Organotin Cations Stabilized by π Coordination – Synthesis and NMR Studies in Solution and in the Solid State

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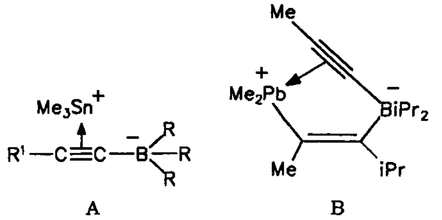
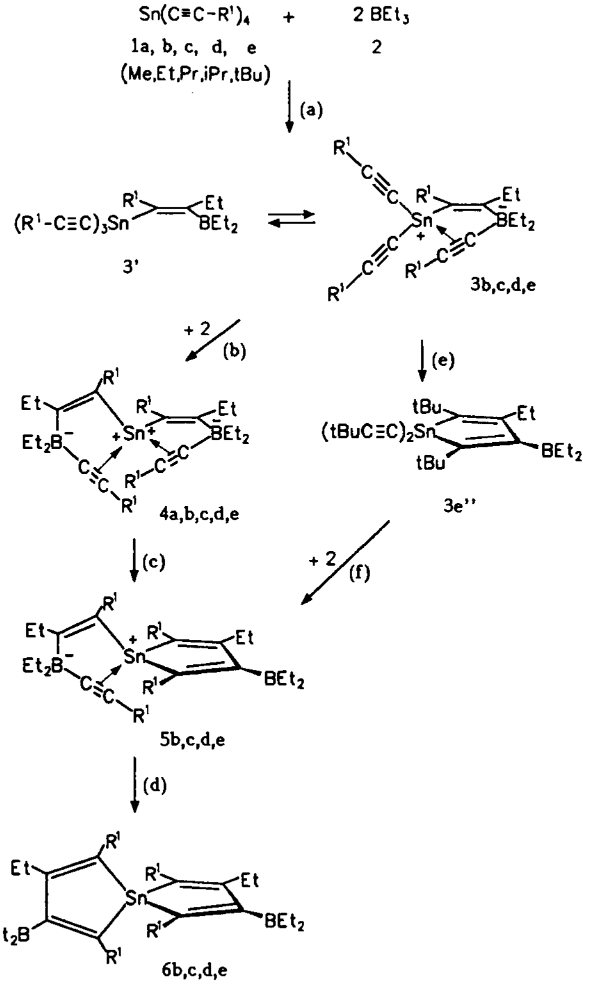
The organoboration of tetraalkynyltin compounds [Sn($C\equiv CR^1$)$_4$ (**1**): R^1 = Me (**a**), Et (**b**), Pr (**c**), *i*Pr (**d**), *t*Bu (**e**)] with triethylborane (**2**) proceeds stepwise. Intermediates with a cationic triorganotin (**3**, **5**) and a dicationic diorganotin fragment (**4**), stabilized by intramolecular coordination of one and two alkynyl moieties, respectively, were isolated (**3e**, **4a**) and/or identified by multinuclear NMR in solution (^{1}H, ^{11}B, ^{13}C, ^{119}Sn) and in the solid state (^{13}C and ^{119}Sn CP/MAS) (**3e**, **4a**). The magnitude of $^1J(^{13}C\equiv^{13}C)$ in **4a** (101.0 Hz) is significantly smaller than that for sodium triethyl-1-propynylborate (**7**) (119.2 Hz), proving the weak coordination of the $C\equiv C$ bond to the dicationic tin fragment. The final products of the organoboration, 1,4,6,9-tetraalkyl-2,7-bis(diethylboryl)-3,8-diethyl-5-stannaspiro[4.4]nona-1,3,6,8-tetraenes (**6b**–**6e**) were obtained in high yield.

The reactivity of the Sn–C≡ bond in alkynyltin compounds is well-known and has been exploited for numerous useful transformations[1–3]. In organoboration reactions[3] the Sn–C≡ bond is cleaved, and organoborate-like intermediates (**A**) have been proposed in which the $C\equiv C$ bond is coordinated to the stannyl group. This assumption could be proved for the first time in the case of the triorganolead cation **B**, stabilized by intramolecular coordination of the $C\equiv C$ bond as part of an alkynylborate moiety. The structure of **B** was established by a complete set of multinuclear magnetic resonance data[4,5] and by an X-ray structure analysis[4]. Although there are NMR-spectroscopic indications that tin analogues of **B** exist in solution[5], attempts to isolate these compounds have not been successful yet. Recently, it was shown that the reaction of tetraalkynyltin compounds **1** with triethylborane (**2**) proceeds stepwise, and a diorganotin dication **4a**, stabilized by two intramolecular π coordinations from $C\equiv C$ bonds, could be isolated and characterized by NMR data in solution as well as by an X-ray structure analysis in the solid state[6]. In the present work, we report on the organoboration of compounds **1** (Scheme 2) in more detail. It was hoped to find evidence for other

Scheme 1



Scheme 2



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possible intermediates, including those containing a cationic triorganotin fragment. Multinuclear NMR, both in solution (^{1}H, ^{11}B, ^{13}C, ^{119}Sn) and in the solid state (^{13}C and ^{119}Sn CP/MAS), was used to provide structural information.

Results and Discussion

Tetraalkynyltin compounds **1** were obtained by the reaction of the respective lithiated alkyne with tin(IV) chloride in moderate to high yields (see Table 1 for ^{13}C- and ^{119}Sn-NMR data).

