Nitrogen Base Adducts of Tetraorganodiboroxanes[1]

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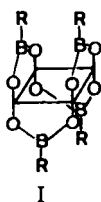
Max-Planck-Institut für Kohlenforschung,
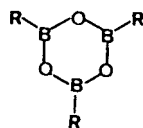Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr

The tetraorganodiboroxanes R_2BOBR_2 [R = C_2H_5 (1); R_2 = 1,5-C_8H_{14} (2)] react with N-bases [pyridine (P); 4-methylpyridine (4-MeP), 4-EtP, 4-*t*BuP, 3,5-Me₂P, DMAP; quinuclidine (Q); 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)] to form stable liquid (N-base-1) and solid (N-base-2) 1:1 adducts (e. g. P-2, Q-2, and DBN-2). In solution, the rates of fluctuation of the N-base between the two boron atoms of the R_2B groups depend on the Lewis acidities of **1** and **2**, the basicities of the bases, as well as the steric factors of the donor-acceptor pairs. At low temperatures (e. g. ≤ −20 °C for P-2 and ≤ −50 °C for P-1), bonding of the base to only one of the boron atoms is indicated. When Q-2 is dissolved in $CDCl_3$ or [D_8]toluene at room temperature it dissociates completly (¹¹B and ¹³C NMR). Below −60 °C interaction between the base and the borane was observed. Low-temperature (−50 °C) ¹¹B-NMR data indicate that in the presence of excess base (Do) a species of the type (Do)₂-1 may be present.

Stickstoffbase-Addukte von Tetraorganodiboroxanen

Tetraorganodiboroxane R_2BOBR_2 [R = C_2H_5 (1); R_2 = 1,5-C_8H_{14} (2)] bilden mit Stickstoffbasen [Pyridin (P); 4-Methylpyridin (4-MeP), 4-EtP, 4-*t*BuP, 3,5-Me₂P, DMAP; Chinuclidin (Q); 1,5-Diazabicyclo[4.3.0]non-5-en (DBN)] stabile, flüssige (N-Base-1) und feste (N-Base-2) 1:1-Additionsverbindungen (z. B. Q-2, DBN-2). In Lösung hängen die Geschwindigkeiten des B,B'-Platzwechsels der N-Base von der Lewis-Acidität von **1** oder **2**, von der Basizität der Stickstoff-Verbindungen sowie von sterischen Einflüssen ab. Bei z. B. ≤ −20 °C für Q-2 oder bei ≤ −50 °C für P-1 ist die Base scheinbar an nur eines der Bor-Atome gebunden. In CDCl₃ oder [D₈]Toluol gelöstes Q-2 ist bei Raumtemperatur vollständig dissoziiert (¹¹B- und ¹³C-NMR). Erst bei < −60 °C sind Base-Boran-Wechselwirkungen nachzuweisen. In Gegenwart von überschüssiger N-Base (Do) liegen ab ca. −50 °C vermutlich Verbindungen vom Typ (Do)₂-1 vor (¹¹B-NMR).
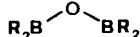
Simple organoboron alkoxy compounds such as diethoxyethylborane, ethyl-1,3,2-dioxaborolane, ethoxydiethylborane, or 9-alkoxy-9-borabicyclo[3.3.1]nonanes do not possess sufficient Lewis acidity to form stable adducts with nitrogen bases. Their ¹¹B-NMR spectra reveal that no significant shifts of their boron resonances are observed on treating these compounds with nitrogen bases[2]. In these compounds efficient π-bond interactions of the oxygen lone pair electrons with the boron vacant orbital apparently decreases their Lewis acidities. By introducing to these organoboron oxygen compounds structural features which either inductively remove electron density from the boron atom, as in the case of the fused tetrakis-1,3,2-dioxaborolane[3] (I), or spread the π-bond interactions of the oxygen lone pair electrons over an additional electron deficient atom, as in the triorganoboroxins (II), or the tetraorganodiboroxanes (III), the effective Lewis acidity increases and addition compounds with appropriate donors can be formed. Crystal structures of both I and II have been determined by X-ray diffraction[2,4].
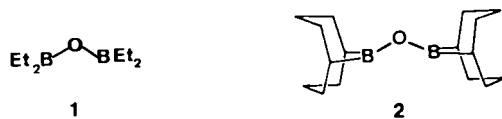
atom, which results in pronounced single bond character of the bonds to the neighbouring two oxygen atoms. These in turn increase their π-bond interactions with the adjoining two boron atoms and thus diminish their Lewis acidity towards additional base molecules. This would explain why hitherto all claims of boroxin adducts with two[5] or even three[6] coordinated N-bases have to be discounted[7].

