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Alkylderivatives of Stanna-*closo*-dodecaborate

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Abstract

The reactions of $[SnB_{11}H_{11}]^{2-}$ with organic halides like 1-chloro-3-iodopropane, allylbromide, propargylbromide and 2,6-bis-(bromomethyl)pyridine lead in a nucleophilic substitution at room temperature to the products $[Bu_3MeN][Cl(CH_2)_3SnB_{11}H_{11}]$ (**4**), $[Bu_3MeN][H_2C{=}CH{-}CH_2{-}SnB_{11}H_{11}]$ (**6**), $[Bu_4N][HCC{-}CH_2SnB_{11}H_{11}]$ (**7**), and $[Bu_4N]_2[2,6\text{-}(H_{11}B_{11}Sn{-}CH_2)_2(C_5H_3N)]$ (**8**). In water $Na_2[SnB_{11}H_{11}]$ reacts with 2-bromoethylamine hydrobromide at 50 °C and 3-bromopropylamine hydrobromide at 70 °C to the zwitterionic products $[H_{11}B_{11}Sn{-}(CH_2)_nNH_3]$ ($n = 2$, 3), which were characterized by X-ray crystal structure analysis. $[H_{11}B_{11}Sn{-}(CH_2)_2NH_3]$ crystallizes with one equivalent of water under the formation of N–H–O hydrogen bonding. In the case of chloroiodomethane and diiodomethane the substitution reaction proceeds differently and the monosubstituted components were not detected. The disubstituted compound $[Bu_3MeN]_2[H_2C(SnB_{11}H_{11})_2]$ (**5**), whose structure could be confirmed by X-ray crystal structure analysis, is the only observed reaction product.

Keywords: Cluster; Boron; Tin; Nucleophilic substitution; Zwitterions; Hydrogen bridging

1. Introduction

The possibility to incorporate *closo*-heteroborane or borane clusters into organic compounds by simple nucleophilic substitution of a suitable leaving group against a Lewis-basic cluster skeleton is well known in the literature from the dicarba-*closo*-dodecaborane $[C_2B_{10}H_{12}]$ and carba-*closo*-dodecaborate $[CB_{11}H_{11}]^-$ [1,2]. Typically, in the first step a nucleophilic center has to be generated for example by metallation before the cluster reacts as a nucleophile. In the case of carboranes many ways of derivatization have been explored, especially to be able to synthesize new agents for BNCT or to get carborane substituted phosphines as a new kind of ligands in organometallic chemistry [3]. In 1992 Todd reported on the synthesis of dianionic icosahedral group-(IV)-*closo*-heteroborates of germanium, tin and lead with the general formula $[EB_{11}H_{11}]^{2-}$. In these clusters one negative charge is located at the incorporated heteroatom E as a lone-pair of electrons, and the other is delocalized inside the cluster skeleton [4]. Todd has demonstrated that the lone-pair at the heteroatom E = Ge and Sn reacts with methyliodide to give the methylated derivatives $[H_3C{-}EB_{11}H_{11}]^-$. The first organometallic derivatives of the dianionic stannaborate have been published in 1999. Transition metal complexes like $[CpFe(CO)_2(SnB_{11}H_{11})]^-$, $[(C_7H_7)Mo(CO)_2(SnB_{11}H_{11})]^-$ and $[CpNi(PPh_3)(SnB_{11}H_{11})]^-$ have been synthesized by reaction of $[SnB_{11}H_{11}]^{2-}$ with the respective organometallic halides [5]. In contrast to this behaviour the carboranyl–tin derivatives (i.e. 2,3-$(CH_3)_2$–1-Sn–2,3-$C_2B_9H_9$ and 2,3-$(Si(CH_3)_3)_2$–1-Sn–2,3-$C_2B_4H_4$) do not show any tendency to react as Lewis-bases [6]. Instead, these clusters are known to form adducts with Lewis-bases like bipyridine [6]. In this paper the substitution behaviour of *closo*-$[SnB_{11}H_{11}]^{2-}$ against organic halides is studied. In a simple nucleophilic substitution the halide should be replaced by the cluster to give anionic derivatives of the type $[R{-}SnB_{11}H_{11}]^-$, which might serve as starting materials for the synthesis of BNCT

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reagents or ligands carrying a weakly co-ordinating anion.

2. Results and discussion

The starting material $[SnB_{11}H_{11}]^{2-}$ was synthesized by an optimized procedure based on the way described by Todd and co-workers [4]. Generally, the nucleophile $[SnB_{11}H_{11}]^{2-}$ was reacted as the $[Bu_4N]^+$ or $[Bu_3MeN]^+$ salt with the respective organic halide in dichloromethane and the progress of the reaction was controlled by ^{11}B-NMR spectroscopy. In view of Todd's result that $[SnB_{11}H_{11}]^{2-}$ reacts as a nucleophile with methyliodide it was not surprising to us that the cluster dianion shows no reactivity towards alkylbromides at room temperature. In order to introduce the cluster into an organic reaction sequence obviously a good leaving group like iodide is necessary. Because of further organic transformations at the alkylchain we started our investigations by reacting the stannaborate with iodides like 1-chloro-3-iodopropane, diiodomethane and chloroiodomethane. The 1-chloro-3-iodopropane electrophile reacts in the desired manner and compound **4** was isolated in 80% yield after recrystallisation (Scheme 1).