Table 1. ^{13}C- and ^{119}Sn-NMR data[a] of tetraalkynyltin compounds **1a−1e**

R^1	Compound	$\delta^{13}C$			$\delta^{119}Sn$
		C^1	C^2	R^1	
Me	**1a**	75.8 [1166.2]	107.8 [242.0]	4.4 [19.6]	-345.3
Et	**1b**	75.6 [1160.2]	113.0 [234.3]	13.6,13.4 [18.5][9.8]	-343.6
Pr	**1c**	76.5 [1156.0]	111.6 [230.0]	22.1,22.1,13.5 [18.1]	-344.4
iPr	**1d**	75.4 [1153.1]	116.9 [227.8]	21.8,22.6 [17.4][8.7]	-341.0
tBu	**1e**	74.9 [1148.4]	119.7 [223.8]	28.4,30.6 [17.0][7.9]	-338.1

[a] In C_6D_6, at 25 °C; $^{n}J(^{119}Sn,^{13}C)$ in Hz are given in [ ].

Mixtures of **1** and triethylborane (**2**) (ratio ca. 1:2) were prepared at −78 °C in CH_2Cl_2 or toluene and kept at temperatures between 0 °C and −50 °C, depending on R^1. The reactivity of **1** decreases for R^1 = Me > Et ≈ PR > *i*Pr ≫ *t*Bu. Changes in the mixtures were monitored regularly by ^{119}Sn-NMR spectroscopy at −40 or −50 °C (see Figure 1).

There was no NMR-spectroscopic evidence available for **3a**, but NMR data for **3b−3d** could be measured, and compound **3e** (R^1 = *t*Bu) was isolated as a colorless solid. Table 2 lists ^{13}C- and ^{119}Sn-NMR data of compounds **3**. Compound **4a** is the first detectable intermediate if R^1 = Me. All other compounds **3** react with **2** to give the analogous intermediates **4b−4e** (see Table 3 for ^{11}B-, ^{13}C-, and ^{119}Sn-NMR data). Interestingly, **4e** is much less stable as compared to the other derivatives of **4**. NMR data of **4e** could only be obtained from samples which had been stored for several weeks at −20 °C, allowing for a very slow conversion of **3e** into **4e** and partly suppressing the otherwise fast rearrangement of **4e** to the compound **5e**. Since the intermediates **4a−4d** are rather stable in solution up to −20 °C (**4a**) or even up to 0 °C (**4b−4d**), steric crowding, favoring a different structure of the intermediate **4e** (vide infra), is believed to be responsible for its instability. Whereas **4a** decomposes above −20 °C to a large number of unidentified products, all other intermediates **4b−4e** rearrange first to give stannol derivatives **5b−5e** where the tin atom is still a cationic center, stabilized by π coordination (^{11}B-, ^{13}C- and ^{119}Sn-NMR data are given in Table 4). These compounds are present as mixtures with their precursors and/or with the final products, the spiro compounds **6b−6e** (see Table 5 for NMR data).

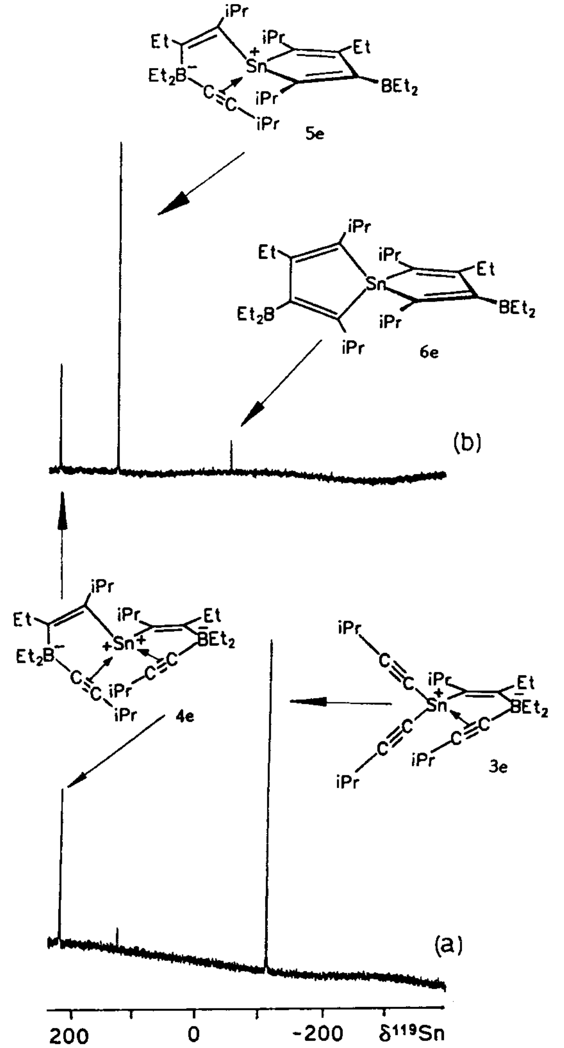


Figure 1. 111.9-MHz ^{119}Sn{^{1}H inverse gated}-NMR spectrum of a reaction solution of **1d** and **2**, showing that the progress of the organoboration can be readily monitored; the assignment of the ^{119}Sn resonances is based on their change in intensity as a function of time and corresponding changes in the ^{1}H-, ^{11}B- and ^{13}C-NMR spectra; (a) spectrum taken after mixing the components at −78 °C and warming to room temperature; (b) the same spectrum after 30 min at room temperature

Heating to 60 °C in toluene for 6−48 h completes the reaction of **1** with **2** to give the spiro compounds **6b−6e** in high yield. The compounds **6b−6d** are colorless or yellowish, oily, slightly air-sensitive liquids or a colorless solid (**6e**) which may be purified by fractional distillation or better by chromatography on silica gel with hexane. These compounds are of condiserable interest for reactions with electrophiles or cycloaddition reactions, either before or after protodeborylation has been carried out[7].

