Phosphane-Borane Chemistry. – Borane Adducts of Two Polyfunctional Phosphanes

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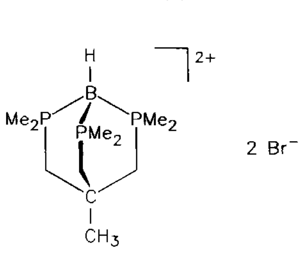
The tris(borane) adduct $MeC(CH_2PMe_2BH_3)_3$ (**2**) of 1,1,1-tris[(dimethylphosphino)methyl]ethane has been prepared from the tripodal phosphane and Me_2S-BH_3 as the borane source. The crystal structure of **2** · 1/2 toluene has been determined by single-crystal X-ray diffraction methods. The molecules display crystallographic C_3 symmetry and an overall staggered conformation. In an analogous way the bis(borane) adduct $CH_2(PH_2BH_3)_2$ (**3**) of 1,3-diphosphapropane has been synthesized, which decomposes above 50°C to give insoluble products, whose elemental analysis indicated that termal P–C bond cleavage is more frequent than P–B bond cleavage.

Phosphane-borane adducts containing P–B bonds are an interesting class of compounds because of their unusual chemical and physical properties. Many efforts have been made to gain a better insight into the interaction between the phosphorus donor and the boron acceptor, but owing to the complexity of the problem no final conclusion has been reached[1,2]. In more recent years, research in the chemistry of compounds containing P–B bonds has focussed largely on monomeric phosphinoboranes ($R_2P=BR_2$, isoelectronic with $R_2Si=CR_2$) with multiple bond character[3]. Other studies, including our own, have been oriented towards the synthesis of precursors and model substances for boron phosphides (PB; isoelectronic with SiC). As a continuation of our previous work on phosphane-boranes based on tetramethyldiphosphane[4] we now have investigated the borane adducts of two carbon-bridged polyfunctional phosphanes, $CH_3C(CH_2PMe_2)_3$ and $CH_2(PH_2)_2$.

Preparation, Properties, NMR Data, and Crystal Structure of the Tris(borane) Adduct of the Tripodal $MeC(CH_2PMe_2)_3$

The hexamethylated tripodal phosphane $MeC(CH_2PMe_2)_3$ has recently been shown to react with the trifunctional adduct $Br_2HB \cdot SMe_2$ to give the dibromide salt of a phosphane-borane cage dication (**1**)[5].



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This dication has been found to have a quinuclidine-type configuration by an X-ray structure analysis. We have now investigated the adduct of the parent phosphane with three BH_3 units.

1,1,1-Tris[(dimethylphosphino)methyl]ethane-tris(borane) (**2**) is readily prepared by the reaction of the tripodal phosphane $MeC(CH_2PMe_2)_3$ with three equivalents of $H_3B \cdot SMe_2$ in toluene as solvent. Removal of SMe_2 liberated in the process, together with part of the solvent, in vacuo followed by warming of the mixture to 80°C gives a clear solution. On slow cooling to room temperature the product crystallizes in high yield. The initial crop contains crystal toluene, but upon drying in a stream of nitrogen or in vacuo the material looses its solvate molecules, and a colorless powder is obtained, which melts without decomposition at 148°C. **2** is stable towards air and moisture and highly soluble in aromatic hydrocarbons, chloroform, and alcohols.

$$MeC(CH_2PMe_2)_3 + 3\,H_3B \cdot SMe_2 \xrightarrow{-3\,SMe_2} \underset{\mathbf{2}}{MeC(CH_2PMe_2BH_3)_3}$$

The ^1H-NMR spectrum of compound **2** shows four resonances in the range from $\delta = 0.2$ to 2.3 in the intensity ratio 3:6:1:2. The BH_3 functions are represented by a broad 1:1:1:1 quadruplet, while the protons of the methyl and methylene groups bound to the phosphonium centers show $[A_6X]_3$ and $[A_2X]_3$ spin systems, respectively. For the methyl group at the bridgehead carbon atom a singlet is observed. In the ^{13}C-NMR spectrum, the quaternary C-atom verifies the equivalence of the three phosphorus atoms in a quadruplet signal. The signals of the methylene carbon atoms appear as a typical first order AX_2X' spin system with a doublet of triplets.

The 1:1:1:1 quadruplet in the ^{31}P-NMR spectrum is also proof for three equivalent phosphorus atoms each bound to a boron atom. In the ^1H-decoupled ^{11}B-NMR spectrum a doublet with $J(PB) = 50$ Hz is observed.

