Ethyloboration of Selenium Dioxide and Selenium Bis(*tert*-butylimide) – Molecular Structure of an Organo-Substituted Eight-Membered [–BOSeO–]$_2$ Heterocycle[1]

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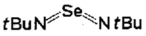
Both selenium dioxide (**1**) and selenium bis(*tert*-butylimide) (**2**) react with triethylborane (**A**) by 1,2-ethyloboration. In the case of **1**, ethane, ethene, diethylselane (**4a**), tetraethyldiboroxane (Et$_2$B)$_2$O (**B**), triethylboroxine (EtBO)$_3$ (**D**) and a cyclic compound [–Et$_2$BOSe(Et)O–]$_2$ (**5$_2$**) are formed after heating to 65 °C. Compound **5$_2$** is also formed when **1** reacts with **B**. Treatment of selenous acid (**3**) with **A** or, preferentially for synthetic purposes, with **B** provides further routes to **5$_2$**. The reaction of the diimide **2** with **A** starts already below –50 °C: a cyclic ethaneselenic acid derivative **6**, $\overline{\mathrm{Et_2BN}}(t\mathrm{Bu})\text{-}\overline{\mathrm{Se(Et)N}}t\mathrm{Bu}$, is formed, and **6** starts to decompose at –50 °C by elimination of ethene to give finally (*tert*-butylamino)diethylborane (**8**), bis(diethylboryl)-*tert*-butylamine (**9**), and Et$_2$Se (**4a**). Transborylation of **5$_2$** with (9-BBN)$_2$O (**C**) affords [–(9-BBN)OSe(Et)O–]$_2$ (**10$_2$**), which crystallizes in the monoclinic space group $P2_1/n$ with the lattice constants (118 K) a = 667.1(1), b = 1282.5(1), c = 1289.1(1) pm and β = 93.06(1)°. All reactions were monitored by ^{11}B- and ^{77}Se-NMR spectroscopy. Furthermore, the reactions of **1** with **A** and **B** and the transborylations were studied by ^{17}O-NMR spectroscopy using the ^{17}O-enriched compounds **1**(^{17}O), **B**(^{17}O), **C**(^{17}O), and **D**(^{17}O).

More than 20 years ago it was shwon that selenium dioxide (**1**) reacts with triethylborane (**A**) in aqueous solution or in tetrahydrofuran (THF) to give diethylselane (**4a**) and diethyldiselane (**4b**)[2]. The formation and isolation of potential intermediates was not considered, and a radical mechanism was proposed for the *B*/*Se* alkyl transfer[2]. In continuing studies of the reactivity and synthetic application of **A** and organoboron-oxygen compounds such as (Et$_2$B)O (**B**), (9-BBN)$_2$O (**C**), and (EtBO)$_3$ (**D**)[3], we have investigated their reactions with selenium dioxide (**1**), selenium bis(*tert*-butylimide) (**2**)[4], and selenous acid (**3**). In addition, transborylations using **C** were attempted in order to prepare reasonably stable intermediates, hoping to take advantage of the higher crystallization tendency of the 9-BBN derivatives[3f].

SeO_2
1

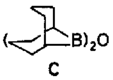


$t\mathrm{BuN{=}Se{=}N}t\mathrm{Bu}$
2

H_2SeO_3
3

Et_3B
A

$(Et_2B)_2O$
B


C

$(EtBO)_3$
D

Results and Discussion

1,2-Ethyloboration of Selenium Dioxide (1): Synthesis of 2,4,4,6,8,8-Hexaethyl-1,3,5,7,2,6,4,8-tetraoxadiselenadiboratocane (5$_2$)

