Pyrazole-Organoboranes, VII[1]

Addition Complexes of Pyrazolylboranes

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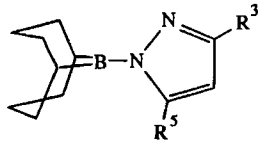
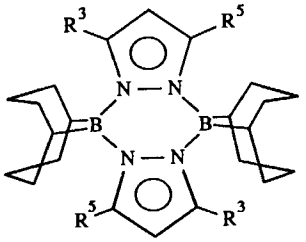
The monomeric 9-pyrazolyl-9-borabicyclo[3.3.1]nonanes react in situ with either excess of **9H-9-BBN** or of some pyrazoles to form the 2:1 or 1:2 adducts **1**–**5** or **7**–**11**, respectively. Spectroscopic data (NMR, IR) suggest and the solid state structure of **4** confirms the presence of a central $\overline{BHBN}_2$ heterocycle in complexes of the type **1**–**5**. In solutions of **7**–**11** NMR data at room temperature indicate a rapid exchange of the four nitrogen atoms of the two pyrazole rings at the boron atom of the 9-BBN moiety. In the solid state (X-ray structure of **8**) intermolecular N–H ··· N bonds lead to dimeric structures. In the almost insoluble adduct **7** a polymeric structure is suggested. Pyrazoles with large substituents, e. g. 3,5-diphenylpyrazole (**p_2Pz**) give addition complexes of the type **1**–**5** only in solution in equilibrium with the corresponding monomeric species (^{11}B NMR) and none of the type **7**–**11**.

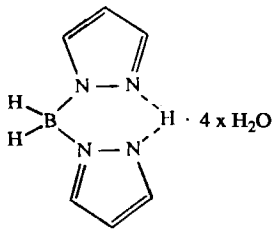
In a previous communication[2] and in the preceeding publication[3] we have reported that the reaction of bis(9*H*-9-borabicyclo[3.3.1]nonane) **(9H-9-BBN)$_2$** with pyrazoles leads, depending on the type and number of substituents in the 3- and/or 5-position on the pyrazoles, to the formation of the monomeric or the dimeric 9-borabicyclo[3.3.1]nonanes **I** and **II**, respectively.



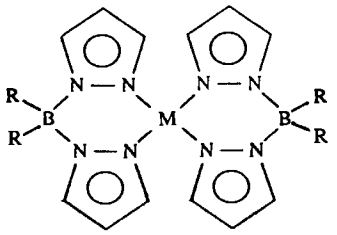
I



II



III



IV

The monomer **I**, the likely initial reaction product, readily dimerizes to form **II**, when the reacting pyrazole is unsubstituted, carries substituents in the C^4 position, or has a methyl group at C^3. This facile dimerization tendency of **I** suggests the presence of a potentially reactive Lewis acid centre on the boron atom and a Lewis base character on the second nitrogen atom of the pyrazole group. The monomer **I** should therefore be regarded as a reactive donor-acceptor species that should show interesting coordinative activities with either a sterically undemanding Lewis acid, or a suitable base molecule. Such tendencies are already evident during the preparatory work leading to **I** or **II** and in some cases have forced us to adopt special procedures to avoid side reactions[3]. In this paper we describe the utilization of one aspect of the donor-acceptor potentials of **I**.

Results and Discussion

As mentioned above, in the initial experimental procedure employed for the preparation of the pyrazolylboranes we have noticed that, depending on the sequence of addition of one reagent to the solutions of the other, the products were either mixtures of the compound sought and a second component, or consisted solely of the latter. Employing the technique of very slow addition of a dilute solution of one component to that of the other, we have obtained two types of addition complexes of **I**.

a) Addition Complexes 1–6 of 9H-9-BBN

The slow addition of a toluene solution of one equivalent of pyrazole (**Pz**) to a solution of one equivalent of **(9H-9-BBN)$_2$** at 50°C gives a solid **1**, the 1:1 addition complex of 9-pyrazolyl-9*H*-9-borabicyclo[3.3.1]nonane **(I)** with **9H-9-BBN**. The mass spectrum of the addition complex **1**, m.p. 138–139°C, shows a molecular ion peak at m/z = 310 (B_2-

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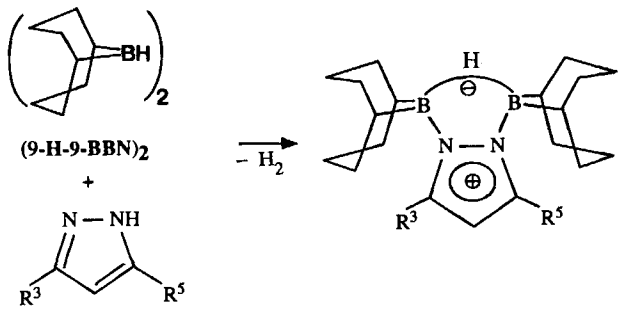
Table 1. NMR data for the addition complexes **1**–**5** and **7**–**11**. Measurements were carried out in $CDCl_3$ as solvent and, unless otherwise denoted, at room temperature

