DOI: 10.1002/ejic.201001324

A Spirocyclic Borate and a Dihydroborate Derived from the 1,2-Diselenolato-1,2-dicarba-*closo*-dodecaborane(12) Dianion $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})Se_2]^{2-}$: Structures, NMR Spectroscopy, and DFT Calculations

Bernd Wrackmeyer,*[a] Elena V. Klimkina,[a] and Wolfgang Milius[a]

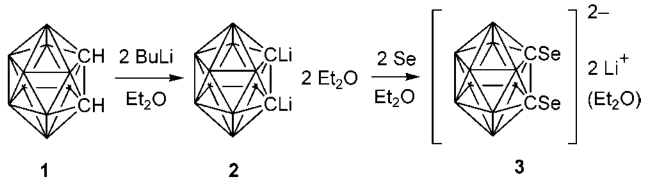
Keywords: Borates / Carboranes / Selenium / NMR spectroscopy / X-ray diffraction

The reaction of the diselenolato-1,2-dicarba-*closo*-dodecaborane(12) dianion with BF_3–OEt_2 affords selectively a spirocyclic bis(1,2-dicarba-*closo*-dodecaborane-1,2-diselena)borate, whereas the analogous reaction with boron trichloride leads mainly to 1,2-bis(ethylseleno)-1,2-dicarba-*closo*-dodecaborane(12) through ether cleavage. The spirocyclic borate reacts with methanol by cleavage of both Se–B and Se–C bonds. With borane in THF (BH_3/THF) and also with $LiBH_4$ exchange reactions take place, which afford the 1,2-dicarba-*closo*-dodecaborane-1,2-diselenadihydroborate. The molecular structures of both borates as tetrabutylammonium salts were determined by X-ray analysis. In solution, the borates were characterized by multinuclear magnetic resonance spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{77}Se). The gas-phase geometries of the borate anions were optimized [RB3LYP/6-3111+G(d,p) level of theory], and the NMR spectroscopic parameters (chemical shifts and coupling constants) were calculated.

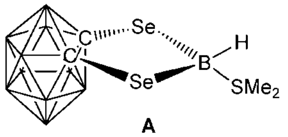
Introduction

A major part of the rich chemistry of 1,2-dicarba-*closo*-dodecaborane(12) **1** ("*ortho*-carborane")[1,2] results from metalation [e.g., dilithiation (**2**)][1–3] followed by various reactions of the reactive metal–carbon bond, among which the insertion of chalcogens is particularly attractive (Scheme 1). Indeed, the dianions of type **3** have proved to be valuable ligands in transition-metal chemistry,[4–7] and their main-group-element chemistry is also a developing and promising field.[8–14] The selenium derivative **3** is particularly attractive, since the ^{77}Se nucleus (natural abundance 7.58%; I = ½) possesses favorable NMR spectroscopic properties, and thus ^{77}Se NMR spectroscopy is well suited to monitor reactions and characterize products, even in mixtures.[15] We have shown that it is advisable for many purposes to use **3** after careful isolation[10,12,14] instead of relying on the seemingly more convenient in situ preparation of the reagent, since this may give rise to side reactions.

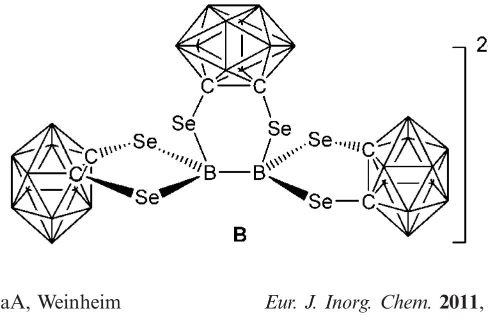
In the present work, we report on the treatment of **3** with boron halides such as Et_2O–BF_3 and boron trichloride BCl_3, with an aim toward the synthesis of boranes, borane adducts, or borates. Although the latter are well known in the chemistry of boron–oxygen compounds,[16,17] well-characterized examples for sulfur[18] or selenium[19] are scarce. The products observed here were characterized by NMR spectroscopy, in two cases by X-ray structural analysis, and gas-phase geometries were optimized by DFT methods, which also served for the calculation of NMR spectroscopic parameters (chemical shits and spin–spin coupling constants). So far, solely the dimethyl sulfide borane adduct **A** has been isolated and structurally characterized,[10] and one diborate **B** derived from the 1,2-diselenolato-1,2-dicarba-



Scheme 1. Dilithiation of *ortho*-carborane (**1**) to give **2**, and insertion of selenium into the C–Li bonds.



A



B

---

[a] Laboratorium für Anorganische Chemie II, Universität Bayreuth,
95440 Bayreuth, Germany
Fax: +49-921-552157
E-mail: b.wrack@uni-bayreuth.de

closo-dodecaborane(12) dianion in **3** has been reported.[8] Using the sulfur analogue of **3**, $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})S_2]^{2-}$, in reactions with boron halides, the formation of a spiroborate anion $\{[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})S_2]_2B\}^-$ has been proposed mainly on the basis of the ^{11}B NMR spectroscopic signal ($\delta^{11}B$ = 13.4 ppm) of the central tetracoordinate boron atom.[9]

Results and Discussion

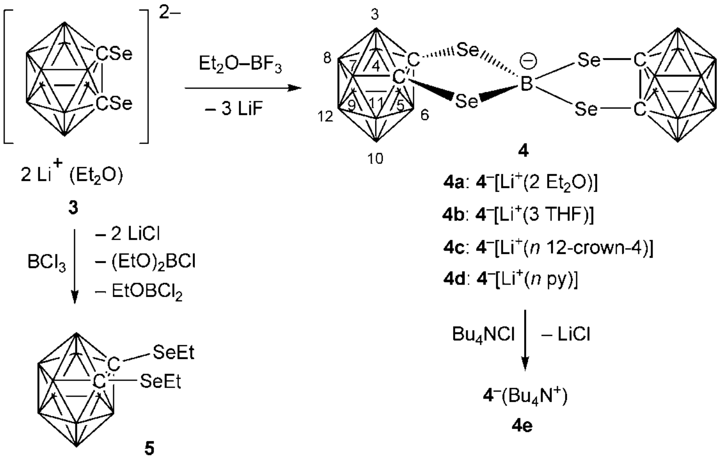
Reaction of 3 with BCl_3 and with $Et_2O–BF_3$

The results for the reactions of **3** with BCl_3 and $BF_3–OEt_2$ are summarized in Scheme 2. Treatment of **3** with $BF_3–OEt_2$ afforded selectively the spirocyclic borate **4**, and three-coordinate boron compounds were found to be absent in the reaction mixture. The borate **4** is stable in the presence of ether, THF, crown ether, and pyridine (py), and was analyzed by NMR spectroscopy in solution (Table 1, Figure 1). It could be converted into the tetrabutylammonium salt **4e**, which could be crystallized for X-ray structural analysis (vide infra).

The analogous treatment of the lithium salt **3** (in the presence of ether) with BCl_3 gave LiCl accompanied by ether cleavage and formation of the seleno ether **5** (ca. 80 %), the ether adduct of the 2-chloro-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-borolane (ca. 10 %),[10] and some unidentified products. The other conceivable product, the borate anion **4**, was not observed.

