifts of B-methyl protons in B(CH₃)₃ adducts revealed¹⁵ a correlation with gas phase dissociation data relating to the stability of the adducts. Of seventeen complexes for which the comparison was made, there was one reversal in order. Less success was achieved, however, when internal chemical shifts of ethyl groups (*i.e.*, the shift between the methyl and methylene peaks) were used to correlate base strength.^{15,16} In agreement with the internal chemical shift criterion it is noted from the appearance of the B(CH₂CH₃)₃ spectra in Fig. 2a-c that the internal shift, $\delta_{CH_3} - \delta_{CH_2}$, becomes increasingly more negative in going from B(CH₂CH₃)₃ to CH₃P[N(CH₃)₂]₂·B(CH₂CH₃)₃ to (CH₃)₃N·B(CH₂CH₃)₃, *i.e.*, as the electronegativity of boron is being progressively lowered by adduct formation with bases of increasing strength. The poor resolution of the B-CH₂CH₃ groups (presumably caused by quadruple relaxation of the boron nucleus) prevented a reliable calculation of the internal shifts. Using the moment method,¹² however, a value of +0.18 p.p.m. resulted for B(CH₂CH₃)₃ and -0.34 p.p.m. for (CH₃)₃N·B(CH₂CH₃)₃. Using the Dailey-Shoolery relationship,^{16,17}

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electronegativity = 0.695($\delta_{CH^*} - \delta_{CH_2}$) + 2.1, an electronegativity of 2.2 for the boron atom in B(CH₂CH₃)₃ and 1.9 for the boron atom in (CH₃)₃N·B(CH₂CH₃)₃ resulted. These values compare with orbital electronegativities of 2.01 for tricoordinated boron (sp² hybridization) and 1.85 for tetracoordinated boron (sp³ hybridization) cited by Ferreira.¹⁸

The proton n.m.r. data yield little information concerning the point of attachment of B(CH₂CH₃)₃ in the aminophosphine adducts. However, in the case of the two bases, (CH₃)₃P and (CH₃)₃N, having only one basic center, there is little question concerning the point of attachment of B(CH₂CH₃)₃. The order of base strength observed here with B(CH₂CH₃)₃, (CH₃)₃P > (CH₃)₃N, is opposite to the order of these two bases with B(CH₃)₃.¹⁹ The reversal most likely is associated with the larger size of the ethyl groups resulting in an increased steric effect²⁰ on bonding of the B(CH₂CH₃)₃ to (CH₃)₃N compared to (CH₃)₃P.

If one assumes that steric effects are important in the aminophosphine series, it might be speculated that P-B bonding would be preferred over N-B bonding and that the base strengths toward B(CH₂CH₃)₃ should decrease in going from (CH₃)₂PN(CH₃)₂ to P[N(CH₃)₂]₃, as observed. However, the present data do not establish that P-B bonding is preferred nor does it say anything about the importance of PN π_{d-p} bonding that might be present.

In the adduct, (NH₂)₃P·BH₃ (first prepared by Kodama and Parry²¹), X-ray information²² has shown P-B bonding. Indirect evidence has been used to infer P-B bonding in P[N(CH₃)₂]₃·BH₃.²³ However, it is known that borine forms complexes of "unexpected" stability when the phosphorus atom is involved.²⁴ For example, the stability of (CH₃)₃P·BH₃ is greater than that of (CH₃)₃P·BF₃ or of (CH₃)₃N·BH₃. Also F₃P·BH₃ exists, whereas F₃P·BF₃ does not. Hence the existence of P-B bonding in (NH₂)₃P·BH₃ does not allow similar bonding to be inferred in the aminophosphine·B(CH₂CH₃)₃ adducts.

Acknowledgment.—The determination of the proton spectra of the pure liquid samples by Professor W. Patrick Gallagher, Adelphi University, and some of the solutions by E. Anderson is gratefully acknowledged.

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