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Molecular Structures, Reactivity, and NMR Spectroscopic Studies of Cyclic and Non-cyclic Silyl-substituted 1,2-Dicarba-*closo*-dodecaborane(12) Derivatives

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Dedicated to Professor Wolfgang Beck on the Occasion of His 80th Birthday

Keywords: Silane; Carboranes; Selenium; Tellurium; Heterocycles; NMR spectroscopy; DFT calculations; X-ray analysis

Abstract. Non-cyclic and cyclic silyl-substituted 1,2-dicarba-*closo*-dodecaborane(12) derivatives were prepared mainly by salt elimination methods. Several known and new compounds were structurally characterized by X-ray analysis in the solid state and by mulinuclear magnetic resonance (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{77}Se, and ^{125}Te NMR) in solution. This includes the 1,2-bis(trimethylsilyl) and 1,2-bis(chlorodimethylsilyl) derivatives as examples for non-cyclic compounds and a series of 1,1,3,3-tetramethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-2-element-cyclopentanes (element = S, Se, Te). Numerous spin-spin coupling constants were determined together with their signs. Molecular gas phase geometries for most compounds studied were optimized by calculations [B3Lyp/6-311+G(d,p)], and NMR parameters were calculated at the same level of theory. The conversion of silyl-substituted *ortho*-carboranes into their respective 7,8-dicarba-*nido*-undecaborate(1-) derivatives was explored successfully for several examples.

Introduction

The remarkable thermal stability and versatile chemistry of 1,2-dicarba-*closo*-docecaborane(12) (**1**) ("*ortho*-carborane") has been well documented in the last five decades.[1–3] In particular, various routes to C-derivatization were established, such as C-lithiation (e.g. **2**), which appears to be highly convenient.[1–3] This has opened the way to 1,2-disilyl-substituted carboranes, some of them (**3**–**6a**) are shown in Scheme 1. In spite of the interest in silyl-substituted carboranes for applications in some fields of materials sciences[1,4] and numerous fields of chemistry,[5] only few simple examples have been structurally characterized in the solid state[6,7] (e.g. **5**[8] and **6a**[8]), and a fairly complete set of important solution-state NMR spectroscopic data is not available at all. For instance, the magnitude of spin-spin coupling constants $^{1}J(^{29}\text{Si},^{13}\text{C})$ for some diphenylsilyl-substituted carboranes[9] is smaller than expected at a first glance, considering the large magnitude of $^{1}J(^{13}\text{C},^{1}\text{H})$ in **1** [$^{1}J(^{13}\text{C},^{1}\text{H})$ = 193 Hz][10] or in mono-substituted *ortho*-carboranes.[10] This was attributed to high s electron density in the C–H hybrid orbital.

In the presented work, we have set out to prepare the missing heavy homologues of **6a** with sulfur (**6b**), selenium (**6c**) and tellurium (**6d**), starting from **4** or **5**. Some aspects of the reactivity of **5** was addressed, and first attempts were made to convert some of the silyl-substituted carboranes into the respective 7,8-dicarba-*nido*-undecaborates(1-). The NMR spectra of **3**–**6** were measured (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{77}Se, and ^{125}Te NMR), including the determination of absolute signs of spin-spin coupling constants, if possible. The molecular structures of **3**, **4**, **6c**, and **6d** were determined by X-ray structural analysis, and the gas phase geometries of **3**–**6** were optimized [B3LYP/6-311+G(d,p)] followed by calculation of NMR parameters at the same level of theory (except of **6d**).

Results and Discussion

Syntheses and NMR Spectroscopy

The synthetic routes are summarized in Scheme 2. Clearly, the dichloride **4**[11] offers great synthetic potential for further transformations. It proved necessary to use the salt elimination reaction of **4** with dilthium selenide[12] or -telluride[12] to obtain pure samples of **6c** and in particular of **6d**. In principle, the strained four-membered cycle in **5**[8] appears to be attractive for insertion reactions.[7b] However, it does not react with tellurium, it reacts sluggishly with selenium, and somewhat more readily with sulfur. Surprisingly, **5** does not react with bis(trimethylsilyl)peroxide at room temp., whereas its reaction with trimethylamine N-oxide[13] affords the known disiloxane **6a**[9,11,14] quantitatively under mild conditions.

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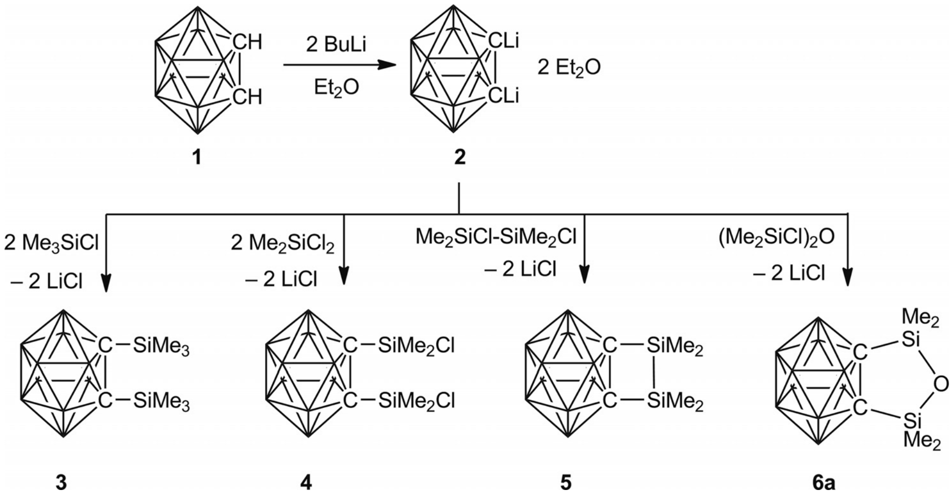
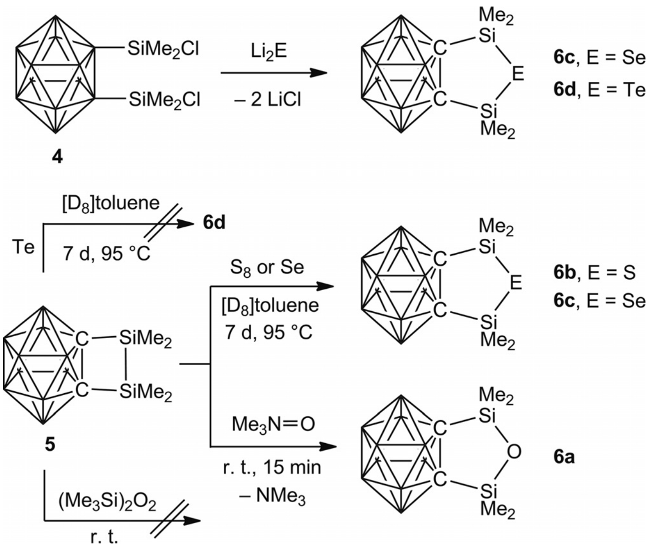


Scheme 1. Some known 1,2-silyl-substituted *ortho*-carborane derivatives, obtained from the reactions of 1,2-dilithio-1,2-dicarba-*closo*-dodecaborane(12) with various chlorosilanes.



Scheme 2. Routes to 1,1,3,3-tetramethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-2-chalkogena-cyclopentanes **6a**–**6d**.

The compounds **6b**,**c**,**d** are crystalline yellowish (**6b**, **6c**) or yellow (**6d**) solids sensitive to moisture and oxygen. In the case of the preparation of **6c** larger amounts of byproducts (ca. 10 %) were observed by ^{29}Si NMR spectroscopy in the crude products. The products **6b**,**c**,**d** are soluble in toluene and CD_2Cl_2. **6b** can be stored for prolonged periods as a solid or in solution at –30 °C. Similarly, **6c** can be stored as a solid or in toluene solution at –30 °C and decomposes slowly in CD_2Cl_2 at –30 °C. Compound **6d** shows low thermal stability. It decomposes under argon as a solid at room temperature and also slowly in [D$_8$]toluene at –30 °C with formation of a black precipitate of elemental tellurium. On contact with moisture and oxygen **6d** decomposes almost immediately.

Similar to **3**–**5** (Table 1), the heterocyclic compounds **6** are readily characterized in solution by their NMR spectroscopic data (Table 2). In the cases of **6c** and **6d**, the presence of magnetically active spin-1/2 ^{77}Se[15] and ^{123,125}Te[16] nuclei reveals additional conclusive structural information, both by determination of chemical shifts and various spin-spin coupling constants. In all cases **3**–**6**, the spin-spin coupling constants $^1J(^{29}Si,^{13}C)$ were measured, in most cases from ^{13}C satellites in the ^{29}Si NMR spectra. The ^{13}C(carborane) NMR signals are only slightly broadened owing to unresolved scalar ^{13}C–^{11}B coupling (^{11}B: I = 3/2; ^{10}B: I = 3).[17] However, they are split due to isotope-induced chemical shifts $^1\Delta^{10/11}B(^{13}C)$.[9] Moreover, longitudinal nuclear spin relaxation times $T_1(^{13}C_{carb})$ are fairly long, and therefore, the signal-to-noise ratio for these NMR signals becomes unfavorable. However, we found that $^1H\rightarrow^{13}C$ polarization transfer, using the refocused INEPT pulse sequence[18] [based on $^3J(^{13}C_{carb},^1H_{SiMe})$], can be applied to circumvent at least the problem associated with $T_1(^{13}C)$ (see Figure 1).

The ^{29}Si NMR spectrum of **6d** is shown (Figure 2) as an instructive example for the information to be gained by observing the respective satellites arising from ^{29}Si–^{13}C and ^{29}Si–$^{123/125}$Te spin-spin coupling.

