Contribution from the Departments of Chemistry, Calvin College, Grand Rapids, Michigan 49506, and the University of Arkansas, Fayetteville, Arkansas 72701

# **Crystal and Molecular Structure of Bis(triphenylphosphine)-Diborane(4)**

WILLIAM VanDOORNE,\* A. W. CORDES, and G. W. HUNT

#### *Received January 11, 1973*

The structure of bis(triphenylphosphine)-diborane(4),  $B_2H_4.2P(C_6H_5)_3$ , 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)  $\overline{A}$ ,  $b = 9.360$  (2)  $\overline{A}$ ,  $c = 1.19$ 11.201 (2) A,  $\alpha = 77.574$  (8)<sup>°</sup>,  $\beta = 109.831$  (8)<sup>°</sup>, and  $\gamma = 119.202$  (8)<sup>°</sup>. The space group is  $P\bar{T}$  with one molecule per unit cell. Manual diffractometer methods (Mo radiation, y 0.71069 **A)** 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 in the anti conformation. The B-B and P-B distances are 1.76 (2) and 1.935 (9) A, respectively while the average P-C and C-C lengths are 1.83 (1) and 1.38 (1) A. 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 Massey' 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 Ruff' synthesized  $B_2H_4.2P(C_6H_5)_3$  by cleavage of a  $B_3H_7$  group. By a similar reaction  $B_2H_4.2PF_3$  has been prepared,<sup>9</sup> as well as  $B_2H_4$  :  $2PF_2H$  and  $B_2H_4$  :  $2PF_2N(CH_3)_2$  .<sup>10</sup> Diamine and diphosphine adducts of  $B_2Cl_4$  and  $B_2F_4$  have been reported, but they apparently form tetramers.<sup>11,12</sup>

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

\* To whom correspondence should be addressed at the Depart- **(1)** H. Noeth and P. Fritz, *Z.* Anorg. Allg. Chem., **324, 129**  ment of Chemistry, University of Hawaii, Honolulu, Hawaii **96822.** 

- **(2) C.** N. Welch and *S.* G. Shore, Inorg. Chem., **7, 225 (1968). (1963).**
- **(3) H. J.** Becher, W. Sawodny, H. Noeth, and W. Meister, *Z.*
- **(4)** L. Trefonas and W. **N.** Lipscomb, *J.* Chem. Phys., **28, 54**  Anorg. Allg. Chem., **314, 226 (1962).**
- **(1958).**
- **(5)** M. Atoji, P. **J.** Wheatly, and W. N. Lipscomb, *J.* Chem. Phys., **27, 196 (1957).** 
	- **(6)** D. **E.** Mann and L. Fano, *J.* Chem. Phys., **26, 1665 (1957). (7) A.** K. Holliday and A. **G.** Massey, Chem. Rev., **62, 303 (1962).**
	-
- **(8)** B. M. Graybill and **J.** K. Ruff, *J.* Amer. Chem. **SOC.,** 84, **1062 (1962).**
- (9) W. **R.** Deever, **E.** R. Lory, and D. M. Ritter, Inorg. Chem., 8, **1263 (1969).**
- (10) E. R. Lory and D. M. Ritter, *Inorg. Chem.*, 10, 939 (1971). **(1 1)** A. **K.** Holliday, F. J. Marsden, and **A.** G. Massey, *J.* Chem. *SOC.,* **3348 (1961).**
- **(12) A.** Finch and H. I. Schlessinger, *J.* Amer. Chem. **SOC., 80, 3573 (1958).**
- **(13) E. R.** Lory, R. F. Porter, and **S.** H. **Bauer,** *Inorg.* Chern., **10, 1072 (1971).**

report of an X-ray diffraction study of the bis(tripheny1 phosphine) adduct of  $B_2H_4$ .

### **Collection and Treatment of Data**

The sample of  $B_2H_4$  2P( $C_6H_5$ ), was prepared by a method similar to that of Graybill and Ruff<sup>8</sup> using  $B_3H_7$ .  $PF_2N(CH_3)_2$  as the starting material, rather than  $B_3H_7 \cdot NCH_3$ , 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 X  $0.30 \times 0.25$  mm in the *a*, *b*, and *c* directions. The crystal was mounted on a glass fiber with the  $a$  axis nearly parallel to the  $\phi$  axis of the diffractometer. Preliminary Weissenberg photographs showed the crystal to be triclinic (space group  $P1$  or  $\overline{P1}$ ).

