1,1-Organoboration of tri-1-alkynyltin compounds: novel triorganotin cations, stannoles, 3-stannolenes and 1-stanna-4-bora-2,5-cyclohexadienes

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Abstract

Tri-1-alkynyltin compounds [$R^2Sn(C\equiv CR^1)_3$ (**1**), R^2 = Me, R^1 = Me (**a**), ^{n}Bu (**b**), ^{t}Bu (**c**), Me_3Si (**d**), 1-(1-cyclohexenyl) (**e**); R^2 = Et, R^1 = Me (**a**(Et)), ^{n}Bu (**b**(Et)), ^{t}Bu (**c**(Et)), $SiMe_3$ (**d**(Et)); R^2 = ^{n}Bu, R^1 = Me (**a**(Bu)), ^{n}Bu (**b**(Bu))] were prepared, and their reactivity towards trialkylboranes Et_3B (**2**) and $^iPr_3B$ (**3**) in 1,1-organoboration reactions was studied. The first step in each reaction is an intermolecular 1,1-alkyloboration. Afterwards, intramolecular 1,1-vinyloboration or 1,1-alkyloboration compete with further intermolecular 1,1-alkyloboration. Various triorganotin cations (**4**–**7**), stabilized by intramolecular side-on coordination to the C≡C bond of an alkynylborate moiety, were detected as highly fluxional intermediates prior to rearrangement into heterocyclic systems such as stannoles (**9**–**11**), 1-stanna-4-bora-2,5-cyclohexadienes (**8**, **12**). The reactions between **1a** or **1a**(Bu) and an excess of Et_3B (**2**) afford the tris(alkenyl)tin compounds **13** via threefold intermolecular 1,1-ethyloboration. **13** rearrange to the 3-stannolenes (**14a** or **14a**(Bu)). The intermediates and final products were characterized by multinuclear one- and two-dimensional ^1H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn NMR.

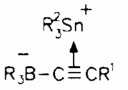
Key words: Organoboration; Tin complexes; Zwitterion alkynyl complexes; NMR multinuclear

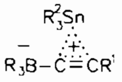
Introduction

Alkynyltin compounds possess reactive Sn–C≡ bonds [1, 2] which are readily attacked by electrophiles. In many cases, exchange reactions take place in which the alkynyl group is transferred from the tin atom to the electrophile E (eqn. (1)). If the electrophile is a tri-

$$.nC\equiv CR^1 + E-R \longrightarrow R^2_3Sn-R + E-C\equiv CR^1 \qquad (1)$$

organoborane, the zwitterionic intermediate **A** is formed [3]. The Sn–C≡ bond has been cleaved, but the formally positive-charged triorganotin fragment is still coordinated to the C≡C bond, ready for further reactions, including attractive alternatives to simple exchange processes. One can also consider intermediates of type **A** as vinyl cations, stabilized by σ-π delocalization [4, 5] typical of β-metal substitution (**B**). Similar shortlived intermediates can be considered in the reaction of alkynylborates with electrophiles [6] such as organosilicon [7] or organotin halides [8].


A


B

Recently, such zwitterionic intermediates have been isolated and fully characterized from 1,1-organoboration reactions between trialkylboranes and di-1-alkynyllead [9], di-1-alkynyltin [10, 11], diamino-di-1-alkynyltin [12] or tetra-1-alkynyltin compounds [13, 14]. This opened convenient routes to the synthesis of various heterocyclic compounds [9–16], useful for further transformations in organic and organometallic synthesis.

In the present work, we report on the reactions between tri-1-alkynyltin compounds (**1**) and triethylborane, Et_3B (**2**), and triisopropylborane, $^iPr_3B$ (**3**). It was intended to detect and to characterize new organotin cations, and it was of interest whether one alkynyl group more (as compared to the di-1-alkynyltin compounds) or less (as compared to the tetra-1-alkynyltin compounds) exerts a marked influence on the principle structure of the intermediates and the final products. It was also hoped that the determination of the structure of the intermediates and final products would shed

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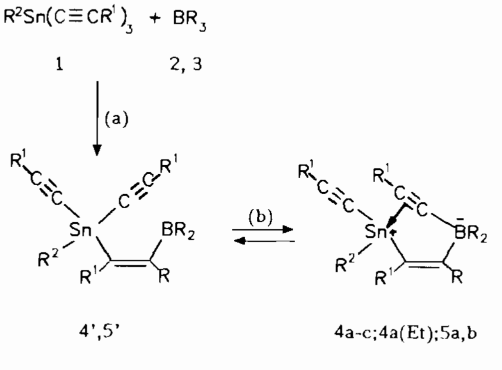
light on the reaction mechanism, in particular with respect to the competition between inter- and intramolecular 1,1-organoboration.

Results and discussion

All reactions between tri-1-alkynyltin compounds (**1**) (if a group other than methyl is linked to tin, this is indicated by its symbol in parentheses) and the trialkylboranes **2** or **3** start with an intermolecular 1,1-alkyloboration and lead to the zwitterionic compounds **4** and **5** which are in equilibrium with **4′** and **5′**, as shown in Scheme 1. NMR studies (*vide infra*) prove that **4** and **5** are the dominant species at low temperature (Fig. 1).

In the case of **4** and **5**, intramolecular 1,1-alkyloboration (Scheme 2(b)) and intramolecular 1,1-vinyloboration (Scheme 2(d)) may compete with further intermolecular 1,1-alkyloboration (Schemes 3 and 4). So far, the formation of **9c** and **9c**(Et) (Scheme 2(d)) are the only examples of intramolecular 1,1-vinyloboration starting from **4c** or **4c**(Et). The intramolecular 1,1-alkyloboration of **5** (Scheme 2(b)) is more common with $R = {}^{i}Pr$ and has been established for four examples of the 1-stanna-4-bora-2,5-cyclohexadienes (**8**, **8′**). Since there are two isomers **8**, **8′** (**8a**:**8a′** = 3:1; **8b**:**8b′** = 10:3; **8b**(Et):**8b**(Et)′ = 6:1), the six-membered ring systems are non-planar and ring-inversion must be slow as compared to the NMR time scale. Both molecular mechanics and semiempirical calculations based on MM+ and PM3 [17] suggest that the boron atom moves out of the plane and a distorted half-chair conformation is preferred. In all types of calculations it turns out that the tin atom is also shifted slightly out of the plane (in the same direction as the boron atom) built by the four olefinic carbon atoms.



Scheme 1. First step in the 1,1-organoboration of tri-1-alkynyltin compounds (**1**); the first detectable zwitterionic intermediates **4a–c**(Et) and **5a,b** were characterized by NMR measurements (Table 2; letters **a–c**, **a**(Et), etc. correspond to numbering of **1** as given in Table 1).

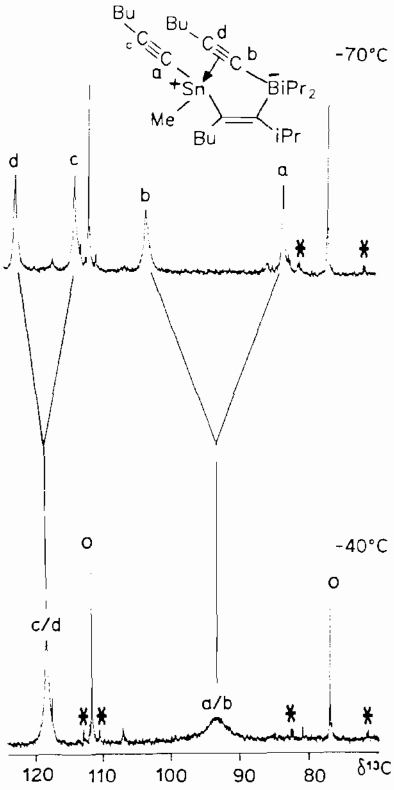
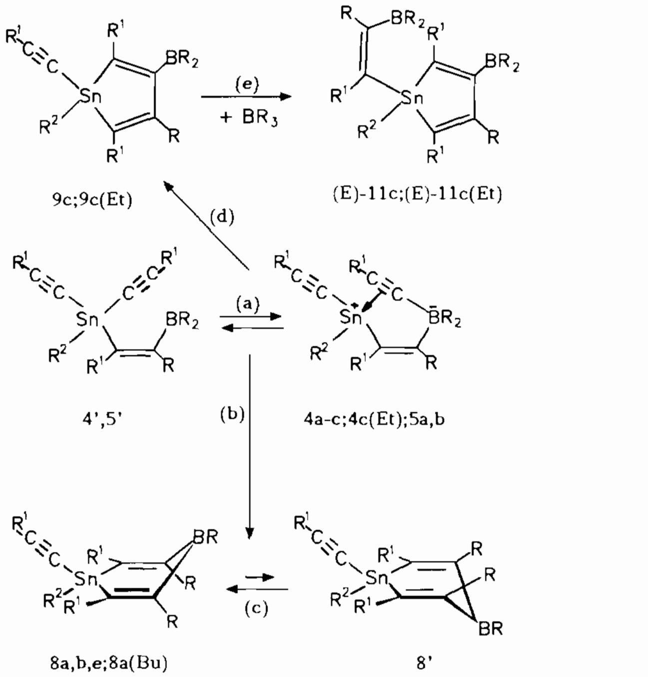


Fig. 1. 75.4 MHz $^{13}C\{^1H\}$ NMR spectrum of **5b** (see Scheme 1(a) and (b)) in CD_2Cl_2; the range for the alkynyl carbon atoms is shown (the $^{117/119}Sn$ satellites are marked by asterisks; ^{13}C NMR signals of the alkynyltin compound **1b** are marked by ○). At −70 °C, the exchange between terminal and bridging alkynyl groups is slow, giving rise to two sets of NMR signals.

In Scheme 3 it is shown that the compounds **4** and **5** react with an excess of the trialkylboranes **2** and **3** to give the intermediates **6** and **7**. Again (see Scheme 1(b)) there is an equilibrium between the zwitterionic compounds **6**, **7** and **6′**, **7′**, the former being dominant at low temperature (Fig. 2). From **6** and in two examples of **7**, the stannoles **10** or **11** are formed via intramolecular 1,1-vinyloboration (Scheme 3(d)), whereas the 1-stanna-4-bora-2,5-cyclohexadienes (**12**) are the result of intramolecular 1,1-alkyloboration starting from **7** (Scheme 3(e)). If **8** or **8′** are present in the mixtures (see Fig. 3), the compounds **12** are also formed in the presence of an excess of **3**. In contrast with **8** and **8′**, the compounds **12** exist only as a single isomer at room temperature. It appears that ring inversion in **12** is severely hindered (see also Fig. 4) owing to the bulky alkenyl group linked to the tin atom.