NMR Spectra

All NMR data support the proposed structures. The compounds **3b−3e** are in equilibrium with **3b′−3e′**, the posi-

Table 2. ^{13}C- and ^{119}Sn-NMR data[a] of (η^2-alkyne)tin compounds **3b–3e**

Temp.(K)	245	233	233	245	198
Compound	**3b**	**3c**	**3d**	**3e**	**3′**
R^1	Et	Pr[b]	iPr	tBu[c]	tBu
Sn-**C**=	136.4 [893.7]	135.1 [892.6]	144.7 [857.8	146.2 [880.6]	144.9 [875.8]
B-**C**=	174.3 [n.o.] (br)	178.1 [168.4] (br)	178.3 [192.0 (br)	180.2 [n.o.] (br)	180.3 [207.4] (br)
M-**C**≡C[d]	83.1 [595.1]	86.4 [510.6]	88.7 [391.3	86.2 [368.0]	81.0 93.1[e] [591.8] [-79.6]
M-C≡**C**[d]	116.5 [115.5]	116.2 [101.4]]	123.4 [74.1]	129.1 [69.7]	121.1 143.1[e] [121.9] [-34.7]
R^1-C=	26.2 [127.5] 16.5 [34.9]	34.8 [134.1] 25.8 [n.o.]	32.2 [146.1] 25.8 [28.3]	39.7 [153.1] 33.2 [54.5]	39.1 [149.9] 32.7 [48.5]
R^1-C≡	14.4, 14.0	22.7, 22.3	22.7, 22.4	29.4, 30.1	30.5,29.1 28.0,29.5
Et-C=	24.5 [166.8] 14.2 [11.4]	25.1 [n.o] 13.7 [n.o.]	25.4 [206.0] 15.0 [21.8]	25.7 [249.6] 15.1 [22.9]	25.2{br} [242.6] 14.7 [23.5]
B**Et$_2$**	n.o. 10.6	19.1(br) 11.3	17.6(br) 11.9	19.2(br) 12.0	17.9(br) 11.6
δ^{119}Sn	-198.1	-147.3	-111.2	-154.2	-150.6

[a] 20% in CD_2Cl_2; $^nJ(^{119}Sn,^{13}C)$ in Hz are given in [ ]; (br) denotes broad ^{13}C resonances of boron-bound carbon atoms; {br} denotes broad ^{13}C resonances due to dynamic effects; n.o.: not observed. – [b] δ^{13}C(Pr) = 13.6, 13.6 (Me). – [c] δ^{11}B: CD_2Cl_2, 263 K = +1.7 ($h_{1/2}$ = 250 Hz). – [d] M = Sn or B; fast exchange of alkynyl groups between tin and boron atoms causes averaged ^{13}C resonances of the C≡C carbon atoms. – [e] Calculated from 2 $^nJ[^{119}Sn,^{13}C(Sn)]$ + $^nJ[^{119}Sn,^{13}C(B)]$ = 3 $^nJ[^{119}Sn,^{13}C(average)]$.

Table 3. ^{11}B-, ^{13}C- and ^{119}Sn-NMR data[a] of bis(η^2-alkyne)tin compounds **4a–4e**

Compound	**4a**	**4b**	**4c**	**4d**	**4e**
R^1	Me[b]	Et	Pr[c]	iPr	tBu
Sn-**C**=	130.8 [522.6][c]	143.4 [488.3]	141.1 [488.8]	151.1 [446.3]	155.7 [477.3]
B-**C**=	190.0(br) [n.b.]	187.1(br) [143.3]	186.3(br) [149.3]	186.0(br) [146.1]	182.6(br) [n.o.]
B-**C**≡C	109.1(br) [134.1][c]	109.1(br) [129.6]	110.4 [130.8]	108.9(br) [126.4]	96.3(br) [127.1]
B-C≡**C**	124.9 [66.7]	132.4 [71.4]	130.4 [69.8]	140.4 [65.4]	160.4 [31.3]
R^1-C=	19.5[c] [174.0] --- ---	25.9 [150.4] 17.8 [34.9]	35.2 [150.4] 26.9 [31.6]	32.3 [143.9] 26.9,26.1 [24.0][20.7]	40.1 [142.1] 32.1 [n.o.]
R^1-C≡	6.8	15.7, 12.4	23.7,22.2	24.3,23.0, 22.1	30.8, 30.3
Et-C=	25.7[c] [154.0] 14.0 [14.1]	26.3 [158.0] 14.8 [9.3]	26.1 [156.3] 14.9 [n.o.]	26.0 [156.9] 15.3 [9.0]	26.5 [n.o.] 14.7 [n.o.]
B**Et$_2$**	16.8(br) 13.0	19.9(br) 13.6	18.0(br), 15.1(br) 12.4,12.3	17.9(br), 15.9(br) 13.1,12.1	23.1(br) 13.3,13.2
δ^{11}B[e]	-5.6	-4.9	-4.5	-4.3	3.2
δ^{119}Sn	165.6	207.5	203.1	223.2	130.7

[a] See footnote [a] of Table 2. – [b] $^1J(^{13}C{\equiv}^{13}C)$ = 101.0 Hz. – [c] δ^{13}C(Pr) = 13.8, 13.0 (Me). – [d] Correction to ref.[6]. – [e] $^{11}B\{^1H\}$NMR (253 K): $h_{1/2}$ = 275 ± 25 Hz.