When a suspension of SeO$_2$ (**1**) in Et$_3$B (**A**) is heated at 65 °C, a colorless solution is formed, and a mixture of ethane and ethene is liberated. In the ^{11}B-NMR spectra[5] of the reaction solution signals for (Et$_2$B)$_2$O (**B**) at δ = 53.0, and for (EtBO)$_3$ (**D**) at δ = 33.0 are observed, and an additional broad ^{11}B resonance signal at δ = 14.0 ($\Delta\nu_{1/2}$ = 300 ± 10 Hz) is assigned to **5$_2$**, the dimer of the 1,2-ethyloboration product of **1** [eq. (1)]. The ^{77}Se-NMR spectra[4b,6] show two signals, one at δ = 235.0 for Et$_2$Se (**4a**) and the other one at δ = 1168.0 for **5$_2$**. Compound **5$_2$** is left as a colorless solid after all volatile material has been removed. If the reaction is carried out with ^{17}O-enriched **1**(^{17}O), ^{17}O-NMR spectra[7] show signals for **B**(^{17}O) (δ = 224.0), **D**(^{17}O) (δ = 146.0), and **5$_2$**(^{17}O) (δ = 130) in accord with the ^{11}B-NMR spectra.

Compound **5$_2$** is also formed in the reaction of **1** with an excess of (Et$_2$B)$_2$O (**B**). The ^{17}O-NMR spectrum shows signals for **B**(^{17}O), **D**(^{17}O), and the broad signal at δ = 130 corresponding to **5$_2$**, by using **B**(^{17}O). In contrast, the reaction of (EtBO)$_3$ (**D**) with **1** does not lead to **5$_2$** but to a red-

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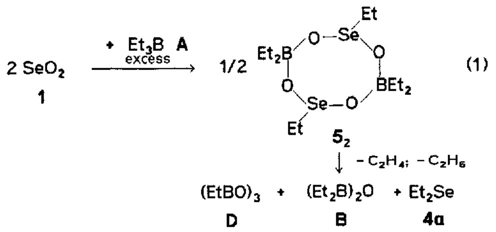
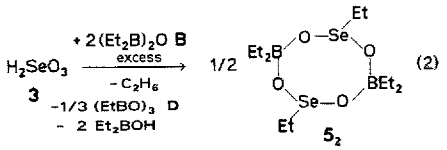


brown reaction solution containing a mixture of compounds, some of which possess a BO_3 fragment ($\delta^{11}B$ = 17.6).

Treatment of selenous acid (**3**) with an excess of Et_3B (**A**) leads to complex mixtures consisting of **B**, **D**, Et_2BOH, Et_2Se (**4a**), Et_2Se_2 (**4b**) ($\delta^{77}Se$ = 336.0), $\mathbf{5_2}$, and at least another selenium compound ($\delta^{77}Se$ = 176.0) which was not identified. The formation of **4a** and **4b** recalls previous findings for the reaction of **1** with **A** in water or THF[2]. The reaction of **3** with an excess of **B** [eq. (2)] affords **D**, Et_2BOH, a small amount of ethane and the dimer $\mathbf{5_2}$ (>70% yield), which can be purified by recrystallization or sublimation (>85°C/0.01 Torr, with partial decomposition). Triethylboroxine (**D**) reacts with **3** without a defined result as observed for **1** and **D** (vide supra).

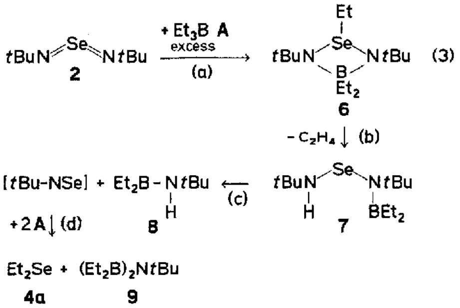


The molecular structures of $\mathbf{5_2}$ in solution and in the solid state must be similar, considering the almost identical isotropic $\delta^{77}Se$ values in both phases (solution: δ = 1168; solid state: 1174.5).

1,2-Ethyloboration of Selenium Bis(*tert*-butylimide) (2)

