

Stepwise synthesis of organometallic-substituted stannoles via stabilized triorganotin cations

Bernd Wrackmeyer*, Klaus Horchler von Locquenghien, Sabine Kundler

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

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Abstract

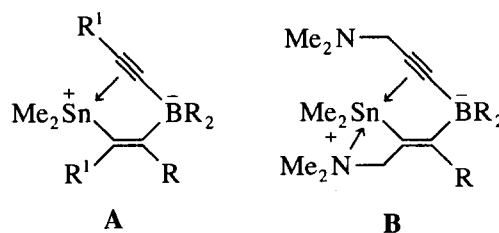
A new triorganotin chloride, (*E*)-2-Chloro(dimethyl)stannyl-3-diethylboryl-*N,N*-dimethyl-2-pentenylamine (**4**), was prepared via 1,1-ethyloboration. Compound **4** reacts with alkynyltin compounds of the type $R^1-C\equiv C-SnMe_3$ [$R^1 = Me$ (**a**) ¹Bu (**b**), $SiMe_3$ (**c**), $SnMe_3$ (**d**), CH_2OMe (**f**) and $Me_3Pb-C\equiv C-PbMe_3$ (**e**) via elimination of Me_3SnCl or Me_3PbCl (**e**) to give zwitterionic intermediates **5a,c-f** in which a cationic triorganotin fragment is stabilized by side-on coordination to the $C\equiv C$ bond of an alkynylborate group and by a coordinative $N-Sn$ bond. The intermediates **5c-e** are the first examples of $(\eta^2\text{-alkyne})_2tin$ compounds where an organometallic substituent is linked to the bridging alkynyl group. These intermediates rearrange at room temperature to give the pure stannole derivatives **6c-f**. The synthesis of **6b** requires heating under reflux for several hours; no intermediate was detected. The analogous reaction of (*E*)-2-chloro(dimethyl)stannyl-3-diethylboryl-2-pentene (**7**) with $R^1-C\equiv C-SnMe_3$ ($R^1 = SiMe_3, SnMe_3$) or $Me_3Pb-C\equiv C-PbMe_3$ afforded the analogous stannoles **8c-e**, but the intermediates corresponding to **5** were too short-lived for NMR spectroscopic detection. All intermediates and the final products were characterized by extensive one- and two-dimensional multinuclear magnetic resonance studies (¹H, ¹¹B, ¹³C, ¹⁵N, ²⁹Si, ¹¹⁹Sn and ²⁰⁷Pb NMR), including the determination of a negative sign for the coupling constant $^1J(^{207}Pb^{13}C\equiv)$ in the intermediate **5e**.

Keywords: Boron; Borates; Metallacycle; Nuclear magnetic resonance; Stannyl; Tin

1. Introduction

Di-1-alkynyltin compounds react with triorganoboranes via 1,1-organoboration to give stannoles, 1-stanna-4-bora-2,5-cyclohexadienes, or 3-stannolenes, depending on reaction conditions, stoichiometry, the nature of R^1 in the $Sn-C\equiv C-R^1$ unit and the group R in the triorganoborane R_3B [1,2]. The important intermediates created prior to the formation of these heterocycles are thermally unstable zwitterionic compounds in which the cationic triorganotin fragment is stabilized by weak π -coordination to the $C\equiv C$ bond of an alkynylborate unit (**A**) [3]. The interaction between the $C\equiv C$ bond and the tin atom in **A** is of particular interest since it can be described as β -metal-stabilization of a vinyl cation [4], or as σ - π delocalization [5]. Similar types of unsymmetrical metal-bridging of an alkynyl group are

observed more frequently with transition metals [6]. If R^1 represents an organometallic substituent, e.g. $R^1 = SiMe_3$ [7,8], it was not possible so far to detect species like **A**, although the structure of the final products of the 1,1-organoboration reaction clearly suggests the intermediacy of such zwitterionic compounds. Recently we have shown that the intermediates become much more stable if R^1 contains a donor function, e.g. a NMe_2 group, which stabilizes the cationic triorganotin fragment by a coordinative $N-Sn$ bond (**B**) [9].

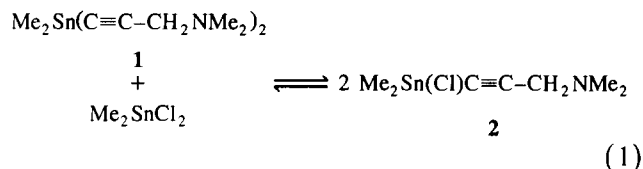


$R^1 = \text{alkyl, phenyl}; R = \text{alkyl}$

* Corresponding author.