Some Aspects of the Reactivity of Tetraselenolatoborate 4

Recently it was shown that pyridine reacts with 4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselenacyclopentane **7** through cage-opening adduct formation followed by deboronation.[14] Thus, we have studied the reaction of **4a** with pyridine in CD_2Cl_2. There was no reaction of **4a** with CD_2Cl_2. However, when pyridine was added to the CD_2Cl_2 solution, a slow reaction took place (Scheme 3). After 2 d at room temperature, the reaction solution contained a mixture of borate **4d**, 1,3-diselenacyclopentane **7**, and *nido*-anion **8**. Since all relevant NMR spectroscopic data of **7** and **8** are known,[14] the analysis of this mixture was straightforward. Deboronation of one or both carborane cages in anion **4**⁻ to give novel di- and trianions was not observed.



Scheme 2. Treatment of the dilithio-1,2-diselenolato-1,2-dicarba-*closo*-dodecaborane(12) **3** with $Et_2O–BF_3$ and BCl_3.

Table 1. ^{11}B, ^{13}C, and ^{77}Se NMR spectroscopic data[a] of the carborane derivatives **4**, **5**, and **9**.

	4a[b] CD_2Cl_2	**4b** CD_2Cl_2	**4c** CD_2Cl_2	**4d** CD_2Cl_2	**4e** CD_2Cl_2	**5** $[D_8]$toluene	**9b** CD_2Cl_2	**9c** CD_2Cl_2	**9e** CD_2Cl_2
$\delta^{13}C$ [C(1,2)]	76.3 [9.3] [158.0]	76.4	76.4 [9.4] [158.2]	76.3 [157.7]	76.4 [9.9] [158.1]	76.0 [163.7]	78.6 [158.6]	78.7 [157.5]	78.7
Other $\delta^{13}C$ data	Et_2O: 14.8 (CH_3), 67.0 (CH_2O)	THF: 25.9 (CH_2), 69.0 (CH_2O)	12-crown-4: 67.8	py: 125.2 (C_β), 138.2 (C_γ), 149.5 (C_α)	NBu_4: 13.7, 20.1, 24.3, 59.4 {2.4}	13.6 [17.6] (CH_3), 26.0 [65.2] (CH_2)	THF: 25.8, 69.0	12-crown-4: 67.1	NBu_4: 13.7, 20.1, 24.3, 59.4 {2.6 Hz}
$\delta^{11}B$ (BSe)	6.0 (56.5)	6.0 (57.8)	6.2 (60.2)	6.0 (56.5)	6.0 (57.5)	–	–9.3	–9.2	–9.2
$\delta^{77}Se$	477.2 (57.5)	478.4 (61.0)	478.4 (60.4)	477.5 (57.0)	477.5 (58.0)[c]	492.8 [163.7][d], $h_{1/2}$ = 7 Hz	396.3 (35), $h_{1/2}$ = 110 Hz	392.4, $h_{1/2}$ = 105 Hz	392.9, $h_{1/2}$ = 80 Hz
$\delta^{77}Se$ (calcd.)	500.7 (–81.8) [–191.5]						460.2 (–47.2) [–192.6]		

[a] Coupling constants $^nJ(^{77}Se,^{13}C)$ are given in square brackets [±0.5 Hz]; $^1J(^{77}Se,^{11}B)$ in parentheses (±0.5 Hz); $^1J(^{14}N,^{13}C)$ in curly brackets; isotope-induced chemical shifts $^1\Delta$ are given in ppb, and the negative sign denotes a shift of the NMR spectroscopic signal of the heavy isotopomer to lower frequency. [b] δ = ^7Li: –0.33 ($h_{1/2}$ = 8 Hz). [c] $^1\Delta^{10/11}B(^{77}Se)$: (–280 ± 20) ppb. [d] $^1\Delta^{12/13}C(1,2)(^{77}Se)$: (–305 ± 5) ppb.

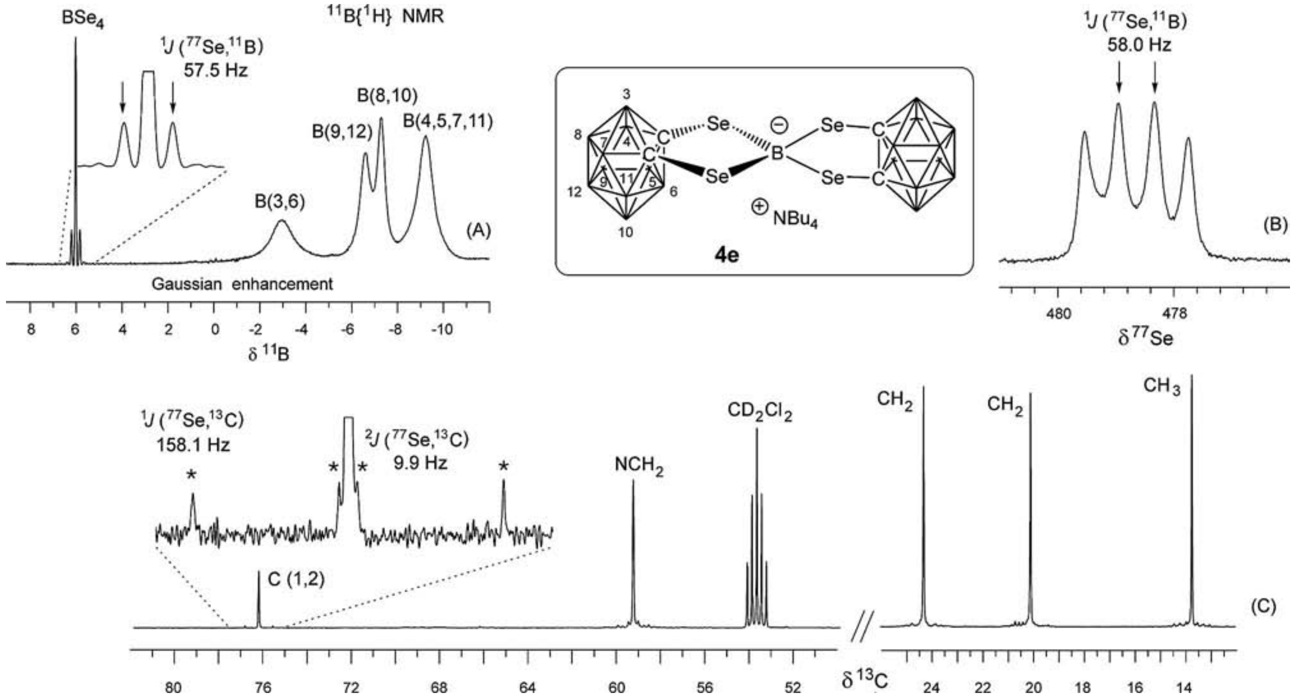
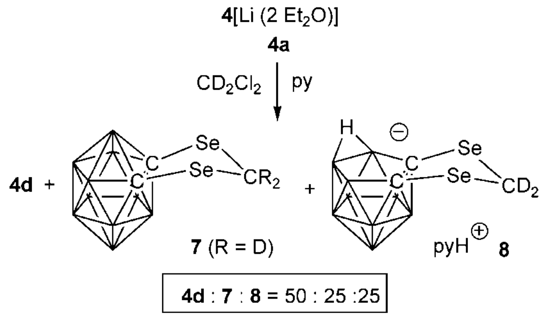


