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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

Keywords: Main group elements / Carboranes / Boron / Selenium / Heterocycles / Density functional calculations / Multinuclear NMR spectroscopy

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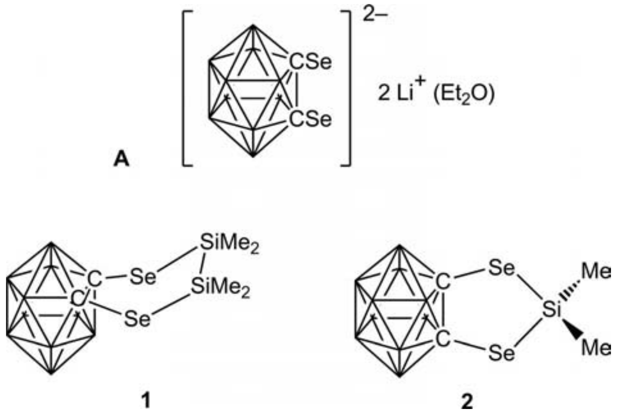
Exchange reactions of 2,2-dimethyl-1,3-diselena-2-silacyclopentane and 2,2,3,3-tetramethyl-1,4-diselena-2,3-disilacyclohexane, as the 4,5- and 5,6-[1,2-dicarba-*closo*-dodecaborano(12)] derivatives, respectively, with boron trihalides (BCl_3, BBr_3, BI_3) and dichlorides ($PhBCl_2$, iPr_2NBCl_2) afford the corresponding 1,3,2-diselenaborolanes in essentially quantitative yield. The products were characterized in solution by multinuclear magnetic resonance spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{77}Se), and for two products, in the solid state by X-ray 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.

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 main-group-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.



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**.

As part of the main group chemistry of **A**, the synthesis of cyclic borane derivatives presents a major challenge. So far, the products derived from **A**, structurally characterized in solution and in the solid state, contain tetracoordinate boron.[12,14] It was shown for reactions of **A** with boron halides that the unavoidable presence of diethyl ether in reagent **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 1,3,2-diselanaborolanes. 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.

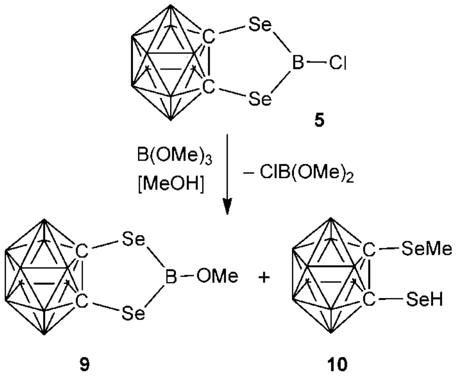
Results and Discussion

Exchange Reactions of the Selenasilanes 1 and 2 with Boron Halides

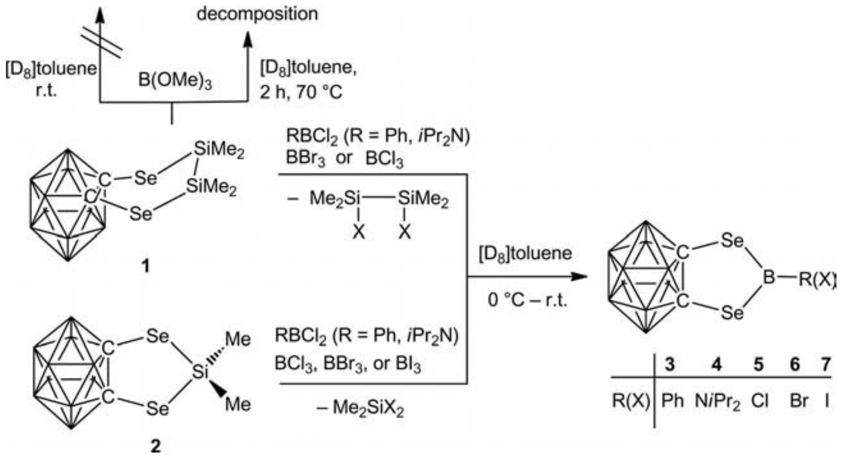
In a previous study,[9] the cyclic disilane derivative **1** was found to be somewhat more reactive than **2** in exchange reactions with chlorosilanes. Therefore, both silanes **1** and **2** are attractive starting materials to explore exchange reactions with boron halides (Scheme 2). All reactions 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 ^{29}Si NMR spectroscopy, following the changes in the intensities of the ^{29}Si NMR signals for **1** or **2** and $Me_4Si_2X_2$ or Me_2SiX_2, 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.

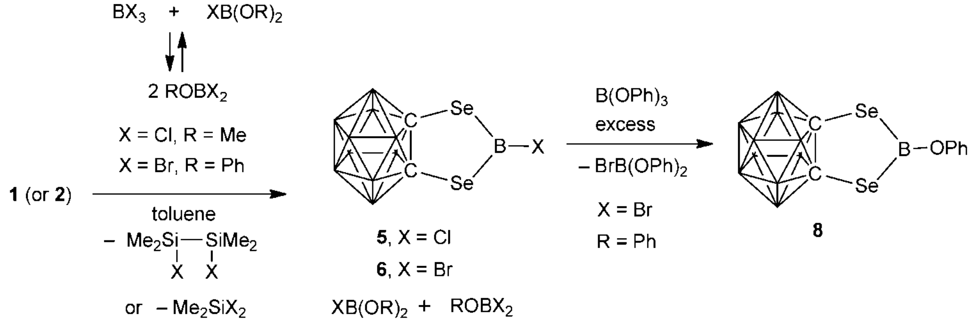
To obtain better evidence for the methoxy derivative, the reaction of **5** with $B(OMe)_3$ was studied (Scheme 4). The NMR spectra of the reaction mixture showed the presence of the desired compound **9** along with decomposition products, of which **10** could be identified by NMR spectroscopy. It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



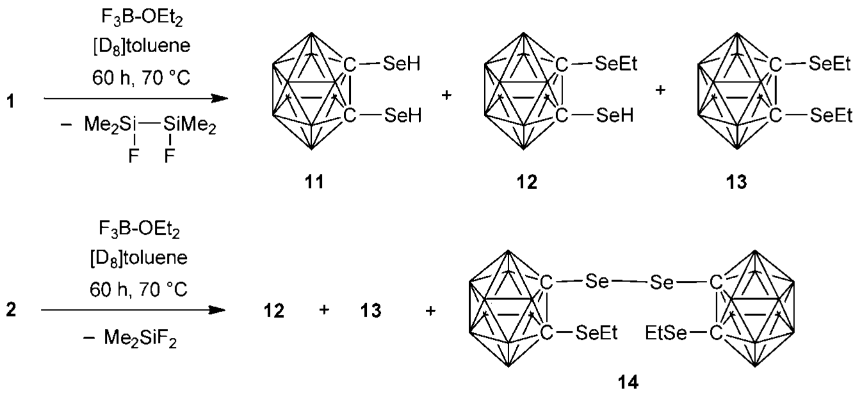
Scheme 4. Exchange reaction of the boron chloride **5** with $B(OMe)_3$.



