CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON 98105

# Bis(trifluorophosphine)-Diborane(4)[1]

BY WILLIAM R. DEEVER, EARL R. LORY, AND D. M. RITTER[2]

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Bis(trifluorophosphine)–diborane(4) has been prepared from trifluorophosphine and the dimethyl ether adduct of triborane(7). The composition was established by vapor density, by solvolysis, and by quantitative reaction with hydrogen and with diborane to give trifluorophosphine–borane and tetraborane(10), respectively. With 1,2-dimethyldiborane methyltetraboranes were obtained. The adduct decomposes in successive second-order reactions to give hexaborane(12) and pentaborane(9). From formation and behavior of the adduct, generalizations are made concerning base-displacement reactions, and from the decomposition, conclusions are reached concerning reactions which contribute to hydride interconversions.

This paper is a more detailed report of the synthesis and of some reactions of bis(trifluorophosphine)–diborane(4) than was given in a communication.[3] The new adduct shows prospect as a versatile reagent in synthesis, and its preparation and behavior promise to afford new insight concerning reactions of boron hydrides and their adducts. The accidental discovery of the species while the synthesis of trifluorophosphine–triborane(7) was being attempted has stimulated development of a growing chemistry concerning diborane(4) derivatives.[4]

## Results

**Characterization.**—The vapor density (MW (obsd) ≈ 195; MW (calcd) = 202) and the parent peak (202) in the mass spectrum establish the molecularity of the new substance. These values and the easy separation from trifluorophosphine–borane preclude confusion with the latter substance of almost the same empirical composition. The solvolyses gave per mole of adduct close to 4 mol of hydrogen in acid solution at 25° and close to 5 mol in hot alkaline solution, as shown in Table I. Since previous experience has shown that B–B bonds resist acid solvolysis but succumb in basic solution,[5] the results are consistent with those expected from a substance containing four B–H bonds and one B–B bond. The structure as that of the 1,2-bis adduct of the 0012 diborane(4)[6] is not demonstrated by these data, but the inference is strong from the mass spectrometric cracking pattern that the molecule is divisible into two $H_2BPF_3$ fragments (*cf.* Table VI). An ionic structure is excluded by the low melting point (−114°) and by a normal value for the heat of sublimation. The latter cannot exceed ~10 kcal/mol considering that the substance is essentially nonvolatile at −120° (*i.e.*, $10^{-3} > P_{\text{vap}} > 10^{-4}$ Torr; *cf.* Table VI).

TABLE I

SOLVOLYSIS OF $B_2H_4(PF_3)_2$

| Sample[a] | $H_2$ recovered[a] Obsd | Calcd |
|---|---|---|
| 0.342 ± 0.001[b] | 1.37 ± 0.06 | 1.37 |
| 0.210 ± 0.001[c] | 1.09 ± 0.05 | 1.05 |

[a] Quantities in millimoles. [b] Acid solution. [c] Basic solution.

**Reactions.**—The hydrogenolysis at room temperature and below gives trifluorophosphine–borane quantitatively. This constitutes another analysis as seen from the data in Table II. Here the diborane(4) adduct resembles the other B–B bonded substances, $B_2Cl_4$ and $B_2F_4$,[7] which contributes to belief in the 0012 structure. The total absence of side reaction products shows the reaction velocity with hydrogen to exceed that of the self-decomposition from which they would arise.

TABLE II[a]

DATA FOR $B_2H_4(PF_3)_2 + H_2 \longrightarrow 2BH_3PF_3$

| $B_2H_4(PF_3)_2$ | $H_2$ consumed | | $(CH_3)_3N$ consumed | | $PF_3$ recovered | | $BH_3N(CH_3)_3$ recovered | | $H_2$[b] formed | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Calcd | Obsd | Calcd | Obsd | Calcd | Obsd | Calcd | Obsd | Calcd | Obsd |
| 0.35 | 0.35 | 0.32 | 0.69 | 0.64 | 0.69 | 0.69 | 0.69 | 0.63 | 1.89 | 1.90 |
| 0.40 | 0.40 | 0.41 | 0.80 | 0.83 | 0.80 | 0.79 | 0.80 | 0.79 | 2.39 | 2.38 |

[a] Quantities in millimoles. [b] From hydrolysis of $BH_3N(CH_3)_3$.

