

Open-Chain and Cyclic Phosphane-Boranes Based on Tetramethyldiphosphane

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1:2 addition compounds of tetramethyldiphosphane with BH_3 , BH_2Br , $\text{B}(\text{H})\text{Br}_2$, and BBr_3 (**1a–d**) have been prepared from the parent diphosphane and the dimethyl sulfide complexes of the boranes in the appropriate stoichiometric ratio. Open-chain and cyclic phosphane-borane cations were obtained from Me_4P_2 and $\text{H}_2\text{BrB} \cdot \text{SMe}_2$ in the molar ratio 2:1 or 1:1, respectively: $[\text{Me}_2\text{P} - \text{PMe}_2 \cdot \text{BH}_2 \cdot \text{PMe}_2 - \text{PMe}_2]^+ \text{Br}^-$ (**2**) or $[\text{H}_2\text{B}(\text{Me}_2\text{P} - \text{PMe}_2)_2 \cdot \text{BH}_2]^{2+} 2 \text{Br}^-$ (**3**). Treatment of **1b** with trimethylphosphane yields the salt $[\text{H}_2\text{BrB} \cdot \text{Me}_2\text{P} - \text{PMe}_2 \cdot \text{BH}_2 \cdot \text{PMe}_3]^+ \text{Br}^-$ (**4**). — The crystal structures of **1b** and **3** · 2 MeOH have been determined by single-crystal X-ray diffraction methods. Molecules **1b** have crystallographic C_{2h} symmetry corresponding to the *anti*-configuration of the diphosphane and staggered conformation of the BH_2Br moieties. The monomers are arranged in layers with $\text{Br} \cdots \text{Br}$ contacts of 3.66 Å. — Crystals of **3** · 2 MeOH have an ionic structure built from bromide ions, interstitial methanol molecules, and crystallographically centrosymmetric dications $[\text{H}_2\text{B}(\text{Me}_2\text{P} - \text{PMe}_2)_2 \cdot \text{BH}_2]^{2+}$. These dications are in a chair configuration approaching (non-crystallographical) mirror symmetry. The intra-ring valence angles at boron [$116.2(2)^\circ$] are significantly larger than those at phosphorus (108.4° , average). The B–P distances are shorter than in standard reference compounds (e.g. **1b**), indicating extra stabilisation in the dicationic phosphane-borane ring system. In the unit cell there are no sub-van der Waals contacts between the individual components.

Phosphane-borane chemistry has been advancing relatively slowly. This is surprising, since compounds based on a PB skeleton (isoelectronic with SiC) show some intriguing chemical and physical properties, some of which are not yet well understood^{1,2}. Recent interest in new refractive and insulating materials of high thermal stability and in III/V semiconductors lead to an increase in pertinent activities, however, focusing *inter alia* on new precursors featuring PB bonds³.

In the course of our studies on phosphane-boranes we have initiated an investigation of diphosphane-bis(boranes), in which two PB moieties are linked by a P–P bond. The prototype of such compounds has been synthesized in the pioneering work by Nöth⁴ and Burg⁵ in the early 60's, but very few contributions to this field have since been made⁶.

Following the synthetic procedures developed for simple functional phosphane-boranes^{1–3,7} of the type $\text{Me}_3\text{P} \cdot$

Zur Chemie der Phosphan-Borane: Offenkettige und cyclische Phosphan-Borane aus Tetramethyldiphosphan

Durch Umsetzung von Tetramethyldiphosphan mit zwei Äquivalenten der Dimethylsulfid-Komplexe von BH_3 , BH_2Br , $\text{B}(\text{H})\text{Br}_2$ und BBr_3 werden die neutralen 1:2-Addukte **1a–d** mit dem Grundgerüst BPPB erhalten. Offenkettige und cyclische Phosphan-Boran-Kationen entstehen bei den entsprechenden Reaktionen von Me_4P_2 mit $\text{H}_2\text{BrB} \cdot \text{SMe}_2$ in den Molverhältnissen 2:1 bzw. 1:1: $[\text{Me}_2\text{P} - \text{PMe}_2 \cdot \text{BH}_2 \cdot \text{Me}_2\text{P} - \text{PMe}_2]^+ \text{Br}^-$ (**2**) bzw. $[\text{H}_2\text{B}(\text{Me}_2\text{P} - \text{PMe}_2)_2 \cdot \text{BH}_2]^{2+} 2 \text{Br}^-$ (**3**). Aus **1b** und Trimethylphosphan wird das Salz $[\text{H}_2\text{BrB} \cdot \text{Me}_2\text{P} - \text{PMe}_2 \cdot \text{BH}_2 \cdot \text{PMe}_3]^+ \text{Br}^-$ (**4**) gebildet. — Durch Einkristall-Röntgenbeugungsmethoden wurden die Kristallstrukturen von **1b** und **3** bestimmt. Die Moleküle **1b** besitzen kristallographische C_{2h} -Symmetrie, was einer *anti*-Konfiguration mit den BH_2Br -Gruppen in der gestaffelten Konformation entspricht. Die Monomeren sind in Schichten mit $\text{Br} \cdots \text{Br}$ -Kontakten von 3.66 Å angeordnet. — Die Kristalle von **3** · 2 MeOH haben eine ionische Struktur bestehend aus Br^- -Ionen, zwei Mol interstitiellem Methanol und cyclischen Dikationen mit kristallographischer Zentrosymmetrie. Die Ringatome bilden eine Sesselform aus und entsprechen einschließlich der Substituenten annähernd einer nicht-kristallographischen Spiegelsymmetrie. Die Ringwinkel an den Boratomen [$116.2(2)^\circ$] sind größer als jene an den Phosphoratomen (im Mittel 108.4°). Die B–P-Abstände sind deutlich kürzer als in Standardverbindungen (wie etwa **1b**), was eine zusätzliche Stabilisierung des Phosphan-Boran-Gerüsts andeutet. In der Zelle werden keine ungewöhnlichen Kontakte zwischen den Baueinheiten beobachtet.