In the case of CH_2I_2 and Cl–CH_2–I the substitution reaction proceeds differently. By reacting the halides H_2CXY (X = I,Y = Cl, I) and the stannaborate in a 1:1 stoichiometric ratio the disubstituted methane derivative **5** and half of an equivalent of unreacted dihalogenomethane were isolated (Scheme 2).

We are of the opinion that in both cases in the first step the iodine is substituted by one equivalent of the nucleophile. Presumably, the resulting intermediate $[Y–CH_2–SnB_{11}H_{11}]^-$ (Y = I, Cl), which was the desired reaction product, is more reactive than the starting material. The second substitution is much more preferred in comparison to the first substitution at another CH_2XY molecule. This is especially remarkable for the hypothetical intermediate $[Cl–CH_2–SnB_{11}H_{11}]^-$ because there is no other example known where a C–Cl bond is cleaved by the relatively weak nucleophile $[SnB_{11}H_{11}]^{2-}$. The cluster seems to have an activating influence on the carbon–halide bond in the anionic compounds $[X–CH_2–SnB_{11}H_{11}]^-$. Enhanced electrostatic repulsion of the anionic leaving group X^- in this intermediate might be the reason for this phenomenon.

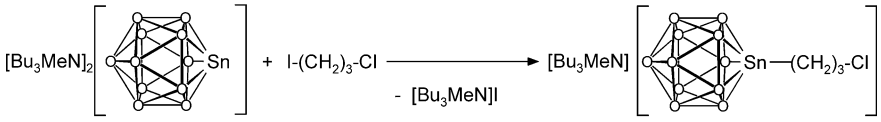
As expected by using the stoichiometric ratio of 1:2 of H_2CXY (X = I, Y = Cl, I) and $[SnB_{11}H_{11}]^{2-}$ only the disubstituted reaction product was isolated in 85% yield as colourless crystals, which are resistant towards air and moisture. After recrystallisation from dichloromethane–benzene we were able to isolate single crystals suitable for X-ray diffraction studies. Fig. 1 shows the ORTEP plot of the anion of **5**.

The observed Sn–B distances for both cluster skeletons are in the range of 2.286(5)–2.314(5) Å and are very similar to the analogous interatomic distances in $[CH_3–SnB_{11}H_{11}]^-$ [2.288(3)–2.306(3) Å] published in the literature [4]. The bond length Sn1–C1 [2.120(4) Å] and Sn2–C1 [2.109(5) Å] are nearly equal and also nearly the same like the C–Sn bond observed in the methylated stannaborate cluster [2.105(3) Å]. As expected the Sn1–C1–Sn2 angle is a bit enlarged [112.4(2)°] with respect to the idealized tetrahedral angle. A similar reaction behaviour of dihalogenated compounds reacting with $[SnB_{11}H_{11}]^{2-}$ in the ratio of 1:1 was found by treating the co-ordination compounds of the type L_2PtCl_2 with one equivalent of the stannaborate cluster [5b].

Besides dihalogenated alkanes activated halides like allylbromide, propargylbromide and 2,6-bis-(bromomethyl)pyridine were successfully reacted with the borate nucleophile. Because of the linkage to a weakly coordinating anion, these molecules are interesting ligands in co-ordination chemistry. The reactions of the unsaturated halogenides with one equivalent of $[SnB_{11}H_{11}]^{2-}$ yielded in almost quantitative isolation of compounds **6**, **7** and **8**. After purification by washing with water up to 91% yield of these salts were isolated as a colourless crystalline material (Scheme 3).

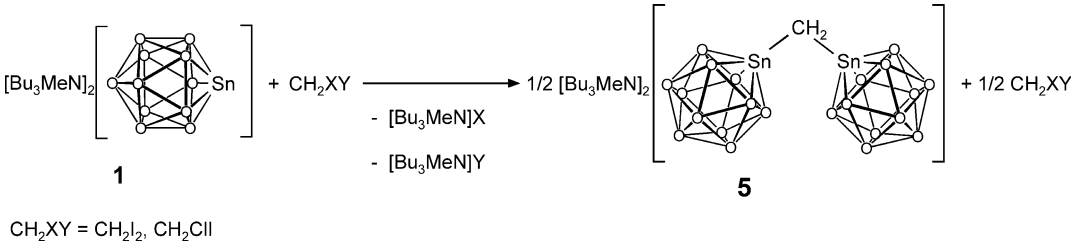
In order to link the *closo*-borate with a primary amine we reacted the nucleophile **1** as the sodium salt with the water soluble bromides 2-bromoethylamine hydrobromide and 3-bromopropylamine hydrobromide. Both electrophiles show no reaction with the tin reagent at room temperature. However, at 50 °C the reaction starts and slowly the water insoluble product precipitates out of solution (Scheme 4).

