acterized by combustion over CuO to water and water plus CO_2 at 300 and 800°, respectively.

Reaction of $[(CH_3)_2AlH]_3$ with $[(CH_3)_2NAl(CH_3)_2]$.—Treatment of $[(CH_3)_2AlNR_2]_2$, 1.46 mmol, with $[(CH_3)_2AlH]_3$, 1.95 mmol, was effected in a sealed ampoule at various temperatures from 25 to 84°. Subsequent separations of the reaction mixtures *via* fractional condensation afforded only starting materials as characterized by those infrared spectra.

Preliminary X-Ray Single Crystal Study.—A crystal of sublimed $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$ was mounted in a 0.5-mm X-ray capillary tube and sealed under a nitrogen atmosphere. The space group $P2_1/n$ was determined by the systematic absences $k = 2n + 1$ for $0k0$ and $h + 1 = 2n + 1$ for $h01$ observed in two zero-level and two first-level precession photographs. The crystal was then mounted on a Picker four-circle X-ray diffraction apparatus and 18 reflections were located. A least-squares refinement of these 18 data points gave cell dimensions a = 14.177 (0.009), b = 10.371 (0.007), c = 7.693 (0.005) Å, and cos β = −0.0129 (0.0004)°. The density calculated from these dimensions, a molecular weight of 318.37, and $Z = 2$ is 0.934 g/cm^3. The experimental density could not be determined due to the reactive nature of this substance. Collection of data and solution of the structure will be published at a later date.

Acknowledgment.—We wish to thank the National Science Foundation for support of this work under Grants GP 9308 and GP 21118.

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The Microwave Spectra, Structures, and Dipole Moments of Trimethylphosphine–Borane and Methylphosphine–Borane

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Received June 3, 1971

The microwave spectra of four isotopic species of $(CH_3)_3P\cdot BH_3$ and nine isotopic species of $CH_3PH_2\cdot BH_3$ have been assigned. For $(CH_3)_3P\cdot BH_3$, the following structural parameters were determined: $r(PB) = 1.901 \pm 0.007$ Å; $r(PC) = 1.819 \pm 0.010$ Å; $r(CH) = 1.08 \pm 0.02$ Å; $r(BH) = 1.212 \pm 0.010$ Å; $\angle CPC = 105.0 \pm 0.4°$; $\angle HCH = 109.3 \pm 1.0°$; $\angle HBH = 113.5 \pm 0.5°$. In deriving the structure, the methyl groups were assumed to be symmetric with a hydrogen–hydrogen distance of 1.760 Å. For $CH_3PH_2\cdot BH_3$, the following structural parameters were determined: $r(PH) = 1.404 \pm 0.006$ Å; $r(PB) = 1.906 \pm 0.006$ Å; $r(PC) = 1.809 \pm 0.006$ Å; $r(BH_s) = 1.234 \pm 0.023$ Å; $r(BH_a) = 1.229 \pm 0.022$ Å; $r(CH_a) = 1.087 \pm 0.004$ Å; $r(CH_s) = 1.098 \pm 0.016$ Å; $\angle H_aBH_s = 116.1 \pm 0.8°$; $\angle H_aBH_a = 112.3 \pm 1.2°$; $\angle H_aCH_s = 110.4 \pm 0.6°$; $\angle H_aCH_a = 108.1 \pm 0.4°$; $\angle HPH = 99.9 \pm 0.4°$; $\angle HPC = 103.2 \pm 0.6°$; $\angle CPB = 115.7 \pm 0.4°$; $\angle HPB = 116.3 \pm 0.6°$; $\angle PBH_a = 102.9 \pm 0.6°$; $\angle PBH_s = 104.2 \pm 1.0°$; $\angle PCH_a = 108.3 \pm 0.4°$; $\angle PCH_s = 111.3 \pm 1.0°$. The BH_3 and CH_3 groups were staggered with respect to the PH bonds. Dipole moments of 4.99 ± 0.2 D for $(CH_3)_3P\cdot BH_3$ and 4.66 ± 0.05 D for $CH_3PH_2\cdot BH_3$ were obtained from Stark splittings.

Introduction

Trimethylphosphine–borane and methylphosphine–borane are addition compounds formed by the reaction of B_2H_6 with $(CH_3)_3P$ and CH_3PH_2, respectively. Burg and Wagner first characterized the compounds.[1] They discovered that $(CH_3)_3P\cdot BH_3$ is a crystalline solid which melts at 103°, while $CH_3PH_2\cdot BH_3$ is a liquid at room temperature. The adducts are quite stable; $(CH_3)_3P\cdot BH_3$ can be heated to about 200° before decomposing slightly, while $CH_3PH_2\cdot BH_3$ produces H_2 and polymeric material above 80°. There was no evidence for dissociation of either adduct at room temperature.

Several structural studies have been completed for various borane adducts,[2-4] but no structural data exist for the simple methylphosphine–boranes. Consequently, a study of $(CH_3)_3P\cdot BH_3$ and $CH_3PH_2\cdot BH_3$ was undertaken in order to relate their structures and stabilities to other phosphorus–boron compounds. Since these adducts are stable toward dissociation, it was of particular interest to compare their P–B bond distances to that in $F_3P\cdot BH_3$ which is extensively dissociated at room temperature.

A detailed structural determination of $CH_3PH_2\cdot BH_3$ was also prompted by the recent study of $HF_2P\cdot BH_3$ which found a pronounced tilt of the borane group away from the fluorine atoms.[4] Since both adducts contain an asymmetrically substituted phosphorus atom, it was hoped that the structural results for $CH_3PH_2\cdot BH_3$ would aid in identifying the origin of the tilt found in $HF_2P\cdot BH_3$.

Experimental Section

Apparatus.—The spectra were measured with a Stark-modulation microwave spectrometer which employed 80-kHz square-wave modulation.[5] The transition frequencies were measured using both oscilloscope display and pen recordings. The recordings were obtained by using a gear assembly to sweep the klystron slowly through a narrow frequency range. The frequencies were measured directly from the traces which were marked at frequency intervals of 1.0 MHz. All measurements were made at about 0°. The transitions for $(CH_3)_3P\cdot BH_3$ and its isotopic species were reproducible to ±0.2 MHz except for the $(CH_3)_3BH_2D$ species where the uncertainties were ±0.3 MHz. The transitions for the $CH_3PH_2\cdot BH_3$ species were measured with a precision of about ±0.1 MHz.

