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N-(2,4,6-Trimethylborazinyl)-Substituted Phosphanes, Arsanes, and Stibanes[‡]

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Reaction of the *N*-lithioborazine $LiH_2N_3B_3Me_3{\cdot}OEt_2$ (**2**) in diethyl ether with PCl_3 or PBr_3 leads to the borazinylphosphanes $(Me_3B_3N_3H_2)PX_2$, $(Me_3B_3N_3H_2)_2PX$ (X = Cl, Br), and $(Me_3B_3N_3H_2)_3P$, depending on the initial stoichiometry. The analogous arsane and stibane derivatives were obtained in a similar manner. While $(Me_3B_3N_3H_2)_2PBr$ is reduced by $LiAlH_4$ in diethyl ether/hexane to give the monophosphane $(Me_3B_3N_3H_2)_2PH$ (**13**), the reaction of $(Me_3B_3N_3H_2)PBr_2$ (**5**) with $LiAlH_4$ in diethyl ether/hexane produces the zwitterionic compound $[Me_3B_3N_2(HN)]^-P^+H_2Et$ (**14**). Dehalogenation of $(Me_3B_3N_3H_2)_2PBr$ (**6**) with Na yields the diphosphane $(Me_3B_3N_3H_2)_2PP(H_2N_3B_3Me_3)_2$ (**18**), while the mixed diphosphane $(Me_3B_3N_3H)_2PPmes_2$ (**17**) is obtained from **6** and $LiPmes_2$. Dehalogenation of $Me_3B_3N_3H_2PBr_2$ with Na results in the exclusive formation of $(Me_3B_3N_3H_2)_4P_4$ (**19**), while the reaction of **5** with Li_2Pmes leads to a mixture of cyclotetraphosphanes $(mes)_{4-n}(Me_3B_3N_3H_2)_nP_4$ (**A**–**F**) along with bicyclic P_4mes_2. The new compounds have been characterized by NMR and IR spectroscopy and partly by mass spectrometry. X-ray structures for compounds, **4**, **5**, **6**, **9**, **13**, **14**, **17**, **18**, **19**, and **E** have been determined. All show different B–N bond lengths within the borazine rings, and some have borazine rings in a half-chair conformation.

Introduction

The deprotonation of borazines $R_3B_3N_3H_3$ by organolithium reagents was first described by Wagner and Bradford,[2] although none of the resulting *N*-lithioborazines were isolated and characterized – their formation was based on the observation that the products reacted with alkyl halides (R′X) to generate borazines of the type $R_3B_3N_3H_{3-n}R'_n$ (*n* = 1–3), thereby indicating that the lithiation is not specific and yields a mixture of *N*-lithioborazines. Recently, we reported the isolation and structural characterization of ligand-stabilized *N*-monolithioborazines $R_3B_3N_3H_2Li{\cdot}L$ (e.g. R = Me, *i*Pr, *t*Bu, Ph; L = Et_2O, thf, tmeda, pmtda).[3,4] These proved to be versatile reagents for the preparation of hitherto unknown borazine derivatives of, for example, B, Al, Ge, or Ti.[5,6] Here, we describe borazinyl-substituted phosphanes, arsanes, and stibanes. Known P-containing borazines are derivatives of phosphorus esters in which either $(RO)_2P(O)_2$ groups are bonded to the B atoms[7] or an $(RO)PO_3$ group connects two borazine units through a B–O–B bond.[8] Other P-containing borazine derivatives include the interesting borazine cations $[Cl_{3-n}B_3(N{=}PPh_3)_3]^{+n}(Cl^-)_n$ (*n* = 1, 2, 3).[9,10] However, no borazine derivatives have been reported to date where R_2P groups are bonded to either B or N. These may be interesting ligands for transition metal complexes, particularly those which act as catalysts, because they will change the catalytic properties of triarylphosphane-based catalysts. Here, we describe the synthesis, structures, and reactivity of some of the heavier group 15 element 2,4,6-trimethylborazinyl compounds, with an emphasis on phosphane derivatives.

Results and Discussion

(2,4,6-Trimethylborazinyl)-halogeno-phosphanes, -arsanes, and -stibanes

Synthesis

2,4,6-Trimethylborazine (**1**) does not react with PCl_3 or PBr_3 in the presence of triethylamine to form borazinylhalogeno-phosphanes $(Me_3B_3N_3H_2)_nPX_{3-n}$ (*n* = 1, 2, 3; X = Cl, Br) as the ring N atoms are not sufficiently nucleophilic to attack the P atoms of the halogenophosphanes to allow NEt_3-assisted HX elimination. This contrasts with the reactivity of dialkylamines with phosphorus halides.[11,12] We therefore studied the reactions of phosphorus trichloride and tribromide, and their arsenic and antimony analogs, with the diethyl ether adduct of 1-lithio-2,4,6-trimethylborazine (**2**) in diethyl ether solution. Depending on the molar ratios employed, we obtained the borazinyldihalogenophosphanes **3** and **5**, as well as the bis(borazinyl)halogenophosphanes **4** and **6** in acceptable yields (>75%). The tris(borazinyl)phosphane **11** could, however, not be prepared in pure state; it was always slightly contaminated with **4**. The borazinyl-arsanes **7**, **8** and borazinyl-stibanes **9**, **10** were prepared analogously. The formation of

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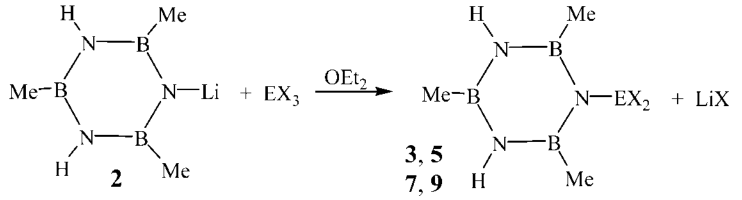

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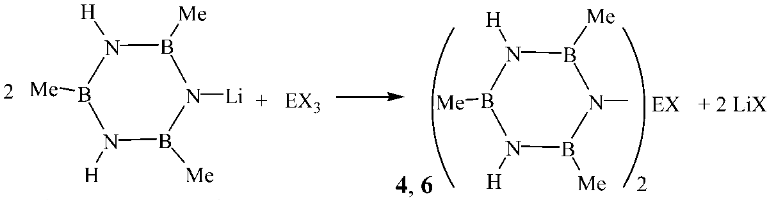

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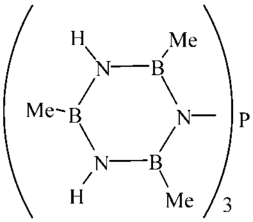


11

	3	**4**	**5**	**6**	**7**	**8**	**9**	**10**
X =	Cl	Cl	Br	Br	Cl	Cl	Cl	Cl
E =	P	P	P	P	As	As	Sb	Sb

$(Me_3B_3N_3H_2)_3E$ (E = As, Sb) was observed only by NMR spectroscopy, and these compounds could not be isolated in pure state. Compounds **4**, **5**, **6**, and **9** were obtained as single crystals.

Spectra

Table 1 lists the NMR spectroscopic data of compounds **3**–**11**. Each of these compounds is characterized by two ^{11}B NMR signals in a 2:1 ratio. The signal at lower field results from the B atoms adjacent to the N1(4) atom(s) carrying the P, As, or Sb atoms (see Figures 1 and 3 for the numbering). The signals at higher field result from the *para* boron atoms B2(5). The shielding is practically unaffected by the number of halogen atoms at P, As, or Sb. The replacement of P by As or Sb leads to an exceptionally small low-field shift of 1–1.5 ppm, which is only a little bit larger for the bromides **5** and **6** (approx. 2.6 ppm). This shows that the charge distribution within the borazine ring is negligibly affected by the *N*-substitution. Even the replacement of the $Li(OEt_2)$ group by EX_2 or EX groups has little effect. The ^{11}B NMR shift of compound **2**, for example, is δ = 35.4 ppm[3] and that of the parent borazine **1** is δ = 32.3 ppm.[13]

There is a ^{31}P chemical shift difference of only 8.6 ppm between the borazinyl-chloro-phosphanes **3** and **4**, whereas this difference is 54.7 ppm for **3** and **11**. Similarly, $\Delta\delta^{31}P$ for the bromides **5** and **6** is only 1.5 ppm but 69.0 ppm for **5** and **11**. The corresponding $\Delta\delta^{31}P$ data for the series $Ph_{3-n}PCl_n$ (n = 0, 1, 2) are 64 and 91.2 ppm and in the $(Me_2N)_{3-n}PCl_n$ series they are 6.3 and 37 ppm, respectively.[14] These latter data are similar to those of the borazinyl-chloro-phosphanes.

While the shielding of the boron nuclei is only slightly affected by the EX_{2-n} groups, the methyl protons in the *para* position of the borazine rings show differences of 0.06 and 0.09 ppm for **3** and **4** and for **5** and **6**, respectively, in contrast to a difference of only 0.01 ppm for the *ortho* methyl groups. This trend is also observed for the arsenic and antimony compounds **7**–**10**.

The proton of the *o*-Me groups of compounds **3** to **6** couples with the ^{31}P nucleus. The resulting $^4J_{^{31}P,^1H}$ coupling constants cover the range 3.3–5.7 Hz, with those of the dihalides being larger than those of the monohalide species. A similar coupling has been observed in borylamino phosphanes.[15]

Table 2 contains a selection of the typical strong IR bands recorded in Hostaflon/Nujol mulls. There are two ν(NH) bands for compounds **3** and **5**, while three ν(NH) bands are observed for **4** and **6**, although either two or four are to be expected. The two borazinyl groups of **4** and **6** are obviously not equivalent in the solid state. All of these bands are comparatively sharp, and the bands at highest

Table 1. Chemical shifts of (trimethylborazinyl)-halogeno-phosphanes, -arsanes, and -stibanes (in ppm; solvent C_6D_6).

	2·OEt₂	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
$\delta_{^{11}B}$	35.4	34.6, 37.1	34.6, 37.2	36.1, 38.6	36.0, 38.8	35.7, 9.5	35.6, 37.9	36.0, 38.3	35.4, 37.8	35.5, 37.7
$\delta_{^{31}P}$	–	183.6	175.0	189.3	190.9	120.3	–	–	–	120.3
$\delta_{^1H}$ CH_3	0.47, 0.59	0.06, 0.66[a]	0.12, 0.65[b]	–0.01, 0.69[c]	0.10, 0.66[d]	0.18, 0.64	0.15, 0.56	0.05, 0.52	0.11, 0.46	0.18, 0.50
$\delta_{^1H}$ NH	4.66	4.48	4.55	4.31	4.41	4.55	4.42	4.41	4.33	4.4

[a] $^4J_{^{31}P,^1H}$ = 3.6 Hz. [b] $^4J_{^{31}P,^1H}$ = 3.6 Hz. [c] $^4J_{^{31}P,^1H}$ = 5.7 Hz. [d] $^4J_{^{31}P,^1H}$ = 3.3 Hz.

wavenumbers are almost the same for all four compounds, whereas the others are lower for the bromides than for the chlorides. BN ring vibrations are found in the regions from 1500 to 1490 cm^{-1} and 1430 to 1380 cm^{-1} as strong bands. Those of the chlorides are observed at somewhat higher wavenumbers than those of the bromides, which suggests an inductive effect of the halides. Only one ν(PN) band is observed for compounds **3** and **5**. As expected, there are two PN$_2$ bands (ν_{sym}PN$_2$ and ν_{asym}PN$_2$) for compounds **4** and **6** and their values suggest that the PN bonds of the chlorides are stronger than those of the bromides. This conclusion is also supported by the PN bonds lengths of these compounds (see below).

X-ray Structures

Single crystals suitable for X-ray structure determinations were obtained for compounds **4**, **5**, **6**, and **9**. The dibromoborazinylphosphane **5** crystallizes in the orthorhombic space group *Pnma* with $Z = 8$, which means that there are two independent molecules in the unit cell (see Figure 1a). As expected, the structural parameters of the two molecules do not differ much, but they are nevertheless significantly different (see Table 3). Both molecules show C_s symmetry, with the P, N, B, C, and some of the H atoms occupying special positions on a mirror plane. The symmetry-related bromine atoms are perpendicularly oriented with respect to the ring plane.

The P1–N1–B3 and P2–N4–B4 angles [119.8(6)° and 112.7(5)°, respectively] of compound **5** demonstrate that the PBr$_2$ groups lie closer to atoms C3 and C6, respectively. The P–N bond lengths of molecules **5A** and **5B** are equal within standard deviations. The B–N bond lengths of the borazine units show distortions relative to the parent molecule Me$_3$B$_3$N$_3$H$_3$.[16] For example, the P substituent induces a significant B–N bond lengthening for the B–N bonds involving the P-bonded atoms N1 and N4. The remaining B–N bonds are shorter than those observed for borazines of the type (RB=NH)$_3$ (1.42–1.44 Å).[17] The B–N–B angles at atoms N1 and N4 [119.8(6)° and 118.6(6)°, respectively] are more acute than all other B–N–B bond angles [125.5(6)–126.7(6)°] while all N–B–N bond angles are smaller than 120° (by an average of 4°).

