1,3,2-Diselenaborolanes with an Annelated Dicarba-*closo*-dodecaborane(12) Unit: Synthesis, Molecular Structure and Reactivity

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Dedicated to Professor Max Herberhold on the occasion of his 75th birthday

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Exchange reactions of 2,2-dimethyl-1,3-diselena-2-silacyclopentane and 2,2,3,3-tetramethyl-1,4-diselena-2,3-disilacyclohexane, as the 4,5- and 5,6-[1,2-dicarba-*closo*-dodecaborano(12)] derivatives, respectively, with boron trihalides (BCl₃, BBr₃, BI₃) and dichlorides (PhBCl₂, *i*Pr₂NBCl₂) afford the corresponding 1,3,2-diselenaborolanes in essentially quantitative yield. The products were characterized in solution by multinuclear magnetic resonance spectroscopy (¹H, ¹¹B, ¹³C, ²⁹Si, ⁷⁷Se), and for two products, in the solid state by X-ray

Introduction

The multifaceted chemistry of 1.2-dicarba-closo-dodecaborane(12) ("ortho-carborane")^[1,2] is based to a great extent on metalation, for example, 1,2-dilithiation,^[1-3] taking advantage of the reactive metal-carbon bonds. Thus, insertion of chalcogens into the C-Li bonds is an obvious option, which was originally developed and exploited for sulfur.^[3c-3e] The development of selenium chemistry in this field appears to be particularly attractive, considering the rather favorable NMR spectroscopic properties of 77 Se (I = 1/2; nat. abund. 7.58%).^[4] The dianion A (used as its lithium salt) has already proved valuable as a versatile ligand in transition metal chemistry^[5-8] and applications in maingroup-element chemistry are also emerging.^[9-15] In our experience, it is preferable to use A after careful isolation^[9] to avoid side reactions. Observing these precautions, the cyclic selenasilanes 1 and $2^{[9]}$ could be obtained in good yield (Scheme 1) as useful starting materials for further syntheses.

As part of the main group chemistry of \mathbf{A} , the synthesis of cyclic borane derivatives presents a major challenge. So far, the products derived from \mathbf{A} , structurally characterized in solution and in the solid state, contain tetracoordinate boron.^[12,14] It was shown for reactions of \mathbf{A} with boron halides that the unavoidable presence of diethyl ether in rea-

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structural analysis. Attempts to synthesize the boron fluoride failed, and the methoxy derivative was obtained in a mixture with a decomposition product. The gas-phase structures of all relevant products were optimized by DFT hybrid methods [RB3LYP/6-311+G(d.p) level of theory], and NMR parameters (shielding constants and spin–spin coupling constants) were calculated. The calculated data compare well with experimental data, both for the structures and the NMR spectroscopic parameters.



Scheme 1. 1,2-Diselenolato-1,2-dicarba-*closo*-dodecaborane(12) dianion **A** as its dilithium salt, the precursor to cyclic selenasilanes **1** and **2**.

gent A gives rise to problems (e.g., diethyl ether cleavage).^[14] Therefore, in the present work, we report on the exchange reactions of the cyclic selenasilanes **1** and **2** with boron halides aiming for the synthesis of the first 1,3,2diselanaborolanes. With the exception of 1,2,4,3,5-triselenadiborolanes,^[16] and the poorly characterized iodide (MeSe)₂B-I,^[17] no other noncyclic or cyclic boron halides containing two B–Se bonds are known. The products observed or obtained here were studied by multinuclear magnetic resonance spectroscopy, and in two cases by X-ray structural analysis. Gas phase geometries were optimized

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for many of the products by DFT hybrid methods, and NMR parameters (chemical shifts and spin–spin coupling constants) were calculated and compared with experimental data.

Results and Discussion

Exchange Reactions of the Selenasilanes 1 and 2 with Boron Halides

In a previous study,^[9] the cyclic disilane derivative 1 was found to be somewhat more reactive than 2 in exchange reactions with chlorosilanes. Therefore, both silanes 1 and 2 are attractive starting materials to explore exchange reactions with boron halides (Scheme 2). All reactions proceeded smoothly to afford the 1,3,2-diselanaborolanes in essentially quantitative yield as air- and moisture-sensitive oils (4, 5) or solids (3, 6, 7). The progress of the reactions was conveniently monitored by ²⁹Si NMR spectroscopy, following the changes in the intensities of the ²⁹Si NMR signals for 1 or 2 and Me₄Si₂X₂ or Me₂SiX₂, respectively. By contrast, B(OMe)₃ did not react with 1 at ambient temperature. Heating of the mixture in toluene led to decomposition.

The reaction of 1 or 2 with $MeOBCl_2$ or $PhOBBr_2$ gave the boron halides 5 and 6 instead of the methoxy or phenoxy derivatives, respectively. Addition of an excess of $B(OPh)_3$ to this mixture shifted the equilibrium into the direction of the phenoxy derivative **8** (Scheme 3) accompanied by slow decomposition.

To obtain better evidence for the methoxy derivative, the reaction of **5** with $B(OMe)_3$ was studied (Scheme 4). The NMR spectra of the reaction mixture showed the presence of the desired compound **9** along with decomposition products, of which **10** could be identified by NMR spectroscopy. It cannot be excluded that $B(OMe)_3$ contained traces of MeOH.



Scheme 4. Exchange reaction of the boron chloride 5 with $B(OMe)_3$.



Scheme 2. Synthesis of 1,3,2-diselenaborolanes 3-7 by exchange reactions of selenasilanes with the respective boron halides.



Scheme 3. Exchange reactions of 1 or 2 with MeOBCl₂ and PhOBBr₂.



Scheme 5. Products identified in the reaction of 1 and 2 with BF_3 -OEt₂.

Various attempts to prepare the boron fluoride analogous to 5–7 were unsuccessful; the treatment of 1 or 2 with a solution of gaseous BF₃ in toluene gave decomposition products of which only the diselenol $1,2-(HSe)_2-1,2-C_2B_{10}H_{10}^{[12]}$ (11) could be identified. The reaction of 1 with BF₃–OEt₂ proceeded slowly after heating to give Me₄Si₂F₂ along with a mixture of three products 11–13 without B–Se bonds. The analogous reaction of 2 proceeded in a similar way, and the compounds 12, 13, and 14 as a mixture, all without B–Se bonds, could be identified by NMR spectroscopy (Scheme 5). A final attempt failed to convert 5 by treatment with SbF₃ into the corresponding fluoride.