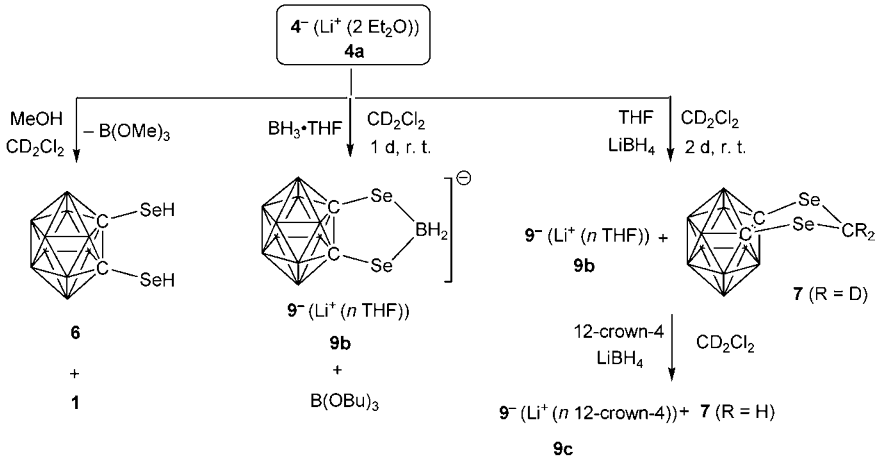
Figure 1. Tetrabutylammonium bis(1,2-dicarba-*closo*-dodecaborane-1,2-diselena)borate **4e**: (A) 128.3 MHz ^{11}B NMR spectra. The ^{77}Se satellites that correspond to $^1J(^{77}Se,^{11}B)$ are marked by arrows. (B) 76.2 MHz ^{77}Se NMR spectrum of **4e** (in CD_2Cl_2, at 23 °C). (C) 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of **4e** (in CD_2Cl_2, at 23 °C). The ^{77}Se satellites for $^nJ(^{77}Se,^{13}C)$ are marked by asterisks.



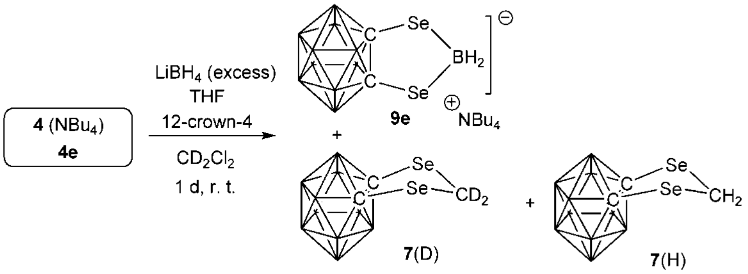
Scheme 3. Reaction of tetraselenolatoborate **4a** with pyridine in CD_2Cl_2.

Treatment of **4a** with methanol (Scheme 4) proceeded expectedly to give $B(OMe)_3$ along with diselenol **6**[10] and the parent *ortho*-carborane **1**. The formation of **1** indicates that cleavage of the B–Se bonds leading to **6** is accompanied by cleavage of the C–Se bonds as well.

Exchange reactions took place (Scheme 4) when **4a** reacted with borane in THF (BH_3/THF). In the reaction solution, only borate **9b** could be identified by its NMR spectroscopic data (Table 1). To confirm this result, another route[18a] was followed towards the same borate **9b**. Thus, **9b** was formed along with **7** (R = D) when a solution of **4a** in CD_2Cl_2 was treated with $LiBH_4$ in THF. Borate **9b** appears to be surprisingly stable in THF or in CD_2Cl_2 (only



Scheme 4. Some reactions of **4a** {**4**$^-$[Li$^+$(2Et$_2$O)]} with MeOH, BH_3/THF, and $LiBH_4$.



Scheme 5. Treatment of the tetrabutylammonium salt **4e** with $LiBH_4$ in CD_2Cl_2/THF followed by 12-crown-4-induced D/H exchange in **7** (R = D) to give **7** (R = H).

after 2 d at room temperature does decomposition become noticeable). In contrast, lithium dihydrido-1,3,2-benzenethiolatoborate disproportionates in THF/toluene solution to give $LiBH_4$, and the spirocyclic lithium bis(benzene-1,2-dithiolato)borate.[18a] Treatment of this mixture [**9b** and **7** (R = D)], which still contained $LiBH_4$ in an excess amount, with crown ether (12-crown-4) caused selective D/H exchange[20] to give **7** as the CH_2 derivative. Under the experimental conditions, the C(H)D derivative was not observed. When the reaction of **4e** with $LiBH_4$ was carried out in THF together with CD_2Cl_2 and 12-crown-4 (Scheme 5), borate **9e** was formed along with **7** as the CD_2 and CH_2 derivative, and the tetrabutylammonium salt **9e** was isolated and characterized by X-ray diffraction (vide infra).

NMR Spectroscopy

Expectedly, the $^{11}B\{^1H\}$ NMR spectrum of **4**$^-$ (Figure 1A) shows four signals for the carborane cage, thereby indicating fast inversion of both nonplanar five-membered C_2Se_2B rings. The assignment is based on relative intensities and selective $^1H\{^{11}B\}$ decoupling experiments together with calculations of chemical shifts (vide infra). In addition, there is one sharp signal for the tetracoordinate central boron atom surrounded by four selenium atoms. Indeed, the ^{77}Se satellites observed here represent the first example of a nicely resolved splitting due to one-bond ^{77}Se–^{11}B spin–spin coupling in ^{11}B NMR spectra. This is confirmed by the ^{77}Se NMR spectrum, which shows a single resonance split into four lines on account of $^1J(^{77}Se,^{11}B)$ (Figure 1, B). The somewhat distorted shape of the quartet can be traced to the still rapid nuclear spin relaxation rate of the quadrupolar ^{11}B nucleus, which causes a shortening of the scalar relaxation time $T_2^{SC}(^{77}Se)$ (scalar relaxation of the second kind[21]). This causes the decrease in the intensities of the outer lines of the quartet. Another noticeable feature in Figure 1 (B) is a hump underneath of the quartet that is shifted to higher frequencies with respect to the center of the quartet. This hump results from unresolved splitting due to one-bond ^{77}Se–^{10}B spin–spin coupling accompanied by an isotope induced chemical shift $^1\Delta^{10/11}B(^{77}Se)$ of around –300 ppb. Finally, the $^{13}C\{^1H\}$ NMR spectrum (Figure 1, C) shows just one signal for the carborane carbon atoms, accompanied by the ^{77}Se satellites, in addition to the $^{13}C(Bu)$ NMR spectroscopic signals of the $[NBu_4]^+$ ion.

The analogous NMR spectroscopic study of the dihydroborate **9** reveals a smaller coupling constant $^1J(^{77}Se,^{11}B)$. The corresponding splitting in the ^{77}Se NMR spectrum (Figure 2) is much less well resolved relative to **4**. This can be traced to the smaller magnitude of $^1J(^{77}Se,^{11}B)$ in **9** and faster ^{11}B nuclear spin relaxation on account of the reduced symmetry around the quadrupolar ^{11}B nucleus. The $^{11}B(BH_2)$ NMR spectroscopic signal ($\delta^{11}B$ = –9.2 ppm) of **9**, hidden underneath of the ^{11}B(carborane) NMR spectroscopic signals, was located by selective $^1H\{^{11}B\}$, selective $^{11}B\{^1H\}$, as well as by observing the *J*-modulated $^{11}B\{^1H\}$ NMR spectrum to make use of the opposite phases of ^{11}BH and $^{11}BH_2$ NMR spectroscopic signals.

