Contributions to the Chemistry of Boron, 188[1]

Synthesis and Structures of New 1,3,2,4-Diphosphadiboretanes

Peter Kölle[a], Gerald Linti[a], Heinrich Nöth*[a], Gary L. Wood[b], Chaitanya K. Narula[b], and Robert T. Paine*[b]

Institut für Anorganische Chemie der Universität München[a],
Meiserstraße 1, D-8000 München 2, FRG

Department of Chemistry, University of New Mexico[b],
Albuquerque, New Mexico, USA

Received November 6, 1987

Three methods have been devised to prepare new diphosphadiboretanes: a) Base-induced hydrogen halide elimination from (amino)phosphinoboron halides precursors, b) tris(trimethylsilyl)phosphane elimination from $R_2N-B[P(SiMe_3)_2]_2$ intermediates prepared in situ from combinations of $R_2N-B(Cl)-P(SiMe_3)_2$ and $LiP(SiMe_3)_2$, and c) organylphosphane elimination from aminobis(organylphosphino)boranes $R_2N-B(PHR')_2$. The molecular structures of three new 1,3,2,4-diphosphadiboretanes (3, 4a, 4c) were determined by X-ray diffractometry. These are characterized by a planar four-membered B_2P_2 ring with the phosphorus substituents in *trans* positions. Their BP bonds represent single bond distances. Experimental results are compared with MNDO III calculations which reveal a low barrier (ΔE = 5 kcal/mol) for the dimerization of the boraphosphene $H_2N-B=PMe$ to the diphosphadiboretane $(H_2N-BPMe)_2$.

Beiträge zur Chemie des Bors, 188[1]. – Synthese und Strukturen neuer 1,3,2,4-Diphosphadiboretane

Drei Methoden wurden zur Darstellung neuer Diphosphadiboretane entwickelt: a) Die baseninduzierte Elimierung von Halogenwasserstoff aus (Amino)phosphinobor-halogeniden, b) Tris(trimethylsilyl)phosphan-Abspaltung aus $R_2N-B[P(SiMe_3)_2]_2$-Zwischenprodukten und c) Organylphosphan-Eliminierung aus Aminobis(organylphosphino)boranen $R_2N-B(PHR')_2$. Die Molekülstrukturen von drei neuen 1,3,2,4-Diphosphadiboretanen (**3**, **4a**, **4c**) wurden mittels Röntgenbeugung bestimmt. Sie sind durch planare B_2P_2-Ringe charakterisiert. Die *P*-Substituenten stehen *trans* zueinander. Experimentelle Ergebnisse werden mit MNDO III Rechnungen verglichen; letztere ergeben eine geringe Aktivierungsbarriere (ΔE = 5 kcal/mol) für die Dimerisierung von $H_2N-B=PMe$ zu $(H_2N-BPMe)_2$.

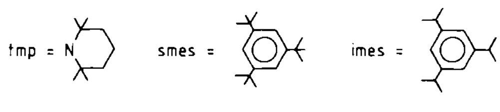
Efforts to "disprove" the so-called double-bond rule have recently resulted in considerable interest in compounds of main group elements involving multiple bonding[2]. The majority of the multiple bonded compounds contain homoelement pairs, e.g. P = P and Si = Si double bonds[3]; however, new hetero-element combinations have also been described, e.g. $-B=C\lt$[4] and $-B\equiv N-$[5]. In hetero-element examples relatively little attention has been given in boron chemistry to the isolation or even detection of compounds containing heavier elements, although gas phase species of the type $X-B=S$ and $X-B=Se$[6] are well characterized. Reports of transient[7,8] and stable[9–11] compounds containing boron-phosphorus multiple bonds have also appeared. During the search for monomeric boraphosphene species $RB=PR'$, it has been observed that potential synthetic routes to these compounds often result in the formation of four-membered 1,3,2,4-diphosphadiboretane rings, examples being $(tmp\text{-}BPR)_2$ (tmp = 2,2,6,6-tetramethylpiperidino, R = phenyl[12], mesityl, and 2,4,6-$C_6H_2tBu_3$[7,8,13], CEt_3[14]), $(PhBPPh)_2$[15], $(Me_2NBPSiMe_3)_2$[16], and $(PhBPSiMe_3)_2$[16]. In our efforts to examine the chemistry of transient or stable monomeric boraphosphenes we have explored additional possible precursors to BP multiple bonds, and several new diphosphadiboretanes have been obtained, on which we report here.

Reactions

(Diorganylphosphino)boranes are generally prepared by reaction of a boron halide with a metal phosphide, and they remain monomeric when the boron atom is electronically stabilized or sterically shielded. The former is the case for (dimethylamino)(phosphino)boranes[17], and an example of the latter is (diorganylphosphino)dimesitylborane[10]. As has now been shown this is also true for certain (amino)(monoorganylphosphino)boranes **1**.

$$R_2N\text{-}BX_2 + LiPHR' \xrightarrow{-LiX} + \underset{\mathbf{1}}{R_2N\text{-}B(X)\text{-}PHR'} \qquad (1)$$

	1a	**1b**	**1c**	**1d**	**1e**	**1f**
X	F	Cl	F	F	F	Cl
R'	smes	imes	imes	$CH(SiMe_3)_2$	imes	CMe_3
R_2N	tmp	tmp	tmp	tmp	$N(CMe_3)_2$	tmp

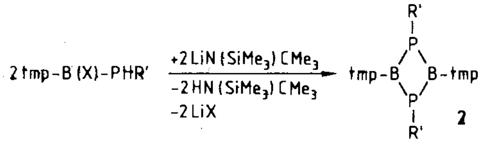


These compounds are readily accessible by reactions according to eq. (1) performed in hydrocarbon solvents. The monomeric nature of these compounds can be unequivocally deduced from their ^{11}B- and ^{31}P-NMR spectra, and this has also been demonstrated recently for $tmp-B(Cl)-P(H)-C_6H_2tBu_3$ by an X-ray structure determination[13]. $tmpBCl_2$ did not react with $LiP(H)CH(SiMe_3)_2$ in contrast to $tmpBF_2$. Similarly, $LiP(H)(C_6H_2iPr_3)$ reacted only with tBu_2NBF_2 but not with tBu_2NBCl_2. These examples clearly demonstrate

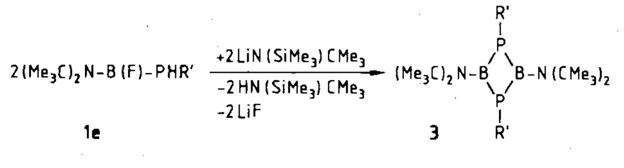
Chem. Ber. **121**, 871–879 (1988) 0009–2940/88/0505–0871 $ 02.50/0

the steric limitations for the nucleophilic substitution at the boron center.

Dehydrohalogenation of tmpB(Cl)P(H)CEt$_3$ was readily achieved by strong and sterically demanding bases[14]. This method did not allow, however, the synthesis of the known diboretane **2a**[13] from **1a** and either NaN(SiMe$_3$)$_2$ or LiN(SiMe$_3$)*t*Bu even in boiling toluene. This lack of reactivity is obviously due to the steric shielding of the P atom by the supermesityl substituent because the [(2,4,6-triisopropylphenyl)phosphino]boranes **1b,c** provide the diboretane **2b** readily.


(2)

	2a	2b	2c	2d
X	Cl	F/Cl	F	Cl
R'	smes	imes	CH(SiMe$_3$)$_2$	CMe$_3$


(3)

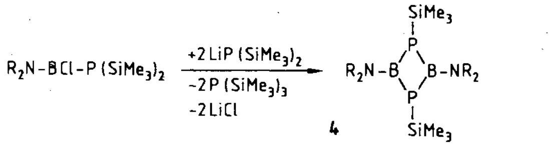
R' = imes

NMR spectra taken during the course of the reactions gave no indication for the presence of a boraphosphene tmp$-$B$=$PR in solution. The same holds for the formation of the diboretane **2c**, where HF elimination requires prolonged heating in boiling benzene. In contrast, the dehydrofluorination of **1e** by the base LiN(SiMe$_3$)*t*Bu according to eq. (3) was successful already at ambient temperature within 24 h, although the *t*Bu$_2$N group is sterically more demanding than the tetramethylpiperidino group. **3** was obtained in 76% yield.

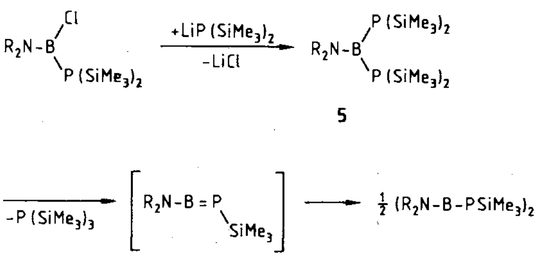
There are, therefore, limitations to the synthesis of diphosphadiboretanes by HX elimination a) with respect to the preparation of the phosphinoborane precursor and b) related to the ease of HX eliminations from these compounds. There are indications that boraphosphenes exist as highly reactive intermediates in these eliminations; however, they will dimerize more readily than react with, e.g., the amine produced during this process. Attempts to trap a boraphosphene during the course of reaction (2) with the amino(imino)borane tmp$-$B$\equiv$N$-$CMe$_3$ remained unsuccessful[18].

