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Selective Consecutive Insertion of Alkynes into the B–Se Bonds of 1,3,2-Diselenaborolane Derivatives: Synthesis and Molecular Structures of Nine-Membered Rings

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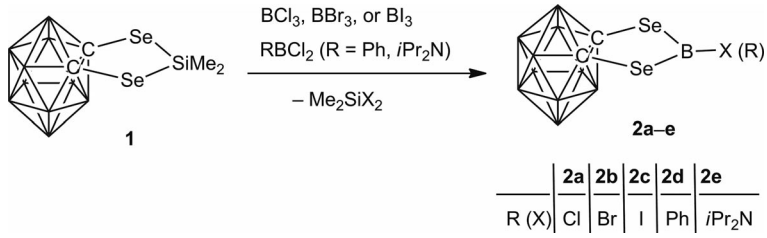
Various alkynes have been inserted selectively and stepwise into the B–Se bond(s) of 1,3,2-diselenaboracyclopentanes {as the 4,5-[1,2-dicarba-*closo*-dodecaborano(12)] derivatives}. The *B*-phenyl derivative was much less reactive than the *B*-halogeno derivatives. The proposed structures were confirmed in solution by multinuclear NMR studies (^{1}H, ^{11}B, ^{13}C and ^{77}Se NMR), also supported by DFT calculations of the gas-phase molecular geometries and NMR parameters [B3LYP/6-311+G(d,p) level of theory]. Isotope-induced nuclear shielding $^{2}\Delta^{10/11}B(^{13}C)$ across weak intramolecular coordinative Se–B bonding was observed in the ^{13}C NMR spectra of the nine-membered-ring compounds. The molecular structures of two nine-membered-ring structures with B–Cl and B–Br functions were determined by X-ray diffraction. In addition, it was shown that the slow hydrolysis of these boron halides afforded the corresponding diboroxanes and borinic acids, the structures of the former being determined by X-ray diffraction.

Introduction

Straightforward routes to various well-characterized, simple selenoboranes have previously been reported.[1,2] Although some applications of noncyclic selenoboranes[1,2] have been described,[3] their cyclic analogues appear to be even more intriguing due to their potential use in heterocyclic synthesis[4,5] or as ligands for transition-metal complexes.[6] The former has been shown by the conversion of 1,3,4,2,5-triselenaborolanes into novel ring systems through reactions with isocyanates[5a] or alkynes.[5b,5c] Recently, we prepared the first stable 1,3,2-diselenaborolane derivatives **2** (Scheme 1)[7] starting from the silane **1**[8] through exchange reactions. Unsaturated substrates can be inserted into the reactive B–Se bond(s) if the boron atom is three-coordinate and strongly Lewis-acidic. Otherwise radical reactions may be induced, which may lead to numerous products.[3a] To detect the first reasonably stable intermediates in the course of the insertion reactions, kinetic stabilization might be necessary. In this respect, it is expected that the bulky annelated 1,2-dicarba-*closo*-dodecaborane(12) unit[9,10] in **2** is particularly useful.

In this paper we report on the first attempts to insert alkynes into the B–Se bond(s) of **2** aiming for the synthesis of larger ring systems in the solid state and in solution and their structural characterization by using multinuclear magnetic resonance methods as well as MO calculations at the B3LYP/6-311+G(d,p) level of theory.



Scheme 1. Formation of 1,3,2-diselenaborolane derivatives **2**.

Results and Discussion

Synthesis and NMR Spectroscopy of Novel Seven- and Nine-Membered Rings

Some alkynes reacted more or less readily with **2a**–**2d**, and some did not react at all, for example, **2a** with 1,4-

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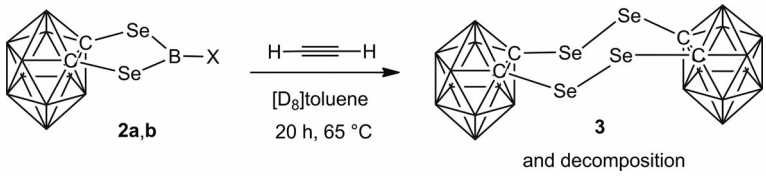
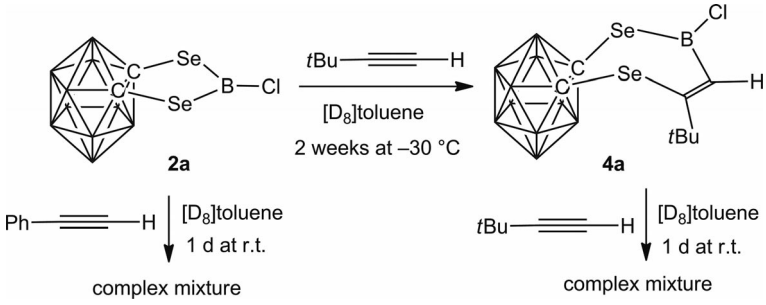


Scheme 2. Reaction of 1,3,2-diselenaborolanes **2a**,**b** with ethyne.

dichlorobut-2-yne or dimethyl acetylenedicarboxylate at room temperature after prolonged periods of time. The reaction of **2a** or **2b** with ethyne (Scheme 2) proceeded slowly, leading to numerous decomposition products of which only the known tetraselenide **3**[9] could be identified by its characteristic ^{13}C and ^{77}Se NMR spectroscopic data. As expected, **2e** was inert towards all alkynes studied, most likely for electronic and steric reasons.

Two different terminal alkynes were used for reactions with **2a** (Scheme 3). In contrast to the reaction of phenylethyne, which afforded a complex mixture not analysed as yet, *tert*-butylethyne gave meaningful results in the first



Scheme 3. Reactions of the 1,3,2-diselenaborolanes **2a** with two terminal alkynes.

Table 1. ^{13}C, ^{11}B and ^{77}Se NMR spectroscopic data[a] for the *ortho*-carborane derivatives **4a**, **5a**–**d** and **7a** in [D_8]toluene.

Compound	**4a**	**5a**	**5b**	**5c**	**5d**[b]	**7a**
$\delta^{13}C$	66.4 [151.7]	69.9 [165.9]	70.2 [163.8]	70.8 [161.4]	70.0 [164.7]	70.9 [165.9]
[$C(2,3)_{carb}$]	{–8.8 ppb}	{–9.0 ppb}	{–9.8 ppb}	{–8.2 ppb}	{–9.6 ppb}	{–9.6 ppb}
	70.1 [169.0]	70.2 [156.7]	73.5 [158.4]	79.3 [164.1]	71.8 [162.5]	71.0 [156.8]
	{–8.8 ppb}	{–7.3 ppb}	{–8.2 ppb}	{–11.5 ppb}	{–9.6 ppb}	{–9.6 ppb}
$\delta^{13}C$[SeC=]	164.6 [111.2]	142.6 [91.5]	141.5 [87.4]	139.6 [81.6]	139.4 [85.3]	135.8 [88.1]
$\delta^{13}C$[=CB]	138.1 [br.]	160.1 [br.]	163.1 [br.]	166.5 [br.]	163.5 [br.]	163.3 [br.]
$\delta^{13}C$[SeC(*R*)]	*t*Bu	Et	Et	Et	Et	Ph
	41.5 [9.4]	29.1 [11.6]	28.4 [11.2]	27.5 [11.4]	28.0 [10.5]	128.5 (C_m)
	28.4 [3.5]	12.8	12.8	12.6	13.19	128.8 (C_o)
						129.2 (C_p)
						137.5 (C_i)
$\delta^{13}C$[=C(*R*)B]	H (δ^1H)	Et	Et	Et	Et	Et
	6.33 $^4J(^{77}Se,^1H)$ = 9.6 Hz	26.1	26.4	26.9	27.4	28.0
		13.5	13.4	13.1	13.22	13.0
$\delta^{11}B$(CBSe)	63.3	56.9	50.4	34.2	55.8	52.0
$\delta^{77}Se$ [SeB]	577.8 [br.]	524.6 [br.]	516.9 [br.]	515.2 [br.]	470.2 [br.]	508.9 [br.]
	$h_{1/2}$ = 105 Hz	$h_{1/2}$ = 100 Hz	$h_{1/2}$ = 110 Hz	$h_{1/2}$ = 150 Hz	$h_{1/2}$ = 60 Hz	$h_{1/2}$ = 85 Hz
$\delta^{77}Se$ [SeC=]	564.0	616.7	616.7	613.4	626.5	661.4
$\delta^{11}B$ (calcd.)	68.7	71.2				70.3
$\delta^{77}Se$ (calcd.)	SeB	SeB				SeB
	553.9 [–180.1] [^1J(carb)]	550.7 [–179.6] [^1J(carb)]				528.3 [–184.4] [^1J(carb)]
	SeC=	SeC=				SeC=
	561.9 [–197.2] [^1J(carb)]	613.0 [–200.1] [^1J(carb)]				687.9 [–200.2] [^1J(carb)]
	[–132.4] [^1J(C=)]	[–124.1] [^1J(C=)]				[–112.3] [^1J(C=)]
	[+2.5] [^2J(C=)]	[+2.9] [^2J(C=)]				[+13.5] [^2J(C=)]
	[+7.9] [$^2J(CMe_3)$]	[+17.3] [$^2J(CH_2)$]				[+8.3] [$^2J(C_i)$]
	[0.0] [$^3J(CH_3)$]	[–2.0] [–2.6] (^3J)				[–1.3] [$^3J(CH_2)$]

[a] Coupling constants $^nJ(^{77}Se,^{13}C)$ are given in brackets [±0.5 Hz], $^1\Delta^{10/11}B(^{13}C(2,3)_{carb})$ ± 0.5 ppb are given in braces {±0.5 Hz}, 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 a lower frequency; n.o. = not observed; [br.] denotes broad ^{13}C or ^{77}Se resonances of boron-bonded carbon atoms. [b] Other $\delta^{13}C$ data: 128.7 (C_m), 132.7 (C_p), 133.8 (C_o), n.o. (C_i) (for Ph).