Tetraorganodiboroxanes are also known to behave as Lewis acids and form 1:1 adducts with Lewis bases[8–10]. But even in the most recent literature the possibility of simultaneous bonding interactions with both of the boron atoms of the diboroxane molecule appear not to have been completly discounted[9,10].

The discovery that bis(1,5-cyclooctanediyl)diborathiane, which is related to **III**, coordinates one base molecule to each of the two boron atoms[11], prompted us to reinvestigate the type of bonding and extent of adduct formation in this class of boron oxygen compounds. Here we report our NMR spectroscopic results on these new adducts.

I   II   III

In the N-base adducts of **II** the nitrogen atom of the base becomes bonded to one of the three boron atoms of the boroxin ring, changes the hybridization around this boron

Results and Discussion

Two tetraalkyldiboroxanes were investigated in this work: tetraethyldiboroxane (**1**) and 1,1:3,3-bis(1,5-cyclooctanediyl)diboroxane (**2**). The adducts were prepared by briefly stirring solutions of **1** or **2** and the appropriate nitrogen base in dichloromethane followed by cooling to −78 °C to affect crystallization. The adducts of **1** are usually liquids at room temperature.

Et_2B—O—BEt_2

1

—B—O—B—

2

The products were investigated by ^{11}B and ^{13}C NMR. The results are presented in Tables 1 and 2, respectively, arranged in order of increasing pK_a values of the N-bases. As can be seen in Table 1 the ^{11}B-NMR signal of the borane at ambient temperature tends to be shifted towards higher field and become broader upon interaction with the nitrogen base. Generally, the position of the new signal is about halfway between the chemical shift of the borane with tricoordinated and that expected for a borane with a tetracoordinated boron atom. The extent of the shift seems to be largely independent of small variations in the basicities of pyridine (**P**) and the pyridine derivatives (cf. Table 1) used (pK_a range of $5.2 - 6.2$[12]) or their concentrations in excess of a 1:1 ratio. This behaviour is similar to the changes observed for the room temperature ^{11}B-chemical shifts of the 1:1 adducts of triorganoboroxins. Only one signal is observed with the chemical shift of a weighted average of one complexed and two uncomplexed boron atoms[2]. This suggests that the base in the tetraorganodiboroxane adducts is involved in a similar exchange process and that the observed chemical shifts are time-averaged. At low temperatures the exchange rate should become slow and two signals, one each for the tri- and for the tetracoordinated boron atom, be present in their ^{11}B-NMR spectra. Thus the ^{11}B-NMR spectra of the 1:1 adducts of the strong bases 4-(dimethylamino)pyridine (**DMAP**, $pK_a = 9.7$[12]) and 1,5-diazabicyclo[4.3.0]non-5-ene (**DBN**, $pK_a = 13.5$[13]) with **2** (**DMAP-2** und **DBN-2**, respectively) show two signals already at room temperature and that of **P-1** on cooling to $-50°C$. This is indicative of the presence of one tri- and one tetracoordinated boron atom (cf. Table 1).

