Contribution to the Chemistry of Boron, 240[◇]

Studies on Benzo-1,3,2-diphosphaborolanes, Benzo-1,4,2,3-diphosphadiborinanes and Benzo-1,5,2,3,4-diphosphatriborepanes☆

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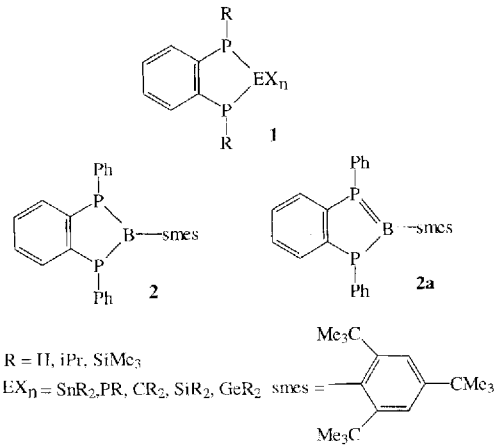
A series of benzo-1,3,2-diphosphaborolanes $C_6H_4(PR)_2BR'$ (R = H, *i*Pr, $SiMe_3$; R' = R_2N, R) has been prepared by several routes and characterized by spectroscopic and – in part – by X-ray diffraction methods. They feature pyramidal P atoms with the substituents in antiperiplanar positions. The P atoms act as coordination sites for the $(CO)_5Cr$ fragment. In contrast to the R_2N-bearing benzo-1,3,2-diphosphaborolanes, the derivative $C_6H_4(PH)_2BCMe_3$ (**4f**) dimerizes by additional B–P bond formation to produce a pentacyclic system $(\mathbf{4f})_2$. – The reaction of $C_6H_4(PHNa)_2$ with $B_2(NMe_2)_2Cl_2$ in THF/hexane yields the acyclic phosphanylborane $Me_2NB(PH{-}C_6H_4PH_2)_2$ (**15**). However, if $C_6H_4[P(iPr)Li]_2$ is allowed to react with $B_2(NMe_2)_2Cl_2$, the benzo-1,4,2,3-diphosphadiborinane **13** is obtained, together with its rearrangement product 2-bis(dimethylamino)borylbenzo-1,3,2-diphosphaborolane **14** which dimerizes to $(\mathbf{14})_2$. – In contrast, the almost planar ring of the 2,3-dimesitylbenzo-1,4,2,3-diphosphadiborinane (**16**) possesses P and B atoms with a planar geometry. Short B–B and B–P bonds suggest that this new heterocycle can be regarded as a 6π electron system. Moreover, the benzo-1,5,2,3,4-diphosphatriborepane **18** forms readily from $C_6H_4(PHNa)_2$ and $Br(Me_2N)B{-}B(NMe_2){-}B(NMe_2)Br$ to give a tub-shaped seven-membered $C_2B_3P_2$ ring system with the P atoms in a pyramidal and the B atoms in a planar environment.

Extensive studies by Issleib et al. on *o*-diphosphanylbenzenes revealed that these are versatile reagents allowing an easy access to a wide variety of benzo-2,1,3-heteroatomdiphospholanes **1**[2]. These heterocycles are of interest not only from the point of view of their remarkable chemical stability, but also with regard to conformational considerations. For instance, the Et_2Ge derivative[2a] shows *cis*/*trans* isomerism. To date, the P atoms in compounds of type **1** have been found to be present in pyramidal environments, as has been demonstrated by NMR techniques. An exception seems to be the borane derivative **2**[3]: Here, based on NMR data, in particular two ^{31}P-NMR signals with considerable shift differences (δ = 12.5, 170.7), a bonding situation as depicted in **2a** has been suggested. Although systems featuring B–P double bond characteristics are well known today[4][5][6][7], the bonding in **2a** might be considered unusual as one might expect the π bonding to involve both of the phosphorus atoms. Taking these aspects into account, we regarded a closer study of benzo-1,3,2-diphosphaborolanes and related heterocycles as both interesting and necessary.



Benzo-1,3,2-diphosphaborolanes

Synthesis: According to procedures designed for other benzo-2,1,3-heteroelement diphospholanes[1][8], three different routes have been examined for the synthesis of benzo-1,3,2-diphosphaborolanes: (i) reactions of the disodium salt of *o*-diphosphanylbenzene, (ii) reactions of the dilithio derivatives of *o*-diphosphanylbenzenes, and (iii) reactions of *o*-bis(trimethylsilylphosphanyl)benzene[2b] with boron dihalides of type R_2NBCl_2, RBX_2 $B_2(NMe_2)_2Cl_2$, $B_2mes_2Cl_2$, and $B_3(NMe_2)_3X_2$ (X = Cl, Br).

According to ^{11}B-NMR data, reactions described by eqs. 1 and 2 proceed quantitatively or almost quantitatively, as shown by the disappearance of the signal for the boron dihalides. However, following the reactions, the ^{31}P-NMR

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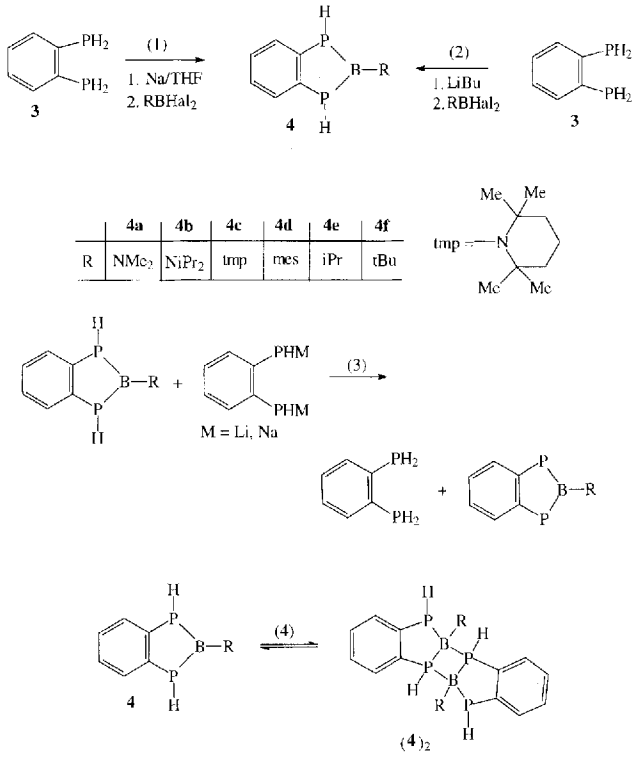
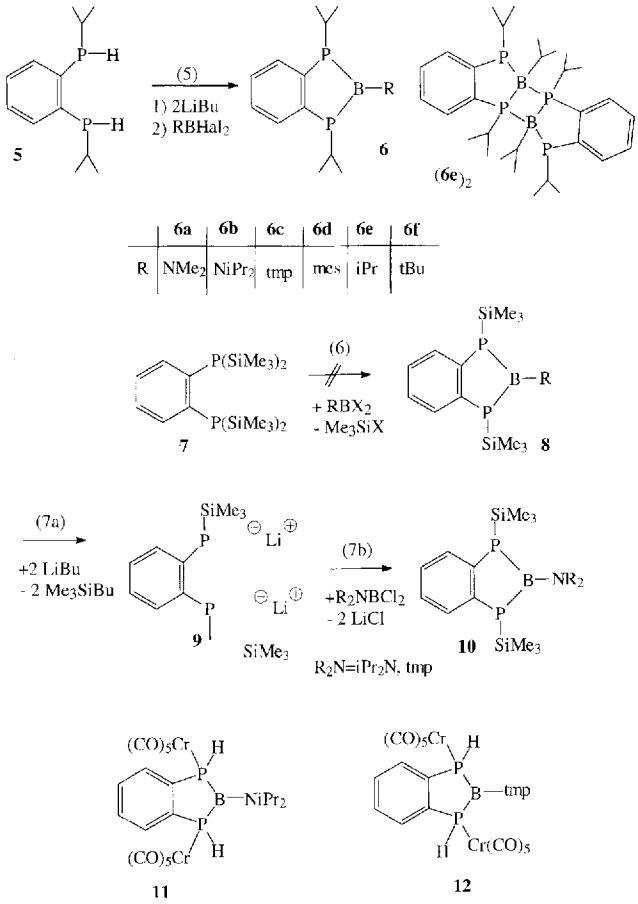
spectra of the solutions invariably indicate the presence of **3**. Its formation was suppressed to a considerable extent, although not completely, when metallated **3** is added to the boron dihalide. We attribute the formation of **3** to a reaction according to eq. 3. It suggests a proton transfer from compounds **4** to the alkali metal salts of **3**, which possess rather basic centers at the P atoms. This process has been checked by allowing **4b** to react with $C_6H_4(PHNa)_2$ in THF, whereupon ^{31}P-NMR spectra show a clean formation of **3**.



Reaction (3) reduces the yield of compounds **4**, and, indeed, the derivatives **4b** and **4c** were obtained only in moderate yield. Moreover, the dimethylamino derivative **4a** could only be characterized in situ by NMR spectroscopy, since after removal of the solvent the solid product that remained proved to be insoluble in THF, toluene or hexane. Furthermore, the mesityl derivative **4d** could not be obtained. Mesitylboroxine $(mesBO)_3$[9] was isolated instead as the only boron-containing material. This boroxine cannot be the product of ether cleavage by mesitylboron dichloride since THF is not attacked by $mesBCl_2$ under the experimental conditions. Therefore, a reaction intermediate must be responsible for the cleavage since oxygen and moisture were rigorously excluded.

Compounds **4e** and **4f** are unstable as monomers and dimerize to pentacyclic compounds via coordinative B–P bonds as depicted in eq. 4. For these compounds, the equilibrium lies fully on the side of the dimers as far as NMR data are concerned.

In order to avoid the proton transfer according to eq. 3, we used the *o*-bis(isopropylphosphanyl)benzene (**5**) for the synthesis of benzo-1,3,2-diphosphaborolanes of type **6**. Metallation of **5** with butyllithium proceeds smoothly, and this holds also for the further reaction with $RBHal_2$. Acceptable to good yields of the derivatives **6a**, **6c**, and **6e** result, but compounds **6b** and **6d** could not be obtained in a pure state.



It is well known that Si–P bond cleavage by boron halides using silylphosphanes $R_{3-n}P(SiMe_3)_n$ allows the synthesis of phosphanylboranes[10]. However, attempts to adapt this method to *o*-bis(trimethylsilyl)phosphanylbenzene (**7**) in order to achieve the synthesis of **8** proved unsuccessful. No Si–P bond cleavage was observed with $PhBCl_2$, BCl_3, or BBr_3 in hexane[11]; precipitates formed, and the small amount of material left in solution showed only ^{11}B-NMR signals for tetracoordinated boron species. No Me_3SiX was found as a volatile material. Clearly, only addition of the boron halides to **7** occurs at ambient temperature and these adducts are stable in refluxing hexane. Their decomposition at higher temperature has not yet been studied[12].

Attempted syntheses of 2-amino-1,3-bis(trimethylsilyl)-benzo-1,3,2-diphosphaborolanes by allowing **7** to react with two equivalents of BuLi (expected formation of $\{C_6H_4[P(SiMe_3)Li]_2\}$ followed by addition of $tmpBCl_2$ and iPr_2NBCl_2, respectively), also proved to be unsuccessful. ^{11}B-NMR signals at $\delta = 65.4$ and 56.9 indicated the formation of **10**. However, the ^{31}P-NMR spectra showed many signals, indicating that no straightforward reactions had occurred, and no pure compound of type **10** could be obtained by fractional crystallization.

It should be possible to use benzo-1,3,2-diphosphaborolanes as ligands. In this context, an interesting question that arises is whether one P atom or both P atoms would add a $Cr(CO)_5$ fragment. It is also of interest to see how the structure of the ligand changes upon coordination. **4b** as well as **4c** react with $THF \cdot Cr(CO)_5$ to give the bis(pentacarbonyl)chromium complexes **11** and **12**, without undergoing a change of configuration at the P atom. This is evident from an X-ray structure analysis of **12**.

NMR Spectra: The results of NMR-spectroscopic investigations on the benzo-1,3,2-diphosphaborolanes are given in Table 1 and in the Experimental Section (^1H, ^{13}C). Heterocycles bearing amino groups give rise to signals in a narrow ^{11}B chemical-shift range of $\delta = 54.1-57.3$, with **6c** ($\delta = 64.7$) being an exception. It appears from these data, particularly by comparison with acyclic aminobis(phosphanyl)boranes[13], that the boron nuclei in compounds **4** and **6** are better shielded, and this is probably the consequence of a planar orientation of the R_2N groups, with the BP_2 unit of the five-membered C_2P_2B ring allowing an excellent π overlap of the p orbitals at the boron and nitrogen atoms[13]. This is in line with $\delta^{11}B = 56.1$ reported for 2-dimethylamino-1,3-diphenyl-1,3,2-diphosphaborolane[14][15]. Consequently, the benzo-1,3,2-diphosphaborolanes do not develop a 6π-electron system.

chemical shifts span only a small range ($\delta = -9.7$ to 1.4). Mass spectra (v.i.) show that compounds **4e–4f** and **6e–6f** are also dimeric in the gaseous phase, and two ^{31}P resonances for solutions demonstrate that dimerization occurs by coordinative B–P bonds. The tetracoordinated P atoms are deshielded with respect to the tricoordinated P atoms and show, in addition, a narrower line width.

^{11}B- and ^{31}P-NMR data for **6f** demonstrate a monomer-dimer equilibrium as shown in eq. 4. However, the *B*-alkylbenzo-1,3,2-diphosphaborolanes **4e**, **4f**, and **6e** are present in solution at ambient temperature as dimers only. Not unexpectedly, equilibria as described by eq. 4 are shifted to the side of the monomer with increasing size of the B and P substituents.