The diffractometer data were obtained with a GE XRD-5 manually operated unit using Zr-filtered Mo Κα radiation (λ 0.71069 A), a scintillation counter, and a pulse height analyzer set for a 90% window. Least-squares refinement<sup>14</sup> of the setting angles of 23 carefully centered reflections gave the following cell parameters at  $23^\circ$ :  $a =$ 9.119(2) A,  $b = 9.360$ (2) A,  $c = 11.201$ (2) A,  $\alpha = 77.574$ (8)°,  $\beta =$ 109.831 (8)<sup>°</sup>,  $\gamma = 119.202$  (8)<sup>°</sup>. The volume of this unit cell is 788.67  $A^3$ . Flotation in a mixture of nitrobenzene and chlorobenzene indicated a density of 1.16 (1)  $g/cm^3$ . Assuming the number of molecules per unit cell to be 1, the calculated density is  $1.16$  g/cm<sup>3</sup>.

a  $\theta$ -2 $\theta$  scan at a rate of  $2^{\circ}/$ min with a takeoff angle of  $3^{\circ}$ . Stationarycrystal, stationary-counter background readings were taken for 10 sec at each of the scans. All peaks with  $2\theta$  between  $0^{\circ}$  and  $40^{\circ}$  were scanned. A total of 798 reflections were observed to have an intensity greater than  $3\sigma$  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  $I = S - BT$ ). For intensity data collection each reflection was scanned 2° with

as a monitor of crystal and electronic stability. No apparent systematic change in their intensities was observed. Absorption corrections were not needed ( $\mu = 1.65$  cm<sup>-1</sup>,  $\mu$ R = 0.023), and extinction corrections were not made. Atomic scattering factors for neutral P, C, **B,** and H were used." The value for phosphorus was corrected to account for the real component of anomalous dispersion.<sup>16</sup> Four reflections (0.12, 113, 104, 223) were measured periodically

#### **Solution and Refinement of Structure**

 $\sum w(\Delta |F|)^2$ . The R factors are defined as  $R_1 = \sum ||F_0| - |F_c||/\sum |F_0|$ and  $R_2 = (\Sigma w || F_0| - |F_c||^2 / \Sigma w F_0^2)^{1/2}$ .<br>A three-dimensional Patterson function<sup>18</sup> revealed the P-P vector The full-matrix least-squares program used<sup>17</sup> minimizes

as the strongest single peak. A Fourier map phased by the phospho-

**A.** Foust, Program **ANGSET,** University of Wisconsin, **1968.**  "International Tables for X-Ray Crystallography," Vol. **111, Press,** Birmingham, England, **1962,** p **202.** 

, See ref **15, p 215.** 

**(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) 815 (TRIPHENYLPHOSPHINE) DIBORANE (4)

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.





B IS (TRIPHENYLPHOSPHINE) DIBORANE (4) 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-A 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 calcplations 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 *R*ratio test.<sup>19</sup> A difference Fourier at this point clearly revealed the positions of the borane hydrogen atoms, at densities of about 0.5 e/A3. These were included, with isotropic temperature factors, in the last two cycles of least-squares refinement. The final values for *R,* and *R,* 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  $0.4 \text{ e}/\text{A}^3$  (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 **1''** while Tables **I1** and 111 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 Eourier programs used were Program FORDAP by R. Shiono and Program ALFF by *C.* R. Hubbard, C. 0. Quicksall, and R. **A.** Jacobson.

(19) W. **C.** Hamilton, *Acta Crysfallogr.,* 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, or \$2.00 for microfiche, referring to code number INORG-73-1686. D. C. 20036. Remit check or money order for \$3.00 for photocopy

### **Discussion**

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 Bauer<sup>13</sup> 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.<sup>9</sup> 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). In the structure of  $B_2H_4.2P(C_6H_5)_3$  the central portion of

The structure found for  $B_2H_4 \cdot 2P(C_6H_5)$ <sub>3</sub> is reasonable in the light of the topological rules for boron hydrides proposed by Lipscomb.<sup>21</sup> 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

$$
B_3H_7L'+3L \rightarrow L'+BH_3L+B_2H_4L_2
$$

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

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

Table II. Final Positional Parameters<sup>a</sup> and Isotropic Temperature Factorsb