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 $MeOBCl_2$ and $PhOBBr_2$.



Scheme 5. Products identified in the reaction of **1** and **2** with BF_3–OEt_2.

Various attempts to prepare the boron fluoride analogous to **5**–**7** were unsuccessful; the treatment of **1** or **2** with a solution of gaseous BF_3 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 BF_3–OEt_2 proceeded slowly after heating to give $Me_4Si_2F_2$ 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 SbF_3 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 ^{11}B(carborane) NMR signals, the ^{11}B 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 ^{77}Se–^{11}B spin–spin coupling. Although the ^{11}B NMR signals are somewhat broad, ^{77}Se satellites are visible under certain conditions in the cases of **6** and **7** (Figure 1). The ^{77}Se NMR spectra are more enlightening in this respect, since at least in the cases of the boron halides **5**–**7**, the ^{77}Se 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 ^{77}Se–^{11}B spin–spin coupling is not resolved in the ^{11}B or ^{77}Se NMR spectra. The ^{77}Se NMR signals for **3**, **4**, and **8** appear as broadened singlets. The ^{77}Se NMR spectrum of **9** (Fig-

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

	3 (R = Ph)			**4** (R = *i*Pr$_2$N)		**5** (X = Cl)	**6** (X = Br)	**7** (X = I)	**8** (R = OPh)	**9** (R = OMe)
	[D$_8$]toluene 298 K	CD_2Cl_2 298 K	CD_2Cl_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
δ^{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 Hz	64.7 [b] $h_{1/2}$ = 70 Hz	52.2 (98.0) $h_{1/2}$ = 75 Hz	55.5 $h_{1/2}$ = 180 Hz	53.9 $h_{1/2}$ = 120 Hz
δ^{11}B(calcd.)	82.8			55.0		80.6	84.6			62.1
δ^{77}Se	609.9 $h_{1/2}$ = 85 Hz	609.7 $h_{1/2}$ = 120 Hz	603.6	441.5 $h_{1/2}$ = 240 Hz	418.4, 449.3	622.0 (83.0)	648.2 (90.0)	694.4 (103.0)	484.6 $h_{1/2}$ = 110 Hz	469.6 (65.0 ± 10)
δ^{77}Se(calcd.)	580.8 [–161.1] (–82.4)			407.0 [–167.9] (–83.4) 442.0 [–167.9] (–83.4)		584.9 [12]	614.1 [12]			445.3 (–80.2) [+8.6] (^3J) [–159.7] (^1J)

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

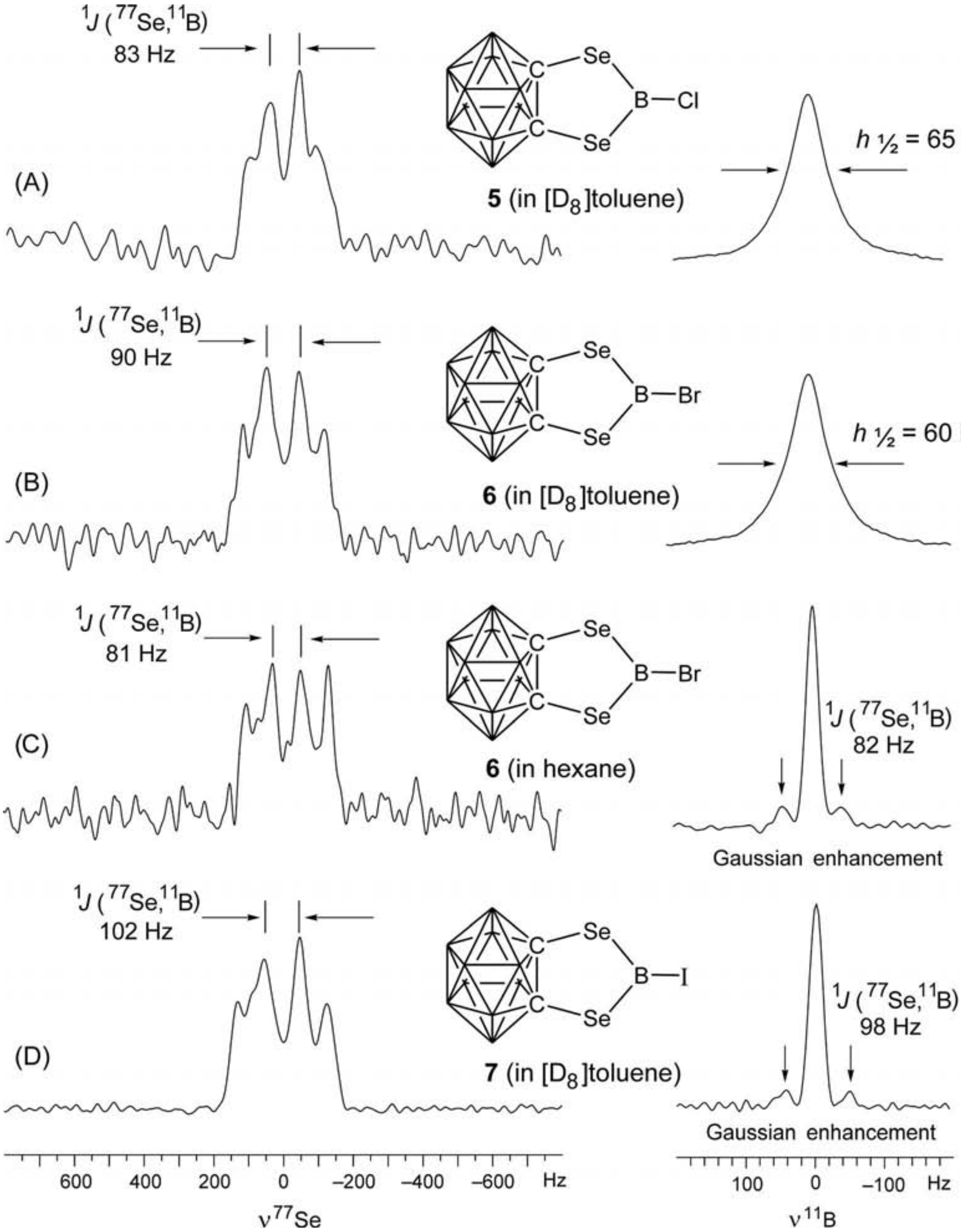


Figure 1. ^{77}Se NMR and ^{11}B NMR spectra of the 1,2-dicarba-*closo*-dodecaborane **5** (A), **6** (B, C), and **7** (D) at 23 °C, 10–15% solution (0.4–0.5 mol/L).