Figure 1 (b) shows a plot of the packing of the two independent molecules in the unit cell. This packing leads to an identical orientation of the bromine atoms of **5A** and **5B** in the stacks of packed borazine rings along the *b*-axis. These stacks are formed by alternating **5A** and **5B** molecules. The closest interatomic distances between the stacks are: B4–B3A = 3.971, B6A–B2A = 3.802, N5A–N3A = 3.940, and N2A–N6A = 3.714 Å. This leads to an average centroid–centroid distance of 3.87 Å, which is larger than the distance between the BN planes of hexagonal boron nitride (3.33 Å). There are no NH···Br interactions and no close Br···Br contacts.

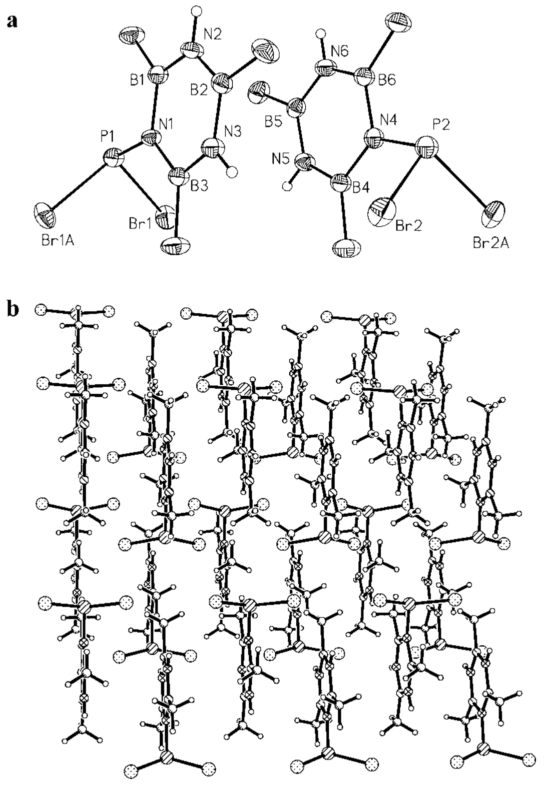


Figure 1. (a) Molecular structure of compound **5** showing the two independent molecules **5A** (left) and **5B** (right). CH hydrogen atoms have been omitted for clarity. The bonding parameters are listed in Table 3. (b) Packing of molecules **5A** and **5B**. These molecules are arranged in strings of alternating **5A** and **5B**.

The structure of **5** can best be compared with that of the dichlorostibane **9**, which crystallizes in the monoclinic system, space group $P2_1/n$, also with $Z = 8$. Relevant structural parameters are summarized in Table 3. The B–N bonds to the Sb-substituted atoms N1 and N4 are significantly longer than all other B–N bonds in the ring, and the B–N(1,4)–B bond angles are smaller (av. 120.95°) than all other B–N–B bond angles (av. 125.6°). The Cl–Sb–Cl bond angles of the two independent molecules differ by 4°, but the two pairs of Cl–Sb–N bond angles differ only by 2.7°.

Table 2. Selected IR data [cm^{-1}] for compounds **3**–**6**, **8**, **9**, and **10**.

Compound	ν(NH)	ν(ring)	ν(EN)	ν(EX)
(Me$_3$B$_3$N$_3$H$_2$)PCl$_2$	3429, 3377	1499, 1402	1295	982, 960
(Me$_3$B$_3$N$_3$H$_2$)$_2$PCl	3431, 3411, 3402	1487, 1435, 1396	1285	973
(Me$_3$B$_3$N$_3$H$_2$)PBr$_2$	3423, 3414	1487, 1432, 1394	1290	975, 940
(Me$_3$B$_3$N$_3$H$_2$)$_2$PBr	3430, 3401, 3391	1483, 1395	1282	962
(Me$_3$B$_3$N$_3$H$_2$)$_2$AsCl	3419, 3411	1478, 1397	1285	920
(Me$_3$B$_3$N$_3$H$_2$)SbCl$_2$	3421, 3406	1474, 1407, 1318	1262	889, 802
(Me$_3$B$_3$N$_3$H$_2$)$_2$SbCl	3438, 3418	1473, 1449, 1400	1261	803

Table 3. Selected bond lengths [Å] and bond angles [°] for $Me_3B_3N_3H_2PBr_2$ (**5**) and $Me_3B_3N_3H_2SbCl_2$ (**8**).

5A		**5B**		**9A**		**9B**	
P1–Br1	2.261(1)	P2–Br2	2.307(2)	Sb1–Cl1	2.387(1)	Sb2–Cl3	2.365(1)
				Sb1–Cl2	2.381(1)	Sb2–Cl4	2.375(1)
P1–N1	1.682(5)	P2–N4	1.674(5)	Sb1–N1	2.022(3)	Sb2–N4	2.027(3)
N1–B1	1.482(9)	N4–B4	1.506(9)	N1–B1	1.470(5)	N4–B4	1.455(5)
B1–N2	1.419(9)	B4–N5	1.411(9)	B1–N2	1.425(6)	B4–N5	1.429(5)
N2–B2	1.416(9)	N5–B5	1.406(9)	N2–B2	1.421(8)	N5–B5	1.425(6)
B2–N3	1.422(9)	B5–N6	1.416(9)	B2–N3	1.430(6)	B5–N6	1.412(6)
N3–B3	1.411(9)	N6–B6	1.386(9)	N3–B3	1.425(5)	N6–B6	1.424(6)
B3–N1	1.486(9)	B6–N4	1.495(9)	B3–N1	1.465(5)	B6–N4	1.465(5)
N1–P1–Br1	104.4(1)	N4–P2–Br2	105.89(1)	N1–Sb1–Cl1	97.50(9)	N4–Sb2–Cl3	99.73(9)
				N1–Sb1–Cl2	100.27(9)	N4–Sb2–Cl4	97.52(9)
Br1–P1–Br1A	99.86(8)	Br2–P2–Br2A	98.99(8)	Cl1–Sb1–Cl2	91.63(4)	Cl3–Sb2–Cl4	95.40(4)
P1–N1–B1	113.2(4)	P2–N4–B4	118.8(6)	Sb1–N1–B1	126.0(3)	Sb2–N4–B4	126.5(2)
B1–N1–B3	119.8(6)	B4–N4–B6	118.8(6)	B1–N1–B3	120.9(3)	B4–N4–B6	121.0(3)
P1–N1–B3	119.8(6)	P2–N4–B6	112.7(5)	Sb1–N1–B3	113.1(2)	Sb2–N4–B6	112.4(3)
B1–N2–B2	125.5(6)	B4–N5–B5	126.7(6)	B1–N2–B2	126.6(4)	B4–N5–B5	121.0(3)
B2–N3–B3	126.5(6)	B4–N6–B6	126.6(6)	B2–N3–B3	125.4(4)	B4–N6–B6	125.3(4)
N1–B1–N2	117.0(6)	N4–B4–N5	115.8(7)	N1–B1–N2	115.9(4)	N4–B4–N5	116.5(3)
N2–B2–N3	115.0(6)	N5–B5–N6	115.0(6)	N2–B2–N3	114.3(4)	N5–B5–N6	115.2(4)
N3–B3–N1	116.1(6)	N6–B6–N4	117.0(6)	N3–B3–N11	116.8(3)	N6–B6–N4	116.9(4)

The packing diagram of the molecules is depicted in part b of Figure 2, which reveals that the molecules are stacked on top of each other with the $SbCl_2$ groups oriented in opposite directions. The planar borazine rings are twisted against each other by 7° and are arranged perpendicularly to the respective $SbCl_2$ planes. Although the orientation of the Sb atoms with respect to the neighboring molecules suggests a higher coordination number than 3, the shortest intermolecular Sb–N distance is 3.693 Å, which is too long to be considered as a weak bond (sum of van der Waals radii: 3.8 Å). Even the intermolecular Sb–Cl interaction is weak because the respective Sb–Cl distance (3.310 Å) is only 0.05 Å shorter than the sum of the van der Waals radii.

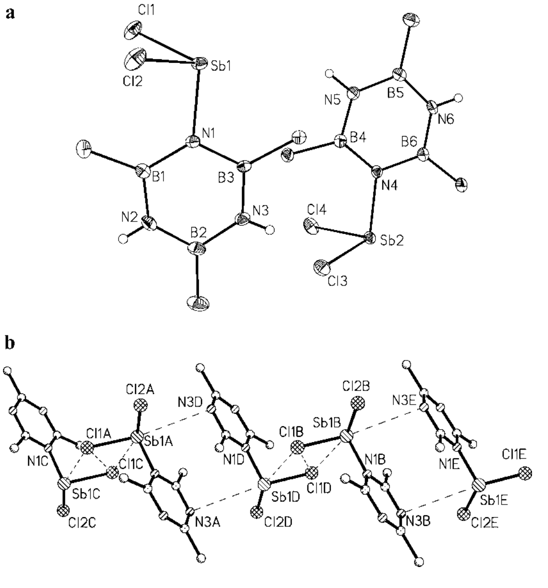


Figure 2. (a) The molecular structure of the two independent molecules in $(Me_3B_3N_3H_2)SbCl_2$ (**9**). Selected bonding parameters are listed in Table 3. CH hydrogen atoms have been omitted. (b) Interaction of one of the two independent molecules of **9**. Dotted lines represent the closests intermolecular interactions.

Figure 3 depicts the molecular structure of the bis(borazinyl)chlorophosphane **4**. This compound crystallizes with two molecules of toluene,[18] which are site disordered. The triclinic space group is $P\bar{1}$ with $Z = 2$. Relevant structural parameters are summarized in Table 4 together with the data for the corresponding bromide **6** (Figure 4). The configuration at the P atom is pyramidal (sum of bond angles: 303.5°). This represents partial sp^3 hybridization similar to that found in triaminophosphanes.[19] The P–Cl bond length [2.307(1) Å] of **4** is longer than that in PCl_3 [2.02(2) Å][20] and is also significantly longer than in most aminochlorophosphanes (2.109–2.197 Å).[21] The largest angle at the P1 atom is N1–P1–N4 (106.7°), while the angles N1–P1–Cl1 and N4–P1–Cl1 are only 100.3(1)° and 96.4(1)°, respectively. The opening of the N1–P1–N4 bond angle is most likely due to the steric demand of the trimethylborazinyl groups. The rings of these groups are not planar, as shown by the position of the atoms N1 and N4, which are bent out of the ring plane by 17° and 7°, respectively. The consequence of this ring distortion is that the methyl groups are also bent away from the ring plane in the opposite direction of the N1(4) atoms. Atoms C1 and C3 are more strongly affected, as shown by the value of 10° for

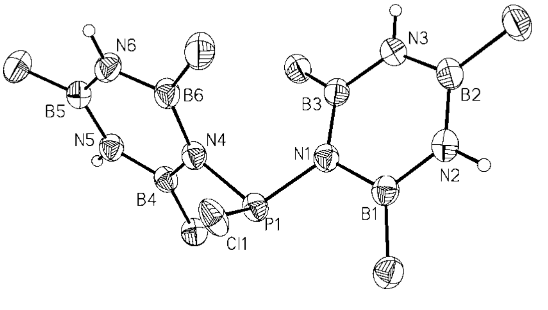


Figure 3. The molecular structure of compound $(Me_3P_3N_3H_2)_2PCl$ (**4**). Hydrogen atoms and the disordered toluene molecule have been omitted. See Table 4 for selected molecular parameters.

C1 and 13° for C3 (C4 and C6 are displaced only by 5° and 9°, respectively). Nevertheless, the sum of the bond angles at atoms N1 and N4 is 360°. It is also worthy to note that the B1–N1–P1 bond angle is 114.5(3)°, which contrasts with the value of 126.2° for the angle B3–N1–P1 [similarly B4–N3–P1 = 113.6(3)° and B6–N4–P1 = 125.7(3)°].

Table 4. Selected bonding parameters for the bis(trimethylborazinyl)halogenophosphanes **5** (X = Cl) and **6** (X = Br).

