Nitrogen Base – Dialkyl-1,2,4,3,5-triselenadiborolanes[1)]

Mohamed Yalpani[a]*, Roland Boese[b], and Roland Köster[a]

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

Institut für Anorganische Chemie der Universität Essen[b],
Universitätsstraße 5–7, D-4300 Essen

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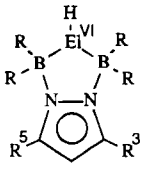
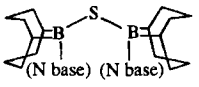
Stickstoffbase–Dialkyl-1,2,4,3,5-triselenadiborolane[1)]

3,5-Dialkyl-1,2,4,3,5-triselenadiborolane $RBSe_3BR$ (**1**) [R = C_2H_5 (**1a**) und R = C_3H_7 (**1b**)] bilden bei Raumtemperatur mit überschüssigen N-Basen [Pyridin (**P**), 3,5-Dimethylpyridin ($\mathbf{m_2P}$), 3-Chlorpyridin (**cP**) und Chinuclidin (**Q**)] stabile 2:1-Additionsverbindungen [$\mathbf{P_2}$-**1a, b**, ($\mathbf{m_2P})_2$-**1a**, **cP-1a**, $\mathbf{Q_2}$-**1a, b**]. In Lösung existieren Gemische von (*syn*/*anti*)$\mathbf{Q_2}$-**1a** (^{1}H-, ^{11}B-NMR). (*syn*)$\mathbf{Q_2}$-**1a** steht bei −80°C mit **Q-1a** und **Q** im Gleichgewicht. Festes $\mathbf{Q_2}$-**1a** liegt als (*anti*)$\mathbf{Q_2}$-**1a** vor (Kristallstrukturanalyse). In Lösung bilden **1** bei Raumtemperatur mit äquimolaren Mengen an N-Basen die 1:1-Addukte [**(N-Base)-1**], in denen nur ein Bor-Atom vierfach koordiniert ist. 1:1-Addukte mit fluktuierender N-Base zwischen den beiden Bor-Atomen werden bei Temperatursteigerung beobachtet (120°C: ^{11}B-NMR). Hexamethylentetramin (**Ur**) bildet stabile, feste 1:1- und 2:1-Addukte (**Ur-1a**, $\mathbf{Ur_2}$-**1a**).

Previously, we have reported on the reactions of a number of N-bases with triorganoboroxins[2)] and bis(diorganoboryl) oxides[3,4)]. In all cases we could conclusively show (NMR, X-ray) that only one of the boron atoms of these >B–O–B< compounds becomes coordinated by the N-base. Using the dibasic pyrazoles we found that as a result of simultaneous bidental coordination of both nitrogen atoms to the two boron atoms of bis(1,5-cyclooctanediylboryl) oxide, sulfide, and selenide the novel stable $B_2El^{VI}N_2$ heterocycles **I** are formed[5,6)]. Bis(9-borabicyclo[3.3.1]nonyl) sulfide was also found to readily react with pyridine bases to form the adducts **II**, in which both boron atoms are coordinated[7,8)].



I

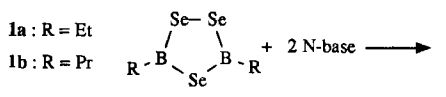


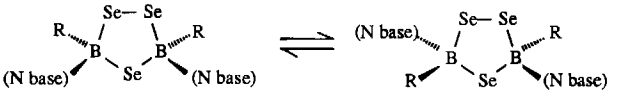
II

We now have extended our studies to the investigation of the adduct forming potentials of 3,5-dialkyl-1,2,4,3,5-triselenadiborolanes[9)] (**1**), which have both the BSeB and the BSe_2B groups, and the boron atoms of which can a priori be thought to have an analogous coordination tendency as in the triorganoboroxins. In this report we show that **1** readily forms doubly N-base-coordinated adducts, and that when the N-base and the $R_2B_2Se_3$ Lewis acid **1** are mixed in a 1:1 ratio only one of the boron atoms becomes coordinated by the N-base without undergoing fluctuation at room temperature.

Results and Discussion

3,5-Dialkyl-1,2,4,3,5-triselenadiborolanes (alkyl = ethyl: **1a**; propyl: **1b**) were prepared by treating a toluene solution of the corresponding tetraalkyldiborane(6) with elemental selenium at reflux[9)]. They could be easily purified by high vacuum distillation to give yellow liquids with disagreeable odour. Reaction of toluene solutions of **1a** or **1b** with excess of an N-base [pyridine (**P**), 3,5-dimethylpyridine ($\mathbf{m_2P}$), 3-chloropyridine (**cP**), quinuclidine (**Q**), and hexamethylenetetramine (**Ur**)] was generally instantaneous as seen by an immidiate change of colour of the solution from yellow to orange or to orange-red, accompanied by heat generation. In some cases the crystalline product separated directly from the reaction mixture. In other cases the solution had to be cooled to −60°C to affect crystallization. Elemental analyses of the crystalline materials isolated showed the ratio of N-base to the triselenadiborolane **1** to be 2:1.





syn anti

Generally the mass spectra of these 2:1 adducts show only the spectra of the individual components. The ^{13}C-NMR spectra are also uninformative, showing only minor shifts

