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Molecular Addition Compounds of Boron. III. Trivinylphosphine–Trimethylborane and Related Adducts[1,2]

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In order to determine the relative effects of methyl, ethyl and vinyl groups on the electron-pair donor power of phosphorus the liquid saturation pressures and gas-phase dissociations of the addition compounds $(CH_2{:}CH)_3P{\cdot}BMe_3$, $Et_3P{\cdot}BMe_3$, $EtMe_2P{\cdot}BMe_3$, $(CH_2{:}CH)Me_2P{\cdot}BMe_3$ and $Me_3P{\cdot}BMe_3$ were investigated. In this manner, towards trimethylborane, the sequence of base strength, $EtMe_2P > Me_3P > (CH_2{:}CH)Me_2P \gg Et_3P > (CH_2{:}CH)_3P$, was established. The gas-phase enthalpy of dissociation of dimethylethylphosphine–trimethylborane is 2.7 kcal. $mole^{-1}$ greater than that of dimethylvinylphosphine–trimethylborane. Whereas towards trimethylborane, dimethylethylphosphine is a stronger base than trimethylphosphine, with the First Row donor nitrogen, dimethylethylamine is a weaker base than trimethylamine.

Introduction

The ability of trialkylphosphines to donate electron pairs to electron acceptors has long been recognized and is demonstrated by the existence of phosphonium salts like $[Et_3PH]Cl$, molecular addition compounds like $Me_3P{\cdot}AlMe_3$, and complex compounds like $(Pr_3P)_2PtCl_2$. As is well known, however, the tendency for trivalent derivatives of elements of the Fifth Group to combine with electron-pair acceptors is affected markedly by the kind of atoms or groups bonded to the Group Vb atoms. Usually electronegative substituents decrease Lewis base strength, whereas electron-releasing groups increase base strength. For example, trimethylphosphine combines with boron trifluoride to produce $Me_3P{\cdot}BF_3$,[4] but phosphorus trifluoride does not form $F_3P{\cdot}BF_3$.[5] Similarly, trialkylamines and trialkylphosphines are much stronger bases than triphenylamine or triphenylphosphine. Although the opposing effects of phenyl and alkyl groups on base strength are well established, little is known about the effect of vinyl groups on the behavior of donor atoms. Because of the absence of any quantitative data on this subject it seemed appropriate to compare the stabilities of the trimethylborane adducts of a series of phosphines in order to determine the relative effects of vinyl, ethyl and methyl groups on the electron donor power of phosphorus. The problem of relative base strength was approached through an investigation of the partial dissociation of molecular addition compounds in the gas phase because a study of this kind provides information of a less ambiguous and more complete nature than that obtainable using other techniques.[6,7] Phosphorus was chosen as the donor atom for this investigation because it was not possible to predict with certainty whether a vinyl group would enhance or diminish, relative to an alkyl group, the donor power of this particular element.[8]

Because of an inductive effect a vinylphosphine might be a weaker base than an alkylphosphine.

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[1] Previous paper, T. D. Coyle, H. D. Kaesz and F. G. A. Stone, THIS JOURNAL, **81**, 2989 (1959).

[2] Presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959. This work was made possible by the award of a grant (G5106) from the National Science Foundation, and is taken from the thesis of H. D. Kaesz submitted to the Graduate School of Arts and Sciences of Harvard University in partial fulfillment of the requirements of the Ph.D. degree.

[3] Public Health Predoctoral Fellow of the National Heart Institute.

[4] (a) H. C. Brown, *J. Chem. Soc.*, 1248 (1956); (b) E. A. Fletcher, Ph.D. Thesis, Purdue University, 1952.

[5] H. S. Booth and J. H. Walkup, THIS JOURNAL, **65**, 2334 (1943).

[6] (a) H. C. Brown, *Record Chem. Progress* (Kresge-Hooker Sci. Lib.), **14**, 83 (1953); (b) H. C. Brown, D. H. McDaniel and O. Häfliger, "Determination of Organic Structures by Physical Methods," Ed. E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1956, p. 567.

[7] F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958).

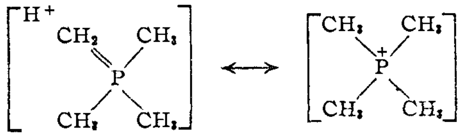
[8] Equilibria, $Base{:}Acid_{(g)} \rightleftarrows Base_{(g)} + Acid_{(g)}$, are frequently upset by irreversible side reactions. Trimethylborane was selected as the reference acid for our work because this acceptor molecule rarely brings about decomposition of the base with which it is paired. It is true that for some donors trimethylborane has high steric requirements, but for Second Row donors such as phosphorus these requirements are unimportant.[6a,7]

