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Tetramethylbiphosphine: Synthesis, Thermal Condensation, Ethylene Addition, Borine Adducts and Conversion to Phosphinoborine Polymers[1]

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Tetramethylbiphosphine, $P_2(CH_3)_4$ (m.p. $-2°$; b.p. est. $140°$), has been made by various reactions using $(CH_3)_2PH$ or $(CH_3)_2NP(CH_3)_2$, or both. It decomposes above $300°$, forming $(CH_3)_2PH$, $(CH_3)_3P$, phosphorus-rich sublimates and nonvolatile condensation products of interest from a high-polymer viewpoint. It adds to C_2H_4 below $300°$, forming mostly $(CH_3)_2PC_2H_4P(CH_3)_2$ (m.p. $0°$; b.p. est. $188°$). This easily forms an air-stable $2BH_3$ adduct (sublimable *in vacuo* at $150°$) and a more volatile single-BH_3 adduct. The air-stable adduct $P_2(CH_3)_4 \cdot 2BH_3$ forms slightly volatile needles or stabler and less volatile (1 mm. at $102.5°$) crystal-lumps; but the infrared spectra fail to prove a solid-state stabilization of the rotational isomers. This double-BH_3 adduct is converted by heat directly to high yields of the trimer and tetramer of $(CH_3)_2 PBH_2$. It also reacts quantitatively with $P_2(CH_3)_4$ to form the air-reactive and relatively volatile but poorly characterized $P_2(CH_3)_4 \cdot BH_3$. Heat decomposes this to form $(CH_3)_2PBH_2$ units and $(CH_3)_2PH$, which supports an open-chain polymer of these units by dative bonding. On further heating, this chain polymer is converted almost entirely to $(CH_3)_2PBH_2$ trimer and tetramer.

The recently-new substance $P_2(CH_3)_4$ (tetramethylbiphosphine)[2] shows considerable promise as a starting point for a wide variety of new chemistry. It can be made rather easily from dimethylphosphine and the aminophosphine $(CH_3)_2NP(CH_3)_2$[3] by several different specific processes, the simplest of which is based upon the somewhat reversible reaction $(CH_3)_2NP(CH_3)_2 + (CH_3)_2PH \rightarrow (CH_3)_2NH + P_2(CH_3)_4$. The equilibrium constants of this indicate $\Delta F^0 = -1.79 + 0.00226T$ kcal. Apparently the net change of bond energy favors the biphosphine; however, it would be difficult to argue a net increase of purely sigma bonding energy, since H and P have the same electronegativity (on the Pauling scale, based on bond-energies) and the changes of sigma-bond overlap energy should nearly cancel out. Hence the negative ΔH (-1.79 kcal.) seems to correlate with two $P_{3p}-P_{3d}$ pi bonds in the biphosphine, *versus* only one $N_{2p}-P_{3d}$ pi bond in the aminophosphine.

Pure $P_2(CH_3)_4$ (in contact only with Pyrex glass) withstands temperatures around $300°$ but decomposes slowly at $350°$. Initially, the non-volatile products seem to be composed of short $(CH_3PCH_2-)_n$ chains, but further heating leads to cross-linking with loss of volatiles, eventually forming a dark brown or black material much like high-polymeric phosphorus. Typical empirical formulas such as $(P_3C_2H_3)_x$ would suggest that the dark flakes have the P_x type of two-layer sheet structure, with many P—P groupings replaced by HC—P patterns and with P–CH₂–P bridging along the edges or connecting between microflake

aggregates. A few open CH_3—P corners also are possible.

Another kind of hydrocarbon connection occurs when $P_2(CH_3)_4$ adds to ethylene at temperatures approaching $300°$, to form the slightly volatile liquid 1,2-bis-(dimethylphosphino)-ethane, $(CH_3)_2PC_2H_4P(CH_3)_2$. This diphosphine reacts with B_5H_9 much in the manner of trimethylamine,[4] forming the difficultly volatile single and double borine complexes and becoming incorporated in a boron hydride resin having considerable thermal stability.[5]

The addition of $P_2(CH_3)_4$ to ethylene might be regarded as pseudohalogen behavior, with the P–P bond analogous to Cl–Cl. This analogy becomes especially appropriate in the case of $P_2(CF_3)_4$, for the highly electronegative CF_3 groups strongly enhance the halogen character of the P–P bond. Thus it has been found by Louis R. Grant (in these Laboratories) that $P_2(CF_3)_4$ adds to ethylene quite easily at room temperature, to form mostly the diphosphine $(CF_3)_2PC_2H_4P(CF_3)_2$ with minor by-products. This work, along with the numerous consequences of adding $P_2(CF_3)_4$ to C_2F_4 and to acetylene, will be the subject of later publications.