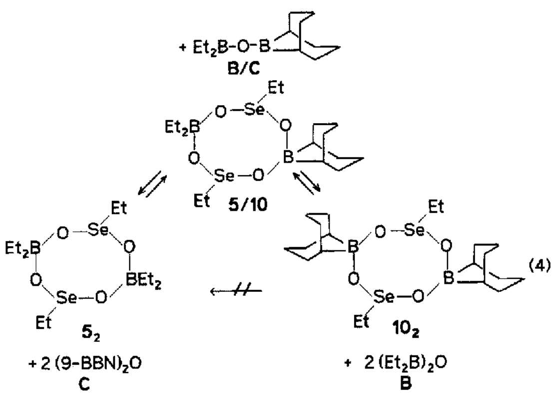
The reaction of **2** with **A** [eq. (3)] starts already far below room temperature. After mixing of the compounds in $[D_8]$toluene at −78°C and warming of the mixture to −50°C, all NMR data show that the selenium diimide **2** ($\delta^{77}Se$ = 1653.8[4b]) is no longer present. Under these conditions, there is clear evidence for the formation of Et_2Se (**4a**), the four-membered ethaneseleninimidic amide derivative **6** ($\delta^{11}B$ = 17.7; $\delta^{77}Se$ = 1010.0), ethene (no ethane), (*tert*-butylamino)diethylborane (**8**) ($\delta^{11}B$ = 46.5), and bis(diethylboryl)-*tert*-butylamine (**9**) ($\delta^{11}B$ = 57.9). A weak signal in the ^{77}Se-NMR spectrum (−50°C) at δ = 711.0 is tentatively assigned to {*tert*-butyl[(*tert*-butylamino)-selenyl]amino}diethylborane (**7**), the most likely precursor of **8**. After a few minutes at room temperature, compound **6** decomposes completely to **8**, **9**, and **4a**. At room temperature, the ^{77}Se resonance at δ = 711.0, tentatively assigned to **7**, can no longer be detected.

Compound **6** results from 1,2-ethyloboration, corresponding to the reaction of **1** with **A** [eq. (1)]. The proposed structure for **6** as a monomer is based on the line width of its ^{11}B-NMR signal ($\Delta\nu_{1/2}$ = 80 ± 5 Hz) which is too small for a dimer (compare with $\Delta\nu_{1/2}$ ≈ 300 Hz for the ^{11}B-NMR signal of the dimer $\mathbf{5_2}$ or an oligomer. Furthermore, all ^{13}C-NMR signals of **6** are very similar to those of its sulfur analogue which was prepared recently by a different route[8]. The decomposition of **6** with C_2H_4 elimination takes place in the same way as observed for the sulfur analogue of **6**; however, the sulfur compounds analogous to **7** and **8** are stable at room temperature for several days[8]. The olefin elimination was frequently observed to take place under mild reaction conditions in the case of alkanesulfinic acid derivatives[9] including ethane derivatives[10]. As expected, compound **7** must be much less stable than its sulfur analogue, and the apparently (indicated by the NMR spectra) more or less synchronous formation of the aminoborane **8**, diborylamine **9**, and Et_2Se (**4a**) [eq. (3c,d)] suggests the intermediacy of [*t*Bu−NSe] analogous to [R−NS] which is known to originate from derivatives of the type $R(H)N-S-NR'_2$[11]. In the presence of an excess of Et_3B, [*t*Bu−NSe] can be trapped to give the diborylamine **9** and Et_2Se (**4a**) [eq. (3d)].



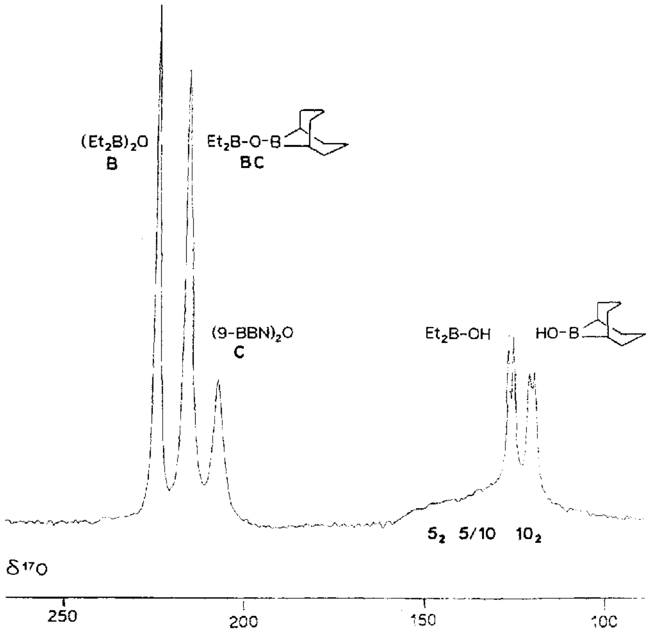
Exchange of Boryl Groups Between Organoboron-Oxygen Compounds: Synthesis of Compound $\mathbf{10_2}$