After stirring overnight under heating both derivatives **9** (50 °C) and **10** (70 °C) were obtained as zwitterionic molecules in high yield. The structure of these polar molecules was determined in the solid state by X-ray single crystal structure analysis and in Figs. 2 and 3 an ORTEP plot of the molecules is depicted. The



1 **4**

Scheme 1.



Scheme 2.

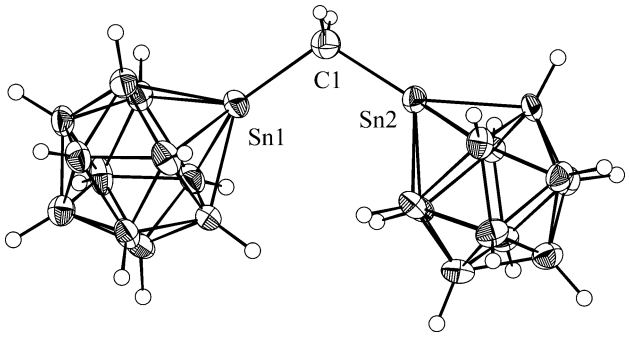


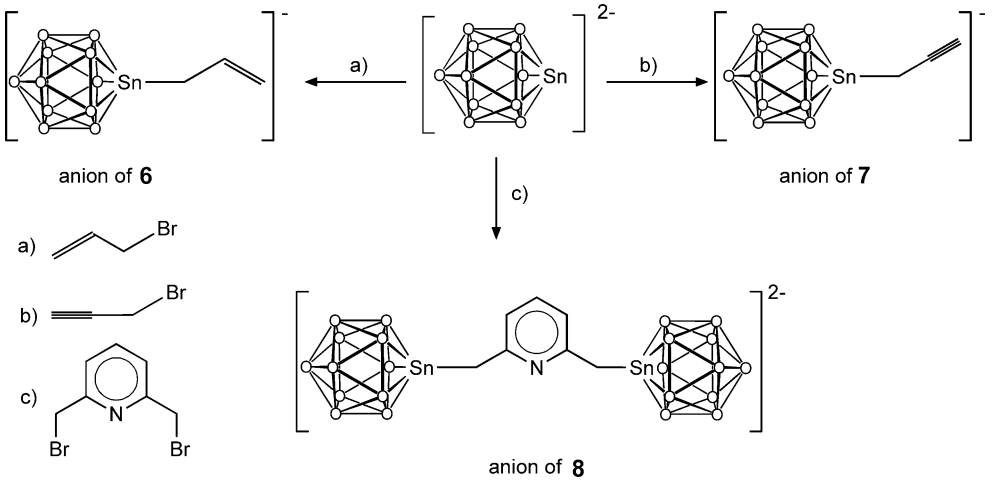
Fig. 1. ORTEP plot of the anion of **5**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms (except at C1) are omitted for the sake of clarity. Selected interatomic distances (Å), angles (°): Sn1–C1 2.120(4), Sn2–C1 2.109(5), Sn1–C1–Sn2 112.4(2).

interatomic distances and angles of both molecules exhibit no peculiarities. Interestingly, the derivative **9** crystallizes with one equivalent of water. All protons in the structure of **9**·H_2O were found and in Fig. 2 the hydrogen bonds between the water molecules and the alkylammonium groups are shown. Recently, Steiner has published a very helpful overview on hydrogen bonding in the solid state [7]. On the basis of studies on the solid state structure the hydrogen bonds are classified into three groups of different bond strength. According to these statistical data the found H-bridges in **9**·H_2O range in the group of intermediate bond strength. Furthermore, the bond distances of the hydrogen bridges described in this publication are in the range of 95% of 370 examples discussed in the literature.

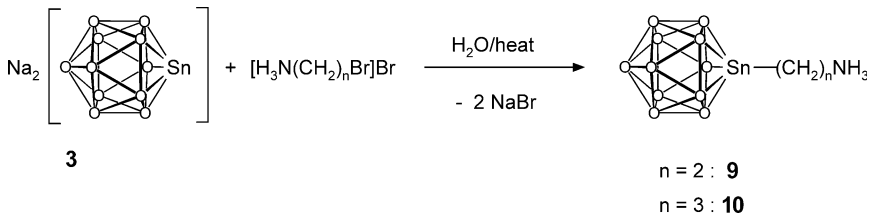
The propyl derivative **10** cyrstallizes in the monoclinic space group $P2_1/m$ and lies on the mirror plane. In Fig. 4, the arrangement of these dipoles in the solid state is shown.

3. Conclusion

The stanna-*closo*-dodecaborate dianion is a strong enough nucleophile to react quantitatively with alkyliodides and activated alkylbromides like allylbromide and propagylbromide. By increasing the reaction temperature two less reactive alkylbromides $[Br(CH_2)_nNH_3]Br$ ($n = 2$, 3) are straightforwardly substituted. In the case of diiodomethane and chloroiodomethane the monosubstitution is not possible. Here the first stannaborate substituent activates even an alkylchloride bond for substitution.