The proposed structures of 3-9 in solution follow conclusively from the characteristic NMR spectroscopic data set (Table 1). In addition to the typical set of four ¹¹B(carbor-

ane) NMR signals, the ¹¹B NMR spectra clearly indicate the presence of three-coordinate boron, and each δ^{11} B value is typical of the effect exerted by the respective substituent at the boron atom in the 1,3,2-diselenaborolane.^[18] The neighborhood to selenium should give rise to one-bond ⁷⁷Se-¹¹B spin-spin coupling. Although the ¹¹B NMR signals are somewhat broad, ⁷⁷Se satellites are visible under certain conditions in the cases of **6** and **7** (Figure 1). The ⁷⁷Se NMR spectra are more enlightening in this respect, since at least in the cases of **1** the boron halides **5**–**7**, the ⁷⁷Se NMR signals are split into partially relaxed 1:1:1:1 quartets (Figure 1). In the cases of **3**, **4**, and **8**, splitting due to ⁷⁷Se-¹¹B spin-spin coupling is not resolved in the ¹¹B or ⁷⁷Se NMR spectra. The ⁷⁷Se NMR signals for **3**, **4**, and **8** appear as broadened singlets. The ⁷⁷Se NMR spectrum of **9** (Fig-

	3 (R = Ph)			$4 (R = iPr_2N)$		5 (X = Cl)	6 (X = Br)	7 (X = I)	8 (R = OPh)	9 (R = OMe)
	[D ₈]toluene 298 K	CD ₂ Cl ₂ 298 K	CD ₂ Cl ₂ 243 K	[D ₈]toluene 298 K	[D ₈]toluene 238 K	[D ₈]toluene 298 K	[D ₈]toluene 298 K	[D ₈]toluene 298 K	[D ₈]toluene 298 K	[D ₈]toluene 298 K
$\delta^{13}C[C(1,2)]$	75.6 [10.6] [140.4]	75.7 [10.4] [141.0]	74.9	71.0	68.9, 73.2	73.5 [10.2] [137.8]	75.7 [138.2]	79.7 [10.1] [142.1]	69.7	69.5
Other δ^{13} C data	Ph: 128.8 (C_m), 133.6 (C_p), 133.8 (C_o) [9.0], n.o. (C_i)	Ph: $129.2 (C_m),$ $134.2 (C_p),$ $134.0 (C_o)$ [8.6], n.o. (C _i)	Ph: 128.6 (C _m), 133.8 (C _p), 133.7 (C _o), 132.9 [br] (C _i)	NMe ₂ : 21.7 (Me) 53.2 (br) (NCH)	NMe ₂ : 19.8, 22.3 (Me), 45.6, 60.6 (NCH)	_	-	-	OPh: 118.5 (C _m), 126.2 (C _p), 130.4 (C _o) 156.3 (C _i)	OMe: 60.3 [10.4]
δ^{11} B(BSe)	76.2	76.3	n.o.	45.7	n.o.	68.6 $h_{1/2} = 71 \text{ Hz}$	64.7 ^[b] $h_{1/2} = 70 \text{ Hz}$	52.2 (98.0) h _{1/2} = 75 Hz	55.5 $h_{1/2} = 180 \text{ Hz}$	53.9 $h_{1/2} = 120 \text{ Hz}$
δ^{11} B(calcd.)	82.8			55.0		80.6	84.6			62.1
δ^{77} Se	609.9 $h_{1/2} = 85 \text{ Hz}$	609.7 $h_{1/2} = 120 \text{ Hz}$	603.6	441.5 $h_{1/2} = 240 \text{ Hz}$	418.4, 449.3	622.0 (83.0)	648.2 (90.0)	694.4 (103.0)	484.6 $h_{1/2} = 110 \text{ Hz}$	469.6 (65.0±10)
δ^{77} Se(calcd.)	580.8 [-161.1]] (-82.4)		407.0 [–167.9] 442.0 [–167.9]	(-83.4) (-83.4)	584.9 ^[12]	614.1 [12]			445.3 (-80.2) [+8.6] (³ J) [-159.7] (¹ J)

Table 1. ¹³C, ¹¹B, and ⁷⁷Se NMR spectroscopic data^[a] of the carborane derivatives 3–9.

[a] Coupling constants ${}^{n}J({}^{77}\text{Se},{}^{13}\text{C})$ are given in brackets [± 0.5 Hz]; ${}^{1}J({}^{77}\text{Se},{}^{11}\text{B})$ in parentheses (± 0.5 Hz); [br] denotes broad ${}^{13}\text{C}$ resonances of boron-bonded carbon atoms; n.o. = not observed. [b] In hexane: $\delta {}^{11}\text{B}$: 65.5 [BSe, ${}^{1}J({}^{77}\text{Se},{}^{11}\text{B})$ = 82 Hz].



Figure 1. 77 Se NMR and 11 B NMR spectra of the 1,2-dicarba-*closo*-dodecaborane **5** (A), **6** (B, C), and **7** (D) at 23 °C, 10–15% solution (0.4–0.5 mol/L).

ure 3), however, shows a partially relaxed quartet, of which the separation of the inner lines can just be measured to give a coupling constant of ${}^{1}J({}^{77}\text{Se},{}^{11}\text{B}) = 65 \text{ Hz}.$

The ¹H(NCH) and ¹³C(NC) NMR signals of the diisopropylamino derivative **4** are broad at room temperature, sharpen upon heating, and change into separate signals at lower temperature. At low temperature, there are also two signals each for the methyl groups, the ¹³C(carborane), as well as for the ⁷⁷Se nuclei (Figure 2). This is in agreement with restricted rotation about the NC(*i*Pr) bonds and a preference of the structure as determined for the crystalline material (see below). Apparently, this involves a so-called gear-mesh mechanism.^[19] This mechanism has been properly analyzed for aminoboranes solely in the case of { η^5 -[1(diisopropylamino)borole]}metal complexes.^[20] In the case of compound **4**, it is noteworthy that the barrier to rotation is rather high, when compared with the aforementioned complexes (for the borole–Cr(CO)₃ complex: $\Delta G^{\#}_{coal} = 42 \pm 2 \text{ kJ mol}^{-1}$ ^[20]) as shown by the evaluated^[21] energy of activation for **4** ($\Delta G^{\#}_{coal} = 52 \pm 2 \text{ kJ mol}^{-1}$).

In the ¹³C{¹H} NMR spectrum of **9**, the ¹³C(OMe) NMR signal is accompanied by ⁷⁷Se satellites (Figure 3, A), proving the absence of fast exchange in solution. This is the first example of this type of vicinal coupling in boranes. The value ${}^{3}J({}^{77}\text{Se},{}^{13}\text{C}) = 10.4$ Hz represents the average for conceivable rotamers. Calculations predict a minimum in energy for the coplanar arrangement of the atoms in the Se₂BOC unit, and the mean value of the calculated coupling



Figure 2. 62.9 MHz ${}^{13}C{}^{1}H$ NMR and 47.7 MHz 77 Se NMR spectra of **4** (in [D₈]toluene) (upper trace: at 378 K, middle trace: at 298 K, lower trace: at 238 K; given assignments follow calculated chemical shifts).



Figure 3. (A) 125.8 MHz ${}^{13}C{}^{1}H$ NMR spectrum of the mixture of 9 and 10 (in [D₈]toluene, at 25 °C). (B) 47.7 MHz ${}^{77}Se$ NMR spectrum from 9 (in [D₈]toluene, at 25 °C).

constants (+8.6 Hz) for the *cis*- (+3.1 Hz) and *trans*-coupling pathways (+14.1 Hz) is close to the experimental value.