When a large amount of base (**Do**) is present and at low temperature, the ^{11}B-NMR signal is shifted to a higher field. Thus the spectra of mixtures of **1** with a fivefold excess of **P**, 3,5-dimethylpyridine (**3,5-Me$_2$P**), or quinuclidine (**Q**) at $-50°C$ show broad peaks at $\delta^{11}B = 27.0$, 23.9, and 11.2, respectively. These results suggest the formation of a new complex in which two base molecules have become bonded to the two boron atoms of **1**. Such doubly coordinated species (**Do$_2$-1**), being in equilibrium with the monocoordinated molecule, results in a time-averaged ^{11}B-NMR signal, and the progressive high-field shift of the peaks would be a reflection of the increasing concentration of the new species as the strength of the base increases (**P** $<$ **3,5-Me$_2$P** $\ll$ **Q**).
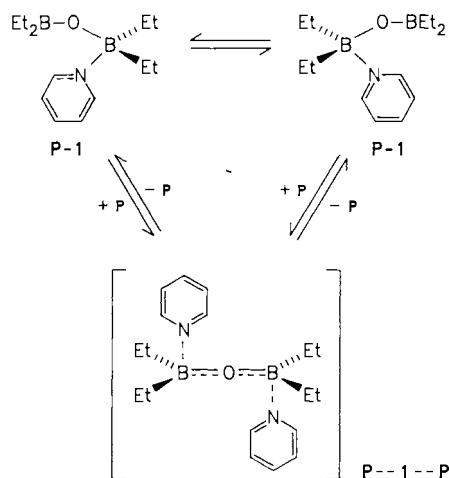
When the even stronger base ($pK_a \approx 13.5$[13]) 1,5-diazabicyclo[4.3.0]non-5-ene (**DBN**) is present in excess and at $-50°C$, the ^{11}B-NMR spectrum showed two very broad peaks of about equal intensities at $\delta^{11}B \approx 40$ and 4.0 indicating mono complexation of **1**.

This unexpected result suggests that in the presence of very strong bases the formation of a strong $B-N$ bond precludes the formation of the species **Do$_2$-1** . This apparent antonymy can be resolved if it is assumed that in the species

Table 1. ^{11}B-NMR chemical shifts of adducts of **1** and **2** with N-bases (r. t. = room temp.)

N-Base	Ratio of N-Base : Diboroxane	Solvent (Temp. °C)	δ ^{11}B [Δv$_{1/2}$[a], Hz], (integral ratio) 1	2
—	—	CDCl$_3$ (r.t.)	55.4 [120]	58.8 [180]
P	1:1	CDCl$_3$ (r.t.)	30.4 [300]	32.5 [500]
	5:1	CDCl$_3$ (r.t.)	29.1 [360]	30.3 [520]
	1:1	d$_8$-THF (-20)	30.0 [900]	50 [1000], 5.6 [500] (1:1)
	1:1	d$_8$-THF (-50)	-45 [3000], 6.8 [2200](1:1)	—
	5:1	d$_8$-THF -50	27.2 [1900]	—
4-MeP	1:1	CDCl$_3$ (r.t.)	31.0 [300]	30.3 [980]
	5:1	CDCl$_3$ (r.t.)	29.0 [400]	30.1 [750]
	5:1	Hexane (-50)	27.0 [1200]	—
4-EtP	1:1	CDCl$_3$ (r.t.)	30.0 [340]	—
4-t-BuP	1:1	CDCl$_3$ (r.t.)	32.1 [360]	31.9 [600]
3,5-Me$_2$P	1:1	CDCl$_3$ (r.t.)	29.9 [400]	30.6 [900]
	5:1	CDCl$_3$ (r.t.)	28.8 [500]	—
	5:1	Hexane (-50)	23.9 [1100]	—
DMAP	1:1	CDCl$_3$ (r.t.)	30.5	—
	1:1	CD$_2$Cl$_2$ (r.t.)	—	52.5 [450], 4.70 [330] (1:1)
Q	1:1	CDCl$_3$ (r.t.)	38.7 [110]	57.6 [180]
	5:1	CDCl$_3$ (r.t.)	28.9 [360]	—
	5:1	CDCl$_3$ (-50)	11.2 [3900]	—
	1:1	d$_8$-THF (r.t.)	—	42.6 [360]
2DBN	1:1	Hexane (r.t.)	27.5 [400]	—
	1:1	THF (r.t.)	—	50.9 [360], 4.0 [160] (1:1)
	1:1	THF (-20)	-53 [1700], 6.0 [770] (1:1)	—
	1:5	Hexane (-50)	-40 [2500], 4.0 [1900](1:1)	—

[a] $\Delta v_{1/2}$ = peak width at half hight.

Do$_2$-1 the bonds of the moderately strong base molecules to both of the boron atoms, as a result of very fast exchange between an incoming and a leaving base molecule, are incompletely developed[14]. These equilibria are shown in Scheme 1.