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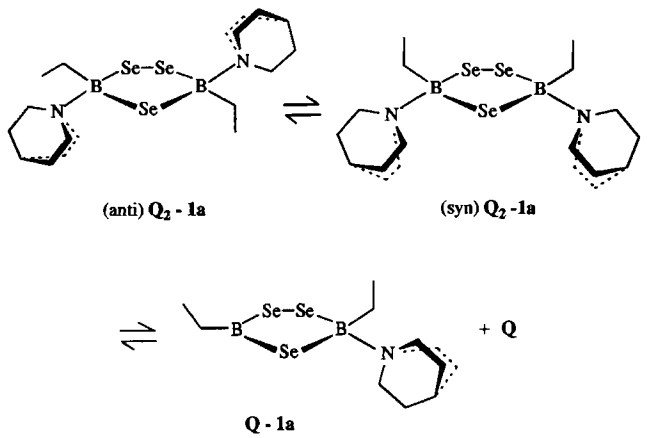
when compared to the ^{13}C resonances of the individual components (see Table 1). Only the adducts with the strong base **Q** show major shifts of the signals of the carbon atoms of the alkyl substituents of **1a** or **1b**. A greater indication for interaction of the N-base with **1** may be obtained from the ^1H-NMR spectra of 2:1 adducts. In these, the association of the N-base with the boron atom reveals itself in an upfield shift and generally the typical separation of the proton signals into a quadruplet for the boron-bonded CH_2 and a triplet for the CH_3 groups. Unlike the case of the amine adducts of trialkylboroxins[2], the extent of these chemical shift separations does not give an indication of the differential strength of the N-base. In the ^1H-NMR spectra of both $\mathbf{Q_2}$-**1a** and $\mathbf{Q_2}$-**1b** the resonance signals for the corresponding α-methylene protons of the **Q** moieties at $\delta = 3.39$ and 3.48 are unusually broad. Furthermore, the signals for the $B-CH_2$ groups appear as two multiplets at $\delta = 0.86/0.70$ (see Figure 1a) and 0.74/0.68, respectively. The shape of these multiplets suggests the existence of a 1:1 equilibrium mixture of species with *syn* and *anti* arrangement of substituents on the respective two boron atoms of $\mathbf{Q_2}$-**1a** and $\mathbf{Q_2}$-**1b**.



We have investigated the behaviour of $\mathbf{Q_2}$-**1a** in solution at various temperatures by ^1H- and ^{11}B-NMR techniques. At +100°C the ^1H-NMR ([D_8]toluene) signals for the α-methylene protons of the **Q** moiety sharpen and appear in the usual multiplet shape. The $B-CH_2$ groups form a single well resolved quartet. At −30°C the overall shape of the $B-CH_2$ signals remain similar to the room temperature spectrum. However, the signal for the α-methylene protons of the **Q** moieties is broadened, ranging from $\delta = 2.8$ to 4.2 with protrusions centred at about $\delta = 3.0$ and 3.5. Additionally a multiplet peak, characteristic for the α-methylene protons of free **Q**, appears at $\delta = 3.36$. The complex ^1H-NMR spectrum of $\mathbf{Q_2}$-**1a** at −80°C is shown in Figure 1b and compared to that obtained at room temperature (Figure 1a). The resonance signals (designated by **Q** in Figure 1b) of unbound **Q** are readily identifiable and comprise about 20% of total **Q** in solution. Since the integral ratio of the peaks for total **Q** to the peaks for the *B*-ethyl groups continues to be 2:1, it is inferred that from about 50% of $\mathbf{Q_2}$-**1a** one **Q** molecule is dissociated. Indications for this process was evident in the ^1H-NMR spectrum at −30°C (see above) and also from the ^{11}B-NMR spectrum obtained at −30°C. In this a peak appears at $\delta^{11}B = 78.6$ ($h_{1/2} = 580$ Hz) [not identical to the ^{11}B resonance signal for **1a** (79.4, $h_{1/2} = 150$ Hz)] in addition to one at $\delta^{11}B = 16.8$ ($h_{1/2} = 200$ Hz) for the tetravalent boron atom in a 1:6 ratio.