Scheme 3.



Scheme 4.

4. Experimental

4.1. General methods

All manipulations were carried out under dry N_2 in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under N_2. — NMR Bruker AC 200 (^{1}H: 200 MHz, int. Me_4Si; $^{13}C\{^1H\}$: 50 MHz, int. Me_4Si; $^{11}B\{^1H\}$: 64 MHz, ext. $BF_3\cdot Et_2O$) — Elemental analysis: Institut für Anorganische Chemie der Universität zu Köln, Heraeus C,H,N,O-Rapid elemental analyzer. Alkylhalogenides were purchased from Aldrich. $[Bu_3MeN]_2[SnB_{11}H_{11}]$ (**1**), $[Bu_4N]_2[SnB_{11}H_{11}]$ (**2**) and $Na_2[SnB_{11}H_{11}]$ (**3**): the cluster was synthesized following a modification of Todd's procedure; the Na salt was generated via the $[Bu_3NH]$ salt. The $[Bu_3NH]$ cation was replaced by Na in reaction with NaH.

4.2. Preparation of *[Bu$_3$MeN][Cl–C$_3$H$_6$–SnB$_{11}$H$_{11}$]* (*4*)

1-Chloro-3-iodopropane (0.41 g, $M = 204.44$ g mol^{-1}, 2.00 mmol, 0.22 mL) was added to a solution of 1.29 g ($M = 649.48$ g mol^{-1}, 1.99 mmol) $[Bu_3MeN]_2[SnB_{11}H_{11}]$ (**1**) in 30 mL CH_2Cl_2 at room temperature (r.t.). After stirring for 12 h all volatiles were removed in vacuum and the residue was washed properly with water. The colourless product was isolated by filtration and after drying in vacuum the product was recrystallized from CH_2Cl_2 by diffusion of C_6H_{14} at +8 °C to give 0.84 g (80% yield) of **4**. — ^{1}H-NMR (C_3H_6O-d_6): $\delta = 0.98$ (t, 9H, $^3J = 7.3$ Hz, $-CH_2-CH_3$), 1.42 (m, 6H, $-CH_2-CH_2-CH_3$), 1.84 (m, 6H, $-CH_2-CH_2-CH_2-$), 2.46 (m, 2H, $^3J_{H-Sn} = 127$ Hz, $Sn-CH_2-CH_2-CH_2-$), 2.78 (t, 2H, $^3J = 7.3$, $^2J_{H-Sn} = 84$ Hz, $Sn-CH_2-CH_2-$), 3.21 (s, 3H, $-N-CH_3$), 3.45 (m, 6H, $-N-CH_2-CH_2-$), 3.88 (t, 2H, $^3J = 6.4$, $^4J_{H-Sn} = 323$ Hz, $-CH_2-CH_2-Cl$). — $^{11}B\{^1H\}$-NMR (C_3H_6O-d_6): $\delta = -11.5$ (s, B12), -16.6 (s, B7/B8/B9/B10/B11), -17.1 (s, B2/B3/B4/B5/B6). — $^{13}C\{^1H\}$-NMR (C_3H_6O-d_6): $\delta = 11.4$ (s, $Sn-CH_2-CH_2-$), 13.8 (s, $-CH_2-CH_3$), 20.3 (s, $-CH_2-CH_2-CH_3$), 24.8 (s, $-CH_2-CH_2-CH_2-$), 31.8 (s, $^2J_{C-Sn} = 41.7$ Hz, $Sn-CH_2-CH_2-CH_2-Cl$), 47.3 (s, $^3J_{C-Sn} = 91.5$ Hz, $-CH_2-CH_2-Cl$), 48.9 (s, $N-CH_3$), 62.5 (s, $N-CH_2-CH_2-$). — Anal. Calc. for $C_{16}H_{47}B_{11}ClNSn$ (526.6): C, 36.49; H, 8.99; N, 2.66. Found: C, 36.13; H, 8.81; N, 2.60%.

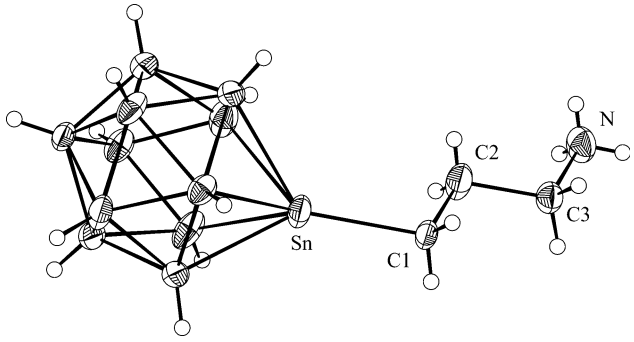


Fig. 3. ORTEP plot of **10**. Thermal ellipsoids are drawn at 50% probability level. Selected interatomic distances (Å): Sn–C1 2.119(4), C1–C2 1.513(6), C2–C3 1.511(5), C3–N 1.497(5).