Electronegativity of carbon (x_C) in its compounds is considered to be related to the type of carbon atom hybridization, *viz.*. $x_{C(sp^3)} < x_{C(sp^2)} < x_{C(sp)}$.[9] The vinyl group should, therefore, be more electronegative than the ethyl group and of comparable electronegativity to the phenyl group. The behavior of the vinyl group in organic chemistry is in agreement with this idea, and it is further supported by dipole moment studies[10] and the relative position of the vinyl group in the cleavage series.[11] However, base strength is determined by several other effects besides the inductive factor.[7]

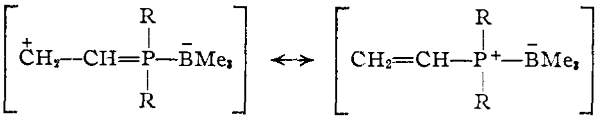
An important consideration is the energy state of the final complex which, for example, might be substantially lowered by resonance. In this connection some recent work of Doering and his coworkers[12] is of interest. Hydroxide ion rapidly brings about elimination of hydrogen bromide from $(BrCH_2CH_2SMe_2)^+$ forming $(CH_2{:}CHSMe_2)^+$, whereas $(BrCH_2CH_2NMe_3)^+$ reacts only slowly with hydroxide, giving $(HOCH_2CH_2NMe_3)^+$ rather than neurine, $(CH_2{:}CHNMe_3)^+$.[12a] This behavior led to the suggestion that the vinyldimethylsulfonium ion is stabilized by resonance, made possible by the ability of sulfur to use orbitals above the $2sp^3$ level.

$$[\overset{+}{C}H_2{-}CH{=}SMe_2] \longleftrightarrow [CH_2{=}CH{-}\overset{+}{S}Me_2]$$

Neurine cannot be stabilized in a similar way since nitrogen has no vacant orbitals of low enough energy to partake in chemical bonding. In organophosphorus and organosulfur chemistry there are many other effects relatable to expanded valence shells. Thus tetramethylphosphonium salts exchange protons readily, whereas tetramethylammonium hydroxide in alkaline deuterium oxide only slowly exchanges.[12b] To account for this, it has been suggested that the tetramethylphosphonium ion is stabilized by resonance, *viz.*



Furthermore, the fact that methylphosphines are very much stronger bases than phosphine also has been attributed[13] to added stabilization of the adducts of the methylphosphines as a result of resonance involving methyl hyperconjugation into the expanded valency shell of phosphorus. If this occurs, a vinyl group with its electrons of π-symmetry would be far more effective than an alkyl group in coupling with the phosphorus 3d-orbitals so as to partially neutralize positive charge on phosphorus. In an addition compound of a vinylphosphine, therefore, it is possible that resonance similar to that suggested for the vinyldimethylsulfonium and tetramethylphosphonium ions might occur and be of such a magnitude as to lead to vinylphosphines being stronger bases than their ethyl or methyl analogs.



$$\left[\overset{+}{C}H_2{-}CH{=}\underset{R}{\overset{R}{P}}{-}\overset{-}{B}Me_3\right] \longleftrightarrow \left[CH_2{=}CH{-}\underset{R}{\overset{R}{P}}{}^{+}{-}\overset{-}{B}Me_3\right]$$

It seemed worthwhile, therefore, to settle by experiment the actual effect of a vinyl group on the base strength of phosphorus, and it was for this reason that the investigation here described was made. The phosphines selected for study were trivinylphosphine, triethylphosphine, dimethylvinylphosphine, dimethylethylphosphine and trimethylphosphine.

Experimental

1. **Starting Materials.**—The phosphines used in this work were prepared by methods described previously.[14] The compounds dimethylvinyl-, dimethylethyl-, trivinyl- and triethylphosphine were fractionally distilled until they were tensimetrically homogeneous, and their vapor pressures are reported elsewhere.[14] The trimethylphosphine used by us had a vapor pressure of 160 mm. at 0° (lit.[15] 160.9 mm.). Trimethylborane was prepared by the Grignard method and purified by forming the complex $Et_3N{\cdot}BMe_3$. Trimethylborane was released from the complex by distillation[16] (vapor pressure 31.4 mm. at −78°; lit.[17] 31.3 mm.).

Dimethylethylamine was obtained by reduction of N,N-dimethylacetamide with lithium aluminum hydride. The crude product of this reduction was treated with phosphorus pentoxide for several days in order to remove secondary amines. Fractional distillation yielded a center fraction distilling at 36.4° (762 mm.) (lit.[18] 37.5°) with n^{24}_D 1.3700.

Anal. Calcd. for $C_4H_{11}N$: C, 65.7; H, 15.2; N, 19.2. Found: C, 65.6; H, 15.2; N, 19.3.

The center fraction was found to be tensimetrically homogeneous and vapor phase chromatography established that the amine had 99.9% minimum purity. Since the vapor pressures of dimethylethylamine do not appear to have been recorded previously, they were studied and found to conform to the equation $\log p_{mm.} = 7.748 - 1500\,T^{-1}$. This equation implies a normal boiling point of 35.0° and a Trouton constant of 22.3 e.u.

