Cyclic bis(amino)organotin cations, stabilized by π-coordination and new spirocyclic stannole derivatives

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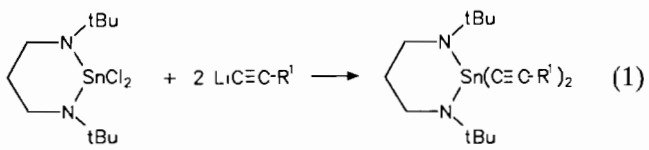
Abstract

The 1,1-organoboration of 2,2-di-1-alkynyl-1,3-di-tertbutyl-1,3,2-diazastannacyclohexanes (**1**) has been studied. Treatment of **1** with triethylborane (**2**) gave first a zwitterionic intermediate **6** in which a diamino(organo)tin cation is stabilized by side-on π-coordination to the C≡C bond of an alkynylborate moiety. The final products proved to be the spirocyclic stannoles **7**. In the reaction between **1** and triisopropylborane (**3**) the intermediate of type **6** could not be detected, but the final product **8** has the same spirocyclic structure as **7**. Multinuclear ^{1}H, ^{11}B, ^{13}C, ^{15}N and ^{119}Sn NMR served for monitoring the reactions and characterization of intermediates and final products.

Key words: Tin complexes; Organotin complexes; Amino complexes

Introduction

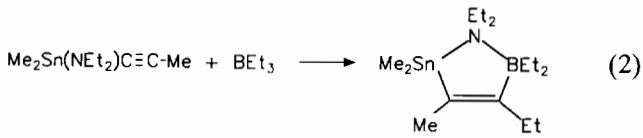
The well documented synthetic potential of tin compounds can be further enhanced if reactive Sn–N [1] and Sn–C≡ bonds [2] are combined in the same molecule as in alkynyl(amino)tin compounds. Non-cyclic compounds of this type are always in equilibrium with other redistribution products [3], whereas cyclic alkynyl(amino)tin compounds should be kinetically more stable. Recently, we have used the readily accessible 1,3-di-tertbutyl-2,2-dichloro-1,3,2-diazastannacyclohexane [4] to prepare the cyclic derivatives **1** [3] (eqn. (1)).



(1)

1a, b
R' = Me, Bu

The reaction of **1** with triorganoboranes (**2**, **3**) is of particular interest since 1,1-organoboration [5] of di-1-alkynyltin compounds has opened convenient routes to various useful heterocyclic systems, such as stannoles [6, 7] or 1-stanna-4-bora-2,5-cyclohexadienes [8, 9]. On the other hand, the influence of Sn–amino groups on the product distribution in organoboration reactions as well as on the stabilization of potential intermediates is unknown. Thus, in the case of **4** (in equilibrium with $Me_2Sn(C{\equiv}CMe)_2$ and $Me_2Sn(NEt_2)_2$), the sole alkynyl(amino)tin compound studied so far, 1,1-organoboration leads to the heterocycle **5** (eqn. (2)) [10] which turned out to be the starting material for various useful transformations [11, 12].



(2)

4 **2** **5**

We have studied the reaction between compounds **1** and trialkylboranes (Et_3B (**2**) and $^{i}Pr_3B$ (**3**)) between −78 and +60 °C. Multinuclear magnetic resonance (^{1}H, ^{11}B, ^{13}C, ^{15}N and ^{119}Sn NMR) served for characterizing intermediates and products.

Results and discussion

The reaction between **1** and Et_3B (**2**) was monitored by ^{13}C and ^{119}Sn NMR. The compounds **6a,b** are the

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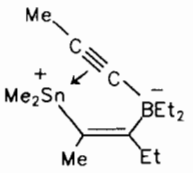
first detectable intermediates, the products of an intermolecular 1,1-ethyloboration, which are formed at temperatures more than −20 °C and slowly rearrange (> 0 °C) via intramolecular 1,1-vinyloboration into the stannole derivatives **7a,b** (Scheme 1). The reaction between **1a** and triisopropylborane (**3**) is too slow even at room temperature. When the mixture is heated to 60 °C for 12 h the stannole derivative **8a**, analogous to **7a**, is formed quantitatively.

