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Chemistry of P–B Bonding: The Phosphinoborines and Their Polymers

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The well-bonded complex $Me_2PH \cdot BH_3$ loses H_2 at 150° to form the very stable and chemically resistant $(Me_2PBH_2)_3$ (orthorhombic, m.p. 86°, b.p. est. 235°), less of the somewhat less stable $(Me_2PBH_2)_4$ (twinned crystals, m.p. 161°, b.p. est. 310°), and a trace of higher polymer convertible by heat to the trimer. The trimer and tetramer hydrolyze slowly at 300° to form $B(OH)_3$, Me_2POOH and $4H_2$ per Me_2PBH_2 unit. The Me_2POOH has m.p. 92° and b.p. est. 377°; vapor dimeric. $(Me_2PBH_2)_3$ very slowly reacts with sodium in liquid ammonia to form $Me_5P_3NH_2(BH_2)_3$ (m.p. 35°; v.t. 6.3 mm. at 97.5°) and unknown by-products. The trimer $(Me_2PBMe_2)_3$ (m.p. 334°, b.p. nearly the same), produced from $Me_2PH \cdot Me_2BBr$ by action of Et_3N, is as inert and stable as $(Me_2PBH_2)_3$, and $(Me_2PBHMe)_x$ may well be likewise, but H_2PBMe_2 forms a monomer which changes to a high polymer or reacts with methanol to form the new compound Me_2BOMe (b.p. 21°). $(MePHBH_2)_n$ occurs as a non-volatile oil and $(PBH_{3.75})_n$, as a refractory solid. New methyl derivatives of H_3PBH_3 are described in relation to the synthesis of the phosphinoborines. The reasons for the chemically inert character of the polymeric phosphinoborines and for the high-polymer character of the H_2P and MePH borines are sought in the nature of covalent bonding involving the 3d orbitals of phosphorus.

The prospect of the development of a very extensive and diversified chemistry of aminoboron compounds[2-4] evokes the question whether a large chemistry of phosphinoboron compounds also is possible. The work of Gamble and Gilmont on "diborane diphosphine"[5] showed some promise of this, but the base-weakness of phosphine itself was a disadvantage, and the attempt to make a volatile phosphinolysis product of diborane led only to an unintelligible polymer. On the other hand, the methylphosphines are far stronger bases,[6] and if dimethylphosphine is chosen as a reagent, the limitation of only one P–H bond per molecule should prevent phosphinolysis reactions from becoming too complex for study.

In accord with expectations, dimethylphosphine reacts with diborane to form an adduct having the molecular formula $(CH_3)_2PH \cdot BH_3$, and this substance is converted by heat to a mixture of $(CH_3)_2PBH_2$ polymers—mostly trimer, some tetramer and a trace of higher polymer. The structural patterns of these substances have not been determined by physical means, but the formation of $(CH_3)_2POOH$ as a major product of hydrolysis leaves no doubt that they are composed of $(CH_3)_2P$ and BH_2 groups. Nevertheless both the trimer and tetramer are astonishingly unreactive toward air, acids, bases and water, hydrolyzing only very slowly in the presence of HCl at 300°. They also are highly resistant to thermal decomposition; especially the trimer may well be the most stable B–H compound ever obtained as a definite substance. The polymer bonding is so strong that it has not been possible to form any phosphinodiborane by addition of BH_3 groups —in contrast to the easy formation of $(CH_3)_2NB_2H_5$ from $(CH_3)_2NBH_2$.[2,3]

The structure of the trimer may well be based upon a $(P–B)_3$ hexatomic ring for which one would write as a first approximation a simple Lewis-type electronic structure with six equivalent P–B bonds and alternating P^+ and B^- formal charges; but some explanation still is needed for the extreme difficulty of hydrolysis. A steric hindrance by the methyl groups, against a close approach by water molecules, might be part of the cause, but the failure of hydrogen chloride to attack either the trimer or the tetramer at ordinary temperatures, as it does all other compounds in which a B–H link is one of four bonds to boron, implies clearly that the B–H bonds in these phosphinoborines are very hard to activate for reaction in the sense of hydride ion. Such inertness toward protonic reagents could well be due to a weak but multiplex B–P π-bonding in which the B–H bonding electrons enter hybrid orbitals involving the 3d (and perhaps partly 4s) states of the adjacent P atoms; thus the electron density on H would be lower, and H less hydridic, than in other quaternary boron compounds. This use of B–H electrons would tend to compensate the $[(CH_3)_2P]^+—B^-$ formal charge and should be more important than a similar use of C–H electrons to increase the electron density on P and so to strengthen the P–B σ-bonding. The whole bonding system thus should be much stronger than that in the easily dissociable dimer of $(CH_3)_2NBH_2$,[3] since nitrogen can offer no such wealth of possible bonding orbitals as those of phosphorus.

The extreme stability of trimeric $(CH_3)_2PBH_2$ is nearly matched by the trimer of $(CH_3)_2PB(CH_3)_2$, which also requires temperatures above 300° for a hydrolytic break-down of the P–B bonding. In this case an interpretation of the polymer bonding in terms of the simple Lewis structure would be quite incredible, since the substitution of CH_3 for H on B lowers the acceptor-bonding strength of boron very sharply.[7] Without the postulated extra bonding between B and P, one should expect $(CH_3)_2PB(CH_3)_2$ to be far less firmly associated than $(CH_3)_2PBH_2$. But the use of electrons from the $(CH_3)_2B$ bond-system for $B \rightarrow P$ π-bonding should be more important than a similar use of BH_2-group electrons, so that the lesser $P \rightarrow B$ σ-bonding effect in the trimer of $(CH_3)_2PB(CH_3)_2$ would be compensated.

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[1] This paper represents some of the research studies reported by Ross Irving Wagner in partial fulfillment of the requirements for the degrees of Master of Science (August, 1950) and Doctor of Philosophy (January, 1953). Other aspects of his work are being published in separate papers. Fuller details are presented in his M.S. thesis and Ph.D. dissertation, microfilm copies of which can be obtained from the University of Southern California Libraries.

[2] A. B. Burg and C. L. Randolph, Jr., THIS JOURNAL, **71**, 3451 (1949).