2. **Apparatus for the Study of Molecular Addition Compounds.**—The apparatus and techniques used in this work have been described previously.[1] Again as in the previous work,[1] in order to check our equipment and techniques the gas-phase dissociation of trimethylamine-trimethylborane was studied immediately prior to our study of the various trimethylborane-phosphine adducts. For $Me_3N{\cdot}BMe_3$ we obtained $\Delta H^0 = 17.59 \pm 0.2$ kcal. mole^{-1} and $\Delta S^0 = 45.8$ e.u. (lit.[19] 17.62 kcal. mole^{-1} and 45.7 e.u., respectively).

3. **Preparation and Study of Complexes. Trivinylphosphine-Trimethylborane.**—A 30.4 cc.[20] sample of trivinylphosphine treated with 30.2 cc. of trimethylborane in the saturation pressure tensimeter at −78° gave a white solid (melting range −6 to −4°). Saturation pressures[21] recorded in Table I enabled the constants for $(CH_2{:}CH)_3P{\cdot}BMe_3$ in Table X to be calculated.

In the dissociation tensimeter (volume 362.1 cc.), 3.77 cc. of trivinylphosphine and 3.78 cc. of trimethylborane were brought together and the following pressure–temperature data obtained.

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[9] C. A. Coulson, "Valence," Oxford University Press, 1952, p. 207.

[10] H. C. Brown, This Journal, **61**, 1483 (1939).

[11] D. Seyferth, *ibid.*, **79**, 2133 (1957).

[12] (a) W. von E. Doering and K. C. Schreiber, *ibid.*, **77**, 514 (1955); (b) W. von E. Doering and A. K. Hoffmann, *ibid.*, **77**, 521 (1955).

[13] D. H. McDaniel, *Science*, **125**, 545 (1957); it must be added, however, that the large base strength difference between phosphine and methylphosphines may also be due in part to the large rehybridization energy necessary for phosphine to form addition compounds (J. H. Gibbs, *J. Chem. Phys.*, **22**, 1460 (1954).

[14] H. D. Kaesz and F. G. A. Stone, *J. Org. Chem.*, **24**, 635 (1959).

[15] N. Davidson and H. C. Brown, This Journal, **64**, 316 (1942).

[16] H. C. Brown, *ibid.*, **67**, 374 (1945).

[17] A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921).

[18] M. Kohn and O. Morgenstern, *Monatsh.*, **28**, 495 (1907).

[19] H. C. Brown, M. D. Taylor and M. Gerstein, This Journal, **66**, 431 (1944).

[20] Throughout this paper the abbreviation cc. refers to gases at standard conditions.

[21] Volume of the saturation pressure tensimeter used in this work was 94 cc.

t, °C.	$P_{\text{(obsd.}}$ mm.,	"α"	Satn. P, mm., complex	Satn. P, mm., free ligand	Appearance, contents tensimeter
15.4	15.42	0.766	45.2	13.6	Liquid present
17.8	17.48	0.986	51.0	15.4	Barely getting dry
21.5	18.27	1.03	61.1	20.1	Dry
28.3	18.69	1.02	84.5	26.3	Dry
35.3	19.15	1.05	116.0	36.9	Dry

It is well known that saturation pressures of a weak complex, obtained with a large sample and in a small tensimeter, cannot be used to predict whether or not a liquid phase will be present in the large tensimeter.[1] Indeed, without observation of the contents of the tensimeter, the degree of dissociation obtained at 15.4° might have been taken as reliable, for at this temperature the previously recorded saturation pressure was 30 mm. higher, suggesting that liquid phase would not be present. It is interesting to note that so long as liquid phase is present in the large tensimeter, pressure–temperature measurements follow more closely those to be expected for the free ligand rather than those expected for the complex. This behavior is typical for a very weak complex. At 21.5°, however, 4° above the disappearance of the last traces of liquid, the complex is fully dissociated, and above 21.5° expansion follows that expected for an ideal gas.

TABLE I

SATURATION PRESSURES OF LIQUID $(CH_2:CH)_3P\cdot BMe_3$

t, °C.	0.0	6.8	14.2	20.8	28.1	35.0
$P_{\text{mm.}}$ (obsd.)	19.6	28.9	42.6	59.5	84.0	113.3
$P_{\text{mm.}}$ (calcd.)	19.8	28.8	42.5	59.1	83.7	114.5

A second experiment was made with a 9.70 cc. sample of trivinylphosphine and 9.58 cc. of trimethylborane. Again liquid phase remained present far beyond the point at which saturation pressure data would predict that the liquid would have vanished. At 48°, a temperature 3° above that at which the liquid disappeared, the volumes were additive.

