Cyclic and Bicyclic Poly(phosphane)borane Cations

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The reactions of $(Me_2S)BH_2Br$ and $(Me_2S)BHBr_2$ with equimolar quantities of 1,2-bis(diphenylphosphanyl)ethene (**1**) or -benzene (**2**) lead to cyclic, cationic bis(phosphane)boranes {**4**: $[(\mathbf{1})BH_2]^+ Br^-$; **5**: $[(\mathbf{1})BHBr]^+ Br^-$; **6**: $[(\mathbf{2})BH_2]^+ Br^-$; **7**: $[(\mathbf{2})BHBr]^+ Br^-$}. The Br^- counterions can be exchanged in metathesis reactions (e.g. with $AgBF_4$ to afford **4a**). The tritertiary phosphane bis[2-(diphenylphosphanyl)phenyl]phenylphosphane (**3**), reacts with $(Me_2S)BHBr_2$ to give bicyclic dicationic tris(phosphane)borane **8**, $[(\mathbf{3})BH]^{2+} \cdot 2\,Br^-$, which can be converted into the bis(hexafluorophosphate) **8a** using NH_4PF_6. All compounds have been characterized by analytical and NMR-spectroscopic data. The crystal and molecular structures of **5**–**7** have been determined by single-crystal X-ray diffraction.The five-membered rings C_2P_2B have an envelope conformation and show no sign of electron delocalization. Attempts to deprotonate the B–H functions in **5**–**8** have not been successful. Clearly, the two (**5**–**7**) or three phosphonium centers (**8**) adjacent to the boron atom are not sufficient to induce an "umpolung" of the B–H group

Introduction

Phosphane–boranes of the type $(R_3P)BH_3$ are zwitterionic molecules with exceedingly high thermal and chemical stability.[1] Hydrolytic decomposition is slow even with strong aqueous acid, and the compounds are not attacked by elemental bromine at room temperature. This robustness is indicative of an "umpolung", or at least a reduction of the inherent $(\delta+)B-H(\delta-)$ polarity in these compounds containing the otherwise quite sensitive B–H bond. To account for these phenomena, various theoretical models based on resonance structures with an increased bond order of the R_3P-BH_3 linkage have been proposed, focusing initially on d-orbital participation, and later on contributions from symmetry-equivalent π^*-orbitals of the σ-framework.[2] There are analogous effects in the chemistry of the isoelectronic phosphonium cations $[R_3P-CH_3]^+$ and silanes $[R_3Si-CH_3]$, in that the deprotonated species derived from them, $[R_3P=CH_2]$ and $[R_3Si-CH_2]^-$, also show unusual stability.[3] State-of-the-art ab initio or density-functional methods give much more satisfactory results, but are less pictorial in their description of bonding.

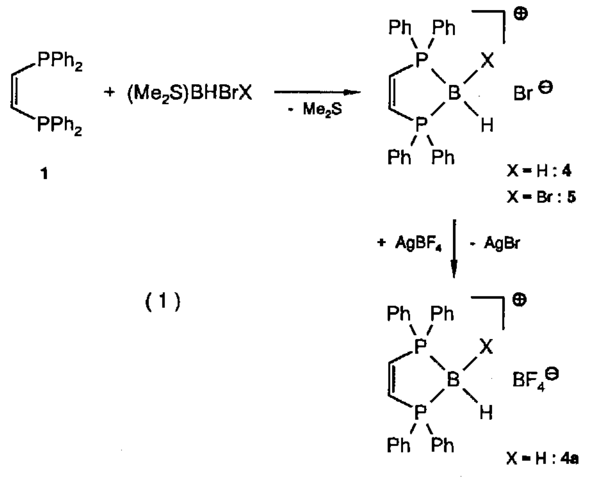
Introducing a second phosphonium substituent at a given boron center, as in cation $[(R_3P)_2BH_2]^+$, leads to a further decrease of the B–H polarity at the BH_2 bridging unit, as judged from the high thermal and chemical stability of salts containing this type of cation.[4] Chemical behaviour of these species is often dominated by the reactivity of the alkyl groups at phosphorus rather than of the BH_2 group.[5] With strong base, deprotonation of the alkyl groups in the α-position to the phosphorus atom is observed, which leads to a variety of novel ylidic species.[5]

To pursue further the trends in borane reactivity as a function of the number and the nature of neighboring phosphonium centers, we have now investigated a set of cyclic phosphane–borane cations with bi- and tridentate phosphanes. For this study, the phosphane ligands *cis*-1,2-bis(diphenylphosphanyl)ethene (**1**), 1,2-bis(diphenylphosphanyl)benzene (**2**), and bis[2-(diphenylphosphanyl)phenyl)]phenylphosphane (**3**) were chosen, which do not offer any acidic α-protons and thus cannot give rise to ylide formation when treated with base. If therefore the "umpolung" of the B–H units is sufficiently advanced in poly(phosphane)borane cations, deprotonation at boron upon treatment with strong base should become feasible.