[3] A. B. Burg and C. L. Randolph, Jr., *ibid.*, **73**, 953 (1951).

[4] A. B. Burg and E. S. Kuljian, *ibid.*, **72**, 3103 (1950). See also earlier references cited in these papers.

[5] E. L. Gamble and P. Gilmont, *ibid.*, **62**, 717 (1940).

[6] H. C. Brown, E. A. Fletcher, E. Lawton and S. Sujishi, Abstracts of Papers Presented at the 121st National Meeting of the American Chemical Society, p. 9N (1952).

[7] H. I. Schlesinger, N. W. Flodin and A. B. Burg, THIS JOURNAL, **61**, 1078 (1939).

Another shift in the relative importance of the P→B σ- and B→P π-bonding effects should occur in polymeric $(CH_3)_2PBHCH_3$. A product roughly corresponding to this was found to be as difficult to hydrolyze as the other $(CH_3)_2PB{=}$ compounds, but the facts concerning it are not yet sufficient for a full discussion.

Phosphinoborines derived from PH_3 or CH_3PH_2 would be expected to form P→B σ-bonds weaker than those in the $(CH_3)_2P$ compounds of the same borine radicals, but the B→P π-bonding should be stronger. And since the B→P π-bonding should be more multiplex than the P→B σ-bonding, a tendency toward linearity should work against the formation of trimer rings. Actually, a product corresponding to CH_3PHBH_2 was obtained as a viscous oil which could not be distilled under high vacuum at temperatures up to 100° (dec.); if it were a low polymer, such as a trimer or tetramer, it should have been at least slightly volatile at lower temperatures. Also, an attempt to obtain H_2PBH_2 from PH_3 and B_2H_6 at 65° led only to non-volatile material. Finally, a nearly monomeric sample of $H_2PB(CH_3)_2$ was made and shown to change slowly to a high polymer without evidencing any stable low-polymer stage. Some 55% of the original sample of $H_2PB(CH_3)_2$ reacted easily with methanol, forming PH_3 and the new compound $(CH_3)_2BOCH_3$—the one case in which a phosphinoborine proved to be highly susceptible to solvolytic break-down, presumably for lack of polymeric condition.

Experimental Part

I. New Complex Compounds of the Phosphine–Borine Type

A number of new compounds which might be described as methyl substitution derivatives of the prototype substance H_3PBH_3[8] were involved in experimental work toward the preparation of various phosphinoborine derivatives and are here described in that relation. Of the fifteen possible methyl derivatives of H_3PBH_3, the four which involve $B(CH_3)_3$ have been thoroughly studied by Brown, *et al.*, who showed that the P→B bond strength increases sharply as CH_3 replaces H on P.[6] Our results show qualitatively similar trends with $(CH_3)_2BH$ and BH_3 complexes of the methyl phosphines. It is noted also that substitution of CH_3 for H on B weakens the P→B bond, as expected from earlier knowledge of $(CH_3)_3N$ complexes,[7] although the phosphine complexes of the CH_3BH_2 group have not been directly studied.

Trimethylphosphine Borine.—A sample of trimethylphosphine was prepared in 38% yield by the reaction between PBr_3 and CH_3MgI in *n*-butyl ether, and purified by distillation in the high-vacuum system. Its vapor tension at 0° was measured as 161.0 mm. (lit. 161.3).[9] A 3.61-cc.[10] portion of $(CH_3)_3P$ reacted vigorously with 1.82 cc. of diborane at −78°, with a decrease of pressure to zero, as demanded by the formation of the compound $(CH_3)_3PBH_3$. The solid product melted in the range 103.0 to 103.5° (orthobaric) and its vapor density just above the condensation point indicated a molecular weight value of 95.4 (calcd., 89.9)—essentially monomeric. The vapor tensions of the solid $(CH_3)_3PBH_3$ were measured in an immersible tensimeter[11] and are presented in Table I. They determine the equation $\log_{10} p_{\text{mm.}} = 9.531 - 2933/T$.

TABLE I

VAPOR TENSIONS OF SOLID $(CH_3)_3PBH_3$

t, °C.	p, mm. Calcd.	p, mm. Found	t, °C.	p, mm. Calcd.	p, mm. Found
45.7	2.15	2.20	65.2	7.30	7.29
50.5	2.94	3.02	75.1	12.85	12.78
55.3	3.99	3.91	80.9	17.66	17.70
61.0	5.68	5.64	85.3	22.34	22.35

The 3.61-cc. sample of $(CH_3)_3PBH_3$ was heated for five hours at 200°, forming only 0.27 cc. of hydrogen. A larger sample (50.5 cc.) was made and heated in a 70-ml. sealed tube for 24 hours at 260°, yielding 6.63 cc. of pure hydrogen; then during an additional 174 hours, an additional 8.45 cc. of H_2 formed, along with 0.72 cc. of methane; also 8.50 cc. of free $(CH_3)_3P$ was found (16.8%). Apparently the main decomposition involved the BH_3 group; such a pyrolysis does not lead to polymers of $(CH_3)_2PBH_2$.

Dimethylphosphine Borine.—Dimethylphosphine was prepared in good yields by a liquid ammonia method (described in a separate paper)[12] and a 30.0-cc. sample was treated with 15.0 cc. of diborane in the immersible tensimeter,[11] with a rapid decrease of pressure to zero. The product melted at −22.6° and its vapor density just above the condensation point indicated a molecular weight of 83 (calcd., 76)—evidently monomeric $(CH_3)_2PH{\cdot}BH_3$. The vapor tensions of the liquid, presented in Table II, determine the equation $\log_{10} p_{\text{mm.}} = 8.100 - 2337/T$, indicating that the normal boiling point would be near 174° and the Trouton constant 23.9 cal./deg. mole.

TABLE II

VAPOR TENSIONS OF LIQUID $(CH_3)_2PH{\cdot}BH_3$

t, °C.	p, mm. Calcd.	p, mm. Found	t, °C.	p, mm. Calcd.	p, mm. Found
29.5	2.39	2.36	75.2	24.6	25.0
39.9	4.33	4.25	90.0	46.3	46.2
50.0	7.40	7.44	100.1	69.2	68.7
60.7	12.62	12.67	110.2	100.9	100.0

Dimethylphosphine borine could be heated to 150° without rapid decomposition, but during 40 hours at that temperature, the 30.0-cc. sample formed 30.12 cc. of H_2—shown by CuO combustion to contain no methane. The products of this phosphinolysis are described in Section II.