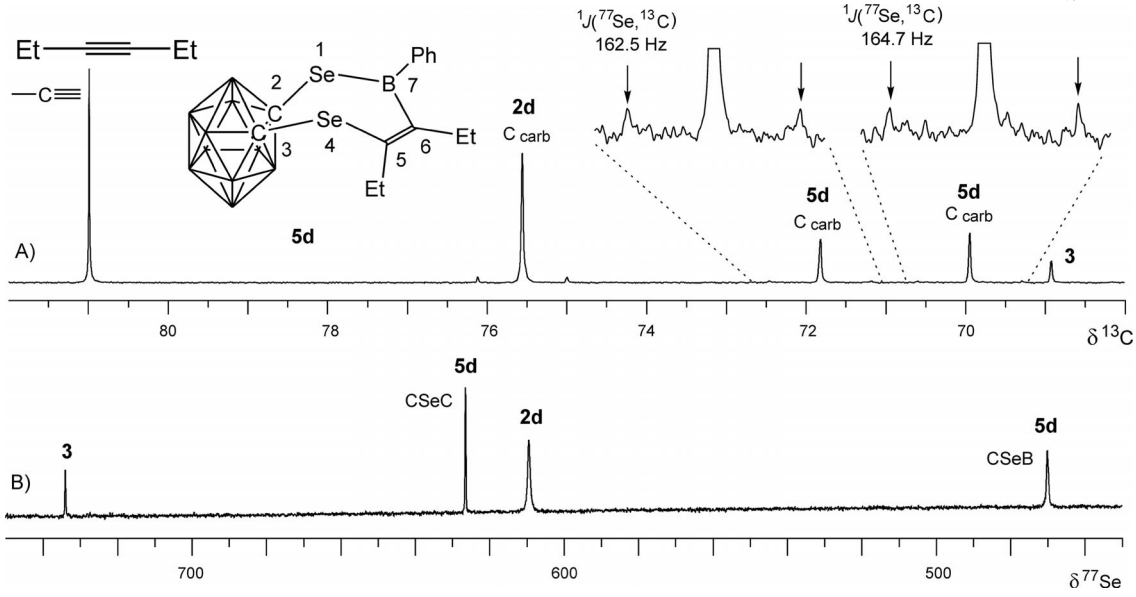


Figure 1. Reaction mixture of **5d**, **2d**, **3** and hex-3-yne obtained from the reaction of **2d** with hex-3-yne (molar ratio 1:2, in [D_8]toluene) after 2 h at 50 °C (**3** is a decomposition product; see Scheme 1). (A) Part of the 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum. The ^{77}Se satellites are marked by arrows. (B) 95.4 MHz ^{77}Se NMR spectrum.

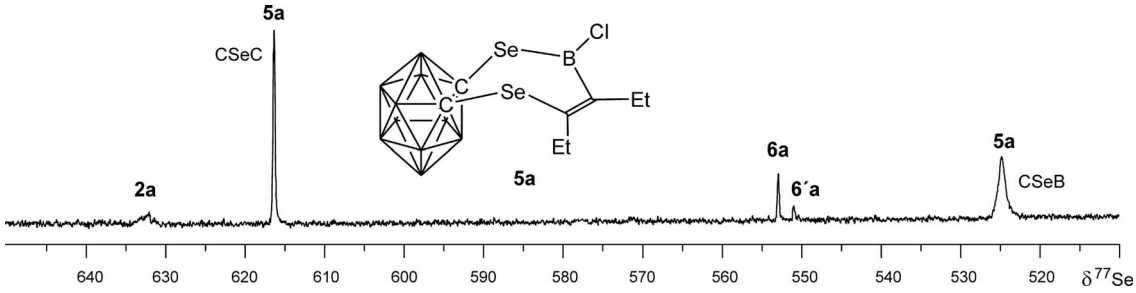
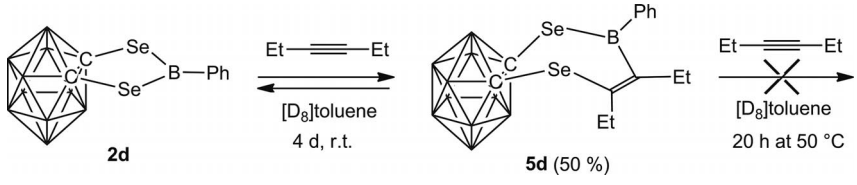


Figure 2. 95.4 MHz ^{77}Se NMR spectrum of the reaction mixture of **5a** together with small amounts of **6a**, **6′a** and **2a** (ca. 10%) obtained from the reaction of **2a** with hex-3-yne (molar ratio 1:1, in [D_8]toluene) after 2 d at room temp.

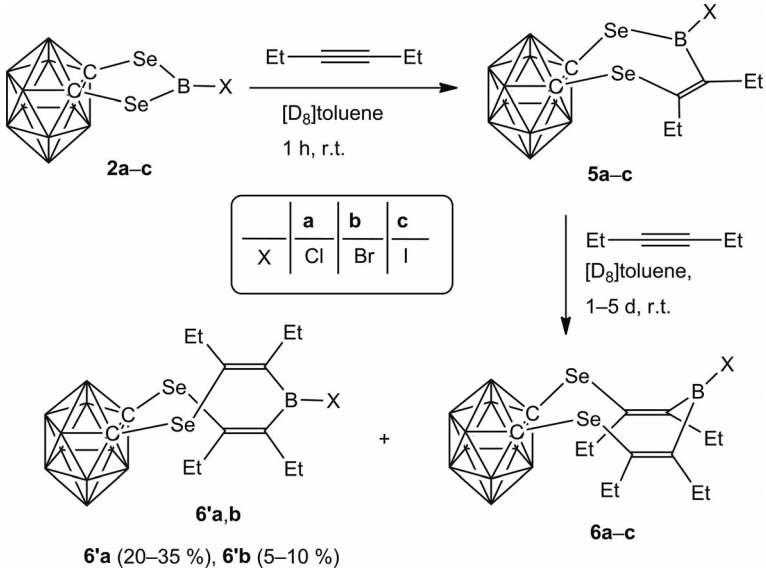
step. The carborane derivative **4a**, containing a seven-membered cycle, was obtained from the slow 1:1 reaction at –30 °C. According to the ^1H, ^{11}B, ^{13}C and ^{77}Se NMR spectra (Table 1), the insertion of the alkyne into one of the B–Se bonds had taken place selectively. The ^{77}Se NMR spectra[11] of the reaction solutions are particularly instructive, because compounds of type **4** give rise to two signals, one broad[7] (B–Se–C) and one sharp (C–Se–C; see Figure 1B or Figure 2). In the presence of an excess of *tert*-butylethyne, further slow reactions occurred, accompanied by decomposition. The complex mixtures were not analysed.

Even more promising results were obtained with hex-3-yne. When **2d** was used, the reaction never went beyond 1:1 stoichiometry. Indeed, an equilibrium exists between **2d** and **5d** in the presence of an excess of hex-3-yne (Scheme 4). It is conceivable that the Lewis acidity of the boron atom plays an important role in the insertion of the alkyne into the B–Se bond(s). In the case of a B–Ph moiety as in **2d** or **5d**, the Lewis acidity is too low to favour a second insertion, and even the first insertion appears to be readily reversible.

When the boron halides **2a**,**b**,**c** were used instead of **2d**, the situation was markedly different (Scheme 5). The first insertion products **5a**,**b**,**c** were detected by NMR spectroscopy used to monitor the reactions. It proved difficult to obtain the products **5a**,**b**,**c** of the 1:1 reactions in a pure state (see the ^{77}Se NMR spectra in Figure 2 and Figure 3).



Scheme 4. Reversible reaction of 1,3,2-diselenaborolane **2d** with hex-3-yne.



Scheme 5. Stepwise reactions of the 1,3,2-diselenaborolanes **2a**,**b**,**c** with hex-3-yne.

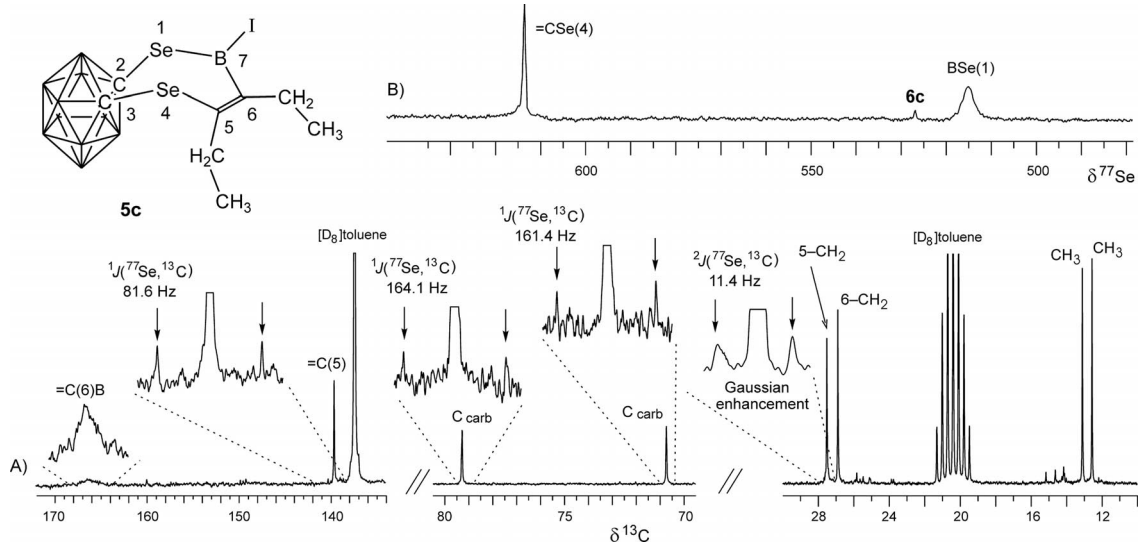


Figure 3. NMR spectra of reaction solutions containing **5c** together with a very small amount of **6c** (in [D_8]toluene, at 23 °C). (A) 62.9 MHz $^{13}C\{^1H\}$ NMR spectrum. In the expansions, the ^{77}Se satellites are marked by arrows. (B) 47.7 MHz ^{77}Se NMR spectrum.

Solely in the case of the iodide **5c** was the product obtained almost pure (see Figure 3). The ^{11}B chemical shifts (Table 1) indicate weak intramolecular coordinative Se–B bonds, slightly stronger in the bromide **5b** and iodide **5c** than in the chloride **5a**. In all three cases the ^{11}B NMR signals are shifted to a lower frequency with respect to the range expected[12] for trigonal boranes in which the boron atoms are surrounded by carbon, selenium and a halogen.

In the presence of an excess of hex-3-yne, the second addition or insertion into the remaining B–Se bond took place readily to give the nine-membered heterocycles **6a**,**b**,**c** and **6′a**,**b** as mixtures of isomers. Nine-membered heterocycles containing boron are rare[13] and so far unknown with a boron–halogen bond. The amount of the isomers **6′** changed in repeated experiments, ranging from ca. 10 to 33% for X = Cl and <5–10% for X = Br. For X = I, the presence of isomer **6′c** could not be detected with any certainty in the ^1H, ^{13}C or ^{77}Se NMR spectra. The solution-state structures of **6a**,**b**,**c** and **6′a**,**b** were assigned on the basis of the ^1H and ^{13}C NMR spectra with the various ^{77}Se satellites arising from ^{77}Se–^{13}C spin–spin coupling across one, two and three bonds (Table 2 and Figure 4). The $^{13}C(CH_2)$ signals were assigned to the $^1H(CH_2)$ multiplets (Figure 5), typical of diastereotopic ^1H nuclei, as expected for the structures **6** and **6′**. Because pure crystalline samples of **6** could be isolated (see below for the X-ray structural analysis) and redissolved, the assignment of the NMR signals was straightforward. In solution, there was no indication of a rapid interconversion between **6** and **6′**.

