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Synthesis of 1,6-dihalogeno-2,3,4,5-tetracarba-*nido*-hexaborane(6) derivatives ☆

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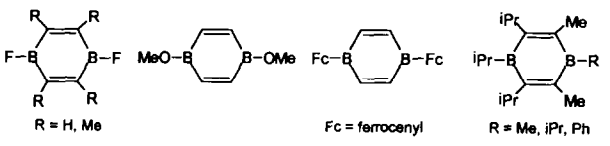
Abstract

1,4,6,9-Tetraalkyl-3,8-diethyl-2,7-bis(diethylboryl)-5-stannaspiro[4.4]nona-1,3,6,8-tetraenes (alkyl = Et (**2a**), Pr (**2b**), ^{i}Pr (**2c**), ^{n}Bu (**2d**)) react with four equivalents of boron tribromide to give 2,3,4,5-tetraalkyl-1,6-dibromo-2,3,4,5-tetracarba-*nido*-hexaboranes(6) (**3a–d**) in high yield. By monitoring the progress of the reactions using ^{13}C NMR spectroscopy, 2,5-diboryl-substituted 3-borolenes (**10**) were identified as intermediates that rearrange to the carboranes via elimination of ethylboron dibromide. Treatment of **2** with boron triiodide affords the analogous 1,6-diodo-substituted carboranes **4**. The reaction of **2** with an excess of boron trichloride proceeds rather slowly, again with a 3-borolene (**9**) as intermediate, and leads finally to a mixture of the carboranes **5** and **6** as a result of elimination of $EtBCl_2$ or BCl_3. Treatment of **2** with BF_3 leads to decomposition without any defined products. The carboranes **3** react stepwise with $Li[Et_3BH]$ to give first the monohydride with a B(6)–H bond (**17**) and the dihydride with B(6)–H and B(1)–H bonds (**18**).

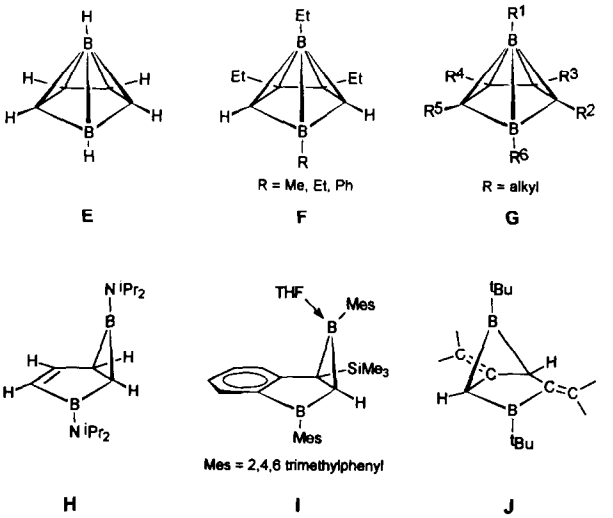
Keywords: Boron; 2,3,4,5-Tetracarba-*nido*-hexaboranes(6); 3-Borolenes; Multinuclear NMR spectroscopy; Tin; Halide

1. Introduction

The intriguing competition between two-center and multi-center bonding becomes frequently apparent in carbon-rich carboranes [1]. In this context the C_4B_2-system is particularly noteworthy since the classical isomers **A** [2], **B**, **C** [3], **D** [4], the 1,4-dibora-2,5-cyclohexadienes, and the typical nonclassical isomers **E** [5], **F** [6], **G** [7], the 2,3,4,5-tetracarba-*nido*-hexaboranes(6), are well known, and there are also various compounds, e.g. **H** [8], **I** [9] and **J** [10], displaying structural features between these extremes.



A B C D



E F G H I J

The direct interconversion between 1,4-dibora-2,5-cyclohexadienes and 2,3,4,5-tetracarba-*nido*-hexaboranes(6) is forbidden by symmetry [11]. Recently, we have shown that **D** rearranges to **G**, not directly, but via cleavage of the six-membered ring into two borirene rings which recombine to give the carboranes of type **G**

☆ Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

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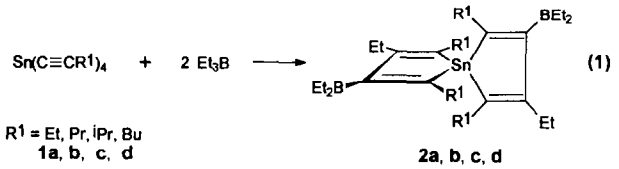
[4]. Another link between classical and nonclassical structures is the 1,3-diboratabenzene dianion which was obtained by reducing a 2,3,4,5-tetracarba-*nido*-hexaborane(6) derivative with two equivalents of lithium [12]. In order to establish more links between the valence isomers of the C_4B_2-system, functional groups at the boron atoms, preferably B–halogen bonds, in the *nido*-carborane system are required.