If steric hindrance is relatively low ($R^1 = Me$; $R^2 = Me$, Bu; $R = Et$), further intermolecular 1,1-ethyloboration of **6a′** or **6a**(Bu)′ leads to **13a** (Scheme 4(b); **13a**(Bu) was not detected) which finally rearrange stereoselectively to the 3-stannolene derivatives **14a** and **14a**(Bu) (Scheme 4(c)). The complex mechanism of this rear-

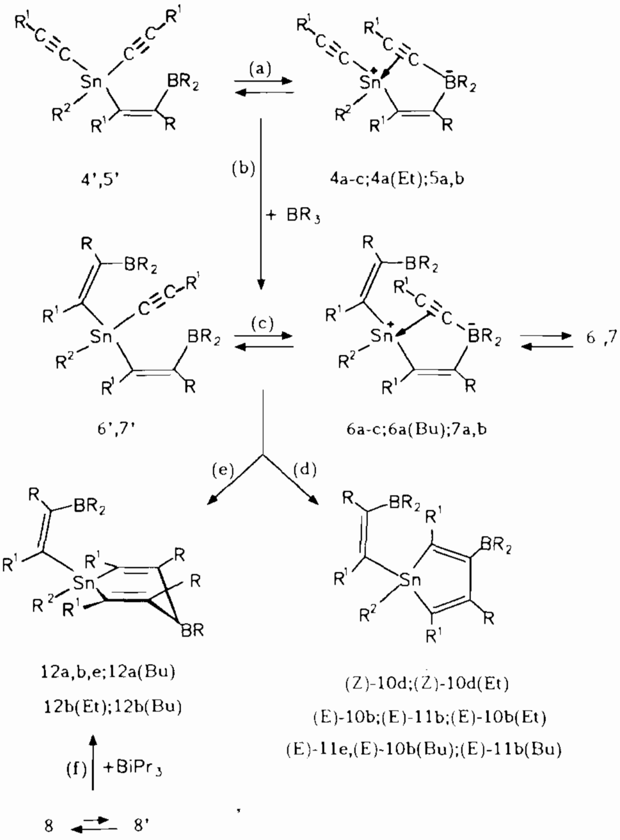


Scheme 2. Further intramolecular 1,1-organoboration starting from the first detectable zwitterionic intermediates **4** and **5** (for NMR data see Tables 4 and 6).

rangement has been discussed previously [18, 19]. Here it is interesting to note that only one diastereomer of **14** is formed (with respect to the exocyclic substituents at the tin atom), presumably as the result of steric crowding [16a].

The structure of the zwitterionic intermediates is analogous to that observed in the organoboration of di-1-alkynyltin [10–12] and tetra-1-alkynyltin compounds [13, 14]. Similarly, the structure of the final products depends in a complex way on the combination of R (from R_3B) and R^1 (from $C{\equiv}CR^1$), whereas R^2 (R^2 = Me, Et, Bu in $R^2Sn(C{\equiv}CR^1)_3$) seems to have little influence. Intermolecular 1,1-ethyloboration competes very efficiently with intramolecular 1,1-organoboration if R^1 is not too bulky. Thus, in the case of **1a**, the reaction with an excess of Et_3B runs readily through to **13a** which rearranges irreversibly to the 3-stannolene **14a**.

Zwitterionic intermediates were not detected in the organoboration of **1d** or **1d**(Et) ($R^1 = SiMe_3$). In this case the intermolecular 1,1-ethyloboration gives at first more than 90% of the product with boryl and silyl groups in *cis*-position at the C=C bond (**4d''**) which is the wrong stereochemistry for further intramolecular organoboration. However, it has been found that organoboration is reversible for this type of alkene, already slightly above room temperature [20, 21]. Thus, any time the correct stereochemistry is present, further



Scheme 3. Further intermolecular 1,1-organoboration starting from the first detectable zwitterionic intermediates **4** and **5** (for NMR data see Table 3 (**6**, **7**), Table 5 (**12**) and Table 6 (**10**, **11**)).

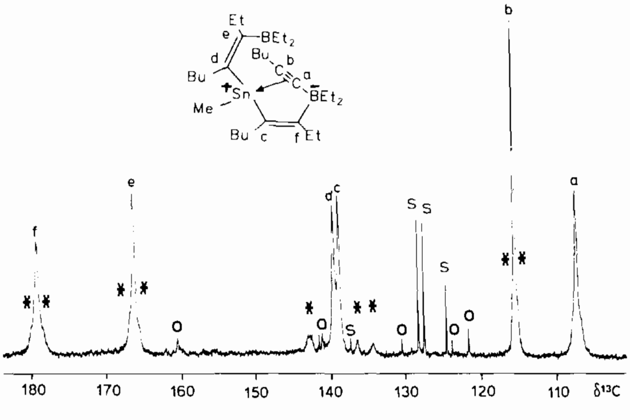


Fig. 2. 67.9 MHz $^{13}C\{^1H\}$ NMR of **6b** (see Scheme 3(b) and (c)) in CD_2Cl_2 at −100 °C; the range of alkynyl and olefinic carbon atoms is shown ($^{117/119}Sn$ satellites are marked by asterisks; a small amount of toluene is still present, marked by S; small signals marked by O arise from the precursor of **6b** and rearrangement products). The non-equivalence of the alkenyl groups as the result of slow exchange of the alkynyl group between boron, tin and the second boron atom is clearly evident.

irreversible intramolecular organoboration takes place, and zwitterionic intermediates are not sufficiently stable under these conditions.

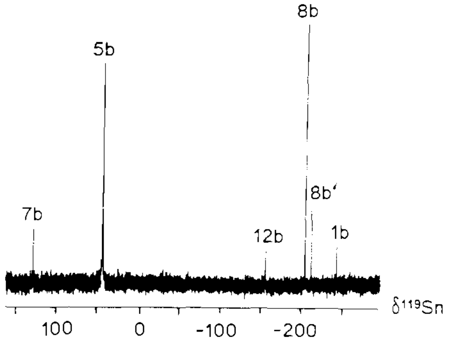
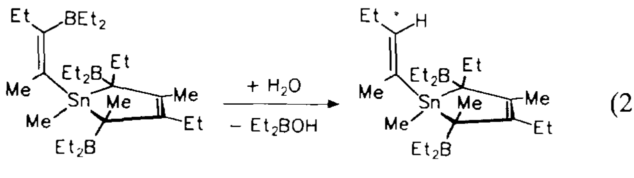


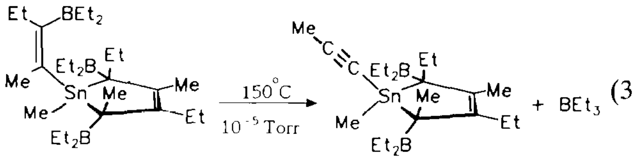
Fig. 3. 111.9 MHz ^{119}Sn{^{1}H inverse gated} NMR spectrum of a mixture obtained from the reaction between **1b** and excess of triisopropylborane (**3**), measured at −20 °C after keeping the reaction mixture for 20 min at room temperature. The ^{119}Sn NMR signals of the zwitterionic intermediates **5b** (Scheme 1(a) and (b)) and **7b** (Scheme 3(b) and (c)) are still visible, together with the ^{119}Sn resonances of the 1-stanna-4-bora-2,5-cyclohexadienes **8b**, **8b'** (Scheme 2(b)) and **12b** (Scheme 3(e)). If the reaction mixture is kept at room temperature for several hours, only the signal of **12b** is observed.

All final products contain reactive B–C and Sn–C bonds. Systematic studies of the reactivity of these compounds are in progress. In the case of compound **14a**, hydrolysis in benzene leads to **15a** (eqn. (2)).



14a 15a (2)

Attempts to purify **14a** by distillation at reduced pressure afford a mixture (≈1:1) of **14a** and **16a** (eqn. (3)).



14a 16a (3)

The formation of **16a** can be understood as a deorganoboration reaction [20, 21] in order to relieve **14a** of some of its steric strain.

NMR spectroscopic results

The tri-1-alkynyltin compounds (**1**) were characterized by ^{1}H (see 'Experimental'), ^{13}C, ^{29}Si and ^{119}Sn NMR, in some cases also by solid-state CP/MAS ^{119}Sn NMR (Table 1).

The organoboration reactions were monitored first by ^{119}Sn NMR at variable temperature in order to find optimum conditions for ^{13}C NMR. A typical example of the potential of ^{119}Sn NMR in the analysis of complex mixtures [22] is given in Fig. 3, showing the presence of six different compounds in the mixture and allowing for structural assignment of the components. In the case of the organoboration of **1d** or **1d**(Et), the presence of the Me$_3$Si group allowed the use of ^{29}Si NMR as an additional tool. This is shown in Fig. 5 for a reaction solution containing the final product (*Z*)-**10d** and a small amount of one of its precursors. By using ^{119}Sn NMR at variable temperature first, the structural assignment of many intermediates was then feasible by ^{13}C NMR, also at variable temperature (in the case of the highly fluxional intermediates **4** to **7**, see Figs. 1 and 2). $^{117/119}$Sn satellite signals owing to coupling constants $^nJ(^{117/119}Sn^{13}C)$ ($n = 1$–4) were used in all assignments of ^{13}C resonance signals, together with the broadening of ^{13}C resonance signals of boron-bonded carbon atoms as a result of scalar relaxation of the second kind [23]. In ambiguous cases, 2D heteronuclear shift correlations (HETCOR) of the type ^{13}C/^{1}H (based on $^1J(^{13}C^1H)$ and on long range coupling constants