We treated 1-phenylbut-1-yne with **2a** to study the selectivity of the insertion reactions (Scheme 6). The reaction proved to be selective in both steps, affording at first **7a** and

Table 2. ^{13}C, ^{11}B and ^{77}Se NMR spectroscopic data[a] of the *ortho*-carborane derivatives **6a–c**, **8a**, **6′a–b** and **8′a** in [D_8]toluene.

Compound	**6a**	**6b**	**6c**	**8a**	**6′a**	**6′b**	**8′a**
$\delta^{13}C$	79.2	75.5	72.7	80.1	59.4	58.5	60.6
[$C(2,3)_{carb}$]	[174.1]	[171.3]	[168.8]	[174.4]	[174.8]	[172.0]	
	{–10.4 ppb}	{–9.6 ppb}	{–8.7 ppb}	{–10.5 ppb}	{–9.6 ppb}	{–9.6 ppb}	
	(+21 ppb)	(+12 ppb)	(+13 ppb)	(+22 ppb)			
$\delta^{13}C$	136.8 [95.7]	137.98 [91.1]	138.6 [87.0]	131.8 [96.1]	138.4 [94.9]	137.9	133.9
[SeC=]	(–12 ppb)	(–10 ppb)		(–12 ppb)			
$\delta^{13}C$[=CB]	162.6 [br.]	164.0 [br.]	165.3 [br.]	163.4 [br.]	163.6 [br.]	165.0 [br.]	164.4 [br.]
$\delta^{13}C$	Et	Et	Et	Ph	Et	Et	Ph
[SeC(*R*)]	28.1 [9.7]	27.7 [10.3]	27.7 [10.5]	128.7 (C_m)	30.3 [8.7]	32.5	139.9 (C_i)
	13.7	13.5	13.1	129.2 (C_o)	13.0	12.8	
				128.6 (C_p)			
				139.3 [8.2] (C_i)			
$\delta^{13}C$	Et	Et	Et	Et	Et	Et	Et
[=C(*R*)B]	26.0 [6.7]	25.8 [7.3]	25.7 [7.5]	27.6	26.6	27.9	28.7
	14.3	14.3	14.3	14.0	13.7	13.5	13.8
$\delta^{11}B$ (=CBC=)	42.0	27.0	9.0	28.0	48.5	n.o.	n.o.
$\delta^{77}Se$ [SeC=]	556.1	541.6	526.9	608.4	554.7	540.4	574.5
$\delta^{11}B$ (calcd.)	61.3						
$\delta^{77}Se$ (calcd.)	548						

[a] Coupling constants $^nJ(^{77}Se,^{13}C)$ are given in brackets [±0.5 Hz], $^1\Delta^{10/11}B(^{13}C(2,3)) \pm 0.5$ ppb are given in braces {±0.5 Hz}, $^2\Delta^{10/11}B(^{13}C(2,3))$ and $^2\Delta^{10/11}B(^{13}C(SeC=)) \pm 0.5$ ppb are given in parentheses (±0.5 Hz), isotope-induced chemical shifts $^{1,2}\Delta$ are given in ppb, and the negative sign denotes a shift of NMR signal of the heavy isotopomer to a lower frequency; n.o. = not observed; [br.] denotes broad ^{13}C or ^{77}Se resonances of boron-bonded carbon atoms.

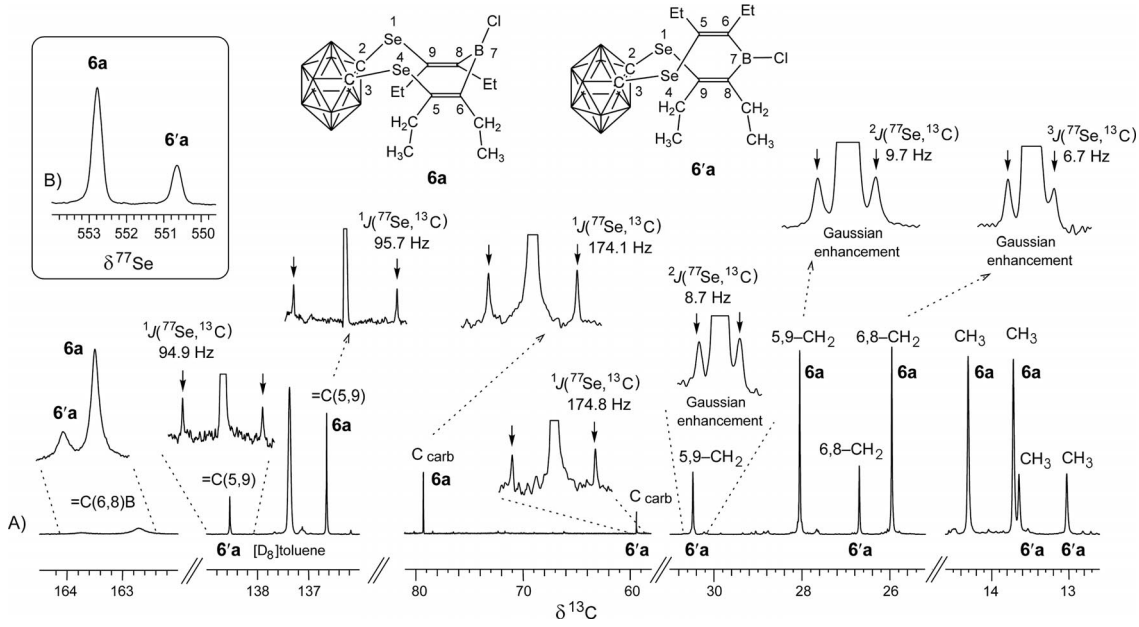


Figure 4. NMR spectra of the mixture of **6a** and **6′a** (ca. 3:1, in [D_8]toluene, at 23 °C) obtained from the reaction of **2a** with hex-3-yne (molar ratio 1:2, in [D_8]toluene) after 5 d at room temp. (A) 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum. In the expansions, the ^{77}Se satellites are marked by arrows. (B) 95.4 MHz ^{77}Se NMR spectrum.

then a mixture containing mainly **8a** together with a small amount of its isomer **8′a** (see Table 2 for the NMR spectroscopic data).

For both **6** and **8**, the ^{11}B nuclear shielding is increased with respect to trigonal diorgano(seleno)boranes[12] even more significantly than for the seven-membered cycles **4a**, **5a**,**b**,**c** and **7a**. Supported by the solid-state structures (see below), this points towards marked intramolecular coordinative Se–B interactions in which both the selenium atoms in **6** and **8** are involved. On the basis of the $\delta^{11}B$ data, these interactions appear to be somewhat weaker in the isomers **6′** (the ^{11}B NMR signal of **8′a** was not observed in the neighbourhood of the broad ^{11}B NMR signal of **8a** because of the low concentration of **8′a**). In principle, this coordinative Se–B bonding should also be evident by isotope-induced nuclear shielding (secondary isotope effects[14]), as has already been shown for $^2\Delta^{10/11}B(^{29}Si)$ in bridging B···E–Si units for E = H or O.[15,16] In the present examples, we deal with B···Se–C units, and therefore one might expect to see additional ^{13}C NMR signals due to $^2\Delta^{10/11}B(^{13}C)$. Although neither the sign nor the magnitude of this effect can be predicted yet, it is clearly visible in the ^{13}C NMR

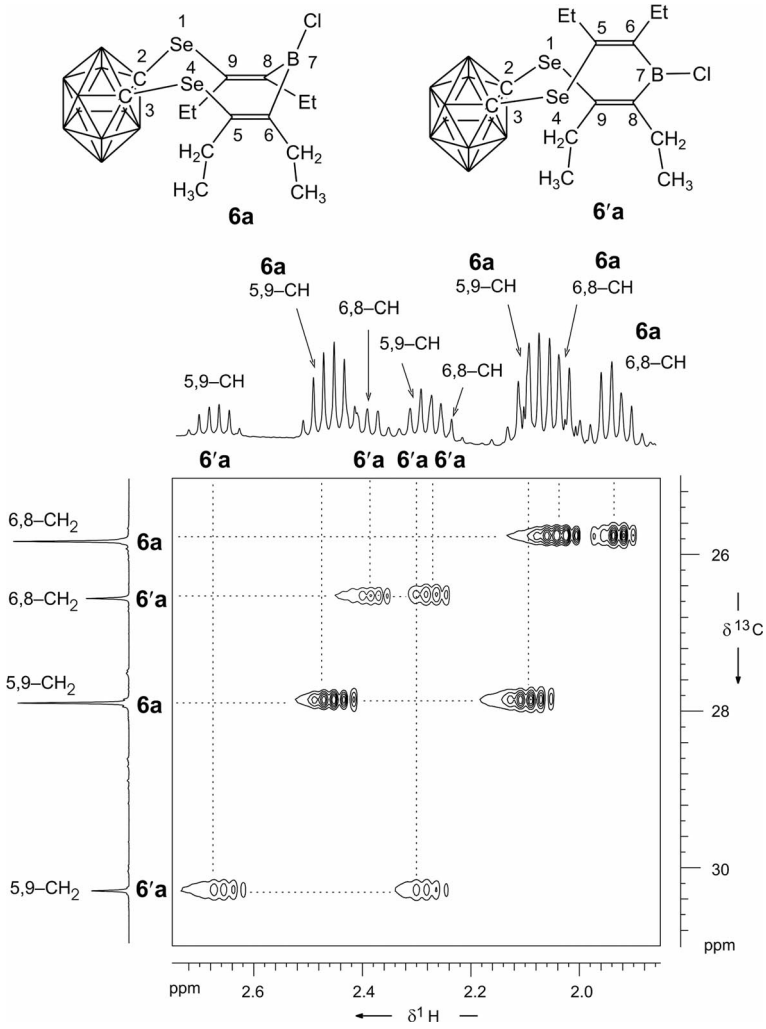
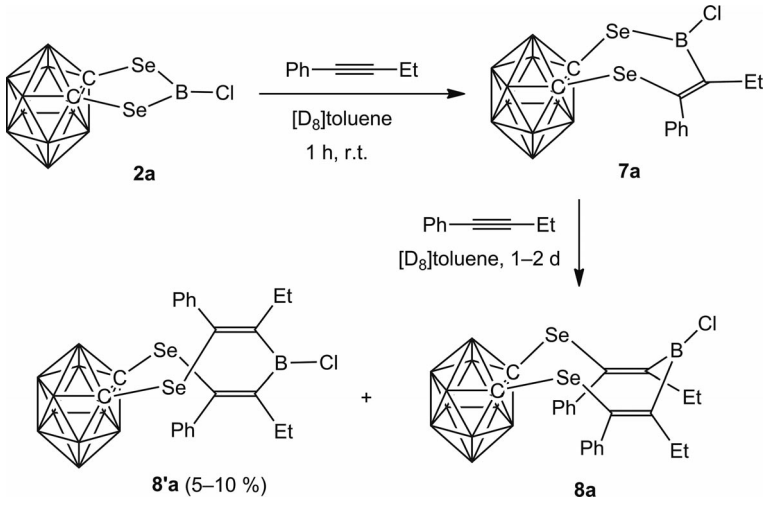


Figure 5. Contour plot of part of the 400 MHz 2D ^{1}H–^{13}C HSQC spectrum (in [D_8]toluene, at 23 °C) of a mixture containing **6a** and **6′a** (3:1).