Methylphosphine Borine.—A rapid and clean reaction between 36.5 cc. of CH_3PH_2 and 18.3 cc. of B_2H_6 occurred when the mixed condensate was warmed from −196°, yielding a product which melted in the range −49.9 to −49.3°. The average molecular weight of the vapor (at 83° and 55 mm., slightly above the condensation point) was determined as 62.0 (calcd., 61.9); the result might have been affected either by a slight dissociation into CH_3PH_2 and B_2H_6 or the formation of a trace of hydrogen, or both—since the borine complexes of the more methylated phosphines showed high molecular weights under similar conditions. However, it was possible to measure consistent vapor tensions up to 81°, as shown in Table III.

TABLE III

VAPOR TENSIONS OF LIQUID $CH_3PH_2{\cdot}BH_3$

t, °C.	p, mm. Calcd.	p, mm. Found	t, °C.	p, mm. Calcd.	p, mm. Found
23.6	3.6	3.5	66.3	34.7	34.8
35.7	7.2	7.1	71.3	43.6	43.4
46.1	12.8	12.7	76.4	54.7	54.6
51.0	16.4	16.5	81.3	67.6	67.3
56.2	21.4	21.5			

These results determine equation $\log_{10} p_{\text{mm.}} = 8,400 - 2329/T$, which means that the normal boiling point would be 150° and the Trouton constant 25.3 cal./deg. mole.

The same 36.5-cc. sample of methylphosphine borine was heated for 20 hours at 100°, finally yielding the theoretical 36.4 cc. of H_2, in accord with the equation $CH_3PH_2{\cdot}BH_3 \rightarrow H_2 + CH_3PHBH_2$. The main product was a viscous oil which could not be distilled—probably a fairly high polymer. When the container was heated by a free flame, the oil changed to a brown non-volatile solid, yielding a further

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[8] This may exist as one form of the "$B_2H_6{\cdot}2PH_3$" which was discovered by E. L. Gamble and P. Gilmont and independently by H. I. Schlesinger and A. B. Burg. *Cf.* ref. 5.

[9] E. J. Rosenbaum and C. R. Sandberg, THIS JOURNAL, **62**, 1622 (1940).

[10] Throughout this paper, the abbreviation "cc." refers to gases at standard conditions.

[11] A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 785 (1937).

[12] R. I. Wagner and A. B. Burg, *ibid.*, **75**, 3869 (1953).

34.8 cc. of H_2. Another sample of the same oil was found to resist hydrolysis by 4 *M* HCl, refluxing *in vacuo* for 10 minutes.

Dimethylphosphine Dimethylborine.—A 44.7-cc. sample of $(CH_3)_2PH$ and 22.2 cc. of $(CH_3)_4B_2H_2$ were condensed together and warmed slowly for reaction; then cooled to −78° to permit removal of the slight excess of $(CH_3)_2PH$. Above 40° the product, $(CH_3)_2PH{\cdot}HB(CH_3)_2$, suffered disproportionation, as indicated by the formation of the highly volatile $B(CH_3)_3$ and $(CH_3)_2PH$ which are only very weakly combined at such a temperature. At lower temperatures the vapor tensions—2.58 mm. at 19.5°, 5.44 mm. at 29.3° and 10.9 mm. at 39.5°—determined the equation $\log_{10} p_{mm.} = 10.177 - 2857/T$, from which the check values 2.60, 5.40 and 11.0 mm. can be calculated. A quick measurement at 49.9° gave 23.3 mm. (calcd., 21.6); at 60.0°, 48.7 mm. (calcd., 40.1)—high values indicative of the disproportionation.

Dimethylphosphine Trimethylborine.—Equal portions of $(CH_3)_2PH$ and $B(CH_3)_3$ (each 48.0 cc. gas) were brought together in an immersible tensimeter,[11] in which they showed an average molecular weight of 63.8 at 78 mm. and 39°, suggesting that the compound $(CH_3)_2PH{\cdot}B(CH_3)_3$ was 92% dissociated under the stated conditions. The vapor tensions of the liquid product, shown in Table IV, determine the equation $\log_{10} p_{mm.} = 10.205 - 2580/T$, according to which the normal boiling point would be 79° and the Trouton constant 33.5 cal./deg. mole—a value suggesting that the compound is almost completely formed in the liquid state, although highly dissociated as a vapor. The orthobaric melting range was measured as −2.8 to −1.8°.

TABLE IV

VAPOR TENSIONS OF LIQUID $(CH_3)_2PH{\cdot}B(CH_3)_3$

t, °C.	*p*, mm. Calcd.	*p*, mm. Found	*t*, °C.	*p*, mm. Calcd.	*p*, mm. Found
0.0	5.8	5.3	49.3	160	164
19.6	24.8	23.8	60.6	299	296
30.8	52.2	52.6	70.5	499	497
41.2	100	101			

II. Polymers of Dimethylphosphinoborine

The Phosphinolysis Products.—A 602-cc. sample of $(CH_3)_2PH{\cdot}BH_3$ (*cf.* Section I) was heated at 150° for 40 hours and the white crystalline products were separated by fractional sublimation under high vacuum. The most volatile fraction (89.5% of the total) had a molecular weight of 234 in the vapor phase, corresponding to the trimer $[(CH_3)_2PBH_2]_3$ (calcd. mol. wt., 222). Its composition was fully confirmed by more than one method of analysis, as described below. Its inertness toward moist air was demonstrated by exposing a sample in an open tube for several weeks, during which no appreciable change occurred. For final purification, it was crystallized from methanol in the open air. Its orthobaric melting range was 85.0–86.0° and a recheck of the molecular weight by the micro-Rast method (freezing point of a solution in camphor) gave the value 214.