In all silyl-substituted *ortho*-carboranes studied here, the magnititude of $^1J(^{29}Si,^{13}C_{carb})$ is relatively small, e.g. when compared with $^1J(^{29}Si,^{13}C_{Me})$, although in *ortho*-carborane the value for $^1J(^{13}C,^1H)$ = 193 Hz indicates that much of the carbons electron density is localized in the C–H bond. However, the Si–C(carborane) bond is polar, and polarizability reduces positive contributions to the Fermi contact term as the dominating mechanism for nuclear spin-spin coupling between nuclei with an open s shell configuration. This is also evident by comparing $^1J(^{13}C,^1H)$ in alkynes R–C≡C–H with $^1J(^{29}Si,^{13}C_{carb})$[19] and $^1J(^{29}Si,^{13}C_{Me})$ in R–C≡C–$SiMe_3$.[20a] If this analogy is correct, the comparable trend should be even more obvious for R–C≅C–$SnMe_3$[20] and stannyl-stubstituted *ortho*-carboranes. Therefore, we have measured the NMR spectroscopic data of **7**(Sn) and coupling constants for **7** and three alkynes are summarized in Scheme 3. Clearly, the data for **7**(Sn) follow the pattern found for silyl-substituted *ortho*-carboranes.

The relative sign of coupling constants can be determined in NMR experiments involving one passive and two active

Table 1. ^{13}C and ^{29}Si NMR spectroscopic data[a)] of the *ortho*-carborane derivatives **3**, **4**, **5**, **7**, and **7**(Sn).

	3	**4**	**5**		**7**[b)]	**7**(Sn)
	[D$_8$]toluene	[D$_8$]toluene	[D$_8$]toluene	CD$_2$Cl$_2$	[D$_8$]toluene	C$_6$D$_6$
δ^{13}C[SiCH$_3$]	1.2 [55.7]	4.4 [64.6]	–3.5	–2.7 [47.7] [4.6]	–2.0 [55.7]	–8.3 (370.2)
δ^{13}C[C(1,2)]	74.8 [46.8]	73.5 [55.8]	80.1	80.9 [38.4]	59.8 (CH), 67.1 [46.6] (CSiMe$_3$)	59.3(CH) 61.5 (CSn) (165.0)
$^1\Delta^{10/11}$B[^{13}C(1,2)] ± 0.5 ppb	–11.8	–10.8	–12.0	–10.5	–8.5	–8.0
δ^{29}Si/^{119}Sn	10.0 [55.8] [47.1]	24.3 [64.7] [55.8]	17.8	19.1 [47.8] [38.4]	9.7 [55.6] [46.1]	56.9
^1J(^{29}Si,^{13}C) (calcd.)	–48.6 (Me) –41.9 (C(1,2))	–56.3 (Me) –51.7 (C(1,2))	–40.1 (Me) –9.9 (^2J)) –34.1 (C(1,2)		–48.9 (Me) –42.8 (C(1))	–

a) Coupling constants ^nJ(^{29}Si,^{13}C) are given in brackets [± 0.5 Hz], coupling constants ^1J(^{119}Sn,^{13}C) are given in parentheses (± 0.5 Hz); isotope-induced chemical shifts $^1\Delta$ are given in ppb, and the negative sign denotes a shift of NMR signal of the heavy isotopomer to lower frequency. b) Ref.[19].

Table 2. ^{13}C, ^{29}Si, ^{77}Se, and ^{125}Te / ^{123}Te NMR spectroscopic data[a)] of the cyclic *ortho*-carborane derivatives **6a**–**6d**.

	6a *E* = O [D$_8$]toluene	CD$_2$Cl$_2$	**6b** *E* = S [D$_8$]toluene	CD$_2$Cl$_2$	**6c** *E* = Se [D$_8$]toluene	CD$_2$Cl$_2$	**6d** *E* = Te [D$_8$]toluene
δ^{13}C[SiCH$_3$]	–1.7 [66.4]	–1.1 [66.4]	2.1 [59.3]	2.6	3.5 [57.4] <8.5>	3.5 [57.6] <8.5>	4.6 [55.0] <14.3>
δ^{13}C[C(1,2)]	73.6 [55.7]	74.1	75.0 [53.5]	75.3	76.9 [51.2]	76.9 [51.2] <8.9>	79.3 [48.4] <26.1>
$^1\Delta^{10/11}$B(^{13}C(1,2)) ± 0.5 ppb	–11.4		–11.1		–10.5	–10.5	–10.5
δ^{29}Si	16.8	16.8	31.8	32.3	30.5	30.9 (123.4)	17.2 (328.1) /272.2/
	[66.4] [55.5]	[66.6] [55.4]	[59.4] [53.4]		[123.5]	[57.6] [51.4] [4.2]	[54.8] [48.6]
δ^{77}Se / δ^{125}Te	–	–	–	–	–358.5 (123.7)	–356.3 (123.4) {4.4}	–895.3[b)] (328.4) {7.6}
$^1\Delta^{28/29}$Si(^{77}Se / ^{125}Te) ± 1 ppb	–	–	–	–	–22.5	–25.6	–36.7
^nJ(^{29}Si,^{13}C) (calcd.)	–60.3 (Me)		–52.4 (Me)		–50.1 (Me)		–
δ^{77}Se (calcd.)	–50.5 (C(1,2)) –3.3 (^2J) –	–	–47.3 (C(1,2)) –4.5 (^2J) –	–	–45.6 (C(1,2)) –4.5 (^2J) –486.8 (+155.5) <+6.0>(^2J(^{77}Se,^{13}C$_{Me}$)) <–10.0> (^2J(^{77}Se,^{13}C$_{carb}$))		–

a) Coupling constants ^nJ(^{29}Si,^{13}C) are given in brackets [± 0.5 Hz]; ^1J(^{77}Se,^{29}Si) and ^1J(^{125}Te,^{29}Si) are given in parentheses (± 0.5 Hz); ^1J(^{123}Te,^{29}Si) are given in / / /± 0.5 Hz/; ^2J(^{77}Se,^{13}C) and ^2J(^{125}Te,^{13}C) are given in < > <± 0.5 Hz>; ^3J(^{77}Se,^{1}H), ^3J(^{125}Te,^{1}H) and ^3J(^{123}Te,^{1}H) in braces {± 0.5 Hz}; isotope-induced chemical shifts $^1\Delta$ are given in ppb, and the negative sign denotes a shift of NMR signal of the heavy isotopomer to lower frequency. b) δ^{123}Te: –895.0 {7.0}.

spins. This can be done using appropriate 1D heteronuclear double resonance experiments[21] or, more conveniently, 2D heteronuclear shift correlations, observing the tilt of relevant cross peaks.[22] If any of the nuclei have a negative gyromagnetic ratio, such as γ(^{29}Si) and γ(^{125}Te), it is advisable to use the notation of reduced coupling constants *K* before converting the sign information to *J* (see Figure 3 and Figure 4).

7,8-Dicarba-nido-undecaborates(1-) from Silyl-substituted ortho-Carboranes

Decapping of the silyl-substituted *ortho*-carboranes to obtain 7,8-dicarba-*nido*-undecaborate(1-) derivatives would greatly enhance their synthetic potential. We started with 1-trimethylsilyl-*ortho*-carborane **7** (Scheme 4) to explore this field. Apparently the reaction with an excess of piperidine worked in the normal way[3,24] to give the monoanion **8**, readily apparent from the typical set of multinuclear magnetic resonance data (Experimental Section and Table 4).

However, the procedure did not work in the case of the disilane derivative **5**. Instead, cleavage of one of the Si–C(carborane) bonds was observed to give **9** (Scheme 5), readily evident from the NMR spectroscopic data set (Table 3). More bulky secondary amines, such as dicyclohexylamine, did not react, whereas primary amines, such as cyclohexylamine or aniline, gave results analogous to piperidine. Traces of moisture as an impurity in all these amines, caused also cleavage of the Si–C(carborane) bond to give **10**, present in the reaction mixtures. The comparable reaction of **5** with ethanol has been reported.[8] Although the desired borates were not formed, the

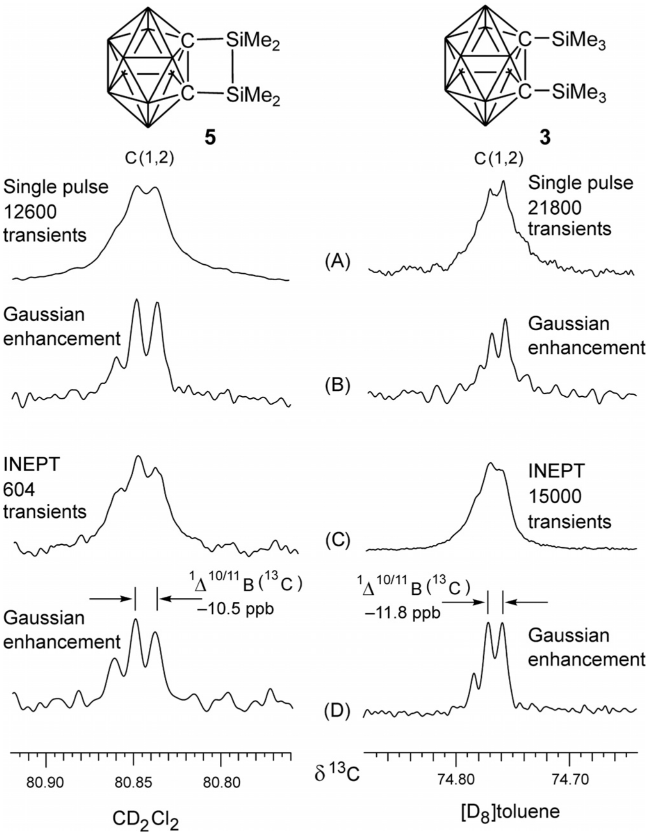


Figure 1. 125.8 MHz $^{13}C\{^1H\}$ NMR spectra of the carborane derivatives **3** (right; in [D_8]toluene at 23 °C) and **5** (left; in CD_2Cl_2, at 23 °C), showing the ^{13}C(carborane) signals. The typical pattern can be seen, caused by isotope-induced chemical shifts $^1\Delta^{10/11}B(^{13}C)$.[9] The performance of the refocused INEPT pulse sequence with ^1H decoupling[18] is markedly better than single pulse methods, using 30° pulses.

reactions shown in Scheme 5 provide a convenient route towards new disilane derivatives, of which those (e.g. **11**, **12**) derived from primary amines may be particularly useful for further transformations.

In contrast with **5**, the cyclic derivatives **6c** and **6d** react with an excess of piperidine (Scheme 6) to afford the desired 7,8-dicarba-*nido*-undecaborate(1-) derivatives **13** (Figure 4; see NMR spectroscopic data in Table 4 and in the Experimental Section). The reactions proceed readily, as monitored by NMR spectroscopy, accompanied by slow side reactions most likely owing to cleavage of the Si–Se or Si–Te bonds, respectively.