Triethylphosphine–Trimethylborane.—In the saturation pressure tensimeter 35.8 cc. of triethylphosphine combined with 35.6 cc. of trimethylborane to give a white solid, m.p. −3 to −4°. Saturation pressures given in Table II led to the constants listed in Table X.

TABLE II

SATURATION PRESSURES OF LIQUID $Et_3P\cdot BMe_3$

t, °C.	58.8	65.9	75.1	82.2	89.8
$P_{\text{mm.}}$ (obsd.)	23.8	33.0	51.0	71.1	102.3
$P_{\text{mm.}}$ (calcd.)	22.7	32.7	51.3	71.4	100.5

In the dissociation tensimeter (volume 362.1 cc.) at 70.5°, 11° above the temperature at which the liquid phase disappeared, 4.91 cc. of trimethylborane and 4.84 cc. of triethylphosphine exhibited a pressure of 25.75 mm. The pressure expected for complete dissociation is 25.74 mm.

Dimethylvinylphosphine–Trimethylborane.—A 31.5 cc. sample of trimethylborane combined with 31.4 cc. of dimethylvinylphosphine at −78° to form a solid (m.p. 50–52°). Saturation pressure measurements tabulated below for liquid dimethylvinylphosphine-trimethylborane permitted calculation of the constants reported in Table X.

TABLE III

SATURATION PRESSURES OF LIQUID $(CH_2:CH)Me_2P\cdot BMe_3$

t, °C.	58.0	60.1	64.7	70.2	74.8	79.8	84.1
$P_{\text{mm.}}$ (obsd.)	49.4	55.8	72.1	96.7	124.0	161.9	200.8
$P_{\text{mm.}}$ (calcd.)	49.3	55.6	72.1	97.5	124.5	161.2	200.2

Saturation pressures for solid dimethylvinylphosphine trimethylborane also were recorded (Table IV).

TABLE IV

SATURATION PRESSURES OF SOLID $(CH_2:CH)Me_2P\cdot BMe_3$

t, °C.	29.9	26.3	35.6	42.9	49.6	54.5
$P_{\text{mm.}}$ (obsd.)	8.4	9.9	14.8	21.6	31.0	40.7

Gas-phase dissociation of dimethylvinylphosphine–trimethylborane was studied several times using different samples over the range 60–102° in the dissociation tensimeter. The pressure reading at 60° was checked three times during any run to make certain that no irreversible reaction had taken place. This was necessary because experience showed that unless the tensimeter had been thoroughly baked at 150° *in vacuo*, prior to a dissociation study, a sample of dimethylvinylphosphine–trimethylborane would decompose irreversibly. Solid appeared in the tensimeter and pressure readings were less than expected.

In a representative experiment, 8.251 cc. of dimethylvinylphosphine and 8.230 cc. of trimethylborane were brought together in the dissociation tensimeter of volume 362.1 cc. The results presented in Table V were obtained.

TABLE V

GAS-PHASE DISSOCIATION OF $(CH_2:CH)Me_2P\cdot BMe_3$

t, °C.	$P_{\text{mm.}}$ (obsd.)	$P_{\text{calcd., mm.}}$		K_p (atm.)[a]	α
		P'_{Me_3B}	$P'_{(CH_2:CH)PMe_2}$		
60.0	39.18	21.067	21.121	0.144	0.857
65.0	40.50	21.383	21.437	.206	.891
70.0	41.64	21.699	21.754	.288	.916
75.5	42.72	22.047	22.103	.392	.935
81.0	43.74	22.394	22.452	.540	.950
60.0[b]	39.18	....	....	...	...
91.5	45.57	23.058	23.117	1.10	.974
60.0[b]	39.18	....	....	...	...
102.0	47.09	23.722	23.783	1.73	.982
60.0[b]	39.16	....	....	...	...

[a] Calculated from the relationship, $K_p(\text{atm.}) = \dfrac{(P_{\text{obsd.}} - P'_{\text{acid}})(P_{\text{obsd.}} - P'_{\text{base}})}{(P'_{\text{acid}} + P'_{\text{base}} - P_{\text{obsd.}})760}$. [b] Check point on cooling.

The variation of K_p with temperature is represented by the equation

$$\log K_p\,(\text{atm.}) = 8.920 - 3250\,T^{-1}$$

whence

$$\Delta F^0_T = 14{,}870 - 40.87\,T \text{ cal. mole}^{-1}$$

Therefore, for the reaction

$$(CH_2:CH)Me_2P\cdot BMe_{3(g)} \longrightarrow (CH_2:CH)PMe_{2(g)} + Me_3B_{(g)}$$

$\Delta H^0 = 14.87$ kcal. mole^{-1} and $\Delta S^0 = 40.87$ e.u.

