Pyrazole – Organoboranes, VIII[1,2)]

Thermal *C* – Borylation in Crowded Pyrazolylboranes

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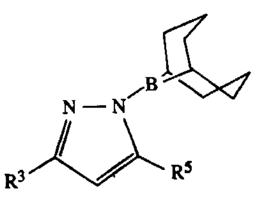
Crowded 3,5-disubstituted pyrazoles, e. g. 3,5-di-*tert*-butyl-, 3,5-di-*tert*-butyl-4-methyl-, or 3,5-di-*tert*-butyl-4-ethylpyrazole [**(tb)$_2$Pz, (tb)$_2$mPz,** or **(tb)$_2$ePz,** respectively], fail to react with activated trialkylboranes (e. g. BEt_3^* or BPr_3^*) at 110°C, even after prolonged heating. At 170°C the reaction of **(tb)$_2$Pz** with activated triethylborane gives the monomeric diethyl(3,5-di-*tert*-butyl-1-pyrazolyl)borane (**3**). At 220–230°C the dimeric boracycles **(4)$_2$** are mainly formed [X-ray structure of **(4a)$_2$**]. In contrast, the reactions of these crowded pyrazoles with tetraalkyldiboranes(6) commence just above room temperature. Diethylhydroborane adducts (**5**) of **3** and dimeric alkyl(3,5-di-*tert*-butyl-1-pyrazolyl)-boranes **(2b)$_2$** and **(2c)$_2$** are the main products.

In recent reports we have shown that 9-pyrazolyl-9-borabicyclo[3.3.1]nonanes **1** are monomeric when the pyrazole ring carries very large substituents (e.g. *tert*-butyl) in the 3,5-positions[2–4)]. Intramolecular steric interactions of these substituents with the bulky and rigid 1,5-cyclooctanediylboryl group of **1** hinder the otherwise facile formation of the very stable dimers of the type **(2)$_2$**[5,6)]. It has been of interest to examine the effect of a combination of small substituents of the boron atom and large ones in the 3,5-positions of the pyrazole ring. In this communication we report on the results of the reaction at high temperatures of pyrazoles bearing very large substituents with a number of trialkylboranes and tetraalkyldiboranes(6).



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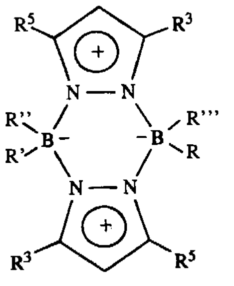
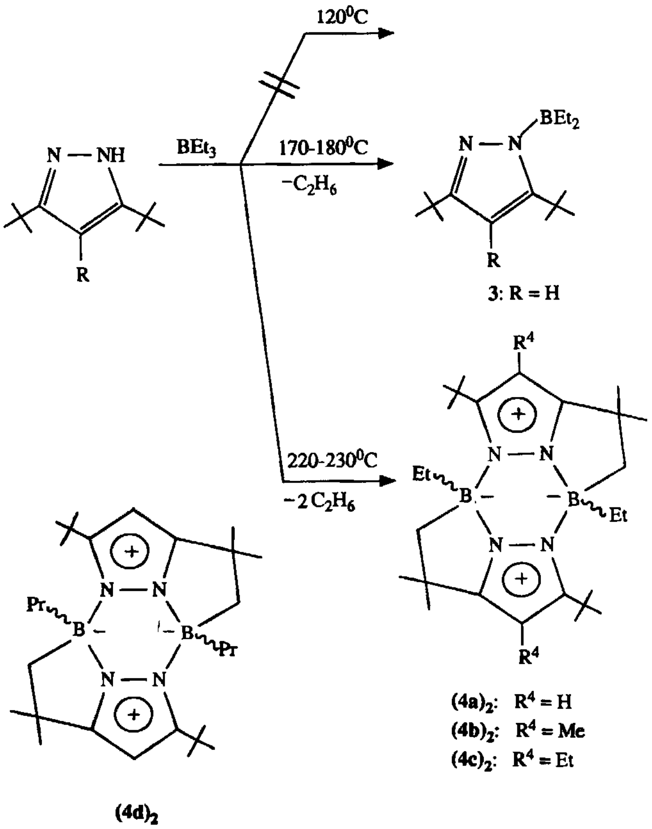


(2a)$_2$: R^3, R^5 = i-Pr; R, R', R'', R''' = Et
(2b)$_2$: R^3, R^5 = t-Bu; R, R' = H; R'', R''' = Et
(2c)$_2$: R^3, R^5 = t-Bu; R, R' = H; R'', R''' = Pr