Materials.—The $(CH_3)_3P\cdot BH_2$ was prepared by the reaction of $(CH_3)_3P$ with B_2H_6.[1] The spectra of both $(CH_3)_3P\cdot {}^{11}BH_3$ and $(CH_3)_3P\cdot {}^{10}BH_3$ were obtained from this sample. The $(CD_3)(CH_3)_2P\cdot BH_3$ was prepared by allowing $(CD_3)(CH_3)_2P$ to react with B_2H_6. The $(CD_3)(CH_3)_2P$ was prepared by treating $(CH_3)_2PH$ with 99.5% CD_3I.[6] The $(CH_3)_3P\cdot BH_2D$ was prepared by allowing $(CH_3)_3P$ to react with a gaseous mixture consisting of two parts B_2H_6 and one part B_2D_6. This diborane mix-

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[1] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, **75**, 3872 (1953).

[2] R. L. Kuczkowski and D. R. Lide, Jr., *J. Chem. Phys.*, **46**, 357 (1967).

[3] C. E. Nordman, *Acta Crystallogr.*, **13**, 535 (1960).

[4] J. P. Pasinski and R. L. Kuczkowski, *J. Chem. Phys.*, **54**, 1903 (1971).

[5] R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **90**, 1705 (1968).

[6] W. L. Jolly, *Inorg. Syn.*, **11**, 124 (1968).

ture was allowed to equilibrate for 1 day before reaction with $(CH_3)_3P$. This stoichiometry gave a mixture in which the main component was the singly deuterated $(CH_3)_3P \cdot BH_2D$ species (*ca.* 44%).

For $CH_3PH_2 \cdot BH_3$, the spectra of the ^{11}B, the ^{10}B, and the $CH_3PH_2 \cdot BH_2D$ species were obtained from samples prepared in a similar manner as described above for $(CH_3)_3P \cdot BH_3$ except for the substitution of CH_3PH_2[6] for $(CH_3)_3P$. The samples of $^{13}CH_3PH_2 \cdot BH_3$ and $CH_2DPH_2 \cdot BH_3$ were prepared by treating enriched samples of CH_3PH_2 with B_2H_6. Methyl-^{13}C iodide (61%) and methyl-d_1 iodide (97%) were used to make $^{13}CH_3PH_2$ and CH_2DPH_2, respectively, by reaction with PH_3.[7]

The samples of $CH_3PDH \cdot BH_3$ and $CH_3PD_2 \cdot BH_3$ were prepared from a mixture of approximately 60% CH_3PDH, 35% CH_3PD_2, and 5% CH_3PH_2. This mixture was prepared by treating CH_3PH_2 with excess DCl *in vacuo*. The amount of deuteration was increased by alternately heating and cooling the resulting solid. The deuterated methylphosphine mixture was liberated by adding a less than equivalent amount of trimethylamine.

Spectra. $(CH_3)_3P \cdot BH_3$.—Both $(CH_3)_3P \cdot {}^{11}BH_3$ and $(CH_3)_3P \cdot {}^{10}BH_3$ exhibited symmetric-top spectra and Stark effects. The assigned transitions and the average rotational constants are listed in Table I. Each transition region consisted of an intense ground-state line and a number of weaker lines arising from rotational transitions in excited vibrational states. Although the vibrational satellite patterns were similar in both isotopic species, no extensive attempt was made to measure and assign these transitions. The $(CH_3)_3P \cdot {}^{10}BH_3$ was studied in natural abundance. The expected intensity relative to that of $(CH_3)_3P \cdot {}^{11}BH_3$ (natural abundance: ^{10}B, 19.6%; ^{11}B, 80.4%), as well as the isotope shifts and vibrational satellite patterns, was useful for the assignment of the spectra. Neither ground-state spectrum exhibited splitting due to boron quadrupole coupling, internal rotation, or centrifugal distortion.

TABLE I

OBSERVED TRANSITIONS AND ROTATIONAL CONSTANTS (MHz) OF $(CH_3)_3P \cdot {}^{11}BH_3$ AND $(CH_3)_3P \cdot {}^{10}BH_3$

$(J+1)$–J	$(CH_3)_3P \cdot {}^{11}BH_3$	$(CH_3)_3P \cdot {}^{10}BH_3$
4–3	25725.16	26384.15
5–4	32156.23	32980.45
6–5	38587.32	
B	3215.63 ± 0.03	3298.04 ± 0.03

The "a" type transitions which were assigned for both the $(CH_3)_3P \cdot BH_2D$ and the $(CD_3)(CH_3)_2P \cdot BH_3$ species are listed in Table II. The measurements were obtained from numerous pen recordings of the spectra. The assignments were based on the frequency fit, the expected isotope shifts, and the intensities of the transitions. The rotational constants, which were obtained by a least-squares fit of the transition frequencies, are shown in Table III.

TABLE II

OBSERVED TRANSITIONS (MHz) FOR $CD_3(CH_3)_2P \cdot BH_3$ AND $(CH_3)_3P \cdot BH_2D$

Transition	$CD_3(CH_3)_2$-$P \cdot BH_3$	$\Delta\nu^a$	$(CH_3)_3P \cdot BH_2D$	$\Delta\nu$
5_{23}–4_{22}	30,346.55	0.00	30,963.31	−0.31
5_{05}–4_{04}	29,547.04	0.09	30,939.92	−0.36
5_{14}–4_{13}	30,015.46	0.31	30,994.72	0.39
5_{15}–4_{14}	29,538.58	0.22	30,905.62	0.17
5_{24}–4_{23}	29,899.72	0.18	*c*	
6_{24}–5_{23}	36,319.80	−0.27	*c*	
6_{06}–5_{05}	35,410.14	−0.38	37,121.90	−0.05
6_{15}–5_{14}	35,859.13	−0.15	*b*	
6_{16}–5_{15}	35,407.90	−0.06	37,085.21	0.19
6_{25}–5_{24}	35,801.09	0.20	*c*	

[a] $\Delta\nu = \nu(\text{obsd}) - \nu(\text{calcd})$. [b] Not observed because spectral region was not accessible. [c] Not measured because these transitions overlapped other $K = 3$, $K = 4$, etc. transitions.

$CH_3PH_2 \cdot BH_3$.—The transitions which were assigned for the nine isotopic species are listed in Tables IV–VI. The assignments, which were greatly facilitated by the increased isotopic enrichment of the samples, were based on the Stark effect, frequency fit, intensities, and the expected isotope shifts. No splittings due to boron quadrupole coupling or internal rotation were observed. Several weaker vibrational satellites were noted; they were not measured or assigned.

