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Crystal and Molecular Structure of Bis(triphenylphosphine)–Diborane(4)

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The structure of bis(triphenylphosphine)-diborane(4), $B_2H_4 \cdot 2P(C_6H_5)_3$, has been determined from X-ray diffraction data obtained from a single crystal by counter methods. The unit cell is triclinic, with a = 9.119 (2) Å, b = 9.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, b = 0.360 (2) Å, c = 0.119 (2) Å, c = 0.119 (2) Å, c = 0.360 (2) Å, c = 0.119 (2) Å, c = 0.360 (2) Å, c = 0.119 (2) Å, c = 0.360 (2) Å, c =11.201 (2) Å, $\alpha = 77.574$ (8)°, $\beta = 109.831$ (8)°, and $\gamma = 119.202$ (8)°. The space group is $P\overline{1}$ with one molecule per unit cell. Manual diffractometer methods (Mo radiation, γ 0.71069 Å) were used to obtain 798 reflections at 23°. Full-matrix least-squares refinement of the structure with anisotropic thermal parameters for all atoms except hydrogen gave a final conventional R index of 7.2%. As required by the space group symmetry, the molecule is centrosymmetric and consists of two triphenylphosphine groups attached to a B_2H_4 moiety. The central $B_2H_4P_2$ part of the molecule has an ethane-like structure structure in the structure of the molecule has an ethane-like structure of the structure of th ture in the anti conformation. The B-B and P-B distances are 1.76 (2) and 1.935 (9) Å, respectively, while the average P-C and C-C lengths are 1.83 (1) and 1.38 (1) Å. The P-B bond is longer than in the isostructural, but less stable, bis-(trifluorophosphine)-diborane(4).

Introduction

There are numerous examples in the chemical literature of diborane(4) derivatives in which each boron atom is threecoordinate, one of the bonded groups being the second boron atom.^{1,2} The structures of several of these compounds have been determined and have been shown to have a molecular skeleton in which the three bonds of each boron atom are planar. Depending on the relative orientation of these planes, these molecules may have either D_{2h} or D_{2d} symmetry, the physical state apparently being the controlling factor.³⁻⁶ Although derivatives of this type are relatively stable, the parent compound, B_2H_4 , has not been isolated. In fact, as Holliday and Massey⁷ pointed out, stable molecules of the type B_2X_4 have only been reported for those cases in which one or more of the X groups has a free electron pair which can be used to stabilize the molecular framework.

Adducts of the parent B_2H_4 compound, which should have an ethane-like structure (i.e., with four-coordinate boron atoms), are known but are less common. Graybill and Ruff⁸ synthesized $B_2H_4 \cdot 2P(C_6H_5)_3$ by cleavage of a B_3H_7 group. By a similar reaction B_2H_4 ·2PF₃ has been prepared,⁹ as well as $B_2H_4 \cdot 2PF_2H$ and $B_2H_4 \cdot 2PF_2N(CH_3)_2$.¹⁰ Diamine and diphosphine adducts of B_2Cl_4 and B_2F_4 have been reported, but they apparently form tetramers.^{11,12}

Of these ethane-like diborane(4) derivatives only one has been subject to a detailed structure determination, namely, an electron diffraction study of $B_2H_4 \cdot 2PF_3$.¹³ This is a

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report of an X-ray diffraction study of the bis(triphenylphosphine) adduct of B_2H_4 .

Collection and Treatment of Data

The sample of $B_2H_4 \cdot 2P(C_6H_5)_3$ was prepared by a method similar to that of Graybill and Ruff⁸ using B_3H_7 PF₂N(CH₃)₂ as the starting material, rather than $B_3H_7 \cdot N(CH_3)_3$. Considerable difficulty was encountered in obtaining a single crystal since fractures appeared to be common in the crystals. A usable crystal was grown by slow evaporation of a solution of the compound in a mixture of benzene and dichloromethane. The dimensions of the crystal were 0.47 \times 0.30×0.25 mm in the a, b, and c directions. The crystal was mounted on a glass fiber with the a axis nearly parallel to the ϕ axis of the diffractometer. Preliminary Weissenberg photographs showed the crystal to be triclinic (space group P1 or $P\overline{1}$).