At room temperature both the ^{11}B- and the ^{13}C-NMR spectra of **DMAP-2** and **DBN-2** appear anomalous. Thus, the ^{11}B-NMR spectra show two peaks assignable to a tri- and a tetracoordinated boron atom, while **DMAP-1** and **DBN-1** as well as all other adducts show only a single time-averaged signal. In the ^{13}C-NMR spectra of **DMAP-2** and **DBN-2** the peaks for the β and γ carbon atoms are broad, indicating coalescence of two sets of nonequivalent carbon atoms, while in all other adducts of **2** these signals, due to rapid exchange, are sharp. These results show that the rate of exchange of the N-base between the two boron atoms of
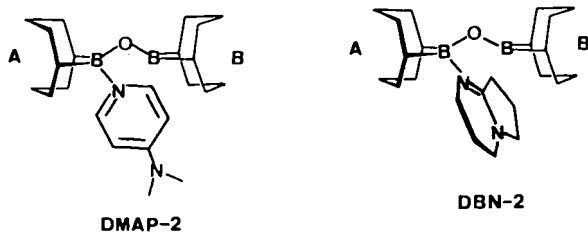
Scheme 1

Table 2. ^{13}C-NMR chemical shifts (ppm) (1 and 2 moieties) of the adducts with N-bases

N–Base	Solvent	Temp. [°C]	1 α-C (br,t)	β-C (q)	2 α-C (br,d)	β-C (t)	γ-C (t)
–	[D$_8$]THF	30	–	–	25.3	34.2	24.0
–	CDCl$_3$	30	15.3	8.7	27.6	33.1	22.84
P	CDCl$_3$	30	15.2	8.2	25.9	32.3	23.4
4-MeP	CDCl$_3$	30	15.0	8.2	25.9	32.3	23.5
4-EtP	CDCl$_3$	30	15.0	8.3	–	–	–
4-t-BuP	CDCl$_3$	30	14.9	8.2	26.2	32.2	23.4
3,5-Me$_2$P	CDCl$_3$	30	14.8	8.3	26.0	32.2	23.5
DMAP	CDCl$_3$	30	14.9	8.4	26.8	33.1 (br)	25.2 (br)
Q	CDCl$_3$	30	13.2	8.5	27.6	33.1	22.8
	[D$_8$]THF	30	–	–	27.3	34.3	24.3
DBN	CDCl$_3$	30	14.0	8.8	26.0	32.7 (br)	23.6 (br)
	[D$_8$]Toluene	30	–	–	27.2	34.1 (br)	24.7 (br)

the tetraorganodiboroxanes is strongly dependent on the attractive forces of the donor-acceptor pair and imply that 2 is a stronger Lewis acid than 1.

The B — N bond strengths also affect the coalescence temperatures of the NMR spectra. Thus for P-1 a two-peak ^{11}B-NMR spectrum indicating a "frozen" adduct is first obtained at − 50°C while a corresponding spectrum for P-2 is already obtained at − 20°C. Similarly, in the ^{13}C-NMR spectrum of P-2 coalescence of the carbon chemical shifts of the 2 moiety are first observed at about − 40°C, while the stronger bases DMAP and DBN bring about coalescence of the corresponding signals of 2 already at room temperature.

Below the coalescence temperatures the ^{13}C-NMR spectra are resolved, and sharp peaks are obtained. For P-2 the spectrum shows eight signals for the 2 moiety. These can be assigned to the carbon atoms of ring A and those of ring B, as listed in Table 3. It can also be seen that the β and the γ carbon atoms of ring A are separated into those on the same and those on the opposite sides of the coordinating base. The corresponding carbon atoms of ring B do not show this differentiation as this ring apparently continues its free rotation about the B — O bond.

For DBN-2 the ^{13}C-NMR spectrum is even more complex. It shows a total of twelve peaks. This is brought about by the conformation (probably perpendicular to the B — O − B plane) of the nonsymmetrical base DBN resulting in the separation of each of the eight carbon atoms of ring A and the β-carbon atoms of the freely rotating ring B.