Previously, compounds of type **F** were obtained in moderate yield from the reaction between 4-ethyl-3-diethylboryl-1,1-dimethyl-stannole and organoboron dihalides [6]. The analogous reaction with BCl_3 or BBr_3 gives complex mixtures containing only a small amount of the 6-halogeno derivative which is difficult to separate [13]. Therefore, we have looked for other stannoles as potential precursors of B-halogen substituted carboranes. Since 1,1-organoboration of tetra-1-alkynyltin compounds (**1**) has opened a convenient route to the 1,1′-spirobistannoles (**2**) (Eq. (1)) [14], it was of interest to study the reactivity of **2** towards boron halides.

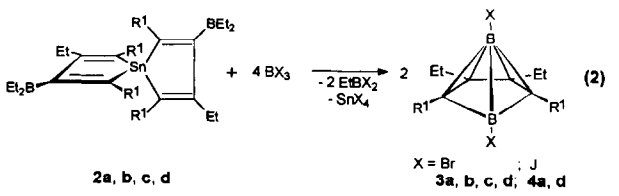
2. Results and discussion

2.1. Synthesis

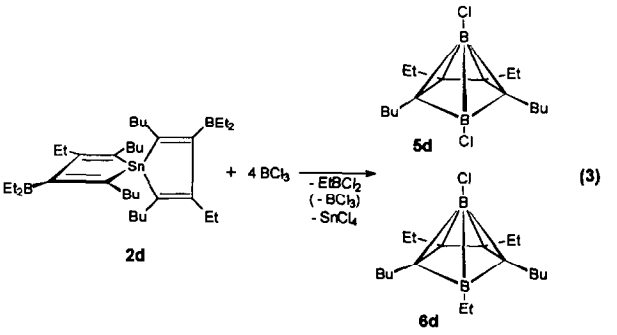
The 1,1′-spirobistannoles (**2**) are prepared according to Eq. (1), starting from the tetra-1-alkynyltin compounds (**1**). The products (**2**) can be used without further purification. In addition to the known compounds **2a** (R = Et), **2b** (R = Pr) and **2c** (R = ^{i}Pr) [14], we have also obtained **2d** (R = ^{n}Bu).



As shown in Eq. (2), the reaction of the compounds **2** with four equivalents of BBr_3 or BI_3 affords the 1,6-dibromo- (**3**) or 1,6-diiodo-tetraalkyl-*nido*-carborane derivatives (**4**) in high yield (> 90%). The reactions are essentially complete as soon as the reaction mixtures are allowed to reach room temperature. The carboranes **3** can be purified by distillation at reduced pressure. The reaction with BI_3 was studied only on a small scale for NMR spectroscopic measurements.

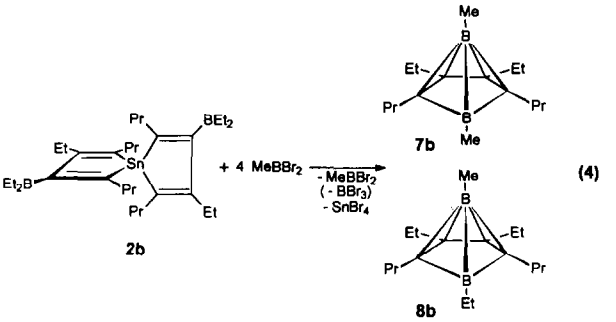


In the case of the reaction between **2** and BCl_3, the conversion into carboranes requires several weeks at ambient temperature, and mixtures are obtained consisting of the 1,6-dichloro-tetraalkyl- (**5**) and 1-chloro-pentaalkyl-*nido*-carborane derivatives (**6**) (Eq. (3)).