The diffractometer data were obtained with a GE XRD-5 manually operated unit using Zr-filtered Mo K α radiation (λ 0.71069 Å), a scintillation counter, and a pulse height analyzer set for a 90% window. Least-squares refinement¹⁴ of the setting angles of 23 carefully centered reflections gave the following cell parameters at 23° : a =9.119 (2) Å, b = 9.360 (2) Å, c = 11.201 (2) Å, $\alpha = 77.574$ (8)°, $\beta = 109.831$ (8)°, $\gamma = 119.202$ (8)°. The volume of this unit cell is 788.67 Å³. Flotation in a mixture of nitrobenzene and chlorobenzene indicated a density of 1.16 (1) g/cm³. Assuming the number of molecules per unit cell to be 1, the calculated density is 1.16 g/cm^3 .

For intensity data collection each reflection was scanned 2° with a θ -2 θ scan at a rate of 2°/min with a takeoff angle of 3°. Stationarycrystal, stationary-counter background readings were taken for 10 sec at each of the scans. All peaks with 2θ between 0° and 40° were scanned. A total of 798 reflections were observed to have an intensity greater than 3σ and these were used for subsequent structure determination and refinement. The standard deviations were calculated by $\sigma_1 = (S + BT^2 + 0.0016I^2)^{1/2}$ (where S = total scan count, B = sum of background counts, T = (scan time)/(total background)time), and I = S - BT).

Four reflections $(0.1\overline{2}, 11\overline{3}, 104, 2\overline{2}3)$ were measured periodically as a monitor of crystal and electronic stability. No apparent systematic change in their intensities was observed. Absorption corrections were not needed ($\mu = 1.65 \text{ cm}^{-1}$, $\mu R = 0.023$), and extinction corrections were not made. Atomic scattering factors for neutral P, C, B, and H were used.¹⁵ The value for phosphorus was corrected to account for the real component of anomalous dispersion.¹⁶

Solution and Refinement of Structure

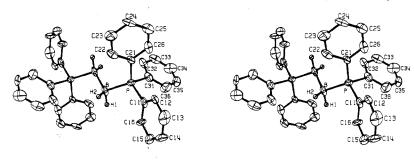
The full-matrix least-squares program used¹⁷ minimizes $\Sigma w(\Delta |F|)^2$. The R factors are defined as $R_1 = \Sigma ||F_0| - |F_0| / \Sigma |F_0|$ and $R_2 = (\Sigma w ||F_0| - |F_c||^2 / \Sigma w F_0^2)^{1/2}$.

A three-dimensional Patterson function¹⁸ revealed the P-P vector as the strongest single peak. A Fourier map phased by the phospho-

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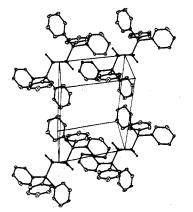
(17) P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, Program UCLALS4, American Crystallographic Association Program Library (old), No. 317 (modified).



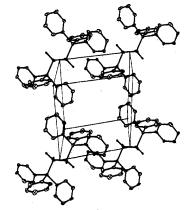
BIS (TRIPHENYLPHOSPHINE) DIBORANE (4)

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Figure 1. Stereoview of bis(triphenylphosphine)-diborane(4). All atoms in the asymmetric unit are labeled. Phenyl hydrogen atoms are not shown. Ellipsoids of 50% probability are used. Borane hydrogen atoms are spheres of 0.1-A radius. The view is nearly perpendicular to the P-B-B-P plane.







BIS (TRIPHENYLPHOSPHINE) DIBORANE (4)

Figure 2. Stereoview of four molecules of bis(triphenylphosphine)-diborane(4). Ellipsoids of 10% probability are shown. Borane hydrogen atoms are spheres of 0.1-Å radius. In this view +a runs into the page away from the reader, +b is nearly horizontal to the left, and +c is vertical upward.

rus atom (R = 55%) revealed the positions of the boron atom and the three carbon atoms directly bonded to the phosphorus. Inclusion of these atoms in a second Fourier synthesis (R = 50%) revealed the positions of all other nonhydrogen atoms.

Four cycles of least-squares refinement with isotropic temperature factors reduced the value of the R index to 15.0%. At this point the positions of the hydrogen atoms on the phenyl groups were calculated using a C-H distance of 0.95 A. In all further refinements the positions of these hydrogen atoms (recalculated after each cycle) were included in the structure factor calculations but were not refined. As a result the value of the residual dropped to 9.4%. The use of anisotropic temperature factors gave a further decrease in R to 8.1%, a significant decrease at the 0.005 level according to Hamilton's Rratio test.¹⁹ A difference Fourier at this point clearly revealed the positions of the borane hydrogen atoms, at densities of about 0.5 e/A^3 . These were included, with isotropic temperature factors, in the last two cycles of least-squares refinement. The final values for R_1 and R_2 are 7.2 and 9.3%; respectively. In the last cycle of refinement all parameter shifts were less than 25% of their standard deviation. A final difference Fourier synthesis revealed no peaks larger than 0.4 e/A^3 (8% of the electron density of a carbon atom). The goodness of fit, defined as $[\Sigma w (F_0 - F_c)^2 / (m - s)]^{1/2}$ is 1.89.