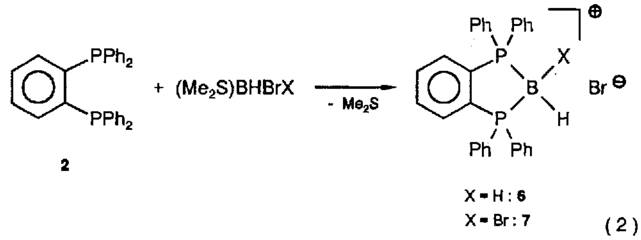
Preparative Results

For the preparation of the new phosphane–boranes, where trimethyl- and triethylphosphane and 1,2-bis(diphenylphosphanyl)ethane (dppe) were employed as ligands, the synthetic pathways which already proved successful in earlier work could be followed.[6]

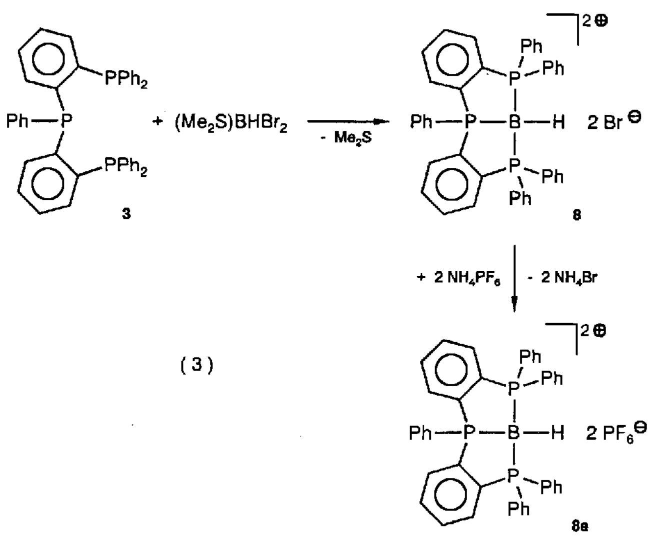
The reaction of dimethyl sulfide–bromoborane with equivalent quantities of ligand **1** leads to a liberation of the thioether and gives high yields of a crystalline product (**4**), which can subsequently be converted into the corresponding tetrafluoroborate salt **4a** by metathesis with $AgBF_4$. If dimethyl sulfide–*di*bromoborane is used instead of the *mono*bromoborane complex, the B–bromo analogue **5** is generated (Eq. 1). Ligand **2** affords the benzo homologues **6** and **7** in much the same way and in high yields (Eq. 2). All products are colorless, air- and water-stable crystalline solids with high melting points, soluble in di- and trichloromethane, methanol, ethanol, and tetrahydrofuran. The compositions of the compounds were confirmed by elemental analysis and mass spectrometry (Experimental Section).



(1)



(2)



(3)

Compounds **5** and **7** do not react further with an excess of the ligands **1** or **2**, and they are also recovered unchanged if treated with another tertiary phosphane like PPh_3. It appears that the last B−Br function in the cation is sterically well protected, and the formation of a third onium center next to the boron atom is not a sufficiently strong driving force for heterolytic B−Br bond breaking.

The structures of compounds **4**−**7** are readily verified by NMR-spectroscopic data. In solution ($CDCl_3$ or CD_2Cl_2) the cations of compounds **4, 4a**, and **6** have virtual C_{2v} symmetry as suggested by only one set of Ph_2P resonances (four equivalent Ph groups, two equivalent phosphorus atoms). In compounds **5** and **7** the symmetry is reduced to C_s, rendering the phenyl groups at each phosphorus atom inequivalent. This inequivalence of the Ph groups is also proof that at ambient temperature there is no rapid ligand exchange at the boron atoms in solution, and that there is no dissociation of the remaining second bromine atom. The agreement of the spectroscopic data of the two complexes **4** and **4a** shows that the anion does not co-determine the parameters of the phosphane−borane group in solution because of the ionic character of the compounds. The crystal structures of compounds **5**−**7** have been determined, and the results confirm the conclusions drawn from spectroscopic data (below).