Dimethylethylphosphine–Trimethylborane.—In the saturation pressure tensimeter 44.3 cc. of trimethylborane combined with 44.1 cc. of dimethylethylphosphine at −78° forming a white solid adduct (m.p. 30–32°). The saturation pressure measurements (Table VI) gave the constants listed in Table X.

TABLE VI

SATURATION PRESSURES OF LIQUID $EtMe_2P\cdot BMe_3$

t, °C.	51.0	59.4	66.3	75.4	85.5
$P_{\text{mm.}}$ (obsd.)	9.96	16.4	23.9	41.0	67.0
$P_{\text{mm.}}$ (calcd.)	10.1	16.7	24.9	40.9	69.0

Gas-phase dissociation of dimethylethylphosphine-trimethylborane was studied several times using different samples in the dissociation tensimeter (volume 362.1 cc.). In a typical experiment using 8.342 cc. of trimethylborane and 8.348 cc. of dimethylethylphosphine the results presented in Table VII were obtained.

Therefore, for the reaction

$$(Et)(Me)_2P\cdot BMe_{3(g)} \longrightarrow (Et)(Me)_2P_{(g)} + Me_3B_{(g)}$$

$\Delta H^0 = 17.58$ kcal. mole^{-1} and $\Delta S^0 = 44.42$ e.u. As in the case of the adduct $(CH_2:CH)Me_2P\cdot BMe_3$, the precision of the measurements was established by conducting other independent studies. Thus, using volumes of $EtMe_2P$ and of Me_3B of 8.127 and 8.174 cc., respectively, the values $\Delta H^0 = 17.51$ kcal. mole^{-1} and $\Delta S^0 = 44.20$ e.u. were obtained.

Trimethylphosphine–Trimethylborane.—This compound has been studied by Sujishi,[22] but the detailed results have

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[22] S. Sujishi, Ph.D. Thesis, Purdue University, 1949.

TABLE VII

GAS-PHASE DISSOCIATION OF $EtMe_2P \cdot BMe_3$

t, °C.	$P_{(obsd.)}$ mm.	$P_{(calcd.)}$ mm.	α	K_p (atm.)[a]
76.4	38.42	22.422	0.713	0.0524
82.0	40.40	22.781	.773	.0790
88.5	42.49	23.198	.832	.126
95.5	44.35	23.647	.875	.191
103.0	46.17	24.128	.913	.306
112.0	48.08	24.705	.946	.540
121.0	49.73	25.282	.967	.944
130.0	51.16	25.859	.978	1.51

[a] Calculated from the relationship $K_p(\text{atm.}) = \frac{\alpha^2}{1-\alpha} \cdot \frac{P_{\text{obsd.}}}{760}$, where $\alpha = \left(\frac{P_{\text{obsd.}}}{P_{\text{calcd.}}} - 1\right)$.

not been published, although Brown has quoted ΔH^0 and ΔS^0 values for the reaction

$$Me_3P \cdot BMe_{3(g)} \longrightarrow Me_3P_{(g)} + Me_3B_{(g)}$$

in several review articles.[4a,6] We reinvestigated the compound both in order to make sure that the experimental techniques being used in this Laboratory were giving results having the accuracy and reproducibility of those reported by Brown and his co-workers, and because reliable information on $Me_3P \cdot BMe_3$ was needed so as to be able to compare the effect of a methyl group on the donor power of phosphorus with that of the ethyl and vinyl groups.

In a representative experiment, an 8.387 cc. sample of trimethylphosphine–trimethylborane was studied in the dissociation tensimeter (volume 362.1 cc.). The results given in Table VIII were used to determine by the method of least squares the equation

$$\log K_p \text{ (atm.)} = 8.7898 - 3612\ T^{-1}$$

Therefore, for the reaction

$$Me_3P \cdot BMe_{3(g)} \longrightarrow Me_3P_{(g)} + Me_3B_{(g)}$$

$\Delta H^0 = 16.53$ kcal. mole^{-1} and $\Delta S^0 = 40.23$ e.u. These results are in excellent agreement with those of Sujishi (Table XI).

TABLE VIII

GAS-PHASE DISSOCIATION OF $Me_3P \cdot BMe_3$

t, °C.	$P_{mm.}$ (obsd.)	$P_{mm.}$ (calcd.)	α	K_p (atm.)[a]
86.5	39.74	23.178	0.714	0.0547
93.0	41.93	23.597	.781	.0864
99.0	43.73	23.983	.823	.121
107.0	45.90	24.499	.874	.195
115.0	47.77	25.014	.909	.301
125.0	49.86	25.659	.943	.529

[a] See footnote to Table VII.

Dimethylethylamine–Trimethylborane.—This complex was studied for the reason given in the Discussion. A 30.4 cc. sample of dimethylethylamine–trimethylborane melted over the range 11–12°. Saturation pressures, recorded in Table IX, conform to the equation $\log P_{mm.} = 11.233 - 3042\ T^{-1}$, implying a normal "boiling point" of 91°, $\Delta H_{vap.} = 13.9$ kcal. mole^{-1}, and Trouton's constant of 38.2 e.u.

