B_2N_4Se-Bicyclo[2.2.1]heptanes and $B_2N_4Se_2$-Bicyclo[2.2.2]octanes[1)]

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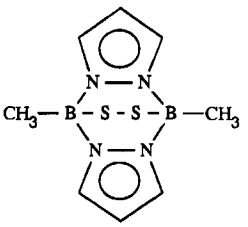
Aus 3,5-Dialkyl-1,2,4,3,5-triselenadiborolanen [Alkyl = C_2H_5 (**1a**) und Alkyl = n-C_3H_7 (**1b**)] werden mit Pyrazol (**Pz**), 3-Methylpyrazol (**mPz**) und 3-Phenylpyrazol (**pPz**) die Diselenabicyclo[2.2.2]octane **2**–**4** hergestellt. Demgegenüber reagieren 3,5-Dimethyl- und 3,5-Diphenylpyrazol ($\mathbf{m_2Pz}$, $\mathbf{p_2Pz}$) mit **1a** zu den Monoselenabicyclo[2.2.1]heptanen **5** und **6**. Von **2a** und **5** liegen Kristallstrukturanalysen vor.

As part of our ongoing interest in the potentials of chalcogeno-organoboranes to form adducts with N-bases[2–9] we report in the preceding publication on addition complexes of 3,5-dialkyl-1,2,4,3,5-triselenadiborolanes (**1**)[10] with a number of N-bases[7]. In this report we describe the reaction of **1** with the dibasic pyrazole (**Pz**) and with a number of monosubstituted pyrazole derivatives, leading to $B_2N_4Se_2$-bicyclo[2.2.2]octanes, which are analogues of the recently described so-called disulfide-bridged pyrazabole **I**[11], and the reaction of certain disubstituted pyrazoles to form the correspondingly novel B_2N_4Se-bicyclo[2.2.1]heptane species.



I

Results and Discussion

Addition of two equivalents of **Pz** to a hexane solution of 3,5-diethyl-1,2,4,3,5-triselenadiborolane (**1a**)[10] at room temperature results in a rapid colour change from yellow to orange. A brown suspension was obtained. From the yellow solution light yellow crystals of **2a** were obtained at −80°C; m.p. 221–223°C. The mass spectrum of **2a** showed a molecular ion at m/z = 374 (14%), corresponding to the molecular formula $C_{10}H_{16}B_2N_4Se_2$. The ^{11}B-NMR spectrum like the ^{1}H- and ^{13}C-NMR data (see Table 1) is in agreement with the structure **2a**, which was also confirmed by an X-ray crystal analysis (see below).

Using a similar procedure the *B*-propyl derivative **2b** was obtained from **Pz** and 3,5-dipropyl-1,2,4,3,5-triselenadiborolane (**1b**).

The molecular structure of **2a** (see below) revealed considerable crowding within the molecule. It could therefore be expected that substitution with either a bulky substituent at the boron atoms of **1** or substituent(s) at the 3- and/or 5-position of the pyrazoles employed would destabilize the diselenide bridge enhancing its transformation into the novel monoselenide-bridged heterocyclic analogue.

The diselenium derivatives **3** and **4** obtained from the reaction of 3-methyl- and 3-phenylpyrazole (**mPz** and **pPz**, respectively) in good yields are, however, thermally stable and in their mass spectra show only a slight increase of the M^+ − Se fragment ions compared to that found for **2a** or **2b**. On the other hand, reaction of 3,5-dimethyl- and 3,5-diphenylpyrazole ($\mathbf{m_2Pz}$ and $\mathbf{p_2Pz}$, respectively) with **1a** gave almost exclusively the novel B_2N_4Se-bicyclo[2.2.1]heptane derivative **5** and exclusively the tetraphenyl analogue **6**. In the former case the mass spectrum of the crude reaction product also revealed a trace of a diselenium derivative. Attempts to increase the yield of this material by carrying out the reaction at lower or higher temperatures were unsuccessful. It appears therefore that the substituents on the pyrazoles only influence the initial stages of the reactions leading to either mono- or diselenium bridged products. One probable mechanistic pathway is shown in Scheme 1. Of the two possible initial reaction intermediates **A** and **B** that can be envisaged, the more flexible six membered ring in **A** should allow a better steric relief of the strains caused by the mutual interactions of the substituents on pyrazole- and of the methylene protons on the boron atom. This would render the trigonal boron atom of **B** a more reactive Lewis acid site for approach of the second pyrazole molecule.