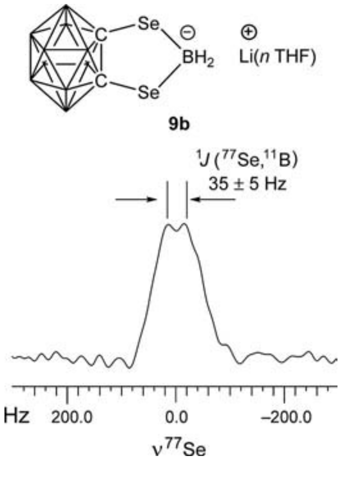


Figure 2. The 47.7 MHz $^{77}Se\{^1H\}$ NMR spectrum of **9b** (in CD_2Cl_2, at 23 °C).

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

The molecular structures of the anions **4** and **9** were optimized at the B3LYP/6-311+G(d,p) level of theory. The experimental data for **4** and **9** (as the NBu_4^+ salts) were reproduced, shown, for example, by the four different surroundings of the selenium atoms in **4** on account of the nonplanar C_2Se_2B rings. It appears that the calculated Se–B bond lengths are slightly too long when compared with the experimental data. The calculated nuclear shieldings agree satisfactorily with the experimental data (Table 2) for the ^{11}B(carborane) nuclei,[22] whereas the calculations underestimate the shielding of the ^{11}B(borate) nuclei in both **4** and **9** when compared with experimental data. This deviation increases with the number of selenium atoms attached to boron. Similarly, the calculated shielding of the ^{77}Se nuclei in both **4** and **9** is slightly too low (Table 1), although the trend is correctly predicted. The calculated $^{1}J(^{77}Se,^{11}B)$ coupling constants are numerically larger than the experimental values. This is the same trend as found for $^{1}J(^{77}Se,^{13}C)$.[23] For both $^{1}J(^{77}Se,^{11}B)$ and $^{1}J(^{77}Se,^{13}C)$, the calculations predict a negative sign which, in the case of $^{1}J(^{77}Se,^{13}C)$, is in agreement with experimentally determined signs.[15]

Table 2. $^{11}B\{^{1}H\}$ NMR spectroscopic data of the carborane derivatives **4e**, **4** (calcd.), **9e**, and **9** (calcd.).

	4e CD_2Cl_2	**4** (calcd.)	**9e** CD_2Cl_2	**9** (calcd.)
B(3,6)	–3.0	–7.0, –1.7, –7.5, –1.6	–3.9	–10.4, 0.2
B(4,5,7,11)	–9.2	–9.4, –12.1, –9.2, –11.3, –9.1, –11.5, –12.3, –9.2	–9.2	–8.1, –11.8, –8.1, –11.8
B(8,10)	–7.3	–9.6, –7.9, –9.9, –7.9	–7.4	–10.6, –7.9
B(9,12)	–6.6	–7.8, –7.5, –7.7, –7.3		–9.4, –9.4
B(13)	6.0	33.3	–9.2	–1.8

X-ray Structural Analyses of the *ortho*-Carborane Derivatives 4e and 9e

To gain structural information on the "free" borate anions, the tetrabutylammonium salts **4e** and **9e** were crystallized and studied by X-ray diffraction. The molecular structure of the borate anions **4** and **9** (Figures 3 and 4) show the tetrahedral environments of the central boron atoms. The five-membered C_2Se_2B rings in the spirocyclic system **4** as well as in **9** deviate from planarity (Figure 3, B; Figure 4). This causes different surroundings for the four selenium atoms in **4** and a slight deviation from ideal tetrahedral environments at the boron atom. The experimental and calculated structural parameters for **4** and **9** are compared in Table 3. There are no examples of this type of surroundings of the boron atom in molecular chemistry. Some examples with BSe_4 structures are known from solid-state chemistry.[19] The structural data (Table 3) of the carborane moiety and of the C_2Se_2B rings are similar to those found previously for **A**[10] and they are similar to those reported for **B**, although the standard deviations in the latter are fairly large.[8] To the best of our knowledge, the borate anion **9** is the first example of this type of borate that has been structurally characterized.

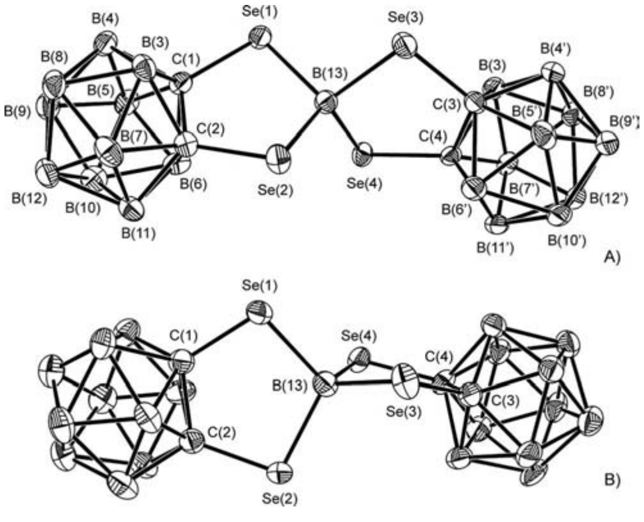


Figure 3. ORTEP plot (40% probabilities; hydrogen atoms are omitted for clarity) of the molecular structure of the tetrabutylammonium bis(1,2-dicarba-*closo*-dodecaborane-1,2-diselena)borate (**4e**) (tetrabutylammonium cation and toluene are omitted for clarity). For selected distances and angles, see Table 3.

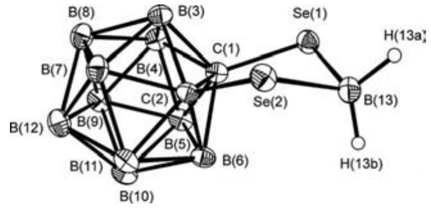


Figure 4. ORTEP plot (50% probabilities; hydrogen atoms, except for $SeBH_2$, are omitted for clarity) of the molecular structure of the tetrabutylammonium 1,2-dicarba-*closo*-dodecaborane-1,2-diselenaborate (**9e**) (tetrabutylammonium cation is omitted for clarity). For selected distances and angles, see Table 3.

Table 3. Selected bond lengths [pm] and angles [°] of **4e**, **4** (calcd.), **9e**, and **9** (calcd.).

	4e T = 133 K	**4** (calcd.)	**9e** T = 133 K	**9** (calcd.)
C(1)–Se(1)	193.1(5)	195.6	193.6(3)	195.9
C(2)–Se(2)	193.5(5)	195.8	194.4(3)	195.9
C(3)–Se(3)	192.5(5)	195.8		
C(4)–Se(4)	192.6(5)	195.5		
C(1)–C(2)	165.2(7)	165.7	167.8(4)	168.0
C(3)–C(4)	166.8(7)	165.4		
Se(1)–B(13)	205.6(6)	209.4	208.0(4)	210.9
Se(2)–B(13)	205.9(6)	208.4	208.1(4)	210.9
Se(3)–B(13)	205.3(6)	208.2		
Se(4)–B(13)	207.3(6)	209.5		
Se(1)–B(13)–Se(2)	107.9(3)	107.0	103.60(17)	104.8
Se(1)–B(13)–Se(3)	106.4(3)	109.0		
Se(1)–B(13)–Se(4)	109.3(3)	116.0		
Se(2)–B(13)–Se(3)	109.8(3)	107.5		
Se(2)–B(13)–Se(4)	115.9(3)	109.7		
Se(3)–B(13)–Se(4)	107.3(3)	107.4		
B(13)–Se(1)–C(1)	97.1(2)	97.5	95.23(15)	95.5
B(13)–Se(2)–C(2)	97.4(2)	97.5	95.22(15)	95.5
B(13)–Se(3)–C(3)	97.7(2)	97.9		
B(13)–Se(4)–C(4)	97.6(2)	97.8		
Se(1)–C(1)–C(2)	116.1(3)	115.6	114.7(2)	115.1
Se(2)–C(2)–C(1)	115.3(3)	115.9	113.8(2)	115.1
Se(3)–C(3)–C(4)	115.6(3)	116.1		
Se(4)–C(4)–C(3)	115.3(3)	115.8		
Se(1)–C(1)–C(2)–Se(2)	0		0.9	
Se(3)–C(3)–C(4)–Se(4)	0			
Distance of B(13) from the plane				
Se(1)–C(1)–C(2)–Se(2)	53.5		87.4	
Se(3)–C(3)–C(4)–Se(4)	54.3			
Plane C(1)–C(2)–B(13) to plane C(3)–C(4)–B(13) [°]	90.2			