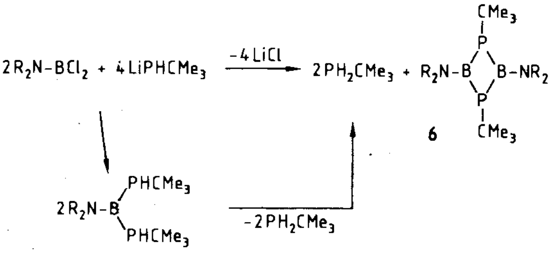
Three diphosphadiboretanes **4a$-$c** carrying a trimethylsilyl group at the phosphorus atoms were obtained in good yield by addition of the phosphide LiP(SiMe$_3$)$_2$ · 2 THF to the respective (amino)(phosphino)boron chlorides as shown in eq. (4).

It is suggested that the first step in this reaction is a nucleophilic substitution of the chloride, followed by an intramolecular P(SiMe$_3$)$_3$ elimination to produce a highly reactive boraphosphene intermediate which dimerizes rapidly to **4**. This reaction sequence is depicted in eq. (5), as based on previous results by Fritz and Hölderich[16] and on those reported here.


(4)

	4a	4b	4c
R$_2$N	N(CHMe$_2$)$_2$	NPh$_2$	tmp


(5)


(6)

7

	6a	6b
R$_2$N	NMe$_2$	N(SiMe$_3$)$_2$

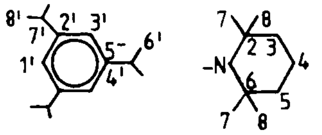
[Bis(trimethylsilyl)phosphino](dimethylamino)borane (**5**, R = Me) can be readily isolated, and the decomposition of Me$_2$NB[P(SiMe$_3$)$_2$]$_2$ proceeds at 150°C with formation of P(SiMe$_3$)$_3$ and [Me$_2$NBPSiMe$_3$]$_2$[16]. Larger amino groups appear to destabilize compounds of type **5**. For example it has been observed[19] that Ph$_2$NB[P(SiMe$_3$)$_2$]$_2$ decomposes in refluxing benzene while *i*Pr$_2$NB[P(SiMe$_3$)$_2$]$_2$ cannot be isolated due to rapid phosphane elimination.

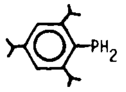
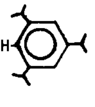
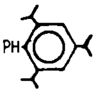
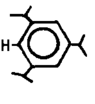
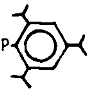
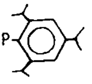
A similar reaction pattern holds for the synthesis of diphosphadiboretanes via bis(*tert*-butylphosphino)boranes R$_2$NB[P(H)*t*Bu]$_2$ (**7**) as shown in eq. (6). The latter could not be isolated due to rapid phosphane elimination even under relatively mild reaction conditions. However, NMR spectroscopy provides unambiguous evidence for their existence, e.g. in the case of (Me$_3$Si)$_2$NB[P(H)*t*Bu]$_2$. Our experiments indicate that the *t*BuPH$_2$ elimination from R$_2$NB[P(H)*t*Bu]$_2$ proceeds faster than the P(SiMe$_3$)$_3$ elimination from R$_2$NB[P(SiMe$_3$)$_2$]$_2$. Reaction (6) is reminiscent to one reported by Cowley et al.[13], who obtained [tmpBPC$_6$H$_2$*t*Bu$_3$]$_2$ from tmpBCl$_2$ and a 1:1 mixture of LiPHR and Li$_2$PR.

Spectra

The mass spectra of **4a$-$c** show the parent ion, an ion corresponding to R$_2$NBP(SiMe$_3$)$^+$, and several expected

Table 1. NMR data of diphosphadiboretanes and their precursors



		$\delta^{11}B$	$\delta^{31}P$	$\delta^{13}C$	δ^1H
a)		-	-158,6	121.7(1'), 152.2(2'), 121.1(3'), 148.9(4') 34.6(5'), 28.8(6'), 33.1(7'), 24.3(8)'	3.79(PH), 7.03(m,Ph) 2.79, 1.22 (para) 3.42, 1.19 (ortho)
b)	$(Me_3Si)_2CHPH_2$	-	-147.2	-0.01(1') -3.2(2')	0.05(Me) 0.04(CH) 2.75(PH)
c)	tmp-BCl-PH 	45.4	-128.7	57.3(2,6), 35.9(3,5), 14.7(4) 31.8(7,8) 121.7(1'), 152.2(2'), 121.1(3'), 148.9(4') 34.6(5'), 23.8(6'), 33.1(7'), 24.3(8')	3.96(PH), 7.10(m,Ph) 2.60, 1.20 (para) 3.84, 1.35 (ortho), 1.49, 1.45 (Me, tmp)
d)	tmp-BF-PH 	37.4	-149.5	54.4(2,6), 37.6(3,5), 15.4(4), 30.1(7,8) 121.1(1'), 154.3(2'), 121.2(3'), 149.1(4') 34.3(5'), 24.1(6'), 33.7(7'), 24.3(8')	4.11(PH), 7.33(m,Ph) 2.95, 1.39 (para) 4.17, 1.55 (ortho) 1.58, 1.52 (Me, tmp)
e)	$(Me_3C)_2N$-BF-PH 	37.9	-144.1	56.4(CMe$_3$), 34.1(CMe$_3$), 121.1(1'), 153.2(2'), 121.3(3'), 148.9(4') 33.9(5'), 24.2(6'), 33.6(7'), 24.4(8')	4.20(PH), 7.30(m,Ph) 2.93, 1.44 (para) 4.17, 1.55 (ortho) 1.53 (Me$_3$C)
f)	tmp-BF-PH-CH$(SiMe_3)_2$	37.7	-142.1	54.4(2,6), 38.1(3,5), 15.6(4), 33.4, 31.5(7,8) 0.6(CH), -1,5(Si$\underline{C}$)	2.77(PH), 135(Me,tmp) 0.19(SiMe$_3$)
g)	[tmp-BP ]$_2$	55.0	-101.0	56.3(2,6), 37.4(3,5), 15.4(4), 32.0(7,8) 122.2(1'), 155.0(2'), 134.8(3'), 149.7(4') 34.4(5'), 23.9(6'), 32.8(7'), 25.7(8')	7.17(m,Ph) 2.78, 1.20 (para) 4.87, 1.48 (ortho) 1.52 (Me, tmp)
h)	[$^tBu_2$NBP ]$_2$	55.4	-94.4	58.8(CMe$_3$), 35.9(CMe$_3$) 122.2(1'), 155.0(2'), 135.7(3'), 149.8(4') 34.4(5'), 23.9(6'), 32.7(7'), 27.7(8')	7.15(m,Ph) 2.78, 1.21 (para) 4.87, 1.32 (ortho)
i)	[tmpBPCH$(SiMe_3)_2]_2$	59.0	-83.4	55.4(2,6), 38.8(3,5), 16.8(4), 36.6(7,8) 18.8(CH), 2.9(SiMe$_3$)	1.62(CH), 0.36(SiMe$_3$) 1.33 (Me,tmp)
k)	$[Me_3Si)_2NBPCMe_3]_2$	68.3	-2.2	4.3(SiMe$_3$), 30.1($\underline{C}$Me$_3$), 32.4(C$\underline{Me}_3$)	0.41(SiMe$_3$) 1.27(C$\underline{Me}_3$)
l)	$[iPr_2NBPSiMe_3]_2$	50.6	-133.6	51.8(CH), 24.5(C$\underline{Me}$), 3.4(SiMe)	3.8(CH), 1.3(CMe) 0.5(SiMe)
m)	$[Ph_2NBPSiMe_3]_2$	58.0	-122.6	161.0(1), 130.0(3), 128.4(2), 126.0(4) 2.7(Me)	7.4(m,Ph) -0.2(Me)
n)	$[tmpBPSiMe_3]_2$	60.8	-55.0	57.3(2,6), 37.8(3.5), 35.3(7,8) 16.3(4), 4.6(SiMe)	1.6, 1.7(CMe) 0.4(SiMe)
o)	$[Me_2NBPCMe_3]_2$	50.2	-46.8	45.2(NMe) 34.0 (C$\underline{Me}$)	2.87 (NMe$_2$), 1.30 (CMe$_3$), Pseudotriplett