The reaction with diborane(6) proceeds at room temperature almost quantitatively to give tetraborane, as shown in Table III. The trace of pentaborane(9) formed when the excess of diborane was threefold can be assigned to self-decomposition of the adduct. Use of a 20-fold excess of diborane possibly suppressed higher hydride formation by the adduct but in turn furnished extra tetraborane and pentaborane(11) from the diborane(6) itself. These observations probably indi-

TABLE III[a]

DATA FOR $B_2H_4(PF_3)_2 + B_2H_6 \longrightarrow B_4H_{10} + 2PF_3$

| $B_2H_4(PF_3)_2$ | $B_2H_6$ added | $B_2H_6 + PF_3$ recovered | | $B_4H_{10}$ recovered | |
|---|---|---|---|---|---|
| | | Calcd | Obsd | Calcd | Obsd |
| 0.22[b] | 0.76 | 0.44[d] | 0.43[d] | 0.22 | 0.18[e] |
| 0.18[c] | 3.81 | 3.99 | 4.00 | 0.18 | 0.21[f] |

[a] Quantities in millimoles. [b] Time 3 hr. [c] Time 12 hr. [d] $PF_3$ only. [e] Also found 0.017 mmol of $B_5H_9$; no $H_2$. [f] Also found 0.008 mmol each of $B_5H_9$ and $B_5H_{11}$ and a trace of $H_2$.

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[1] Research supported by funds from National Science Foundation Grants GP-3459 and GP-7888.

[2] Addressee for correspondence.

[3] W. R. Deever and D. M. Ritter, *J. Am. Chem. Soc.*, **89**, 5073 (1967).

[4] W. R. Deever, F. M. Miller, E. R. Lory, and D. M. Ritter, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. M215.

[5] T. Wartig and E. F. Apple, *J. Am. Chem. Soc.*, **77**, 6400 (1955).

[6] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 44.

[7] G. Urry, T. Wartig, R. E. Moore, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5293 (1954); A. Finch and H. I. Schlesinger, *ibid.*, **80**, 3573 (1958).

cate that the self-decomposition is very slightly competitive, thus establishing the diborane reaction as somewhat slower than the hydrogenolysis. The analogous reaction with 1,2-dimethyldiborane is even slower (*cf.* Table IV).

Table IV

Reaction of $B_2H_4(PF_3)_2$ and $(BH_2CH_3)_2$

| Reactants[a] | | Products[a] | | | |
|---|---|---|---|---|---|
| $B_2H_4(PF_3)_2$ | $(BH_2CH_3)_2$ | $B_4H_{10}$ | $B_4H_9CH_3$ | $B_4H_8(CH_3)_2$ | $B_6H_{12}$ |
| 0.66[b] | 3.80 | 0.10 | 0.05 | 0.33[f] | 0.03 |
| 1.15[b] | *e* | 0.09 | 0.10 | 0.39[f] | 0.10 |
| 1.10[c] | 6.60 | | | 0.23 | |
| 0.28[d] | 5.50 | | | 0.06 | <0.1 |

[a] Quantities in millimoles. [b] Time 1 hr at 23°. [c] Time 2 hr at −45°. [d] Time 6 hr at −95°. [e] Large excess. [f] Proportions of isomers: 2,4, 42%; 1,2, 44%; 2,2, 14%.

Unlike the decomposition of other unstable base–borane adducts[8] the self-reaction of bis(trifluorophosphine)–diborane(4) appears to be second order for 70% of the reaction as shown in Figure 2. The earliest appearing product seems to be hexaborane(12), which, as the reaction proceeds, diminishes proportionately in favor of pentaborane(9) and tetraborane(10). After longer standing there are found also pentaborane(11) and diborane(6) as the additional products formed in part from the trifluorophosphine-catalyzed decomposition of hexaborane(12), through which it all finally vanishes.

## Discussion

Some comparative chemistry can be found in considering how diborane(4) adducts may be formed. In addition to the base-displacement process for forming new adducts from existing ones, there should be considered another category, namely, the adduct-displacement reaction, of which the preparation of bis(triphenylphosphine)–diborane(4) from trimethylamine–triborane(7) was the first example known with certainty.[9] Triphenylphosphine–triborane(7) was obtained from the adduct with tetrahydrofuran.[9] Graybill and Ruff recognized that "there thus appears to be a correlation between the strength of the ligand bond in $XB_3H_7$ and the mode of reaction toward a stronger nucleophile: the stronger the initial ligand bond the greater the extent of degradation of the triborane." The adduct-displacement synthesis of bis(trifluorophosphine)–diborane(4) demonstrates a need to modify this generalization. The base pairs TPP–TMA and TFP–DME[10] are found so differently placed on the scale of base strength as to indicate that there must exist a relative as well as an absolute base strength relation which determines whether there is to occur predominantly: (1) formation of another triborane(7) adduct, (2) transformation to a diborane(4) adduct, or (3) degradation to a borane adduct and a polymer. This is developed further in Figure 1 where there is presented a rationale for the various ways in which bases are reported to react with triborane(7) adducts. Steps **1** → **2** and **2** → **6** are the concerted transformation through which the transition states (**2** and **3**) are established by the attack of the base b′ on the adduct $B_3H_7$–b (formula **1**). In view of the reaction