Atom	x	у	z	B, A <sup>2</sup>
P	0150(5)	$-1886(5)$	1775 (4)	
B	$-0828(11)$	$-0951(11)$	0186(8)	
C11c	$-1479(10)$	$-3774(9)$	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)	
C <sub>21</sub>	1174 (9)	$-0556(9)$	3126(7)	
C22	0697(8)	0647 (10)	3027(6)	
C <sub>23</sub>	1362 (10)	1649(8)	4026 (7)	
C <sub>24</sub>	2546 (9)	1445 (11)	5080 (7)	
C <sub>25</sub>	3066 (10)	0294 (11)	5170 (7)	
C <sub>26</sub>	2395 (10)	$-0706(8)$	4185 (7)	
C <sub>31</sub>	1846 (9)	$-2407(10)$	1775 (6)	
C <sub>32</sub>	3346 (11)	$-1129(10)$	1480 (7)	
C <sub>33</sub>	4659 (11)	$-1460(12)$	1467 (7)	
C <sub>34</sub>	4491 (13)	$-2988(14)$	1650(8)	
C35	3033(13)	$-4245(11)$	1956 (8)	
C <sub>36</sub>	1650 (10)	$-4011(10)$	1994 (9)	
H1 <sup>d</sup>	$-145(4)$	$-189(3)$	$-068(3)$	5(1)
H <sub>2</sub>	$-198(4)$	$-106(3)$	047(3)	4(1)
H12 <sup>e</sup>	$-079$	$-340$	411	6.0
H13	$-320$	$-588$	463	6.0
H <sub>1</sub> 4	$-515$	$-763$	305	6.0
H <sub>15</sub>	$-492$	$-695$	099	6.0
H16	$-269$	$-462$	052	6.0
H22	$-010$	077	230	6.0
H <sub>2</sub> 3	101	246	397	6.0
H <sub>24</sub>	300	212	574	6.0
H <sub>25</sub>	388	018	589	6.0
H <sub>26</sub>	275	$-150$	424	6.0
H32	347	$-005$	132	6.0
H33	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<sup>a</sup>

Atom	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
P	065(7)	065 (7)	063(5)	034 (12)	042 (9)	$-014(8)$
B	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)	$-02(4)$
C <sub>23</sub>	21 (4)	16 (3)	06(2)	16 (6)	05(5)	$-09(4)$
C <sub>24</sub>	09(3)	19 (4)	07(2)	05 (6)	$-05(4)$	$-11(4)$
C <sub>25</sub>	13 (4)	20(4)	09(2)	23(7)	00(4)	$-14(5)$
C <sub>26</sub>	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)
C <sub>33</sub>	15 (4)	24 (4)	08 (2)	12 (7)	$-01(4)$	$-09(5)$
C <sub>34</sub>	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



 $\alpha B'$  is related to B by  $-x$ ,  $-y$ ,  $-z$ .

Table **V.** Least-Squares Planes<sup>*a*</sup> of the Form  $AX + BY + CZ + D = 0$ 

Phenyl group	A		В	С	D	
	0.517		$-0.833$	0.200	1.438	
2	$-0.885$		$-0.229$	0.405	1.383	
3	0.168		0.149 0.974		1.575	
Phenyl group 1		Phenyl group 2		Phenyl group 3		
	Dist from	Dist from			Dist from	
	mean plane,		mean plane,		mean plane,	
Atom	Å	Atom	Å	Atom	Ä	
C11	0.01	C <sub>21</sub>	0.02	C <sub>31</sub>	0.01	
C12	0.00	C <sub>22</sub>	$-0.02$	C <sub>32</sub>	$-0.01$	
C13	$-0.02$	C <sub>23</sub>	0.01	C <sub>33</sub>	0.02	
C <sub>14</sub>	0.02	C <sub>24</sub>	0.01	C <sub>34</sub>	$-0.02$	
C15	$-0.01$	C <sub>25</sub>	0.00	C <sub>35</sub>	0.02	
C16	$-0.01$	C <sub>26</sub>	$-0.01$	C <sub>36</sub>	0.01	
P	$-0.11$	P	0.06	P	$-0.03$	

*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  $BH<sub>3</sub>$  group during cleavage and the gain of two from the additional B-L bond formed result in a  $B_2H_4.2L$  molecule with 14 valence electrons. This is isoelectronic with the  $B_2H_6^2$ <sup>-</sup> ion considered by Lipscomb,<sup>21</sup> 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*  $H_3B-BHL_2$  or  $LH_2B-BH_2L$ ), 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  $1.775 \text{ Å}^{22}$  This is identical, within experimental error, with the  $\sigma$ -bonded B-B distance found for  $B_2H_4:2P(C_6H_5)$ <sub>3</sub> and close to that for  $B_2H_4:2PF_3$ <sup>13</sup> As a result, the positions of the nonhydrogen atoms in structures I and I1 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  $B_2H_4$ .  $2P(C_6H_5)$ <sub>3</sub> clearly showed two hydrogen atoms in positions corresponding to those in structure 11, which is therefore assumed to be correct.