Scheme 6. Reaction of 1,3,2-diselenaborolane **2a** with 1-phenylbut-1-yne.

spectra of compounds **6** and **8** when spectra could be recorded with a sufficient signal-to-noise ratio and high resolution (Figure 6).

Both the boron–carbon and boron–halogen bonds in **6** and **8** are susceptible to further transformations. First, we studied the slow oxidation/hydrolysis of samples with X =

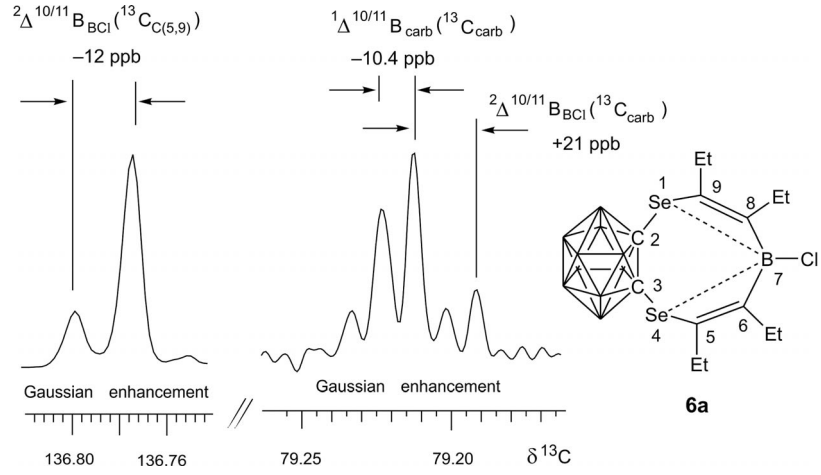
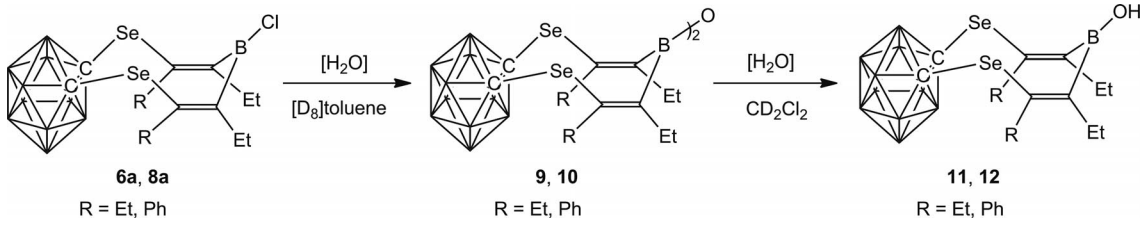


Figure 6. Expansions of the 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of **6a** for the ^{13}C(carb) and the olefinic ^{13}C(5,9) NMR signals showing secondary isotope effects due to the presence of ^{10}B and ^{11}B (ratio ca. 1:4). The characteristic splitting due to $^1\Delta^{10/11}B(^{13}C)$ has been discussed for dicarba-*closo*-dodecaboranes,[17] whereas the effects across selenium, $^2\Delta^{10/11}B(^{13}C)$ of opposite signs (!), were observed here for the first time.



Scheme 7. Slow hydrolysis of the B–Cl bond affording diboroxanes or borinic acids.

Cl (Scheme 7). Toluene solutions containing mainly **6a** or **8a** were kept unsealed for several days until a crystalline solid separated. The supernatant solution still contained compound **6** or **8**. The solid materials were collected and studied by X-ray crystallography (see below); they were identified as the diboroxanes **9** and **10**. When **9** or **10** were dissolved in CD_2Cl_2 and the samples again kept unsealed, after some time (1 d for **9**, 7 d for **10**) traces of moisture generated the borinic acids **11** and **12** (see Table 3 for the NMR spectroscopic data). Thus, slow hydrolysis of the B–Cl bond in **6** or **8** is preferred over slow oxidation.

DFT Calculations of Molecular Geometries, Chemical Shifts $\delta^{11}B$ and $\delta^{77}Se$, and Coupling Constants

The gas-phase molecular structures of the seven-membered rings **4a**, **5a**,**b** and **7a**, and the nine-membered rings **6a**,**b**, **6′a**,**b** and **11** were calculated and optimized at the B3LYP/6-311+G(d,p) level of theory.[18] In the case of the nine-membered rings, **6a** is slightly more stable (by 6.7 kcal/mol) than **6′a**. The calculated structures are similar to the experimental solid-state structures (**6a**,**b**, see below), although coordinative Se–B interactions are underestimated in the calculations. The mean Se–B distances are longer and the sums of bond angles deviate less from 360° for the calculated structures. This is regarded as a major reason for the differences in the calculated[19–21] and experimental NMR parameters, in particular with respect to $^{11}B(7)$ nuclear shielding. The calculated ^{77}Se nuclear shielding[22,23] as well as the trend in the calculated coupling constants $^nJ(^{77}Se,^{13}C)$[24,25] agree well with the experimental data given the inaccuracy of the calculated geometries.

Table 3. ^{13}C, ^{11}B and ^{77}Se NMR spectroscopic data for the *ortho*-carborane derivatives **10**–**12** in CD_2Cl_2.

Compound	**10**	**11**	**12**
$\delta^{13}C$ [$C(2,3)_{carb}$]	84.9	85.1	85.5
$\delta^{13}C$ [SeC=]	140.49	135.5	140.53
$\delta^{13}C$[=CB]	161.2 [br.]	162.2 [br.]	162.5 [br.]
$\delta^{13}C$ [SeC(*R*)]	Ph	Et	Ph
	128.7 (C_m)	29.5	128.5 (C_m)
	130.0 (C_o)	14.3	130.3 (C_o)
	128.5 (C_p)		128.2 (C_p)
	131.2 (C_i)		130.4 (C_i)
$\delta^{13}C$ [=C(*R*)B]	Et	Et	Et
	27.96	26.2	27.93
	14.4	14.6	14.1
$\delta^{11}B$ (=CBC=)	28.0	41.8	25.0
$\delta^{77}Se$ [SeC=]	626.5	560.5	625.6

X-ray Structural Analyses of the *ortho*-Carborane Derivatives 6a,b, 9 and 10

The molecular structures of the boron halides **6a**,**b** and boroxanes **9** and **10** are shown in Figures 7, 8 and 9 (see

Table 4 for the structural parameters). Intermolecular interactions appear to be negligible in all cases studied, although the arrangement of the molecules of **10** in the unit cell is remarkable (Figure 9B). All the relevant structural features of the carborane units agree with reported data.[10] The question of intramolecular Se–B bonding, already apparent from the δ^{11}B data, is also answered by inspecting the changes in the mean Se–B distances and the sums of the angles at the respective boron atoms. The longest mean Se–B distances are observed for the diboroxanes **9** and **10** (313.4 and 315.4 pm) followed by **6a** (299.8 pm) and **6b** (290.1 pm). This fits to changes in the sums of bond angles, which are close to 360° for the trigonal-planar surroundings of the boron atoms in **9** and **10** (358.7 and 359.1°), and point towards increasing pyramidalization in **6a** (356.2°) and **6b** (352.1°). The Se(1)–B(13) bonding interaction is also mirrored by the widening of the corresponding C(1)–Se(1)–C(3) angle when compared with C(12)–Se(2)–C(2), as is clearly evident for **6a** and **6b** and expectedly less so for **9** and **10**. The wide B–O–B bond angles in the diboroxanes **9** and **10** [169.3(3) and 178.2(8)°] are typical of this class of compounds.[26,27]

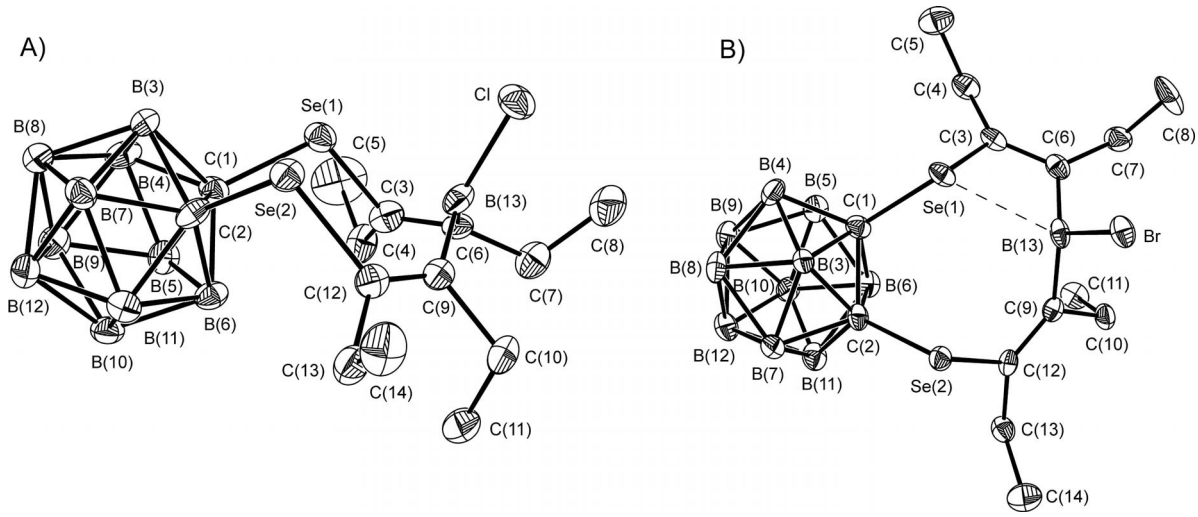


Figure 7. Molecular structures of (A) **6a** and (B) **6b** (ORTEP plots drawn at the 50% probability level, hydrogen atoms have been omitted for clarity; for selected distances and angles, see Table 4). The dashed line in (B) indicates the relatively short Se–B distance, typical of a coordinative interaction, supported by the sum of the bond angles at B(13) (356.2° for **6a** and 352.7° for **6b**).