Table 4. ^{11}B-, ^{13}C- and ^{119}Sn-NMR data[a] of stannol derivatives **5b–5e**

Compound	**5b**	**5c**	**5d**	**5e**	**3e′′**
R^1	Et[b]	Pr[c]	iPr[d]	tBu[e]	tBu[f]
Sn-**C**=	142.2 [576.6]	140.1 [574.9]	148.5 [548.2]	151.7 [551.7]	---
B-**C**=	184.5(br)	183.9(br)	182.1(br)	181.1(br)	---
Sn**C(2)**=	140.6 [321.5]	137.4 [320.4]	145.1 [311.7]	155.1 [318.9]	149.7 [571.2]
=**C(3)**B	164.4(br) [n.o.]	164.3(br) [56.7]	161.8(br) [56.4]	158.9(br) [59.7]	161.5(br) [n.o.]
C(4)=	152.6 [130.8]	152.4 [130.8]	150.9 [128.6]	150.1 [150.6]	151.8 [202.5]
Sn**C(5)**=	140.1 [379.3]	136.9 [381.5]	144.6 [361.9]	149.1 [365.8]	145.4 [632.8]
M-**C**≡C[g]	106.9(br) [n.o.]	107.1(br) [91.6]	102.9(br) [93.7]	93.0(br) [89.0]	79.5 [586.9]
M-C≡**C**[g]	119.7 [56.7]	116.8 [57.8]	126.7 [51.2]	144.9 [27.4]	121.2 [116.4]
δ^{11}B	89.5,-4.2	87.0,-5.1	87.5,-5.4	87.0,1.9	88.4
δ^{119}Sn	130.2	131.1	124.1	79.0	-192.3

[a] See footnote [a] of Table 2. – [b] 293 K, CD_2Cl_2; reaction solution; δ^{13}C(ring fragment) = 28.3 [80.7], 24.7 [70.8], 17.7 [16.9], 17.5 [16.9] (Et); 27.0 [55.6], 14.6 [7.4] (4-Et); 23.0 (br.), 9.6 (BEt_2); δ^{13}C(alkene fragment) = 26.7 [146.0], 14.4 [19.5] (=CEt); 26.5 [141.7], 17.9 [59.0] {=C(Sn)Et}; 18.3 (br.), 12.7 (BEt_2); δ^{13}C(≡CEt) = 15.5, 14.0. – [c] 233 K, CD_2Cl_2; reaction solution; δ^{13}C(ring fragment) = 37.8 [76.3], 33.1 [69.8], 27.2, 26.6 (Pr); 26.2 (Et); 22.8 (br.), 22.6 (br.), 9.7, 9.3 (BEt_2); δ^{13}C(alkene fragment) = 35.4 [140.6], 26.6 (Pr); 23.3 (Et); 18.1 (br.), 12.5 (BEt_2); δ^{13}C(≡CPr) = 23.8, 22.4 (CH_2); δ^{13}C(Me; without assignment) = 14.5, 14.5, 14.4, 14.2, 14.2, 13.7. – [d] 233 K, CD_2Cl_2; reaction solution; δ^{13}C(ring fragment) = 34.7 [73.0], 30.1 [64.7] (*i*Pr); 26.0, 14.4 (Et); 22.9 (br.), 9.4, 9.4 (BEt_2); δ^{13}C(alkene fragment) = 32.0 [131.2], (*i*Pr); 26.5, 15.4 (Et); 17.5 (br.), 12.7, 12.6 (BEt_2); δ^{13}C(≡C*i*Pr) = 24.0, 22.7, 22.6; δ^{13}C(Me; without assignment) = 26.6, 26.5, 26.3, 26.3, 25.7, 25.7. – [e] 233 K, CD_2Cl_2; reaction solution; δ^{13}C(ring fragment) = 38.4 [69.8], 37.0 [64.3], 34.2, 33.6 (*t*Bu); 27.1 [66.5], 15.4 [16.4] (Et); 23.6 (br.), 22.1 (br.), 10.5, 9.6 (BEt_2); δ^{13}C(alkene fragment) = 39.4 [128.6], 33.3 (*t*Bu); 26.3 [160.4], 14.2 [7.2] (Et); 19.2 (br.), 15.2 (br.), 12.8, 12.5 (BEt_2); δ^{13}C(≡C*t*Bu) = 31.3, 29.6. – [f] δ^{13}C: CD_2Cl_2, 298 K = 38.6 [66.5], 37.6 [62.6], 33.9 [23.5], 33.5 [24.4] (*t*BuC=); 31.1, 30.9 [7.8] (tBuC≡); 27.7 [94.9], 15.6 [11.7] (Et); 22.8 (br.), 10.0 (BEt_2). – [g] M = B for **5b–5e**; M = Sn for **3e″**.

tion of equilibrium being dependent on R^1. In the case of **3b–3d**, it was not possible to "freeze" the exchange between alkynyl groups in terminal and bridging positions, although the change in the δ^{119}Sn and $^1J(^{119}Sn,^{13}C{\equiv})$ values from **3b–3d** indicates an increasing contribution from compound **3d** as compared to **3d′**. However, in the case of **3e** the exchange becomes slow at low temperature (coalescence at −60°C), and terminal and bridging alkynyl groups are clearly distinguished in the ^{13}C-NMR spectra (see Figure 2). Therefore, **3e** is the first example of a triorgantin cation, stabilized by π coordination, which could be isolated. An interesting feature of the low-temperature ^{13}C-NMR measurement concerns the sign of $^1J(^{119}Sn,^{13}C{\equiv})$ which must be regarded as negative for a terminal alkynyl group[8]. Since the mean value of $^1J(^{119}Sn,^{13}C{\equiv})$ is known for the fast exchange limit, the sign of $^1J(^{119}Sn,^{13}C{\equiv})$ for the bridging alkynyl group turns out to be positive. Similarly, negative and positive signs result for $^2J(^{119}Sn,C{\equiv}^{13}C)$ for the terminal and

Table 5. ^{11}B-, ^{13}C- and ^{119}Sn-NMR data[a] of 1,4,6,9-tetraalkyl-2,7-bis(diethylboryl)-3,8-diethyl-5-stannaspiro[4.4]nona-1,3,6,8-tetraenes **6b**–**6e**