Since we failed to obtain crystals of $\mathbf{5_2}$ suitable for X-ray structural analysis, an *O*-transborylation reaction was carried out in order to exchange the Et_2B groups in $\mathbf{5_2}$ for 9-BBN groups. The equilibria shown in eq. (4) are shifted towards $\mathbf{10_2}$ because of its stability as a dimer and its low solubility in toluene. Crystals of $\mathbf{10_2}$ obtained from this reaction were directly suitable for X-ray structure analysis (vide infra). The ^{11}B-NMR spectrum of the reaction solution shows signals for $\mathbf{5_2}$, **5/10**, and $\mathbf{10_2}$ (not resolved) at δ = 13−14, for **C** (δ = 58.0) and **B** (δ = 53), and at δ = 55.0 (two signals, just resolved) for the mixed oxide Et_2B-O-9-BBN (**B/C**).



The exchange of boryl groups becomes readily evident by studying the reaction of **5**$_2$ with either **B**(^{17}O) or **C**(^{17}O). In the former case, the exchange takes place at room temperature in C_6D_6 solution as shown by the ^{17}O-NMR spectrum with signals at $\delta = 224.0$ for **B** and 130 for **5**$_2$. If **C**(^{17}O) is used, after heating at 50 °C in C_6D_6 for 30 min the ^{17}O-NMR spectrum shows signals for **C** ($\delta = 207.0$), **B** (224), and the mixed oxide Et_2B-O-9-BBN (**B/C**) (216.0). In the range between $\delta^{17}O$ 110 and 140, there are broad overlapping signals of the dimer **5**$_2$, the derivate **5/10** built formally from the monomers **5** and **10**, containing one Et_2B and one 9-BBN group, and of the dimer **10**$_2$. This exchange reaction is accompanied by decomposition (ethene elimination) and formation of Et_2B-OH and 9-BBN−9-OH (see Figure 1). The exchange between **5**$_2$ and **D**(^{17}O) proceeds fast at room temperature, and a ^{17}O-NMR spectrum of the C_6D_6 solution shows the broad signal of **5**$_2$(^{17}O) ($\delta = 130$) in addition to the sharp signal of **D**(^{17}O) (146).

Figure 1. 54.2-MHz ^{17}O-NMR spectrum (110000 transients, acquisition time 0.02 s): exchange reaction between **5**$_2$ and **C**(^{17}O) after heating to 50 °C in [D$_8$]toluene; both doublets on top of the broad resonance for **5**$_2$, **5/10**, and **10**$_2$ change to singlets by ^1H decoupling and are assigned to Et_2BOH and (9-BBN)−9-OH[7b,c] as a result of partial decomposition of **5**$_2$

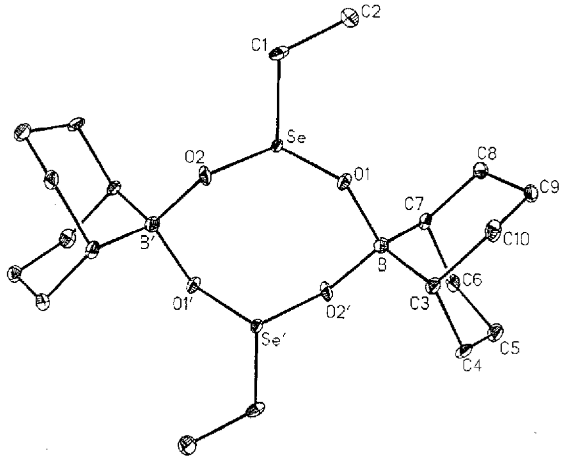


These experiments demonstrate that the eight-membered ring in **10**$_2$, **5/10** and in particular in **5**$_2$ is readily opened and closed. Therefore, one can also assume that the dimer **5**$_2$ is in equilibrium with its monomer **5**, at least at elevated temperatures (>80 °C). Then it is conceivable that the oxygen compound **5** behaves in a way analogous to the nitrogen derivative **6** [eq. (3b)], suffering C_2H_4 elimination followed by further reactions leading to the formation of ethane, Et_2BOH, $(Et_2B)_2O$ (**B**), and Et_2Se (**4a**).