In an attempt to trap the proposed intermediates **A** or **B** we also treated **Pz** with **1a** in a 1:1 molar ratio, however, the only product isolated was **2** in less than 50% yield, based on the amount of **1a** employed. Therefore, it is evident that any initially formed addition complex of **1** with one molecule of pyrazole is a very reactive species.

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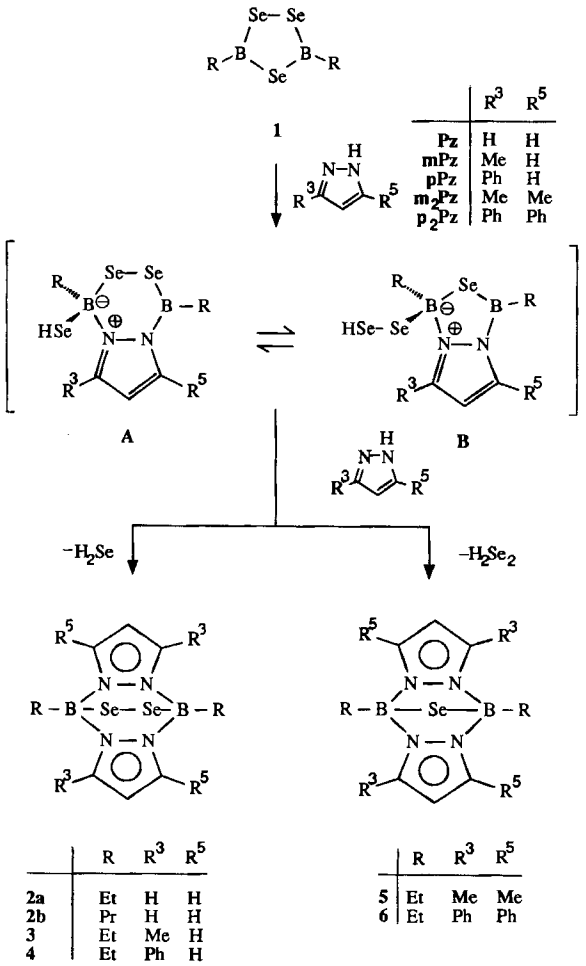
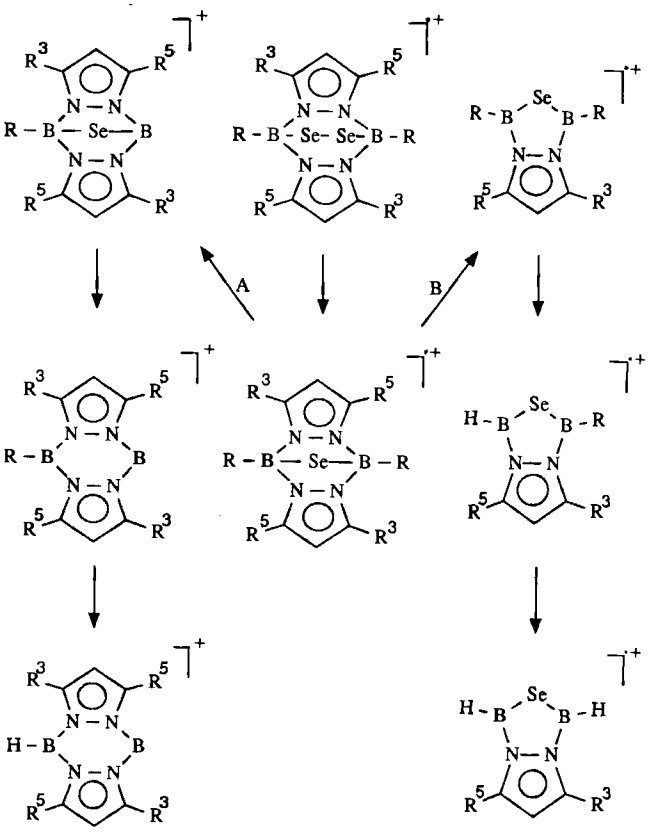
Table 1. NMR data for compounds **2**–**6**