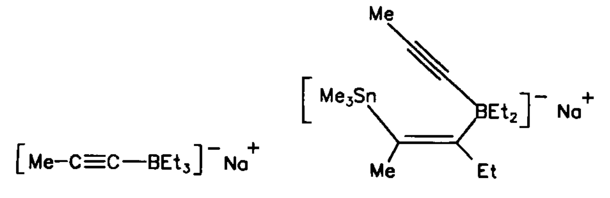
Compound	**6b**	**6c**	**6d**	**6e**
R¹	**Et**	**Pr**	**iPr**	**tBu**
SnC(1)	142.7 [383.7]	140.7 [380.9]	148.6 [372.8]	155.6 [373.8]
=C(2)	164.7 [51.8] (br)	165.2 [49.6] (br)	163.0 [47.4] (br)	162.6 (br)
=C(3)	152.2 [113.4]	152.5 [112.3]	150.7 [113.4]	152.6 [124.2]
SnC(4)	142.2 [434.9]	140.0 [432.2]	147.7 [422.9]	150.0 [417.4]
R¹(C(1))	29.4,18.6 [73.6][19.6]	38.2,27.2[b] [71.4][17.4]	35.4, [c] [67.6]	37.8,33.7 [64.3][21.8]
R¹(C(4))	25.8,18.3 [65.4][21.3]	34.6,26.7[b] [63.8][18.5]	31.1, [c] [60.0]	37.0,34.1 [58.9][20.7]
C(3)Et	26.8,14.5 [54.5][9.3]	26.6,14.2 [53.4][9.6]	26.5,14.8 [54.5][9.3]	27.6,15.3 [64.3][10.9]
BEt₂	23.0(br) 9.6	22.8(br) 9.3	22.9(br) 9.5	23.2(br),23.0(br) 10.3,10.1
δ^{11}B	83.0	84.3	86.3	87.2
δ^{119}Sn	-19.7	-13.7	-48.3	+9.4

[a] Ca. 50% in C_6D_6, 27 ± 1 °C; $J(^{119}Sn,^{13}C)$ in Hz are given in [ ]; (br) denotes broad ^{13}C resonances of boron-bound carbon atoms. — [b] $\delta^{13}C(Pr)$ = 14.5, 14.4 (Me, without assignment). — [c] $\delta^{13}C(iPr)$ = 27.4 [13.1], 27.3 [12.0], 26.7 [13.1], 26.6 [14.2] (Me, without assignment).

bridging alkynyl groups, respectively. As compound **3e** could be isolated as a solid, solid-state ^{119}Sn CP/MAS-NMR spectra were recorded (see Figure 3) in order to compare the δ^{119}Sn values in both phases. The good agreement proves that the low-temperature NMR spectra in solution are representative of the main features of the molecular structure in the solid state. The pattern of the spinning side bands deviates greatly from axial symmetry and seems to be perturbed by some kind of modulation. This points towards motional processes in the solid state which have not been analysed yet.

Since the X-ray structure of **4a** has been determined[6], we have now aimed for a more complete set of NMR data. In this context, it was necessary to find out how π coordination of the C≡C bond to the cationic center affects the $\delta^{13}C(C\equiv)$ values. Furthermore, it was hoped that a comparison of the coupling constants $^1J(^{13}C\equiv^{13}C)$ in **4a** and related alkynes would reveal additional information. Thus, we studied the alkynylborates **7** and **8** as model compounds for both $\delta^{13}C(C\equiv)$ (**7**, **8**) and $^1J(^{13}C\equiv^{13}C)$ values (**7**) (see Table 6 for ^{11}B-, ^{13}C-, and ^{119}Sn-NMR data of **7** and **8**). We also succeeded in measuring $^1J(^{13}C\equiv^{13}C)$ in **4a**.

Scheme 3



7 **8**

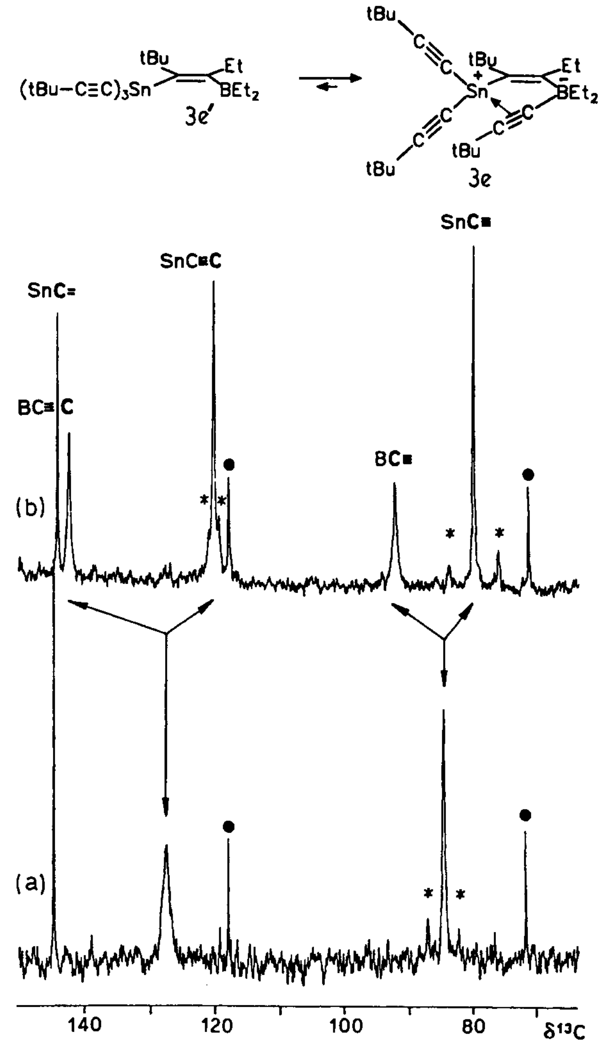


Figure 2. 75.5-MHz ^{13}C-NMR spectra (^{1}H-decoupled) of **3e** in CD_2Cl_2, showing the range of alkynyl and – in part – olefinic ^{13}C resonances; the $^{13}C(C\equiv)$ resonances of the starting material **1e** are marked by dots; (a) at −30 °C; the exchange of terminal and bridging alkynyl groups is still fast as compared to the NMR time scale; the averaged $^{117/119}$Sn satellites are marked by asterisks; (b) at −75 °C; as indicated, the $^{13}C(C\equiv)$ resonances are now split into those for terminal (Sn*C*≡C and SnC≡*C*) and bridging akynyl groups (B*C*≡C and BC≡*C*); again the $^{117/119}$Sn satellites are marked by asterisks; missing data may be calculated from the mean values or vice versa