The reaction between tetramethylbiphosphine and diborane affords an interesting opportunity to compare the single-borine complex $P_2(CH_3)_4 \cdot BH_3$ with the double-borine complex $P_2(CH_3)_4 \cdot 2BH_3$. Each shows two solid forms, but those of the double complex are more recognizably distinct and can be interconverted only at higher temperatures. The question whether the two bimorphisms have a similar molecular-structural cause has not been decided. Both complexes make $(CH_3)_2PBH_2$ polymers on heating, but only the single-borine complex forms also $(CH_3)_2PH$, which supports the formation of major proportions of the open-chain high polymer instead of mostly trimer. The single-borine complex is not to be made in pure form by direct addition of diborane to excess $P_2(CH_3)_4$, for some of the double-borine complex always forms; however, the quantitative reaction $P_2(CH_3)_4 \cdot 2BH_3 + P_2(CH_3)_4 \rightarrow 2P_2(CH_3)_4 \cdot BH_3$ does

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(2) (a) A. B. Burg, P. J. Slota, Jr., and W. Mahler, Abstracts of the 134th National A.C.S. Meeting, 78P (1958). (b) A. B. Burg, *J. Inorg. Nuclear Chem.*, 11, 258 (1959). (c) H. Nöth, *Z. Naturforsch.*, 15b, 328 (1960). (d) G. W. Parshall, *J. Inorg. Nuclear Chem.*, 14, 292 (1960).

(3) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, 80, 1107 (1958).

(4) A. B. Burg, *ibid.*, 79, 2129 (1957).

(5) A. B. Burg, *Angew. Chem.*, 72, 191 (1960).

TABLE I

Expt. no.	Reactants (mmole) Me₂PH	Me₂NPMe₂	Time, hr.	Temp., °C.	Components of mixture (mmole) P₂Me₄	Me₂NH	Me₂NPMe₂	Me₂PH
1	10.58	11.05	4	62	6.83	a	a	a
	a	a	20	64	9.22	9.22	1.65	1.36
2	39.24	30.65	19	60	23.22	a	a	a
	a	+9.32	19	67	33.47	....	5.10	...
3	11.506	12.174	1.14[b]	26	10.407	10.481	1.541	1.120
4	6.773	7.385	181	78.5	5.760	5.626	1.404	0.61
5	15.091	16.030	168	99	12.92	13.41	2.719	1.820

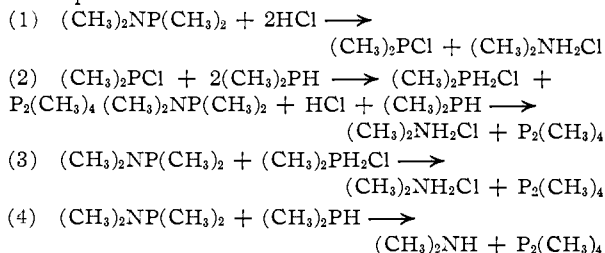[a] Unresolved mixture, reused in a supplementary experiments.   [b] Years.

show that the P–B bonding is stronger in the single-borine adduct.

The weaker attachment of the second BH_3 in $P_2(CH_3)_4 \cdot 2BH_3$ might be attributed partly to steric hindrance but more to the inductive effect of one polar P–B dative bond against the formation of the second such bond. Working against this inductive effect would be the interaction of the B–H bonding electrons with P-3d orbitals,[6] partly overcoming the polarity of the P–B dative bonds and attaching the BH_3 groups more firmly. Without this effect, $P_2(CH_3)_4 \cdot 2BH_3$ could be expected to dissociate appreciably into $P_2(CH_3)_4 \cdot BH_3 + {}^1/_2B_2H_6$; instead, it is easier to cleave the P–P bond to form $[(CH_3)_2PBH_2]_n$.

The $[(CH_3)_2PBH_2]_n$ open chain, formed by heating $P_2(CH_3)_4 \cdot BH_3$, must be P→B dative bonded from unit to unit, with a supporting $(CH_3)_2HP$→B dative bond at one end and lone-pair electrons on P at the other end.[2b,7] The chain-ending $-\underset{..}{P}$-$(CH_3)_2$ group can close a trimer ring by displacing a dative bond three units down the chain. This happens as the temperature is raised, so that the plastic product is nearly all converted to trimeric $(CH_3)_2PBH_2$ and a trace of $(CH_3)_2PH$. Some of this secondary process may occur during the main reaction, accounting for early yields of trimer comparable to the plastic higher polymer.

Synthesis and Properties of Tetramethylbiphosphine

Methods of Synthesis.—The four different specific methods whereby $P_2(CH_3)_4$ was made from $(CH_3)_2NP(CH_3)_2$ and $(CH_3)_2PH$ are represented by the equations

(1) $(CH_3)_2NP(CH_3)_2 + 2HCl \longrightarrow$
$$(CH_3)_2PCl + (CH_3)_2NH_2Cl$$

(2) $(CH_3)_2PCl + 2(CH_3)_2PH \longrightarrow (CH_3)_2PH_2Cl +$
$$P_2(CH_3)_4 \; (CH_3)_2NP(CH_3)_2 + HCl + (CH_3)_2PH \longrightarrow$$
$$(CH_3)_2NH_2Cl + P_2(CH_3)_4$$

(3) $(CH_3)_2NP(CH_3)_2 + (CH_3)_2PH_2Cl \longrightarrow$
$$(CH_3)_2NH_2Cl + P_2(CH_3)_4$$

(4) $(CH_3)_2NP(CH_3)_2 + (CH_3)_2PH \longrightarrow$
$$(CH_3)_2NH + P_2(CH_3)_4$$

Process (1) can be made fairly efficient, especially if it is combined with (3) to employ the phosphonium chloride; however, it requires special efforts for avoiding side reactions in the synthesis of $(CH_3)_2PCl$. For this it is important to employ a slight excess of the aminophosphine[3]; and for full efficacy it is important to distil the volatile components back and forth between two reaction tubes (under high vacuum, using liquid nitrogen) with heating of the non-volatile residues. Thus more direct methods of making $P_2(CH_3)_4$ are preferred.

