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# Synthesis of Tellurasila Cycles Containing an Annelated Dicarba-*closo*-dodecaborane(12) Unit: Structure of a 1,4-Ditellura-2,3-disilacyclohexane Derivative

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Insertion of tellurium into C–Li bonds of dilithiated 1,2-dicarba-*closo*-dodecaborane(12) gave 1,2-dicarba-*closo*-dodecaborano(12)-1,2-ditellurolate  $[(1,2-C_2B_{10}H_{10})Te_2Li_2](Et_2O)$ which, after reaction with 1,2-dichlorotetramethyldisilane, afforded a six-membered heterocycle containing the Te–Si– Si–Te unit with an annelated carborane moiety, characterized by multinuclear magnetic resonance and X-ray structural analysis. As a byproduct, a five-membered ring containing a Si–Si–Te unit was formed, which was obtained as a major

### Introduction

The chemistry of 1,2-dithio- and 1,2-diselenolato-1,2-dicarba-closo-dodecaborane(12) dianions [1,2-(1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)- $E_2$ <sup>2-</sup> (E = S, Se), prepared in situ as the dilithium salts<sup>[1-4]</sup> (sodium,<sup>[5a,5b]</sup> potassium<sup>[5b,5c]</sup> or ammonium<sup>[5c,5d]</sup> salts), been exploited in transition-metal chemishas try<sup>[1,3a,3b,4a,4b,5a,6-11]</sup> and, more recently, also in maingroup-element chemistry.<sup>[1,3a,12-18]</sup> In contrast, the heavy congener [1,2-(1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)Te<sub>2</sub>]<sup>2-</sup> has received much less attention.<sup>[4a,19]</sup> It appears that its synthesis is less straightforward and its reactivity is less predictable than in the cases of the sulfur and selenium analogues. The most notable derivatives are 1 and 2, isolated in low yield and characterized in the solid state by X-ray structural analysis.<sup>[19]</sup> however, without relevant solution-state NMR spectroscopic data.

product, using conditions favouring partial insertion of tellurium into C-Li bonds. Treatment of  $[(1,2-C_2B_{10}H_{10})Te_2Li_2]$ -(Et<sub>2</sub>O) with dichlorodimethylsilane led to a five-membered heterocycle as a major product containing a Te-Te-Si unit. Various decomposition/hydrolysis/oxidation products could be identified by multinuclear magnetic resonance, among them most notably 1,2-di(hydrotelluro)-1,2-dicarba-*closo*-dodecaborane(12).



Starting from the parent *ortho*-carborane 3, careful preparation of 4 and 5 enabled the synthesis of diselenasila cycles in good yield and high purity,<sup>[4c]</sup> as shown for 6 in Scheme 1. Such diselenasila cycles turned out to be useful



Scheme 1. Synthesis of the 1,2-diselenolato-1,2-dicarba-closo-dodecaborane(12) dianion, and its conversion into a diselenadisila cycle.

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starting materials for the synthesis of other novel heterocycles, since the Si–Se bonds are readily split in exchange reactions with various element halides.<sup>[20–22]</sup>

In the present work, we have set out to prepare the 1,2ditellurato-1,2-dicarba-*closo*-dodecaborane(12) dianion,

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 $[1,2-(1,2-C_2B_{10}H_{10})Te_2]^{2-}$  (7), and to study its reactivity towards chlorosilanes. Considering the favourable NMR spectroscopic properties of <sup>125</sup>Te (I = 1/2; natural abundance 6.99 %),<sup>[23]</sup> it was hoped that <sup>125</sup>Te NMR spectroscopy could play a similarly important role as <sup>77</sup>Se NMR spectroscopy in comparable selenium chemistry.

### **Results and Discussion**

### Synthesis and NMR Spectroscopy

In addition to the usual precautions to exclude air and moisture, the tellurium compounds are thermally less stable than their selenium analogues and they are sensitive to daylight. In Scheme 2, the seemingly simple route to disilane derivative **8** is shown. A small amount of an impurity was present in the reaction solution, later on identified as heterocycle **9** (see below). Disilane **8** is sparingly soluble in toluene, and therefore, it can be separated from impurities and isolated in a pure state.

Samples of 8 could not be kept for prolonged periods of time, neither in solution nor in the solid state. Decomposition, noticeable by elimination of elemental tellurium, took place readily. However, mass spectra, all relevant solution-state NMR spectroscopic data (see the Exp. Sect., Table 1 and Figure 1), and suitable crystals for X-ray structural analysis were obtained (see below).

Models from B3LYP/LANL2DZ calculations suggest a nonplanar six-membered ring, in which the SiMe groups should be different. At room temperature, inversion of the ring appears to be fast on the NMR spectroscopy timescale, since only single <sup>1</sup>H(SiMe) and <sup>13</sup>C(SiMe) NMR spectroscopy signals were observed, similar to the situation in 6.<sup>[4c]</sup> The <sup>13</sup>C, <sup>29</sup>Si and <sup>125</sup>Te NMR spectra of 8 are instructive (Figure 1); they show numerous satellites owing to spin-spin coupling, splitting owing to isotope-induced chemical shifts (<sup>13</sup>C NMR spectrum, Figure 1, A), and remarkable, for I = 1/2 nuclei, differences in line widths. The <sup>13</sup>C<sub>carb</sub> NMR spectroscopy signal is shifted towards low frequencies relative to other carborane derivatives,<sup>[4a,24]</sup> typical of those in the neighbourhood of heavy tellurium. The isotope-induced chemical shift  ${}^{1}\Delta^{10/11}B({}^{13}C_{carb})$  is similar in magnitude to that of other carboranes.<sup>[25]</sup> The spin-spin coupling constant  ${}^{1}J({}^{125}\text{Te}, {}^{13}\text{C})$  has been measured here for the first time for this type of carbon atom. Its magnitude follows the trend found for  ${}^{1}J({}^{77}\text{Se}, {}^{13}\text{C}).{}^{[4c,26]}$  The magnitude of  ${}^{1}J({}^{125}\text{Te}, {}^{29}\text{Si})$  is in the usual range for Te–Si bonds, as has been reported for numerous examples.<sup>[27,28]</sup> In the disilane unit, two-bond couplings  ${}^{2}J({}^{126}\text{Te},\text{Si},{}^{13}\text{C})$  and  ${}^{2}J({}^{29}Si,Si,{}^{13}C)$  are observed, the latter proving unambiguously the presence of the Si-Si bond. The considerable line width of the <sup>125</sup>Te NMR spectroscopy signal can be traced to relaxation by chemical-shift anisotropy, typical for heavy



Scheme 2. Synthesis of  $[1,2-(1,2-C_2B_{10}H_{10})Te_2]^{2-}$  as dilithium salt 7 and conversion into disilane derivative 8.