Although the intermediates **6** could not be isolated in pure state as yet, their proposed structure is based on consistent multinuclear NMR data (*vide infra*). Compounds **7** and **8** are obtained as yellowish, oily, air- and moisture-sensitive liquids which are left in high purity once the solvent and excess of trialkylborane have been removed. Attempts at the distillation of **7** or **8** at reduced pressure leads to decomposition.

Stabilization of organotin cations by π-coordination has been reported previously [13–15]. The present intermediates **6** are the first examples of this type of compound with tin–nitrogen bonds. The NtBu groups may exert a kinetically stabilizing effect and, in principle, the nitrogen atoms could delocalize some of the positive charge. The selective formation of the products **7a** and **8a** is rather surprising in the light of previous studies dealing with organoboration of di-1-propynyl- and tetra-1-propynyltin compounds: stannole derivatives were never obtained in pure state [13, 14] and with $^{i}Pr_3B$ selective formation of 1-stanna-4-bora-2,5-cyclohexadiene derivatives was observed [8, 9]. The intermediacy of organotin cations, such as **9** [15] (observed at low temperature in the reaction between $Me_2Sn(C{\equiv}CMe)_2$ and **2** which is analogous to **6**, has been



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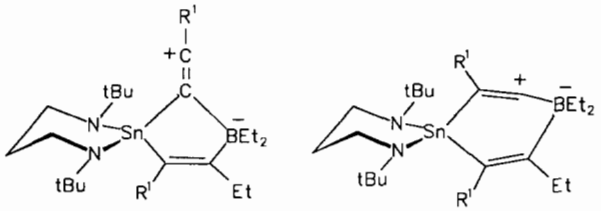
firmly established in 1,1-organoboration reactions. Therefore, it is tempting to consider differing contributions from structures of vinyl cations **A** and **B** to the ground state of organotin cations. While hyperconjugation via the B–C [16] and in particular via the Sn–C bond [17] can stabilize both cations, structure **B** represents the most likely immediate precursor of the stannole and the 1-stanna-4-bora-2,5-cyclohexadiene system.

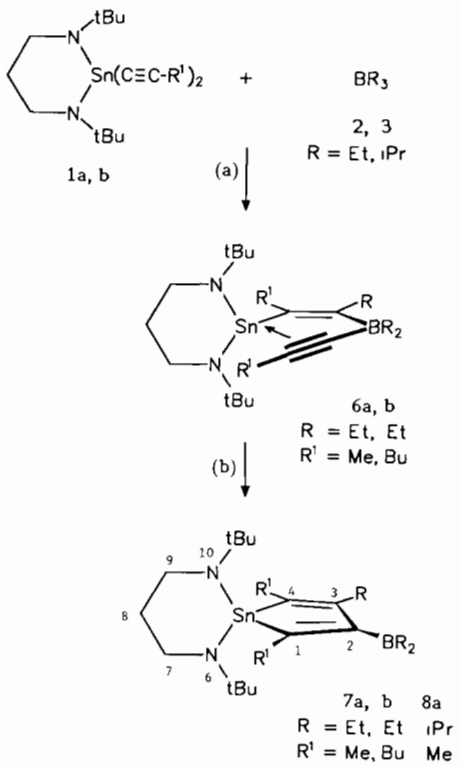


A **B**

The new type of stannoles **7** and **8** contain numerous reactive sites which are promising for a rich chemistry. Most noteworthy are the reactivity of Sn–N bonds [1] and the diene system, the latter being an interesting group for various cycloadditions.