---

Kopplungskonstanten(Hz): a) $^1J(^{31}P^1H)$ 202, $^1J(^{31}P^{13}C)$ 57.2, $^2J(^{31}P^{13}C)$ 10.0); b) $^1J(^{31}P^1H)$ 189, $^1J(^{31}P^{13}C)$ 28.6, $^3J(^{31}P^{13}C)$ 4,0, $^4J(^{31}P^1H)$ 0.8, $^3J(^1H^1H)$ 7.6; c) $^1J(^{31}P^{11}B)$ 62(ber.), $^1J(^{31}P^1H)$ 238 Hz, $^1J(^{31}P^{13}C)$ 57.2, $^2J(^{31}P^{13}C)$ 10.0; d) $^1J(^{31}P^{11}B)$ 72(ber.), $^1J(^{31}P^1H)$ 230, $^1J(^{31}P^{13}C)$ 57.1, $^2J(^{31}P^{13}C)$ 10.3, $^3J(^{19}F^1H)$ 14.0; d) $^1J(^{31}P^{11}B)$ 72, $^1J(^{31}P^1H)$ 230, $^1J(^{31}P^{13}C)$ 57.1, $^2J(^{31}P^{13}C)$ 10.3, $^3J(^{19}F^1H)$ 14.0; e) $^1J(^{31}P^1H$ 209, $^1J(^{31}P^{11}B)$ 72 (ber.), $^3J(^{31}P^{13}C)$ 6.0, $^3J(^{19}F^{13}C)$ 6.4, $^1J(^{31}P^{13}C)$ 31.0, $^1J(^{19}F^1H)$ 3.2, $^1J(^1H^1H)$ 7.5; f) $^1J(^{31}P^{11}B)$ 83 (ber.); g) $^1J(^{31}P^{11}B)$ 88 (ber.), $^3J(^{31}P^{13}C(CMe_3)$ 6,4, $^3J(^{31}P^{13}C(ipso)$ 8.7, $^3J(^{31}P^{13}C(m)$, $^3J(^{31}P^{13}C)$ 6.0 ($\underline{C}HMe_2$); h) $^1J(^{31}P^{11}B)$ 79, $^3J(^{31}P^{13}C)$ 5.4 (N$\underline{C}$), $J(^{31}P^{13}C)$ 7.7, $^1J(^{31}P^{13}C)$ 34.5 (CH), $^2J(^{31}P^1H)$ 15.4; i) $^1J(^{31}P^{11}B)$ 91 (ber.), $^1J(^{31}P^{13}C)$ 11.2 ($\underline{C}Me_3$); k) $^3J(^{31}P^{13}C)$ 6.9, $^2J(^{31}P^{13}C)$ 4,5; l) $^2J(^{31}P^{13}C)$ 4.5, $^3J(^{31}P^{13}C)$ 6.9, $^3J(HH)$ 7.0, $J(^{31}P^1H)$ 1.8; m) $^2J(^{31}P^{13}C)$ 4.8, $^3J(^{31}P^{13}C)$ 4.8, $^3J(^{31}P^1H$ 4.3; n) $^3J(^{31}P^{13}C)$ 4.0, $^4J(^{31}P^{13}C)$ 6.3, $^2J(^{31}P^{13}C)$ 3.0, $J(^{31}P^1H)$ 1.5.

fragments. However, the spectra are very sensitive to sample inlet conditions and ionisation voltage. Similarly, $[tmpBPCEt_3]_2$[14] at 70 or 15 eV did not produce the parent ion even under carefully controlled conditions, and a fragment $[M - Et_2C{=}CHMe]^+$ (m/z = 464) had only 3% relative intensity. It breaks further down with loss of $Et_2C{=}CHMe$ to give $(tmpBPH)_2^{+\cdot}$ (m/z = 366, 5%). In contrast, the dominate fragmentation of M^+ leads to $tmpBPCEt_3^{+\cdot}$ (m/z = 281, 100%) which looses CH_3, C_2H_5, and $(C_2H_5)_3C$ radicals. Therefore, care should be exercised in suggesting the presence of a boraphosphene monomer as a neutral progenitor to $R_2NB{=}PR'^+$ on the basis of mass spectral analysis, provided that both P and B carry bulky groups. On the other hand, the mass spectrum of **6b** exhibits the parent ion M^+ in 25% relative intensity, and three successive fragmentations involving the loss of a *tert*-butyl radical, of isopropene and P_2 is ascertained by metastable peaks. This result differs considerably from those of sterically crowded diphosphadiboretanes.

All the compounds reported in this study show a single signal in the $^{31}P\{^1H\}$-NMR spectrum. Substitution of an RPH_2 proton by an aminohaloboryl group results in deshielding. This effect is more pronounced for $R_2N(Cl)B$ substituents (20 – 30 ppm) than for $R_2N(F)B$ groups (5 – 15 pm) (see Table 1).

A similar trend is observed for the shifts of the diphosphadiboretanes, as their ^{31}P resonance appears at lower field than those of their $R_2NB(X)P(H)R'$ precursor molecules. The shift difference $\Delta^{31}P$ is larger for the boron fluoride precursor and the resulting diphosphadiboretane ($\Delta^{31}P$ 48 – 59 ppm) than for the boron chloride precursor and the B_2P_2 ring ($\Delta^{31}P$ 37 – 47 ppm). These values increase for the pairs of compounds $R_2NB(Cl)P(SiMe_3)_2/(R_2NBPSiMe_3)_2$ ($\Delta^{31}P$ 79.8 – 89 ppm) which match closely with $\Delta^{31}P$ = 70 ppm previously reported for $(Me_2NBPSiMe_3)_2$[16]. However a surprisingly high $\Delta^{31}P$ value results (124.5 ppm) for the pair $tmpB(Cl)P(SiMe_3)_2$/**4c**. The origin of this larger shift difference is not certain although the steric influence suggests a greater electronic deshielding effect at phosphorus.

The proton decoupled ^{11}B-NMR spectra of compounds $R_2NB(X)P(H)R'$ exhibit δ values between 46.1 and 45.4 for the chlorides and 37.9 – 36.5 for the fluorides. These data match with those found for analogous compounds with sterically less demanding amino groups, e.g. $Et_2NB(Cl)PEt_2$ ($\delta^{11}B$ 40.4)[20]. Also the trimethylsilyl groups exhibit little influence on the ^{11}B chemical shifts, and the data reported here are comparable with $Me_2NB(Cl)P(SiMe_3)_2$ ($\delta^{11}B$ 40.0)[19] or $Et_2NB(PEt_2)_2$ ($\delta^{11}B$ 50.9)[21]. The line width of the ^{11}B-NMR signals are observed in the range of 400 – 600 Hz. This precludes the observation of BF or BP coupling. However, an estimate for the upper limit of $^1J(^{31}P^{11}B)$ can be made from the line width using the relation $J(PB) = (0.2\ h_{1/2}\ (^{11}B)\Delta\nu\text{-}^{31}P)^{1/2}$ [22]. Values between 60 and 80 Hz result from this estimation.

The formation of diphosphadiboretanes is accompanied by a decrease in the shielding at the boron nucleus, and this has also been observed for the phosphorus atom. *P*-aryl group-substituted diphosphadiboretanes exhibit signals at $\delta^{11}B \approx 55$, *P*-alkyl-substituted ones at $\delta^{11}B \approx 60$, while the *P*-trimethylsilyl-substituted diphosphadiboretanes span the range 50 – 61 ppm, their boron atoms becoming increasingly deshielded as the steric requirements of the R_2N group increases. In accord with this stands the shift $\delta^{11}B$ = 52.2 for $(Me_2NBPSiMe_3)_2$[19] which matches that of **4a**. The shielding at the boron atom is, therefore, rather similar to that of (amino)bis(phosphino)boranes, containing also a BP_2N structural unit as typical for the diphosphadiboretane.

The ^1H- and ^{13}C-NMR data are in agreement with the proposed structures, and the ^{13}C-NMR spectra of the (amino)(phosphino)boron halides are of first order. The carbon atom of the phosphorus bound organyl or trimethylsilyl groups do not show simple first order coupling patterns. They rather display an AXX′ "triplet" resulting from near equivalence of the two phosphorus atoms in the $^{13}C\{^1H\}$-NMR spectra. A similar effect is seen in the ^1H-NMR spectra for the Me_3Si protons in **4a,c** while a "normal" doublet is resolved in the spectrum of **4b**.

Crystal and Molecular Structures

Since the NMR spectra of the diphosphadiboretanes provide no evidence for the ring structure (planar or bent) or the configuration at the *P*-substituents (*cis* or *trans*), the molecular structure of three of these ring compounds (**3**, **4a**, and **4c**) were determined by single crystal X-ray diffraction analysis. Views of these molecules are presented by the ORTEP-plots in Figures 1 – 3, and relevant bond distances and bond angles are summarized in Table 2.