Results and Discussions

The reaction of activated trialkylboranes[7)] with pyrazoles is usually very facile[2–6)]. Commencement of the reaction can be observed at just above room temperature and in the case of activated triethylborane (BEt_3^*)[7)] the progress of the reaction can be monitored by measuring the ethane gas evolved. In agreement with this, 3,5-diisopropylpyrazole [**(ip)$_2$Pz**] reacts with BEt_3^* to form the dimeric diethyl(3,5-diisopropyl-1-pyrazolyl)borane **(2a)$_2$** in quantitative yield. When the more crowded 3,5-di-*tert*-butylpyrazole [**(tb)$_2$Pz**] is heated with an excess of BEt_3^* at reflux no gas evolution is observed, and only unreacted **(tb)$_2$Pz** can be recovered



3: R = H

(4a)$_2$: R^4 = H
(4b)$_2$: R^4 = Me
(4c)$_2$: R^4 = Et

(4d)$_2$

Table 1. NMR data for pyrazolylboranes **(2)**$_2$, **3**, **(4)**$_2$, and **5** ($CDCl_3$ as solvent, ambient temperature)

Com-pound No	$\delta^{13}C$ (50.4 MHz)						$\delta^{11}B$ 64.2 MHz	$\delta^{1}H$ (200 MHz)					
	Pyrazolyl moiety			B-alkyl group				Pyrazolyl moiety			B-alkyl group		
	C^3 R^3	C^4 R^4	C^5 R^5	B-CH_2 (br,t)	CH_2 (t)	CH_3 (q)		R^3	H^4 R^4	R^5	BCH_2	CH_2	CH_3
(2a)$_2$	156.9(s) 26.3(d) 23.6(q)	102.0(d)	156.9(s)	17.4	–	9.3	3.8	3.48(2H) 1.15(12H)	6.14(2H)	3.48(2H) 1.15(12H)	0.64(8H)	–	0.24(12H)
(2b)$_2$	158.9(s) 32.3(s) 30.2(q)	103.8(d)	158.9(s) 32.3(s) 30.2(q)	19.5	–	9.9	-2.4	1.39(18H)	5.94(2H)	1.39(18H)	0.1(4H)	–	0.1(6H)
(2c)$_2$	159.2(s) 32.3(s) 30.1(q)	103.7	159.2(s) 32.3(s) 30.1(q)	31.0	18.6	17.7	-3.0	1.39(18H)	5.94(2H)	1.39(18H)	0.02(4H)	0.27(4H)	0.48(6H)
3	161.5(s) 31.8(s) 30.5(q)	104.4(d)	161.5(s) 31.8(s) 30.5(q)	17.1	–	8.2	63.8	1.35(9H)	6.10(1H)	1.35(9H)	1.61(4H)	–	1.05(6H)
(4a)$_2$	161.4(s) 36.5(s) 32.8(q) 30.2(q)	96.4(d)	160.3(s) 33.0(s) 31.4(q)	40.8 17.1	–	10.9	5.6	1.52(d,2H) 1.45(d,2H) 1.40(6H) 1.27(6H)	5.66(2H)	1.39(18H)	0.82(4H)	–	0.82(6H)
(4b)$_2$	157.6(s) 36.4(s) 33.1(q) 31.5(q)	105.7(s) 28.4(q)	156.8(s) 31.4(s) 30.0(q)	42.0 17.0	–	10.0	5.3	1.30(6H) 1.20(4H) 1.18(6H)	– 2.05(6H)	1.27(18H)	0.89(4H)	–	0.48(6H)
(4c)$_2$	156.9(s) 36.8(s) 31.9(q) 29.3(q)	113.3(s) 17.3(q) 16.4(t)	156.6(s) 32.2(s) 31.0(q)	43.6 16.2	–	10.2	5.7	1.35(4H) 1.33(6H) 1.28(6H)	– 2.58(4H) 1.18(6H)	1.39(18H)	0.88(4H)	–	0.64(6H)
(4d)$_2$	160.4(s) 35.9(s) 32.7(q) 31.0(q)	95.6	159.6(s) 32.3(q) 29.9(q)	40.5 30.0	19.9	17.9	5.3	1.48(d,2H) 1.35(d,2H) 1.31(3H) 1.20(3H)	5.70(2H)	1.30(18H)	0.79(4H)	1.32(4H)	0.82(6H)
5	154.3(s) 31.1(s) 30.2(q)	103.4(d)	154.3(s) 31.1(s) 30.2(q)	14.5	–	9.8	16.0	1.21(9H)	5.94(1H)	1.21(9H)	0.8(8H)	–	0.8(12H)

after removing the borane reagent under reduced pressure. When however, the two reagents are heated at 170–220°C in a closed vessel for 6–12 h, depending on the temperature and the reaction time, up to about two equivalents of ethane gas are formed, and either a liquid or a crystalline solid product is obtained. The homogeneous liquid product, formed at 170°C after 6 h, can be identified by its mass (M^+ = 248) and NMR spectra (see Table 1) as the monomeric diethyl(3,5-di-*tert*-butyl-1-pyrazolyl)borane (**3**). The principal product formed at about 220°C is the novel crystalline air-stable dimer **(4a)**$_2$ in which as a result of *C*-borylation boracycles are formed.

