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B–N bond formation at stanna-*closo*-dodecaborate†

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The heteroborate stanna-*closo*-dodecaborate shows double substitution in the reaction with alkylated acetonitrile. The reaction product, the charge compensated *E*,*E*-isomer, was isomerized into the *Z*,*Z*-isomer and hydrogenated at the double bonds. Furthermore the methylated cluster shows less reactivity and the monosubstituted cluster was isolated. The reaction products were characterized by elemental analysis and NMR spectroscopy. Three of the substitution products were also characterized by single crystal structure analysis.

Introduction

In borane and heteroborane cluster chemistry the research is focused on reactions changing the cluster skeleton or derivatizing the cluster sphere.[1–4] The reactivity at the BH-units of the cluster can be compared with reactions of C–H-units in unsaturated organic molecules like benzene. A large variety of different elements like halides, oxygen, sulphur, nitrogen, phosphorus and carbon can be placed by substitution reactions at the borane cluster.[1,5–25] In 1964 the amination of *closo*-borates $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ with hydroxylamine-*o*-sulfonic acid was published.[26] The product of this reaction with *closo*-dodecaborate, the ammonioundecahydro-*closo*-dodecaborate(1–), is a versatile starting material for many applications of boron cluster derivatives.[27,28] Furthermore the reaction of Lewis bases like ammonia or other nitrogen donors with boranes is another possibility for the formation of a B–N bond at a borane cluster.[29–31] Protonated *closo*-borates like $[B_{10}H_{11}]^{-}$ were reacted with nitriles to give in high yield the borylated nitrile exhibiting a B–N bond.[32] Aminocarboranes were synthesized by a cluster closure reaction of *nido*-carboranes with aminodichloroborane.[33] Furthermore a successful approach to the field of aminocarboranes was published with the palladium catalyzed Buchwald–Hartwig amidation starting with iodo-carboranes.[34,35] Stone and co-workers have found a hydroboration reaction of alkylnitrilium salts. Transition metal complexes of the monocarbollide and dicarbollide ligands react with a mixture of acetonitrile and CF_3SO_3Me to give the hydroboration product with the N(Me)=C(H)Me group connected *via* the nitrogen atom at the boron cluster.[36–39]

We are investigating the chemistry of group 14 heteroboranes and especially of the mono- and di-hetero-*closo*-dodecaborates of germanium and tin.[40–52] In the last few years we have published our results on the coordination properties of the germanium and tin ligands $[GeB_{11}H_{11}]^{2-}$, $[SnB_{11}H_{11}]^{2-}$ and $[Sn_2B_{10}H_{10}]^{2-}$. In this publication we present the first substitution reaction at the BH-units of stanna-*closo*-dodecaborate $[SnB_{11}H_{11}]^{2-}$.

Results and discussion

Synthesis

The nucleophilic stanna-*closo*-dodecaborate cluster was reacted with *in situ* generated alkylated acetonitrile $[MeC{\equiv}NEt]^{+}$ (Scheme 1).

Two cations react with two BH-units of the upper boron belt of the dianionic heteroborate to give a charge compensated molecule **2**. Although the tin vertex has shown its high nucleophilicity in many reactions no indications for a reaction at the tin atom are found with the *N*-ethylnitrilium cation. In contrast to the work of Stone *et al.*, who exclusively obtained monosubstitution at the cluster sphere in the reaction of metallacarboranes even with an excess of alkylated nitrile $[Me–C{\equiv}N–R]^{+}$, stanna-*closo*-dodecaborate shows a higher reactivity and forms two exopolyhedral B–N bonds. This reaction is stereoselective since we only isolated one stereoisomer with *E* geometry at the double bonds in high yield. In the case of metallacarboranes both isomers, the *E* and *Z* product, were isolated as a mixture. Assuming the pathway of Stone *et al.* which includes hydride abstraction leading to generation of free imine, the exclusive formation of the sterically more demanding *E* isomer can be rationalized since the corresponding free imine is thermodynamically more stable.[53–55] The disubstituted product **2** was characterized by elemental analysis, NMR spectroscopy and single crystal structure analysis. The *E* isomer was transformed into the sterically less demanding