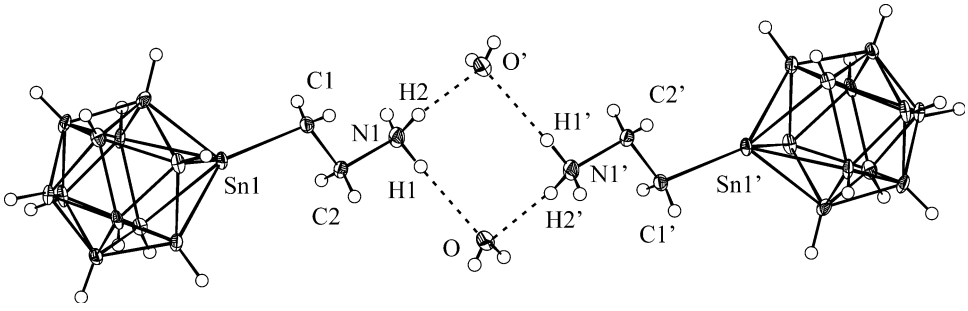


Fig. 2. ORTEP plot of $\mathbf{9}\cdot H_2O$. Thermal ellipsoids are drawn at 50% probability level. Selected interatomic distances (Å), angles (°): Sn1–C1 2140(4), C1–C2 1.496(6), C2–N1 1.503(5), N1–H1 0.93(6), H1–O 2.02(5), O–H2′ 2.13(5), H2–N1 0.86(6), N1–O 2.892(5), N1′–O 2.974(5), O–H1–N1 157(1), O–H2′–N1′ 170(1).

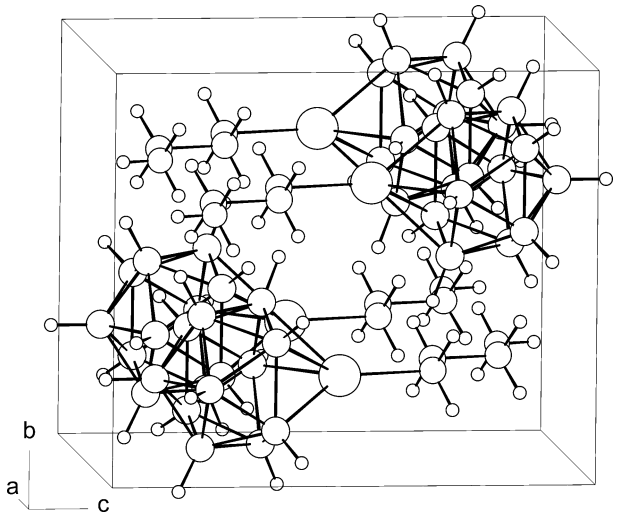


Fig. 4. Perspective view of the arrangement of **10** in the cell along axis *a*.

4.3. Preparation of $[Bu_3MeN]_2[CH_2(SnB_{11}H_{11})_2]$ (5)

At r.t. 0.39 g ($M = 267.83$ g mol^{-1}, 1.46 mmol, 0.12 mL) CH_2I_2 were added to a solution of 1.89 g (649.48 g mol^{-1}, 2.91 mmol) $[Bu_3NMe]_2[SnB_{11}H_{11}]$ (**1**) in 20 mL CH_2Cl_2. After stirring for 12 h, the mixture was evaporated in vacuum and the waxy residue was properly treated with water to remove the $[Bu_3NMe]I$. The resulting powder was dried in vacuum and recrystallized from CH_2Cl_2 by diffusion of C_6H_6 at +8 °C to give 1.13 g (85% yield) of **5**. — ^{1}H-NMR (C_3H_6O-d_6): $\delta = 0.98$ (t, 18H, $^3J = 7.3$ Hz, $-CH_2-CH_3$), 1.43 (m, 12H, $^3J = 7.3$ Hz, $-CH_2-CH_2-CH_3$), 1.84 (m, 12H, $-CH_2-CH_2-CH_2-$), 2.96 (s, 2H, $Sn-CH_2-Sn$, $^2J_{H-Sn} = 80$ Hz), 3.21 (s, 6H, $-N-CH_3$), 3.45 (m, 12H, $-N-CH_2-CH_2-$). — ^{11}B{^{1}H}-NMR (C_3H_6O-d_6): $\delta = -12.5$ (s, B12), −16.9 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). — ^{13}C{^{1}H}-NMR (C_3H_6O-d_6): $\delta = -20.6$ (s, $Sn-CH_2-Sn$), 13.9 (s, $-CH_2-CH_3$), 20.4 (s, $-CH_2-CH_2-CH_3$), 24.8 (s, $-CH_2-CH_2-CH_2-$), 49.0 (s, $N-CH_3$), 62.4 (s, $N-CH_2-CH_2-$). — Anal. Calc. for $C_{27}H_{84}B_{22}N_2Sn_2$ (912.3): C, 35.55; H, 9.28; N, 3.07. Found: C, 35.40; H, 9.31; N, 3.13%.