Conclusion

The spirocyclic bis(1,2-dicarba-*closo*-dodecaborane-1,2-diselena)borate **4** is readily accessible from the treatment of the diselenolato-1,2-dicarba-*closo*-dodecaborane(12) dianion **3** with BF_3–OEt_2. The borate **4** can be handled as a solid and is stable in various polar and nonpolar solvents. It undergoes decomposition with methanol and exchange reactions with borane in THF (BH_3/THF) and also with $LiBH_4$. These exchange reactions afford the 1,2-dicarba-*closo*-dodecaborane-1,2-diselenadihydroborate **9**, which appears to be stable towards disproportionation reactions. Both borates **4** and **9** were characterized by multinuclear magnetic resonance methods in solution, thereby establishing ^{77}Se NMR spectroscopy as a useful tool in boron–selenium chemistry, and as tetrabutylammonium salts by X-ray diffraction in the solid state.

Experimental Section

General: All syntheses and the handling of the samples were carried out by observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The CD_2Cl_2 was distilled from CaH_2 under an atmosphere of argon. All other solvents were distilled from Na metal under an atmosphere of argon. $[(1,2\text{-}C_2B_{10}H_{10})Se_2Li_2](Et_2O)$[12] was prepared according to the published procedure. Other starting materials were purchased from Aldrich [butyllithium (1.6 M in hexane), BCl_3 (1.0 M in toluene), BF_3–OEt_2 (purified by redistillation), pyridine (anhydrous, 99.8%), $LiBH_4$ (≥95.0%), 12-crown-4 (98%)], Fluka [selenium metal “gray,” Bu_4NCl (>97%)], and KatChem. (*ortho*-carborane **1**), and used as received. NMR spectroscopic measurements were carried out with the following devices: Bruker DRX 500 and Bruker ARX 250: ^{1}H, ^{11}B, ^{13}C, and ^{77}Se NMR; Varian INOVA 400: ^{1}H, ^{11}B, ^{13}C, ^{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) 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 $\Xi(^{11}B)$ = 32.083971 MHz], neat Me_2Se [δ^{77}Se = (0 ± 0.1) ppm for $\Xi(^{77}Se)$ = 19.071523 MHz]. Assignments of ^{1}H and ^{11}B NMR spectroscopic signals are based on selective $^1H\{^{11}B\}$ heteronuclear decoupling experiments. IR spectra were determined with a Perkin–Elmer Spectrum 2000 FTIR. Melting points (uncorrected) were determined with a Büchi 510 melting point apparatus. Elemental analyses [C(H)] of the borates **4** did not give reproducible results, most likely on account of boron carbide formation and the slightly varying amount of solvent coordinated to the Li^+ cation.

All quantum chemical calculations were carried out with the Gaussian 03 program package (Revision B.02).[24] Optimized gas-phase geometries at the B3LYP/6-311+g(d,p) level of theory were found to be minima by the absence of imaginary frequencies. NMR spectroscopic parameters (nuclear magnetic shielding by the gauge including atomic orbitals (GIAO) method,[25] and spin–spin coupling constants[26]) were calculated at the same level of theory. Calculated nuclear shieldings σ^{11}B and σ^{77}Se were converted by δ^{11}B (calcd.) = $\sigma(^{11}B) - \sigma(^{11}B, B_2H_6)$, with $\sigma(^{11}B, B_2H_6)$ = +84.1 [δ^{11}B (B_2H_6) = 18 and δ^{11}B (BF_3–OEt_2) = 0], and δ^{77}Se (calcd.) = $\sigma(^{77}Se) - \sigma(^{77}Se, SeMe_2)$ with $\sigma(^{77}Se, SeMe_2)$ = +1621.7.

Lithium Bis(1,2-dicarba-*closo*-dodecaborane-1,2-diselena)borate (4)

4[Li(2Et$_2$O)] (4a): Freshly prepared $[(1,2\text{-}C_2B_{10}H_{10})Se_2Li_2](Et_2O)$ (**3**; 1065 mg, 2.82 mmol) was dissolved in toluene (20 mL). The solution was cooled to –30 °C, and BF_3–OEt_2 (0.35 mL; 2.84 mmol) was injected slowly (30 min) through a syringe, then Et_2O (0.5 mL) was added. The reaction mixture was stirred at room temp. for 20 h. Volatile materials were removed in vacuo, and the remaining solid was dissolved in toluene (5 mL). The formation of an oily phase and a white precipitate (LiF) was observed, and the supernatant liquid was decanted. The remaining oil was separated from the white solid, washed with toluene (5 mL), and dried in vacuo to give 563 mg (52%) of **4a** as a white powder. Compound **4a**: $^1H\{^{11}B\}$ NMR (399.8 MHz, CD_2Cl_2, 25 °C): δ = 1.31 [t, ^3J(H,H) = 7.1 Hz, 12 H, CH_3 from Et_2O], 2.06 [br. s, 4 H, HB(9,12) for $\delta(^{11}B)$ = –6.6], 2.19 [br. s, 4 H, HB(8,10) for $\delta(^{11}B)$ = –7.3], 2.35 (s, CH_3 toluene), 2.44 [br. s, 8 H, HB(4,5,7,11) for $\delta(^{11}B)$ = –9.2], 2.74 [br. s, 4 H, HB(3,6) for $\delta(^{11}B)$ = –3.0], 3.75 [q, ^3J(H,H) = 7.1 Hz, 8 H, OCH_2 from Et_2O], 7.19 (m, Ar from toluene) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, CD_2Cl_2; 25 °C): δ = –9.2 [8 B, B(4,5,7,11)], –7.3 [4 B, B(8,10)], –6.6 [4 B, B(9,12)], –3.0 [4 B, B(3,6)], 6.0 [$^1J(^{77}Se,^{11}B)$ = 56.5 Hz, 1 B, BSe_4) ppm. ^{11}B NMR (160.5 MHz, CD_2Cl_2; 25 °C): δ = –9.2 [d, J = 160 Hz, 8 B, B(4,5,7,11)], –7.3 [d, J = 140 Hz, 4 B, B(8,10)], –6.6 [d, 4 B, B(9,12)], –3.0 [d, J = 160 Hz, 4 B, B(3,6)], 6.0 [s, $^1J(^{77}Se,^{11}B)$ = 56.5 Hz, 1 B, BSe_4) ppm.