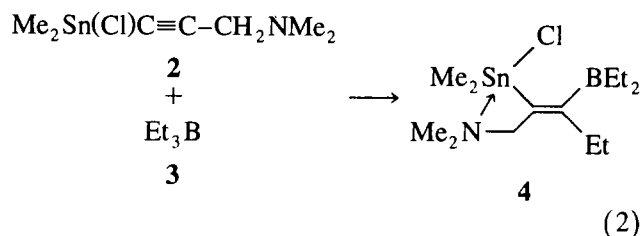
2. Results and discussion

A strategy for the stepwise synthesis of stannoles has already been developed [7,8], and in the present work we have adapted this route in order to obtain species in which coordinative N–Sn interactions are likely to exist. According to Eq. (1), a mixture of **1** and dimethyltin dichloride equilibrates with the alkynyltin compound **2**, the balance being towards the right-hand side. An excess of ca. 20% of Me_2SnCl_2 shifts the equilibrium completely towards **2**, as shown by the ^{119}Sn NMR spectra.



Treatment of this mixture with an excess of triethylborane (Et_3B , **3**) affords selectively and quantitatively (based on the amount of **2**) the (*E*)-alkene derivative **4**, the product of an 1,1-ethyloboration (Eq. (2)).

Compound **4** is an air- and moisture-sensitive yellowish liquid. The $\delta^{119}\text{Sn}$ value for **4** ($\delta - 5.6$) indicates the presence of a coordinative N–Sn bond. This is apparent from the comparison with the $\delta^{119}\text{Sn}$ value of the analogous compound where the Me_2NCH_2 group in **4** is replaced by a propyl group ($\delta + 90.9$). The increased ^{119}Sn nuclear shielding in **4** indicates [10] an increase in the coordination number of the tin atom.



Compound **4** is an ideal starting point for further transformations, taking advantage of the reactive Sn–Cl bond. Thus, exchange reactions with alkynyltin or alkynyllead compounds, as shown in Eqs. (3a) and (3b), respectively, proceed under mild conditions, leading first to the species **5'** which are in equilibrium with the zwitterionic compounds **5**. Finally, the intermediates **5** rearrange, via an intramolecular 1,1-vinyloboration, to the stannoles **6** (Eq. (3c)). The stannoles **6b–d,f** are formed quantitatively and can be used for further reactions without purification. The lead derivative **6e** appears to be fairly unstable and its formation is accompanied by ca. 25% of unknown decomposition products. In the case of **6a**, the stannole (ca. 35%; $\delta^{119}\text{Sn} - 4.7$) was identified among various other organoboration products. It has been observed previously that 1-propynyltin derivatives undergo side reactions, mainly because of the competition between intra- and intermolecular organoboration reactions [3d,11,12]. It was possible to prove by multinuclear magnetic resonance the presence of all compounds **5** as intermediates in their respective reactions (except in the case of **5b**),

Table 1
 ^{11}B , ^{13}C , ^{29}Si , ^{119}Sn and ^{207}Pb NMR data ^a of the zwitterionic intermediates **5**

R ¹ No.	Me 5a	SiMe ₃ ^b 5c	SnMe ₃ ^c 5d	PbMe ₃ ^d 5e	MeOCH ₂ ^e 5f
$\delta^{13}\text{C}(\text{Me}_2\text{Sn})$	-1.2 [301.9]	1.4 [327.5]	1.2 [333.5]	1.1 [335.2]	0.1 [306.3]
$\delta^{13}\text{C}(\text{Sn}-\text{C}=\text{C})$	138.4 [871.9]	138.4 [864.8]	138.5 [852.1]	138.7 [848.0]	142.5 [858.1]
$\delta^{13}\text{C}(\text{B}-\text{C}=\text{C})$	178.7 (br)	177.8 (br)	177.3 (br)	177.4 (br)	177.3 (br)
$\delta^{13}\text{C}(\text{B}-\text{C}=\text{C})$	115.4 (br)	165.5 (br)	173.8 (br)	174.9 (br)	126.1 (br)
$\delta^{13}\text{C}(\text{R}^1-\text{C}=\text{C})$	103.7 [45.2]	106.0 [87.2]	98.8 [112.3] [244.1]	96.3 [126.4] (393.5) ^e	101.4 [44.7]
$\delta^{13}\text{C}(\text{Et}_2\text{B})$	16.9 (br) 12.1	15.5 (br) 12.3	15.3 (br) 12.4	15.2 (br) 12.4	16.2 (br) 12.3
$\delta^{13}\text{C}(\text{Et}-\text{C}=\text{C})$	25.5 [173.3] 13.6 [19.5]	25.8 [171.1] 14.2 [20.2]	25.8 [156.9] 14.2 [n.m.]	25.9 [160.2] 14.4 [n.m.]	25.5 [165.7] 13.9 [19.5]
$\delta^{13}\text{C}(\text{CH}_2\text{NMe}_2)$	62.8 [88.3] 47.6	62.4 [86.7] 45.9	62.0 [88.8] 45.7	61.8 [87.7] 45.7	63.3 [80.1] 45.0
$\delta^{13}\text{C}(\text{R}^1-\text{C}=\text{C})$	9.4	0.9 ^f	-6.1	5.5	60.2
$\delta^{11}\text{B}$	-9.2	-11.7	-12.8	-12.8	-10.7
$\delta^{119}\text{Sn}$	+131.6	+107.5	+100.9 [14.2]	+100.8 [24.4]	+142.5