A less volatile fraction, amounting to 8.8% of the original solid phosphinolysis product, showed a molecular weight of 280.5 by the micro-Rast method; hence this fraction evidently was the tetramer $[(CH_3)_2PBH_2]_4$ (calcd. mol. wt., 295). It was easily purified by recrystallization from benzene in the open air; m.p. 160–161° (orthobaric).

A trace of non-volatile residue, which could not be sublimed *in vacuo* by brief application of a free flame, was heated for 88 hours in a sealed tube at 173°, yielding 22.9 mg. (1% of the original product) of the trimer; evidently the non-sublimable fraction was a higher polymer which was far less stable than the trimer. The tetramer also was shown to be less stable than the trimer: a 15.7-mg. sample of pure tetramer (after showing no change during two weeks at 255°) was wholly decomposed during 140 hours in a sealed tube at 350°, yielding 1.5 cc. of CH_4, 1.86 cc. of H_2 and a golden-brown solid from which 2.6 mg. of the trimer was extracted by methanol and identified by its volatility and melting point. The yield of trimer from tetramer thus was at least 16%, in spite of the long heating at 350°.

Combustion Analysis of the Dimethylphosphinoborines.—Carbon–hydrogen analyses by the standard micro-method gave 32.23% C for the trimer and 32.39% C for the tetramer (calcd., 32.51%); the corresponding values for hydrogen were 11.11 and 11.32% (calcd., 10.91%). For phosphorus and boron, weighed samples of the trimer were vaporized in a stream of hydrogen which burned at a small quartz tip in an atmosphere of oxygen within a water-cooled Pyrex chamber. The excess gas bubbled out through water in the same all-glass apparatus. The resulting phosphoric acid was precipitated as $MgNH_4PO_4$ (using a very slight excess of Mg^{++}) and weighed as $Mg_2P_2O_7$. The filtrate was boiled to remove ammonia, neutralized to the methyl red end-point, and titrated to the phenolphthalein end-point in the presence of mannitol; the magnesium was at a concentration too low for any interference. Phosphorus found: 42.9, 40.5 and 40.1% (calcd., 41.9%); boron found: 14.2 and 14.5% (calcd., 14.6%). In view of the quantitative (99.2% or better) synthesis, these results left no doubt of the composition of either the trimer or the tetramer.

Hydrolysis Experiments.—Before the possible structures of the new polymers could be considered, it was necessary to determine whether the methyl groups remained on phosphorus, and hydrogen on boron, after the original phosphinolysis reaction at 150°. Hydrolysis reactions yielding boric acid and an identifiable compound of the $(CH_3)_2P$ group would give a positive answer.

In a preliminary experiment, a 51.3-mg. sample of the trimer (5.18 cc.) was heated with water at 100° for 44 hours without appreciable effect, and with 4 *M* HCl at 240° for 15 hours to yield only 0.6 cc. of H_2—2% of what would be expected if every B–H bond yielded one H_2. A mixed sample of trimer and tetramer was tried with concd. NaOH at 100° for four hours and with 4 *M* HCl at 100° for 35 hours—yielding no appreciable hydrogen at all. Next the trimer was tried with dry HCl (excess) and during 43 hours at 300° it yielded only 52% of the amount of hydrogen which should have resulted if each BH_2 unit were converted to a BHCl unit.

The most nearly complete hydrolysis of the trimer occurred when a 37.1-mg. sample (0.1669 mmole) was heated in a 60-ml. Pyrex bomb tube with 5.55 mmoles of water and 2.13 mmoles of HCl for 256 hours at 300°. The resulting 42.8 cc. (1.910 mmoles) of H_2 corresponded to a 95.1% completion of the reaction $[(CH_3)_2PBH_2]_3 + 15H_2O \rightarrow 12H_2 + 3(CH_3)_2POOH + 3B(OH)_3$. Only such an equation could account for the nearly double yield of hydrogen and the absence of any methane. The tetramer was hydrolyzed in the same manner: 8.5-mg. sample gave 10.17 cc. of pure H_2—99% of the amount expected if the other products were $(CH_3)_2POOH$ and $B(OH)_3$.

Three other samples of the trimer and one of the tetramer were partially hydrolyzed in soda-glass tubes to avoid spurious boric acid; however, the hydrolysis was far less extensive, apparently on account of some obscure effect of the more alkaline glass. Thus 0.282 mmole of the trimer in a 150-ml. tube yielded only 21% of the expected hydrogen during 334 hours at 300°; 0.154 mmole in a 60-ml. tube, 44% during 297 hours at 300°; 0.155 mmole in a 60 ml. tube, 66% during 473 hours at 315°. In accord with its lesser stability, the tetramer went a little farther: a 0.114-mmole sample was 89% hydrolyzed in a 60-ml. tube during 473 hours at 315°.

In order to compare the products of these hydrolyses with known material, an authentic sample of dimethylphosphinic acid, $(CH_3)_2POOH$, was prepared as described in the following paragraph, and a mixture containing 79.3 mg. of it (0.84 meq.) with 0.84 meq. of boric acid was titrated by standard base with a *p*H meter as indicator. The first inflection was sharp, with the center at a *p*H of 6.0 when 0.87 meq. of base had been added; the second inflection, corresponding to boric acid, was found by the differential method at *p*H 10.3, after 0.86 meq. more base had been added. Now the mixtures resulting from the hydrolyses of the trimer and tetramer (in soda-glass tubes) were titrated in just the same manner, giving inflection ranges virtually superimposable upon those of the known mixture: first inflection center at *p*H 6.0 to 6.1; second at 10.3 to 10.6. Thus it was quite clear that the hydrolysis products were qualitatively the same as the known mixture of $(CH_3)_2POOH$ and $B(OH)_3$. The results indicated proportions of $(CH_3)_2POOH$ fairly comparable to the extent of hydrolysis, while the results for boric acid usually ran considerably lower. Hence the results were only qualitative, but they left no doubt that the methyl groups remained on the phosphorus during the phosphinolysis of diborane and the hydrolysis of the products at elevated temperatures. Hence it was reasonable to assume that the trimer and tetramer were composed of $(CH_3)_2PBH_2$ units, presumably forming rings of alternating P and B atoms.