No.	$\delta^{13}C$ (50.4 MHz)						$\delta^{11}B$	$\delta^{1}H$ (200 MHz)					
	Pyrazole moiety			R			(64.2 MHz)	Pyrazole moiety			R		
	C^3 R'^3	C^4	C^5 R'^5	B–CH_2	CH_2	CH_3		H^3 R'^3	H^4	H^5 R'^5	B–CH_2	CH_2	CH_3
2a	137.2	107.2	137.2	8.0	–	8.9	–0.9	7.76	6.45	7.76	1.47	–	1.15
2b	132.3	107.0	132.0	20.0	17.7	18.8	–1.4	7.73	6.45	7.73	1.54	1.30	1.09
3	144.9	109.5	136.4	9.1	–	9.0	–0.4	– 2.44	6.21	7.70	1.47	–	1.06
4	148.3 130.4 129.2 129.1 127.6	109.4	133.1	9.0	–	8.0	0.3	– 7.67 7.42	6.36	7.79	1.08	–	0.54
5	142.3 11.6	108.0	142.3 11.6	10.0	–	12.4	6.5	– 2.15	5.50	– 2.15	1.30	–	1.18
6	146.9 129.8 129.1 128.7 127.4	109.5	146.9 129.8 129.1 128.7 127.4	11.6	–	10.0	7.6	– 7.30	6.05	– 7.30	1.20	–	1.20

Scheme 1



Scheme 2



Finally it should be mentioned that reactions of **1** with pyrazoles in some cases give also traces of side products which have a higher selenium content. Thus, in the mass spectra of a number of crude products trace amounts of a more volatile compound (observed by

differential evaporation of the sample in the mass spectometer) are found, which show a molecular mass corresponding to $(Pz)_2(RBSe)_3$. The volatile component in the crude product from the reaction of **1a** with **pPz**, e. g., shows an apparent molecular ion at $m/z = 646$ with an isotopic abundance pattern corresponding to $C_{24}H_{29}B_3N_4Se_3$. So far, we have been unable to isolate and further analyze the structure of this side product.

Mass Spectra of 2–6

The fragmentation pattern of the Se_2-bicyclo[2.2.2]-octanes **2**–**4** exhibit certain common features differentiating them from the Se_1-bicyclo[2.2.1]heptanes **5** and **6**, which also reflect the steric influence of the substituents on the 3,5-positions of the pyrazoles. Thus the Se_2-compounds **2**–**4**, similar to their S_2-analogue **I**[11], after loss of one selenium atom from the molecular ion, form the Se_1-bridged species. The latter fragment mainly loses one of the boron substituents (pathway, A, Scheme 2), followed by the loss of the last selenium atom. On the other hand, the tetrasubstituted Se_1-bridged molecules **5** and **6** fragment mainly by the initial loss of one pyrazole group (pathway B, Scheme 2), followed by the further loss of the *B*-ethyl substituent. As seen by the more abundant fragment ions, this pathway is clearly even more favoured in the case of the tetraphenyl derivative **6**. This shows that starting from an assumed common monoselenium atom containing species, the steric factor of the pyrazole substituents leads to differing fragmentations.

X-ray Crystal Structures of 2a and 5

a) *Structure of* **2a**: The molecular structure of **2a** as determined by X-ray crystallography is shown in Figure 1a, and selected bond lengths and angles are listed in Table 2 and compared to that of **5** (see below). In contrast to the structure of **I**[11], the molecule of **2a** has no crystallographic symmetry. This is due to the *near anti* conformation of the