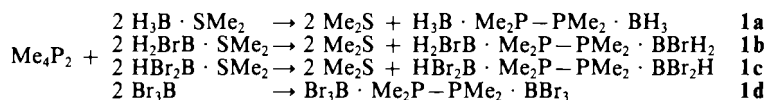
BH_2X or $\text{Me}_3\text{P} \cdot \text{BHX}_2$, we prepared $\text{H}_3\text{B} \cdot \text{Me}_2\text{P} - \text{PMe}_2 \cdot \text{BH}_3$ and its BBr functionalized derivatives, which are key compounds for the synthesis of larger open-chain and cyclic phosphane-boranes.

Preparation and Properties of Compounds

Tetramethyldiphosphane-bis(borane) (**1a**) is obtained by the reaction of the diphosphane with the dimethyl sulfide borane adduct in benzene as solvent. The product is a crystalline solid, which can be sublimed *in vacuo*. Only one of the melting points quoted in the literature could be confirmed^{4–6}. The NMR data collected are useful for identification of the derivatives (see Experimental).

The mono-, di- and tribromoborane adducts of Me_4P_2 were obtained similarly, but a correct 2:1 stoichiometric ratio of the reactants and a suitable direction and rate of addition of the components are important in these cases,

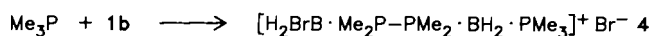
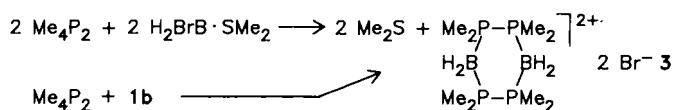
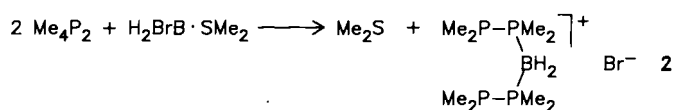
Scheme 1



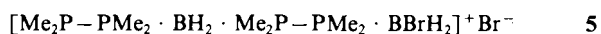
since secondary reactions can otherwise reduce the yields and lead to other products (Scheme 1). BBr_3 was introduced without the SMe_2 donor and in dichloromethane solvent, where better solubility is secured.

When $\text{H}_2\text{BrB} \cdot \text{SMe}_2$ is treated with Me_4P_2 in the molar ratio 1:2, the bromine atom is substituted by the second equivalent of Me_4P_2 to give the ionic product **2**.

Reaction of equimolar amounts of $\text{H}_2\text{BrB} \cdot \text{SMe}_2$ with Me_4P_2 , or treatment of **1b** with a second equivalent of Me_4P_2 , also leads to complete substitution of the bromine atoms with formation of a cyclic dicationic phosphane-borane species, which is isolated in high yield as the dibromide **3**. Monosubstitution of bromine in **1b** can be accomplished with one equivalent of Me_3P to give the mixed phosphane-borane salt **4**. The secondary reaction with an excess of Me_3P obviously is very slowly, probably due to the low solubility of the primary product (**4**).



There is experimental evidence for an intermediate in the reaction of **1b** with Me_4P_2 . This compound, probably a salt **5**, precipitates in almost quantitative yield from the benzene solution of the reactants. Final cyclisation is accomplished by dissolution in methanol. **3** crystallizes from methanol at -25°C with two molecules of crystal methanol. Intermediate **5** has not been definitely identified owing to its low solubility and limited stability.



All other compounds gave satisfactory elemental analyses and were characterized by their NMR and IR spectra. The structures of **1b** and **3** · 2 MeOH were determined by single-crystal X-ray methods (see below).