Preparation of Dimethylphosphinic Acid.—Pure $(CH_3)_2POOH$ was made by the reaction $5(CH_3)_2PH + 4HIO_3 \rightarrow 5(CH_3)_2POOH + 2I_2 + 2H_2O$—an adaptation of a method which has been used for the quantitative oxidation of phosphine to phosphoric acid.[13] The dimethylphosphine (9.95 mmoles) was condensed upon a frozen solution of 9.97 mmoles of I_2O_5 in 5 ml. of water, in a 50-ml. flask attached to the vacuum system. The vigorous reaction was controlled by holding an ice-water slush around the flask. Finally, the excess iodic acid was destroyed by HI and the I_2, HI and H_2O were removed by vacuum evaporation. The last of the water was removed by dissolving the product in benzene and boiling. After crystallization from benzene, the substance melted at 91–92°, and again had the same m.p. after sublimation *in vacuo*. Combustion analysis gave 25.68% C and 7.36% H (calcd., 25.54 and 7.50).

Representative vapor tensions of dimethylphosphinic acid are given by Table V. They conform to the equation $\log_{10} p_{\text{mm.}} = 7.313 - 2880/T$; b.p. 377°; Trouton constant 20.2 cal./deg. mole. Determinations of the vapor density indicate that the vapor is dimeric at or near equilibrium with the liquid, but dissociates into a monomer at higher temperatures.

TABLE V

VAPOR TENSIONS OF LIQUID $[(CH_3)_2POOH]_2$

t, °C.	p, mm.		t, °C.	p, mm.	
	Calcd.	Found		Calcd.	Found
94.8	0.31	0.29	119.8	0.96	0.98
102.3	.44	.44	129.7	1.46	1.46
109.8	.62	.60	134.6	1.78	1.76
114.9	.78	.75	139.7	2.17	2.13

Vapor Tensions of the Trimer and Tetramer.—Purified samples of the trimer and tetramer of dimethylphosphinoborine were resublimed in high vacuum to remove the solvent and adhering traces of dimethylphosphine (the odor of which remained faintly evident even after the most repetitious process of purification) and their vapor tensions were measured in an immersible tensimeter like that previously described[11] but designed for higher precision.[14] The results for the trimer, shown in Table VI, determine the equation $\log_{10} p_{\text{mm.}} = 13.10 - 4515/T$ for the solid (values below 85°) and $\log_{10} p_{\text{mm.}} = 8.557 - 2887/T$ for the liquid. The calculated boiling point is 235° and the Trouton constant 26.0 cal./deg. mole. The heat of fusion is estimated as 7.4 kcal./mole.

TABLE VI

VAPOR TENSIONS OF DIMETHYLPHOSPHINOBORINE TRIMER

t, °C.	p, mm.		t, °C.	p, mm.	
	Calcd.	Found		Calcd.	Found
	Solid			Liquid	
59.75	0.35	0.40	89.50	3.95	3.95
65.00	.56	.54	95.25	5.25	5.33
69.60	.85	.82	100.00	6.58	6.79
74.67	1.32	1.29	104.85	8.30	8.41
79.55	2.00	2.04	109.87	10.47	10.50
84.87	3.09	2.88	114.87	13.09	13.27
			120.17	16.48	16.56
			124.86	20.09	20.07

The vapor tension measurements on the tetramer were a little more difficult on account of the higher temperature range, and the results for the solid were slightly disturbed by a trace of a more volatile impurity. Allowing for this, the equation $\log_{10} p_{\text{mm.}} = 12.28 - 4900/T$ is roughly representative. The values for the liquid tetramer, as presented in Table VII, determine the equation $\log_{10} p_{\text{mm.}} = 8.364 - 3196/T$, from which the normal boiling point is computed to be 310° and the Trouton constant 25.1 cal./deg. mole. The heat of fusion is near 8.0 kcal./mole.

TABLE VII

VAPOR TENSIONS OF LIQUID DIMETHYLPHOSPHINOBORINE TETRAMER

t, °C.	p, mm.		t, °C.	p, mm.	
	Calcd.	Found		Calcd.	Found
161.9	10.44	10.4	175.2	17.2	17.2
165.1	11.75	11.8	179.8	20.3	20.3
170.5	14.5	14.6	189.8	28.9	28.9

Crystallography of the Trimer and Tetramer.[15]—A single crystal of the trimer of dimethylphosphinoborine showed parallel extinction between crossed Nicol prisms and also gave a diaxial interference figure. These indications of an orthorhombic unit cell were confirmed by X-ray rotation and Weissenberg photographs from which a_1 = 11.1, a_2 = 13.1 and a_3 = 10.4 Å. Crystal fragments of the substance floated on water but sank in a water–ethanol mixture of density 0.96; hence the density is such as to require twelve $(CH_3)_2PBH_2$ units per unit cell. Inasmuch as the crystallographically equivalent general positions in any orthorhombic crystal occur in sets of 4, 8, or 16, the 12-unit result indicates three sets of fourfold position: *i.e.*, four equivalent trimer molecules. The task of lattice placement of the molecules has not been completed.

The crystals of the tetramer have a lath-like shape and apparently are biaxial. X-Ray examination by Weissenberg photography proved each crystal to be a parallel twin. Rotation photographs, with the long direction of the crystal as axis, did not demonstrate the twinning; hence the twinning plane is parallel to the long direction.

The Behavior of the Trimer toward Sodium in Liquid Ammonia.—It is generally assumed that most bonds between atoms of different elements can be broken by the action of the electron in liquid ammonia; hence attempts were made to obtain a clean break-down of the trimer of dimethylphosphinoborine by that reagent. A preliminary experiment, involving 0.109 mmole of trimer and 2.09 mmoles of sodium in 2 ml. of liquid ammonia (65 days at 0°) showed that some reaction occurred, yielding 1.04 mmoles of H_2, probably some sodium amide, and soluble material more volatile than the trimer. Some free sodium remained.