	$\delta^{13}C$ (50.4 MHz)						$\delta^{11}B$	$\delta^{1}H$ (200 MHz)					
	Pyrazole moiety			9-BBN moiety			(64.2 MHz)	Pyrazole moiety			9-BBN moiety		
	C^3 R^3	C^4	C^5 R^5	αC (br,d)	βC (t)	γC (t)		H^3 R^3	H^4	H^5 R^5	αH(br)	βH(γH)	γH
1	130.4(d)	107.6(d)	130.4(d)	22.5	32.3	24.0	18.8	7.52	6.39	7.52	0.95(4H)	1.7-2.0 (m,20H)	1.58 (m,4H)
2	141.0(s) 13.5(q)	109.0(d)	131.1(d)	23.6 22.4	34.3 32.2 31.2 30.8	24.0 23.9 23.1 22.9	21.3 16.2	- 2.39	6.12	7.42	1.07(2H) 0.94(2H)	1.7-2.0 (m,20H)	1.54 (m,4H)
3	146.3	110.2(d)	127.9(d)	23.3 22.8	33.1 33.0 32.3 31.2	24.0 23.8 23.5 23.2	21.6 16.0	- 7.39	6.36	7.70	1.17(2H) 1.09(2H)	1.7-2.0 (m,20H)	1.44 (m,4H)
4	141.8(s) 13.6(q)	111.3(d)	141.8(s) 13.6(q)	23.5	34.2 30.8	24.0 23.0	18.7	- 2.41	6.02	- 2.41	1.1(4H)	1.7-2.1 (m,20H)	1.58 (m,4H)
5	142.4(s) 13.7(q)	111.8(d)	147.7(s) 131.1(s) 129.9(d) 128.7(d) 127.5(d)	26.0 24.1	34.3 33.8 30.9 30.3	24.1 23.8 23.2 22.9	18.8	- 2.42	6.08	- 7.33	1.13(2H) 0.91(2H)	1.3-2.0 (m,20H)	≈1.3 (m,3H) 0.64 (m,1H)
8	144.7 12.2(q)	104.5(d)	133.7	21.2	30.8	23.3	1.2	7.52	5.94	- 2.12	1.6(2H)	1.4-1.9 (m,10H)	1.2 (m,2H)
9	147.9(s) 130.5(s) 128.5(d) 128.2(d) 125.3(d)	101.8(d)	135.1(d)	22.9	31.1	23.8	2.7	7.79	6.50 (13.75, N-H-N)	- 7.68(4H) 7.33(6H)	1.64(2H)	1.8-2.0 (m,10H)	1.51 (m,2H)
10	144.3(s) 12.3(q)	106.1(d)	144.3(s) 12.3(q)	22.6	30.7	23.4	4.6	- 2.30(6H) 2.35(6H)	5.70 5.75(2H)	- 2.30(6H) 2.17(6H)	≈1.7(2H) ≈1.7(2H)	1.6-2.0 (m,10H) 1.5-2.0 (m,10H)	1.36 (m,2H) 1.3 (m,2H)
-80°C													
11	145.9(s) 12.8(q)	103.8(d)	147.2(s) 130.9(s) 128.4(d) 127.9(d) 125.2(d)	23.1	30.9	23.4	6.0	- 2.39(6H)	6.12	- 7.52(4H) 7.21(6H)	≈1.7(2H)	1.7-1.9 (m,10H)	1.36 (m,2H)

85%), corresponding to the molecular formula $C_{19}H_{32}B_2N_2$. The relatively high intensities of the fragement ions assigned to **9H-9-BBN** [m/z = 122 (60%)] and that of **I** [m/z = 216 (100%)] are an indication for the lability of **1**.