The structure of **(4a)**$_2$ has been deduced on the basis of its mass and NMR stectra (Table 1) and confirmed by an X-ray diffraction. The molecular structure of **(4a)**$_2$ is shown in Figure 1. The *cis* configuration of the *B*-ethyl substituents imparts a boat conformation to the central B_2N_4 six-membered ring with a folding angle between the two planes B1N1N2B2 and B1N3N4B2 of 44.5° and between those of N2B1N3 and N1B2N4 of 60.9°. These are larger than those found in the disulfur-[8] and diselenium[9]-bridged diorganopyrazolylborane dimers. The pyrazole rings are not coplanar with the planes B1N1N2B2 and B1N3N4B2 and deviate from these by 5.9 and 4.8°, respectively.

The fused pentacyclic ring system of **(4a)**$_2$ shows a number of abnormally distorted bonds and angles (see legend to Figure 1). Predominant among these are the rather short C1C9 and C4C17 (1.510 Å) and the elongated C9C12 and C17C18 (1.572 Å) single bonds. Furthermore, all four BN

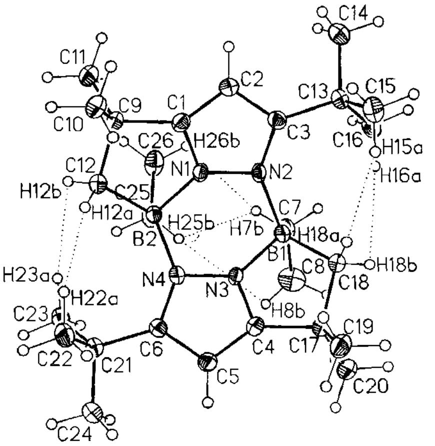
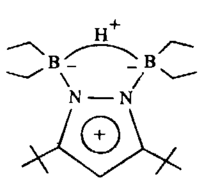


Figure 1. Molecular structure of **(4a)**$_2$ (dotted lines indicate very short non-bonded intramolecular distances). Bond lengths (Å): B1N2 1.607(2), B1N3 1.599(3), N1N2 1.369(2), B2N1 1.589(3), B2N4 1.609(2), N4N3 1.372(2), B1C7 1.610(3), B1C18 1.641(2), C17C18 1.572(2), C4C17 1.510(2), N3C4 1.330(2), N4C6 1.358(2). – Bond angles (°): N1B2N4 101.7(1), N2N1B2 133.3(1), N1N2B1 111.8(1), B1N2C3 141.4(1), B2N1C1 115.9(1), C9C1C2 138.9(1), C2C3C13 125.5(2), N2C3C13 126.0(1), C1C9C12 102.6(1), C12B2N1 95.6(1), C12B2C25 115.8(9), B2C25C26 116.1(1), N4B2C12 119.3(1)

bonds are significantly longer (1.601 Å$_{av}$) than the corresponding BN bonds in the usual dimeric pyrazolylboranes[10,11] and in the sulfur- and selenium-bridged derivatives[8,9]. Several angles are excessively widened, e.g. N4B2C12, C9C1C2, N2N1B2, and B1N2C3 (119.3, 138.9, 133.3, and 141.4°, respectively). Others are very small, e.g. C1C9C12 and C12B2N1 (102.6 and 95.6°, respectively). Finally, a large number of very short intramolecular nonbonding H···H distances (Figure 1, dotted lines) add to the strains prevailing in this molecule.

The above reaction appears to be a general one for pyrazoles with *tert*-butyl groups in the 3,5-positions. Thus, the reaction of either 3,5-di-*tert*-butyl-4-methyl- or 3,5-di-*tert*-butyl-4-ethylpyrazole [**(tb)$_2$mPz** or **(tb)$_2$ePz**, respectively] with BEt_3^* at 220–230 °C gives the crystalline dimer **(4b)$_2$** or **(4c)$_2$**, respectively. Similarly, the propyl derivative **(4d)$_2$** is obtained from **(tb)$_2$Pz** and activated tripropylborane (BPr_3^*) at 220 °C. In all cases the ^{1}H-and ^{13}C-NMR spectra of the raw products show the presence of mixtures of both possible *cis* and *trans* isomers of the corresponding dimer **(4)$_2$**[12]. Recrystallization from hexane results in the preferential crystallization and isolation of only one isomer [based on the X-ray structure analysis of **(4a)$_2$**, in all cases presumably the *cis* isomer].