The observed and calculated structure factors are given in Table I^{20} while Tables II and III give the final positional parameters and the thermal vibration parameters (all anisotropic except the two borane hydrogen atoms). Table IV gives the molecular dimensions of the molecule. The least-squares best planes for the three phenyl groups and the distances of the carbon atoms and the phosphorus atom from the planes are given in Table V.

(18) The Fourier programs used were Program FORDAP by R. Shiono and Program ALFF by C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson.

(19) W. C. Hamilton, Acta Crystallogr., 18, 502 (1965).
(20) Table I, a listing of observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1686.

Discussion

In the structure of $B_2H_4 \cdot 2P(C_6H_5)_3$ the central portion of the molecule, *i.e.*, the two phosphorus and the two boron atoms, assumes a planar trans configuration, such that the structure is analogous to the anti conformation of a disubstituted ethane molecule (Figure 1). In the electron diffraction study by Lory, Porter, and Bauer¹³ two trial structures were considered. The first is analogous to that described above for $B_2H_4 \cdot 2P(C_6H_5)_3$. The second is the trans isomer of a disubstituted diborane(6) framework, with two bridging hydrogen atoms. The second model would require the presence of two electrons, unpaired, in high-energy orbitals of the boron atoms. Although the electron diffraction data favored the first model slightly, the basis for rejecting the second model was primarily chemical evidence and infrared spectra reported in a previous paper.⁹ The overall structures of the trifluorophosphine and the triphenylphosphine adducts of B_2H_4 are thus the same, although differences in molecular geometries do exist (see below).

The structure found for $B_2H_4 \cdot 2P(C_6H_5)_3$ is reasonable in the light of the topological rules for boron hydrides proposed by Lipscomb.²¹ If one considers the formation of $B_2H_4L_2$ from the triborane adduct B_3H_7L' (where L and L' are monodentate bases) to be a combination of base displacement and cleavage of the B_3 framework, the reaction may be written

$$\mathbf{B_3H_7L'} + \mathbf{3L} \rightarrow \mathbf{L'} + \mathbf{BH_3L} + \mathbf{B_2H_4L_2}$$

In the original synthesis of $B_2H_4 \cdot 2P(C_6H_5)_3$ by Ruff and Graybill,⁸ L was triphenylphosphine and L' was trimethylamine. The neutral $B_3H_7 \cdot L'$ molecule has 18 valence electrons

(21) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 49.

Table II.Final Positional Parameters a and IsotropicTemperature Factors b

iemperature	te l'actors.				
Atom	x	у	Ζ	<i>B</i> , Å ²	
Р	0150 (5)	-1886 (5)	1775 (4)		
В	-0828(11)	-0951 (11)	0186 (8)		
C11 ^c	-1479 (10)	-3774 (9)	2292 (8)		
C12	-1635 (10)	-4138 (8)	3485 (8)		
C13	-3070 (12)	-5609 (11)	3794 (7)		
C14	-4233 (11)	-6653 (9)	2851 (9)		
C15	-4094 (12)	-6246 (9)	1627 (7)		
C16	-2765 (10)	-4860 (9)	1351 (7)		
C21	1174 (9)	-0556 (9)	3126 (7)		
C22	0697 (8)	0647 (10)	3027 (6)		
C23	1362 (10)	1649 (8)	4026 (7)		
C24	2546 (9)	1445 (11)	5080 (7)		
C25	3066 (10)	0294 (11)	5170 (7)		
C26	2395 (10)	-0706 (8)	4185 (7)		
C31	1846 (9)	-2407 (10)	1775 (6)		
C32	3346 (11)	-1129 (10)	1480 (7)		
C33	4659 (11)	-1460 (12)	1467 (7)		
C34	4491 (13)	-2988 (14)	1650 (8)		
C35	3033 (13)	-4245 (11)	1956 (8)		
C36	1650 (10)	-4011 (10)	1994 (9)		
$H1^d$	-145 (4)	-189 (3)	-068 (3)	5(1)	
H2	-198 (4)	-106 (3)	047 (3)	4 (1)	
$H12^{e}$	-079	-340	411	6.0	
H13	-320	-588	463	6.0	
H14	-515	-763	305	6.0	
H15	-492	-695	0 99	6.0	
H16	-269	-462	052	6.0	
H22	-010	077	230	6.0	
H23	101	246	397	6.0	
H24	300	212	574	6.0	
H25	388	018	589	6.0	
H26	275	-150	424	6.0	
H32	347	-005	132	6.0	
Н33	567	-062	130	6.0	
H34	538	-319	160	6.0	
H35	293	-529	212	6.0	
H36	062	-489	218	6.0	

