PENTAALKYL-6-TRIORGANOSTANNYL-2,3,4,5-TETRACARBA-*NIDO*-HEXABORANES(6)

Bernd Wrackmeyer* and Alexandra Glöckle

Anorganische Chemie II, Universität Bayreuth, , D-95440 Bayreuth, Germany

Abstract

Pentaalkyl-6-bromo-2,3,4,5-tetracarba-*nido*-hexaboranes(6) (carb-Br **2**) react with trimethylstannyl- and triphenylstannyl-lithium to give the 6-stannyl subtituted carbaboranes carb-$SnMe_3$ **3a** and carb-$SnPh_3$ **3b**. The reactivity of **3b** towards various electrophiles was studied. It reacts with tin tetrachloride and tin tetrabromide preferably by cleavage of the Sn-C bond, leading finally to novel inorganic tin(IV) halides carb-$SnCl_3$ **6(Cl)** or carb-$SnBr_3$ **6(Br)**. This is also true for the reaction with boron tribromide. In this case, carb-$SnBr_3$ **6(Br)** proved to be stable even in the presence of an excess of BBr_3; heating of this mixture at 60°C leads back to **2** and to $SnBr_2$. In the reaction with bromine, it appears that both Sn-C and Sn-**B** bonds are attacked since the formation of carb-$SnPh_2Br$ **4(Br)**, carb-$SnPhBr_2$ **5(Br)** and **2** can be detected by ^{119}Sn and ^{11}B NMR. No reaction of **3b** with zirconium tetrachloride was observed, whereas titanium tetrachloride reacts very slowly, again by cleavage of one of the Sn-C bonds. All products were characterized by ^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR spectroscopy.

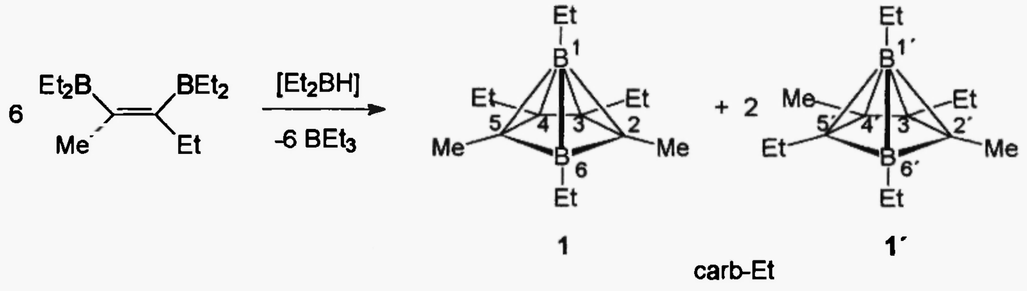
1. Introduction

Although peralkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(6) have been known since the mid-sixties [1] as exceptionally stable compounds (in contrast with the parent derivative $C_4B_2H_6$ [2]), their chemistry has not been explored in great detail. Only recently, the synthesis of tetraalkyl-1,6-dibromo- [3] and pentaalkyl-6-bromo-derivatives [4] was reported, together with the corresponding B-H derivatives, and the basic structure of such alkylated carbaboranes determined by an X-ray diffraction analysis of another pentamethyl derivative with the N-bonded $Fe_2(CO)_6$-μ-SN fragment in 6-position [5]. Various polyhedral boranes are known in which triorganostannyl groups are linked to boron either in bridging or in terminal position [6]. The synthetic potential of simple stannylboranes [7] is increasing since it was found that compounds such as $Me_3SnB(NEt_2)_2$ can be used in the palladium-catalyzed stannylboration of alkynes [8]. Therefore, we report in the present work on the synthesis of pentaalkyl-6-triorganostannyl-2,3,4,5-tetracarba-*nido*-hexaboranes(6) **3**, together with the results of a first screening of the reactivity of **3** towards various element halides.

2. Results and discussion

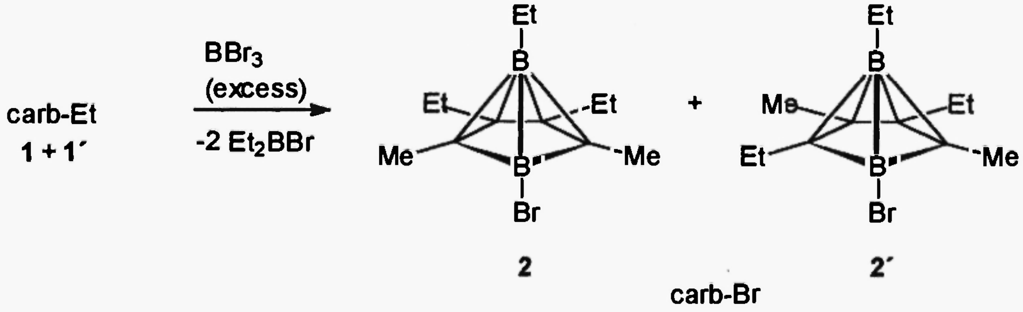
2.1 Syntheses of 6-triorganotin substituted carbaboranes

The most convenient route to peralkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(6) is shown in Eq.(1), leading to a 2:1 mixture of isomers **1** + **1′** [1]. These isomers have almost identical physical and chemical properties, and therefore the mixture **1** + **1′** was used as starting material.