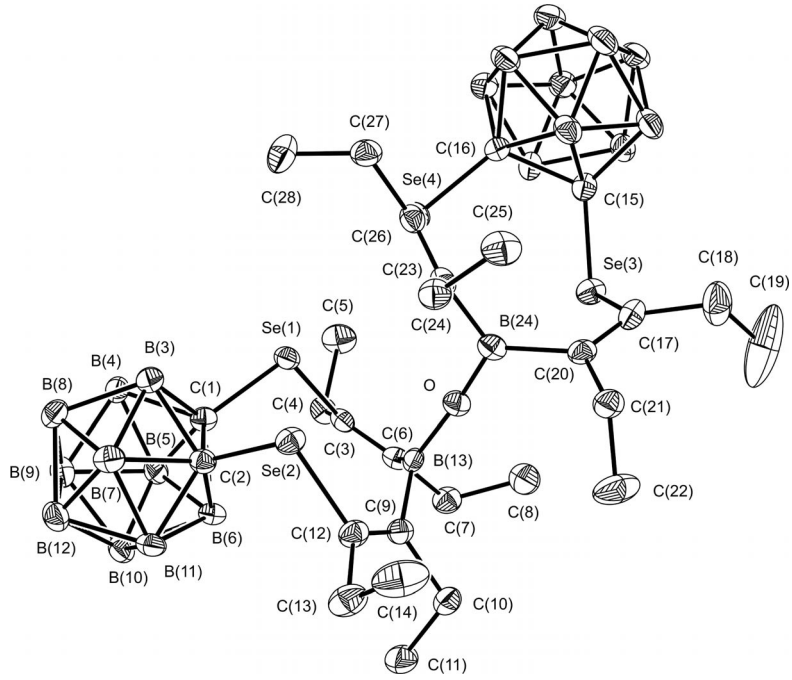


Figure 8. Molecular structure of 7,7′-oxobis{2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-5,6,8,9-tetraethyl-1,4-diselena-7-boracyclohepta-5,8-diene} (**9**; ORTEP plots drawn at the 50% probability level, hydrogen atoms have been omitted for clarity; for selected distances and angles, see Table 4).

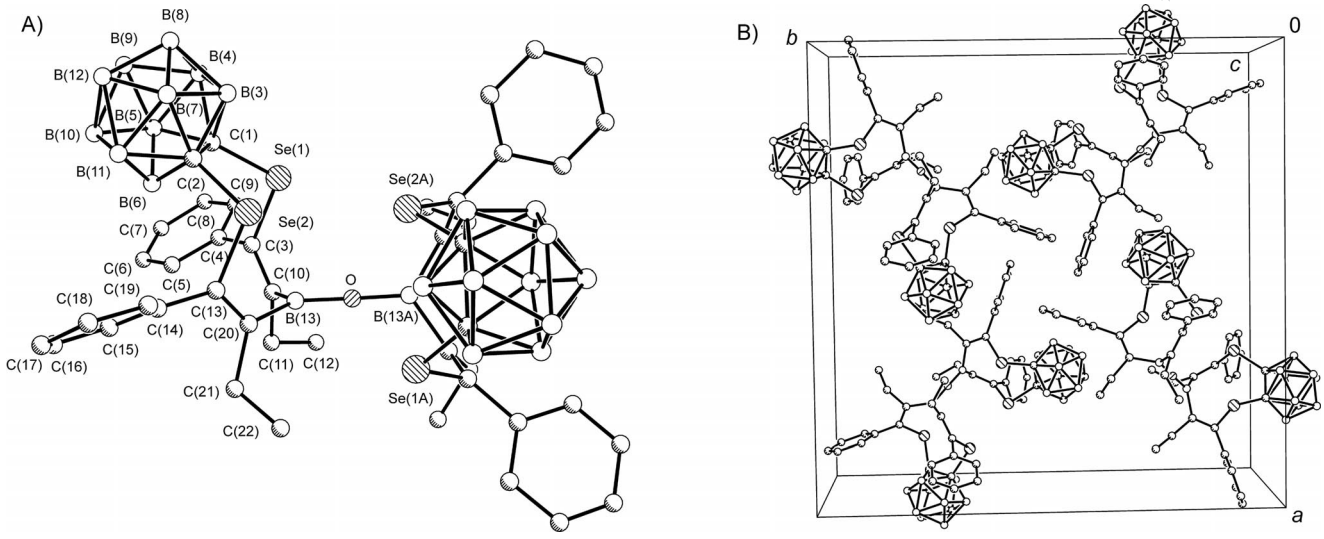


Figure 9. A) Molecular structure of 7,7′-oxybis{2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-6,8-diethyl-5,9-diphenyl-1,4-diselena-7-boracyclohepta-5,8-diene} (**10**; ball-and-stick model, hydrogen atoms have been omitted for clarity; for selected distances and angles, see Table 4). (B) Positions of molecules of **10** in the cryatal lattice.

Table 4. Selected bond lengths [pm] and angles [°] of the *ortho*-carborane derivatives **6a** and **6b**, (calcd. for the tetramethyl derivative), **9** (calcd. for the tetramethyl-BOH derivative) at 133 K and **10** at 293 K.

	6a X = Cl	Calcd. X = Cl	**6b** X = Br	Calcd. X = Br	**9** X = O	Calcd. X = OH		**10**[a] X = O
C(1)–Se(1)	193.0(6)	195.4	195.4(6)	195.5	192.9(3)	195.4	C(1)–Se(1)	193.3(6)
C(2)–Se(2)	193.7(7)	195.5	193.1(5)	195.6	192.1(3)	195.4	C(2)–Se(2)	194.1(6)
C(1)–C(2)	172.3(9)	178.9	169.8(8)	178.8	175.5(5)	179.9	C(1)–C(2)	174.5(8)
C(3)–Se(1)	193.7(7)	195.3	192.8(6)	195.4	194.9(3)	195.8	C(3)–Se(1)	193.3(6)
C(12)–Se(2)	194.0(7)	195.4	193.7(6)	195.4	194.3(3)	195.8	C(13)–Se(2)	191.6(7)
C(3)–C(6)	132.4(10)	134.2	134.4(9)	134.2	133.6(5)	133.7	C(3)–C(10)	132.8(8)
C(12)–C(9)	133.7(10)	134.3	133.6(8)	134.3	132.6(5)	133.7	C(13)–C(20)	133.5(9)
C(6)–B(13)	158.6(10)	157.5	158.0(9)	157.0	157.2(5)	158.7	C(10)–B(13)	157.4(9)
C(9)–B(13)	157.4(10)	157.6	157.6(9)	157.4	158.4(5)	158.8	C(20)–B(13)	157.5(10)
B(13)–X	177.7(8)	178.6	198.0(6)	195.7	135.7(4)	136.1	B(13)–O	134.8(6)
B(24)–X					133.8(4)		B(13A)–O	
Se(1)···B(13)	264.7	316.8	247.9	315.3	306.7	307.9	Se(1)···B(13)	310.8
Se(2)···B(13)	334.8	320.3	332.2	322.3	319.0	318.0	Se(2)···B(13)	320.0
Se(3)···B(24)					302.9			
Se(4)···B(24)					324.8			
C(3)–Se(1)–C(1)	109.1(3)	104.3	110.2(2)	103.8	103.39(13)	104.8	C(3)–Se(1)–C(1)	105.1(2)
C(12)–Se(2)–C(2)	100.6(3)	104.5	101.1(2)	104.5	101.21(14)	104.5	C(13)–Se(2)–C(2)	103.8(2)
Se(1)–C(1)–C(2)	116.0(4)	117.5	114.3(3)	117.7	116.7(2)	117.2	Se(1)–C(1)–C(2)	117.0(3)
Se(2)–C(2)–C(1)	116.9(4)	117.3	116.9(3)	117.3	118.2(2)	118.0	Se(2)–C(2)–C(1)	116.0(4)
Se(1)–C(3)–C(6)	107.0(5)	117.7	103.9(4)	118.0	116.5(3)	117.2	Se(1)–C(3)–C(10)	114.7(4)
Se(2)–C(12)–C(9)	119.4(5)	117.1	118.6(5)	116.9	118.6(3)	118.8	Se(2)–C(13)–C(20)	116.8(5)
C(3)–C(6)–B(13)	114.6(6)	125.5	111.6(5)	126.0	121.9(3)	123.5	C(3)–C(10)–B(13)	123.2(5)
C(12)–C(9)–B(13)	130.4(6)	124.6	130.2(5)	124.2	124.9(3)	126.4	C(13)–C(20)–B(13)	125.5(6)
C(6)–B(13)–C(9)	117.9(6)	122.0	120.3(5)	122.6	124.8(3)	120.3	C(10)–B(13)–C(20)	114.9(5)
C(6)–B(13)–X	121.5(5)	117.8	119.6(4)	117.3	117.9(3)	117.0	C(10)–B(13)–O	121.4(6)
C(9)–B(13)–X	116.8(5)	117.8	112.8(4)	117.3	116.0(3)	121.3	C(20)–B(13)–O	122.8(5)
Se(1)–C(3)–C(4)	121.4(5)	114.7	123.1(5)	114.7	113.5(2)	114.5	Se(1)–C(3)–C(4)	117.5(4)
Se(2)–C(12)–C(13)	112.8(5)	114.7	113.2(4)	114.7	113.8(3)	114.0	Se(2)–C(13)–C(14)	116.4(5)
C(7)–C(6)–B(13)	122.0(6)	113.1	125.1(5)	112.8	115.9(3)	114.6	C(11)–C(10)–B(13)	116.3(5)
C(10)–C(9)–B(13)	112.2(6)	113.4	110.6(5)	113.6	114.7(3)	113.1	C(21)–C(20)–B(13)	114.6(6)
B(24)–O–B(13)					169.3(3)		B(13)–O–B(13A)	178.2(8)

[a] The crystal structure contains about $0.2CD_2Cl_2$ per formula unit.

The molecule of **10** shows the symmetry C_2. The twofold axis runs through the oxygen atom at the center of the B–O–B bond (Figure 9A). Thus, only four molecules are found in the unit cell. The four molecules in the unit cell are generated by a $\bar{4}$ axis in the center of the *ab* plane running parallel to the *c* axis (Figure 9B).

Conclusions

The C≡C bond of various alkynes, except those of electron-deficient alkynes, inserts readily into the B–Se bond(s) of 1,3,2-diselenaborolanes, provided the boron atom is sufficiently Lewis-acidic and preferably in the presence of a B–X function (X = Cl, Br, I). In the first step, the reactions afforded novel seven-membered rings, and – for the first time – nine-membered rings containing six carbon, two selenium and one boron atom were formed in the second step. The insertion of 1-phenylbut-1-yne led selectively to heterocycles in which the selenium atoms and the phenyl groups are in geminal positions. In both the seven- and nine-membered rings, weak intramolecular coordinative Se–B interactions are indicated by NMR spectroscopy, confirmed by X-ray structural analysis. The new heterocycles are susceptible to further transformations; in the case of the nine-membered-ring compounds, the conversion of B–Cl into B–O functions was shown to take place selectively by slow hydrolysis.