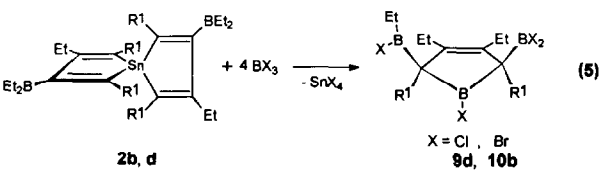


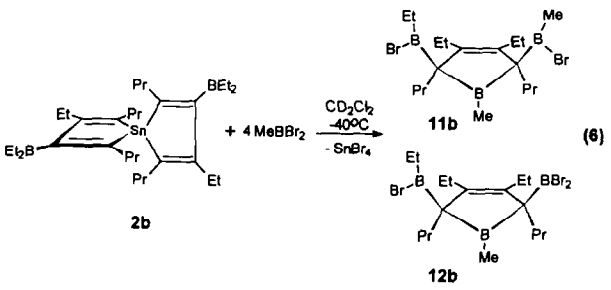
Treatment of **2** with an excess of BF_3 induces decomposition, and so far we have failed to identify any products.

Mixtures of hexaalkyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**7**, **8** corresponding to type **G**) are formed if **2** reacts with $MeBBr_2$ (Eq. (4)). In the case of **8**, the methyl group prefers the apical position.

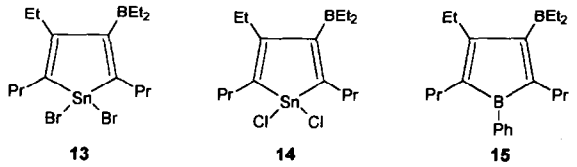


In most cases studied (Eqs. (1)–(4)), intermediates prior to the formation of the carboranes were detected and characterized by NMR spectroscopy. These intermediates are 3-borolenes (**9**–**12**) bearing boryl groups in 2,5-positions with the boryl groups at the same side of the ring, as shown in Eqs. (5) and (6).

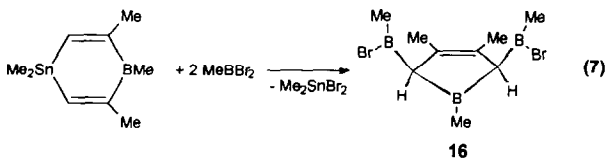




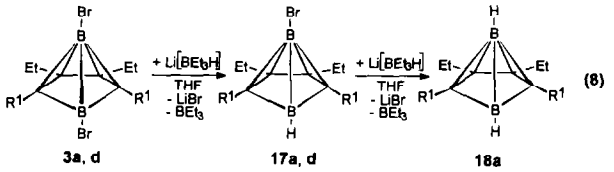
If the reaction according to Eq. (6) is conducted in a 1:2 ratio of the educts, NMR data (see Section 4) indicate that the reaction mixture contains a 1,1-dibromo-stannole **13** among many other unidentified products. Treatment of **2** with $PhBCl_2$ does not give a 3-borolene or carboranes, but the 1,1-dichloro-stannole **14** can be identified by its NMR data (see Section 4). The other potential products, the borole **15** or its Diels–Alder dimer [15], could not be identified with certainty in the reaction mixture.



Another 2,5-diborylated 3-borolene **16**, as a precursor of carboranes of type **F**, had already been obtained from the reaction (Eq. (7)) between 1,1,2,4,6-pentamethyl-1,4-stannabora-2,5-cyclohexadiene and $MeBBr_2$ (1:2 ratio) [6b]. It was shown that **16** can be converted into the carborane of type **F** via elimination of $MeBBr_2$, although this required rather harsh reaction conditions [6b]. The comparatively smooth conversion of the 3-borolenes **9–12**, via elimination of boron halides, to the carboranes **3–8** can be explained considering the crowded situation in the 3-borolenes **9–12** with R^1 = alkyl as compared to R^1 = H (**16**).



First attempts to make use of the B–Br bonds in the carboranes **3** were successful. The reaction between **3** and $Li[Et_3BH]$ leads stepwise to the carboranes **17** and **18**. At first, the B(6)–Br bond is attacked selectively (Eq. (8a)) to give **17a,d** which can be isolated. The selective formation of **17** indicates an exocyclic Br/H exchange process. The reaction of the carborane **17a** with a second equivalent of $Li[Et_3BH]$ affords the 2,3,4,5-tetraalkyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**18a**).