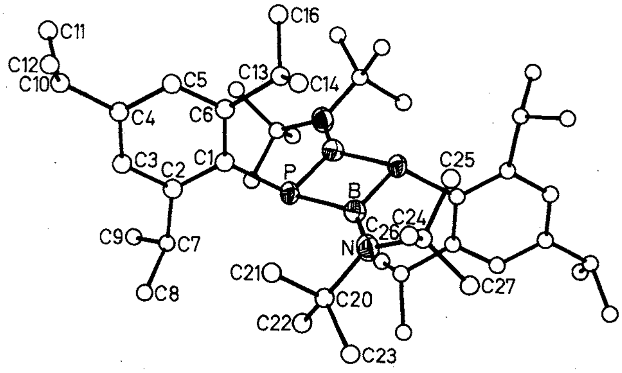


Figure 1. ORTEP plot of the molecular structure of 2,4-bis(di-*tert*-butylamino)-1,3-bis(2,4,6-triisopropylphenyl)-1,3,2,4-diphosphadiboretane (**3**). Thermal ellipsoids represent a 50% probability

The structures are closely related to the recently reported structures of $(tmpBPCEt_3)_2$[14], $(tmpBPC_6H_2Me_3)_2$[13], and $(tmpBPC_6H_2tBu_3)$[27]. The B_2P_2 rings are planar, and in the case of **3** and **4a** the planarity results from a crystallographically imposed center of inversion. As a consequence, the substituents at the phosphorus atoms are in *trans* orientation to each other, as has been found in the previously determined structures of diphosphadiboretanes. The nitrogen atoms lie in the B_2P_2 plane, and the boron atoms and nitrogen atoms have trigonal planar geometry, with sums of bond angles of 360(±0.5)°. All molecules possess pyramidal phosphorus atoms, but the sums of angles differ considerably [**3**: 327.4°, **4a**: 284.6°, **4c**: 283.5° at P(1), 302.0° at

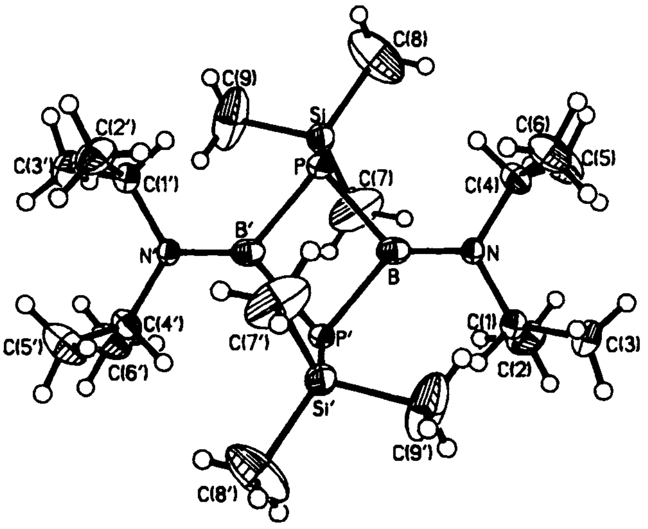


Figure 2. Molecular structure of 2,4-bis(diisopropylamino)-1,3-bis(trimethylsilyl)-1,3,2,4-diphosphadiboretane (**4a**). Thermal ellipsoids represent a 25% probability

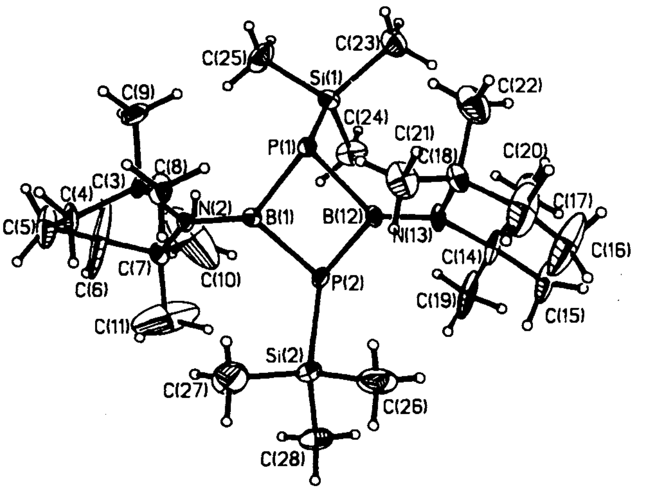


Figure 3. ORTEP plot of 2,4-bis(2,2,6,6-tetramethylpiperidino)-1,3-bis(trimethylsilyl)-1,3,2,4-diphosphadiboretane (**4c**). Thermal ellipsoids represent a 25% probability

P(2)]. In this respect, **3** resembles $(tmpBPCEt_3)_2$ (329.2°)[14]. These data reflect the steric interactions between the amino groups and the phosphorus substituents.

The BP bonds in **4a** and **4c** can be considered to be equally long within experimental error (3σ criterion) and are longer than the BP bonds in **3**. Those in **4a,c** compare well with the BP bond distance in $(tmpBPC_6H_2tBu_3)_2$[12], whose bond lengths have been taken as evidence for possible cycloreversion to the monomer in the gas phase. All of these BP bonds can be considered as weak single bonds since they are of comparable lengths with phosphane borane adducts, e.g. $Me_3P \cdot BX_3$ [X = Cl, Br, I; d(BP) being 1.957, 1.92, and 1.92 Å respectively][23] or $H_3P \cdot BH_3$ [d(BP) 1.937(5) Å][24]. However, since both the boron and the phosphorus atoms are tetracoordinated in these adducts, a single BP bond between tricoordinate B and P atoms should be shorter. In any event, the BP bond lengths reported for diphosphadiboretanes are significantly longer than the BP multiple bond lengths reported by Power and co-workers[11].

Table 2. Selected bond lengths and nonbonding distances (in Å) as well as bond angles (in °) for diphosphadiboretanes

Bond Lengths			
	3a	4a	4c
BP	1.926(5)	1.947(4)	1.948(10)
BP	1.921(5)	1.955(5)	1.969(12)
			1.950(11)
			1.957(12)
BN	1.430(6)	1.384(5)	1.417(13)
			1.397(14)
PSi(C)	1.861(5)	2.254(2)	2.261(4)
			2.262(4)
Nonbonding distances			
B...B	2.710	2.534	2.602
P...P	2.729	2.968	2.900
Bond angles			
B-P-Si(C)	121.9(2)	101.5(1)	110.0(3)
		102.1(1)	108.5(3)
			100.5(3)
			99.8(3)
B-P-B	89.6(2)	81.0(2)	83.2(5)
			83.5(5)
P-B-P	90.4(2)	99.0(2)	95.9(5)
			95.4(5)
N-B-P	134.7	131.4(3)	132.1(8)
N-B-P	134.8	129.6(3)	132.0(7)
			130.5(8)
			134.0(8)
B-N-C	119.3(4)	119.6(3)	122.6(8)
	121.9(4)	120.1(4)	123.5(8)
			118.0(7)
			119.5(8)

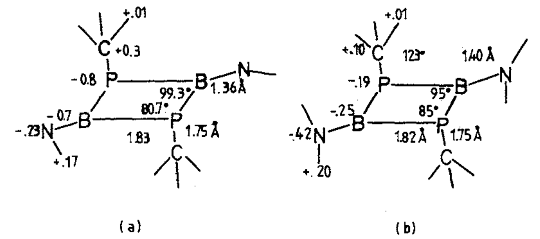
The BN bond lengths range from 1.384(5) Å in **4a** via 1.397(14) and 1.417(13) Å in **4c** to 1.430(6) Å in **3**, reflecting various degrees of π orbital overlap. They compare with 1.393(3) Å in $(tmpBPC_6H_2tBu_3)_2$[7], 1.431(2) Å in $(tmpBPCEt_3)_2$[14] and 1.465(3) Å in $(tmpBNtBu)_2$[25]. The data suggest that increasing steric congestion both by the R_2N and the RP groups lengthens the BN bond, and this effect is reflected, at least in part, by the torsion angle of the R_2N group made with the B_2P_2 plane which is less in **4c** (35°) than in $(tmpBPCEt_3)_2$ (46.5°)[14]. Lastly, the PSi bond lengths – 2.254(2) Å in **4a** and 2.261(4) Å in **4c** – are similar in these two compounds and are close to the 2.287(4) Å found in $P_7(SiMe_3)_3$[26].

MNDO Calculation

There are a number of interesting features in the formation and configuration of diphosphadiboretanes as compared with their nitrogen analogues, the 1,3,2,4-diazadiboretidines. While amino(imino)boranes $R_2N-B{\equiv}NR$ are readily accessible[5] and dimerize to diazadiboretidines in a second order rate process[27], no aminoboraphosphene $R_2N-B{=}PR'$ has yet been observed. Its dimerisation to a

1,3,2,4-diphosphadiboretane occurs obviously very rapidly, suggesting that the activation energy for their [2 + 2] cycloaddition should be much lower than for amino(imino)-boranes. One reason for this difference is associated with the different ground state structures of iminoboranes and boraphosphenes. The former possess a linear structure involving a BN triple bond[28], while calculations for the latter favour a BP double bond with a bent arrangement of the substituent at the phosphorus atom[8].