	4	**6**		**4**	**6**
P1–X	2.307(2)	2.334(1)			
P1–N1	1.702(4)	1.704(3)	P1–N4	1.698(4)	1.717(3)
B1–N1	1.474(7)	1.475(5)	B4–N4	1.463(6)	1.475(5)
B1–N2	1.423(6)	1.410(6)	Be4–N5	1.422(7)	1.419(5)
B2–N2	1.405(7)	1.418(5)	B5–N5	1.422(7)	1.420(6)
B2–N3	1.425(8)	1.416(6)	B5–N6	1.424(7)	1.425(6)
B3–N3	1.437(6)	1.414(5)	B6–N6	1.425(7)	1.415(5)
B3–N1	1.481(7)	1.469(5)	B6–N4	1.481(6)	1.469(5)
X–P1–N1	100.3(1)	99.2(1)	X–P1–N4	96.4(1)	101.1(1)
N1–P1–N4	106.7(2)	106.2(1)	N1–P1–N4	108.7(4)	106.2(2)
P1–N1–B1	114.5(3)	126.5(2)	P1–N4–B4	125.7(3)	126.6(2)
P1–N1–B3	126.2(3)	112.9(2)	P1–N4–B6	120.6(4)	114.0(2)
B1–N1–B3	119.1(4)	120.5(3)	B4–N4–B6	126.1(4)	118.9(3)
B1–N2–B2	125.9(5)	126.9(4)	B4–N5–B5	125.8(4)	115.6(3)
B2–N3–B3	125.6(5)	126.5(4)	B5–N6–B6	126.1(4)	126.3(4)
N1–B1–N2	116.6(5)	115.8(3)	N5–B5–N6	114.5(4)	113.0(4)
N3–B3–N1	115.2(5)	116.3(3)	N6–B6–N4	116.0(4)	116.6(3)

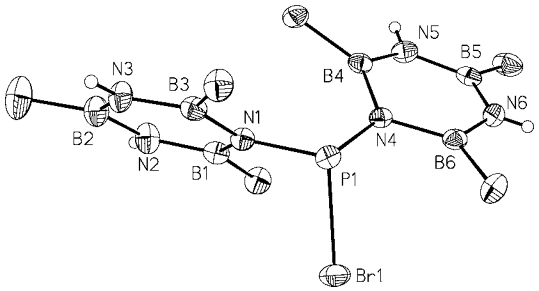


Figure 4. ORTEP plot of the molecular structure of $(Me_3B_3N_3H_2)_2$-PBr (**6**). Selected bonding parameters are listed in Table 4. CH hydrogen atoms have been omitted.

Amongst the B–N–B bond angles, those at atoms N1 and N4 are almost identical [119.1(4)° and 120.6(4)°, respectively]. The N–B–N bond angles to the B atoms opposite to N1 and N4 are only 114.7(4)° and 114.5(4)°, respectively, and are thus the smallest N–B–N bond angles of the two borazine moieties. In contrast, the B1–N2–B2 and B4–N5–B5 angles are quite wide [125.9(4)°]. The two borazine rings are twisted against each other by 56.6°.

Compound **6** crystallizes free of solvent molecules in the orthorhombic system, space group *Pbca*, with $Z = 8$. It is thus not isomorphous with **4** although the structural parameters of its trimethylborazinyl units are similar to those of **4**. This can readily be seen by comparing the data in Table 4. The sum of bond angles at the P1 atom is 306.4°, and, in analogy to **4**, the largest angle at the P atom is 106.2(1)° for N1–P1–N4.

The two borazine rings are twisted against each other by 51°. One of the borazine rings (N1 to B3) is planar, and the P1 atom is coplanar with this ring. The other borazine ring (N4 to B6) shows a half-chair conformation, with the plane B3–N4–B6 forming an angle of 15.9° with the B3–N5–B5–N6–B6 plane. Atoms C4 and C6 are placed below the plane of these five atoms. As observed in **4**, the N5–B4 and N6–B6 bonds are no longer parallel to one another, as would be expected for a planar borazine moiety, but are twisted against each other by 5°. This results in torsion angles of 7° for C6–B6–N5–P1 and 14° for C4–B4–N4–P1.

Once again, the B–N bonds to atoms N1 and N4 are longer [1.475(5) and 1.469(5)°] than all other B–N bonds in the rings. The shortest B–N bonds are B1–N2, B3–N3, B4–N5, and B6–N6, while those to the *p*-B atoms correspond best with those of symmetrically substituted borazines [1.418(6) Å].[17] The N–B–N bond angles vary from 113.9° to 115.8(3)°. While the bond angles B–N(1,4)–B are close to 120°, all other B–N–B bond angles are on average 126.7°. The P–Br bond length is 2.333(1) Å, which is 0.07 Å longer than in the dibromophosphane **5**.

Reactions of the Bromo(trimethylborazinyl)phosphanes with Lithium Tetrahydridoaluminate

The reaction of the bromides **5** and **6** with $LiAlH_4$ should allow the synthesis of the corresponding phosphanes, $(Me_3B_3N_3H_2)PH_2$ and $(Me_3B_3N_3H_2)_2PH$, as shown in Equations (3) and (4), although it is known that aminophosphanes $(R_2N)_{2-n}PH_{n+1}$ are prone to undergo amine elimination.[22]

As shown in Equation (4), the reaction of **6** with $LiAlH_4$ in diethyl ether/hexane gives the compound bis(trimethylborazinyl)phosphane (**13**) in 75% yield. In contrast, the expected reaction [Equation (3)] between the dibromophosphane **5** and $LiAlH_4$ in the same solvents takes a different course. Thus, after removing the solid formed, the filtrate was found to be free of bromide. The crystals that separated from the concentrated filtrate within a week were found to exhibit three ^{11}B NMR signals at δ = 34.1, 35.3, and 36.8 ppm (in a ratio of about 1:1:1) but only a single ^{31}P NMR signal as a triplet at δ = 6.5 ppm ($^1J_{^{31}P,^1H}$ = 430 Hz) when dissolved in C_6D_6 (Figure 5, a). These data give evidence for the presence of a phosphonium $R(X)PH_2^+$ unit, and this was confirmed by the ^1H NMR spectrum, which shows two doublets (see Figure 5, b).

The signal of one of the doublets is further split into a triplet, while the other doublet is split into a quartet (see Figure 5, b). This gives convincing evidence that an ethyl group is attached to the P atom and that the solid is definitely not compound **12**, as would be expected from Equation (3). At this stage we assumed that the compound was most likely the zwitterionic phosphonium borazinate **14**. The $^1J_{^{31}P,^1H}$ coupling constant for the doublet of quartets is 380 Hz, while the $^1J_{^{31}P,^1H}$ coupling constant of the doublet of triplets is 370 Hz. Each of these resonances displays a further coupling of 7 Hz corresponding to $^3J_{^1H,^1H}$. Neither

$$2\,(Me_3B_3N_3H_2)PBr_2 + LiAlH_4 \rightarrow 2\,(Me_3B_3N_3H_2)PH_2 + LiAlBr_4 \quad (3)$$

12

$$4\,(Me_3B_3N_3H_2)_2PBr + LiAlH_4 \rightarrow 4\,(Me_3B_3N_3H_2)_2PH + LiAlBr_4 \quad (4)$$

13

$$Me_3B_3N_3H_2\text{-}PBr_2 + LiAlH_4 + OEt_2 \rightarrow Me_3B_3N_3H_2\text{-}PH_2 + LiBr + AlH_2Br{\cdot}OEt_2 \quad (5)$$

$$AlH_2Br^{\cdot}\,OEt_2 \rightarrow AlH_2(OEt)] + EtBr \quad (6)$$

$$Me_3B_3N_3H_2\text{-}PH_2 + EtBr \rightarrow [(Me_3B_3N_3H_2)PH_2Et]Br \quad (7)$$

$$[(Mc_3B_3N_3H_2)PH_2Et]Br + AlH_2(OEt) \rightarrow (Mc_3B_3(NH)(N^-)N)\text{-}P^+H_2Et + HAl(OEt)Br + H_2 \quad (8)$$

14

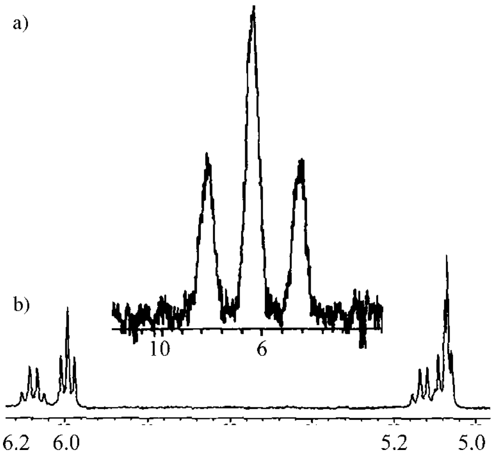
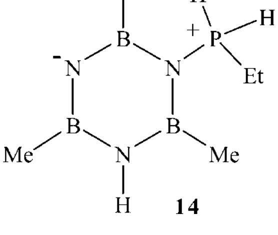


Figure 5. (a) ^{31}P NMR spectrum of **14**. (b) ^{1}H NMR spectrum of **14**.

of the signals shows a roof effect. This assignment was verified by recording a two dimensional ^{1}H-^{31}P spectrum.[5] The structure of **14** was finally confirmed by an X-ray structure determination. The ^{11}B NMR spectrum, with its three ^{11}B NMR signals, is also in line with these arguments.



14

It is clear that the formation of **14** requires a number of steps. One hypothesis for its formation is summarized in Equations (5) to (8). The crucial step here is the formation of EtBr by an ether cleavage with $AlBr_3$, which is a well known process. EtBr is needed to form the phosphonium salt shown in Equation (7), which is the logical precursor to compound **14**. This reaction sequence is unique as no zwitterionic borazine is yet known and nor is a noncoordinated singly deprotonated borazine ring.

X-ray Structures

The monophosphane **13** crystallizes from hexane as colorless needles (orthorhombic, space group *Pbca* with $Z = 8$). Its molecular structure is shown in Figure 6 and structural parameters are listed in Table 5. Its P–N bonds are significantly longer than those in compounds **4**, **5**, and **6**. The sum of bond angles at the P1 atom is 311°, which is a few degrees larger than in any of the borazinylphosphanes described previously. This results primarily from an N1–P1–H bond angle of 102.5(9)°. On the other hand, the N1–P1–N4 bond angle is 105.7(1)°, which corresponds with those found in **4** and **6**. The angles at the P1 atom are, in general, smaller than those found for aminophosphanes.[19]

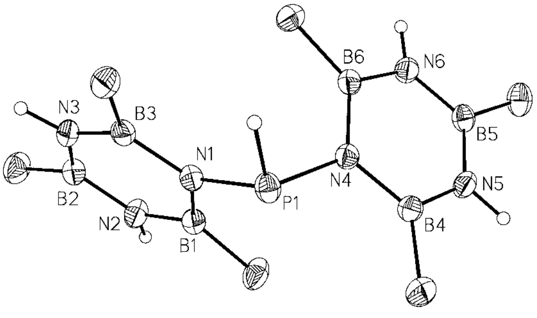


Figure 6. Molecular structure of the phosphane derivative **13**. Selected bonding parameters are listed in Table 5. CH hydrogen atoms have been omitted.

The two borazine units of **13** are almost planar and are twisted against each other by 84°, an angle that is significantly larger than in **4** or **6**, where the angle between the planes B1–N1–B3 and B1–B2–B3 is 5.2° and 8.0°, respectively. The exocyclic angles at N1 are 119.0(2)° for B1–N1–P1 and 120.0(2)° for B3–N1–P1, while the P1–N1–B2–C2 torsion angle is 177°. The B4–N4–P1 and B6–N4–P1 angles are 118.2(2)° and 121.7(2)°, respectively, whereas the P1–

Table 5. Selected bonding parameters for $(Me_3B_3N_3H_2)_2PH$ (**13**) and $(Me_3B_3N_3H)PH_2Et$ (**14**).

13				**14**			
P1–N1	1.742(2)	P1–N4	1.734(2)	P1–N1	1.694(2)		
P1–H1	1.42(1)			P1–C4	1.930(3)		
N1–B1	1.435(4)	N4–B4	1.454(4)	P1–H1	1.23(4)		
B1–N2	1.429(4)	B4–N5	1.413(4)	P1–H2	1.32(4)		
N2–B2	1.427(4)	N5–B5	1.415(4)	N1–B1	1.462(3)		
B2–N3	1.407(5)	B5–N6	1.418(4)	B1–N3	1.413(3)		
N3–B3	1.433(4)	N6–B6	1.419(4)	N2–B2	1.439(3)		
B3–N1	1.464(4)	B6–N4	1.460(4)	B2–N3	11.428(3)		
N1–P1–N4	105.7(1)	N1–P1–H1	102.5(9)	N3–B3	1.421(3)		
N4–P1–H1	102.8(9)			B3–N1	1.439(3)		
B1–N1–P1	119.0(2)	B4–N4–P1	118.2(2)	B1–N1–P1	119.5(2)	H1–P1–H2	103.4(9)
B3–N1–P1	120.0(2)	N6–N4–P1	121.8(2)	B2–N1–P1	119.0(2)	H1–P1–C4	114.1(9)
B1–N1–B3	120.4(2)	B4–N4–B6	120.0(2)	B1–N1–B3	121.3(2)	H2–P1–C4	113.6(4)
B1–N2–B2	124.8(3)	B4–N5–B5	125.5(2)	B1–N2–B2	125.0(2)	H1–P1–N1	107.3(4)
B2–N3–B3	125.8(2)	B5–N6–B6	125.4(2)	N2–N3–B3	125.3(2)	H2–P1–N1	102.6(4)
N1–B1–N2	117.3(3)	N4–B4–N5	117.0(2)	N1–B1–N2	116.9(2)	N1–P1–C4	114.53(9)
N2–B2–N3	115.0(3)	N5–B5–N6	114.7(3)	N2–B2–N3	114.9(2)	P1–C4–C5	112.2(3)
N3–B3–N1	116.4(3)	N6–B6–N4	116.9(2)	N3–B3–N1	116.5(2)		

N4–B5–C5 torsion angle is only 33°, which deviates significantly from the corresponding P1–N1–B2–C2 torsion angle. Once again, the B–N bonds to N1 and N4 are longer [1.452(4), 1.464(4), 1.454(4), and 1.460(4) Å] than all other B–N bonds (av. 1.43 Å).