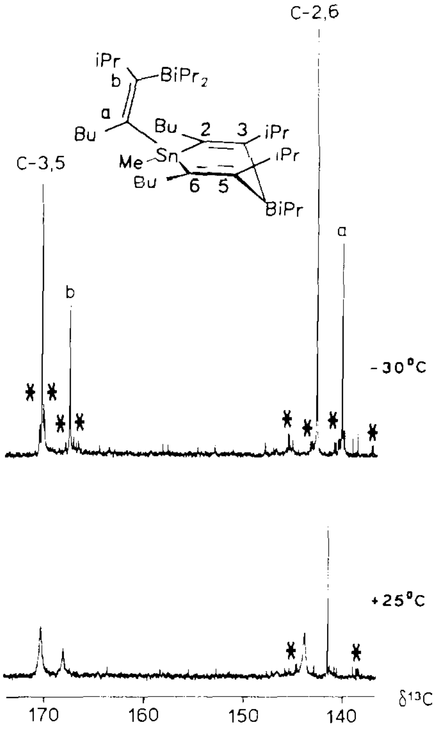
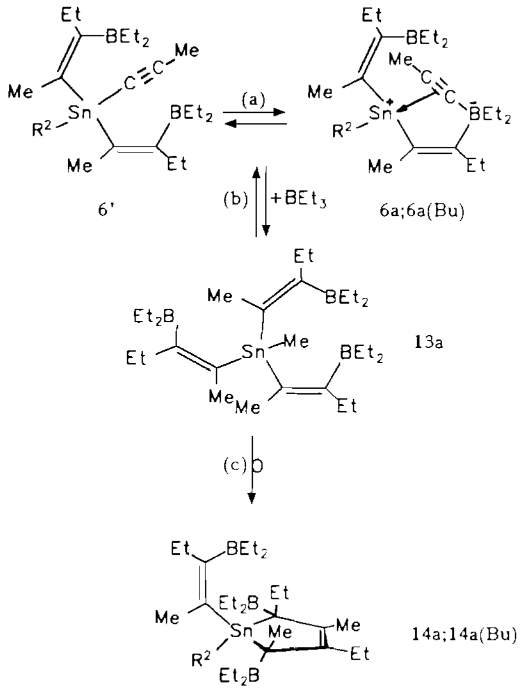


Fig. 4. 75.4 MHz ^{13}C{^{1}H} NMR spectra of **12b** (Scheme 3(e)) in CD$_2$Cl$_2$, showing the region of olefinic carbon atoms ($^{117/119}$Sn satellites are marked by asterisks). At room temperature, the ^{13}C(2,6) resonance signal is broad because of ring inversion; the C(3,5) and the C(b) NMR signals are broad owing to partially relaxed scalar coupling $^1J(^{13}C^{11}B)$. At −30 °C, ring inversion processes become slower and the ^{13}C(2,6) signal is sharp; there is only one isomer of **12b** (note the slight change in the δ^{13}C(2,6) and δ^{13}C(3,5) values when the ring adopts a more rigid conformation). The ^{13}C(3,5) resonances of the boron-bonded carbon atoms become sharp as a result of 'quadrupolar decoupling' at lower temperatures.



Scheme 4. Further intermolecular 1,1-organoboration starting from the second detectable zwitterionic intermediates **6** (for NMR data see Table 7 (**13**, **14**)).

$^nJ(^{13}C^1H)$ ($n=2,3$)), $^{29}Si/^1H$ (based on $^nJ(^{29}Si^1H)$ ($n=2,3$)) and $^{119}Sn/^1H$ (based on $^nJ(^{119}Sn^1H)$ ($n=2,3$)) were used to confirm the assignments. ^{13}C NMR and heteronuclear NMR together with the HETCOR experiments proved extremely valuable for the structural assignments because ^1H NMR spectra, even at 500 MHz, were very complex in most cases. Relevant NMR data are given in Table 2 (η^2-alkynyltin compounds **4** and **5**), Table 3 (η^2-alkynyltin compounds **6** and **7**), Tables 4 and 5 (1-stanna-4-bora-2,5-cyclohexadienes **8** and **12**, respectively), Table 6 (stannole derivatives **9** to **11**) and Table 7 (tris(alkenyl)tin derivative **13a** and 3-stannolenes **14a** to **16a** and **14a**(Bu)).

η^2-Alkynyltin compounds 4, 5, 6 and 7

The dynamic behaviour of the zwitterionic compounds is shown by examples of ^{13}C NMR spectra in Figs. 1 (**5b**) and 2 (**6b**). The activation energy of the alkynyl exchange process [13, 14] can be evaluated [24] at the coalescence temperature for **4c** ($\Delta G^{\neq}$ (223 K) = 44.0 ± 1 kJ/mol), **5b** ($\Delta G^{\neq}$ (223 K) = 39.0 ± 1 kJ/mol), **6a** ($\Delta G^{\neq}$ (213 K) = 38.0 ± 1 kJ/mol) and **6b** ($\Delta G^{\neq}$ (203 K) = 36.0 ± 1 kJ/mol). The changes in the $\delta^{13}C$ values of the bridging as compared to the terminal alkynyl group are typical [10] of the side-on coordination to the cationic organotin fragment. The coupling constants $^1J(^{119}Sn^{13}C)$ in compounds **4** and **5** are instructive. The largest value $|^1J(^{119}Sn^{13}C)|$ is always observed for the olefinic carbon atom (e.g. **4c** at −90 °C: 737.9 Hz) whereas the values $|^1J(^{119}Sn^{13}C_{Me})|$ (**4c**: 349.2 Hz) and $|^1J(^{119}Sn^{13}C_{C\equiv})|$ (**4c**: 352.8 Hz) are of comparable magnitude. This is surprising at first sight since expectations based on the hybridization of the carbon atom would suggest a completely different sequence. It appears that the electronegative alkynyl group induces rehybridization [25] at the readily polarizable tin atom, even to a greater extent than in other mono-1-alkynyltin compounds [26], and the highest s-character must be ascribed to the Sn–C≡ hybrid orbital. In some cases (e.g. **4c** or **6b**), it was possible to observe ^{119}Sn–^{13}C coupling for the bridging alkynyl group which provides firm evidence for the interaction between the C≡C bond and the cationic tin fragment.

^{11}B NMR spectra of the compounds **4** and **5** gave rather broad signals in the range of $\delta^{11}B$ 0 to −10 at low temperature, typical of tetracoordinate boron atoms [23b,c], similar to other zwitterionic intermediates described previously [9–14]. In the case of **6** and **7**, broad ^{11}B NMR signals were found with $\delta^{11}B$ values $\approx +40$, about half way between those of compounds **4** and **5** and alkenylboranes ($\delta^{11}B \approx +80$), as expected for a fast equilibrium between **6**, **7** and **6'**, **7'**. If the equilibrium was shifted more to **7**, as for **7b**, the ^{11}B resonance signal of the tetracoordinate boron atom appeared at $\delta^{11}B$ +3.4; the one of the alkenylborane moiety was too broad for assignment. There was little change of the $\delta^{119}Sn$ values of **4**, **5** or **6**, **7** with lower temperature (a slight shift to higher frequency at lower temperature) indicating that the preferred structure of the cationic tin fragment with side-on coordination to the C≡C bond is already the major contributor to ^{119}Sn nuclear shielding. The $\delta^{119}Sn$ values of **6** and **7** are rather similar to those of the corresponding intermediates obtained via organoboration of di-1-alkynyltin compounds [10]. The increased ^{119}Sn nuclear shielding in **4** and **5** with respect to that in **6** and **7** is mainly the result of the shielding influence of the terminal alkynyl group [22]. However, it turned out that $\delta^{119}Sn$ values of these zwitterionic compounds are very sensitive towards small structural changes which may affect the nature of the side-on coordination (compare, for example, the $\delta^{119}Sn$ values of **4a** (−26.8), **4b** (+52.9) and **4c** (0.7) with those of **1a** (−250.4), **1b** (−249.3) and **1c** (−245.0)).

1-Stanna-4-bora-2,5-cyclohexadienes 8, 8' and 12

All NMR data of the compounds **8**, **8'** (Table 4) and **12** (Table 5) support the proposed structures. They correspond closely to the data measured for other 1-stanna-4-bora-2,5-cyclohexadiene derivatives which were obtained from organoboration of di-1-alkynyltin compounds [10]. Replacement of an exocyclic SnMe group by an alkenyl group (**12**) or an alkynyl group (**8**, **8'**) leads to the expected increase in ^{119}Sn nuclear

TABLE 1. ^{119}Sn and ^{13}C NMR data[a] of tri-1-alkynyltin compounds $R^2Sn(C{\equiv}CR^1)_3$ (**1**)

No. R^1/R^2	δ^{119}Sn	δ^{13}C			
		R^2	Sn*C*≡	≡*C*R^1	R^1
1a Me/Me	−250.4 [b]	−5.6 [617.1]	77.7 [873.9]	107.3 [184.2]	4.6 [16.2]
1b Me/Bu	−249.3	−5.1 [613.3]	78.1 [874.4]	111.4 [180.0]	13.8, 20.0, 22.1, 30.9 [15.7] [6.8]
1c Me/^{t}Bu	−245.0	−4.7 [612.5]	76.3 [864.3]	119.7 [171.1]	28.5, 30.8 [14.2][6.5]
1d Me/SiMe$_3$	−273.4 [c, d]	−5.2 [603.8]	106.2 [760.3] (10.0)	119.6 [126.8] (74.5)	−0.4 [n.o.] (56.7)
1e Me/[e]	−239.2	−5.0 [618.2]	85.2 [857.4]	112.1 [176.2]	21.6, 22.4, 25.8, 29.2 121.2[19.7], 136.7[10.8]
1a(Et) Et/Me	−242.9	7.0, 9.7 [639.2][33.8]	77.1 [815.3]	107.6 [170.0]	4.6 [15.3]
1b(Et) Et/Bu	−242.9	7.2, 9.8 [640.0][32.3]	77.8 [809.9]	112.2 [164.3]	13.6, 20.0, 22.1, 30.8 [15.7] [7.8]
1c(Et) Et/^{t}Bu	−236.9 [f]	7.5, 9.8 [634.2][33.8]	75.8 [806.4]	120.3 [157.0]	28.6, 30.9 [13.1][6.5]
1d(Et) Et/SiMe$_3$	−267.9 [g]	7.4, 9.6 [622.1][32.3]	105.7 [704.6] (n.o.)	119.7 [115.5] (n.o.)	−0.4 [n.o.] (56.7)
1a(Bu) Bu/Me	−249.2	13.6, 14.7 [627.1] 26.4, 28.0 [85.0][30.5]	77.6 [813.1]	107.5 [169.5]	4.6 [15.3]
1b(Bu) Bu/Bu	−249.6	13.8, 14.9 26.3, 28.1	78.2 [808.4]	112.2 [165.5]	13.8, 20.0, 22.1, 30.9

[a] In C_6D_6 at 25 °C, $^nJ(^{119}SnX)$ ($X = {}^{29}Si$, ^{13}C) in Hz are given in square brackets []; $^nJ(^{29}Si^{13}C)$ in Hz are given in parentheses (); n.o.: not observed. [b] δ^{119}Sn (solid state) = −244.6. [c] δ^{119}Sn (solid state) = −279.7. [d] δ^{29}Si = −18.6 [15.3]. [e] R^1 = 1-(1-cyclohexenyl). [f] δ^{119}Sn (solid state) = −237.2. [g] δ^{29}Si = −18.4 [14.0].

shielding. In most cases the isomerization of **8** to **8′** is slow already at room temperature as indicated by broadened ^{13}C NMR signals. ^{13}C NMR measurements at −30 to −40 °C gave sharp ^{13}C resonances and allowed the $^{117/119}$Sn satellite signals to be observed. For coalescence of the ^{13}C(SnMe) resonances the activation energy of the isomerization was evaluated for **8a** ($\Delta G^{\#}$ (298 K) = 58 ± 1 kJ/mol) and **8b** ($\Delta G^{\#}$ (313 K) = 60.0 ± 1 kJ/mol). Such an isomerization does not take place in the case of compound **12**. As shown in Fig. 4, the olefinic ^{13}C(2,6) resonance signals are broadened at room temperature and become sharp at lower temperature. This indicates that the preferred structure of the ring is already present at room temperature as a result of steric repulsion between the bulky alkenyl group at the tin atom and the ^{i}Pr–B moiety.