4.4. Preparation of $[Bu_3MeN][H_2C{=}CH-CH_2-SnB_{11}H_{11}]$ (6)

At r.t. 1.04 g (M = 649.48 g mol^{-1}, 1.60 mmol) $[Bu_3MeN]_2[SnB_{11}H_{11}]$ (**1**) were dissolved in 20 mL of dichloromethane and 1.60 mmol allylbromide were added. After stirring overnight all volatiles were removed and the residue was treated with water to remove the $[Bu_3MeN]Br$. The resulting powder was washed with water and Et_2O before drying in vacuum. Recrystallization from CH_2Cl_2 by slow diffusion of C_6H_{14} at +8 °C yielded in 0.72 g (91% yield) of **6**. — ^{1}H-NMR (CD_2Cl_2): $\delta = 1.02$ (t, 9H, $^3J = 7.3$ Hz, $-CH_2-CH_3$), 1.43 (m, 6H, $^3J = 7.3$ Hz, $-CH_2-CH_2-CH_3$), 1.67 (m, 6H, $-CH_2-CH_2-CH_2-$), 3.02 (s, 3H, $-N-CH_3$), 3.18 (m, 6H, $-N-CH_2-CH_2-$), 3.43 (d, 2H, $^3J = 7.9$, $^2J_{H-Sn} = 110$ Hz, $Sn-CH_2-CH{=}CH_2$), 5.14 (d, 1H, $^3J = 10.1$ Hz, $-CH{=}CH_2$ (in *trans* position to $Sn-CH_2$)), 5.40 (d, 1H, $^3J = 16.8$ Hz, $-CH{=}CH_2$ (in *cis* position to $Sn-CH_2$)), 6.20 (m, 1H, $-CH_2-CH{=}CH_2$). — ^{11}B{^{1}H}-NMR (CD_2Cl_2): $\delta = -12.3$ (s, B12), −16.9 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). — ^{13}C{^{1}H}-NMR (CD_2Cl_2): $\delta = 13.7$ (s, $-CH_2-CH_3$), 19.2 (s, $Sn-CH_2-CH{=}CH_2$), 20.0 (s, $-CH_2-CH_2-CH_3$), 24.7 (s, $-CH_2-CH_2-CH_2-$), 49.4 (s, $N-CH_3$), 62.5 (s, $N-CH_2-CH_2-$), 117.6 (s, $-CH{=}CH_2$), 133.0 (s, $Sn-CH_2-CH{=}CH_2$). — Anal. Calc. for $C_{16}H_{46}B_{11}NSn$ (490.2): C, 39.21; H, 9.46; N, 2.86. Found: C, 38.52; H, 9.16; N, 2.66%.

4.5. Preparation of $[Bu_4N][HC{\equiv}C-CH_2-SnB_{11}H_{11}]$ (7)

At r.t. 0.53 g ($M = 733.80$ g mol^{-1}, 0.72 mmol) $[Bu_4N]_2[SnB_{11}H_{11}]$ (**2**) were dissolved in 20 mL of CH_2Cl_2 and 0.09 g ($M = 119.10$ g mol^{-1}, 0.71 mmol, 0.08 mL 80% solution in $C_6H_5CH_3$) propargylbromide were added. After stirring overnight all volatiles were removed and the residue was treated with water to remove the $[Bu_4N]Br$. The resulting powder was washed twice with water and finally with Et_2O before drying in vacuum. Recrystallization from CH_2Cl_2 by slow diffusion of C_6H_{14} at +8 °C resulted in the isolation of 0.35 g (91% yield) of **7**. — ^{1}H-NMR (CD_2Cl_2): $\delta = 1.02$ (t, 12H, $^3J = 7.3$ Hz, $-CH_2-CH_3$), 1.44 (m, 8H, $^3J = 7.3$ Hz, $-CH_2-CH_2-CH_3$), 1.62 (m, 8H, $-CH_2-CH_2-CH_2-$), 3.20 (s, 8H, $-N-CH_2-CH_2-$), 4.89 (d, 2H, $^4J = 6.7$, $^2J_{H-Sn} = 90$ Hz, $Sn-CH_2-C$), 5.78 (t, 1H, $^4J = 6.7$, $^4J_{H-Sn} = 57$ Hz, $-CH_2-C{\equiv}C-H$). — ^{11}B{^{1}H}-NMR (CD_2Cl_2): $\delta = -12.9$ (s, B12), −17.3 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). — ^{13}C{^{1}H}-NMR (CD_2Cl_2): $\delta = 13.7$ (s, $-CH_2-CH_3$), 20.1 (s, $-CH_2-CH_2-CH_3$), 24.3 (s, $-CH_2-CH_2-CH_2-$), 59.4 (s, $N-CH_2-CH_2-$), 66.1 (s, $-C{\equiv}C-H$), 71.0 (s, $Sn-CH_2-C$), 214.5 (s, $-CH_2-C{\equiv}C-$). — Anal. Calc. for $C_{19}H_{50}B_{11}NSn$ (530.2): C, 43.04; H, 9.50; N, 2.64. Found: C, 43.81; H, 9.52; N, 2.40%.