2 · 1/2 toluene crystallizes in the hexagonal space group $R\bar{3}$ with six formula units in the unit cell. The three

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$CH_2PMe_2BH_3$ groups are related by a crystallographic threefold axis coinciding with the bond through the quaternary C-atom and the attached methyl carbon atom (Figure 1). The position of the toluene is disordered relative to this threefold axis.

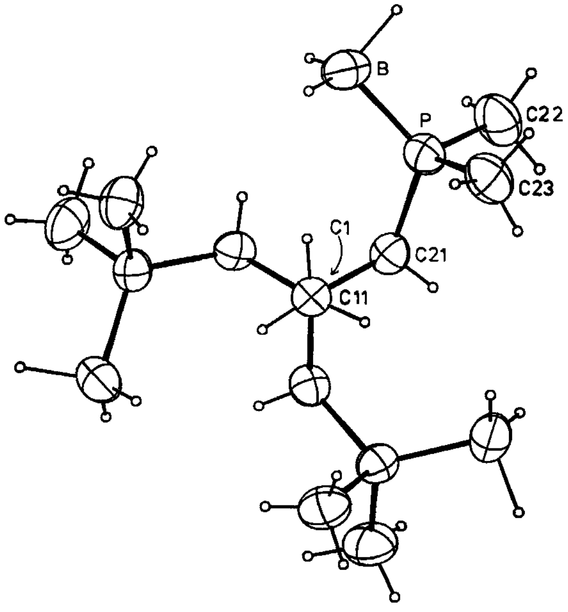

Figure 1. Molecular structure of $MeC(CH_2PMe_2BH_3)_3$ (**2**) and atomic numbering (50% probability ellipsoids are shown for the heavier atoms, arbitrary radii were used for hydrogen atoms). The molecule has a crystallographic threefold axis through the bridgehead carbon atom C1 (not visible) and the methyl carbon atom C11

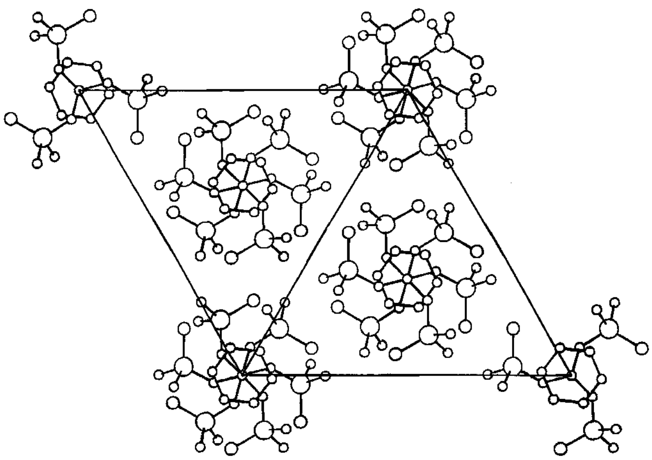

Figure 2. Packing of the $MeC(CH_2PMe_2BH_3)_3$ (**2**) molecules and the solvent (toluene, methyl groups omitted) projected onto the *xy* plane of the unit cell

The B–P bond lengths in **2** (Table 1) differ significantly from those reported for the cage cation in **1**[5], but are in good agreement with P–B distances found for other simple phosphane-boranes such as Me_3P-BH_3 (1.901 Å)[6]. Projections onto every bond in molecule **2** show, that this highly flexible species exists in a staggered ground state (Figure 2). Obviously, the molecular structure is governed by the repulsion between all neighboring groups, with electrostatic contributions from the dipolar phosphane-borane units operative in the same direction.

Table 1. Bond distances [Å] and angles [°] in compound **2**

P–B	1.917(7)	P–C21	1.829(5)
P–C22	1.804(5)	P–C23	1.811(5)
C1–C11	1.537(9)	C1–C21	1.553(5)
B–P–C21	120.0(3)	B–P–C22	111.9(3)
B–P–C23	111.1(3)	C21–P–C22	101.1(3)
C21–P–C23	107.3(3)	C22–P–C23	103.9(3)
C21–C1–C11	111.2(3)	C21–C1–C21′	107.8(3)
P–C21–C1	120.1(3)		

Preparation, Properties, and NMR Data of the Bis(borane) Adduct $CH_2(PH_2BH_3)_2$

In search of potential precursors applicable in chemical vapor deposition (CVD) experiments to give boron phosphide (BP), the preparation of borane adducts of small phosphanes with a minimum carbon content has been investigated. The adduct H_3P-BH_3, first obtained by Gamble and Gilmont in 1940[7], contains no carbon at all, but readily dissociates at temperatures as low as –30°C. The borane adduct of methylphosphane $MePH_2-BH_3$ is thermally more stable and decomposes above 80°C[8].