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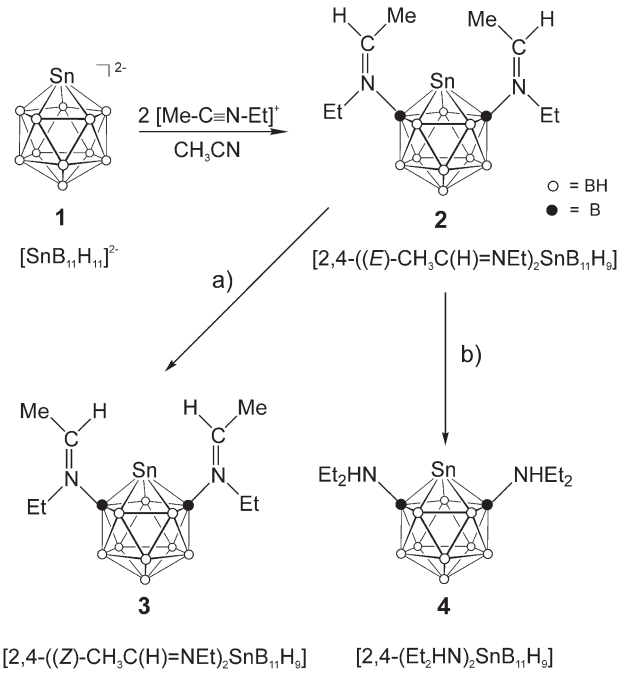
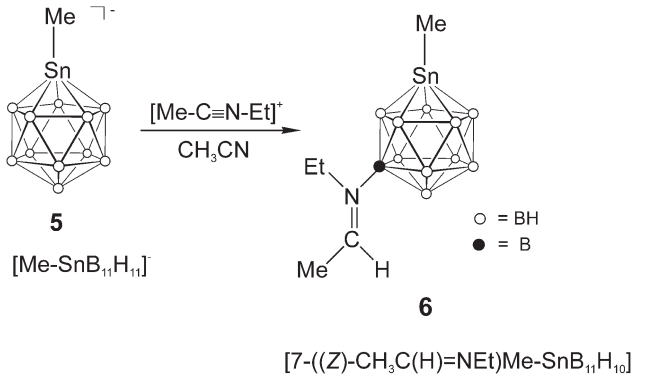


Scheme 1 Reaction of $[SnB_{11}H_{11}]^{2-}$ with $[Me–C{\equiv}N–Et]^{+}$, isomerization and hydrogenation of the disubstitution product. (a) THF, H_2O, PMe_3 stirring overnight; (b) $NaBH_4$, ethanol, stirring overnight.



Scheme 2 Reaction of the methylated stanna-*closo*-dodecaborate with $[Me–C{\equiv}N–Et]^{+}$.

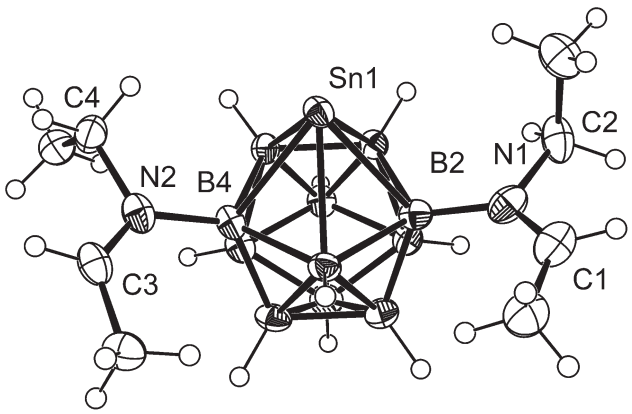


Fig. 1 ORTEP plot of the molecular structure of 2,4-bis-((*E*)-*N*-ethylideneethylamino)-stanna-*closo*-dodecaborane (**2**). Ellipsoids at 50% probability, interatomic distances [Å] and bond angles [°]: Sn1–B2 2.410(5), Sn1–B3 2.421(5), Sn1–B4 2.418(5), Sn1–B5 2.405(4), Sn1–B6 2.410(5), N2–C3 1.266(6), N2–C4 1.529(6), N2–B4 1.535(6), N1–C1 1.268(6), N1–C2 1.529(6), N1–B2 1.568(6), N2–B4–Sn1 112.8(3), N1–B1–Sn1 107.7(3), C3–N2–C4 111.5(4), C3–N2–B4 131.5(4), C4–N2–B4 117.0(4), C2–N1–C1 114.4(4), C1–N1–B2 128.5(4), C2–N1–B2 117.0(3).