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 solvents CH_2Cl_2 and CD_2Cl_2 were distilled from CaH_2 under argon. All other solvents were distilled from Na under argon. The starting materials, that is, **2a**–**e**, were prepared as described previously.[7] Dried [D_8]toluene was saturated with acetylene (1 atm) at 0 °C. Other starting materials were purchased from Aldrich [hex-3-yne (99%), 3,3-dimethylbut-1-yne (98%), 1-phenylbut-1-yne (99%), 1,4-dichlorobut-2-yne (99%), phenylethyne (98%), dimethyl acetylenedicarboxylate (99%)], and used as received. NMR measurements: Bruker DRX 500 and Bruker ARX 250: ^{1}H, ^{10}B, ^{11}B, ^{13}C, ^{29}Si and ^{77}Se; Varian INOVA 400: ^{1}H, ^{11}B, ^{13}C and ^{77}Se; chemical shifts are given relative to Me_4Si [δ^1H ($CHDCl_2$) = 5.33, ($C_6D_5CD_2H$) = 2.08 (±0.01) ppm; δ^{13}C (CD_2Cl_2) = 53.8, ($C_6D_5CD_3$) = 20.4 (±0.1) ppm], external BF_3·OEt_2 [δ^{11}B = 0 (±0.3) ppm for Ξ(^{11}B) = 32.083971 MHz], external BF_3·OEt_2 [δ^{10}B = 0 (±0.3) ppm for Ξ(^{10}B) = 10.743657 MHz], neat Me_2Se [δ^{77}Se = 0 (±0.1) ppm for Ξ(^{77}Se) = 19.071523 MHz]. ^{10}B NMR spectra were recorded to observe the extremely broad ^{10}B NMR signals of diluted samples. In the ^{11}B NMR spectra, these signals were partially covered by the probe head background signal. Assignments of ^{1}H and ^{11}B NMR signals are based on selective ^{1}H{^{11}B selective} heteronuclear decoupling experiments.[28] Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for ^{12}C, ^{1}H, ^{11}B, ^{16}O and ^{80}Se). Routinely carried out elemental analyses of the products as bulk samples did not give satisfactory and reproducible results. Possible reasons for this are the formation of boron carbide, the great sensitivity of the compounds (see the formation of **9**–**12**), and the presence of minor impurities (e.g., **3**). Melting points were determined with a Büchi 510 melting point apparatus. All quantum chemical calculations were carried out by using the Gaussian 09 program package.[29] Optimized geometries at the B3LYP/6-311+g(d.p) level of theory[18] were found to be minima by the absence of imaginary frequencies. NMR parameters were calculated[21,30] at the same level of theory. Calculated nuclear magnetic shieldings σ^{11}B and σ^{77}Se were converted into δ values by using δ^{11}B (calcd.) = σ(^{11}B) – σ(^{11}B, B_2H_6) with σ(^{11}B, B_2H_6) = +84.1 [δ^{11}B (B_2H_6) = 18 and δ^{11}B (BF_3·OEt_2) = 0] and δ^{77}Se(calcd.) = σ(^{77}Se) – σ(^{77}Se, $SeMe_2$) with σ(^{77}Se, $SeMe_2$) = +1621.7.

5-(*tert*-Butyl)-7-chloro-2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-1,4-diselena-7-boracyclohept-3-ene (4a): A solution of **2a** (0.26 mmol) in [D_8]toluene (0.6 mL) [from **1** (93.5 mg; 0.26 mmol) and BCl_3 (0.5 mL of a 1.0 M solution in toluene, 0.5 mmol)[7]] was cooled to –50 °C, and *tert*-butylethyne (0.032 mL, 21 mg, 0.26 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B and ^{1}H NMR spectroscopy. After 2 weeks at –30 °C, volatile materials were removed in vacuo to give **4a** as a white oil. ^{1}H{^{11}B} NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 0.79 (s, 9 H, CH_3), 2.58, 2.75 [2 br. s, 3 H, 5 H, HB for δ(^{11}B) = –11.8, –8.5 ppm], 2.90 [br. s, 1 H, HB for δ(^{11}B) = –3.0 ppm], 2.96 [br. s, 1 H, HB for δ(^{11}B) = –0.9 ppm], 6.34 [s, ^3J(^{77}Se,^{1}H) = 9.6 Hz, 1 H, SeC=CH] ppm. ^{11}B{^{1}H} NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –11.8 (1 B), –8.5 (7 B), –3.0 (1 B), –0.9 (1 B), 63.3 (1 B, BCl) ppm. ^{11}B NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –11.8 [d, ^1J(^{11}B,^{1}H) = 164 Hz, 1 B], –8.5 (m, 7 B), –3.0 [d, ^1J(^{11}B,^{1}H) = 151 Hz, 1 B], –0.9 [d, ^1J(^{11}B,^{1}H) = 151 Hz, 1 B], 63.3 (s, 1 B, BCl) ppm.

7-Chloro-2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-5,6-diethyl-1,4-diselena-7-boracyclohept-3-ene (5a): A solution of **2a** (0.24 mmol) in [D_8]toluene (0.6 mL) [from **1** (85 mg; 0.24 mmol) and BCl_3 (0.45 mL of a 1.0 M solution in toluene, 0.45 mmol)[7]] was cooled to –50 °C, and hex-3-yne (0.027 mL, 19.5 mg, 0.24 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B and ^{1}H NMR spectroscopy. After 1 h at room temp., the mixture contained **5a** together with **2a** (ca. 5%, by ^{77}Se NMR). ^{1}H{^{11}B} NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 0.71 [t, ^3J(H,H) = 7.4 Hz, 3 H, C(5)CCH_3], 0.83 [t, ^3J(H,H) = 7.6 Hz, 3 H, C(6)CCH_3], 1.85 [dq, ^2J(H,H) = 14.8 Hz, ^3J(H,H) = 7.4 Hz, 1 H, C(5)CH(a)], 1.91 [dq, ^2J(H,H) = 15.2 Hz, ^3J(H,H) = 7.6 Hz, 1 H, C(6)CH(a)], 2.03 [dq, ^2J(H,H) = 15.2 Hz, ^3J(H,H) = 7.6 Hz, 1 H, C(6)CH(b)], 2.12 [dq, ^2J(H,H) = 14.8 Hz, ^3J(H,H) = 7.4 Hz, 1 H, C(5)CH(b)], 2.50 [br. m, 1 H, HB for δ(^{11}B) = –9.3 ppm], 2.55 [br. m, 2 H, HB for δ(^{11}B) = –6.3, –12.0 ppm], 2.63 [br. m, 1 H, HB for δ(^{11}B) = –8.8 ppm], 2.68 [br. m, 2 H, HB for δ(^{11}B) = –7.9, –8.8 ppm], 2.72 [br. m, 1 H, HB for δ(^{11}B) = –7.9 ppm], 2.83 [br. s, 1 H, HB for δ(^{11}B) = –7.9 ppm], 2.86 [br. s, 1 H, HB for δ(^{11}B) = –3.3 ppm], 3.00 [br. s, 1 H, HB for δ(^{11}B) = –0.8 ppm] ppm. ^{11}B{^{1}H} NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –12.0 (1 B), –9.3 (1 B), –8.8 (2 B), –7.9 (3 B), –6.3 (1 B), –3.3 (1 B), –0.8 (1 B), 57.2 (1 B, BCl) ppm. ^{11}B NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –12.0 [d, ^1J(^{11}B,^{1}H) = 194 Hz, 1 B], –9.3 [d, ^1J(^{11}B,^{1}H) = 169 Hz, 1 B], –8.8 [d, ^1J(^{11}B,^{1}H) = 150 Hz, 2 B], –7.9 [d, ^1J(^{11}B,^{1}H) = 145 Hz, 3 B], –6.3 (d, 1 B), –3.3 [d, ^1J(^{11}B,^{1}H) = 150 Hz, 1 B], –0.8 [d, ^1J(^{11}B,^{1}H) = 151 Hz, 1 B], 57.2 (s, 1 B, BCl) ppm.

7-Bromo-2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-5,6-diethyl-1,4-diselena-7-boracyclohept-3-ene (5b): A solution of **2b** (0.24 mmol) in [D_8]toluene (0.6 mL) [from **1** (85 mg; 0.24 mmol) and BBr_3 (0.4 mL of a 1.0 M solution in hexane, 0.4 mmol)[7]] was cooled to –50 °C, and hex-3-yne (0.027 mL, 19.5 mg, 0.24 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B and ^{1}H NMR spectroscopy. After 1 h at room temp., the mixture contained **5b** together with **6b** (<5%, by ^{77}Se NMR). ^{1}H{^{11}B} NMR (250.13 MHz, [D_8]toluene, 25 °C): δ = 0.71 [t, ^3J(H,H) = 7.5 Hz, 3 H, C(5)CCH_3], 0.88 [t, ^3J(H,H) = 7.6 Hz, 3 H, C(6)CCH_3], 1.84 [dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 1 H, C(5)CH(a)], 1.95 [dq, ^2J(H,H) = 14.8 Hz, ^3J(H,H) = 7.6 Hz, 1 H, C(6)CH(a)], 2.11 [m, 2 H, C(6)CH(b), C(5)CH(b)], 2.45–2.80 [br. m, 8 H, HB for δ(^{11}B) = –8.6, –12.7 ppm], 2.83 [br. s, 1 H, HB

for $\delta(^{11}B)$ = –3.3 ppm], 2.98 [br. s, 1 H, HB for $\delta(^{11}B)$ = –1.2 ppm] ppm. $^{11}B\{^1H\}$ NMR (80.25 MHz, [D$_8$]toluene, 25 °C): δ = –12.7 (1 B), –8.6 (7 B), –3.3 (1 B), –1.2 (1 B), 50.3 (1 B, BBr) ppm. ^{11}B NMR (80.25 MHz, [D$_8$]toluene, 25 °C): δ = –12.7 (d, 1 B), –8.6 (7 B), –3.3 [d, $^1J(^{11}B,^1H)$ = 156 Hz, 1 B], –1.2 [d, $^1J(^{11}B,^1H)$ = 156 Hz, 1 B], 50.3 (s, 1 B, BBr) ppm.