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 ^1J(^{77}Se,^{11}B) = 65 Hz.

The ^{1}H(NCH) and ^{13}C(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 ^{13}C(carborane), as well as for the ^{77}Se 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: $\Delta G^{\#}_{\text{coal}} = 42 \pm 2$ kJ mol^{-1} [20]) as shown by the evaluated[21] energy of activation for **4** ($\Delta G^{\#}_{\text{coal}} = 52 \pm 2$ kJ mol^{-1}).

In the ^{13}C{^{1}H} NMR spectrum of **9**, the ^{13}C(OMe) NMR signal is accompanied by ^{77}Se 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 ^3J(^{77}Se,^{13}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 Se$_2$BOC unit, and the mean value of the calculated coupling

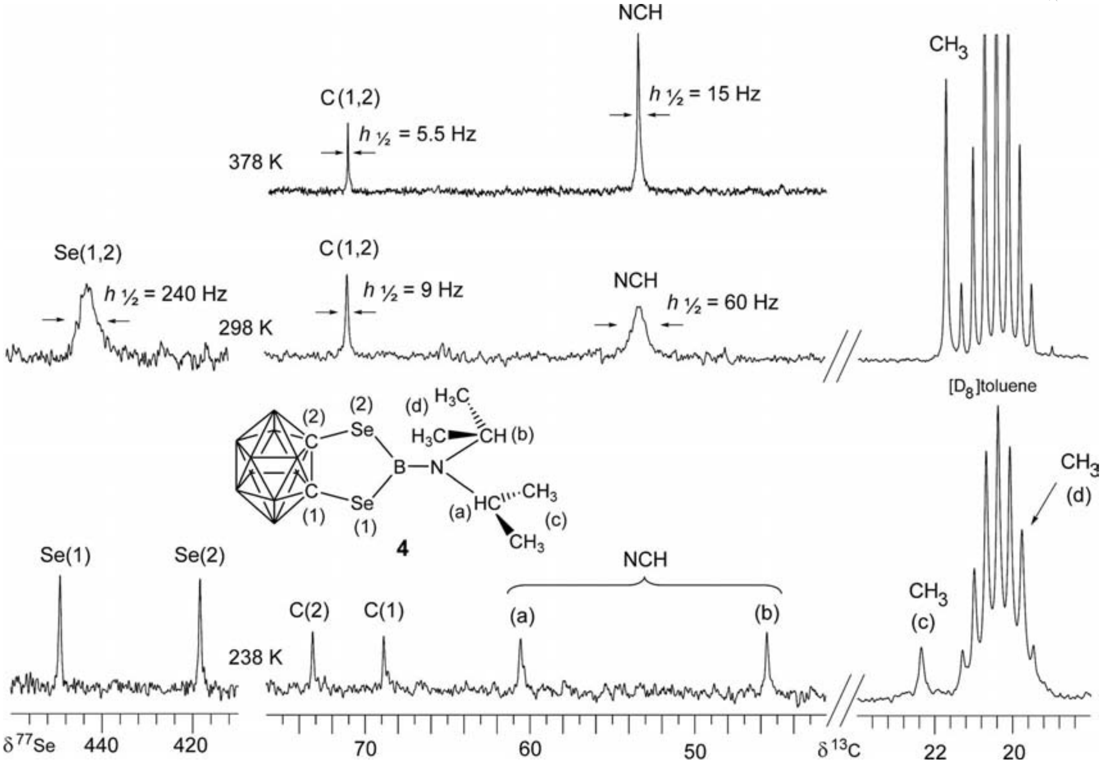


Figure 2. 62.9 MHz $^{13}C\{^1H\}$ NMR and 47.7 MHz ^{77}Se NMR spectra of **4** (in [D$_8$]toluene) (upper trace: at 378 K, middle trace: at 298 K, lower trace: at 238 K; given assignments follow calculated chemical shifts).