DMAP-2   DBN-2

In contrast to the N-bases so far discussed, solutions of the strong N-bases triethylamine, tetramethylethylenediamine or Q (pK_a = 10.8, 9.0, and 10.95, respectively[13]) show

no or only minimal interaction in solution with the boron atoms of the tetraorganodiboroxanes 1 or 2. Thus a 1:1 mixture of Q with 1 results in a shift of the ^{11}B-NMR signal from δ = 58 to only 39 and without an increase of the line width. Only when a fivefold excess of the amine is added, the ^{11}B-NMR signal shifts to 28.9 ppm and becomes broad.

Surprisingly, while a solution of a 1:1 mixture of Q and 2 shows no shift of the boron signal and even at − 50°C its

Table 3. Low-temperature ^{13}C-NMR chemical shifts (ppm) of the 2 moieties of DBN-2, Q-2, and P-2

Adduct	Solvent	Temp. [°C]	Ring A α-C (br,d)	β-C (t)	γ-C (t)	Ring B α-C (br,d)	β-C (t)	γ-C (t)
P-2[a]	CD$_2$Cl$_2$	−60	24.5	31.8 / 30.6	24.4 / 24.3	26.0	32.5	22.8
DBN-2[b]	[D$_8$]Toluene	−50	26.5 / 25.5	35.4 / 32.8 / 32.4 / 32.2	25.8 / 25.6	27.5	34.5 / 34.3	24.6
Q-2[a,c]	[D$_8$]THF	−60	26.6	34.2	24.3	27.7	34.5	24.3
Q-2[a]	[D$_8$]THF	−115	23.4 / 32.3	36.2 / 32.3	25.4 / 24.3	28.2	34.3	30.0

[a] Measured at 75.47 MHz. — [b] Measured at 50.32 MHz. — [c] All peaks were broad.

^{13}C-NMR spectrum has the carbon chemical shifts of the individual components, on further cooling to $-80\,°$C it forms the relatively stable crystalline 1:1 adduct **Q-2** (m. p. $123-125\,°$C). The existence of an interaction between **Q** and **2** and thus the formation of an adduct of the type **Q-2** is not only indicated by the ready formation of a crystalline 1:1 complex, but is also evident in the ^{13}C-NMR spectra obtained at even lower temperatures. Thus at $-60\,°$C, peaks due to the α carbon atoms of the **2** moiety appear at $\delta = 26.6$ and 27.7, for the β carbon atoms at 34.2 and 34.5 and for the γ carbon atoms at $\delta = 24.3$. All of these peaks are very broad. Sharp peaks are observed for the α, β, and γ carbon atoms of the **Q** moiety at $\delta = 48.8$, 25.2, and 21.1, respectively. At this temperature, the peak shapes and the values of the chemical shifts indicate that the commencement of interaction between **Q** and **2** is simultaneous with the tendency for the base to come to rest on one of the boron atoms of **2**. Nevertheless, fluctuation of **Q** between the two boron atoms and tumbling of the $C_8H_{14}B$ rings of **2** continue at a slow rate. At $-80\,°$C the peaks for the **2** moiety are relatively sharp and could be interpreted to indicate coordination of the amine to one of the boron atoms of the diboroxane moiety similar to that found in **DBN-2**, i. e., the carbon atoms of the tetra- and tricoordinated rings A and B can be clearly distinguished. Thus, the α carbon atoms of the A and B rings appear at $\delta = 23.6$ and 28.2, respectively. A dissymmetry in ring A also results as seen by the presence of two signals at $\delta = 36.1$ and 32.2 for the four β carbon atoms, as well as two signals at $\delta = 25.4$ and 24.3 for the two γ carbon atoms of this ring. The signals for the **Q** moiety are unusual: While the peak for the γ carbon atom at $\delta =$ 21.1 is sharp, that of the β carbon atoms at $\delta = 24.9$ is broadened, and for the α carbon atoms two peaks at $\delta = 47.3$ and 49.1 (integral ratio 1:3) are observed which are likewise broad. These results can be interpreted to indicate a restricted rotation of the boron-bonded **Q** within the engulfing environment of **2** and the existence of a preferred conformation in which one α carbon atom appears to be in a different surrounding than the other two. At $-115\,°$C, while other parts of the spectrum remain virtually unchanged, the two peaks assignable to the α carbon atoms of **Q** are shifted to $\delta = 47.9$ and 51.3 and their integral ratio is reversed to 2:1. This indicates the development of a new low-energy conformation of **Q** within the surroundings of **2**.