2,3-[1,2-Dicarba-*closo*-dodecaborano(12)]-5,6-diethyl-7-iodo-1,4-diselena-7-boracyclohept-3-ene 5c): A solution of **2c** (0.20 mmol) in [D$_8$]toluene (0.5 mL) [from **1** (85 mg; 0.20 mmol) and BI_3 (0.2 mmol)[7]] was cooled to –50 °C, and hex-3-yne (0.023 mL, 16.8 mg, 0.20 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B and ^1H NMR spectroscopy. After 3 h at room temp., the mixture contained **5c** together with **6c** (<5%, by ^{77}Se NMR). $^1H\{^{11}B\}$ NMR (250.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.67 [t, ^3J(H,H) = 7.4 Hz, 3 H, C(5)CCH$_3$], 0.90 [t, ^3J(H,H) = 7.6 Hz, 3 H, C(6)CCH$_3$], 1.81 [dq, ^2J(H,H) = 14.8 Hz, ^3J(H,H) = 7.4 Hz, 1 H, C(5)CH(a)], 1.94 [dq, ^2J(H,H) = 15.2 Hz, ^3J(H,H) = 7.6 Hz, 1 H, C(6)CH(a)], 2.11 [m, 2 H, C(6)-CH(b), C(5)CH(b)], 2.50–2.80 [br. m, 8 H, HB for $\delta(^{11}B)$ = –8.6, –11.5 ppm], 2.80 [br. s, 1 H, HB for $\delta(^{11}B)$ = –3.2 ppm], 2.94 [br. s, 1 H, HB for $\delta(^{11}B)$ = –1.6 ppm] ppm. $^{11}B\{^1H\}$ NMR (80.25 MHz, [D$_8$]toluene, 25 °C): δ = –11.5 (1 B), –8.8 (7 B), –3.2 (1 B), –1.6 (1 B), 34.1 (1 B, BI) ppm. ^{11}B NMR (80.25 MHz, [D$_8$]toluene, 25 °C): δ = –11.5 (d, 1 B), –8.8 (7 B), –3.2 [d, $^1J(^{11}B,^1H)$ = 147 Hz, 1 B], –1.6 [d, $^1J(^{11}B,^1H)$ = 142 Hz, 1 B], 34.1 (s, 1 B, BI) ppm.

2,3-[1,2-Dicarba-*closo*-dodecaborano(12)]-5,6-diethyl-7-phenyl-1,4-diselena-7-boracyclohept-3-ene (5d): A solution of **2d** (0.28 mmol) in [D$_8$]toluene (0.6 mL) was cooled to –50 °C, and hex-3-yne (0.031 mL, 23 mg, 0.28 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B and ^1H NMR spectroscopy. After 4 d at room temp., the mixture contained **5d** (ca. 50%) and **2d** (ca. 50%) together with hex-3-yne. After 20 h at 50 °C, the mixture contained **5d** (ca. 40%) and **2d** (ca. 60%) together with tetraselenide **3**, hex-3-yne and $(PhBO)_3$. Data for **5d**: ^1H NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.81 [t, ^3J(H,H) = 7.5 Hz, 3 H, CH$_3$], 0.85 [t, ^3J(H,H) = 7.5 Hz, 3 H, CH$_3$], 1.98 [m, 2 H, C(5)CH(a), C(6)CH(a)], 2.14, 2.39 [2 dq, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1 H, 1 H, C(5)CH(b), C(6)CH(b)], 7.10 (m, 2 H, H$_m$ from Ph), 7.18 (m, 1 H, H$_p$ from Ph), 7.51 (m, 2 H, H$_o$ from Ph) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –18 to 0 for the mixture of **5d** and **2d** (overlapping signals), 56.4 (PhBSe for **5d**), 76.2 (PhBSe for **2d**) ppm.

7-Chloro-2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-6-ethyl-5-phenyl-1,4-diselena-7-boracyclohept-3-ene (7a): A solution of **2a** (0.23 mmol) in [D$_8$]toluene (0.5 mL) [from **1** (85 mg; 0.24 mmol) and BCl_3 (0.5 mL of a 1.0 M solution in toluene, 0.5 mmol)[7]] was cooled to –50 °C, and 1-phenylbut-1-yne (0.033 mL, 29.9 mg, 0.23 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B and ^1H NMR spectroscopy. After 1 h at room temp., the mixture contained **7a** together with **8a** and **2a** (ca. 5%, by ^{77}Se NMR). ^1H NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.86 [t, ^3J(H,H) = 7.6 Hz, 3 H, CH$_3$], 2.21 [dq, ^2J(H,H) = 15.2 Hz, ^3J(H,H) = 7.6 Hz, 1 H, C(6)CH(a)], 2.29 [dq, ^2J(H,H) = 15.2 Hz, ^3J(H,H) = 7.6 Hz, 1 H, C(6)CH(b)], 6.95–7.00 (m, 5 H, Ph) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –11.7 (1 B), –8.5 (7 B), –3.0 (1 B), –1.2 (1 B), 52.3 (1 B, BCl) ppm. ^{11}B NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –11.7 [d, $^1J(^{11}B,^1H)$ = 164 Hz, 1 B], –8.5 (7 B), –3.0 [d, $^1J(^{11}B,^1H)$ = 155 Hz, 1 B], –1.2 [d, $^1J(^{11}B,^1H)$ = 150 Hz, 1 B], 52.3 (s, 1 B, BCl) ppm.

7-Chloro-2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-5,6,8,9-tetraethyl-1,4-diselena-7-boracyclohepta-5,8-diene (6a and 6′a): A solution of **5a** [0.24 mmol; [together with **2a** (ca. 5%), see above] in [D$_8$]-toluene (0.6 mL) was cooled to –50 °C, and hex-3-yne (0.03 mL, 21.5 mg, 0.26 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B, ^1H and ^{77}Se NMR spectroscopy. After 2 d at room temp., the mixture contained **6a**, **6′a** and hex-3-yne. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr). The resulting mixture thus obtained contained **6a** (ca. 70%) and **6′a** (ca. 30%). Transparent single crystals of **6a** for X-ray analysis were grown from [D$_8$]toluene after 3 weeks at –30 °C; m.p. 100–103 °C. Data for **6a**: ^1H NMR (399.8 MHz, [D$_8$]-toluene, 25 °C): δ = 0.91 [t, ^3J(H,H) = 7.5 Hz, 6 H, C(5,9)CCH$_3$], 0.94 [t, ^3J(H,H) = 7.5 Hz, 6 H, C(6,8)CCH$_3$], 1.94 [dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 2 H, C(6,8)CH(a)], 2.05 [dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 2 H, C(6,8)CH(b)], 2.09 [dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 2 H, C(5,9)CH(a)], 2.45 [dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 2 H, C(5,9)CH(b)] ppm. Data for **6′a**: ^1H NMR (399.8 MHz, [D$_8$]toluene, 25 °C): δ = 0.93 [t, ^3J(H,H) = 7.5 Hz, 6 H, C(5,9)CCH$_3$], 0.94 [t, ^3J(H,H) = 7.5 Hz, 6 H, C(6,8)-CCH$_3$], 2.26 [dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 2 H, C(6,8)CH(a)], 2.28 [dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 2 H, C(5,9)CH(a)], 2.39 [dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 2 H, C(6,8)CH(b)], 2.65 [dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 2 H, C(5,9)CH(b)] ppm. Data for **6a** + **6′a**: $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –12.0 to –5.0 (8 B), –1.6 (2 B) for the mixture of **6a** and **6′a** (overlapping signals), 42.0 (1 B, BCl for **6a**), 48.5 (1 B, BCl for **6′a**) ppm.

7-Bromo-2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-5,6,8,9-tetraethyl-1,4-diselena-7-boracyclohepta-5,8-diene (6b and 6′b): A solution of **5b** (0.24 mmol; see above) in [D$_8$]toluene (0.6 mL) was cooled to –50 °C, and hex-3-yne (0.03 mL, 21.7 mg, 0.26 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B, ^1H and ^{77}Se NMR spectroscopy. After 5 d at room temp., the mixture contained **6b**, **6′b** and hex-3-yne. Volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr). The resulting mixture thus obtained contained **6b** (ca. 90%) and **6′b** (ca. 5–10%) together with tetraselenide **3** (2–3%). Transparent single crystals of **6b** for X-ray analysis were grown from [D$_8$]toluene after 2 weeks at –30 °C; m.p. 115–120 °C. Data for **6b**: $^1H\{^{11}B\}$ NMR (399.8 MHz, [D$_8$]toluene, 25 °C): δ = 0.88 [t, ^3J(H,H) = 7.4 Hz, 6 H, C(5,9)-CCH$_3$], 1.01 [t, ^3J(H,H) = 7.6 Hz, 6 H, C(6,8)CCH$_3$], 2.03 [m, 6 H, C(6,8)CH$_2$, C(5,9)CH(a)], 2.42 [dq, ^2J(H,H) = 14.8 Hz, ^3J(H,H) = 7.4 Hz, 2 H, C(5,9)CH(b)], 2.61 [br. m, 6 H, HB for $\delta(^{11}B)$ = –9.4 ppm], 2.80 [br. m, 2 H, HB for $\delta(^{11}B)$ = –8.0 ppm], 2.94 [br. m, 2 H, HB for $\delta(^{11}B)$ = –1.6 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –9.4 (6 B), –8.0 (2 B), –1.5 (2 B), 28.0 (1 B, BBr) ppm. ^1H and ^{11}B NMR signals for **6′b** could not be assigned with certainty owing to low concentration and severe overlap with signals for **6b**.

2,3-[1,2-Dicarba-*closo*-dodecaborano(12)]-5,6,8,9-tetraethyl-7-iodo-1,4-diselena-7-boracyclohepta-5,8-diene (6c): A solution of **5c** (0.20 mmol; see above) in [D$_8$]toluene (0.6 mL) was cooled to –50 °C, and hex-3-yne (0.025 mL, 18 mg, 0.22 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B, ^1H and ^{77}Se NMR spectroscopy. After 5 d at room temp., volatile materials were removed in vacuo (3 h, 8×10^{-3} Torr). The resulting mixture thus obtained contained **6c** (ca. 90%) together with several unidentified side-products (ca. 10%). $^1H\{^{11}B\}$ NMR (399.8 MHz, [D$_8$]toluene, 25 °C): δ = 0.82 [t, ^3J(H,H) = 7.4 Hz, 6 H, C(5,9)CCH$_3$], 1.02 [t, ^3J(H,H) = 7.6 Hz, 6 H, C(6,8)-CCH$_3$], 2.02 [m, 6 H, C(6,8)CH$_2$, C(5,9)CH(a)], 2.36 [dq, ^2J(H,H) = 14.8 Hz, ^3J(H,H) = 7.4 Hz, 2 H, C(5,9)CH(b)], 2.45–2.80 (m, 8 H, HB), 2.94 [br. m, 2 H, HB for $\delta(^{11}B)$ = –1.6 ppm] ppm. $^{11}B\{^1H\}$

NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –12.0 to –5.0 (8 B), –1.6 (2 B), 9.0 (1 B, BI) ppm.