TABLE III

ROTATIONAL CONSTANTS (MHz) FOR $CD_3(CH_3)_2P \cdot BH_3$ AND $(CH_3)_3P \cdot BH_2D$

	$CD_3(CH_3)_2P \cdot BH_3$	$(CH_3)_3P \cdot BH_2D$
A	3247.33 ± 0.50	3472 ± 10
B	3070.15 ± 0.20	3104.18 ± 0.10
C	2933.47 ± 0.10	3086.35 ± 0.10

Intense "a" and much weaker "b" type transitions were observed for all the species except the two BH_2D adducts (*cf.* below) and the $CH_3PD_2 \cdot BH_3$ species. The "b" type transitions in the last three species were too weak (due to a smaller isotopic enrichment) to be assigned unequivocally because they occurred in a rich region of the spectra. The "b" dipole spectrum for the ^{10}B species in natural abundance was also weak, but the transitions fortunately occurred in a sparse region of the spectrum where they could be identified rather easily.

The $CH_3PH_2 \cdot BH_2D$ and $CH_2DPH_2 \cdot BH_3$ species both exist in two forms distinguished by deuterium substitution in the plane of symmetry ($CH_3PH_2 \cdot BH_2D_s$ and $CH_2D_sPH_2 \cdot BH_3$) or at the two equivalent positions above and below the plane of symmetry ($CH_3PH_2 \cdot BH_2D_a$ and $CH_2D_aPH_2 \cdot BH_3$). The spectra of the last two species were observed to be approximately twice as intense as their corresponding in-plane species.

The rotational constants for the various species are listed in Table VII. These were obtained from three low J transitions for the species in Tables IV and V and from a least-squares analysis of all the transitions for the species in Table VI, since no "b" type transitions were obtained for the latter species.

The values of $(I_A + I_B - I_C)$ for several species are given in Table VIII. The near equality of this quantity for these species confirms that the molecule possesses a plane of symmetry as shown in Figure 1. The moments of inertia of the $CH_3PD_2 \cdot BH_3$ species also demonstrate the plane of symmetry. It can be shown that

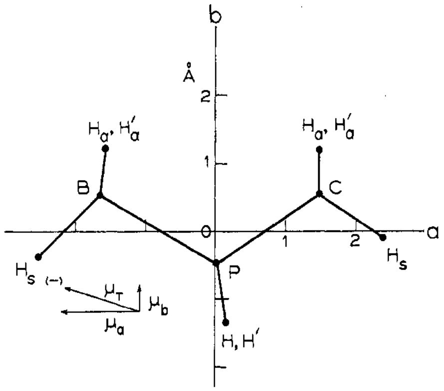

Figure 1.—Projection of $CH_3PH_2 \cdot BH_3$ on the symmetry (*ab*) plane.

$$(I_A + I_B - I_C)_{CH_3PH_2 \cdot BH_3} = (I_A + I_B - I_C)_{CH_3PD_2 \cdot BH_3} - 4\Delta m c_{H(P)}^2$$

where $\Delta m = m_D - m_H$. Using the value of $c_{H(P)}$ from Table XII, the right-hand side of the equation gives 11.805 amu Å², which compares well with the values in Table VIII.

Stark Effect.—The Stark measurements were made with a precision dc power supply (Fluke, Model 412B).[8] The effective guide spacing was determined by using the 1 ← 0 transition of OCS (μ = 0.7152 D).[9] The second-order Stark coefficients measured for the $J = 4 \leftarrow 3$, $K = 0$ transition of $(CH_3)_3P \cdot BH_3$ are listed in Table IX, along with the second-order Stark coefficients for several transitions of $CH_3PH_2 \cdot BH_3$.

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(7) S. D. Gokhale and W. L. Jolly, *Inorg. Syn.*, **9**, 56 (1967).

(8) W. H. Kirchhoff, *J. Amer. Chem. Soc.*, **89**, 1312 (1967).

(9) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

TABLE IV

THE MICROWAVE SPECTRA OF $CH_3PH_2\cdot BH_3$, $^{13}CH_3PH_2\cdot BH_3$, AND $CH_2D_aPH_2\cdot BH_3$ (MHz)

Transition	$CH_3PH_2\cdot BH_3$	$\Delta\nu$[a]	$^{13}CH_3PH_2\cdot BH_3$	$\Delta\nu$	$CH_2D_aPH_2\cdot BH_3$	$\Delta\nu$
			a Type			
$2_{02}-1_{01}$	21,839.78	−0.02	21,292.83	−0.18	21,085.54	−0.04
$2_{11}-1_{10}$	(22,896.79)[b]	0.03	(22,312.72)	−0.01	(22,115.52)	0.02
$2_{12}-1_{11}$	(20,905.60)	0.04	(20,388.28)	0.03	(20,181.74)	0.03
$3_{21}-2_{20}$	33,095.50	0.06	32,253.89	−0.11	31,973.34	0.22
$3_{03}-2_{02}$	32,607.76	−0.40	31,796.87	−0.61	31,472.43	−0.39
$3_{12}-2_{11}$	34,305.11	−0.48	33,431.53	−0.44	32,132.13	−0.33
$3_{13}-2_{12}$	31,320.97	−0.22	30,547.36	−0.07	30,234.30	0.03
$3_{22}-2_{21}$	32,852.72	0.91	32,026.31	0.56	31,723.70	0.76
			b Type			
$1_{11}-0_{00}$	(22,566.12)	0.00	22,274.80	0.04	...	...
$2_{12}-1_{01}$	32,521.21	0.13	(31,987.78)	0.03	(30,813.38)	0.03
$4_{04}-3_{13}$	33,806.56	−2.06	32,691.88	−2.18	33,191.85	−1.77
$3_{21}-3_{12}$	33,697.01	−0.68	33,677.04	−0.90	30,798.02	−0.54
$4_{22}-4_{13}$	32,388.00[c]	0.06	32,392.75	0.31	29,564.60	0.66
	32,389.08	1.14				
$5_{23}-5_{14}$	31,219.53	2.09	31,226.42	2.23	28,497.83	1.83

[a] $\Delta\nu = \nu(\text{obsd}) - \nu(\text{calcd})$. [b] Transitions in parentheses used to calculate rotational constants. [c] An unambiguous assignment was impossible since these two lines overlapped.