Pz:	$R^3 = R^5 = H$	**1**:	$R^3 = R^5 = H$
mPz:	$R^3 = Me$, $R^5 = H$	**2**:	$R^3 = Me$, $R^5 = H$
pPz:	$R^3 = Ph$, $R^5 = H$	**3**:	$R^3 = Ph$, $R^5 = H$
m_2Pz:	$R^3 = R^5 = Me$	**4**:	$R^3 = R^5 = Me$
mpPz:	$R^3 = Me$, $R^5 = Ph$	**5**:	$R^3 = Me$, $R^5 = Ph$
p_2Pz:	$R^3 = R^5 = Ph$	**6**:	$R^3 = R^5 = Ph$

The infrared spectrum of **1**, reveals broad B–H bonds at $\tilde{\nu}$ = 1970 and 1825 cm^{-1}. The single narrow signal in its ^{11}B-NMR spectrum at δ = 18.8 suggests the equivalence of both boron atoms and is significantly shifted to low field compared with simple N-base adducts of **9H-9-BBN**[4]. The symmetrial nature of the bonding of the two 1,5-cyclooctanediylboryl groups with the nitrogen atoms of **Pz** is also evident in the ^{13}C-NMR data (Table 1).

We have determined the crystal structure of **4**, the 3,5-dimethyl derivative of **1**, which like the 3-methyl (**2**), 3-phenyl (**3**), and 3-methyl-5-phenyl (**5**) derivatives (see Table 1) can readily be prepared by the above procedure from the corresponding 3-methyl-, 3-phenyl-, and 3,5-dimethylpyrazoles (**mPz**, **pPz**, **m_2Pz**, and **mpPz**, respectively). The molecular structure of **4** determined by X-ray diffraction is shown in Figure 1, and selected bond lenghts and angles are listed in Table 2.

The molecule of **4** is slightly distorted in the solid state. The hydrogen atom H1, bridging the two boron atoms B1 and B2, appears to have a shorter bond length to B2. This distortion is, however, only minimally extended to other bond lengths and angles around the central N_2B_2H ring. Even though this uneven bonding to the two boron atoms may be the result of disordering of H1 (cf. the very large mean deviations of the bond lengths and angles involving H1, Table 2), it is appealing to regard **4** as a loose association of **9H-9-BBN** and **I** ($R^3 = R^5 = Me$), a notion which is also borne out by the observed MS fragmention pattern

(see above). Intramolecular steric interactions of the methyl groups of the **m_2Pz** moiety with the two 1,5-cyclooctanediylboryl groups [see the very short non-bonded distances (Figure 1, dotted lines) of H4c and H5c with H7b, H9a and H19b, H21a, respectively] and the resulting close approach of the hydrogen atoms (H11a and H13b to H17b and H15b, respectively) of these rings appear to contribute to the weakening of the association of this addition complex.

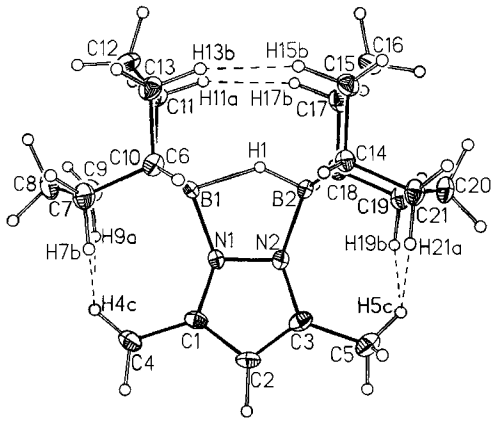


Figure 1. Molecular structure of **4**

Table 2. Selected bond lengths and angles for **4**

Bond lengths (Å)		Bond angles (°)	
B1-H1	1.381(15)	B1H1B2	127.4(16)
B2-H1	1.327(22)	H1B2N2	97.2(8)
B2-N2	1.585(2)	B2N2N1	109.1(1)
N2-N1	1.373(2)	N2N1B1	109.6(1)
N1-B1	1.577(3)	N1B1H1	96.0(10)
B1-C6	1.594(2)	N1B1C6	117.3(1)
B1-C10	1.592(2)	N2B2C14	117.9(1)
B2-C14	1.589(2)	C6B1C10	109.1(2)
B2-C18	1.599(2)	C14B2C18	108.8(1)

It should be expected that these intramolecular steric interactions will render **4** less stable than the unsubstituted derivative **1** and the monosubstituted **2** and **3**. Indeed, the mass spectra of these compounds reflect this tendency: The intensity of the molecular ion peaks decreases progessively from 90 to 25% for **1** and **4**, respectively.