7-Chloro-2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-6,8-diethyl-5,9-diphenyl-1,4-diselena-7-boracyclohepta-5,8-diene (8a and 8′a): A solution of **7a** (0.23 mmol) [together with **8a** and **2a** (ca. 5%), see above] in [D$_8$]toluene (0.6 mL) was cooled to –50 °C, and 1-phenylbut-1-yne (0.035 mL, 32.0 mg, 0.25 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{11}B, ^{1}H and ^{77}Se NMR spectroscopy. After 3 d at room temp., the mixture contained **8a**, **8′a** and 1-phenylbut-1-yne. Volatile materials were removed in vacuo (5 h, 8×10^{-3} Torr). The resulting mixture thus obtained contained **8** (ca. 90%) and **8′a** (ca. 5–10%). Data for **8a**: ^{1}H{^{11}B} NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.88 [t, ^{3}J(H,H) = 7.6 Hz, 6 H, CH$_3$], 2.06 [dq, ^{2}J(H,H) = 15.2 Hz, ^{3}J(H,H) = 7.6 Hz, 2 H, C(6,8)CH(a)], 2.49 [dq, ^{2}J(H,H) = 15.2 Hz, ^{3}J(H,H) = 7.6 Hz, 2 H, C(6,8)CH(b)], 2.89 (m, 10 H, BH), 6.98 (m, 2 H, H$_p$), 7.07 (m, 4 H, H$_m$), 7.16 (m, 4 H, H$_o$) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –9.8 (4 B), –8.0 (4 B), –1.4 (2 B), 28.0 (v. br., 1 B, BCl) ppm. Data for **8′a**: ^{1}H{^{11}B} NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.87 [t, ^{3}J(H,H) = 7.6 Hz, 6 H, CH$_3$], 2.19 [dq, ^{2}J(H,H) = 15.2 Hz, ^{3}J(H,H) = 7.6 Hz, 2 H, C(6,8)CH(a)], 2.60 [dq, ^{2}J(H,H) = 15.2 Hz, ^{3}J(H,H) = 7.6 Hz, 2 H, C(6,8)CH(b)], 2.89 (m, 10 H, BH), 7.01 (m, 2 H, H$_p$), 7.11 (m, 4 H, H$_m$), 7.38 (m, 4 H, H$_o$) ppm.

7,7′-Oxybis{2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-5,6,8,9-tetraethyl-1,4-diselena-7-boracyclohepta-5,8-diene} (9): The mixture containing **6a** and **6′a** slowly formed the anhydride **9** on standing in toluene. Transparent single crystals of **9** for X-ray analysis were grown from CD_2Cl_2 after 1 d at room temp.; m.p. 210–213 °C. MS (EI, 70 eV): calcd. for $C_{28}H_{60}B_{21}Se_4O$ 956; *m*/*z* (%) = 956 (10) [M]$^+$, 927 (5) [M – Et]$^+$, 876 [M – SeH]$^+$.

7,7′-Oxybis{2,3-[1,2-dicarba-*closo*-dodecaborano(12)]-6,8-diethyl-5,9-diphenyl-1,4-diselena-7-boracyclohepta-5,8-diene} (10): The mixture containing **8a** and **8′a** slowly formed the anhydride **10** on standing at –30 °C in [D$_8$]toluene. Insoluble materials were separated by centrifugation and redissolved in CD_2Cl_2. Transparent single crystals of **10** for X-ray analysis were grown from CD_2Cl_2 after 3 d at room temp.; m.p. 210–213 °C. ^{1}H{^{11}B} NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 0.98 [t, ^{3}J(H,H) = 7.6 Hz, 12 H, CH$_3$], 1.56 (br. m, 4 H, HB), 1.90 (br. m, 6 H, HB), 2.22 (br. m, 6 H, HB), 2.38 [dq, ^{2}J(H,H) = 14.5 Hz, ^{3}J(H,H) = 7.6 Hz, 4 H, C(6,8)CH(a)], 2.46 (br. m, 4 H, HB), 2.70 [dq, ^{2}J(H,H) = 14.5 Hz, ^{3}J(H,H) = 7.6 Hz, 4 H, C(6,8)H(b)], 7.32–7.45 (m, 20 H, Ph) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, CD_2Cl_2, 25 °C): δ = –10.6 (6 B), –8.5 (4 B), –7.4 (4 B), –2.2 (6 B), 28.0 (v. br., 2 B, BOB) ppm. ^{10}B{^{1}H} NMR (53.7 MHz, CD_2Cl_2, 25 °C): δ = –10.6 (6 B), –8.7 (8 B), –2.4 (6 B), 28.0 (br., 2 B, BOB) ppm.

2,3-[1,2-Dicarba-*closo*-dodecaborano(12)]-5,6,8,9-tetraethyl-7-hydroxy-1,4-diselena-7-boracyclohepta-5,8-diene (11): Compound **9** is moisture-sensitive and decomposed in CD_2Cl_2 (1 d) at room temp. to form **11**; m.p. 190–195 °C. ^{1}H{^{11}B} NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 1.06 [t, ^{3}J(H,H) = 7.5 Hz, 12 H, CH$_3$], 1.07 [t, ^{3}J(H,H) = 7.4 Hz, 12 H, CH$_3$], 1.97 [br. m, 2 H, HB for δ(^{11}B) = –10.5 ppm], 2.07 [br. m, 2 H, HB for δ(^{11}B) = –8.6 ppm], 2.21 [dq, ^{2}J(H,H) = 15.0 Hz, ^{3}J(H,H) = 7.5 Hz, 4 H, CH from CH$_2$], 2.27 [dq, ^{2}J(H,H) = 14.8 Hz, ^{3}J(H,H) = 7.4 Hz, 4 H, CH from CH$_2$], 2.40 [dq, ^{2}J(H,H) = 15.0 Hz, ^{3}J(H,H) = 7.5 Hz, 4 H, CH from CH$_2$], 2.42 [br. m, 6 H, HB for δ(^{11}B) = –2.3 ppm], 2.51 [br. m, 4 H, HB for δ(^{11}B) = –10.5 ppm], 2.69 [br. m, 6 H, HB for δ(^{11}B) = –6.3 ppm], 2.85 [dq, ^{2}J(H,H) = 15.0 Hz, ^{3}J(H,H) = 7.5 Hz, 4 H, CH from CH$_2$], 5.66 (s, 1 H, BOH) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, CD_2Cl_2, 25 °C): δ = –10.5 (6 B), –8.7 (2 B), –6.3 (6 B), –2.3 (6 B), 41.8 (br., 2 B, BOB) ppm. MS (EI, 70 eV): calcd. for $C_{14}H_{31}B_{11}Se_2O$ 492; *m*/*z* (%) = 493 (30) [MH]$^+$, 463 (50) [M – EtH]$^+$, 329 (70).

2,3-[1,2-Dicarba-*closo*-dodecaborano(12)]-6,8-diethyl-7-hydroxy-5,9-diphenyl-1,4-diselena-7-boracyclohepta-5,8-diene (12): Compound **10** is moisture-sensitive and decomposed slowly (7 d) in CD_2Cl_2 at room temp. to form **12**; m.p. 170–172 °C. ^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 0.93 [t, ^{3}J(H,H) = 7.5 Hz, 6 H, CH$_3$], 2.32 [dq, ^{2}J(H,H) = 14.3 Hz, ^{3}J(H,H) = 7.5 Hz, 2 H, C(6,8)CH(a)], 2.58 [dq, ^{2}J(H,H) = 14.3 Hz, ^{3}J(H,H) = 7.5 Hz, 2 H, C(6,8)H(b)], 6.19 (s, 1 H, BOH), 7.32–7.45 (m, 20 H, Ph) ppm. ^{10}B{^{1}H} NMR (53.7 MHz, CD_2Cl_2, 25 °C): δ = –10.6 (6 B), –8.7 (8 B), –2.3 (6 B),

Table 5. Crystallographic data for the *ortho*-carborane derivatives **6a**, **6b**, **9** and **10**.

	6a	**6b**	**9**	**10**
Empirical formula	$C_{14}H_{30}B_{11}ClSe_2$	$C_{14}H_{30}B_{11}BrSe_2$	$C_{28}H_{60}B_{22}OSe_4$	$C_{44}H_{60}B_{21}OSe_4 \cdot 0.2CD_2Cl_2$
Crystal	colourless prism	colourless prism	colourless block	colourless block
Dimensions [mm]	0.22 × 0.18 × 0.16	0.24 × 0.19 × 0.18	0.30 × 0.23 × 0.20	0.30 × 0.26 × 0.24
T [K]	133(2)	133(2)	133(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic	tetragonal
Space group	$P2_1/n$	$P2_1/n$	Cc	$P\bar{4}n2$
Lattice parameters				
a [pm]	707.66(14)	1053.8(2)	1201.9(2)	2368.4(3)
b [pm]	1789.2(4)	1984.7(4)	1815.6(4)	
c [pm]	1821.1(4)	1128.4(2)	2137.3(4)	1114.6(2)
β [°]	100.49(3)	100.54(3)	100.73(3)	
Z	4	4	4	8
μ [mm^{-1}]	3.379	4.909	3.228	2.466
Diffractometer	STOE IPDS II, Mo-K_α, λ = 71.073 pm, graphite monochromator			
θ range [°]	1.61–25.69	2.05–25.70	1.94–25.70	1.72–29.44
Reflections collected	8071	27639	29173	118921
Independent reflections [$I \geq 2\sigma(I)$]	3230	3294	8091	5035
Absorption correction	none[a]	none[a]	numerical	none[a]
Max./min. transmission			0.9371/0.7414	
Refined parameters	253	253	500	329
wR2/*R1* [$I \geq 2\sigma(I)$]	0.1588/0.0726	0.0925/0.0546	0.0606/0.0280	0.1248/0.0497
Flack parameter			–0.001(7)	0.000(17)
Max./min. residual electron density [10^{-6} e pm^{-3}]	1.576/–0.807	0.758/–0.574	0.529/–0.317	0.505/–0.447

[a] Absorption corrections did not improve the parameter set.

25.0 (br., 2 B, BOB) ppm. MS (EI, 70 eV): calcd. for $C_{22}H_{31}B_{11}Se_2O$ (588); *m/z* (%) = 588 (20) $[M]^+$, 457 (10).

Crystal Structure Determination of 6a, 6b, 9 and 10: Structure solutions and refinements were carried out with the program package SHELX-97.[31] Details pertinent to the crystal structure determination are listed in Table 5. Crystals of an appropriate size were sealed under argon in Lindemann capillaries, and the data collections were carried out at 133 (for **6a**, **6b** and **9**) and 293 K (for **10**).[32]

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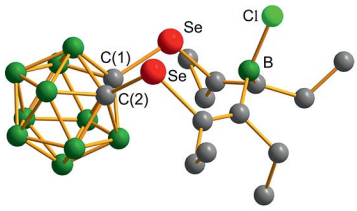
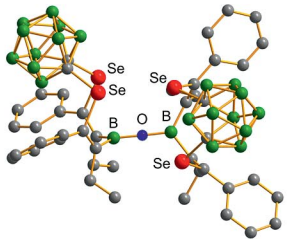
Alkyne Insertion





After two insertions of non-terminal alkynes into the B–Se bonds of 2-halogeno-1,3,2-diselenaborolanes novel nine-membered rings are formed. The reactions were shown to proceed stepwise and also selectively.

Keywords: Carboranes / Selenium / Alkynes / Heterocycles / Insertion / NMR spectroscopy / Density functional calculations