NMR spectra

NMR data (^{11}B, ^{13}C, ^{15}N and ^{119}Sn NMR) for the intermediates **6** and the stannoles **7** and **8** are given in Tables 1 and 2, respectively. The presence of the borylated stannole ring in **7** and **8** is clearly shown by the ^{13}C NMR data of the olefinic carbon atoms (see Fig. 1). The characteristic pattern consists of a broad ^{13}C NMR signal (owing to partially relaxed scalar coupling $^{1}J(^{13}C^{11}B)$ [18]) and three sharp signals, two accompanied by $^{117/119}Sn$ satellites according to large one-bond coupling constants $|^{1}J(^{119}Sn^{13}C)|$ and one with a smaller coupling constant $|^{2}J(^{119}Sn^{13}C)|$. All other ^{13}C resonances, together with ^{1}H NMR data, support the spirocyclic structure of **7** and **8**. The ^{1}H nuclear shielding is affected by steric crowding since the $\delta^{1}H$ values (proved by 2D $^{13}C/^{1}H$ heteronuclear shift correlation) for $=C-CH_2$ ($\delta = 1.85$) in **7a** and in particular that for $=C-CH$ ($\delta = 1.40$) in **8a** are unusual. In compound **8a**, the rotation of the $B^{i}Pr_2$ group about the $=C-B$



Scheme 1.

TABLE 1 ^{13}C, ^{15}N and ^{119}Sn NMR data[a] of the cyclic (η^2-alkyne)bis(amino)tin compounds **6a,b**

$\delta^{13}C$	**6a**	**6b**[b]
Sn–C=, R^1	133.2 [984.0], 18.8 [189.6]	140.6 [955.0]
B–C=, Et	178.0 [br], 24.5 [230.5], 13.1 [24 0]	177.4 [br]
B–C≡	114.7 [br, 130]	116.4 [br]
≡C–R^1, R^1	124.2 [82.8], 6.2 [<3]	128.5
BEt_2	17 0 [br], 13 6	16.9 [br], 13.6
NtBu	56 6 [7.1], 30.5 [22.9]	56.6 [7 0], 30.5 [22.5]
NCH_2CH_2	48.2 [16.9], 35 6 [16 9]	48.7 [17.0], 35 4 [17.5]
$\delta^{11}B$	−7.1	−7 0
$\delta^{15}N$	−295.0 [184.6]	nm
$\delta^{119}Sn$	−32.8	−37 1

[a]In CD_2Cl_2 at −10 °C; coupling constants $J(^{119}Sn^{13}C)$ and $^1J(^{119}Sn^{15}N)$ are given in square brackets; nm = not measured. [b]^{13}C resonances from =C–Et, =C–Bu and ≡C–Bu were not assigned.

TABLE 2 ^{11}B, ^{13}C, ^{15}N and ^{119}Sn NMR data[a] of the stannole derivatives **7a**, **7b** and **8a**

	7a	**7b**	**8a**
=C(1)	136.3 [541.7]	144.2 [529.3]	135.5 [515.5]
R^1	16.2	35.3 [14.0] 31.0, 22.6, 14 3	19.6 [91.9]
=C(2)	160.5 [br]	159.1 [br]	162.8 [br]
BR_2	22.9 [br], 9.2	22.7 [br], 9 2	26.6 [br], 19.6, 19.5
=C(3)	147.3 [186.4]	145 7 [189.2]	150.0 [177.7]
R	26.7 [74.1], 13.0 [10.9]	27.5 [76.8], 13.0 [11.0]	40.2 [79.7], 21.7 [9.3]
=C(4)	133.4 [621.3]	140.8 [611.2]	135.1 [622.3]
R^1	19.4 [nm]	35.3 [14.4] 31.0, 23.4, 14.2	18.9 [73.4]
N(tBu)	55.3 [5.4], 30.2 [20.7]	55.5 [8.7], 29 6 [20.5]	55 2 [7.5], 30 3 [20.7]
NCH_2CH_2	50.0 [7.6], 36.5 [25.1]	48.2 [5.7], 36.3 [17.9]	48.1 [7.6], 36 5 [24.0]
$\delta^{11}B$	86.0	86.0	85.0
$\delta^{15}N$	−317.2 [27.7]	nm	−316.1 [30.8]
$\delta^{119}Sn$	−87.1	−93.8	−76.5