The B-B bond length in  $B_2H_4.2P(C_6H_5)$ <sub>3</sub> is 1.76 (2) Å which is consistent with values found for polyhedral boranes.<sup>21</sup> Similarly, the average B-H bond length of  $1.20(3)$ A is comparable to the value of 1.196 (8) A found for  $B-H_t$ bonds in diborane $(6).^{22}$ 

The length of the P-B bond is of interest. **At** 1.935 (9) **A**  it is similar to the value of 1.93 **A** found both for H3P.BH3 and for  $(CH_3)_3P<sub>1</sub>BH<sub>3</sub><sup>23</sup>$  as well as 1.935 Å in  $[(CH_3)_2$ - $PH<sub>2</sub>$ <sup>24</sup> 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  $B_2H_4$  2PF<sub>3</sub> is 1.848 (28) Å,<sup>13</sup> and in F<sub>3</sub>P·BH<sub>3</sub> it is 1.836 (12) A.<sup>25</sup> 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.<sup>26</sup> Thus  $(C_6H_5)_3P \cdot BH_3$ ,  $B_2H_4$ .  $2P(C_6H_5)_3$ ,  $(CH_3)_3P\cdot BH_3$ , as well as other alkylphosphineboranes,<sup>27</sup> appear to undergo little, if any, measurable dissociation, even at elevated temperatures. However, the BH<sub>3</sub> adduct of the parent compound, PH<sub>3</sub>, is highly dissociated at  $25^{\circ}$ ,<sup>28</sup> and F<sub>3</sub>P.BH<sub>3</sub> also dissociates readily.<sup>29</sup> While com-

**(22) L. S. Bartell and B. L. Carroll,** *J. Chem. Phys.,* **42, 1135 (1965).** 

**(23) E. L. McGandy, Doctoral Dissertation, Boston University, (24) W. C. Hamilton,** *Acta Crystallogr.***, <b>8**, 199 (1955).

**(25) R. L. Kuczkowski and D. R. Lide,** *J. Chem. Phys.,* **46, 357 (26) P. S. Bryan and R. L. Kuczkowski,** *Inorg. Chem.,* **11, 553 (1967).** 

**(27) M. Morris, Doctoral Dissertation, University of Michigan, (1972).** 

**(28) E. L. Gamble and P. Gilmont,** *J. Amer. Chem. SOC., 62,* **717 Ann Arbor, Mich., 1965.** 

**(29) R. W. Parry and T. C. Bissot, J.** *Amer. Chem. Soc., 78,* **1524 (1 940). (1956).** 

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

## $adduct(g) \rightarrow base(g) + \frac{1}{2}B_2H_6(g)$

the values for the enthalpy of dissociation are low for  $F_3P$ . BH<sub>3</sub> (5.49 kcal/mol)<sup>25</sup> and H<sub>3</sub>P·BH<sub>3</sub> (less than 6 kcal/mol)<sup>30</sup> but considerably higher for  $(CH_3)_3P·BH_3$  (greater than 22  $kcal/mol$ .<sup>26</sup> By comparison to measurements in dilute solutions, $31$  which give values comparable to gas-phase reactions,<sup>32</sup> the enthalpy value for  $(C_6H_5)_3P^*BH_3$  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  $B_2H_4.2P(C_6H_5)$ <sub>3</sub> is high while that of  $B_2H_4.2PF_3$  and  $B_2H_4$  2PF<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> is much lower, indicating that similar effects may be involved.

by Weaver and Parry<sup>33</sup> and discussed by Rudolph and Parry $30,34$  may be used to reconcile these observations. Thus, the long weak found in  $H_3P·BH_3$  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.<sup>34</sup> Thus shorter, weaker bonds are observed for  $F_3P·BH_3$  and  $B_2H_4·2PF_3$ . 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  $B_4H_8$ .  $PF_2N(CH_3)_2$ <sup>35</sup> and 1.887  $(13)$  Å for  $(H_2N)_3P<sup>·</sup>BH_3.$ <sup>36</sup> The model for the dipole moments of phosphines proposed

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

**Acknowledgments.** We wish gratefully to acknowledge the National Science Foundation and the Dupont Foundation for financial aid. We are indebted to the Computing Centers of Calvin College, the University of Arkansas, and the University of Hawaii for their support and to Dr. Karl Seff for supplying some of the computer programs used.

- **(31) M. A. Frisch, M. G. Heal, H. MacMe, and I. 0. Madden,** *J. Chem. Soc.,* **899 (1965).**
- **(32) H. C. Brown and R. H. Horowitz,** *J. Amer. Chem.* **SOC., 77, 1730 (1955).**

**(33) J. R. Weaver and R. W. Parry,** *Inorg. Chem.,* **5, 718 (1966). (34) R. W. Rudolph and R.** W. **Parry,** *J. Amer. Chem. SOC.,* **89, 1621 (1967).** 

**(35) M. D. LaPrade and C. E. Nordman,** *Inorg. Chem.,* **8, 1669 (1969).** 

**(36) C. E. Nordman,** *Acta Crystallogr.,* **13, 535 (1960).** 

**<sup>(30)</sup> R. W. Rudolph, Doctoral Dissertation, University** of **Michigan, Ann Arbor, Mich., 1966.**