^a In CDCl_3 (ca. 20%) at 243 K; coupling constants $J(^{119}\text{Sn}^{13}\text{C})$ [Hz, ± 0.5] are given in square brackets; coupling constants $J(^{207}\text{Pb}^{13}\text{C})$ [Hz, ± 0.5] are given in curved brackets; n.m. = not measured; (br) denotes the broadened ^{13}C NMR signal of a boron-bonded carbon atom.

^b $\delta^{29}\text{Si} - 13.9$.

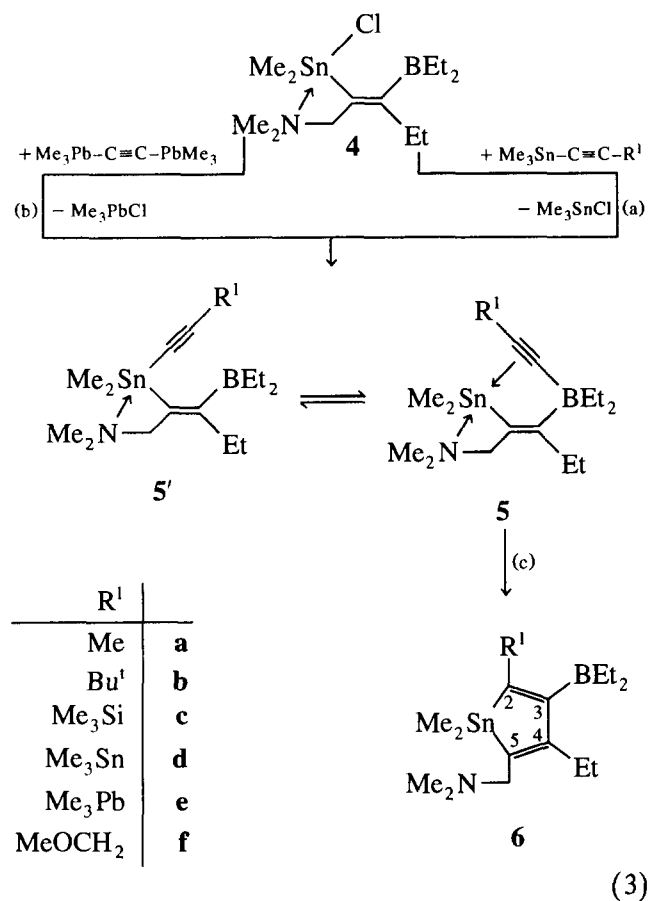
^c $\delta^{119}\text{Sn}(\text{SnMe}_3) - 35.2$ [14.2]

^d $\delta^{207}\text{Pb} - 26.7$ [24.4]

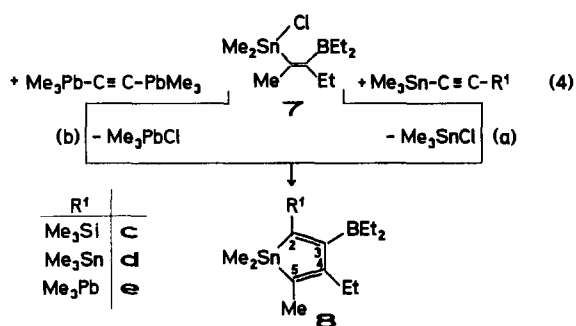
^e See Fig. 2.

^f $J(^{29}\text{Si}^{13}\text{C}) = 56.7 \pm 0.5$ Hz.

even in the presence of the organometallic substituents at the C≡C bond in **5c–e**. This demonstrates the stabilizing effect of intramolecular N–Sn coordination. In the case of R¹ = ^tBu, the exchange reaction requires heating and, since the following intramolecular reactions are faster, only the final product **6b** is obtained.



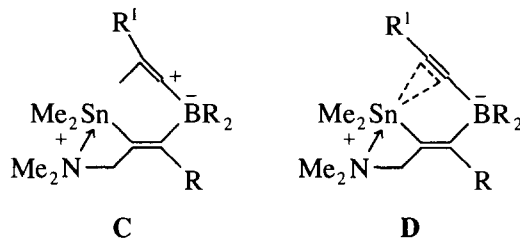
The reactions between **7** and alkynyltin compounds [8a] (Eq. (4a)) were reinvestigated, and, in addition, the reaction between **7** and bis(trimethylplumbyl)ethyne (Eq. (4b)) was studied. We failed to detect any of the zwitterionic intermediates. In agreement with the literature [8a], the stannoles **8c–e** were formed selectively. The stannole **8e** is obtained as an oily red liquid which decomposes after several hours at room temperature.