Treatment of $(Me_2S)BHBr_2$ with equimolar amounts of $(2\text{-}Ph_2P{-}C_6H_4)_2PPh$ (**3**) in toluene at 20 °C gives a colorless precipitate, which can be purified by crystallization from dichloromethane/diethyl ether (**8**, 83 % yield, m.p. 196 °C). Metathesis with excess $NH_4^+PF_6^-$ in ethanol leads to the bis(hexafluorophosphate) salt (**8a**, 71 % yield, m.p. 223 °C, air- and water-stable, soluble in $CHCl_3$, CH_2Cl_2, methanol, and dimethyl sulfoxide) [Eq. (3)]. Both compounds were identified by elemental analysis and mass-spectrometry data (Experimental Section).

The $^{31}P\{^1H\}$-NMR spectrum of **8** (in CD_2Cl_2 at 25 °C) shows an AX_2 pattern suggesting a mirror symmetry for the dication. The ^{11}B resonance is a broad signal at $\delta = -32.3$ with no P−B coupling resolved. Unfortunately, no single crystals could be grown of **8** or **8a**, and therefore further details of the structures are not available.

Compounds **8** and **8a** cannot be deprotonated at the boron atom. Even with stong bases like LiH, *n*BuLi, Et_3N, $KN(SiMe_3)_2$, etc., no reaction was observed. Treatment with $LiNMe_2$, NaOMe, or pyridine (Pyr) leads to decomposition with liberation of the phosphanes, and tris(pyridino)borate salts $[(Pyr)_3BH]^{2+-}\cdot 2\ X^-$ were accordingly obtained in the pyridine reaction. Three phosphonium neighbors to the boron center are therefore not yet sufficient to effect a complete "umpolung" of the hydrogen atom at the boron center. This is surprising since the corresponding monocation $[(R_3P)_3B]^+$ is isoelectronic with the carbon-centered dication $[(R_3P)_3C]^{2+}$ or the bissilylated ylide $[(R_3P)C(SiR_3)_2]$, etc., which are all known to have high stability. The high negative (2−) formal charge of the boron atom in **A** appears to be the main reason for the reluctance of compounds **8** and **8a** to loose a proton to any of the bases applied.

Structural Studies

The crystal structures of compounds **5**−**7** have been determined by single-crystal X-ray diffraction studies (Table 1).

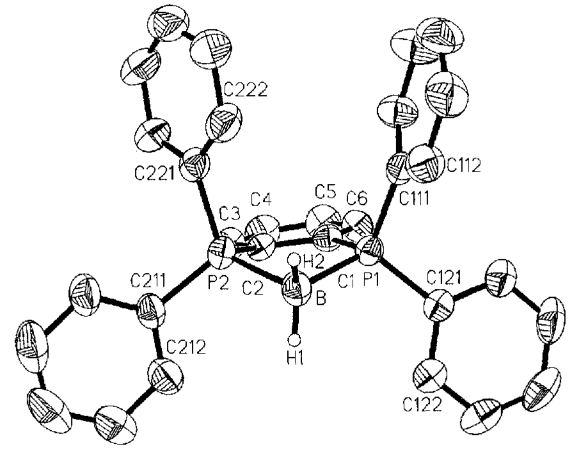
Crystals of compound **6** are orthorhombic, space group *Pna*2$_1$, with 4 molecules in the unit cell. In the lattice there are no unusual connectivities between the cations and anions. The cations feature a five-membered ring in an envelope conformation with the boron atom deviating most strongly from the plane made up of the remaining ring atoms (Figure 1). The two P−B distances are equal within the limit of standard deviations [P1−B 1.941(5), P2−B 1.939(5) Å], and the P−B−P angle [97.9(2) °] is the smallest of the ring angles.