2.2. NMR spectroscopic results

The ^{13}C NMR data of some 3-borolenes are given in Table 1. The presence of the 3-borolene ring and the substituent pattern follows conclusively from these data. The appearence of broad ^{13}C resonance signals typical of boron-bonded carbon atoms are particularly useful for the structural assignment.

^{13}C and ^{11}B NMR data of the carboranes **3–8**, **17** and **18** are given in Table 2. All 2,3,4,5-tetracarba-*nido*-hexaborane(6) derivatives studied here, and also those reported in the literature, are readily identified, even in dilute reaction mixtures, by their typical ^{11}B NMR spectra, showing a sharp ^{11}B NMR signal at low frequencies ($\delta^{11}B$ −36.7 to −52.9) and a much broader signal at higher frequencies ($\delta^{11}B$ + 6.0– + 23). A representative ^{11}B NMR spectrum of a reaction solution is shown in Fig. 1, where it is also possible to identify the

Table 1
^{11}B and ^{13}C NMR data of the 3-borolenes **9–11** and **16** [6b] for comparison

Compound	C(2,5) [a]	C(3,4)	R(2,5) [b]	Et(3,4) [b]
9d [c]	65.8 (br), 63.9 (br)	147.6, 144.1	34.3, 32.1, 31.7, 31.1, 24.3, 24.1, 14,0, 14,0	22.7, 22.5 14.9, 14.8
10b [d]	69.6 (br), 68.6 (br)	148.0, 144.2	38.2, 36.8, 22.4, 21.4, 15.6, 15.3	22.8, 22.3 15.1, 14.9
11b [e]	73.1 (br), 70.3 (br)	151.0, 144.3	38.2, 37.2, 35.6, 34.5, 23.8, 23.4, 23.1, 22.7, 14.3,	21.2, 20.5 15.6, 14.3
	70.3 (br), 69.5 (br)		14.3, 13.8, 13.5	
16	76.6 (br), 76.6 (br)	136.9, 136.9	[f]	[f]

[a] (br) denotes broad ^{13}C resonances of boron-bonded carbon atoms.
[b] Without further assignment.
[c] In C_6D_6 at 298 K, reaction solution. $\delta^{13}C$ = 21.4 (br), 9.5 (B*Et*). $\delta^{11}B$ = +67.7 ($h_{1/2}$ = 1600 Hz).
[d] In CD_2Cl_2 at 233 K, reaction solution. $\delta^{13}C$ = not observed, 11.1 (B*Et*).
[e] In CD_2Cl_2 at 233 K, reaction solution. $\delta^{13}C^{[b]}$ = 20.1, 19.5, 9.2, 8.5 (B*Et*); 18.5, 17.9 (B*Me*); 11.3, 10.8 (> B*Me*).
[f] In $CDCl_3$ at 298 K. $\delta^{13}C$ = 17.8 (br) (BBr*Me*); 16.6 (=C*Me*); 10.3 (br) (> B*Me*). $\delta^{11}B$ = +86.5 B(1); +76.6 B(2, 5); $\delta^{1}H$ = 3.44 H(2, 5).

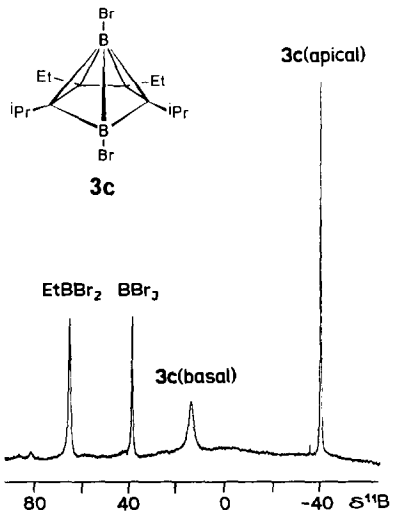


Fig. 1. $^{11}B\{^1H\}$ NMR spectrum (in hexane at 25 °C) at 80.3 MHz of a reaction solution (according to Eq. (2)) containing to the carborane **3c**. A slight excess of BBr_3 is still present, together with $EtBBr_2$ which was eliminated from the intermediate 3-borolene **10c** to give **3c**.