A possible pathway for these transformations is depicted in the reaction coordinate diagram of Figure 1 whereby the contours of the maxima and minima are arbitrary and are made to fit the temperatures at which spectra were obtained.

The results presented above clearly demonstrate that in solution, at room temperature, and when the coordinating N-base is of moderate basicity, the base rapidly fluctuates between the boron atoms of the tetraorganodiboroxane. At room temperature, even in the presence of a large excess of base, only one base undergoes complexation. However, at low temperatures coordination of both boron atoms by base molecules is indicated. As the basicity of the N-base is increased, simultaneous with the choice of **2** which seems to have a larger Lewis acidity than **1**, the base appears to come to rest on one of the boron atoms of the acceptor diboroxane. In the case of the strong, yet apparently sterically disadvantageous, base **Q** both the ^{11}B- and ^{13}C-NMR spectra
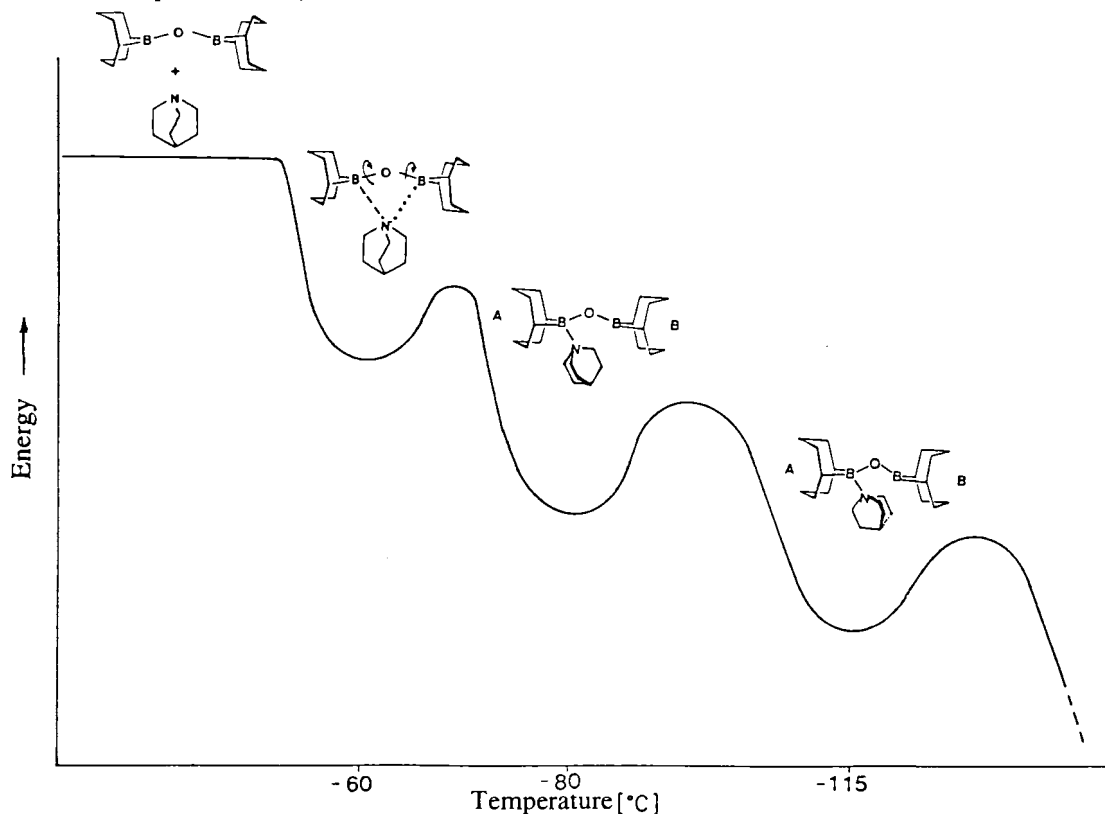

Figure 1. Reaction coordinate showing the temperature-dependent interactions between **Q** and **2**

gave no evidence of any interactions at ordinary temperatures. Only at very low temperatures could significant coordination be demonstrated. Yet the pair **Q** and **2** form a stable crystalline lattice as seen in the relatively high melting point of 123−125°C. We therefore investigated the molecular and lattice structure of **Q-2** and for comparison also that of **P-2**. The discussion of these and of their unusual premelting phase transformations will be the subject of the following publication[15].