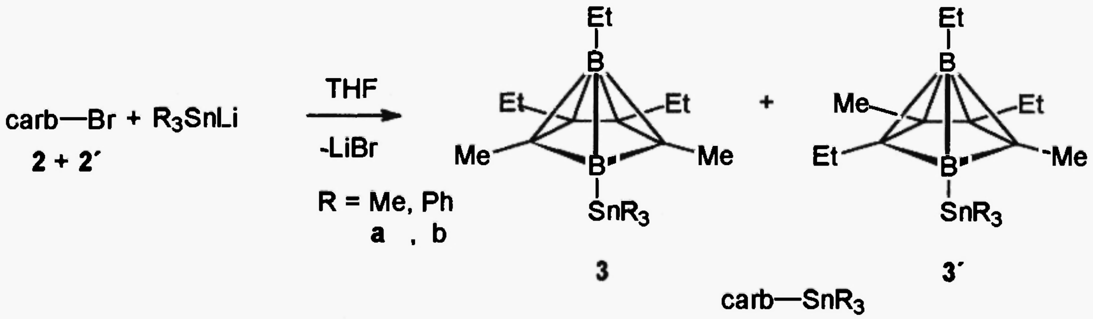
(1)

Following again the literature procedure [4], **1** + **1′** were converted selectively to **2** + **2′** by treatment with boron tribromide [Eq.(2)]. In the following the 6-substituted carboranyl moieties are abbreviated as carb.



(2)

The reaction of the mixture **2** + **2′** with Me_3SnLi or Ph_3SnLi [Eq.(3)] in THF afforded the corresponding mixtures of carbaboranes **3** + **3′** in moderate to good yields.

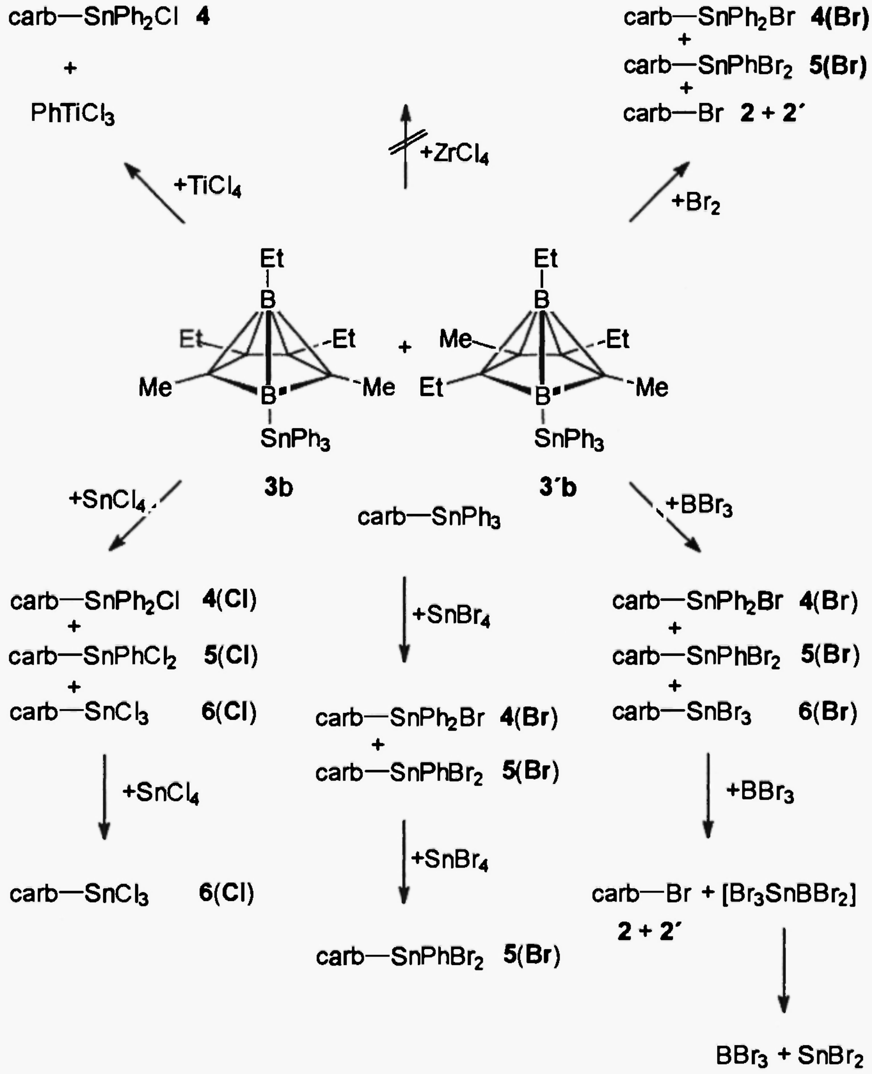


(3)

*2.2 Reactivity of **3b** + **3´b** towards electrophiles*

The reactivity of Sn-C bonds towards electrophiles is well documented [9]. Exchange reactions of tetraorganyltin compounds with tin tetrachloride or tin tetrabromide serve as prominent examples.