	<b>7</b> <sup>[b]</sup>	<b>8</b> <sup>[c]</sup>	9	11	14	21
$\delta^{13}C[C_{carb}]$	41.5 (br)	35.8 [415.5] {-8.8}	32.3 (CTe) [383.0] {-10.0} 75.0 (CSi) [18.0] (48.5) {-11.1}	60.3 (CH) 65.3 (CSi) (39.5) {-9.5}	25.2 (CTe) [380.2] [14.8] {-8.0} 82.1 (CSi) (49.5) [24.1] {-11.1}	28.0 (CTe) [507.4] {-9.3} 75.7 (CSi) {-11.2}
δ <sup>13</sup> C[SiMe <sub>2</sub> ]	-	-2.1 (43.3) (5.4) [28.8]	-2.4 (MeSi $C_{carb}$ ) (48.9) (5.6) -0.7 (MeSiTe) (45.2) (4.5) [12.6]	-1.9 (48.6) (5.3)	3.1 (54.1) [7.5]	-1.4 (MeSiC <sub>carb</sub> ) (48.4) (6.1) 3.1 (MeSiCl) (49.7) (7.0)
δ <sup>29</sup> Si	_	-8.7 <285.7> (43.3) (5.4)	2.0 (SiTe) <283.4> /78.7/ (45.3) (5.8) 17.2 (SiC <sub>carb</sub> ) /78.7/ (48.9) <19.5> (4.5)	-3.3 (48.7) (39.5)	22.3 <329.5> (54.0)	0.3 (MeSiC <sub>carb</sub> ) /101.0/ (48.4) (7.1) 21.4 (MeSiCl) /101.0/(49.6)
δ <sup>125</sup> Te	540 (br.) $h_{1/2} \approx 5500 \text{ Hz}$	615.9 < 285.0 > $h_{1/2} \approx 60 \text{ Hz}$	549.9 <285.0> $h_{1/2} \approx 60 \text{ Hz}$	_	$\begin{array}{l} 878.3 > 2315 < \\ h_{1/2} \approx 50 \text{ Hz} \\ -208.8 > 2315 < <329.5 > \\ h_{1/2} \approx (23 \pm 1) \text{ Hz} \end{array}$	1038.9 $h_{1/2} \approx 50 \text{ Hz}$

Table 1. <sup>13</sup>C, <sup>29</sup>Si and <sup>125</sup>Te NMR spectroscopic data<sup>[a]</sup> of the *ortho*-carborane derivatives 7, 8, 9, 11, 14, and 21 (solvent: [D<sub>8</sub>]toluene).

[a] Coupling constants  ${}^{n}J({}^{125}\text{Te},{}^{13}\text{C})$  are given in brackets  $[\pm 0.5 \text{ Hz}]$ ;  ${}^{n}J({}^{29}\text{Si},{}^{13}\text{C})$  given in parentheses  $(\pm 0.5 \text{ Hz})$ ,  ${}^{n}J({}^{125}\text{Te},{}^{29}\text{Si})$  given in  $< ... > < \pm 0.5 \text{ Hz} >$ ;  ${}^{1}J({}^{29}\text{Si},{}^{29}\text{Si})$  are given between slashes  $/...//\pm 0.5 \text{ Hz}$ ;  ${}^{1}J({}^{125}\text{Te},{}^{125}\text{Te})$  are given between  $> ... < > \pm 0.5 \text{ Hz} <$ ;  ${}^{1}J({}^{29}\text{Si},{}^{29}\text{Si}) \pm 0.5 \text{ ppb}$  are given in braces  $\{\pm 0.5 \text{ Hz}\}$ ; isotope-induced chemical shifts  ${}^{1}\Delta$  are given in ppb, and the negative sign denotes a shift of NMR spectroscopy signal of the heavy isotopomer to lower frequency. [b] Other  $\delta^{13}$ C data: 15.0 (CH<sub>3</sub> from Et<sub>2</sub>O), 66.3 (OCH<sub>2</sub> from Et<sub>2</sub>O) ppm. [c]  $\delta^{123}$ Te: 615.5 ppm.





Figure 1. 2,2,3,3-Tetramethyl-5,6-[1,2-dicarba-*closo*-dodecaborano(12)]-1,4-ditellura-2,3-disilacyclohexane (8). (A) 125.8 MHz  ${}^{13}C{}^{1}H$ NMR spectrum of 8 (in [D<sub>8</sub>]toluene, at 23 °C). The  ${}^{29}Si$  satellites for  ${}^{n}J({}^{29}Si,{}^{13}C_{Me})$  are marked by filled circles; the  ${}^{125}Te$  satellites for  ${}^{n}J({}^{125}Te,{}^{13}C)$  are marked by arrows. The typical isotope-induced chemical shift  ${}^{1}\Delta^{10/11}B({}^{13}C_{carb})$  was observed.<sup>[25]</sup> (B) 157.9 MHz  ${}^{125}Te$  NMR spectrum of 8 (in [D<sub>8</sub>]toluene, at 23 °C). The  ${}^{29}Si$  satellites for  ${}^{1}J({}^{125}Te,{}^{29}Si)$  are marked by  $\nabla$ . (C) 99.4 MHz  ${}^{29}Si{}^{1}H$  NMR spectrum of 8 (in [D<sub>8</sub>]toluene, at 23 °C). The  ${}^{125}Te$  satellites for  ${}^{1}J({}^{125}Te,{}^{29}Si)$  are marked by  $\nabla$ ; the  ${}^{13}C$  satellites for  ${}^{n}J({}^{29}Si,{}^{13}C_{Me})$  are marked by filled circles.

nuclei in unsymmetrical surroundings and high-field NMR spectroscopy measurements.<sup>[29]</sup> Clearly, this has consequences for the line widths of <sup>125</sup>Te satellites in <sup>13</sup>C or <sup>29</sup>Si NMR spectra. Fast <sup>125</sup>Te nuclear spin relaxation gives rise to short-lived spin states representing the spin–spin coupling interaction, noticeable by broadening of the respective satellite signals.

In Scheme 3 (A), we demonstrate the complex and unpredictable behaviour of the starting dianion 7 (see also ref.<sup>[19]</sup>) when it was prepared from 4 under slightly different conditions. Again, 8 was formed in the reaction with 1,2dichlorotetramethyldisilane, however, not as the major product. Instead 9, the minor species mentioned above (Scheme 2), is now the major product, and one other heterocycle, 10,<sup>[30]</sup> could be indentified in the reaction mixture. One may speculate that the Te insertion into the C-Li bonds in 4 was incomplete (see relevant experiments for insertion of Se)<sup>[18]</sup> prior to the following reaction. This was investigated in more detail as shown in Scheme 3 (B). Heterocycle 10 has been prepared independently, studied for its NMR spectroscopy parameters and characterised by X-ray structural analysis.<sup>[30]</sup> Compound 11 has been synthesised previously in another context, and its solid-state structure has been determined.<sup>[31]</sup> However, a more complete NMR

spectroscopic data set is reported in the present work (see Table 1 and the Exp. Sect.), and its identity matched the material reported in the literature<sup>[31]</sup> as evident by X-ray structural analysis.