TABLE IX

SATURATION PRESSURES OF LIQUID $EtMe_2N \cdot BMe_3$

t, °C.	30.4	38.7	49.2	57.5	66.1
$P_{mm.}$ (obsd.)	16.4	30.3	63.5	109.0	184.4
$P_{mm.}$ (calcd.)	16.4	30.3	63.0	108.6	185.8

Samples of dimethylethylamine-trimethylborane were studied in the dissociation tensimeter in order to determine the variation of K_p with temperature. By averaging the results of three determinations the relationships $\log K_p(\text{atm.}) = 8.923 - 3005\ T^{-1}$ and $\Delta F_T{}^0 = 13.750 - 40.84\ T$ were obtained. Therefore, for the reaction

$$EtMe_2N \cdot BMe_{3(g)} \rightarrow EtMe_2N_{(g)} + Me_3B_{(g)}$$

$\Delta H^0 = 13.8 \pm 0.5$ kcal. mole^{-1} and $\Delta S^0 = 40.8 \pm 1$ e.u.

Discussion

The results presented in the Experimental section show that both triethylphosphine and trivinylphosphine are extremely weak bases toward trimethylborane. The trimethylborane adducts of these two phosphines are completely dissociated in the gas phase at the lowest temperatures at which pressure measurements could be made such that no liquid phase was present. Because of the high degree of dissociation of $(CH_2{:}CH)_3P \cdot BMe_3$ and of $Et_3P \cdot BMe_3$, quantitative comparison of their relative stabilities was impossible. However, qualitative comparison of the relative Lewis base strengths of the two phosphines can be made by comparing the volatilities of their trimethylborane adducts. For complexes of low stability, it has long been customary to infer relative stabilities from relative volatilities. For two addition compounds of closely similar structure and molecular weight, the less stable exhibits the higher saturation pressure.[23] In Table X the volatility data for $(CH_2{:}CH)_3P \cdot BMe_3$ and $Et_3P \cdot BMe_3$ show that trivinylphosphine is a weaker base than triethylphosphine. Thus the vinyl group has a weakening effect compared with the ethyl group on the electron-pair donor power of phosphorus.

The addition compounds $(CH_2{:}CH)Me_2P \cdot BMe_3$, $EtMe_2P \cdot BMe_3$ and $Me_3P \cdot BMe_3$ are all only partially dissociated in the gas phase so that it was possible to make an accurate determination of the enthalpy change involved in dissociation of these complexes into their donor-acceptor parts (Table XI). In the case of the two phosphines $CH_2{:}CHPMe_2$ and $EtPMe_2$ there is a 2.7 kcal. stability difference between their respective trimethylborane adducts, with the ethylphosphine the stronger Lewis base. The results summarized in Table XI, in conjunction with the relative volatility considerations mentioned above, show that toward trimethylborane the sequence of base strength is

$$EtMe_2P > Me_3P > (CH_2{:}CH)Me_2P \gg Et_3P > (CH_2{:}CH)_3P$$

The position of dimethylethylphosphine at the head of this series is interesting. It is true that the ethyl group is more electron releasing than the methyl,[24] unless hyperconjugation is involved; however, toward Group III acceptors the greater electron-releasing effect of the ethyl group is often offset by its larger steric requirements. Thus the work of Brown and his co-workers[4a,6] has shown that toward trimethylborane, trimethylamine is a much stronger base than triethylamine. The heat of dissociation of $Me_3N \cdot BMe_3$ in the gas phase is 17.62 kcal., whereas that for $Et_3N \cdot BMe_3$ is only about 10 kcal. Here steric requirements outweigh inductive considerations. With the Second-Row donor atoms, sulfur or phosphorus, donor-acceptor bonds are longer and, therefore, steric requirements must be less important. Perhaps this is why $Me_2S \cdot BMe_3$ exists whereas $Me_2O \cdot BMe_3$ does not.[25] The relatively high base strength of $EtMe_2P$, equal to that of Me_3N toward Me_3B,

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(23) H. C. Brown and H. Pearsall, THIS JOURNAL, **67**, 1765 (1945).

(24) C. K. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University, Ithaca, New York, 1953, p. 90.