^a Values given are $\times 10^4$, except for H atoms, which are $\times 10^3$. ^b In this, and in other tables, the figure in parentheses is the estimated standard deviation in last significant digit. ^c For carbon atoms, the first digit represents the number of the phenyl group and the second digit is the number of the atom in the group. ^d H1 and H2 are attached to the boron atom; the numbers of all other hydrogen atoms are those of the carbon atom to which the hydrogen is attached. ^e Calculated positions used in structure factor calculations but not refined.

Table III. Anisotropic Temperature Factors^a

Atom	<i>b</i> ₁₁	b 22	b 33	<i>b</i> ₁₂	b ₁₃	b 23
Р	065 (7)	065 (7)	063 (5)	034 (12)	042 (9)	-014 (8)
в	08 (3)	13 (3)	06 (1)	12 (15)	05 (3)	11 (3)
C11	11 (3)	13 (3)	05 (2)	15 (5)	05 (4)	10 (4)
C12	08 (3)	10 (3)	10 (2)	07 (5)	-03(4)	06 (4)
C13	25 (5)	20 (4)	09 (2)	21 (8)	21 (6)	13 (5)
C14	19 (4)	09 (3)	10 (2)	-04 (5)	-05 (5)	-05 (4)
C15	21 (4)	10 (3)	06 (2)	09 (6)	-10(4)	02 (3)
C16	12 (3)	06 (3)	07 (2)	-05 (5)	02 (4)	03 (3)
C21	08 (3)	12 (3)	06 (2)	14 (5)	-02(4)	-08(3)
C22	07 (3)	18 (3)	06 (2)	08 (5)	02 (3)	-02 (4)
C23	21 (4)	16 (3)	06 (2)	16 (6)	05 (5)	-09 (4)
C24	09 (3)	19 (4)	07 (2)	05 (6)	-05 (4)	-11 (4)
C25	13 (4)	20 (4)	09 (2)	23 (7)	00 (4)	-14 (5)
C26	14 (3)	16 (3)	06 (2)	20 (6)	08 (4)	06 (4)
C31	13 (3)	16 (3)	06 (1)	21 (6)	02 (3)	-04 (3)
C32	13 (3)	19 (3)	07 (1)	18 (7)	02 (4)	04 (3)
C33	15 (4)	24 (4)	08 (2)	12 (7)	-01 (4)	-09 (5)
C34	16 (4)	22 (4)	15 (2)	15 (8)	14 (5)	-12 (5)
C35	21 (4)	13 (4)	15 (3)	28 (7)	-04 (5)	-06 (4)
C36	15 (4)	13 (4)	19 (3)	12 (6)	13 (5)	01 (4)

^a Values given are $\times 10^3$, except for the P atom, which are $\times 10^4$. The temperature factor is $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Table IV. Bond Lengths and Angles