Amongst the benzo-1,3,2-diphosphaborolanes, the Me_2N derivative **4a** is the only one that shows two ^{31}P-NMR signals, indicating the presence of two isomers, e.g. pairs of PH groups in peri- and antiperiplanar positions. The more intense signal at $\delta^{31}P = -109.1$ most likely stems from the antiperiplanar isomer, since this configuration is obviously preferred, as is found for all derivatives investigated by X-ray structure analysis.

The ^1H- and ^{13}C-NMR spectra of compounds **4** and **6** are in accord with the proposed structures, but the ^1H-NMR spectra are not of first order. Moreover, there are

Table 1. ^{11}B- and ^{31}P-NMR data for benzo-1,3,2-diphosphaborolanes; all spectra were recorded in C_6D_6; numbers in parentheses give the width at half-height of the signals in Hz

	R	R′	$\delta^{11}B$	$\delta^{31}P$		R	R′	$\delta^{11}B$	$\delta^{31}P$
4a	H	NMe_2	57.2 (194)	−107.4 −109.1	**6c**	*i*Pr	tmp	64.7 (427)	−3.4
4b	H	$NiPr_2$	54.1 (206)	−103.3	**6d**	*i*Pr	mes	68.8 (230)	24.1
4c	H	tmp	56.3	−88.6	**6e**	*i*Pr	*i*Pr	1.4 (210)	23.5 (140) −8.1 (50)
4e	H	*i*Pr	−4.9 (215)	−40.4 (180) −73.2 (55)	**6f**	*i*Pr	*t*Bu	87.0 (213) −5.5 (76)	−8.4 (240) 16.1 (90) −3.4 (30)
4f	H	*t*Bu	−9.7 (200)	−28.8 (145) −75.4[a] (41)					
6a	*i*Pr	NMe_2	56.1 (260)	−21.2	**11**	H	$NiPr_2$	49.9 (506)	−49.1
6b	*i*Pr	$NiPr_2$	57.3 (245)	−18.5	**12**	H	tmp	50.5 (700)	−38.1

[a] d, $^1J(^{31}P^1H) = 194$ Hz.

However, even if we note almost no influence of the R_2N groups or of the P substituents on $\delta^{11}B$, we observe that an increasing size of the amino group causes a deshielding of the ^{31}P nuclei. The differences in deshielding are apparently independent of the P substituents, and are ca. 3.5 and 15 ppm, respectively, for the series $Me_2N > iPr_2N >$ tmp. Possibly, the steric effect of the amino group changes σ bonding parameters at the P atoms, and this effect is of course most pronounced for the tmp group.

In contrast to the *B*-amino-substituted compounds, the *B*-organyl derivatives **4e–4f** and **6e**, **6f** exhibit ^{11}B resonances for tetracoordinated boron atoms. Once again, these some ambiguities in the assignments, and in some cases the C atoms next to the P atoms of the heterocycle are not observed as a result of severe line broadening. For instance, only one set of ^1H- and ^{13}C-NMR signals is seen for the *i*Pr groups in **4b**. However, two ^{13}C resonances are observed for the methyl groups of the tmp unit in **4c**, each appearing as a pseudo triplet due to PC coupling. This would be consistent with hindered rotation about the B–N bond. However, only a single ^{13}C-NMR signal has been found for the CH_3 groups of **6c**; this and the deshielded ^{11}B nucleus suggests free rotation of the tmp group about its B–N bond at ambient temperature.

"Double sets" of signals are observed for the dimeric *B*-alkyl derivatives because the twofold axis characterizing the symmetry of the monomeric unit is lost upon dimerization. Signals for the C1 atoms are observed for dimeric **4e** and **4f**.

Complexation of **4b** and **4c** with $Cr(CO)_5$ leads to a better shielding of the ^{11}B nuclei by 4.9 and 6.8 ppm for **11** and **12**, respectively. We assume that this is due to the presence of tetracoordinated "phosphonium" P atoms, which enhance electron deficiency at the boron atom, and this, in turn, leads to stronger B−N-π bonding. As expected, the opposite is true for the P atoms. They are deshielded by 54.2 and 50.5 ppm, respectively. The ^1H- and ^{13}C-NMR spectra of **12** support the suggested formula. There are two signals each for the methyl groups of the tmp moiety, and a broad ^1H multiplet for the CH_2 groups. The ^{13}C signals for the aromatic C1 and C6 atoms are too weak to be reliably detected. Two IR bands at $\tilde{\nu}$ = 2069 cm^{-1} and a broad band at 1953 cm^{-1} for the CO groups are consistent with local C_{4v} point group symmetry of the $Cr(CO)_5$ group, assuming that the broad band results from an overlap of two closely spaced bands. The positions of these bands are intermediate between those of $iPr_3PCr(CO)_5$[16] and $Ph_3PCr(CO)_5$[17], demonstrating a similar σ/π donor-acceptor behaviour. Two bands for ν(PH) at 2330 and 2315 cm^{-1} are also characteristic. Compared to the free ligand [ν(PH) = 2277 and 2243 cm^{-1}] these bands indicate a strengthening of the P−H bond due to tetracoordination of the P atoms[18].

IR Spectra: IR spectra of the benzo-1,3,2-diphosphaborolanes are not very diagnostic, with the exception of the P−H stretching frequencies of compound **4**.

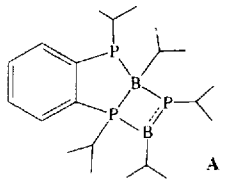
Mass Spectra: The mass spectra show some typical features. Data for the most intense peaks are listed in the Experimental Section, and the assignment of peaks can readily be made by checking the isotopic pattern typical for the $^{10}B/^{11}B$ isotope ratio.

The molecular ions of **4b**, **4c**, and **6a** are the parent peaks. These ions lose CH_3 radicals on fragmentation, as ascertained for $M^{\cdot+}$ of **4b** by a metastable peak. $M^{\cdot+}$ of **4b** also loses an isopropyl fragment, and $[M - CH_3]^+$ of **4b** further decomposes with loss of propene, giving a fairly intense peak at *m/z* (%) = 194 (55) for $C_6H_4(PH)_2B-NH-(CH_2CH_2)$.

In contrast, the molecular ion of the dimethylamino derivative **6a** not only fragments by loss of a CH_3 radical, but also by successive fragmentation of two molecules of propene from the *P*-isopropyl substituents, generating PH-containing ions. However, when the size of the *B*-substituents in monomeric 1,3-diisopropylbenzo-1,3,2-diphosphaborolanes increases then the loss of an *i*Pr fragment from $M^{\cdot+}$ leads to a parent peak $(M - CHMe_2)^+$ for both **6b** and **6c**. Metastable peaks corroborate this fragmentation. In addition, with less probability, $M^{\cdot+}$ species of these compounds lose CH_3 followed by propene.

Two of the dimeric heterocycles, **4f** and **6e**, were also studied. Only **4f** showed the molecular ion, although with only 8% relative intensity. $M^{\cdot+}$ of **4f** readily loses a *tert*-butyl group, but the parent peak is in fact CMe_3^+; thus, a neutral BP-containing species is clearly quite stable. However, whether its formation results from $M^{\cdot+}$ of the dimer or the monomer has yet to be ascertained. $(M/2)^{\cdot+}$ of **4f** is present as a high-intensity peak, reflecting the facile monomerization of $(\mathbf{4f})_2$. The ion $(M/2)^{\cdot+}$ also readily undergoes loss of CMe_3.

No molecular ion was detected for $(\mathbf{6c})_2$ in the 70-eV mass spectrum. It readily disintegrates forming $(M/2)^{\cdot+}$ (28%), and this ion in turn splits off propene. However, a strong peak at *m/z* (%) = 406 (58; 2 B atoms) reveals that $(\mathbf{6e})_2$ must be present in the gaseous phase, at least to a certain extent, because the formation of the peak at *m/z* = 406 can be attributed to a loss of the fragment C_6H_4PiPr from $M^{\cdot+}$ of dimeric **6e**. The high stability of this ion can be explained by the formation of a tricyclic species **A**.

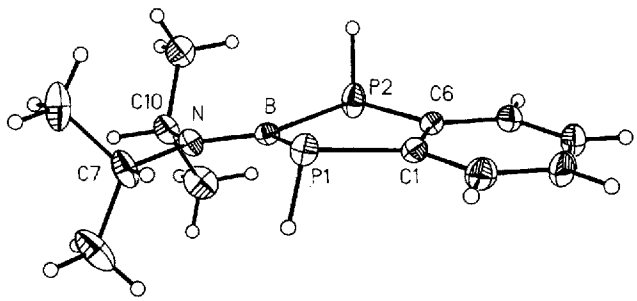


A

In summary, the mass spectra of the benzo-1,3,2-diphosphaborolanes reveal considerable stability of these heterocycles.

Molecular Structures: In order to characterize the structures and conformation of benzo-1,3,2-diphosphaborolanes, the molecular structures of some representative examples were investigated by X-ray structure analysis. Figures 1−6 show the results.

Figure 1. ORTEP representation of the molecular structure of the diisopropylamino derivative **4b**; thermal ellipsoids represent a 25-% probability; estimated standard deviations are given in parentheses[a]



[a] Selected bond lengths [Å]: B−P1 1.936(2), B−P2 1.946(3), B−N 1.381(3), P1−C1 1.828(3), P2−C6 1.823(2), C1−C6 1.409(3), N−C7 1.491(3), N−C10 1.493(3). − Selected bond angles [°]: P1−B−P2 108.5(1), P1−B−N 123.4(2), P2−B−N 128.0(2), B−P1−C1 96.0(1), B−P2−C6 95.8(1), P1−C1−C6 117.9(2), P2−C6−C1 119.0(2), C7−N−C10 114.1(2), C7−N−B 120.8(2), C10−N−B 125.1(2). − Interplanar angles [°]: P1C1C6P2/P1BP2 17.4, P1BP2/C7NC10 2.5.

The C_2P_2B rings of the monomeric heterocycles show only small deviations from planarity. Thus, the angle between the planes BP_2 and P1C1C6P2 varies from 17.4° for **4b**, through 2.6 and 17.1° for the two crystallographically independent molecules of **4c**, to 0.8° for **6c**. However, in the dimer of **4f** this angle is larger (21.1°). In spite of this "close" planarity, there is no delocalization of π-electron

density because the P atoms in all the compounds are present in pyramidal environments, e.g. the lone pairs of electrons at the P atoms are obviously not involved in bonding.

The two B–P bonds in **4b** are of almost equal length and correspond to single bonds between tricoordinated boron and phosphorus atoms[14]. The P–C bond lengths of 1.826(3) Å (average) to the aromatic C atoms are also typical for a $P(\lambda^3)-C(sp^2)$ situation[19]. A short B–N bond [1.381(3) Å] indicates B–N-π bonding and this is supported by the small twist of 2.5° between the planes P_2B and NC_2 of the planar moieties around the B and N atoms. An asymmetry in the two P–B–N bond angles [123.4 and 128.0(2)°] can be rationalized from the orientation of the two isopropyl groups. The Me_2C unit at atom C10 is directed towards atom P2, while it is the H atom at C7 which points in the direction of P1. It is evident that there is an enhanced steric interaction for the first situation, which results in a wider bond angle.

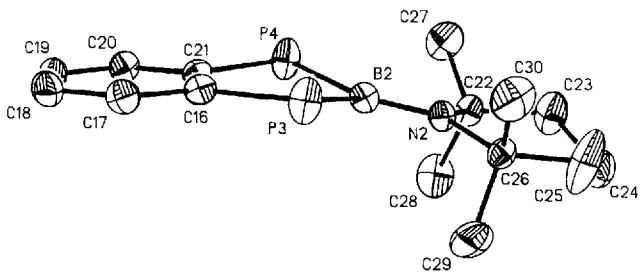
An antiperiplanar orientation of the phosphane hydrogen atoms is another structural feature of **4b**. If its structure were to remain in solution, then four chemically and magnetically non-equivalent CH_3 groups would be detectable by NMR. Since only a single signal is observed in the ^1H- and ^{13}C-NMR spectra, we must conclude that free rotation about the B–N bond occurs in solution.

According to the X-ray structure determination of the tetramethylpiperidino derivative **4c**, there are two molecules in the asymmetric unit of the monoclinic unit cell, space group *P*2(1)/*c*. Figure 2 shows one of these two molecules, which are very similar as far as bonding parameters are concerned. However, they differ significantly in their conformation. Thus, the interplanar angle between the C_2P_2 and P_2B planes on the one hand, and the P_2B and NC_2 planes on the other, are 2.6 and 12.5° for molecule (a) (shown in Figure 2), and 17.1 and 4.3° for molecule (b), respectively. Since the positions of the phosphane hydrogen atoms could not be reliably determined, it remains an open question as to which isomer is present[20].

Compared with the structural parameters of **4b**, the B–P bonds in **4c** are somewhat longer (average 1.97 Å) and the P–C bonds slightly shorter (average 1.80 Å). The higher symmetry of the tmp ligand compared with the $NiPr_2$ group in **4b** is reflected in equal P–B–N bond angles [av. 127.5(2)°]. Somewhat more acute P–B–P bond angles in **4c** compared with those in **4b** [average 104.9(4) vs. 108.6(1)°] probably result from stronger steric interaction of the tmp's CH_3 groups with the PH units.