We are grateful to Dr. *R. Mynott* for the variable-temperature ^{13}C-NMR spectra and for the very valuable discussions.

Experimental

All reactions were carried out under dry oxygen-free argon. All solvents were freshly distilled under argon from appropriate drying agents. − ^{13}C- and ^{11}B-NMR spectra: Bruker (AC 200) and (WM 300) spectrometer. Chemical shifts are given in ppm relative to internal Me$_4$Si or relative to the solvent chemical shift for ^{13}C and from external Et$_2$O−BF$_3$ for ^{11}B shifts. − DSC measurements: DuPont 1090 instrument.

Preparation of the Adducts (General Procedure): Equimolar quantities (1−2 g) of **1**[16] or **2**[17] and the N-base (cf. Tables 1 and 2) in 10−20 ml of the appropriate solvent (toluene or CH$_2$Cl$_2$) were briefly mixed. In the case of the solid adducts (those of **2**) the solution was slowly cooled to −60°C and the resulting crystalline solid collected. Generally, a nearly quantitative yield of product was obtained. In the case of the liquid adducts (those of **1**) the product was isolated as residue after vacuum removal of the solvent. The procedures given below for **P-2** and **Q-2** illustrate this method.

Pyridine-Bis(1,5-cyclooctanediyl)diboroxane (**P-2**): 2.6 g (10.0 mmol) of **2** and 0.79 g (10.0 mmol) of **P** in 6 ml of CH$_2$Cl$_2$ were briefly mixed. After cooling to −78°C the crystals obtained were recrystallized from CH$_2$Cl$_2$ by slow cooling to −60°C to give colourless prisms of **P-2** (3.1 g, 92%), m. p. 138−139°C. − ^{1}H-NMR (CDCl$_3$), **P** moiety: δ = 8.72 (dd, 2H); 7.95 (dt, 1H); 7.51 (dt, 2H); **2** moiety: δ = 1.59 (m, 20H); 1.22 (m, 4H); 1.0 (br, 4H). − ^{11}B-NMR: cf. Table 1. − ^{13}C-NMR (CDCl$_3$), **P** moiety (−60°C): δ = 145.7 (d); 139.6 (d); 124.8 (d); **2** moiety: cf. Tables 2 and 3. − ^{17}O-NMR (CDCl$_3$): δ = 164 ($h_{1/2}$ = 400 Hz) and 123 (trace).

C$_{21}$H$_{33}$B$_2$NO (337.1)   Calcd. C 74.82 H 9.87 B 6.41
                                  Found C 74.95 H 9.80 B 6.52

Quinuclidine-Bis(1,5-cyclooctanediyl)diboroxane (**Q-2**): 3.35 g (13.0 mmol) of **2** and 1.45 g (13.0 mmol) of **Q** in 14 ml of toluene were stirred for 15 min and then cooled to −78°C. The crystalline solid obtained was recrystallized from toluene by slow cooling to −78°C to give colourless prisms of **Q-2** (4.3 g, 90%), m. p. 132−133°C. − DSC: 126−129°C. − ^{1}H-NMR (CDCl$_3$), **Q** moi-

ety: δ = 2.80 (m, 6H); 1.70 (s, 1H); 1.49 (m, 6H); **2** moiety: δ = 1.76 (m, 20H); 1.33 (m, 4H); 1.09 (br, 4H). − ^{11}B-NMR: cf. Table 1. − ^{13}C-NMR (CDCl$_3$), **Q** moiety (−60°C): δ = 48.8 (t); 25.2 (t); 21.1 (d); (−80°C): 47.3 (br), 49.1 (br); 24.9; 21.1; (−115°C): 47.9 (br), 51.3 (v br); 24.8; 21.1; **2** moiety: cf. Tables 2 and 3. − ^{17}O-NMR (CDCl$_3$): δ = 189 ($h_{1/2}$ = 400 Hz) and 153 (trace).