X-Ray Structural Analysis of Compound 10$_2$

The data relevant to the X-ray structure determination[12] are given in the experimental part, and the molecular structure of **10**$_2$ is shown in Figure 2 together with selected bond lengths and angles. The eight-membered ring has C_i symmetry. The B−O bond length [154.2(3) pm] and the angle O−B−O [107.1(2)°] are similar to those in the eight-membered heterocycle [μ-H-9-(MeO)$_2$−9-BBN]$_2$[13] (154.1 pm; 105.3°). This is also true for the almost perpendicular arrangement (94.2°) of the planes O−B−O and C3−B−C7, and the geometry of the 9-BBN skeletons is perfectly comparable. As expected, the bond angles O−Se−O [99.2(1)°], O−Se−C [97.2(1), 96.1(1)°] are small, and the sum of the bond angles at each of the selenium atoms (292.5°) indicates their pyramidal surroundings. The bond lengths Se−O [171.8(1) pm] and Se−C [193.0(2) pm] are found in the expected range. Owing to the bond angles Se−O−B [117.8(1) and 122.7(1)°] the eight-membered ring is strongly folded with an angle of 83.8° between the O−B−O and O−Se−O planes.

Figure 2. Molecular structure of the dimeric 1,5-cyclooctanediylboryl-ethyl-seleninide **10**$_2$[a]



[a] Selected bond lengths [pm] and bond angles [°]: Se−O1 171.8(1), O1−B 154.2(3), O2'−B 154.2(3), Se−C1 193.0(2), C7−B 160.1(3), C1−C2 151.6(3), C7−C8 154.0(3); O1−Se−O2 99.2(1), Se−O2−B' 122.7(1), O1−B−O2' 107.1(2), Se−O1−B 117.8(1), C3−B−C7 108.5(2), Se−C1−C2 112.0(1), O2−Se−C1 96.1(1), O1−Se−C1 97.2(1); angles between planes [°]: O1O2'B/C3C7B 94.2, O1BO2/O1SeO2 83.8, C3BC7/O1SeO2 11.8.

To summarize, it was shown that the reaction of both selenium dioxide (**1**) and selenium bis(*tert*-butylimide) (**2**) with triethylborane (**A**) proceeds stepwise by 1,2-ethyloboration in the first step, followed by ethene and (for the reaction of **1** with **A**) also by ethane elimination. For the first time, intermediates were characterized by multinuclear magnetic resonance in solution, and in the case of **10**$_2$ by X-ray structure analysis.

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Experimental

All reactions and handling of samples for measurements were carried out under argon, strictly observing precautions to exclude air and moisture. − Elemental analyses: Dornis & Kolbe, Mülheim a.d. Ruhr. – The dried solvents were freshly distilled and stored under argon. – DSC[14a]: DuPont 9900. – EI MS (70 eV)[14b]: Finnigan MAT CH5. – NMR: Bruker AC 200, Bruker AC 300, Bruker ARX 250, Bruker WM 400 (all used for ^{1}H, ^{11}B, ^{13}C, ^{17}O[14c] and ^{77}Se NMR in solution) and Bruker MSL 300 (solid-state ^{77}Se CP/MAS NMR); chemical shifts are given with respect to Me_4Si [$\delta^{1}H(C_6D_6) = 7.15$; $\delta^{13}C(C_6D_6) = 128.0$], $Et_2O \cdot BF_3$ [$\delta^{11}B = 0$ with $\Xi(^{11}B) = 32.083971$ MHz], H_2O ($\delta^{17}O = 0$) and Me_2Se [$\delta^{77}Se = 0$ with $\Xi(^{77}Se) = 19.071523$]. – The starting materials **2**[4], Et_3B (**A**)[15], $(Et_2B)_2O$ (**B**)[16], $(9\text{-BBN})_2O$ (**C**)[17], $(EtBO)_3$ (**D**)[18], and the ^{17}O-labeled compounds **B**(^{17}O), **C**(^{17}O), and **D**(^{17}O)[19] were prepared according to literature procedures. SeO_2 (**1**), H_2SeO_3 (**3**) (Merck), and ^{17}O-enriched (≈5% ^{17}O) water (Ventron) were used as commercial products.