	0						
	Bond Len	gths, Å					
B'-Ba	1.76 (2)	C23-C24	1.36 (1)				
B-P	1.935 (9)	C24-C25	1.35 (1)				
B-H1	1.24 (3)	C25-C26	1.38 (1)				
B-H2	1.15 (3)	C26-C21	1.36 (1)				
P-C11	1.802 (8)	C31-C32	1.40 (1)				
P-C21	1.852 (8)	C32-C33	1.38 (1)				
P-C31	1.835 (8)	C33-C34	1.34 (1)				
C11-C12	1.34 (1)	C34-C35	1.37 (1)				
C12-C13	1.44 (1)	C35-C36	1.40(1)				
C13-C14	1.37 (1)	C36-C31	1.40 (1)				
C14-C15	1.37 (1)		. ,				
C15-C16	1.34 (1)	Av B-H	1.20 (3)				
C16-C11	1.41 (1)	Av P-C	1.83 (1)				
C21-C22	1.36 (1)	Av C-C	1.38 (1)				
C22-C23	1.39 (1)						
Bond Angles, deg							
B'-B-H1	110.3 (14)	C14-C15-C16	120.5 (7)				
B'-B-H2	122.8 (16)	C14-C15-C16	120.3 (7)				
B'-B-P	109.0 (5)	C16-C11-C12	121.0(7) 118.3(7)				
B-P-C11	112.3 (4)	C21-C22-C23	110.5(7) 120.8(7)				
B-P-C21	114.1 (4)	C22-C23-C24	120.3(7) 118.5(7)				
B-P-C31	116.0 (4)	C23-C24-C25	121.2 (8)				
P-C11-C12	124.4 (6)	C24-C25-C26	120.2 (8)				
P-C11-C16	117.1 (6)	C25-C26-C21	119.9 (7)				
P-C21-C22	117.7 (5)	C26-C21-C22	119.3 (7)				
P-C21-C26	123.0 (6)	C31-C32-C33	119.1 (8)				
P-C31-C32	117.0 (5)	C32-C33-C34	121.9 (9)				
P-C31-C36	122.9 (6)	C33-C34-C35	119.1 (9)				
Р-В-Н1	110.3 (14)	C34-C35-C36	122.3 (9)				
P-B-H2	96.2 (16)	C35-C36-C31	117.2 (8)				
H1-B-H2	107.2 (20)	C36-C31-C32	120.1 (7)				
C11-P-C21	104.6 (4)		. ,				
C11-P-C31	104.4 (4)	Av P-C-C	120.3 (6)				
C21-P-C31	104.2 (4)	Av B-P-C	114.1 (4)				
C11-C12-C13	120.8 (7)	Av C-P-C	104.4 (4)				
C12-C13-C14	118.1 (8)	Av C-C-C	120.0 (8)				
C13-C14-C15	120.5 (8)						
	1=0.0 (0)						

^a B' is related to B by -x, -y, -z.

Table V. Least-Squares Planes^a of the Form AX + BY + CZ + D = 0

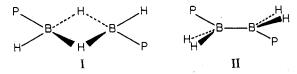
Phenyl grou	ıp A	i	B	C	D
1	0.517	-0.	.833 0.1	200	1.438
2	-0.885	-0.	.229 0	405	1.383
3	0.168	0.	149 0.	974	1.575
Phenyl group 1		Phe	Phenyl group 2 Phenyl grou		nyl group 3
<u></u>	Dist from mean plane,		Dist from mean plane,		Dist from mean plane,
Atom	Å	Atom	Â	Atom	Â
C11	0.01	C21	0.02	C31	0.01
C12	0.00	C22	-0.02	C32	-0.01
C13	-0.02	C23	0.01	C33	0.02
C14	0.02	C24	0.01	C34	-0.02
C15	-0.01	C25	0.00	C35	0.02
C16	-0.01	C26	-0.01	C36	0.01
P	-0.11	Р	0.06	Р	-0.03

 ^{a}A , B, and C are direction cosines for the orthogonal coordinate system with Y coincident with the crystal b axis and Z normal to the crystal ab plane.

(counting the electrons in the borane segment of the molecule plus two in the B-L' bond). Loss of six electrons in the BH₃ group during cleavage and the gain of two from the additional B-L bond formed result in a B₂H₄·2L molecule with 14 valence electrons. This is isoelectronic with the B₂H₆²⁻ ion considered by Lipscomb,²¹ who gave the 0014 (or ethane-like) structure as the only reasonable one for this ion. There are two cleavage directions possible for this reaction (*i.e.*, the product is H₃B-BHL₂ or LH₂B-BH₂L), and the 1,2 isomer has now been found by the work of Lory, Porter, and Bauer as well as by this study.

The choice between a hydrogen-bridged and a nonbridged

structure on the basis of X-ray diffraction results must be made with caution. The two possible structures are



Because of the small bond angles for the bridging H atoms, the nonbonded B-B distance in diborane derivatives may be expected to be quite short. In diborane(6), for example, the distance is 1.775 Å.²² This is identical, within experimental error, with the σ -bonded B-B distance found for $B_2H_4 \cdot 2P(C_6H_5)_3$ and close to that for $B_2H_4 \cdot 2PF_3$.¹³ As a result, the positions of the nonhydrogen atoms in structures I and II above would be nearly identical, except for possible variations in bond angles. The feature that distinguishes between these two models is, of course, the position of the hydrogen atoms. A difference Fourier synthesis for B_2H_4 . $2P(C_6H_5)_3$ clearly showed two hydrogen atoms in positions corresponding to those in structure II, which is therefore assumed to be correct.