While compound **1a** is relatively inert to air and moisture, the brominated derivatives **1b-d** are more sensitive and slowly oxidized or hydrolysed. They are soluble in low-polarity solvents, such as aromatic hydrocarbons or halo-methanes, without decomposition, but are solvolysed in methanol. The salts **2-4** are insoluble in non-polar or low-polarity solvents, but soluble in polar media like water, methanol, or dimethyl sulfoxide. Slow decomposition is also

observed, however, in these solvents at ambient temperature with evolution of hydrogen and other gases, which reduce Ag^+ to elemental silver. Trimethyl borate is the final main methanolysis product, as shown by NMR spectroscopy.

Crystal and Molecular Structure of $\text{H}_2\text{BrB} \cdot \text{Me}_2\text{P}-\text{PMe}_2 \cdot \text{BBrH}_2$ (**1b**)

The structural details of **1b** were of particular interest, since a structure determination of the parent compound **1a** had given ambiguous results. **1a** forms two different crystalline modifications, but only the structure of one of these is known. In this form three different molecules are present which differ in the relative rotation of the two $\text{PMe}_2 \cdot \text{BH}_3$ parts around the P-P bond. A systematic error in the data set, which affected mainly the values calculated for the P-P-B angles, could not be ruled out⁸.

In addition, the structure of tetramethyldiphosphane itself appears to be an open problem, as a series of different experimental⁹ and theoretical methods¹⁰ has given contradictory results. The question of the relative stability of *anti* and *gauche* conformations could not be answered conclusively. For unsubstituted diphosphane the two conformers are believed to be equal in energy¹¹. The crystal structures of two transition metal complexes of Me_4P_2 are known quite accurately, but their geometry may be largely determined by steric and electronic effects of the bulky complex fragments¹².

Compound **1b** crystallises in the orthorhombic space group $Cmca$ (Nr. 64) with four molecules in the unit cell. The molecules have crystallographic C_{2h} symmetry corresponding to the *anti* conformation (Figure 1).

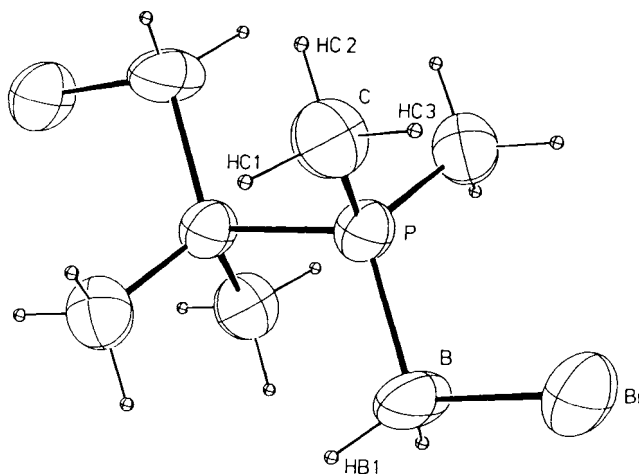


Figure 1. Molecular structure of $\text{BrH}_2\text{B} \cdot \text{Me}_2\text{P}-\text{PMe}_2 \cdot \text{BH}_2\text{Br}$ (**1b**) and atomic numbering. (50% Probability ellipsoids are shown for the heavier atoms; arbitrary radii were used for hydrogen atoms.) The molecule has crystallographic C_{2h} symmetry with the atoms BrBPPBBr in a plane of symmetry and a twofold axis perpendicular to this plane through the center of the P-P bond

Somewhat greater displacement amplitudes of the bromine atoms perpendicular to the plane of symmetry may indicate a slight deviation of the molecules from the *anti* configuration, but normal displacement amplitudes for the carbon atoms make it unlikely that the P–P bond rotation is the dominant factor for this vibrational distortion (Table 1).

Table 1. Selected NMR data of some trimethylphosphane- and tetramethyldiphosphane-boranes [δ values in ppm rel. to TMS, H_3PO_4 , and $B(OMe)_3$, respectively; J values in Hz]