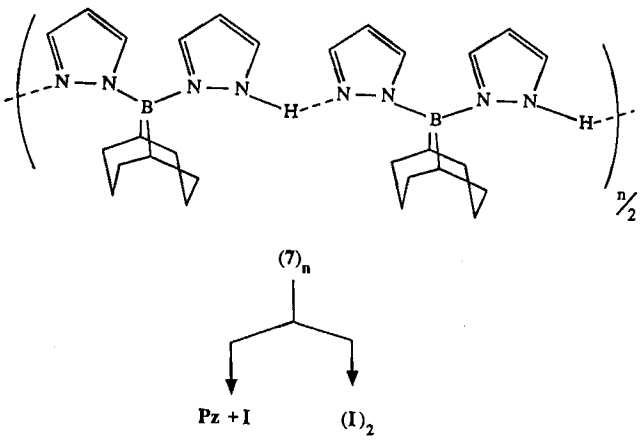
In contrast to the above described cases, 3,5-diphenylpyrazole (**p_2Pz**) reacts with a molar excess of **(9H-9-BBN)$_2$** to give, as indicated by the ^{11}B-NMR signals at δ = 64.0, 27.8, and 18.9, only an equilibrium mixture of the monomeric species **I** (R = Ph)[3], **(9H-9-BBN)$_2$**, and the addition complex **6** in a ratio of about 6:6:1, and the reaction solution of the even more bulky 3,5-di-*tert*-butylpyrazole **[(tb)$_2$Pz]** with excess of **(9H-9-BBN)$_2$** shows only the ^{11}B-NMR resonance signals for the monomeric species **I** (R = *t*Bu) at δ = 63.5 and for the unreacted **(9H-9-BBN)$_2$** at δ = 27.9.

b) Addition Complexes 7–11 of I with Pyrazoles

By reversing the mode of addition of the reagents and by choosing a 1:2 ratio of the reactants, **9H-9-BBN** and the respective pyrazole, a further type of addition complex is formed. Thus, the slow addition of a toluene solution of half an equivalent of **(9H-9-BBN)$_2$** to a toluene solution of two equivalents of **Pz** at 80°C results in the evolution of one equivalent of hydrogen gas. On cooling, from the resulting solution the addition complex **7** separates as colourless microcrystals in >90% yield, m.p. 265–266°C (dec.). The infrared spectrum shows a very broad N–H band centred at $\tilde{\nu}$ = 2700 cm^{-1}. Complex **7** is extremely insoluble in all nonprotic solvents suitable for NMR measurements. Its mass spectrum shows no molecular ion peak corresponding to that of **7**. Instead, analysis of the thermal vaporization curves reveals that at lower temperatures (70–80°C) molecular ion peaks corresponding to those of **Pz** (m/z = 68) and to **I** (m/z = 188) predominate. At higher temperatures the intensity of the molecular ion peak for **Pz** decreases, and at 110°C this peak becomes vanishingly small. The spectrum at this temperature is superimposable with that of the dimer **II** (R^3 = R^5 = H) at the same ion source temperature[3].

These results, together with the observed extreme insolubility and the very high melting/decomposition temperature of **7**, point to a polymeric structure **(7)$_n$** in the solid state from which in the mass spectrometer, as a consequence of gradual thermal decomposition, initially **Pz** and the monomer **I** and at higher temperatures, through reorganization, the dimer **II** separate. These steps, occuring in the mass spectrometer, are shown in the Scheme.

Scheme



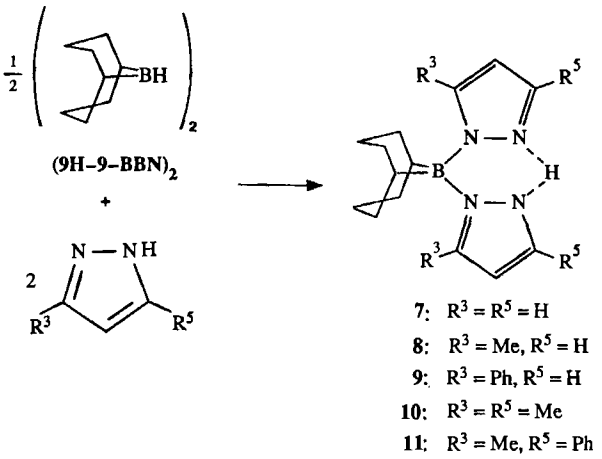
We have been unable to grow suitable crystals of **7** for X-ray study. However, the addition complex **8**, obtained by the reaction of **(9H-9-BBN)$_2$** with **mPz**, has been found to be sufficiently soluble to allow the determination of its structure in solution as well as to grow crystals for X-ray diffraction studies (see below).

In both the ^{1}H- and ^{13}C-NMR spectra of **8** only one set of signals is present for the two **mPz** groups, suggesting the equivalence of these. Similarly, the presence of only one set of signals for the α, β, and γ carbon atoms of the 1,5-C_8H_{14} carbon skeleton indicates the equivalence of both wings of this bicyclic ring. Finally, the ^{11}B chemical shift at δ = 1.2 ($h_{1/2}$ = 340 Hz) implies the existence of a tetravalent boron atom which is in agreement with the structure of **8**.