Table 1. Crystal data, data collection, structure solution and refinement for compounds **5** to **7**

	5	**6**	**7**
Crystal data			
Formula	$C_{27}H_{24}BBr_2Cl_3P_2$	$C_{30}H_{26}BBrP_2$	$C_{31}H_{26}BBr_2Cl_3P_2$
M_r	687.38	539.17	737.44
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P\,2_1/c$	$P\,na2_1$	$P\,2_12_12_1$
a [Å]	11.170(1)	19.935(1)	9.826(1)
b [Å]	9.634(1)	14.045(1)	17.851(2)
c [Å]	28.694(3)	9.389(1)	18.297(2)
α [°]	90	90	90
β [°]	100.99(1)	90	90
γ [°]	90	90	90
V [Å^3]	3031.2(5)	2628.8(4)	3209.4(6)
$\rho_{calcd.}$ [gcm^{-3}]	1.506	1.362	1.526
Z	4	4	4
$F(000)$	1368	1104	1472
μ(Mo-K_α) [cm^{-1}]	30.60	17.02	28.96
Absorption correction	ψ scans	ψ scans	ψ scans
T_{min}/T_{max}	0.69/0.99	0.78/0.99	0.75/0.99
Data collection			
T [°C]	−68	+25	−68
Scan mode	ω	ω	ω
hkl range	$-13 \rightarrow 13, -11 \rightarrow 11, 0 \rightarrow 35$	$0 \rightarrow 21, -17 \rightarrow 0, -11 \rightarrow 11$	$-11 \rightarrow 11, 0 \rightarrow 21, -21 \rightarrow 14$
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.64	0.64	0.64
Measured reflections	7104	4864	7576
Refls. used for refinement	5912 (R_{int} = 0.0281)	4726 (R_{int} = 0.0104)	5128 (R_{int} = 0.0303)
Refinement			
Refined parameters	361	314	347
H atoms (found/calcd.)	3/20	2/24	1/24
Final R values [$I > 2\sigma(I)$]			
$R1$[a]	0.0607	0.0424	0.0498
$wR2$[b]	0.1024	0.0800	0.1223
Goof	1.193	1.067	1.023
Absolute structure param.	–	0.002(9)	0.395(13)
(shift/error)$_{max}$	< 0.001	< 0.001	< 0.001
ρ_{fin}(max/min) [eÅ^{-3}]	0.560/−0.375	0.339/−0.499	0.663/−0.601

[a] $R1 = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$. – [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0774 (**5**), 0.0273 (**6**), 0.0150 (**7**); b = 2.55 (**5**), 1.89 (**6**), 8.03 (**7**). – [c] The value of the absolute structure parameter indicates that the structure is probably a racemic twin.

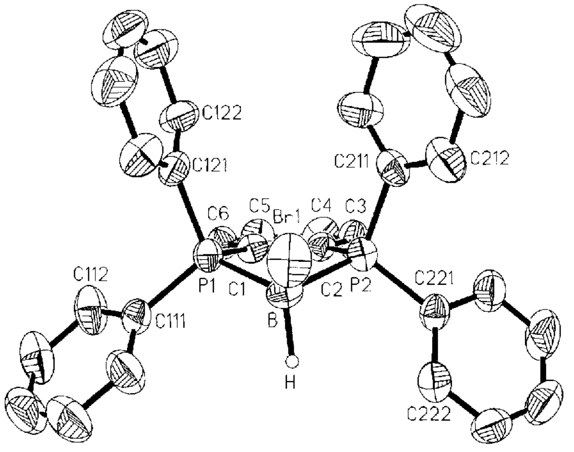
Figure 1. Molecular structure of the cation of compound **6**



Compound **7** crystallizes with one equivalent of chloroform in the lattice, which is disordered. The crystals are orthorhombic, space group $P2_12_12_1$, with 4 molecules in the unit cell. One of the two bromine atoms is an independent bromide anion, while the second is attached to the boron atom. The structure of the cation resembles that of compound **6** very closely. The five-membered ring is also in an envelope conformation with two somewhat larger, but internally equivalent P–B bonds [P1–B 1.975(7), P2–B 1.964(8) Å] and a narrow P–B–P angle [99.2(3) °]. The bromine atom is in a quasi-equatorial position at the boron atom with a distance B–Br1 = 1.975(7) Å. Though not imposed crystallographically, the cation closely approaches mirror symmetry (point group C_s), with the mirror plane defined by the atoms of the group BHBr (Figure 2).