The $^1J(^{13}C\equiv^{13}C)$ values, in particular, were difficult to obtain, since partially relaxed coupling $J(^{13}C,^{11}B)$ broadens the relevant ^{13}C resonances[9]. The problem was solved by measuring the $^{13}C(\equiv CMe)$ value of **7** in THF at −40 °C by the refocused INEPT pulse sequence[8a,c,10], taking advantage of the coupling constant $^2J(\equiv^{13}C,^1H)$ (≈ 10 Hz). The same technique was applied to **4a** at −40 °C and gave $^1J(^{13}C\equiv^{13}C)$ = 101.0 Hz. This is a smaller value than obtained for **7** [$^1J(^{13}C\equiv^{13}C)$ = 119.2 Hz], in agreement with a reduced C≡C bond order in **4a** as a result of the coordinative interaction with the tin atom. It is important to note that

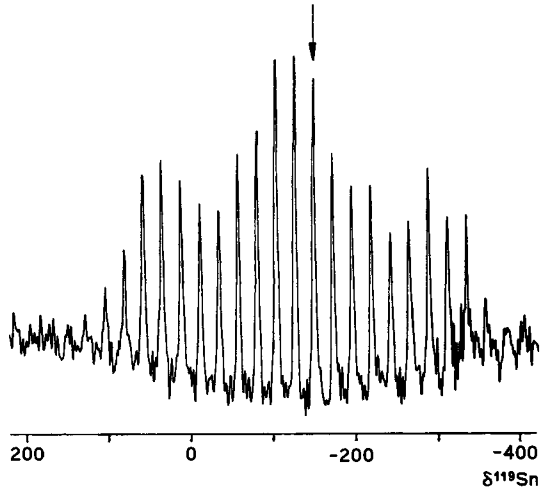


Figure 3. 111.9-MHz solid-state ^{119}Sn CP/MAS-NMR spectrum of compound **3e** at −30 °C, (spinning speed 2585 s^{-1}; recycle delay 5 s; contact time 5 ms; 1056 scans); δ^{119}Sn = −145.6; the apparently modulated pattern of spinning side bands could not be analyzed

Table 6. ^{11}B-, ^{13}C- and ^{119}Sn-NMR data[a] of the alkynylborates **7** and **8**

Compound	δ^{13}C				δ^{11}B	δ^{119}Sn
	SnC=	=CB	BC≡	MeC≡		
7[b]	---	---	109.9 (br{70})	85.7[c]	-18.4	---
8[d]	128.5 [697.7]	177.0 (br{65})	109.9 (br{70})	91.2	-14-2	-79.9

[a] 20% in THF/[D_8]THF; $^nJ(^{119}\mathrm{Sn},^{13}\mathrm{C})$ in Hz are given in [ ]; $^1J(^{13}\mathrm{C},^{11}\mathrm{B})$ in Hz are given in { }; (br) denotes broad ^{13}C resonances for boron-bound carbon atoms. — [b] δ^{13}C(BEt_3) = 15.3 (br.) {50}, 11.8. — $^1J(^{13}\mathrm{C}\equiv{}^{13}\mathrm{C})$ = 119.2 Hz. — [c] $h_{1/2}$ = 12 Hz. — [d] Other δ^{13}C = 25.9 [110.2], 14.9 [15.3] (=CEt); 22.2 [104.3] (=CMe); 20.1 (br.) {47}, 13.0 (BEt_2); −3.5 [301.8] (Me_3Sn).

neither IR data nor the bond distances $d_{C\equiv C}$ could be relied on with regard to such information.

The comparison of the δ^{13}C(C≡) values of **7**, **8**, and **4a** reveals a significant deshielding of the ^{13}C(≡*C*Me) nucleus in **4a**. This supports a significant contribution from a canonic vinyl cation structure **C** which is stabilized by hyperconjugation with a σ-Sn−C (**D**) or a σ-B−C bond (**E**) in β-position. The δ^{13}C(≡*C*R^1) data of **4a**−**4e** show a dramatic change for R^1 = *t*Bu (**4e**) (Table 7). The observed deshielding is much larger than expected on the basis of regular substituent effects. Therefore, it appears that the structures **C**, **D**, and **E** are more important for **4e** than for **4a**−**4d**. Some vinyl cations have been studied by ^{13}C-NMR[11] spectroscopy, showing similarly deshielded ^{13}C(=C^+R^1) nuclei. The exceptional behavior of **4e** is also reflected by its δ^{119}Sn value which differs considerably from those of **4a**−**4d** (see Table 3).