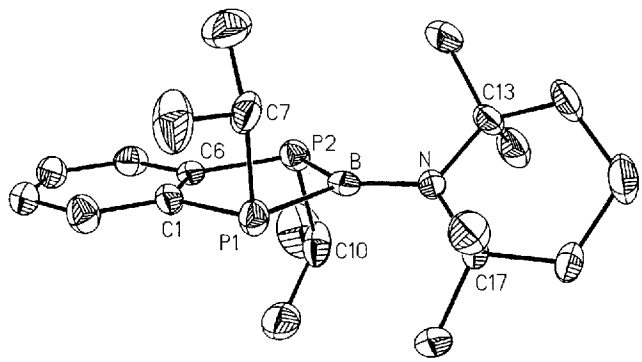
The antiperiplanar orientation of the P substituents is once again demonstrated by the molecular structure of compound **6c** (see Figure 3). B–P bond lengths are similar to those in **4c**, and the P–C bonds are equal to those in **4b**. As expected, the P–C bond to the aliphatic substituent is longer (av. 1.87 Å)[19] than that to the aromatic C atoms (1.83 Å). In contrast to **4b** and **4c**, we note a significantly longer B–N bond [1.418(6) Å], and, most notably, an interplanar angle of 35.2° between the NC_2 and the P_2B planes. Due to this twisting, B–N-π overlap is no longer optimal, resulting in a reduced bond order for the B–N bond. It is evident that this twisting results from steric interaction of the tmp's CH_3 groups with the *i*PrP group, even if the CH part of the isopropyl group points into the direction of the tmp ligand. In contrast to **4c**, where the half-chair conformation is present, the tmp ligand adopts a twist conformation.

Figure 2. ORTEP representations of one (b) of the two independent molecules of the tetramethylpiperidino derivative **4c**; thermal ellipsoids represent a 25-% probability[a]



[a] Selected bond lengths [Å] for (a): B1–P1 1.976(8), B1–P2 1.964(8), P1–C1 1.808(7), P2–C6 1.813(7), B1–N1 1.39(1), N1–C7 1.522(8), N1–C11 1.532(8); (b): B2–P3 1.964(8), B2–P4 1.962(8), P3–C16 1.807(7), P4–C21 1.799(7), B2–N2 1.39(1). – Selected bond angles [°] for (a): P1–B1–P2 105.2(4), P1–B1–N1 127.1(5), P2–B1–N1 127.7(5), B1–P1–C1 98.9(3), B1–P2–C6 99.0(3), C7–N1–C11; (b): P3–B2–P4 104.6(4), P3–B2–N2 127.4(5), P4–B2–N2 128.0(5), B2–P3–C16 98.3(3), B2–P4–C21 98.2(3). – Interplanar angles [°] for (a): P1C1C6P2/P1B1P2 2.6, P1B1P2/C7N1C11 12.5; (b): P3C16C21P4/P3B2P4 17.1, P3B2P4/C22N2C26 4.3.

Figure 3. ORTEP representation of the molecular structure of the tetramethylpiperidino derivative of **6c**; thermal ellipsoids are represented at a 25-% probability level[a]

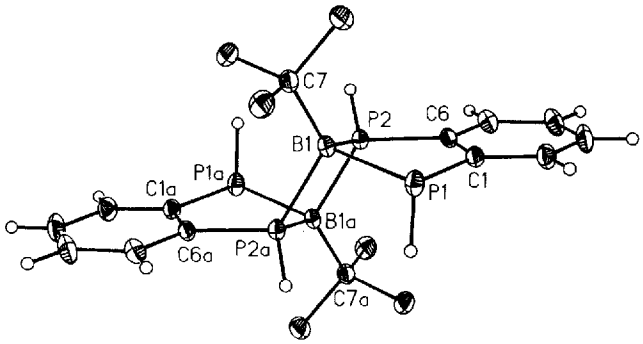


[a] Selected bond lengths [Å]: B–P1 1.948(7), B–P2 1.946(7), P1–C1 1.835(5), P1–C7 1.881(6), P2–C6 1.824(5), P2–C10 1.868(7), C1–C6 1.393(7), B–N 1.418(6). – Selected bond angles [°]: P1–B–P2 109.9(4), B–P1–C1 95.0(4), B–P2–C6 96.3(4), P1–C1–C6 120.5(6), P2–C6–C1 118.2(5), P1–B–N 125.0(5) P2–B–N 126.2(5), B–P1–C7 99.7(3), B–P2–C10 100.5(3). – Interplanar angles [°]: P1C1C6P2/P1BP2 = 0.4, P1BP2/C13NC17 35.2. – Sum of bond angles [°]: B 360.0, P1 296.3, P2 298.2.

Figure 4 depicts the molecular structure of dimeric **4f** and the ladder-type structure of its pentacyclic molecule. In each of the two "molecular halves", we again find an antiperiplanar orientation of the *P*-substituents. $(\mathbf{4f})_2$ crystallizes from hexane in the triclinic system, space group $P\bar{1}$ with $Z = 1$. The molecule, therefore, has a crystallographically imposed center of symmetry. There are two pairs of symmetry-equivalent B–P bonds in the four-membered ring, with bond lengths of 1.981(3) and 1.996(3) Å. Surpris-

ingly, the B1–P1 bond exceeds these slightly [2.013(3) Å], although the P1 phosphorus atom is tricoordinated.

Figure 4. ORTEP representation of the molecular structure of dimeric 2-*tert*-butylbenzo-1,3,2-diphosphaborolane $(\mathbf{4f})_2$; thermal ellipsoids are depicted at a 25% probability level[a]



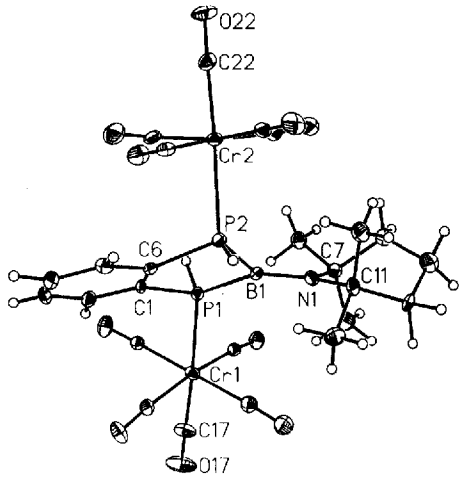
[a] Selected bond lengths [Å]: B1–P1 2.013(3), B1–P2 1.981(3), B1–P2a 1.996(3), B1–C7 1.615(4), P1–C1 1.842(3), P2–C6 1.816(3), P1–H1 1.34(3), P2–H2 1.26(3). – Selected bond angles [°]: P1–B1–P2 98.7(1), P1–B1–P2a 103.9(2), P1–B1–C7 114.1(2), P2–B1–C7 124.0(2), P2a–B1–C7 122.9(2), B1–P1–C1 99.9(1), B1–P1–H1 101(1), C1–P1–H1 97(1), P1–C1–C6 119.0(2), C1–C6–P2 113.7(2), B1–P2–C6 104.0(1), B1a–P2–H2 117(1), C6–P2–H2 102(1). – Interplanar angles [°]: B1P1B1aP1a/P1B1P2 –76.2, C1–C6/B1P1P2 21.1. – Torsion angles [°]: P1C1C6P2 1.4, P1B1P2C6 –19.9.

The hydrogen positions for the PH units have been found experimentally but on refinement they led to shorter distances [1.26(3), 1.34(3) Å] than expected for P–H bonds[21].

Figure 5 shows a stereo view of the unit cell and the packing of the molecules. It is apparent that the packing of the molecules is primarily determined by the planar benzodiphosphaborolane units.

the Cr atom leads to a lengthening of the B–P and P–C bonds due to the tetracoordination of the P atoms (average Δ = 0.022 Å for B–P and 0.019 Å for P–C). However, there is no noticeable difference in the lengths of the B–N bonds. In contrast to compound **4c**, the PH hydrogen atom could be unambiguously located.

Figure 6. ORTEP plot representation of the molecular structure of **12**; thermal ellipsoids are represented at a 25% probability level[a]



[a] Selected bond lengths [Å]: P1–B1 1.998(6), P2–B1 1.981(5), P1–C1 1.842(4), P2–C6 1.812(5). B1–N1 1.407(71), Cr1–P1 2.441(2), Cr2–P2 2.420(2), Cr1–C17 1.864(5), Cr2–C22 1.873(5). – Selected bond angles [°]: P1–B1–P2 103.3(3), C1–P1–B1 98.3(2), C6–P2–B1 98.9(2), P1–Cr1–C17 177.0(2), P2–Cr2–C22 176.9(2), P1–B1–N1 129.7(3), B1–N1–C7 116.2(4), B1–P1–Cr1 125.1(2), C1–P1–Cr1 111.7(2), B1–P2–Cr2 114.6(2), C6–P2–Cr2 109.2(2). Interplanar angles [°]: C1–C6/P1C1C6P2 7.5, P1C1C6P2/P1B1P2 17.1, P1B1P2/N1C7aC11b 33.9, C1–C6/P1C1C6P2 7.3.

Figure 5. Stereo view of the unit cell of compound **4f** to demonstrate the packing of the molecules.

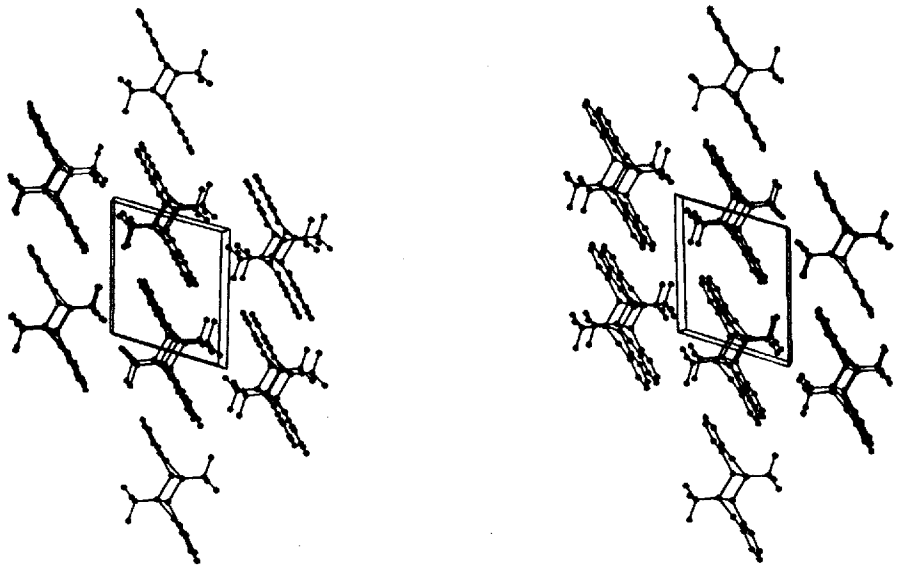


Figure 6 shows the molecular structure of compound **12**, the $Cr(CO)_5$ complex of ligand **4c**. **12** crystallizes in yellow prisms from hexane/toluene mixtures in the monoclinic system. The $Cr(CO)_5$ fragments of the molecule are present, as expected, in antiperiplanar positions. Coordination of

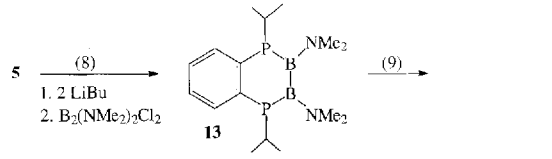
The five-membered BP_2C_2 ring is not planar, as indicated by a 17.1° twist of the P1B1P2 plane with respect to the P1C1C6P2 plane [this corresponds to molecule (b) of ligand **4c**]. Also, the twisting of the tmp group with respect to the P1B1B2 plane (34.0°) is almost the same as in **4c**. Why the

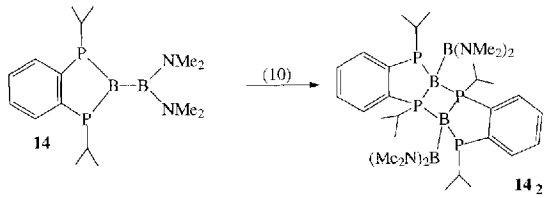
two Cr–P atom distances are significantly different cannot readily be explained. However, similar Cr–P distances have been observed for $Ph_3PCr(CO)_5$[16] and *fac*-$Cr(CO)_4(PEt_3)_2$[17].

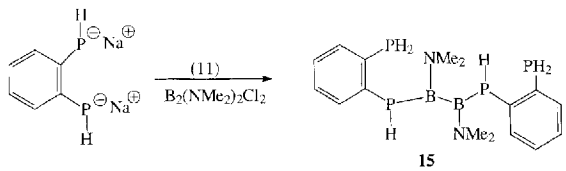
Benzo-1,4,2,3-diphosphadiborinanes and Benzo-1,5,2,3,4-diphosphatriborepanes

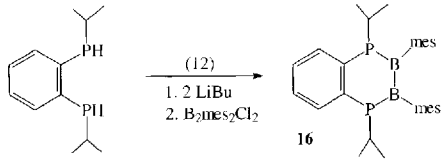
Synthesis: As shown in the previous section, *o*-bis(isopropylphosphanyl)benzene (**5**) proved superior to *o*-bis(phosphanyl)benzene (**3**) for the synthesis of benzo-1,3,2-diphosphaborolanes. Therefore, **5** was used as a building block for the preparation of new BP heterocycles with more than one boron atom.

Dilithiation of **5** followed by reaction with $B_2(NMe_2)_2Cl_2$ is quantitative in accordance with eqs. 8 and 9 as far as LiCl formation is concerned. However, two boron-containing compounds are formed: one with $\delta^{11}B = 53.9$ as the major component (ca. 60%), and a second one with ^{11}B-NMR signals at $\delta = 41.2$ and -14.1 (1:1 ratio). The first one proved to be the expected benzo-1,4,2,3-diphosphadiborinane **13**, while the other was identified as the pentacyclic compound $(\mathbf{14})_2$. We assume that $(\mathbf{14})_2$ forms by rearrangement of **13** to **14**, followed by dimerization of the latter (see eqs. 9 and 10); **13** and $(\mathbf{14})_2$ were separated by fractional crystallization, and were isolated in moderate yields of 20% and 14%, respectively.