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

The optimized calculated [B3LYP/6-311+G(d,p) level of theory] geometries agree reasonably well with experimental data (Table 5, Table 6) given for expected differences between gas and solid phases. Using the calculated geometries, NMR parameters such as nuclear shielding (chemical shift) and spin-spin coupling constants ^nJ can be calculated. This works very well for $\delta^{11}B$[25] and was also shown to predict $\delta^{77}Se$ values[26,27] within an acceptable limit of error. The magnitude of calculated values $^1J(^{29}Si,^{13}C)$, at this level of theory, tends to be smaller by about 10–15 % than experimental data.[23] However, the sign and the trends are predicted correctly. This is also the case for $^1J(^{77}Se,^{29}Si)$ as well as for $^2J(^{77}Se,^{13}C_{Me})$ and $^3J(^{77}Se,^1H_{Me})$,[24b,28–30] again experimentally confirmed in this work.

X-ray Structural Analyses of the ortho-Carborane Derivatives

The molecular structures of the 1,2-bis(silyl)-*ortho*-carboranes **3** and **4** are shown in Figure 5 and Figure 6, respectively. The most notable features are the Si–C bond lengths, which are fairly long for the Si–C(carborane) and in the normal range for Si–C(methyl). The Si–C(carborane) distances are in the range determined previously[5,31] which, however, was not discussed. Apparently, the longer Si–C(carborane) distances mirror the rather small magnitude of the coupling constants $^1J(^{29}Si,^{13}C_{carb})$ (vide supra).

The analogous molecular structures of the selenium and tellurium containing cyclic *ortho*-carborane derivatives are shown in Figure 7. The cycles annealed to the carborane unit deviate markedly from ideal planarity (Table 6), whereas solution state ^1H and ^{13}C NMR spectra indicate fast ring inversion. Again, the Si–C(carborane) distances are slightly elongated,

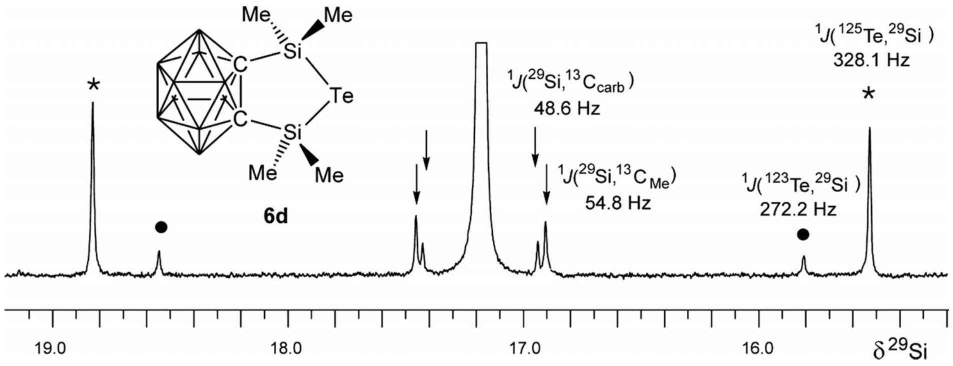
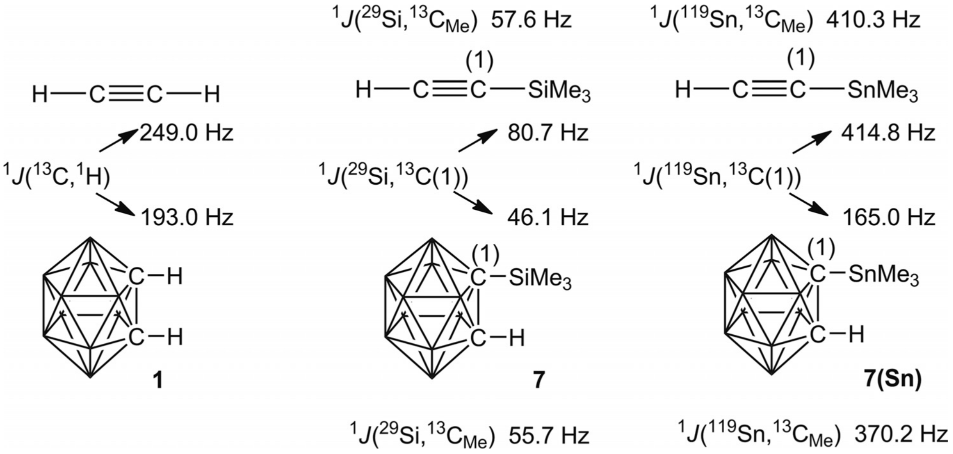


Figure 2. 99.4 MHz $^{29}Si\{^1H\}$ NMR spectrum (INEPT, refocused[18]) of **6d** (in [D_8]toluene, at 23 °C). The ^{125}Te satellites for $^1J(^{125}Te,^{29}Si)$ are marked by asterisks; the ^{123}Te satellites for $^1J(^{123}Te,^{29}Si)$ are marked by filled circles; the ^{13}C satellites for $^1J(^{29}Si,^{13}C_{Me})$ and $^1J(^{29}Si,^{13}C_{carb})$ are marked by arrows.



Scheme 3. Comparison of spin-spin coupling constants for alkynes and *ortho*-carboranes **1**, **7**, and **7**(Sn) (Table 1).

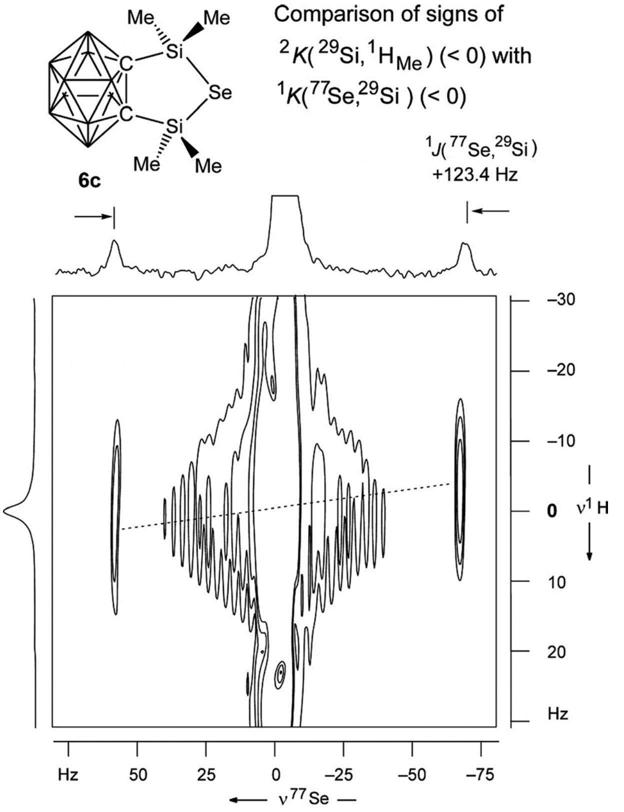


Figure 3. 2D $^{77}Se/^1H$ heteronuclear shift correlation ($\nu^{77}Se$ = 95.4 and ν^1H = 500.13 MHz) of **6c** (in CD_2Cl_2, at 23 °C), based on $^3J(^{77}Se,^1H_{Me})$ = 4.4 Hz. The positive tilt (dashed line) of the cross peaks for the ^{29}Si satellites indicates alike signs of $^2K(^{29}Si,^1H_{Me})$ and $^1K(^{77}Se,^{29}Si)$. Since the former is known to be negative,[23] it follows that $^1K(^{77}Se,^{29}Si) < 0$ and $^1J(^{77}Se,^{29}Si) > 0$ [$\gamma(^{29}Si) < 0$].

when compared with those of Si–C(methyl) bonds. All other bond lengths and angles are in the usual ranges.[12,32]

Conclusions

This work has completed the series of *ortho*-carborane-annealed 1,3-disila-2-element-cyclopentane derivatives (element = O, S, Se, Te), of which the selenium and tellurium compounds could be structurally characterized. All cyclic compounds were characterized in solution by advanced multinuclear magnetic resonance spectroscopic methods. The data obtained were compared with those of noncyclic silyl-substituted *ortho*-carboranes, of which two examples were also characterized by X-ray crystallography. It was found that the comparatively small magnitude of one-bond ^{29}Si–^{13}C(carborane) spin-spin coupling constants, measured herein for the first time in a systematic way, is mirrored by elongated Si–C bond lengths. The scarce data set of ^{13}C NMR spectroscopic data of *ortho*-carboranes presented in the literature could be enlarged by application of polarization transfer techniques (INEPT). In several cases, it could be demonstrated that the conversion of the new *ortho*-carborane derivatives into 7,8-dicarba-*nido*-undecaborate(1-) derivatives proceeds in the usual way. Further exploration of this synthetic potential is in progress.

Experimental Section

General: All syntheses and handling of samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. CH_2Cl_2 and CD_2Cl_2 were distilled over CaH_2 in an atmosphere of argon. All other solvents were distilled from Na metal in an atmosphere of argon. The starting materials were prepared as described in the literature, i.e. **2**,[33] Li_2Se, Li_2Te.[12] Other starting materials were purchased from Aldrich [Me_3SiCl, Me_2SiCl_2, $(Me_2SiCl)_2$, $Li[BEt_3H]$ (1.0 M in THF, Super-Hydride), tellurium (powder, –200 mesh, 99.8 % metals basis), sulfur (powder, 99.98 % metals basis), $Me_3N = O$ (98 %)], Fluka (selenium metal “grey”), ABCR ($Me_3SiOOSiMe_3$, 97 %) and KatChem. (*ortho*-carborane **1**), and used as received.