2.1. NMR spectroscopic measurements

The ¹¹B, ¹³C, ²⁹Si, ¹¹⁹Sn and ²⁰⁷Pb NMR data of the zwitterionic intermediates **5** and the stannoles **6** and **8** are given in Tables 1, 2 and 3, respectively. The reactions between **4** or **7** and the alkynyltin and alkynyl-lead compounds were monitored by ¹¹⁹Sn NMR (Fig. 1) in order to find the best conditions for measuring NMR data of the zwitterionic intermediates **5** and to follow their rearrangement to the stannoles **6** or **8**. There is already a large data set available [3,7–9] for compounds similar to **5** and **6** or **8**, and all NMR data measured for **5**, **6** and **8** are consistently in support of the proposed structures.

NMR data of the bridging R¹-C≡C-B moiety in the intermediates **5** are of particular interest since they may reveal important information about the bonding situation. The δ¹¹B values of **5** are in the range known for tetraorganylborates [13]. The low ¹³C(≡C-B) nuclear shielding, especially in the case of **5c,d**, compared with alkynylborates [3a,14] or alkynes in general [14], indicates an interaction with the cationic tin fragment. The β-metal-stabilizing effect of R¹ = SiMe₃, SnMe₃ or PbMe₃ should favour a strong contribution of the vinyl cationic structure **C** or the σ-π delocalized structure **D**. Indeed, marked deshielding is typical of the positively charged ¹³C nucleus in vinyl cations [15] corresponding to the structure **C**. The shielding of ¹³C(R¹ = Me), ²⁹Si, ¹¹⁹Sn(SnMe₃) and ²⁰⁷Pb in **5a,c–e** is reduced with respect to comparable alkynes, suggesting a significantly bent R¹-C≡C-B group. The ¹¹⁹Sn nuclear shielding in the compounds **5a–e** is increased in comparison with intermediates of type **A** in which the coordinative N–Sn bond is absent, and in contrast with compounds **A** [3a], the temperature dependence of the δ¹¹⁹Sn values is small. The increase in ¹¹⁹Sn nuclear shielding in the series **5a** < **5c** < **5d,e** also points towards an increasing contribution of the structures **C** and **D**, otherwise one would expect a much smaller influence of R¹ on δ¹¹⁹Sn.



The magnitude of the coupling constants [¹J(¹¹⁹Sn¹³C)] for the R¹-C≡ group increases from 45.2 Hz (R¹ = Me) to 126.4 Hz (R¹ = PbMe₃). Although the signs of these coupling constants are unknown, the absolute increase indicates a stronger Sn–C(R₁)≡ interaction in the derivatives **5c–e** than in **5a**, in accord with the increasing (from C to Pb) β-metal-stabilizing effect. The magnitude of the coupling constants ¹J(¹¹⁹Sn(SnMe₃)¹³C≡) and ¹J(²⁰⁷Pb¹³C≡) in **5d**

Table 2
 ^{11}B , ^{13}C , ^{29}Si , ^{119}Sn and ^{207}Pb NMR data ^a of the stannoles **6**

R ¹ No.	Bu ^t 6b	SiMe ₃ ^b 6c	SnMe ₃ ^c 6d	PbMe ₃ ^d 6e	MeOCH ₂ 6f
$\delta^{13}\text{C}(\text{Me}_2\text{Sn})$	-6.6 [360.2]	-6.2 [291.0]	-6.9 [292.6]	-7.0 [298.9]	-8.3 [328.0]
$\delta^{13}\text{C}(\text{C}(2))$	156.7 [410.9]	139.5 [211.7]	137.5 [201.1] [384.2]	144.0 [n.m.] {157.1}	133.0 [376.1]
$\delta^{13}\text{C}(\text{C}(3))$	159.6 (br)	181.0 (br)	184.8 (br)	183.3 (br)	172.3 (br)
$\delta^{13}\text{C}(\text{C}(4))$	151.0 [121.5]	151.7 [164.4]	151.7 [163.4] [111.3]	152.2 [203.9] {188.5}	152.9 [87.6]
$\delta^{13}\text{C}(\text{C}(5))$	140.1 [479.5]	146.4 [467.6]	144.5 [466.7] [13.0]	144.9 [n.m.] {18.0}	142.9 [543.0]
$\delta^{13}\text{C}(\text{Et}_2\text{B})$	22.0 (br) 9.8	22.5 (br) 9.6	21.7 (br) 9.1	22.0 (br) 9.4	19.3 (br) 10.7
$\delta^{13}\text{C}(\text{Et}-\text{C}(4))$	25.9 [57.8]	26.7 [62.1]	26.4 [61.0]	26.8 [61.0]	24.8 [61.0]
$\delta^{13}\text{C}(\text{CH}_2\text{NMe}_2)$	61.3 [48.0]	61.8 [51.8]	61.4 [52.9]	61.6 [54.0]	62.0 [51.2]
$\delta^{13}\text{C}(\text{R}^1-\text{C}(2))$	45.9 37.8 [62.1] 33.3	46.2 2.1 [11.4] ^e	45.9 -7.5 [< 5] [328.5]	46.0 -1.0 [12.6] {209.1}	46.0 87.1 [n.m.] 55.7 (OMe)
$\delta^{11}\text{B}$	+85.0	+85.0	+85.0	+85.0	+26.5
$\delta^{119}\text{Sn}$	+3.4	+66.1	+64.0 [893.3]	+59.6 [1551.0]	-37.2