An amino group in *B*-amino-boraphosphenes will reduce the electron deficiency at the boron atom by π orbital overlap. MNDO III calculations[29] show that the geometry-optimized dimer $(H_2NB-PCH_3)_2$ is 90 kcal/mol more stable than the monomer $H_2NB=PCH_3$. Amongst the various conformations for the dimer the structure containing a planar B_2P_2 ring with equal BP bond lengths and coplanar *B*-amino groups, which allows optimal BN-π bonding, is the most stable one. Parameters are shown in Figure 4.



(a) (b)

Figure 4. Molecular parameters and fractional charges from geometry-optimized structures calculated by the MNDO III method. a) represents data for the most stable conformation; b) shows the data for the molecule with planar NH_2 groups perpendicular to the B_2P_2 plane

According to these calculations the planar B_2P_2 ring should be diamond shaped with acute BPB bond angles at the phosphorus atoms. Structure **4a** compares well with this model. However, the calculated BP bond lengths were found to be noteably too short, generally by 0.1 Å, while the BN bond lengths match much better with experimental values[30].

Since most of the determined structures of 2,4-diamino-1,3,2,4-diphosphadiboretanes contain noncoplanar amino groups we also performed MNDO III calculations for the conformation in which the torsion angle of the amino group was kept at 90°, refining all other parameters freely. The result of this calculation is presented in Figure 4b).

The diamond shape structure of the planar B_2P_2 ring is now less pronounced, and the bond angles are comparable with those found for **4c** or $(tmpBPC_6H_2tBu_3)_2$ (PBP 93.1°, BPB 86.9°)[7]. The most significant result is, however, that the BP bond lengths are little affected in contrast to the BN bond lengths by this conformational change. Also, the phosphorus atoms become less pyramidal, which is also in accord with experimental data. Charge densities suggest that the phosphorus atoms should become more nucleophilic and the boron atoms more electrophilic as compared to the most stable structure.

Since MNDO III calculations on the dimerisation of amino-imino-boranes to 2,4-diamino-1,3,2,4-diazadiboretidines gave very satisfactory results for the activation energy, we also calculated E_A for the dimerisation process of $H_2N-B=PCH_3$. The result is shown in Figure 5. The activation energy for the dimerisation in a synchronous one-step process is only 5 kcal/mol, which is 7 times smaller than for $H_2N-B\equiv N-CH_3$. This low barrier is consistent with the futile attempts made so far to prepare boraphosphenes. Although the absolute values of our calculations may not necessarily match closely with experimental data, they are nevertheless in accord with the chemistry of iminoboranes on the one hand and of boraphosphenes on the other. It remains to been seen how the calculated data change with higher-level calculations.

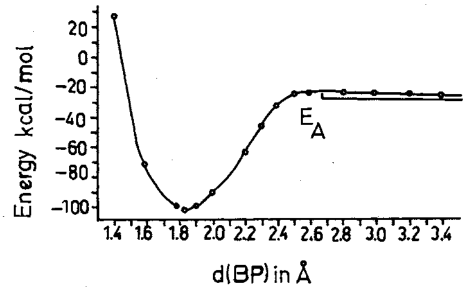


Figure 5. Reaction coordinate for the dimerisation of $H_2NB=PCH_3$ by a synchronous one-step process. The two molecules approach each other "side on"

This work was supported from *Fonds der Chemischen Industrie* and *BASF Aktiengesellschaft* (H. N.) and the *National Science Foundation* (R. T. P.). A *NATO* grant which allowed the cooperation of our research groups is gratefully acknowledged.

Experimental

All investigations were performed under dry nitrogen or argon gas or in vacuo. – Infrared spectra: Nicolet FTIR Model 6000 spectrometer. – Mass spectra: Finnegan GC/MS or Varian CH 7 spectrometers. – NMR spectra: Varian FT 80, GE-NT 360, Jeol FX 90 and Bruker WP 200 instruments. – X-Ray data: Syntex R 3 diffractometers, SHELXTL programs for structure solution.

(2,4,6-Triisopropylphenyl)phosphane: A Grignard solution was prepared from 43.0 g (153 mmol) of 1-bromo-2,4,6-triisopropylbenzene, 8.0 g (340 mmol) of activated Mg powder, and 400 ml of diethyl ether. The reaction was completed by keeping the solution under reflux for 2 h. Excess Mg was removed by filtering the solution directly into a dropping funnel. The Grignard solution was slowly added to a stirred solution of 13.0 ml of PCl_3 (150 mmol) in 150 ml of diethyl ether, kept at −50°C. A thick slurry formed in the course of the reaction. After stirring the mixture over night at ambient temperature, the insoluble material was removed by filtration and carefully washed 3 times with 100-ml portions of ether. The combined filtrates were concentrated in vacuo to remove about 80% of the solvent. The remaining solution was cooled to −18°C. Crystals of dichloro(2,4,6-triisopropylphenyl)phosphane separated. Yield: 21 g (45%), m.p. 90−100°C. – 20 g of this material was dissolved in 100 ml of diethyl ether. At 10°C a fine suspension of 3.0 g of $LiAlH_4$ in 100 ml of diethyl ether was added to the vigorously stirred dichlorophosphane solution. Stirring was continued over night, and hydrolysis was then performed by adding a solution of 10 g of KOH in 30 ml of deoxygenated water. Having separated the organic layer and dried with Na_2SO_4, all of the ether was re-

moved in vacuo, leaving the organylphosphane as a pale yellow liquid in the residue. Yield: 5.9−7.6 g (37−48%). This material was used without further purification to prepare suspensions of $LiPHC_6H_2[CH(CH_3)_2]_3$ by reaction with an equimolar amount of *n*-butyllithium in hexane.

[Bis(trimethylsilyl)methyl]phosphane: 12.3 g (47.3 mmol) of $(Me_3Si)_2CH-PCl_2$[32], dissolved in 50 ml of diethyl ether, was added to a stirred suspension of 2.0 g (52.6 mmol) of $LiAlH_4$ in 100 ml of diethyl ether. After stirring overnight hydrolysis was achieved by carefully adding a solution of 0.5 g of KOH in 20 ml of water. Workup followed the procedure described for $C_6H_2(iPr)_3PH_2$. Yield: 4.8 g (53%) of $(Me_3Si)_2CH-PH_2$, b.p. 78 °C/20 Torr.

$C_7H_{21}PSi_2$ (192.4) Calcd. C 43.70 H 11.00
Found C 42.95 H 10.82

Chloro(2,2,6,6-tetramethylpiperidino)[(2,4,6-triisopropylphenyl)phosphino]borane (**1b**): A suspension of 5.78 g (23.8 mmol) of $LiP(H)C_6H_2[CH(CH_3)_2]_3$ in 60 ml of hexane was added under vigorous stirring within 45 min to a solution of 5.27 g (23.8 mmol) of $tmpBCl_2$[5b], dissolved in 100 ml of hexane. After stirring the suspension for 2 days, the solid material was filtered off and the solvent evaporated. The remaining solid gave 7.85 g (78%) of **1b** by crystallisation from 20 ml of hexane at −78 °C, m.p. 91−94 °C.

$C_{24}H_{42}BClNP$ (422.9)
Calcd. C 68.17 H 10.25 N 3.31
Found C 66.61 H 10.56 N 3.54
mol. mass 422 (MS, ^{11}B, ^{35}Cl; correct isotopic pattern)

Fluoro(2,2,6,6-tetramethylpiperidino)[(2,4,6-triisopropylphenyl)phosphino]borane (**1c**): Preparation in analogy to **1b** from 1.8 g (9.5 mmol) of $tmpBF_2$[31] and 2.3 g (9.5 mmol) of $LiPHC_6H_2[CH(CH_3)_2]_3$. Yield: 2.4 g (63%), m.p. 97−105 °C.

$C_{24}H_{42}BFNP$ (405.4) Calcd. C 71.11 H 10.44 N 3.46
Found C 69.87 H 10.91 N 3.07

2,4-Bis(2,2,6,6-tetramethylpiperidino)-1,3-bis(2,4,6-triisopropylphenyl)-1,3,2,4-diphosphadiboretane (**2b**): A solution of 0.60 g (3.2 mmol) of $NaN(SiMe_3)_2$ in 20 ml of toluene was added dropwise with stirring to 1.25 g (3.0 mmol) of **1b**, dissolved in 40 ml of toluene. Stirring was continued for 2 days, the insoluble material removed, and all volatiles were stripped off in vacuo. The condensate contained $HN(SiMe_3)_2$ ($\delta^1H = 0.04$). The solution of the solid residue in 5 ml of toluene was cooled to −78 °C, when 0.97 g (83%) of **2b** crystallized, m.p. 265−270 °C.