Formation of Adducts

Since the isolation of suitable crystalline materials of the halides 5–7 turned out to be difficult, we tried to isolate

such materials for adducts. The results are shown in Scheme 6 for the reaction of **5** with pyridine, 2,2'-bipyridine and *N*-methylpyrrolidine. In each case, the adduct formation is accompanied by further reactions leading mainly to the spirocyclic borate anion **16**, which we have already prepared and characterized through a different route.^[14] NMR spectroscopic data (Table 2) clearly indicate the formation of the adducts **15a** and **15b**, whereas no adduct was ob-

served in the reaction of **5** with 2,2'-bipyridine. Crystalline material was isolated for **15b** (see below). Additional weak ¹¹B NMR signals, typical of tetracoordinate boron atoms, were observed for the reaction solutions and assigned to the boronium cations **17a** (Figure 4, A) and **17b**. From a mix-

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ture containing **5** and pyridine, crystals of a rather insoluble material were isolated in low yield. Although these crystals were of poor quality for accurate X-ray diffraction studies, the data set collected allowed the deduction of at least the structural features of the boronium cation 17a.



Scheme 6. Reactions of the boron chloride 5 with pyridine, N-methylpyrrolidine and 2,2'-bipyridine.

Table 2. ¹³C, ¹¹B, and ⁷⁷Se NMR spectroscopic data^[a] of the carborane derivatives 10, 12, 14–16.

	10	12	14	15a		15b	16a	16b	16c
	[D ₈]toluene	[D ₈]toluene	[D ₈]toluene	CD ₂ Cl ₂	[D ₈]toluene	[D ₈]toluene	CD ₂ Cl ₂	[D ₈]toluene	CD ₂ Cl ₂
$\delta^{13}C[C(1,2)]$	68.2 [133.0] (SeH), 72.8 [161.0] (SeMe)	68.2 (SeH) 73.3 {-9.6} (SeEt)	72.5 {-11.4} 72.6 {-10.5}	73.7	74.1 [8.7] [151.7] {-8.7}	72.7	76.3	76.9	76.3
Other δ^{13} C data	Me: 11.5 [69.3]	Et: 13.6 [17.6] 26.1 [64.8]	Et: 13.5 [17.6] 26.9 [64.8]	py: 125.4 (C_{β}), 140.0 (C_{γ}), 146.9 (C_{a})	py: 126.0 (C _β), 143.4 (C _γ), 145.9 (C _a)	$\begin{array}{c} C_{4}H_{8}NCH_{3}:\\ 22.5 \ (C_{\beta}),\\ 46.9 \ (Me),\\ 61.1 \ (C_{\alpha}) \end{array}$	pyH ⁺ : 127.0 (C _β), 142.5 (C _γ), 146.5 (C _α)	$C_{4}H_{8}N(CH_{3})H^{+}:$ 23.5 (C _{β}), 40.1 (Me), 54.9 (C _{α})	2,2'-bipyH ⁺ : 123.5, 126.2, 141.1, 147.5, 150.9
δ^{11} B(BSe)	_	_	-	14.0 (45.5) ^[b]	13.9 (45.0)	16.9 (47.6) ^[c]	6.0 (59.0)	6.7 (55.5)	5.9 (58.9)
δ^{77} Se	350.1/54.9/ (SeH), 415.4 (SeMe)	351.7/55.7/ (SeH), 502.2 (SeEt)	489.3 (SeEt), 715.1 (Se–Se)	469.6 (45.4)	467.6 (45.0)	435.6	477.9 (57.1)	477.6 (57.0)	477.9 (61.9)
δ^{77} Se(calcd.)	292.1(SeH), 400.2 (SeMe)	289.4 (SeH), 452.2 (SeEt)	451.2 (SeEt), 841.6 (Se–Se)	436.7 (-70.0) [-18.1]	[-173.7]	413.6 (-72.4) [-179.3], 437.3 (-73.0) [-179.5]	500.7 (-81.8) (for 16 (calcd.	[-191.5]) ^[14])	

[a] Coupling constants ${}^{n}J({}^{77}Se, {}^{13}C)$ are given in brackets [± 0.5 Hz]; ${}^{1}J({}^{77}Se, {}^{11}B)$ in parentheses (± 0.5 Hz), ${}^{1}J({}^{77}Se, {}^{11}H)$ in// / ± 0.5 Hz/; ${}^{1}\Delta^{10/11}B[{}^{13}C(1,2)]$ are given in braces { ± 0.5 ppb}, ${}^{(34)}$ isotope-induced chemical shifts ${}^{1}\Delta$ are given in ppb, and the negative sign denotes a shift of the NMR signal of the heavy isotopomer to lower frequency. [b] $\delta^{11}B$ (calcd.): 24.3 (-70.0). [c] $\delta^{11}B$ (calcd.): 28.0 (-72.4) (-73.0).



Figure 4. ⁷⁷Se NMR and ¹¹B NMR spectra of the reaction solution obtained from the reaction of **5** with pyridine. (A) 47.7 MHz ⁷⁷Se NMR and 80.3 MHz ¹¹B NMR spectra (in CD₂Cl₂, at 25 °C), the mixture of **15a** and **16a** (ratio 2:1) (after 2 h at room temperature in [D₈]toluene). (B) 76.2 MHz ⁷⁷Se NMR and 80.3 MHz ¹¹B NMR spectra (in CD₂Cl₂, at 25 °C), the mixture of **15a** and **16a** (ratio 9:1) (after 1 h at -50 °C and 1 h at room temperature in [D₈]toluene).

DFT Calculations of Molecular Geometries, Chemical Shifts δ^{11} B and δ^{77} Se, and Coupling constants

The optimized geometries calculated at the B3LYP/6-311+G(d,p) level of theory^[22] of **4** and **15b** are in close agreement with the experimental structural data (Table 3).

Table 3. Selected bond lengths [pm] and angles [°] of the of the carborane derivatives 4, 4(calcd.), 15b, and 15b(calcd.).

	4	4 (calcd.)	15b	15b (calcd.)
T [K]	133 K		133 K	
C(1)-Se(1)	192.3(3)	195.5	193.1(4)	195.5
C(2)-Se(2)	193.2(4)	195.6	193.2(5)	195.7
C(1)-C(2)	163.8(5)	163.2	163.4(6)	163.9
Se(1)-B(13)	197.5(4)	200.2	205.9(5)	208.1
Se(2)-B(13)	199.1(4)	199.8	206.5(5)	208.2
B(13)–N	138.0(5)	139.8	160.5(7)	165.8
N-C(3)	147.9(4)	149.1	152.1(6)	152.0
N-C(6)	148.4(4)	149.5	151.2(6)	151.7
N-C(7)			150.4(5)	150.5
B(13)-Cl			185.0(5)	187.1
B(13)-Se(1)-C(1)	96.31(15)	96.5	98.25(19)	98.29
B(13)-Se(2)-C(2)	95.96(15)	96.4	98.03(19)	98.26
Se(1)-C(1)-C(2)	116.5(2)	116.2	116.7(3)	116.87
Se(2)-C(2)-C(1)	116.1(2)	116.4	116.9(3)	116.80
Se(1)-B(13)-Se(2)	115.07(19)	114.5	109.8(2)	109.74
Se(1)-B(13)-N	120.5(3)	120.7	108.1(3)	109.7
Se(2)-B(13)-N	124.5(3)	124.8	110.4(3)	111.1
N-B(13)-Cl			107.3(3)	105.6
Se(1)-B(13)-Cl			111.9(3)	111.10
Se(2)-B(13)-Cl			109.1(2)	109.68
B(13)-N-C(3)	119.6(3)	120.2	111.7(3)	112.3
B(13)-N-C(6)	125.4(3)	125.3	115.1(4)	114.0
B(13)-N-C(7)			110.0(4)	110.5
C(3)-N-C(6)	115.0(3)	114.5	102.6(3)	102.0
Se(1)-C(1)-C(2)-Se(2)-B(13)	1.3		3.0	
Se(1)-C(1)-C(2)-Se(2)	0.2	0.0	1.1	0.1
Distance of B(13) from the				
plane: Se(1)-C(1)-C(2)-Se(2)	5.0		11.8	