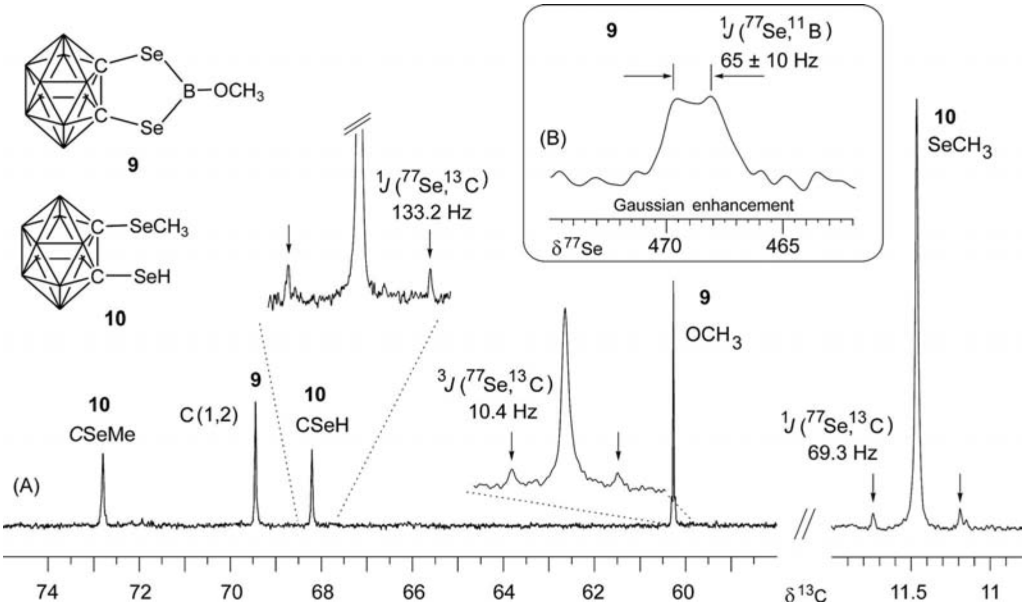
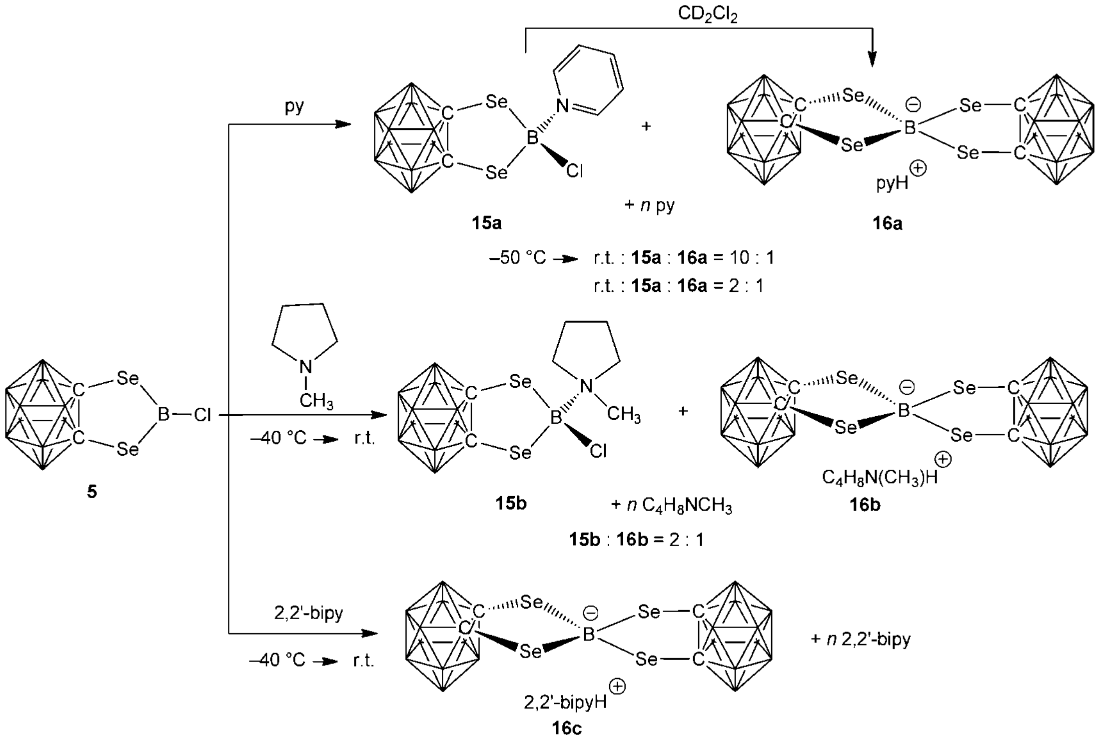


Figure 3. (A) 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the mixture of **9** and **10** (in [D$_8$]toluene, at 25 °C). (B) 47.7 MHz ^{77}Se NMR spectrum from **9** (in [D$_8$]toluene, at 25 °C).

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 observed in the reaction of **5** with 2,2′-bipyridine. Crystalline material was isolated for **15b** (see below). Additional weak ^{11}B 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 mixture 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. ^{13}C, ^{11}B, and ^{77}Se 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$_2$
δ^{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$_\beta$), 140.0 (C$_\gamma$), 146.9 (C$_\alpha$)	py: 126.0 (C$_\beta$), 143.4 (C$_\gamma$), 145.9 (C$_\alpha$)	C$_4$H$_8$NCH$_3$: 22.5 (C$_\beta$), 46.9 (Me), 61.1 (C$_\alpha$)	pyH$^+$: 127.0 (C$_\beta$), 142.5 (C$_\gamma$), 146.5 (C$_\alpha$)	C$_4$H$_8$N(CH$_3$)H$^+$: 23.5 (C$_\beta$), 40.1 (Me), 54.9 (C$_\alpha$)	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) [–191.5] (for **16** (calcd.) [14])		

[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), $^{1}J(^{77}\text{Se},^{1}\text{H})$ in// /± 0.5 Hz/; $^{1}\Delta^{10/11}\text{B}[^{13}\text{C}(1,2)]$ 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] δ^{11}B (calcd.): 24.3 (–70.0). [c] δ^{11}B (calcd.): 28.0 (–72.4) (–73.0).