$C_{48}H_{82}B_2N_2P_2$ (772.8)
Calcd. C 74.60 H 10.96 N 3.62
Found C 74.02 H 10.72 N 3.55
mol. mass 772 (MS, ^{11}B), 776 (cryoscop. in benzene)

[[Bis(trimethylsilyl)methyl]phosphino]fluoro(2,2,6,6-tetramethylpiperidino)borane (**1d**): A suspension of $LiP(H)CH(SiMe_3)_2$, prepared from 7.6 mmol of $(Me_3Si)_2CH-PH_2$ and the equimolar amount of LiBu in diethyl ether at 25 °C in 25 ml of pentane, was dropped into a stirred solution of 1.5 g (7.6 mmol) of $tmpBF_2$. 48 h later, insolubles were removed by filtration and the solvents from the filtrate were evaporated in vacuo. 2.23 g (82%) of **1d** remained as a yellow viscous compound which contained no impurities according to the NMR spectra.

$C_{16}H_{38}BFNPSi_2$ (361.4) Calcd. C 53.17 H 10.60 N 3.88
Found C 50.97 H 10.09 N 3.67

1,3-Bis[bis(trimethylsilyl)methyl]-2,4-bis(2,2,6,6-tetramethylpiperidino)-1,3,2,4-diphosphadiboretane (**2c**): A mixture of 1.36 g (3.8 mmol) of **1d** and 0.58 g (3.9 mmol) of $LiN(SiMe_3)tBu$ in 40 ml of benzene was kept under reflux for 4 days. The solid formed was removed by filtration and the solid obtained after stripping the solvent from the filtrate was crystallized from 20 ml of toluene at −78 °C. Yield: 0.78 g (65%) of **2c** as yellow crystals, m.p. 235−238 °C.

$C_{32}H_{74}B_2N_2P_2Si_4$ (682.9)
Calcd. C 56.29 H 10.92 N 4.10
Found C 53.85 H 10.82 N 4.33
mol. mass 682 (MS, ^{11}B, ^{28}Si)

(Di-tert-butylamino)[(2,4,6-triisopropylphenyl)phosphino]boron Fluoride (**1e**): Prepared according to **1d** from 3.10 g (12.6 mmol) of $LiPHC_6H_2(CHMe_2)_3$ and 2.23 g (12.6 mmol) of tBu_2NBF_2[33] in 60 ml of pentane with stirring over night. Concentration of the filtrate to 25% of its original volume and crystallisation at −78 °C; 3.37 g (68%) of light yellow crystals of **1e**, m.p. 40−46 °C.

$C_{23}H_{42}BFNP$ (398.4) Calcd. C 70.73 H 10.76 N 3.56
Found C 70.67 H 10.78 N 3.30

2,4-Bis(di-tert-butylamino)-1,3-bis(2,4,6-triisopropylphenyl)-1,3,2,4-diphosphadiboretane (**3**): Prepared according to **2c** from 1.25 g (8.5 mmol) of $LiN(SiMe_3)tBu$ in 20 ml of benzene and 3.3 g (8.4 mmol) of **1e** in 40 ml of benzene. Crystallisation from 10 ml of toluene at −78 °C. Yield: 2.4 g (76%) of **3**, m.p. 196−208 °C.

$C_{48}H_{82}B_2N_2P_2$ (746.7) Calcd. C 73.99 H 11.06 N 3.75
Found C 67.76 H 10.08 N 3.15

(tert-Butylphosphino)(2,2,6,6-tetramethylpiperidino)boron Chloride (**1f**): Prepared in analogy to **1b** from 1.03 g (10.7 mmol) of $LiPHtBu$ suspended in 20 ml of hexane and 2.4 g (10.7 mmol) of $tmpBCl_2$. Separation of the insoluble part after 12 h. Isolated by distillation: 1.3 g (45%) **1f** as a lemon yellow, viscous oil; m.p. 42−46 °C.

$C_{13}H_{28}BClNP$ (275.6) Calcd. C 56.65 H 10.24 N 5.08
Found C 55.62 H 10.11 N 5.21

1,3-Di-tert-butyl-2,4-bis(2,2,6,6-tetramethylpiperidino)-1,3,2,4-diphosphadiboretane (**2d**): Dehydrohalogenation of 0.57 g (2.0 mmol) of **1f** in 15 ml of benzene with 0.31 g of $LiN(SiMe_3)tBu$ in 15 ml of benzene in analogy to the preparation of **3a**. Yield: 0.38 g (80%) of **3b**, yellow powder, m.p. 95−101 °C.

$C_{26}H_{54}B_2N_2P_2$ (478.3) Calcd. C 65.29 H 11.38 N 5.86
Found C 63.73 H 11.27 N 5.52

2,4-Bis(diisopropylamino)-1,3-bis(trimethylsilyl)-1,3,2,4-diphosphadiboretane (**4a**): A solution of (diisopropylamino)[bis(trimethylsilyl)phosphino]boron chloride[34] (0.65 g, 2.0 mmol) in 50 ml of dry benzene was added to 0.66 g (2.0 mmol) of $LiP(SiMe_3)_2 \cdot 2\,THF$[16], and the mixture was refluxed for 4 h. The resulting suspension was cooled to room temperature, filtered and the solvent evaporated from the filtrate. The remaining oil was warmed in vacuo at 50 °C to remove $P(SiMe_3)_3$ resulting in isolation of a colourless solid, 0.34 g (79%) of **4a**, m.p. 117−120 °C. − MS (55 eV): *m/z* (%) 430.7 (40, M^+), 357.6 (99, M − $SiMe_3^+$), 214.3 (1, $iPr_2NBSiMe_3^+$) 73.1 (100, $SiMe_3^+$). − IR (hexane, cm^{-1}): 1432 (m), 1379 (m), 1365 (m), 1302 (s), 1261 (m), 1187 (m), 1147 (m), 1109 (w), 1066 (w), 1049 (m), 1044 (w), 1011 (w), 838 (w), 821 (w), 809 (w), 801 (w), 570 (w).

$C_{18}H_{46}B_2N_2P_2Si_2$ (430.4) Calcd. C 50.28 H 10.71 N 6.52
Found C 48.87 H 10.20 N 6.31

2,4-Bis(diphenylamino)-1,3-bis(trimethylsilyl)-1,3,2,4-diphosphadiboretane (**4b**): According to **4a** (diphenylamino)[bis(trimethylsilyl)phosphino]boron chloride[34] (0.78 g, 2.0 mmol) in 50 ml of dry benzene was added to 0.66 g (2.0 mmol) of $LiP(SiMe_3)_2 \cdot 2\,THF$. A yellow oily solid was obtained from the filtrate which was washed with cold hexane (0 °C) leaving a colourless solid, 0.30 g of **4b** (53%), m.p. 199−203 °C. − MS (55 eV): *m/z* (%) = 566.2 (20, M^+), 493.2 (10, M − $SiMe_3^+$), 283.1 (3, $Ph_2NPSiMe_3^+$), 73.1 (100, $SiMe_3^+$). −

IR (benzene, cm^{-1}): 1491 (s), 1466 (m), 1391 (m), 1376 (m), 1366 (m), 1339 (s), 1297 (s), 1286 (m), 1246 (m), 840 (s), 796 (w), 749 (m), 628 (m).

$C_{30}H_{38}B_2N_2P_2Si_2$ (566.4) Calcd. C 63.65 H 6.72 N 4.95
Found C 63.36 H 7.34 N 4.87

2,4-Bis(2,2,6,6-tetramethylpiperidino)-1,3-bis(trimethylsilyl)-1,3,2,4-diphosphadiboretane (**4c**): Prepared in analogy to **4a** from [(2,2,6,6-tetramethylpiperidino)bis(trimethylsilyl)phosphino]boron chloride[34)] (3.63 g, 10 mmol) in 50 ml of benzene and 3.28 g (10 mmol) of $LiP(SiMe_3)_2 \cdot 2$ THF at 25°C. A pale yellow oil remained after evaporating the solvent from the filtrate. The $P(SiMe_3)_3$ formed was removed by gentle warming in vacuo and a bright yellow crystalline solid was isolated. Yield: 2.14 g of **4c** (84%), m.p. 95°C. – MS (50 eV): *m/z* (%) = 509.5 (25, M^+), 437.5 (60, M – $SiMe_3^+$) 254 (40, $tmpBPSiMe_3^+$), 73 (100, $SiMe_3^+$). – IR (cm^{-1}, pentane): 1383 (m), 1365 (s), 1308 (s), 1277 (s), 1242 (s), 1216 (w), 1170 (s), 1128 (m), 1039 (w), 995 (w), 974 (m), 838 (s), 748 (m), 686 (w), 629 (m).