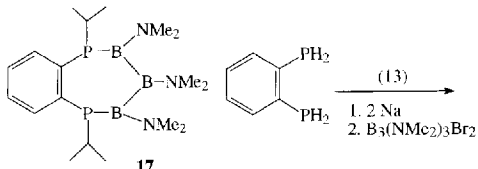


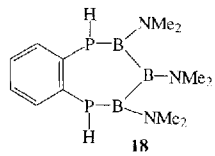


When the same reaction was performed with $C_6H_4(PHNa)_2$ as shown in eq. 11, neither **13** nor $(\mathbf{14})_2$ were formed according to ^{11}B- and ^{31}P-NMR spectroscopy, but rather the bis(phosphanyl)diborane(4) derivative **15**. However, this compound could not be isolated in a pure state, nor did it crystallize. Its characterization is based on NMR data alone, and from these data the structure **15** is derived.

On the other hand, $C_6H_4[P(i\text{Pr})Li]_2$, when treated with $mes_2B_2Cl_2$ according to eq. 12 gave the heterocycle **16** in 53% yield. NMR data of this compound indicate a structure different from that of **13**, and proof of this will be presented later (v.i.).

Attempts to prepare the benzo-1,5,2,3,4-diphosphatriborepane **17** from $C_6H_4[P(i\text{Pr})Li]_2$ and $B_3(NMe_2)_3Cl_2$ failed, although NMR spectra (^{11}B, ^{13}C, ^{31}P) of **17** could be recorded. From its hexane solution, a yellow precipitate forms continuously until the solution is depleted of **17**. Rapid removal of the solvent from solutions of **17** led to a yellow oil (82%), which solidified on attempted redissolution, but was, like the precipitate from the original solution, insoluble in hexane or toluene. The same result was obtained by allowing $B_3(NMe_2)_3Br_2$ to react with $C_6H_4[P(i\text{Pr})Na]_2$. However, a reaction as described by eq. 13 led to the new heterocycle **18** in 56% yield.





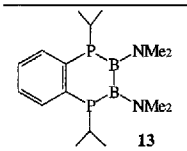
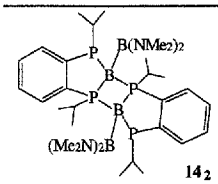
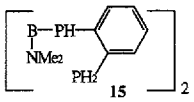
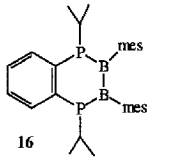
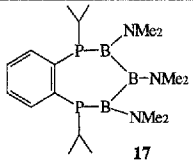
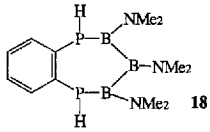
NMR Spectra: ^{11}B- and ^{31}P-NMR data of the benzo-1,4,2,3-diphosphadiborinanes, the benzo-1,5,2,3,4-diphosphatriborepane **18** and the related compounds are compiled in Table 2.

The boron nuclei in **13** are better shielded than in the benzo-1,3,2-diphosphaborolane **6a**, in spite of the fact that a B–B bond is present in **13**. This is somewhat unusual as the ^{11}B resonances of diborane(4) derivatives are generally found at lower field than the corresponding borane derivatives[13]. However, an R_2P group has about the same effect on the shielding of the boron nucleus as a boron atom, as shown by the following data: $\{Et_2NB(PEt_2)_2$: $\delta^{11}B = 50.9$[22]; $Et_2P(Me_2N)B-B(NMe_2)PEt_2$: $\delta^{11}B = 52.9$[23]$\}$. Moreover, the ^{31}P nuclei are also better shielded than in **6a**. This may be due to stronger B–N-π bonding.

$(\mathbf{14})_2$ shows two resonances in the ^{11}B- and ^{31}P-NMR spectra, respectively, and the chemical shifts reveal the presence of both a tricoordinated and a tetracoordinated pair of B and P atoms. These data are consistent with the proposed structure and, particularly, the large line width of the signal at $\delta = 41.5$ is typical of an $(Me_2N)_2B$ group bonded to a boron atom.

For the 1,4-diisopropyl-2,3-dimesityl derivative **16**, almost the same chemical shift $\delta^{11}B$ is noted as for **13**, in spite of the fact that its ^{31}P nuclei are strongly deshielded. Both data provide good evidence of B–P-π bonding. Firstly, the resonance of the boron atom of **16** should be at

Table 2. ^{11}B- and ^{31}P-NMR data (in C_6D_6) for compounds **13** to **18**; half-widths (in Hz) of the signals are given in parentheses

	δ^{11}B	δ^{31}P
 **13**	53.9 (410)	−32.9
 $\mathbf{14}_2$	41.5 (830) −14.2 (350)	33.4 −0.1
 **15**	54.5 (260)	−122.7 −100.6
 **16**	53.1 (760)	68.4
 **17**	55.8 (550)	−34 (237)
 **18**	56.8 (390)	−91.1 (291)

much lower field as compared to **13** because B-bonded aryl groups lead to a deshielding as a consequence of weak or no B−C-π bonding. Secondly, no B−C-π bonding can be expected in **16** for steric reasons: two adjacent mesityl groups will not allow coplanarity of the aryl substituents with the B_2P unit, not even for one of both. Consequently, the comparatively high electron density at the boron atoms as revealed by the δ^{11}B value for **16** must come from π interaction with the phosphorus atoms. The strong deshielding of the nuclei fits with a planar (or almost planar) environment around these atoms, and this has been ascertained by X-ray crystallography (v.i.).

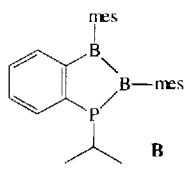
Although one would expect two ^{11}B-NMR resonances each for the triboradiphosphetanes **17** and **18**, only one is observed. This is not unusual for triborane(5) derivatives, as demonstrated by acyclic compounds e.g. $B_3(NMe_2)_3(PPh_2)_2$[23a]. The phosphorus atoms of **17** and **18** are well shielded and are therefore present in a pyramidal configuration. Compared with δ^{31}P for **4a**, there is a deshielding of 17 ppm, which may indicate some differences in the bond angles at these P atoms.

^{1}H and ^{13}C resonances are consistent with the suggested structures for all the boron-rich heterocycles. However, the splitting patterns cannot be explained by first-order rules, particularly for the benzo ring and the isopropyl groups. Nevertheless, the resonances for the Me_2N groups give a clear indication that there is hindered rotation about the B−N bonds in **13** (two ^{1}H and ^{13}C signals), in $(\mathbf{14})_2$ (two ^{1}H and ^{13}C signals) as well as in **17** and **18** (3 signals in a 1:1:1 ratio in the ^{1}H-NMR spectra). These results are supported by two different ^3J(P,C) values for the Me_2N groups, due to *cis* and *trans* orientations of P atoms, and this is of course only possible if there is no rotation about the B−N bond at ambient temperature.

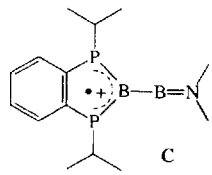
Considering the structure of $(\mathbf{14})_2$, a comparatively complex ^{1}H-NMR spectrum can be expected. Indeed, the signals for the aromatic protons (H2, H3) and the CH proton of the isopropyl group appear as "multisignal peaks", not allowing a resolution of their fine structure. Moreover, the ^{1}H-NMR signals for the methyl groups of the *i*Pr group, which are non-equivalent, are observed as a group of multiplets.

Compound **15** gives rise to one ^{11}B resonance at $\delta = 54.5$ and two ^{31}P resonances. The signal $\delta = -122.7$ appears as a doublet of triplets due to PH and PP coupling [^3J(P,P) = 54 Hz, ^1J(P,H) = 200 Hz], while the signal at $\delta^{31}P = -100.6$ appears as a doublet of doublets [^3J(P,P) = 54 Hz, ^1J(P,H) = 216 Hz]. The former points to the presence of a PH_2 group, while the latter is typical of a PH group. Since the ^{11}B resonance indicates the presence of a diboron unit, the suggested structure seems justified.

Mass Spectra: The molecular entities of compounds **13**, $(\mathbf{14})_2$, **16**, and **18** were ascertained by the observation of the molecular ions. Compared with the benzo-1,3,2-diphosphaborolanes, their stability is less pronounced because the relative intensity was in no case 100%. $M^{\cdot+}$ of **13** fragments in two ways: (i) by loss of $BNMe_2$ to produce the molecular ion of the borolane unit **6a**, and (ii) by loss of an isopropyl radical followed by loss of propene. $M^{\cdot+}$ of $(\mathbf{14})_2$ (15%) on the other hand readily "monomerizes" to the cation of **14**. This is followed by loss of propene and then of Me_2N. Both fragmentations have been ascertained by the observation of the respective metastable peaks. The peak at *m/z* (%) = 248 (41), stemming from a cation containing two boron atoms, may result from a structural unit as shown for **B**.



B



C

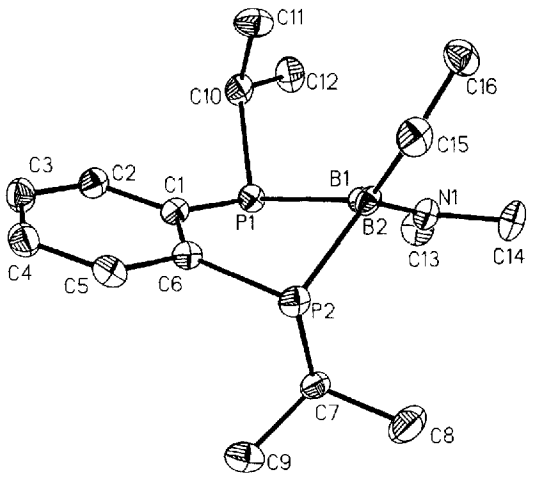
In accord with the proposed structure for **16**, its $M^{\cdot+}$ ion has a relative intensity of 82%, indicating high stability. Three decomposition routes have been observed: (i) $M^{\cdot+}$ loses an *i*Pr radical. This leads to the parent peak [*m/z* (%) = 441 (100), *m** = 401.82]. $(M - i\text{Pr})^+$ then disintegrates with loss of propane, and this fragmentation is ascertained by a metastable ion. (ii) $M^{\cdot+}$ loses P(*i*Pr) by ring contraction, producing a cation of an as yet unknown heterocycle **C** and (iii) finally $M^{\cdot+}$ fragments by loss of CH_3.

A ring contraction is also typical for the radical cation of **18** (35% relative intensity). Loss of a $B_2(NMe_2)_2$ unit, a diborylene, leads to the cation of compound **4a** (13%). In addition, M^{+} decomposes with expulsion of neutral **4a** due to the formation of $B_2(NMe_2)_2$ as a radical cation [*m/z* (%) = 110 (100)], which is the parent peak. Moreover, Me_2N^+ is also formed abundantly (71%).

X-ray Structures: As already indicated, compounds **13** and $(\mathbf{14})_2$ are formed by the interaction of $C_6H_4[P(i\text{Pr})Li]_2$ with $B_2(NMe_2)_2Cl_2$. It was of interest to compare the conformation of **13** with **16** and to ascertain the structure of $(\mathbf{14})_2$ by X-ray structure analysis.

The molecular structure of **13** is shown in Figure 7; **13** is a yellow compound crystallizing triclinically in the space group $P\bar{1}$. A view along the boron–boron bond reveals a non-planar $B_2P_2C_2$ ring system having a twist conformation. The B–P bonds lie in the range for single bonds [av. 1.966(8)Å], similar to those of **6a**, while the B–B bond length [1.691(8)Å] is typical for electron-precise diborane(4) derivatives[23a][24]. There seems to be some slight asymmetry in the bond lengths within the benzene ring, but the significance of this observation may be questionable.

Figure 7. The molecular structure of 1,4-diisopropyl-2,3-dimethylaminobenzo-1,4,2,3-diphosphadiborinane (**13**) in ORTEP representation; thermal ellipsoids represent a 25-% probability[a]

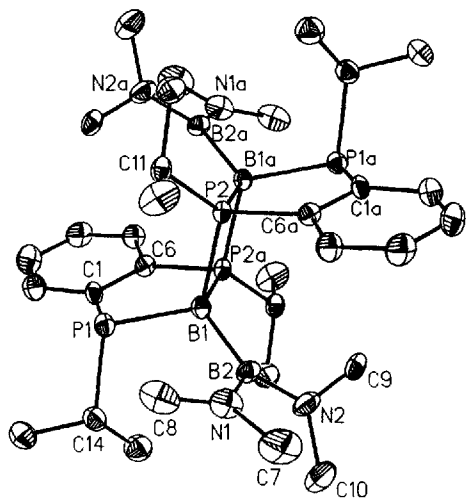


[a] Selected bond lengths [Å]: P1–B1 1.968(7), P2–B2 1.964(8), B1–B2 1.691(8), P1–C1 1.833(7), P1–C10 1.877(7), P2–C6 1.850(7), P2–C7 1.872(6), B1–N1 1.392(9), B2–N2 1.396(7). – Selected bond angles [°]: P1–B1–B2 116.0(5), P1–B1–N1 118.1(4), B2–B1–N1 124.9(5), P2–B2–B1 110.3(4), P2–B2–N2 120.6(4), B1–B2–N2 129.0(6), B1–P1–C1 104.8(3), B1–P1–C10 102.6(3), C1–P1–C10 101.8(3), B2–P2–C6 96.2(3), B2–P2–C7 102.1(3), C6–P2–C7 101.2(3). Interplanar angles [°]: C_1–C_6/P1C1C6P2 4.5, P1C1C6P2/P1B1B2 26.2, P1C1C6P2/P2B2B1 70.0, P1B1B2/N1C7C8 14.4, P2B2B1/N2C9C10 174.9 – Torsion angle [°]: P1B2P2 –53.3.

The B–N bonds are short and, in conjunction with the coplanarity of the C_2N unit with the respective B_2P plane, demonstrate the double-bond characteristics of these bonds. Compared with benzo-1,3,2-diphosphaborolanes, the endocyclic angles at the boron atoms are in this case closer to 120°, as shown by values of 116.0(5) and 110.3(4)°. However, this also demonstrates the asymmetry of the $C_2P_2B_2$ six-membered ring system as shown additionally by two rather sharp endocyclic C–P–B bond angles of 104.8(1) and 96.2(3)°, respectively. Moreover, the sum of bond angles of the two P atoms differs by 10°, and the pyramidal environment at P1 is slightly flatter than at P2. In solution, this asymmetry is lost according to NMR data, thus suggesting that the distortions are due to packing effects in the lattice.