All NMR spectroscopic data of **9** strongly support the proposed structure (Table 1, Figure 2). The presence of the Si–Si bond is evident from one-bond <sup>29</sup>Si,<sup>29</sup>Si spin coupling, shown by satellites in the <sup>29</sup>Si NMR spectrum. One silicon atom is attached to tellurium (<sup>29</sup>Si NMR spectroscopy signal with <sup>125</sup>Te satellites), whereas the other one is not. The information from <sup>13</sup>C NMR spectroscopy signals, together with their <sup>29</sup>Si and <sup>125</sup>Te satellites, is consistent with the <sup>29</sup>Si and <sup>125</sup>Te NMR spectra.

What appeared to be a fairly simple task at first glance, namely, the synthesis of silane 13 by the reaction of dianion 7 with Me<sub>2</sub>SiCl<sub>2</sub>, turned out to pose a formidable problem. Apparently, 13 was not even formed as a minor product in appreciable quantity when we studied the reaction solutions by NMR spectroscopy with spectra recorded immediately after the reactions had been performed. In each of several attempts, solely the cyclic ditellane 14 was formed together with side products, and was identified by NMR spectroscopic data. The results are summarized in Scheme 4. A final attempt to prepare 13, starting from 8, by exchange with



Scheme 3. Preparation of dianion 7 under slightly different conditions gives rise to the formation of a mixture of heterocycles.



Figure 2. (A) 99.4 MHz <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of the mixture of **8**, **9**, **10** and **11** (in  $[D_8]$ toluene, at 23 °C). The <sup>125</sup>Te satellites for <sup>*n*</sup>J(<sup>125</sup>Te, <sup>29</sup>Si) are marked by  $\nabla$ ; the <sup>13</sup>C satellites for <sup>*n*</sup>J(<sup>29</sup>Si, <sup>13</sup>C) are marked by filled circles; the <sup>29</sup>Si satellites for <sup>1</sup>J(<sup>29</sup>Si, <sup>29</sup>Si) are marked by asterisks. (B) Part of the 125.8 MHz <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (SiMe groups) of the mixture of **8** and **9** (in  $[D_8]$ toluene, at 23 °C). The <sup>29</sup>Si satellites for <sup>*n*</sup>J(<sup>29</sup>Si, <sup>13</sup>C) are marked by filled circles; the <sup>125</sup>Te satellites for <sup>*n*</sup>J(<sup>29</sup>Si, <sup>21</sup>C) are marked by arrows.

 $Me_2SiCl_2$  (analogously to experiments in selenium chemistry)<sup>[4c]</sup> also failed completely. When we used (Me\_2SiCl)<sub>2</sub>O in the reaction with 7, hoping that a different ring size might help to stabilise the desired product as a seven-membered ring, we only identified the tellurium-free known cyclic disiloxane **15**.<sup>[30]</sup>





Scheme 4. Reactivity of dianion 7 towards Me<sub>2</sub>SiCl<sub>2</sub> and (Me<sub>2</sub>SiCl<sub>2</sub>O.



Figure 3. 3,3-Dimethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,2-ditellura-3-silacyclopentane (14). (A) 100.5 MHz <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 14 (in [D<sub>8</sub>]toluene, at 23 °C). The <sup>29</sup>Si satellites for  ${}^{n}J({}^{29}\text{Si},{}^{13}\text{C}_{Me})$  are marked by filled circles; the <sup>125</sup>Te satellites for  ${}^{n}J({}^{125}\text{Te},{}^{13}\text{C})$  are marked by arrows. The isotope-induced chemical shift  ${}^{1}\Delta^{10/11}\text{B}({}^{13}\text{C}_{carb})$  observed for 14.<sup>[25]</sup> (B) 126.2 MHz  ${}^{125}\text{Te}$  NMR spectrum of 14 (in [D<sub>8</sub>]toluene, at 23 °C). The <sup>29</sup>Si satellites for  ${}^{1}J({}^{125}\text{Te},{}^{29}\text{Si})$  are marked by  $\nabla$ ; the  ${}^{125}\text{Te}$  satellites for  ${}^{1}J({}^{125}\text{Te},{}^{29}\text{Si})$  are marked by  $\nabla$ ; the  ${}^{125}\text{Te}$  satellites for  ${}^{1}J({}^{125}\text{Te},{}^{29}\text{Si})$  are marked by  $\nabla$ ; the  ${}^{125}\text{Te}$  satellites for  ${}^{1}J({}^{125}\text{Te},{}^{29}\text{Si})$  are marked by  $\nabla$ ; the  ${}^{125}\text{Te}$  satellites for  ${}^{1}J({}^{125}\text{Te},{}^{29}\text{Si})$  are marked by  $\nabla$ ; the  ${}^{125}\text{Te}$  satellites for  ${}^{1}J({}^{125}\text{Te},{}^{29}\text{Si})$  are marked by  $\nabla$ ; the  ${}^{125}\text{Te}$  satellites for  ${}^{1}J({}^{125}\text{Te},{}^{29}\text{Si})$  are marked by  $\nabla$ ; the  ${}^{125}\text{Te}$  satellites for  ${}^{1}J({}^{125}\text{Te},{}^{29}\text{Si})$  are marked by  $\nabla$ ; the  ${}^{13}\text{C}$  satellites for  ${}^{n}J({}^{29}\text{Si},{}^{13}\text{C}_{Me})$  are marked by filled circles.

Cyclic ditellane **14** deserves interest, since the comparable diselane was also observed quite unexpectedly as a side product in connection with the synthesis and reactivity of the diselena analogue to **13**.<sup>[4c]</sup> Since a pure sample of **14** could not be isolated, all relevant NMR spectra (Table 1 and Figure 3) were measured from solutions containing **14**. The <sup>13</sup>C, <sup>29</sup>Si and <sup>125</sup>Te NMR spectra with important information on mutual spin–spin couplings provide convincing evidence for the proposed structure. Perhaps, most note-

worthy is the large magnitude of the coupling constant  ${}^{1}J({}^{125}\text{Te}, {}^{125}\text{Te}) = 2315 \text{ Hz}$ , much larger than in noncyclic ditellanes,  ${}^{[32]}$  which is reminiscent of  ${}^{1}J({}^{77}\text{Se}, {}^{77}\text{Se}) = 313 \text{ Hz}^{[4c]}$  in the corresponding cyclic diselane, also significantly larger than in noncyclic diselanes.  ${}^{[33]}$ 

#### **Reactivity of the Cyclic Tellurasilanes**

When unsealed samples of 8 were kept at room temperature in toluene (Scheme 5) slow hydrolysis took place, ac-



Scheme 5. Slow hydrolysis/oxidation of 8 in toluene.

companied by formation of small amounts of elemental tellurium. After several days, the solutions contained the known ditellane **1**, as a result of partial hydrolysis and oxidation, the parent carborane **3**, and the known<sup>[27a]</sup> cyclic siloxane derivative **16** ( $\delta^{29}$ Si = 1.1 ppm), both due to hydrolysis. According to <sup>29</sup>Si NMR spectra, small amounts of other oligomers (Me<sub>2</sub>SiSiMe<sub>2</sub>O)<sub>n</sub> (n > 2;  $\delta^{29}$ Si = 1.5, 1.6, 2.7 ppm) were also present in the mixture. In spite of the formation of elemental tellurium, there was no NMR spectroscopic evidence for the presence of heterocycle **9**.