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

(7) R. I. Wagner and F. F. Caserio, Jr., *ibid.*, **11**, 259 (1959).

The one-step process (2) proved to be fairly satisfactory: 5.603 mmoles each of the three reactants, warmed together during 1 hr. from −70 to −40° and then briefly heated to 70°, produced immediately 471 mg. (69% yield) of P_2-$(CH_3)_4$. After this had been isolated, the remaining components were reheated to bring the final yield of $P_2(CH_3)_4$ to 557 mg., or 81%.

Process (3) was found to be relatively convenient and highly efficient. A 23.74 mmole sample of $(CH_3)_2PH$ was converted to the hydrochloride, which was heated at 95° with 25.66 mmoles of $(CH_3)_2NP(CH_3)_2$ in a 60 ml. reaction tube attached to the high-vacuum system through a stopcock. The biphosphine was isolated and the remaining volatiles were reheated in the same reaction tube until there was no further yield of biphosphine. The recovered aminophosphine now amounted to 2.13 mmoles; used, 23.53 mmoles. The yield of $P_2(CH_3)_4$, 2.783 g. (22.79 mmoles), represented 96.0% of the dimethylphosphine or 96.9% of the consumed aminophosphine. The solid non-volatile product was extracted by chloroform (a specific solvent for dimethylammonium chloride) and weighed as 1.8968 g., representing 23.26 mmoles of $(CH_3)_2NH_2Cl$. The chloride titration gave 23.0 mmoles (calcd., 23.74). Thus the whole experiment was so nearly quantitative as to constitute a proof of the formula $P_2(CH_3)_4$.

The relatively clean and simple process (4) is convenient for large-scale production. The reaction becomes appreciable within a few minutes at 99° and is 85% complete at equilibrium. For fast production of high yields, one may heat the mixture for an hour, remove the resulting biphosphine by fractional condensation at −40° and reheat the reactants to obtain more biphosphine, finally converting the last traces of the reactants by process (3). At room temperature reaction (4) eventually reaches 89% completion but is so much slower that one must weigh the advantage of a somewhat higher initial yield against the time required for the process.

Equilibria in Process (4).—The quantitative experiments on process (4) are summarized in Table I. In each case the reaction took place in a 20 ml. sealed tube. The resulting mixture was resolved by high-vacuum fractional condensation, with the biphosphine coming out at −40°, the aminophosphine at −78° and the amine–phosphine mixture at −196°. In each case the biphosphine and the aminophosphine were weighed in order to determine the extent of the reaction, and in some cases the result was double-checked (without showing any serious error) by determining $(CH_3)_2NH$ as the hydrochloride, from which the $(CH_3)_2PH_2Cl$ (volatile at room temperature) had been removed by sublimation, for separate weighing.

Most of the experiments of Table I represent incomplete approaches toward equilibrium, but expts. 3 and 5 are believed to have reached it. For the nearly 14-month expt. 3, we can make a comparison with a smaller and much rougher room-temperature experiment (not here listed) which reached a similar stage of completion in half the time. Defining K as the product of the amounts of $(CH_3)_2NH$ and $P_2(CH_3)_4$ divided by the product of the amounts of $(CH_3)_2PH$ and $(CH_3)_2NP(CH_3)_2$,

the results of Expts. 3 and 5 are, respectively, K = 63.2 and K = 35.0, leading to the equation log K = 391/T − 0.493 (ΔF^0 = −1.79 + 0.002267 kcal.). From this the value of K for 78.5° would be calculated as 40.3, only 6.6% above the Q value (37.8) implied by expt. 4. Thus it seems that the higher-temperature expt. 5 must have reached equilibrium, within a small experimental error.

Disproportionative Methods of Synthesis.—The hydrolysis of $(CH_3)_2NP(CH_3)_2$ forms $(CH_3)_2NH$,[3] but the parallel product $(CH_3)_2POH$ is wholly converted to $(CH_3)_2POOH$ and $(CH_3)_2PH$.[8] Thus the treatment of one $(CH_3)_2NP(CH_3)_2$ by 0.67H_2O gives 0.33 $(CH_3)_2PH$, which can react with the remaining 0.33 $(CH_3)_2NP(CH_3)_2$ to form $P_2(CH_3)_4$. This method has not yet been developed to high efficiency.

A similar disproportionation can occur when $(CH_3)_2NP(CH_3)_2$ is ammonolyzed. The initially-formed $(CH_3)_2PNH_2$ at once converts to $[(CH_3)_2P]_2NH$ and some $[(CH_3)_2P]_3N$,[3] but longer heating of the mixture leads also to $(CH_3)_2PH$ and presumably $(CH_3)_2PNHNH_2$ or its condensation products. Then the $(CH_3)_2PH$ can attack any of the aminophosphines to make $P_2(CH_3)_4$. An experiment by Dr. Peter J. Slota, Jr., (in these Laboratories) employed 8.88 mmoles of NH_3 and 26.27 mmoles of $(CH_3)_2NP(CH_3)_2$ in a 100 ml. Pyrex tube, heated at the lower end by an oil-bath at 170–200° for 60 hr. The volatile components (in mmoles) now were 6.89NH_3, 0.134PH_3, 1.0-$(CH_3)_2NP(CH_3)_2$, 22.41 $(CH_3)_2NH$ and 2.82P_2-$(CH_3)_4$, the last representing 22% of the consumed aminophosphine.