Since calculated shielding constants^[23] for ¹¹B, ¹³C, and ⁷⁷Se^[24] agree reasonably well with measured data, the calculated geometries are correct. Considering the large range of δ^{77} Se,^[4] the calculated values are useful for structural assignments (see, for example, Figure 2). In addition to chemical shifts, spin–spin coupling constants can also be calculated^[25] based on optimized geometries. The data in Tables 1 and 2 show that the trend and approximate magnitude of ¹*J*(⁷⁷Se,¹¹B) and ¹*J*(⁷⁷Se,¹³C) coupling constants are predicted correctly. In the case of **9**, the correct prediction of ³*J*(⁷⁷Se,¹³C) (see Figure 3) is noteworthy.

X-ray Structural Analyses of the *ortho*-Carborane Derivatives 4 and 15b

The molecular structures of 4 and 15b are shown in the Figures 5 and 6, respectively, and experimental structural parameters together with calculated data are given in Table 3. The diselenaborolane ring in 4 is almost planar, whereas the analogous ring in 15b is slightly folded. Apparently, the C(1)-C(2) and C-Se bond lengths in both 4 and **15b** are not affected by the nature of the B(13) boron atom. Expectedly,^[26,27] the B(13)–Se bond lengths are shorter in 4 than in 15b. This effect is even more pronounced for the B(13)-N bonds, which in the case of 4 is short [138.0(5)] pm], indicating considerable double-bond character.^[28] The conformation adopted by the N-iPr groups in 4 corresponds closely to the results of NMR spectroscopic measurements at low temperature (Figure 2), in agreement with the calculated gas-phase structure of lowest energy. The B-Se bond lengths in 15b are similar to those reported for the dimethylsulfide adduct of the corresponding B-H derivative.[12]



Figure 5. Two views of the ORTEP plots (50% probabilities; hydrogen atoms have been omitted for clarity) of the molecular structure of the 2-bis(isopropylamino)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-borolane **4** (for selected distances and angles see Table 3).



Figure 6. ORTEP plot (50% probabilities; hydrogen atoms have been omitted for clarity) of the molecular structure of the 2-chloro-2-(*N*-methylpyrrolidine)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-boracyclopentane **15b** (for selected distances and angles see Table 3).

Conclusion

By contrast with previous attempts, a straightforward route to 1,3,2-diselenaborolanes with an annelated dicarba*closo*-dodecaborane(12) unit by the exchange reactions of boron halides with siladiselena heterocycles has been successfully explored. The combination of multinuclear magnetic resonance spectroscopy in solution and DFT calculations of NMR parameters served well even in the characterization of some side products. The X-ray structural analysis of the B–N*i*Pr₂ derivative provided the first structural data of a 1,3,2-diselenaborolane containing a threecoordinate boron atom. Considering the reactivity of B–Se and B–X bonds (X = Cl, Br, I), the new boranes possess synthetic potential for further useful transformations. Of particular interest will be the reactivity towards alkynes with respect to insertion (into B–Se or B–X bonds) or further exchange reactions.

Experimental Section

General: All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The CH₂Cl₂ and CD₂Cl₂ were distilled from CaH₂ under an atmosphere of argon. All other solvents were distilled from Na metal under an argon atmosphere. The starting materials were prepared as described in the literature; 1,^[9] 2,^[9] MeOBCl₂ from B(OMe)₃ and BCl₃ (molar ratio 1:2) in toluene, PhOBBr₂ from B(OPh)₃ and BBr₃ (molar ratio 1:2) in hexane.^[29] Other starting materials were purchased from Aldrich [BCl₃ (1.0 M in toluene), BBr₃ (1.0 M in hexane), BI₃ (\geq 98%), BF₃–OEt₂ (purified by redistillation), PhBCl₂ (97%), *i*Pr₂NBCl₂, B(OMe)₃ (99.999%), B(OPh)₃, pyridine (anhydrous, 99.8%), N-methylpyrrolidine, SbF₃ (98%)], from Messer Griesheim (BF₃) and used as received. 2,2'-Bipyridine (Aldrich, $\geq 99\%$) was sublimed before use (40–45 °C/2 \times 10⁻² Torr). NMR spectroscopic measurements: Bruker DRX 500 and Bruker ARX 250: 1H, 11B, 13C, 77Se, and ²⁹Si NMR [refocused INEPT^[30] based on ${}^{2}J({}^{29}Si,{}^{1}H) = 6-7$ Hz]; Varian INOVA 400: ¹H, ¹¹B, ¹³C, ²⁹Si, ⁷⁷Se NMR; chemical shifts are given relative to Me₄Si [δ^{1} H (CHDCl₂) = 5.33, (C₆D₅CD₂H) = 2.08 (± 0.01); δ^{13} C (CD₂Cl₂) = 53.8, (C₆D₅CD₃) = 20.4 (± 0.1); δ^{29} Si = 0 (±0.1) for Ξ (²⁹Si) = 19.867184 MHz]; external BF₃-OEt₂ $[\delta^{11}B = 0 \ (\pm 0.3) \text{ for } \Xi^{(11}B) = 32.083971 \text{ MHz}], \text{ neat } Me_2Se \ [\delta^{77}Se$ = 0 (\pm 0.1) for Ξ (⁷⁷Se) = 19.071523 MHz]. Assignments of ¹H and ¹¹B NMR spectroscopic signals are based on selective ¹H{¹¹B selective} heteronuclear decoupling experiments. Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet [data for (¹²C, ¹H, ¹¹B, ³⁵Cl, ²⁸Si, ⁸⁰Se)]. Elemental analyses [C(H)] of the boranes 3– 8, and of the adduct 15b did not give satisfactory and reproducible results, most likely on account of boron carbide formation. Melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

All quantum chemical calculations were carried out using the Gaussian 03 program package (Revision-B.02).^[31] Optimized geometries at the RB3LYP/6-311+ g(d.p) level of theory were found to be minima by the absence of imaginary frequencies. NMR parameters were calculated at the same level of theory. Calculated chemical shifts δ^{11} B and δ^{77} Se were converted by δ^{11} B (calcd) = $\sigma(^{11}$ B) – $\sigma(^{11}$ B, B₂H₆), with $\sigma(^{11}$ B, B₂H₆) = +84.1 [δ^{11} B (B₂H₆) = 18 and δ^{11} B (BF₃–OEt₂) = 0] and δ^{77} Se(calcd) = $\sigma(^{77}$ Se) – $\sigma(^{77}$ Se, SeMe₂) with $\sigma(^{77}$ Se, SeMe₂) = +1621.7.