1,3-Diphosphapropane $CH_2(PH_2)_2$ has a phosphorus-to-carbon ratio intermediate between PH_3 and $MePH_2$, and the bis(borane) adduct of this difunctional phosphane is thus of considerable interest. The parent phosphane may be obtained by reduction of tetraisopropyl methylenediphosphonate with diphenylsilane[9]. The bis(borane) adduct **3** of 1,3-diphosphapropane is accessible by addition of two equivalents of $H_3B\cdot SMe_2$ in benzene as a solvent. **3** can be recrystallized from benzene. Evolution of hydrogen is observed with moisture and in protic solvents.

$$H_2P-CH_2-PH_2 + 2\,H_3B\cdot SMe_2 \xrightarrow{-2\,SMe_2} \underset{\mathbf{3}}{H_3B-PH_2-CH_2-PH_2-BH_3}$$

3 decomposes above 50°C before reaching its sublimation temperature and its melting point. This low thermal stability may be due to the presence of protic and hydridic hydrogen atoms within the same molecule. Decomposition also takes place in solution. Refluxing of a solution of **3** in toluene for 10 hours yields a colorless precipitate, which is insoluble in common solvents. Based on elemental analysis, the product has the composition $C_1H_{5.6}B_{1.3}P_{1.2}$. The boron-to-phosphorus ratio is nearly the same as in **3**, but the carbon content has increased, indicative of preferential P–C cleavage.

The ^1H-NMR spectrum of **3** displays separate groups of signals for the hydrogen atoms bound to different elements. The lowest field signal (a doublet of multiplets) is assigned to the two equivalent PH_2 functions. The broadened 1:1:1:1 quadruplet of the BH_3 groups partially overlaps with the signal of the methylene protons, which appears as a well resolved pattern of triplet of quintuplets. The ^1H-decoupled ^{13}C-NMR spectrum features a triplet [J(PC) = 27 Hz], which is split into a triplet of triplets under "off-resonance" conditions. In the ^1H-coupled ^{31}P-NMR spectrum the P−B coupling is not well resolved, and only a triplet of broad signals with J(PH) = 396 Hz is observed. The ^1H-coupled ^{11}B-NMR spectrum exhibits a quadruplet of doublets with one-bond couplings J(BH) = 102 and J(PB) = 29 Hz (Table 2).

Table 2. ^{31}P- and ^{11}B-NMR data of some phosphane-boranes (δ values, J in Hz)

	H_3P-BH_3[10,11]	**3**	$MePH_2-BH_3$[12]
$\delta^{31}P$	−102	−56.9	−68.6
J(HP)	372	384	388
$\delta^{11}B$	−60.8	−56.7	−58.8
J(PB)	27	29	43.5
J(HB)	100	102	103

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Experimental

All experiments were carried out under dry and pure nitrogen. Glassware and solvents were purified, dried, and kept under nitrogen. 1,3-Diphosphapropane was obtained by the method of Issleib[9]. $[D_6]$Benzene and [D]chloroform were used as solvents for NMR spectroscopy with tetramethylsilane, phosphoric acid, and trimethyl borate as reference compounds, respectively (JEOL GX 270 and GX 400 spectrometers).

1,1,1-Tris[(dimethylphosphino)methyl]ethane-tris(borane) (**2**): A solution of $MeC(CH_2PMe_2)_3$[13] (1.26 g, 5.0 mmol) in 15 ml of toluene was treated at 0°C with a solution of borane-dimethyl sulfide complex (1.14 g, 15.0 mmol) in 15 ml of the same solvent. After stirring for 1 h one third of the solvent was removed in vacuo to precipitate most of the product. Warming to 80°C gave a clear solution. On cooling to room temp. compound **2** crystallized with half an equivalent of crystal toluene. The crystals were dried in vacuo to yield 1.41 g of the solvent-free product (96%), m.p. 148°C. − ^1H NMR ($CDCl_3$): δ = 0.65 [q, J(BH) = 110 Hz, BH_3], 1.35 ($[A_6X]_3$, N = 10 Hz, $(CH_3)_2P$], 1.46 (s, CH_3C), 2.27 ($[A_2X]_3$, N = 12 Hz, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 14.2 [AXX′X″, N = 40 Hz, $(CH_3)_2P$], 23.6 [q, J(PC) = 5 Hz, $C-CH_3$], 38.3 (s, $C-CH_3$), 39.6 [dt, ^1J(PC) = 30, ^3J(PC) = 5 Hz, CH_2]. − ^{31}P NMR ($CDCl_3$): δ = 0.3 [q, J(BP) ≈ 43 Hz]. − ^{11}B NMR ($CDCl_3$): δ = −54.7 [d, J(PB) ≈ 50 Hz]. − IR (KBr): $\tilde{\nu}$ = 2979 cm^{-1}, 2970 m, 2947 m, 2914 m, 2372 vs, 2316 s, 2271 m, 1473 w, 1458 w, 1429 m, 1416 m, 1406 m, 1375 m, 1307 m, 1295 s, 1232 w, 1139 m, 1067 s, 1059 s, 1105 w, 965 s, 948 s, 932 vs, 874 s, 795 w, 751 m, 732 w, 704 m, 669 w, 579 m, 555 m, 499 w, 445 w.