The course of the exchange reaction of **3b** + **3´b** with tin tetrachloride (Scheme 1) is evident from the sequence of ^{119}Sn NMR spectra in Figure 1. The first reaction products are carb-$SnPh_2Cl$ **4(Cl)** and carb-$SnPhCl_2$ **5(Cl)**, together with $PhSnCl_3$, Ph_2SnCl_2 and a trace of Ph_3SnCl (Fig. 1a). This indicates that the Sn-C bonds are more reactive than the Sn-B bond. Only in the presence of an excess of $SnCl_4$, the equilibrium is finally shifted towards carb-$SnCl_3$ **6(Cl)** (Fig. 1d) wich may be formed also by cleavage of the Sn-B bond. However, considering the product distribution in the beginning of the reaction, it is more likely that the cleavage of the third Sn-C bond takes place much more slowly than the cleavage of the first and second Sn-C bond, and may still be faster than the cleavage of the Sn-B bond. The reaction with an excess of $SnBr_4$ (Scheme 1) leads to carb-$SnPhBr_2$ **5(Br)**, even after heating for 12 h at 80°C.



Scheme 1. Exchange reactions of carb-$SnPh_3$ **3b** + **3´b** with element halides (The tin halides Ph_3SnX, Ph_2SnX_2, $PhSnX_3$ have been omitted for clarity).

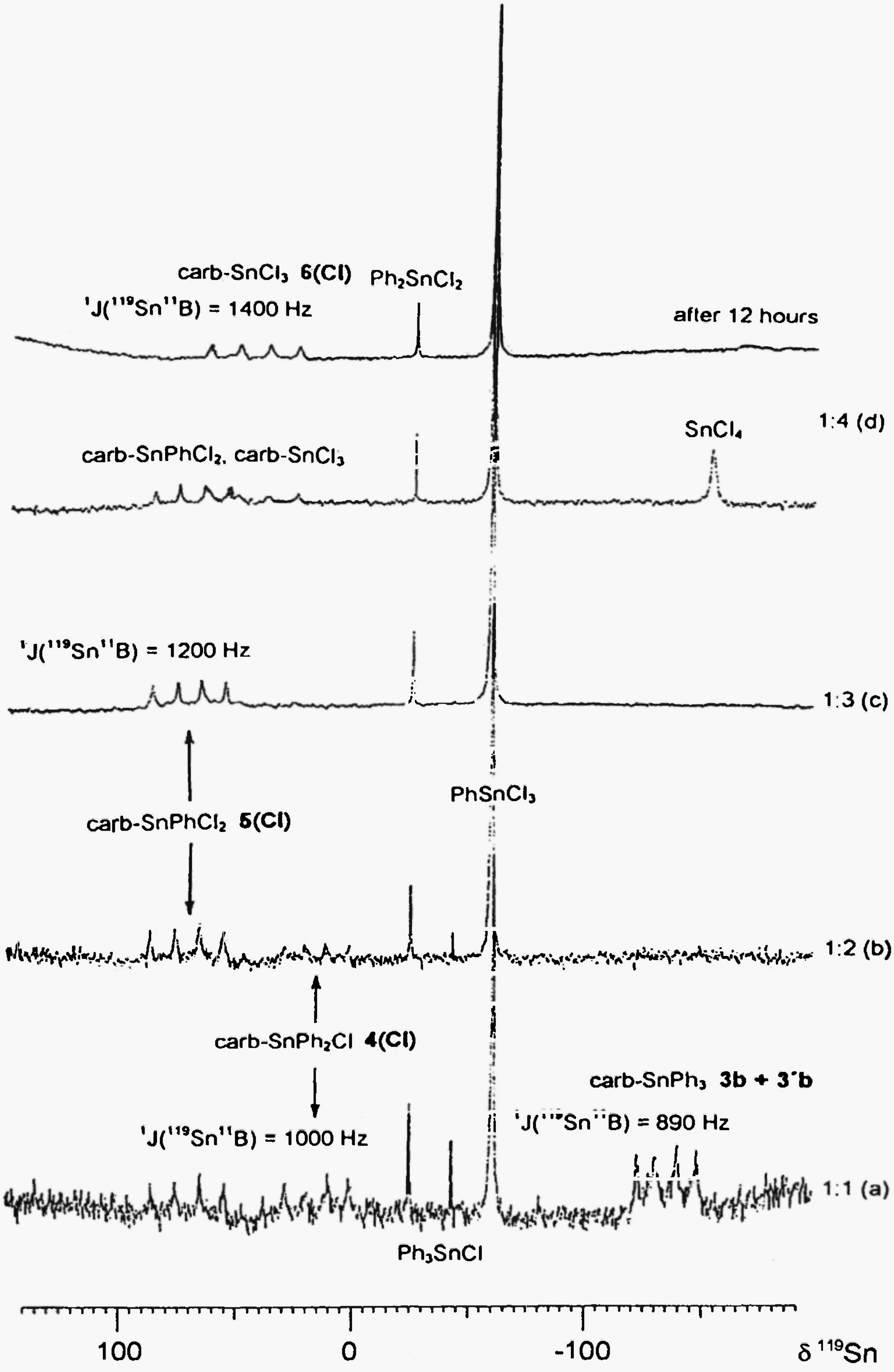


Figure 1. The exchange reaction of **3b + 3'b** with $SnCl_4$ monitored by 112 MHz ^{119}Sn NMR [see text for (a) - (b)].