2-Phenyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2borolane (3). Method A: A suspension of 1 (60 mg, 0.144 mmol) in $[D_8]$ toluene (0.6 mL) was cooled to 0 °C and 1.5 equiv. of PhBCl₂ (0.03 mL, 0.23 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 24 h at r.t., the mixture contained 3 together with Me₂Si(Cl)–SiMe₂(Cl) and PhBCl₂. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr) to give 3 as a white solid.

Method B: A solution of **2** (99 mg, 0.277 mmol) in $[D_8]$ toluene (0.6 mL) was cooled to 0 °C and PhBCl₂ (0.036 mL, 0.28 mmol) was added. The progress of the reaction was monitored by ¹¹B and

²⁹Si NMR spectroscopy. After 24 h at r.t., the mixture contained **3** together with Me₂SiCl₂. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr) to give **3** as a white solid.

3: ¹H{¹¹B} NMR (250.1 MHz; [D₈]toluene; 25 °C): δ = 2.78 (br. m, 10 H, HB), 6.80–7.10 (m, 5 H, Ph) ppm. ¹H NMR (250.1 MHz; [D₈]toluene; -50 °C): δ = 2.93 (br. s, 10 H, HB), 6.80 (m, 3 H, Ph), 7.04 (m, 2 H, Ph) ppm. ¹¹B{¹H} NMR (80.3 MHz; [D₈]toluene; 25 °C): δ = -9.2 (4 B), -7.1 (2 B), -5.9 (2 B), -4.7 (2 B), 76.0 (1 B, SeB) ppm. ¹¹H{¹¹B} NMR (250.1 MHz, CD₂Cl₂; 25 °C): δ = 2.30 [br. s, 2 H, HB for δ (¹¹B) = -6.1], 2.37 [br. s, 2 H, HB for δ (¹¹B) = -7.2], 2.64 [br. s, 4 H, HB for δ (¹¹B) = -9.0], 2.78 [br. s, 2 H, HB for δ (¹¹B) = -4.4], 7.35–7.65 (m, 5 H, Ph) ppm. ¹¹B{¹H} NMR (80.3 MHz, CD₂Cl₂; 25 °C): δ = -9.0 (4 B), -7.2 (2 B), -6.1 (2 B), -4.4 (2 B), 76.4 (1 B, SeB) ppm. ¹¹B NMR (80.3 MHz, CD₂Cl₂; 25 °C): δ = -8.9 (d, 4 B, 175 Hz), -7.1 (d, 2 B, 155 Hz), -6.1 (d, 2 B, 160 Hz), -4.3 (d, 2 B), 76.4 (s, 1 B, SeB) ppm. EI-MS (70 eV) for C₈H₁₅B₁₁Se₂ (388.05): *m/z* (%) = 388 (5) [M⁺], 301 (100) [M⁺ - BC₆H₅], 221 (15), 209 (35), 124 (22), 114 (32).

2-Diisopropylamino-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3diselena-2-borolane (4). Method A: A suspension of 1 (60 mg, 0.144 mmol) in [D₈]toluene (0.6 mL) was cooled to 0 °C and 1.5 equiv. of *i*Pr₂NBCl₂ (39 mL, 0.22 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 1 h at r.t., the mixture contained 4 together with Me₂Si(Cl)–SiMe₂(Cl) and *i*Pr₂NBCl₂. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr) to give 4 as a white oil. Single transparent crystals of 4 for X-ray analysis were grown from [D₈]toluene/hexane (1:2) solution after 2 months at -30 °C; m.p. 128–130 °C.

Method B: A solution of **2** (93 mg, 0.258 mmol) in $[D_8]$ toluene (0.6 mL) was cooled to 0 °C and *i*Pr₂NBCl₂ (0.05 mL, 0.28 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 30 min at r.t., the mixture contained **4** together with Me₂SiCl₂ and *i*Pr₂NBCl₂. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr) to give **4** as a white solid.

4: ¹H{¹¹B} NMR (250.1 MHz; [D₈]toluene; 25 °C): $\delta = 0.71$ [d, ³*J*(H,H) = 6.75 Hz, 12 H, NCMe₂], 2.64 [sep, ³*J*(H,H) = 6.75 Hz, 2 H, NCH], 2.78 [br. s, 4 H, HB for $\delta^{(11}B) = -6.8, -5.4$], 2.88 [br. s, 4 H, HB for $\delta^{(11}B) = -8.8$], 2.94 [br. s, 2 H, HB for $\delta^{(11}B) = -3.1$] ppm. ¹H NMR (250.1 MHz; [D₈]toluene; -50 °C): $\delta = 0.48, 0.73$ (br. s, br. s, 6 H, 6 H, NCMe₂), 2.30, 2.38 (br. m, br. m, 1 H, 1 H, NCH), 3.11 (br. s, 10 H, HB) ppm. ¹¹B{¹H} NMR (80.3 MHz; [D₈]toluene; 25 °C): $\delta = -8.8$ (4 B), -6.8 (2 B), -5.4 (2 B), -3.1 (2 B), 45.7 (1 B, SeB) ppm. ¹¹B NMR (80.3 MHz; [D₈]toluene; 25 °C): $\delta = -8.8$ (d, J = 160 Hz, 2 B), -5.4 (d, J = 160 Hz, 2 B), -3.1 (d, J = 175 Hz, 2 B), 45.7 (s, 1 B, SeB) ppm. EI-MS (70 eV) for C₈H₂₄B₁₁Se₂N (411.12): *m/z* (%) = 411 (15) [M⁺], 396 (100) [M⁺ - CH₃], 353 (45) [M⁺ - C₄H₁₀], 310 (5), 221 (12), 143 (13).

2-Chloro-4,5-[1,2-dicarba-*closo*-**dodecaborano(12)]-1,3-diselena-2-borolane (5).** Method A: A suspension of 1 (70 mg, 0.166 mmol) in [D₈]toluene (0.6 mL) was cooled to 0 °C and 1.5 equiv. of BCl₃ (0.25 mL of a 1.0 M solution in toluene, 0.25 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 2 d at r.t., the mixture contained 5 together with Me₂Si(Cl)–SiMe₂(Cl) and BCl₃. Volatile materials were removed in vacuo (1 h, 8×10^{-3} Torr) to give 5 as a yellowish oil.

Method B: A solution of **2** (78 mg, 0.219 mmol) in $[D_8]$ toluene (0.6 mL) was cooled to 0 °C and ca. 2 equiv. BCl₃ (0.4 mL of a 1.0 M solution in toluene, 0.4 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy.



After 2 h at r.t., the mixture contained 5 together with Me₂SiCl₂ and BCl₃. Volatile materials were removed in vacuo (1 h, 8×10^{-3} Torr) to give 5 as a yellowish oil.