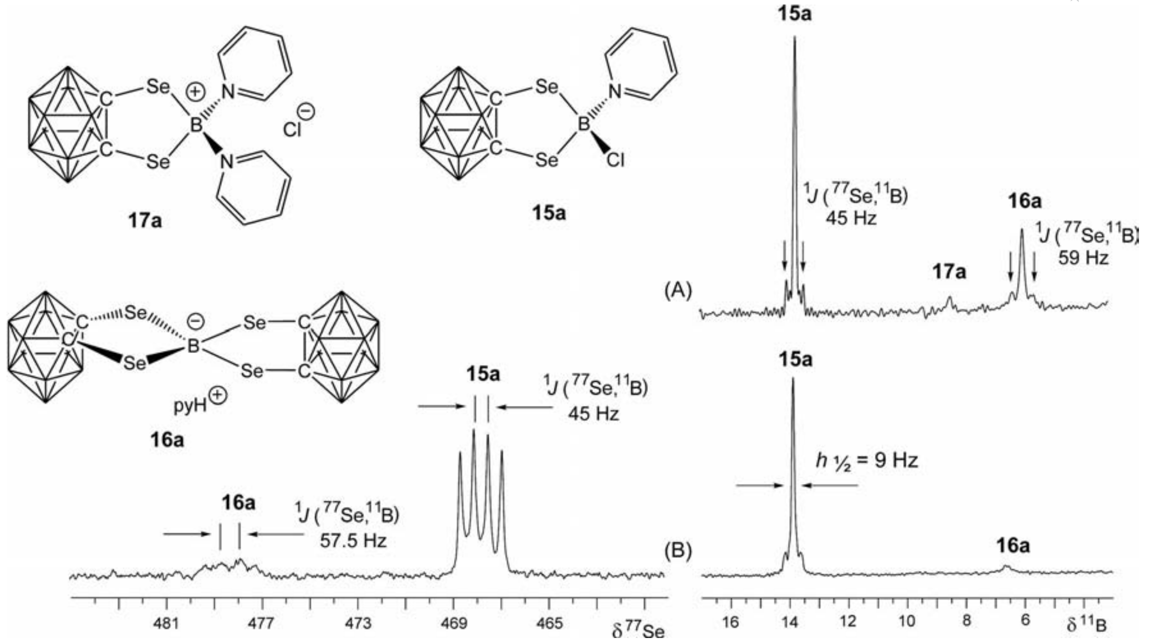


Figure 4. ^{77}Se NMR and ^{11}B NMR spectra of the reaction solution obtained from the reaction of **5** with pyridine. (A) 47.7 MHz ^{77}Se NMR and 80.3 MHz ^{11}B NMR spectra (in CD_2Cl_2, at 25 °C), the mixture of **15a** and **16a** (ratio 2:1) (after 2 h at room temperature in [D$_8$]toluene). (B) 76.2 MHz ^{77}Se NMR and 80.3 MHz ^{11}B NMR spectra (in CD_2Cl_2, 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 [D$_8$]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 ^{11}B, ^{13}C, and ^{77}Se[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 $^{1}J(^{77}\text{Se},^{11}\text{B})$ and $^{1}J(^{77}\text{Se},^{13}\text{C})$ coupling constants are predicted correctly. In the case of **9**, the correct prediction of $^{3}J(^{77}\text{Se},^{13}\text{C})$ (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–*i*Pr 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]

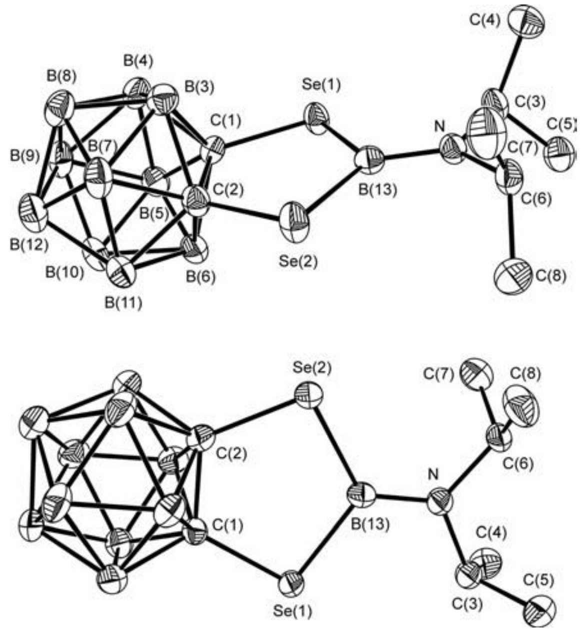


Figure 5. Two views of the ORTEP plots (50% probabilities; hydrogen atoms have been omitted for clarity) of the molecular structure of the 2-bis(isopropylamino)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-borolane **4** (for selected distances and angles see Table 3).

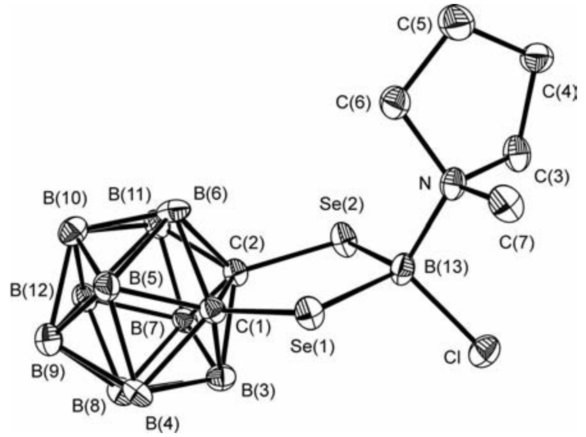


Figure 6. ORTEP plot (50% probabilities; hydrogen atoms have been omitted for clarity) of the molecular structure of the 2-chloro-2-(*N*-methylpyrrolidine)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-boracyclopentane **15b** (for selected distances and angles see Table 3).

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*Pr$_2$ derivative provided the first structural data of a 1,3,2-diselenaborolane containing a three-coordinate 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 CH_2Cl_2 and CD_2Cl_2 were distilled from CaH_2 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] $MeOBCl_2$ from $B(OMe)_3$ and BCl_3 (molar ratio 1:2) in toluene, $PhOBBr_2$ from $B(OPh)_3$ and BBr_3 (molar ratio 1:2) in hexane.[29] Other starting materials were purchased from Aldrich [BCl_3 (1.0 M in toluene), BBr_3 (1.0 M in hexane), BI_3 (≥ 98%), BF_3–OEt_2 (purified by redistillation), $PhBCl_2$ (97%), *i*Pr$_2$NBCl$_2$, $B(OMe)_3$ (99.999%), $B(OPh)_3$, pyridine (anhydrous, 99.8%), *N*-methylpyrrolidine, SbF_3 (98%)], from Messer Griesheim (BF_3) and used as received. 2,2′-Bipyridine (Aldrich, ≥ 99%) was sublimed before use (40–45 °C/2×10^{-2} Torr). NMR spectroscopic measurements: Bruker DRX 500 and Bruker ARX 250: ^1H, ^{11}B, ^{13}C, ^{77}Se, and ^{29}Si NMR [refocused INEPT[30] based on $^2J(^{29}Si,^1H)$ = 6–7 Hz]; Varian INOVA 400: ^1H, ^{11}B, ^{13}C, ^{29}Si, ^{77}Se NMR; chemical shifts are given relative to Me_4Si [δ^1H ($CHDCl_2$) = 5.33, ($C_6D_5CD_2H$) = 2.08 (± 0.01); $\delta^{13}C$ (CD_2Cl_2) = 53.8, ($C_6D_5CD_3$) = 20.4 (± 0.1); $\delta^{29}Si$ = 0 (±0.1) for $\Xi(^{29}Si)$ = 19.867184 MHz]; external BF_3–OEt_2 [$\delta^{11}B$ = 0 (±0.3) for $\Xi(^{11}B)$ = 32.083971 MHz], neat Me_2Se [$\delta^{77}Se$ = 0 (± 0.1) for $\Xi(^{77}Se)$ = 19.071523 MHz]. Assignments of ^1H and ^{11}B NMR spectroscopic signals are based on selective $^1H\{^{11}B$ selective$\}$ heteronuclear decoupling experiments. Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet [data for (^{12}C, ^1H, ^{11}B, ^{35}Cl, ^{28}Si, ^{80}Se)]. 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 $\delta^{11}B$ and $\delta^{77}Se$ were converted by $\delta^{11}B$ (calcd) = $\sigma(^{11}B) - \sigma(^{11}B, B_2H_6)$, with $\sigma(^{11}B, B_2H_6)$ = +84.1 [$\delta^{11}B$ (B_2H_6) = 18 and $\delta^{11}B$ (BF_3–OEt_2) = 0] and $\delta^{77}Se$(calcd) = $\sigma(^{77}Se) - \sigma(^{77}Se, SeMe_2)$ with $\sigma(^{77}Se, SeMe_2)$ = +1621.7.