NMR measurements: Bruker DRX 500 and Bruker ARX 250: ^1H, ^{11}B, ^{13}C, ^{77}Se, ^{125}Te, ^{123}Te, and ^{29}Si NMR [refocused INEPT[18] based on $^2J(^{29}Si,^1H)$ = 6–7 Hz]; Varian INOVA 400: ^1H, ^{11}B, ^{13}C, ^{29}Si, ^{77}Se NMR; chemical shifts are given relative to Me_4Si [δ^1H ($CHDCl_2$) 5.33, ($C_6D_5CD_2H$) = 2.08 (± 0.01); $\delta^{13}C$ (CD_2Cl_2) = 53.8, ($C_6D_5CD_3$) = 20.4 (± 0.1); $\delta^{29}Si = 0$ (±0.1) for $\Xi(^{29}Si)$ = 19.867184 MHz]; external BF_3-OEt_2 [$\delta^{11}B = 0$ (±0.3) for $\Xi(^{11}B)$ = 32.083971 MHz], neat Me_2Se [$\delta^{77}Se = 0$ (± 0.1) for $\Xi(^{77}Se)$ = 19.071523 MHz], neat $SnMe_4$ [[$\delta^{119}Sn = 0$ for $\Xi(^{119}Sn)$ = 37.290665 MHz], neat Me_2Te [$\delta^{125}Te = 0$

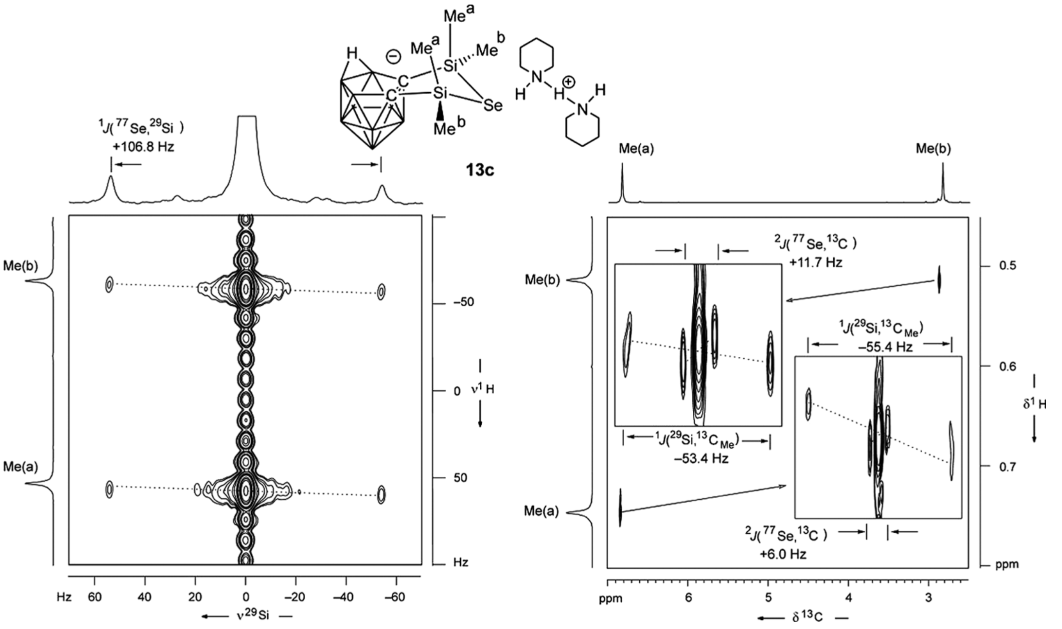
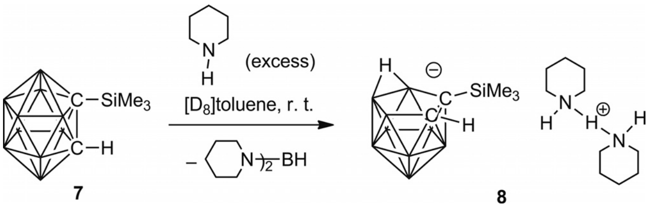


Figure 4. 2D heteronuclear shift correlations (ν^1H = 500.13 MHz) of **13c** (in [D$_8$]toluene, at 25 °C), showing the expected different SiMe groups. Left: $^{29}Si/^1H$-HETCOR experiment using $^2J(^{29}Si,^1H_{Me})$. The negative tilt of the ^{77}Se satellites is indicated by dashed lines. This compares the signs of $^1K(^{77}Se,^{29}Si)$ and $^3K(^{77}Se,^1H_{Me})$. Since $^1K(^{77}Se,^{29}Si) < 0$, $^3K(^{77}Se,^1H_{Me}) > 0$. Right: $^{13}C/^1H$-HETCOR experiment for the Si–Me groups, using $^1J(^{13}C,^1H)$. The positive and negative tilt of the ^{77}Se and ^{29}Si satellites (see expansions), respectively, is indicated by dashed lines. For the ^{77}Se satellites, this compares the signs of $^2J(^{77}Se,^{13}C_{Me})$ and $^3J(^{77}Se,^1H_{Me})$ which are both > 0, for both types of methyl groups, in agreement with calculations.



Scheme 4. Typical reaction of a monosubstituted *ortho*-carborane with piperidine in excess.

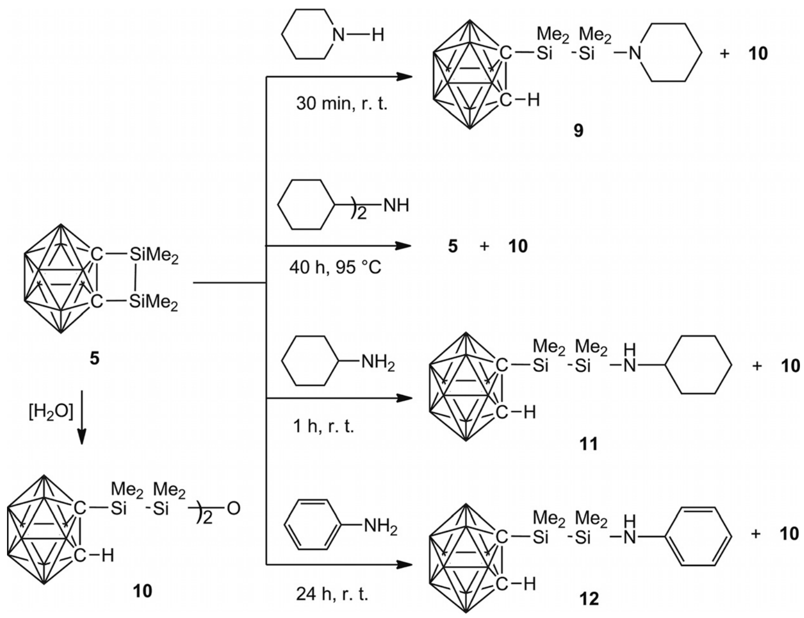
for $\Xi(^{125}Te)$ = 31.549802 MHz], neat Me$_2$Te [$\delta^{123}Te$ = 0 for $\Xi(^{123}Te)$ = 26.169773 MHz]. Assignments of ^1H and ^{11}B NMR signals are based on selective $^1H\{^{11}B$ selective$\}$ heteronuclear decoupling experiments.[34] Melting points (uncorrected) were determined with a Büchi 510 melting point apparatus.

All quantum chemical calculations were carried out using the Gaussian 09 program package.[35] Optimized geometries at the B3LYP/6-311+g(d.p) level of theory were found to be minima by the absence of imaginary frequencies. NMR parameters were calculated at the same level of theory. Calculated chemical shifts $\delta^{11}B$ and $\delta^{77}Se$ were converted by $\delta^{11}B$ (calcd) = $\sigma(^{11}B) - \sigma(^{11}B, B_2H_6)$, with $\sigma(^{11}B, B_2H_6)$ = +84.1 [$\delta^{11}B$ (B$_2$H$_6$) = 18 and $\delta^{11}B$ (BF$_3$-OEt$_2$) = 0] and $\delta^{77}Se$(calcd) = $\sigma(^{77}Se) - \sigma(^{77}Se, SeMe_2)$ with $\sigma(^{77}Se, SeMe_2)$ = +1621.7.

1,2-Bis(trimethylsilyl)-1,2-dicarba-*closo*-dodecaborane(12) (3):[36] Single transparent crystals of **3** for X-ray analysis were grown from [D$_8$]toluene after 2 weeks at –30 °C; m.p. 121–124 °C.

1,2-Bis[chloro(dimethyl)silyl]-1,2-dicarba-*closo*-dodecaborane(12) (4): Freshly prepared [(1,2-C$_2$B$_{10}$H$_{10}$)Li$_2$](2·Et$_2$O) (**2**) (919 mg, 3.14 mmol) was taken up in Et$_2$O (20 mL); the suspension was cooled to 0 °C, and Me$_2$SiCl$_2$ (90 mg, 0.85 mL, 6.98 mmol) was injected slowly (30 min) through a syringe. After stirring the reaction mixture for 20 h at room temperature, insoluble materials were separated by centrifugation, and the clear liquid was collected. Volatile materials were removed in vacuo to give **4** as a white solid (955 mg; 92 %). Single transparent crystals of **4** for X-ray analysis were grown from [D$_8$]toluene after 1 month at –30 °C; m.p. 100–103 °C. **$^1H\{^{11}B\}$ NMR** (250.1 MHz; [D$_8$]toluene; 25 °C): δ [$^2J(^{29}Si,^1H)$] = 0.37 [7.2] (s, 12 H, CH$_3$Si), 2.25 (br. s, 4 H, HB), 2.47 (br. s, 2 H, HB), 2.84 (br. s, 2 H, HB), 3.03 (br. s, 2 H, HB). **$^{11}B\{^1H\}$ NMR** (80.3 MHz; [D$_8$]toluene; 25 °C): δ = –10.8 (2B), –8.8 (4B), –5.1 (2B), 3.2 (2B). **^{11}B NMR** (80.3 MHz; [D$_8$]toluene; 25 °C): δ = –10.8 (d, 2B, 163 Hz), –8.8 (d, 4B, 160 Hz), –5.1 (d, 2B, 150 Hz), 3.2 (d, 2B, 150 Hz). **EI-MS** (70 eV) for C$_6$H$_{22}$B$_{10}$Si$_2$Cl$_2$ (328.16): *m/z* (%) = 328 (2) [M$^+$], 313 (100) [M$^+$ – CH$_3$], 294 (5), 277 (4), 259 (8), 199 (10), 156 (10).