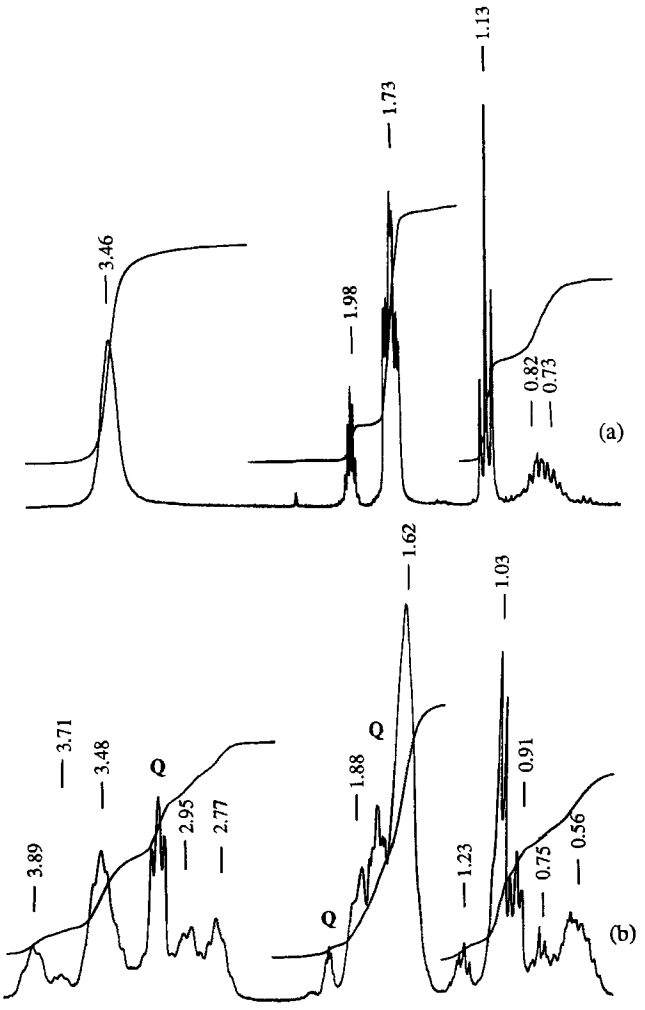


Figure 1. 200-MHz ^1H-NMR spectrum (CD_2Cl_2) of $\mathbf{Q_2}$-**1a**. a) at room temperature; b) at −80°C

The main part of the spectrum shown in Figure 1b can be interpreted by assuming an equilibrium established between the syn/anti configurated $\mathbf{Q_2}$-**1a** species, the mono N-base-**1** adduct (**Q**-**1a**) and free **Q**. Assuming a preferred conformation of **Q** about the N–B bond in the two $\mathbf{Q_2}$-**1** geometric isomers, the multiplet at $\delta^1H = 3.89$ and parts of the multiplets at $\delta = 3.48$ and 2.95 together with the triplet at $\delta = 1.03$ and the multiplet centred at about 0.56 can be assigned to one isomer in about 50% concentration. Part of the ^1H-NMR signals at $\delta = 3.48$, 2.95, 1.03, 0.91, and 0.56 in addition to the peaks at $\delta = 2.77$, 1.23 arise from a **Q**-**1a** species (see also Figure 2b and discussion below). Finally, the small multiplet at $\delta^1H = 3.71$ points also to the possible involvement of another isomer of $\mathbf{Q_2}$-**1a**. Based on spacial consideration and information of the structure of (*anti*)$\mathbf{Q_2}$-**1a** in the solid state (see below), we assign to the major component the *anti* configuration. Consequently, the driving force for the dissociation of the *syn* isomer into **Q**-**1a** and **Q** would be the unfavourable steric interactions between the two neighbouring **Q** moieties in (*syn*)$\mathbf{Q_2}$-**1a**.

In contrast to the relative indifference of the room temperature ^1H- and ^{13}C-NMR chemical shifts to the presence of the N-bases, the ^{11}B-NMR spectra show large shifts and also some sensibility to base strengths as well as to the substituents on the Lewis acid boron atoms. Thus, for the dipyridine adduct $\mathbf{P_2}$-**1a** the ^{11}B-NMR signal (see Table 1)

Table 1. NMR data for 2:1 and 1:1 N-base adducts of **1a** and **1b**. All NMR measurements at room temperature were carried out in $CDCl_3$. The two ^{11}B-NMR measurements at 120°C were obtained in toluene in sealed tubes

	δ^1H (200 MHz)			$\delta^{11}B$	$\delta^{13}C$ (50.4 MHz)			
Compound	1 moiety		N-base moiety	(64.2MHz)	1 moiety		N-base moiety	
1a	1.65(q)	1.26(t)	–	79.1	18.4	13.2	–	
P_2-1a	1.20(q)	0.78(t)	9.52(d), 7.89(tt), 7.45(tt)	12.8	19.0	12.8	145.8(d), 139.8(d), 124.3(d)	
P-1a	1.99(q)	1.08(t)	9.10(br), 6.92(tt), 6.56(tt)	14.5/75.7	19.9	13.7	146.1(d), 140.1(d), 124.7(d)	
P-1a (120°C)		n.m.		47.0		n.m.		
(m_2P)$_2$-1a	1.24(q)	0.89(t)	9.10(s), 7.5(s), 2.35(s)	11.9	18.9	12.8	143.2(d), 140.9(s), 133.8(d)	
(cP)$_2$-1a	1.20(q)	0.88(t)	9.43(d), 9.27(d), 7.82(dt) 7.42(dd)	15.9	18.2	12.8	145.6(d), 144.2(d), 139.1(d), 132.5(s), 124.7(d)	
cP-1a	1.40(q)	1.00(t)	9.20(br), 9.10(d), 7.82(d), 7.58(dd)	15.0/78.0	18.3	12.8	145.0(d), 144.0(d), 140.9(d), 133.5(s), 125.9(d)	
cP-1a (120°C)		n.m.		47.0		n.m.		
Q_2-1a	0.82(m) 0.73(m)	1.13(t)	3.46(br), 1.98(m), 1.73(m)	17.0	13.2	13.8	47.9(t), 24.4(t), 20.6(d)	
Ur$_2$-1a	0.73(br)	1.13(t)	4.73(s)	15.5		n.m.		
Ur-1a	1.06(m)	1.06(m)	4.68(s)	44.3	13.5	13.2	72.9(t)	
1b	1.80(m)	1.80(m)	0.94(t) –	79.0	28.0	22.5	16.7 –	
P_2-1b	1.21(m)	1.21(m)	0.84(t) 9.50(d), 7.90(tt), 7.50(dd)	12.2	30.0	22.5	17.3 146.0(d), 139.5(d), 124.2(d)	
P-1b	1.52(m)	1.52(m)	0.98(t) 9.10(br,d), 7.05(m), 6.85(t)	13.8/77.6	29.7(br)	23.5(br)	17.9(br) 146.1(d), 141.2(d), 125.5	
Q_2-1b	0.74(m) 0.68(m)	1.52(m)	0.88(t) 3.39(br), 1.94(m), 1.67(m)	16.1	24.9	23.1	17.7 47.9(t), 24.6(t), 20.7	
Q-1b	0.80(m)	1.51(m)	0.90(t) 3.58(t), 1.95(m), 1.73(m)	16.5/78.5	28.1	22.7	17.0 48.1(t), 24.3(t), 20.9	