Figure 8 depicts the molecular structure of compound $(\mathbf{14})_2$. It demonstrates that a rearrangement of **13** into a 2-boryl-substituted benzo-1,3,2-diphosphaborolane **14** has occurred, and that this monomer has dimerized by the formation of pairs of B–P-coordinative bonds. However, the B–P bonds to the tetracoordinated boron atoms and the tetracoordinated P atoms are almost of the same length [1.998(7) and 2.018(7) Å], although the somewhat longer bond corresponds to the coordinated B–P bond. The B–P bonds between the tetracoordinated boron atoms and the tricoordinated P atoms [1.978(7) Å] are distinctly shorter.

Figure 8. The molecular structure of the dimeric 2-bis(dimethylaminoboryl)-1,3-diisopropylbenzo-1,3,2-diphosphaborolane $(\mathbf{14})_2$; thermal ellipsoids represent a 25-% probability; hydrogen atoms are omitted for clarity[a]



[a] Selected bond lengths [Å]: P1–B1 1.978(7), B1–P2a 1.998(7), P2–B1 2.018(7), B1–B2 1.744(9), P1–C1 1.826(6), P1–C14 1.888(7), P2–C6a 1.840(6), P2–C11 1.863(6), B2–N1 1.45(1), B2–N2 1.45(1). – Selected bond angles [°]: P1–B1–P2a 103.2(3), B1–P1–C1 100.2(3), P1–B1–P2 112.4(3), P1–B1–B2 115.5(4), B1–P1–C14 106.6(3), C1–P1–C14 102.3(3). – Interplanar angles [°]: P1C1C6P2a/P1B1P2a 2.6, C_6C_4/P1B1P2a 9.1, P1B1P2a/P2B1aP2a 51.1, B2N1N2/P2B1aP2a 81.8, B2N1N2/N1C7C8 22.9, B2N1N2/N2C9C10 137.5, N1C7C8/N2C9C10 123.5.

Although the B–B bond length of 1.744(9) Å lies at the long end of the range for B–B bonds for electron-precise polyboranes[24][25], this might be due to the fact that one of the boron atoms is tetracoordinated. The B–N bond lengths of 1.42(1) and 1.45(1) Å are definitely longer than in **13**, but are in accord with the presence of a bis(dimethylamino)boryl unit, for which a B–N bond order of 1.5 may be expected, provided that both C_2N planes of the amino group are coplanar with the N_2B_2 plane. Steric interaction between the CH_3 groups, however, prevents this arrange-

ment, and this leads to interplanar angles of 137.5° (= 42.5°) for $N2C_2$ and 22.9° for $N1C_2$.

On inspection of the benzo-1,3,2-diphosphaborolane units in $(\mathbf{14})_2$, it is apparent that these seem to be planar, and, indeed, the P1C1C6P2a plane is twisted with respect to the P_2B plane by only 2.6°. Due to the crystallographic inversion center – located at the center of the four-membered B_2P_2 ring – the "monomeric" units are packed parallel to one another, and the B_2P_2 ring plane forms an angle of 108.9° with the C6P2B1P1 plane.

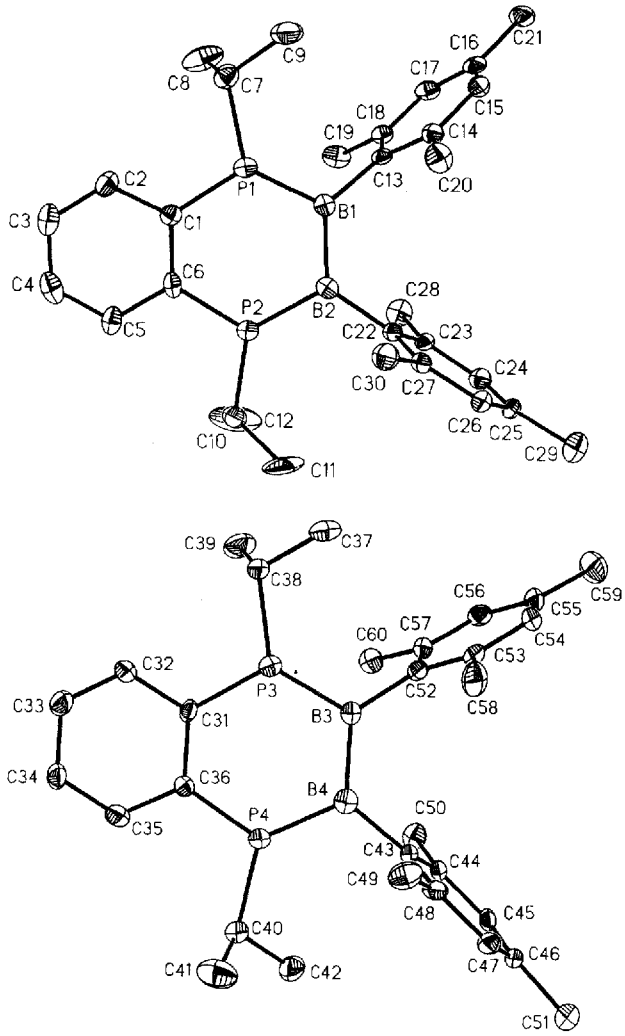
A totally different structure is found for the molecule **16**, as shown in Figure 9. The orange-colored compound crystallizes triclinically in space group $P\bar{1}$ with two independent molecules [(a) and (b)] in the asymmetric unit. Bond lengths and bond angles in these molecules are not significantly different, but the conformations are not alike. The most striking feature of **16** is the "planarity" of the phosphorus atoms, as shown by the sum of bond angles of 357.3° for P1, 359.3° for P2, 358.6° for P3, and 359.9° for P4. Short B–B bonds [1.682(9) and 1.660(8) Å] are complemented by short B–P bonds [av. 1.807(7) Å for (a), 1.817(9) Å for (b)] and this corresponds to a reduction of the B–P bond lengths by 0.16 and 0.15 Å, respectively, compared with those of the dimethylamino derivative **13**. This indicates B–P-π bond characteristics for the B–P bonds in **16**, since the contraction of the bond is larger than would be expected simply for a change in hybridization at the P atoms from p^3 to sp^2[26]. On average, the P–C bond length to the aromatic carbon atom changes by 0.066 Å compared to compound **13**, and this shortening of the bond length corresponds approximately to the change in the effective radius of the P atoms in **16**, supporting the conclusion that B–P-π bonding is present in these molecules. In addition, the endocyclic bond angles at the P atoms are close to 120°, while those at the boron atoms are about 116°. However, the $C_2P_2B_2$ ring system is not fully planar as might be expected for the benzo-1,4,2,3-diphosphadiborinane, which may be considered as being a naphthalene analogue. For both molecules of **16**, twisting of the P_2B_2 moiety with respect to the benzene ring is apparent, and the corresponding torsion angles PBBP are 18 and 16.4°, respectively. Thus, the deviation from planarity is not a marked one.

All boron atoms in **16** are in planar environments, but there is no B–C-π bonding because the mesityl groups are oriented almost orthogonally to the respective B_2P planes [83.8 and 80.4° for (a), 99.3 and 97.3° for (b)]. Moreover, it is interesting to note that one methyl group of each *i*Pr group is oriented towards an adjacent phenyl group (see Figure 9).

A view of the molecular structure of the triborane(5) derivative **18**, the 2,3,4-tris(dimethylamino)benzo-1,5,2,3,4-diphosphatriborepane, is presented in Figure 10. Its seven-membered $C_2P_2B_3$ unit shows a tub-type conformation with folding angles to the P1C1C6P2 plane of only 24° for the benzene ring, but of 49.2° for the B1B2B3 plane.

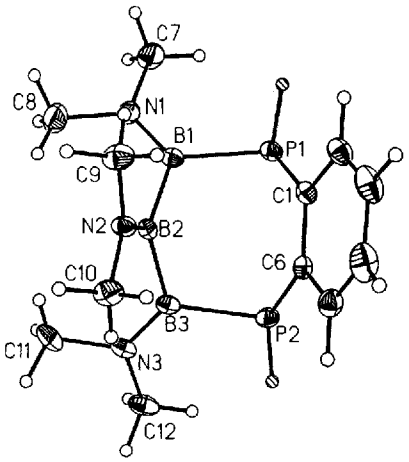
B–P bond lengths correspond to single bonds, and the B–B distances are as expected[25]. All the B–N bond lengths are very similar, the average being 1.394 Å. This is in the range for significant B–N-π bonding and, indeed, the C_2N planes are almost coplanar with the PB_2 (5.5, 7.2°) and B_3 (16.7°) planes, respectively. Furthermore, molecule **18** shows a typical feature for electron-precise polyboranes: the orthogonality between pairs of adjacent Me_2NB groups[25]. The specific values are N1C7C8/N2C9C10

Figure 9. View of the molecular structures of the two independent molecules [top: (a); bottom: (b)] of **16**; thermal ellipsoids represent a 25-% probability[a]



[a] Selected bond lengths [Å] for (a): B1–P1 1.808(6), B2–P2 1.809(5), B1–B2 1.686(7), P1–C1 1.770(5), P2–C6 1.767(5), P1–C7 1.842(5), P2–C10 1.841(5), B1–C13 1.583(7), B2–C22 1.585(7), C1–C6 1.467(7); (b): B3–P3 1.813(5), B4–P4 1.810(6), B3–B4 1.671(7), P3–C31 1.774(5), P4–C36 1.777(5), P3–C38 1.837(5), P4–C40 1.845(5), B3–C52 1.587(7), B4–C43 1.592(7), C31–C36 1.417(6). – Bond angles [°] for (a): B1–P1–C1 120.7(2), B2–P2–C6 121.6(2), P1–B1–B2 115.3(3), B1–B2–P2 115.7(4) P1–C1–C6 122.2(4), P2–C6–C1 121.2(4), B1–B2–C22 126.0(4), B2–B1–C13 117.5(4), B1–P1–C7 125.7(2), B2–P2–C10 125.3(3); (b): B3–P3–C31 121.1(2), B4–P4–C36 121.1(2), P3–B3–B4 115.2(3), P4–B4–B3 116.6(3), P3–C31–C36 122.1(3), P4–C36–C31 121.5(3), B3–B4–C43 127.1(4), B4–B3–C52 125.0(4). – Interplanar angles [°] for (a): C1–C6/P1B1B2 19.5, C1–C6/ P2B2B1 13.2, P1B1B2/P2B2B1 18.0, B1B2P2/C22–C27 99.4, P1B1B2/C13–C18 83.8; (b): C31–36/P3B4 15.9, C31–C36/B3B4P4 9.4, P3B3B4/P4B4B3 16.3, B4B3P3/C52–57 99.3, B3B4P4/C43–C48 97.3.

Figure 10. The molecular structure of the benzo-1,5,2,3,4-diphosphatriborepane **18**; thermal ellipsoids are represented with a 25-% probability[a]

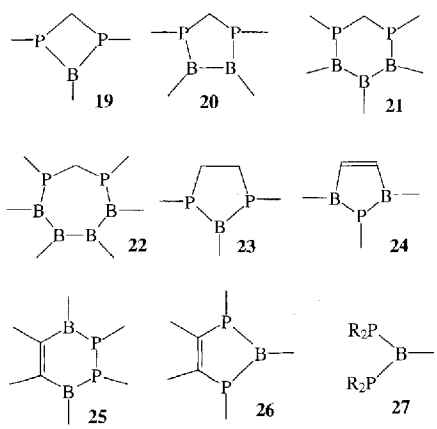


[a] Selected bond lengths [Å]: P1–B1 1.961(5), B1–B2 1.705(5), B2–B3 1.694(6), B3–P2 1.966(5), P2–C6 1.835(4), C1–C6 1.407(5), C1–P1 1.834(4), P1–H1 1.32(4), P2–H2 1.32(4), B1–N1 1.400(5), B2–N2 1.391(5), B3–N3 1.391(5). – Selected bond angles [°]: P1–B1–B2 112.7(3), B1–B2–B3 115.1(3), B2–B3–P2 112.0(3), B3–P2–C6 100.6(2), P2–C6–C1 120.8(3), C6–C1–P1 120.6(3), C1–P1–B1 100.3(2), C1–P1–H1 97(2), B1–P1–H1 99(2), C6–P2–H2 96(2), B3–P2–H2 98(2), P1–B1–N1 120.9(3), B2–B1–N1 126.1(3), B1–B2–N2 121.3(3), B3–B2–N2 122.3(3), B2–B3–N3 127.0(4), P2–B3–N3 120.6(3). – Interplanar angles [°]: C1–C6/P1C1C6P2 2.4, P1C1C6P2/B1B2B3 49.2, P1B1B2/N1C7C8 5.5, B1B2B3/N2C9C10 16.7, P2B3B2/N3C5C 7.2, N1C7C8/N2C9C10 97.5, N2C9C10/N3C11C12 97.7.

97.5°, N2C9C10/N3C11C12 97.7°. This conformation, the tub-form of the seven-membered ring and the comparatively long P–C bonds [1.835, 1.834(4) Å] demonstrate that there is no electron delocalization in this ring system.

Discussion

BP heterocycles containing carbon atoms in the ring system have attracted attention only in recent years. Typical examples are the four-membered 1,3,2-diphosphaboretanes **19**[15], as well as the five-, six- and seven-membered species **20**, **21**, and **22**, having in common the PCP unit[15][26]. Interesting heterocyclic systems are those of the 2,5-dihydro-1*H*-1,2,5-phosphadiborole **24**[27] and the saturated 1,3,2-diphosphaborolanes **23**[15].