2-Phenyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-borolane (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 $PhBCl_2$ (0.03 mL, 0.23 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 24 h at r.t., the mixture contained **3** together with $Me_2Si(Cl)$–$SiMe_2(Cl)$ and $PhBCl_2$. 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 $PhBCl_2$ (0.036 mL, 0.28 mmol) was added. The progress of the reaction was monitored by ^{11}B and

^{29}Si NMR spectroscopy. After 24 h at r.t., the mixture contained **3** together with Me_2SiCl_2. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr) to give **3** as a white solid.

3: $^{1}H\{^{11}B\}$ NMR (250.1 MHz; $[D_8]$toluene; 25 °C): δ = 2.78 (br. m, 10 H, HB), 6.80–7.10 (m, 5 H, Ph) ppm. ^{1}H NMR (250.1 MHz; $[D_8]$toluene; –50 °C): δ = 2.93 (br. s, 10 H, HB), 6.80 (m, 3 H, Ph), 7.04 (m, 2 H, Ph) ppm. $^{11}B\{^{1}H\}$ NMR (80.3 MHz; $[D_8]$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. $^{1}H\{^{11}B\}$ NMR (250.1 MHz, CD_2Cl_2; 25 °C): δ = 2.30 [br. s, 2 H, HB for $\delta(^{11}B)$ = –6.1], 2.37 [br. s, 2 H, HB for $\delta(^{11}B)$ = –7.2], 2.64 [br. s, 4 H, HB for $\delta(^{11}B)$ = –9.0], 2.78 [br. s, 2 H, HB for $\delta(^{11}B)$ = –4.4], 7.35–7.65 (m, 5 H, Ph) ppm. $^{11}B\{^{1}H\}$ NMR (80.3 MHz, CD_2Cl_2; 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. ^{11}B NMR (80.3 MHz, CD_2Cl_2; 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 $C_8H_{15}B_{11}Se_2$ (388.05): m/z (%) = 388 (5) [M^+], 301 (100) [$M^+ - BC_6H_5$], 221 (15), 209 (35), 124 (22), 114 (32).

2-Diisopropylamino-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-borolane (4). 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 iPr_2NBCl_2 (39 mL, 0.22 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 1 h at r.t., the mixture contained **4** together with $Me_2Si(Cl)–SiMe_2(Cl)$ and iPr_2NBCl_2. 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 $[D_8]$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 iPr_2NBCl_2 (0.05 mL, 0.28 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 30 min at r.t., the mixture contained **4** together with Me_2SiCl_2 and iPr_2NBCl_2. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr) to give **4** as a white solid.

4: $^{1}H\{^{11}B\}$ NMR (250.1 MHz; $[D_8]$toluene; 25 °C): δ = 0.71 [d, $^{3}J(H,H)$ = 6.75 Hz, 12 H, $NCMe_2$], 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. ^{1}H NMR (250.1 MHz; $[D_8]$toluene; –50 °C): δ = 0.48, 0.73 (br. s, br. s, 6 H, 6 H, $NCMe_2$), 2.30, 2.38 (br. m, br. m, 1 H, 1 H, NCH), 3.11 (br. s, 10 H, HB) ppm. $^{11}B\{^{1}H\}$ NMR (80.3 MHz; $[D_8]$toluene; 25 °C): δ = –8.8 (4 B), –6.8 (2 B), –5.4 (2 B), –3.1 (2 B), 45.7 (1 B, SeB) ppm. ^{11}B NMR (80.3 MHz; $[D_8]$toluene; 25 °C): δ = –8.8 (d, J = 160 Hz, 4 B), –6.8 (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 $C_8H_{24}B_{11}Se_2N$ (411.12): m/z (%) = 411 (15) [M^+], 396 (100) [$M^+ - CH_3$], 353 (45) [$M^+ - C_4H_{10}$], 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 $[D_8]$toluene (0.6 mL) was cooled to 0 °C and 1.5 equiv. of BCl_3 (0.25 mL of a 1.0 M solution in toluene, 0.25 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 2 d at r.t., the mixture contained **5** together with $Me_2Si(Cl)–SiMe_2(Cl)$ and BCl_3. 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. BCl_3 (0.4 mL of a 1.0 M solution in toluene, 0.4 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 2 h at r.t., the mixture contained **5** together with Me_2SiCl_2 and BCl_3. 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; $[D_8]$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; $[D_8]$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; $[D_8]$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 $C_2H_{10}B_{11}Se_2Cl$ (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-2-borolane (6). Method A: A suspension of **1** (70 mg, 0.166 mmol) in $[D_8]$toluene (0.6 mL) was cooled to 0 °C and BBr_3 (0.25 mL of a 1.0 M solution in hexane, 0.25 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 2 h at r.t., the mixture contained **6** together with $Me_2Si(Br)–SiMe_2(Br)$ and BBr_3. 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 BBr_3 (0.4 mL of a 1.0 M solution in hexane, 0.4 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 1 h at r.t., the mixture contained **6** together with Me_2SiBr_2 and BBr_3. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr) to give **6** as a yellowish solid.

6: $^{1}H\{^{11}B\}$ NMR (250.1 MHz; $[D_8]$toluene; 25 °C): δ = 2.60 [br. s, 6 H, HB for $\delta(^{11}B)$ = –9.1, –5.0], 2.69 [br. s, 4 H, HB for $\delta(^{11}B)$ = –7.0, –5.0] ppm. $^{11}B\{^{1}H\}$ NMR (80.3 MHz; $[D_8]$toluene; 25 °C): δ = –9.1 (4 B), –7.0 (2 B), –5.0 (4 B), 64.7 (1 B, SeB) ppm. ^{11}B NMR (80.3 MHz; $[D_8]$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. ^{11}B 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, $^{1}J(^{77}Se)$ = 81.1 Hz, 1 B, SeB] ppm.