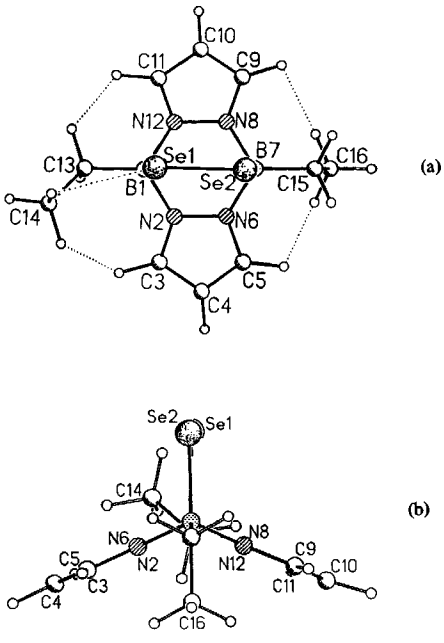


Figure 1. Molecular structure of **2a**

two substituent ethyl groups in **2a**. As in the projection shown in Figure 1b, one of these lies below the N1N2N3N4 plane and is situated equidistant to the two flanking pyrazole rings (torsion angle Se2B7C15C16 = 179.1°). The other is turned towards the selenium atom Se1 (torsion angle Se1B1C13C14 = −45.0°). The two pyrazole rings form an interplanar angle of 46.6°, very close to that found in **I**[11].

Bond lengths and angles around the central bicyclic ring system, with the exception of the longer Se–Se bond (2.350 Å, compared to 2.105 Å for th S–S bond), are also largely the same as those found for **I**[11]. A significant structural difference arises from the increased crowding due the ethyl substituents. In Figure 1 the very close intramolecular H···H and H···Se nonbonded distances are denoted by dotted lines. The conformation of the two ethyl groups as found in solid **2a** should make the two selenium atoms Se1 and Se2 chemically nonequivalent. This is confirmed by the presence of the two signals of equal intensities found in its CP MAS ^{77}Se-NMR spectrum at δ = 66.9 and 69.5[12]. In solution the two ethyl groups appear to rotate freely as only one very narrow signal at δ = −0.9 ($h_{1/2}$ = 100 Hz) is found in the ^{11}B-NMR spectrum and a single set of signals for the methylene and methyl protons and carbon atoms is observed in the ^{1}H- and ^{13}C-NMR spectra (see Table 1).

Table 2. Selected bond lengths (Å) and bond angles (°) for **2a** and **5**

Bond lengths (Å)	2a	5	Bond angles (°)	2a	5
Se1Se2	2.350(1)	–	B1SeB2	–	75.2(4)
Se(1)B1	2.096(6)	2.067(10)	Se2Se1B1	98.1(2)	–
Se(2)B7	2.078(5)	2.081(9)	Se1Se2B7	96.8(2)	–
B1N2	1.549(7)	1.583(12)	Se(1)B1N2	107.8(3)	101.3(6)
B1N12	1.544(7)	1.594(10)	Se(1)B1N12	106.8(3)	101.1(5)
B7N6	1.553(7)	1.573(11)	Se(2)B7N6	107.0(3)	101.2(2)
B7N8	1.548(7)	1.598(13)	Se(2)B7N8	108.5(3)	99.7(6)
N2N6	1.359(5)	1.373(9)	N2B1N12	104.0(4)	101.0(6)
N8N12	1.366(6)	1.374(9)	N6B7N8	103.9(4)	101.9(6)
B1C13	1.579(8)	1.577(13)	B1C13C14	118.6(5)	113.7(8)
			B7C15C16	116.5(4)	114.7(9)

b) *Molecular Structure of* **5**: The molecule of **5** is shown in Figure 2a. Besides the monoselenide bridging the main initially apparant difference to the structure of **2** is the *near syn* conformation of the two *B*-ethyl substituents. In **5** the two C13–C14 and C15–16 bonds of the ethyl groups form torsion angles of −50.8° and −42.2° to the B1Se and B2Se bonds, respectively. In these conformations the nearest nonbonded intramolecular distances between the methyl group hydrogen atoms of the two B1 and B2 ethyl substituents are 3.06 and 3.00 Å, slightly more distant than of the corresponding group in **2a** (in **2a**, nonbonded distance Se1···H14 = 2.807 Å). In the projection shown in Figure 2b it can be seen that the two *B*-ethyl groups of **5** occupy positions of least interactions with their neighbours. The ethyl group in a conformation below the plane formed by the atoms N1N2-N3N4 as found in **2a** would experience extensive crowding with the pyrazole methyl substituents.