X-Ray Structural Analysis of $\mathbf{10_2}$[12]: Crystal size 0.41 × 0.28 × 0.25 mm, colorless, $T = 118$ K, monoclinic: $a = 667.1(1)$, $b = 1282.5(1)$, $c = 1289.1(1)$ pm, $\beta = 93.06(1)°$, $P2_1/n$; $Z = 2$; diffractometer: Nicolet R3m/V, $\mu(\text{Mo-}K_\alpha) = 3.05\ \text{mm}^{-1}$, $\lambda = 0.71069$ Å, ω scan, $2\Theta_{max} = 50°$, $F(000) = 532$ e; reflections: measured 2163, independent 1925, observed 1807 [$F_o > 4\sigma(F)$]; empirical absorption correction: max./min. transmission 0.96/0.76, R_{merg} 0.057/0.046; refined parameters 168; structure solution: direct methods; calculations: SGI Iris Indigo, program: SHELXTL-PLUS; $R = 0.0266$, $R_w = 0.032$; max. residual electron density 0.685 e/Å^3.

^{17}O-Enriched Selenium Dioxide [**1**(^{17}O)] *and Selenous Acid* [**3**(^{17}O)]: Selenium dioxide (**1**) and selenous acid (**3**) exchange ^{16}O for ^{17}O in a mixture of ^{17}O-enriched water and [D$_8$]THF (ratio 1:2 or 1:1) as shown by the ^{17}O-NMR signal at $\delta = 175$ ($\Delta\nu_{1/2} \approx 1200$ Hz). A broad ^{17}O signal of H_2O under these conditions is found at $\delta = -6$ to -8 ($\Delta\nu_{1/2} \approx 700$ to 1200 Hz, depending on concentration). Dry **1**(^{17}O) is obtained after removal of THF and water.

2,4,4,6,8,8-Hexaethyl-1,3,5,7,2,6,4,8-tetraoxadiselenadiboratocane ($\mathbf{5_2}$) *from* **1** *and* **A**: A suspension of 479.4 mg (4.32 mmol) of **1** in 1.26 g (12.8 mmol) of triethylborane (**A**) is heated to 45–65 °C to give a colorless, clear solution and 1.61 mmol of a gas consisting (MS) of ethane (62%) and ethene (38%). After removal of all volatile material (**A**, **B**, **D**, and **4a**) in vacuo (0.001 Torr), a colorless solid is left ($\delta^{11}B = 14.0$; $\delta^{77}Se = 1168.0$) which is identified subsequently as compound $\mathbf{5_2}$. If the clear solution is heated to 80–85 °C, further evolution of 2.23 mmol of gas is observed, consisting (MS) of ethane (85.3%) and ethene (14.7%). The ^{11}B- and ^{77}Se-NMR signals of $\mathbf{5_2}$ are no longer observed, whereas the ^{77}Se-NMR signal of Et_2Se (**4a**) becomes stronger, and a weak ^{77}Se-NMR signal ($\delta = 336.0$) appears for Et_2Se_2 (**4b**).

$\mathbf{5_2}$ (m.p. 70–73 °C, after recrystallization from heptane: 80 °C; DSC: 79.6 °C, dec. >130 °C). – EI MS, *m/z* (%): 391 (<1) [B_2Se_2], 335 (<1) [BSE_2], 277 (<1), 237 (<1). – ^{1}H NMR (C_6D_6): $\delta = 2.17$ (4H, CH_2Se), 1.18 (12H, CH_3CH_2B), 0.8 (14H, CH_2B, CH_3CH_2Se). – ^{11}B NMR (heptane): $\delta = 14.1$ ($\Delta\nu_{1/2} = 300 \pm 10$ Hz). – ^{13}C NMR (C_6D_6): δ [$J(^{77}Se,^{13}C)$] = 46.2 [69.4] (CH_2Se), 16.6 (broad, CH_2B), 10.5 (CH_3CH_2B), 5.6 (CH_3CH_2Se). – ^{17}O NMR (C_6D_6): $\delta = 130.0$. – ^{77}Se NMR (C_6D_6): $\delta = 1168.0$. – Solid-state ^{77}Se CP/MAS NMR (90° pulses ^{1}H and ^{77}Se 5 μs, contact time 5 ms, repetition time 5 s, 160 transients, rotation 2855 and 3695 Hz): $\delta = 1174.5$. – $C_{12}H_{30}B_2O_4Se_2$ (417.9): calcd. C 34.49, H 7.24, B 5.17, Se 37.79; found C 34.42, H 7.40, B 5.02, Se 37.24.