Similarly, **3b** + **3'b** react with BBr_3 preferably by cleavage of the Sn-C bond (Scheme 1) to give carb-$SnBr_3$ **6(Br)** which is stable at room temperature, even in the presence of an excess of BBr_3. Heating of such a mixture at 60°C for 6 hours leads to the formation of carb-Br **2** + **2'** and $SnBr_2$.

The reaction of **3b** + **3'b** with bromine gives carb-$SnPh_2Br$ **4(Br)**, carb-$SnPhBr_2$ **5(Br)** and carb-Br **2** + **2'**, indicating cleavage of the Sn-C as well as of the Sn-B bond.

No reaction was observed between **3b** + **3'b** and $ZrCl_4$, whereas $TiCl_4$ reacts slowly to give carb-$SnPh_2Cl$ **4(Cl)** and $PhTiCl_3$

2.3 NMR spectroscopic results

The consistent data set of ^1H, ^{11}B, ^{13}C and ^{119}Sn NMR data (see Table 1) supports the proposed structure of the 6-stannyl-carbaboranes.

The 2,3,4,5-tetracarba-*nido*-hexaborane(6) structure itself follows unambiguously from the typical $\delta^{11}B$ data for the apical (δ -43.3 to -43.7) and the basal boron atom (δ 11.3 to 13.7). The substituent pattern can be deduced from the $\delta^{13}C$ values of the substituents, and most data could be assigned based on the results of 2D $^1H/^1H$ COSY and 2D $^{13}C/^1H$ HETCOR experiments. The marked broadening of the ^{13}C resonances of boron-bonded carbon atoms (see Figure 2) is an additional criterion for the assignment. The ^{119}Sn nuclear shielding in **3a** ($\delta^{119}Sn$ -117.1) or **3b** ($\delta^{119}Sn$ -137.8) is significantly increased when compared with Ph-$SnMe_3$ ($\delta^{119}Sn$ -28.6) or Ph_4Sn ($\delta^{119}Sn$ -128.1). In contrast, the presence of Cl or Br at the tin atom reduces the ^{119}Sn nuclear shielding much more than in comparable phenyltin halides [e.g., $\delta^{119}Sn$ +44.0 (**6(Cl)**) and $\delta^{119}Sn$ -63.0 ($PhSnCl_3$), or $\delta^{119}Sn$ -96.1 (**6(Br)**) and $\delta^{119}Sn$ -224.6 ($PhSnBr_3$)]. If one fits the $\delta^{119}Sn$ values to pairwise additive parameters [12], strong deshielding interactions carb/Cl or carb/Br must be assumed, whereas carb/Me or carb/Ph interactions contribute to increased ^{119}Sn nuclear shielding.

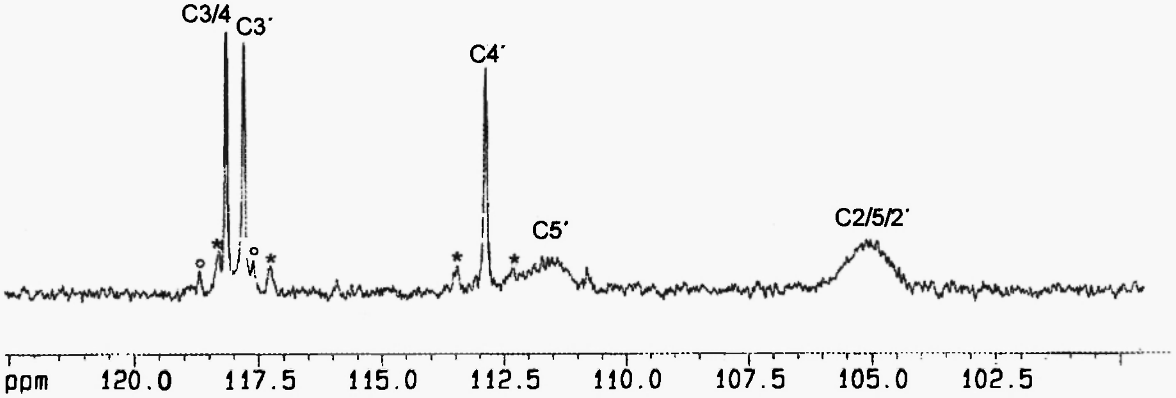


Figure 2. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of carb-$SnCl_3$ **6(Cl)** showing the region for the carbaborane ^{13}C resonances with $^{117/119}Sn$ satellites (marked by asterisks) according to $^3J(^{119}Sn,^{13}C)$. Note the broad ^{13}C resonance signals for the boron-bonded carbon atoms C(2/5).