Compound **14** crystallizes in the orthorhombic space group $Pca2_1$ with $Z = 8$. Its molecular structure, depicted in Figure 7, demonstrates the presence of a phosphonium group. The bond angles at the P1 atom range from 102.6(4)° (N1–P1–H2) to 114.53(9)° (N1–P1–C4). The two P–H bonds seem to be significantly different [1.32(4) and 1.23(4) Å] and the bond angle between them is 103.4°. The P–C bond [1.930(3) Å] is much longer than in other organophosphonium salts [d(PC) = 1.674 to 1.849 Å],[23] and this bond is still 0.1 Å longer than the "normal" P–C single bond length when an electronegativity correction is applied.[24]

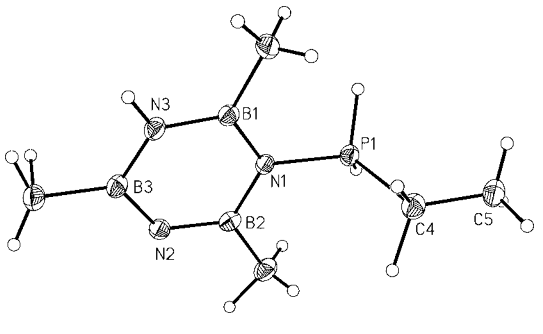


Figure 7. ORTEP plot of the molecular structure of the zwitterion **14**. Selected bonding parameters are listed in Table 5.

The borazine ring of **14** is planar and large B–N–B bond angles at atoms N2 and N3 [125.0(2)° and 125.3(2)°, respectively] are once again observed; the B1–N1–B2 bond angle is 121.3(2)°. The B1–N1–P1 and B2–N1–P1 bond angles are smaller than 120° [119.5(2)° and 119.0(2)°, respectively], and the N–B–N bond angles are also acute [114.9(2)–116.5(2)°]. Equivalent pairs of B–N bond lengths range from 1.462(3) and 1.459(3) Å (to N1) and include short [B1–N2 = 1.413(3), B3–N3 = 1.421(3) Å] and intermediate bond lengths [N2–B2 = 1.439(3), N3–B2 = 1.428(3) Å].

The difference Fourier analysis for NH hydrogen atoms revealed weak peaks on atoms N2 and N3. They refined best with a site occupation factor (SOF) of 0.5 as the U_i values were not compatible with an SOF of 1. Figure 7 shows only one occupied NH position. The X-ray structure analysis excludes an Et/Me exchange between the P atom and a B atom.

Trimethylborazinyldiphosphanes and Cyclotetraphosphanes

The trimethylborazinyl-halogeno-phosphanes appeared to be precursors for borazinyldiphosphanes and cyclophosphanes because it is well known that the dehalogenation of di- and monoorgano-halogeno-phosphanes leads to diphosphosphanes P_2R_4 and cyclophosphanes $(RP)_n$, respectively. Diphosphanes can also be prepared by the reaction of R_2PX with Me_3SiPR_2. However, no reaction was observed on treating the bromide **6** with Me_3SiPR_2 [Equation (9)] even at reflux in toluene.

After replacement of Me_3SiPR_2 with $LiPmes_2$, however, good yields of the diphosphane **17** were obtained [Equation (10)]. The analogous reaction with $LiPPh_2$ generated **16**, although it could not be completely separated from accompanying Ph_2PPPh_2.

As the reaction shown in Equation (11) proceeded without problems, we also decided to treat the dibromide **5** with sodium in toluene. This reaction gave exclusively tetrakis(trimethylborazinyl)cyclotetraphosphane (**19**), as shown in Equation (12). This compound crystallized as strongly intergrown needles, which were also obtained by treating **5** with activated Mg or sodium naphthalide in thf.

While the crystal quality of **16** was insufficient for an X-ray structure determination, single crystals of **17** and **18** were obtained. However, those of **17** were quite small and did not diffract too well. Nevertheless, the refinement converged at $R_1 = 6.5\%$.

$$(Me_3B_3N_3H_2)_2PBr + Me_3SiPR_2 \nrightarrow (Me_3B_3N_3H_2)_2P\text{-}PR_2 + Me_3SiBr \qquad (9)$$

R = Et (**15**), Ph (**16**)

$$(Me_3B_3N_3H_2)_2PBr + LiPmes_2 \rightarrow (Me_3B_3N_3H_2)_2P\text{-}Pmes_2 + LiBr \qquad (10)$$

17

$$2\,(Me_3B_3N_3H_2)_2PBr + 2\,Na \rightarrow (Me_3B_3N_3H_2)_2P\text{-}P(H_2N_2B_3Me_3)_2 + 2\,NaBr \qquad (11)$$

18

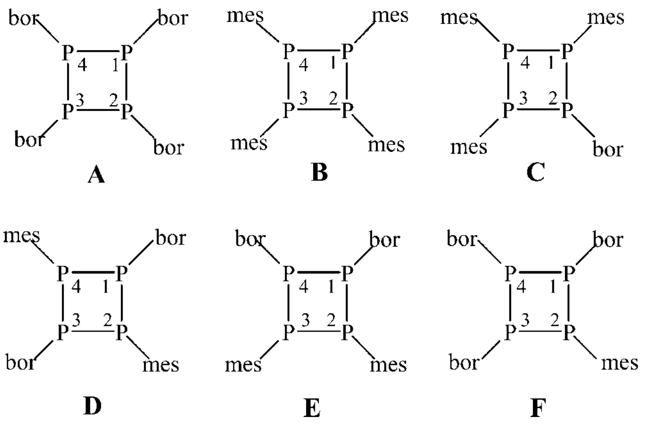
$$4\,(Me_3B_3N_3H_2)PBr_2 + 4\,Na \rightarrow (Me_3B_3N_3H_2)_4P_4 + 4\,NaBr \qquad (12)$$

19

$$2\,(Me_3B_3N_3H_2)PBr_2 + 2\,Li_2Pmes \rightarrow (Me_3B_3N_3H_2)_2P_4(mes)_2 + 4\,LiBr \qquad (13)$$

A – **E**

We expected that the reaction of **5** with Li_2Pmes might yield the 2,4-bis(mesityl)-1,3-bis(trimethylborazinyl)cyclotetraphosphane **D**. However, the ^{31}P NMR spectroscopic data of the solution showed that this ideal composition is not achieved. Rather, a mixture of the cyclotetraphosphanes **A**–**F** (Scheme 1) is formed, with no evidence for cyclotriphosphanes or cyclopentaphosphanes. Isolated single crystals turned out to be the isomer 2,3-bis(mesityl)-1,4-bis(trimethylborazinyl)cyclotetraphosphane (**E**).



Scheme 1. Isomers of dimesitylbis(trimethylborazinyl)cyclotetraphosphane.

NMR Spectra

Table 6 lists the chemical shifts and coupling constants of the nuclei ^{1}H, ^{11}B, and ^{31}P for the diphosphane derivatives. Surprisingly, both diphosphanes **17** and **18** show only a single but very broad ^{11}B resonance, which contrasts with the borazinyl-halogeno-phosphanes. As expected, **18** exhibits a single ^{31}P resonance signal at δ = 108.7 ppm, while there are two doublets at δ = 113.9 and –20.6 ppm for **17**, with a $^{1}J_{^{31}P,^{31}P}$ coupling constant of 223 Hz. Thus, the mesityl-bonded P nuclei are much better shielded than the P nuclei bearing borazine rings. Two sets of proton signals are observed for the BMe groups in **17** and **18**, with those of the *o*-BMe protons being better shielded than the *p*-BMe protons. The former appear as doublets due to $^{4}J_{^{31}P,^{1}H}$ coupling, whereas no such coupling is observed for the *o*-Me groups of the mesityl substituents.

The NMR spectra of compound **19** are rather simple, with only one signal appearing in each of the ^{11}B and ^{31}P NMR spectra. The ^{11}B NMR signal is rather broad. Since there are also single sets of ^{1}H NMR signals for the *o*-BMe and *p*-BMe groups, this suggests that the compound has an all-*trans* conformation. The *o*-BMe protons appear as doublets with a $^{4}J_{^{31}P,^{1}H}$ coupling constant of 5.2 Hz. These data also demonstrate that no cyclotriphosphane or cyclopentaphosphane is generated upon dehalogenation of **5**.

In contrast, the NMR spectra of the solution obtained by treating **5** with Li_2Pmes are surprisingly complex. There are many ^{31}P NMR signals in the range from δ = –60 to –300 ppm, which indicates the presence of cyclotetraphosphanes. Most of these signals could be assigned. Thus, the weak triplets at δ = –171.2 and –299.0 ppm are due to the presence of *cis*-bis(mesityl)bicyclo[1.1.0]tetraphosphane,[24] which is also present as its *trans*-isomer (δ = –292.2 ppm (dd) and two triplets at δ = –155.7 and –161.2 ppm).[24]

Table 6. NMR spectroscopic data for compounds **17**, **18**, **19** and **E**. Half width (Hz) in parentheses.

Compound	$\delta^{11}B$	$\delta^{31}P$	$\delta^{1}H$ *o*-BMe	$\delta^{1}H$ *p*-BMe	$\delta^{1}H$ NH	$\delta^{1}H$ *p*-CMe	$\delta^{1}H$ *o*-CMe	$\delta^{1}H$ CH
17	36.4 (1250)	113.9,[a] –20.6[a]	0.87[b]	0.13	4.39	2.03	2.56	6.67
18[c]	36.3 (1260)	108.7	0.84	0.15	4.49	–	–	–
19	37.1 (1225)	63.0	0.87[d]	0.05	4.48			
E	36.8 (1300)	60.9, –49.2	0.99[e]	0.04		2.80	2.71[f]	

[a] $^{1}J_{^{31}P,^{31}P}$ = 223 Hz. [b] $^{4}J_{^{31}P,^{1}H}$ = 6.8 Hz. [c] bor = $Me_3B_3N_3H_2$. [d] $^{4}J_{^{31}P,^{1}H}$ = 5.2 Hz. [e] $^{4}J_{^{31}P,^{1}H}$ = 5.75 Hz. [f] $^{4}J_{^{31}P,^{1}H}$ = 3.57 Hz.

Fractional crystallization provided crystals of the isomer **E**. A solution of these crystals shows a single but rather broad ^{11}B NMR signal with $h_{1/2}$ = 1300 Hz. This may well result from two overlapping ^{11}B signals because the ^{1}H NMR spectra clearly show the presence of two types of BMe, NH, CMe, and CH signals in the expected intensity ratios. Both the *o*-BMe and *o*-CMe protons appear as doublets due to $^{4}J_{^{31}\text{P},^{1}\text{H}}$ coupling.

A two-dimensional ^{31}P NMR spectrum[5] and high-resolution ^{31}P NMR spectra of the reaction solution give evidence for the presence of all isomers of the cyclotetraphosphanes **A**–**F**. The rings **A** and **B** should lead to an A_4 spin system (^{31}P singlet for the all-*trans* conformer). The singlet at δ = 63.0 ppm demonstrates the presence of isomer **A**, and another singlet at δ = –43.2 ppm stems from compound **B**. Ring **E** should be represented by an AA′XX′ spin system and should therefore show a higher order spectrum, which, in a first approximation, could appear as a doublet of doublets. This doublet of doublets can indeed be observed at δ = 60.9 and –49.2 ppm and these signals show additional signals at higher resolution to give a spectrum of higher order. Ring **D** should give a first-order spectrum, as expected for an A_2X_2 spin system. This is indeed observed, with two triplets at δ = 36.9 and –7.8 ppm ($^{1}J_{^{31}\text{P},^{31}\text{P}}$ = 170 Hz). The P2 atom of ring **C** should give an A_2X type spectrum, in other words a triplet, which is found at δ = 77.3 ppm. Another triplet at δ = 32.5 ppm, with a coupling constant of 232 Hz, can be assigned to the atom P4. Finally, a doublet of doublets is observed at δ = –26.4 ppm representing atoms P1 and P3. The same signal types should result from the presence of isomer **F**. The respective chemical shifts are: a triplet at δ = –30.5 ppm for P2, a doublet of doublets at δ = 41.4 ppm for P1 and P3, and a triplet at δ = 74.9 ppm for P4. The coupling constant is 168 Hz. Examples of the observed and calculated ^{31}P NMR spectra are displayed in Figure 8. The program NUTS[36] was used to obtain the calculated spectra.