C$_{23}$H$_{41}$B$_2$NO (369.2)   Calcd. C 74.82 H 11.19 B 5.85
                                  Found C 74.72 H 11.28 B 5.62

CAS Registry Numbers

1: 7318-84-5 / **4-*t*-BuP-1**: 117497-79-7 / **DBN-1**: 117497-83-3 / **DMAP-1**: 117497-81-1 / **4-EtP-1**: 117497-78-6 / **4-MeP-1**: 117497-77-5 / **3,5-Me$_2$P-1**: 117497-80-0 / **P-1**: 117497-76-4 / **Q-1**: 117497-82-2 / **2**: 74744-62-0 / **4-*t*-BuP-2**: 117497-85-5 / **DBN-2**: 117497-88-8 / **DMAP-2**: 117497-87-7 / **4-MeP-2**: 117497-84-4 / **3,5-Me$_2$P-2**: 117497-86-6 / **P-2**: 116972-69-1 / **Q-2**: 116996-19-1 / **4-*t*BuP**: 3978-81-2 / **DBN**: 3001-72-7 / **DMAP**: 1122-58-3 / **4-EtP**: 536-75-4 / **4-MeP**: 108-89-4 / **3,5-Me$_2$P**: 591-22-0 / **P**: 110-86-1 / **Q**: 100-76-5

[1] [1a] Part 84 of Boron Compounds; Part 83: R. Köster, G. Seidel, G. Müller, R. Boese, B. Wrackmeyer, *Chem. Ber.* **21** (1988) 1381. − [1b] Preliminary experiments on this work were carried out by R. Köster and J. Serwatowski in 1982−84, cf. ref.[1c] and [1d]. − [1c] R. Köster, Lewisbase-Organodiboroxane, in *Methoden der Organischen Chemie* (Houben-Weyl-Müller), 4th ed., vol. XIII/3b (R. Köster, Ed.), p. 621, Thieme, Stuttgart 1983. − [1d] B. Wrackmeyer, R. Köster, Analytik der Organobor-Verbindungen, in *Methoden der Organischen Chemie* (Houben-Weyl-Müller), 4th ed., vol. XIII/3c (R. Köster, Ed.), p. 537, Thieme, Stuttgart 1984.
[2] M. Yalpani, R. Boese, *Chem. Ber.* **116** (1983) 3347.
[3] M. Yalpani, R. Köster, G. Wilke, *Chem. Ber.* **116** (1983) 1336.
[4] C. Krüger, Y. H. Tsay, unpublished result (1982).
[5] J. Bielawski, K. Niedenzu, *Inorg. Chem.* **25** (1986) 1771.
[6] W. L. Fielder, M. M. Chamberlain, C. H. Brown, *J. Org. Chem.* **26** (1961) 2154.
[7] M. Yalpani, R. Köster, *Chem. Ber.* **121** (1988) 1553.
[8] G. F. Lanthier, W. A. G. Graham, *Can. J. Chem.* **47** (1968) 569.
[9] J. D. Odom, A. J. Zozulin, S. A. Johnston, J. R. Durig, S. Riethmüller, E. J. Stampf, *J. Organomet. Chem.* **201** (1980) 351.
[10] H. E. Katz, *J. Org. Chem.* **50** (1985) 2575.
[11] R. Köster, G. Seidel, *Z. Naturforsch., Teil B*, **43** (1988) 687.
[12] D. D. Perin, *Dissociation Constants of Organic Bases in Aqueous Solutions*, Butterworth, London 1965.
[13] D. H. R. Barton, J. D. Elliot, S. D. Gero, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2085.
[14] The existence of adducts with large temperature-dependent variation in their B−N bond lengths are also observed in the solid state and are discussed in the following publication[15].
[15] M. Yalpani, R. Köster, R. Boese, M. Sulkowski, *Chem. Ber.* **122** (1989) 9, following paper.
[16] R. Köster, Tetraorganodiboroxane, in *Methoden der Organischen Chemie* (Houben-Weyl-Müller), 4th ed., vol. XIII/3a (R. Köster, Ed.), p. 814, Thieme, Stuttgart 1982.
[17] R. Köster, W. Schüßler, G. Seidel, *Organometallic Synth.* **4** (1988) 460; see also ref.[16], p. 816.

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