At intermediate temperatures, e.g. 180–200 °C, the reactions produce mixtures: The ^{11}B-NMR spectra show the presence of derivatives of **3** ($\delta \approx 64.0$) and of **(4)$_2$** ($\delta \approx 5.0$). In addition, depending on the duration of the exposure and the temperature, peaks of varying signal intersities can be observed at $\delta^{11}\mathrm{B} \approx 16.0, 11.0, -5.0$. Furthermore, the IR spectra of the products provide evidence for the presence of compounds with $\mathrm{>B-H}$ bonds [$\tilde{\nu}(\mathrm{>B-H}) = 2480$, $(\mathrm{>B-H-B<}) = 1900\ \mathrm{cm^{-1}}$]. A mass spectroscopic analysis of the product mixture formed by the reaction of **(tb)$_2$Pz** with BEt_3^* at 180 °C, carried out by fractional vaporization of the sample into the ion chamber, indicates the presence of the hydroborane derivatives **(2b)$_2$**, **5**, and **6**.



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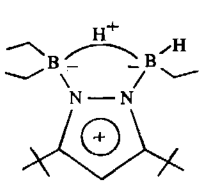

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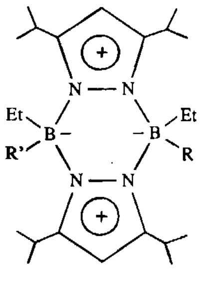


7: R = Et; R' = (iPr)$_2$Pz
8: R, R' = (iPr)$_2$Pz

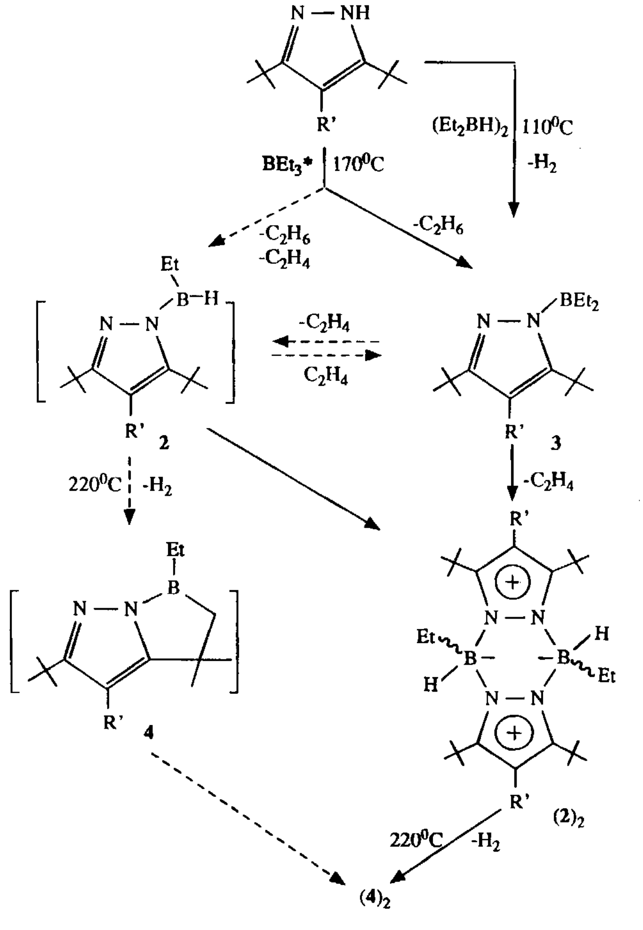
Compounds **5** and **6** are analogues of the 1:1 addition complexes formed by the reaction of 9-borabicyclo[3.3.1]nonane with e.g. monomeric 9-(3,5-di-*tert*-butyl-1-pyrazolyl)-9-borabicyclo[3.3.1]nonane[2–4]. Both **5** and **6** are presumably formed under the above reaction conditions by the addition to **3** of in situ generated diethylhydroborane or monoethyldihydroborane. Compound **5** can be prepared in pure form by the addition of stoichiometric amounts of tetraethyldiborane(6) to **3** at room temperature, or directly by the reaction of **(tb)$_2$Pz** with an excess of tetraethyldiborane(6) in refluxing heptane.

Thermolysis of pure **3** or **5**, or of mixtures containing **3**, **5**, and **6** at 180 °C converted the former to solid **(2b)$_2$**. Compound **(2b)$_2$** and its *B*-propyl derivative **(2c)$_2$** can also be prepared in low yield by the direct reaction of the corresponding pyrazole and tetraalkyldiborane at 120 °C or in higher yieds at 180 °C. The dimeric alkylhydropyrazolylboranes **(2b)$_2$** and **(2c)$_2$** are derivatives of the so-called pyrazaboles[5,6].

Since the further thermal treatment of **(2b)$_2$** or **(2c)$_2$** at 220 °C leads to the formation of the corresponding dimer **(4)$_2$**, they can be regarded as intermediates in the direct thermal reactions of the substituted pyrazoles with trialkylboranes. However, the dimeric diethyl(3,5-diisopropylpyrazolyl)borane **(2a)$_2$** remains unchanged at 220 °C and only prolonged heating at 240–250 °C results in partial decomposition. Amongst the decomposition products mass spectroscopy furnishes evidence for the presence of compounds **7** and **8** in which one and two *i*Pr$_2$Pz groups, respectively, are substituted at the boron atom(s).