1,1,2,2-Tetramethyl-3,4-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-cyclobutane (5): Freshly prepared [(1,2-C$_2$B$_{10}$H$_{10}$)Li$_2$](2 Et$_2$O) **2** (665 mg, 2.27 mmol) was taken up in Et$_2$O (40 mL); the suspension was cooled to 0 °C, and Me$_2$Si(Cl)–Si(Cl)Me$_2$ (43 mg, 0.42 mL, 2.27 mmol) was injected slowly (30 min) through a syringe. After stirring the reaction mixture for 3 h at room temperature, insoluble materials were separated by centrifugation, and the clear liquid was collected. The remaining insoluble materials were washed with Et$_2$O (15 mL) and centrifuged. The centrifuged solutions were combined, and volatile materials were removed in vacuo to give **5** as a white solid (551 mg; 94 %). **$^1H\{^{11}B\}$ NMR** (250.1 MHz; CD$_2$Cl$_2$; 25 °C): δ [$^2J(^{29}Si,^1H)$] = 0.48 [6.9] (s, 12 H, CH$_3$Si), 2.11 [br. s, 4 H, HB for $\delta(^{11}B)$ = –9.8], 2.25 [br. s, 2 H, HB for $\delta(^{11}B)$ = 0.0], 2.42 [br. s, 2 H, HB for $\delta(^{11}B)$ = –4.1], 2.49 [br. s, 2 H, HB for $\delta(^{11}B)$ = –11.9]. **$^{11}B\{^1H\}$ NMR** (80.3 MHz; CD$_2$Cl$_2$; 25 °C): δ = –11.9 (2B), –9.8 (4B), –4.1 (2B), 0.0 (2B). **^{11}B NMR** (80.3 MHz; CD$_2$Cl$_2$; 25 °C): δ = –11.9 (d, 2B, 174 Hz), –9.8 (d, 4B, 164 Hz), –4.1 (d, 2B, 147 Hz), 0.0 (d, 2B, 147 Hz).

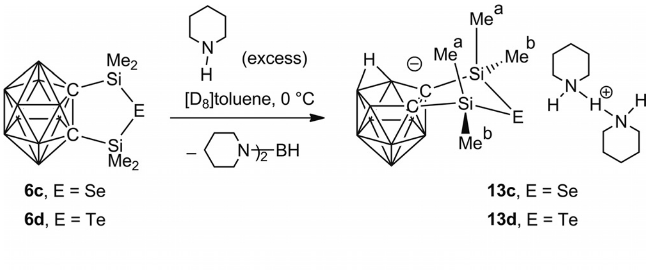


Scheme 5. Cleavage of the Si–C(carborane) bond in **5** with amines.

Table 3. ^{13}C, ^{29}Si NMR spectroscopic data[a)] of the *ortho*-carborane derivatives **9**–**12**.

	9 [D$_8$]toluene	**11** [D$_8$]toluene	**12** [D$_8$]toluene	**10** [D$_8$]toluene
δ^{13}C[C(1)SiCH$_3$]	–1.8 [44.0] [5.4]	–2.6 [44.6] [5.6]	–1.8 [45.6] [5.5]	–3.3 [45.6] [6.3]
δ^{13}C[SiSiCH$_3$]	–1.3 [50.9] [11.1]	0.3 [50.2] [10.1]	–0.2 [51.4] [9.1]	2.7 [51.5] [10.4]
δ^{13}C[C(2)]	60.9	60.9	60.5	60.2
$^{1}\Delta^{10/11}$B(^{13}C(1)) ± 0.5 ppb		–8.6	–7.2	–8.0
δ^{13}C[C(1)Si]	67.1	67.0	66.4	65.6
$^{1}\Delta^{10/11}$B(^{13}C(2)) ± 0.5 ppb	–12.3	–11.8	–11.2	–10.4
Other δ^{13}C data	pip: 25.4 (C$_\gamma$) 28.0 (C$_\beta$) 47.3 (C$_\alpha$)	C$_6$H$_{11}$: 25.4 (C$_p$) 25.8 (C$_m$) 38.9 (C$_o$) 51.8 (C$_i$)	Ph: 117.1 (C$_m$) 119.2 (C$_p$) 129.9 (C$_o$) 146.9 (C$_i$)	–
δ^{29}Si [C(1)Si]	–8.3 (95.0) [44.0] [11.1]	–7.98 [45.0] [10.1]	–6.6 [45.5] [9.2]	–7.5 (106.1) [46.1] [10.4]
δ^{29}Si [SiSi]	–3.8 (95.0) [51.0] [5.4]	–7.97 [50.1] [5.4]	–7.2 [51.4] [5.5]	6.6 (106.2) [51.5] [6.4]
$^{1}J(^{29}$Si,^{29}Si) and $^{n}J(^{29}$Si,^{13}C) (calcd.)	+75.0 (SiSi), –27.1 (C(1)), –34.3 (Me), –58.4 (Me), –13.8 (MeSiSi; ^{2}J), –5.8 (MeSiC(1), ^{2}J)			

a) Coupling constants $^{n}J(^{29}$Si,^{13}C) are given in brackets [± 0.5 Hz]; $^{1}J(^{29}$Si,^{29}Si) are given in parentheses (± 0.5 Hz); isotope-induced chemical shifts $^{1}\Delta$ are given in ppb, and the negative sign denotes a shift of NMR signal of the heavy isotopomer to lower frequency.



Scheme 6. Conversion of the *ortho*-carborane derivatives **6** into the respective 7,8-dicarba-*nido*-undecaborate(1-) derivatives **13**.

1,1,3,3-Tetramethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-2-selena-cyclopentane (6c): Method A: A solution of **4** (372 mg, 1.13 mmol) in toluene (20 mL) was cooled to 0 °C and a solution of freshly prepared Li$_2$Se (1.13 mmol) [from Se (89 mg; 1.13 mmol), Li[BEt$_3$H] (2.26 mL of a 1 M solution in THF; 2.26 mmol), and THF (3 mL)[12]]; afterwards further THF (10 mL) was added. After stirring the reaction mixture for 3h at room temperature, volatile materials were removed in vacuo. The remaining materials were washed with toluene (20 mL) and centrifuged. The centrifuged solutions were combined, and volatile materials were removed in vacuo to give a yellow solid. The residue was extracted with hexane (20 mL), insoluble materials were centrifuged. The clear liquid after centrifugation was dried in vacuo to give 322 mg (85 %) of **6c** as a

Table 4. ^{13}C, ^{29}Si, ^{77}Se, and ^{125}Te NMR spectroscopic data[a)] of the 7,8-dicarba-*nido*-undecaborate(1^-) derivatives **8**, **13c**, and **13d**.

	8 [D_8]toluene	**13c** (*E* = Se) [D_8]toluene	**13d** (*E* = Te) [D_8]toluene
$\delta^{13}C[SiCH_3]$	–1.0 [52.8]	CH_3(b): 2.9 [53.3] <11.7> CH_3(a): 6.8 [55.1] <6.0>	CH_3(b): 4.5 [51.1] <23.7> CH_3(a): 8.4 [53.6] <7.5>
$\delta^{13}C[C(7,8)]$	43.7 (br) (CSi) 46.6 (br) (CH)	55.3 (br)	56.3 (br)
Other $\delta^{13}C$ data	pip: 23.7 (C_γ) 25.5 (C_β) 45.6 (C_α)	pip: 23.9 (C_γ) 25.7 (C_β) 45.7 (C_α)	pip: 24.2 (C_γ) 26.5 (C_β) 46.4 (C_α)
$\delta^{29}Si$	1.2 [53.5]	29.9 (106.8)	20.6 (273.5) /225.2/
$\delta^{77}Se$ / $\delta^{125}Te$	–	–396.5 (106.0)	–1006.0 (279.0) {10.5}[b)]
$^1\Delta^{28/29}Si(^{77}Se$ / $^{125}Te)$ ± 1 ppb	–	–23.0	–34.5
$^1J(^{29}Si,^{13}C)$(calcd.)	–50.2 (Me), –66.4 [C(7)]	–44.9, –47.1[Me(b,a)], –59.5 [C(7,8)]	–
$^1J(^{77}Se,^{29}Si)$ (cacld.)		+130.0	
$^2J(^{77}Se,^{13}C)$ (calcd.)		+9.8, +3.4 [Me(b,a)], –8.1 [C(7,8)]	
$\delta^{77}Se$ (calcd.)	–	–539.0	–

a) Coupling constants $^nJ(^{29}Si,^{13}C)$ are given in brackets [± 0.5 Hz]; $^1J(^{77}Se,^{29}Si)$ and $^1J(^{125}Te,^{29}Si)$ are given in parentheses (± 0.5 Hz); $^1J(^{123}Te,^{29}Si)$ are given in / / /± 0.5 Hz/; $^2J(^{77}Se,^{13}C)$ and $^2J(^{125}Te,^{13}C)$ are given in < > <± 0.5 Hz>; $^3J(^{77}Se,^1H)$, $^3J(^{125}Te,^1H)$ and $^3J(^{123}Te,^1H)$ in braces {± 0.5 Hz}; (br) denotes broad ^{13}C resonances due to dynamic effects; isotope-induced chemical shifts $^1\Delta$ are given in ppb, and the negative sign denotes a shift of NMR signal of the heavy isotopomer to lower frequency. b) $\delta^{123}Te$: –1005.6.

Table 5. Selected bond lengths /pm and angles /° of the *ortho*-carborane derivatives **3**, **3**(calcd.), **4**, **4**(calcd.), and **5**, **5**(calcd.).