Another process was discovered by Louis R. Grant in these Laboratories. Trying to make $[(CH_3)_2P]_3P$, he observed a vigorous reaction on warming 6.786 mmoles of $(CH_3)_2PH$ with 1.146 mmole of PCl_3 to 25°. The resulting volatile phosphine hydrochlorides were treated with $(CH_3)_3N$; recovery of $(CH_3)_2PH$, 4.128 mmoles; yield of $P_2(CH_3)_4$, 1.114 mmoles or 81% of the consumed $(CH_3)_2PH$. The by-product was a non-volatile orange-colored solid.

Physical Properties.—A highly purified sample of the biphosphine $P_2(CH_3)_4$ melted in the range −2.25 to −2.15°. Its vapor tensions, shown in Table II, determined the equation log $p_{mm.}$ = 6.5244 − 0.005588 T + 1.75 log T − 2444/T, according to which the normal b.p. would be 140.2° and the Trouton constant 20.1 cal./deg. mole. Molecular weight determinations in the vapor phase at 100° and 182 mm. (74% satd.) and at 80° and 47 mm. (40% satd.) gave the respective values 123.3 and 122.8; calcd. for $P_2(CH_3)_4$, 122.1.

TABLE II

VAPOR TENSIONS OF LIQUID $P_2(CH_3)_4$

t (°C.)	0.00	21.4	24.8	30.7	41.9	47.7	54.3
$p_{mm.}$ (obsd.)	2.07	7.99	9.69	13.50	23.92	31.6	43.0
$p_{mm.}$ (calcd.)	2.06	8.01	9.70	13.43	23.93	31.7	42.9

Confirmation of the Formula.—A middle fraction (85.8 mg., or 0.703 mmole) of $P_2(CH_3)_4$ was taken by distillation from the weighing tube, in order to minimize the possible catalytic effects of grease and mercury. This sample absorbed 51.7 mg. of CH_3I (from a larger sample)—exactly 0.703 mmole, as calcd. This precisely quantitative formation of the 1:1 adduct left no possible doubt of the formula $P_2(CH_3)_4$, which already was strongly supported by the stoichiometry of the synthesis, the physical evidence of uniformity and the molecular weight.

(8) J. E. Griffiths and A. B. Burg, Proc. Chem. Soc., 12 (1961).

Thermal Stability and Decomposition.—A 169.4 mg. sample (1.388 mmoles) of $P_2(CH_3)_4$ was heated in a sealed 45 ml. tube for 25 hr. at 290° without effect on the m.p. However, after a 6 hr. heating from 300 to 350° the same sample had begun to decompose: the recovery of P_2-$(CH_3)_4$ was 138.4 mg., or 81.7%. The volatile product (13.9 mg.; average mol. wt. 67; 0° vapor tensions 175–215 mm. in various fractions) was recognized as a mixture of 0.12 mmole of $(CH_3)_2PH$ and 0.09 mmole of $(CH_3)_3P$. Therefore the non-volatile product (a colorless oil) could be interpreted as containing 0.09 mmole of CH_3P and 0.12 mmole of CH_3PCH_2 as ring-forming or chain-connecting units, with 0.09 mmole of $(CH_3)_2P$ as chain end-groups. The presence of CH_3P units would imply a process analogous to the very clean formation of $(CF_3)_3P$ and $(CF_3P)_n$ by the pyrolysis of $P_2(CF_3)_4$,[9] but in the present case some P–CH$_2$–P linkages must have been established.

Longer periods at 350° led to virtually complete conversion, with the formation of methane instead of dimethylphosphine. For the results shown in Table III the samples were heated in sealed 50 ml. tubes, in an electric tube-furnace varying ± 8° from the average 350°. The CH_4 was recognized by its 12 mm. vapor tension at −196° and proved to be free of hydrogen. The slight "C_2H_6" fractions were identified only by the depth of temperature required to trap them under high vacuum. The $(CH_3)_3P$ was recognized by its 160 mm. vapor tension at 0° and 77.0 mol. wt. (calcd., 76.1). In each case the product delivered under high vacuum at 100° was a mixture of yellow oily droplets and a white sublimate. Acetone extracted nothing from the final residue.

TABLE III

DECOMPOSITION OF $P_2(CH_3)_4$ AT 350°

Expt. no.	$P_2(CH_3)_4$ (mmole) Start	End	Time, hr.	Volatile products (mmoles) CH_4	"C_2H_6"	$(CH_3)_3P$	Volatile at 100° (mg.)
1	2.193	0.061	21	0.673	0.013	2.387	29.0
2	3.353	.054	122	1.715	.027	3.470	70.0
3	2.252	.014	120	1.500	.021	2.149	38.1

The 100° product from expt. 3 was analyzed by O_2-combustion leading to 1.164 mmoles of H_3PO_4 and 0.155 mmole of CO_2. If it had the same H:C ratio as the final residue, the formula of this residue would be close to $(P_3-C_2H_3)_x$. By similar estimation the final residue of expt. 2 would be written as $(P_4C_3H_4)_x$. The less advanced expt. 1 had a 17:10 ratio of H to C in the room-temperature residue, implying more CH_3–P and P–CH$_2$–P connections

$$HC\overset{\displaystyle/P}{\underset{\displaystyle\backslash P}{-}}\!\!-P$$

and fewer $HC \overset{P}{\underset{P}{}}$—P connections than would be found in the final residues of expts. 2 and 3.