Scheme 4

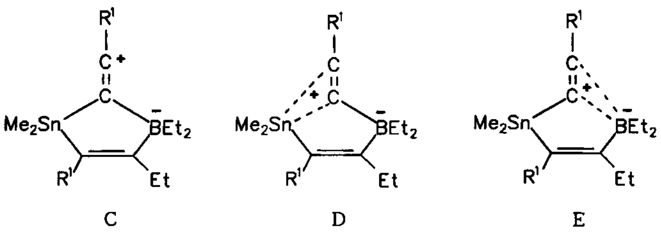


Table 7. Comparison of δ^{13}C(≡*C*R^1) values for bis(η^2-alkyne)tin compounds **4a**−**4e**

Compound (R^1)	**4a** (Me)	**4b** (Et)	**4c** (Pr)	**4d** (*i*Pr)	**4e** (*t*Bu)
δ^{13}C(≡*C*R^1)	124.9	132.4	130.4	140.4	160.4

The solid-state ^{13}C and ^{119}Sn CP/MAS-NMR spectra of **4a** (Figure 4) are in accord with the results of the X-ray analysis[6]. A twin set of relevant ^{13}C resonances is observed as expected on the basis of slightly differing bond distances and bond angles for the two halves of the molecule. The solid-state δ^{119}Sn value (+168.5) is close to the solution-state δ^{119}Sn value (+165.6), indicating that the molecular structure, as determined for the crystalline state, is retained in solution. The large ^{119}Sn chemical-shift anisotropy [$\Delta\sigma(^{119}\mathrm{Sn})$ = 837] is in agreement with the extremely distorted tetrahedral surrounding of the tin atom in **4a**. There is only one other example of Sn(IV) compounds known with a similarly large $\Delta\sigma(^{119}\mathrm{Sn})$ value (725), namely for a spiro compound analogous to **6**, but with Me_3Si substituents in 1,4,6,9-positions, in which the surrounding of the tin atom also corresponds to a severely distorted tetrahedron[12].

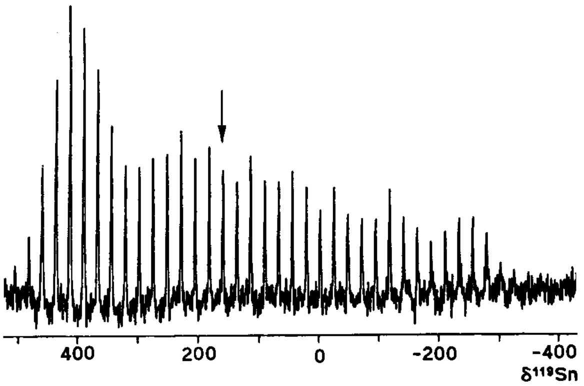


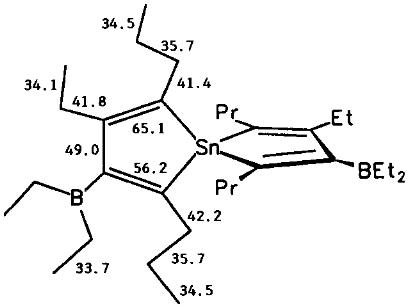
Figure 4. 111.9-MHz solid-state ^{119}Sn CP/MAS-NMR spectrum of compound **4a** at −30 °C (spinning speed 2582 s^{-1}; recycle delay 5 s; contact time 5 ms; 1080 scans); δ^{119}Sn = +168.5; the pattern of the spinning side bands was analyzed[16] to give $\Delta\sigma$ = 837; σ_{11} = −492.0, σ_{22} = −402.7, σ_{33} = 331.5; asymmetry parameter η = 0.16

The proposed structure of the stannol derivatives **5b**−**5d** can be deduced unambiguously from characteristic ^{13}C-NMR data (Table 4). The ^{13}C resonances of the stannol rings are readily identified due to the coupling constants $J(^{119}\mathrm{Sn},^{13}\mathrm{C})$, the broad signal of the boron-bound carbon atom, as well as on the basis of many ^{13}C-NMR data of other stannoles for comparison[3c,5,13].

The spiro compounds **6b**−**6e** show the expected pattern of ^{13}C-NMR signals (Table 5). In the case of **6c**, ^{13}C-IN-

ADEQUATE spectra[14] have been recorded in order to determine coupling constants $^1J(^{13}C,^{13}C)$ and to confirm the assignment of all ^{13}C resonances [Scheme 5; coupling constants $^1J(^{13}C,^{13}C)$ are given in Hz].

Scheme 5



6c

Interestingly, the ^{119}Sn nuclear shielding in compounds of type **6** is significantly higher than in the corresponding 1,3,6,9-tetrakis(trimethylsilyl) derivatives[12].

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Experimental

All compounds were handled under N_2 or Ar by using carefully dried glassware and solvents. – Starting materials such as tin(IV) chloride, terminal alkynes (Fluka), solutions of butyllithium (1.6 M) in hexane (Aldrich) were commercial products. – Deuterated solvents were stored over molecular sieve and saturated with N_2. – IR: Perkin-Elmer 983. – $^1H/^{13}C$ NMR: Bruker AC 300, Bruker AM 500 (300.13 MHz/75.5 MHz and 500.13 MHz/125.8 MHz, respectively); ^{11}B NMR: Bruker AC 300 (96.3 MHz) and JEOL FX90Q (28.7 MHz), $Et_2O \cdot BF_3$ as external standard; ^{119}Sn NMR: Bruker AC 300 (111.8 MHz), Bruker AM 500 (186.3 MHz), and JEOL FX90Q (33.3 MHz), $SnMe_4$ as external standard. – Solid-state NMR: Bruker MSL 300; ^{13}C and ^{119}Sn CP/MAS-NMR spectra were recorded at –30°C. The air-sensitive compounds were placed into air-tight inserts[15], fitting into the commercial ZrO_2 rotors of the double-bearing probehead. All ^{119}Sn-CP/MAS spectra were run at least at two different spinning speeds for assignment of the isotropic $\delta^{119}Sn$ values (tetracyclohexyltin served as a secondary external reference). – MS: EI-MS (70 eV) VARIAN MAT CH 7. – Elemental analyses were carried out by Dornis & Kolbe, Mülheim, and Pascher, Remagen.

Tetraalkynylstannanes **1a–e**: A freshly prepared suspension of 85 mmol of the respective lithiated alkyne in 100 ml of toluene is stirred at –78°C before a solution of 2.2 ml (19 mmol) of tin tetrachloride in 10 ml of toluene is added dropwise within 0.5 h. The mixture is warmed to ambient temperature, heated to 60°C for 12 h, and filtered through dry Na_2SO_4. The solvent is removed in vacuo (10^{-3} Torr) leaving the pure products in 80–95% yield (see Table 1 for ^{119}Sn- and ^{13}C-NMR data).