5: ${}^{1}H{}^{11}B{}$ NMR (250.1 MHz; [D₈]toluene; 25 °C): δ = 2.60 [br. s, 6 H, HB for $\delta({}^{11}B)$ = -9.0, -4.9], 2.69 [br. s, 4 H, HB for $\delta({}^{11}B)$ = -7.2, -4.9] ppm. ${}^{11}B{}^{1}H{}$ NMR (80.3 MHz; [D₈]toluene; 25 °C): δ = -9.0 (4 B), -7.2 (2 B), -4.9 (4 B), 68.6 (1 B, SeB) ppm. ${}^{11}B$ NMR (80.3 MHz; [D₈]toluene; 25 °C): δ = -9.0 (d, *J* = 180 Hz, 4 B), -7.2 (d, *J* = 158 Hz, 2 B), -4.9 (d, *J* = 150 Hz, 4 B), 68.6 (s, 1 B, SeB) ppm. EI-MS (70 eV) for C₂H₁₀B₁₁Se₂Cl (346.40): *m/z* (%) = 346 (100) [M⁺], 301 (20) [M⁺ – BCl], 253 (5), 218 (8), 207 (7), 161 (6), 124 (22), 112 (18).

2-Bromo-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2borolane (6). Method A: A suspension of 1 (70 mg, 0.166 mmol) in [D₈]toluene (0.6 mL) was cooled to 0 °C and BBr₃ (0.25 mL of a 1.0 M solution in hexane, 0.25 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 2 h at r.t., the mixture contained 6 together with Me₂Si(Br)– SiMe₂(Br) and BBr₃. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr) to give 6 as a yellowish solid.

Method B: A solution of **2** (85 mg, 0.238 mmol) in $[D_8]$ toluene (0.6 mL) was cooled to 0 °C and BBr₃ (0.4 mL of a 1.0 M solution in hexane, 0.4 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 1 h at r.t., the mixture contained **6** together with Me₂SiBr₂ and BBr₃. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr) to give **6** as a yellowish solid.

6: ¹H{¹¹B} NMR (250.1 MHz; [D₈]toluene; 25 °C): δ = 2.60 [br. s, 6 H, HB for δ (¹¹B) = -9.1, -5.0], 2.69 [br. s, 4 H, HB for δ (¹¹B) = -7.0, -5.0] ppm. ¹¹B{¹H} NMR (80.3 MHz; [D₈]toluene; 25 °C): δ = -9.1 (4 B), -7.0 (2 B), -5.0 (4 B), 64.7 (1 B, SeB) ppm. ¹¹B NMR (80.3 MHz; [D₈]toluene; 25 °C): δ = -9.1 (d, *J* = 165 Hz, 4 B), -7.0 (d, *J* = 160 Hz, 2 B), -5.0 (d, *J* = 162 Hz, 2 B), 64.7 (s, 1 B, SeB) ppm. ¹¹B NMR (80.3 MHz; hexane; 25 °C): δ = -8.4 (d, *J* = 167 Hz, 4 B), -6.4 (d, *J* = 160 Hz, 2 B), -4.3 (d, *J* = 169 Hz, 2 B), 65.5 [s, ¹*J*(⁷⁷Se) = 81.1 Hz, 1 B, SeB] ppm.

2-Iodo-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2borolane (7): A solution of **2** (85 mg, 0.238 mmol) in [D₈]toluene (0.6 mL) was cooled to 0 °C and ca. 1.5 equiv. BI₃ (157 mg, 0.4 mmol) was added. The formation of a red solution was observed. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 10 min at r.t., the mixture contained 7 together with Me₂SiI₂ and BI₃. Volatile materials were removed in vacuo (5 h, 40 °C at 8×10^{-3} Torr) to give 7 as a rosè-colored solid.

7: ¹H{¹¹B} NMR (250.1 MHz; [D₈]toluene; 25 °C): δ = 2.57 [br. s, 2 H, HB for δ (¹¹B) = -5.2], 2.61 [br. s, 4 H, HB for δ (¹¹B) = -9.2], 2.64 [br. s, 2 H, HB for δ (¹¹B) = -5.2], 2.71 [br. s, 2 H, HB for δ (¹¹B) = -6.8] ppm. ¹¹B{¹H} NMR (80.3 MHz; [D₈]toluene; 25 °C): δ = -9.2 (4 B), -6.8 (2 B), -5.3 (4 B), 52.2 (1 B, SeB) ppm. ¹¹B NMR (80.3 MHz; [D₈]toluene; 25 °C): δ = -9.2 (d, *J* = 165 Hz, 4 B), -6.8 (d, *J* = 170 Hz, 2 B), -5.3 (d, *J* = 170 Hz, 4 B), 52.2 [¹*J*(⁷⁷Se, ¹¹B) = 93.0 Hz, 1 B, SeB] ppm.

Reaction of 1 with MeOBCl₂: A suspension of 1 (70 mg, 0.166 mmol) in $[D_8]$ toluene (0.6 mL) was cooled to 0 °C and a solution of freshly prepared MeOBCl₂ in toluene (0.35 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 1 h at r.t., the mixture contained **5** together with Me₂Si(Cl)–SiMe₂(Cl), (MeO)₂BCl, and MeOBCl₂. Volatile materials were removed in vacuo (2 h, 8×10^{-3} Torr) to give **5** as a yellowish oil.

FULL PAPER

Synthesis of PhOBBr₂: A solution of (PhO)₃B (154 mg, 0.53 mmol) in hexane (1 mL) was cooled to 0 °C and BBr₃ (1.06 mL of a 1.0 M solution in hexane, 1.06 mmol) was added. After 30 min at 0 °C, the mixture contained PhOBBr₂ (90%), (PhO)₂BBr (5%), and BBr₃ (5%). ¹¹B NMR (80.3 MHz; hexane; 25 °C): δ = 22.5 [(PhO)₂BBr], 28.1 (PhOBBr₂), 39.4 (BBr₃) ppm.

Reaction of 2 with PhOBBr₂: A solution of **2** (85 mg, 0.238 mmol) in $[D_8]$ toluene (0.6 mL) was cooled to 0 °C and a solution of freshly prepared PhOBBr₂ in hexane (0.45 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 1 h at r.t., the mixture contained **6** together with Me₂SiBr₂, (PhO)₂BBr, and PhOBBr₂.

Reaction of 1 with PhOBBr₂ and B(OPh)₃. 2-Phenoxy-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-borolane (8): A suspension of 1 (70 mg, 0.166 mmol) in [D₈]toluene (0.6 mL) was cooled to 0 °C and a solution of freshly prepared PhOBBr₂ in hexane (0.30 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 1 h at r.t., the mixture contained **6** together with Me₂Si(Br)–SiMe₂(Br), (PhO)₂BBr, and PhOBBr₂. B(OPh)₃ (87 mg, 0.30 mmol) was added to this mixture at 0 °C. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr). The resulting mixture thus obtained contained **8** (50%), **11** (25%), **6** (25%), BrB(OPh)₂, and B(OPh)₃ (⁷⁷Se, ¹³C, ¹¹B NMR).