is shifted from δ = 79.1 to 12.8 showing the tetravalency of the boron atoms. While the more basic 3,5-dimethylpyridine ($\delta^{11}B$ = 11.9) appears to develop only insignificantly stronger bonds to the boron atoms, the weaker base 3-chloropyridine forms the adduct **cP$_2$-1a** with a ^{11}B-NMR signal at δ = 15.9, suggesting a weaker association of the Lewis acid-base pairs. The ^{11}B resonances for the 2:1 adducts **Q$_2$-1a** and **Q$_2$-1b** at δ = 17.0 and 16.1, respectively, do not reflect the relative strength of this base. Both **Q** and the much weaker base **Ur** appear to experience steric hindrance in approaching the Lewis acid boron atoms[3] and therefore seem to be only weakly coordinated (see also discussion of the ^1H-NMR spectra above and the X-ray structure of **Q$_2$-1a**, below).

In solution with a 1:1 stoichiometry of the Lewis acid/base pairs, a fluctuation of the N-base between the two boron atoms of **1a** or **1b** could be expected, as observed for the N-base adducts of triorganoboroxins[2] and tetraorganodiboroxanes[3]. The ^{11}B-NMR spectra of the 1:1 adducts **P-1a**, **P-1b**, **cP-1a**, **Q-1**, and **Q-1b**, however, all show two signals, one at about δ_{av} = 78 ($h_{½} \approx$ 700 Hz) and another at δ_{av} = 14 ($h_{½} \approx$ 200 Hz) with an integral ratio of approximately 1:1. At elevated temperatures (e.g. 120°C), however, both peaks coalesce at about δ = 47 (for **P-1a** and **cP-1a**) as expected for a 1:1 adduct in which there is fluxional movement of the N-base between the two boron atoms of **1**.

From the ^1H-NMR spectrum of **Q-1a** at room temperature (Figure 2a) it is seen that the peak for the α-methylene protons of the **Q** moiety at δ^1H = 3.33, in contrast to that shown for **Q$_2$-1a** (Figure 1a), are sharp indicating unhindered rotation of **Q** about the B–N bond. Of the groups of peaks between about δ^1H = 0.5 and 1.5 for the two ethyl groups of the **1a** moiety, the broad peak at δ = 1.34 integrates for one B–CH_2 group. The two protons of the other B–CH_2 group appear separately, one as a quadruplet at δ = 0.86 and the other broad at 0.70. At −80°C (Figure 2b) the peak at δ^1H = 1.23 is resolved into a quadruplet, both peaks at δ = 0.74 and 0.55 constitute partially resolved quadruplet and two triplets are observed at δ = 0.98 and 0.90. Furthermore, the group of peaks for the α-methylene protons of **Q**, centred at about δ^1H = 3.2, show a similar pattern as observed in the spectrum of **Q$_2$-1a** at −80°C (compare Figure 1b). These results clearly indicate the presence of two types of ethyl groups, one freely rotating, substituted at a trigonal boron atom, and another at a tetragonal boron atom with hindered rotation, even at room temperature. Finally the complex pattern of peaks assignable to the α-methylene protons of the **Q** moiety at about δ = 3.2 show also the impeded rotation and the existence of a preferred conformation about the B–N bond.