1,2,3,6-Tetrahydrodiphosphadiborines **25** are particularly interesting because they are potential candidates for a delocalized 6π-electron system containing P atoms in a planar geometry. However, to date only *B,B'*-dialkylamino derivatives are known, and strong B–N-π bonding obviously prevents the 6π-electron delocalization[27].

Benzo-1,3,2-diphosphaborolanes contain the structure elements of the as yet unknown 1,3,2-diphosphaboroles **26** and of diphosphanylboranes **27**. There is ^{31}P-NMR evidence that in the case of **27** (R = *t*Bu; R' = Et, Me, Br) the pyramidal geometry at the P atoms becomes flatter with increasing Lewis acidity at the boron atom since the P atoms are strongly deshielded (δ = 45.5–51.6)[28]. Therefore, there was a chance that benzo-1,3-diphosphaborolanes might allow the delocalization of π electrons in the presence of suitable substituents.

Both NMR spectra as well as the molecular parameters of the *B*-dialkylamino derivatives of the benzo-1,3,2-diphosphaborolanes **4** and **6** provide clear evidence that the electron pairs at the P atoms are not involved in π bonding. However, δ^{11}B data and, in particular, the B–N bond lengths, are in accord with B–N-π bonding, which strongly reduces the Lewis acidity at the boron center. This is particularly relevant for the Me_2N group and less so for the bulky tetramethylpiperidino group, the NC_2 unit of which cannot be coplanar with the P_2B skeleton in **6c**. The resulting weakening of the B–N bond, as shown by an increase of the B–N bond length to > 1.4 Å, will reduce electron density at the boron atom, but the bulkiness of the tmp ligand will sterically shield the boron center. In no case was there any indication of the formation of a compound akin to **2a**. Considering the result for **15**, one may speculate that **2a** is actually mesB(PPh–C_6H_4–PHPh)$_2$. This would account for the observation of two different ^{31}P-NMR signals.

That the Lewis acidity at the boron atom is considerably increased when R_2N groups are replaced by alkyl groups is demonstrated by compounds **4e**, **4f**, and **6e** which dimerize; the dimer present in the solid state is in equilibrium with its monomer in solution when there are bulky organyl groups present both at B and the P atoms (**6f**). The low-field shift of the P atom in the ^{31}P-NMR spectra for the monomeric units indicates, however, that these atoms may reside in a flat, pyramidal environment. Enlarging the ring to six members indeed leads to an almost planar $C_2P_2B_2$ ring with P atoms in planar or almost planar geometries, as realized in compound **16**. The boron atoms are clearly electron-deficient since their substituent mesityl groups cannot donate π-electron density owing to an almost perpendicular arrangement of these in relation to the $C_2P_2B_2$ ring. Short P–C and B–P bond lengths are compatible with B–P-π bonding, and the 70-eV mass spectrum of **16** provides additional evidence that **16** can be regarded as a 6π-electron system, i.e. as an analogue of naphthalene. Indeed, the bonding parameters are comparable and compatible with the planar six-membered (cyBPmes)$_3$ ring[29], which has short B–P bonds (1.84 Å). The B–P bonds in **16** are actually even shorter than in (cyBPmes)$_3$. In contrast, the non-

benzo system **25** as well as the benzo system **16** have both a non-planar $C_2P_2B_2$ ring and P atoms in pyramidal surroundings. As far as the hetero ring is concerned, compounds **13** and **25** are positional isomers. Both bear amino groups at the boron atom, resulting in strong B−N-π bonding, thus reducing the Lewis acidity at the boron atom. Therefore, there is no chance of B−P-π bonding. Interestingly, the six-membered hetero ring of compound **13** is unstable because the isomer **14** is formed by ring contraction. This generates a rather acidic boron atom, but instead of inducing planarity at the P atoms and leading to formation of a 6π-electron heterocycle, the compound dimerizes to $(\mathbf{14})_2$. This is obviously the better alternative for the system to become more stable. In contrast, no such ring contraction occurs for the seven-membered **18**. Our conclusion is that the formation of BP heterocycles containing planar-coordinated P atoms, and short B−P bonds with double-bond characteristics is only possible if the boron center acts as a strong Lewis acid. At the same time, it must also be sterically shielded in order to prevent dimerization or oligomerization.

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Experimental Section

Schlenk techniques have been used throughout for maintaining an atmosphere of oxygen-free argon or nitrogen. Solvents were dried by conventional methods ($LiAlH_4$, P_4O_{10}, K), distilled and stored under N_2. The *o*-diphosphanylbenzenes were prepared as described[2] as well as Me_2NBCl_2[30], iPr_2NBCl_2[31], $tmpBCl_2$[32], $mesBCl_2$[33], and $RBCl_2$ or $RBBr_2$ (R = Me, *i*Pr, *t*Bu)[34]. The institute's microanalytical laboratory performed all elemental analyses. In the case of sensitive compounds and compounds containing the mesitylboron groups, larger deviations between calculated and observed values resulted. − NMR: Jeol 270 (^{11}B, ^{31}P), Jeol 400 (^1H, ^{13}C), Bruker WP 200 (^{11}B). Standards: C_6D_6, $SiMe_4$, 85% H_3PO_4, $BF_3{\cdot}OEt_2$. − IR: Perkin-Elmer FT (only medium to very strong bands are reported). − MS: Atlas CH7. − X-ray: Siemens R3m and P4, Mo-K_α radiation, graphite monochromator, SHELXR-PLUS and SHELX-93 programs[35].

General Procedure A for Preparing Compounds **4a**−**4c**: *o*-Diphosphanylbenzene was dissolved in anhydrous tetrahydrofuran (20 ml) and two equivalents of elemental sodium pieces were added. Hydrogen evolution started readily from the stirred solution, which turned yellow. Stirring was continued overnight, then any insoluble material was removed by filtration. The filtrate was cooled to −78 °C and the boron halide (1 equiv.), dissolved in hexane (ca. 20 ml), was added. After the resulting suspension had attained ambient temperature, all volatile material was removed in vacuo; 30 ml of hexane was added to the residue, and after stirring for ca. 15 min, the insoluble material was filtered off, and the product was allowed to crystallize from the solution at −30 °C.

2-Dimethylaminobenzo-1,3,2-diphosphaborolane (**4a**): $C_6H_4(PH_2)_2$ (310 mg, 2.4 mmol), Na (110 mg, 4.8 mmol), and Me_2NBCl_2 (280 mg, 2.3 mmol) were treated according to General Procedure A. After the reaction, the filtrate showed ^{31}P-NMR signals for $C_6H_4(PH_2)_2$ besides those of **4a**, while only a single ^{11}B-NMR signal of **4a** (δ = 57) was observed. On cooling, a colorless powder separated within a few hours. It did not dissolve in diethyl ether, THF, hexane or toluene. Neither the yield of this solid nor its analytical data were determined.

2-Diisopropylaminobenzo-1,3,2-diphosphaborolane (**4b**): $C_6H_4(PH_2)_2$ (550 mg, 3.9 mmol), Na (180 mg, 7.8 mmol) and iPr_2NBCl_2 (700 mg, 3.9 mmol) were treated according to General Procedure A. Yield: 420 mg of **4b** (43%) as colorless crystals; m.p. ca. 140 °C (dec.). − ^1H NMR (C_6D_6): δ = 0.99 [5-H, d, ^3J(HH) = 5.4 Hz], 3.32 (4-H), 4.52 [PH, d, ^1J(PH) = 200 Hz], 6.99 (3-H, m, *N* = 13 Hz), 7.64 (2-H, m, *N* = 15 Hz). − ^{13}C NMR (C_6D_6): δ = 22.8 (C-5), 53.4 (C-4), 127.0 (C-3, XX′ part of AA′XX′ spin system, *N* = 8 Hz), 132.1 (C-2, XX′ part), 142.4 (C-1). − IR (Nujol/Hostaflon): $\tilde{\nu}$ = 2965 cm^{-1} (s), 2924 (m), 2869 (m), 2291 (m), 2275 (m), 2258 (m), 1485 (m), 1471 (s), 1444 (s), 1439 (m), 1382 (m), 1368 (s), 1333 (m), 1322 (s), 1184 (s), 1164 (m), 1146 (s), 1138 (s), 1111 (m), 1002 (m), 877 (m), 860 (m), 852 (m), 745 (s), 681 (m), 568 (s). − MS; *m/z* (%): 251 (100) ($M^{\cdot+}$), 236 (77) [$M^{\cdot+}$ − CH_3], *m** = 221.90, 208 (89) [$M^{\cdot+}$ − $CH(CH_3)_2$], 194 (56) [$M^{\cdot+}$ − isopropene − CH_3], 188 (54), 174 (29) [$M^{\cdot+}$ − C_6H_4], 77 (38) [C_6H_4]. − $C_{12}H_{20}BNP_2$ (251.06): calcd. C 57.41, H 8.03, N 5.58; found C 56.95, H 8.28, N 5.37.

2-(2,2,6,6-Tetramethylpiperidino)benzo-1,3,2-diphosphaborolane (**4c**): $C_6H_4(PH_2)_2$ (320 mg, 2.3 mmol), Na (110 mg, 4.8 mmol), and $tmpBCl_2$ (500 mg, 2.2 mmol) were treated according to General Procedure A. Yield: 140 mg (21%), colorless crystals (1st fraction). A second fraction was obtained from the concentrated solution, but the additional yield was not determined; m.p. 92−94 °C. − ^1H NMR (C_6D_6): δ = 1.32 (tmp), 1.38 (tmp), 4.74 [PH, d, ^1J(PH) = 214 Hz], 7.00 (3-H, m, *N* = 17 Hz), 7.63 (2-H, m, *N* = 18 Hz). − ^{13}C NMR (C_6D_6): δ = 15.7 (C-6), 32.7 [C-7, t, ^4J(PC) = 21.0 Hz], 40.5 (C-5), 59.4 (C-4), 126.9 (C-3), 130.5 (C-2), 142.1 (C-1). − IR (Nujol/Hostaflon): ν(= 3048 cm^{-1} (m), 2994 (m), 2966 (s), 2939 (s), 2930 (s), 2870 (m), 2286 (m), 2276 (m), 2247 (m), 1585 (m), 1467 (m), 1458 (m), 1441 (m), 1428 (m), 1388 (s), 1370 (s), 1363 (s), 1341 (m), 1324 (s), 1302 (s), 1293 (s), 1276 (s), 1246 (s), 1231 (s), 1194 (m), 1165 (m), 1125 (s), 1091 (m), 1069 (m), 1044 (m), 1027 (m), 1009 (m), 997 (m), 989 (m), 974 (m), 949 (m), 883 (s), 852 (s), 925 (m), 741 (s), 712 (m), 674 (m), 561 (m). − MS; *m/z* (%): 291 (100) [$M^{\cdot+}$], 276 (79) [$M^{\cdot+}$ − CH_3], *m** = 261.77, 207 (28), 142 (44) [$C_6H_4(PH_2)_2$], 126 (70) [tmp-$H^{\cdot+}$ − CH_3], 109 (68) [$C_6H_4PH_2$]. − $C_{15}H_{24}BNP_2$ (291.12): calcd. C 61.89, H 8.31, N 4.81; found C 62.03, H 8.07, N 4.82.

General Procedure B for Preparing Compounds **4d**−**4f**: *o*-Diphosphanylbenzene was dissolved in hexane (ca. 20 ml/1 mmol). To the stirred solution, a BuLi solution in hexane (1.56 M, 2 equiv.) was added through a dropping funnel. A yellow suspension formed, which was stirred for 14 h at ambient temperature. Subsequently, a hexane solution of the alkylboron dihalide was added; at this stage the yellow suspension turned white. After several hours (1−5 h) the supernatant liquid was checked by ^{11}B-NMR for completeness of the reaction. ^{31}P-NMR spectra invariably showed the signal for $C_6H_4(PH_2)_2$ as a minor constituent. Removal of the solid by filtration and of the solvent from the filtrate led to **4e**−**4f**, which were crystallized from hexane.

Dimeric 2-Isopropylbenzo-1,3,2-diphosphaborolane (**4e**): $C_6H_4(PHLi)_2$ (1.41 mmol) and $iPrBBr_2$ (300 mg, 1.41 mmol) were treated according to General Procedure B. In this case the $iPrBBr_2$ solution was cooled to −50 °C and the phosphide suspension was added. 140 mg of insoluble material was present after stirring for 14 h. A colorless oil was obtained. From its hexane solution no

crystals separated at −30 °C. Attempted distillation led to decomposition at approximately 85 °C/0.01 Torr. The compound was characterized only by NMR methods (before thermal treatment). – NMR (C_6D_6): $\delta^{11}B = -4.9$; $\delta^{31}P = -40.4, -73.2$.

Dimeric 2-tert-Butylbenzo-1,3,2-diphosphaborolane (**4f**): $C_6H_4(PHLi)_2$ (1.2 mmol) and *t*BuBBr$_2$ (280 mg, 120 mmol) were treated according to General Procedure B. A light-yellow oil (290 mg) remained after removal of solvent. On addition of 4 ml of hexane, some solid formed, which was removed by filtration. The yellow filtrate was kept at −18 °C, giving 80 mg (32%) of yellowish, well-formed single crystals; m.p. 181 °C (dec.). – ^{1}H NMR: δ = 0.95 (5-H), 3.73 [PH, dd, ^1J(PH) = 194 Hz, ^3J(PH) = 28 Hz], 4.87 [PH, d, ^1J(PH) = 208 Hz], 6.91 (3-H, m, *N* = 10 Hz), 7.65 (2-H, m, *N* = 9 Hz). – ^{13}C NMR (C_6D_6): δ = 30.2 (C-5), 130.0 (C-3'), 130.6 (C-3), 133.8 (C-2'), 134.3 (C-2), 143.1 (C-1). – IR (Nujol/Hostaflon): $\tilde{\nu}$ = 3063 cm^{-1} (m), 2923 (s), 2950 (s), 2279 (m), 1479 (m), 1464 (s), 1444 (m), 1397 (m), 1375 (s), 1357 (s), 1262 (m), 1202 (m), 1147 (m), 1070 (m), 857 (s), 747 (s). – MS (70 eV); *m/z* (%): 416 (8) [M$^{\cdot+}$], 359 (34) [M$^{\cdot+}$ − *t*Bu], 208 (21) [M$^{\cdot+}$/2], 151 (59) [M$^{\cdot+}$/2 − *t*Bu], 57 (100) [*t*Bu$^+$]. – $C_{20}H_{30}B_2P_4$ (415.96): calcd. C 57.75, H 7.27; found C 56.71, H 7.39.