Reaction of 5 with B(OMe)₃. 2-Methoxy-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-borolane (9) and 1-Hydroseleno-2methylseleno-1,2-dicarba-*closo*-dodecaborane(12) (10): A solution of 5 (68 mg, 0.20 mmol) in [D₈]toluene (0.6 mL) was cooled to 0 °C and B(OMe)₃ (0.03 mL, 0.27 mmol) was added. The progress of the reaction was monitored by ¹¹B NMR spectroscopy. Volatile materials were removed in vacuo (1 h, 8×10^{-3} Torr). The mixture thus obtained contained 9 (80%) and 10 (20%) (⁷⁷Se, ¹³C, ¹¹B NMR; see also Figure 3).

9: ${}^{1}H{}^{11}B{}$ NMR (250.1 MHz; [D₈]toluene; 25 °C): δ = 2.75 (m, 10 H, HB), 2.84 (s, 3 H, OMe) ppm. ${}^{11}B{}^{1}H{}$ NMR (80.3 MHz; [D₈]toluene; 25 °C): δ = -8.7 (4 B), -7.1 (2 B), -4.8 (2 B), -3.6 (2 B), 53.9 (1 B, SeB) ppm.

10: ${}^{11}\text{H}{}^{11}\text{B}$ NMR (250.1 MHz; [D₈]toluene; 25 °C): δ = 1.64 [s, ${}^{2}J({}^{77}\text{Si},{}^{1}\text{H})$ = 13.4 Hz, 3 H, SeMe], 1.71 [s, ${}^{1}J({}^{77}\text{Si},{}^{1}\text{H})$ = 54.9 Hz, 1 H, SeH], 2.15 [br. s, 2 H, HB for $\delta({}^{11}\text{B})$ = -8.8], 2.54 [br. s, 2 H, HB for $\delta({}^{11}\text{B})$ = -8.1], 2.66 [br. s, 2 H, HB for $\delta({}^{11}\text{B})$ = -8.1], 2.75 [br. s, 2 H, HB for $\delta({}^{11}\text{B})$ = -7.5], 2.87 [br. s, 2 H, HB for $\delta({}^{11}\text{B})$ = -2.1, -2.8] ppm. ${}^{11}\text{B}{}^{1}\text{H}$ NMR (80.3 MHz; [D₈]toluene; 25 °C): δ = -8.8 (2 B), -8.1 (4 B), -7.5 (2 B), -2.8 (1 B), -2.1 (1 B) ppm.

Reaction of 1 (or 2) with BF₃: A saturated solution of BF₃ in toluene (5 mL) was added to **1** (or **2**) (0.5 mmol) in $[D_8]$ toluene (1 mL) at 0 °C. The mixture was stirred for 2 d at room temperature. Volatile materials were removed in vacuo to give **11** along with other decomposition products.

Reaction of 1 with BF₃–OEt₂: A suspension of 1 (70 mg, 0.168 mmol) in [D₈]toluene (0.6 mL) was cooled to 0 °C and BF₃–OEt₂ (0.05 mL, 0.41 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 60 h at 70 °C, the mixture contained **11**, **12**, and **13** together with Me₂Si(F)–SiMe₂(F) and BF₃–OEt₂. Volatile materials were removed in vacuo. The solution thus obtained contained **11** (30%), **12** (60%), and **13** (10%) (⁷⁷Se NMR).

11 + 12 + 13: ¹H NMR (250.1 MHz, CD₂Cl₂; 25 °C): δ = 1.35–1.45 (m, Me from Et), 2.61 [s, ¹J(⁷⁷Se, ¹H) = 53.0 Hz, SeH from **11**],

2.68 [s, ${}^{1}J({}^{77}\text{Se},{}^{1}\text{H}) = 52.3 \text{ Hz}$, SeH from **12**], 2.95–3.05 (m, CH₂ from Et) ppm. ${}^{77}\text{Se}$ NMR (47.7 MHz, CD₂Cl₂; 25 °C): δ = 355.1 [d, ${}^{1}J({}^{77}\text{Se},{}^{1}\text{H}) = 52.3 \text{ Hz}$, SeH from **12**], 370.4 [d, ${}^{1}J({}^{77}\text{Se},{}^{1}\text{H}) = 53.0 \text{ Hz}$, SeH from **11**], 489.1 (**13**), 501.7 (**12**) ppm.

Me₂Si(F)–SiF(Me₂): ²⁹Si NMR (49.7 MHz; [D₈]toluene; 25 °C): δ = 28.5 [dd, ¹*J*(²⁹Si, ¹⁹F) = 303.6, ²*J*(²⁹Si, ¹⁹F) = 33.8 Hz, SiMe] ppm. ¹H NMR (250.1 MHz; [D₈]toluene; 25 °C): δ = 0.22 [dm, SiMe, ³*J*(¹⁹F, ¹H) = 9.0 Hz] ppm.

Reaction of 2 with BF₃–OEt₂: A solution of **2** (67 mg, 0.187 mmol) in $[D_8]$ toluene (0.6 mL) was cooled to 0 °C and BF₃–OEt₂ (0.05 mL, 0.41 mmol) was added. The progress of the reaction was monitored by ¹¹B and ²⁹Si NMR spectroscopy. After 60 h at 70 °C, the mixture contained **12**, **13**, and **14** together with Me₂SiF₂ and BF₃–OEt₂. Volatile materials were removed in vacuo. The solution thus obtained contained **12** (25%), **13** (30%), and **14** (45%) (⁷⁷Se NMR).

12 + **13** + **14**: ¹H NMR (250.1 MHz; $[D_8]$ toluene; 25 °C): $\delta = 0.85$ (m, Me from Et), 1.76 [s, ¹*J*(⁷⁷Se, ¹H) = 55.7 Hz, SeH from **12**], 2.40–2.55 (m, CH₂ from Et) ppm. ⁷⁷Se NMR (95.4 MHz, CD₂Cl₂; 25 °C): $\delta = 351.7$ [d, ¹*J*(⁷⁷Se, ¹H) = 55.7 Hz, SeH from **12**], 489.3 (SeEt from **14**), 491.9 (**13**), 502.2 (SeEt from **12**), 715.1 (Se-Se from **14**) ppm.

Me₂SiF₂: ²⁹Si NMR (49.7 MHz; [D₈]toluene; 25 °C): δ = 5.7 [t, ¹*J*(²⁹Si,¹⁹F) = 289.8 Hz, SiMe] ppm. ¹H NMR (250.1 MHz; [D₈]-toluene; 25 °C): δ = 0.03 [t, ³*J*(¹⁹F,¹H) = 6.2 Hz, SiMe] ppm.

Reaction of 5 with Pyridine. 2-Chloro-2-pyridine-4,5-[1,2-dicarbacloso-dodecaborano(12)]-1,3-diselena-2-boracyclopentane (15a) and Pyridinium Bis(1,2-dicarba-closo-dodecaborane-1,2-diselena)borate (16a): A solution of 5 (70 mg, 0.196 mmol) in [D₈]toluene (0.6 mL) was cooled to -50 °C and pyridine (0.1 mL, 1.2 mmol) was added. The formation of a yellow solution was observed. The progress of the reaction was monitored by ¹¹B NMR spectroscopy. Volatile materials were removed in vacuo (1 h, 8×10^{-3} Torr). The mixture thus obtained contained 15a (90%) and 16a (10%) (⁷⁷Se, ¹³C, ¹¹B NMR). The same reaction at room temperature resulted in a mixture, containing 15a (70%) and 16a (30%) (⁷⁷Se, ¹³C, ¹¹B NMR).