The B-B bond length in $B_2H_4 \cdot 2P(C_6H_5)_3$ is 1.76 (2) Å which is consistent with values found for polyhedral boranes.²¹ Similarly, the average B-H bond length of 1.20 (3) Å is comparable to the value of 1.196 (8) Å found for $B-H_t$ bonds in diborane(6).²²

The length of the P-B bond is of interest. At 1.935 (9) Å it is similar to the value of 1.93 Å found both for $H_3P \cdot BH_3$ and for (CH₃)₃P BH₃,²³ as well as 1.935 Å in [(CH₃)₂- $PBH_2]_3$.²⁴ These values may be contrasted with the significantly shorter values found for fluorophosphine derivatives of borane acids. For example, the P-B bond length in $B_2H_4 \cdot 2PF_3$ is 1.848 (28) Å,¹³ and in $F_3P \cdot BH_3$ it is 1.836 (12) Å.²⁵ These shorter bonds would seem to indicate that the fluorophosphine derivatives are more strongly bound to the borane acids than the alkyl- and arylphosphine adducts. The opposite effect, however, is indicated by the observed stabilities of these compounds, which has been pointed our earlier by Bryan and Kuczkowski.²⁶ Thus $(C_6H_5)_3P \cdot BH_3$, $B_2H_4 \cdot$ $2P(C_6H_5)_3$, $(CH_3)_3P$ ·BH₃, as well as other alkylphosphineboranes,²⁷ appear to undergo little, if any, measurable dissociation, even at elevated temperatures. However, the BH3 adduct of the parent compound, PH₃, is highly dissociated at 25° ,²⁸ and F₃P·BH₃ also dissociates readily.²⁹ While com-

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parable thermodynamic data are not complete, the values that are available in the literature do show the alkyl- and arylphosphine-boranes (which have the longer bonds) to be more stable than fluorophosphine-boranes (with shorter bonds). For the reaction

adduct (g) \rightarrow base (g) + $1/{_2B_2H_6(g)}$

the values for the enthalpy of dissociation are low for F₃P. BH₃ $(5.49 \text{ kcal/mol})^{25}$ and H₃P·BH₃ (less than 6 kcal/mol)³⁰ but considerably higher for (CH₃)₃P·BH₃ (greater than 22 kcal/mol).²⁶ By comparison to measurements in dilute solutions,³¹ which give values comparable to gas-phase reactions,³² the enthalpy value for $(C_6H_5)_3P \cdot BH_3$ is about 20 kcal/mol. While few thermodynamic data are available for the adducts of the reference acid B_2H_4 , the chemical stability of $B_2H_4 \cdot 2P(C_6H_5)_3$ is high while that of $B_2H_4 \cdot 2PF_3$ and $B_2H_4 \cdot 2PF_2N(CH_3)_2$ is much lower, indicating that similar effects may be involved.

The model for the dipole moments of phosphines proposed by Weaver and Parry³³ and discussed by Rudolph and Parry^{30,34} may be used to reconcile these observations. Thus, the long weak found in $H_3P \cdot BH_3$ is due to the fact that the free electron pair on the P atom is closely held and is not very polarizable. Replacement of the P-H bonds by P-C bonds increases the polarizability of the phosphorus electron pair, producing stronger bonds in those adducts in which the phosphorus bears alkyl or phenyl groups. Although a similar loosening of the electron pair might be expected for the molecule PF_3 , the high electronegativity of the fluorines causes a shift of negative charge away from the phosphorus atom. The ligand therefore becomes a weaker donor, which must approach the acceptor atom more closely for the formation of a bond.³⁴ Thus shorter, weaker bonds are observed for $F_3P \cdot BH_3$ and $B_2H_4 \cdot 2PF_3$. As less strongly electronegative groups replace the fluorine atoms, a lengthening of the P-B bond should occur. Support for this is found in the values of 1.856 (8) Å for $B_4H_8 \cdot PF_2N(CH_3)_2^{35}$ and 1.887 (13) Å for (H₂N)₃P·BH₃.³⁶

Registry No. $B_2H_4 \cdot 2P(C_6H_5)_3$, 39678-68-7.

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