^a In $[\text{D}_8]\text{toluene}$ (**6e**), in C_6D_6 (**6c,6f**) and in CDCl_3 (**5b,5d**), all ca. 20% at 298 ± 1 K; coupling constants to ^{119}Sn [Hz, ± 0.5] and ^{207}Pb [Hz, ± 0.5] are given in square and curved brackets, respectively; (n.m.) = not measured; (br) denotes the broadened ^{13}C NMR signals for a boron-bonded carbon atom.

^b $\delta^{29}\text{Si} - 10.1$.

^c $\delta^{119}\text{Sn}(\text{SnMe}_3) - 38.9$ [893.3].

^d $\delta^{207}\text{Pb} - 38.0$ [1551.0].

^e $^1J(^{29}\text{Si}^{13}\text{C}) = 51.2 \pm 0.5$ Hz.

and **5e** is unusual for alkynyl(trimethyl)tin and particularly for alkynyl(trimethyl)lead compounds [14,16]. Therefore, the sign of $^1J(^{207}\text{Pb}^{13}\text{C}\equiv)$ was determined as

Table 3
 ^{11}B , ^{13}C , ^{29}Si , ^{119}Sn and ^{207}Pb NMR data ^a of the stannoles **8**

R ¹ No.	SiMe ₃ ^b 8c	SnMe ₃ ^c 8d	PbMe ₃ ^d 8e
$\delta^{13}\text{C}(\text{Me}_2\text{Sn})$	-7.6 [278.2]	-8.1 [276.0]	-8.2 [282.3]
$\delta^{13}\text{C}(\text{C}(2))$	136.1 [231.1] (66.8)	134.4 [223.8] [336.7]	140.7 [226.7] {168.4}
$\delta^{13}\text{C}(\text{C}(3))$	182.2 (br)	186.2 (br)	184.6 (br)
$\delta^{13}\text{C}(\text{C}(4))$	153.3 [173.2]	154.0 [173.0] [106.8]	154.3 [162.9] {178.2}
$\delta^{13}\text{C}(\text{C}(5))$	139.0 [451.4]	138.1 [454.0]	137.6 [453.4] {16.3}
$\delta^{13}\text{C}(\text{Et}_2\text{B})$	22.2 (br) 9.2	22.1 (br) 9.4	22.2 (br) 9.5
$\delta^{13}\text{C}(\text{Et}-\text{C}(4))$	27.2 [58.2]	25.7 [59.8]	25.8 [71.0]
$\delta^{13}\text{C}(\text{CH}_3-\text{C}(5))$	13.9 [7.5]	14.1 [8.9]	{3.2}, 14.1 [9.8]
$\delta^{13}\text{C}(\text{R}^1-\text{C}(2))$	17.4 [75.2]	17.6 [76.3]	17.7 [75.2] {< 2}
$\delta^{13}\text{C}(\text{R}^1-\text{C}(2))$	1.8 [13.1] (50.9)	-7.2 [11.5] [331.9]	-0.8 [13.1] {216.4}
$\delta^{11}\text{B}$	+86.0	+86.0	+86.0
$\delta^{119}\text{Sn}$	+59.2 (93.7)	+57.1 [978.5]	+52.3 [1632.0]

^a In C_6D_6 (ca. 20% at 298 ± 1 K); coupling constants ^{29}Si [Hz, ± 0.5], ^{119}Sn [Hz, ± 0.5] and ^{207}Pb [Hz, ± 0.5] are given in parentheses, square and curved brackets, respectively; (br) denotes the broadened ^{13}C NMR signals for a boron bonded carbon atom; data for **8c** and **8d** are taken from the literature [8a].

^b $\delta^{29}\text{Si} - 10.0$ [93.7].

^c $\delta^{119}\text{Sn}(\text{SnMe}_3) - 38.4$ [978.5].