15a: ${}^{1}H{}^{11}B{}$ NMR (250.1 MHz, CD₂Cl₂; 25 °C): δ = 2.1–3.2 (m, 10 H, HB), 7.85 (m, H_β-py), 8.17 (m, H_γ-py), 9.42 (m, H_a-py) ppm. ${}^{11}B{}^{1}H{}$ NMR (80.3 MHz, CD₂Cl₂; 25 °C): δ = -11.8, -9.5, -8.5, -6.1, -1.3 (10 BH), 13.9 [${}^{1}J({}^{77}Se, {}^{11}B{})$ = 45.0 Hz, 1 B, BSe₂] ppm.

16a: ${}^{1}H{}^{11}B{}$ NMR (250.1 MHz, CD₂Cl₂; 25 °C): δ = 2.07 (br. s, 4 H, HB), 2.20 (br. s, 4 H, HB), 2.45 (br. s, 8 H, HB), 2.76 (br. s, 4 H, HB), 8.05 (m, H_{\beta}-py), 8.51 (m, H_{\gamma}-py), 8.77 (m, H_{\alpha}-py), 16.5 (br. s, pyH⁺) ppm. ${}^{11}B{}^{1}H{}$ NMR (80.3 MHz, CD₂Cl₂, 25 °C): δ = -9.2 (8 B), -7.2 (8 B), -3.0 (4 B), 6.0 [${}^{1}J({}^{77}Se,{}^{11}B)$ = 59.0 Hz, 1 B, BSe₂] ppm.

Reaction of 5 with *N*-Methylpyrrolidine. 2-Chloro-2-(*N*-methylpyrrolidine)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2boracyclopentane (15b) and *N*-Methylpyrrolidinium Bis(1,2-dicarba*closo*-dodecaborane-1,2-diselena)borate (16b): The synthesis was carried out as described for 15a, starting from 5 (35 mg, 0.10 mmol) in [D₈]toluene (0.6 mL) and *N*-methylpyrrolidine (25 mg, 0.29 mmol) at -40 °C. The formation of a yellow solution was observed. Volatile materials were removed in vacuo (1 h, 8×10^{-3} Torr). The mixture thus obtained contained 15b (70%) and 16b (30%) (⁷⁷Se, ¹³C, ¹¹B NMR). Single transparent crystals of 15b were grown from [D₈]toluene solution after 1 d at r.t.; m.p. 160– 165 °C (dec.).

15b: ¹H NMR (500.1 MHz; [D₈]toluene; 25 °C): δ = 0.90, 1.00 (m, m, 2 H, 2 H, H_β-pyrrolidine), 1.82 (m, 3 H, CH₃), 2.83 (m, 4 H,

H_α-pyrrolidine) ppm. ¹¹B{¹H} NMR (160.5 MHz; [D₈]toluene; 25 °C): δ = -15-0 (overlapping signals for **16b**), 16.9 [¹*J*(⁷⁷Se,¹¹B) = 46.6 Hz, 1 B, BSe₂] ppm.

16b: ¹H NMR (500.1 MHz; [D₈]toluene; 25 °C): δ = 1.42 (m, H_β-pyrrolidine), 2.03 (m, NCH₃-pyrrolidine), 2.41 (m, H_α-pyrrolidine), 11.6 (br. s, NH⁺-pyrrolidine) ppm. ¹¹B{¹H} NMR (160.5 MHz; [D₈]toluene; 25 °C): δ = -15–0 (overlapping signals for **15b**), 6.7 [¹J(⁷⁷Se, ¹¹B) = 55.5 Hz, 1 B, BSe₂] ppm.

Reaction of 5 with 2,2'-Bipyridine. 2,2'-Bipyridinium Bis(1,2-dicarba-*closo*-dodecaborane-1,2-diselena)borate (16c): When the synthesis was carried out as described for 15a, starting from 5 (79 mg, 0.228 mmol) in [D₈]toluene (0.6 mL) and 2,2'-bipyridine (36 mg, 0.23 mmol) at -40 °C, the formation of a layer of red oil formed at the bottom. The top layer was decanted, the residual oil was dried in vacuo. The mixture thus obtained contained 16c (70 %), 11 (20 %) and *ortho*-carborane (10 %) (⁷⁷Se, ¹³C, ¹¹B NMR).

16c: ${}^{1}H{}^{11}B{}$ NMR (250.1 MHz; CD₂Cl₂; 25 °C): $\delta = 2.0-3.0$ (m, 20H, HB), 7.73 (m, 2,2'-bipy), 8.27 (m, 2,2'-bipy), 8.72 (m, 2,2'-bipy), 8.89 (m, 2,2'-bipy), 16.9 (br. s, 2,2'-bipyH⁺). ${}^{11}B{}^{1}H{}$ NMR (80.3 MHz; CD₂Cl₂; 25 °C): $\delta = -13$ to 0 (overlapping signals for **11** and *ortho*-carborane), 6.0 [${}^{1}J({}^{77}Se, {}^{11}B) = 56.5$ Hz, 1 B, BSe₄].

Crystal Structure Determination of 4 and 15b: Details pertinent to the crystal structure determinations^[32] are listed in Table 4.^[33] Crystals of appropriate size were sealed under argon in Lindemann capillaries. The data collections were carried out at 133 K for 4 and **15b** by using a STOE IPDS II diffractometer with graphitemonochromated Mo- K_a ($\lambda = 71.073$ pm) radiation.

Table 4. Crystallographic data of the carborane derivatives $\mathbf{4}$ and $\mathbf{15b}$.

	4	15b
Formula	C ₈ H ₂₄ B ₁₁ NSe ₂	C ₇ H ₂₁ B ₁₁ ClNSe ₂
Crystal	colorless prism	colorless prism
Dimensions [mm ³]	$0.42 \times 0.22 \times 0.18$	$0.25 \times 0.19 \times 0.18$
Temperature [K]	133(2)	133(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_{1}/c$	<i>P</i> 2(1)
<i>a</i> [pm]	700.29(14)	705.02(14)
b [pm]	1740.3(4)	1134.6(2)
c [pm]	1529.0(3)	1073.2(2)
β[°]	96.65(3)	93.08(3)
Z	4	2
Absorption coefficient,	3.981	4.452
$\mu [{\rm mm}^{-1}]$		
Measuring range (ϑ) [°]	1.78-25.68	1.90-25.61
Reflections collected	17976	27891
Independent reflections	3072	1613
$[I \ge 2\sigma(I)]$		
Absorption correction	none ^[a]	numerical
Refined parameters	199	200
Absolute structure pa-	-	0.52(3)
rameter		
$wR_2 / R1 [I \ge 2\sigma(I)]$	0.095 / 0.039	0.060 / 0.023 ^[b]
Max. / min. residual e^- density [e pm ⁻³ 10 ⁻⁶]	1.010 / -0.397	0.797 / -0.388

[a] Absorption corrections did not improve the parameter set. [b] The crystal structure was solved and refined taking into account racemic twinning.

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