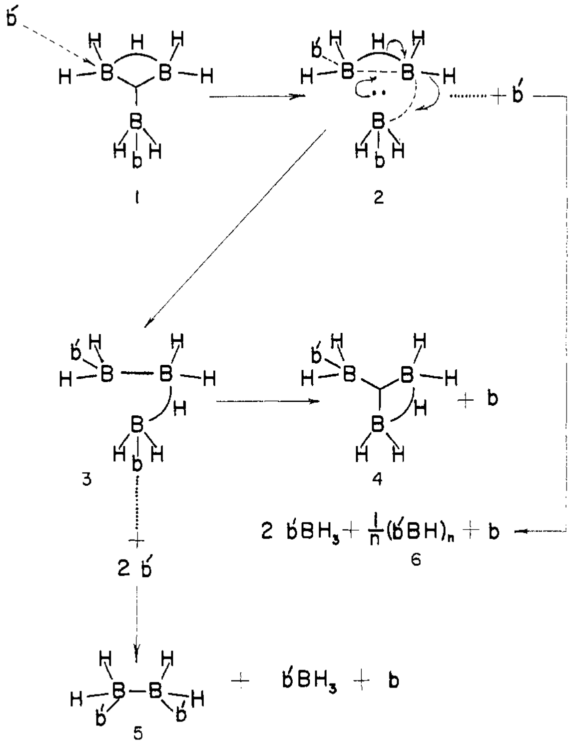

Figure 1.

$$B_2H_4(PF_3)_2 + 2N(CH_3)_3 \longrightarrow H_3B\text{-}N(CH_3)_3 + (1/n)(HBN(CH_3)_3)_n + 2PF_3$$

where stepwise base displacement can produce dissimilarly substituted boron atoms and lead to polymer through strong base–strong acid adduct elimination, a concerted process, yielding a long-lived transition state or short-lived intermediates with a second attack by base following, seems a more logical explanation than an immediate expulsion of borane adduct. The single hydrogen bridge in **3** should be considered the same as that found in $B_2H_6N(CH_3)_3$.[11] Step **3** → **4**, giving only net base displacement, is the path largely taken when the base pairs[10] are TPP–THF,[9] A–THP,[12] and TMA–THP,[12] etc. Path **3** → **5** is the adduct elimination step found for the base pairs TPP–TMA[9] and TFP–DME. There remains route **2** → **6** taken when the attacking base is the one in the adduct or another of nearly the same strength and both are relatively strong. Such cases are those involving the base pairs TMA–TMA,[13] A–THF,[12] TMA–A,[12] TMA–THP,[14] TPP–DMS,[9] TPP–TMA,[9] and TPP–THF.[9] In the first of these latter examples the evidence was an observed degradation, and in the others a less than optimum yield of

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[8] A. B. Burg, *J. Am. Chem. Soc.*, **74**, 3482 (1952); A. B. Burg and Y.-C. Fu, *ibid.*, **88**, 1147 (1966).

[9] B. M. Graybill and J. K. Ruff, *ibid.*, **84**, 1062 (1962).

[10] The abbreviations in this paper are: TPP, triphenylphosphine; TMA, trimethylamine; TFP, trifluorophosphine; DME, dimethyl ether; THP, tetrahydropyran; THF, tetrahydrofuran; DMS, dimethyl sulfide; A, ammonia.

[11] S. G. Shore and C. L. Hall, *J. Am. Chem. Soc.*, **88**, 5346 (1966); **89**, 3947 (1967).

[12] G. Kodoma, R. W. Parry, and J. C. Carter, *ibid.*, **81**, 3534 (1959).

[13] R. W. Parry and L. J. Edwards, *ibid.*, **81**, 3556 (1959); A. B. Burg and F. G. A. Stone, *ibid.*, **75**, 228 (1953).

[14] N. E. Lewtin, E. F. Westrum, and J. C. Carter, *ibid.*, **81**, 3547 (1959).

product was obtained by route **3** → **4** or **3** → **5** together with an unidentified nonvolatile residue. When the attacking base is identical with the ligand and it is relatively weak, the route appears to be **3** → **5** as found for the reaction[15] of dimethylaminodifluorophosphine on the adduct of that base with triborane(7).[16]