The 1:1 adduct **Ur-1a** is not only an exception since it crystallizes as such from the reaction medium in 85% yield, it also has, compared to the other 1:1 adducts, an unusual

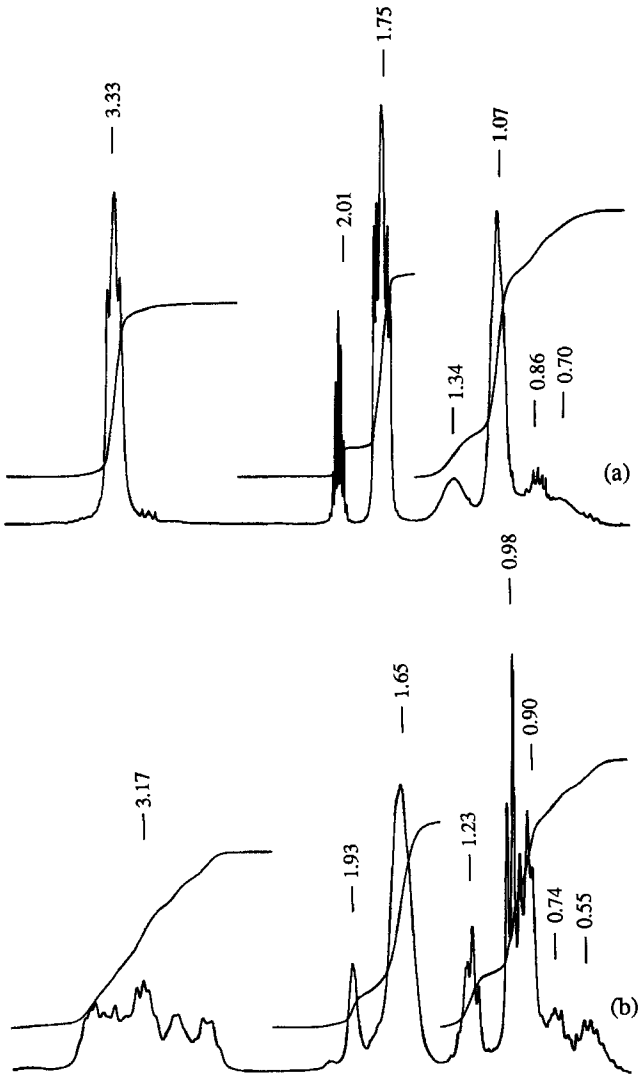


Figure 2. 200-MHz ^{1}H-NMR spectrum (CD_2Cl_2) of **Q-1a**. a) at room temperature; b) at −80°C

room temperature ^{11}B-NMR signal at $\delta = 44.3$. This value, being median between the chemical shift of the free **1a** and that of the doubly coordinated species **(base)$_2$-1a**, suggests a structure in which an N-base fluctuates between the two boron atom sites. The low solubility of this 1:1 adduct together with its high melting/decomposition point at 197°C may be interpreted in terms of a polymeric structure in which two nitrogen atoms of each urotropine molecule simultaneously but weakly interact with two separate molecules of **1a**. So far we have been unable to grow suitable crystals of **Ur-1a** for X-ray crystallographic analysis. We have, however, obtained the crystal structure of the diquinuclidine adduct **Q_2-1a**, which is depicted in Figure 3.

Selected bond lengths and angles are shown in Tables 2 and 3. The central B_2Se_3 ring is nonplanar, with a torsional angle between atoms B1Se2Se1B2 of −32.4° and between B1Se3B2Se1 of 11.7°. The two quinuclidine molecules and ethyl substituents adopt an *anti* configuration. The environments around the two boron atoms B1 and B2 are not identical. Thus while the four atoms around B1 form a regular tetragon, B2 is situated in the centre of a distorted tetragon: The two angles C17B2Se1 (105.7°) and C17B2Se3 (113.2°) demonstrate this deformity. An inspection of the intramolecular nonbonded H···H and H···Se distances shows that a number of these approach each other close to, or are within the van der Waals radii. These nonbonded distances are also listed in Table 2, and in Figure 3 they are shown by dotted lines.

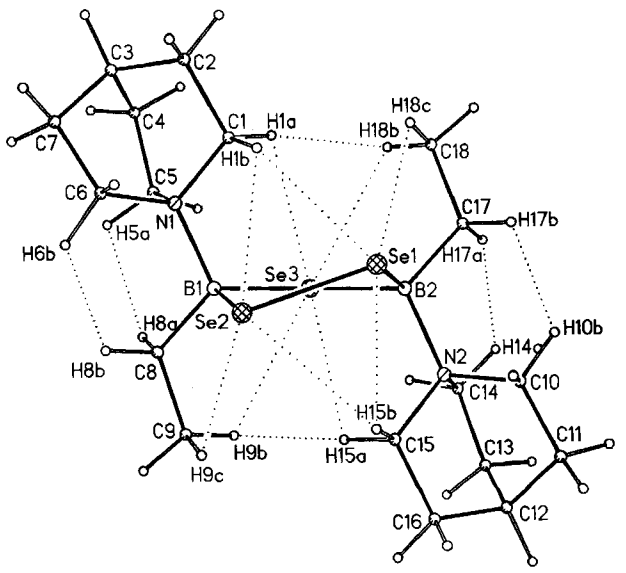


Figure 3. Molecular structure of **Q_2-1a**. Dotted lines show short nonbonded intramolecular distances

Table 2. Selected bond lengths and very short intramolecular nonbonded distances in **Q_2−1a**