TABLE V

THE MICROWAVE SPECTRA OF $CH_3PH_2\cdot {}^{10}BH_3$, $CH_3PDH\cdot BH_3$, AND $CH_2D_sPH_2\cdot BH_3$ (MHz)

Transition	$CH_3PH_2\cdot {}^{10}BH_3$	$\Delta\nu$	$CH_3PDH\cdot BH_3$	$\Delta\nu$	$CH_2D_sPH_2\cdot BH_3$	$\Delta\nu$
			a Type			
$2_{02}-1_{01}$	22,530.90	−0.01	21,495.21	−0.36	20,565.29	0.01
$2_{11}-1_{10}$	(23,637.91)	−0.02	(22,581.51)	0.01	(21,494.58)	0.00
$2_{12}-1_{11}$	(21,557.76)	0.00	(20,554.97)	−0.01	(19,730.02)	0.00
$3_{21}-2_{20}$	34,162.00	−0.56	32,640.21	−0.23	31,105.44	0.13
$3_{03}-2_{02}$	33,630.72	−0.07	32,063.85	−0.37	30,731.48	−0.08
$3_{12}-2_{11}$	35,413.61	0.10	33,824.60	−0.45	32,211.59	−0.05
$3_{13}-2_{12}$	32,295.70	−0.31	30,788.41	−0.05	29,566.48	0.21
$3_{22}-2_{21}$	33,897.68	0.93	32,352.90	0.52	30,919.36	0.92
			b Type			
$2_{12}-1_{01}$	(33,144.45)	0.01	(30,631.18)	0.01	(31,711.10)	0.03
$3_{21}-3_{12}$	33,576.60	0.60	...	...	...	...
$3_{22}-3_{13}$	...	...	34,831.10	−1.15	...	...
$4_{04}-3_{13}$	...	...	...	...	30,781.13	−0.99
$4_{22}-4_{13}$	32,237.90	−1.04	27,893.66	−0.03	33,642.40	−0.54
$5_{23}-5_{14}$	31,073.42	0.04	26,904.64	0.76	32,456.80	0.74

TABLE VI

THE MICROWAVE SPECTRA OF $CH_3PD_2\cdot BH_3$, $CH_3PH_2\cdot BH_2D_a$, AND $CH_3PH_2\cdot BH_2D_s$ (MHz)

Transition (a type)	$CH_3PD_2\cdot BH_3$	$\Delta\nu$	$CH_3PH_2\cdot BH_2D_a$	$\Delta\nu$	$CH_3PH_2\cdot BH_2D_s$	$\Delta\nu$
$2_{02}-1_{01}$	21,154.84	−0.08	21,004.79	−0.07	20,439.08	0.29
$2_{11}-1_{10}$	22,233.85	0.09	22,016.99	0.29	21,361.63	0.11
$2_{12}-1_{11}$	20,236.18	0.09	20,116.52	0.29	19,609.04	−0.04
$3_{21}-2_{20}$	32,168.84	−0.22	31,844.03	−0.28	30,912.74	−0.20
$3_{03}-2_{02}$	31,535.56	−0.16	31,354.94	−0.13	30,542.93	−0.23
$3_{12}-2_{11}$	33,298.34	−0.12	32,985.00	−0.20	32,012.20	−0.26
$3_{13}-2_{12}$	30,305.86	−0.12	30,136.83	−0.13	29,385.21	−0.09
$3_{22}-2_{21}$	31,852.98	0.59	31,600.41	0.72	30,728.78	0.78

TABLE VII

ROTATIONAL CONSTANTS FOR $CH_3PH_2\cdot BH_3$ (MHz)

Species	A	B	C
$CH_3PH_2\cdot BH_3$	17,588.62 ± 0.25	5973.10 ± 0.05	4977.50 ± 0.05
$CH_3PH_2\cdot {}^{10}BH_3$	17,756.19 ± 0.25	6169.50 ± 0.05	5129.42 ± 0.05
$^{13}CH_3PH_2\cdot BH_3$	17,418.25 ± 0.25	5818.74 ± 0.05	4856.51 ± 0.05
$CH_3PDH\cdot BH_3$	15,974.89 ± 0.25	5898.69 ± 0.05	4885.43 ± 0.05
$CH_3PD_2\cdot BH_3$	14,641 ± 7	5808.15 ± 0.06	4809.31 ± 0.06
$CH_2D_aPH_2\cdot BH_3$	16,402.25 ± 0.25	5770.60 ± 0.05	4803.71 ± 0.05
$CH_2D_sPH_2\cdot BH_3$	17,575.28 ± 0.25	5594.21 ± 0.05	4711.94 ± 0.05
$CH_3PH_2\cdot BH_2D_s$	17,507 ± 20	5559.44 ± 0.08	4683.23 ± 0.08
$CH_3PH_2\cdot BH_2D_a$	16,249 ± 14	5741.73 ± 0.09	4791.50 ± 0.09

TABLE VIII
VALUES OF $I_A + I_B - I_C$ FOR $CH_3PH_2 \cdot BH_3$ (AMU Å^2)

Species	$I_A + I_B - I_C$	Species	$I_A + I_B - I_C$
$CH_3PH_2 \cdot BH_3$	11.813	$CH_2D_sPH_2 \cdot BH_3$	11.843
$CH_3PH_2 \cdot {}^{10}BH_3$	11.856	$CH_2PH_2 \cdot BH_2D_s$	11.863
${}^{13}CH_3PH_2 \cdot BH_3$	11.809		

TABLE IX
STARK COEFFICIENTS ($10^6 \times$ MHz CM^2/V^2) AND
DIPOLE MOMENT COMPONENTS (D) FOR
$CH_3PH_2 \cdot BH_3$ AND $(CH_3)_3P \cdot BH_3$

Transition	Obsd	Calcd
	$(CH_3)_3P \cdot BH_3$	
$J = 4–3, K = 0, \|M\| = 2$	5.23 ± 0.15	5.10
$\|M\| = 1$	-5.38 ± 0.38	-5.52
	$\|\mu\| = 4.99 \pm 0.2$	
	$CH_3PH_2 \cdot BH_3$	
$3_{12}–2_{11}, M = 0$	-2.42 ± 0.03	-2.39
$2_{11}–1_{10}, M = 0$	5.32 ± 0.04	5.29
$3_{03}–2_{02}, M = 0$	3.20 ± 0.04	3.21
$\|\mu_a\| = 4.36 \pm 0.04$	$\|\mu_b\| = 1.65 \pm 0.03$	$\|\mu_t\| = 4.66 \pm 0.05$

Data Analysis

Structure of $(CH_3)_3P \cdot BH_3$.—The substitution coordinates[10] of the BH_3 group were calculated from the moments of inertia of the normal, the $(CH_3)_3P \cdot {}^{10}BH_3$, and the $(CH_3)_3P \cdot BH_2D$ species. The coordinates of the methyl group hydrogen atoms were calculated using the moments of inertia of $CD_3(CH_3)_2P \cdot BH_3$ with Kraitchman's equations modified for a triply deuterated methyl group.