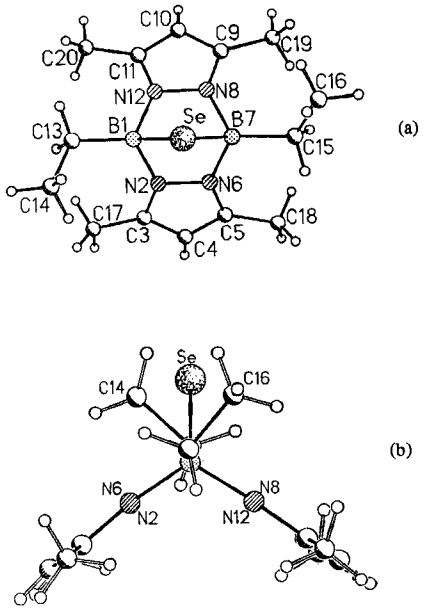


Figure 2. Molecular structure of **5**

Furthermore, the monoselenide bridging in **5** causes changes of some of the bond lengths and angles from those found in **2a** (Table 2). The bridging selenium atom forms a very narrow angle of 75.2° with the two boron atoms B1 and B2. This brings about a greater folding of the two planes N1B2N3 and N2B1N4 forming an interplanar angle of 133.9°. The pyrazole rings in **5** have an interplanar angle of 106.0° (in **2a**, 133.4°). Finally, it is noteworthy that some of the bond lengths have also changed, e.g. the B–N bonds are significantly elongated (by an average of 0.039 Å) compared to the corresponding bonds in **2a** (see Table 2).

Experimental

Instruments: Büchi melting point apparatus, sealed capillary tubes. – Mass spectra: MAT CH 5. – ^{1}H-, ^{11}B-, ^{13}C-NMR: Bruker AC 200 with $(CH_3)_4Si$ as internal and Et_2O-BF_3 as external standards. – CP MAS ^{77}Se-NMR[12a]: Bruker MSL 300 (57.3 MHz), contact time 5 ms; $\delta^{77}Se = 0$ for $(CH_3)_2Se$ (external) for CP MAS relation over $(NH_4)_2SeO_4$ ($\delta^{77}Se = 1040.2$) using a heat-sealed Kel-F rotor insert[12b]. – The boron reagents **1a** and **1b** were prepared as described in ref.[7]. The pyrazoles **pPz** and **p_2Pz**, unavailable commercially, were prepared from the corresponding 1,3-ketoaldehyde and diketone with hydrazine hydrate[13]. All operations were carried out under a strictly oxygen-free and dry atmosphere.

1,7-Dialkyl-13,14-diselena-2,8-diaza-6,12-diazonia-1,7-diboratatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradeca-3,5,9,11-tetraenes **2**–**4** *and 13-Selena-2,8-diaza-6,12-diazonia-1,7-diboratatetracyclo[5.5.1.0^{2,6}.0^{8,12}]-trideca-3,5,9,11-tetraenes* **7** *and* **8** *(General Procedure):* A mixture of **1** and a two-molar excess of the corresponding pyrazole in an appropriate hydrocarbon solvent was stirred at 25–130°C for 1–20 h (see Table 3). On completion of the reaction the solution was filtered and the filtrate cooled to –78°C to effect crystallization. In some cases the product separates directly from the reaction mixture at room temperature. Recrystallization was generally carried out in heptane or toluene. In Table 3 the detailed reaction

Table 3. Experimental data for the preparation of compounds **2**–**6** and their mass spectra and elemental analyses