Z isomer in the reaction with PMe_3. The isomerization is quantitative on the basis of NMR spectroscopy. No equilibrium between **2** and **3** is observed and no back reaction takes place. However, only 12.5% of the product **3** were isolated after column chromatography. The stereochemistry of compound **3** was determined by two dimensional NMR experiments including $^{1}H–^{13}C\{^{1}H\}$ HSQC and $^{1}H–^{1}H$ NOESY. Hydrogenation of the diiminium substituted product **2** was carried out by stirring with sodium tetrahydroborate in ethanol over the course of 24 h (Scheme 1). In product **4** the cluster is substituted by two diethylamino groups. Compound **4** was characterized by single crystal structure analysis, elemental analysis and NMR spectroscopy.

In order to study the influence of an alkylation at the tin vertex we reacted the methylated stanna-*closo*-dodecaborate **5** with the *N*-ethylnitrilium salt. After stirring at room temperature for three days the reaction product **6** was isolated in moderate yield (Scheme 2). The product was characterized by single crystal structure analysis, elemental analysis and NMR spectroscopy.

In contrast to the free stanna-*closo*-dodecaborate the methylated cluster shows a higher reactivity of the BH-units at the lower boron belt. This behaviour can be rationalized by the electron withdrawing effect of the methyl group attached to the tin vertex[56] which is directing the substitution to the "*meta*" position of the cluster. Since the tin atom shows a signal typical for tin(IV) in the Mössbauer spectrum after methylation, the cluster loses electron density especially at the tin vertex.[57,58] This presumably also renders the hydrogen atoms of the upper boron belt less ready for hydride abstraction by the nitrilium cation ultimately leading to reaction at the lower boron belt. Furthermore it is interesting to note that in the case of the methylated stanna-*closo*-dodecaborate only the sterically less hindered *Z* isomer is formed, suggesting either a mechanism which does not include formation of the free imine or a much faster isomerization reaction.

Solid-state structures

In Fig. 1–3 the structures of the substitution products **2**, **4**, **6** together with selected distances and angles are presented. Details of the crystal and structure refinement parameters are listed in Table 1. The interatomic distances between the cluster atoms are in the range known from other stanna-*closo*-dodecaborate structures.[40,44,58,59] The B–N bond lengths are common in a variety of nitrogen substituted borane clusters and the C–N bond lengths are in consistency with the double bond character in **2** and **6** and the single bonds in the hydrogenation product **4**.[30,32,36–39] The B–B distances in the clusters do not significantly change due to introduction of

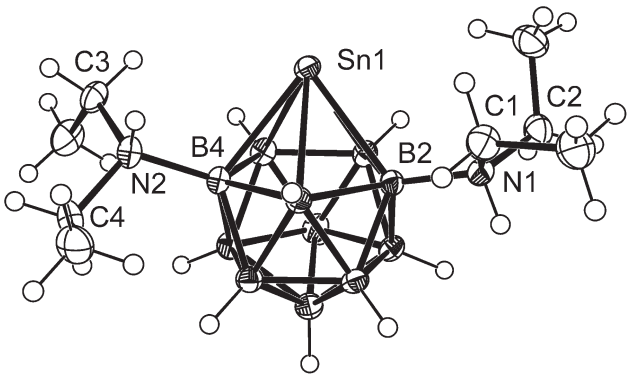


Fig. 2 ORTEP plot of the molecular structure of 2,4-bis-(diethylamino)-stanna-*closo*-dodecaborane (**4**). Ellipsoids at 50% probability, interatomic distances [Å] and bond angles [°]: Sn1–B2 2.396(2), B3–Sn1 2.413(2), B4–Sn1 2.420(2), B5–Sn1 2.407(2), Sn1–B6 2.405(2), B4–N2 1.605(3), N1–B2 1.593(3), N2–C3 1.5101 (3), N2–C4 1.513(4), N1–C1 1.495(3), N1–C2 1.507(3), N2–B4–Sn1 108.1(1), N1–B2–Sn1 116.2(1).