2-Iodo-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-borolane (7): A solution of **2** (85 mg, 0.238 mmol) in $[D_8]$toluene (0.6 mL) was cooled to 0 °C and ca. 1.5 equiv. BI_3 (157 mg, 0.4 mmol) was added. The formation of a red solution was observed. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 10 min at r.t., the mixture contained **7** together with Me_2SiI_2 and BI_3. Volatile materials were removed in vacuo (5 h, 40 °C at 8×10^{-3} Torr) to give **7** as a rosè-colored solid.

7: $^{1}H\{^{11}B\}$ NMR (250.1 MHz; $[D_8]$toluene; 25 °C): δ = 2.57 [br. s, 2 H, HB for $\delta(^{11}B)$ = –5.2], 2.61 [br. s, 4 H, HB for $\delta(^{11}B)$ = –9.2], 2.64 [br. s, 2 H, HB for $\delta(^{11}B)$ = –5.2], 2.71 [br. s, 2 H, HB for $\delta(^{11}B)$ = –6.8] ppm. $^{11}B\{^{1}H\}$ NMR (80.3 MHz; $[D_8]$toluene; 25 °C): δ = –9.2 (4 B), –6.8 (2 B), –5.3 (4 B), 52.2 (1 B, SeB) ppm. ^{11}B NMR (80.3 MHz; $[D_8]$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 [$^{1}J(^{77}Se,^{11}B)$ = 93.0 Hz, 1 B, SeB] ppm.

Reaction of 1 with $MeOBCl_2$: 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 $MeOBCl_2$ in toluene (0.35 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 1 h at r.t., the mixture contained **5** together with $Me_2Si(Cl)–SiMe_2(Cl)$, $(MeO)_2BCl$, and $MeOBCl_2$. Volatile atile materials were removed in vacuo (2 h, 8×10^{-3} Torr) to give **5** as a yellowish oil.

Synthesis of $PhOBBr_2$: A solution of $(PhO)_3B$ (154 mg, 0.53 mmol) in hexane (1 mL) was cooled to 0 °C and BBr_3 (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 $PhOBBr_2$ (90%), $(PhO)_2BBr$ (5%), and BBr_3 (5%). ^{11}B NMR (80.3 MHz; hexane; 25 °C): δ = 22.5 [$(PhO)_2BBr$], 28.1 ($PhOBBr_2$), 39.4 (BBr_3) ppm.

Reaction of 2 with $PhOBBr_2$: 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 $PhOBBr_2$ in hexane (0.45 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 1 h at r.t., the mixture contained **6** together with Me_2SiBr_2, $(PhO)_2BBr$, and $PhOBBr_2$.

Reaction of 1 with $PhOBBr_2$ 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 [D$_8$]toluene (0.6 mL) was cooled to 0 °C and a solution of freshly prepared $PhOBBr_2$ in hexane (0.30 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 1 h at r.t., the mixture contained **6** together with $Me_2Si(Br)–SiMe_2(Br)$, $(PhO)_2BBr$, and $PhOBBr_2$. $B(OPh)_3$ (87 mg, 0.30 mmol) was added to this mixture at 0 °C. The progress of the reaction was monitored by ^{11}B and ^{29}Si 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 $B(OPh)_3$ (^{77}Se, ^{13}C, ^{11}B 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-2-methylseleno-1,2-dicarba-*closo*-dodecaborane(12) (10): A solution of **5** (68 mg, 0.20 mmol) in [D$_8$]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 ^{11}B NMR spectroscopy. Volatile materials were removed in vacuo (1 h, 8×10^{-3} Torr). The mixture thus obtained contained **9** (80%) and **10** (20%) (^{77}Se, ^{13}C, ^{11}B NMR; see also Figure 3).

9: ^{1}H{^{11}B} NMR (250.1 MHz; [D$_8$]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; [D$_8$]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: ^{1}H{^{11}B} NMR (250.1 MHz; [D$_8$]toluene; 25 °C): δ = 1.64 [s, $^2J(^{77}Si,^1H)$ = 13.4 Hz, 3 H, SeMe], 1.71 [s, $^1J(^{77}Si,^1H)$ = 54.9 Hz, 1 H, SeH], 2.15 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.8], 2.54 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.1], 2.66 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.1], 2.75 [br. s, 2 H, HB for $\delta(^{11}B)$ = –7.5], 2.87 [br. s, 2 H, HB for $\delta(^{11}B)$ = –2.1, –2.8] ppm. ^{11}B{^{1}H} NMR (80.3 MHz; [D$_8$]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 BF_3: A saturated solution of BF_3 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 $BF_3–OEt_2$: A suspension of **1** (70 mg, 0.168 mmol) in [D$_8$]toluene (0.6 mL) was cooled to 0 °C and $BF_3–OEt_2$ (0.05 mL, 0.41 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 60 h at 70 °C, the mixture contained **11**, **12**, and **13** together with $Me_2Si(F)–SiMe_2(F)$ and $BF_3–OEt_2$. Volatile materials were removed in vacuo. The solution thus obtained contained **11** (30%), **12** (60%), and **13** (10%) (^{77}Se NMR).

11 + 12 + 13: ^{1}H NMR (250.1 MHz, CD$_2$Cl$_2$; 25 °C): δ = 1.35–1.45 (m, Me from Et), 2.61 [s, $^1J(^{77}Se,^1H)$ = 53.0 Hz, SeH from **11**], 2.68 [s, $^1J(^{77}Se,^1H)$ = 52.3 Hz, SeH from **12**], 2.95–3.05 (m, CH$_2$ from Et) ppm. ^{77}Se NMR (47.7 MHz, CD$_2$Cl$_2$; 25 °C): δ = 355.1 [d, $^1J(^{77}Se,^1H)$ = 52.3 Hz, SeH from **12**], 370.4 [d, $^1J(^{77}Se,^1H)$ = 53.0 Hz, SeH from **11**], 489.1 (**13**), 501.7 (**12**) ppm.