4.6. Preparation of $[Bu_4N]_2[2,6\text{-}(H_{11}B_{11}Sn-CH_2)_2(C_5H_3N)]$ (8)

To a solution of 0.61 g (733.80 g mol^{-1}, 0.84 mmol) $[Bu_4N]_2[SnB_{11}H_{11}]$ (**2**) in 20 mL CH_2Cl_2 0.11 g ($M =$ 265.00 g mol^{-1}, 0.42 mmol) 2,6-bis-(bromomethyl)pyridine dissolved in 10 mL CH_2Cl_2 were added at r.t. After stirring overnight, the mixture was evaporated in vacuum and the white waxy residue was properly treated

Table 1
Crystal data and structure refinement parameters for **5**, **9**, and **10**

	5	**9**	**10**
Empirical formula	$C_{27}H_{84}B_{22}N_2Sn_2$	$C_2H_{20}B_{11}NOSn$	$C_3H_{20}B_{11}NSn$
Temperature (K)	170(2)	170(2)	170(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)	$P2_1/m$ (No. 11)
a (pm)	1519.9(2)	1023.8(2)	703.2(1)
b (pm)	2178.0(3)	1125.9(1)	898.2(1)
c (pm)	1570.9(2)	1139.5(2)	1039.1(2)
β (°)	110.52(2)	102.27(2)	93.91(1)
V (nm^3)	4.8702(9)	1.2834(3)	0.6548(2)
Z	4	4	2
M (g mol^{-1})	912.16	311.79	307.80
ρ_{calc} (g cm^{-3})	1.244	1.614	1.561
μ (mm^{-1})	1.049	1.954	1.909
Absorption correction	Numerical	Numerical	Numerical
$F(000)$	1880	608	300
θ Range (°)	1.86–24.16	1.83–24.13	1.96–29.49
Index range	$-17 \le h \le 17$, $-25 \le k \le 25$, $-17 \le l \le 17$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-13 \le l \le 13$	$-9 \le h \le 9$, $-12 \le k \le 11$, $-14 \le l \le 14$
Diffractometer	STOE *I*mage *P*late *D*iffraction *S*ystem		
Radiation	Mo–K_α (graphite monochromator, $\lambda = 71.073$ pm)		
Total data collected	38 595	9959	12 222
Unique data	7355	2015	1920
Observed data	5772	1724	1650
Max/min transmission	0.8037/0.9237	0.4342/0.7211	0.6602/0.8047
Variables	480	225	130
R_{merg}	0.0483	0.1101	0.0721
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0414$, $wR_2 = 0.0974$	$R_1 = 0.0279$, $wR_2 = 0.0693$	$R_1 = 0.0312$, $wR_2 = 0.0673$
R indexes (all data)	$R_1 = 0.0554$, $wR_2 = 0.1026$	$R_1 = 0.0346$, $wR_2 = 0.0717$	$R_1 = 0.0402$, $wR_2 = 0.0701$
Goodness-of-fit (S_{obs})	1.109	1.062	1.087
Goodness-of-fit (S_{all})	1.024	1.005	1.044
Largest difference map hole/peak [e 10^{-6} pm^{-3}]	−0.636/2.380	−0.931/0.533	−1.244/1.159

$R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma\ |F_o|$, $wR_2 = [\Sigma\ w(|F_o|^2 - |F_c|^2)^2/\Sigma\ w(|F_o|^2)^2]^{1/2}$, $S_2 = [\Sigma\ w(|F_o|^2 - |F_c|^2)^2/(n-p)]^{1/2}$, with $w = 1/[\sigma^2(F_o)^2 + (0.0576P)^2 + 6.0770P]$ for **5**, $w = 1/[\sigma^2(F_o)^2 + (0.0362P)^2]$ for **9** and $w = 1/[\sigma^2(F_o)^2 + (0.0341P)^2 + 0.5039P]$ for **10** were $P = (F_o^2 + 2F_c^2)/3$. $F_c^* = kF_c[1 + 0.001|F_c|^2\lambda^3/\sin(2\theta)]^{-1/4}$.