The steps shown in Scheme 1 rationalize the formation of **(4a)$_2$** from either triethylborane or tetraethyldiborane(6).

Scheme 1. Pathways for the formation of **3** and the dimers **(2)$_2$** and **(4)$_2$** from e. g. BEt$_3$ or (Et$_2$BH)$_2$ (dotted arrows represent alternative routes)



As mentioned above the key precursor is thought to be the dimeric hydroborane **(2b)$_2$**. The initial formation of monomeric **4a**, however, cannot be ruled out. The conversion of **(2b)$_2$** to **(4a)$_2$** at 220°C proceeds probably in a similar manner as the pyrolysis of trialkylboranes to boracycles above 250°C[13]. Another noteworthy aspect of the present reaction is thus the relatively mild temperature required for the cyclization step and also for the proposed dehydroboration(s) leading to **(2b)$_2$** and ethylene. Since ethane is the only gaseous end-product found in this reaction, it has to be assumed that the ethylene formed in accordance with Scheme 1 is rapidly hydrogenated in a borane-catalysed reaction[14,15]. [The direct conversion of compound **3** to **(4)$_2$** and release of ethane gas cannot be ruled out.][16]

The special air and water stability of the dimeric structures **(2)$_2$** have been attributed to both steric and electronic factors[5b]. Since both dimers **(2)$_2$** and **(4)$_2$** have basically identical electronic structures, the driving force for the relatively facile thermal conversion of **(2)$_2$** to **(4)$_2$** can be attributed to a decrease in internal crowding in the vicinity of the boron atom and the neighbouring *tert*-butyl group.

The progressive increase of strain and therefore the instability of the dimers **(4a)$_2$**, **(4b)$_2$**, and **(4c)$_2$**, resulting from the substitution of methyl or ethyl groups, respectively, in the 4-positions of the pyrazole rings, become only evident in the fragment ion intensities found in their mass spectra (Table 2): None of these spectra show a molecular ion. However, while the intensity of the primary fragment ion [M^+ − Et] progressively decreases from 100% in **(4a)$_2$** to 8% in **(4c)$_2$**, there is an increase of the $M^+/2$ ion intensity from 20% in **(4a)$_2$** to 99% in **(4c)$_2$**. As expected, the change of the *B*-substituents from ethyl to propyl does not significantly alter the crowding and therefore the stability of the dimers; both **(4a)$_2$** and **(4d)$_2$** have similar intense corresponding fragment ion peaks in their mass spectra. Generally, the observation of fragments derived from the dimer molecular ion point to the persistent stability of the B_2N_4 heterocycle despite the severity of the intramolecular crowding in **(4a)$_2$**–**(4d)$_2$**.

Experimental

Instruments: Büchi melting point apparatus, sealed capillary tubes. – IR: Perkin Elmer 297. – MS: MAT CH 5. – ^{1}H, ^{11}B, ^{13}C NMR: Bruker AC 200, Me_4Si as internal and Et_2O-BF_3 as external standard. Sources of the reagents are cited in refs.[2,16]. All operations were carried out under oxygen-free dry argon. Solvents were freshly dried and distilled.

Bis[(3,5-diisopropyl-1-pyrazolyl)diethylborane] [**(2a)$_2$**]: To a solution of 1.5 g (9.9 mmol) of **(ip)$_2$Pz** in 20 ml of toluene was added a solution of 1.5 g (15.3 mmol) of triethylborane (activated with 2% pivalic acid)[7] in 10 ml of toluene. The mixture was slowly heated to reflux. Gas evolution commenced at above 50°C. A total of 220 ml of ethane gas evolved after 1 h at reflux. The solvent and volatiles were removed under reduced pressure. The solid residue **(2a)$_2$** was recrystallized from hexane. (For NMR data see Table 1 and for m.p., yield, MS, and microanalysis see Table 2.
Table 2

Bis[(3,5-di-tert-butyl-1-pyrazolyl)ethylborane] [**(2b)$_2$**]: A suspension of 1.8 g (10.0 mmol) of **(tb)$_2$Pz** in 4.4 ml (≈38.8 mmol $>$BH borane) of tetraethyldiborane(6) was first heated at 70°C for 3 h until gas evolution ceased, then heated to 110°C for an additional 1 h. A total of 10 mmol of gas evolved. From the colourless solution the volatiles were removed under reduced pressure, and under vacuum (10^{-3} Torr) at ≈100°C bath temperature, the liquid fraction (0.6 g) was removed from a solid residue. ^{11}B NMR of the liquid fraction: δ = 16.3 (**5**) and 8.5 (**6**) (≈2:1 integral ratio). The solid residue was recrystallized from hexane to give 1.2 g of colourless solid **(2b)$_2$**. – IR (KBr): $\tilde{\nu}$($>$B−H) = 2480 cm^{-1}. (For NMR data see Table 1 and for m.p., yield, MS, and microanalysis see Table 2.)