4[Li(3THF)] (4b) and 4[Li(12-crown-4)] (4c): A solution of **4a** (50 mg, 0.065 mmol) in CD_2Cl_2 (1.0 mL) was cooled to 0 °C, and THF (1.0 mmol) or 12-crown-4 (0.08 mmol) was added. The formation of a yellow solution was observed. Volatile materials were removed in vacuo, the remaining solid was dissolved in [D$_8$]toluene (1 mL), during which a layer of oil formed at the bottom. The liquid phase was separated by centrifugation, and the residue at the bottom was dried in vacuo to leave a yellow oil of **4b** (or **4c**).

Compound 4b: $^1H\{^{11}B\}$ NMR (250.1 MHz, CD_2Cl_2; 25 °C): δ = 1.97 (m, 12 H, CH_2 from THF), 2.02 [br. s, 4 H, HB(9,12) for $\delta(^{11}B)$ = –7.3], 2.16 [br. s, 4 H, HB(8,10) for $\delta(^{11}B)$ = –7.3], 2.42 [br. s, 8 H, HB(4,5,7,11) for $\delta(^{11}B)$ = –9.3], 2.72 [br. s, 4 H, HB(3,6) for $\delta(^{11}B)$ = –2.8], 3.78 (t, 12 H, OCH_2 from THF) ppm. $^{11}B\{^1H\}$ NMR (80.3 MHz, CD_2Cl_2; 25 °C): δ = –9.3 [8 B, B(4,5,7,11)], –7.3 [8 B, B(8,10), B(9,12)], –2.8 [4 B, B(3,6)], 6.0 [$^1J(^{77}Se,^{11}B)$ = 57.8 Hz, 1B, BSe_4] ppm.

Compound 4c: $^1H\{^{11}B\}$ NMR (250.1 MHz, CD_2Cl_2; 25 °C): δ = 2.16 [br. s, 4 H, HB(9,12) for $\delta(^{11}B)$ = –7.1], 2.29 [br. s, 4 H, HB(8,10) for $\delta(^{11}B)$ = –7.1], 2.54 [br. s, 8 H, HB(4,5,7,11) for $\delta(^{11}B)$ = –9.1], 2.85 [br. s, 4 H, HB(3,6) for $\delta(^{11}B)$ = –2.9], 3.68 (s, approx. 20 H CH_2 from 12-crown-4 in slight excess amount) ppm. $^{11}B\{^1H\}$ NMR (80.3 MHz, CD_2Cl_2; 25 °C): δ = –9.1 [8 B, B(4,5,7,11)], –7.1 [8 B, B(8,10), B(9,12)], –2.9 [4 B, B(3,6)], 6.2 [$^1J(^{77}Se,^{11}B)$ = 60.2 Hz, 1 B, BSe_4] ppm.

4[Li(*n*py)] (4d): A solution of **4a** (50 mg, 0.065 mmol) in CD_2Cl_2 (1.0 mL) was cooled to 0 °C and pyridine (1 mL) was added in excess amount. The formation of a yellow solution was observed. After 2 d at room temp., volatile materials were removed in vacuo to leave an orange-red residue that contained **4d** (50%), **7** (25%), and **8** (25%) (^{1}H and ^{11}B NMR spectroscopy). Compound **4d**: $^1H\{^{11}B\}$ NMR (399.8 MHz, CD_2Cl_2; 25 °C): δ = 2.04 [br. s, 4 H, HB(9,12)], 2.17 [br. s, 4 H, HB(8,10)], 2.42 [br. s, 8 H, HB(4,5,7,11)], 2.73 [br. s, 4 H, HB(3,6)], 7.43 (m, H_β-py), 7.86 (m, H_γ-py), 8.49 (m, H_α-py) ppm. $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2; 25 °C): δ = –20–0 (overlapping signals for **4d**, **7**, and **8**), 6.0 [$^1J(^{77}Se,^{11}B)$ = 56.5 Hz, 1 B, BSe_4] ppm.

Tetrabutylammonium Bis(1,2-dicarba-*closo*-dodecaborane-1,2-diselena)borate (4e): A solution of **4a** (100 mg, 0.13 mmol) in CD_2Cl_2 (1.5 mL) was cooled to 0 °C, and degassed Bu_4NCl (50 mg, 0.18 mmol) was added. After stirring the reaction mixture for 1 h at room temp., insoluble materials (LiCl) were separated by centrifugation, and the clear liquid was collected. Volatile materials were removed in vacuo to give a yellow solid. This solid was washed with [D_8]toluene (1 mL) and Et_2O (1 mL), and dried in vacuo to give **4e** as a yellow crystalline solid. Single transparent crystals of **4e** for X-ray analysis were grown from CD_2Cl_2/[D_8]toluene (5:1) solution after 2 d at –30 °C; m.p. 185–190 °C (decomp.). $^1H\{^{11}B\}$ NMR (399.8 MHz, CD_2Cl_2; 25 °C): δ = 1.02 [t, $^3J(H,H)$ = 7.2 Hz, 12 H, CH_3 from Bu], 1.43 [sextet, $^3J(H,H)$ = 7.2 Hz, 8 H, CH_2 from Bu], 1.61 (m, 8 H, CH_2 from Bu), 2.05 [br. s, 4 H, HB(9,12) for $\delta(^{11}B)$ = –6.6], 2.18 [br. s, 4 H, HB(8,10) for $\delta(^{11}B)$ = –7.3], 2.43 [br. s, 8 H, HB(4,5,7,11) for $\delta(^{11}B)$ = –9.2], 2.74 [br. s, 4 H, HB(3,6) for $\delta(^{11}B)$ = –3.0], 3.18 (m, 8 H, NCH_2) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, CD_2Cl_2; 25 °C): δ = –9.2 [8 B, B(4,5,7,11)], –7.3 [4 B, B(8,10)], –6.6 [4 B, B(9,12)], –3.0 [4 B, B(3,6)], 6.0 [$^1J(^{77}Se,^{11}B)$ = 57.5 Hz, 1 B, BSe_4] ppm. ^{11}B NMR (160.5 MHz, CD_2Cl_2; 25 °C): δ = –9.2 [d, J = 170 Hz, 8 B, B(4,5,7,11)], –7.3 [d, J = 145 Hz, 4 B, B(8,10)], –6.6 [d, 4 B, B(9,12)], –3.0 [d, J = 185 Hz, 4 B, B(3,6)], 6.0 [s, $^1J(^{77}Se,^{11}B)$ = 57.5 Hz, 1 B, BSe_4] ppm.

1,2-Bis(ethylseleno)-1,2-dicarba-*closo*-dodecaborane(12) (5): Freshly prepared **3** (990 mg, 2.55 mmol) was taken up in toluene (30 mL); the solution was cooled to –40 °C, and BCl_3 (2.55 mL of a 1.0 M solution in toluene; 2.55 mmol) was injected slowly through a syringe. After stirring the reaction mixture for 18 h at room temp., insoluble materials were separated by centrifugation, and the clear yellowish liquid was collected. Volatile materials were removed in vacuo to leave a yellowish oil that contained about 80% of **5** along with the ether adduct of the 2-chloro-1,2,3-diselenoborolane (10%) and some unidentified products (^1H and ^{13}C NMR spectroscopy). Compound **5**: $^1H\{^{11}B\}$ NMR (399.8 MHz; [D_8]toluene; 25 °C): δ = 1.00 [t, $^3J(H,H)$ = 7.7 Hz, 6 H, 2 CH_3 from Et], 2.25 (br. s, 2 H, HB for $\delta^{11}B$ = –10.3), 2.56 [q, $^3J(H,H)$ = 7.7 Hz, 4 H, 2 CH_2 from Et], 2.74 (br. s, 6 H, HB for $\delta^{11}B$ = –8.3), 2.89 (br. s, 2 H, HB for $\delta^{11}B$ = –2.4) ppm. $^{11}B\{^1H\}$ NMR (128.3 MHz; [D_8]toluene; 25 °C): δ = –10.3 (2 B), –8.3 (6 B), –2.4 (2 B) ppm.