	$\delta^{11}B$	$\delta^{13}C$	$\delta^{31}P$
Me_3P-BH_3	-55.2 ($J = 60$)	12.5 ($J = 38$)	-1.7 ($J = 60$)
Me_3P-BH_2Br	-40.5 ($J = 86$)	8.0 ($J = 42$)	-11.9 ($J = 86$)
$Me_3P-BHBr_2$	-33.1 ($J = 118$)	6.1 ($J = 45$)	-14.2 ($J = 118$)
Me_3P-BBr_3	-32.7 ($J = 157$)	5.7 ($J = 47$)	-11.1 ($J = 157$)
$[Me_3P-BH_2-PMe_3]^+ Br^-$	-50.6 ($J = 92$)	11.5 ($J = 49$)	-8.7 ($J = 92$)
$Me_4P_2 \cdot 2 BH_3$ (1a)	-57.8	6.9 ($N = 36$)	-4.4
$Me_4P_2 \cdot 2 BH_2Br$ (1b)	-42.1	4.4 ($N = 36$)	-17.1
$Me_4P_2 \cdot 2 BHBr_2$ (1c)	-34.4	3.5 ($N = 37$)	-23.0
$Me_4P_2 \cdot 2 BBr_3$ (1d)	-34.4	6.0 ($N = 37$)	-20.0
$[2 Me_4P_2 \cdot 2 BH_2]^{2+} 2 Br^-$ (3)	-53.6	6.4 ($N = 40$)	-13.1

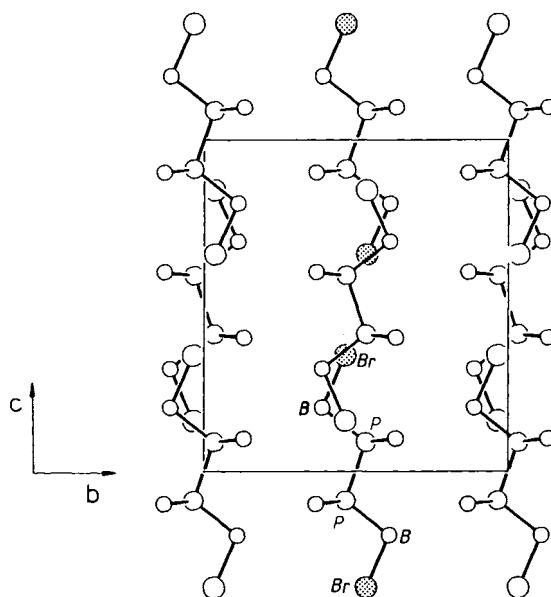


Figure 2. Packing of molecules **1b** in the orthorhombic unit cell. Layers are extending parallel to the *a/c* plane

Crystal and Molecular Structure of $[H_2B(Me_2P-PMe_2)_2BH_2]^{2+} 2 Br^- \cdot 2 MeOH$ (3**)**

The salt **3** crystallises with two equivalents of methanol in the monoclinic space group $P2_1/n$ with two formula units in the unit cell. This implies that the cations of **3** strictly adhere to crystallographic centrosymmetry (Figure 3).

The bond lengths in molecules **1b** differ only slightly from those reported for **1a** (average values), as shown in Table 2. The B–Br distance agrees well with that found in $Me_3P \cdot BBr_3$ ¹³. The P'–P–B angle of 107.4(2)° detected in **1b** is much smaller, however, than in **1a** [114.4(6)°], but it was exactly this angle, where uncertainties had arisen about the quality of the data set⁸). It appears, therefore, that the value obtained for **1b** is the more reliable data for the series of compounds in question.

Table 2. Bond distances [Å] and angles [°] in compound **1b**. (Esd's in units of the last significant figure in parentheses)

P–P	2.189(5)	P'–P–B	107.4(2)
P–B	1.97(1)	P'–P–C	104.9(2)
P–C	1.778(7)	B–P–C	115.0(2)
B–Br	2.01(1)	C–P–C'	106.6(4)
		P–B–Br	104.4(5)

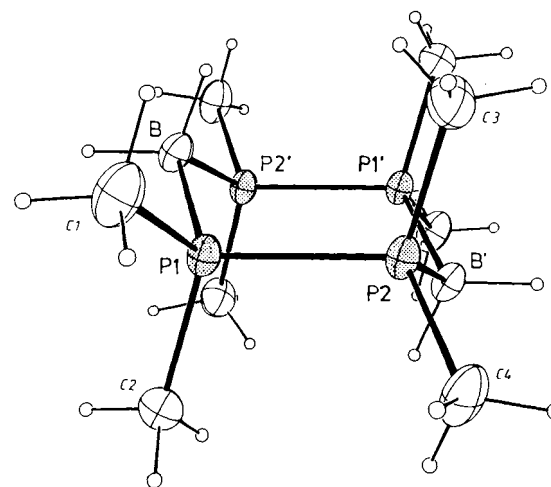


Figure 3. Structure of the cation $[H_2B(Me_2P-PMe_2)_2BH_2]^{2+}$ in the ionic crystal of $[H_2B(Me_2P-PMe_2)_2BH_2]^{2+} 2 Br^- \cdot 2 MeOH$ (**3**) with atomic numbering. The chair-form ring system has a crystallographic center of symmetry. (50% Probability ellipsoids are shown for the heavier atoms; arbitrary radii were used for hydrogen atoms)

In the crystal the molecules **1b** are arranged in layers with $Br \cdots Br$ contacts of 3.66 Å (average), significantly lower than the assumed van der Waals distance of 3.70–4.00 Å¹⁴). The packing is illustrated in Figure 2.