Table 2. Melting (boiling) points, yields (%), mass spectra, and elemental analyses for pyrazolylboranes **(2)$_2$**, **3**, **(4)$_2$**, **5**, and **6**

Compound No	m.p. (b.p.) °C/Torr	Yield (%)	Mass spectrum (m/z % rel. int.)	Elemental analysis			
				Mol.for. (mol.wt.)	Calcd. Found C	H	B
(2a)$_2$	173-174	99	411(M^+-29,B_2,100), 259(15), 191(15)	$C_{26}H_{50}B_2N_4$ (440.3)	70.92 70.81	11.45 11.52	4.91 4.95
(2b)$_2$	217-218	54	411(M^+-29,B_2,100), 381(11), 191(28)	$C_{26}H_{50}B_2N_4$ (440.3)	70.92 70.71	11.45 11.49	4.91 4.83
(2c)$_2$	212-213	70	425(M^+-43,B_2,100), 383(43), 191(26)	$C_{28}H_{54}B_2N_4$ (468.4)	71.80 71.69	11.62 11.53	4.62 4.80
3	(50-52/ 10^{-3})	68	248(M^+,B_1,15), 219 (100), 136(55), 108(28)	$C_{15}H_{29}BN_2$ (248.2)	72.58 72.40	11.78 11.91	4.36 4.58
(4a)$_2$	172-173	72	407(M^+-29,B_2,100), 218(M^+/2,20), 217(20), 203(25), 189(22)	$C_{26}H_{46}B_2N_4$ (436.3)	71.58 71.51	10.63 10.68	4.96 4.72
(4b)$_2$	186-188	71	435(M^+-29,B_2,18), 232 (M^+/2,84), 231(76), 217 (68), 190(100), 189(76)	$C_{28}H_{50}B_2N_4$ (464.4)	72.42 72.28	10.85 10.93	4.66 4.58
(4c)$_2$	161-162	51	463(M^+-29,B_2,8), 246 (M^+/2,99), 231(100), 217(30), 203(60)	$C_{30}H_{54}B_2N_4$ (492.4)	73.18 73.01	11.05 11.21	4.39 4.52
(4d)$_2$	157-158	68	421(M^+-29,B_2,100), 379(12), 232(M^+/2,8), 217(52), 204(33), 189(38), 175(20)	$C_{28}H_{50}B_2N_4$ (464.4)	72.42 72.51	10.85 10.81	4.66 4.71
5	(108-109/ 10^{-3})	62	289(M^+-29,55), 288 (44), 287(100), 286 (45), 259(15)	$C_{19}H_{40}B_2N_2$ (318.2)	71.73 72.02	12.67 12.50	6.80 6.61
6	—	—	261(M^+-29,30), 260 (30), 259(100), 258(45)	$C_{17}H_{36}B_2N_2$ (290.1)		n. d.	

Bis[(3,5-di-tert-butyl-1-pyrazolyl)propylborane] [**(2c)$_2$**]: To a stirred suspension of 1.5 g (8.3 mol) of **(tb)$_2$Pz** in 15 ml of toluene, initially at 80°C, was added dropwise a solution of 3.8 g (19.4 mmol $>$BH borane) of tetrapropyldiborane(6) in 15 ml of toluene. After gas evolution had ceased (2 h) the mixture was further heated at reflux for 2 h. The solvent and volatiles were removed in vacuo. The residue, a sticky solid, was sublimed at 120°C/10^{-3} Torr. Recrystallization of the solid sublimate from hexane gave 1.2 g of colourless solid **(2c)$_2$**. – IR (KBr): $\tilde{\nu}$($>$B−H) = 2480 cm^{-1}. (For NMR data see Table 1 and for m.p., yield, MS, and microanalysis see Table 2.)

(3,5-Di-tert-butyl-1-pyrazolyl)diethylborane (**3**): A mixture of 2.9 g (16.1 mmol) of 3,5-di-*tert*-butylpyrazole [**(tb)$_2$Pz**] and 4.0 g (40.8 mmol) of activated triethylborane (BEt_3^*) was heated in a 100-ml stainless steel autoclave at 170°C for 6 h. After cooling to room temp., 20 ml of hexane was added and the product removed from the autoclave. The volatiles were evaporated under reduced pressure, and the liquid residue was distilled in vacuo. (For NMR data see Table 1 and for b.p., yield, MS, and microanalysis see Table 2.