As told previously the decomposition of bis(trifluorophosphine)–diborane(4) is over-all second order with products reminiscent of association processes. A series of consecutive second-order reactions (followed for these equations and subsequent eq 7–12 by $-\Delta G_{300}$, kcal/mol, in parentheses) can be used to describe the several steps as shown in eq 1–6. If, among

$$2B_2H_4(PF_3)_2 \longrightarrow i\text{-}B_4H_8(PF_3)_2 + 2PF_3 \quad (27.7) \qquad (1)$$

$$B_2H_4(PF_3)_2 + i\text{-}B_4H_8(PF_3)_2 \longrightarrow B_6H_{12} + 4PF_3 \quad (71.0) \qquad (2)$$

$$B_6H_{12} + B_2H_4(PF_3)_2 \longrightarrow B_5H_9 + B_3H_7 + 2PF_3 \quad (30.3) \qquad (3)$$

$$B_6H_{12} + B_3H_7 \longrightarrow B_5H_9 + B_4H_{10} \quad (18.0) \qquad (4)$$

$$B_2H_4(PF_3)_2 + B_3H_7 \longrightarrow B_5H_{11} + 2PF_3 \quad (44.4) \qquad (5)$$

$$B_6H_{12} \xrightarrow{PF_3} B_5H_9 + xB_4H_{10} + yB_2H_6 \qquad (6)$$

these reactions, (1) and (3) are considered as rate determining, reaction 2 is taken as a steady-state process, and the rate of (4) is greater than the rate of (5), both fast, the products can be accounted for, and a steady-state tretament gives a rate equation which is over-all second order in disappearance of bis(trifluorophosphine)–diborane(4).

The steady-state intermediate, $i\text{-}B_4H_8(PF_3)_2$, may be supposed to stem from a hydride with the linear 2022 structure, which provides a diacid function located at boron atoms 1 and 4. Another more descriptive name is 1,2-bis(trifluorophosphine boranyl)diborane(6). Here the known reactions between diborane derivatives and bis(trifluorophosphine)–diborane(4) represent a basis for belief that the conjectured intermediate should react similarly to give a substituted tetraborane which can rearrange to hexaborane(12). A simultaneous decomposition of the 2202 $B_4H_8(PF_3)$ and $B_2H_4(PF_3)_2$ indicated, as well as product analysis might show, that the two substances decomposed independently, which eliminates that $B_4$ adduct as an intermediate.

Reactions 3 and 6 together are required to account for the attrition of the hexaborane(12), as seen from the control experiments. There trifluorophosphine catalysis promoted less conversion of hexaborane(12) than the over-all disappearance in the self-reaction of the diborane(4) adduct. Reactions 4 and 5 account for the tetraborane(10) and pentaborane(11) found in the products. As will be seen the proposed reactions have thermochemical justification.

Because $BH_2$ was observed in the mass spectrum of diborane determined during pyrolysis[17] the radical and its dimer have been proposed as intermediates in the diborane decomposition and from less evidence in the formation of the higher hydrides.[18] Though not the slightest evidence of free $B_2H_4$ has appeared in the examination of the $PF_3$ adduct, some deductions about diborane(4) may be possible by comparison between the behavior of this adduct and that of other diborane(4) derivatives. The pertinent reactions are those with hydrogen, with diborane, and with itself. They can be considered kinetically and thermochemically.

There are reaction rates with hydrogen which rank qualitatively in the order $B_2H_4(PF_3)_2 \approx B_2Cl_4 \gg B_2H_4[N(CH_3)_3]_2 > B_2Cl_4[N(CH_3)_3]_2 \approx 0$.[4,5] In the reaction with diborane the rates are in the order $B_2H_4(PF_3)_2 \gg B_2H_4[N(CH_3)_3]_2$.[4,5] Apparently, the weaker the base in the adduct, the faster the reactions proceed. That $B_2H_4$ must be very reactive in these same ways can be decided by extrapolative reasoning. In this way a basis becomes established for considering that the over-all reaction cited in ref 18 is directly reversible. as seen in eq 7. For the formation of tetraborane(10),

$$B_2H_6 \rightleftarrows B_2H_4 + H_2 \quad (-24.3) \qquad (7)$$

see eq 8. Plausible reactions (eq 9–12) can be written

$$B_2H_4 + B_2H_6 \longrightarrow B_4H_{10} \quad (22.0) \qquad (8)$$

$$2B_2H_4 \longrightarrow i\text{-}B_4H_8 \quad (22.2) \qquad (9)$$

$$i\text{-}B_4H_8 + B_2H_6 \longrightarrow B_5H_{11} + BH_3 \quad (12.7) \qquad (10)$$

$$i\text{-}B_4H_8 + B_2H_4 \longrightarrow B_6H_{12} \quad (50.6) \qquad (11)$$

$$B_6H_{12} + B_2H_4 \longrightarrow B_5H_9 + B_3H_7 \quad (21.7) \qquad (12)$$

for other steps in hydride interconversion. Thermochemical justification can be found for many of these reactions. To do so in the absence of accurate state functions requires the calculation of approximate values as listed in Table V. The values for $\Delta H_a$ are heats of atomization deduced from calorimetry[19] assuming bond additivity which applies reasonably well to boron hydrides. The values of $S'$ are approximate entropies[20] so designated to avoid any confusion with an accurate standard entropy. A few values are from other sources.