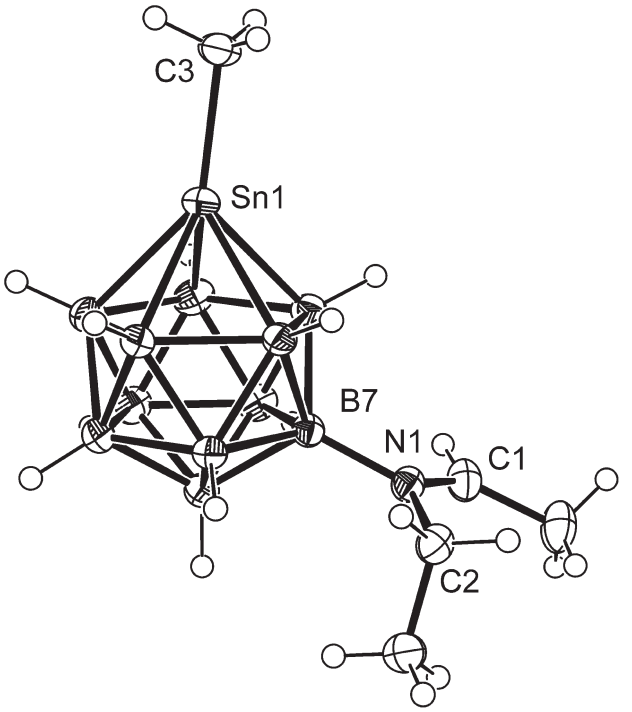


Fig. 3 ORTEP plot of the molecular structure of 7-((*Z*)-*N*-ethylideneethylamino)-1-(methyl)-stanna-*closo*-dodecaborane (**6**). Ellipsoids at 50% probability, interatomic distances [Å] and bond angles [°]: N1–C1 1.282(2), N1–C2 1.486(2), N1–B7 1.557(2), Sn1–B2 2.291(2), Sn1–B6 2.292(2), Sn1–B5 2.294(2), Sn1–B4 2.297(2), Sn1–B3 2.301(2), C3–Sn1 2.100(2), C2–N1–B7 121.0(2), C1–N1–B7 118.3(1), N1–B7–B2 117.3(1), N1–B7–B3 118.8(1).

substituents. However, slightly increased values are observed for the Sn to upper B_5 belt distances in the case of the substituted clusters **2** and **4**.

NMR spectroscopy

The molecular structures of the charge compensated clusters **2–4** and **6** were confirmed by heteronuclear NMR spectroscopy. In the proton NMR we have detected the resonances for the HC═N proton at low field for the iminium substitution products **2** (7.8 ppm), **3** (8.22 ppm) and **6** (8.5 ppm) which correlate with the respective signal in the carbon NMR spectrum for the HC═N group [**2**: 174.5 ppm; **3**: 171.0; **6**: 177.0]. In the case of cluster **4** the NH protons show a resonance at 4.2 ppm. The signals of the hydrogen atoms attached to boron atoms of the cluster can not be seen as isolated signals in the ^{1}H NMR spectrum. They give rise to a very broad baseline elevation between 1 and 2.5 ppm.

The nitrogen substituted boron atom of the cluster exhibits a resonance, which shows no coupling to hydrogen atoms and is shifted significantly to lower field in comparison to the other cluster signals.

The signals in the ^{119}Sn NMR spectrum give clear evidence for the unsubstituted situation in **2–4** (−560, −563, −656 ppm) and for the methylated cluster **6** (−206 ppm).

Experimental

General

All manipulations were carried out under exclusion of air and moisture in an argon atmosphere using standard Schlenk techniques. Solvents were purified by standard methods. Elemental analyses were performed by the Institut für Anorganische Chemie Universität Tübingen using a Vario EL analyzer and a Vario MICRO EL analyzer. The starting materials $[Et_3NH]_2$-$[SnB_{11}H_{11}]$ and $[Et_3NH][Me–SnB_{11}H_{11}]$ were synthesized by a modified protocol of the work of Todd.[57] All further chemicals used were purchased commercially and were not further purified.