In deriving the modified equations, it was assumed that the methyl group was symmetrical with a C_3 symmetry axis that was coincident with the P–C bond axis. The geometry of a methyl group projected in a symmetry plane is shown in Figure 2. It is convenient to relate the coordinates of the three hydrogen atoms to a point which lies at the intersection of the C_3 symmetry axis and the bisector of the $H_1H_2H_1'$ triangle. The four parameters associated with this point are x and z which define the position of the point in the principal-axis system of $(CH_3)_3P \cdot BH_3$, angle θ which describes the orientation of the plane formed by the three H atoms relative to the z axis (or PB bond axis), and d which is related to the distance between two H atoms through the equation $3d = r_{HH'} \sin 60°$. The equations locating the H atoms are

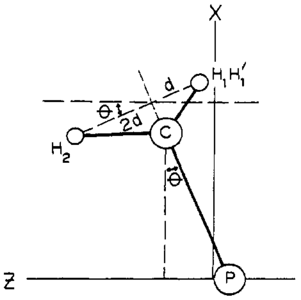

Figure 2.—Projection of the methyl group on the symmetry plane (xz) in $(CH_3)_3P \cdot BH_3$.

$$x_1 = x_1' = x + d \sin \theta \qquad x_2 = x - 2d \sin \theta$$

$$z_1 = z_1' = z - d \cos \theta \qquad z_2 = z + 2d \cos \theta$$

$$y_1 = -y_1' = \pm\sqrt{3}d \qquad y_2 = 0$$

With these, the following inertial dyadic elements for $CD_3(CH_3)_2P \cdot BH_3$ were derived in the principal coordinate system of the normal isotopic species

$$I'_{zz} = I_Z + \mu x^2 + 2\Delta m y_1^2 + 6\Delta m d^2 \sin^2 \theta$$

$$I'_{yy} = I_Y + \mu(x^2 + z^2) + 6\Delta m d^2 = I'_Y$$

$$I'_{xx} = I_X + \mu z^2 + 2\Delta m y_1^2 + 6\Delta m d^2 \cos^2 \theta$$

$$I'_{xz} = -\mu xz - 6\Delta m d^2 \sin \theta \cos \theta$$

$$I'_{xy} = I'_{yz} = 0$$

The notation of Kraitchman has been employed throughout,[10] except that $\mu = 3M\Delta m/M + 3\Delta m$ where $\Delta m = M_D - M_H$ and M is the mass of the normal isotopic species. Since all the cross terms involving y are zero, the moment of inertia derived spectroscopically, I'_Y, is identical to the expression for I'_{yy}. Also, the following useful equation can be derived

$$I_Z = I'_X + I'_Z - I'_Y - 4\Delta m y_1^2$$

Therefore a value for the moment of inertia about the symmetry axis of $(CH_3)_3P \cdot BH_3$ (I_Z) can be obtained from the moments of inertia of the $CD_3(CH_3)_2P \cdot BH_3$ species provided that a value is assumed for y_1, where $2y_1 = r_{HH'}$.

With a value assumed for $r_{HH'}$, the inertial dyadic can be reduced to a 2 × 2 matrix involving the three parameters x, z, and θ. If the θ is known from other experiments or can be reasonably assumed, x, z, and the hydrogen coordinates can be obtained.

In the case of $(CH_3)_3P \cdot BH_3$, the value of θ was constrained to be equal to $\angle CPB - 90°$. However, $\angle CPB$ was not known initially and was dependent upon the carbon and phosphorus coordinates. These could be obtained once the hydrogen atoms were located by using the first- and second-moment equations for $(CH_3)_3P \cdot BH_3$, as well as a geometrical relationship ($\tan \theta = (z_p - z_c)/x_c$; see Figure 2) which aligned the P–C bond parallel to the assumed C_3 methyl group symmetry axis.

Hence a cyclical procedure was employed in which the first step was to assume $r_{HH'}$ and θ. Next, x and z of the hydrogens were determined and, finally, the carbon and phosphorus coordinates were obtained. If the assumed value of θ did not agree with that calculated from the final $\angle CPB$ or if the methyl groups were not symmetric, then a new θ was assumed. The calculation was recycled until a consistent set of data was obtained for a range of six r_{HH} values based on typical values for r(CH) and $\angle HCH$ in methyl groups. The structures obtained from these calculations are shown in Table X. These results show that the heavy-atom parameters are rather insensitive to the assumption of

TABLE X
STRUCTURAL PARAMETERS FOR $(CH_3)_3P \cdot BH_3$
vs. ASSUMED r(HH) VALUES

r(HH), Å (assumed)	∠HCH, deg	r(CH), Å	r(PB), Å	∠CPC, deg	r(PC), Å
1.736	109.1	1.066	1.901	105.0	1.822
1.752	109.2	1.075	1.902	105.1	1.820
1.769	109.5	1.084	1.900	104.9	1.819
1.785	109.7	1.091	1.903	105.2	1.818
1.802	109.9	1.100	1.901	105.0	1.817
1.818	110.1	1.109	1.902	105.0	1.815

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(10) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

$r_{HH'}$ but the methyl group parameters are quite dependent upon it.

It is reasonable to limit the assumed value of $r_{HH'}$ close to the experimental values of 1.760 and 1.763 Å, obtained, respectively, for the closely related $CH_3PH_2 \cdot BH_3$ (*cf.* below) and $(CH_3)_3P$.[11] The value of 1.760 Å gave the final structural values listed in Table XI. The error limits for the values were estimated from the experimental uncertainties in the rotational constants.

TABLE XI

STRUCTURAL PARAMETERS FOR $(CH_3)_3P \cdot BH_3$

$r(PB) = 1.901 \pm 0.007$ Å $\angle CPC = 105.0 \pm 0.4°$
$r(PC) = 1.819 \pm 0.010$ Å $\angle HCH = 109.3 \pm 1.0$
$r(CH) = 1.08 \pm 0.02$ Å $\angle HBH = 113.5 \pm 0.5°$
$r(BH) = 1.212 \pm 0.010$ Å

A calculation was also carried out to determine the effect of vibrations on the structural results by assuming that deuterium substitution caused a 0.005-Å shortening of a particular bond. This produced changes that were well within the experimental uncertainties listed in Table XI.