The magnitude of the coupling constants $|^1J(^{119}Sn,^{11}B)|$ in **3** is similar to that observed for simple stannylboranes [7] or polyhedral stannylboranes [6]. The magnitude of $|^1J(^{119}Sn,^{11}B)|$ increases with the number of halogen atoms attached to the tin atom, in particular in the series with Cl. This is an expected trend and fits into the concept of rehybridization [13] at the tin atom,

Table 1. ^{11}B, ^{13}C, ^{119}Sn NMR data [a] of 6-stannyl-2,3,4,5-tetracarba-*nido*-hexaboranes(6)

		carb-SnMe$_3$ **3a + 3'a**	carb-SnPh$_3$ **3b + 3'b**	carb-SnCl$_3$ [d] **6(Cl)**	carb-SnPhBr$_2$ **5(Br)**	carb-SnBr$_3$ [f] **6(Br)**
δ^{11}B	B(1)	-43.6	-43.7	-43.3	-43.3	-43.3
	B(6)	13.7	13.5	11.3	12.5	12.0
δ^{119}Sn	[$^1J(^{119}Sn^{11}B)$]	-117.1 [944]	-137.8 [926]	44.0 [1400]	13.9 [1150]	-96.1 [1255]
δ^{13}C	B(1)-Et	-4.3 br[c] (80); 11.5	-3.9 br (84); 11.1	-5.9 br (97); 11.5	-5.2 br (92); 11.3	-5.6 br (95); 11.3
	C(2/2')	104.3/104.3	105.2/105.2	105.2/105.2	105.1/105.1	104.4/104.4
	C(5/5')	104.3/111.1	105.2/112.1	105.2/111.6	105.1/111.9	104.4/111.1
	C(3/3')	117.4/117.0	118.3 [60]/117.8 [61]	118.3 [140]/117.9 [140]	117.9 [100]/117.5 [100]	117.5 [129]/117.1 [128]
	C(4/4')	117.4/111.5	118.3 [60]/112.5 [61]	118.3 [140]/112.9 [145]	117.9 [100]/112.3 [101]	117.5 [129]/112.1 [135]
	C(2)-Me	13.0	13.4	11.8 [22.4]	12.3 [17.4]	11.5 [19.4];
	C(2')-Me	13.0	13.4	11.9 [19.6]	12.4 [14.9]	11.6 [18.4];
	C(3)-Et	21.5; 15.7	21.5; 15.4	20.5 [16.0]; 15.5	20.7 [14.3]; 15.7	21.6 [16.1]; 15.5
	C(3')-Et	18.0; 13.7	18.2; 13.7	17.9 [14.7]; 13.4	17.9 [11.0]; 13.6	17.8 [14.4]; 13.4
	C(4)-Et	21.5, 15.7	21.5; 15.4	20.5 [16.0]; 15.5	20.7 [14.3]; 15.7	21.6 [16.1]; 15.5
	C(4')-Me	9.3	9.6	9.3 [17.2]	9.3 [12.4]	9.1 [17.3];
	C(5)-Me	13.0	13.4	11.8 [22.4]	12.3 [17.4]	11.5 [19.4]
	C(5')-Et	18.0; 12.9	18.3; 12.9	17.9 [16.0]; 12.6	17.9 [11.0]; 12.8	17.8 [14.4]; 12.7
	Sn-Me	-10.2 / -10.1 [256]	-	-	-	-
	Sn-Ph(C$_i$) [b]	-	142.8 [392]	-	[e]	-

[a] Coupling constants $^1J(^{119}Sn, ^{11}B)$ and $^nJ(^{119}Sn, ^{13}C)$ in Hz are given in square brackets, $^1J(^{13}C, ^{11}B)$ in parantheses. [b] δ^{13}C 138.2 [36] (Sn-Ph(C$_o$)), 128.5 [40] (Sn-Ph(C$_m$), 128.5 [10] (Sn-Ph(C$_p$). [c] Broad signal due to partially relaxed $J(^{13}C,^{11}B)$ spin spin coupling. [d] δ^{11}B -43.3 (B(1)), 12.4 (B(6)) (**4(Cl)**); δ^{119}Sn 14.8 [1000] (**4(Cl)**); δ^{11}B -43.3 (B(1)), 12.4 (B(6)) (**5(Cl)**); δ^{119}Sn 70.5 [1200] (**5(Cl)**). [e] not assigned. [f] δ^{11}B -43.3 (B(1)), 12.5 (B(6)) (**4(Br)**); δ^{119}Sn -11.9 [1035] (**4(Br)**).

induced by strongly electronegative ligands. The smaller values of $|^1J(^{119}Sn, ^{13}C)|$ in **3a** + **3´a** (256 Hz) and **3b** + **3´b** (392 Hz), when compared with data for Me_4Sn (338 Hz) or Ph_4Sn (531 Hz) indicate that the carb substituent is more electropositive than a phenyl or an alkyl group. It is difficult to observe small coupling constants $^nJ(^{119}Sn, ^{13}C)$ ($n > 1$). This is the result of broadening of the ^{13}C NMR signals for carbon atoms not directly adjacent to boron, owing to partially relaxed scalar ^{13}C-^{11}B coupling across two or three bonds. However, in the case of **3b** the vicinal coupling constant $^3J(^{119}Sn, ^{13}C(3/4))$ = 60 Hz is resolved. Much larger values $|^3J(^{119}Sn, ^{13}C(3/4))|$ are observed for **6**(Br) and **6**(Cl) (see Figure 2). For the latter compounds, other three-bond and also four-bond ^{119}Sn-^{13}C coupling constants in the order of 10 to 22 Hz (see Table 1) are resolved. It is remarkable that the magnitude of the vicinal ^{119}Sn-$^{13}C(3/4)$ coupling constants is so large in comparison with $^3J(^{119}Sn, ^{13}C(2/5\text{-}CH_3$ or $\text{-}CH_2))$. Although, in general, the magnitude of four-bond couplings is smaller than that of three-bond couplings, this is not found in **6(Cl)** and **6**(Br).