The present study has confirmed earlier findings, according to which many diphosphane compounds adopt the *anti* configuration as their ground state. For a long time $I_2P-P I_2$ has been the classical example in this context¹⁵.

The cations of **3** have a chair conformation. The angles between the planes containing the four P atoms and those through P1,B,P2' (P1',B',P2) are 126.6° (Table 3). The six-membered rings have approximate mirror symmetry with respect to a plane containing the boron and the hydrogen

atoms at boron. Along the P–P axes the conformation is *gauche* with torsion angles B–P1–P2–B' of -53.1° . The intra-ring valence angles at the boron atoms [$116.2(2)^\circ$] are significantly larger than those at the phosphorus atoms (108.4° , average), which come close to the tetrahedral standard.

Table 3. Bond distances [\AA] and angles [$^\circ$] in compound 3

P1–P2	2.190(1)	P1–C2	1.796(4)
P1–B	1.924(4)	P2–C3	1.798(4)
P2'–B	1.918(4)	P2–C4	1.797(4)
P1–C1	1.801(4)	P2–P1–B	108.5(1)
		P1–P2–B'	108.3(1)
		P1–B–P2'	116.2(2)
Plane P1P2P1'P2' / Plane P1BP2'	126.6 $^\circ$		
P1P2P1'P2' / Plane P2B'P1'	126.6 $^\circ$		

The P–P bond lengths [$2.190(1) \text{\AA}$] agree reasonably well with those in **1a** [$2.205(4) \text{\AA}$] and in **1b** [$2.189(5) \text{\AA}$], but the P–B bond lengths differ significantly from those in the reference compounds. The average P–B distance in **3** is 1.921\AA , noticeably shorter than in **1a** and in **1b**, where $1.95(2)$ and $1.97(1) \text{\AA}$, respectively, are observed. It agrees, however, with the P–B distances in a variety of six-membered rings containing the $R_2P-BH_2-PR_2$ fragment. Once again, this result substantiates the exceptional stability of cumulated P–B bonds in phosphane-boranes¹⁶.

In the crystal the shortest intermolecular contacts between phosphorus and bromine are 4.70\AA , substantially larger than the van der Waals limit.

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Experimental

All experiments were carried out under dry and pure nitrogen. Glassware and solvents were purified and dried accordingly. Great care was taken to avoid contact with potentially hazardous fumes of boranes and their derivatives.

Tetramethyldiphosphane-Bis(borane) (1a): A solution of the borane-dimethyl sulfide complex (1.52 g , 20.0 mmol) in 15 ml of benzene was treated at room temp. with a solution of tetramethyldiphosphane (1.22 g , 10.0 mmol) in 15 ml of the same solvent. The solvent was evaporated from the reaction mixture in vacuo after 45 min , and the residue was purified by sublimation at $80^\circ\text{C}/0.05 \text{ Torr}$. Colourless crystals were obtained in 86% yield (1.29 g), m.p. $106-108^\circ\text{C}$ (ref. 106°C^4 , 190°C^5). – $^1\text{H NMR}$ (C_6D_6): $\delta = 0.86$ (br. s, CH_3), 1.10 [br. q, $^1J(\text{BH}) = 100 \text{ Hz}$, BH_3]. – $^{13}\text{C NMR}$ (C_6D_6): $\delta = 6.9$ (AXX', $N = 36 \text{ Hz}$). – $^{31}\text{P NMR}$ (C_6D_6): $\delta = -4.4$, br. – $^{11}\text{B NMR}$ (C_6D_6): $\delta = -57.8$, br.

Tetramethyldiphosphane-Bis(dibromoborane) (1c): Tetramethyldiphosphane (1.22 g , 10.0 mmol) and the bromoborane complex of dimethyl sulfide (4.68 g , 20.0 mmol) were allowed to react for 1 h at room temp. in 25 ml of benzene as solvent. Removal of the solvent to one half of the original volume led to complete precip-

itation of the product. Large colorless crystals can be obtained from hot benzene upon slow cooling in 84% yield (3.92 g), m.p. $120-122^\circ\text{C}$. – $^1\text{H NMR}$ (C_6D_6): $\delta = 1.12$ ($A_6XX'A'_6$, $N = 4 \text{ Hz}$, CH_3). – $^{13}\text{C NMR}$ (C_6D_6): $\delta = 3.48$ (AXX', $N = 37 \text{ Hz}$). – $^{31}\text{P NMR}$ (C_6D_6): $\delta = -23.0$, br. – $^{11}\text{B NMR}$ (C_6D_6): $\delta = -34.4$, br. – IR (KBr): 2977 w ; 2909 w ; 2476 m ; 1407 s ; 1291 s ; 978 m ; 950 vs ; 887 vs ; 844 s ; 762 w ; 714 m ; 603 m ; 569 s ; $517 \text{ cm}^{-1} \text{ w}$.