Bis(3-tert-butyl-8-ethyl-6,6-dimethyl-1,2-diaza-8-borabicyclo-[3.3.0]octa-2,4-diene) [**(4a)$_2$**]: A mixture of 3.1 g (17.2 mmol) of **(tb)$_2$Pz** and 5.0 g (51.0 mmol) of BEt_3^* was heated as above at 220°C for 12 h. The solid product was recrystallized from hexane to give colourless crystalline **(4a)$_2$**. (For NMR data see Table 1 and for m.p., yield, MS, and microanalysis see Table 2.

X-ray Single-Crystal Structure Determination of **(4a)$_2$**: Data collection and calculations were carried out on a Nicolet R 3 m/v four-cycle diffractometer with Microvax II and SHELXTL-PLUS software[18]. The structure solution was performed by direct methods, and all hydrogen atoms were included as rigid groups (C—H bond lengths at 0.96 Å, C—C—H and H—C—H angles at 109.5 and 120°C, respectively). The isotropic displacement parameters (IDP's) of all the H atoms were refined without constraints.

Structural Data for **(4a)$_2$**: Crystal size 0.27 × 0.22 × 0.19 mm, space groups $P\bar{1}$, $Z = 2$, $a = 10.114(1)$, $b = 10.545(1)$, $c = 13.781(1)$ Å, $V = 1310.5(2)$ Å^3, $\beta = 93.32(1)°$, $d_{calc.} = 1.103$ g/cm^3, $\mu = 0.06$ mm^{-1} radiation Mo/K_α, $2\Theta = 50$ deg, number of unique reflections = 4658, observed reflections = 3789 [$F_o \geq 4\sigma(F)$], $R = 0.0413$, $R_w = 0.0435$ [$w^{-1} = \sigma^2(F_o) + gF_o^2$] with $g = 0.00062$, residual electron density = 0.248 e/Å^3 (0.79 Å for B2). The atomic coordinates of **(4a)$_2$** are listed in Table 3[18,19].

Table 3. Atomic coordinates (× 10^4) and equivalent isotropic displacement factors (Å^2 × 10^4) of **(4a)$_2$**. *Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
N(1)	3403(1)	2663(1)	1992(1)	174(5)*
N(2)	3490(1)	4018(1)	2115(1)	174(5)*
N(3)	5882(1)	4401(1)	2999(1)	163(5)*
N(4)	5821(1)	3048(1)	2814(1)	168(5)*
B(1)	5136(2)	5173(2)	2415(1)	192(7)*
B(2)	4570(2)	1993(2)	1891(1)	188(7)*
C(1)	2026(2)	1741(2)	1854(1)	198(6)*
C(2)	1161(2)	2488(2)	1841(1)	222(6)*
C(3)	2104(2)	3915(2)	1994(1)	197(6)*
C(4)	6810(2)	5223(2)	3828(1)	173(6)*
C(5)	7450(2)	4424(2)	4186(1)	198(6)*
C(6)	6807(2)	3059(2)	3533(1)	178(6)*
C(7)	5720(2)	5468(2)	1389(1)	239(7)*
C(25)	5270(2)	2014(2)	869(1)	248(7)*
C(9)	1865(2)	246(2)	1807(1)	224(6)*
C(10)	1027(2)	-276(2)	2631(1)	289(7)*
C(11)	1040(2)	-769(2)	791(1)	317(7)*
C(12)	3481(2)	424(2)	1995(1)	236(6)*
C(13)	1647(2)	5141(2)	2022(1)	222(6)*
C(14)	177(2)	4557(2)	1335(2)	339(8)*
C(15)	1467(2)	5763(2)	3088(1)	301(7)*
C(16)	2717(2)	6312(2)	1620(1)	284(7)*
C(17)	6787(2)	6676(2)	4142(1)	205(6)*
C(18)	5512(2)	6555(2)	3368(1)	219(6)*
C(19)	6490(2)	6964(2)	5222(1)	277(7)*
C(20)	8239(2)	7835(2)	4081(1)	277(7)*
C(21)	7128(2)	1782(2)	3620(1)	202(6)*
C(22)	6137(2)	979(2)	4287(1)	264(7)*
C(23)	6961(2)	783(2)	2595(1)	246(7)*
C(24)	8702(2)	2320(2)	4133(1)	281(7)*
C(26)	4218(2)	1615(2)	-98(1)	308(7)*
C(8)	7340(2)	6211(2)	1418(2)	383(8)*

Bis(3-tert-butyl-8-ethyl-4,6,6-trimethyl-1,2-diaza-8-borabicyclo-[3.3.0]octa-2,4-diene)[**(4b)$_2$**]: A mixture of 0.99 g (5.1 mmol) of **(tb)$_2$mPz** and 3.5 ml (25.0 mmol) of **BEt_3^*** was heated as above at 220°C for 12 h. The solid product recrystallized from hexane to give 0.8 g of**(4b)$_2$**. (For NMR data see Table 1 and for m.p., yield, MS, and microanalysis see Table 2.)