3. Conclusions

Pentaalkyl-6-stannyl-2,3,4,5-tetracarba-*nido*-hexaboranes(6) (carb-SnR_3 **3**) are readily accessible by conventional organometallic procedures. The reactivity of **3b** + **3´b** towards electrophiles showed that the Sn-C bonds are cleaved preferably except in the reaction with bromine where a radical mechanism is conceivable. Although these reactions of compounds **3b**+ **3´b** were not successful with respect to the formation of new element-boron bonds, the derivatives carb-$SnCl_3$ **6(Cl)** or carb-$SnBr_3$ **6**(Br) are new types of inorganic tin(IV) halides, and their chemistry may have a number of interesting aspects for future studies.

4. Experimental

All reactions were carried out in an inert atmosphere of Ar or N_2, observing necessary precautions to exclude moisture and oxygen. A 2:1 mixture of the isomers 2,4-dimethyl-1,3,5-triethyl- and 2,5-dimethyl-1,3,4-triethyl-2,3,4,5-tetracarba-*nido*-hexaboranes(6) [1] served as starting materials. These were converted into carb-Br **2** + **2´** [4]. The THF solutions of Me_3SnLi [10] and Ph_3SnLi [11] were prepared following literature procedures. The reactions 4.3 to 4.7 were carried out in NMR tubes.

^1H, ^{11}B, ^{13}C and ^{119}Sn NMR spectra were recorded by using Bruker DRX 500, Bruker AC 300 and Bruker ARX 250 instruments equipped with multinuclear probe heads (samples ca. 10 - 20% in C_6D_6 at 25 ± 1°C in 5mm o.d. tubes were measured if not mentioned otherwise). Chemical shifts are given with respect to the chemical shift of the solvent (second external reference Me_4Si) [δ^1H 7.15 (C_6D_5H); 7.24 ($CHCl_3$), $\delta^{13}C$ 128.0 (C_6D_6); 77.0 ($CDCl_3$)] and external Et_2O-BF_3 [$\delta^{11}B$ 0 for $\Xi(^{11}B)$ = 32.083971 MHz], $SnMe_4$ [$\delta^{119}Sn$ 0 for $\Xi(^{119}Sn)$ = 37.290665 MHz].

4.1 Pentaalkyl-6-trimethylstannyl-2,3,4,5-tetracarba-nido-hexaboranes(6) ***3a*** *+* ***3´a***

6-Bromo-pentaalkyl-2,3,4,5-tetracarba-*nido*-hexaboranes(6) **2** + **2´** (2.2ml; 11 mmol) were added to a cooled (-78°C) solution of Me_3SnLi (11 mmol) in 50ml THF. After the reaction mixture was warmed to room temperature and stirred for further 12 h, solid material was filtered off. The solvent was removed *in vacuo* and the oily residue was distilled to give **3a** + **3´a** (b.p. 36.5°C/10^{-4} Torr; 2.32g; 56%) as a colourless liquid. - ^1H-NMR: δ^1H [$^nJ(^{119}Sn,^1H)$] 0.08 br (q), 0.68 br (t) (15H, B(1)-Et); 1.77 (s, 12H, C(2/2´/5)-Me); 1.95 to 2.07 and 2.14 to 2.28 (m), 1.11 (t), (10H, C(3/4)-Et); 1.87 to 2.00 (m), 0.92 (t), (10H, C(3´)-Et); 1.87 to 2.00 (m), 0.88 (t),(10H, C(5´)-Et); 1.53 (s, 6H, C(4´)-Me); 0.41 and 0.40 (1 : 2), (s, 27H, $SnMe_3$) [46 Hz].

4.2 Pentaalkyl-6-triphenylstannyl-2,3,4,5-tetracarba-nido-hexaboranes(6) ***3b + 3´b***

6-Bromo-pentaalkyl-2,3,4,5-tetracarba-*nido*-hexaboranes(6) **2 + 2´** (1.7ml; 8.3 mmol) were added to a solution of Ph$_3$SnLi (8.3 mmol) in THF (25ml) at room temperature. The mixture was stirred for 12 h at room temperature and then filtered. After removing the solvent, the mixture of **3b + 3´b** (3.22g; 72%) was obtained as a yellowish wax. - ^{1}H-NMR: δ^{1}H [^{n}J(^{119}Sn,^{1}H)] 0.18 br(q), 0.65 br (t), (15H, B(1)-Et); 1.77 (s, 6H, C(2´)-Me); 1.76 (s, 6H, C(2/5)-Me), 1.88 to 1.96 and 2.23 to 2.31 (m), 0.95 (t), (10H, C(3/4)-Et); 1.81 to 1.93 (m), 0.88 (t), (10H, C(3´)-Et); 1.93 to 1.81 (m), 0.84 (t), (10H, C(5´)-Et); 1.50 (s, 6H, C(4´)-Me); 7.83 (m) [42 Hz] and 7.17 to 7.27 (m, 45H, SnPh$_3$).- EI-MS (70 eV): *m/z* (%) = 537 (15) [M^{+}], 459 (25) [M-Ph]$^{+}$, 382 (5) [M-2Ph]$^{+}$, 264 (100) [M-SnPh$_2$]$^{+}$.