$\text{C}_4\text{H}_{14}\text{B}_2\text{Br}_4\text{P}_2$ (465.3) Calcd. C 10.32 H 3.03
Found C 10.42 H 3.03

Tetramethyldiphosphane-Bis(tribromoborane) (1d): A solution of tribromoborane (2.51 g , 10.0 mmol) in 15 ml of dichloromethane was treated slowly with a solution of tetramethyldiphosphane (0.61 g , 5.0 mmol) in 15 ml of the same solvent at room temperature. After stirring for 12 h the solvent was removed in vacuo to leave a colourless crystalline product in 85% yield (2.66 g), m.p. 203°C . – $^1\text{H NMR}$ (C_6D_6): $\delta = 1.41$ (br., CH_3). – $^{13}\text{C NMR}$ (C_6D_6): $\delta = 6.00$ (AXX', $N = 37 \text{ Hz}$). – $^{31}\text{P NMR}$ (C_6D_6): $\delta = -20.0$, br. – $^{11}\text{B NMR}$ (C_6D_6): $\delta = -34.4$, br. – IR (KBr): 2985 w ; 2908 w ; 1411 m ; 1397 s ; 1295 w ; 1288 m ; 955 s ; 898 s ; 761 w ; 713 m ; 668 s ; 640 vs ; $614 \text{ cm}^{-1} \text{ vs}$.

$\text{C}_4\text{H}_{12}\text{B}_2\text{Br}_6\text{P}_2$ (623.2) Calcd. C 7.71 H 1.94
Found C 7.74 H 1.98

Tetramethyldiphosphane-Bis(bromoborane) (1b): The preparation of this compound followed that of the dibromo analogue with 2.44 g (20.0 mmol) of tetramethyldiphosphane and 6.19 g (40.0 mmol) of the bromoborane-dimethyl sulfide complex. Colourless crystals were obtained in 79% yield (4.88 g), m.p. 145°C . – $^1\text{H NMR}$ (C_6D_6): $\delta = 0.96$ ($A_6XX'A'_6$, $N = 3 \text{ Hz}$, CH_3). – $^{13}\text{C NMR}$ (C_6D_6): $\delta = 4.39$ (AXX', $N = 36 \text{ Hz}$). – $^{31}\text{P NMR}$ (C_6D_6): $\delta = -17.1$, br. – $^{11}\text{B NMR}$ (C_6D_6): $\delta = -42.1$, br. – IR (KBr): 2981 w ; 2914 w ; 2458 m ; 2403 m ; 1411 s ; 1296 s ; 1122 s ; 1007 s ; 951 s ; 880 s ; 765 m ; 717 m ; 567 w ; $507 \text{ cm}^{-1} \text{ m}$.

$\text{C}_4\text{H}_{16}\text{B}_2\text{Br}_2\text{P}_2$ (307.5) Calcd. C 15.62 H 5.24
Found C 15.62 H 5.10

1,1,2,2,4,4,5,5-Octamethyl-1,2,4,5-tetraphosphonia-3,6-diboranatocyclohexane Dibromide (3): A solution of **1b** (3.08 g , 10.0 mmol) in 50 ml of benzene is treated slowly with a solution of tetramethyldiphosphane (1.22 g , 10.0 mmol) in 20 ml of the same solvent. The reaction mixture became turbid after 5 min and was stirred for 60 h at room temperature. After filtration and washing of the primary product with benzene the yield was 95% (4.08 g). Purification and crystal growth were accomplished by dissolving the material in 50 ml of methanol (a slight effervescence was observed), concentration of the solution to $1/3$ of the initial volume in vacuo at -10°C , followed by filtration and cooling of the filtrate to -25°C . This pure product was isolated by decantation of the mother liquor and drying in a stream of nitrogen, yield 2.18 g (51%), decomposition without melting at 160°C . – $^1\text{H NMR}$ (CD_3OD): $\delta = 2.10$ (br., CH_3). – $^{13}\text{C NMR}$ (CD_3OD): $\delta = 6.4$ (AXX', $N = 40 \text{ Hz}$). – $^{31}\text{P NMR}$ (CD_3OD): $\delta = -13.0$, br. – $^{11}\text{B NMR}$ (CD_3OD): $\delta = -53.6$, br. – IR (KBr): 2977 m ; 2961 s ; 2473 s ; 2461 s ; 2406 s ; 1622 m ; 1420 m ; 1408 m ; 1399 m ; 1313 w ; 1296 w ; 1109 w ; 966 s ; 949 vs ; 935 vs ; 852 w ; 820 w ; 770 w ; 732 m ; 720 m ; 636 w ; $554 \text{ cm}^{-1} \text{ w}$.