Stannole derivatives 9, 10 and 11

The stannoles were readily identified by their typical pattern of olefinic ^{13}C NMR signals. There are three sharp signals, two of which (C(2,5)) have $^{117/119}$Sn satellites according to $^1J(^{119}Sn^{13}C)$, and one (C(4)) with $^{117/119}$Sn satellites according to smaller values $|^{2,3}J(^{119}Sn^{13}C)|$. Finally, there is always a broad signal typical of the boron-bonded C(3) (see Fig. 5). The magnitude of the $J(^{119}Sn^{13}C)$ and δ^{13}C values depends on the nature of the other substituents in the same way as was found previously for similar stannoles [10, 12, 14, 15, 21d]. Similarly, the decrease in ^{119}Sn nuclear shielding has already been noted [15, 21d] if Me$_3$Si groups are in 2,5-position ((*Z*)-**10d** and (*Z*)-**10d**(Et)), whereas the alkynyl group attached to the tin atom in **9c** causes the expected increase in ^{119}Sn nuclear shielding. The magnitude of the geminal coupling constants $^2J(^{119}Sn^{29}Si)$ does not reflect the coupling pathway across and olefinic ring carbon or an exocyclic olefinic carbon atom. In the course of the experiments for mutual assignment of the ^{29}Si, ^{1}H and ^{13}C resonances it turned out that the sign of the long range coupling constant $^4J(^{117/119}SnCSiC^1H)$ changes from +0.5 Hz (C(2)), ≈0 Hz (C(5)) across olefinic ring carbon atoms to −0.3 Hz across the exocyclic olefinic carbon atom.

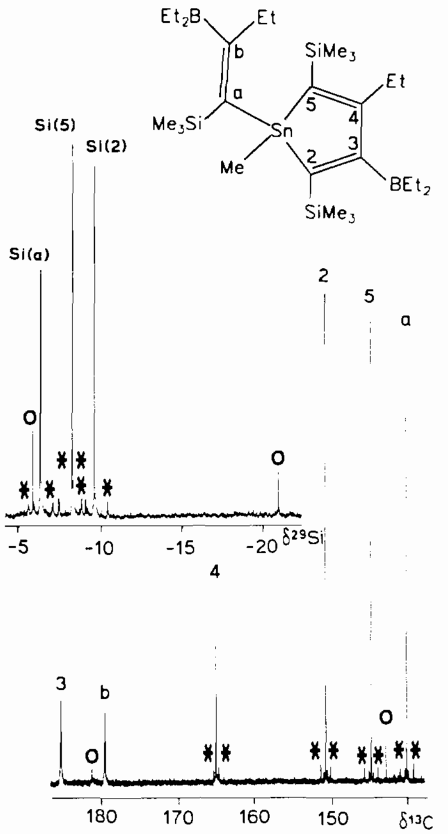


Fig. 5. 75.4 MHz ^{13}C{^{1}H} and 59.6 MHz ^{29}Si (refocused INEPT with ^{1}H decoupling) NMR spectra of **10d** (Scheme 3(d)) in C_6D_6 at 25 °C ($^{117/119}$Sn satellites are marked by asterisks; a small amount of a precursor of **10d** is still present, marked by ○). The ^{13}C NMR spectrum shows the olefinic region with the typical pattern of three sharp (C(2,4,5)) and one broad ^{13}C NMR signal (C(3)) for the stannole ring, together with one sharp (C(a)) and one broad (C(b)) signal for the alkenyl group. Three different ^{29}Si NMR signals (Si(2), Si(5) and Si(a)) are required for **10d**. Their assignment is based on 2D heteronuclear shift correlations ^{13}C/^{1}H (using $^3J(^{13}$CSiC^{1}H)) and ^{29}Si/^{1}H (using $^2J(^{29}$SiC^{1}H)).

Tris(alkenyl)tin compound 13a and 3-stannolene derivatives 14a, 15a and 16a

The structure of the tris(alkenyl)tin derivative **13a** followed conclusively from the ^{13}C NMR data and from the δ^{119}Sn value (Table 7). The 3-stannolene ring in **14** to **16** displayed a typical pattern of ^{13}C NMR signals [10, 17, 18]: two broad resonances of boron-bonded aliphatic quaternary carbon atoms and two sharp olefinic ^{13}C resonances with $^{117/119}$Sn satellites according to small values $|^{2,3}J(^{119}Sn^{13}C)|$. The small values $|^1J(^{119}Sn^{13}C(2,5))|$ (**14a**: 67.1 Hz) are due to the influence of the boryl group as an electropositive substituent and should also result from σ-π delocalization involving the Sn–C(2,5) σ bond and the unoccupied p_z orbital of the boryl groups in 2,5-position. This interaction should also lead to increased shielding of the involved boron nuclei which is evident from $\delta^{11}B = 74.7$ as compared to ≈ 85 for boron atoms of C–BEt$_2$ groups without tin at the carbon atom.

Experimental

All compounds were handled in a dry N_2 atmosphere using carefully purified solvents and dry glassware. The alkyltin trichlorides [27], the 1-alkynyltin compounds **1** [28] and the trialkylboranes **2** [29] and **3** [30] were prepared following literature procedures. All organoboration reactions were first carried out on a small scale for NMR studies. NMR spectra were measured by using Jeol EX 270 (^{1}H, ^{13}C NMR), Bruker AC 300 and Bruker AM 500 NMR spectrometers, the latter two being equipped with a multinuclear unit. Chemical shifts are given with respect to Me$_4$Si (internal) for δ^1H and δ^{13}C ($\delta^{13}C(C_6D_6) = 128.0$), Me$_4$Si (external: $\Xi(^{29}Si) = 19.867184$ MHz), Me$_4$Sn (external: $\Xi(^{119}Sn) = 37.290665$ MHz) and Et$_2$O·BF$_3$ (external: $\Xi(^{11}B) = 32.083971$ MHz). Solid-state NMR: Bruker MSL 300; ^{119}Sn CP/MAS NMR spectra were recorded at 25 °C. The compounds were packed into air-tight inserts, fitting into the commercial ZrO$_2$ rotors of the double-bearing probehead [31]. All ^{119}Sn CP/MAS NMR spectra were run at two different spinning speeds for assignment of the isotropic δ^{119}Sn values. IR: Perkin-Elmer 983. MS: EI-MS (70 eV) Varian MAT CH 7.

IR and ^{1}H NMR data of the tri-1-alkynyltin compounds (1)

1a: $\nu(C{\equiv}C)$ (hexane) = 2280, 2170 cm^{-1}. δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.29 [79.2] s (*Me*Sn); 1.47 [15.1] s (≡C*Me*).

1b: $\nu(C{\equiv}C)$ (hexane) = 2280, 2159 cm^{-1}. δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.24 [78.5] s (*Me*Sn); 0.69 t (*Me*); 1.24 m (CH_2); 1.99 t (≡CCH_2).

1c: $\nu(C{\equiv}C)$ (hexane) = 2279 cm^{-1}. δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.33 [77.9] s (*Me*Sn); 1.09 s (^{t}*Bu*).

1d: δ^1H (C_6D_6, 25 °C) ($^nJ(^{29}Si^1H)$) [$^nJ(^{119}Sn^1H)$] = 0.06 [n.o.] (6.8) s (Si*Me*$_3$); 0.24 [79.5] s (*Me*Sn).

1e: $\nu(C{\equiv}C)$ (toluene) = 2135.0 cm^{-1}. δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.32 [79.9] s (*Me*Sn); cyclohexenyl: 1.25 m, 1.73 m, 2.03 m (CH_2), 6.11 m (=C*H*).

1a(Et): $\nu(C{\equiv}C)$ (hexane) = 2168 cm^{-1}. δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.94 q, 1.13 t (*Et*Sn); 1.52 [14.5] s (≡C*Me*).

1b(Et): $\nu(C{\equiv}C)$ (hexane) = 2281 cm^{-1}. δ^1H (C_6D_6, 25 °C) = 0.69 t, 1.03 q (*Et*Sn); 1.24 m, 1.99 t (≡C*Bu*).

1c(Et): $\nu(C{\equiv}C)$ (hexane) = 2137 cm^{-1}. δ^1H (C_6D_6, 25 °C) = 1.03 t, 1.22 q (*Et*Sn); 1.08 s (^{t}*Bu*).

1d(Et): δ^1H (C_7D_8, 25 °C) ($^nJ(^{29}Si^1H)$) = −0.03 (6.8) s (Si*Me*$_3$); 0.86 q, 1.05 t (*Et*Sn).

1a(Bu): $\nu(C{\equiv}C)$ (toluene) = 2168.0 cm^{-1}. δ^1H (C_6D_6, 25 °C) = 0.75 t, 1.06 t, 1.27 m, 1.58 m (*Bu*Sn); 1.49 s (≡C*Me*).