^d $\delta^{207}\text{Pb} - 47.2$ [1632.0].

described [16b] (see Fig. 2) and found to be negative. A large negative value of $^1J(^{207}\text{Pb}^{13}\text{C}\equiv)$ (-335.2 Hz) implies an extremely polarized Pb-C \equiv bond, in agreement with the proposed bonding situation in **5e**. The fairly small values $|^2J(^{119}\text{Sn}^{119}\text{Sn})|$ (14.2 Hz) in **5d** and $|^2J(^{207}\text{Pb}^{119}\text{Sn})|$ (24.4 Hz) in **5e** seem to be more consistent with the structure **D** rather than with **C**, considering the large absolute magnitude of such geminal coupling constants across a formally sp^2 hybridized carbon atom (see the data for the stannoles **6d** and **6e** in Table 2). However, fairly small values of $^2J(^{119}\text{Sn}^{119}\text{Sn})$ have been also found in the case of allenes bearing two, three or four SnMe₃ groups [17].

The existence of a coordinative N-Sn bond in the

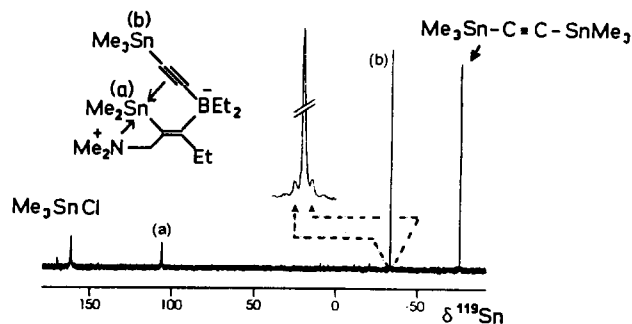


Fig. 1. 33.3 MHz $^{119}\text{Sn}\{^1\text{H}$ inverse gated} NMR spectrum of a reaction solution containing the zwitterionic intermediate **5d**, Me_3SnCl and excess of $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SnMe}_3$. The arrows mark the expanded spectrum of the $^{119}\text{Sn}(\text{Me}_3\text{Sn}-\text{C}\equiv)$ NMR signal for **5d**, showing $^{117/119}\text{Sn}$ satellites corresponding to $^2J(\text{SnSn}) = 14.2$ Hz.

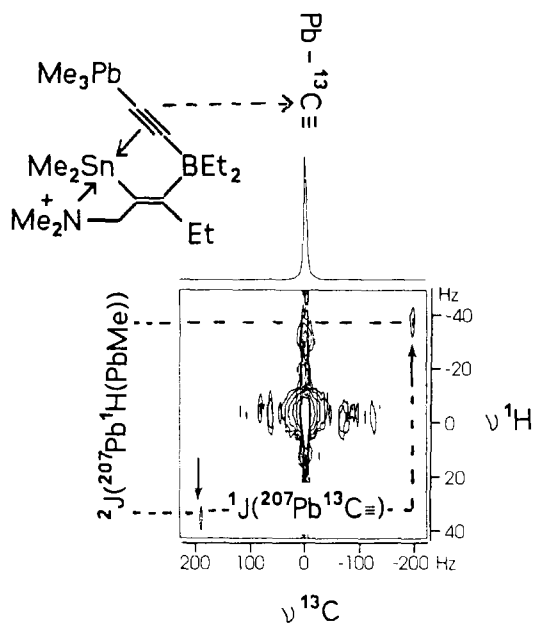
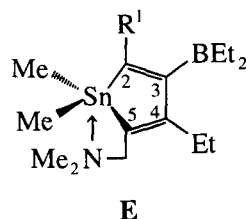


Fig. 2. 125.7 MHz 2D $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlation based on the long-range coupling constant $^3J \equiv ^{13}\text{C}-\text{Pb}-\text{C}-^1\text{H} \approx 2$ Hz. The passive nucleus is ^{207}Pb and the signs of the coupling constants $^2J(^{207}\text{Pb}^1\text{H})$ (< 0 [24]) and $^1J(^{207}\text{Pb}^{13}\text{C} \equiv)$ are compared; the positive tilt of the cross peaks marked by arrows indicates alike signs [24,25].

stannoles **6b–e**, as shown in **E**, cannot be ascertained by comparing the chemical shifts $\delta^{13}\text{C}$ and $\delta^{119}\text{Sn}$ with other stannoles [e.g., **8b–d** [8a], **8e** (Table 3)]. From these data it appears that there is no coordinative N–Sn interaction. However, inspection of the magnitudes of the coupling constants $^1J(^{119}\text{Sn}^{13}\text{C})$ indicates at least weak coordinative N–Sn bonding. According to structure **E**, the nitrogen atom and the C(2) atom of the stannol ring occupy the axial positions of a distorted trigonal bipyramid. Since changes in the magnitude of $|^1J(^{119}\text{Sn}^{13}\text{C})|$ depend to some extent on the “s-character” of the Sn–C bond hybrid orbitals [10] (at least for a series of closely related tetra-organyltin compounds), one would expect smaller $|^1J(^{119}\text{Sn}^{13}\text{C}(2))|$ values in **6** as compared with **8**. Conversely, the $|^1J(^{119}\text{Sn}^{13}\text{C}(5))|$ and $|^1J(^{119}\text{Sn}^{13}\text{C}(\text{Me}))|$ values for the carbon atoms occupying preferentially the equatorial positions, should be larger in **6** than in **8**. This is indeed observed in all cases.