Exchange reactions of 8 with an excess amount of dimethyldichlorosilane and dichlorophenylborane (Scheme 6) were studied. In the former case, the expected product 13 (see Scheme 4) was not observed. Instead, after several days, telluranes 1 and 2 were formed. Since these compounds were formed in various reactions, their NMR spectroscopic characterisation proved possible (Table 2). The reaction of **8** with PhBCl<sub>2</sub> at room temperature proceeded surprisingly slowly, indicated by formation of Me<sub>2</sub>(Cl)Si-Si(Cl)Me<sub>2</sub> (<sup>29</sup>Si NMR spectroscopy). The desired borane **17** might have been present in low concentration as indicated by a broad <sup>11</sup>B NMR spectroscopy signal at  $\delta^{11}B =$ 39.4 ppm. However, after three weeks, the major reaction pathway leads to various decomposition products, of which **2**, **18**, **19** and **20** could be identified. Among these, ditellurol **18** is of interest since it is apparently sufficiently stable in solution for further transformations, as already shown here by its oxidation products **19** and **2**. The presence of **18** follows conclusively from the characteristic NMR spectra (Figure 4). Simple slow hydrolysis/oxidation of **2** afforded ditellane **1** together with elemental tellurium.

Similarly to **8**, heterocycle **9** reacted only slowly at room temperature with PhBCl<sub>2</sub> (Scheme 7). Compounds with Te–



Scheme 6. Attempted exchange reactions of 8 with Me<sub>2</sub>SiCl<sub>2</sub> and PhBCl<sub>2</sub>.

Table 2. <sup>13</sup>C and <sup>125</sup>Te NMR spectroscopic data<sup>[a]</sup> of the *ortho*-carborane derivatives 1, 2, 17, 18, and 19 (solvent: [D<sub>8</sub>]toluene).

	1 <sup>[b]</sup>	<b>2</b> <sup>[b]</sup>	17 <sup>[c]</sup>	18	19
$\delta^{13}$ C[C(carb)] $\delta^{125}$ Te	30.3 (CTe), 66.3 (CH) 1071.1	30.3 (CTe) 1093.5	n.o. 1074.2 [br.] $h_{1/2} \approx 700 \text{ Hz}$	40.8 790.2 ( $\approx$ 45.0) $h_{1/2} \approx$ 90 Hz	37.7, 39.0 743.1 ( $\approx$ 50.0) (TeH) $h_{1/2} \approx$ 75 Hz 1102.2 (Te-Te)
$\delta^{1}$ H (TeH)	_	-	_	-0.38 (46.0) (8.2)	-0.48 (54.0)

[a] Coupling constants  ${}^{n}J({}^{125}\text{Te}, {}^{13}\text{C})$  are given in brackets [ $\pm 0.5 \text{ Hz}$ ];  ${}^{n}J({}^{125}\text{Te}, {}^{1}\text{H})$  in parentheses ( $\pm 1 \text{ Hz}$ ); [br] denotes broad  ${}^{125}\text{Te}$  resonances of boron-bonded tellurium atoms; n.o.: not observed. [b] Ref. [22] [c]  $\delta^{11}\text{B} = 39.4 \text{ ppm}$ .







Figure 4. 157.8 MHz <sup>125</sup>Te NMR, 500.13 MHz <sup>1</sup>H and <sup>1</sup>H{<sup>125</sup>Te} NMR spectra of 1,2-di(hydrotelluro)-1,2-dicarba-*closo*-dodecaborane(12) (18) (23 °C, in [D<sub>8</sub>]toluene).

B bonds could not be identified with certainty. Instead the parent carborane 3, triphenylboroxine 20 and the ditellane derivative 21 were major products.



Scheme 7. Attempted exchange reaction of 9 with PhBCl<sub>2</sub>.

### X-ray Structural Analyses of the Six-Membered Ring 8 Containing the Te–Si–Si–Te Unit

The molecular structure of 8 is shown in Figure 5, and relevant structural parameters are given in Table 3, together with those for the analogous selenium derivative 6 for comparison.



Figure 5. ORTEP plot (50 % probability; hydrogen atoms are omitted for clarity) of the molecular structure of the 2,2,3,3-tetramethyl-5,6-[1,2-dicarba-*closo*-dodecaborano(12)]-1,4-ditellura-2,3-disilacyclohexane (8) (for selected distances and angles see Table 3).

The main structural features of 8 and 6 are similar. As expected, the major differences concern the bond lengths

Table 3.	Selected	bond	lengths	[pm]	and	angles	[°]	of	the	ortho-
carborar	ne derivat	ive 8 a	and <b>6</b> .							

	8	<b>6</b> <sup>[a]</sup>
	E = Te	E = Se
C(1)–E(1)	213.8(4)	193.8(4)
C(2)–E(2)	214.3(4)	193.5(4)
C(1)-C(2)	168.4(5)	171.4(5)
E(1)-Si(1)	253.54(12)	232.37(14)
E(2)-Si(2)	253.35(12)	232.84(15)
Si(1)-Si(2)	236.22(18)	235.94(18)
C(1)-E(1)-Si(1)	99.02(11)	103.68(13)
C(2)-E(2)-Si(2)	99.62(11)	104.03(13)
E(1)-Si(1)-Si(2)	106.59(5)	106.18(6)
E(2)-Si(2)-Si(1)	108.73(5)	106.31(7)
E(1)-C(1)-C(2)	121.6(2)	120.3(2)
E(2)-C(2)-C(1)	120.8(2)	120.1(3)
C(3)-Si(1)-C(4)	108.6(2)	109.3(3)
C(5)-Si(2)-C(6)	109.7(2)	111.4(3)
Plane $E(1)-C(1)-C(2)-E(2)$	0.0	0.7
Plane $E(1)-Si(1)-Si(2)-E(2)$	2.1	1.5
Distance of Si(1) from the plane	224.4	199.8
E(1)-C(1)-C(2)-E(2)		
Distance of Si(2) from the plane	219.8	197.1
E(1)-C(1)-C(2)-E(2)		
[a] Ref. <sup>[4c]</sup>	·	

 $E-Si^{[27]}$  and E-C as well as the bond angles at Te and Se, which are more acute in the case of E = Te. Intra- and intermolecular Te-Te distances in solid **8** are slightly shorter than the sum of van der Waals radii, which may account for the instability with respect to formation of elemental tellurium.