NMR

NMR spectra were recorded with a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 250.13 (^{1}H), 80.25 (^{11}B), 62.90 (^{13}C), and 93.25 MHz (^{119}Sn), a Bruker Avance AVII+ 400 NMR spectrometer equipped with a 5 mm QNP head and operating at 400.13 (^{1}H) and 100.13 (^{13}C) and a Bruker Avance AVII+ 500 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 186.50 (^{119}Sn). Chemical shifts are reported in δ values in parts per million (ppm) relative to external TMS (^{1}H, Θ = 100%; ^{13}C, Θ = 25.145020%), $BF_3{\cdot}Et_2O$ (^{11}B, Θ = 32.083974%), $SnMe_4$ (^{119}Sn, Θ = 37.290632%) using the chemical shift of the solvent ^{2}H resonance frequency.[60]

Crystallography

X-Ray data for compounds **2** and **6** (Table 1) were collected with a Stoe IPDS 2T diffractometer and corrected for Lorentz and polarization effects and absorption by air. The programs used in this work were Stoe's X-Area and WinGX suite of programs including SHELXS and SHELXL for structure solution and refinement.[61,62]

X-Ray data for compound **4** were collected with a Bruker Smart APEX II diffractometer with graphite monochromated

Table 1 Crystal and structure refinement parameters of **2**, **4**, **6**

	2	**4**	**6**
Formula	$C_8H_{27}B_{11}N_2Sn$	$C_8H_{31}B_{11}N_2Sn$	$C_5H_{22}B_{11}NSn$
M_r [g mol^{-1}]	388.92	392.95	333.84
Wavelength [Å]	0.71073	0.71073	0.71073
Temperature [K]	110(2)	173(2)	150(2)
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*Pbca*	*Pbca*	$P\bar{1}$
Z	8	8	2
a [Å]	11.7586(6)	11.7237(4)	7.1933(4)
b [Å]	12.7204(6)	12.1615(4)	9.7884(6)
c [Å]	23.8490(12)	25.9327(9)	11.3155(7)
α [°]			86.106(5)
β [°]			87.949(5)
γ [°]			69.275(4)
V [Å^3]	3567.2(3)	3697.4(2)	743.40(8)
ρ_{calc} [g cm^{-3}]	1.448	1.412	1.491
μ [mm^{-1}]	1.420	1.370	1.688
F(000)	1552	1584	328
Crystal size [mm^3]	0.30 × 0.25 × 0.22	0.25 × 0.13 × 0.10	0.17 × 0.16 × 0.14
θ range [°]	1.71–27.06	5.70–26.37	2.78–29.17
Limiting indices	$-15 \le h \le 13$, $-16 \le k \le 15$, $-30 \le l \le 29$	$-14 \le h \le 14$, $-15 \le k \le 14$, $-32 \le l \le 32$	$-9 \le h \le 9$, $-13 \le k \le 13$, $-15 \le l \le 15$
Reflections collected	51 530	50 793	13 903
Independent reflections (R_{int})	3894/0.0497	3744/0.0399	3999/0.0312
Completeness	99.6	98.9	99.6
Absorption correction	Multi-scan	Numerical	Numerical
Max./min. transmission	0.7455 and 0.6717	0.9060/0.7251	0.8710/0.6267
Parameters/restraints	203/0	212/1	165/0
R_1/wR_2 [$I > 2\sigma(I)$]	0.0417/0.1013	0.0241/0.0482	0.0221/0.0501
R_1/wR_2 for all data	0.0476/0.1046	0.0277/0.0494	0.0254/0.0510
GOF on F^2	1.142	1.157	1.113
Largest diff. peak and hole [e A^{-3}]	2.358 and −1.194	0.656 and −0.451	1.148 and −0.596

Mo Kα radiation. The programs used were Bruker's APEX2 v2011.8-0 including SADABS for multiscan absorption correction and SAINT for structure solution[63] as well as the WinGX suite of programs v1.70.01 including SHELXL for structure refinement.