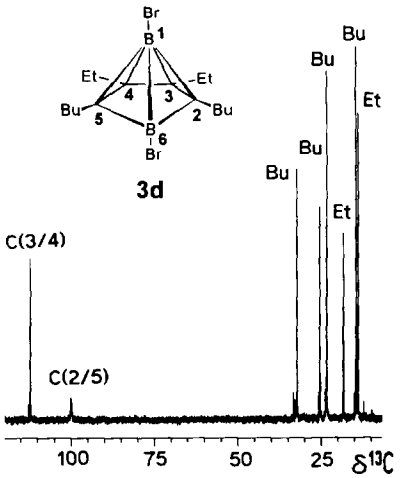


Fig. 2. $^{13}C\{^1H\}$ NMR spectrum (in C_6D_6 at 25 °C) at 62.8 MHz of the carborane **3d** (crude product after removal of the solvent). Assignment of ^{13}C(Bu) and ^{13}C(Et) resonance signals was achieved by 2D $^{13}C/^1H$ heteronuclear shift correlations; note the broadening of the $^{13}C(2,5)$ resonance signals as a result of partially relaxed scalar $^{13}C-^{11}B$ coupling.

boron halide which is eliminated from the intermediate 2,5-diboryl-substituted 3-borolene. As can be seen from Table 1, there are characteristic differences in the $\delta^{11}B$ data which allow to distinguish the type of substituent linked to B(1) and/or B(6).

There is also a typical pattern of the ^{13}C NMR

Table 2
^{11}B and ^{13}C NMR data [a] of substituted 2,3,4,5-tetracarba-*nido*-hexa-boranes(6)

Compound	$\delta^{13}C$						$\delta^{11}B$ [d]	
	C(2,5)	*C*(3,4)	*R*(2,5)	*Et*(3,4)	B*R*(1)	B*R*(6)	*B*(1)	*B*(6)
3a	101.2 (br)	112.1	18.9, 14.5	18.0, 13.6	—	—	−40.3	+14.8
3b	100.1 (br)	112.4	27.7, 23.3 14.6	18.6, 13.6	—	—	−40.2	+15.5
3c	104.6 (br)	111.5	27.0, 20.8 23.7	18.2, 13.7	—	—	−41.3	+13.8
3d	100.2 (br)	112.2	33.3, 25.4 23.1, 14.5	18.2, 13.6	—	—	−40.1	+15.5
4a	105.1 (br)	114.3	20.8, 14.3	19.1, 13.6	—	—	−52.4	+6.0
4d	104.2 (br)	114.2	32.2, 27.2 23.1, 14.1	19.0, 13.4	—	—	−52.2	+6.6
5d [b]	99.7 (br)	110.7	32.3, 25.4 23.5, 14.4	18.0, 13.8	—	—	−36.7	+14.6
6d [b]	97.3 (br)	110.7	32.3, 25.1 23.1, 14.3	17.9, 13.6	—	3.8 (br), 12.0	−36.7	+18.9
7b [c]	98.6 (br)	110.4	28.2, 25.0 14.7	17.8, 14.4	−15.4 (br)	−5.9 (br)	−45.5	+17.8
8b [c]	98.6 (br)	110.1	28.2, 24.7 14.8	17.8, 14.4	−15.4 (br)	4.1 (br), 14.7	−45.5	+17.8
17a	105.9 (br)	114.9	20.1, 14.8	18.2, 13.2	—	—	−40.9	+10.9 [e]
17d	104.9 (br)	114.8	32.7, 26.7 23.2, 14.3	18.2, 13.3	—	—	−40.8	+11.0 [f]
18a	103.6 (br)	112.0	20.2, 15.9	17.7, 14.9	—	—	−52.9	+8.4 [g]

[a] In C_6D_6 (50% v/v, 25 °C); (br) denotes broad ^{13}C resonances of boron-bonded carbon atoms.
[b] A 2:1 mixture of **5b** and **6d**.
[c] A 1:1 mixture of **7b** and **8b**.
[d] Full width at half height $h_{1/2}$ ($^{11}B(1)\{^1H\}$) = 10 ± 5 Hz; $h_{1/2}$ ($^{11}B(6)\{^1H\}$) = 250 ± 30 Hz.
[e] $^1J(^{11}B(6)^1H)$ = 145.0 Hz.
[f] $^1J(^{11}B(6)^1H)$ = 149.0 Hz.
[g] $^1J(^{11}B(6)^1H)$ = 136.0 Hz; $^1J(^{11}B(1)^1H)$ = 199.0 Hz.