The methyl group parameters for $CH_3PH_2 \cdot BH_3$ (*cf.* below) and for $(CH_3)_3P$[11] suggest that the methyl groups are slightly asymmetric and possess small tilts. Therefore it is quite important to ascertain what effect such asymmetries would have on the $(CH_3)_3P \cdot BH_3$ structure where symmetrical methyl groups with no tilts have been assumed. The effects were estimated based on $CH_3PH_2 \cdot BH_3$ and $(CH_3)_3P$ and they had only a slight effect on the heavy-atom parameters, but they so increased the number of possible methyl group parameters that it was impossible to determine anything definite about the methyl groups. Thus, it still appears that the heavy-atom results in Table XI are reliable, but the methyl group parameters listed are somewhat arbitrary and depend quite strongly on any assumed geometry. A 50% increase in the experimental uncertainty for the heavy-atom parameters in Table XI should cover the changes in their parameters for plausible asymmetries of the methyl groups.

Structure of $CH_3PH_2 \cdot BH_3$.—Substitution coordinates[10] were calculated for all the atoms except the phosphorus. The phosphorus coordinates were calculated directly from the first-moment conditions. The coordinates of the atoms are shown in Table XII. The H(P) coordinates were calculated using the more accurate $CH_3PDH \cdot BH_3$ species. The results from $CH_3PD_2 \cdot BH_3$ were quite similar which served to verify the two assignments. The two small substitution coordinates were checked for possible sign ambiguities. Only the negative value of $b_{H_s(C)}$ yields a reasonable result for $r(CH_s)$. A positive sign for $a_{H(P)}$ was determined by computing the product of inertia, $\Sigma m_i a_i b_i$. The value of 0.398 amu Å^2 that was obtained with a positive value for $a_{H(P)}$ was clearly more acceptable than 1.442 amu Å^2 calculated with a negative value.

TABLE XII

COORDINATES OF $CH_3PH_2 \cdot BH_3$ IN PRINCIPAL-AXIS SYSTEM (Å)[a]

Atom	*a*	*b*	*c*
P	−0.0044	−0.4521	0.0
H(P)	0.1940	−1.3338	±1.0742
B	−1.6414	0.5238	0.0
H_s(B)	−2.5136	−0.3495	0.0
H_a(B)	−1.5555	1.2028	±1.0204
C	1.5045	0.5460	0.0
H_s(C)	2.4021	−0.0869	0.0
H_a(C)	1.4920	1.1845	±0.8800

[a] Masses employed for both molecules in this work were from C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955, p 644. The conversion factor 5.05531×10^5 amu Å^2 MHz was used to calculate the moments of inertia.

The structural parameters were calculated directly from the coordinates in Table XII and the values are shown in Table XIII. The coordinate system and the structure are illustrated in Figures 1 and 3, respectively. The coordinates establish that both the BH_3 and the CH_3 groups are staggered with respect to the P–H bonds.

TABLE XIII

STRUCTURAL PARAMETERS FOR $CH_3PH_2 \cdot BH_3$

Bonds	Value, Å	Bond angles	Value, deg	Bond angles	Value, deg
CH_s	1.098 ± 0.016	H_aBH_s	116.1 ± 0.8	HPB	116.3 ± 0.6
CH_a	1.087 ± 0.004	H_aBH_a'	112.3 ± 1.2	PBH_a	102.9 ± 0.6
BH_a	1.229 ± 0.022	H_aCH_s	110.4 ± 0.6	PBH_s	104.2 ± 1.0
BH_s	1.234 ± 0.023	H_aCH_a'	108.1 ± 0.4	PCH_a	108.3 ± 0.4
PC	1.809 ± 0.006	HPH′	99.9 ± 0.4	PCH_s	111.3 ± 1.0
PB	1.906 ± 0.006	HPC	103.2 ± 0.6		
PH	1.404 ± 0.006	CPB	115.7 ± 0.4		

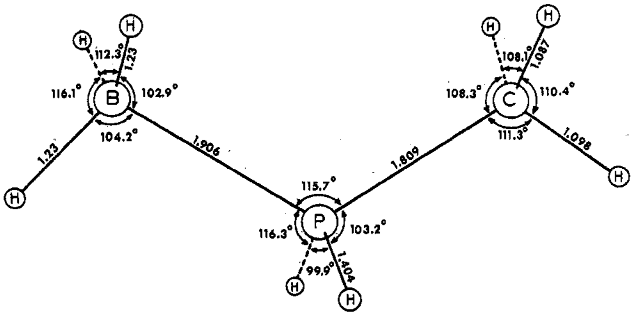

Figure 3.—Structure of $CH_3PH_2 \cdot BH_3$.

Since substitution coordinates were determined for all atoms except phosphorus, a routine compound errors analysis was carried out based on the experimental uncertainties in the rotational constants.[12] The experimental uncertainties that resulted for most of the bond lengths and angles seemed quite low and hence were doubled, with the exception of the parameters involving the BH_3 group which already seemed reasonable. These uncertainties are listed in Table XIII.

An estimate of the effect of vibrations on the structure was made by assuming that deuterium substitution caused a 0.005-Å shortening of a particular bond.[13] This resulted in B–H, C–H, and P–H bond lengths that were about 0.01 Å larger than are listed in Table XIII.

Dipole Moments.—The average dipole moment for $(CH_3)_3P \cdot BH_3$ calculated from the Stark coefficients in Table IX is 4.99 ± 0.2 D. The large uncertainty in this value is due mainly to the experimental uncertainty in the frequency measurements on the rather

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[11] P. S. Bryan and R. L. Kuczkowski, *J. Chem. Phys.*, **55**, 3049 (1971).

[12] E. B. Wilson, Jr., "An Introduction to Scientific Research," McGraw-Hill, New York, N. Y., 1952, p 272.

[13] D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **37**, 1668 (1962).

weak transitions. The data in Table IX gave values for $CH_3PH_2 \cdot BH_3$ of $|\mu_a| = 4.36$ D, $|\mu_b| = 1.65$ D, and $|\mu_t| = 4.66 \pm 0.05$ D. The total dipole makes an angle of 20.8° with the *a* axis. The orientation of the total dipole shown in Figure 1 is based on the bond dipole moment orientations discussed below.

These values agree well with those obtained by Morse[14] from measurements in benzene. He obtained 4.97 ± 0.01 D for $(CH_3)_3P \cdot BH_3$ and 4.58 ± 0.01 D for $CH_3PH_2 \cdot BH_3$.