## Experimental Part

**Preparation of $B_2H_4(PF_3)_2$.**—Treatment of dimethyl ether–triborane(7)[21] with phosphorus trifluoride[22] was performed in a Pyrex vessel of 30-cm length, 9-mm o.d., and 5-mm i.d. intended to withstand a pressure in excess of 35 atm. One end was fitted with a 4-mm Teflon plug glass needle valve.[23] Reac-

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[15] E. R. Lory and D. M. Ritter, Abstracts, 23rd Annual Northwest Regional Meeting of the American Chemical Society, Portland, Ore., June 12–14, 1968, No. 23–55.

[16] M. A. Fleming, Dissertation, University of Michigan, 1963.

[17] T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 2733 (1964).

[18] T. P. Fehlner, *ibid.*, **87**, 4200 (1965).

[19] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961); S. R. Gunn and J. H. Kindsvater, *ibid.*, **70**, 1114 (1966).

[20] An approximate entropy was estimated for diborane(4) from a relation found to hold for the series of compounds $BCl_3$, $BF_3$, and $BH_3$ where log $S° \approx$ log MW. A parallel relation was assumed for $B_2Cl_4$ and $B_2H_4$ from which was deduced $S'_{298} \cong 56$ eu. Other approximate entropy values were calculated using the Sachur–Tetrode equation for $S'_T$ (*cf.* Taylor and Glasstone, "Treatise on Physical Chemistry," Van Nostrand Co., Inc., New York, N. Y., 1942, p 554) and rigid-rotor models for $S'_R$ (*cf.* F. D. Rossini, "Chemical Thermodynamics," John Wiley & Sons, Inc., New York, N. Y., 1950). The ethane configuration was assumed for trifluorophosphine–borane and the *trans* configuration was assigned to bis(trifluorophosphine)–diborane(4) and to $i\text{-}B_4H_8(PF_3)_2$. Tetrahedral bond angles were assumed and bond lengths used were those collected by L. E. Sutton, Ed., "Tables of Interatomic Distances," Special Publication No. 11 and 18, The Chemical Society, London, 1958, 1965. For each possible restricted rotation 1 eu was added. The contribution from vibrational modes was estimated from the characteristic frequencies.

[21] W. R. Deever and D. M. Ritter, *Inorg. Chem.*, **7**, 1036 (1968).

[22] Purified by treatment with trimethylamine at 25° followed by fractional condensation from −80 to −145 to −196°, repetitively until no more reaction with the amine was observed; *cf.* J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960).

[23] Fischer and Porter Co., Catalog No. 795-120-0004.

TABLE V

APPROXIMATE THERMOCHEMICAL DATA

| | $\Delta H_a$,[a,c] kcal/mol | $S'$, eu |
|---|---|---|
| $BH_3PF_3$ | 282 | 64 |
| $B_2H_4(PF_3)_2$ | 461 | 79 |
| *i*-$B_4H_8(PF_3)_2$ | 933 | 83 |
| $BH_3$ | 270 | 45[b] |
| $B_2H_4$ | 437 | 56 |
| $B_2H_6$ | 575 | 55.5[b] |
| $B_3H_7$ | 742 | 54 |
| *i*-$B_4H_8$ | 909 | 65 |
| $B_4H_{10}$ | 1048 | 63 |
| $B_5H_9$ | 1130 | 66[d] |
| $B_5H_{11}$ | 1227 | 71 |
| $B_6H_{12}$ | 1410 | 75 |
| $PF_3$ | 12 | 65[b] |
| $H_2$ | 103 | 34[b] |

[a] Bond energies (kcal/mol): B–H, 90; B–B, 77; B–H–B, 107.5; $\mathrm{B{-}}\!<^{\mathrm{B}}_{\mathrm{B}}$, 90. Resonance energies per $B_3$ bond (kcal/mol): $B_5H_9$, 5; $B_5H_{11}$, 2; $B_6H_{12}$, 1.[19] [b] "JANAF Thermochemical Tables." [c] Bond energy for $\geqslant$B–$PF_3$, 12 kcal/mol.[8] [d] H. J. Hrostowski and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954).