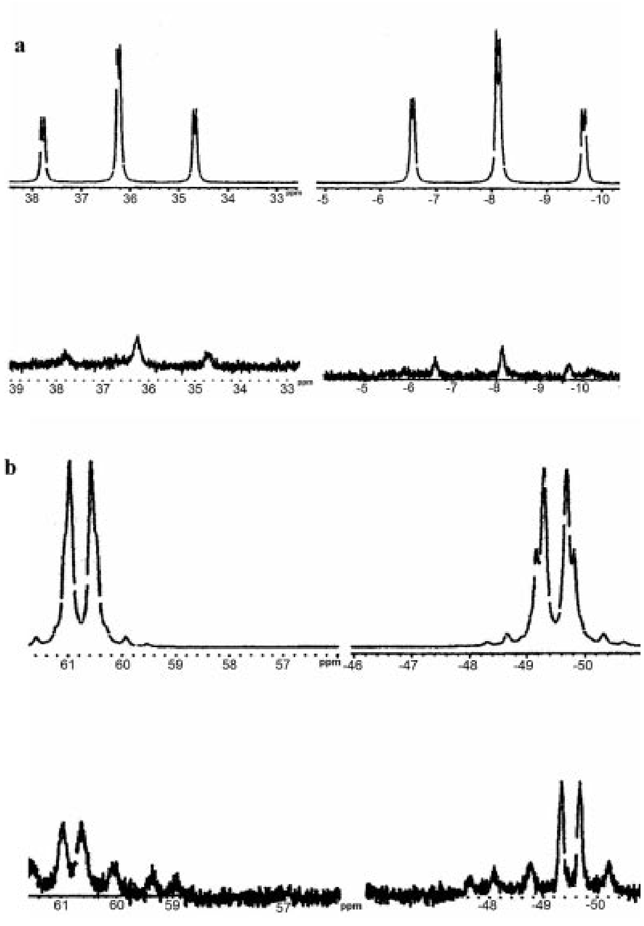


Figure 8. (a) Observed (bottom) and calculated (top) ^{31}P NMR spectra for the isomer 1,3-diborazinyl-2,4-dimesitylcyclotetraphosphane. (b) Observed (bottom) and calculated (top) ^{31}P NMR spectrum of the isomer 1,2-diborazinyl-3,4-dimesitylcyclotetraphosphane (**E**).

The mes and borazinyl substituents (or PX groups) therefore appear to have exchanged during the course of reaction to give a more or less random distribution of the cyclotetraphosphanes.

X-ray Structures

The tetrakis(trimethylborazinyl)diphosphane **18** crystallizes from toluene as **18**$(C_6H_5Me)_2$ in the triclinic space group $P\bar{1}$; its molecular structure is depicted in Figure 9 and relevant bonding parameters are listed in Table 7. The borazinyl units in this compound are present in a staggered conformation. The dihedral angles of opposite rings are 164° for both ring pairs while the dihedral angles of adjacent rings differ by 30°. The N4–P1–P2 angle is 108.4(2)° while the N1–P1–P2 angle exceeds this angle by 7.8°. A twist of 32° is found for the borazinyl rings containing N1 and N7, and this value is even larger for N4 and N10 (97°). While the borazine rings containing N1 and N7 are planar, those including atoms N4 and N10 are slightly bent into a half-chair conformation, with N4 bent out of the plane by 11° and N10 by 9.2°. The BMe groups at the *ortho* positions are bent backwards, with the respective NBC angles ranging from 124.3(7)° to 127.4(7)°. Additional bonding parameters are listed in Table 7.

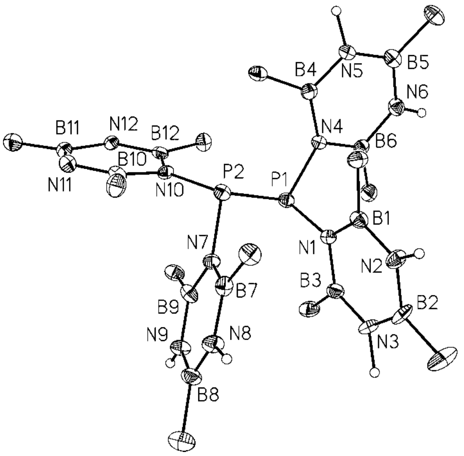


Figure 9. The molecular structure of tetrakis(trimethylborazinyl)diphosphane (**18**). The H atoms of the methyl groups are not shown. Selected bonding parameters are listed in Table 7.

Table 7. Selected bonding parameters for $P_2(H_2N_3B_3Me_3)_4$ (**18**).

P1–P2	2.287(2)						
P1–N1	1.735(6)	P1–N4	1.748(5)	P2–N7	1.755(6)	P2–N10	1.740(5)
B1–N1	1.44(1)	B4–N4	1.462(9)	B7–N7	1.472(9)	B10–N10	1.461(9)
B1–N2	1.44(1)	B4–N5	1.418(9)	B7–N8	1.42(1)	B10–N11	1.45(1)
N2–B2	1.42(1)	N5–B5	1.430(9)	N8–B8	1.42(1)	N11–B11	1.40(1)
B2–N3	1.45(1)	B5–N6	1.43(1)	B8–N9	1–40(1)	B11–N12	1.443(9)
N3–B3	1.41(1)	N6–B6	1.430(9)	N9–B9	1.42(1)	N12–B12	1.433(9)
B3–N1	1.49(1)	B6–N4	1.468(9)	B9–N7	1.452(9)	B12–N10	1.459(9)
P2–P1–N1	94.3(2)	P2–P1–N4	108.5(2)	P1–P2–N7	94.8(2)	P1–P2–N10	109.1(2)
N1–P1–N4	101.8(5)			N7–P2–N10	102.7(3)		
P1–N1–B1	126.6(5)	P1–N4–B4	130.1(5)	P2–N7–B7	113.6(5)	P2–N10–B10	111.8(5)
P1–N1–B3	115.4(5)	P1–N4–B7	111.3(5)	P2–N7–B9	126.7(5)	P2–N10–B12	130.6(5)
B1–N1–B3	118.0(7)	B4–N4–B6	118.6(6)	B7–N7–B9	119.6(5)	B10–N10–B12	117.5(5)
B1–N2–B2	126.21(7)	B4–N5–B5	126.4(7)	B7–N8–B8	126.1(4)	B10–N11–B11	124.7(5)
B2–N3–B3	124.4(7)	B5–N6–B6	126.4(7)	B8–N9–B9	125.6(5)	B11–N12–B12	123.5(6)
N1–B1–N2	117.5(7)	N4–B4–N5	117.6(6)	N7–B7–N8	116.6(6)	N10–B10–N11	118.6(5)
N2–B2–N3	114.3(8)	N5–B5–N6	113.3(7)	N8–B8–N9	114.4(6)	N11–B11–N12	115.5(5)
N3–B3–N1	119.4(7)	N6–B6–N4	117.6(6)	N9–B9–N7	117.7(5)	N12–B12–N10	119.5(5)

Figure 10 shows the molecular structure of the "mixed" diphosphane **17**, and Table 8 contains its bonding parameters. The P–P bond in **18** [2.287(1) Å] is longer than in **17** [2.268(1) Å], which may be a steric effect because the P–N bond in **18** is about 0.03 Å shorter than in **17**.

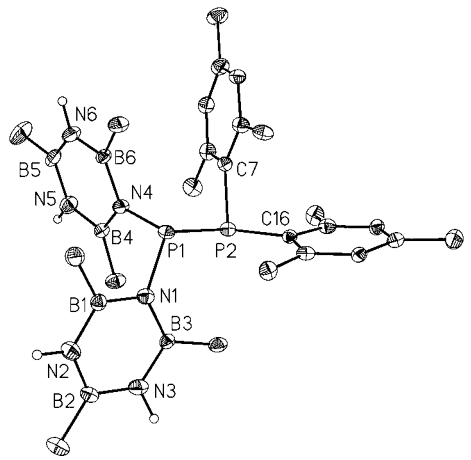


Figure 10. Molecular structure of *P*,*P*-dimesityl-*P*′,*P*′-bis(trimethylborazinyl)diphosphane (**17**). Hydrogen atoms, with the exception of the NH hydrogens, have been omitted. Selected bonding parameters are listed in Table 8.

The first fraction to crystallize from a hexane solution obtained by treating $Me_3B_3N_3H_2PBr_2$ with Li_2Pmes proved to be uniform when inspected by microscopy. The crystals are monoclinic, space group $P\bar{1}$, with $Z = 2$. There is also one molecule of hexane in the unit cell. In a first attempt we solved the structure by assuming that the crystal might have the composition $P_4(H_2N_3B_3Me_3)_4$. The structure solution indeed revealed a cyclotetraphosphane ring, with each of the four P atoms carrying a six-membered ring. The structure refined to $R = 6.6\%$ with attached B_3N_3 rings. However, the thermal parameters and bond lengths clearly showed that this assumption was wrong as there are two long P–N bonds and two shorter ones, and the B–C bond lengths are also shorter for those rings with "long" P–N distances. This result suggests that these latter rings are mesityl rings rather than borazines. In this case the R value improved to $R_1 = 5.99\%$. The result of this latter refinement is shown in Figure 11, where it is clear that the crystal contains species **E**. Selected bonding parameters are summarized in Table 9.

Table 8. Selected bonding parameters for $(Me_3B_3N_3H_2)_2P\text{-}P(C_6H_2Me_3)_2$ (**17**).

P1–P2	2.268(1)						
P1–N1	1.778(2)	P1–N4	1.771(3)	P2–C7	1.831(3)	P2–C16	1.829(3)
N1–B1	1.451(5)	N4–B4	1.451(4)	C7–C8	1.422(4)	C16–C17	1.420(4)
B1–N2	1.415(4)	B4–N5	1.416t(5)	C8–C9	1.391(4)	C17–C18	1.388(5)
N2–B2	1.416(5)	N5–B5	1.412(5)	C9–C10	1.401(5)	C18–C19	1.391(4)
B2–N3	1.413(5)	B5–N6	1.420(5)	C10–C11	1.393(4)	C19–C20	1.394(5)
N3–B3	1.424(4)	N6–B6	1.409(5)	C11–C12	1.402(4)	C20 C21	1.393(5)
B3–N1	1.454(4)	B6–N4	1.456(4)	C12–C7	1.429(4)	C21–C16	1.426(4)
P2–P1–N1	108.7(1)	P2–P1–N4	102.4(1)	P1–P2–C7	96.3(1)	P1–P2–C16	110.9(9)
N1–P1–N4	102.4(1)			C7–P2–C16	102.1(1)		
B1–N1–B3	118.4(3)	B4–N4–B6	119.(3)	C8–C7–C16	117.2(3)	C17–C16–C21	117.2(3)
B1–N2–B2	124.1(3)	B4–N5–B5	125.3(3)	C8–C9–C10	122.9(3)	C17–C18–C19	123.1(3)
B2–N3–B3	125.8(3)	B5–N6–B6	124.9(3)	C10–C11–C12	123.3(3)	C19–C20–C21	123.3(3)
N1–B1–N2	119.0(3)	N4–B4–N5	117.7(3)	C7–C8–C9	119.9(3)	C16–C17–C18	120.0(3)
N2–B2–N3	114.5(3)	N5–B5–N6	114.8(3)	C9–C10–C11	116.6(3)	C18–C19–C20	116.4(3)
N3–B3–N1	117.1(3)	N6–B6–N4	118.0(3)	C11–C12–C7	119.0(3)	C19–C20–C21	123.3(3)

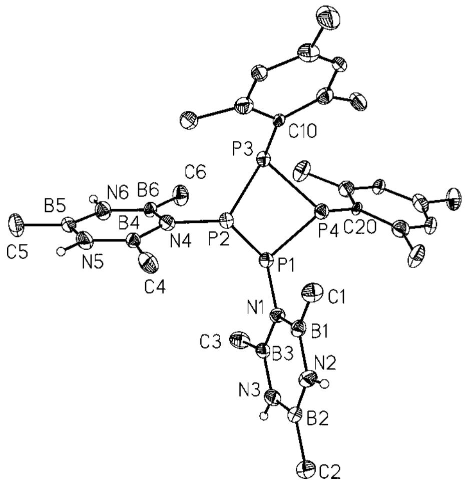


Figure 11. The molecular structure of 3,4-dimesityl-1,2-bis(trimethylborazinyl)cyclotetraphosphane (**E**). Hydrogen atoms at the methyl groups have been omitted. Selected bonding parameters are listed in Table 9.