3. Conclusions

The tin chloride **4** appears to be a useful starting material in organometallic synthesis, considering the

rich chemistry of the analogous tin chloride **7** [18]. Like other metalloles [19], the stannoles **6** will have a considerable synthetic potential. Unique properties may be related to the presence of the dimethylamino group in **6** which is available for electrophilic attack and by this selective ring opening reactions can be controlled. The coordinative N–Sn bond helps to stabilize (η^2 -alkyne)tin compounds which otherwise are extremely instable and short-lived.

4. Experimental details

All synthetic work and handling of compounds was carried out under an atmosphere of dry N_2 or Ar, using carefully dried glassware and dry solvents. The starting materials were commercial products except for Me_3PbBr which was prepared from Me_4Pb and Br_2 [20]. The alkynyltin compounds **1** [9] and $\text{R}^1-\text{C}\equiv\text{C}-\text{SnMe}_3$ [21], bis(trimethylplumbyl)ethyne [22], and (*E*)-2-chlorodimethylstannyl-3-diethylboryl-2-pentene (**7**) [23] were obtained as described in the literature.

EI MS spectra (70 eV) were recorded with a Varian MAT CH 7 spectrometer. NMR spectra were measured at $25 \pm 1^\circ\text{C}$, if not mentioned otherwise, from solutions (ca. 5–20%) in 5 mm tubes (see also Tables 1–3), using Jeol FX 90 Q, Bruker AC 300 and Bruker AM 500 spectrometers, equipped with variable temperature and multinuclear units. Chemical shifts are given with respect to Me_4Si [$\delta^1\text{H}$ ($\text{CHCl}_3/\text{CDCl}_3$) = 7.24 $\delta^1\text{H}$ (CH_2Cl_2) = 5.33; $\delta^1\text{H}$ ($\text{C}_6\text{D}_5\text{CHD}_2$) = 2.03; $\delta^1\text{H}$ ($\text{C}_6\text{D}_5\text{H}$) = 7.14; $\delta^{13}\text{C}$ (CDCl_3) = 77.0; $\delta^{13}\text{C}$ (CD_2Cl_2) = 53.8; $\delta^{13}\text{C}$ ($\text{C}_6\text{D}_5\text{CD}_3$) = 20.4; $\delta^{29}\text{Si}$ with $\bar{\nu}(^{29}\text{Si}) = 19.867184$ MHz], $\text{Et}_2\text{O}-\text{BF}_3$ [$\delta^{11}\text{B}$ with $\bar{\nu}(^{11}\text{B}) = 32.083971$ MHz], Me_4Sn [$\delta^{119}\text{Sn}$ with $\bar{\nu}(^{119}\text{Sn}) = 37.290665$ MHz] and Me_4Pb [$\delta^{207}\text{Pb}$ with $\bar{\nu}(^{207}\text{Pb}) = 20.920597$ MHz].

4.1. (*E*)-2-Chloro(dimethyl)stannyl-3-diethylboryl-*N,N*-dimethyl-2-pentenylamine (**4**)

A mixture of 31.3 g (100 mmol) of $\text{Me}_2\text{Sn}(\text{C}\equiv\text{CCH}_2\text{NMe}_2)$ (**1**) and 25.3 g (120 mmol) of Me_2SnCl_2 in 100 ml of hexane was heated to reflux for 3 h. Then the reaction mixture was cooled to -78°C and 31 ml (220 mmol) of Et_3B were added in one portion. After warming to room temperature and heating to reflux for 4 h, the solvent and the excess Et_3B were removed in vacuo, leaving a brown residue. Fractional distillation afforded first the excess of Me_2SnCl_2 and then 29.1 g (80%) of the product **2** as a yellowish oil (b.p. $143^\circ\text{C}/.01$ Torr. EI-MS: m/z (%) = 336 (67) [$\text{M}^+ - 29$], 229 (50), 212 (63), 196 (58), 185 (57), 165 (83), 135 (76), 110 (100), 58 (80). ^1H NMR (300 MHz; CDCl_3): $\delta^1\text{H}$ [$J(^{119}\text{Sn}^1\text{H})$] = 0.46 [59.8] s, 6H, SnMe_2 ; 1.09 q, 0.86 t, 10H, BEt_2 ; 1.88 q, 0.81 t, 5H, $=\text{CET}$; 3.22 [70.1] s, 2.21 s, 8H, CH_2NMe_2 .