TABLE 2. ^{119}Sn and ^{13}C NMR data[a, b] of η^2-alkynyltin compounds **4** and **5** at variable temperature

	4a	**5a**	**4b**	**5b**	**5b**	**4c**	**4c**
	Temperature (K)						
	233	233	233	233	203	243	183
Sn*C*=	128.0 [766.2]	128.4 [767.9]	137.2 [755.6]	139.1 [746.6]	138.7 [742.2]	147.2 [745.9]	146.5 [737.9]
B*C*=	176.9 [137.3]	181.1 [136.8]	181.9 [157.5]	183.5 [147.2]	182.9 [146.0]	179.0 (br){br}	178.7 [161.1]
M*C*≡	88.6[c] [317.7]	89.3[c] [238.2]	95.2[c] [163.6]	93.2[c] {br}	103.1[d] [n.o.] 83.1[e] [363.5]	89.7[c] {br}	94.5[d] [82.4] 83.0[e] [352.8]
≡*C*R^1	111.3[c] [58.9]	112.2[c] [43.3]	118.0[c] [23.2]	118.1[c] {br}	122.3[d] [n.o.] 113.6[e] [70.0]	130.3[c] {br}	137.9[d] [36.6] 121.2[e] [77.5]
Sn*Me*	−2.1 [402.7]	−1.9 [371.1]	1.8 [347.9]	1.7 [334.6]	1.3 [337.7]	5.2 [344.7]	4.9 [349.2]
=C*R*^{1}	19.0 [141.7]	21.8 [151.6]	32.8[f] [147.7] 36.0 [41.5]	35.4[g] [141.7] 36.5 [45.8]	35.0[h] [145.0] 36.0 [n.o.]	39.3 [136.7] 33.0 [49.4]	38.9 [136.1] 32.5 [48.8]
≡C*R*^{1}	5.5[c] [7.1]	5.4[c] [n.o.]	21.2, 30.8 22.3, 13.9[c]	20.5, 30.5 22.1, 13.7[c]	19.7, 30.3 21.9, 13.7[i]	29.5, 30.0[c]	29.3, 29.5 29.7, 29.9
=C*R*	24.2, 13.6 [145.2][16.3]	32.3, 17.3 [169.6]	26.1, 13.9 [168.5]	32.9, 17.4 [187.5]	32.8, 19.3 [186.4]	25.7, 15.1 [199.6][20.1]	22.7, 14.7 [198.4][19.5]
δ^{119}Sn	-26.8[j]	−22.8[j]	52.9	39.0[k]	40.9	0.7[l]	3.4

[a] In C_7D_8 or CD_2Cl_2; $^nJ(^{119}Sn^{13}C)$ in Hz are given in []; {br} denotes broad signals due to dynamic effects; n.o.: not observed. [b] $\delta^{13}C(Et_2B) = 19.0 \pm 1$ (CH_2), 10.5 ± 1 (CH_3). $\delta^{13}C(^iPr_2B) = 20.9 \pm 1$ (CH); 19 ± 2 (CH_3). [c] M = Sn or B; fast exchange of alkynyl groups between tin and boron atoms causes averaged ^{13}C resonances. [d] (B*C*≡*C*) group. [e] (Sn*C*≡*C*) group. [f] δ^{13}C(Bu) = 22.9, 14.6. [g] δ^{13}C(Bu) = 22.6, 14.3. [h] δ^{13}C(Bu) = 21.9, 14.2. [i] Broad signals. [j] At 243 K. [k] $\delta^{11}B(CD_2Cl_2$, 253 K) = −1.7. [l] δ^{119}Sn(**4c**(Et), C_7D_8, 233) = 9.5.

1b(Bu): ν(C≡C) (toluene) = 2156 cm^{-1}. δ^1H (C_6D_6, 25 °C) = 0.68 t, 1.23 m, 1.99 t (*Bu*); 0.77 t, 1.26 m, 2.08 t (*Bu*Sn).

Organoboration of trialkynylstannanes 1 with trialkylboranes. General procedure

A solution of 8.00 mmol of **1** in 40 ml of toluene is cooled to −78 °C, then the neat borane (25 mmol) is added in one portion. The mixtures are warmed to room temperature. NMR spectroscopic control shows whether the reaction is complete. In some cases heating to reflux for 30 min is necessary. After removal of the solvent *in vacuo* the residue is characterized by NMR.

12a: yield 4.2 g (98%). δ^1H (CD_2Cl_2, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.08 [52.1] s (*Me*Sn); 0.90–1.20 m (without assignment); 1.53 m (C*H*); 1.74 m (C*H*); 1.96 [54.7] s (*Me*); 2.06 [52.1] s (*Me*); 2.79 m (C*H*); 2.92 m (C*H*). MS: *m*/*z* (%) = 517 (1), 489 (3), 353 (19), 310 (7), 43 (100), 129 (40).

12b: mixture with (*E*)-**11b** (10:1), yield 4.7 g/0.5 g (100%). δ^1H (CD_2Cl_2, 25 °C) = 0.17 s (*Me*Sn); 0.94–1.23 m, 1.31 m, 1.45 m, 1.73 m, 2.18 m, 2.39 m, 2.68 m, 2.78 m, 2.96 m (without assignment).

12b(Bu): mixture with (*E*)-**11b**(Bu) (4:1), yield 4.4 g/1.1 g (100%). δ^1H (C_6D_6, 25 °C) = 0.89, 1.32 m (*Bu*Sn); 0.92, 1.33, 2.41 m (*Bu*C=); 0.95, 1.33/1.38, 1.36/1.51, 2.28/2.76 m (*Bu*C(2/6)); 2.91 m, 1.08 d, 1.13 d (^{i}*Pr*(C3/5)); 2.64 m, 1.20 d (^{i}*Pr*C=); not assigned: ^{i}*Pr*B.

(*E*)-**10b**: 3.7 g (80% product; 20% not identified compounds). δ^1H (CD_2Cl_2, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.26 [50.4] s (*Me*Sn); 0.89–1.02 m, (C*H*$_3$, Bu/Et); 1.32, 1.36/1.43, 1.39, 1.39, 1.40/1.49, 1.41, 2.02/2.15, 2.31/2.45, 2.42 m (C*H*$_2$, Bu); 1.80/2.21, 2.25 m (C*H*$_2$, Et).

(*Z*)-**10d**: yield 4.9 g (98%). δ^1H (CD_2Cl_2, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.16 (5.9) s (*Me*$_3$SiC=); 0.18 (6.4) s (*Me*$_3$SiC(2)); 0.27 (6.4) s (*Me*$_3$SiC(5)); 0.55 [45.3] s (*Me*Sn); 0.79 t, 2.15 q (*Et*C=); 1.04, 2.12/2.37 m 5H, (*Et*C(4)); 0.91 (br), 1.30 (br) (20H, *Et*$_2$B). MS: m/z (%) = 537 (19), 401 (3), 360 (5), 261 (19), 73 (100).

(*E*)-**10b**(Bu): 4.2 g (90% product; 10% not identified compounds). δ^1H (C_6D_6, 25 °C) = 0.85, 0.87/0.98, 0.92, 0.93, 0.95, 1.05 m (C*H*$_3$, *Et*/*Bu*); 1.35, 1.86/2.13 m (C*H*$_2$, *Et*); 1.30/1.38, 1.35, 1.37, 1.46, 1.46, 1.48, 1.60, 2.09/2.18, 2.15, 2.41, 2.46 m (C*H*$_2$, *Bu*).

8a: mixture with **12a** and **1a** (9:2:5), yield 1.8 g/0.5 g/0.6 g (100%). δ^1H (CD_2Cl_2, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.29

TABLE 3. ^{119}Sn and ^{13}C NMR data[a] of η^2-alkyltin compounds **6** and **7** at variable temperature

	6a	**6a**	**6a**(Bu)	**6b**	**6b**	**7a**	**7b**
Temperature (K)	243	183	223	233	173	233	245
Sn*C*=	131.2^b [529.7]	132.5^c [n.o.] 127.8^d [n.o.]	131.6^b [480.8]	140.0^b [512.7]	139.7^c [425.0] 139.0^d [594.0]	137.3 [541.1]	142.5 [n.o.]
B*C*=	176.0^b [104.0]	167.9^c [n.o.] 181.5^d [n.o.]	177.2^b {br}	174.7^b [81.0]	166.4^c [95.0] 179.4^d [113.0]	177.7 {br}	182.2 {br}
M*C*≡	108.3 [77.9]	106.5 [n.o.]	109.2 [75.2]	109.5 [78.1]	107.4 [86.0]	106.6 [n.o]	107.6 [91.6]
≡*C*R^1	111.3 [49.1]	110.2 [56.7]	110.9 [50.0]	117.6 [50.0]	115.6 [47.0]	112.5 [49.8]	118.0 [49.1]
Sn*Me*	−0.7 [227.8]	−1.6 [237.6]	^{e}	2.0 [216.1]	0.8 [218.5]	0.0 [211.7]	2.8 [198.4]
=C*R*^{1}	18.9 [113.9]	18.2 [n.o.]	17.7	33.5^f [97.7] 34.9 [22.0]	32.3^g [n.o.] 35.1 [n.o.]	17.8	^{h}
≡C*R*^{1}	6.0	5.6	5.5	20.7, 30.8 22.3, 14.7	20.5, 29.8 21.6, 13.9	6.0	^{h}
=C*R*	24.0, 13.5^b [109.0][n.o.]	23.7, 22.2 13.6, 13.2	24.7, 14.3^b [n.o.]	24.6, 13.8^b [109.9][n.o.]	24.7, 22.3 13.7, 13.3	32.1 ^{h}	^{h}
δ^{119}Sn	146.5	154.5	141.7	154.5^i	162.3^j	113.5	124.2
δ^{11}B	41.1^{b,k}			39.1^{b,k}			3.4^l

[a] In C_7D_8 or CD_2Cl_2; $^nJ(^{119}Sn^{13}C)$ in Hz are given in []; {br} denotes broad signals due to dynamic effects; n.o.: not observed. [b] M(C≡C) = Sn or B; fast exchange of alkynyl groups between tin and boron atoms causes averaged ^{13}C resonances. [c] Alkenyl fragment. [d] Ring fragment. [e] δ^{13}C (*Bu*Sn) = 14.3, 14.3, 27.8, 28.8. [f] δ^{13}C (Bu) = 23.4, 14.7. [g] δ^{13}C (Bu) = 22.8, 13.9. [h] No further assignment. [i] δ^{119}Sn (**6c**, CD_2Cl_2) = 92.1. [j] δ^{119}Sn (203 K). [k] δ^{11}B (263 K). [l] δ^{11}B (273 K).