2,4-Bis-((*E*)-*N*-ethylideneethylamino)-stanna-*closo*-dodecaborane (2). $[Et_3O][BF_4]$ (2.0 g, 10.5 mmol) was dissolved in 10 mL acetonitrile and stirred at room temperature overnight. $[Et_3NH]_2[SnB_{11}H_{11}]$ (**1**) (2.38 g, 5.25 mmol) was dissolved in 50 mL acetonitrile and the *N*-ethyl-acetonitrilium solution was added dropwise over the course of 30 min. The reaction was stirred overnight and the solvent was removed *in vacuo*. The oily residue was dissolved in 30 mL DCM and washed twice with 30 mL aqueous NaCl solution (1 M) and once with 50 mL water. After removal of the solvent 2.0 g (5.14 mmol, 97.9%) of the product were isolated as a slightly yellow powder. The product can be further purified by column chromatography on silica gel using hexane : acetone (2 : 1) as the eluent. ^{1}H NMR (500 MHz, CD_2Cl_2, 26 °C): δ = 7.8 (s, br, 2H, C*H*), 4.0–3.9 (m, 4H, CH_2), 2.55 (d, 6H, $^3J(^1H–^1H)$ = 6.1 Hz, CH–CH_3), 1.41 (t, 6H, $^3J(^1H–^1H)$ = 7.3 Hz, CH_2–CH_3), $^{11}B\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 26 °C): δ = 3.3 (s, 2B, *B*–N), −9.1 (s, 1B), −10 to −13 (m, 8B), $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 26 °C): δ = 174.5 (s, *C*H), 59.8 (s, *C*H_2), 21.2 (s, CH–*C*H_3), 17.0 (s, CH_2–*C*H_3), $^{119}Sn\{^1H\}$ NMR (187 MHz, CD_2Cl_2, 26 °C): δ = −560 (s); elemental analysis calcd (%) for $C_8H_{27}N_2B_{11}Sn$ (388.95 g mol^{-1}): C 24.70, H 7.00, N 7.20; found: C 24.94, H 6.93, N 7.33.

2,4-Bis-((*Z*)-*N*-ethylideneethylamino)-stanna-*closo*-dodecaborane (3). 2,4-((*E*)-$CH_3C(H)$=$NEt)_2SnB_{11}H_9$ (**2**) (200 mg, 0.51 mmol) was dissolved in 10 mL THF and 1 mL water. One drop of a PMe_3 solution in THF (1 M) was added and the reaction was stirred overnight. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel using hexane : acetone (2 : 1) as the eluent. After evaporation of the solvent 25 mg (0.06 mmol, 12.5%) of the product were isolated as a colorless powder. ^{1}H NMR (500 MHz, CD_2Cl_2, 26 °C): δ = 8.22 (q, 2H, $^3J(^1H–^1H)$ = 5.8 Hz, C*H*), 3.76 (q, 4H, $^3J(^1H–^1H)$ = 7.3 Hz, CH_2), 2.11 (d, 6H, $^3J(^1H–^1H)$ = 6.0 Hz, CH–CH_3), 1.34 (t, 6H, $^3J(^1H–^1H)$ = 7.3 Hz, CH_2–CH_3), $^{11}B\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 26 °C): δ = 5.5 (s, 2B, *B*–N), −7.7 (s, 1B), −10 to −13 (m, 6B), −13.7 (s, 2B), $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 26 °C): δ = 171.0 (s, *C*H), 48.3 (s, *C*H_2), 18.2 (s, CH–*C*H_3), 14.2 (s, CH_2–*C*H_3), $^{119}Sn\{^1H\}$ NMR (187 MHz, CD_2Cl_2, 26 °C): δ = −563 (s); elemental analysis calcd (%) for $C_8H_{27}N_2B_{11}Sn$ (388.95 g mol^{-1}): C 24.70, H 7.00, N 7.20; found: C 25.08, H 6.90, N 7.17.