In another small-scale experiment, 0.116 mmole of trimer and 2.43 mmoles of sodium were sealed off with 3 ml. of liquid ammonia in a heavy-walled H-tube (tested at 13 atm.) and left for 36 days at room temperature. The blue color was discharged, leaving a light yellow solution and a white precipitate. The solution was decanted into the empty arm of the H-tube; then the tube was opened and 26.0 cc. of H_2 (1.16 mmoles, corresponding to all but 5% of sodium) was pumped off. With it was 0.026 mmole of methane. Now the ammonia was evaporated off and the two arms of the H-tube were separated by sealing. Hydrolysis of the insoluble solid yielded 2.10 mmoles of ammonia, consistent with the assumption of sodium amide. The ammonia-soluble fraction upon treatment with 1 ml. of 12 M HCl yielded 0.244 mmole of H_2 and 4.7 mg. of a solid somewhat more volatile than the trimer: it melted in the range 35.5–35.7°.

In the final experiment, a solution of 236.1 mg. (1.066 mmoles) of the trimer and 100.0 mg. (4.346 mmoles) of sodium in 4.0 ml. of liquid ammonia was allowed to stand in the H-tube for 62 days at room temperature, with a complete discharge of the blue color during the first 32 days. The gaseous products were found to be 1.713 mmoles of H_2 and 0.2606 mmole of methane. After evaporation of the solvent ammonia, the residual solids were heated to 100° and the volatile components sublimed into the other arm of the H-tube at −196°. Under these circumstances, the previously-observed volatile solid product remained with the sodium amide (presumably in some kind of combination), for the melting point of the sublimate indicated it to be pure trimer; weight 109.5 mg., or 46.4% of the original.

An Amido Derivative of the Trimer.—The residue now was treated with 0.2 ml. of water, yielding 0.37 cc. of H_2 (0.016_5 mmole); then the water and ammonia were removed from the low-melting solid with the aid of anhydrous calcium sulfate. The crude product (melting range 33.7–35.6°) was purified in the high-vacuum system, with 95% recovery,

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(13) L. Moser and A. Brukl, *Z. anorg. allgem. Chem.*, **121**, 76 (1922).

(14) C. L. Randolph, Jr., Ph.D. Dissertation, University of Southern California Libraries, Los Angeles, 1949, p. 37.

(15) This work was done by Arthur J. Stosick of this Department, in the year 1950.

57.0 mg. The average of three vapor density measurements showed a molecular weight of 227; hence the sample amounted to 0.256 mmole, closely corresponding to the previously-mentioned 0.2606 mmole of methane, and representing 45% of the unrecovered trimer. It appeared that the product might be the result of substitution of one NH_2 group for CH_3 on P in the trimer. This hypothesis was supported by a C–H–N microanalysis giving 26.0% C, 9.85% H, and 6.26% N; calcd. values for $(CH_3)_5NH_2P_3(BH_2)_3$, 27.0% C, 10.41% H, and 6.29% N. These results, taken with the molecular weight value and the source of the substance, left little doubt that the product was the same as the original trimer except that one CH_3 group had been replaced by NH_2. The character and manner of formation of other reaction products are yet to be learned.

Representative vapor tensions of the amido derivative are shown in Table VIII. They correspond to the equation $\log_{10} p_{\text{mm.}} = -(5407.9/T) + 1.75 \log_{10} T - 0.01949T + 18.121$, which is not applicable above 150°.

TABLE VIII

VAPOR TENSIONS OF LIQUID $(CH_3)_5NH_2P_3(BH_2)_3$

t, °C.	p, mm. Calcd.	p, mm. Found	t, °C.	p, mm. Calcd.	p, mm. Found
36.1	0.09	0.08	84.8	3.22	3.27
45.0	.21	.21	97.5	6.36	6.27
55.2	.45	.45	112.4	12.7	12.5
65.0	.93	.92	127.4	23.4	23.8
77.5	2.08	2.11			

III. Other Phosphinoborine Polymers

The Fully Methylated Trimer.—An efficient preparation of the trimer of $(CH_3)_2PB(CH_3)_2$ was achieved through the reaction of $(CH_3)_2PH$ with $(CH_3)_2BBr$ in the presence of triethylamine—an adaptation of a method which has been used before for the synthesis of B–N compounds.[16] This was done after it had been shown that the dimethylborine group in $(CH_3)_2PH\cdot HB(CH_3)_2$ disproportionated before appreciable loss of hydrogen occurred, and after attempts at the phosphinolysis of $B(CH_3)_3$ at 250 to 380° had led to serious disproportionation of the $(CH_3)_2PH$ and considerable formation of red and white phosphorus.

In the successful experiment, 80.3 cc. each of $(CH_3)_2PH$ and $(CH_3)_2BBr$ were brought together in 10 ml. of benzene and treated with 80.3 cc. of triethylamine, to form a precipitate of $(C_2H_5)_3NHBr$. The benzene was evaporated *in vacuo* and replaced by ether; then after filtration the product was recrystallized from methanol, in a yield of 30%. Further use of the same method has indicated that it would be feasible to use ether as the solvent throughout the process, filtering off the salt and crystallizing the desired product, probably in higher yield.

The molecular weight of the purified solid was determined by its effect upon the freezing point of camphor (micro-Rast method), as 334 (calcd. for trimeric Me_2PBMe_2, 306). Its melting range was sharp: 333–334°. Its vapor tensions, given by Table IX, determine the equation $\log_{10} p_{\text{mm.}} = 9.883 - 4184/T$, according to which the molar heat of sublimation is 19.2 kcal. and the boiling point is nearly the same as the melting point—a situation consistent with the high symmetry which a dodecamethyl hexagonal-ring structure would have.

TABLE IX

VAPOR TENSIONS OF SOLID $[(CH_3)_2PB(CH_3)_2]_3$

, °C.	p, mm. Calcd.	p, mm. Found	t, °C.	p, mm. Calcd.	p, mm. Found
120.0	0.18	0.18	170.0	2.78	2.98
130.0	.32	.27	180.0	4.46	4.27
140.0	.57	.54	190.0	7.08	7.10
150.0	.99	.85	197.5	9.84	9.83
160.0	1.68	1.72			

The trimer of dimethylphosphinodimethylborine proved to be inert toward the open air, and required at least 300° for hydrolysis at an appreciable rate in an acid medium. A 13.8-mg. sample (1.01 cc.) was heated with 0.1 ml. of concd. HCl in a tube of 60 ml. volume for seven days at 325°, yielding 5.48 cc. of H_2, 5.96 cc. of CH_4, and an unmeasured amount of $(CH_3)_2POOH$, which was identified by a mixed melting point determination with an authentic sample. The hydrolysis evidently proceeded in accordance with the equation $[(CH_3)_2PB(CH_3)_2]_3 + 15HOH \rightarrow 3(CH_3)_2POOH + 3B(OH)_3 + 6H_2 + 6CH_4$, but was not strictly complete. However, the result left no reasonable doubt of the identity of the new compound.