The same reaction, carried out with **1**(^{17}O), leads to the formation of **B**(^{17}O) ($\delta = 224.0$); **D**(^{17}O) ($\delta = 146.0$), and $\mathbf{5_2}$(^{17}O) ($\delta = 130$) as shown by ^{17}O-NMR spectroscopy.

$\mathbf{5_2}$ *from* **1** *and* **B**: A mixture of 111.0 g of **1** (1 mol) and a threefold excess of tetraethyldiboroxane (**B**) is heated at 120 °C for 25 min. The color of the mixture turns first to red-brown and then to yellow, and 0.4 mol of gas is set free. ^{11}B-NMR spectra showed the presence of a small amount of $\mathbf{5_2}$ ($\delta = 14.0$) and **D** (33.0) in addition to **B** (53.0). The same reaction with **B**(^{17}O), performed on a small scale for NMR measurements, shows the formation of $\mathbf{5_2}$(^{17}O) and **D**(^{17}O) as revealed by ^{17}O-NMR spectroscopy.

Reaction between **1** *and* **D**: A suspension of 0.55 g (5 mmol) of **1** in an excess of triethylboroxine (**D**) (2.5 g, 15 mmol) is heated at 145 °C for 3 h to give a red-brown liquid. The ^{11}B-NMR spectrum shows the signal for **D** ($\delta = 33.0$) and a signal at $\delta = 17.6$ for compounds with a BO_3 structure.

Selenous Acid (**3**) *and Ethylboron Compounds* **A**, **B**, *and* **D**: Heating of a mixture of 223.7 mg (1.73 mmol) of selenous acid (**3**) and an excess of **A** (1.6 g, 16.4 mmol) at 55 °C for 1 h gives 2.2 mmol of ethane (MS). ^{11}B- and ^{77}Se-NMR spectra show that the mixture contains **A**, **B**, **D**, Et_2BOH, and the selenium compounds $\mathbf{5_2}$ ($\delta^{77}Se = 1168.0$), **4a** ($\delta^{77}Se = 235.0$), and **4b** ($\delta^{77}Se = 330.0$), and at least one unidentified selenium compound ($\delta^{77}Se = 176.0$). Addition of 1361.5 mg (11.24 mmol) of 9-H-9-BBN in 2 ml of mesitylene and heating at 130 °C for 1.5 h gives 1.74 mmol of H_2. The color of the solution turns from yellow-green over red-brown to dark-green, and black selenium precipitates; then the color of the clear solution changes to green, and then to yellowish.

A suspension of 0.64 g (5 mmol) of **3** in an excess of **D** (2.5 g, 15 mmol) is heated at 145 °C for 3 h to give a green solid covered by an orange liquid. The ^{11}B-NMR spectrum shows the signal for **D** ($\delta = 33.0$) and a weak signal at $\delta = 18.0$ for compounds with a BO_3 structure.

$\mathbf{5_2}$ *from* **3** *and* **B**: A mixture of 1.2 g (9.3 mmol) of **3** and 4.5 g (29.2 mmol) of **B** is heated to 80 °C to liberate 0.79 mmol of ethane. The resulting yellow, clear solution is heated at 110 °C for 30 min. Fractional distillation (14 Torr, <25 °C) gives first 1.5 g of a mixture of Et_2BOH [$\delta^{1}H(OH) = 6.07$[16b]] and **D** and then 2.0 g (0.01 Torr, <50 °C) of a yellowish liquid (**B**, **D**, and, according to ^{77}Se NMR, **4a** and a small amount of **4b**), leaving 1.4 g (72%) of $\mathbf{5_2}$ (with analytical data identical with those obtained from the reaction of **1** with **A**).