The Ethylene-connected Diphosphine

The Ethylene-addition Reaction.—The conditions and results of four experiments on the addition of $P_2(CH_3)_4$ to C_2H_4 are shown in Table IV. In expt. 1 the mixture had been heated in a 50 ml. sealed Pyrex tube for 44 hr. at 232° without effect upon the m.p. of the $P_2(CH_3)_4$, whereas in expt. 2 (also in a 50 ml. tube) a tiny crystal of iodine (ca. 5 mg.) led to some reaction at 207°. In expt. 1 the desired diphosphine was fractionated out after each heating but not separately weighed; and the −12 to −5° melting range could not be improved by more fractional distillation. In expt. 2 the diphosphine came to no harm through further heating with the remaining reactants in the later stages; the pure diphosphine showed slight melting between −1.8 and −1.0° and major melting in the range −1.0 to 0.0°. Good samples were obtained also from the single-heat expts. 3 and 4 (100 ml. Pyrex tubes).

(9) W. Mahler and A. B. Burg, J. Am. Chem. Soc., 80, 6161 (1958).

TABLE IV

ADDITION OF P₂(CH₃)₄ TO ETHYLENE (Quantities in mmoles)

Expt. no.	Reactants employed P₂(CH₃)₄	C₂H₄	Time, hr.	Temp., °C.	Reactants recovered P₂(CH₃)₄	C₂H₄	Reactants consumed P₂(CH₃)₄	C₂H₄	Products (CH₃)₃P	(CH₃)₂PH	Diphosphine
1	1.125	1.423	20	292	...	1.06	...	0.36	...	...	....
	(Remainders)		72	300	...	0.77	...	.65	...	...	....
	(Remainders)		160	303	0.081	0.544	1.044	.879	0.393	Nil	0.666 (64%)
2	4.417	7.616	118	207	...	6.826	...	.790	...	...	....
	(Remainders)		145	258	...	2.930	...	4.686	...	...	....
	(Remainders)		120	267	1.39	2.043	3.027	5.573	.306	0.236	2.396 (79%)
3	2.59	11.31	410	280	0.28	6.49	2.31	4.82	.490	0.134	1.512 (66%)
4	5.748	13.153	760	260	0.18	6.023	5.57	7.13	1.693	Nil	3.526 (63%)

The per cent. yields of $(CH_3)_2PC_2H_4P(CH_3)_2$ shown in Table IV are based upon the consumed $P_2(CH_3)_4$, and it is evident that considerable proportions of this biphosphine went into side reactions which consumed still more ethylene. The persistent formation of trimethylphosphine shows that CH_3 groups transferred from one phosphorus atom to another. It would appear that some of the non-volatile products could be explained as polymers involving $C_2H_4PCH_3$ units. Perhaps also some of the missing ethylene was converted to longer-chain material.

Physical Properties of the Diphosphine.—The diphosphine sample which melted mostly in the range -1.0 to $0.0°$ (expt. 2, Table IV) yielded the vapor-tension data shown in Table V. These values are correlated by the equation $\log p_{mm.} = 6.7232_4 - 0.005070T + 1.75 \log T - 2844/T$, according to which the normal b.p. would be $188.1°$ and the Trouton constant 21.00 cal./deg. mole.

TABLE V

VAPOR TENSIONS OF $(CH_3)_2PC_2H_4P(CH_3)_2$

t (°C.)	25.6	37.1	49.8	63.8	91.2	114.4	130.2
$p_{mm.}$ (obsd.)	1.05	2.23	4.69	9.92	35.68	89.1	154.0
$p_{mm.}$ (calcd.)	1.05	2.21	4.69	9.95	35.74	89.1	154.0

The vapor-tension sample was heated further in the 135 ml. immersible bulb-manometer system, evaporating completely at $133°$. Then the standard volumes of the vapor were determined at 140.0 and $151.5°$, leading to mol. wt. values of 154.0 and 152.0, respectively. This approach toward the calculated value (150.1) left no doubt that the compound was $(CH_3)_2PC_2H_4P(CH_3)_2$.

The Double-borine Adduct of the Diphosphine.—The identity of the diphosphine was further confirmed by the stoichiometry of formation of the adduct $(CH_3)_2PC_2H_4P(CH_3)_2 \cdot 2BH_3$. A 65.5 mg. sample of the diphosphine smoothly absorbed 0.436 mmole of B_2H_6 (from a measured larger sample); calcd. for the double-borine adduct, 0.436_4 mmole. The adduct sublimed slowly at $150°$ under high vacuum. It seemed to be unaffected by the open air. It proved to be sparingly soluble in acetone, with a fairly high temperature-coefficient permitting recrystallization. The crystals appeared as short parallelopipeds, showing red and green stripes on opposite edges when viewed between crossed Polaroid films. An attempt to remove the BH_3 groups by heating with $(CH_3)_3N$ (8 hr. at $100°$) was partially successful: some 15% of the BH_3 groups were taken off in the form of $(CH_3)_3NBH_3$.

At this point there was no attempt to make the single-BH_3 adduct; however this was later recognized as one of the products of the reaction of $(CH_3)_2PC_2H_4P(CH_3)_2$ with B_5H_9.[5] Its presence in a slightly volatile oily fraction was demonstrated by a quantitative experiment on its conversion to the double-BH_3 adduct by absorption of a measured amount of diborane. Since it can be distilled slowly under high vacuum at room temperature, it clearly is more volatile than the double-BH_3 adduct, quite as expected for one dative bond per molecule rather than two.