No.	**1** g (mmol)	Pyrazole g (mmol)	Solvent (ml)	Temp. °C Time (h)	Yield g (%)	m.p. °C	MS Spectrum m/z (%)	Elemental Analysis Mol.for. (mol.wt.) Calcd. C H B N Se Found
2a	**1a** 3.97 (11.9)	**Pz** 1.63 (23.9)	hexane (30)	25 (1)	3.6 (82)	221–223	374(M^+,B_2Se_2,14), 294(2), 256(8), 214(B_2,41), 185(B_2, 100), 157(B_2,39)	$C_{10}H_{16}B_2N_4Se_2$ (371.8) 32.30 4.34 5.82 15.07 42.47 32.42 4.39 5.69 15.15 42.27
2b	**1b** 1.75 (5.1)	**Pz** 0.69 (10.1)	hexane (15)	30 (20)		210–212	402(M^+,B_2Se_2,16), 280(2), 242(B_2, 46), 199(B_2,100), 157 (B_2,60)	$C_{12}H_{20}B_2N_4Se_2$ (399.9) 36.05 5.04 5.41 14.01 39.49 36.18 5.00 5.61 14.23 39.31
3	**1a** 1.89 (6.0)	**MePz** 1.02 (12.4)	heptane (15)	100 (18)	1.81 (75)	140 dec.	402(M^+,B_2Se_2,4), 322(6), 293(17), 242(B_2,20), 213(B_2, 100), 185(B_2,25)	$C_{12}H_{20}B_2N_4Se_2$ (399.9) 36.05 5.04 5.41 14.01 39.49 36.22 4.91 5.38 13.91 39.58
4	**1a** 1.02 (3.2)	**PhPz** 0.93 (6.5)	nonane (15)	130 (24)	1.41 (84)	256–257	526(M^+,B_2Se_2,10), 446(B_2Se,8), 417(25), 366(B_2,13), 337(B_2, 100), 309(B_2,26)	$C_{22}H_{24}B_2N_4Se_2$ (524.0) 50.43 4.62 4.13 10.69 30.14 49.99 4.39 4.19 11.08 30.94
5	**1a** 2.01 (6.4)	**Me_2Pz** 1.22 (12.7)	hexane (15)	70 (15)	1.61 (72)	261–262	350(M^+,B_2Se,51), 321(87), 293(6), 255 (B_2Se,17), 241(B_2, 100), 213(B_2,32)	$C_{14}H_{24}B_2N_4Se$ (349.0) 48.19 6.93 6.20 16.06 22.63 48.30 6.71 6.18 16.15 22.79
6	**1a** 1.87 (5.91)	**Ph_2Pz** 2.60 (11.80)	nonane (15)	130 (18)	2.30 (65)	267–268	598(M^+,B_2Se,88), 569 (91), 489(43), 461 (32), 379(B_2Se,100), 323(B_2Se,44), 77(96)	$C_{34}H_{32}B_2N_4Se$ (597.2) 68.38 5.40 3.62 9.39 13.22 67.94 5.40 3.79 9.51 13.69

conditions, yields, mass spectra, and elemental analyses of the products are listed. The NMR data are compiled in Table 1. The procedure for the preparation of **2a**, given below, demonstrates the facility of this reaction.

Table 4. Crystallographic data for **2a** and **5** and data collection procedures

	2a	**5**
Formula	$C_{10}H_{16}B_2N_4Se_2$	$C_{14}H_{24}B_2N_4Se$
Crystal size (mm)	0.51 x 0.45 x 0.43	0.36 x 0.31 x 0.28
Space group	$P2_1/n$	$P2_1/c$
Z	4	4
a (Å)	8.744(1)	7.915(1)
b (Å)	14.411(3)	13.494(2)
c (Å)	11.143(2)	16.648(3)
β (deg)	95.88(1)	104.32(1)
T (K)	room temp.	room temp.
V (Å^3)	1396.9(4)	1722.7(5)
$d_{calc.}$ (g/cm^3)	1.768	1.345
μ (mm^{-1})	4.76	1.96
Radiation	Mo-K_α	Mo-K_α
$2\Theta_{max}$ (deg)	55	45
Total no. of unique reflections	2244	2244
Observed reflections [$F_o \geq 4\sigma(F)$]	1919	1480
R	0.042	0.55
R_w [$w^{-1}=\sigma^2(F_o+g(F_o^2)]$	0.042	0.56
g	5.1 x 10^{-4}	3.5 x 10^{-4}
Number of parameters refined	191	230
Residual electron density (e/Å^3)	0.63	0.48

Table 5. Atomic coordinates (x 10^4) [Å] and equivalent isotropic displacement factors (x 10^{-1}) [pm] for **2a**

	x	y	z	U_{eq}
Se(1)	611(1)	3484(1)	6519(1)	42(1)*
Se(2)	756(1)	2925(1)	8509(1)	37(1)*
B(1)	2444(6)	4426(4)	6749(5)	32(2)*
N(2)	3880(4)	3891(3)	7310(3)	28(1)*
C(3)	5180(6)	3624(4)	6882(5)	37(2)*
C(4)	6072(6)	3145(4)	7746(5)	40(2)*
C(5)	5262(6)	3132(3)	8732(5)	35(2)*
N(6)	3926(4)	3585(2)	8467(3)	25(1)*
B(7)	2550(6)	3774(4)	9210(5)	26(2)*
N(8)	2110(4)	4795(3)	8910(4)	29(1)*
C(9)	1660(5)	5499(3)	9583(5)	32(2)*
C(10)	1384(6)	6254(4)	8873(6)	41(2)*
C(11)	1651(6)	6001(4)	7736(5)	39(2)*
N(12)	2083(4)	5107(3)	7750(3)	28(1)*
C(13)	2625(7)	4916(4)	5504(5)	45(2)*
C(14)	2556(8)	4322(5)	4369(5)	62(3)*
C(15)	2908(6)	3574(3)	10606(4)	33(2)*
C(16)	4237(6)	4136(4)	11281(5)	41(2)*