Material Corresponding to Dimethylphosphinomethylborine.—In view of the disproportionation of $(CH_3)_3N\cdot HB(CH_3)_2$ at 75°,[7] the compound $(CH_3)_2PH\cdot HB(CH_3)_2$ might be expected to change to $(CH_3)_2PH\cdot B(CH_3)_3$ and $(CH_3)_2PH\cdot H_2BCH_3$ at temperatures below that required for the loss of hydrogen from the latter product—whereby this complex would be converted to a polymeric form of $(CH_3)_2PBHCH_3$. However, one should not discount the possibility of some further disproportionation whereby $(CH_3)_2PBH_2$ and $(CH_3)_2PB(CH_3)_2$ units would be formed. And since the formation of some $B(CH_3)_3$ in the early stages of the process should result in partial suppression of the disproportionation at later stages one might well expect a mixture of polymers and copolymers in which the $(CH_3)_2PBHCH_3$ units would predominate, with $(CH_3)_2PB(CH_3)_2$ units second in importance, and with some $(CH_3)_2PBH_2$ units also present.

In a preliminary experiment, 44.4 cc. of the complex $(CH_3)_2PH\cdot HB(CH_3)_2$ (*cf.* Section I) was heated 17 hours at 90°, without yielding more than a trace of hydrogen; then during 48 hours at 165° the phosphinolysis yielded 19.8 cc. (89% of the calculated amount) of H_2 and 19.0 cc. of $(CH_3)_2PH\cdot B(CH_3)_3$. The latter was isolated by sublimation *in vacuo* and identified by comparison of properties with those of the directly synthesized sample which was described in Section I. The main reaction thus appeared to be $2(CH_3)_2PH\cdot HB(CH_3)_2 \rightarrow H_2 + (CH_3)_2PH\cdot B(CH_3)_3 + (CH_3)_2PBHCH_3$ (polymer), but the presence or absence of $(CH_3)_2PB(CH_3)_2$ units or $(CH_3)_2PBH_2$ units in the product was not decided.

In the next experiment some $(CH_3)_2PH\cdot B(CH_3)_3$ was employed from the start, and this time there was definite evidence of the presence of $(CH_3)_2PB(CH_3)_2$ units in the polymeric product. A sealed tube containing 200 cc. of $(CH_3)_2PH\cdot HB(CH_3)_2$ and 48.0 cc. of $(CH_3)_2PH\cdot B(CH_2)_3$ was heated for 26 hours at 165°; then it was opened and found to contain 110.8 cc. of H_2, 132.0 cc. of $(CH_3)_2PH\cdot B(CH_3)_3$ and a difficultly volatile solid residue. Since the hydrogen was 10.8% above that calculated according to the equation given at the end of the preceding paragraph, it could be assumed that the 12% deficit of $(CH_3)_2PH\cdot B(CH_3)_3$ was due to the formation of some $(CH_3)_2PB(CH_3)_2$ units. Accordingly the waxy solid product (inert toward water and oxygen) was twice recrystallized from ethanol, with 10% final recovery, but with a rise of melting point only from 120 to 132°. An excess of $(CH_3)_2B$ over BH_2 groups still was indicated by the high C:H atomic ratio of 0.315 (by combustion analysis) and by the results of hydrolysis. The attempt to isolate $[(CH_3)_2PBHCH_3]_x$ as a single substance thus did not succeed, perhaps because of solid solutions or copolymerization, or both.

The waxy white solid was hydrolyzed during 7 days at 320°, with 0.1 ml. of concd. HCl, producing 3.91 cc. of CH_4 and 7.74 cc. of H_2 from a 12.2-mg. sample. A polymer composed only of $(CH_3)_2PBHCH_3$ units would have yielded only 3.11 cc. of CH_4, or less if one considers that hydrolysis may not have been quite complete.

Pyrolysis of Phosphine Borine.—The solid reaction product of phosphine with diborane was heated at 200° by Gamble and Gilmont[5] in the hope of getting an analog of borazole. Instead, they got only a waxy solid and about 1.3 H_2 per P–B unit used up. Considering that the decomposition of diborane probably played a great part in their experiment, we heated a mixture of 21.7 cc. of PH_3 and 10.7 cc. of B_2H_6 for 19 days at a temperature of only 65°, obtaining 22.0 cc. of H_2 and recovering 0.69 cc. of B_2H_6 with 4.3 cc. of PH_3. Hence the non-volatile product had the empirical formula $PB_{1.15}H_{3.91}$—presumably to be interpreted as $(PBH_{3.75})_n$ with a little BH polymer. It was insoluble and chemically inert, in ether, benzene, methanol, water and aqueous HCl under mild conditions. Its insolubility could be due to cross-linking to induce a stage of polymerization far beyond that of the methyl derivatives of phosphinoborine.

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[16] J. F. Brown, Jr., THIS JOURNAL, **74**, 1219 (1952).

Phosphinodimethylborine.—In view of the base-weakness of phosphine and the electron-acceptor weakness of dimethylboron groups, it could be expected that the combination $H_2PB(CH_3)_2$ would be the most weakly bonded and least strongly polymerized of all of the phosphinoborines. In order to investigate it, four methods of synthesis were tried, with success only from the fourth. The first method was to heat a 2:1 mixture of PH_3 and $(CH_3)_4B_2H_2$; the main result was the disproportionation of the latter. The second method was the pyrolysis of an equimolar mixture of PH_3 and $B(CH_3)_3$, resulting chiefly in the decomposition of the phosphine. Next the reaction between $NaPH_2$ and $(CH_3)_2BBr$ was tried, without a solvent, and nothing seemed to happen until at a fairly elevated temperature there was a sudden and violent reaction with much evolution of hydrogen. Perhaps a reaction of this type could be controlled if $LiPH_2$ were used in ether; however, the success of the fourth method made it unnecessary to try this.