$\text{C}_8\text{H}_{28}\text{B}_2\text{Br}_2\text{P}_4$ (429.6) Calcd. C 22.37 H 6.57
Found C 22.15 H 6.60

1,3-Bis(dimethylphosphano)-1,1,3,3-tetramethyl-1,3-diphosphonia-2-boranatopropane Bromide (2): A solution of Tetramethyldiphosphane (3.66 g , 30.0 mmol) in 50 ml of benzene was treated with a solution of the bromoborane-dimethyl sulfide complex (2.32 g , 15.0 mmol) in 25 ml of the same solvent at room temperature. After

2 d the precipitate was filtered, washed with benzene (10 ml) and pentane (10 ml), and dried in vacuo. This primary product was suspended in 50 ml of warm toluene, and acetonitrile was added until almost all of the material had dissolved. Filtration and slow cooling of the filtrate to -25°C gave a pure, colorless, crystalline compound in 84% yield (4.26 g), m.p. $102-104^{\circ}\text{C}$ with decomposition. $^1\text{H NMR}$ (CD_3CN): $\delta = 1.31$ [dd, $J(\text{PH}) = 15.6$ and 3.9 Hz, MeP(III)]; 1.63 [dd, $J(\text{PH}) = 11.2$ and 3.9 Hz, MeP(V)]. $^{13}\text{C NMR}$ (CD_3CN): $\delta = 7.15$ [AA'X, $N = 23$ Hz, $\text{CH}_3\text{P(III)}$]; 7.62 [AXX', $N = 42$ Hz, $\text{CH}_3\text{P(V)}$]. $^{31}\text{P NMR}$ (CD_3CN): $\delta = -14.1$ [dq, $J(\text{PP}) = 236$, $J(\text{PB}) = 79$ Hz, P(V)]; -58.3 [d, P(III)]. $^{11}\text{B NMR}$ (CD_3CN): $\delta = -52.9$ [t, $J(\text{PB}) = 79$ Hz]. $-\text{IR}$ (KBr): 2957 m; 2896 m; 2409 m; 2369 m; 1415 s; 1405 s; 1311 w; 1293 m; 1105 w; 998 w; 965 s; 952 s; 943 s; 928 m; 913 s; 902 s; 880 m; 758 m; 729 s; 666 m; 659 m; 624 w; 572 cm^{-1} w.

$\text{C}_8\text{H}_{26}\text{BBrP}_4$ (336.9) Calcd. C 28.52 H 7.78
Found C 27.93 H 7.51

Table 4. Crystal structure data for **1b** and **3**

	1b	3
Formula	$\text{C}_4\text{H}_{16}\text{B}_2\text{Br}_2\text{P}_2$	$\text{C}_{10}\text{H}_{36}\text{B}_2\text{Br}_2\text{O}_2\text{P}_4$
M_r	307.550	493.722
Crystal system	orthorhombic	monoclinic
Space group	$Cmca$ (No. 64)	$P2_1/n$ (No. 14)
a [\AA]	9.854(1)	10.198(1)
b [\AA]	10.760(1)	10.903(1)
c [\AA]	11.781(2)	10.643(1)
β [deg.]	90	105.66(1)
V [\AA^3]	1249.1	1139.5
Z	4	2
$d_{\text{calcd.}}$ [g/cm^3]	1.635	1.439
$\mu(\text{Mo-K}\alpha)$ [cm^{-1}]	66.3	38.0
$F(000)$ [e]	600	504
T [$^{\circ}\text{C}$]	23	-50
Diffractometer	Enraf-Nonius CAD4	Syntex-P2 ₁
Scan	$\Theta/2\Theta$	ω
Scan width (in ω)	$1.0 + 0.35 \tan \Theta$	0.9
$(\sin \Theta/\lambda)_{\text{max}}$, \AA^{-1}	0.637	0.617
hkl range	$+12, \pm 13, \pm 15$	$+12, +13, \pm 13$
Refl. measd./unique	3653/722	3336/2246
R_{int}	0.017	0.029
Reflexes obs.	503	1880
Rel. transmission	0.65–1.00	0.69–1.00
Structure solution	Patterson methods	direct methods
H atoms (found/calcd.)	all calculated	all found
Parameters refined	28	91
R^a	0.056	0.036
R_w^b	0.039	0.040
$\Delta\rho_{\text{fin}}$ (max/min) [$e/\text{\AA}^3$]	1.17/–0.89	0.47/–0.39

^a $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w F_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. Function minimized: $\sum w(|F_o| - |F_c|)^2$.