Table 3. Selected bond lengths and angles for **8**

Bond lengths (Å)		Bond angles (°)	
B-N1	1.567(4)	N1BN3	104.5(2)
B-N3	1.613(3)	C7BC11	106.0(2)
B-C7	1.623(4)	N1BC7	111.4(2)
B-C11	1.605(4)	N3BC7	107.7(2)
N1-N2	1.373(3)	N3BC11	113.1(2)
N3-N4	1.354(3)	N1BC11	114.0(2)
N2-C1	1.347(3)	BN3C6	126.7(2)
N4-C4	1.337(3)	BN1C3	127.7(2)
N1-C3	1.345(3)	BN1N2	123.1(2)
N3-C6	1.334(3)	BN3N4	126.7(2)
C1-C2	1.394(4)	N2N1C3	106.2(2)
C4-C5	1.380(4)	N4N3C6	109.1(2)
C2-C3	1.370(4)	N1N2C1	106.0(2)
C5-C6	1.379(4)	N3N4C4	110.6(2)

Although the NMR data for **8** suggest a simultaneous H bonding between the two nitrogen atoms of the **mPz** units as shown, the nature of the N–H and B–N bonding in solutions of this and other addition complexes must be regarded as a dynamic one as seen in the data of the ^{1}H- and ^{13}C-NMR spectra of the addition complex **10**, obtained from **m_2Pz** and **(9H-9-BBN)$_2$**. In **10** only one signal for the two methyl groups and one signal for both of the C^3 and C^5 carbon atoms of **m_2Pz** are found. The slightly broadened signals for the carbon atoms of the pyrazolyl groups in the ^{13}C-NMR spectrum at room temperature suggest that the interchange of the two nitrogen atoms of each of the two 3,5-dimethylpyrazolyl groups is relatively slow at this temperature. The rate of this exchange process decreases further at lower temperatures, and at −80 °C two signals for two non-equivalent methyl groups are found in the ^{1}H-NMR spectrum (see Table 1).



7: $R^3 = R^5 = H$
8: $R^3 = Me$, $R^5 = H$
9: $R^3 = Ph$, $R^5 = H$
10: $R^3 = R^5 = Me$
11: $R^3 = Me$, $R^5 = Ph$

Structures of the type **7**–**11** have been variously mentioned in the past, but to our knowledge only in one case, that of the parent molecule **III**, has the addition complex

Table 4. Experimental data for the preparation of the addition complexes **1**–**11**, their mass spectra and elemental analyses

No.	Pyrazole g (mmol)	(9-H-9-BBN)$_2$ g (mmol)	Toluene ml	Temp. °C	Yield g (%)	m.p. °C	Mass Spectrum	Elemental Analysis Mol.for. (mol.wt.)	Calcd / Found C	H	B
1	**Pz** 1.10 (16.2)	3.95 (16.2)	25	60	4.5 (90)	138-139	310 (M^+,B_2,90), 199 (B_2,100), 188(18), 187(30)	$C_{19}H_{32}B_2N_2$ (310.1)	73.59 / 73.38	10.40 / 10.58	6.97 / 6.90
2	**mPz** 1.21 (14.7)	3.78 (15.5)	20	60	3.67 (77)	176-177	324 (M^+,B_2,45), 213 (B_2,100), 202(50), 201 (60), 94(60)	$C_{20}H_{34}B_2N_2$ (324.1)	74.11 / 73.93	10.57 / 10.51	6.67 / 6.54
3	**pPz** 0.54 (3.8)	0.92 (3.8)	10	80	1.22 (83)	103-106	386 (M^+,B_2,5), 275 (B_2,15), 264(85), 263 (100), 221(60), 122(25)	$C_{25}H_{36}B_2N_2$ (386.2)	77.75 / 77.56	9.40 / 9.75	5.60 / 5.61
4	**m_2Pz** 0.82 (8.5)	2.09 (8.6)	10	50	2.74 (95)	181-183	338 (M^+, B_2,25), 227(98). 216(100), 215(85)	$C_{21}H_{36}B_2N_2$ (338.2)	74.59 / 74.50	10.73 / 10.87	6.39 / 6.51
5	**mpPz** 0.42 (2.66)	0.65 (2.65)	10	90	0.78 (73)	116-118	400 (M^+, B_2,2), 278 (75), 277(100), 249(38), 235(50), 169(47)	$C_{26}H_{38}B_2N_2$ (400.2)	78.03 / 77.81	9.57 / 9.85	5.40 / 5.62
7	**Pz** 1.45 (21.3)	1.30 (5.3)	20	60	2.60 (96)	265-266	188 (M^+-**Pz**,50), 187(80), 160(58), 159(48), 145(50), 132(55), 81(45), 68(100)	$C_{14}H_{21}BN_4$ (256.2)	65.64 / 65.58	8.26 / 8.32	4.22 / 4.30
8	**mPz** 2.01 (24.5)	1.50 (6.2)	20	60	2.95 (84)	193-195	284 (M^+, B_1,1), 202(65), 201(70), 174(38), 173(40), 82(100)	$C_{16}H_{25}BN_4$ (284.2)	67.62 / 67.55	8.87 / 8.75	3.80 / 3.92
9	**pPz** 1.10 (7.6)	0.466 (1.9)	10	80	1.35 (87)	156-158	264 (M^+-**pPz**,64),263(76), 236(30), 235(35), 221(47), 208(30), 144(100)	$C_{26}H_{29}BN_4$ (408.4)	76.47 / 76.32	7.16 / 7.05	2.65 / 2.81
10	**m_2Pz** 1.94 (20.2)	1.24 (5.1)	40	80	3.04 (95)	107	216 (M^+-**m_2Pz**,46), 215 (40), 188(25), 187(40), 173(40), 160(30), 96(100)	$C_{18}H_{29}BN_4$ (312.2)	69.23 / 69.51	9.36 / 9.21	3.46 / 3.59
11	**mpPz** 2.36 (14.92)	0.87 (3.6)	60	110	2.48 (80)	156-158	278 (M^+-**mpPz**,45), 277 (65), 250(15), 249(25), 235(55), 158(100)	$C_{28}H_{33}BN_4$ (436.4)	77.06 / 76.95	7.62 / 7.62	2.48 / 2.91