Selenium Bis(tert-butylimide) (**2**) *and Triethylborane* (**A**): A solution of freshly prepared **2** (0.33 g, 1.5 mmol) in 2 ml of [D$_8$]toluene is cooled to −78 °C before an excess of **A** (0.49 g, 5 mmol) is added by means of a syringe. The mixture is allowed to warm up to −50 °C for NMR measurements. This allowed the identification of the 1,2-ethyloboration product **6**, Et_2Se (**4a**), aminoborane **8**, diborylamine **9**, and ethene. The weak ^{77}Se-NMR signal at $\delta = 711.0$ is assigned tentatively to the intermediate **7**.

6: ^{11}B NMR ([D$_8$]toluene, 25 °C): $\delta = 17.7$ ($\Delta\nu_{1/2} = 80 \pm 5$ Hz). – ^{13}C NMR ([D$_8$]toluene, −50 °C): $\delta = 45.6$ (CH_2Se), 31.5, 53.7 [$(CH_3)_3CN$], 22.9, 16.9 (broad, CH_2B), 12.4, 11.8 (CH_3CH_2B), 4.4 (CH_3CH_2Se). – ^{77}Se NMR: $\delta = 1010.0$.

8: ^{11}B NMR ([D$_8$]toluene, 25 °C): $\delta = 46.5$. – ^{13}C NMR ([D$_8$]toluene, −50 °C): $\delta = 33.2$, 52.1 [$(CH_3)_3CN$], 13.1, 11.5 (broad, CH_2B), 10.4, 10.1 (CH_3CH_2B).

9: ^{11}B NMR ([D$_8$]toluene, 25 °C): $\delta = 57.9$. – ^{13}C NMR ([D$_8$]toluene, −50 °C): $\delta = 32.5$, 49.2 [$(CH_3)_3CN$], 14.8 (broad, CH_2B), 9.6 (CH_3CH_2B).

4,4:8,8-Bis(1,5-cyclooctanediyl)-2,6-diethyl-1,3,5,7,2,6,4,8-tetraoxadiselenadiboratocane ($\mathbf{10_2}$) *from* $\mathbf{5_2}$ *and* **C**: A solution containing 693.5 mg (1.66 mmol) of $\mathbf{5_2}$ and 993.3 mg (3.85 mmol) of **C** in 20 ml of toluene is clear at first and then becomes cloudy. After heating at 70 °C for 20 min, the solution becomes clear again, but on cooling to room temp. colorless crystals of $\mathbf{10_2}$ precipitate. After decantion of the solution, the crystals are washed with heptane and dried in vacuo (0.001 Torr). The yields is 760 mg (88%)

of compound **10_2** as colorless needles [dec. >168 °C (DSC)]. – EI MS, *m/z* (%): 399 (<1), 387 (<1), 304 (ca. 1), 275 (2). – ^1H NMR ([D_8]toluene, 90 °C): δ = 2.35 (H_2CSe), 2.0, 1.8, 1.62, 0.73 ($H_{14}C_8B$), 0.94 ($C\textit{H}_3CH_2Se$). – ^{11}B NMR ([D_8]toluene, 90 °C): δ = 13.7 ($\Delta\nu_{1/2}$ = 400 Hz). – ^{13}C NMR ([D_8]toluene, 90 °C): δ = 46.6 (CH_2Se), 33.3, 33.6 (β-C), 28.0 (broad, α-CB), 25.0 (γ-C), 5.2 ($\textit{C}H_3CH_2Se$). – $C_{20}H_{38}B_2O_4Se_2$ (522.1): calcd. C 46.01, H 7.34, B 4.14, Se 30.25; found C 45.93, H 7.24, B 4.05, Se 30.24.

The O-exchange reactions between **5_2** and the ^{17}O-enriched boranes **B**(^{17}O), **C**(^{17}O), and **D**(^{17}O) are carried out on a small scale for ^{17}O-NMR measurements as described in the text (see also Figure 1).

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