4.3 Pentaalkyl-6-chlorodiphenylstannyl- ***4(Cl)****, 6-dichlorophenylstannyl-* ***5(Cl)*** *and 6-trichloro-stannyl-2,3,4,5-tetracarba-nido-hexaboranes(6)* ***6(Cl)***

Tin tetrachloride (0.05ml; 0.394 mmol) was added to a solution of **3b + 3´b** (0.211g; 0.394 mmol) in C$_6$D$_6$. After 10 minutes, ^{119}Sn NMR spectrum showed signals of carb-SnPh$_2$Cl **4(Cl)** and carb-SnPhCl$_2$ **5(Cl)** besides the carb-SnPh$_3$ **3b + 3´b** and phenyltin chlorides. Shortly after the addition of another 0.05ml (0.394 mmol) of SnCl$_4$ to the reaction mixture, the ^{119}Sn NMR signals of carb-SnPhCl$_2$ **5**(Cl) as main product and weak signal of carb-SnPh$_2$Cl **4(Cl)** were detected. After adding a four fold excess of SnCl$_4$, the formation of carb-SnCl$_3$ **6(Cl)** became evident from its ^{119}Sn NMR signal, and after 12 h the carb-SnCl$_3$ **6(Cl)** was the only stannyl carborane present. - ^{1}H-NMR (**6(Cl)**): δ^{1}H 0.03 br (q), 0.62 br (t), (15H, B(1)-Et); 1.71 (s, 6H, C(2´)-Me); 1.69 (s, 6H, C(2/5)-Me); 1.89 to 1.98 and 2.14 to 2.23 (m), 1.04 (t), (10H, C(3/4)-Et); 1.71 to 1.93(m), 0.86 (t),, (10H, C(3´)-Et); 1.71 to 1.93 (m), 0.84 (t), (10H, C(5´)-Et); 1.50 (s, 6H, C(4´)-Me).

The reaction with SnBr$_4$ was carried out in the analogous way. The substitution of the last phenyl group didn´t take place even after heating the reaction mixture 12 h to 80°C. δ^{119}Sn-58.2 (Ph$_3$SnBr); δ^{119}Sn -70.9 (Ph$_2$SnBr$_2$); δ^{119}Sn -224.6 (PhSnBr$_3$), δ^{13}C137.8 [966] (Ph-C1130.0 [118]), (Ph-C2/6), 133.3 [78] (Ph-C3/5), 132.6 [25] (Ph-C4). - ^{1}H-NMR (**5**(Br)): δ^{1}H 0.13 br (q), 0.67 br (t), (15H, B(1)-Et); 1.80 (s, 6H, C(2´)-Me); 1.80 (s, 6H, C(2/5)-Me); 1.79 to 1.93 and 2.38 to 2.47 (m), 1.05 (t), (10H, C(3/4)-Et); 1.75 to 1.90 (m), 0.83 (t), (10H, C(3´)-Et); 1.75 to 1.90 (m), 0.80 (t), (10H, C(5´)-Et); 1.45 (s, 6H, C(4´)-Me).

4.4 Reaction of pentaalkyl-6-(triphenyl)stannyl-2,3,4,5-tetracarba-nido-hexaboranes(6) ***3b + 3´b*** *with boron tribromide*

Boron tribromide (0.05ml; 0.133g; 0.53 mmol) was added to a solution of **3b + 3´b** in C$_6$D$_6$ (0.4ml). After 1 h at room temperature the ^{11}B NMR signals showed the presence of Ph$_2$BBr (δ^{11}B 66.2) and starting material. The ^{119}Sn NMR spectrum showed along with the signal for the starting material signals for carb-SnPh$_3$ **3b + 3´b**, Ph$_3$SnBr (δ^{119}Sn -58.2) and Ph$_2$SnBr$_2$ (δ^{119}Sn -70.9) in a ratio 1:1, carb-SnPh$_2$Br **4**(Br) and carb-SnPhBr$_2$ **5**(Br) and a small amount of carb-SnBr$_3$ **6**(Br). After the addition of an excess of BBr$_3$ (0.17ml; 0.45g; 1.7 mmol) to the reaction mixture fast substitution of all phenyl groups at the tin atom took place. This was indicated by a strong ^{119}Sn NMR signal for carb-SnBr$_3$ **6**(Br). The ^{11}B NMR spectrum showed the signal of an excess of BBr$_3$. After heating this solution for 6 h at 60°C, the ^{11}B NMR signals indicated the formation of carb-Br **2 + 2´** and a solid (SnBr$_2$) was formed. - ^{1}H-NMR (**6**(Br)): δ'H 0.05 br (q), 0.62 br (t), (15H, B(1)-Et); 1.72 (s, 6H, C(2´)-Me); 1.71 (s, 6H, C(2/5)-Me); 1.79 to 1.93 and 2.26 to 2.43 (m), 1.04 (t), (10H, C(3/4)-Et); 1.73 to 1.83 (m), 0.79 (t), (10H, C(3´)-Et); 1.73 to 1.83 (m), 0.77 (t), (10H, C(5´)-Et); 1.40 (s, 6H, C(4´)-Me).