The method finally used to make $H_2PB(CH_3)_2$ was like that used for $[(CH_3)_2PB(CH_3)_2]_3$: a reaction between phosphine and $(CH_3)_2BBr$ in the presence of triethylamine, in benzene as a solvent. The three reactants (each 95 cc.) were put together in 10 ml. of benzene, and the resulting precipitate of triethylammonium bromide was filtered off and weighed; yield 96.5%. Now the benzene solution was evaporated and the product taken up in ether (5 ml.); in later experiments ether was used as the original solvent. On cooling of the ether solution to −78°, a thick white precipitate appeared; then after evaporation of the ether at that temperature, the wettish solid melted in the range 45–50°. When the ether solution was evaporated at ordinary temperatures, the product was a viscous oil, convertible to the solid by the ether freeze-out method.

A combustion analysis of the oil gave 33.1% C (calcd. 32.5) and 10.5% H (calcd. 10.9), as expected for the formula $H_2PB(CH_3)_2$. An attempt to distil a sample of the product under high vacuum resulted in some profound change, for the distillate melted in the range 41–125°, and gave a low analysis for both carbon and hydrogen.

Another sample of the $H_2PB(CH_3)_2$ material (19.2 mg.) was used for a determination of the molecular weight by the isopiestic method in ether, using 34.2 mg. of $[(CH_3)_2PBH_2]_3$ as the reference substance. By this method, one places the two solids in separate arms of an inverted U-tube and distils in pure ether through a connection at the top, which then is sealed shut *in vacuo*. From the comparison of heights of ether in the two arms, the molecular weights are compared on an inverse basis. Soon after the start of the experiment (75 minutes), the average molecular weight of the $H_2PB(CH_3)_2$ material was 94.2 (calcd. for monomer, 73.9); at 140 min., 98.2; at 300 min., 110; at 1410 min., 182; at 3350 min., 418; at 4665 min., 686; and at 8555 min., 2080. Thus it was clearly evident that in ether solution the material gradually forms a high polymer. The same tendency toward high polymerization probably also is shown by methylphosphinoborine, and it seems that only the dimethylphosphinoborines are more stable as trimers than as higher polymers.

Methanol Reaction to Form the New Compound $(CH_3)_2BOCH_3$.—A fresh sample of $H_2PB(CH_3)_2$ material, prepared from 94.3-cc. portions of PH_3, $(CH_3)_2BBr$ and $(C_2H_5)_3N$, was treated with more methanol than required by the equation $H_2PB(CH_3)_2 + CH_3OH \rightarrow PH_3 + (CH_3)_2BOCH_3$, but yielded only 55.7 cc. of PH_3 and 52.1 cc. of $(CH_3)_2BOCH_3$. An insoluble oily residue was noticed, and it is reasonable to suppose that the polymeric forms of $H_2PB(CH_3)_2$ did not react—a conclusion supported by the initial value of the molecular weight in ether, as compared to the yield of phosphine.

Since $(CH_3)_2BOCH_3$ is a new compound, some of its properties were investigated. The molecular weight of the vapor was measured as 72.7 (calcd., 71.9) and the vapor tensions, shown in Table X, determined the equation $\log_{10} p_{\text{mm.}} = 7.935 - 1490/T$, according to which the normal boiling point is 21° and the Trouton constant 23.2 cal./deg. mole.

TABLE X

VAPOR TENSIONS OF LIQUID $(CH_3)_2BOCH_3$

t, °C.	−78.5	−63.5	−45.2	−22.9	0.0
$p_{\text{mm.}}$ (obsd.)	2.0	6.5	24.9	96.6	301
$p_{\text{mm.}}$ (calcd.)	1.9	6.8	25.1	95.9	303

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[CONTRIBUTION FROM RESEARCH LABORATORIES, TITANIUM DIVISION, NATIONAL LEAD COMPANY]

Organotitanium Compounds. I. Isolation of a Compound Containing the Titanium–Carbon Bond[1]

BY DANIEL F. HERMAN AND WALTER K. NELSON

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The reaction of phenyllithium with isopropyl titanate in equimolar proportions led to the formation of a thermally stable crystalline complex possessing the formula $C_6H_5Ti(OC_3H_7)_3{\cdot}LiOC_3H_7{\cdot}LiBr{\cdot}(C_2H_5)_2O$ as indicated by elementary analyses and chemical properties. The complex was rapidly oxidized and hydrolyzed on exposure to the atmosphere. Treatment with titanium tetrachloride converted the lithium isopropylate portion of the complex to lithium chloride and isopropyl titanate, thus freeing phenyltitanium triisopropylate from the complex. The latter was isolated as a crystalline material, m.p. 88–90°, and was stable on storage at 10° for at least a year, although it decomposed rapidly with oxygen and water. It was unaffected by carbon dioxide but reaction with benzophenone gave triphenylcarbinol. These reactions indicate phenyltitanium triisopropylate to be an organometallic compound of a somewhat lower order of activity than the common Grignard reagents. Thermal decomposition of the phenyl–titanium bond gave rise to reduced titanium compounds and free phenyl radicals, the latter being shown by the ability of the product to catalyze the polymerization of styrene. The free radicals in turn formed benzene, biphenyl and more highly condensed hydrocarbons.

Introduction

A study of the organic chemistry of titanium has been undertaken to examine the properties of compounds containing covalent titanium–carbon bonds. The preparation of such compounds has been attempted repeatedly and unsuccessfully in the past since the first study by Cahours in 1861.[2-4]

The non-existence or instability of organometallic compounds of the transition elements, including titanium, was attributed by von Grosse to the distribution of the valence electrons of the metal

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[1] A preliminary presentation of this material appeared as a "Communication to the Editor," THIS JOURNAL, **74**, 2693 (1952), and was delivered at the 123rd Meeting of the American Chemical Society in Los Angeles, California, March 15 to 19, 1953.

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(4) Y. M. Plets, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1298 (1938).