Bond lengths [Å]		nonbonded distances [Å]			
B1–Se2	2.073(7)	H1a···H18b	2.23	H1b···Se1	2.90
Se2–Se1	2.341(1)	H5a···H8a	2.18	H9b···Se3	2.99
Se1–B2	2.083(7)	H6b···H8b	1.99	H9c···Se2	2.93
B2–Se3	2.065(6)	H9b···H15a	2.18	H15a···Se3	2.87
Se3–B1	2.072(7)	H14a···H17a	2.10	H15b···Se1	2.77
B1–C8	1.604(9)	H10b···H17a	2.04	H15b···Se2	2.98
B1–N1	1.647(9)	H1a···Se3	2.92	H18b···Se3	2.94
B2–C17	1.607(10)	H1b···Se2	2.88	H18c···Se1	2.95
B2–N2	1.650(8)				

Table 3. Selected bond angles in **Q_2−1a**

Bond angles [°]			
B1Se2Se1	101.1(2)	Se3B1C8	110.8(4)
Se2Se1B2	101.3(2)	Se3B1N1	108.1(4)
Se1B2Se3	109.4(3)	Se3B2N2	107.8(4)
B2Se3B1	108.1(3)	Se3B2C17	113.2(4)
Se3B1Se2	109.4(3)	Se1B2N2	110.0(4)
Se2B1N1	109.7(4)	Se1B2C17	105.7(4)
Se2B1C8	108.2(5)	C17B2N2	111.1(5)
N1B1C8	110.6(5)		

The two coordinating quinuclidine molecules in **Q_2-1a** thus experience a large number of close interactions with

the substituents on their respective boron atom acceptors. These steric interactions can be considered to be the underlying cause for the distortions of the central B_2Se_3 five-membered ring. Furthermore, these nonbonded interactions probably also lead to the low field shifts observed in the ^{11}B-NMR spectra of **Q_2-1a** and **Q_2-1b** compared to those of the other N-base adducts of **1a** and **1b** as they prevent the close approach of the **Q's** to the boron atoms (see also discussion above). Finally, the nearly equal distances of both H17a and H17b to H10a and H14a, respectively, observed in the solid state molecule of **Q_2-1a** (see Table 2), may change by slight rotation of the ethyl groups in solution, resulting in nonequivalence of the two protons as discussed above.

Experimental

Instruments: Büchi melting point apparatus, sealed capillary tubes. Mass spectra: MAT CH 5. – ^1H-, ^{11}B-, and ^{13}C-NMR: Bruker AC 200 with $(CH_3)_4Si$ as internal and Et_2O-BF_3 as external standards. – ^{77}Se-NMR[10]: Bruker MSL 300 (57.3 MHz), CP MAS[10], contact time 5 ms; $\delta^{77}Se = 0$ for $(CH_3)_2Se$ (external), for CP MAS relation over $(NH_4)_2SeO_4$ ($\delta^{77}Se = 1040.2$). – All operations were carried out under very dry oxygen-free argon. All solvents were freshly distilled under argon from appropriate drying agents.

3,5-Diethyl-1,2,4,3,5-triselenadiborolane (**1a**)[9]: A suspension of 11.7 g (160.7 mmol) of tetraethyldiborane(6) (13.7‰ BH) and 10.0 g (126.7 mol) of selenium in 20 ml of toluene was heated for 27 h at reflux. After filtration and removal of the solvent, the residue was distilled in vacuo, b.p. 54–58°C at 0.001 Torr. 10.1 g (75.8%) of an evil smelling, extremely air-sensitive, yellow liquid **1a** was obtained. – MS: Cluster of ions centred at $m/z = 320$ (M^+, 30%, B_2Se_3). – $\delta(^1H)$ ($CDCl_3$): 1.65 (q); 1.26 (t). – $\delta(^{13}C)$ ($CDCl_3$): 18.4 (br, t); 13.2 (q). – $\delta(^{11}B)$ ($CDCl_3$): 79.1 ($h_{1/2} = 210$ Hz). – $\delta(^{77}Se)$ (CD_2Cl_2): 555.8, 417.9 (2:1)[10].

$C_4H_{10}B_2Se_3$ (316.6) Calcd. C 15.17 H 3.18 B 6.83
Found C 15.31 H 3.29 B 7.01

3,5-Dipropyl-1,2,4,3,5-triselenadiborolane (**1b**)[9]: A suspension of 4.18 g (53 mmol) of elemental selenium and 6.7 g (68.1 mmol) of tetrapropyldiborane(6) (8.85‰ ≥BH) in 30 ml of toluene was refluxed for 48 h. After filtration and removal of the solvent and volatiles, the residue was distilled, b.p. 71–73°C/0.001 Torr, to give 4.9 g (80%) of a yellow, very air-sensitive liquid **1b**. – MS: cluster of ions centred at $m/z = 346$ (M^+, 45%, B_2Se_3). – $\delta(^1H)$ ($CDCl_3$): 1.80 (m, 8H); 0.94 (t, 6H). – $\delta(^{13}C)$ ($CDCl_3$): 28.0 (br, t); 22.5 (t); 16.7 (q). – $\delta(^{11}B)$ ($CDCl_3$): 79.0 ($h_{1/2} = 240$ Hz).