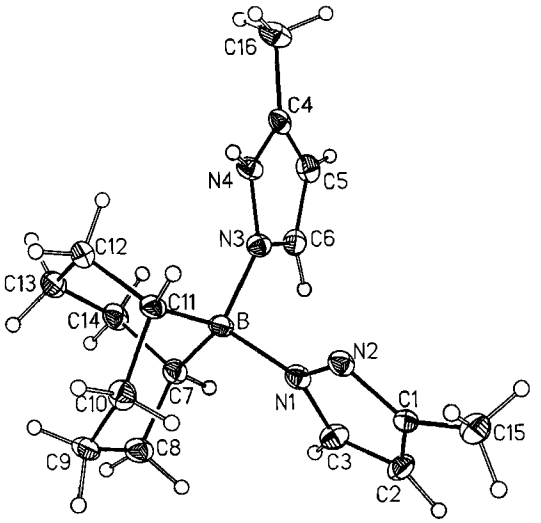


Figure 2. Molecular structure of **8**

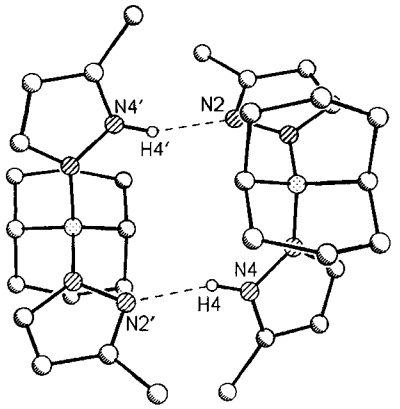


Figure 3. Pairing of molecules in the lattice of **8**

been actually prepared in the form of its tetrahydrate[5]. On the other hand, a large number of the metal bidentate chelates **IV** have been prepared by the action of pyrazoles on e.g. metal boron hydrides[5] or of trialkylboranes on the metal pyrazolides[6,7]. X-ray structure determinations of two transition metal chelates have confirmed the equidistant bonding of the metal to both nitrogen atoms of **IV**[7,8].

We have determined the molecular structure of **8** by X-ray diffraction in order to find out if, in analogy to the bidentate metal chelates, the hydrogen atom is shared between the two pyrazolyl groups. Figure 2 depicts the molecular structure of **8**. It shows, that the two pyrazole rings do not have a planar conformation with respect to each other, rather the planes of the two rings face each other tilting at an angle determined by that of the N1BN3 atoms of 104.3° (interplanar angle between the planes defined by the atoms C7BC11 of the 9-BBN ring and N1N2C2C4C5 of the pyrazole ring at 50.6° and to the second pyrazole ring with the atoms N3N4C4C5C6 at 63.0°).

Selected bond lengths and angles are listed in Table 3. It can be seen that some of the equivalent bond lengths and angles in the two pyrazole rings vary significantly, e.g. the N3N4 bond is shorter by about 0.02 Å than the corresponding N1N2 bond, and similarly the angle between the atoms N3N4C4 is larger than the equivalent angle between the atoms N1N2C1 by about 4.6°. Also, the bond lengths of the two nitrogen atoms N1 and N3 to the boron atom show significant differences, BN1 being shorter by about 0.05 Å. These differences can be attributed to the presence of the acidic hydrogen atom on N4 rendering the two rings non-equivalent.