Tetramethylbiphosphine with Diborane

The Double-borine Adduct.—The formation of the double complex $P_2(CH_3)_4 \cdot 2BH_3$ is fairly straightforward: one condenses a weighed sample of $P_2(CH_3)_4$ thinly upon the walls of the reaction tube and exposes it to diborane (present in excess) during a slow warming from $-78°$ to room temperature. Sometimes a little of the $P_2(CH_3)_4$ or $P_2(CH_3)_4 \cdot BH_3$ is trapped in the solid $P_2(CH_3)_4 \cdot 2BH_3$. In such a case, the tube is heated briefly to $100°$, cooled, evacuated of diborane, closed and heated at $100°$ to sublime the double-BH_3 adduct. With return of the diborane, the reaction now can be completed. The quantitative data of three such syntheses are shown in Table VI.

TABLE VI

FORMATION OF $P_2(CH_3)_4 \cdot 2BH_3$

Expt. no.	Reactants (mmole) P₂(CH₃)₄	B₂H₆	Mmole B₂H₆ recovered	Reaction ratio B₂H₆/ P₂(CH₃)₄
1	1.154	1.159	0.006	0.999
2	1.191	1.405	.214	1.000
3	0.413	1.076	.667	0.990

In a fourth experiment, the double-BH_3 adduct was formed directly in an immersible tensimeter,[10] within which it was vacuum-sublimed for purification. Its vapor tensions (Table VII) determined the equation $\log p_{mm.} = 14.214 - 5340/T$, indicating 1.00 mm. at $102.5°$.

TABLE VII

VAPOR TENSIONS OF SOLID $P_2(CH_3)_4 \cdot 2BH_3$

t (°C.)	72	78	85	88	93
$p_{mm.}$ (obsd.)	0.05	0.10	0.20	0.28	0.42
$p_{mm.}$ (calcd.)	0.056	0.100	0.198	0.264	0.420

Such low volatility was surprising because an earlier sample of the same material, formed below

(10) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 785 (1937).

room temperature and never warmed above 25°, had undergone major sublimation during 24 hr. under high vacuum at 22–25°. Such a rate of evaporation would have been quite impossible for a solid substance having only 2×10^{-4} mm. vapor tension at 25°, as calculated from the equation. By microscopic inspection, however, an unheated sample of $P_2(CH_3)_4 \cdot 2BH_3$ was found to be a mixture of irregular striated-lump crystals and well formed needles or flat blades. The needles often extended from common centers to form spiny clusters. They sublimed under high vacuum at 25°, condensing as lumps at room temperature and as needles just above a trap at 0°. Under static heating, the needles converted entirely to the lump form, and accordingly it was this form which gave the data of Table VII. However, when the lump form was sublimed (very slowly at 60° under high vacuum) the sublimate consisted of lump-crystals near the warm zone and needles in the cooler regions farther down the tube. Thus it appeared that the two crystal forms interconverted through the vapor phase. Both forms proved to be birefringent, for microscopic observation between crossed polarizers showed delicate blue-green and red fringes on the needles and sometimes the same colors on the lumps, which mostly appeared golden-yellow.

Neither with the pure lump-crystals nor with a mixture of the two forms was it possible to reproduce the 106° m.p. given by Nöth for $P_2(CH_3)_4$ $2BH_3$.[2c] In fact, no melting occurred when a sealed tube containing the crystal-mixture was immersed suddenly in oil at 112°; all that happened was that the needles lost their linear shape and became striated, evidently converting to the less volatile form. The lumps finally melted at 194° (in a sealed 1 ml. tube), but then the evolution of hydrogen indicated enough formation of the $(CH_3)_2PBH_2$ trimer and tetramer to account for a solution effect.

In an effort to recognize a possible chemical reason for the different crystal forms of $P_2(CH_3)_4$ $2BH_3$, the molecular weight of a mixed sample was determined. The 25.2 mg. sample lowered the vapor tension of 15.34 mmoles of diethyl ether by 3.59 mm. from the pure-ether value of 328 mm. at 12.5°. Thus the apparent mol. wt. was 156.2, or 4.4% above the calculated 149.7. Since the solution was nearly saturated, this result is consistent with the absence of any appreciable proportion of material having a higher molecular weight.

Infrared Spectrum of the Double Adduct.—A possible reason for the two differently-volatile crystal forms of $P_2(CH_3)_4 \cdot 2BH_3$ would be a stabilization of the rotational isomers (one *trans* and two 60°-*cis*, or *gauche*, forms of a pattern almost like hexamethylethane) through interaction of dative-bond dipoles in the solid state. Evidence bearing upon this hypothesis was sought through a relatively detailed study of the infrared spectra of two samples. One of these was obtained as a high-vacuum sublimate far from the hot region, and under the 160-power microscope it seemed to be about 30% lumps with 70% needles. The other

sample was taken as the sublimate nearest to the 100° bath and seemed to be pure lump-form. These air-stable (and acetone-soluble) samples were pulverized in Nujol to make mulls of similar crystal-size (as judged under the microscope), for mounting between salt-windows.