Ether Adduct of 2-Chloro-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-borolane: ^{77}Se NMR (76.2 MHz; [D_8]toluene; 25 °C): δ = 469.0 (br.) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz; [D_8]toluene; 25 °C): δ = 16.0 (CH_3 from Et_2O), 70.8 (CH_2 from Et_2O), 73.4 [C(1,2)] ppm.

Treatment of 4a with MeOH: A solution of **4a** (50 mg, 0.065 mmol) in CD_2Cl_2 (1.5 mL) was cooled to 0 °C, and MeOH (1 mL) was added. The progress of the reaction was monitored by ^{11}B NMR spectroscopy. After 24 h at room temp., the mixture contained **4a** (50%), **6** (30%),[10] **1** (20%), and $B(OMe)_3$. After 2 h at 60 °C, the mixture contained **6** (20%), **1** (80%), and $B(OMe)_3$ (^1H, ^{11}B, ^{13}C NMR spectroscopy).

Treatment of 4a with BH_3/THF: A solution of **4a** (50 mg, 0.065 mmol) in CD_2Cl_2 (1.5 mL) was cooled to 0 °C, and BH_3–THF (0.2 mL of a 1.0 M solution in THF, 0.2 mmol) was added. The progress of the reaction was monitored by ^{11}B NMR spectroscopy. After 12 h at room temp., the mixture contained lithium 1,2-dicarba-*closo*-dodecaborane-1,2-diselenaborate {**9b**; **9**[Li(*n*THF)]} together with $B(OBu)_3$.

Treatment of 4a with $LiBH_4$, CD_2Cl_2, and 12-crown-4: A solution of **4a** (50 mg, 0.065 mmol) in CD_2Cl_2 (1.5 mL) was cooled to 0 °C and added to degassed $LiBH_4$ (approx. 2 mg, 0.09 mmol). Then THF (0.3 mL) was added to this reaction mixture. The progress of the reaction was monitored by ^{11}B NMR spectroscopy. After 24 h at room temp., volatile materials were removed in vacuo, the remaining mixture was dissolved in CD_2Cl_2 (1 mL), and the liquid phase was separated by centrifugation. The mixture contained **9b** (80%), **7** (R = D) (20%),[14] and $LiBH_4$. Then 12-crown-4 (0.016 mL, 0.10 mmol) was added to this reaction mixture. Volatile materials were removed in vacuo, the remaining mixture was dissolved in [D_8]toluene (1 mL), and the liquid phase was separated by centrifugation. The remaining oil at the bottom was dried in vacuo to leave an orange-red residue. After 2 d in CD_2Cl_2 at room temp., the mixture contained **9c** (90%), **7** (R = H) (10%),[14] and $LiBH_4$.

9[Li(*n*THF)] (9b): $^1H\{^{11}B\}$ NMR (399.8 MHz, CD_2Cl_2; 25 °C): δ = 1.91 (m, CH_2 from THF, BH), 2.33 (br. s, 2 H, BH), 2.42 (br. s, 4 H, BH), 2.80 (br. s, 2 H, BH), 3.54 (br. s, 2 H, $SeBH_2$), 3.80 (m, CH_2 from THF) ppm. $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2; 25 °C): δ = –9.3 (5B, BSe_2), –7.5 [4B, B(8,10), B(9,12)], –3.8 [2B, B(3,6)] ppm. ^{11}B NMR (128.3 MHz, CD_2Cl_2; 25 °C): δ = –9.3 [5B, B(4,5,7,11), BSe_2], –7.5 [d, J = 150 Hz, 4B, B(8,10), B(9,12)], –3.8 [d, J = 175 Hz, 2B, B(3,6)] ppm.

9[Li(*n*12-crown-4)] (9c): $^1H\{^{11}B\}$ NMR (399.8 MHz, CD_2Cl_2; 25 °C): δ = 2.03 (br. s, 2 H, BH), 2.07 (br. s, 2 H, BH), 2.43 (br. s, 4 H, BH), 2.81 (br. s, 2 H, BH), 3.56 (br. s, 2 H, $SeBH_2$), 3.78 (s, CH_2 from 12-crown-4) ppm. $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2; 25 °C): δ = –9.2 (5 B), –7.5 (4 B), –3.9 (2 B) ppm. IR (CD_2Cl_2): $\tilde{\nu}$ = (B–H) = 2198, 2303 (BH_2), 2588 (br) (BH for *o*-carborane) cm^{-1}.

Treatment of 4e with $LiBH_4$, CD_2Cl_2, and 12-crown-4: A solution of **4e** (50 mg, 0.059 mmol) in CD_2Cl_2 (1.5 mL) was cooled to 0 °C and added to degassed $LiBH_4$ (approx. 2 mg, 0.09 mmol). Then 12-crown-4 (0.016 mL, 0.10 mmol) was added to this reaction mixture. The progress of the reaction was monitored by ^{11}B NMR spectroscopy. After 12 h at room temp., the mixture contained tetrabutylammonium 1,2-dicarba-*closo*-dodecaborane-1,2-diselenaborate (**9e**) (70%), **7** (R = D, H) (30%), $LiBH_4$, and 12-crown-4. Single transparent crystals of **9e** were grown from CD_2Cl_2/[D_8]toluene (1:1) solution after 5 d at –30 °C; m.p. 95–100 °C (decomp.). Compound **9e**: $^1H\{^{11}B\}$ NMR (399.8 MHz, CD_2Cl_2; 25 °C): δ = 1.02

Table 4. Crystallographic data of the carborane derivatives **4e** and **9e**.[a]

	4e	**9e**
Formula	$C_{20}H_{56}B_{21}NSe_4\cdot0.5$toluene	$C_{18}H_{48}B_{11}NSe_2$
Crystal	yellowish prism	colorless prism
Dimensions [mm^3]	0.24 × 0.15 × 0.16	0.24 × 0.18 × 0.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [pm]	1129.6(2)	1101.8(2)
b [pm]	1904.9(4)	2157.3(4)
c [pm]	2005.1(4)	1228.4(3)
β [°]	97.94(3)	100.38(3)
Z	4	4
Abs. coeff. μ [mm^{-1}]	3.454	2.583
Measuring range (θ) [°]	1.48–25.77	1.89–25.66
Reflections collected	51076	37953
Independent reflections [$I \geq 2\sigma(I)$]	6653	4091
Refined parameters	435	289
wR_2/R_1 [$I \geq 2\sigma(I)$]	0.128/0.058	0.103/0.040
Max./min. resid. electron density [$e\,pm^{-3} \times 10^{-6}$]	1.185/–0.491	0.619/–0.730

[a] No absorption corrections were carried out because they did not improve the parameter set. In both cases, the temperature was 133(2) K.