Another aspect of the structure which is at first sight surprising is the *syn*-arrangement of the methyl substituents. On closer inspection of the molecular packing in the cell, however, it is evident that molecules of **8** appear in pairs. Figure 3 shows one of these pairs in which the two molecules are held together by intramolecular hydrogen bonding between H4 of one molecule and N2′ of its neighbour [d(H4···N2′) = 1.95 Å, cf. Fig. 3]. It is this pairing that forces the *syn*-arrangement of the methyl substituents. A further aspect of the pair is the sterically more favorable *anti*-packing of the two 9-BBN rings.

In solutions of **8** the non-equivalence of the two **mPz** rings is removed, as seen in its NMR spectra, and it can be assumed that at least as one component in an equilibrium mixture of hydrogen-bonded species the intramolecular H-bonded structure is also present.

The addition complexes **9**–**11** with more bulky substituent(s) on the pyrazolyl rings can also be readily obtained by the reaction of **(9H-9-BBN)$_2$** with an excess of **pPz**, **m$_2$Pz**,

Table 5. Crystallographic data for **4** and **8** and data collection procedures

	4	**8**
Formula	$C_{21}H_{36}B_2N_2$	$C_{16}H_{25}BN_4$
Crystal size (mm)	0.28 x 0.25 x 0.10	0.29 x 0.17 x 0.15
Space group	$P\bar{1}$	$P2_1/n$
Z	2	4
a (Å)	9.7634(11)	8.097(2)
b (Å)	10.3355(8)	16.116(4)
c (Å)	10.9660(9)	11.922(4)
α (deg)	78.245(6)	
β (deg)	83.589(8)	96.21(3)
γ (deg)	63.895(7)	
T (K)	120	110
V (Å)	972.45(16)	1546.6(8)
d_{calcd} (g/cm^3)	1.192	1.238
μ (mm^{-1})	0.07	0.07
Radiation	M_o-K_α	M_o-K_α
$2\Theta_{max}$ (deg)	50	45
Total no. of unique reflections	3456	2055
Observed reflections [$F_o \geq 4\sigma(F)$]	2985	1762
R	0.044	0.045
R_w [$w=\sigma^2(F_o+g(F_o^2)$]	0.057	0.047
g	2.4 x 10^{-3}	2.7 x 10^{-4}
Residual electron density (e/Å^3)	0.299	0.204

and **mpPz**, respectively. However, when the pyrazoles **p_2Pz** and **$(tb)_2$Pz** are used only the corresponding monomeric species are obtained. Even in solution no trace of addition complexes has been detected.

The reactions of the donor-acceptor molecules **I** with other Lewis acids and bases are currently being investigated.

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, $(CH_3)_4Si$ as internal and Et_2O-BF_3 as external standards. – Sources of the reagents are cited in ref.[9]. All operations were carried out under oxygen-free dry argon. Solvents were freshly dried and distilled.

General Procuedure for the Preparation of the Addition Complexes **1–6** *of* **I** *and* **9H-9-BBN**: One molar equivalent of **$(9H\text{-}9\text{-}BBN)_2$**, dissolved in toluene, was placed into a three-necked flask equipped with a gas inlet/outlet tube and a dropping funnel. One molar equivalent of the respective pyrazole (**Pz**, **mPz**, **pPz**, **mpPz**, or **m_2Pz**, dissolved in toluene) was added dropwise from the funnel to the stirred solution at 50–80°C. Gas evolution was complete after about 1 h, and the mixture was stirred and heated for a further hour. The product solution was slowly cooled to –60°C. If crystallization did not set in, the solvent was replaced by hexane. Yields and other relevant data are listed in Table 1 and 4.

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors ($Å^2 \times 10^3$) for **4**