The cyclotetraphosphane ring is folded, as expected, and it substituents are present in the *trans* orientation that is typical for other P_4R_4 rings.[25–28] The rings at atoms P1 and P3 are twisted against each other by 20° while those at atoms P2 and P4 make an angle of 93°. Amongst the P–P bonds, those to atom P4 are significantly longer than those to atom P2. The longer bonds match with those found for tetrakis(2,2,6,6-tetramethylpiperidino)cyclotetraphosphane or diphenylbis(tetramethylpiperidino)cyclotetraphosphane (2.245 Å).[26]

The endocyclic P–P–P angles span the range from 78.99(5)° (P4) to 84.35(5)° (P3) and are compatible with those of other cyclotetraphosphanes.[25–28] The four-membered ring is not uniformly bent, however, as the non-bonding P–P distances are 3.6 Å for P2–P4 and 2.8 Å for P1–P3.

Discussion and Conclusion

The chemistry of borazines is well documented,[29–31] although neither *B*- nor *N*-phosphanylborazines have been reported. We now show that (2,4,6-trimethylborazinyl)-halogeno-phosphanes are readily available and may serve as starting materials for *N*-(diorganophosphanyl)borazines. *B*-Phosphanylborazines should also be accessible by treating *B*-haloborazines with alkali metal organophosphides.

Because halophosphanes do not react with borazines of the type $R_3B_3N_3H_3$, even in the presence of an HX acceptor, we have used the recently characterized *N*-monolithio-trimethylborazine (**2**) as a stronger nucleophile to bind the borazinyl unit to P^{III}, As^{III}, and Sb^{III} centers. This gives access to all members of the series $(Me_3B_3N_3H_2)_n$-EX_{3-n} (E = P, As, Sb), although the compounds with $n = 3$ were not obtained in pure state. We have also found that the borazinyl-halogeno-phosphanes are suitable reagents for preparing the corresponding bis(borazinyl)phosphane (**13**) as well as borazinyldiphosphanes or borazinylcyclotetraphosphanes. However, the reaction of $LiAlH_4$ with $Me_3B_3N_3H_2PBr_2$ in hexane/diethyl ether does not provide $Me_3B_3N_3H_2PH_2$; rather, this provides the zwitterionic phosphonium borazinate **14**, which shows that the P atom of $(Me_3B_3N_3H_2)PHEt$ is a stronger basic center than the ring N atoms because one of the NH atoms migrates to the P atom. This generates a new type of borazine derivative.[29–31] We are convinced that the reaction of $LiAlH_4$ with $Me_3B_3N_3H_2PBr_2$ in the absence of diethyl ether will lead to $Me_3B_3N_3H_2PH_2$, whose P atom should be less basic than that of the PHEt group.

The dehalogenation of organohalophosphanes with Na or other metals is often employed as a route to organodiphosphanes or organocyclophosphanes.[32] While the dehalogenation of **6** with Na or Mg produced the corresponding diphosphane derivative **18**, its reaction with $LiPmes_2$ gives access to the mixed substituted diphosphane **17**. However, in the case of $LiPPh_2$ the formation of P_2Ph_4 is also

Table 9. Selected bonding parameters for $(Me_3B_3N_3H_2)_2P_4mes_2$ (**E**).[a]

P1–P4	2.215(2)	P1–P2	2.207(2)	P2–P3	2.251(2)	P3–P4	2.256(2)
P4–C20	1.804(4)	P1–N1	1.754(4)	P2–N4	1.769(4)	P3–C10	1.801(4)
C20–C21	1.428(7)	N1–B1	1.449(7)	N4–B4	1.451(6)	C10–C11	1.433(6)
C21–C22	1.379(7)	B1–N2	1.434(7)	B4–N5	1.402(7)	C11–C12	1.406(6)
C23–C24	1.395(7)	N2–B2	1.420(7)	N5–B5	1.411(8)	C13–C14	1.404(7)
C22–C23	1.407(7)	B2–N3	1.409(8)	B5–N6	1.396(7)	C12–C13	1.396(7)
C21–C22	1.379(7)	N3–B3	1.441(7)	N6–B6	1.410(8)	C11–C10	1.433(7)
C20–C21	1.428(7)	B3–N1	1.468(6)	B6–N4	1.450(7)	C10–C15	1.441(7)
P1–P4–P3	84.34(6)	P1–P2–P3	84.34(6)	P2–P1–P4	80.95(6)	P2–P3–P4	79.11(6)
P1–P4–C20	104.8(1)	P2–P3–N1	107.0(1)	P4–P3–N4	111.27(6)	P1–P4–C20	104.8(1)
P3–P4–C20	114.4(2)	P4–P2–N1	109.5(1)	P1–P2–N4	106.8(1)	P3–P4–C20	114.4(21)
P4–C20–C25	128.3(3)	P2–N1–B1	127.2(3)	P2–N4–B4	113.3(1)	P4–C20–C21	113.6(3)
P4–C20–C21	113.7(4)	P2–N1–B3	122.2(4)	P2–N4–B6	127.6(4)	P4–C20–C25	128.3(3)
C25–C20–C21	118.0(5)	B1–N1–B3	120.6(4)	B4–N4–B6	119.0(4)	C15–C10–C11	117.8(4)
C24–C25–C20	118.5(5)	N1–B1–N2	117.4(5)	N4–B4–N5	118.0(5)	C14–C15–C10	119.1(4)
C23–C24–C25	124.1(4)	B1–N2–B2	124.8(6)	B4–N5–B5	124.8(5)	C13–C14–C15	123.5(4)
C24–C23–C22	115.8(5)	N2–B2–N3	115.1(5)	N5–B5–N6	115.0(4)	C14–C13–C12	115.9(4)
C21–C22–C23	122.9(4)	B2–N3–B3	126.0(5)	B5–N6–B6	125.5(5)	C11–C12–C13	123.9(4)

[a] Average B–C bond length: 1.557 Å; average C–C(*exo*) bond length: 1.529 Å.

observed along with $(Me_3B_3N_3H_2)_2PPPh_2$ (**16**). This indicates that a Li/Br exchange occurs during the reaction, and this also occurs during the reaction of Li_2Pmes with **4**, as shown by the formation of compounds **A**–**F**, which is also accompanied by the formation of small amounts of bicylo[1.1.0]tetraphosphanes. The tetra(borazinyl)cyclotetraphosphane (**19**) shows only one ^{31}P signal (δ = 63 ppm),which fits nicely with the other ^{31}P data recorded for cyclotetraphosphanes of the type $(R_2NP)_4$.[26] As far as we are aware the exchange of organo substituents in organophosphorus chemistry is not common, although the borazinyl group, with its P–N bond, is a species with higher bond polarity and is therefore more likely to be more reactive, similar to the aminophosphanes.

This higher reactivity of the borazinylphosphanes with respect to the *N*-unsubstituted borazines seems to be a consequence of the changes in the structures of the new compounds. As shown by X-ray structure determinations, the P atom induces asymmetry in the borazine ring as shown by the comparatively long B–N bonds to the P-carrying N atom. This weakens the B1–N2 and B3–N4 bonds to the neighboring boron atoms. Atoms B1(3), on the other hand, usually form the shortest B–N bonds to atoms N2(5), while the B–N bonds to B2(5) (*para*-position) show B–N bond lengths that correspond to those found in symmetrically substituted borazines $(RB{=}NH)_3$.[30,31] In contrast, the lithium borazine **2**$\cdot OEt_2$, which is dimeric, shows a different distortion. Here, the bonds N1–B1(3) are the shortest bonds in the borazine ring while the B1–N2 and N3–B3 bonds are the longest.[3] This demonstrates that the P substituents have an opposite effect on the B1(3)–N1 bonds, and therefore on the electron distribution in the P-substituted borazine rings, to the Li atom. Moreover, although most of the borazine rings in the new compounds are planar, several show a semi-chair distortion. The distortion is only weak but is nevertheless significant. We assume that this might be a packing effect. We will report shortly on new boron-, aluminum-, and titanium-substituted borazines, the latter of which show the strongest BN bond differences to date, and we are continuing to explore further aspects of this new field of borazine chemistry.

Experimental Section

All experiments were performed using inert gas techniques. Solvents were dried by conventional methods and distilled under an N_2 atmosphere. Compounds **1** and **2** were prepared as described in the literature,[2] as were $LiPmes_2$, LiPmes, and $LiPPh_2$.[32] All other reagents were commercially available. NMR spectroscopic data were recorded in C_6D_6 solutions with TMS (int.), 85% H_3PO_4, or $BF_3\cdot OEt_2$ (external) as standards with Bruker ACP 200 or Jeol FX 400 instruments. IR spectra were recorded as Nujol/Hostaflon mulls. Mass spectroscopy was performed with a Varian Atlas CH-7 instrument. A Siemens P4 four-circle diffractometer equipped with an area detector and a low temperature device was used for recording X-ray reflection data. Elemental analyses were performed by the analytical laboratory of the department. C/N values often deviate by more than 1%, particularly when the compounds contain aryl groups. This is due to incomplete combustion due to boron carbide or nitride formation or to partial hydrolysis.

Dichloro(2,4,6-trimethylborazinyl)phosphane (3): A solution of **2** (0.60 g, 2.96 mmol) in a mixture of hexane (10 mL) and diethyl ether (5 mL) was slowly added to a solution of PCl_3 (0.26 mL, 2.96 mmol) in hexane (30 mL). LiCl precipitated rapidly. After stirring overnight the solid was removed by filtration (yield 95% of LiCl) and the solvents were evaporated from the filtrate in vacuo. The oil which remained was distilled at 55 °C/1 Torr to give pure **3**. Yield 0.56 g (85%). $C_3H_{11}B_3Cl_2N_3P$ (223.45): calcd. C 16.12, H 4.96, N 18.80; found C 16.40, H 5.03, N 18.40. IR: $\tilde{\nu}$ = 3428 s, 3377 m, 3243 w, 2960 s, 2491 w, 2293 w, 2227 w, 2190 w, 2000 w, 1955 w, 1898 w, 1499 s, 1402 s, 1321 s, 1295 s, 1179 m, 1147 m, 1083 m, 1040 w, 1006 m, 982 s, 891 s, 811 m, 729 m, 626 w, 587 m, 532 w, 500 m. 459 m, 426 w, 362 w cm^{-1}.

Chlorobis(2,4,6-trimethylborazinyl)phosphane (4): Prepared in analogy to **3** from PCl_3 (0.18 mL, 2.02 mmol) in hexane (30 mL) and **2** (0.82 g, 4.05 mmol) in hexane/diethyl ether (10:5 mL). The filtrate was reduced to a fifth of its original volume in vacuo and then kept at –25 °C. Yellowish crystals of **4** separated within 5 d. After drying they melted at 110 °C (b.p. 140 °C/1 Torr). Yield 0.50 g (80%). $C_6H_{22}B_6ClN_6P$ (309.57): calcd. C 23.28, H 7.16, N 27.15; found C 22.95, H 6.96, N 26.43. IR: $\tilde{\nu}$ = 3441 s, 3411 s, 3402 s, 2988 m, 2956 m, 2941 m, 2911 m, 1487 s, 1435 s, 1396 s, 1302 s, 1285 s, 1193 m, 1176 m, 1159 s, 1145 s, 1080 m, 1010 w, 973 s, 960 s, 891 s, 808 m, 751 m, 735 m, 721 m, 704 m, 640 w, 591 m, 578 m, 566 m, 539 w, 503 w, 493 w, 468 w, 446 w, 431 w, 405 w, 366 w, 320 w, 296 w cm^{-1}.

Dibromo(2,4,6-trimethylborazinyl)phosphane (5): Prepared in analogy to **3** from PBr_3 (0.17 mL, 1.78 mmol) in hexane (30 mL) and **2** (360 mg, 1.78 mmol) in hexane/diethyl ether (10 mL each). LiBr precipitated rapidly and the solution turned yellow. After stirring overnight, filtration and evaporation of the solvents from the filtrate left a yellow oil (b.p. 95 °C/1 Torr). Within a month the liquid turned into yellow needles (m.p. 50 °C). Yield 0.5 g (85%). $C_3H_{11}B_3Br_2N_3P$ (312.35): calcd. C 11.54, H 3.55, N 13.45; found C 11.50, H 3.62, N 13.47. IR: $\tilde{\nu}$ = 3423 s, 3414 s, 2950 m, 2856 w, 2284 w, 2218 w, 1993 w, 1947 w, 1859 w, 1867 w, 1487 s, 1432 s, 1394 s, 1369 m, 1355 m, 1320 m, 1290 s, 1191 s, 1176 s, 1144 s, 1079 s, 975 s, 940 m, 889 s, 809 s, 731 s, 687 s, 569 s, 480 w, 465 w, 436 m, 389 s, 351 s, 286 w, 258 m cm^{-1}.