$C_6H_{14}B_2Se_3$ (344.7) Calcd. C 20.91 H 4.09 B 6.27
Found C 21.23 H 4.03 B 6.39

2:1 Adducts of N-Bases with **1a** *and* **1b** *(General Procedure):* A solution of 2 mole equivalents of the N-base in 5–10 ml of a hydrocarbon solvent was added to a solution of 1 mole equivalent of **1a** or **1b** in 5–10 ml of the same solvent. The solution immediately changed colour from yellow to orange or orange-red. After a few minutes, if no crystals form, the solution is slowly cooled to –60°C and the crystalline solid formed collected by filtration. Experimental details for the individual adducts prepared are given in Table 4 and NMR data in Table 1. The two procedures given below examplify this method.

3,5-Dipyridine–3,5-Diethyl-1,2,4,3,5-triselenadiborolane (**P_2-1a**): To a solution of 1.28 g (4.04 mmol) of **1a** in 5 ml of toluene was added 0.64 g (8.09 mmol) of pyridine (P) in 5 ml of toluene. The resulting orange-red solution is stirred for 1 h at room temp. Slow cooling to –60°C yields 1.84 g (96%) of orange-red microcrystals of **P_2-1a**, m.p. 137–138°C. – ^{77}Se-NMR ($CDCl_3$): $\delta = 211.3$[10]. – CP MAS: $\delta = 266.7, 239.4, -42.1$[10]. – For other NMR data and for elemental analysis see Tables 1 and 4, respectively.

Table 4. Experimental data for the preparation of N-base adducts of **1a** and **1b**

Product	1 g (mmol)	N-base g (mmol)	Solvent (ml)	Yield g (%)	m.p. °C	Analysis Mol.for. (mol.wt.)	Calcd. / Found	C	H	B	N
P_2-1a	1.28 (4.04)	0.64 (8.09)	toluene (10)	1.84 (96)	137.8	$C_{14}H_{20}B_2N_2Se_3$ (474.8)	Calcd.	35.41	4.24	4.55	5.99
							Found	35.63	4.08	4.80	5.89
$(m_2P)_2$-1a	1.73 (5.46)	1.13 (10.55)	toluene (10)	2.12 (73)	197(dec)	$C_{18}H_{28}B_2N_2Se_3$ (530.9)	Calcd.	40.72	5.32	4.07	5.27
							Found	40.32	5.63	4.45	5.51
$(cP)_2$-1a	1.16 (3.66)	0.83 (7.31)	toluene (20)	1.39 (70)	92–93	$C_{14}H_{18}B_2Cl_2N_2Se_3$ (567.7)	Calcd.	30.92	3.37	3.98	5.15
							Found	30.41	3.63	4.03	4.92
Q_2-1a	1.91 (6.04)	1.31 (11.78)	toluene (10)	2.29 (70)	192–193	$C_{18}H_{36}B_2N_2Se_3$ (538.5)	Calcd.	40.14	6.74	4.01	5.20
							Found	40.00	6.79	4.08	5.19
Ur_2-1a	1.14 (3.60)	1.01 (7.20)	toluene (20)	1.82 (85)	188(dec)	$C_{16}H_{34}B_2N_8Se_3$ (597.0)	Calcd.	32.19	5.74	3.62	18.77
							Found	33.46	5.79	3.79	19.01
Ur-1a	1.68 (5.30)	0.72 (5.13)	toluene (20)	1.99 (85)	197(dec)	$C_{10}H_{22}B_2N_4Se_3$ (456.8)	Calcd.	26.29	4.85	4.73	12.26
							Found	26.59	5.03	4.39	12.02
P_2-1b	1.14 (3.30)	0.60 (7.6)	toluene (10)	1.50 (90)	113(dec)	$C_{16}H_{24}B_2N_2Se_3$ (502.9)	Calcd.	38.21	4.81	4.30	5.57
							Found	38.05	4.89	4.52	5.49
Q_2-1b	0.62 (1.79)	0.40 (3.59)	hexane (10)	1.43 (80)	165–166	$C_{20}H_{40}B_2N_2Se_3$ (567.0)	Calcd.	42.36	7.11	3.81	4.94
							Found	42.47	7.15	3.75	4.90

3,5-Diquinuclidine–3,5-Diethyl-1,2,4,3,5-triselenadiborolane (**Q_2-1a**): For experimental data see Table 4 and for NMR data Table 1.

X-ray Single-Crystal Structure Determination of **Q_2-1a**: Data collection and calculations were carried out on a Nicolet R 3 m/V four-cycle diffractometer with Microvax II and SHELXTL-PLUS software[11]. 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°, respectively). The isotropic displacement parameters (IDP's) of all the H atoms were refined without constraints.

Structural Data for **Q_2-1a**: Crystal size 0.48 × 0.42 × 0.31 mm, monoclinic, $P2_1/c$, $Z = 4$, $a = 12.084(2)$, $b = 9.133(1)$, $c = 19.191(4)$ Å, $V = 2109.3(5)$ Å^3, $\beta = 95.12(1)°$, $d_{calc.} = 1.695$ g/cm^3, $\mu = 5.18$ mm^{-1}, radiation Mo-K_α, $2\Theta_{max} = 45$ deg, empirical absorption correction, max/min transmission 1.00/0.35, number of unique reflections = 2704, observed reflections = 2301 [$F_o \geq 4\sigma(F)$], $R = 0.039$, $R_w = 0.043$ [$w^{-1} = \sigma^2(F_o) + gF_o^2$] with $g = 1.97 \times 0.001$, residual electron density = 0.82 e/Å^3 (0.89 Å from C17). The atomic coordinates of **Q_2-1a** are listed in Table 5[11,12].