2-(Dimethylamino)-1,3-diisopropylbenzo-1,3,2-diphosphaborolane (**6a**): According to General Procedure B, $C_6H_4(PHiPr)_2$ (220 mg, 0.97 mmol) was metallated with BuLi (1.25 ml, 1.56 M) and the intermediate thus formed was allowed to react with Me_2NBCl_2 (120 mg, 0.97 mmol). Yield: 110 mg of **6a** (39%), colorless crystals, m.p. 53 °C. A second crop was obtained from the filtrate after concentration. – ^{1}H NMR (C_6D_6): δ = 1.16 (5-H, m, A_3A_3' part of an $A_3A_3'MXX'$, spin system), 2.19 (4-H, m, M part), 2.73 (6-H, NMe_2), 7.08 (3-H, m, AA' part of AA'XX' spin system), 7.65 (2-H, m, AA' part). – ^{13}C NMR (C_6D_6): δ = 23.4 (C-5, pseudo-t, *N* = 6 Hz), 27.8 (C-4, pseudo-t, *N* = 34 Hz), 45.3 [C-6, t, ^3J(P, C) = 10 Hz], 127.3 (C-3, m, XX' part of AA'XX' spin system, *N* = 4 Hz), 133.5 (C-2, m, XX' part), 147.7 (C-1). – IR (Nujol/Hostaflon): $\tilde{\nu}$ = 3049 cm^{-1} (m), 2949 (s), 2923 (s), 2863 (s), 1523 (s), 1509 (s), 1473 (m), 1452 (m), 1443 (s), 1425 (m), 1407 (s), 1381 (m), 1361 (m), 1236 (s), 1190 (s), 1151 (s), 1137 (s), 1097 (m), 1052 (m), 1030 (s), 886 (m), 856 (m), 848 (m), 761 (s), 735 (m), 593 (m), 533 (m), 496 (m), 483 (m). – MS (70 eV); m/z (%): 279 (100) [M$^{\cdot+}$], 264 (4) [M − Me]$^+$, 237 (74) [M − C_3H_6]$^+$, *m** = 201.32, 195 (35) [M − 2 C_3H_6]$^+$, 183 (22) [$C_6H_4(PH)_2iPr$], 132 (40), 70 (56).

1,3-Diisopropyl-2-(tetramethylpiperidino)benzo-1,3,2-diphosphaborolane (**6c**): Procedure B; $C_6H_4(PHiPr)_2$ (330 mg, 1.5 mmol) in 10 ml of hexane, BuLi (2.92 mmol) in 15 ml of hexane, tmpBCl$_2$ (320 mg, 1.5 mmol). Yield: 340 mg of **6c** (62%), yellow-orange crystals from hexane, m.p. 80 °C. – ^{1}H NMR (C_6D_6): δ = 1.00 (5-H, A_3A_3' part of $A_3A'_3MXX'$ spin system, *N* = 19.1 Hz), 1.64 (9-H), 1.81 (7-H, 8-H, m, *N* = 24.4 Hz), 2.19 (4-H, m, *N* = 19.5 Hz), 7.24 (3-H, m, *N* = 16.1 Hz), 7.63 (2-H, m, *N* = 15.2 Hz). – ^{13}C NMR (C_6D_6): δ = 14.1 (C-8), 23.1 (C-5, pseudo-t, *N* = 8 Hz), 28.5 (C-4, m, *N* = 14.8 Hz), 34.5 (C-7), 35.8 (C-9), 58.1 [C-6, t, ^3J(PC) = 8.1 Hz], 127.0 (C-3, XX' part of AA'XX' spin system, *N* = 8 Hz), 132.3 (C-2, XX' part, *N* = 26.9 Hz), 146.1 (C-1, XX' part, *N* = 5.1 Hz). – IR (Nujol/Hostaflon): $\tilde{\nu}$ = 2990 cm^{-1} (m), 2962 (s), 2944 (s), 2918 (s), 2897 (s), 2874 (m), 2959 (s), 1459 (s), 1448 (m), 1424 (m), 1405 (m), 1383 (s), 1364 (s), 1359 (s), 1349 (m), 1340 (m), 1323 (s), 1281 (s), 1249 (m), 1244 (m), 1231 (m), 1170 (s), 1124 (s), 1025 (m), 991 (m), 975 (m), 776 (m), 752 (s), 736 (m), 585 (m), 572 (m), 516 (m). – MS (70 eV); *m/z* (%): 375 (63) [M$^{\cdot+}$], 360 (34) [M − CH_3]$^+$, 332 (100) [M − *i*Pr]$^+$, *m** = 293.93, 318 (32) [M − Me − C_3H_6]$^+$, 290 (33) [M − *i*Pr − C_3H_6]$^+$, *m** = 253.31, 250 (24), 224 (22) [M − Btmp]$^+$, 182 (32), 126 (24) [tmpH$^+$ − Me]. – $C_{21}H_{36}BNP_2$ (375.28), calcd. C 67.21, H 9.67, N 3.73; found C 66.43, H 9.83, N 3.62.

1,3-Diisopropyl-2-mesitylbenzo-1,3,2-diphosphaborolane (**6d**): Procedure B; $C_6H_4(PHiPr)_2$ (270 mg, 1.2 mmol) in 5 ml of hexane, BuLi (210 mg, 2.38 mmol in 1.52 ml of hexane), mesBCl$_2$ (240 mg, 1.2 mmol) in 5 ml of hexane; 210 mg "LiCl" removed. The waxy residue obtained upon concentration of the filtrate did not crystallize. – MS (70 eV); *m/z* (%): 354 (49) [M$^{\cdot+}$], 339 (8) [M − CH_3]$^+$, 311 (100) [M − $CHMe_2$]$^+$, *m** = 273.22, 297 (15) [M − CH_3 − C_3H_6]$^+$, 269 (11) [M − $CHMe_2$ − C_3H_6]$^+$, 205 (26), 119 (35) [mes$^+$], 77 (21) [$C_6H^+_5$].

1,2,3-Triisopropylbenzo-1,3,2-diphosphaborolane (**6e**): Procedure B; a suspension of $C_6H_4(PiPrLi)_2$ (0.88 mmol) in 10 ml of hexane was added to 190 mg (0.88 mmol) of *i*PrBBr$_2$ in 15 ml of hexane; 200 mg of insoluble residue was removed. Some yellow crystals (30 mg, 12%) were isolated, m.p. 128 °C. – ^{1}H NMR (C_6D_6): δ = 0.55 (5'''-H, m, *N* = 26 Hz), 0.67 (5''-H, m, *N* = 30 Hz), 1.20 (5'-H, m, *N* = 31 Hz), 1.30 (5-H, m, *N* = 28 Hz), 1.40 (7'-H, m, *N* = 23 Hz), 1.59 (7-H, m, *N* = 30 Hz), 1.93 (6-H, m, *N* = 25 Hz), 2.15 (4'-H, m, *N* = 20 Hz), 2.63 (4-H, m, *N* = 20 Hz), 6.73 (3'-H, m, *N* = 13 Hz), 7.05 (2'-H, m, *N* = 15 Hz), 7.55 (2-H, m, *N* = 14 Hz). – ^{13}C NMR (C_6D_6): δ = 18.7 (C-7'), 21.7 (C-7), 22.2 (C-5''', m, *N* = 28 Hz), 23.0 (C-5'', m, *N* = 14 Hz), 23.9 (C-5', m, *N* = 29 Hz), 24.2 (C-5, m, *N* = 13 Hz), 25.6 (C-4', m, *N* = 24 Hz), 26.8 (C-4, m, *N* = 23 Hz), 30.2 (C-6), 125.4 (C-3', XX' part of an AA'XX' spin system, *N* = 8 Hz), 128.6 (C-3), 130.8 (C2', XX' part of an AA'XX' spin system, *N* = 20 Hz), 133.8 (C-2, XX' part of an AA'XX' spin system, *N* = 24 Hz), 141.8 (C-1). – IR (Nujol/Hostaflon): $\tilde{\nu}$ = 3055 cm^{-1} (m), 2980 (s), 2922 (s), 2876 (s), 1575 (m), 1475 (s), 1445 (s), 1427 (m), 1383 (m), 1373 (m), 1364 (s), 1353 (m), 1250 (m), 1240 (s), 1152 (m), 1104 (m), 1051 (m), 1031 (s), 933 (m), 884 (m), 752 (s), 683 (s), 653 (m), 621 (s), 594 (m), 524 (s), 503 (s), 493 (m), 420 (m), 408 (m). – MS (70 eV); *m/z* (%): 406 (58) [M$^{\cdot+}$ − C_6H_4PiPr], 364 (100) [M$^{\cdot+}$ − C_6H_4PiPr − *i*Pr], 322 (83), 278 (28) [M$^{\cdot+}$/2], 235 (43) [M$^{\cdot+}$/2 − isopropene], 42 (35) [isopropene].

2-tert-Butyl-1,3-diisopropylbenzo-1,3,2-diphosphaborolane (**6f**): Procedure B; $C_6H_4(PiPrLi)_2$ (0.90 mmol) in 10 ml of hexane was added to 200 mg (0.90 mmol) of *t*BuBBr$_2$ in 15 ml hexane; 180 mg of insoluble residue was present after the reaction. Removal of all volatile material led to an oily residue which was found to be a mixture of the monomeric and dimeric species. No separation (distillation, crystallization) could be achieved. – NMR (C_6D_6): $\delta^{11}B = 87.0$; $\delta^{31}P = -5.5$ (monomeric); $\delta^{11}B = -8.4$; $\delta^{31}P = 16.1/-3.4$ (dimeric).

μ-[2-(Tetramethylpiperidino)benzo-1,3,2-diphosphaborolane]bis(pentacarbonylchromium) (**12**): Cr(CO)$_6$ was dissolved in THF (420 mg, 1.9 mmol, 70 ml). After irradiation of the solution with a mercury lamp (3 h), the resulting solution of $(CO)_5Cr\cdot THF$ was added to a solution of $C_6H_4(PH)_2Btmp$ in hexane (140 mg, 0.48 mmol, 30 ml). After stirring for 14 h, removal of all volatile material in vacuo and redissolution of the remaining oil in hexane/toluene (10 ml/2 ml), the yellow solution was filtered and kept at −30 °C for several days. Yellow-orange cubes separated within a few days; **12** was found to be more susceptible to hydrolysis than the ligand **4c**. Yield: 130 mg of **12** (39%); m.p. 108 °C (dec.). – ^{1}H NMR (C_6D_6): δ = 0.95 (m, 6 H), 1.21 (CH_3, 6 H), 1.37 (CH_3, 6 H), 4.14 [PH, 2 H, d, ^1J(PH) = 102.7 Hz], 6.72 (3-H, 2 H), 7.42 (2-H, 2 H). – ^{13}C NMR (C_6D_6): δ = 13.8 (C-6), 30.2 (C-7'), 35.6 (C-7), 36.1 (C-5), 60.4 (C-4), 130.7 (C-3), 131.7 (C-2, XX' part of an AA'XX' spin system, *N* = 19.8 Hz), 216.8 [*C*O, pseudo-t, ^2J(PC) = 4.9 Hz], 221.4 (*C*O). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2329.8 cm^{-1} (m), 2315 [w, ν(PH)],

2069.2 (s), 1953.1 [s, br., ν(CO)]. – $C_{25}H_{24}BCr_2NO_{10}P_2$ (675.22): calcd. C 44.47, H 3.58, N 2.07; found C 43.59, H 3.99, N 1.98.

2,3-Bis(dimethylamino)-1,4-diisopropylbenzo-1,4,2,3-diphosphadiborinane (**13**) *and Dimeric 2-[Bis(dimethylamino)boryl]-1,3-diisopropylbenzo-1,3,2-diphosphaborolane* $(\mathbf{14})_2$: $C_6H_4(PHiPr)_2$ (240 mg, 1.1 mmol) was dissolved in 20 ml of diethyl ether, cooled to −40 °C and metallated with 2.12 mmol of BuLi in 11.3 ml of hexane. The mixture was stirred for 14 h and then added to a solution of $B_2(NMe_2)_2Cl_2$ (190 mg, 1.1 mmol) in 20 ml of hexane at −78 °C. Insoluble material that had been formed was rapidly removed by filtration. On standing at −78 °C crystals separated within 10 h. Yield: 70 mg of **13** (20%), m.p. 64 °C. The filtrate was reduced in vacuo to half its volume, and further colorless crystals of different shape formed at −78 °C within a few hours. Yield: 50 mg of $(\mathbf{14})_2$ (14%), m.p. 174−179 °C.