signals of the carboranes in the region for the carbon atoms in 2,3,4,5-position (δ^{13}C(2,5) 97.3–105.9 and δ^{13}C(3,4) 110.1–114.9) with broad ^{13}C(2,5) NMR signals owing to partially relaxed scalar ^{13}C(2,5)–^{11}B coupling (Fig. 2). The influence of substituents at the boron atoms on the range of the δ^{13}C(2,3,4,5) values is surprisingly small. The assignment of the ^{13}C(alkyl) resonance signals and parts of the extremely complex pattern of the ^{1}H NMR spectra was achieved by 2D ^{13}C/^{1}H heteronuclear shift correlations (HETCOR) based on coupling constants $^{1}J(^{13}C^{1}H)$ and long-range coupling constants $^{n}J(^{13}C^{1}H)$ (n = 2 or 3) together with 2D ^{1}H/^{1}H COSY experiments.

The coupling constants $^{1}J(^{11}B^{1}H)$ for the carboranes **17** and **18** are typical of the bonding situation [16], with a large value (199.0 Hz) for the apical ^{11}B(1) which is formally sp hybridized, and smaller values (136–149 Hz) for the ^{11}B(6) nuclei, formally sp^2 hybridized.

3. Conclusions

The first examples of 1,6-dihalogeno 2,3,4,5-tetracarba-*nido*-hexaborane(6) derivatives, e.g. **3** (halogen = Br) have been prepared in high yield. In all cases studied, the precursors of the carboranes were identified as 2,5-diboryl-substituted 3-borolenes. The new 1,6-dibromo-substituted carboranes **3** will serve as starting materials in order to explore the chemistry of these carboranes and to find further links between various valence isomers of the C_4B_2 system. The conversion of the carboranes **3** to the monohydride (**17**) and the dihydride (**18**) is the first proof of the reactivity and the synthetic potential of these 1,6-dihalogeno-2,3,4,5-tetracarba-*nido*-hexaborane(6) derivatives.

4. Experimental details

All preparative work and handling of the samples was carried out under N_2, using dry glassware and dry solvents. Deuterated solvents were stored over molecular sieves and saturated with N_2. Starting materials such as BCl_3 (Merck), BBr_3 (Fluka) and $LiBEt_3H$ (Aldrich, 1M in THF) were commercial products. BI_3 [17], $MeBBr_2$ [18], the alkynyl tin compounds **1a–d** [19] and the 5-stannaspiro [4.4]nona-1,3,6,8-tetraenes **2a–c** [14] were prepared according to literature procedures. EI–MS spectra (70 eV): Varian MAT CH 7 with direct inlet. NMR spectra: Jeol FX 90 Q (^{11}B), Jeol EX 270 (^{1}H, ^{13}C) Bruker ARX 250 and Bruker AC 300 (^{1}H, ^{11}B, ^{13}C); chemical shifts are given with respect to Me_4Si (δ^{1}H(C_6D_5H) = 7.15; δ^{13}C(C_6D_6) = 128.0; Et_2O–BF_3 (δ^{11}B: $\Xi(^{11}B)$ = 32.083971 MHz).

4.1. 1,4,6,9-Tetrabutyl-3,8-diethyl-2,7-bis(diethylboryl)-5-stannaspiro[4.4]nona-1,3,6,8-tetraene (2d)

A solution of 3.55 g (8.0 mmol) of **1d** in 40 mml of toluene was cooled to −78 °C and 3.30 ml (25 mmol) of BEt_3 were added in one portion. The mixture was warmed to room temperature and heated to 60 °C for 12 h. After removal of the solvent together with the excess of Et_3B in vacuo, the oily residue consisted already of pure (> 95% according to ^{1}H and ^{13}C NMR spectroscopies) **2d**. Further purification by distillation (b.p. 185–190 °C/10^{-3} Torr), accompanied by decomposition, gave 3.8 g (75%) of **2d**.