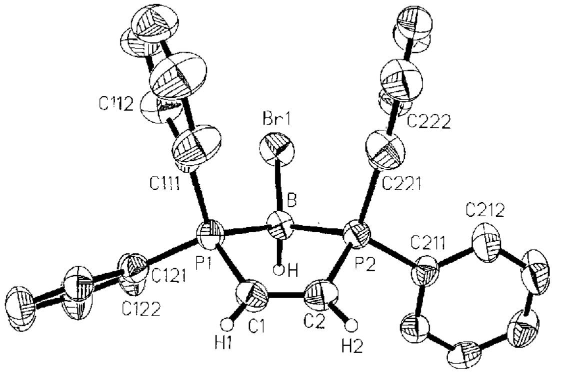
Compound **5** also crystallizes with one mole-equivalent of chloroform, which is severely disordered in the lattice. The crystals are monoclinic, space group $P2_1/c$, with 4 molecules in the unit cell. The conformation of the five-membered ring of the cation and its substituents is virtually the same as in the benzo analogue **7**. The bromine atom is again in an equatorial position and a non-crystallographic mirror plane through the atoms B, H, and Br1 is easily recognized as bisecting the olefinic double bond (C1–C2) (Figure 3). The narrow P–B–P angle [96.8(3) °] is flanked by two nearly equidistant P–B bonds [P1–B 1.947(6), P2–B 1.946(6) Å], and the B–Br1 bond length [1.979(6) Å] is virtually identical with the corresponding distance in

Figure 2. Molecular structure of the cation of compound **7**



the benzo analogue [**7**: 1.975(7) Å]. The olefinic double bond C1−C2 = 1.321(7) Å shows no anomalies.

Figure 3. Molecular structure of the cation of compound **5**



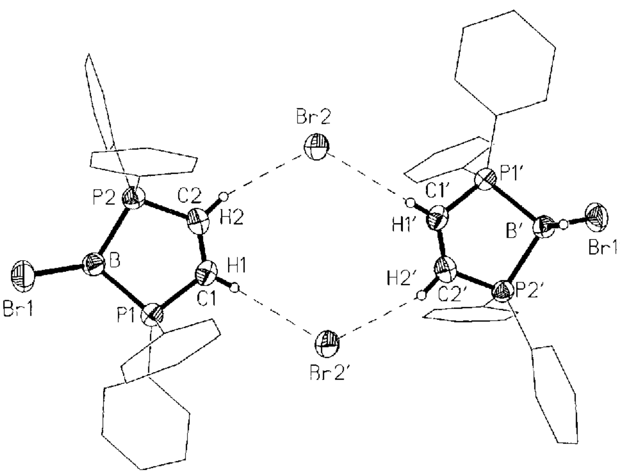
Formula units of **5** are arranged in pairs in the unit cell of the crystal (Figure 4). The bromide anions (Br2) are close and almost colinear to the hydrogen−carbon bonds of the ethene bridge (H1, H2) suggesting some directed orientation reminiscent of hydrogen bonding. The long distances Br2···H1′ and Br2···H2 [2.762 and 2.745 Å, respectively] are almost equal and indicate equivalent, but weak interactions.

In summary, it appears that all three structures represent classical geometries as expected for an architecture involving combinations of independent olefin, arene, and phosphane−borane units without any significant delocalization of electron density in more extended π-systems.

Experimental Section

General: All experiments were carried out routinely in purified dry nitrogen. Solvents were dried and kept under nitrogen, and glassware was oven-dried and filled with nitrogen. 1,2-Bis(diphenylphosphanyl)benzene[3e] and bis[2-(diphenylphosphanyl)phenyl]phenylphosphane[7] were prepared according to literature procedures, all other starting materials are commercially available.

Figure 4. Pairwise arrangement of molecules in the crystals of compound **5**



[(Z)-1,2-Bis(diphenylphosphanyl)ethene]dihydroboron Bromide (**4**): Dimethyl sulfide−bromoborane (1.03 ml, 9.61 mmol) is added to a solution of (*Z*)-1,2-bis(diphenylphosphanyl)ethene (3.81 g, 9.61 mmol) in 25 ml of toluene. A white precipitate is formed almost immediately, but the solution is allowed to reflux for 1 h before collection of the solid by filtration. After washing with toluene and pentane, **4** is recrystallized from chloroform/diethyl ether. Yield 3.16 g (67 %), colorless solid, m. p. 249°C. − ^{1}H NMR ($CDCl_3$, 20°C): δ = 7.35−7.65 (m, 20 H, Ph), 8.71 (m, AA′XX′, 2 H, PCH). − ^{13}C NMR (v. s.): δ = 122.9, 129.7, 132.3, 133.3 [m, AXX′, Ph (*ipso, meta, ortho, para*)], 144.2 (m, AXX′, PCH). − ^{11}B NMR (v. s.): δ = −35.2 (br. s). − ^{31}P NMR (v. s.): δ = 34.7 (br. s). − $C_{26}H_{24}BBrP_2$ (489.15): calcd. C 63.84, H 4.94, Br 16.33; found C 62.17, H 4.95, Br 16.89.