TABLE 4. ^{119}Sn and ^{13}C NMR data[a, b] of 1-alkyl-1-alkynyl-1-stanna-4-boracyclohexa-2,5-dienes (**8**)

	8a^c	**8a**	**8′a**	**8b**^{d}	**8′b**	**8b**	**8′b**	**8e**	**8a**(Bu)^e
Temperature (K)	298	243		298		233		298	298
R^{2}Sn	−8.4{br} [393.4]	−8.2 [398.9]	−10.5 [n.o]	−4.5 {br}	n.o. {br}	−4.5 [388.6]	−9.2 [382.0]	−7.6 {br}	13.4^e [408.9]
Sn*C*(2/6)=	136.8{br} [534.2]	137.4 [539.0]	134.5 [543.3]	143.8 {br}	141.1 {br}	144.1 [523.7]	140.7 [524.6]	144.2 {br}	137.3{br} [520.3]
B*C*(3/5)=	169.8 {br}(br)	168.0 [66.5]	170.0 [35.6]	168.1 {br}(br)	170.9 {br}(br)	167.6 [58.1]	169.7 [38.4]	168.7 {br}(br)	169.2 {br}(br)
Sn*C*≡	81.5 [441.4]	81.0 [423.2]	81.1 [n.o.]	81.9 {br}	83.0 {br}	81.6 [439.7]	82.9 [475.5]	71.8 {br}	81.1 [423.4]
≡*C*R^1	106.9{br} [170.0]	107.2 [83.9]	105.0 [90.5]	111.8 {br}	110.0 {br}	111.9 [86.1]	109.1 [94.5]	111.5 {br}	107.0 [76.3]
δ^{119}Sn^f	−202.4{br}	−204.1	−208.3	−207.6	−214.3	−209.3	−217.0	−210.2	−196.2

[a] In C_7D_8, CD_2Cl_2 or C_6D_6; $^nJ(^{119}Sn^{13}C)$ in Hz are given in []; {br} denotes broad signals due to dynamic effects; n.o.: not observed. [b] (br) denotes broad ^{13}C resonances of boron-bound carbon atoms. [c] **8a**:**8′a** = 1:3; δ^{13}C (CD_2Cl_2, 298 K) = 5.1 (*Me*C≡); 20.7, 25.8 (br) (^{i}*Pr*$_2$B); 21.0 [51.2] (*Me*C(2/6)); 22.6 [5.4], 22.8 [6.4], 31.2 [85.0] (^{i}*Pr*C(3/5)). [d] **8b**:**8′b** = 10:3; δ^{13}C (CD_2Cl_2, 298 K) = 14.0, 22.6, 34.4 [14.4], 34.7 [43.1] (*Bu*C(2/6)); 14.6, 20.3, 22.4, 31.8 (*Bu*C≡); 23.5 [7.2], 31.5 [86.2] (^{i}*Pr*C(3/5)). **8b**(Et):**8′b**(Et) = 1:6; δ^{119}Sn (C_6D_6, 298 K) = −192.3/−209.1. [e] δ^{13}C (C_6D_6, 298 K) = 5.0 [9.9] (*Me*C≡); 13.8, 27.3, 29.6 [27.5] (*Bu*Sn); 20.8, 25.7 (br) (^{i}*Pr*$_2$B); 21.3 [48.8] (*Me*C(2/6)); 22.6 [5.3], 22.8 [9.2], 31.2 [81.6] (^{i}*Pr*C(3/5)). [f] δ^{11}B (**8b**, **8′b**; CD_2Cl_2, 298 K) = 70.5; −δ^{11}B (**8a**(Bu); C_6D_6, 298 K) = 71.6.

TABLE 5. ^{119}Sn and ^{13}C NMR data[a,b] of 1-alkenyl-1-alkyl-1-stanna-4-boracyclohexa-2,5-dienes (**12**)

	12a[c]	**12a**(Bu)[d]	**12b**[e,f,g]		**12b**(Bu)[h]	**12e**[j]
Temperature (K)	298	298	298	253	298	298
R^{2}Sn	−7.9 [284.6]	12.3[313.9], 30.1[20.7], 27.8[70.8], 13.8	−4.2 [273.9]	−4.9 [272.9]	14.1[294.4]{br}, 30.8[20.0], 28.1[74.5], 13.7	−4.3 [276.7]
Sn*C*(2/6)=	137.9 [447.0]	138.2 [427.2]	143.1{br} [433.7]	141.6 [432.1]	143.4{br} [402.1]	147.5 [404.9]
B*C*(3/5)=	169.6 [40.0]	170.1 [33.6]	169.8 (br)	169.4 [35.4]	170.4 (br){br}	168.6 [34.6]
Sn*C*=	131.9 [501.8]	133.1 [468.4]	140.9 [488.1]	138.9 [487.1]	141.4 [452.4]	142.5 [488.3]
B*C*=	167.1 [63.0]	167.1 [62.6]	167.5 (br)	166.5 [61.0]	166.8 (br){br}	166.5 [42.7]
δ^{119}Sn	−160.0	−149.3	−161.2	−160.7	−138.3	−167.1

[a] In C_7D_8, CD_2Cl_2 or C_6D_6; $^nJ(^{119}Sn^{13}C)$ in Hz are given in []; {br} denotes broad signals due to dynamic effects; n.o.: not observed. [b] (br) denotes broad ^{13}C resonances of boron-bound carbon atoms. [c] δ^{13}C (CD_2Cl_2, 298 K) = 19.6 [n.o.] (C(2)*Me*); 20.3 [52.3] (SnC=*Me*); 19.6, 20.8 [6.8], 22.1 [6.8], 22.7, 30.8 [67.0], 31.2 [84.0] (^{i}*Pr*, without assignment); 17.5, 17.5, 25.8, 26.2 (^{i}*Pr*B, without assignment). [d] δ^{13}C (C_6D_6, 298 K) = 21.7 [n.o.] (SnC=*Me*); 21.7 [49.0] (C(2/6)Me); 22.4 [6.5], 22.9 [7.1], 23.1 [6.1], 31.2 [64.3], 31.4 [81.7] (^{i}*Pr*, without assignment); 17.8, 21.1, 25.6(br), 26.8(br) (^{i}*Pr*B, without assignment). [e] δ^{13}C (C_6D_6, 298 K) = 14.8, 14.8, 24.0, 24.3, 35.2 [n.o.], 35.2 [9.6], 36.0 [46.6], 37.0 [57.8] (*Bu*, without assignment); 18.2, 21.9, 23.6, 23.7, 31.4 [65.9], 31.5 [85.1] (^{i}*Pr*, without assignment). [f] δ^{13}C (CD_2Cl_2, 253 K) = 14.4, 14.6, 23.7, 24.0, 34.8 [91.6], 34.8, 35.4 [50.0], 35.9 (*Bu*, without assignment); 19.0, 20.1, 21.6, 22.9, 23.2, 24.8, 25.9, 26.9, 30.6 [63.5], 31.0 (^{i}*Pr*, without assignment). [g] δ^{119}Sn (C_6D_6, 298 K) **12b**(Et) = −133.6. [h] δ^{13}C (C_6D_6, 298 K) = 14.3, 14.4, 23.7, 24.0, 33.0{br}, 34.7 [9.0], 35.8 [46.7], 36.6 [52.1] (*Bu* without assignment); 21.7, 23.3, 23.5, 31.1 [83.5], 31.3 [65.5] (i*Pr*, without assignment); 17.8, 19.5, 20.3, 25.9(br), 27.0(br) (^{i}*Pr*B, without assignment). [j] δ^{13}C (C_6D_6) = 119.6 [31.5], 121.7 [34.6] (H*C*=); 141.9 [n.o.], 142.1 [28.5] (=*C*−).

[61.0] s (*Me*Sn); 0.95 (br), 1.76 m (^{i}*Pr*B); 1.87 s (*Me*C≡); 1.18 (d), 1.19 (d), 2.87 sept (^{i}*Pr*C(3/5)); 2.12 [58.4] s (*Me*C(2/6)).

8a(Bu): yield 3.4 g (98%). δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.84, 1.32, 1.66 [69.4] m (*Bu*Sn); 0.97 (br), 1.71 m (7H, ^{i}*Pr*B); 1.64 s (*Me*C≡); 1.10 d, 1.12 d, 2.79 [5.5] sept (^{i}*Pr*C(3/5)); 2.15 [56.8] s (*Me*C(2/6)).

Organoboration of 1a or 1a(Bu) in neat triethylborane (2)

The alkynyltin compounds **1a** or **1a**(Bu) (8.00 mmol) are cooled to −78 °C. After addition of an excess of 5 ml of triethylborane (**2**), the suspension is allowed to reach room temperature and stirring is continued for further 12 h. Removal of the excess of **2** *in vacuo* leads to pure **14** as colourless oils.

14a: yield 4.3 g (98%). δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = −0.16 [46.0] s (*Me*Sn); 0.98/1.15, 0.99/1.24 m (*Et*$_2$B); 1.01, 2.04/2.11 m (=C*Et*); 1.11 t [3.0], 2.24/2.48 m (C(2)*Et*); 1.12 1.75/2.53 m (C(4)Et); 1.79 [5.8] s (C(3)*Me*); 1.86 [68.8] s (C(5)*Me*); 2.16 [50.0] s (=C*Me*).

14a(Bu): yield 4.6 g (99%). δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.77 [45.6]/0.87 [43.5], 1.32 [37.3], 1.25 [<2.0], 0.83 m (*Bu*Sn); 0.87 [<2.0], 1.98 [6.0]/2.07 [6.2] m (=C*Et*); 0.97/1.19, 0.97, 1.26/1.29 m (*Et*$_2$B); 0.91 [2.0], 2.05/2.09 m (C(2)*Et*); 1.04, 1.58 [>2.0]/2.45 [6.2] m (C(4)*Et*); 1.58 [2.0] s (C(3)*Me*); 1.58 [68.4] s (C(5)*Me*); 1.94 [49.8] s (=C*Me*).

Partial hydrolysis of **14a** in benzene gives **15a** (mixture with **14a** (1:1)): δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.10 [48.1] s (*Me*Sn); 1.01, 2.27 m (C(2)*Et*); 1.03, 2.20 [9.4] m (C(4)*Et*); 1.12, 1.80/2.55 m (=C*Et*); 1.74 [3.0] s (C(3)*Me*); 1.81 [68.8] s (C(5)*Me*); 1.95 [56.3] s (=C*Me*); 5.65 [81.0] s (=C*H*).

Distillation of the 3-stannolene **14a** under reduced pressure (10^{-5} Torr, 150 °C) afforded a 1:1 mixture of **14a** and the deorganoborated 3-stannolene **16a**: δ^1H (C_6D_6, 25 °C) = −0.15 s (*Me*Sn); 0.90–1.20 m (without assignment); 1.60 s, 1.60 s, 1.70 s, 1.80 s, 1.90 s, 2.00 s, 2.10 m, 2.30 m, 2.40 m (without assignment).