Discussion

Table XIV contains several of the structural parameters for free and coordinated $(CH_3)_3P$ and CH_3PH_2.

TABLE XIV

COMPARISON OF STRUCTURAL PARAMETERS

	Microwave spectroscopy		Electron diffraction
	$(CH_3)_3P \cdot BH_3$[a]	$(CH_3)_3P$[b]	$(CH_3)_3P$[c]
P–C, Å	1.819 ± 0.010	1.843 ± 0.003	1.846 ± 0.003
∠CPC, deg	105.0 ± 0.4	98.9 ± 0.2	98.6 ± 0.3
	$CH_3PH_2 \cdot BH_3$[a]	CH_3PH_2[d]	CH_3PH_2[e]
P–C, Å	1.809 ± 0.006	1.863	1.858 ± 0.003
P–H, Å	1.404 ± 0.006	1.414	1.423 ± 0.007
∠CPH, deg	103.2 ± 0.6	97.5	96.5 (assumed)
∠HPH′, deg	99.9 ± 0.4	93.4	

[a] This work. [b] Reference 11. [c] L. S. Bartell and L. O. Brockway, *ibid.*, **32**, 512 (1960). [d] T. Kojima, E. L. Breig, and C. C. Lin, *J. Chem. Phys.*, **35**, 2139 (1961). [e] L. S. Bartell, *ibid.*, **32**, 832 (1960).

A systematic decrease in the bond distances and an increase in the bond angles upon coordination is observed. A similar effect was observed in other borane complexes such as $F_3P \cdot BH_3$ and $HF_2P \cdot BH_3$. Such changes have been discussed previously[4,15] and are quite consistent with several semiempirical structural models such as the electron pair repulsion theory[16] or the second-order hybridization theory.[17] There is one structural change which is particularly noteworthy. It is seen that the P–C bond length in free $(CH_3)_3P$ is shorter than in CH_3PH_2. Upon coordination the opposite is observed. The significance of this more pronounced shortening of the P–C bond in CH_3PH_2 is not clear. It might be argued that the experimental uncertainties are too large to establish the effect unambiguously. Hence it would be interesting to know if a similar trend occurs in other methylphosphine complexes and also if the same trend occurs for C–N bond lengths in methylamine complexes.

TABLE XV

PHOSPHORUS–BORON BOND DISTANCES IN BORANE ADDUCTS

Compd	P–B, Å	Compd	P–B, Å
$H_3P \cdot BH_3$	1.93 ± 0.012[a]	$(NH_2)_3P \cdot BH_3$	1.887 ± 0.013[c]
$CH_3PH_2 \cdot BH_3$	1.906 ± 0.006[b]	$F_3P \cdot BH_3$	1.836 ± 0.012[d]
$(CH_3)_3P \cdot BH_3$	1.901 ± 0.007[b]	$F_2HP \cdot BH_3$	1.832 ± 0.009[e]

[a] E. L. McGandy, Ph.D. Thesis, Boston University, Boston, Mass., 1961. [b] This work. [c] Reference 3. [d] Reference 2. [e] Reference 4.

The value for r(PB) in $(CH_3)_3P \cdot BH_3$ is listed in Table XV along with the values for several other borane complexes. The P–B bond lengths for the two methylphosphine adducts are quite close; the difference between them is probably not significant in view of the attached uncertainties. Thus, although $(CH_3)_3P$ is a stronger donor than CH_3PH_2 based on their reactions with other acids such as $B(CH_3)_3$ and BF_3,[18,19] there seems to be little difference in the P–B bond lengths in their borane adducts.

From the values in Table XV, it is apparent that when electronegative atoms such as fluorines are attached to phosphorus, a much shorter central bond results than when electropositive CH_3 groups or H atoms are attached. This contrast in r(PB) values is generally (except for $HF_2P \cdot BH_3$)[4] in agreement with the semiempirical structural models mentioned above.[16,17] The long bonds in $(CH_3)_3P \cdot BH_3$, $CH_3PH_2 \cdot BH_3$, and $H_3P \cdot BH_3$ are also consistent with the proposal that the classical σ dative bond can be supplemented by d_π–p_π bonding involving the phosphorus d orbitals and the borane group.[20] Such a contribution should be smaller in these adducts than in the fluorinated phosphines.

While the long P–B bonds in $(CH_3)_3P \cdot BH_3$ and $CH_3PH_2 \cdot BH_3$ are reasonable based on these semiempirical models, they nevertheless appear inconsistent with the fact that CH_3PH_2 and especially $(CH_3)_3P$ are considered better Lewis bases than PF_3 toward other group III acids. The long P–B bonds also appear inconsistent with the stability of $(CH_3)_3P \cdot BH_3$ and $CH_3PH_2 \cdot BH_3$ compared to $F_3P \cdot BH_3$; employing evidence for dissociation as the criterion of stability, only $F_3P \cdot BH_3$ and $H_3P \cdot BH_3$ in Table XV are extensively dissociated at room temperature.

The comparison of the stabilities of $(CH_3)_3P \cdot BH_3$ and $F_3P \cdot BH_3$ can be further analyzed by considering the criterion of stability suggested by Coyle and Stone, *viz.*, the enthalpy change, ΔH, for the dissociation of the adduct in the gas phase into its component donor and acceptor molecules.[21] A value for the dissociation of $F_3P \cdot BH_3$ is already known.[2] Since $(CH_3)_3P \cdot BH_3$ does not readily dissociate, a value cannot be directly measured. However, a lower limit was obtained for the reaction

$$2(CH_3)_3P \cdot BH_3(g) \longrightarrow 2(CH_3)_3P(g) + B_2H_6(g)$$

by estimating the minimum values for ΔG and ΔS at 298°. The ΔG was estimated as ≥ 14 kcal since no microwave spectrum for $(CH_3)_3P$ was observed. This indicated that less than 1% of the complex dissociated in the absorption cell at pressures of 0.1–0.01 Torr. The ΔS was estimated as 28 eu by using the reported value of $S°$ for B_2H_6[22] and calculated $S°$ values for $(CH_3)_3P$ and $(CH_3)_3P \cdot BH_3$. The latter were calculated from the known rotational constants and vibrational spectra.[23–26] Using the ΔG and ΔS values, the ΔH for the reaction was estimated to be ≥ 22.4 kcal.

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(14) J. G. Morse, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1965.

(15) Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969).

(16) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970).

(17) H. A. Bent, *J. Inorg. Nucl. Chem.*, **19**, 43 (1961).

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

(19) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(20) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

(21) T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 137 (1964).