[a]In [D_8]toluene at 25±1 °C, coupling constants $^nJ(^{119}Sn^{13}C)$ and $^1J(^{119}Sn^{15}N)$ are given in square brackets; nm = not measured

bond is hindered, as indicated by the two $^{13}C(CH_3)$ resonances for the diastereotopic methyl groups. The ^{119}Sn nuclear shielding in **7** and **8** is increased by ≈100 ppm with respect to that in comparable stannoles containing an Me_2Sn moiety. However, this difference is in the same order of magnitude as for the respective bis(alkynyl)tin compounds ($\delta^{119}Sn$ for $Me_2Sn(C{\equiv}CMe)_2$: −156.0 [19] and for **1a**: −265.4 [3]). Therefore, the influence of the cyclic bis(amino) ligand on $\delta^{119}Sn$ remains fairly constant. The $\delta^{15}N$ values of **7a** and **8a** are in the typical range for bis(dialkylamino)diorganotin compounds [20] and there is only a slight change as compared to **1a** ($\delta^{15}N$ −321.4). The magnitude of the coupling constants $|^1J(^{119}Sn^{15}N)|$ in **7a** (27.7 Hz) and **8a** (30.8 Hz) is much smaller than in **1a** (100.1 Hz), indicating the influence of the strongly electronegative alkynyl group upon rehybridization at the tin atom in **1a** [3].

The similarity with characteristic ^{13}C NMR data for organotin cations analogous to **6** strongly supports the proposed structure of **6**. There are two ^{13}C resonance signals for olefinic carbon atoms, one broad for =C–B with a characteristic high frequency shift and the other one sharp accompanied by $^{117/119}Sn$ satellites corresponding to a large coupling constant $|^1J(^{119}Sn^{13}C{=})|$ (984 (**6a**), 955 (**6b**) Hz). The two ^{13}C resonances for the bridging alkynyl group are also broad (B–C≡) and sharp (≡C–R^1) but with much smaller coupling constants $|J(^{119}Sn^{13}C{\equiv})|$. The ^{13}C nuclear shielding in this group, in particular that of the alkynyl carbon atom

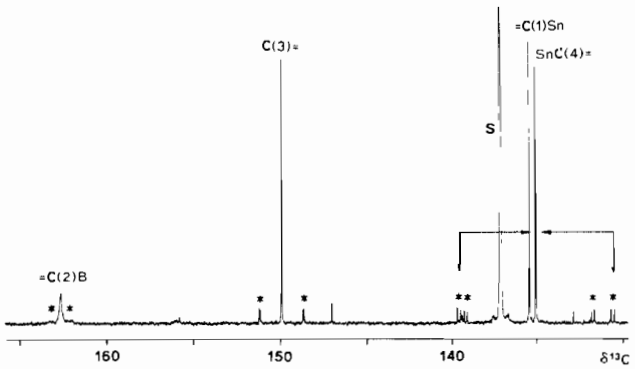


Fig. 1. 75.5 MHz $^{13}C\{^1H\}$ NMR spectrum (olefinic region) of compound **8a** (~15% in [D_8]-toluene (marked S) at 25 °C). The assignment is based on the broadening owing to partially relaxed scalar ^{13}C–^{11}B coupling (=C(2)–B) and the magnitude of $|^nJ(^{119}Sn^{13}C)|$ (=C(3), $n=2$, =C(1)–Sn and =C(4)–Sn, $n=1$) The $^{117/119}Sn$ satellite signals are marked by asterisks

linked to R^1, is considerably reduced as compared to alkynylborates and also with respect to **9**:

	6a	$[Et_3B-C\equiv C-Me]^-$ [14]	**9** [15]
$\delta^{13}C$ (B–C≡)	114.7	109.9	108.2
(≡C–)	124.2	85.7	112.1