Organoboration of 1c or 1c(Et) in neat triethylborane (2)

The same procedure was followed as described for **1a**. After a reaction time of 12 h at room temperature the stannoles **9c** and **9c**(Et) are obtained as oily liquids, contaminated by ≈15% of unidentified compounds.

9c(Et): yield 3.3 g (85%). δ^1H (C_6D_6, 25 °C) [$^nJ(^{119}Sn^1H)$] = 0.93, 1.22 m, (*Et*Sn); 1.15 s, 1.17 s, 1.32 s (^{t}*Bu* groups); 0.95, 1.93, 1.97 m (=C*Et*); 1.05, 1.06 m (*Et*$_2$B).

TABLE 6. ^{119}Sn, ^{29}Si and ^{13}C NMR data[a] of 1-alkenyl-1-alkyl-3-dialkylboryl-1-stannacyclopenta-2,4-dienes (**10**, **11**) and 1-alkynyl-1-methyl-1-stannacyclopenta-2,4-diene (**9**)

	(*Z*)-**10d**[b]	(*Z*)-**10d**(Et)[c]	(*E*)-**10b**[d]	(*E*)-**11b**[e]	(*E*)-**10b**(Et)[f]	(*E*)-**11e**[g]	(*E*)-**10b**(Bu)[h]	(*E*)-**11b**(Bu)[i]	**9c**[j]	**9c**(Et)[k]
R^{2}Sn	−2.6 [219.2]	10.4, 31.9	−6.6 [269.2]	−5.5 [253.8]	11.1, 32.5	−5.6 [253.3]	14.2 [299.8]	14.0, 27.2, 29.8, 38.2	−3.0 [358.0]	8.2, 9.1 [62.0][373.9]
Sn*C*(5)=	144.8 [228.0] (63.6)	143.5 [214.2] (62.6)	143.0 [448.6]	145.2 [446.5]	141.7 [429.9]	147.3 [417.3]	142.5 [429.9]	144.5 [425.5]	147.3 [537.6]	146.9 [507.6]
=*C*(4)	165.0 [90.7]	166.5 [83.1]	152.3 [110.5]	155.8 [105.2]	152.8 [102.7]	154.8 [96.6]	152.6 [104.1]	156.2 [98.7]	151.6 [161.8]	152.3 [154.4]
B*C*(3)	185.2 (br)	181.3 (br)	165.3 (br)	168.3 (br)	166.1 [43.5](br)	166.6 [51.9](br)	165.9 [44.9]	167.9 (br)	161.5 (br)	162.0 (br)
Sn*C*(2)=	150.7 [161.1] (64.4)	149.2 [146.7] (64.6)	144.5 [405.3]	143.1 [395.1]	142.9 [381.5]	147.5 [380.5]	143.6 [382.4]	142.4 [375.2]	152.0 [485.9]	151.7 [458.5]
Sn*C*=	140.2 [216.2] (60.2)	141.0 [187.8] (60.6)	140.0 [483.2]	140.7 [473.8]	140.3 [453.9]	142.4 [455.7]	140.7 [453.3]	141.2 [441.6]	81.4[l] [420.2]	80.9[l] [385.1]
B*C*=	179.5 (br)	184.9(br) [41.1]	163.9 (br)	168.5 (br)	163.5 [69.9](br)	166.1 [64.1](br)	163.4 [68.2]	167.9 (br)	120.7[m] [82.2]	121.5[m] [72.6]
δ^{119}Sn	55.6	74.1	−48.5	−33.5	−32.8	−42.8	−39.0	−25.2	−86.1	−72.3

[a] In C_6D_6 at 25 °C; $^nJ(^{119}SnX)$ (X = ^{29}Si, ^{13}C) in Hz are given in square brackets []; $^nJ(^{29}Si^{13}C)$ in Hz are given in parentheses (); (br) denotes broad ^{13}C resonances of boron-bound carbon atoms; n.o.: not observed. [b] δ^{13}C (C_6D_6) = 2.1 [11.0] (50.9) (*Me*$_3$SiC=); 2.3 [11.9] (52.6) (*Me*$_3$SiC(2)); 2.6 [10.2] (50.9) (*Me*$_3$SiC(5)); 9.7, 9.8, 19.5 (br) (*Et*$_2$B); 13.8 [7.2], 35.7 [128.9] (31.4) (=C*Et*); 16.2 [10.2], 31.8 [88.2] (=C(4)*Et*). δ^{29}Si (C_6D_6) [$^2J(^{119}Sn^{29}Si)$] = −6.4 [89.3] (Me$_3$*Si*C=); −8.3 [97.3] (Me$_3$*Si*C(5)); −9.6 [97.5] (Me$_3$*Si*C(2)). [c] δ^{13}C (C_6D_6) = 2.1 [n.o.] (50.9), 2.3 [n.o.] (52.8), 2.5 [9.8] (50.7) (Si*Me*$_3$, without assignment); 13.6, 36.1 [121.3] (11.7) (*Et*C=); 16.2, 32.0 [84.1] (*Et*C(4)); 9.7, 9.7, 22.3 (br), 22.5 (br) (*Et*$_2$B). δ^{29}Si (C_6D_6) = −6.4, −8.7, −10.0. [d] δ^{13}C (C_6D_6) = 14.4, 14.5, 14.6, 14.6, 14.7 (*CH*$_3$, Bu/Et, without assignment); 23.7 [n.o.], 26.5 [53.4] (*CH*$_2$, Et, without assignment); 23.6, 23.7, 23.8, 32.5 [61.0], 33.8 [n.o.], 35.2 [62.2], 36.2 [14.2], 36.4 [24.0], 36.5 [13.1] (*CH*$_2$, Bu, without assignment). [e] δ^{13}C (C_6D_6) = 6.3; 9.3; 9.4; 11.1; 14.4; 22.1; 23.5; 23.6; 24.1; 32.5; 33.5; 33.6; 36.0; 36.2; 36.4 (without assignment). [f] δ^{13}C (C_6D_6) = 14.4, 14.4, 14.5, 14.5, 14.6 (*CH*$_3$, Bu/Et, without assignment); 24.1, 26.4 (*CH*$_2$, Et, without assignment); 23.5, 23.5, 23.7, 32.5, 33.6, 35.2, 36.0, 36.2, 36.4 (*CH*$_2$, Bu, without assignment). δ^{11}B = 87.2. [g] δ^{13}C (C_7D_8) = 118.2 [29.5], 19.8 [32.6], 21.2 [36.6] (*HC*=, without assignment); 141.9 [40.7], 142.3 [38.7], 143.0 [58.0] (=C−, without assignment). [h] δ^{13}C (C_6D_6) = 13.9, 14.3, 14.4, 14.4, 14.5, 14.5 [9.9] (*C*H$_3$, Bu/Et, without assignment); 26.4 [52.1], 27.4 [57.4] (*CH*$_2$, Et, without assignment); 23.4, 23.5, 23.5, 23.6, 29.8 [17.1], 32.5 [59.2], 33.6 [10.8], 35.3 [59.2], 36.1 [14.4], 36.4 [12.6], 36.4 [67.3] (*CH*$_2$, Bu, without assignment). [i] δ^{13}C (C_6D_6) = 14.3, 14.4, 14.4, 23.8, 23.8, 33.9, 34.3, 35.1, 36.1, 36.1, 37.0, 37.1 (*Bu*, without assignment); 18.2, 18.5, 19.8, 19.9, 20.0, 22.9, 23.1 (^{i}*Pr*, without assignment). [j] δ^{13}C (C_6D_6) = 10.1, 10.3, 22.7 (br), 22.8 (br) (*Et*$_2$B); 15.7, 27.5 [77.5] (=C*Et*); 28.7 [7.0], 31.3 (≡C^t*Bu*); 33.6 [21.1], 33.9 [21.1], 37.3 [62.2], 38.0 [70.4] (=C^t*Bu*). [k] δ^{13}C (C_6D_6) = 10.3, 10.5, 22.7 (br), 23.0 (br) (*Et*$_2$B); 15.8 [14.0], 27.6 [76.0] (=C*Et*); 28.6 [7.5], 29.9 [5.8] (≡C^t*Bu*); 33.5 [21.1], 33.9 [21.1], 36.9 [60.3], 37.6 [67.0] (=C^t*Bu*). δ^{119}Sn(C_6D_6) (*E*)–**10c**(Et) = −27.1. [l] δ^{13}C (Sn*C*≡). [m] δ^{13}C (≡*C*–^{t}Bu).

TABLE 7. ^{119}Sn and ^{13}C NMR data[a] of 1-stanna-3-cyclopentene derivatives **14**, **15** and **16** and one trialkenylstannane **13**

	δ^{13}C						δ^{119}Sn
	Stannacyclopentene fragment				Alkenyl fragment		
	Sn*C*(2)	=*C*(3)	=*C*(4)	Sn*C*(5)	Sn*C*=	=*C*B	
13a[b]					137.0	162.7	−123.7
					[491.6]	[63.2]	
14a[c]	65.8(br)	145.6	136.3	74.6(br)	132.8	167.6	−25.5
	[67.1]	[12.0]	[13.2]	[67.1]	[465.0]	[74.3]	
14a(Bu)[d]	64.4(br)	144.9	134.6	73.0	136.9	164.6(br)	−28.7
	[59.5]	[9.2]	[13.0]	[62.6]	[419.6]	[64.8]	
15a[e]	66.6	145.6	135.3	74.7	138.0	146.0	−34.7
	(br)	[12.0]	[13.2]	(br)	[419.1]	[26.5]	
					Alkynyl fragment		
16a[f]	65.8	145.7	134.9	73.6	80.3	110.1	−16.6
	(br)	[13.1]	[n.o.]	(br)	[n.o.]	[n.o.]	