MS ($C_{36}H_{66}B_2Sn$): m/z (%) = 640 (3) [M^+], 611 (3), 380 (4), 57 (100). ^{1}H NMR (C_6D_6, 298 K): δ = 2.43 m, 2.16 m, 1.49–1.15 m, 0.85 t, 0.82 t, 18H, *Bu*; 2.03 q, 0.99 t, 5H *Et*(4); 1.49–1.15 m, 1.09 m 10H, B*Et*$_2$. ^{13}C NMR (C_6D_6, 298 K): δ [$^{n}J(^{119}Sn^{13}C)$] = 165.0 [50.1] (br) (=*C*B); 152.4 [112.3] (=*C*Et); 140.8 [382.6] (=*C*Bu); 140.1 [433.8] (=*C*Bu); 35.7 [69.2]/32.2 [62.1], 36.4 [18.0]/36.7 [17.4], 23.3/23.1, 14.4/14.4 (*Bu*); 26.7 [53.0], 14.4 [9.0] (*Et*); 22.7 (br), 9.5 (B*Et*$_2$); $^{1}J(^{13}C(1)^{13}C(2))$ = 56.0 Hz; $^{1}J(^{13}C(3)^{13}C(4))$ = 65.5 Hz.

4.2. Reaction of 2 with boron tribromide to give 2,3,4,5-tetraalkyl-1,6-dibromo-2,3,4,5-tetracarba-nido-hexaboranes(6) (3) (general procedure)

Boron tribromide (2.5 ml, 26.4 mmol) was added in one portion to cooled solutions (−78 °C) of **2a–d** (3.4 mmol) in 20 ml of hexane. After warming to room temperature, the red reaction solutions were stirred for further 3 h. After filtration from insoluble material, followed by removal of the solvent and BBr_3 in vacuo, crude red products were left. Fractional distillation gave the pure 2,3,4,5-tetraalkyl-1,6-dibromo-2,3,4,5-tetracarba-*nido*-hexaboranes(6) **3** in high yield (up to 98% with respect to **2**).

3a: b.p. 80–85 °C/3 × 10^{-3} Torr. MS ($C_{12}H_{20}B_2Br_2$) m/z (%) = 346 (100) [M^+]. ^{1}H NMR (C_6D_6, 298 K): δ = 2.45 m, 1.92 m, 1.13 t, 10H, *Et*(2,5); 2.00 m, 1.99 m, 0.95 t, 10H, *Et*(3,4).

3b: b.p. 85–90 °C/3 × 10^{-3} Torr. MS ($C_{14}H_{24}B_2Br_2$): m/z (%) = 374 (100) [M^+]. ^{1}H NMR (C_6D_6, 298 K): δ = 2.20 m, 1.87 m, 1.59 m, 0.92 t, 14H, *Pr*(2,5); 2.08 m, 2.04 m, 1.00 t, 10H, *Et*(3,4).

3c: b.p. 75–90 °C/3 × 10^{-3} Torr. MS ($C_{14}H_{24}B_2Br_2$): m/z (%) = 374 (100) [M^+]. ^{1}H NMR (C_6D_6, 298 K): δ = 2.52 sp, 1.32 d, 1.23 d, 14H, ^{i}*Pr*(2,5); 2.09 m, 2.08 m, 1.01 t, 10H, *Et*(3,4).

3d: b.p. 85–95 °C/3 × 10^{-3} Torr. MS($C_{16}H_{28}B_2Br_2$): m/z (%) = 402 (100) [M^+]. ^{1}H NMR (C_6D_6, 298 K): δ = 2.21 m, 1.88 m, 1.58 m, 1.50 m, 1.21 m, 0.87 t, 18H, *Bu*(2,5); 2.08 m, 1.02 t, 10H, *Et*(3,4).

The reactions between **2a**, **2d** and boron triiodide were carried out as described for BBr_3, but on a smaller scale for NMR measurements. The reactions were complete as soon as the mixtures had reached room temperature. According to the NMR spectra quantitative conversion to the 1,6-diiodo-carboranes **4a** and **4d** had taken place.

The reaction between **1d** and boron trichloride was also carried out as described for BBr_3 and monitored by NMR. The reaction was complete only after three weeks at room temperature and gave a mixture of **5d** and **6d**.

4.3. Reaction of 2b with BBr_3 to give 1-bromo-2-dibromoboryl-5-bromo(ethyl)boryl-3,4-diethyl-2,5-dipropyl-3-borolene (10b)

An excess of boron tribromide was injected into a cooled solution (−78 °C) of **2d** (0.2 mmol) in 1.5 ml of CD_2Cl_2. The reaction was monitored by NMR spectroscopy between −78 and +25 °C. The formation of the 3-borolene **10b** was observed at −40 °C. After 2 h at room temperature, **10b** was completely converted, by elimination of $EtBBr_2$ (^{11}B NMR; see also Fig. 1) to the 2,3,4,5-tetracarba-*nido*-hexaborane(6) (**3b**).