This deshielding of $^{13}C(\equiv C-)$ is typical of the corresponding carbon atom in vinyl cations [21] and therefore, it corroborates the assumption that the canonic structure **A** is important for compounds **6**. All other ^{13}C NMR signals were also assigned in agreement with the proposed structure of **6**. Noteworthy are the $^{13}C(=CCH_3)$ and $^{13}C(=CCH_2)$ resonances for which the expected [13–15] large coupling constants $|^2J(^{119}Sn^{13}C)| = 189.6$ Hz and $|^3J(^{119}Sn^{13}C)| = 230.5$ Hz were measured.

The ^{119}Sn resonances of compounds **6** are at rather high field (**6a**: −32.8, **6b**: −37.1) as compared to triorganotin cations (e.g. **9** (−70 °C) [15]: +203.0). This difference is more than twice the effect which can be attributed to the cyclic bis(amino) ligand (*vide supra*), another indication that the nature of the side-on π-coordination of the tin atom in **6** is different from that in **9** and that structure **A** may play a more important role in the case of compounds **6**.

It proved possible to measure the ^{15}N NMR spectrum of a diluted reaction solution containing **6a**. The ^{15}N nuclear shielding is reduced by 25 ppm relative to **7a** which is not a particularly large effect. However, magnitude and sign of coupling constants $^1J(^{119}Sn^{15}N)$ are known to be very sensitive to changes in the electronic structure of the tin atom [20], as demonstrated by the value of $^1J(^{119}Sn^{15}N)$ for **6a** (184.6 Hz). This large magnitude of $|^1J(^{119}Sn^{15}N)|$ can only be understood by assuming a negative sign of this coupling constant, implying little 's-character' of the Sn–N bond hybrid orbitals and high 's-character' of the Sn–C= bond hybrid orbital (rehybridization [22]), in agreement with the large coupling constant $|^1J(^{119}Sn^{13}C_{(C=)})| = 984$ Hz. Similarly, coupling constants $|^1J(^{119}Sn^{13}C_{(Me)}|$ in compounds like **9** are fairly small (**9**: 249.6 Hz [15] compared with Me_4Sn: 340 Hz) in particular if compared with $|^1J(^{119}Sn^{13}C_{(C=)})| > 625$ Hz (**9**: 660.5 Hz [15]).

Experimental

All experiments and handling of the compounds were carried out in an atmosphere of N_2 observing all necessary precautions to exclude oxygen and moisture. Starting materials such as solutions of butyllithium (1.6 M) in hexane (Aldrich), tin tetrachloride (Merck) and the terminal alkynes were commercial products. Triethylborane [23], triisopropylborane [24] and 1,3-di-tert-butyl-2,2-dichloro-1,3,2-diazastannacyclohexane [4] were obtained as described. Elemental analyses: Pascher, Remagen. EI-MS (70 eV), Varian MAT CH-7 with direct inlet. $^1H/^{13}C$ NMR: Bruker AM 500 (500.13/125.77 MHz), Bruker AC 300 (300.13/75.5 MHz) and Jeol EX 270 (270.0/67.95 MHz). ^{11}B NMR: Bruker AC 300 (96.3 MHz) and Jeol FX 90 Q (28.7 MHz), $Et_2O \cdot BF_3$ as external standard ($\Xi(^{11}B) = 32.083971$ MHz). ^{15}N NMR: Bruker AC 300 (30.4 MHz), neat $MeNO_2$ as external standard ($\Xi(^{15}N) = 10.136767$ MHz). ^{119}Sn NMR: Bruker AC 300 (111.9 MHz) and Jeol FX90 Q (33.3 MHz), Me_4Sn as external standard ($\Xi(^{119}Sn) = 37.290665$ MHz).