2,4-Bis-(diethylamino)-stanna-*closo*-dodecaborane (4). 2,4-((*E*)-$CH_3C(H)$=$NEt)_2SnB_{11}H_9$ (**2**) (110 mg, 0.28 mmol) and Na$[BH_4]$ (23 mg, 0.62 mmol) were dissolved in 10 mL ethanol and stirred at room temperature overnight. The solvent was removed *in vacuo*. The oily residue was redissolved in 10 mL DCM and washed three times with 10 mL water. After removal of the solvent 100 mg (0.25 mmol, 90.9%) of the product were obtained as a colorless powder. The product can be further purified by column chromatography on silica gel using

hexane : acetone (3 : 1) as the eluent. ^{1}H NMR (500 MHz, CD_2Cl_2, 26 °C): δ = 4.2 (s, br, 2H, N*H*), 3.3–3.2 (m, 2H, CH_2), 3.0–2.8 (m, 2H, CH_2), 1.3–1.2 (m, 12H, CH_3), ^{11}B{^{1}H} NMR (161 MHz, CD_2Cl_2, 26 °C): δ = 6.0 (s, 2B, *B*–N), −8.6 (s, 1B), −11 to −14 (m, 6B), −14.6 (s, 2B), ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 26 °C): δ = 49.5 (s, *C*H_2), 49.4 (s, *C*H_2), 11.7 (s, *C*H_3), 11.7 (s, *C*H_3), ^{119}Sn{^{1}H} NMR (187 MHz, CD_2Cl_2, 26 °C): δ = −656 (s); elemental analysis calcd (%) for $C_8H_{31}N_2B_{11}Sn$ (392.98 g mol^{-1}): C 24.45, H 7.95, N 7.13; found: C 24.71, H 7.97, N 7.10.

7-((*Z*)-*N*-Ethylideneethylamino)-1-(methyl)-stanna-*closo*-dodecaborane (6). [Et_3O][BF_4] (900 mg, 4.74 mmol) was dissolved in 10 mL acetonitrile and stirred at room temperature overnight. Thereafter [Et_3NH][$MeSnB_{11}H_{11}$] (**5**) (340 mg, 0.94 mmol) was added in one portion. After further stirring at room temperature for 3 days the solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel using hexane : acetone (3 : 1) as the eluent. After evaporation of the solvent 118 mg (0.35 mmol, 37.2%) of the product were isolated as a colorless powder. ^{1}H NMR (500 MHz, CD_2Cl_2, 26 °C): δ = 8.5 (s, br, 1H, C*H*), 3.90 (q, 2H, ^{3}J(^{1}H–^{1}H) = 7.2 Hz, CH_2), 2.28 (d, 3H, ^{3}J(^{1}H–^{1}H) = 5.9 Hz, CH–CH_3), 1.84 (s, 3H, ^{2}J(^{119}Sn–^{1}H) = 96.5 Hz, ^{2}J(^{117}Sn–^{1}H) = 92.3 Hz, Sn–CH_3) 1.33 (t, 3H, ^{3}J(^{1}H–^{1}H) = 7.4 Hz, CH_2–CH_3), ^{11}B{^{1}H} NMR (161 MHz, CD_2Cl_2, 26 °C): δ = −2.7 (s, 1B, *B*–N), −12.8 (s, 1B), −14 to −19 (s, br, 8B), −20.4 (s, 1B), ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 26 °C): δ = 177.0 (s, *C*H), 49.5 (s, *C*H_2), 19.4 (s, CH–*C*H_3), 14.1 (s, CH_2–*C*H_3), −8.1 (s, Sn–*C*H_3), ^{119}Sn{^{1}H} NMR (187 MHz, CD_2Cl_2, 26 °C): δ = −206 (s); elemental analysis calcd (%) for $C_5H_{22}NB_{11}Sn$ (388.95 g mol^{-1}): C 17.99, H 6.64, N 4.20; found: C 18.28, H 6.34, N 4.28.

Conclusions

In conclusion we have found a way to regioselectively activate the BH-units of stanna-*closo*-dodecaborate. The heteroborate can be substituted at the cluster sphere two times at the upper boron belt in the reaction with alkylated acetonitrile. Due to alkylation at the tin atom of the cluster the reactivity towards BH-substitution with the *N*-ethylnitrilium cation drops and monosubstitution is achieved regioselectively at the lower boron belt. These reaction products could be starting materials for further ligand development.

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