4.4. Reaction between 2b and $MeBBr_2$ in a 1:1 ratio, leading to 1,1-dibromo-3-diethylboryl-4-ethyl-2,5-dipropyl-stannole (13)

The reaction was carried out as described for the other boron halides. ^{13}C NMR (CD_2Cl_2; −40 °C): δ [$J(^{119}Sn^{13}C)$] = 158.3 (br) [104.5] C(3); 147.0 [269.8] C(4); 131.5 [698.8] C(5); 131.1 [590.6] C(2); 35.0 [98.9], 31.7 [85.8], 26.0 [17.2], 25.8, 15.0, 14.6 Pr(2,5); 27.4 [105.5], 14.2 Et(4); 22.2 (br), 8.9 BEt_2. ^{119}Sn NMR (CD_2Cl_2; −40 °C): δ = −33.7.

4.5. Reaction between 2b and $PhBCl_2$ in excess, leading to 1,1-dichloro-3-diethylboryl-4-ethyl-2,5-dipropyl-stannole (14)

The reaction was carried out as described for the other boron halides. ^{13}C NMR (CD_2Cl_2; 25 °C): δ[$J(^{119}Sn^{13}C)$] = 160.5 (br) C(3); 149.1 [275.2] C(4); 131.9 [809.0] C(2); 130.9 [641.9] C(5); 35.6 [95.8], 32.3 [85.2], 26.5 [19.5], 26.1 [17.4], 14.5, 14.4 Pr(2,5); 28.3 [102.1], 13.9 [11.6] Et(4); 22.8 (br), 9.3 BEt_2. ^{119}Sn NMR (CD_2Cl_2; 25 °C): δ = +13.1.

4.6. 2,3,4,5-Tetraalkyl-1-bromo-2,3,4,5-tetracarba-nido-hexaborane(6) (17a,d) (general procedure)

Solutions of the 1,6-dibromo-carborane (10 mmol) in 30 ml of THF were cooled to −78 °C and 10 ml of a solution of $Li[BEt_3H]$ in THF (1 M) was added. The reaction solution was warmed to room temperature and after stirring for 12 h the solvent was removed in vacuo (10^{-3} Torr). Fractional distillation gave the pure products **17a** and **17d** in high yield (> 90%) as colorless, air-sensitive liquids.

17a: b.p. 70–75 °C/10^{-3} Torr. ^1H NMR (C_6D_6, 298 K): δ = 3.88 (br) [$^1J(^{11}B(6)^1H)$ = 145.0 Hz] 1H, B(6)*H*; 2.06 m, 1.20 t, 10H, *Et*(2,5); 2.06 m, 1.01 t, 10H, *Et*(3,4).

17d: b.p. 78–82 °C/10^{-3}Torr. ^1H NMR (C_6D_6, 298 K): δ = 3.98 (br) [$^1J(^{11}B(6)^1H)$ = 149.0 Hz] 1H, B(6)*H*; 2.07 m, 1.67 m, 1.37 m, 1.01 t, 18H, *Bu*(2,5); 2.06 m, 0.90 t, 10H, *Et*(3,4).

4.7. 2,3,4,5-Tetraethyl-2,3,4,5-tetracarba-nido-hexaborane(6) (18a)

The reaction between **3a** (3.45 g, 10 mmol) and an excess of $Li[BEt_3H]$ (30 ml of a 1M THF solution) was carried out as described for **17**. Fractional distillation gave 1.6 g (85%) of pure **18a** as a colorless, air-sensitive liquid (b.p. 30–34°C/10^{-3} Torr). ^1H NMR (C_6D_6, 298 K): δ = 3.88 (br) [$^1J(^{11}B(6)^1H)$ = 136.0 Hz] 1H, B(6)*H*; 2.23 m, 1.13 t, 10H, *Et*(2,5); 2.05 m, 0.99 t, 10H, *Et*(3,4); −0.85 [$^1J(^{11}B(1)^1H)$ = 199.0 Hz] 1:1:1:1 q, 1H, B(1)*H*.

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