$C_{24}H_{54}B_2N_2P_2Si_2$ (510.4) Calcd. C 56.52 H 10.60 N 5.50
Found C 53.61 H 10.18 N 4.63

1,3-Di-tert-butyl-2,4-bis(dimethylamino)-1,3,2,4-diphosphadiboretane (**6a**): A solution of 9.10 g (42.4 mmol) of Me_2NBBr_2 (or the

Table 3. Crystallographic data of the diphosphadiboretanes **3**, **4a**, and **4c** as well as data concerning data collection and refinement

	3	**4c**	**4a**
Formula	$C_{46}H_{82}B_2N_2P_2$	$C_{24}H_{54}B_2N_2P_2Si_2$	$C_{18}H_{46}B_2N_2P_2Si_2$
mol. mass	746.94	509.6	429.6
a [Å]	9.371(2)	12.587(3)	9.425(3)
b [Å]	10.936(3)	15.433(4)	13.189(4)
c [Å]	12.718(4)	16.418(4)	11.361(3)
α [°]	89.00(2)	90	90
β [°]	78.65(2)	94.62(2)	98.81(2)
γ [°]	74.01(3)	90	90
V [Å^3]	1227.4(14)	3179(1)	1395.6(7)
d_r [gcm^{-3}]	1.011	1.07	1.024
Z	1	4	2
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
μ [cm^{-1}]	1.14	2.21	2.42
F (000)	411.9	1120	472
crystal size (mm)	0.33x0.17x0.44	0.16x0.32x0.35	0.21x0.32x0.35
temperature (°C)	18	20	-35
reciprocal space	±h,±k,±l	hk±l	±h±kl
2Θ-range [°]	2-48	2-45	2-50
Scan mode	ω/2Θ	Θ/2Θ	ω
Scan range	ω(o)±1.2	$K_{d1,2}$±1.25	+0.92/-0.97
Scan speed (°/min)	3.5-29.3	4-30	4-30
Reflections measured	5818	6399	5308
Unique reflections	2340	4202	2455
Observed reflections (2σ(F))	1787	2265	1870
Parameters refined	335	289	118
R	0.10	0.111	0.077
R_w	0.094	0.094	0.072
g	0.0005	0.00168	0.00055
highest residual electron density (e/Å^3)	0.4	0.6	0.6

Table 4. Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters U_{eq} (× 10^3 Å^2) of the diphosphadiboretane **3**

	x	y	z	U
P	4617(1)	557(1)	4089(1)	50(1)
B	4407(6)	1137(5)	5547(4)	48(2)
N	3726(4)	2328(4)	6131(3)	57(2)
C(1)	5581(5)	1288(4)	2928(3)	50(2)
C(2)	4802(5)	1759(5)	2078(4)	59(2)
C(3)	5538(6)	2281(5)	1189(4)	74(2)
C(4)	7009(7)	2359(6)	1089(4)	79(3)
C(5)	7765(6)	1921(5)	1916(4)	73(2)
C(6)	7092(5)	1389(4)	2830(4)	58(2)
C(7)	3166(6)	1747(5)	2072(4)	67(2)
C(8)	2095(8)	3091(7)	2130(6)	97(3)
C(9)	3035(7)	1011(6)	1107(4)	93(3)
C(10)	7799(8)	2966(7)	102(5)	118(4)
C(11)	8918(12)	1963(9)	-606(6)	197(6)
C(12)	8378(16)	4027(10)	307(8)	137(8)
C(12a)	6950(25)	4110(19)	-231(15)	128(11)
C(13)	8018(6)	972(5)	3717(4)	64(2)
C(14)	8023(9)	2101(7)	4376(6)	119(4)
C(16)	9603(7)	147(7)	3310(5)	112(4)
C(20)	2525(6)	3355(4)	5695(4)	60(2)
C(21)	3341(7)	4035(6)	4818(5)	92(3)
C(22)	1514(7)	2727(6)	5228(6)	92(3)
C(23)	1362(8)	4315(7)	6522(6)	111(4)
C(24)	4203(7)	2635(5)	7160(4)	79(3)
C(25)	5631(10)	1663(7)	7315(7)	164(5)
C(26)	4634(8)	3898(6)	7118(5)	95(3)
C(27)	2988(18)	2586(11)	8136(7)	159(8)

Table 5. Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters U_{eq} (× 10^3 Å^2) of the diphosphadiboretane **4a**

ATOM	x/a	y/b	z/c	U(Å^2)
P	-.00155(12)	.93827 (8)	.10902(10)	.0430 (4)*
B	.0735 (5)	1.0675 (4)	.0609 (4)	.0384(15)*
N	.1517 (3)	1.1428 (3)	.1265 (3)	.0400(11)*
C(1)	.1825 (5)	1.2394 (3)	.0671 (4)	.0533(16)*
C(2)	.0750 (7)	1.3212 (4)	.0817 (5)	.0895(26)*
C(3)	.3358 (5)	1.2773 (4)	.0939 (5)	.0876(24)*
C(4)	.2021 (5)	1.1282 (4)	.2546 (4)	.0574(17)*
C(5)	.1581 (7)	1.2034 (5)	.3367 (5)	.1121(32)*
C(6)	.3500 (6)	1.0887 (5)	.2819 (5)	.0895(25)*
Si	-.19714(15)	.98922(11)	.18488(12)	.0584 (5)*
C(7)	-.2576 (7)	1.1166 (6)	.1360 (8)	.1445(43)*
C(8)	-.1591 (9)	.9914 (9)	.3474 (6)	.1790(55)*
C(9)	-.3497 (7)	.9021 (6)	.1419 (8)	.1543(45)*

Table 6. Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters U_{eq} (× 10^3 Å^2) of the diphosphadiboretane **4c**

ATOM	x/a	y/b	z/c	U(Å^2)
P(1)	.47651(22)	.61714(16)	.24346(17)	.0418 (9)*
P(2)	.56850(22)	.77066(16)	.17542(16)	.0418 (9)*
Si(1)	.53172(27)	.64408(20)	.37546(19)	.0575(12)*
C(23)	.6086(10)	.5509 (7)	.4195 (7)	.087 (6)*
C(24)	.6196(10)	.7402 (7)	.3919 (7)	.084 (6)*
C(25)	.4142 (9)	.6598 (9)	.4343 (6)	.095 (6)*
Si(2)	.55754(30)	.80003(21)	.04003(20)	.0630(13)*
C(26)	.6316(13)	.7143 (8)	-.0171 (7)	.125 (8)*
C(27)	.4211(12)	.7958(11)	-.0078 (7)	.149 (9)*
C(28)	.6182(11)	.9082 (7)	.0237 (8)	.107 (7)*
B(1)	.4298 (9)	.7324 (6)	.2078 (6)	.032 (4)*
N(2)	.3293 (6)	.7742 (4)	.2057 (4)	.036 (3)*
C(3)	.2307 (7)	.7191 (6)	.1914 (6)	.045 (4)*
C(4)	.1371 (8)	.7759 (8)	.1557 (8)	.077 (5)*
C(5)	.1153(11)	.8545 (9)	.2029(10)	.120 (8)*
C(6)	.2180(12)	.8914(11)	.2415(21)	.320(22)*
C(7)	.3179 (9)	.8669 (6)	.2247 (7)	.052 (4)*
C(8)	.2440 (9)	.6493 (6)	.1278 (7)	.067 (5)*
C(9)	.2023 (9)	.6755 (7)	.2703 (6)	.071 (5)*
C(10)	.3840(22)	.8916(10)	.2928(13)	.284(18)*
C(11)	.3519(25)	.9222 (9)	.1653(16)	.332(22)*
B(12)	.6064 (9)	.6490 (7)	.1911 (7)	.038 (4)*
N(13)	.6920 (6)	.5981 (4)	.1704 (5)	.046 (3)*
C(14)	.8055 (9)	.6283 (9)	.1782 (8)	.072 (5)*
C(15)	.8686 (9)	.5929 (9)	.1098 (9)	.101 (7)*
C(16)	.8498(14)	.5019(12)	.0911(14)	.206(13)*
C(17)	.7584(14)	.4714(10)	.0939(12)	.154(10)*
C(18)	.6742(10)	.5050 (7)	.1497 (7)	.059 (5)*
C(19)	.8135 (9)	.7270 (8)	.1799(11)	.138 (9)*
C(20)	.8593(10)	.5973(10)	.2595 (9)	.125 (8)*
C(21)	.5708(10)	.4908 (7)	.1015 (7)	.086 (6)*
C(22)	.6773(12)	.4463 (8)	.2220 (9)	.117 (7)*

equivalent amount of Me_2NBCl_2) in 150 ml of pentane was cooled to −45°C and a suspension of 8.18 g (85.2 mmol) of LiPH*t*Bu in 100 ml of pentane slowly added while stirring. The mixture was then allowed to attain ambient temperature. The insoluble material was removed by filtration. Yellow crystals remained after all volatiles had been stripped from the filtrate. $tBuPH_2$ was found in the condensate ($\delta^{31}P$ −80.5). Yield: 5.73 g (95%) of **6a**.