## Conclusion

The preparation of the 1,2-ditellurato-1,2-dicarba-*closo*-dodecaborane(12) dianion  $[1,2-(1,2-C_2B_{10}H_{10})Te_2]^{2-}$  as its dilithium salt 7 is more difficult and less reproducible than



its lighter congeners. Moreover, in the case of tellurium, the dianion itself and the products appear to be light sensitive and decompose readily. However, disilane derivative **8**, prepared by the reaction of **7** with 1,2-dichlorotetramethyldisilane, containing a six-membered ring, could be isolated in a pure state in reasonably good yield, and may well serve for further transformations. In this study, two interesting five-membered rings **9** and **14**, containing the Si–Si–Te and the Si–Te–Te unit, respectively, were also identified by using multinuclear magnetic resonance spectroscopy. Clearly, this tellurium chemistry is less predictable than the corresponding selenium chemistry. However, this is also a stimulating fact, inspiring further activity.

# **Experimental Section**

General: All syntheses and the handling of the samples were performed by observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The deuterated solvent  $CD_2Cl_2$  was distilled from CaH2 under an atmosphere of argon. All other solvents were distilled from Na metal under an atmosphere of argon. [(1,2- $C_2B_{10}H_{10}$ Li<sub>2</sub>](2Et<sub>2</sub>O)<sup>[4c]</sup> (4) was prepared according to the published procedure. The starting materials were purchased from Aldrich {butyllithium (1.6 m in hexane), Me<sub>2</sub>SiCl<sub>2</sub>, [Me<sub>2</sub>(Cl)Si]<sub>2</sub>, [Me<sub>2</sub>(Cl)Si]<sub>2</sub>O, tellurium (powder, 200 mesh, 99.8 % metals basis), PhBCl<sub>2</sub> (97%)}, and KatChem. (*ortho*-carborane 3), and used without further purification. NMR spectroscopy measurements: Bruker DRX 500: <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>125</sup>Te, and <sup>29</sup>Si NMR [refocused INEPT<sup>[34]</sup> based on  ${}^{2}J({}^{29}Si,{}^{1}H) = 6-7$  Hz]; Varian INOVA 400:  ${}^{1}H$ , <sup>11</sup>B, <sup>13</sup>C, <sup>125</sup>Te, <sup>29</sup>Si NMR; chemical shifts are given relative to Me<sub>4</sub>Si [ $\delta^{1}$ H (CHDCl<sub>2</sub>) = 5.33 ppm,  $\delta^{1}$ H (C<sub>6</sub>D<sub>5</sub>CD<sub>2</sub>H) = 2.08  $(\pm 0.01)$  ppm;  $\delta^{13}$ C (CD<sub>2</sub>Cl<sub>2</sub>) = 53.8 ppm, (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>) = 20.4 (\pm 0.1) ppm]; external BF<sub>3</sub>-OEt<sub>2</sub> [ $\delta^{11}B = 0 \ (\pm 0.3)$  ppm for  $\Xi(^{11}B) =$ 32.083971 MHz], neat Me<sub>2</sub>Te [ $\delta^{125}$ Te = 0 ppm for  $\Xi$ (<sup>125</sup>Te) = 31.549802 MHz]. Assignments of <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy signals are based on  ${}^{1}H{}^{11}B{}$  selective heteronuclear decoupling experiments.<sup>[35]</sup> Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for <sup>12</sup>C, <sup>1</sup>H, <sup>11</sup>B, <sup>28</sup>Si, <sup>130</sup>Te). Melting points (uncorrected) were determined using a Büchi 510 melting point apparatus. Owing to the extreme sensitivity of compounds 8 and 9 elemental analysis was not performed. All preparative work as well as handling of the samples was performed in the dark to shield samples as much as possible from light. Thus, reaction flasks and NMR spectroscopy sample tubes were wrapped in aluminium foil. All tellurium-containing compounds studied here decompose under Ar as solids and in the solution at room temp. as well as in the presence of light accompanied by formation of black elemental tellurium.

**1,2-Dicarba**-*closo*-dodecaborano(12)-1,2-ditellurolate [(1,2- $C_2B_{10}H_{10}$ )Te<sub>2</sub>Li<sub>2</sub>](Et<sub>2</sub>O) (7): Degassed elemental tellurium (911 mg, 7.14 mmol) was added to freshly prepared [(1,2- $C_2B_{10}H_{10}$ )Li<sub>2</sub>](2-Et<sub>2</sub>O) (4) (1045 mg, 3.57 mmol). The mixture was cooled to 0 °C, and Et<sub>2</sub>O (25 mL) was added in the dark. The reaction flask was wrapped in aluminium foil, and the suspension was stirred at room temp. (or 0 °C) for 18 h. The formation of a red oily phase and a green precipitate was observed. The suspension was separated using a centrifuge, and the yellow supernatant liquid was decanted. The residue after centrifugation (oil and solid) was dried under vacuum (4 h,  $8 \times 10^{-3}$  Torr) to give 7 as a yellow-green powder (1606 mg, 82 %). Compound 7 decomposes slowly under Ar as a solid at room temp. as well as in the presence of light and remains relatively

stable in the absence of light at  $-30 \,^{\circ}\text{C} \cdot {}^{1}\text{H} \{ {}^{11}\text{B} \}$  NMR (399.8 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta$  = 1.22, 3.56 (t, q, ca. 20 H, OEt<sub>2</sub>), 2.65, 3.05, 3.25, 3.35 (br. m, 10 H, HB) ppm. {}^{11}\text{B} \{ {}^{1}\text{H} \} NMR (128.3 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta$  = -0.9 (br., 10 B) ppm.