13: ^{1}H NMR ($CDCl_3$): δ = 1.16 [5′-H, dd, ^3J(PH) = 13.2 Hz, ^3J(H,H) = 6.8 Hz], 1.18 [5-H, dd, ^3J(PH) = 14.4 Hz, ^3J(H,H), 6.8 Hz], 2.47 (4-H, m, N = 33 Hz), 2.66 (6′-H), 3.03 [6-H, d, ^3J(PH) = 1.5 Hz], 7.02 (3-H, m, N = 13 Hz), 7.75 (2-H, m, N = 20 Hz). – ^{13}C NMR ($CDCl_3$): δ = 22.7 (C-5, pseudo-t, N = 29 Hz), 26.6 [C-4, d, ^1J(PC) = 10 Hz], 41.9 [C-6′, d, ^3J(PC) = 28 Hz], 46.8 [C-6, d, ^3J(PC) = 5 Hz], 126.7 (C-3, m, N = 12 Hz), 137.8 (C-2, m, N = 35 Hz), 145.0 (C-1, m, N = 19 Hz). – IR (Nujol/Hostaflon): $\tilde{\nu}$ = 2946 cm^{-1} (s), 2929 (s), 2893 (s), 2864 (s), 2802 (m), 1500 (s), 1451 (s), 1409 (s), 1391 (s), 1377 (m), 1358 (m), 1236 (m), 1187 (s), 1158 (s), 1119 (s), 1093 (m), 1046 (m), 1027 (m), 988 (m), 975 (m), 878 (m), 747 (s), 636 (m), 609 (m), 473 (m), 459 (m). – MS (70 eV); *m/z* (%): 334 (24) [$M^{\cdot+}$], 291 (51) [$M^{\cdot+}$ − *i*Pr], 279 (12) [$M^{\cdot+}$ − $BNMe_2$], 249 (11) [291 − C_3H_6], 226 (80) [$C_6H_4(PHiPr)_2^{\cdot+}$], 183 (100) [226 − *i*Pr], m^* = 148.18, 141 (90) [183 − C_3H_6], m^* = 108.64, 109 (83) [C_6H_4PH], 77 (76) [C_6H_4]. – $C_{16}H_{30}B_2N_2P_2$ (333.99): calcd. C 57.54, H 9.05, N 8.39; found C 56.93, H 8.84, N 7.94.

$(\mathbf{14})_2$: ^{1}H NMR ($CDCl_3$): δ = 0.94−1.49 (5-H, m), 2.30 (6′-H), 2.58 (4′-H), 2.75 (4-H), 2.86 (6-H), 7.12 (3-H, br., N = 17 Hz),

Table 3. Crystallographic data and data relating to data collection and structure determination of the benzodiphosphaboron heterocycles

Compound	**4b**	**4c**	**6c**	**4f**	**12**	**13**	$(\mathbf{14})_2$	**16**	**18**
Chem. formula	$C_{12}H_{20}BNP_2$	$C_{15}H_{22}BNP_2$	$C_{21}H_{36}BNP_2$	$C_{30}H_{40}B_2P_2 \cdot 0.16\,C_7H_8$	$C_{57}H_{56}B_2Cr_4N_2O_{20}P_4$	$C_{16}H_{30}B_2N_2P_2$	$C_{31.75}H_{42}B_2P_2$	$C_{16}H_{30}B_2N_2P_2$	$C_{12}H_{24}B_3N_3P_2$
Form. wght.	251.04	289.1	375.26	499.5	1442.54	333.98	507.21	333.98	304.71
Cryst. size [mm]	0.55×0.5×0.5	0.4×0.4×0.4	0.32×0.45×0.6	0.49×0.4×0.35	0.2×0.3×0.3	0.32×0.4×0.4	0.35×0.4×0.49	0.35×0.44×0.58	0.4×0.4×0.6
Cryst. system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/c	*P*2(1)/c	*Pbca*	$P\bar{1}$	*P*2(1)/c	$P\bar{1}$	$P\bar{1}$	*P*2(1)/n	*P*2(1)/n
a [Å]	14.195(1)	14.105(7)	14.350(8)	11.625(4)	9.924(6)	8.270(2)	11.625(4)	12.018(5)	8.222(4)
b [Å]	7.972(1)	12.318(8)	13.565(10)	13.993(4)	27.378(20)	10.384(10)	13.993(4)	12.766(3)	13.206(6)
c [Å]	13.649(2)	19.264(14)	23.506(15)	19.088(5)	12.712(9)	12.354(8)	19.088(5)	12.215(6)	16.355(9)
α [°]	90.00	90.00	90.00	102.70(2)	90.00	98.72(1)	102.70(2)	90.00	90.00
β [°]	108.93(1)	101.86(5)	90.00	93.79(3)	111.62(4)	106.20(1)	93.79(3)	90.01(1)	93.40(4)
γ [°]	90.00	90.00	90.00	94.17(2)	90.00	97.85(1)	94.17(2)	90.00	90.00
V [Å^3]	1460.9(3)	3276(4)	4575.6(51)	3011(2)	3210.9(38)	989.0(12)	3010.3(16)	1863.7(13)	1772.7(15)
Z	4	4	8	4	2	2	4	4	4
ρ(calcd.) [Mg/m^3]	1.141	1.172	1.089	1.102	1.492	1.122	1.119	1.190	1.142
μ [mm^{-1}]	0.273	0.246	0.194	0.162	0.832	0.217	0.163	0.231	0.237
F(000)	536	1232	1632	1073.16	1476	360	1090	720	648
Index range	−17≤*h*≤16	−15≤*h*≤15	−1≤*h*≤16	0≤*h*≤11	0≤*h*≤6	0≤*h*≤9	−9≤*h*≤11	−1≤*h*≤13	0≤*h*≤7
Index range	−9≤*k*≤1	−13≤*k*≤1	0≤*k*≤7	−12≤*k*≤12	−20≤*k*≤32	−12≤*k*≤11	−5≤*k*≤15	0≤*k*≤14	−14≤*k*≤0
Index range	0≤*l*≤16	0≤*l*≤21	−26≤*l*≤26	−19≤*l*≤18	−15≤*l*≤14	−14≤*l*≤13	−21≤*l*≤21	−13≤*l*≤13	−18≤*l*≤18
2 θ [°]	51.98	50.8	48.94	44	50.02	49.00	48.00	48.02	47.08
Temp.[K]	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Refl. collected	2712	5621	4803	9554	4068	3252	9554	3340	2631
Refl. unique	2580	5166	2295	9036	3729	3106	9036	2911	2435
Refl. observed (4σ)	1969	2641	1139	5270	2631	2151	5519	1943	1997
R (int.)	0.0229	0.035	0.1071	0.0661	0.0491	0.9725	0.0820	0.0934	0.0236
No. variables	145	343	233	631	376	202	651	207	187
Weighting scheme[a]	0.0442/	0.053/	0.0283/	0.994	0.0623/	0.2002/	0.0835/	0.1896/	0.0550/
x/y	0.7667	0.8455	0.0000	–	4.0825	1.3317	4.1160	4.9973	1.7840
GOOF	1.030	2.050	0.983	1.035	1.035	1.531	1.027	1.040	1.238
Final R (4σ)	0.0433	0.0758	0.0541	0.0678	0.0464	0.1137	0.0694	0.1002	0.0439
Final *wR2*	0.1055	0.1211	0.0893	0.0892	0.1057	0.3282	0.1576	0.2618	0.1340
Larg. res. peak [e/Å^3]	0.235	0.466	0.158	1.28	0.502	1.048	0.509	1.578	0.236

[a] $w^{-1} = \sigma^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2\,F_c^2)/3$.

7.50 (2-H, br., N = 14 Hz), 7.89 (2-H, br., N = 19 Hz). – ^{13}C NMR ($CDCl_3$): δ = 21.3 (C-5,5', m, N = 44 Hz), 28.1 (C-4,4', N = 35 Hz), 41.8, 43.1 (C-6,6'), 126.5, 132.2 (C-3,3'), 133.6, 134.1 (C-2,2'). – IR (Nujol/Hostaflon): $\tilde{\nu}$ = 2987 cm^{-1} (m), 2957 (s), 2946 (s), 2923 (s), 2864 (s), 2835 (m), 2776 (s), 1496 (s), 1468 (s), 1444 (s), 1380 (m), 1350 (s), 1335 (s), 1209 (s), 1183 (m), 1110 (m), 1106 (m), 1085 (s), 1074 (s), 1054 (s), 1037 (m), 1028 (m), 749 (s), 501 (m). – MS (70 eV); *m/z* (%): 668 (15) [M^{+}], 624 (46) [M^{+} – NMe_2], 615 (30), 334 (38) [$M^{+}/2$], 292 (100) [334 – C_3H_6], m^* = 225.28, 248 (41) [292 – NMe_2], m^* = 210.63, 99 (93) [$(B(NMe_2)_2^+$]. – $C_{32}H_{60}B_4P_4N_4$ (667.98): calcd. C 57.54, H 9.05, N 8.39; found C 57.19, H 8.94, N 7.92.

1,4-Diisopropyl-2,3-dimesitylbenzo-1,4,2,3-diphosphadiborinane (**16**): Prepared according to General Procedure B from $C_6H_4(PHiPr)_2$ (310 mg, 1.4 mmol), BuLi (2.74 mmol) and $mes_2B_2Cl_2$ (450 mg, 1.4 mmol). Yellow crystals from hexane solution. Yield: 350 mg of **16** (53%), m.p. 155 °C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 1.32 [5-H, dd, ^3J(PH) = 16.1 Hz, ^3J(HH) = 7.3 Hz], 2.16 (10-H), 2.19 (11-H), 3.22 [4-H, sept, ^3J(HH) = 6.2 Hz], 6.66 (8-H), 7.35 (3-H, br.) 7.89 (2-H, br.). – ^{13}C NMR ($CDCl_3$): δ = 21.1 (C-11), 21.5 (C-5), 24.2 (C-10), 24.7 [C-4, pseudo-t, ^1J(PC) + ^3J(PC) = 10 Hz], 123.9 (C-8), 127.0 (C-7), 127.6 (C-3, N = 10 Hz), 133.4 (C-2, br.), 135.1 (C-9), 137.3 (C-6), 140.2 (C-1, br.). – IR (Nujol/Hostaflon): $\tilde{\nu}$ = 2972 cm^{-1} (s), 2958 (s), 2945 (s), 2924 (s), 2910 (s), 2866 (m), 1606 (m), 1462 (s), 1439 (s), 1418 (s), 1385 (m), 1370 (s), 1237 (m), 1041 (m), 884 (m), 848 (s), 732 (s), 623 (m), 492 (m). – MS (70 eV); *m/z* (%): 484 (82) [M^{+}], 469 (36) [M^{+} – Me], 441 (100) [M^{+} – *i*Pr], m^* = 401.82, 410 (36) [M^{+} – $PCHMe_2$], 399 (34) [441 – C_3H_6], m^* = 361.00, 321 (47) [441 – mesH], 311 (36) [441 – Bmes], 286 (74), 279 (69), 249 (53) [$C_6H_4PHB_2$mes], 217 (57) [$C_6H_4B_2$mes], 120 (47) [$mesH^+$]. – $C_{30}H_{40}B_2P_2$ (484.22): calcd. C 74.42, H. 8.33; found C 74.37, H 8.21.

2,3,4-Tris(dimethylamino)benzo-1,5,2,3,4-diphosphatriborepane (**18**): According to General Proceedure A, a solution of $C_6H_4(PHNa)_2$ was prepared from 1.18 mmol of $C_6H_4(PH_2)_2$ and added at −78 °C to a stirred solution of $B_3(NMe_2)_3Br_2$ (380 mg, 1.18 mmol). A yellow suspension resulted after stirring overnight. All volatile material was then removed and the residue was treated with 20 ml of hexane. Solid material was removed by filtration (270 mg) and the solution cooled to −20 °C whereupon colorless needles separated within a few hours. Yield: 200 mg of **18**, 56%, m.p. 263–265 °C. Single crystals were obtained after several recrystallizations from hexane. – ^{1}H NMR (C_6D_6): δ = 2.38 (4,4'-H'), 2.51 (5,5'-H'), 2.62 (6,6'-H'), 4.17 [PH, d, ^1J(PH) = 226 Hz], 6.95 (3-H, m, N = 12 Hz), 7.47 (2-H, m, N = 20 Hz). – ^{13}C NMR (C_6D_6): δ = 41.7 [C-4, d, ^3J(P,C) = 8 Hz], 45.4 [C-5, d, ^3J(P,C) = 11 Hz], 46.2 (C-6), 126.0 (C-3), 134.3 (C-2). – IR (Nujol/Hostaflon): $\tilde{\nu}$ = 2940 cm^{-1} (s), 2862 (s), 2779 (m), 2276 (s), 1551 (m), 1494 (s), 1440 (s), 1413 (s), 1397 (s), 1194 (s), 1157 (s), 1141 (m), 1118 (s), 1047 (m), 989 (m), 943 (m), 894 (m), 868 (m), 610 (m). – MS (70 eV); *m/z* (%): 305 (63) [M^{+}], 195 (13) [M^{+} – $B_2(NMe_2)_2$], 151 (28) [$C_6H_4(PH)_2B^+$], 110 (100) [$(BNMe_2)_2^+$], 44 (71) [Me_2N^+]. – $C_{12}H_{24}B_3N_3P_2$ (304.59): calcd. C 47.30, H 7.94, N 13.79; found C 47.06, H 7.46, N 13.45.

X-ray Crystallographic Investigations: Selected single crystals were transferred under argon into glass capillaries which were then sealed. Siemens R3 and P4 four-circle X-ray diffractometers using graphite-monochromated Mo-K_α radiation were used for data collection. Cell parameters were calculated from 18–30 centered reflections in the 2θ range of 14–28°. Data collection was performed by checking the stability of the instruments with 3 check reflections after every 97 intensity measurements, and the intensity data were corrected according to any intensity variation (usually less than 2%). Lorentz and polarization correction was also applied. The structures of the compounds were solved by direct methods[35]. Non-hydrogen atoms were refined in anisotropic description. Hydrogen atoms in calculated positions were included in the final refinement using a riding model (SHELX-93 program[35]). Table 3 contains a summary of relevant data. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-100507. Copies of the data can be obtained free of charge on application to The Director, CCCD, 12, Union Park, Cambridge CB2 1EZ, U.K. [Fax (internat.): + 44(0)1223/336033; E-mail: deposit@chemchrys.cam.ac.uk].

☆ Dedicated to my friend Prof. Dr. *A. Meller* on the occasion of his 65th birthday.

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