[(Z)-1,2-Bis(diphenylphosphanyl)ethene]dihydroboron Tetrafluoroborate (**4a**): Silver tetrafluoroborate (1.26 g, 6.46 mmol) in 8 ml of THF is added to a solution of **4** (3.16 g, 6.46 mmol) in 25 ml of dichloromethane. After filtration of the silver bromide, **4a** is precipitated with pentane. Yield 2.69 g (84 %), colorless solid, m. p. 210°C.

[(Z)-1,2-Bis(diphenylphosphanyl)ethene]bromohydroboron Bromide (**5**): Like compound **4**, with dimethyl sulfide−dibromoborane (2.65 ml, 21.1 mmol) and (*Z*)-1,2-bis(diphenylphosphanyl)ethene (8.35 g, 21.1 mmol) in 50 ml of toluene. Yield 7.70 g (64 %), colorless crystals, m. p. 195°C. − ^{1}H NMR ($CDCl_3$, 20°C): δ = 7.40−7.79 (m, 20 H, Ph), 8.98 (m, AA′XX′, 2 H, PCH). − ^{13}C NMR (v. s.): δ = 120.8, 122.9, 129.6, 130.0, 132.8, 133.1, 133.6, 134.0 [m, AXX′, Ph (*ipso, meta, ortho, para*)], 143.9 (m, AXX′, PCH). − ^{11}B NMR (v. s.): δ = −22.6 (br. s). − ^{31}P NMR (v. s.): δ = 15.4 (br. s). − $C_{26}H_{23}BBr_2P_2$ (568.04): calcd. C 54.98, H 4.08, Br 28.13; found C 53.23, H 3.93, Br 28.17.

[1,2-Bis(diphenylphosphanyl)benzene]dihydroboron Bromide (**6**): Like compound **4**, with dimethyl sulfide−bromoborane (0.36 ml, 3.36 mmol) and 1,2-bis(diphenylphosphanyl)benzene (1.50 g, 3.36 mmol) in 25 ml of toluene. Yield 1.53 g (84 %), colorless crystals, m. p. 255°C. − ^{1}H NMR ($CDCl_3$, 20°C): δ = 8.15−7.51 (m, Ph). − ^{13}C NMR (v. s.): δ = 133.5 (m, AXX′, C3/C6), 133.6 (m, AXX′, C1/C2), 135.3 (m, AXX′, C4/C5), 121.4, 129.7, 132.6, 133.4 [m, AXX′, Ph (*ipso, meta, ortho, para*)]. − ^{11}B NMR (v. s.): δ = −32.9 (br. s). − ^{31}P NMR (v. s.): δ = 23.9 (br. s). − $C_{30}H_{26}BBrP_2$ (539.21) calcd. C 66.83, H 4.86, Br 14.82; found C 64.81, H 4.80, Br 14.86.

[1,2-Bis(diphenylphosphanyl)benzene]bromohydroboron Bromide (**7**): Like compound **4**, with dimethyl sulfide−dibromoborane (0.59

Table 2. Selected bond lengths [Å] and angles [°] of compounds **5**, **6**, and **7**

	5		**6**		**7**
B−P1	1.947(6)	B−P1	1.941(5)	B−P1	1.964(8)
B−P2	1.946(6)	B−P2	1.939(5)	B−P2	1.954(8)
B−Br1	1.979(6)	B−H1	0.97(4)	B−Br1	1.975(7)
B−H	1.13(5)	B−H2	1.48(4)	B−H	1.26(8)
P1−C1	1.789(6)	P1−C1	1.809(4)	P1−C1	1.817(6)
P2−C2	1.797(5)	P2−C2	1.803(4)	P2−C2	1.792(7)
C1−C2	1.321(7)	C1−C2	1.400(5)	C1−C2	1.403(9)
P1−B−P2	96.8(3)	P1−B−P2	97.9(2)	P1−B−P2	99.2(3)
B−P2−C2	98.0(3)	B−P2−C2	101.8(2)	B−P2−C2	100.9(3)
P2−C2−C1	116.7(4)	P2−C2−C1	114.3(3)	P2−C2−C1	116.9(5)
C2−C1−P1	115.9(4)	C2−C1−P1	115.1(3)	C2−C1−P1	116.9(5)
C1−P1−B	98.7(3)	C1−P−B	102.5(2)	C1−P1−B	100.4(3)