Bis(3-tert-butyl-4,8-diethyl-6,6-dimethyl-1,2-diaza-8-borabicyclo-[3.3.0]octa-2,4-diene) [**(4c)$_2$**]: A mixture of 0.60 g (2.9 mmol) of **(tb$_2$)ePz** and 5 ml (35.7 mmol) of triethylborane was heated as above at 230°C for 14 h. The solid product was recrystallized from hexane to give colourless crystalline **(4c)$_2$**. (For NMR data see Table 1 and for m.p., yield, MS, and microanalysis see Table 2.)

*Bis(3-tert-butyl-6,6-dimethyl-8-propyl-1,2-diaza-8-borabicyclo-[3.3.0]octa-2,4-diene)***(4d)$_2$**: A mixture of 2.0 g (11.1 mmol) of **(tb)$_2$Pz** and 8.1 g (57.9 mmol) of activated tripropylborane (**BPr_3^***)[7] was stirred in a 100-ml autoclave at 180°C for 14 h. The product was worked up as above to give 2.5 g of a sticky solid. Sublimation at 120°C/10^{-3} Torr afforded a colourless solid which was recrystallized from hexane to give 1.9 g of **(4d)$_2$**. (For NMR data see Table 1 and for m.p., yield, MS, and microanalysis see Table 2.)

Diethylborane Adduct of (3,5-Di-tert-butyl-1-pyrazolyl)diethylborane **(5)**: To a suspension of 1.0 g (5.8 mmol) of **(tb)$_2$Pz** in 15 ml of heptane heated at 50°C was added dropwise a solution of 1.5 ml (13.8 mmol >BH borane) of tetraethyldiborane(6) in 15 ml of heptane. Gas was evolved and after the borane addition was completed 130 ml (5.8 mmol) of hydrogen gas was collected. The solution was heated to reflux for 2 h, the solvent evaporated at reduced pressure, and the slightly viscous colourless residue distilled in vacuo. A colourless liquid was collected. — IR (film): $\tilde{\nu}(\gtrdot B-H-B\lessdot) = 1900$ cm^{-1}(br.). (For NMR data see Table 1 and for b.p., yield, MS, and microanalysis see Table 2.)

CAS Registry Numbers

(2a)$_2$: 133778-77-5 / **(2b)$_2$**: 133778-78-6 / **(2c)$_2$**: 133778-79-7 / **3**: 133778-76-4 / *cis*-**(4a)$_2$**: 133778-82-2 / *trans*-**(4a)$_2$**: 133814-68-3 / *cis*-**(4b)$_2$**: 133778-83-3 / *trans*-**(4b)$_2$**: 133814-69-4 / *cis*-**(4c)$_2$**: 133778-84-4 / *trans*-**(4c)$_2$**: 133814-70-7 / *cis*-**(4d)$_2$**: 133778-85-5 / *trans*-**(4d)$_2$**: 133814-71-8 / **5**: 133778-80-0 / **6**: 133778-81-1 / BEt_3: 97-94-9 / BPr_3: 1116-61-6 / **(ip)$_2$Pz**: 17536-00-4 / **(tb)$_2$Pz**: 1132-14-5 / **(tb)$_2$mPz**: 18712-47-5 / **(tb)$_2$ePz**: 125281-21-2 / pivalic acid: 75-98-9 / tetraethyldiborane(6): 12081-54-8 / tetrapropyldiborane(6): 22784-01-6

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[1] Dedicated to Professor Dr. *P. Binger* on the occasion of his 60th birthday.

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[12] The presence of a second component, presumably the *trans* isomer e.g. of **(4a)$_2$**, is clearly indicated by additional peaks in the ^{1}H-NMR spectra of the crude product: A singlet at $\delta = 5.88$ for H^4 of the pyrazolyl moiety and a triplet at $\delta = -0.08$ for the methyl protons of the BEt groups. In the ^{13}C-NMR spectrum the following peaks can be assigned to about 15% *trans* **(4a)$_2$**: $\delta = 165.3$ (s), 160.1 (s), 98.4 (d), 36.7 (s), 32.5 (s), 30.9 (q), 28.8 (q), and 8.6 (q).

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[15] When triethylborane is heated under D_2 pressure (7 bar) at 180°C for 7 h, besides the release of C_2H_6 and C_2H_5D, as seen by the formation of HD and H_2, a significant isotope exchange is also observed. At higher temperatures (e.g. 220°C), D_2 is efficiently consumed, and mainly C_2H_6,C_2H_5D and $C_2H_4D_2$ are formed. At both temperatures, the non-gaseous products consist of mixtures of triethylborane and a number of ethylhydro-(deuterio)diboranes(6), as well as diborane(6) and polyboranes[16] (^{11}B NMR). The infrared spectra of the products show also the presence of C—D vibrations at 2280 cm^{-1}. The results show

that besides straightforward B—C bond deuterolysis also dehydroboration-deuterioboration reactions are involved.

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