2,2,3,3-Tetramethyl-5,6-[1,2-dicarba-closo-dodecaborano(12)]-1,4-ditellura-2,3-disilacyclohexane (8): Freshly prepared  $[(1,2-C_2B_{10}H_{10})-$ Te<sub>2</sub>Li<sub>2</sub>](2Et<sub>2</sub>O) 7 (692 mg, 1.26 mmol) was cooled to -20 °C, and was dissolved in toluene (20 mL); the suspension was cooled to -40 °C, and Me<sub>2</sub>Si(Cl)-Si(Cl)Me<sub>2</sub> (237 mg, 0.235 mL, 1.26 mmol) was injected slowly through a syringe. After stirring the reaction mixture for 1.5 h at -30 °C and 30 min at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The remaining insoluble materials were washed with toluene (10 mL) and centrifuged. The centrifuged solutions were combined, and volatile materials were removed under vacuum to give a yellow-brown solid (447 mg). The resulting mixture thus obtained contained 8 (ca. 70%), 9 (ca. 20%) and side product 11 (10%) (from <sup>29</sup>Si and <sup>13</sup>C NMR). The remaining insoluble materials were washed with toluene (30 mL) and centrifuged. Compound 8 was only sparingly soluble in both hexane and toluene. Yellowish single crystals of 8 for X-ray analysis were grown from [D<sub>8</sub>]toluene solution after 1 week at -30 °C; m.p. 155-165 °C (decomposition). Compound 8 decomposes under Ar as a solid at room temp., also slowly in [D<sub>8</sub>]toluene at -30 °C as well as in the presence of light with formation of black elemental tellurium. <sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz,  $[D_8]$ toluene, 25 °C):  $\delta = 0.30$  (s, 12 H, CH<sub>3</sub>Si), 2.69 [br. s, 2 H, HB for  $\delta(^{11}B) = -6.1$  ppm], 2.81 [br. s, 2 H, HB for  $\delta^{(11B)} = -6.1 \text{ ppm}$ ], 3.09 [br. s, 2 H, HB for  $\delta^{(11B)} = -0.5 \text{ ppm}$ ], 3.21 [br. s, 4 H, HB for  $\delta(^{11}B) = -6.1$  ppm] ppm.  $^{11}B{^{1}H}$  NMR (160.5 MHz,  $[D_8]$ toluene, 25 °C):  $\delta = -6.1$  (8 B), -0.5 (2 B) ppm. <sup>11</sup>B NMR (160.5 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta = -6.1$  [d, <sup>1</sup>J(<sup>11</sup>B, <sup>1</sup>H) = 157 Hz, 8 B], -0.5 [d,  ${}^{1}J({}^{11}B,{}^{1}H)$  = 147 Hz, 2 B] ppm. EI-MS (70 eV) for  $C_6H_{22}B_{10}Si_2Te_2$  (513.7): m/z (%) = 514 (20) [M<sup>+</sup>], 499 (5) [M<sup>+</sup> - CH<sub>3</sub>], 445 (5) [M<sup>+</sup> - HSi(CH<sub>3</sub>)<sub>2</sub>], 387 (7) [M - Te], 372 (18)  $[M - CH_3 - Te]$ , 357 (15)  $[C_3H_9Te_2Si_2]$ , 326 (5)  $[M - CH_3 - CH_3 - Te]$ TeSi(CH<sub>3</sub>)<sub>2</sub>], 245 (20) [C<sub>4</sub>H<sub>11</sub>TeSi<sub>2</sub>], 188 (40) [TeSi(CH<sub>3</sub>)<sub>2</sub>], 73 (100) [Si(CH<sub>3</sub>)<sub>3</sub>].

Reaction of 4 with Tellurium and Me<sub>2</sub>Si(Cl)-Si(Cl)Me<sub>2</sub>: 2,2,3,3-Tetramethyl-4,5-[1,2-dicarba-closo-dodecaborano(12)]-1-tellura-2,3disilacyclopentane (9): (A) Degassed elemental tellurium (1130 mg, 8.85 mmol) was added to freshly prepared [(1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)Li<sub>2</sub>](2-Et<sub>2</sub>O) 4 (1305 mg, 4.46 mmol). The mixture was cooled to 0 °C, and Et<sub>2</sub>O (30 mL) was added. The suspension was stirred for 1 h at 0 °C and for 1 h at room temp. The formation of a green precipitate was observed, which was separated using a centrifuge. The yellow supernatant liquid was decanted. The residue after centrifugation was dried under vacuum (1 h,  $8 \times 10^{-3}$  Torr) to give a yellowgreen powder (2654 mg). The solid was cooled to 0 °C, and was dissolved in toluene (40 mL); the suspension was cooled to -30 °C, and Me<sub>4</sub>Si<sub>2</sub>Cl<sub>2</sub> (800 mg, 0.796 mL, 4.27 mmol) was injected slowly through a syringe. After stirring the reaction mixture for 1.5 h at -20 °C, insoluble materials were separated by centrifugation at 0 °C, and the clear yellow-brown liquid was collected. Volatile materials were removed under vacuum to give a brown solid (1360 mg). The resulting mixture thus obtained contained 8 (ca. 35 %), 9 (ca. 55 %), 10 (ca. 5 %), 11 (ca. 5 %) and several unidentified side products (from <sup>29</sup>Si and <sup>13</sup>C NMR spectra). The remaining mixture was dissolved in hexane (20 mL), and the liquid phase was separated by centrifugation. Transparent crystals of 9 [m.p. 140-150 °C (decomposition)] were grown from a [D<sub>8</sub>]toluene solution after 5 days at -30 °C. Compound 9: 1H{11B} NMR (250.13 MHz,  $[D_8]$ toluene, 25 °C):  $\delta = 0.06$  (s, 6 H, CH<sub>3</sub>Si), 0.32 (s, 6 H, CH<sub>3</sub>Si), 2.18 [br. s, 2 H, HB for  $\delta(^{11}B) = -9.4$  ppm], 2.69 [br. s, 2 H, HB for



$$\begin{split} & \delta(^{11}\text{B}) = -7.3 \text{ ppm}], 2.77 \text{ [br. s, 1 H, HB for } \delta(^{11}\text{B}) = 1.1 \text{ ppm}], 2.91 \\ & [\text{br. s, 4 H, HB for } \delta(^{11}\text{B}) = -6.6, -3.4 \text{ ppm}], 3.04 \text{ [br. s, 1 H, HB for } \delta(^{11}\text{B}) = -2.4 \text{ ppm}] \text{ ppm}. \ ^{11}\text{B}\{^{1}\text{H}\} \text{ NMR } (160.5 \text{ MHz, } [D_8]\text{toluene}, \\ & 25 ^{\circ}\text{C}): \delta = -9.4 (2 \text{ B}), -7.3 (2 \text{ B}), -6.7 (2 \text{ B}), -3.4 (2 \text{ B}), -2.4 (1 \text{ B}), \\ & 1.0 (1 \text{ B}) \text{ ppm}. \ ^{11}\text{B} \text{ NMR } (160.5 \text{ MHz, } [D_8]\text{toluene}, 25 ^{\circ}\text{C}): \delta = -9.4 \\ & [d, \ ^{1}J(^{11}\text{B},^{1}\text{H}) = 168 \text{ Hz}, 2 \text{ B}], -7.3 \ [d, \ ^{1}J(^{11}\text{B},^{1}\text{H}) = 168 \text{ Hz}, 2 \text{ B}], \\ & -6.7 \ [d, \ ^{1}J(^{11}\text{B},^{1}\text{H}) = 165 \text{ Hz}, 2 \text{ B}], -3.4 \ [d, \ ^{1}J(^{11}\text{B},^{1}\text{H}) = 155 \text{ Hz}, 2 \\ & \text{B}], -2.4 \ [d, \ ^{1}J(^{11}\text{B},^{1}\text{H}) = 155 \text{ Hz}, 1 \text{ B}], 1.0 \ [d, \ ^{1}J(^{11}\text{B},^{1}\text{H}) = 150 \text{ Hz}, \\ & 1 \text{ B}] \text{ ppm}. \text{ EI-MS } (70 \text{ eV}) \text{ for } \text{C}_6\text{H}_{22}\text{B}_{10}\text{S}_{12}\text{Te} (386.1): m/z \ (\%) = 387 \\ & (80) \ [\text{M}^+], 372 \ (100) \ [\text{M}^+ - \text{CH}_3], 258 \ (5) \ [\text{M}^+ - \text{Te}], 243 \ (6) \ [\text{M}^+ - \\ & \text{Te} - \text{CH}_3], 223 \ (4), 210 \ (10), 198 \ (8) \ [\text{M} - \text{Te} - 4\text{CH}_3], 188 \ (10) \\ & [\text{TeSi}(\text{CH}_3)_2], 73 \ (70) \ [Si(\text{CH}_3)_3]. \end{split}$$