(22) S. Sundram, *Z. Phys. Chem. (Frankfurt am Main)*, **36**, 376 (1963).

(23) Several low-frequency vibrational modes for $(CH_3)_3P \cdot BH_3$ had to be estimated from comparison with similar molecules; the choice for their frequencies did not significantly alter the conclusions that follow.

(24) D. R. Lide, Jr., *J. Chem. Phys.*, **27**, 343 (1957).

(25) E. J. Rosenbaum, D. J. Rubin, and C. R. Sandberg, *ibid.*, **8**, 366 (1940).

(26) R. J. Wyma, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1964.

This can be compared with the value of 11–12 kcal measured for the dissociation of $F_3P \cdot BH_3$.[2,27] A similar calculation of the ΔH for the dissociation of CH_3PH_2 was not made, partly due to the lack of vibrational data for $CH_3PH_2 \cdot BH_3$.

The possibility that $(CH_3)_3P \cdot BH_3$ is stable for kinetic reasons must also be considered. This possibility seems unlikely because strong coordination compounds ordinarily have nearly zero activation energies for formation[21] and because mixtures of diborane and $(CH_3)_3P$ readily react to form the adduct. The same is true of $CH_3PH_2 \cdot BH_3$ and $(CH_3)_2PH \cdot BH_3$.[28]

In summary, the data for $(CH_3)_3P \cdot BH_3$ support the deduction that $(CH_3)_3P$ forms a more stable borane adduct than F_3P, even though $F_3P \cdot BH_3$ has a significantly shorter P–B bond. The same is true for $CH_3PH_2 \cdot BH_3$ *vs.* $F_3P \cdot BH_3$ based on the tendency to dissociate at room temperature. Presumably then, the usually accepted correlation between bond length and stability should be applied cautiously for addition compounds. It is important to point out, however, that there is a distinction between the stability of the complex and the strength of the central bond. Thus, the enthalpy of dissociation (ΔH_G) can be considered as arising from two contributions: an enthalpy of reorganization (ΔH_R) and an enthalpy of dative bond formation (ΔH_T).[21] It is interesting to speculate on the relative contributions of ΔH_R and ΔH_T toward ΔH_G. If it is assumed that the traditional concept of bond strength holds, *i.e.*, that the strongest bond is the shortest, then it must be concluded that the reorganization enthalpy is much larger for F_3P than $(CH_3)_3P$. This view emphasizes the role of the reorganization step of the donor in the formation of the borane complexes. Unfortunately, the changes in structural parameters of both F_3P and $(CH_3)_3P$ upon coordination are similar and do not suggest a large difference in reorganization enthalpies. It is also possible that quite different values of ΔH_R may not show up as changes in the bond lengths and angles.

On the other hand, if the reorganization step is similar for both reactions, the conclusion is that $(CH_3)_3P \cdot BH_3$ has a longer yet a stronger PB bond than $F_3P \cdot BH_3$. In this regard, it is interesting that Rudolph and Parry have proposed a model which accounts for a short but weak bond in $F_3P \cdot BH_3$.[29] Additional experiments or quantitative estimates from theoretical calculations as guidelines for ΔH_R and ΔH_T would be useful in determining unambiguously which interpretation applies for $(CH_3)_3P \cdot BH_3$ and $F_3P \cdot BH_3$.

The structure of $CH_3PH_2 \cdot BH_3$ is also interesting because the phosphorus is asymmetrically substituted. In another asymmetric adduct, $HF_2P \cdot BH_3$, a pronounced tilt of the borane group away from the fluorines was reported.[4] The structural parameters for $CH_3PH_2 \cdot BH_3$ do not indicate a similar pronounced tilt. The two PBH angles (Figure 3) do differ by 1.3°; however, the uncertainties are quite large for the borane group and can account for the difference. The 3° difference in the PCH angles of the methyl group is beyond experimental uncertainty and appears to be real.

The tilt of the methyl group can be explained by a similar mechanism as was employed regarding the borane tilt in HF_2PBH_3. In the latter, bond dipole interactions or nonbonded electrostatic effects involving a repulsion between the fluorine atoms and the hydridic hydrogens attached to borane was proposed. Applying a similar argument to the methyl group in $CH_3PH_2 \cdot BH_3$, the tilt can be considered in terms of electrostatic interactions of the protonic methyl hydrogens with the protonic hydrogen on phosphorus and the negative boron. The boron is thought to possess a residual negative charge due to the formation of the donor–acceptor bond with phosphorus. Such an interaction could qualitatively rationalize the direction of tilt of the methyl group toward the borane group. Alternatively, this proposal suggests that the methyl tilt arises from an interaction with a very polar P–B bond. Similarly, a pronounced tilt of the borane group compared to $HF_2P \cdot BH_3$ is not found because the BH bonds interact with two PH bond moments and a PC bond moment which are similar in magnitude and direction.

An estimate of the magnitude of the P–BH_3 bond dipole moment can be obtained from the dipole moments and structures measured for $(CH_3)_3P \cdot BH_3$ and $CH_3PH_2 \cdot BH_3$. Parry and Weaver have deduced bond moment values for the methylphosphines.[30] Using their value for the P–CH_3 moment in $(CH_3)_3P$, a value of 3.97 D can be calculated for the P–BH_3 moment in $(CH_3)_3P \cdot BH_3$. With their values for the P–CH_3 and PH bond moments in CH_3PH_2, values of 3.92 and 3.44 D were calculated for the P–BH_3 bond moment in $CH_3PH_2 \cdot BH_3$ depending on whether the μ_a or μ_b dipole components were used. In these calculations, it was assumed that the methyl groups and the hydrogens were positive while the borane group was negative with respect to phosphorus. The lack of perfect correspondence for the calculations probably arises from the fact that the bond moments calculated from three-coordinate phosphorus compounds are not expected to be exactly transferable to four-coordinate phosphorus. Nevertheless, the reasonable consistency between the three calculations indicates that the P–BH_3 bond dipole moment is approximately 3.4–4.0 D.

Acknowledgment.—This work was supported by a grant (GP 11388) from the National Science Foundation. Discussions on aspects of coordination chemistry with Dr. Ralph Rudolph are also acknowledged.

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(27) A. B. Burg and Y. C. Fu, *J. Amer. Chem. Soc.*, **88**, 1147 (1966).

(28) H. Brumberger and W. H. Smith, *J. Phys. Chem.*, **72**, 3340 (1968).

(29) R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, **89**, 1621 (1967).

(30) J. R. Weaver and R. W. Parry, *Inorg. Chem.*, **5**, 718 (1966).