$C_{12}H_{30}B_2N_2P_2$ (285.9)
Calcd. C 50.40 H 10.57 N 9.80
Found C 49.50 H 10.16 N 9.69
mol. mass 286 (MS, ^{11}B)

2,4-Bis[bis(trimethylsilyl)amino]-1,3-di-tert-butyl-1,3,2,4-diphosphadiboretane (**6b**): Reaction in analogy to **6a**. 0.54 g (2.6 mmol) of $(Me_3Si)_2NBF_2$ in 10 ml of pentane, 0.49 g (5.1 mmol) of LiPH*t*Bu in 50 ml of pentane, −20°C. The NMR spectra of the solution recorded after the mixture had reached ambient temperature are in accord with the formation of $(Me_3Si)_2NB(PHtBu)_2$ (**7**): $\delta^{11}B$ 73.2, $h_{1/2}$ = 160 Hz, $\delta^{31}P$ −34.5, d, $^1J(^{31}P^1H)$ = 215 Hz. The yellow residue of the filtrate remained oily; crystallisation from diethyl ether or toluene was unsuccessful. NMR spectra of the oil showed no impurities.

$C_{20}H_{54}B_2N_2P_2Si_4$ (518.6) Calcd. C 46.32 H 10.50 N 5.40
Found C 40.99 H 9.12 N 3.88

X-Ray Structure Determinations: The crystals were sealed under argon in glass capillaries. Lp and absorption correction (ψ-scan) was applied for **4a,c** and Lp correction only for **3**. The structures were solved by Direct Methods. Nonhydrogen atoms were refined anisotropically, hydrogen atoms isotropically with $U_i = 1.2 \cdot U_i$ of the respective carbon atom. A summary of crystallographic data and information on data collection and refinement is given in Table 3. Tables 4 to 6 contain the atomic coordinates of the nonhydrogen atoms[35]. Some remarks are necessary for compound **3**.

3 CH_3 groups were included in the final refinement as rigid groups. The isopropyl group in *para* position of the phenyl ring was disordered, and was refined with occupancy factors of 0.36 and 0.64, respectively, for the two orientations.

CAS Registry Numbers

1b: 112438-23-0 / **1c**: 112459-36-6 / **1d**: 112438-25-2 / **1e**: 112438-27-4 / **1f**: 112438-29-6 / **2b**: 112438-24-1 / **2c**: 112438-26-3 / **2d**: 112459-35-5 / **3**: 112438-28-5 / **4a**: 112438-30-9 / **4b**: 112438-31-0 / **4c**: 112438-32-1 / **6a**: 112438-33-2 / **6b**: 112438-34-3 / **7**: 112438-38-7 / $H_2NB{=}PCH_3$: 112438-40-1 / $(H_2NBPCH_3)_2$: 112438-39-8 / $iPr_3C_6H_2Br$: 21524-34-5 / $iPr_3C_6H_2PCl_2$: 53356-73-3 / $iPr_3C_6H_2PH_2$: 112438-22-9 / $(Me_3Si)_2CHPCl_2$: 76505-20-9 / $(Me_3Si)_2CHPH_2$: 96082-33-6 / $tmpBCl_2$: 79855-29-1 / $tmpBF_2$: 103547-63-3 / tBu_2NBF_2: 666-59-1 / $NaN(SiMe_3)_2$: 1070-89-9 / $LiN(SiMe_3)tBu$: 18270-42-3 / $LiP(SiMe_3)_2 \cdot 2\,THF$: 59610-41-2 / LiPH*t*Bu: 67877-34-3 / $(iPr)_2NB(Cl)P(SiMe_3)_2$: 112438-35-4 / $Ph_2NB(Cl)P(SiMe_3)_2$: 112438-36-5 / $tmpB(Cl)P(SiMe_3)_2$: 112438-37-6 / Me_2NBBr_2: 7360-64-7 / $(Me_3Si)_2NBF_2$: 2251-46-9 / PCl_3: 7719-12-2

---

[1] Part 187: H. Nöth, *Z. Anorg. Allg. Chem.*, in press.

[2] Chemie der Hauptgruppenelemente, *Nova Acta Leopold., Neue Folge*, Vol. 59 (1985); Symposium on Multiple Bonding Involving the Heavier Main Group Elements, 192, ACS National Meeting, Anaheim, Sept. 1986.

[3] A. H. Cowley, *Acc. Chem. Res.* **17** (1984) 386; R. West, M. J. Fink, J. Michl, *Science* **214** (1981) 1343; M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **103** (1981) 4587.

[4] H. Klusik, A. Berndt, *Angew. Chem.* **95** (1983) 895; *Angew. Chem. Int. Ed. Engl.* **22** (1983) 877; B. Glaser, H. Nöth, *Angew. Chem.* **97** (1985) 424; *Angew. Chem. Int. Ed. Engl.* **24** (1985) 416.

[5] [5a] P. Paetzold, *Adv. Inorg. Chem. Radiochem.* **31** (1987) 123. – [5b] H. Nöth, S. Weber, *Z. Naturforsch., Teil B*, **37** (1983) 1460.

[6] H. Kroto, *Chem. Soc. Rev.* **11** (1982) 436.

[7] A. M. Arif, J. E. Boggs, A. H. Cowley, J. G. Lee, M. Pakulski, J. M. Power, *J. Am. Chem. Soc.* **108** (1986) 6083.

[8] A. H. Cowley, *Phosphorus Sulfur* **30** (1987) 129.

[9] R. A. Bartlett, X. Feng, M. M. Olmstead, P. P. Power, *Phosphorus Sulfur* **30** (1987) 245.

[10] X. Feng, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **25** (1985) 4615.

[11] R. A. Bartlett, X. Feng, P. P. Power, *J. Am. Chem. Soc.* **108** (1986) 6817.

[12] J. Escudie, C. Courét, M. Lazraq, B. Garrigues, *Synth. React. Inorg. Metalorg. Chem.* **17** (1987) 379.

[13] A. M. Arif, A. H. Cowley, M. Pakulski, J. M. Power, *J. Chem. Soc., Chem. Commun.* **1986**, 889.

[14] P. Kölle, H. Nöth, R. T. Paine, *Chem. Ber.* **119** (1986) 2681.

[15] G. E. Coates, J. G. Livingstone, *J. Chem. Soc.* **1961**, 5053; A. D. Tevebaugh, *Inorg. Chem.* **3** (1964) 302. The problem, whether PhBPPh is a monomer as suggested by Coates or possibly a trimer as suggested by Tevebaugh is still unsettled.

[16] G. Fritz, W. Hölderich, *Z. Anorg. Allg. Chem.* **431** (1977) 61.

[17] H. Nöth, W. Schrägle, *Chem. Ber.* **97** (1964) 2218, 2374.

[18] Similar unsuccessful experiments are reported in ref.[12] using olefins as scavengers.

[19] G. L. Wood, *Ph. D. Thesis*, University of New Mexico, 1987.

[20] W. Becker, *Diploma Thesis*, Univ. Marburg, 1969.

[21] W. Becker, H. Nöth, *Chem. Ber.* **105** (1972) 1962.

[22] H. O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie*, G. Thieme, Stuttgart, New York 1984.

[23] L. Black, R. C. Taylor, *Acta Crystallogr., Sect. B*, **31** (1975) 1116.

[24] P. S. Bryan, R. L. Kuczkowski, *Inorg. Chem.* **11** (1972) 553.

[25] H. Nöth, M. Schwartz, S. Weber, *Chem. Ber.* **118** (1985) 4716.

[26] H. G. von Schnering, W. Hönle, *Z. Anorg. Allg. Chem.* **440** (1978) 171.

[27] E. Salzbrenner, *Diploma Thesis*, Univ. München, 1987.

[28] P. Paetzold, Ch. von Plotho, G. Schmid, R. Boese, B. Schrader, D. Bougeard, U. Pfeiffer, R. Gleiter, W. Schäfer, *Chem. Ber.* **117** (1984) 1089.

[29] *MNDO III, QCPE Program 353* by J. D. Bowden, G. S. Owen as modified by W. Thiel.

[30] Using the MNDO III method we calculated a PP bond length of 2.04 Å for P_2H_4. This is 0.18 Å shorter than the experimental value. According to W. Thiel (private communication to P. Kölle) the program generally provides bond lengths which are too short for elements of the 3rd period.

[31] S. Weber, *PhD Thesis*, Univ. München, 1984.

[32] R. R. Ford, R. H. Neilson, *Polyhedron* **5** (1986) 643; M. J. S. Gynane, A. Hudson, M. F. Lappert, P. P. Power, *J. Chem. Soc., Dalton Trans*, **1980**, 2428.

[33] P. Kölle, H. Nöth, *Chem. Ber.* **119** (1986) 313.

[34] G. L. Wood, R. T. Paine, H. Nöth, to be submitted for publication.

[35] Additional information concerning the X-ray structure determinations are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (W. Germany) and can be requested by quoting the registry number CSD 52740, the authors, and the reference to this publication.

[308/87]