g, 2.52 mmol) and 1,2-bis(diphenylphosphanyl)benzene (1.13 g, 2.52 mmol) in 20 ml of toluene. Yield 1.50 g (96 %), colorless crystals, m. p. 233°C. – ^{1}H NMR (CDCl$_3$, 20°C): δ = 8.22–7.35 (m, Ph). – ^{13}C NMR (v. s.): δ = 131.2 (m, AXX′, C1/C2), 134.8 (m, AXX′, C3/C6), 136.7 (m, AXX′, C4/C5), 111.8, 119.8, 129.6, 130.4, 133.7, 133.7, 133.9, 134.5 [m, AXX′, Ph (*ipso*, *meta*, *ortho*, *para*)]. – ^{11}B NMR (v. s.): δ = −21.6 (br. s). – ^{31}P NMR (v. s.): δ = 6.4 (br. s). – $C_{30}H_{25}BBr_2P_2 \cdot CHCl_3$ (618.10 + 116.64): calcd. C 50.48, H 3.55; found C 50.47, H 3.58.

{Bis[2-(diphenylphosphanyl)phenyl]phenylphosphane}hydroboron Dibromide (**8**): Dimethyl sulfide−dibromoborane (96 mg, 0.41 mmol) is added to a solution of bis[2-(diphenylphosphanyl)phenyl]phenylphosphane (259 mg, 0.41 mmol) in 20 ml of toluene and stirred for 2 h at room temperature. The white precipitate is collected and recrystallized twice from dichloromethane/diethyl ether. Yield 272 mg (83 %), colorless solid, m. p. 196°C. – ^{11}B NMR (CD$_2$Cl$_2$, −90°C): δ = −32.3 (br. s). – ^{31}P NMR (v. s.): δ = 44.3 [t, 1, J(P,P) = 29 Hz, $P^{cent.}$], 24.6 (d, 2, $P^{term.}$). – MS (FAB): 723.5 [M$^+$ − Br], 641.6 [M$^+$ − 2 Br].

{Bis[2-(diphenylphosphanyl)phenyl]phenylphosphane}hydroboron Bis(hexafluorophosphate) (**8a**): A solution of **8** (182 mg, 0.23 mmol) in aqueous ethanol is treated with an ethanolic solution of ammonium hexafluorophosphate. The precipitated PF_6^- salt is collected by filtration, washed twice with ethanol and recrystallized from methanol. Yield 152 mg (71 %), colorless crystals, m. p. 223°C. – MS (FD): 787.3 [M$^+$ − PF$_6$] – $C_{42}H_{34}BF_{12}P_5$ (932.72): calcd. C 54.10, H 3.68, Br 0; found C 53.07, H 3.90, Br 0.

Crystal-Structure Determinations: Specimens of suitable quality and size of compounds **5**, **6**, and **7** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection with an Enraf Nonius CAD4 diffractometer, using Mo-K_α radiation [λ(Mo-K_α) = 0.71073 Å]. During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for all compounds. Lp correction was applied and intensity data were corrected for absorption effects (ψ scans). The structures were solved by direct (**6**, **7**) and Patterson methods (**5**) (SHELXS 86), and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically, except for those of the (partly disordered) CHCl$_3$ molecules in the crystals of **5** and **7**. All phenyl hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)}$ = 1.5 U_{eq} of the attached C atom), whereas all B−*H* and the *H*C=C*H* atoms (**5**) were found and refined isotropically, or were included with fixed isotropic contributions (B−*H* of compound **7**). The solvent molecules in compounds **5** and **7** were refined in split positions with isotropic displacement parameters. Their H atoms were neglected. Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in Table 2.

Anisotropic thermal parameters, tables of interatomic distances and angles, and atomic coordinates have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting depository numbers CSD-406848 (**5**), -406849 (**6**), -406850 (**7**).

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[1] [1a] H. Schmidbaur, *J. Organomet. Chem.* **1980**, *200*, 287–306. – [1b] P. P. Power, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 449–460; *Angew. Chem.* **1990**, *102*, 527–538. – [1c] T. Imamoto, *Pure Appl. Chem.* **1993**, *65*, 655–660. – [1d] R. T. Paine, H. Nöth, *Chem. Rev.* **1995**, *95*, 343–379. – [1e] G. W. Parshall in E. L. Muetterties, *The Chemistry of Boron and its Compounds*, Wiley, New York, **1967**, p. 617–634. – [1f] J. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, London, **1976**, p. 446–449. – [1g] D. E. C. Corbridge, *Phosphorus – An Outline of its Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam, **1990**, p. 675–684.