(B) Degassed elemental tellurium (516 mg, 4.04 mmol) was added to freshly prepared  $[(1,2-C_2B_{10}H_{10})Li_2](2Et_2O)$  (4) (1185 mg, 4.05 mmol). The mixture was cooled to 0 °C, and Et<sub>2</sub>O (20 mL) was added. The suspension was stirred for 15 h at room temp. to give a green precipitate and a red-brown oil, both of which were dried without separation under vacuum (3 h,  $8 \times 10^{-3}$  Torr) to give a yellow-green powder. The solid was cooled to -30 °C, and was dissolved in toluene (50 mL); the suspension was cooled to -40 °C, and Me<sub>4</sub>Si<sub>2</sub>Cl<sub>2</sub> (753 mg, 0.75 mL, 4.02 mmol) was injected slowly through a syringe. After stirring the reaction mixture for 1 h at -40 °C and for 1 h at room temp., insoluble materials were separated by centrifugation, and the clear yellow-brown liquid was collected. The remaining insoluble materials were washed with toluene (30 mL) and centrifuged. The centrifuged solutions were combined, and volatile materials were removed under vacuum to give a yellowbrown solid (1443 mg). The resulting mixture thus obtained contained 8 (ca. 20%), 7 (ca. 60%), 10 (ca. 5%), 11 (ca. 15%) and several unidentified side products (from <sup>29</sup>Si and <sup>13</sup>C NMR spectra). The remaining mixture was dissolved in hexane (20 mL), and the liquid phase was separated by centrifugation. The remaining insoluble materials were dissolved in Et<sub>2</sub>O (10 mL), centrifuged, and the liquid phase was separated and dried under vacuum. Transparent crystals of 11 for X-ray analysis<sup>[31]</sup> were grown from a  $[D_8]$ toluene solution after 3 days at -30 °C. Compound 11: <sup>1</sup>H NMR (250.13 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta = -0.04$  (s, 12 H, CH<sub>3</sub>Si), 2.67 (br. s, 2 H, CH) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (160.5 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta = -13.5$  (4 B), -11.7 (4 B), -10.9 (4 B), -6.5 (6 B), -1.0 (2 B) ppm. <sup>11</sup>B NMR (160.5 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta = -13.5$  [d,  ${}^{1}J({}^{11}B,{}^{1}H) = 172 \text{ Hz}, 4 \text{ B}, -11.7 \text{ [d, } {}^{1}J({}^{11}B,{}^{1}H) = 160 \text{ Hz}, 4 \text{ B},$  $-10.9 \text{ [d, } {}^{1}J({}^{11}\text{B},{}^{1}\text{H}) = 150 \text{ Hz}, 4 \text{ B]}, -6.5 \text{ [d, } {}^{1}J({}^{11}\text{B},{}^{1}\text{H}) = 150 \text{ Hz},$ 6 B], -1.0 [d,  ${}^{1}J({}^{11}B, {}^{1}H) = 150$  Hz, 2 B] ppm.

Reaction of 7 with Me<sub>2</sub>SiCl<sub>2</sub>: 3,3-Dimethyl-4,5-[1,2-dicarba-*closo*dodecaborano(12)]-1,2-ditellura-3-silacyclopentane (14): Freshly prepared [(1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)Te<sub>2</sub>Li<sub>2</sub>](2Et<sub>2</sub>O) (7) (1546 mg, 2.82 mmol) was cooled to -20 °C, and was dissolved in toluene (30 mL); the suspension was cooled to -40 °C, and Me<sub>2</sub>SiCl<sub>2</sub> (360 mg, 0.336 mL, 2.79 mmol) was injected slowly through a syringe. After stirring the reaction mixture for 1 h at -40 °C and 1 h at room temp., insoluble materials were separated by centrifugation, and the clear blue liquid was collected. Volatile materials were removed under vacuum to give a brown oil (825 mg). The resulting mixture thus obtained contained 14 (ca. 50 %) and several side products (from <sup>29</sup>Si NMR spectra). The remaining oil was washed with hexane (10 mL), dried under vacuum to give a brown oil (250 mg) of 14 (80 %) and several unidentified materials (from <sup>29</sup>Si and <sup>13</sup>C NMR spectra). 14: <sup>1</sup>H NMR (399.8 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta = 0.37$  (s, 6 H, CH<sub>3</sub>Si).

Reaction of 7 with  $[Me_2(Cl)Si]_2O: 1,1,3,3$ -Tetramethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-disila-2-oxa-cyclopentane (15): Freshly prepared  $[(1,2-C_2B_{10}H_{10})Te_2Li_2](2Et_2O)$  (7) (696 mg, 1.27 mmol) was cooled to -40 °C, dissolved in toluene (20 mL) and  $[Me_2(Cl)Si]_2O$  (258 mg, 0.249 mL, 1.27 mmol) was injected slowly through a syringe. After stirring the reaction mixture for 1.5 h at -30 °C and 15 min at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. Volatile materials were removed under vacuum to give a yellow-brown oil (250 mg). The resulting mixture thus obtained contained **15** (ca. 80 %)<sup>[30]</sup> and several unidentified side products (from <sup>29</sup>Si NMR spectra).