	3	**3**(calcd.)		**4**	**4**(calcd.)	**5**[a)]	**5**(calcd.)
T /K	133 K			133 K		293 K	
C(1)–Si(1)	193.5(3)	195.4	C(1)–Si(1)	191.5(4)	194.0	193.0(2)	194.6
C(2)–Si(2)	193.3(3)	195.4	C(2)–Si(2)	192.2(4)	194.0		194.5
Si(1)–C(3)	185.7(3)	188.5	Si(1)–C(3)	186.6(4)	187.0	187.4	188.3
Si(1)–C(4)	185.9(3)	188.3	Si(1)–C(4)	189.5(3)	186.6	186.1	188.3
Si(1)–C(5)	186.0(3)	188.3	Si(2)–C(5)	191.7(7)	186.6		188.3
Si(2)–C(6)	185.0(3)	188.5	Si(2)–C(6)	186.8(4)	187.0		188.3
Si(2)–C(7)	186.0(3)	188.3					
Si(2)–C(8)	186.3(3)	188.3					
C(1)–C(2)	171.4(4)	172.6	C(1)–C(2)	170.3(5)	171.5	170.6(3)	170.4
			Si(1)–Si(2)			236.40(9)	239.2
Si(1)–C(1)–C(2)	127.03(17)	127.24	Si(1)–C(1)–C(2)	127.2(2)	128.0	99.81(5)	100.2
Si(2)–C(2)–C(1)	126.31(17)	127.23	Si(2)–C(2)–C(1)	127.6(2)	128.0		
Plane Si(1)–C(1)–C(2)–Si(2)	0.8	3.1	Plane Si(1)–C(1)–C(2)–Si(2)	1.3	6.75	0.2	0.0

a) Ref.[8].

yellowish solid (larger amounts of byproducts were observed by ^{29}Si NMR spectroscopy in the crude products). Yellowish single crystals of **6c** for X-ray analysis were grown from [D_8]toluene solution after 7 d at –30 °C; m.p. 118–122 °C.

Method B: A solution of **5** (90 mg, 0.35 mmol) in [D_8]toluene (1 mL) was added at room temperature to an excess of dry and degassed elemental selenium (40 mg). The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 7 d at 95 °C, the solution was centrifuged from selenium. The clear liquid was dried in vacuo to give **6c** as a yellowish solid (the solid thus obtained contained about 10 % of **6a**).

6c: **$^1H\{^{11}B\}$ NMR** (399.8 MHz; CD_2Cl_2; 25 °C): δ = 0.67 (s, 12 H, CH_3Si), 2.16 [br. s, 4 H, $HB^{4,5,7,11}$ for $\delta(^{11}B)$ = –10.2], 2.29 [br. s, 2 H, $HB^{3,6}$ for $\delta(^{11}B)$ = –12.3], 2.33 [br. s, 2 H, HB for $\delta(^{11}B)$ = –0.6], 2.52 [br. s, 2 H, HB for $\delta(^{11}B)$ = –3.7]. **$^{11}B\{^1H\}$ NMR** (128.3 MHz; CD_2Cl_2; 25 °C): δ = –12.3 (2B, $B^{3,6}$), –10.2 (4B, $B^{4,5,7,11}$), –3.7 (2B), –0.6 (2B). **^{11}B NMR** (128.3 MHz; CD_2Cl_2; 25 °C): δ = –12.3 (d, 2B, $B^{3,6}$, 170 Hz), –10.2 (d, 4B, $B^{4,5,7,11}$, 156 Hz), –3.7 (d, 2B, 151 Hz), –0.6 (d, 2B, 156 Hz). **EI-MS** (70 eV) for $C_6H_{22}B_{10}Si_2Se$ (338.14): *m/z* (%) = 338 (65) [M^+], 323 (100) [$M^+ - CH_3$], 275 (5), 259 (18), 210 (10).

1,1,3,3-Tetramethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-2-tellura-cyclopentane (6d): A solution of **4** (255 mg, 0.77 mmol) in THF (8 mL) was cooled to 0 °C and a solution of freshly prepared Li_2Te (0.77 mmol) [from Te (99 mg; 0.77 mmol) and Li[BEt_3H] (1.55 mL of a 1 M solution in THF; 1.55 mmol)[12]] was added. After stirring the reaction mixture for 2h at 0 °C, volatile materials were removed in vacuo. The remaining materials were washed with toluene (20 mL) and centrifuged. The clear liquid was dried in vacuo to give 241 mg (81 %) of **6d** as a yellow solid. Yellowish single crystals of **6d** for X-ray analysis were grown from [D_8]toluene solution after 3 d at –30 °C; m.p. 135–139 °C. **6d** decomposes slowly in an argon atmosphere as a solid at room temperature and also slowly in

Table 6. Selected bond lengths /pm and angles /° of the cyclic *ortho*-carborane derivatives **6** and **6**(calcd.).

	6a[a]	**6a**(calcd.)	**6b**(calcd.)	**6c**	**6c**(calcd.)	**6d**
	(E = O)	(E = O)	(E = S)	(E = Se)	(E = Se)	(E = Te)
T /K	198 K			133 K		133 K
C(1)–Si(1)	191.4(2)	193.1	192.6	190.3(4)	192.9	191.0(3)
C(2)–Si(2)		193.1	192.6	190.2(4)	192.9	191.0(3)
Si(1)–C(3)	183.3	186.6	187.3	185.1(5)	187.5	185.0(3)
Si(1)–C(4)	184.2	186.6	187.3	185.1(5)	187.5	185.4(3)
Si(2)–C(5)	183.3	186.6	187.3	184.9(5)	187.5	185.7(3)
Si(2)–C(6)	184.2	186.6	187.3	185.1(5)	187.5	185.2(3)
C(1)–C(2)	169.1(4)	169.2	167.2	168.5(5)	167.6	167.8(4)
E–Si(1)	164.2(1)	167.4	217.4	226.30(14)	231.5	249.07(10)
E–Si(2)		167.4	217.4	227.24(13)	231.5	248.87(9)
Si(1)–C(1)–C(2)	108.97(6)	109.34	115.81	117.3(2)	117.31	119.90(18)
Si(2)–C(2)–C(1)		109.34	115.81	116.0(2)	117.31	119.09(18)
C(1)–Si(1)–E	98.15(9)	98.12	103.83	104.02(12)	104.62	103.86(9)
C(2)–Si(2)–E		98.12	103.83	104.47(12)	104.62	104.22(9)
Si(1)–E–Si(2)	125.84(13)	125.09	100.72	96.70(4)	96.15	91.26(3)
Plane Si(1)–C(1)–C(2)–Si(2)	0	0	0	0.2	0	0.4
Distance of E from the plane Si(1)–C(1)–C(2)–Si(2)	8.0	0	0	31.9	0	37.2
Plane C(1)–Si(1)–E–Si(2)–C(2)	2.2	0	0	7.6	0	8.4

a) Ref.[8].

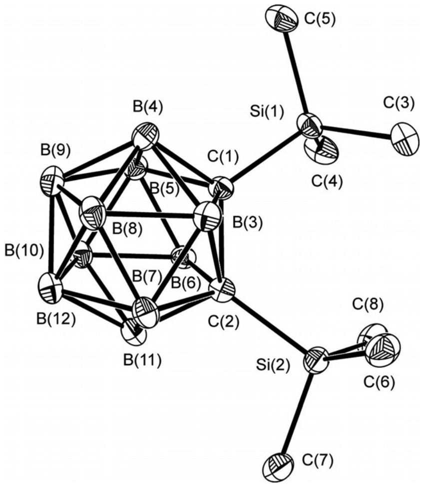


Figure 5. ORTEP plot (50 % probabilities; hydrogen atoms are omitted for clarity) of the molecular structure of the 1,2-bis(trimethysilyl)-1,2-dicarba-*closo*-dodecaborane(12) **3** (for selected distances and angles see Table 5).

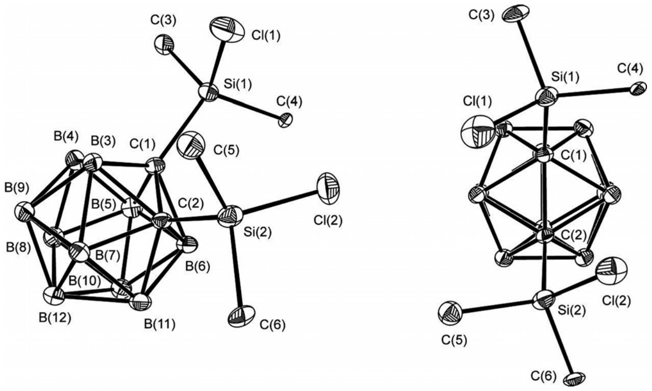


Figure 6. Two views of the ORTEP plots (50 % probabilities; hydrogen atoms are omitted for clarity) of the molecular structure of the 1,2-bis(chloro-dimethysilyl)-1,2-dicarba-*closo*-dodecaborane(12) **4** (for selected distances and angles see Table 5). In one of the dimethylchlorosilyl groups disorder [between Cl(2) and C(5)] was observed.

[D_8]toluene at –30 °C with formation of a black precipitate of elemental tellurium. **^{1}H{^{11}B} NMR** (399.8 MHz; [D_8]toluene; 25 °C): δ [$^2J(^{29}Si,^1H)$] = 0.38 [7.6] (s, 12 H, CH_3Si), 2.22 (br. s, 6 H,), 2.72 (br. s, 2 H, HB), 2.91 (br. s, 2 H, HB). **^{11}B{^{1}H} NMR** (128.3 MHz; [D_8]toluene; 25 °C): δ = –12.3 (2B, $B^{3,6}$), –9.9 (4B, B), –3.1 (2B), –0.1 (2B). **^{11}B NMR** (128.3 MHz; [D_8]toluene; 25 °C): δ = –12.3 (d, 2B, B, 162 Hz), –9.9 (d, 4B, B, 160 Hz), –3.1 (d, 2B, 148 Hz), –0.1 (d, 2B, 150 Hz).

1,1,3,3-Tetramethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-2-thia-cyclopentane (6b): A solution of **5** (70 mg, 0.27 mmol) in [D_8]toluene (1 mL) was added at room temperature to an excess of dry and degassed elemental sulfur (10 mg). The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 7 d at 85 °C, the solution was centrifuged from sulfur. The clear liquid was dried in vacuo to give **6b** as a yellowish solid. **^{1}H{^{11}B} NMR** (399.8 MHz; [D_8]toluene; 25 °C): δ [$^2J(^{29}Si,^1H)$] = 0.2 [6.8] (s, 12 H, CH_3Si), 2.22 (br. s, 6 H, HB), 2.93 (br. s, 2 H, HB), 2.99 (br. s, 2 H, HB). **^{11}B{^{1}H} NMR** (128.3 MHz; [D_8]toluene; 25 °C): δ = –12.5 (2B, B), –10.1 (4B, B), –3.3 (2B), 0.1 (2B). **^{11}B NMR** (128.3 MHz; [D_8]toluene; 25 °C): δ = –12.5 (d, 2B, 170 Hz), –10.1 (d, 4B, 164 Hz), –3.3 (d, 2B, 149 Hz), 0.1 (d, 2B, 152 Hz). **EI-MS** (70 eV) for $C_6H_{22}B_{10}Si_2S$ (290.20): m/z (%) = 290 (30) [M^+], 275 (100) [$M^+ - CH_3$], 259 (5), 211 (4), 137 (7).