$Me_2Si(F)–SiF(Me_2)$: ^{29}Si NMR (49.7 MHz; [D$_8$]toluene; 25 °C): δ = 28.5 [dd, $^1J(^{29}Si,^{19}F)$ = 303.6, $^2J(^{29}Si,^{19}F)$ = 33.8 Hz, SiMe] ppm. ^{1}H NMR (250.1 MHz; [D$_8$]toluene; 25 °C): δ = 0.22 [dm, SiMe, $^3J(^{19}F,^1H)$ = 9.0 Hz] ppm.

Reaction of 2 with $BF_3–OEt_2$: A solution of **2** (67 mg, 0.187 mmol) in [D$_8$]toluene (0.6 mL) was cooled to 0 °C and $BF_3–OEt_2$ (0.05 mL, 0.41 mmol) was added. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 60 h at 70 °C, the mixture contained **12**, **13**, and **14** together with Me_2SiF_2 and $BF_3–OEt_2$. Volatile materials were removed in vacuo. The solution thus obtained contained **12** (25%), **13** (30%), and **14** (45%) (^{77}Se NMR).

12 + 13 + 14: ^{1}H NMR (250.1 MHz; [D$_8$]toluene; 25 °C): δ = 0.85 (m, Me from Et), 1.76 [s, $^1J(^{77}Se,^1H)$ = 55.7 Hz, SeH from **12**], 2.40–2.55 (m, CH$_2$ from Et) ppm. ^{77}Se NMR (95.4 MHz, CD$_2$Cl$_2$; 25 °C): δ = 351.7 [d, $^1J(^{77}Se,^1H)$ = 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.

Me_2SiF_2: ^{29}Si NMR (49.7 MHz; [D$_8$]toluene; 25 °C): δ = 5.7 [t, $^1J(^{29}Si,^{19}F)$ = 289.8 Hz, SiMe] ppm. ^{1}H NMR (250.1 MHz; [D$_8$]toluene; 25 °C): δ = 0.03 [t, $^3J(^{19}F,^1H)$ = 6.2 Hz, SiMe] ppm.

Reaction of 5 with Pyridine. 2-Chloro-2-pyridine-4,5-[1,2-dicarba-*closo*-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 [D$_8$]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 ^{11}B NMR spectroscopy. Volatile materials were removed in vacuo (1 h, 8×10^{-3} Torr). The mixture thus obtained contained **15a** (90%) and **16a** (10%) (^{77}Se, ^{13}C, ^{11}B NMR). The same reaction at room temperature resulted in a mixture, containing **15a** (70%) and **16a** (30%) (^{77}Se, ^{13}C, ^{11}B NMR).

15a: ^{1}H{^{11}B} NMR (250.1 MHz, CD$_2$Cl$_2$; 25 °C): δ = 2.1–3.2 (m, 10 H, HB), 7.85 (m, H$_\beta$-py), 8.17 (m, H$_\gamma$-py), 9.42 (m, H$_\alpha$-py) ppm. ^{11}B{^{1}H} NMR (80.3 MHz, CD$_2$Cl$_2$; 25 °C): δ = –11.8, –9.5, –8.5, –6.1, –1.3 (10 BH), 13.9 [$^1J(^{77}Se,^{11}B)$ = 45.0 Hz, 1 B, BSe$_2$] ppm.

16a: ^{1}H{^{11}B} NMR (250.1 MHz, CD$_2$Cl$_2$; 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, CD$_2$Cl$_2$, 25 °C): δ = –9.2 (8 B), –7.2 (8 B), –3.0 (4 B), 6.0 [$^1J(^{77}Se,^{11}B)$ = 59.0 Hz, 1 B, BSe$_2$] ppm.

Reaction of 5 with *N*-Methylpyrrolidine. 2-Chloro-2-(*N*-methylpyrrolidine)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-boracyclopentane (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 [D$_8$]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%) (^{77}Se, ^{13}C, ^{11}B NMR). Single transparent crystals of **15b** were grown from [D$_8$]toluene solution after 1 d at r.t.; m.p. 160–165 °C (dec.).

15b: ^{1}H NMR (500.1 MHz; [D$_8$]toluene; 25 °C): δ = 0.90, 1.00 (m, m, 2 H, 2 H, H$_\beta$-pyrrolidine), 1.82 (m, 3 H, CH$_3$), 2.83 (m, 4 H,

H_α-pyrrolidine) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –15–0 (overlapping signals for **16b**), 16.9 [$^1J(^{77}Se,^{11}B)$ = 46.6 Hz, 1 B, BSe$_2$] ppm.

16b: ^1H NMR (500.1 MHz; [D$_8$]toluene; 25 °C): δ = 1.42 (m, H_β-pyrrolidine), 2.03 (m, NCH$_3$-pyrrolidine), 2.41 (m, H_α-pyrrolidine), 11.6 (br. s, NH$^+$-pyrrolidine) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –15–0 (overlapping signals for **15b**), 6.7 [$^1J(^{77}Se,^{11}B)$ = 55.5 Hz, 1 B, BSe$_2$] 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 [D$_8$]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 %) (^{77}Se, ^{13}C, ^{11}B NMR).

16c: $^1H\{^{11}B\}$ NMR (250.1 MHz; CD$_2$Cl$_2$; 25 °C): δ = 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$^+$). $^{11}B\{^1H\}$ NMR (80.3 MHz; CD$_2$Cl$_2$; 25 °C): δ = –13 to 0 (overlapping signals for **11** and *ortho*-carborane), 6.0 [$^1J(^{77}Se,^{11}B)$ = 56.5 Hz, 1 B, BSe$_4$].

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 graphite-monochromated Mo-K_α (λ = 71.073 pm) radiation.

Table 4. Crystallographic data of the carborane derivatives **4** and **15b**.

	4	15b
Formula	$C_8H_{24}B_{11}NSe_2$	$C_7H_{21}B_{11}ClNSe_2$
Crystal	colorless prism	colorless prism
Dimensions [mm^3]	0.42 × 0.22 × 0.18	0.25 × 0.19 × 0.18
Temperature [K]	133(2)	133(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2(1)$
a [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, μ [mm^{-1}]	3.981	4.452
Measuring range (ϑ) [°]	1.78–25.68	1.90–25.61
Reflections collected	17976	27891
Independent reflections [$I \geq 2\sigma(I)$]	3072	1613
Absorption correction	none[a]	numerical
Refined parameters	199	200
Absolute structure parameter	–	0.52(3)
wR_2 / $R1$ [$I \geq 2\sigma(I)$]	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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