Bromobis(2,4,6-trimethylborazinyl)phosphane (6): Prepared in analogy to **4** from PBr_3 (0.18 mL, 1.63 mmol) dissolved in hexane (30 mL) and **2** (0.66 g, 3.26 mmol) in hexane/diethyl ether (10 mL each). After stirring overnight the precipitate (LiBr, 90%) was removed by filtration and two thirds of the solvent was removed in vacuo. Colorless crystals of **6** separated from the slightly yellow solution at 5 °C within a week. Yield 0.40 g (80%), m.p. 145 °C. $C_6H_{22}B_6BrN_6P$ (354.03): calcd. C 20.36, H 6.26, N 23.74; found C 19.27, H 6.19, N 23.23. IR: $\tilde{\nu}$ = 3430 s, 3401 s, 3391 s, 3314 m, 3142 m, 2989 s, 2859 m, 2808 m, 2459 w, 2296 w, 2224 w, 1993 w, 1945 w, 1747 w, 1682 w, 1483 s, 1395 s, 1282 s, 1224 m, 1192 m, 1174 m, 1158 s, 1142 s, 1037 w, 1006 w, 962 s, 889 s, 806 m, 759 m, 741 m, 704 m, 624 m, 596 m, 689 m, 567 m, 493 w, 454 w, 439 w, 423 w, 384 w, 362 w, 309 w, 284 w cm^{-1}. MS (70 eV): *m*/*z* (%) 354 (20) $[M^+]$, 339 (15) $[M^+ - Me]$, 309 (10) $[M^+ - 3Me]$, 274 (100) $[M^+ - Br]$, 259 (55), $[M^+ - Br - Me]$, 244 (15) $[M^+ - Br - 2Me]$, 121 (20) $[B_3N_3Me_3H_2^+]$, 111 (65) $[PBr^+]$.

Dichloro(2,4,6-trimethylborazinyl)arsane (7): A toluene solution of **2** (0.58 g, 2.86 mmol in 20 mL) was added dropwise to a solution of $AsCl_3$ (0.24 mL, 2.86 mmol) in hexane (30 mL). A white precipitate formed immediately. After stirring overnight the solid was removed by filtration and the solvents evaporated in vacuo. A slightly yellow oil (0.5 g) remained as residue which decomposed on attempted distillation. Yield 500 mg (65%). ^{1}H NMR: δ = 0.15 (s, 3 H, BMe), 0.56 (s, 6 H, BMe), 4.42 ppm (br. s, 2 H, NH). ^{11}B NMR: δ = 35.6, 37.9 ppm (1:2).

Chlorobis(2,4,6-trimethylborazinyl)arsane (8): Prepared in analogy to **4** from $AsCl_3$ (0.30 mL, 3.58 mmol) in hexane (30 mL) and **2** (1.45 g, 7.16 mmol) in toluene (20 mL). LiCl was recovered in 95% yield. The filtrate was concentrated and the white amorphous precipitate that formed within a week was isolated. Yield 0.9 g (75%), m.p. 64 °C. No single crystals were obtained from toluene, diethyl ether, or thf solutions. $C_6H_{22}AsB_6ClN_6$ (353.49): calcd. C 20.38, H 6.27, N 23.37; found C 20.81, H 6.09, N 22.96. IR: $\tilde{\nu}$ = 3445 m, 3419 s, 3411 s, 2942 s, 2951 s, 2909 s, 2858 m, 1478 s, 1397 s, 1303 s, 1285 s, 1193 m, 1177 m, 1161 m, 1154 m, 1118 w, 1083 m, 1045 w, 1026 w, 920 s, 889 s, 805 m, 753 w, 734 m, 717 s, 573 s, 539 m, 505 w, 485 w, 458 w, 430 w, 416 w, 344 m, 322 w, 288 w, 282 w, 274 w cm^{-1}.

Dichloro(2,4,6-trimethylborazinyl)stibane (9): Freshly sublimed $SbCl_3$ (0.60 g, 2.62 mmol) was suspended in hexane (30 mL) and a solution of **2** (0.53 g, 1.57 mmol) in hexane (20 mL) was added. After keeping the suspension at reflux overnight the insoluble white material was removed by filtration. The solvent was evaporated from the filtrate in vacuo and the residue dissolved in a small quantity of hexane. Colorless crystals separated from this solution at –5 °C within a week. Yield 0.62 g (75%), m.p. 148–149 °C. $C_3H_{11}B_3Cl_2N_3Sb$ (314.23): calcd. C 11.47, H 3.53, Cl 22.56, N 13.37; found C 12.86, H 3.84, Cl 22.34, N 12.48. IR: $\tilde{\nu}$ = 3448 w, 3421 s, 3406 s, 2964 s, 2964 m, 2946 m, 2910 w, 1474 s, 1407 s, 1332 m, 1317 s, 1303 s, 1292 s, 1262 s, 1191 m, 1172 m, 1153 m, 1082 s, 1020 m, 889 s, 802 s, 757 m, 740 m, 715 s, 661 w, 569 s, 531 m, 400 w, 392 w, 342 s, 331 s, 318 st cm^{-1}. MS (50 eV): *m*/*z* (%) 314 (5) [M$^+$], 299 (45) [M$^+$ – Me], 207 (20) [$MeSbCl_2^+$], 192 (100) [$SbCl_2^+$], 156 (65) [$SbCl^+$], 122 (80) [$Me_3B_3N_3H_2^+$].

Tris(2,4,6-trimethylborazinyl)arsane was obtained from **2** (0.96 g, 4.69 mmol) in a solution of hexane (30 mL) and $AsCl_3$ (0.11 mL, 1.56 mmol) in 10 mL of hexane. After keeping the mixture at reflux for 3 d the solid was filtered off and the filtrate reduced to one third of its original volume. The solution still contained small amounts of chloride. The ^{11}B NMR spectrum showed the formation of $(Me_3B_3N_3H_2)_3As$. ^{1}H NMR (C_6D_6): δ = 0.07 (s, 3 H, BMe), 0.61 (s, 6 H, BMe), 4.42 ppm (br. s, 2 H, NH) with some weak signals from impurities. ^{11}B NMR (C_6D_6): δ = 35.5, 36.9 ppm.

Chlorobis(2,4,6-trimethylborazinyl)stibane (10): A suspension of $SbCl_3$ (0.37 g, 1.62 mmol) in hexane (30 mL) was allowed to react with a solution of **2** (0.657 g, 3.24 mmol) in hexane (20 mL). After refluxing overnight the solid was removed by filtration and the filtrate reduced in volume by 3/4. From the solution settled a white powder at –25 °C. Yield 0.50 g of **10** (75%), dec. > 200 °C. $C_6H_{22}B_6ClN_6Sb$ (400.36): calcd. C 17.99, H 5.53, N 20.99; found C 20.47, H 5.38, N 21.79. IR: $\tilde{\nu}$ = 3438 s, 3418 s, 2963 s, 2932 m, 2861 m, 2791 w, 1473 s, 1449 m, 1429 m, 1300 s, 1370 m, 1360 w, 1321 m, 1282 w, 1261 s, 1193 w, 1170 w, 1095 s, 1021 w, 956 w, 893 w, 833 w, 803 w, 755 w, 700 m, 670 m, 658 m, 614 s, 533 w, 528 w, 477 w, 404 w cm^{-1}.

Tris(2,4,6-trimethylborazinyl)phosphane (11): PBr_3 (1.64 mmol) dissolved in toluene (10 mL) was added to a solution of **2** (1.00 g, 4.93 mmol) in toluene (30 mL). A white precipitate formed rapidly. After keeping the mixture at reflux for one day the solid was removed by filtration. A ^{31}P NMR spectrum showed the formation of **11** (δ = 120.3 ppm) along with minor amounts of **6** (δ = 191 ppm). The latter could not totally be removed from **6** despite repeated crystallization from toluene/hexane at –20 °C. ^{1}H NMR (C_6D_6): δ = 0.18 (s, 3 H, BMe), 0.64 (d, 6 H, BMe), 4.55 ppm (br. s, NH) ppm. ^{11}B NMR (C_6D_6): δ = 35.7, 39.5 ppm (2:1). ^{31}P NMR (C_6D_6): δ = 120.3 ppm.

Tris(2,4,6-trimethylborazinyl)stibane (impure) was obtained as a white powder upon treatment of a suspension of $SbCl_3$ (0.488 g, 2.13 mmol) in hexane (20 mL) with a solution of **2** (1.30 g, 6.24 mmol) in hexane (30 mL). After heating the mixture overnight to reflux and removing the insoluble material a white powder remained after evaporation of the solvent. The product was characterized only by NMR spectroscopy. ^{1}H NMR: δ = 0.19 (s, 9 H, Me), 0.52 (s, 18 H, Me), 4.31 ppm (s, 6 H, Me) and some additional weak signals. ^{11}B NMR: δ = 35.1, 37.3 ppm (1:2).

Bis(2,4,6-trimethylborazinyl)phosphane (13): Compound **6** (1.65 g, 4.67 mmol) was dissolved in hexane (30 mL) and a solution of $LiAlH_4$ in diethyl ether (0.83 mL of a 1.3 M solution) was added to this stirred solution to give a white precipitate. After stirring overnight the solid was removed by filtration and three quarters of the solvents were evaporated from the filtrate in vacuo. Storing the solution at +5 °C gave platelets of **13** within two weeks (m.p. 82 °C). Yield 0.95 g (75%). $C_6H_{23}B_6N_6P$ (275.12): calcd. C 26.19, H 8.43, N 30.54; found C 26.69, H 9.01, N 29.96. IR: $\tilde{\nu}$ = 3424 s, 3402 s, 2958 s, 2942 s, 2932 s, 2846 w, 2489 w. 2293 s, 2254 s, 2175 w, 2122 w, 2080 w, 1980 w, 1915 w, 1901 w, 1879 w, 1483 s, 1397 s, 1371 m, 1316 s, 1291 s, 1206 m, 1196 m, 1186 w, 1163 s, 1143 w, 1105 w, 1093 w, 1065 m, 1040 w, 1021 w, 991 m, 962 s, 895 s, 834 w, 912 m, 785 w, 748 s, 725 w, 636 w. 605 m, 592 m, 572 m, 492 w, 479 w, 440 w, 394 w. 371 m, 356 w cm^{-1}.

Zwitterionic Ethylphosphonium 2,4,6-Trimethylborazinate 14: A diethyl ether solution of $LiAlH_4$ (0.29 mmol, 1.4 M) was added to a hexane solution (30 mL) of **5** (0.52 g, 1.66 mmol) with stirring. The solid formed was removed by filtration after stirring the mixture overnight. The volume of the filtrate was then reduced to one fifth. Crystals separated within a week on storing this solution at –5 °C. Yield 0.20 g (65%). $C_5H_{17}B_3N_3P$ (182.59): calcd. C 32.89, H 9.37, N 23.01; found C 32.19, H 9.12, N 22.54. IR: $\tilde{\nu}$ = 3443 s, 3407 s, 2950 s, 2911 s, 2900 s, 2853 s, 2332 s, 1490 s, 1407 s, 1370 s, 1360 s, 1262 s, 1199 s, 1183 s, 1166 s, 1144 s, 1098 s, 1059 s, 1021 s, 997 s, 943 s, 888 s, 806 s, 748 s, 730 m, 715 m, 676 m, 667 m, 649 m, 642 m, 603 m, 567 m, 546 w, 397 w, 378 m cm^{-1}. ^{1}H NMR: δ = 0.14 (s, 3 H, BMe), 0.30 (m, 5 H, Et). 0.35–0.47 (m, 5 H, P*Me*, PC*H*$_2$), 0.54 (d, $^4J_{^{31}P,^1H}$ = 1.9 Hz, 6 H, BMe), 5.52 (dt, $^1J_{^{31}P,^1H}$ = 370, $^3J_{^{31}P,^1H}$ = 7 Hz, 2 H, PH_2), 5.59 ppm (dq, $^1J_{^{31}P,^1H}$ = 379, $^3J_{^1H,^1H}$ = 7 Hz, 2 H, P*H*$_2$). ^{11}B NMR: δ = 34.1, 35.3 ppm. ^{31}P NMR: δ = 5.5 ppm (t, $^1J_{^{31}P,^1H}$ = 430 Hz).