1,1,3,3-Tetramethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-2-oxa-cyclopentane (6a): A solution of **5** (70 mg, 0.27 mmol) in [D_8]toluene (1 mL) was added at room temperature to $Me_3N{=}O$ (25 mg; 0.33 mmol). Volatile materials were removed in vacuo to give **6a** as a white oil (the solid thus obtained contained about 10 % of $Me_3N{=}O$). **^{1}H{^{11}B} NMR** (500.1 MHz; [D_8]toluene; 25 °C): δ [$^2J(^{29}Si,^1H)$] = 0.03 [7.0] (s, 12 H, CH_3Si), 2.21 (br. s, 2 H, HB), 2.26 (br. s, 4 H, HB), 2.99 (br. s, 2 H, HB), 3.04 (br. s, 2 H, HB). **^{11}B{^{1}H} NMR** (160.5 MHz; [D_8]toluene; 25 °C): δ = –12.5 (2B, B), –10.5 (4B, B), –3.2 (2B), 0.2 (2B). **^{11}B NMR** (160.5 MHz; [D_8]toluene; 25 °C):

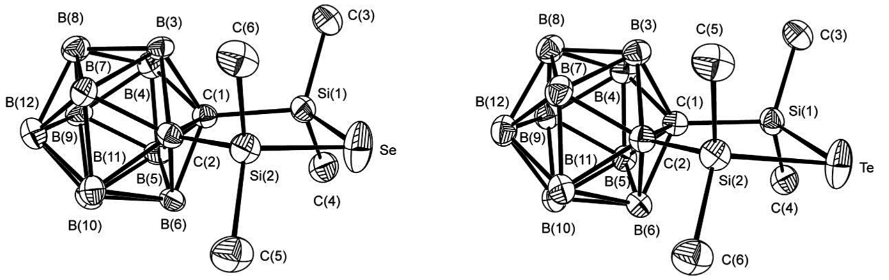


Figure 7. ORTEP plot (50 % probabilities; hydrogen atoms are omitted for clarity) of the molecular structure of the 1,1,3,3-tetramethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-2-selenacyclopentane (**6c**) and of the 1,1,3,3-tetramethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-2-telluracyclopentane (**6d**) (for selected distances and angles see Table 6).

δ = –12.5 (d, 2B, 165 Hz), –10.5 (d, 4B, 157 Hz), –3.2 (d, 2B, 145 Hz), 0.2 (d, 2B, 145 Hz).

Piperidinium 9,10-µ-hydro-7-trimethylsilyl-7,8-dicarba-*nido*-undecaborate(1-) Piperidine Adduct, $[(C_5H_{10}NH)_2H]^+[7\text{-}Si(CH_3)_3\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (8): A solution of 1-trimethylsilyl-1,2-dicarba-*closo*-dodecaborane(12) (100 mg; 0.46 mmol) in [D$_8$]toluene (0.6 mL) was cooled to 0 °C, and piperidine (0.02 mL; 17 mg; 2.0 mmol) was added through a syringe. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 60 h at room temp., volatile materials were removed in vacuo, and the remaining oil was washed with hexane (1 mL), dried in vacuo to give a white oil of **8**. **^{1}H NMR** (500.1 MHz; [D$_8$]toluene; 25 °C): δ [$^2J(^{29}$Si,^{1}H)] = –2.15 [br. m, 1 H, B(10)H$_{bridge}$ for $\delta(^{11}$B) = –32.1], 0.15 [6.8] (s, 9 H, SiCH$_3$), 1.33 (m, H-pip), 2.54 (m, H-pip), 6.18 (br. s, NH). **^{11}B{^{1}H} NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –36.0 [1B, B(1)], –32.1 [1B, B(10)], –21.0 (1B), –18.8 (1B), –17.2 (1B), –16.0 (1B), –12.6 (1B), –9.7 (1B), –8.7 (1B). **^{11}B NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –36.0 [d, 1B, B(1), 140 Hz], –32.1 [d, 1B, B(10), 129 Hz], –21.0 (d, 1B, 129 Hz), –18.8 (d, 1B, 130 Hz), –17.2 (d, 1B), –16.0 (d, 1B), –12.6 (d, 1B, 128 Hz), –9.7 (d, 1B, 150 Hz), –8.7 (d, 1B, 145 Hz).

1-(1,1,2,2-Tetramethyl-2-(N-piperidinyl)disilanyl)-1,2-dicarba-*closo*-dodecaborane(12) (9): A suspension of **5** (150 mg, 0.58 mmol) in [D$_8$]toluene (3.0 mL) was cooled to –10 °C and piperidine (0.079 mL; 68 mg; 0.80 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 30 min at room temp., the transparent solution contained **9** together with **10** (ca. 25 %) and piperidine. Volatile materials were removed in vacuo (1 h, 8 × 10^{-3} Torr). The mixture thus obtained contained **9** (60 %) and **10** (40 %) (^{29}Si, ^{13}C, ^{1}H NMR).

9: **^{1}H{^{11}B} NMR** (500.1 MHz; [D$_8$]toluene; 25 °C): δ [$^2J(^{29}$Si,^{1}H)] = –0.01 [6.4] (s, 6 H, SiCH$_3$), –0.02 [6.5] (s, 6 H, SiCH$_3$), 1.20 (m, 4H, H$_\beta$-pip), 1.37 (m, 2H, H$_\gamma$-pip), 2.17 [br. s, 1 H, HB for $\delta(^{11}$B) = –13.3], 2.22 [br. s, 2 H, HB for $\delta(^{11}$B) = –13.3 and –10.7], 2.25 [br. s, 1 H, HB for $\delta(^{11}$B) = –10.7], 2.35 [m, 1H, HB for $\delta(^{11}$B) = –11.8], 2.39 [br. s, 1 H, HB for $\delta(^{11}$B) = –1.8], 2.51 (m, 4H, H$_\alpha$-pip), 2.78 [br. s, 2 H, HB for $\delta(^{11}$B) = –6.6], 2.84 [br. s, 1 H, HB for $\delta(^{11}$B) = –1.1], 2.91 [br. s, 1 H, HB for $\delta(^{11}$B) = 0.1], 3.42 (s, 1H, CH). **^{1}H NMR** (500.1 MHz; CD$_2$Cl$_2$; 25 °C): δ [$^2J(^{29}$Si,^{1}H)] = 0.23 [6.4] (s, 6 H, SiCH$_3$), 0.27 (s, 6 H, SiCH$_3$), 1.39 (m, 4H, H$_\beta$-pip), 1.55 (m, 2H, H$_\gamma$-pip), 2.76 (m, 4H, H$_\alpha$-pip), 3.87 (s, 1H, CH). **^{11}B{^{1}H} NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –13.3 (2B), –11.8 (2B), –10.7 (2B), –6.6 (2B), –1.1 (1B), 0.1 (1B). **^{11}B NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –13.3 (d, 2B, 179 Hz), –11.8 (d, 2B, 173 Hz), –10.7 (d, 2B, 165 Hz), –6.6 (d, 2B, 150 Hz), –1.1 (d, 1B, 157 Hz), 0.1 (d, 1B, 174 Hz).

10: **^{1}H NMR** (500.1 MHz; [D$_8$]toluene; 25 °C): δ [$^2J(^{29}$Si,^{1}H)] = –0.06 [6.4] (s, 6 H, SiCH$_3$), 0.12 [6.4] (s, 6 H, SiCH$_3$), 2.94 (s, 1H, CH). **^{1}H NMR** (500.1 MHz; CD$_2$Cl$_2$; 25 °C): δ [$^2J(^{29}$Si,^{1}H)] = 0.27 (s, 6 H, SiCH$_3$), 0.33 (s, 6 H, SiCH$_3$), 3.48 (s, 1H, CH). **^{11}B{^{1}H} NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –13.3 (2B), –11.8 (2B), –10.7 (2B), –6.6 (2B), –1.1 (1B), 0.1 (1B). **^{11}B NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –13.3 (d, 2B, 179 Hz), –11.8 (d, 2B, 173 Hz), –10.7 (d, 2B, 165 Hz), –6.6 (d, 2B, 150 Hz), –1.1 (d, 1B, 157 Hz), 0.1 (d, 1B, 174 Hz).

Reaction of 5 with Dicyclohexylamine: 1,1,3,3-Tetramethyl-1,3-bis(1,2-dicarba-*closo*-dodecaborane(12)-1-yldimethylsilyl) disiloxane (10): A suspension of **5** (50 mg, 0.19 mmol) in [D$_8$]toluene (0.7 mL) was cooled to –10 °C and dicyclohexylamine (0.08 mL; 73 mg; 0.4 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 24 h at room temp., the solution contained only **5** and dicyclohexylamine. After 24 h at 95 °C, the solution contained **5** (ca. 70 %), **10** (ca. 30 %), and dicyclohexylamine. **EI-MS** (70 eV) for $C_{12}H_{26}Si_4OB_{20}$ (514.9): *m/z* (%) = 350 (10), 334 (100) [M$^+$ – $C_4H_{17}B_{10}Si$], 250 (10), 238 (32), 200 (5).