[t, ^3J(H,H) = 7.2 Hz, 12 H, CH_3 from Bu], 1.43 [sextet, ^3J(H,H) = 7.2 Hz, 8 H, CH_2 from Bu], 1.61 (m, 8 H, CH_2 from Bu), 2.03 (br. s, 2 H, BH), 2.07 (br. s, 2 H, BH), 2.43 (br. s, 4 H, BH), 2.81 (br. s, 2 H, BH), 3.56 (br. s, 2 H, $SeBH_2$), 3.12 (m, 8 H, NCH_2) ppm. $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2; 25 °C): δ = –9.2 (5 B), –7.4 (4 B), –3.9 (2 B) ppm.

Crystal Structure Determination of Complexes 4e and 9e: Details pertinent to the crystal structure determinations are listed in Table 4. Crystals of appropriate size were sealed under an atmosphere of argon in Lindemann capillaries. The data collections were carried out at 133 K for **4e** and **9e** with a STOE IPDS II diffractometer with graphite-monochromated Mo-K_α (λ = 71.073 pm) radiation.

CCDC-804607 (for **4e**, at 133 K) and -804608 (for **9e**, at 133 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Support of this work by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

---

[1] R. N. Grimes, *Carboranes*, Academic Press, New York, **1970**.

[2] a) V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209–223; b) F. Teixidor, C. Viñas, *Science of Synthesis* **2004**, *6*, 1235–1275.

[3] a) A. Laromaine, F. Teixidor, R. Kivekäs, R. Sillanpää, R. Benakki, B. Grüner, C. Viñas, *Dalton Trans.* **2005**, 1785–1795; b) H. Beall, in E. L. Muetterties (Eds.), *Boron Hydride Chemistry*, Academic Press, London **1975**, p. 316, and references cited therein.

[4] a) X. Meng, F. Wang, G.-X. Jin, *Coord. Chem. Rev.* **2010**, *254*, 1260–1272; b) S. Liu, Y.-F. Han, G.-X. Jin, *Chem. Soc. Rev.* **2007**, *36*, 1543–1560; c) G.-X. Jin, *Coord. Chem. Rev.* **2004**, *248*, 587–602.

[5] a) W.-G. Jia, Y.-F. Han, G.-X. Jin, *Organometallics* **2008**, *27*, 6035–6038; b) X.-Q. Xiao, Y.-J. Lin, G.-X. Jin, *Dalton Trans.* **2008**, 2615–2619; c) Y.-Q. Chen, J.-Q. Wang, G.-X. Jin, *J. Organomet. Chem.* **2007**, *692*, 5190–5194; d) Y.-F. Han, J.-S. Zhang, Y.-J. Lin, J. Dai, G.-X. Jin, *J. Organomet. Chem.* **2007**, *692*, 4545–4550; e) X.-F. Hou, S. Liu, H. Wang, Y.-Q. Chen, G.-X. Jin, *Dalton Trans.* **2006**, 5231–5239; f) S. Cai, Y. Lin, G.-X. Jin, *Dalton Trans.* **2006**, 912–918; g) G.-X. Jin, J.-Q. Wang, *Dalton Trans.* **2006**, 86–90.

[6] a) D.-H. Wu, C.-H. Wu, Y.-Z. Li, D.-D. Guo, X.-M. Wang, H. Yan, *Dalton Trans.* **2009**, 285–290; b) B.-H. Xu, J.-C. Tao, Y.-Z. Li, S.-H. Li, H. Yan, *Organometallics* **2008**, *27*, 334–340; c) B.-H. Xu, X.-Q. Peng, Y.-Z. Li, H. Yan, *Chem. Eur. J.* **2008**, *14*, 9347–9356.

[7] a) S. Lu, G.-X. Jin, St. Eibl, M. Herberhold, Y. Xin, *Organometallics* **2002**, *21*, 2533–2535; b) B. Wrackmeyer, H. Yan, W. Milius, M. Herberhold, *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 1518–1524; c) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *Eur. J. Inorg. Chem.* **1999**, 873–875; d) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **1999**, *587*, 252–257.

[8] N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, *New J. Chem.* **2000**, *24*, 837–839.

[9] H. D. Smith Jr., L. F. Hohnstedt, *Inorg. Chem.* **1968**, *7*, 1061–1066.

[10] B. Wrackmeyer, E. V. Klimkina, W. Milius, *Polyhedron* **2010**, *29*, 2324–2334.

[11] a) B. Wrackmeyer, Z. García Hernández, R. Kempe, M. Herberhold, *Appl. Organomet. Chem.* **2007**, *21*, 108–116; b) Z. García Hernández, B. Wrackmeyer, R. Kempe, M. Herberhold, *ARKIVOC* **2008**, 65–80.

[12] B. Wrackmeyer, E. V. Klimkina, W. Milius, *Appl. Organomet. Chem.* **2010**, *25*, 25–32.

[13] B. Wrackmeyer, Z. García Hernández, R. Kempe, M. Herberhold, *Z. Anorg. Allg. Chem.* **2007**, *633*, 851–857.

[14] B. Wrackmeyer, E. V. Klimkina, W. Milius, T. Bauer, R. Kempe, *Chem. Eur. J.* **2011**, *17*, 3238–3251.

[15] a) H. Duddeck, *Prog. Nucl. Magn. Reson. Spectrosc.* **1995**, *27*, 1–323; b) H. Duddeck, *Annu. Rep. NMR Spectrosc.* **2004**, *52*, 105–166.

[16] K. Ishihara, H. Yamamoto, *Science of Synthesis* **2004**, *6*, 423–436.

[17] a) T. Tu, T. Maris, J. D. Wuest, *Cryst. Growth Des.* **2008**, *8*, 1541–1546; b) S. Yu, S. Lindeman, C. D. Tran, *J. Org. Chem.* **2008**, *73*, 2576–2591; c) S. H. Chikkali, D. Gudat, F. Lissner, M. Nieger, T. Schleid, *Dalton Trans.* **2007**, 3906–3913; d) R. Gausepohl, P. Buskens, J. Kleinen, A. Bruckmann, C. W. Lehmann, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2006**, *45*, 3689–3692; e) D. B. Llewellyn, B. A. Arndtsen, *Tetrahedron: Asymmetry* **2005**, *16*, 1789–1799.

[18] a) J. Knizek, H. Nöth, *J. Organomet. Chem.* **2000**, *614–615*, 168–187; b) B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus, B. Scott, F. H. Stephens, *Angew. Chem. Int. Ed.* **2009**, *48*, 6812–6816.

[19] A. Lindemann, J. Kuchinke, C. Köster, A. Hammerschmidt, M. Döch, T. Pruss, B. Krebs, *Phosphorus Sulfur Silicon Relat. Elem.* **2001**, *169*, 169–172.

[20] B. Davis, *J. Labelled Compd. Radiopharm.* **1987**, *24*, 199–204.

[21] A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, Oxford, **1961**, pp. 305–315.

[22] a) M. Bühl, in: *Encyclopedia of Computational Chemistry* (Ed.: P. v. R. Schleyer), vol. 3, Wiley, Chichester, **1999**, pp. 1835–1845; b) M. Bühl, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1992**, *114*, 477–491.

[23] B. Wrackmeyer, Z. García Hernández, M. Herberhold, *Magn. Reson. Chem.* **2007**, *45*, 198–204.

[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, rev. B.02, Gaussian, Inc., Pittsburgh, PA, **2003**.

[25] K. Wollinski, J. F. Hinton, P. J. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260.

[26] T. Helgaker, M. Jaszunski, M. Pecul, *Prog. Nucl. Magn. Reson. Spectrosc.* **2008**, *53*, 249–268.

Received: December 17, 2010