**Bis[1,2-dicarba-***closo***-dodecaborane-1-yl]ditellane (1):** A solution of **8** (50 mg, 0.097 mmol) in [D<sub>8</sub>]toluene (0.6 mL) was added to an NMR spectroscopy tube, and stored at room temp. for 2 weeks. The progress of the reaction was monitored by <sup>1</sup>H, <sup>29</sup>Si and <sup>13</sup>C NMR spectroscopy. The solution thus obtained contained **1**, **16**<sup>[27a]</sup> and *ortho*-carborane **3**. Compound **1**: <sup>1</sup>H NMR (500.13 MHz, [D<sub>8</sub>]-toluene, 25 °C):  $\delta$  = 2.55 (br. s, 2 H, CH) ppm. <sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta$  = 2.20 [br. s, 4 H, HB for  $\delta$ (<sup>11</sup>B) = -11.0 ppm], 2.36 [br. s, 4 H, HB for  $\delta$ (<sup>11</sup>B) = -11.5 ppm], 2.55 (br. s, 2 H, CH), 2.57 [br. s, 4 H, HB for  $\delta$ (<sup>11</sup>B) = -8.5 ppm], 2.61 [br. s, 4 H, HB for  $\delta$ (<sup>11</sup>B) = -6.8 ppm], 2.79 [br. s, 2 H, HB for  $\delta$ (<sup>11</sup>B) = 0.2 ppm], 2.92 [br. s, 2 H, HB for  $\delta$ (<sup>11</sup>B) = -2.2 ppm] ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (160.5 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta$  = -11.5 (4 B), -11.0 (4 B), -8.5 (4 B), 6.8 (4 B), -2.2 (2 B), 0.2 (2 B) ppm.

**Reaction of 8 with PhBCl<sub>2</sub>: 3,4,7,8-Bis[1,2-dicarba-***closo***-dodecabor-ano(12)]-1,2,5,6-tetratelluracyclooctane (2) and 1,2-Di(hydrotelluro)-1,2-dicarba-***closo***-dodecaborane(12) (18):** A solution of 8 (23 mg, 0.045 mmol) in [D<sub>8</sub>]toluene (0.6 mL) was added to an NMR spectroscopy tube, cooled to 0 °C and PhBCl<sub>2</sub> (0.012 mL, 14.5 mg, 0.091 mmol) was added through a microsyringe. A solution was stored at room temp. for 3 weeks. The progress of the reaction was monitored by <sup>1</sup>H, <sup>11</sup>B, <sup>29</sup>Si, <sup>125</sup>Te and <sup>13</sup>C NMR spectroscopy. The formation of red-orange crystals of 2 was observed. The solid of **2** was separated, and the yellow supernatant liquid was collected. The solution thus obtained contained **18, 19** and **20** together with Me<sub>4</sub>-Si<sub>2</sub>Cl<sub>2</sub> and PhBCl<sub>2</sub>.

**Compound 2:** <sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta$  = 2.26 [br. s, 2 H, HB for  $\delta(^{11}B) = -9.3$  ppm], 2.63 [br. s, 1 H, HB for  $\delta(^{11}B) = -9.3$  ppm], 2.68, 2.87, 3.06 [br. s, br. s, br. s, 2 H, 4 H, 4 H, HB for  $\delta(^{11}B) = -5.7$  ppm], 3.11 [br. s, 6 H, HB for  $\delta(^{11}B) = -1.1$  ppm], 3.15 [br. s, 1 H, HB for  $\delta(^{11}B) = -9.3$  ppm] ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (160.5 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta = -9.3$  (6 B), -5.7 (10 B), 1.1 (6 B) ppm. <sup>11</sup>B NMR (160.5 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta = -9.3$  [d, <sup>1</sup>J(<sup>11</sup>B,<sup>1</sup>H) = 150 Hz, 6 B], -5.7 (2 B), 1.1 [d, <sup>1</sup>J(<sup>11</sup>B,<sup>1</sup>H) = 145 Hz, 6 B] ppm.

**Compound 18:** <sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta$ = -0.38 [s, 2 H, TeH, <sup>1</sup>*J*(<sup>125</sup>Te,<sup>1</sup>H) = 46.0 Hz, <sup>4</sup>*J*(<sup>125</sup>Te,<sup>1</sup>H) = 8.2 Hz], 2.56 [br. s, 1 H, HB for  $\delta$ (<sup>11</sup>B) = -5.3 ppm], 2.66 [br. s, 2 H, HB for  $\delta$ (<sup>11</sup>B) = -5.9 ppm], 2.87 [br. s, 1 H, HB for  $\delta$ (<sup>11</sup>B) = -7.1 ppm], 3.00 [br. s, 3 H, HB for  $\delta$ (<sup>11</sup>B) = -7.2, -0.3 ppm], 3.05 [br. s, 3 H, HB for  $\delta$ (<sup>11</sup>B) = -5.9 ppm] ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (160.5 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta$  = -7.2 (2 B), -5.9 (5 B), -5.3 (1 B), -0.3 (2 B) ppm.

**Compound 19:** <sup>1</sup>H NMR (500.13 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta = -0.48$  [s, 2 H, TeH, <sup>1</sup>*J*(<sup>125</sup>Te,<sup>1</sup>H) = 53.5 Hz] ppm.

**Reaction of 9 with PhBCl<sub>2</sub>:** A solution of **9** (50 mg, 0.13 mmol) in  $[D_8]$ toluene (0.6 mL) was added to an NMR spectroscopy tube, cooled to 0 °C and PhBCl<sub>2</sub> (0.034 mL, 41.3 mg, 0.26 mmol) was added through a microsyringe. The solution was stored at room temp. for 2 weeks. The progress of the reaction was monitored by <sup>1</sup>H, <sup>11</sup>B, <sup>29</sup>Si, <sup>125</sup>Te and <sup>13</sup>C NMR spectroscopy. The solution thus obtained contained **21** together with **20**, **3** and PhBCl<sub>2</sub>. Compound **21**: <sup>1</sup>H NMR (500.13 MHz, [D<sub>8</sub>]toluene, 25 °C):  $\delta = 0.30$  (s, 12 H, CH<sub>3</sub>Si), 0.37 (s, 12 H, CH<sub>3</sub>Si) ppm.



**Crystal Structure Determination of 8:** Structure solutions and refinements were carried out with the program package SHELXTL-97.<sup>[36]</sup> Details pertinent to the crystal structure determination are listed in Table 4. Crystals of appropriate size were sealed under argon in Lindemann capillaries, and the data collections were carried out at 133 K.<sup>[37]</sup>

Table 4. Crystallographic data of *ortho*-carborane derivative 8.

	8
Formula	$C_6H_{22}B_{10}Si_2Te_2$
Crystal	yellowish block
Dimensions [mm <sup>3</sup> ]	$0.24 \times 0.19 \times 0.18$
<i>T</i> [K]	133(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a [pm]	830.41(17)
<i>b</i> [pm]	1971.0(4)
<i>c</i> [pm]	1172.4(2)
β [°]	98.20(3)
Z	4
$\mu [{ m mm^{-1}}]$	3.178
Diffractometer	STOE IPDS II
	Mo- $K_{\alpha}$ , $\lambda = 71.073$ pm,
	graphite monochromator
Measuring range $(\Theta)$ [°]	2.04-25.65
Reflections collected	3578
Independent reflections $[I \ge 2\sigma(I)]$	2290
Absorption correction	numerical
Max./min. transmission	0.6927/0.5123
Refined parameters	181
$wR2/R1$ [ $I \ge 2\sigma(I)$ ]	0.0457/0.0210
Max./min. residual electron density	0.925/-0.627
$[e pm^{-3} 10^{-6}]$	

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