with water to remove the [Bu_4N]Br. The resulting powder was dried in vacuum and recrystallized from CH_2Cl_2 by diffusion of C_6H_6 at +8 °C to give 0.37 g (80% yield) of **8**. — ^{1}H-NMR (CD_2Cl_2): $\delta = 1.00$ (t, 12H, $^3J = 7.3$ Hz, –CH_2–CH_3), 1.42 (m, 8H, $^3J = 7.3$ Hz, –CH_2–CH_2–CH_3), 1.62 (m, 8H, –CH_2–CH_2–CH_2–), 3.20 (s, 8H, –N–CH_2–CH_2–), 4.16 (s, 4H, C2/6–CH_2–Sn), 7.31 (q, 2H, C3/5-*H*), 7.66 (m, 1H, C4–*H*). — ^{11}B{^{1}H}-NMR (CD_2Cl_2): $\delta = -12.9$ (s, B12), −17.1 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). — ^{13}C{^{1}H}-NMR (CD_2Cl_2): $\delta = 13.8$ (s, –CH_2–CH_3), 20.1 (s, –CH_2–CH_2–CH_3), 24.3 (s, –CH_2–CH_2–CH_2–), 26.0 (s, C2/6–CH_2–), 59.4 (s, N–CH_2–CH_2–), 120.7 (s, *C*3/5–H), 138.6 (s, *C*4–H), 120.7 (s, *C*3/5–H). — Anal. Calc. for $C_{39}H_{101}B_{22}N_3Sn_2$ (1087.5): C, 43.07; H, 9.36; N, 3.86. Found: C, 42.87; H, 9.44; N, 3.82%.

4.7. Preparation of [H_3N–$(CH_2)_2$–$SnB_{11}H_{11}$] (**9**)

$Na_2[SnB_{11}H_{11}]$ (**3**) (0.91 g, $M = 294.70$ g mol^{-1}, 3.07 mmol) was dissolved in 20 mL of water and added to a water solution of 0.63 g ($M = 204.90$ g mol^{-1}, 3.08 mmol) 2-bromoethylamine hydrobromide. After a reaction time of 24 h at 50 °C the heating bath was removed and upon cooling to r.t. colourless crystals started to grow. The crystals were collected by filtration and washed with water. Drying in high vacuum resulted in the isolation of 0.51 g (53% yield) of **9**. — ^{1}H-NMR (CD_3CN): $\delta = 2.72$ (t, 2H, –CH_2–$SnB_{11}H_{11}$), 3.52 (t, 2H, H_3N–CH_2–). — ^{11}B{^{1}H}-NMR (CD_3CN): $\delta = -11.9$ (s, B12), −17.0 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). — Anal. Calc. for $C_2H_{20}B_{11}NOSn$ (311.817): C, 7.70; H, 6.46; N, 4.49. Found: C, 7.96; H, 6.50; N, 4.29%.

4.8. Preparation of $[H_3N{-}(CH_2)_3{-}SnB_{11}H_{11}]$ (10)

A solution of 1.15 g ($M = 294.70$ g mol^{-1}, 3.90 mmol) $Na_2SnB_{11}H_{11}$ in 30 mL water was added to 30 mL of a water solution of 0.89 g ($M = 218.93$ g mol^{-1}, 4.07 mmol) 3-bromopropylamine hydrobromide. After stirring for 24 h stirring at 70 °C the heating bath is removed and upon cooling to r.t. without stirring the formation of colourless crystals starts immediately. Washing of the crystalline material with water and subsequent drying in high vacuum led to isolation of 0.71 g (59% yield) of **10**. — ^{1}H-NMR (C_3H_6O-d_6): $\delta = 2.56$ (m, 2H, $-CH_2-CH_2-SnB_{11}H_{11}$), 2.78 (t, 2H, $-CH_2-SnB_{11}H_{11}$), 3.57 (t, 2H, H_3N-CH_2-). — ^{11}B{^{1}H}-NMR (C_3H_6O-d_6): $\delta = -11.1$ (s, B12), −16.9 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). — Anal. Calc. for $C_3H_{20}B_{11}NSn$ (307.817): C, 11.79; H, 6.61; N, 4.50. Found: C, 11.71; H, 6.55; N, 4.55%.

4.9. X-ray crystal structure determination of 5, 9 and 10

A suitable single crystal of each compound was carefully selected under a polarizing microscope and mounted in a glass capillary. The scattering intensities were collected by an imaging plate diffractometer (IPDSI/IPDSII, STOE & CIE) equipped with a normal focus, 1.75 kW, sealed tube X-ray source (Mo–K_α, $\lambda = 0.71073$ Å) operating at 50 kV and 35 mA. Intensity data for **5** and **9** were collected at 170 K by ψ-scans in 125 frames ($0 \le \psi \le 250°$, $\Delta\psi = 2°$, exposure time of 4 min) in the 2θ range of 2.9–48.4°. Intensity data for **10** were collected at 170 K in 180 frames with ω-scans ($0 \le \omega \le 180°$; $\psi = 0°$, $0 \le \omega \le 180°$; $\psi = 90°$, $\Delta\omega = 2°$, exposure time of 3 min) in the 2θ range of 2.3–59.5°. Structure solution and refinement were carried out using the programs SHELXS-97 [8] and SHELXL-93 [9]. The H atom positions for **9** and **10** were taken from the difference Fourier card at the end of the refinement. The hydrogen atoms in **5** were placed geometrically and held in the riding mode. A numerical absorption correction was applied after optimization of the crystal shape (X-RED [10] and X-SHAPE [11]). The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Details of the refinements are given in Table 1.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 187397–187399 for compounds **5**, **9** and **10**. Copies of the data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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