4.2. (*gh*²-alkyne)tin Compounds (5)

A solution of 4 mmol of the alkynyltin compound $R^1-C\equiv C-SnMe_3$ or $Me_3Pb-C\equiv C-PbMe_3$ in 8 ml of $CHCl_3$ was cooled to $-78^\circ C$. After addition of 1.45 g (4 mmol) of **4** in one portion, the mixtures were warmed to $0^\circ C$ and kept at that temperature for 24 h (**5a**), 2 d (**5c**), 12 h (**5d**), 4 h (**5e**) and 2 d (**5f**). In the case of **5e**, insoluble Me_3PbCl was filtered off after 4 h. In the case of $R^1 = ^tBu$, no reaction had occurred after 4 d at $0^\circ C$. All reactions were monitored by ^{119}Sn NMR and the compounds **4** were characterized by other NMR data once the reactions were found to be complete.

5a: 1H NMR ($CDCl_3$; $-30^\circ C$; 300 MHz): δ^1H [$J(^{119}Sn^1H)$] = 0.48 [52.5] s, 6H, $SnMe_2$; -0.02 m, 0.51 m, 10H, BEt_2 ; 1.70 m, 0.70 t, 5H, $-CEt$; 1.79 s, 3H, $=CMe$; 3.22 [78.5] s, 2.25 s, 8H, CH_2NMe_2 .

5c: 1H NMR ($CDCl_3$; 300 MHz): δ^1H [$J(^{119}Sn^1H)$] = 0.16 s, 9H, $SiMe_3$; 0.67 [51.6] s, 6H, $SnMe_2$; 0.00 m, 0.71 t, 10H, BEt_2 ; 1.89 q, 0.84 t, 5H, $=CEt$; 3.28 [77.8] s, 2.32 s, 8H, CH_2NMe_2 .

5d: 1H NMR ($CDCl_3$; 300 MHz): 0.28 [58.0] s, 9H, $SnMe_3$; 0.51 [51.6] s, 6H, $SnMe_2$; 0.00 m, 0.64 t, 10H, BEt_2 ; 1.84 q, 0.76 t, 5H, $=CEt$; 3.21 [77.3] s, 2.26 s, 8H, CH_2NMe_2 .

5e: 1H NMR ($CDCl_3$; $-30^\circ C$; 300 MHz): δ^1H [$J(^{119}Sn^1H)$] { $J(^{207}Pb^1H)$ } = 0.43 [51.5] s, 6H, $SnMe_2$; -0.01 m, 0.60 t, 10H, BEt_2 ; 1.08 [74.5] s, 9H, $PbMe_3$; 1.81 q, 0.72 t, 5H, $-CEt$; 3.12 [77.2] s, 2.19 s, 8H, CH_2NMe_2 .

5f: 1H NMR ($CDCl_3$; 500 MHz): δ^1H [$J(^{119}Sn^1H)$] = 0.62 [52.4] s, 6H, $SnMe_2$; 0.16 m, 0.67 t, 10H, BEt_2 ; 1.86 q, 0.81 t, 5H, $=CEt$; 3.36 [78.0] s, 2.34 s, 8H, CH_2NMe_2 ; 4.10 s, 3.25 s, 5H, CH_2OMe .

4.3. Stannoles (6)

The reaction solutions containing the intermediates **5** were kept for several days at room temperature. The reaction mixture for $R^1 = ^tBu$ was heated under reflux for 4 h. The solvent was removed in vacuo and the Me_3SnCl (**6a–d,f**) was removed by sublimation (10^{-4} Torr). The pure stannoles **6b–f** (satisfactory elemental analyses) were left as yellow, oily liquids which decompose on attempted distillation ($> 100^\circ C/10^{-4}$ Torr). The stannole **6a** is part of a complex mixture which has not been analysed as yet.

4.4. 3-Diethylboryl-4-ethyl-1,1,5-trimethyl-2-trimethylplumbylstannole (8e)

A suspension of 0.53 g (1 mmol) of $Me_3Pb-C\equiv C-PbMe_3$ in 20 ml of hexane was cooled to $-78^\circ C$. After addition of 0.321 g (1 mmol) of **7** in one portion through a syringe the mixture was slowly warmed to room temperature, the progress of the reaction being

monitored by ^{119}Sn NMR at regular intervals. The colour of the reaction solution changed to red and a colourless precipitate (Me_3PbCl) was formed. The stannole **8e** was formed without a detectable intermediate. Filtration and removal of the solvent in vacuo gave 0.30 g (54%) of pure ($> 95\%$ according to 1H NMR) **8e** as a red oil. The red colour arises from small amounts of impurities and is typical of many organolead compounds prepared by 1,1-organoboration reactions. 1H NMR (C_6D_6 ; 300 MHz): δ^1H [$J(^{119}Sn^1H)$] { $J(^{207}Pb^1H)$ } = 0.29 [53.2] s, 6H, $SnMe_2$; 0.80 [56.4] s, 9H, $PbMe_3$; 1.39 m, 1.04 t, 10H, BEt_2 ; 2.12 q, 0.99 t, 5H, $=CEt$; 2.04 [44.0] s, 3H, $=CMe$.

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