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters of **1b** [$U_{\text{eq}} = (U_1 U_2 U_3)^{1/3}$, where U_i are the eigenvalues of the U_{ij} matrix]

Atom	x/a	y/b	z/c	U_{eq}
Br	0.00000	0.0350(1)	0.34788(8)	0.076
P	0.00000	0.0328(3)	0.0879(2)	0.052
C	0.1446(8)	0.1309(6)	0.0985(5)	0.070
B	0.00000	–0.111(1)	0.1917(8)	0.066

Table 6. Fractional atomic coordinates and equivalent isotropic displacement parameters of **3** (U_{eq} see Table 5)

Atom	x/a	y/b	z/c	U_{eq}
Br	0.02639(4)	0.75759(4)	0.94321(4)	0.033
P1	0.10403(9)	0.93844(9)	0.38275(8)	0.018
P2	0.17027(9)	0.91921(9)	0.59537(8)	0.018
C3	0.1217(4)	0.7658(4)	0.6257(4)	0.028
C1	0.1534(4)	0.8017(4)	0.3121(4)	0.028
C2	0.1971(4)	1.0664(4)	0.3441(4)	0.029
C4	0.3526(4)	0.9322(4)	0.6496(4)	0.026
B	–0.0915(4)	0.9497(4)	0.3293(4)	0.020
O	0.6726(3)	1.1302(3)	1.0358(3)	0.036
C5	0.6614(5)	1.0398(4)	0.9371(5)	0.040

1-Bromo-2,2,3,3,5,5-hexamethyl-2,3,5-triphosphonia-1,4-diboran-apatentane Bromide (4): Compound **1b** (3.08 g, 10.0 mmol), when treated with trimethylphosphane (1.52 g, 20.0 mmol) in a total of 40 ml of benzene, showed an instantaneous reaction with formation of a colorless precipitate. Filtration after 1 h, washing with benzene, and drying in vacuo yielded 3.44 g of the product (90%), m.p. 185°C . $-\text{H NMR}$ (CD_2Cl_2): $\delta = 1.75$ (m, $N = 18$ Hz, $\text{CH}_3\text{PBH}_2\text{P}$); 1.87 [d, $J(\text{PH}) = 12$ Hz, $(\text{CH}_3)_3\text{P}$]; 2.34 [dd, $J(\text{PH}) = 11.5$ and 8 Hz, CH_3PBBR]. $^{13}\text{C NMR}$ (CD_2Cl_2): $\delta = 7.5$ (AA'X, $N = 45$ Hz); 9.0 [d, $J(\text{PC}) = 42$ Hz]; 12.5 (AXX', $N = 87$ Hz). $^{31}\text{P NMR}$ (CD_2Cl_2): $\delta = 6$, br; 10 , br; 13 , br. $-\text{IR}$ (KBr): 2960 s; 2938 m; 2898 m; 2880 m; 2470 m; 2450 m; 2419 m; 2400 m; 1414 m; 1297 m; 1129 m; 1111 w; 1008 vs; 981 vs; 966 vs; 925 s; 909 vs; 859 m; 764 m; 740 m; 707 m; 636 w; 544 w; 523 cm^{-1} w.

$\text{C}_7\text{H}_{25}\text{B}_2\text{Br}_2\text{P}_3$ (383.6) Calcd. C 21.92 H 6.57
Found C 21.46 H 6.19

X-Ray Structure Analyses of Compounds 1b and 3: Suitable single crystals of **1b** and **3** were mounted in glass capillaries under argon and examined directly on the diffractometer. Crystal data and important numbers pertinent to data collection and refinement are collected in Table 4. The data sets were recorded with Mo-K α radiation, $\lambda = 0.71069$ \AA , using graphite monochromators. They were corrected for Lp effects and empirically for those of absorption. Structure factors with $F_o \geq 4.0\sigma(F_o)$ were considered 'observed' and used for the refinement. Tables 5 and 6 contain the atomic coordinates of the non-H atoms. Further crystal data and complete lists of atomic parameters and observed and calculated structure factors have been deposited¹⁷. Programs used were DELOS, LE-PAGE (cell reduction), SHELXS-86 (structure solution), SHELX-76 (structure refinement), and local routines.

CAS Registry Numbers

1a: 13327-53-2 / **1b**: 120333-10-0 / **1c**: 120333-11-1 / **1d**: 120333-12-2 / **2**: 120333-13-3 / **3**: 120333-14-4 / **3**·2 MeOH: 120333-16-6 / **4**: 120333-15-5 / $\text{H}_3\text{B}\cdot\text{SMe}_2$: 13292-87-0 / $\text{H}_3\text{BrB}\cdot\text{SMe}_2$: 55652-52-3 / $\text{HBr}_2\text{B}\cdot\text{SMe}_2$: 55671-55-1 / Br_3B : 10294-33-4

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- ¹⁷⁾ Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2. Inquiries should be accompanied by the depository number CSD-53747, the names of the authors, and the literature citation.

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