1-(2-(Cyclohexylamino)-1,1,2,2-tetramethyl-disilanyl)-1,2-dicarba-*closo*-dodecaborane(12) (11): A suspension of **5** (66 mg, 0.26 mmol) in [D$_8$]toluene (0.7 mL) was cooled to –20 °C and cyclohexylamine (0.055 mL; 48 mg; 0.48 mmol) was added through a microsyringe. The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 1 h at room temp., the transparent solution contained **11** together with **10** (ca. 20 %) and cyclohexylamine. Volatile materials were removed in vacuo (3 h, 8 × 10^{-3} Torr). The mixture thus obtained contained **11** (80 %) and **10** (20 %) (^{29}Si, ^{13}C, ^{1}H NMR). **^{1}H{^{11}B} NMR** (500.1 MHz; [D$_8$]toluene; 25 °C): δ [$^2J(^{29}$Si,^{1}H)] = 0.00 [6.2] (s, 6 H, SiCH$_3$), 0.05 [6.4] (s, 6 H, SiCH$_3$), 0.78 (m, 2H, cyclohexyl), 0.91 (m, 1H, cyclohexyl), 1.12 (m, 2H, cyclohexyl), 1.45 (m, 1H, cyclohexyl), 1.58 (m, 4H, cyclohexyl), 2.18 (br. s, 2 H, HB for $\delta(^{11}$B) = –13.3 and –10.8), 2.25 [br. s, 2 H, HB for $\delta(^{11}$B) = –13.3 and –10.8], 2.33 [br. s, 2 H, HB for $\delta(^{11}$B) = –11.8], 2.33 (m, 1H, cyclohexyl), 2.73 [br. s, 2 H, HB for $\delta(^{11}$B) = –6.6], 2.80 [br. s, 1 H, HB for $\delta(^{11}$B) = –1.1], 2.86 [br. s, 1 H, HB for $\delta(^{11}$B) = 0.0], 3.41 (s, 1H, CH). **^{11}B{^{1}H} NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –13.3 (2B), –11.8 (2B), –10.8 (2B), –6.6 (2B), –1.1 (1B), 0.0 (1B). **^{11}B NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –13.3 (d, 2B, 179 Hz), –11.8 (d, 2B, 170 Hz), –10.8 (d, 2B, 165 Hz), –6.6 (d, 2B, 150 Hz), –1.1 (d, 1B, 160 Hz), 0.0 (d, 1B, 170 Hz).

1-(1,1,2,2-Tetramethyl-2-(phenylamino)disilanyl)-1,2-dicarba-*closo*-dodecaborane(12) (12): A suspension of **5** (56 mg, 0.22 mmol) in [D$_8$]toluene (0.7 mL) was cooled to 0 °C and aniline (0.1 mL;

102 mg; 1.1 mmol) was added through a syringe. The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 40 h at room temp., the transparent solution contained **12** together with **10** (ca. 25 %) and aniline. Volatile materials were removed in vacuo (5 h, 8×10^{-3} Torr). The mixture thus obtained contained **12** (75 %) and **10** (25 %) (^{29}Si, ^{13}C, ^{1}H NMR). **^{1}H{^{11}B} NMR** (500.1 MHz; [D$_8$]toluene; 25 °C): δ [$^{2}J(^{29}Si,^{1}H)$] = –0.03 [5.7] (s, 6 H, SiCH$_3$), 0.15 (6.0) (s, 6 H, SiCH$_3$), 2.08 [br. s, 1 H, HB for $\delta(^{11}B)$ = –13.3], 2.19 [br. s, 2 H, HB for $\delta(^{11}B)$ = –13.3 and –10.8], 2.22 [br. s, 1 H, HB for $\delta(^{11}B)$ = –10.8], 2.26 [m, 1 H, HB for $\delta(^{11}B)$ = –11.7], 2.35 [br. s, 1 H, HB for $\delta(^{11}B)$ = –11.7], 2.73 [br. s, 1 H, HB for $\delta(^{11}B)$ = –6.7], 2.78 [br. s, 1 H, HB for $\delta(^{11}B)$ = –6.7], 2.85 [br. s, 1 H, HB for $\delta(^{11}B)$ = –1.1], 2.86 [br. s, 1 H, HB for $\delta(^{11}B)$ = 0.1], 2.92 (s, 1H, CH), 6.37 (m, 2H, Ph), 6.68 (m, 1H, Ph), 7.03 (m, 2H, Ph). **^{11}B{^{1}H} NMR** (160.5 MHz; D$_8$]toluene; 25 °C): δ = –13.3 (2B), –11.7 (2B), –10.8 (2B), –6.7 (2B), –1.1 (1B), 0.1 (1B). **^{11}B NMR** (160.5 MHz; D$_8$]toluene; 25 °C): δ = –13.3 (d, 2B, 180 Hz), –11.7 (d, 2B, 158 Hz), –10.8 (d, 2B, 155 Hz), –6.7 (d, 2B, 150 Hz), –1.1 (d, 1B, 158 Hz), 0.0 (d, 1B, 175 Hz).

Piperidinium 9,10-µ-Hydro-7,8-µ-(1′,1′,3′,3′-tetramethyl-1′,3′-disila-2′-selena-1′,3′-diyl)-7,8-dicarba-*nido*-undecaborate(1-) Piperidine Adduct, $[(C_5H_{10}NH)_2H]^+[7,8\text{-}\mu\text{-}Si(CH_3)_2SeSi(CH_3)_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (13c): A solution of **6c** (80 mg; 0.24 mmol) in [D$_8$]toluene (0.6 mL) was cooled to 0 °C, and piperidine (0.07 mL; 60 mg; 0.71 mmol) was added through a microsyringe. The formation of a orange solution was observed. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 40 h at room temp., the mixture contained **13c** together with $(C_5H_{10}N)_2BH$ and piperidine. **^{1}H NMR** (500.1 MHz; [D$_8$]toluene; 25 °C): δ [$^{2}J(^{29}Si,^{1}H)$] {$^{3}J(^{77}Se,^{1}H)$} = –1.94 [br. m, 1 H, B(10)H$_{bridge}$ for $\delta(^{11}B)$ = –29.7], 0.52 [7.2] {4.6} [s, 6 H, SiCH$_3$(b)], 0.75 [7.2] [s, 6 H, SiCH$_3$(a)], 1.35 (m, H-pip), 1.52 (m, H-pip), 3.02 (m, H$_\alpha$-pip), 5.90 (br. s, NH). **^{11}B{^{1}H} NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –33.9 [1B, B(1)], –29.7 [1B, B(10)], –17.6 (2B), –14.0 (3B), –11.4 (1B), –8.4 (1B), 27.8 [1B, $(C_5H_{10}N)_2BH$].

Piperidinium 9,10-µ-Hydro-7,8-µ-(1′,1′,3′,3′-tetramethyl-1′,3′-disila-2′-tellura-1′,3′-diyl)-7,8-dicarba-*nido*-undecaborate(1-) Piperidine Adduct, $[(C_5H_{10}NH)_2H]^+[7,8\text{-}\mu\text{-}Si(CH_3)_2TeSi(CH_3)_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (13d): A solution of **6d** (90 mg; 0.23 mmol) in [D$_8$]toluene (0.6 mL) was cooled to 0 °C, and piperidine (0.07 mL; 60 mg; 0.71 mmol) was added through a microsyringe. The formation of a crimson dark solution was observed. The progress of the reaction was monitored by ^{11}B and ^{29}Si NMR spectroscopy. After 40 h at room temp., the mixture contained **13d** together with $(C_5H_{10}N)_2BH$, piperidine and larger amounts of byproducts. **13d** decomposes in an argon atmosphere slowly and in [D$_8$]toluene at –30 °C with formation of a black precipitate of elemental tellurium. **^{1}H NMR** (500.1 MHz; [D$_8$]toluene; 25 °C): δ [$^{2}J(^{29}Si,^{1}H)$] {$^{3}J(^{125}Te,^{1}H)$} = –2.03 [br. m, 1 H, B(10)H$_{bridge}$ for $\delta(^{11}B)$ = –29.7], 0.60 [7.2] {10.5} [s, 6 H, SiCH$_3$(b)], 0.88 [7.0] [s, 6 H, SiCH$_3$(a)], 1.35 (m, H-pip), 1.55 (m, H-pip), 3.00 (m, H$_\alpha$-pip), 4.16 (br. s, NH). **^{11}B{^{1}H} NMR** (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –34.0 [1B, B(1)], –29.7 [1B, B(10)], –13–0 (overlapping signals for **13d** and byproducts), 27.3 [1B, $(C_5H_{10}N)_2BH$].

Crystal Structure Determination of 3, 4, 6c, and 6d: Structure solutions and refinements were carried out with the program package SHELXTL-PLUS V.5.1.[37] Details pertinent to the crystal structure determination are listed in Table 7. Crystals of appropriate size were sealed in an argon atmosphere in Lindeman capillaries and the data collections were carried out at 133 K.[38]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-862717 (**3**), -862719 (**4**), -862720 (**6c**), and -862718 (**6d**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Table 7. Crystallographic data of the *ortho*-carborane derivatives **3**, **4**, **6c**, and **6d**.

	3	4	6c	6d
Formula	$C_8H_{28}B_{10}Si_2$	$C_6H_{22}B_{10}Cl_2Si_2$	$C_6H_{22}B_{10}SeSi_2$	$C_6H_{22}B_{10}Si_2Te$
Crystal	colorless prism	colorless block	yellowish prism	yellowish prism
Dimensions /mm^3	0.28 × 0.22 × 0.20	0.18 × 0.16 × 0.15	0.29 × 0.24 × 0.22	0.25 × 0.19 × 0.18
Temperature /K	133(2)	133(2) K	133(2) K	133(2) K
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
Lattice parameters				
a /pm	908.56(18)	904.43(18)	686.94(14)	683.52(14)
b /pm	1447.2(3)	1445.8(3)	1404.8(3)	1445.0(3)
c /pm	1346.1(3)	1337.0(3)	1776.1(4)	1771.9(4)
β /deg	90.42(3)	90.69(3)	96.90(3)	96.27(3)
Z	4	4	4	4
Absorption coefficient μ /mm^{-1}	0.180	0.486	2.322	1.823
Diffractometer	STOE IPDS II, Mo-K_α, λ = 71.073 pm, graphite monochromator			
Measuring range (ϑ) /deg	2.07–25.74	2.07–25.73	1.85–25.75	1.82–25.60
Reflections collected	20647	21647	18333	22839
Independent reflections [$I \geq 2\sigma(I)$]	2569	2836	2470	3009
Absorption correction[a)]	none	none	none	none
Refined parameters	181	185	172	172
wR_2/R_1 [$I \geq 2\sigma(I)$]	0.129 / 0.058	0.173 / 0.063	0.125 / 0.055	0.081 / 0.032
Max./min. residual electron density /e·pm^{-3}·10^{-6}	0.525 / –0.237	0.719 / –0.612	0.848 / –0.393	1.497 / –0.956

a) Absorption corrections did not improve the parameter set.

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