Table VIII describes the spectra of both samples, with mention of the observable differences. Except where the Infracord instrument is mentioned, the bands were recorded at high resolution by a Perkin–Elmer Model 13 double-beam spectrophotometer, using sodium chloride optics. For purposes of structure confirmation, both spectra are virtually the same, showing only geminal methyl groups (as by the split rocking modes) and BH_3 groups rather than some other deployment of 2B and 6H. For such results the P atoms cannot be different. Minor differences in bands from the two samples would admit the possibility of rotational isomers; however, the different crystal-field effects in two different crystal structures might alone account for the differences. Hence the stabilization of rotational isomers in the solid state remains an interesting hypothesis, requiring a different basis for decision.

TABLE VIII

INFRARED SPECTRUM OF $P_2(CH_3)_4 \cdot 2BH_3$[a]

Frequency (cm.$^{-1}$)	Intensity and character	Interpretation
2920 2880	Very strong doublet	C–H stretching (Infracord)
2220	Medium peak	Uncertain; probable CO_2 effect
2345 2315	Strong doublet	B–H stretch, affected by CO_2
1400	Broad medium peak	C–H bending, δ-e
1305	Weak peak	Probably a Nujol effect
1297	Weak shoulder	Uncertain
1286	Sharp medium peak	C–H bending, δ-a
1150	Broad weak peak	(Present only for lump-form)
1125	Medium peak	B–H bending, δ-e
1101	Weak shoulder	(Present only for lump-form)
1068	Medium shoulder (submerged peak)	Uncertain; more evident for the needle-form
1057	High shoulder on 1049 peak	Uncertain; more evident for the needle-form
1049	Strong peak	B–H bending, δ-a
945 895	Med. strong peak Strong peak	CH_3 group rocking (Infracord)
849	Weak peak	Uncertain
834	Weak peak	Uncertain
768 759 731	Weak peak Weak peak Med. peak	Could represent the three peaks expected for gauche-BH_3 rocking, but not surely
722	Medium peak	Probably a Nujol effect
693 681	Weak peak Weak peak	Probably P–C stretch

[a] It is a pleasure to acknowledge valuable aid by Dr. David A. Dows in the recording and interpretation of these data.

The bands in which one would seek differences due to the stabilization of rotational isomers would be those representing B-H bending and BH_3-group rocking, for these aspects would be different for *trans* and *gauche* placement of the BH_3 groups. No differences would be expected for the methyl groups, since both *trans* and *gauche* relations between methyl groups occur in both kinds of rotational isomers. And in fact, the bands concerning the methyl groups are identical in shape (with only slight differences of intensity of some shoulders), whereas noticeable qualitative differ-

ences occur in the B–H bending bands. For example, the high shoulder indicating a submerged peak at 1057 cm.$^{-1}$ is noticeably broader for the pure-lump sample than for the 70%-needle sample, as though it might not be found at all for pure needles. However, the three peaks at 768, 759 and 731 are identically related to each other in shape and intensity for the two samples, only showing somewhat less over-all intensity for the needle-crystal sample. One may well consider that crystal-field effects might be most important for the groups which are associated with dipoles, namely, the dative-bonded BH_3 groups.

Decomposition of the Double Adduct.—A pure sample of $P_2(CH_3)_4\cdot2BH_3$ (from expt. 2 of Table VI) was unaffected by a 5-hr. heating in a sealed tube at 154° but showed a minor formation of oily material after 11 hr. at 170°. After 11 hr. longer at 290° the sample had formed 1.262 mmole of H_2, or 6.0% more than required by the equation $P_2(CH_3)_4\cdot2BH_3 \rightarrow H_2 + {}^2/_n[(CH_3)_2PBH_2]_n$. The yield of $(CH_3)_2PH$ was 0.094 mmole, or 4%. Also present were 129 mg. of $[(CH_3)_2PBH_2]_3$ (m.p. 88°), 25.3 mg. of $[(CH_3)_2PBH_2]_4$ (m.p. 160°) and 15.5 mg. of a white gum, not volatile under high vacuum at 100°. Its easy solubility in acetone would suggest that this gum was no very high polymer, or at least not extensively cross-linked. The reaction-balance would give its empirical formula as $[(Me_2P)_6B_9H_{11}]_x$, which could be interpreted in terms of $(PB)_3$ rings connected together by small boron-hydride units attached to the ring-boron atoms. However, the stoichiometry lacked precision, since almost 90% of the material went to form $[(CH_3)_2PBH_2]_{3,4}$.

The Single-Boron Adduct: Formation and Polymerization.—The initial experiment on the synthesis of $P_2(CH_3)_4\cdot BH_3$ employed the reactants in the calculated ratio: 0.960 mmole of $P_2(CH_3)_4$ with 0.480 mmole of B_2H_6. The biphosphine was condensed as a thin solid layer on the inner wall of the 50 ml. reaction tube (connected through a stopcock to the high-vacuum system) and warmed with the diborane from −60 to −8° during 10 hr. The main product appeared as a slightly volatile liquid with a little solid. The formation of 0.056 mmole of $(CH_3)_2PH$ would have been due to a catalytic effect of the stopcock grease (Apiezon L) upon $P_2(CH_3)_4$, of which 0.136 mmole (14%) was recovered. The failure to absorb this 14% meant that an equal part of the initially-formed $P_2(CH_3)_4\cdot BH_3$ had reacted further to make $P_2(CH_3)_4\cdot2BH_3$. This secondary reaction was not appreciably reversed by heating the product with the unused biphosphine for 20 min. at 100°, but a later experiment showed that longer heating would have converted the mixture almost entirely to $P_2(CH_3)_4\cdot BH_3$. Hence the following account of the conversion of the present mixture to polymers must represent almost wholly a reaction of this single-borine adduct.