[2] [2a] A. B. Burg, *Rec. Chem. Rev.* **1958**, *58*, 101. – [2b] T. D. Coyle, H. D. Kaesz, F. G. A. Stone, *J. Am. Chem. Soc.* **1959**, *81*, 2989. – [2c] A. H. Cowley, M. C. Damasco, *J. Am. Chem. Soc.* **1971**, *93*, 6815–21. – [2d] J. Demuynck, A. Veillard, *Chem. Commun.* **1970**, 873. – [2e] I. H. Hillier, J. C. Marriott, V. R. Saunders, M. J. Ware, *Chem. Commun.* **1970**, 1586. – [2f] A. H. Cowley, R. A. Kemp, M. Lattman, M. L. McKee, *Inorg. Chem.* **1982**, *21*, 85–88.

[3] [3a] H. Schmidbaur, *Adv. Organomet. Chem.* **1970**, *9*, 260. – [3b] H. Schmidbaur, *Acc. Chem. Res.* **1975**, *8*, 62. – [3c] H. Schmidbaur, *Adv. Organomet. Chem.* **1976**, *14*, 205. – [3d] H. Schmidbaur, *Pure Appl. Chem.* **1978**, *50*, 19. – [3e] G. A. Bowmaker, R. Herr, H. Schmidbaur, *Chem. Ber.* **1983**, *116*, 3567–79.

[4] [4a] N. E. Miller, E. L. Muetterties, *J. Am. Chem. Soc.* **1964**, *86*, 1033–38. – [4b] G. E. Ryschkewitsch in E. L. Muetterties, *Boron Hydride Chemistry*, Academic Press, New York, **1975**, p. 223–239.

[5] [5a] H. Schmidbaur, G. Müller, U. Schubert, O. Orama, *Angew. Chem.* **1978**, *90*, 126; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 126. – [5b] H. Schmidbaur, G. Müller, U. Schubert, O. Orama, *Chem. Ber.* **1979**, *112*, 3302–10. – [5c] H. Schmidbaur, H. J. Füller, G. Müller, A. Frank, *Chem. Ber.* **1979**, *112*, 1448. – [5d] H. Schmidbaur, G. Müller, K. C. Dash, B. Milewski-Mahrla, *Chem. Ber.* **1981**, *114*, 441. – [5e] H. Schmidbaur, G. Müller, *Monatsh. Chem.* **1980**, *111*, 1233. – [5f] H. Schmidbaur, G.

Müller, D. Neugebauer, W. Geike, F. H. Köhler, J. Pebler, *Organometallics* **1983**, *2*, 257. – [5g] H. Schmidbaur, E. Weiß, W. Graf, *Organometallics* **1985**, *4*, 1233.

[6] [6a] H. C. Kelly, G. L. Smith, *Inorg. Chem.* **1969**, *8*, 2000. – [6b] N. E. Miller, *Inorg. Synth.* **1970**, *12*, 13. – [6c] B. T. Pennington, M. A. Chiusano, D. J. Dye, E. D. Martin, D. R. Martin, *J. Inorg. Nucl. Chem.* **1978**, *40*, 389. – [6d] D. R. Martin, C. M. Merkel, J. P. Ruiz, J. U. Mondal, *Inorg. Chim. Acta* **1985**, *100*, 293. – [6e] H. Schmidbaur, T. Wimmer, G. Reber, G. Müller, *Angew. Chem.* **1988**, *100*, 1135–38; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1071–74. – [6f] H. Schmidbaur, C. Paschalidis, O. Steigelmann, G. Müller, *Chem. Ber.* **1989**, *122*, 1851. – [6g] M. F. Hawthorne, W. S. Rees, C. B. Knobler, D. M. Schubert, *Organometallics* **1990**, *9*, 2938. – [6h] S. A. Westcott, H. P. Blom, T. B. Marder, R. T. Baker, J. C. Calabrese, *Inorg. Chem.* **1993**, *32*, 2175.

[7] J. G. Hartley, L. M. Venanzi, D. C. Goodall, *J. Chem. Soc.* **1963**, 3930.

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