	x	y	z	U_{eq}
N(1)	4821(1)	4422(1)	2418(1)	15(1)*
N(2)	4071(1)	5679(1)	2916(1)	16(1)*
B(1)	3623(2)	3947(2)	2034(2)	15(1)*
B(2)	2292(2)	6276(2)	2753(2)	16(1)*
C(1)	6341(2)	3987(2)	2474(1)	18(1)*
C(2)	6545(2)	4976(2)	3016(1)	20(1)*
C(3)	5124(2)	6021(2)	3299(1)	20(1)*
C(4)	7571(2)	2693(2)	1997(2)	25(1)*
C(5)	4807(2)	7250(2)	3965(2)	32(1)*
C(6)	3435(2)	2600(2)	2913(1)	19(1)*
C(7)	4840(2)	1186(2)	2686(2)	28(1)*
C(8)	5159(2)	989(2)	1318(2)	33(1)*
C(9)	4934(2)	2375(2)	359(2)	28(1)*
C(10)	3597(2)	3812(2)	617(1)	18(1)*
C(11)	2039(2)	3888(2)	375(2)	21(1)*
C(12)	1646(2)	2729(2)	1249(2)	25(1)*
C(13)	1923(2)	2596(2)	2630(2)	24(1)*
C(14)	1238(2)	6370(2)	3976(1)	17(1)*
C(15)	-333(2)	6525(2)	3653(2)	23(1)*
C(16)	-1137(2)	7772(2)	2590(2)	26(1)*
C(17)	-84(2)	7856(2)	1451(2)	23(1)*
C(18)	1476(2)	7727(2)	1755(1)	18(1)*
C(19)	1346(2)	9049(2)	2289(2)	22(1)*
C(20)	672(2)	9134(2)	3625(2)	24(1)*
C(21)	1118(2)	7671(2)	4535(2)	22(1)*
H(1)	2350(20)	5198(19)	2236(16)	25(5)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

General Procedure for the Preparation of the Addition Complexes **7–10**: As above, except that a solution of two molar equivalents of the pyrazole was placed into the three-necked flask and a solution of half a molar equivalent of **$(9H\text{-}9\text{-}BBN)_2$** was added dropwise.

X-ray Single-Crystal Structure Determination of **4** *and* **8**: Data collection and calculations were carried out on a Nicolet R 3 mV four-circle diffractometer with Microvax II and SHELXTL-PLUS software[10]. Structural data for **4** and **8** are compiled in Table 5.

Table 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors ($Å^2 \times 10^3$) for **8**

	x	y	z	U_{eq}
B	1263(4)	1414(2)	4392(3)	17(1)*
N(1)	1369(3)	932(1)	3260(2)	17(1)*
N(2)	565(3)	194(1)	3011(2)	17(1)*
N(3)	2593(3)	957(1)	5291(2)	16(1)*
N(4)	2258(3)	519(1)	6208(2)	17(1)*
C(1)	952(3)	-28(2)	1983(2)	18(1)*
C(2)	2004(3)	556(2)	1569(2)	20(1)*
C(3)	2233(3)	1143(2)	2402(2)	20(1)*
C(4)	3665(3)	310(2)	6837(2)	18(1)*
C(5)	4968(3)	616(2)	6304(2)	20(1)*
C(6)	4244(3)	1014(2)	5350(2)	20(1)*
C(7)	1845(3)	2372(2)	4292(2)	19(1)*
C(8)	643(3)	2843(2)	3424(2)	23(1)*
C(9)	-1203(3)	2749(2)	3561(2)	22(1)*
C(10)	-1711(3)	1861(2)	3826(2)	21(1)*
C(11)	-571(3)	1447(2)	4786(2)	18(1)*
C(12)	-589(3)	1911(2)	5915(2)	20(1)*
C(13)	346(3)	2741(2)	6030(2)	22(1)*
C(14)	1958(3)	2776(2)	5466(2)	22(1)*
C(15)	297(3)	-806(2)	1416(2)	24(1)*
C(16)	3656(3)	-141(2)	7926(2)	25(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The structures were determined by direct methods, and all but the boron- or the nitrogen-bound hydrogen atoms were included as rigid groups (C–H bond lengths 0.96 Å, C–C–H and H–C–H angles 109.5 or 120°). The isotropic displacement parameters (IDP's) of all the H atoms were refined without constraints. The boron- or the nitrogen-bound hydrogen atom was located by means of the difference Fourier synthesis and refined without distance constraints. The atom coordinates for compounds **4** and **8** are listed in Tables 6 and 7[11].

CAS Registry Numbers

1: 125878-52-6 / **2**: 125878-53-7 / **3**: 125878-54-8 / **4**: 125878-55-9 / **5**: 125878-56-0 / **6**: 125878-57-1 / 7: 125050-96-6 / **8**: 125878-58-2 / **9**: 125878-59-3 / **10**: 125878-60-6 / **11**: 125878-61-7 / **I** (R = Ph): 125950-19-8 / **I** (R = *t*Bu): 125303-72-2 / **$(9H\text{-}9\text{-}BBN)_2$**: 21205-91-4 / **Pz**: 288-13-1 / **mPz**: 1453-58-3 / **pPz**: 2458-26-6 / **m_2Pz**: 67-51-6 / **mpPz**: 3347-62-4 / **p_2Pz**: 1145-01-3 / **$(tb)_2$Pz**: 1132-14-5

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