The entire mixture next was heated in the sealed-off reaction tube for 70 hr. at 174°, producing 0.06 mmole of H_2. The recovery of $P_2(CH_3)_4$ now was only 0.02 mmole (2%). The yield of $(CH_3)_2PH$ (0.93 mmole) was 97% of that calculated from the equation $P_2(CH_3)_4\cdot BH_3 \rightarrow (CH_3)_2-PH + {}^1/_n[(CH_3)_2PBH_2]_n$. Only 42% of the expected $(CH_3)_2PBH_2$ units (30.0 mg., or 0.405 mmole) appeared as trimer and tetramer; these were separated by vacuum sublimation and identified by their melting points. A slightly higher yield of $(CH_3)_2PBH_2$ units was present in the white residue, which remained non-volatile even after brief heating above its melting range (about 180–200°).

This residue was heated in the resealed and evacuated tube for 20 hr. at 330°, yielding 0.07 mmole of H_2, 0.021 mmole of $(CH_3)_2PH$, 31.0 mg. of $[(CH_3)_2PBH_2]_3$ and 2.1 mg. of $[(CH_3)_2PBH_2]_4$. Hence this residue accounted for 0.447 mmole (46.5%) of the expected $(CH_3)_2PBH_2$ units, evidently in the form of a higher polymer which could be broken down to the trimer and tetramer. Assuming that the $(CH_3)_2PH$ was present as such in this non-volatile material, it would appear that it served as a base to support a chain polymer averaging $22(CH_3)_2PBH_2$ per molecule, through successive P–B dative bonds. Soon after this observation, the same principle of base-support of open-chain phosphinoborine polymerization was studied much more fully elsewhere.[7]

At this point the yield of $(CH_3)_2PBH_2$ units was 89% of the calculated value. The rest of the material could be accounted for by a cream-colored final residue, partly soluble in acetone but all dissolved by hot nitric acid, with a negative phosphate test. Such behavior toward nitric acid is characteristic of various highly condensed phosphorus-boron-hydride resins which have been made in these Laboratories.

Further Study of the Single-Borine Adduct.—Later attempts at a direct quantitative synthesis of $P_2(CH_3)_4\cdot BH_3$ invariably led to some formation of the double-borine adduct; and the isolation of the desired single-borine adduct by distillation methods was made difficult by the repeated formation of small quantities of $(CH_3)_2PH$ and a slow disengagement of the last of the excess $P_2(CH_3)_4$. For a quantitative synthesis the best procedure was to form the adduct $P_2(CH_3)_4\cdot2BH_3$ and heat it with more $P_2(CH_3)_4$.

For this purpose the sample from Expt. 3 of Table VI was heated with 62.5 mg. (0.512 mmole) of $P_2(CH_3)_4$ for 4 hr. at 80°. The recovered $P_2(CH_3)_4$ amounted to 11.3 mg. Thus the reaction (with stoichiometry in mmoles) was

$$P_2(CH_3)_4\cdot2BH_3 + P_2(CH_3)_4 \longrightarrow 2P_2(CH_3)_4\cdot BH_3$$
$$0.413 \qquad\qquad 0.419 \qquad\qquad (0.830)$$
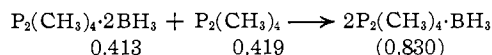
The stability of the product was tested by a series of 4 to 7 hr. heatings at 80°, each liberating a trace (0.005 to 0.001 mmole) of $P_2(CH_3)_4$ but each time less than before. It was not quite possible to decide whether any of the biphosphine came from a reversal of the above reaction.

Attempts to observe the m.p. and volatility of $P_2(CH_3)_4\cdot BH_3$ were made difficult by its sensitivity to stopcock greases and by behavior suggesting more than one solid form. An opaque-crystalline sublimate, taken by high-vacuum fractional condensation in a U-tube at 0°, developed less than 0.02 mm. pressure during 20 min. at 25°; and to sublime away this 0.2 mmole sample under high vacuum required 5 hr. at 28°. But when the same opaque crystals were resublimed by briefly heating the closed U-tube at 50°, the more transparent sublimate now could be sublimed out in 0.5 hr. at 28°. The opaque form was largely converted to the more volatile transparent form during a day-long warming from 10 to 19°. A melting range of 41–45° was fairly typical but might correspond to a mixture including some of the yet unconverted low-temperature form.

Consistent vapor-tension measurements could not be obtained for the solid $P_2(CH_3)_4\cdot BH_3$, but the roughly useful values shown in Table VIII could be obtained for the liquid, by subtracting 0.40 mm. from each measurement, to correct for the $(CH_3)_2PH$ which was isolated and measured afterwards. On this basis, log $p_{mm.} = 8.37 − 2744/T$; b.p. 254°; Trouton constant 25 cal./deg. mole, a normal result for a fairly polar substance.

TABLE IX

ROUGH VAPOR TENSIONS OF LIQUID $P_2(CH_3)_4\cdot BH_3$

t (°C.)	54.0	61.0	68.6	78.2	85.0
$p_{mm.}$ (corr.)	0.99	1.44	2.10	3.63	5.18
$p_{mm.}$ (calcd.)	0.96	1.44	2.19	3.63	5.12