[a] In CD_2Cl_2 or C_6D_6; $^{n}J(^{119}Sn^{13}C)$ in Hz are given in []; (br) denotes broad ^{13}C resonances of boron-bound carbon atoms; n.o.: not observed. [b] δ^{13}C (CD_2Cl_2, 233 K) = −7.1 [266.9] (Sn*Me*); 9.6, 22.0 (br) (*Et*$_2$B); 14.1, 23.2 (=C*Et*). [c] δ^{13}C (C_6D_6) = −7.6 [216.7] (Sn*Me*); 9.5, 16.2 (br) (*Et*$_2$B); 9.0, 21.4 (br) (=C*Et*$_2$B); 13.2 [12.2], 23.1 [91.6] (=C*Et*); 15.2, 30.0 [61.0] (C(4)*Et*); 17.4 [40.3], 28.3 [28.5] (C(2)*Et*); 21.1 [28.5] (C(5)*Me*); 21.7 [67.1] (C(3)*Me*); 22.8 [61.0] (=C*Me*). [d] δ^{11}B (C_6D_6) = 74.7. δ^{13}C (C_6D_6) = 8.6, 16.2 (br) (*Et*$_2$B); 9.3, 21.5 (br) (=C*Et*$_2$B); 13.4 [250.2], 30.0 [18.3], 27.9 [70.2], 13.7 (*Bu*Sn); 13.5 [10.7], 23.6 [79.4] (=C*Et*); 15.3 [29.8], 24.4 [26.7] (C(2)*Et*); 15.3, 30.1 [62.6] (C(4)*Et*); 19.5 [59.5] (C(3)*Me*); 20.8 [28.2] (C(5)*Me*); 21.7 [61.0] (=C*Me*). [e] δ^{13}C (C_6D_6) = −8.2 [241.1] (Sn*Me*); 8.5 {br}, 15.7 (br), 16.5 (br) (*Et*$_2$B); 14.3 [8.1], 22.1 [66.1] (C(4)*Et*); 15.2, 29.9 [97.7] (=C*Et*); 15.9 [30.5], 25.3 [30.5] (C(2)*Et*); 19.6 [48.8] =C*Me*); 20.0 [65.1] (C(3)*Me*); 20.3 [30.5] (C(5)*Me*). [f] δ^{13}C (C_6D_6) = −6.4 [n.o.] (Sn*Me*); 4.9 [9.8] (≡C*Me*); 9.0; 9.4, 15.9 (br), 15.9 (br) (*Et*$_2$B); 12.8, 29.6 (C(4)*Et*); 15.6, 28.2 (C(2)*Et*); 19.9 (C(5)*Me*), 20.6 (C(3)*Me*).

η^2-Alkynetin compound 6a

The tri-1-propynyltin compound **1a** (1.1 g, 4.4 mmol) is added to a stirred solution of 1.2 g (12 mmol) of Et_3B in 40 ml of toluene at −78 °C. The mixture is slowly warmed to 0 °C and, after 0.5 h, the solvent and the excess of Et_3B are removed *in vacuo* (10^{-3} Torr). The solid, light yellowish residue is recrystallized from pentane at −78 °C to give 1.9 g (98%) of pure **6a**.

6a: δ^{1}H (CD_2Cl_2, −30 °C) [$^{n}J(^{119}Sn^{1}H)$] = 0.54 [44.4] s (*Me*Sn); 0.82 t, 1.21 q (*Et*$_2$B); 0.93 t, 2.17 q (*Et*); 1.98 [73.2] s (*Me*C=); 2.04 [8.1] s (*Me*C≡).

5b: δ^{1}H (C_6D_6, −40 °C) [$^{n}J(^{119}Sn^{1}H)$] = 0.36 [41.5] s (*Me*Sn); 0.62 t, 1.96 q (*Et*); 0.72, 1.10, 1.14, 1.93 m (9H, *Bu*C≡); 0.72, 1.19, 1.20/1.35, 2.22/2.42 m (*Bu*C=); 0.85 q, 0.90 t (*Et*$_2$B).

4b: δ^{1}H (C_6D_6, −40 °C) [$^{n}J(^{119}Sn^{1}H)$] = 0.50 [52.5] s (*Me*Sn); 0.62 q, 0.96 t(*Et*$_2$B); 0.62 t, 2.08 q (*Et*); 0.62, 1.10, 1.14, 1.83 m (*Bu*C=); 0.85, 1.15, 1.19, 2.30 m (9H, *Bu*C=).

4c: δ^{1}H (CD_2Cl_2, −30 °C) [$^{n}J(^{119}Sn^{1}H)$] = 0.53 [80.9] s (*Me*Sn); 0.28 m, 0.72 t (*Et*$_2$B); 0.88 t, 2.09 q (*Et*); 1.21 s, 1.27 s (three ^{t}*Bu* groups). δ^{1}H (CD_2Cl_2, −87 °C) [$^{n}J(^{119}Sn^{1}H)$] = 0.50 [84.0] s (*Me*Sn); 0.01, 0.23, 0.29, 0.54 m (*Et*$_2$B); 1.96, 2.11 m (*Et*); 1.15 (s), 1.18 (s), 1.30 (s) (three ^{t}*Bu* groups).

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References

1 (a)M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1987, pp. 129–184; (b) I. Omae, *J. Organomet. Chem. Libr., 21* (1989) 209.

2 C. Cauletti, C. Furlani and A. Sebald, *Gazz. Chim. Ital., 119* (1988) 1.

3 (a) B. Wrackmeyer, *Rev. Silicion, Germanium, Tin, Lead Compd., 6* (1982) 75–148; (b) B. Wrackmeyer, in S. Hermanek (ed.), *Boron Chemistry, Proc. 6th Int. Meet. Boron Chemistry (IMEBORON VI)*, World Scientific, Singapore, 1987, pp. 387–415.

4 (a) P.J. Stang, Z. Rappoport, M. Hannack and L.R. Subramanian, *Vinyl Cations*, Academic Press, New York, 1979; (b) H.-U. Siehl, F.-P. Kaufmann, Y. Apeloig, V. Braude, D. Danovich, A. Berndt and N. Stamatis, *Angew. Chem., 103* (1991) 1546; *Angew. Chem. Int. Ed. Engl., 30* (1991) 1479; (c) C. Dallaire and M.A. Brook, *Organometallics, 12* (1993) 2332.

5 (a) P. Buzek, P. v. Rague Schleyer and S. Sieber, *Chem. Unserer Zeit, 28* (1992) 116; (b) A. Berndt, *Angew. Chem., 105* (1993) 1034.

6 (a) P. Binger and R. Köster, *Tetrahedron Lett.,* (1965) 1901; (b) A. Suzuki, *Acc. Chem. Res., 15* (1982) 178; (c) A. Pelter, *Chem. Soc. Rev., 11* (1982) 203; (d) E. Negishi, *J. Organomet. Chem., 108* (1976) 281.

7 R. Köster, *Pure Appl. Chem., 49* (1977) 765.

8 (a) J. Hooz and R. Mortimer, *Tetrahedron Lett.,* (1976) 805; (b) K.K. Wang, K.-H. Chu, Y. Lin and H. Chen, *Tetrahedron, 45* (1989) 1105.

9 B. Wrackmeyer, K. Horchler and R. Boese, *Angew. Chem., 101* (1989) 1563; *Angew. Chem., Int. Ed. Engl., 28* (1989) 1500.

10 B. Wrackmeyer, S. Kundler and R. Boese, *Chem. Ber., 126* (1993) 1361.

11 B. Wrackmeyer, S. Kundler, W. Milius and R. Boese, *Chem. Ber., 127* (1994) 333.

12 B. Wrackmeyer, G. Kehr and S. Ali, *Inorg. Chim. Acta, 256* (1994) 51.

13 B. Wrackmeyer, G. Kehr and R. Boese, *Angew. Chem., 103* (1991) 1374; *Angew. Chem., Int. Ed. Engl., 30* (1991) 1370.

14 B. Wrackmeyer, G. Kehr, A. Sebald and J. Kümmerlen, *Chem. Ber., 125* (1992) 1597.

15 B. Wrackmeyer, G. Kehr and R. Boese, *Chem. Ber., 125* (1992) 643.

16 (a)R. Köster, G. Seidel, B. Wrackmeyer and J. Süss, *Chem. Ber., 126* (1993) 1107; (b) R. Köster, G. Seidel, I. Klopp, C. Krüger, B. Wrackmeyer, G. Kehr and J. Süss, *Chem. Ber., 126* (1993) 1385; (c) B. Wrackmeyer, G. Kehr and J. Süss, *Chem. Ber., 126* (1993) 2221.

17 *HYPERCHEM Software Package*; based on J.J.P. Stewart, *J. Comput. Chem., 12* (1991) 320.

18 B. Wrackmeyer and S. Kerschl, *Z. Naturforsch., Teil B, 39* (1984) 1037.

19 B. Wrackmeyer and K. Horchler, *Z. Naturforsch., Teil B, 45* (1990) 437.

20 L.A. Hagelee and R. Köster, *Synth. React. Inorg. Met.-Org. Chem., 7* (1977) 53.

21 (a) B. Wrackmeyer, *Z. Naturforsch., Teil B, 33* (1978) 385; (b) A. Schmidt and B. Wrackmeyer, *Z. Naturforsch., Teil B, 33* (1978) 855; (c) B. Wrackmeyer and K. Horchler, *Organometallics, 9* (1990) 1881; (d) B. Wrackmeyer, *J. Organomet. Chem., 364* (1989) 331.

22 B. Wrackmeyer, *Annu. Rep. NMR Spectrosc., 16* (1985) 73–185.

23 (a) B. Wrackmeyer, *Prog. NMR Spectrosc., 12* (1979) 227; (b) B. Wrackmeyer and R. Köster, in R. Köster (ed.), *Houben-Weyl-Müller, Methoden der Organischen Chemie,* Vol. XIII/3c, Thieme, Stuttgart, 1984, pp. 377–611; (c) B. Wrackmeyer, *Annu. Rep. NMR Spectrosc., 20* (1988) 61–203.

24 J. Sandström, *Dynamic NMR Spectroscopy,* Academic Press, New York, 1982, p. 96.

25 H.A. Bent, *Chem. Rev., 61* (1961) 275.

26 B. Wrackmeyer, *J. Magn. Reson., 42* (1981) 287.

27 (a) G. Bär and S. Pawlenko, in *Houben-Weyl-Müller, Methoden der Organischen Chemie,* Vol. XIII/6, Thieme, Stuttgart, 1978, p. 265; (b) W.P. Neumann and G. Burkhardt, *Liebigs. Ann. Chem.,* (1963) 11.

28 (a) W.E. Davidsohn and M.C. Henry, *Chem. Rev., 67* (1967) 73; (b) B. Wrackmeyer, G. Kehr, D. Wettinger and W. Milius, *Main Group Met. Chem., 16* (1993) 433.

29 R. Köster, P. Binger and W.V. Dahlhoff, *Synth. React. Inorg. Met.-Org. Chem., 3* (1973) 359.

30 E. Krause and P. Nobbe, *Ber. Dtsch. Chem. Ges., 64* (1931) 2112.

31 L.H. Merwin, A. Sebald, J.E. Espidel and R.K. Harris, *J. Magn. Reson., 84* (1989) 367.