tion was observed as low as −23°. At −16° the solid etherate disappeared in about 0.5 hr, but the time necessary for complete reaction was 5–6 hr. If the volatile reaction components were removed prior to this, a white solid precipitated which was identified as unreacted dimethyl ether–triborane(7), judging from the melting range 10.5–11.1°. In a typical case dimethyl ether–triborane(7) (1.37 mmol) was made in the reaction tube. On this was condensed trifluorophosphine (10.92 mmol). After the mixture had remained at −16° for 6 hr, it was distilled into a U tube where it was mixed with boron trifluoride (4 mmol). The U tube was surrounded by a bath cooled to −45°, and a separation by slow fractional condensation was carried out through U tubes cooled to −95, −120, and −145° into one at −196°. Needle-shaped crystals of bis(trifluorophosphine)–diborane(4) were collected at −120° (1.01 mmol, 74% yield). During a too rapid fractionation, liquid product will accumulate at −95°. The products can be separated also by glpc. A column of 120-cm length and 0.9-cm i.d. was packed with acid-washed "Silaclad-treated" firebrick[24] loaded with 35% mineral oil. It was well conditioned by several hours of exposure to boron hydrides. At 40 cm³/min flow of helium carrier gas with the column at 0°, the retention times in minutes for some components of a preparative mixture were: $PF_3$, 2.0; $B_2H_6$, 2.4; $B_2H_4(PF_3)_2$, 6.5; $(CH_3)_2O$, 8.0; $B_4H_{10}$, 49. With dimethyl ether in the mixture the loss of product was as much as 50%. Starting with purified $B_2H_4(PF_3)_2$ the loss through decomposition on the same column at 0° was 10%. The decomposition products were $B_4H_{10}$, $B_5H_9$, $B_5H_{11}$, and $B_6H_{12}$ with 1:1:1.5:3.5 as the relative proportions.

**Physical Characterization.—Melting points** were determined by the collapsing ring-dropping plunger method.[25] Values of −114.5, −114.3, and −114.2° were obtained for individually purified samples. Successive measurements without purification gave a melting point depression of about 1.4°.

**Gas density molecular weight** measurement was complicated by decomposition of the sample while it was warmed to room temperature to measure the pressure. The only remedy was to perform these operations as swiftly as possible. Values obtained were 188, 192, and 195 g/mol (calcd, 202 g/mol).

**Vapor pressures** were observed manometrically in a static system at a few fixed points using samples freshly purified for each determination. After each measurement the temperature was lowered to −126°, where any decomposition was shown by a residual pressure of $PF_3$. The results are given in Table VI. The constants for the van't Hoff isochore were calculated from pressures corrected for the decomposition.

**Infrared absorption frequencies** were determined on a Perkin-Elmer Model 21 spectrometer with sodium chloride optics for the range 3000–800 cm$^{-1}$ and on a Beckman IR 10 grating spectrometer using AgCl cell windows for the range 800–300 cm$^{-1}$. The absorbances (cm$^{-1}$) observed were: 2403 (s) and 2353 (s) for $BH_2$ stretching; 1120 (m) for $BH_2$ wagging; a PQR branched system centered on 940 (vs) for $PF_3$ stretching and 612 (s) for P–B stretching.

TABLE VI

VAPOR PRESSURES[a]

| | Temp, °C | | | | | |
|---|---|---|---|---|---|---|
| | −79 | −71 | −63 | −54 | −48 | −44 |
| $P_{mm}$(obsd) | 2 | 3 | 8 | 16[b] | 24[b] | 33[c] |
| Log $P$(calcd) | 0.28 | 0.55 | 0.88 | 1.18 | 1.38 | 1.50 |

[a] Log $P = 8.20 - (1536/T)$; $\Delta H_v = 7.03$ kcal/mol; $\Delta H_v/289 = 23.5$. [b] Correction, 1 mm. [c] Correction, 1.5 mm.

**Mass spectra** were obtained on an AEI Model MS-9 double-focusing spectrometer.[26] A tungsten carbide emitting surface was established on the tungsten filament by several hours of treatment with 2-butene. Through external cooling the source temperature was kept at 110–140°. An operating ionizing potential of 24 V was selected to give the highest ion current consistent with the least cracking. Polyisotopic spectra were obtained at low resolving power (1 part in 200) to ensure complete integration of all of the contributions assigned to each single mass number. The polyisotopic spectrum contained $B_5$, $B_4$, and $B_3$ envelopes. To ensure that these species originated in the source and not from prior decomposition, purified bis(trifluorophosphine)–diborane(4) was slowly distilled directly into the source through a trap cooled to −95°. For inclusion in Table VII those masses were selected for which the individual intensities equaled or exceeded 0.5% of that for the most intense peak at *m/e* 88. The average of intensity for the 63 masses thus rejected as background was 0.15 ± 0.02. Not considered were 79 masses for which the intensity was zero. The species assignments are suggested ones not verified by high-resolution mass determination.

**Chemical Reactions.—Solvolysis** of the adduct gave hydrogen gas which was collected for volume measurement by means of a Toepler pump with the results given in Table I. The reaction in acid solution was performed at 25° for 3 hr in 2 ml of a degassed 1:3 mixture of trifluoroacetic acid in 95% ethanol.[9] The reaction bulb was fitted with a Teflon stem needle valve[23] to equip it for use as a weighing bottle. The reactions in basic solution were performed in sealed tubes provided with hook break-seals. A weighed sample of the adduct was condensed in the tube which contained 2 ml of degassed 10% ethanolic potassium hydroxide solution. After the tube was sealed from the vacuum line, it was heated for 18 hr in a steam bath.