$C_{11}H_{36}B_3P_3$ (293.8)	Calcd.	C 44.98	H 12.35
	Found	C 44.99	H 12.16

Crystal Structure Determination of the Tris(borane) Adduct $MeC(CH_2PMe_2BH_3)_3$ (**2**): Syntex $P2_1$ diffractometer, Mo-K_α radiation, λ = 0.71069 Å, graphite monochromator, T = −50°C. − Crystal data: $C_{11}H_{36}B_3P_3 \cdot (C_7H_8)_{0.5}$, M = 339.83, space group $R\bar{3}$ with $a = b$ = 16.274(1), c = 15.219(1) Å, V = 3490.64 $Å^3$, Z = 6, $d_{calcd.}$ = 0.9793 gcm^{-3}, μ(Mo-K_α) = 2.11 cm^{-1}, $F(000)$ = 1122. The intensities of 1364 reflexions were collected up to (sin Θ/ϑ) = 0.572 $Å^{-1}$ (hkl range: ±18, +18, +17) and averaged to 1220 independent data, 1010 of which with $F_o \geq 4.0\sigma(F_o)$ were considered "observed". The structure was solved with direct methods (SHELXS-86[14]) and refined using anisotropic displacement parameters for the non-hydrogen atoms and the hydrogen atoms of the BH_3 groups. All other hydrogen atoms were assigned constant values U_{iso} = 0.5 $Å^2$ (CH_3 as rigid groups). R (R_w) = 0.066 (0.088), $w = 1/\sigma^2(F_o)$ for 91 refined parameters. Residual electron density 0.70/−0.41 $eÅ^{-3}$[15]. Fractional atomic coordinates see Table 3.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters for **2**

Atom	X/A	Y/B	Z/C	$U_{eq.}$
P	0.47322(9)	0.17084(9)	0.03268(8)	0.068
B	0.4075(5)	0.2379(6)	0.0051(6)	0.107
C21	0.5928(3)	0.2345(3)	0.0792(3)	0.072
C22	0.4117(4)	0.0807(4)	0.1150(4)	0.085
C23	0.4775(4)	0.1052(4)	−0.0616(4)	0.082
C1	0.66670	0.33330	0.0423(4)	0.063
C11	0.66670	0.33330	−0.0586(5)	0.062
CTol	0.084(4)	−0.013(5)	0.002(1)	0.432

2,4-Diphosphonia-1,5-diboratapentane (**3**): A solution of 1,3-diphosphapropane (0.80 g, 10.0 mmol) in 15 ml of benzene was treated at 5°C with a solution of borane-dimethyl sulfide complex (1.52 g, 20.0 mmol) in 15 ml of the same solvent and stirred at room temperature for 2 h. Purification was accomplished by concentration of the solution to 1/5 of the initial volume in vacuo, followed by cooling to 0°C. The obtained precipitate was isolated by decantation of the mother liquor and drying in vacuo, yield 0.69 g (64%), decomposition without melting at 50°C. − ^1H NMR (C_6D_6): δ = 0.81 [tquint, J(PH) = 10.6, J(HH) = 6.0 Hz, CH_2], 1.07 [q, broad, J(BH) = 100 Hz, BH_3], 3.71 [m, N = 420, ^1J(PH) = 396 Hz, PH_2]. − ^{13}C NMR (off resonance, C_6D_6): δ = 2.7 [tt, J(PC) = 28 Hz]. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −56.9 [q, J(BP) = 28 Hz]. − ^{11}B NMR (C_6D_6): δ = −56.7 [qd, J(HB) = 102, J(PB) = 29 Hz]. − IR (KBr): $\tilde{\nu}$ = 2965 cm^{-1} m, 2916 m, 2380 vs, 1977 w, 1373 m, 1176 m, 1136 m, 1085 m, 1054 s, 943 vs, 884 s, 815 w, 799 s, 789 m, 631 m, 607 w, 567 m, 554 m.

$CH_{12}B_2P_2$ (107.7)	Calcd.	C 11.15	H 11.23
	Found	C 11.51	H 11.02

CAS Registry Numbers

2: 128923-83-1 / **2** · 0.5 C_7H_8: 128923-84-2 / **3**: 128923-85-3

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