4.5 Reaction of pentaalkyl-6-(triphenyl)stannyl-2,3,4,5-tetracarba-nido-hexaboranes(6) ***3b + 3'b*** *with bromine*

Bromine (0.02g; 0.10 mmol) was added to 0.113g (0.21 mmol) of **3b + 3'b** in C_6D_6 (0.4ml). After 12 h at room temperature ^{11}B NMR signals for carb-Br **2 + 2'** indicated cleavage of the Sn-B bond, and in the ^{119}Sn NMR spectrum signals for carb-$SnPh_2Br$ **4(Br)**, Ph_3SnBr and Ph_2SnBr_2 were detected as a result of cleavage of the Sn-C bond.

4.6 Reaction of pentaalkyl-6-(triphenyl)stannyl-2,3,4,5-tetracarba-nido-hexaboranes(6) ***3b + 3'b*** *with zirconium tetrachloride*

An excess of $ZrCl_4$ was added to a solution of **3b + 3'b** (0.100g; 0.18 mmol) in C_6D_6 (0.4ml) at room temperature. After 12 h at 70°C there was no reaction observed.

4.7 Reaction of pentaalkyl-6-(triphenyl)stannyl-2,3,4,5-tetracarba-nido-hexaboranes(6) ***3b + 3'b*** *with titanium tetrachloride*

An excess of $TiCl_4$ was added to a solution of **3b + 3'b** (0.104g; 0.19 mmol) in C_6D_6 (0.4ml) at room temperature. After 12 h at room temperature the ^{119}Sn NMR spectrum of the reaction mixture indicated cleavage of the Sn-C bond, by the ^{119}Sn NMR signal of carb-$SnPh_2Cl$ **4(Cl)**, in addition to that of the starting material carb-$SnPh_3$ **3b + 3'b**.

References:

[1] a) P. Binger Tetrahedron Lett. **24** (1966) 2675;
    b) P. Binger, Angew. Chem. **80** (1968) 288; Angew. Chem., Int. Ed. Engl. **7** (1968) 286;
    c) R. Köster, M. A. Grassberger, Angew. Chem. **79** (1967) 197; Angew. Chem., Int. Ed. Engl. **6** (1967) 218.
[2] a) T. P. Onak, G. T. F. Wong, J. Am. Chem. Soc. **92** (1970) 5226;
    b) V. R. Miller, R. N. Grimes, Inorg. Chem. **11** (1972) 862.
[3] B. Wrackmeyer, G. Kehr, J. Organomet. Chem. **501** (1995) 87.
[4] B. Wrackmeyer, A. Glöckle, Z. Naturforsch. **51b** (1996) 859.
[5] M. Herberhold, U. Bertholdt, W. Milius, A. Glöckle, B. Wrackmeyer, J. Chem. Soc. Chem. Commun. (**1996**) 1296.
[6] a) M. L. Thomson, R. N. Grimes, Inorg. Chem. **11** (1972) 1925;
    b) D. K. Srivastava, N. P. Rath, L. Barton, Organometallics **11** (1992) 2263.
    c) H. Fang, D. Zhao, N. P. Rath, L. Brammer, L. Barton, Organometallics **14** (1995) 1700.
[7] a) W. Biffar, H. Nöth, R. Schwerthöffer, Liebigs Ann. Chem. (**1981**) 2067;
    b) W. Biffar, H. Nöth, H. Pommerening, R. Schwerthöffer, W. Storch, B. Wrackmeyer, Chem. Ber. **114** (1981) 49;
    c) B. Frankhauter, H. Pritzkow, W. Siebert, Z. Naturforsch., **49b** (1994) 250.
[8] M. Tanaka, S. Onozawa, T. Sakakura, Y. Hatanaka, IMEBORON IX, Abstracts CB16, Heidelberg, 1996.
[9] I. Omae, Organotin Chemistry, Journal of Organometallic Chemistry Library 21, pp 167 - 187, Elsevier, Amsterdam (1989).
[10] C. Tamborski, F.E. Ford, E.J.Soloski, J. Org. Chem. 28 (1963) 237.
[11] H. Gilman, O.L. Marrs, S.-Y. Sim, J. Org. Chem. **27** (1962) 4232.
[12] T. Vladimiroff, E. R. Malinowski, J. Chem. Phys. **46** (1967) 1830.
[13] H. A. Bent, Chem. Rev. **61** (1961) 275.

Received: November 7, 1996 - Accepted: December 12, 1996 - Accepted in revised camera-ready format: December 20, 1996