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

1,7-Diethyl-13,14-diselena-2,8-diaza-6,12-diazonia-1,7-diboratatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradeca-3,5,9,11-tetraene (**2a**): A solution of 3.97 g (11.9 mmol) of **1a** in 15 ml of hexane was added to a stirred solution of 1.63 g (23.9 mmol) of pyrazole (**Pz**). The resulting initially yellow solution rapidly changed to an orange colour, and after about 1 h a brown suspension was obtained. Filtration from traces of elemental selenium gave a yellow solution. On slow cooling to −80°C 3.6 g (82%) of crystalline **2a**, m.p. 221−223°C, was collected. For elemental analysis, mass spectrum, ^{1}H-, ^{11}B-, and ^{13}C-NMR analyses see Tables 3 and 1. − CP MAS ^{77}Se-NMR: δ = 66.9 and 69.5 (intensity ratio 1:1)[12].

X-ray Single-Crystal Structure Determination of **2a** *and* **5**: Data collection and calculations were carried out on a Nicolet R 3 m/V four-cycle diffractometer with Microvax II and SHELXTL-PLUS software[14]. After empirical absorption corrections the structure solutions were performed by direct methods, and for refinements 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 in groups without constraints. Structural data for **2a** and **5** are listed in Table 4 and the atomic coordinates in Tables 5 and 6, respectively[15].

Table 6. Atomic coordinates (x 10^4) [Å] and equivalent isotropic displacement factors (x 10^{-1}) [pm] for **5**

	x	y	z	U_{eq}
Se	7235(1)	2519(1)	2664(1)	64(1)*
B(1)	8613(11)	1217(7)	2670(6)	52(4)*
N(2)	8038(7)	610(5)	3371(4)	46(2)*
C(3)	7718(10)	-325(7)	3564(6)	59(4)*
C(4)	7455(12)	-322(8)	4344(7)	69(4)*
C(5)	7667(10)	627(8)	4639(5)	58(4)*
N(6)	7995(8)	1200(5)	4037(4)	48(2)*
B(7)	8528(13)	2298(6)	3900(6)	53(4)*
N(8)	10475(8)	2164(5)	3805(4)	52(3)*
C(9)	12128(11)	2420(6)	4198(5)	56(3)*
C(10)	13173(14)	1968(8)	3754(6)	66(4)*
C(11)	12165(10)	1432(6)	3116(6)	56(3)*
N(12)	10526(8)	1557(4)	3149(4)	49(3)*
C(13)	8438(11)	685(7)	1809(5)	62(4)*
C(14)	6544(11)	532(10)	1316(6)	95(5)*
C(15)	8219(12)	3089(7)	4563(6)	69(4)*
C(16)	8210(18)	4143(7)	4291(8)	110(6)*
C(17)	7710(14)	-1204(8)	3003(7)	96(5)*
C(18)	7534(14)	1016(8)	5471(6)	86(5)*
C(19)	12592(12)	3074(8)	4939(6)	79(4)*
C(20)	12730(11)	780(8)	2507(6)	79(5)*

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

CAS Registry Numbers

1a: 115706-03-1 / **1b**: 41453-09-2 / **2a**: 124177-22-6 / **2b**: 124177-23-7 / **3**: 124177-24-8 / **4**: 124177-25-9 / **5**: 124177-26-0 / **6**: 124177-27-1 / **Pz**: 288-13-1 / **MePz**: 1453-58-3 / **PhPz**: 2458-26-6 / **Me_2Pz**: 67-51-6 / **Ph_2Pz**: 1145-01-3

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[15] 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 numbers CSD-320035, -320036, the names of the authors, and the journal citation.

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