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TABLE X

PHOSPHINE ADDUCTS OF TRIMETHYLBORANE

Compound	Melting point, °C.	Boiling point,[a] °C.	$\log_{10} P_{(mm.)} = -A/T + B$ A	B	Trouton constant,[a] e.u.	Satn. P at t, mm./°C.
$(CH_2:CH)_3P \cdot BMe_3$[b]	−6 to −4	84.4	1835	8.012	23.5	91.2/30
$Et_3P \cdot BMe_3$[b]	−3 to −4	142.7	2508	8.911	27.6	5.3/30
$(CH_2:CH)Me_2P \cdot BMe_3$	50–52	113.1	2761	10.028	32.7	55.2/60
$EtMe_2P \cdot BMe_3$	30–32	141.0	2809	9.670	31.1	17.4/60
$Me_3P \cdot BMe_3$[c]	118–121	...	..	....	..	Solid 18.1/60

[a] By extrapolation of the vapor pressure equation. [b] The fact that the b.p. of $(CH_2:CH)_3P \cdot BMe_3$ is less than that of trivinylphosphine whereas the b.p. of $Et_3P \cdot BMe_3$ is greater than that of triethylphosphine is strongly indicative that the vinyl compound is the weaker base (see ref. 1). [c] Data from ref. 22.

provides another example of how electronic considerations outweigh steric requirements when Second-Row atoms are involved, whereas the reverse often is true for First-Row atoms. In order to place this idea on a firmer basis, as described in the Experimental section, the stability of the addition compound $EtMe_2N \cdot BMe_3$ was examined. Unlike the case of $EtMe_2P$ *versus* Me_3P, $EtMe_2N$ was found to be a weaker base by 3.8 kcal. than Me_3N toward trimethylborane. Nevertheless, in certain instances steric effects are important in organophosphine addition compounds. Thus with three groups on phosphorus larger than methyl, as in trivinyl- and triethylphosphine, a marked reduction in base strength toward trimethylborane is observed.

TABLE XI

GAS-PHASE DISSOCIATION DATA[a] FOR THE TRIMETHYLBORANE ADDUCTS OF THE ORGANOPHOSPHINES

Compound	$\log K_p$ (atm.) = $-A/T + B$ A	B	ΔH^0, kcal. mole^{-1}	ΔS^0, e.u.	ΔF^0_T at 100°, kcal.
$(CH_2:CH)_3P \cdot BMe_3$	Highly dissociated as gas				
$Et_3P \cdot BMe_3$	Highly dissociated as gas				
$(CH_2:CH)Me_2P \cdot BMe_3$	3239	8.903	14.83	40.7	−3.79
$EtMe_2P \cdot BMe_3$	3833	9.682	17.54	44.3	+1.01
$Me_3P \cdot BMe_3$	3612	8.790	16.53	40.2	+1.52
	..	...	16.47[b]	40.0[b]	+1.52[b]

[a] The values reported represent averages for the dissociations $R_3P \cdot BMe_{3(g)} \rightarrow R_3P_{(g)} + Me_3B_{(g)}$. [b] From the work of Sujishi (ref. 22).

Since the vinyl group has a weakening effect on the donor power of phosphorus, it is evident that the trimethylborane adducts of vinylphosphines are not significantly stabilized by d-orbital resonance of a kind involving transfer of positive charge from phosphorus to the vinyl group, a possibility suggested in the Introduction following consideration of the ideas of Doering and his coworkers.[12] Indeed, in view of the experimental findings reported in this paper it is worthwhile considering an important distinction between the phosphorus compounds studied here and the sulfur and phosphorusco mpounds studied by Doering, *et al.* In the latter work the Second Row elements bear a positive charge whereas in an adduct $R_3P \cdot BMe_3$ although there must be some charge transfer in the dative σ-bond, it may not be sufficient to make the phosphorus atom positive relative to boron. Because of this the phosphorus d-orbitals may be too diffuse to be effective in π-bonding with the vinyl group in, for example, $(CH_2:CH)Me_2P \cdot BMe_3$, in spite of the fact that the phosphorus atom in the adduct probably is tetrahedral so that there are phosphorus d-orbitals having the correct symmetry for interaction with the vinyl group's π-electrons. Furthermore, since vinylphosphines are weak donors, there can be no strong mesomeric effect in the free bases themselves involving electron release of the vinyl group's π-electrons into the phosphorus 3d-orbitals. Although such an effect would be analogous to the p_π–p_π bonding present in the alkylvinylboranes,[26] its absence in the vinylphosphines is in agreement with the idea[27] that in phosphorus compounds in which phosphorus shares electrons with three neighboring atoms the three bonds to phosphorus have little or no π-character. It is interesting to note in passing that in the case of *neutral* organosulfur compounds in which a phenyl group is bonded to sulfur, evidence has been presented both for [28] and against[29,30] the idea of mesomerism between the phenyl group's π-electrons and the vacant sulfur d-orbitals.