Organoboration of the di-1-alkynyltin compounds 1 leading to 1,3,4,6,10-pentaalkyl-2-dialkylboryl-6,10-diaza-5-stannaspiro[4,5]deca-1,3-dienes (7, 8). General procedure

The trialkylboranes **2** or **3** (slight excess: 12–15 mmol) are added in one portion to a stirred solution of 10 mmol of the alkynyltin compounds **1** in 30 ml of hexane at −78 °C. This mixture is allowed to reach ambient temperature. After 24 h the formation of **7a,b** is complete (^{11}B, ^{119}Sn NMR). In the case of **8a**, the reaction mixture was heated to reflux for 12 h. The solvent was removed *in vacuo* (0.1 Torr) and analysis of the oily, yellowish residues shows that **7a,b** and **8a** are obtained in quantitative yield. The products decompose during distillation (> 70 °C/10^{-3} Torr). For ^{11}B, ^{13}C, ^{15}N and ^{119}Sn NMR data see Table 2.

7a: ^1H NMR (500.13 MHz, [D_8]toluene): $\delta[^nJ(^{119}Sn^1H)] = 0.83$ [t, 6H, BEt]; 0.99 [t, 3H, Et]; 1.0–1.2 [m, 4H, BCH_2]; 1.06 [s, 18H, N^{t}Bu]; 1.85 [m, 2H, $=CCH_2$]; 1.78 [m, 2H, $-CH_2-$]; 1.86 [57.6] [s, 3H, =CMe]; 2.00 [53.0] [s, 3H, =CMe]; 3.00 [43.0] [m, 4H, NCH_2]. MS: *m/z* (%) = 480 M^+ (3), 465 $M-Me^+$ (45),

86 (100). *Anal.* Calc. for $C_{23}H_{45}BN_2Sn$ (479.1): C, 57.66; H, 9.47; N, 5.84. Found: C, 57.45; H, 9.38; N, 5.64%.

8a: ^{1}H NMR (500.13 MHz, [D_8]toluene): $\delta[^nJ(^{119}Sn^1H)]$ = 0.96 [d, 6H, B^{i}Pr]; 0.98 [d, 6H, B^{i}Pr]; 1.04 [s, 9H, N^{t}Bu]; 1.10 [d, 6H, ^{i}Pr]; 1.35 [m, 2H, BCH]; 1.40 [sp, 1H, =CCH]; 1.74 [m, 2H, $-CH_2-$]; 1.90 [56.5] [s, 3H, =CMe]; 2.12 [58.7] [s, 3H, =CMe]; 2.97 [38.5] [m, 4H, NCH_2]. *Anal.* Calc. for $C_{26}H_{51}BN_2Sn$ (521.18): C, 59.92; H, 9.86; N, 5.37. Found: C, 59.60; H, 9.55; N. 5.25%.

Organoboration of ***1a*** *with* Et_3B *(NMR tube, monitored by* ^1H, ^{11}B, ^{13}C *and* ^{119}Sn *NMR)*

A 5 mm (o.d.) NMR tube containing a solution of 100 mg of **1a** (0.26 mmol) in 0.5 ml of [D_8]toluene is cooled to −78 °C and 0.04 ml of Et_3B is injected. The reaction starts at −20 °C to give the intermediate **6a** and is complete after 30 min at −5 °C. Attempts to isolate **6a** gave mainly **7a** and some other unidentified products.

6a: ^{1}H NMR (300.13 MHz, [D_8]toluene, −20 °C): $\delta[^nJ(^{119}Sn^1H)]$ = 0.55 [broad, 4H, BCH_2]; 0.84, 0.86 [t, 6H, BEt]; 1.03 [t, 3H, Et]; 1.08 [s, 18H, N^{t}Bu]; 1.65 [m, 2H, $-CH_2-$]; 1.71 [<3] [s, 3H, ≡CMe]; 1.88 [122.5] [s, 3H, =CMe]; 2.13 [q, 2H, $=CCH_2$]; 2.93 [76.0] [m, 4H, NCH_2].

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