Bis(mesityl)bis(2,4,6-trimethylborazinyl)diphosphane (17): A solution of **6** (0.88 g, 25 mmol) in hexane (20 mL) was added slowly to a stirred suspension of $LiPmes_2$ (0.69 g, 2.5 mmol) in hexane (50 mL) at –78 °C. The mixture was then kept at reflux for 14 h. Insoluble material was removed by filtration and about half of the solvent was removed in vacuo. The filtrate was kept at –25 °C and the microcrystalline material recrystallized from toluene at –30 °C as colorless prisms. Two crystals were selected for the X-ray structure determination and proved to contain toluene. The crystals became opaque in vacuo. After keeping them in vacuo for 3 h the yield was 1.15 g (85%), m.p. 182 °C. $C_{24}H_{44}B_6N_6P_2$ (542.47): calcd. 53.04, H 8.16, N 15.46; found C 51.71, H 8.66, N 14.74. IR: $\tilde{\nu}$ = 3424 m, 3414 m, 3403 w, 3100 w, 3089 m, 3025 m, 2965 s, 2924 s, 2864 m, 2731 w, 1667 w, 1601 m, 1549 w, 1478 s, 1432 s, 1396 m, 1298 s, 1277 s, 1188 m, 1178 m, 1152 m, 1083 m, 1031 w, 1016 w, 930 m, 896 m, 953 m, 861 m, 807 m, 787 w, 734 m, 699 w, 602 w, 581 s, 568 m, 559 m, 546 w, 521 w, 499 w, 453 w, 375 m, 365 m cm^{-1}.

Tetrakis(2,4,6-trimethylborazinyl)diphosphane (18): Freshly cut pieces of elemental Na (300 mg) were added to a solution of **6** (1.61 g, 5.0 mmol) in toluene (50 mL). There was no reaction at ambient temperature. The mixture was then kept at reflux (about 3 d) until the ^{31}P NMR signal of the **6** could no longer be observed. The solid material was then removed by filtration. The filtrate was free of bromide. Two thirds of the toluene was then evaporated in vacuo and the remaining solution kept at –25 °C. Crystals of **18** separated within 10 d. Yield 1.02 g (70%). $C_{12}H_{44}B_{12}N_{12}P_2$ (548.24): calcd. C 26.29, H 8.09, N 30.66; found C 28.34, H 8.36, N 29.86. IR: $\tilde{\nu}$ = 3432 s, 3413 s, 2956 m, 2943 m, 2855 m, 1483 s, 1399 s, 1293 s, 1280 s, 1200 m, 1190 s, 1177 s, 1153 s, 1084 m, 1041 w, 1030 w, 1019 w, 933 s, 889 s, 808 m, 736 s, 727 s, 715 m, 649 m, 683 s, 563 m, 518 w, 491 w 431 w, 374 m, 358 m cm^{-1}. ^{1}H NMR: δ = 0.15 (s, 12 H, BMe), 0.84 (s, 24 H, BMe), 4.49 ppm (s, 8 H, NH). ^{11}B NMR: = 36.3 ppm (br., $h_{1/2}$ = 1260 Hz). ^{31}P NMR: = 108.7 ppm (s).

Tetrakis(2,4,6-trimethylborazinyl)cyclotetraphosphane (19): A solution of **5** (0.33 g, 1.04 mmol) in hexane (50 mL) was treated with a suspension of finely cut sodium chips (ca. 0.5 g). The reaction started after heating the mixture to reflux. After 3 d the ^{31}P NMR signal of **5** could no longer be detected. The insoluble material was removed by filtration. No bromide was found in the filtrate. After reducing the volume of the filtrate by about 60% slightly yellowish crystals separated within two weeks at –50 °C. Attempts to obtain single crystals from hexane, toluene, or thf were unsuccessful. Yield 0.18 g (60%), m.p. 200 °C. $C_{12}H_{44}B_{12}N_{12}P_4$ (610.18): calcd. C 23.62, H 7.26, N 27.55; found C 24.12, H 7.34, N 24.89. IR: $\tilde{\nu}$ = 3437 w, 3422 w, 2969 m, 2890 w, 1483 s, 1397 s, 1380 m, 1364 w, 1282 s, 1261 m, 1193 m, 1178 m, 1150 m, 1131 w, 1082 m, 939 s, 878 s, 850 m, 808 m, 701 wm, 613 w, 574 w, 351 w, 343 w cm^{-1}.

Dimesitylbis(2,4,6-trimethylborazinyl)cyclotetraphosphane (A–F): A solution of **4** (0.33 g, 1.04 mmol) in toluene (20 mL) was slowly added at –78 °C to a suspension of mesPLi$_2$ (0.17 g, 1.04 mmol) in the same solvent (20 mL). The stirred mixture was allowed to reach room temperature and stirring was continued overnight. The insoluble material was then removed by filtration. The filtrate contained no bromide and was investigated by NMR spectroscopy. The volume of the filtrate was further reduced to one fifth. Colorless, prismatic crystals were isolated after two weeks which proved to be compound **E**. Yield 0.27 g (45%), m.p. 189 °C. Further fractional crystallizations yielded no other pure product. $C_{24}H_{44}B_6N_6P_4$ (605.35): calcd. C 42.55, H 7.37, N 14.61; found C 44.46, H 7.63, N 13. 84. IR: $\tilde{\nu}$ = 3437 w, 3428 w, 3409 w, 3400 m, 3025 w, 2959 m, 2860 w, 1602 m, 1481 s, 1399 s, 1370 m, 1361 w, 1285 s, 1263 m, 1201 m, 1191 m, 1178 m, 1150 m, 1130 w, 1084 m, 1028 w, 939 s, 888 s, 850 m, 733 m, 701 m, 607 w, 571 m, 467 w, 353 w cm^{-1}. ^{1}H NMR: δ = 0.043 (s, 6 H, BMe), 0.99 (d, $^{4}J_{^{31}P,^{1}H}$ = 5.75 Hz, 12 H, BMe), 2.80 (d, $^{4}J_{^{31}P,^{1}H}$ = 3.57 Hz, 12 H, CMe), 2.82 (s, 6 H, CMe), 4.47 (s, 4 H, NH), 6.68 ppm (s, 4 H, CMe). ^{31}P NMR: δ = 74.9 (t, $^{1}J_{^{31}P,^{31}P}$ = 168.3 Hz), –30.5 (t, $^{1}J_{^{31}P,^{31}P}$ = 168.4 Hz), 48.6 (dd, $^{1}J_{^{31}P,^{31}P}$ = 168.2 Hz), 63.4 (s), 60.7 (dd, $^{1}J_{^{31}P,^{31}P}$ = 57.0 Hz), –49.5 (dd, $^{1}J_{^{31}P,^{31}P}$ = 57.0 Hz), 36.2 (t, $^{1}J_{^{31}P,^{31}P}$ = 171.7 Hz), –8.1 (t, $^{1}J_{^{31}P,^{31}P}$ = 168.4 Hz), 77.3 (t, $^{1}J_{^{31}P,^{31}P}$ = 170.2 Hz), –26.4 (dd, $^{1}J_{^{31}P,^{31}P}$ = 170.2 Hz), –32 ppm (t, $^{1}J_{^{31}P,^{31}P}$ = 170.2 Hz).

X-ray Structure Determinations: Single crystals were covered with perfluoro ether oil under dinitrogen and a specimen selected. The selected crystal was mounted on the top of a glass fiber and placed

Table 10. Crystallographic data and data collection and structure solution parameters.

Compound	**4**	**5**	**6**	**9**
Empirical formula	$C_{13}H_{26}B_6ClN_6P$	$C_3H_{11}B_3Br_2N_3P$	$C_6H_{22}B_6BrN_6P$	$C_3H_{11}B_3Cl_2N_3Sb$
Formula mass	398.17	312.37	354.04	314.23
Crystal size [mm]	0.10 × 0.20 × 0.20	0.35 × 0.26 × 0.19	0.20 × 0.20 × 0.30	0.25 × 0.298 × 0.42
Crystal system	triclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P\bar{1}$	*Pnma* (62)	*Pbca*	$P2_1/n$
a [Å]	8.0317(6)	19.963(1)	16.0349(4)	8.1660(2)
b [Å]	11.4558(9)	7.4737(3)	8.2488(2)	9.7796(3)
c [Å]	13.658(1)	15.2362(8)	27.1422(5)	28.1685(8)
α [°]	83.692(2)	90	90	90
β [°]	74.337(2)	90	90	90.5608(2)
γ [°]	74.062(2)	90	90	90
V [Å^3]	1162.6(2)	2273.1(2)	3590.1(1)	2249.4(1)
Z	2	8	8	8
ρ(calcd.) [Mg m^{-3}]	1.135	1.825	1.310	1.856
μ [mm^{-1}]	0.243	7.225	2.373	2.879
F(000)	415	1200	1440	1200
Index ranges	$-10 \le h \le 8$, $14 \le k \le 14$, $-17 \le l \le 17$	$-26 \le h \le 26$, $8 \le k \le 9$, $-20 \le l \le 17$	$-19 \le h \le 19$, $10 \le k \le 10$, $-32 \le l \le 32$	$-10 \le h \le 10$, $12 \le k \le 12$, $-32 \le l \le 35$
2θ [°]	57.54	56.00	52.74	57.84
Temp. [K]	193(2)	200(2)	183	193
Reflections collected	6838	12290	18337	12381
Reflections unique	3581	2933	3515	4446
Reflections observed (4σ)	2646	1696	2337	4047
R (int.)	0.0195	0.0540	0.0624	0.0186
Number of variables	270	139	203	233
Weighting scheme[a] x/y	0.1907/0.612	0.0758/0.00	0.0297/3.5073	0.0339/3.4530
GOOF	1.118	0.926	1.104	1.140
Final R(4σ)	0.0881	0.0462	0.0519	0.0304
Final $wR2$	0.2748	0.1184	0.0904	0.0719
Largest residual peak [e/Å^3]	1.270	1.277	0.319	0.696

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

Table 11. Crystallographic data and data collection and structure solution parameters.

Compound	**13**	**14**	**17**·$2C_6H_8$	**E**
Empirical formula	$C_6H_{23}B_6N_6P$	$C_5H_{17}B_3N_3P$	$C_{38}H_{56}B_6N_6P_2$	$C_{24}H_{44}B_6N_6P_4$
Formula mass	275.13	182.62	723.69	605.80
Crystal size [mm]	0.05 × 0.4 × 0.5	0.2 × 0.3 × 0.3	0.2 × 0.3 × 0.4	0.2 × 0.23 × 0.3
Crystal system	orthorhombic	orthorhombic	triclinic	triclinic
Space group	*Pbca*	$Pca2_1$	$P\bar{1}$	$P\bar{1}$
a [Å]	15.860(1)	16.997(1)	11.173(2)	8.9312(7)
b [Å]	8.0674(6)	4.5201(3)	11.495(3)	11.2962(9)
c [Å]	25.886(2)	14.537(1)	16.176(4)	19.757(2)
α [°]	90	90	77.833(9)	81.619(2)
β [°]	90	90	80.90(1)	89.161(2)
γ [°]	90	90	84.69(1)	70.801(2)
V [Å^3]	3312.2(4)	1116.9(1)	2001.6(8)	1861.1(3)
Z	8	4	2	2
ρ(calcd.) [Mg m^{-3}]	1.104	1.086	1.131	1.129
μ [mm^{-1}]	0.157	0.199	0.141	0.14
F(000)	1168	392	730	706
Index ranges	$-16 \le h \le 19$, $10 \le k \le 10$, $-31 \le l \le 32$	$-21 \le h \le 21$, $5 \le k \le 5$, $-18 \le l \le 18$	$-11 \le h \le 15$, $14 \le k \le 14$, $-20 \le l \le 20$	$-12 \le h \le 10$, $13 \le k \le 13$, $-25 \le l \le 25$
2θ [°]	58.58	58.48	58.46	57.64
Temp. [K]	193(2)	193(2)	193(2)	183(2)
Reflections collected	17739	5956	11732	10765
Reflections unique	3361	2381	6286	5627
Reflections observed (4σ)	2060	2085	4531	3103
R (int.)	0.0621	0.0244	0.0251	0.0521
Number of variables	183	181	423	407
Weighting scheme[a] x/y	0.0772/1.4325	0.0806/0.0039	0.200/0.000	0.3621//0.000
GOOF	1.029	0.926	1.034	0.960
Final R(4σ)	0.0601	0.0393	0.0650	0 054
Final $wR2$	0.1431	0.1100	0.1728	0.1144
Largest residual peak [e/Å^3]	0.229	0.214	0.604	0.245

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

on the goniometer head flushed with a cold stream of N_2. Data for the determination of the unit cell were colleted at –80 °C for a total of 75 frames. The unit cell was determined with the program SMART.[33] Data collection was performed in the hemisphere mode. After data reduction the model structure was determined with the program SAINT.[34] The structure determination package SHELXTL[35] was used to refine the data. Non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and refined using a riding model. The NH hydrogen atoms were located in the difference Fourier map and their positions were refined with isotropic thermal parameters. The thermal ellipsoids in the figures are shown at the 25% probability level. Distances are given in Ångstroms and bond angles in degrees. Crystallographic data and data related to data collection and refinement are summarized in Tables 10 and 11.

CCDC-620997 to -621005 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[18] Both toluene molecules are disordered with an SOF of close to 0.5. This value was fixed to 0.5 in the refinement. One toluene looks like a xylene whereas the other is more differently disordered: the benzene rings are shifted so that the *p*-C atoms are centered in the middle of the other six-membered ring. However, the C–C distances are not equal. No H atoms have been added to these disordered molecules.

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