The sequence of base strength found as a result of this work is not unexpected. As mentioned in the Introduction, it was entirely possible on the basis of a simple electronegativity effect that replacement of an alkyl group on phosphorus by a vinyl group would result in a decrease in base strength. However, an alternative explanation for the low Lewis base character of vinylphosphines merits some consideration. The ultraviolet spectra of the triphenyl derivatives $(C_6H_5)_3M$ (M = N, P, As or Sb) have been interpreted by Jaffé[31] in terms of delocalization of the lone pair of the Group Vb atom amongst the phenyl group's π-orbitals. Such an effect is also possible in vinyl derivatives of the Group Vb elements, although if it occurs it must be less effective than in phenyl derivatives since fewer atoms are involved. Appreciable coupling of π-electrons of phenyl or vinyl groups through a lone-pair of a Group Vb atom would lead to a hybridization state for the donor atom different from sp^3. This in turn would cause phenyl and vinyl derivatives of the Group Vb elements to be weak bases since a relatively large rehybridization would be required by the base before it could

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acquire the tetrahedral configuration of a molecular addition compound. In the case of phenyl derivatives of the Group Vb atoms recent structural data on triphenylamine provide some support for Jaffé's suggestion.[31] The CNC angle is 116°,[32] considerably greater than that in trimethylamine.

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Organoboron Halides. II. The Vinylhaloboranes, A Preliminary Study of their Preparation and Properties[1,2]

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The new compound vinyldifluoroborane may be obtained by vinylation of boron trifluoride with divinylmercury, divinylzinc, tetravinyltin or di-*n*-butyldivinyltin. Vinyldichloro- and divinylchloroborane can be prepared by treating boron trichloride with tetravinyltin. Although vinyl groups are preferentially cleaved by boron halides from alkylvinyltin compounds, tetraalkyltin compounds react with boron halides to give a variety of alkylhaloboranes. Since many tetraorganotin compounds are commercially available, these reactions represent a useful route for the small-scale preparation of organohaloboranes. Vinyldifluoroborane is not further vinylated when heated with a variety of vinylmetallic reagents. For this reason divinylfluoroborane was prepared by treating divinylchloroborane with antimony trifluoride. A number of physical properties of the new vinylhaloboranes are reported, including the main features of their infrared spectra. Thermal stability of the vinylhaloboranes increases in the sequence $(CH_2{:}CH)_2BF < (CH_2{:}CH)_2BCl < CH_2{:}CHBCl_2 < CH_2{:}CHBF_2$. Modes of decomposition of the compounds are discussed. Vinyldifluoroborane has a high thermal stability, comparable with that of ethyldifluoroborane. The vinylhaloboranes react with water at elevated temperatures with either complete or partial removal of their vinyl groups as ethylene. With ammoniacal silver(I) ion the vinylhaloboranes react in a manner more similar to that of arylboron compounds than alkylboron compounds. Vinyldifluoroborane reacts with diethylzinc to give triethylborane and with trimethylaluminum to give trimethylborane.

In the century since the first report of an organoborane,[4] ever-increasing numbers of alkyl- and aryl-boron compounds have been prepared.[5] However, of the many characterized organoboron compounds only a few contain the $>C{=}CH{-}B$ configuration, *e.g.*, trivinylborane,[6] alkylvinyl-[6a] and alkylpropenylboranes,[6a] β-chlorovinylchloroboranes[7] and certain unsaturated boronic acids.[8] This scarcity of vinylboron compounds is disappointing since, as Ritter and his co-workers[6a,9] have pointed out, B–C π-bonding might occur if a vinyl group is one of three groups bonded to a boron atom. Such a mesomeric effect would be related to the stabilization of Lewis acids such as boron trifluoride by internal dative bonding and to the existence of certain boron compounds such as the dialkoxyboranes as monomers. It is thus clear that a study of vinylboron compounds might well allow a better understanding of the energetics of molecular addition compound formation and of the polymerization of some derivatives of the Group III elements.

Furthermore, from the purely preparative point of view compounds containing the $>C{=}CH{-}B$ grouping should be valuable intermediates in the synthesis of new boron compounds, provided cleavage of vinyl groups from boron is not too facile. With these ideas in mind, and in order to extend vinylboron chemistry, we were led to devise methods for preparing some unreported vinylhaloboranes. This paper describes these methods and also gives a preliminary account of the properties of the new compounds.

In our initial work it was found that vinyldifluoroborane could be prepared by treating boron trifluoride with divinylmercury[10a], or divinylzinc.[11] Later it was discovered that vinyldifluoroborane could be made in even better yield from the reaction between boron trifluoride and the recently described tetravinyltin.[12] Since divinylmercury is toxic and since divinylzinc is inflammable in air and thermally somewhat unstable, use of these reagents was largely abandoned in favor of tetravinyltin. Vinylation of boron trifluoride by the various vinylmetallics occurs slowly at ambient temperatures, but even at elevated temperatures. using a large excess of vinylmetallic, no di- or trivinylation of boron trifluoride occurs. Furthermore, vinyldifluoroborane resists vinylation by divinylmercury and tetravinyltin at temperatures from 100 to 200°.

In contrast to boron trifluoride's inertness to further vinylation both boron trichloride and

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(1) Previous paper, B. Bartocha, W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, **6**, 119 (1958).

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