**Treatment with hydrogen** was carried out in a 106-ml reaction bulb fitted with a 4 mm Teflon stem needle valve.[23] A purified sample of the adduct was transferred by condensation to the previously weighed bulb. Without warming the bulb or its contents enough hydrogen was added quantitatively to obtain a pressure of 1 atm when the bulb was warmed to room temperature. Prior to use the hydrogen was deoxygenated over BTS catalyst[27] and then dehydrated at −196°. The bulb was kept at room temperature for 3–5 hr. During this time it was weighed, and the amount of sample was determined by difference, including in the tare weight the amount of hydrogen previously

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(24) Johns Manville "Chromosorb" treated with 12 *M* hydrochloric acid and after thorough washing, with "Siliclad"; *cf.* S. D. Nogare and R. S. Juvet, "Gas-Liquid Chromatography," Interscience Publishers, New York, N. Y., 1962, p 146. Treatment was followed by vacuum drying at 110°.

(25) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 184.

(26) Purchased with funds supplied under National Science Foundation Instrument Grant GP-5418.

(27) Badische Anilin und Soda Fabrik, A. G., Ludwigshafen am Rhein.

TABLE VII

POLYISOTOPIC MASS SPECTRUM OF $B_2H_4(PF_3)_2$

| m/e | Relative abundance | Assignment[a] | m/e | Relative abundance | Assignment[a] |
|---|---|---|---|---|---|
| 202 | 0.07 | $B_2H_4P_2F_6$ | 52 | 0.34 | $B_4$[b] |
| 201 | 0.10 | | 51 | 1.42 | HPF |
| 200 | 2.75 | | 50 | 4.69 | PF |
| 199 | 1.41 | | 49 | 3.45 | |
| 198 | 0.20 | | 48 | 2.81 | |
| 114 | 0.81 | $B_2H_4PF_3$ | 47 | 2.18 | |
| 113 | 0.78 | | 46 | 2.66 | |
| 112 | 3.47 | | 45 | 3.79 | |
| 111 | 1.92 | | 43 | 1.71 | BHP |
| 110 | 0.42 | | 42 | 1.05 | BP |
| 102 | 0.91 | $BH_3PF_3$ | 38 | 1.37 | $B_3$ |
| 101 | 63.63 | | 37 | 1.22 | |
| 100 | 6.86 | | 36 | 1.12 | |
| 99 | 1.38 | | 35 | 0.70 | |
| 89 | 0.59 | | 33 | 0.70 | $PH_2$ |
| 88 | 100.00 | $PF_3$ | 31 | 1.81 | P |
| 69 | 62.97 | $PF_2$ | 27 | 2.03 | $B_2$ |
| 64 | 0.45 | $BH_3PF$<br>$B_5$[b] | 26 | 3.37 | |
| 63 | 1.10 | | 25 | 1.96 | |
| 62 | 1.03 | | 24 | 1.59 | |
| 61 | 1.00 | | 23 | 0.64 | |
| 60 | 0.89 | | 22 | 0.10 | |
| 59 | 0.72 | | 13 | 1.08 | $B_1$ |
| 58 | 0.49 | | 12 | 0.50 | |
| 57 | 0.49 | | 11 | 0.32 | |
| | | | 10 | 0.08 | |

[a] For each species envelope only the parent peak is listed.
[b] The species shown are considered to overlap in this mass range.

added. The surplus hydrogen was measured, and, still using the bulb as the reactor, the diborane and trifluorophosphine–borane portion of the condensable gas was converted to trimethylamine–borane with a known excess of trimethylamine.[28] The excess trimethylamine and trifluorophosphine were removed while the bulb was cooled to −23°, and they were separated by glpc using mineral oil on firebrick.[29] The trimethylamine–borane was determined by weighing. To confirm its identity the sample was hydrolyzed with 5 ml of 6 *N* hydrochloric acid, first at room temperature and then at 100° until, upon periodic examination, hydrogen evolution was found to have ceased. The results can be found in Table II.

**Reaction with diborane,** purified by glpc[30] and measured volumetrically, was performed in the 106-ml reaction bulb. Following condensation of the diborane, the bulb was weighed. Purified $B_2H_4(PF_3)_2$ was then added by condensation, and the flask was reweighed. The reaction mixture was left at room temperature for 3 and 12 hr in separate experiments. The products were separated by glpc with the results shown in Table II.

**Reaction with 1,2-dimethyldiborane** was performed in the 106-ml bulb. For the room-temperature reactions the amount of bis(trifluorophosphine)–diborane(4) was determined by weight difference, but for reactions at lower temperatures the sample size was estimated from the trifluorophosphine found in the products, which were separated by glpc. The components were identified by their relative retention times,[30] and the proportions of the dimethyltetraboranes[31] were estimated from the chromatographic trace using a five-channel Du Pont curve analyzer.[32] Table IV contains the results except those for the methyldiboranes which are always formed in such reactions.