3,5-Diquinuclidine–3,5-Dipropyl-1,2,4,3,5-triselenadiborolane (**Q_2-1b**): To a stirred solution of 0.62 g (1.79 mmol) of **1b** in 5 ml of hexane was added dropwise a solution of 0.40 g (3.59 mmol) of quinuclidine (**Q**) in 5 ml of hexane. After 1 h at room temp. the product was filtered from small amounts of a yellow powder. The filtrate on slow cooling to −60°C gave orange crystals of **Q_2-1b**, m.p. 165–166°C.

1:1 Adducts of N-Bases with **1a** *or* **1b** *(General Procedure):* Equimolar quantities (1–2 g) of **1a** or **1b** in 5–10 ml of toluene were mixed with a toluene solution of the corresponding N-base. After stirring for 1 h at room temp. the solvent and all volatiles were removed in vacuo (0.001 Torr) at 40–50°C. The residue (>95% yield), usually a red or orange-red viscous material, was used as such for NMR spectroscopic studies. An exception to this procedure was the case of **Ur-1a** which is given separately below.

Hexamethylenetetramine–3,5-Diethyl-1,2,4,3,5-triselenadiborolane (**Ur-1a**): A solution of 1.68 g (5.3 mmol) of **1a** in 10 ml of toluene was mixed with a solution of 0.73 g (5.2 mmol) of urotropine (**Ur**) in 10 ml of toluene. The mixture was left at room temp. for 20 h. The microcrystalline solid of **Ur-1a** that separated was filtered, 1.99 g (85%), m.p. 197°C (dec.).

Table 5. Atomic coordinates (× 10^4) [Å] and equivalent isotropic displacement factors (× 10^{-1}) [pm] for **Q_2-1a**

Atom[a]	x	y	z	U_{eq}
Se1	3200(1)	2115(1)	9003(1)	13(1)*
Se2	4400(1)	167(1)	8822(1)	13(1)*
Se3	1766(1)	−700(1)	8219(1)	11(1)*
N1	3085(4)	−2377(5)	9368(3)	11(2)*
N2	1893(4)	2280(5)	7559(3)	14(2)*
B1	3280(7)	−1535(7)	8630(4)	14(2)*
B2	1809(6)	1546(7)	8339(3)	9(2)*
C1	2557(5)	−1404(6)	9887(3)	12(2)*
C2	2613(6)	−2119(6)	10603(3)	14(2)*
C3	2762(5)	−3758(7)	10519(3)	16(2)*
C4	1946(5)	−4272(6)	9916(3)	14(2)*
C5	2327(5)	−3693(6)	9235(3)	15(2)*
C6	4162(5)	−2930(6)	9734(3)	14(2)*
C7	3920(6)	−4036(7)	10306(3)	19(2)*
C8	3777(5)	−2644(7)	8090(3)	15(2)*
C9	3985(6)	−2038(7)	7373(3)	19(2)*
C10	1876(7)	3916(7)	7597(4)	29(3)*
C11	1841(7)	4616(7)	6898(4)	25(2)*
C12	1986(6)	3460(6)	6345(3)	20(2)*
C13	1016(6)	2390(7)	6333(3)	20(2)*
C14	918(6)	1828(7)	7066(3)	22(2)*
C15	2931(6)	1838(8)	7243(3)	24(2)*
C16	3055(6)	2636(8)	6559(3)	21(2)*
C17	760(5)	2182(6)	8700(3)	14(2)*
C18	514(6)	1467(7)	9381(3)	19(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.
[a] Number of the atoms s. Figure 3.

CAS Registry Numbers

1a: 115706-03-1 / **P_2-1a**: 124176-79-0 / **P-1a**: 124176-80-3 / **$(m_2P)_2$-1a**: 124176-81-4 / **$(cP)_2$-1a**: 124176-82-5 / **cP-1a**: 124176-83-6 / **Q_2-1a**: 124176-84-7 / **Ur_2-1a**: 124176-85-8 / **Ur-1a**: 124176-86-9 / **1b**: 41453-09-2 / **P_2-1b**: 124176-87-0 / **P-1b**: 124176-88-1 / **Q_2-1b**: 124176-89-2 / **Q-1b**: 124176-90-5 / **m_2P**: 591-22-0 / **cP**: 626-60-8 / **Q**: 100-76-5 / **Ur**: 100-97-0 / ^{77}Se: 14681-72-2 / ^{11}B: 14798-13-1 / tetraethyldiborane(6): 12081-54-8 / tetrapropyldiborane(6): 22784-01-6

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[10] We are greatful to Professor Dr. *B. Wrackmeyer* (Laboratorium für Anorganische Chemie der Universität Bayreuth) for ^{77}Se-NMR measurements in solution and to Dr. *A. Sebald* (Bayrisches Geoinstitut, Universität Bayreuth) for the CP MAS analysis.
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[12] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-320037, the names of the authors, and the journal citation.

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