**Decomposition** was determined at 25° by observing the decay of intensity for the infrared absorption frequency at 2353 $cm^{-1}$ which belongs uniquely to $B_2H_4(PF_3)_2$. A purified sample (0.161 mmol) was transferred to the cell (5-cm path length, 129 ml). The sample was kept at −126° while the cell was pumped to remove any residual $PF_3$. The cooled portion of the cell was warmed quickly to room temperature, and the recording of the infrared signal intensity, $T_t$, was begun. After 30 hr the reaction was deemed finished, and the products were separated by glpc. The infrared signal intensity at this time was taken as $T_\infty$ corresponding to $C_\infty = 0$ for the adduct reactant. To transform the values $T_t$ into absorbance values, $A_t$, proportional to concentrations, the values read from the strip chart were substituted in the equation

$$A_t = \log \frac{T_\infty - T_0}{T_t - T_0}$$

The results plotted in first- and second-order form are found in Figure 2. The products at the end were diborane(6), tetraborane(10), pentaborane(9), a trace of hexaborane(12), and no noncondensable gas.

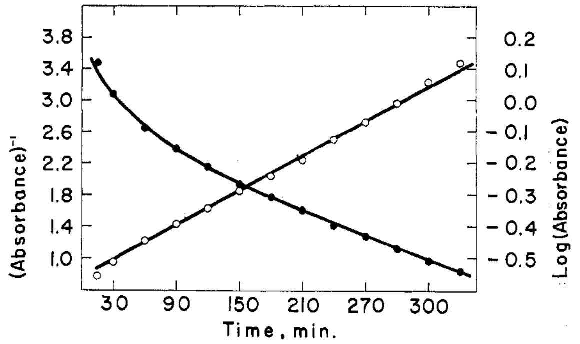

Figure 2.—Kinetics of decomposition: ●, first order; ○, second order.

A solution of $B_2H_4(PF_3)_2$ (10 mol %) in propane remained unaltered at −80° for 26.5 hr; glpc showed only the propane solvent, the adduct, a minute amount of $PF_3$, and no $B_4$, $B_5$, or $B_6$ species in the sample.

A neat sample decomposed 3% in 32 hr at −95° as judged by the trifluorophosphine formed. A further 7% decomposition occurred in 105 hr at −80°. In each case the extent of reaction was judged by measuring the trifluorophosphine removed when the sample was cooled to −145°.

Hexaborane(12) (0.178 mmol at 26.1 Torr) and trifluorophosphine (0.480 mmol at 70.5 Torr) were mixed for 36 hr. The products were separated by glpc; they were identified by relative retention time. The amounts in millimoles as determined by gas volume were: $B_4H_{10}$, 0.01; $B_5H_9$, 0.02; $B_5H_{11}$, 0.01; $B_2H_6$, 0.03; recovered $B_6H_{12}$, 0.135.

Joint decomposition of $B_2H_4(PF_3)_2$ and $B_4H_8(PF_3)$[33] was observed with a mixture containing 0.45 and 0.21 mmol of those substances, respectively. The mixture was kept at −112° for 6 hr while 0.10 mmol of $PF_3$ was removed. During the succeeding 5 hr at −95° an additional 0.035 mmol appeared. Then the remaining material was kept at 23° for 1 hr while 0.015 mmol of hydrogen was formed. The amounts of volatile material measured in millimoles were: $B_4H_{10}$, 0.060; $B_5H_9$, 0.036; $B_5H_{11}$, 0.006; $B_6H_{12}$, 0.091; $BH_3PF_3$, a trace. A nonvolatile oil remained.

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(28) Purified over $P_4O_{10}$ and by fractional condensation.

(29) Trifluorophosphine alone or mixed with trimethylamine was subject to 5% loss per pass over the glpc column. A corresponding correction has been applied to the quantities of $PF_3$ listed in the tables. When the glpc-separated components were recombined or when glpc-purified trimethylamine was mixed with trifluorophosphine, inexplicably a small amount of white solid was formed at room temperature. This was not found if trimethylamine was purified by fractional condensation: W. R. Deever, Ph.D. Thesis, University of Washington, 1968, p 51.

(30) G. R. Seely, J. P. Oliver, and D. M. Ritter, *Anal. Chem.*, **31**, 1993 (1959).

(31) W. R. Deever and D. M. Ritter, forthcoming publication; see W. R. Deever, Ph.D. Thesis, University of Washington, 1968.

(32) The instrument was available through the cooperation of Professor D. C. Teller, Department of Biochemistry, University of Washington.

(33) T. R. Spellman and A. B. Burg, *Inorg. Chem.*, **2**, 1139 (1963).