1a: Yield 4.5 g (86%); m.p. 150–152°C. – IR (toluene): $\tilde{\nu}$ = 2174.0 cm^{-1} [ν(C≡C)]; (hexane): $\tilde{\nu}$ = 2179.0 cm^{-1} [ν(C≡C)]. – ^1H NMR (C_6D_6): δ [$^nJ(^{119}Sn,^1H)$] = 1.41 [17.5] {$^1J(^{13}C,^1H)$ = 131.9 Hz, s, Me}.

$C_{12}H_{12}Sn$ (274.92) Calcd. C 52.43 H 4.40 Sn 43.17
Found C 53.08 H 4.52 Sn 43.00

1b: Yield 5.2 g (83%); m.p. 83–85°C. – IR (hexane): $\tilde{\nu}$ = 2167.0 cm^{-1} [ν(C≡C)]. – ^1H NMR (C_6D_6): δ [$^nJ(^{119}Sn^1H)$] = 1.80 {$^1J(^{13}C,^1H)$ = 130.8 Hz, q, 2H, CH_2}; 0.77 [5.1] {$^1J(^{13}C,^1H)$ = 128.7 Hz, t, 3H, CH_3}. – MS: *m/z* (%) = 279 (84), 226 (52), 173 (100), 120 (64).

$C_{16}H_{20}Sn$ (331.02) Calcd. C 58.06 H 6.09 Sn 35.85
Found C 58.12 H 6.12 Sn 35.97

1c: Yield 6.6 g (90%). – IR (hexane): $\tilde{\nu}$ = 2169.0 cm^{-1} [ν(C≡C)]. – ^1H NMR (C_6D_6): δ = 1.93 (t, 2H, CH_2); 1.27 (m, 2H, CH_2); 0.77 (t, 3H, CH_3). – MS: *m/z* (%) = 388 (4) [M^+], 321 (100), 254 (80), 187 (84), 120 (50).

$C_{20}H_{28}Sn$ (387.13) Calcd. C 62.05 H 7.29 Sn 30.66
Found C 62.59 H 7.35 Sn 30.60

1d: Yield 6.5 g (88%); m.p. 114–116°C. – ^1H NMR (C_6D_6): δ [$^nJ(^{119}Sn,^1H)$] = 2.24 (sept, 1H, CH); 0.86 (d, 6H, CH_3). – MS: *m/z* (%) = 321 (100), 253 (26), 187 (48), 120 (16). – IR (hexane): $\tilde{\nu}$ = 2165.0 cm^{-1} [ν(C≡C)].

$C_{20}H_{28}Sn$ (387.13) Calcd. C 62.05 H 7.29 Sn 30.66
Found C 62.32 H 7.41 Sn 30.75

1e: Yield 6.8 g (80%); m.p. 187–189°C. – IR (toluene): $\tilde{\nu}$ = 2142.0 cm^{-1}, 2175 [ν(C≡C)]. – ^1H NMR (C_6D_6): δ = 1.01 (s, *t*Bu).

$C_{24}H_{36}Sn$ (443.24) Calcd. C 65.04 H 8.19 Sn 26.78
Found C 65.19 H 8.31 Sn 26.88

Organoboration of Tetraalkynylstannanes **1** [R^1 = Et (**b**), Pr (**c**), *i*Pr (**d**), *t*Bu (**e**)] *with Triethylborane* (**2**) *Leading to 1,4,6,9-Tetraalkyl-2,7-bis(diethylboryl)-3,8-diethyl-5-stannaspiro[4.4]nona-1,3,6,8-tetraenes* **6** (General Procedure): Solutions of 8.00 mmol of **1b–e** in 40 ml of toluene are cooled to –78°C, then 3.30 ml (25.0 mmol) of **2** is added in one portion; the mixtures are warmed to room temperature and finally heated to 60°C for 12 h. After removal of the solvent in vacuo, the residues are purified either by fractional distillation (<10^{-3} Torr) (e.g., **6b**, **6c**) or by chromatography (SiO_2 with hexane) to give pure products (e.g. **6d**, **6e**).

6b: Yield 3.1 g (73%); b.p. 175–180°C/10^{-3}Torr, viscous yellowish liquid (distillation accompanied by decomposition; there is also ca. 15% of 2-(diethylboryl)-1,3,4,6,7,8,9,10-octaethyl-8-bora-5-stannaspiro[4.5]deca-1,3,6,9-tetraene present). – ^1H NMR (in CD_2Cl_2): δ [$^nJ(^{119}Sn^1H)$] = 2.37 [22.1] (q), 1.06 (t) (5H, 4-Et); 2.08 [35.5] (q), 1.01 (t) (5H, 1-Et); 1.99 (q), 0.94 (t) (5H, 3-Et); 1.33 (br.), 1.01 (10H, BEt_2).

$C_{28}H_{50}B_2Sn$ (527.01)
Calcd. C 63.81 H 9.56 B 4.10 Sn 22.52
Found C 64.00 H 9.74 B 4.38 Sn 22.63

6c: Yield 3.8 g (82%); b.p. 180–190°C/10^{-3} Torr, viscous yellowish liquid (distillation is accompanied by decomposition; there is also ca. 15% of 2-(diethylboryl)-3,7,8,9-tetraethyl-1,4,6,10-tetrapropyl-8-bora-5-stannaspiro[4.5]deca-1,3,6,9-tetraene present). – ^1H NMR (C_6D_6): δ = 2.36 (t), 1.46 (m), 0.84 (t) (7H, 4-Pr); 2.09 (t), 1.46 (m), 0.87 (t) (7H, 1-Pr); 2.04 (q), 0.95 (t) (5H, 3-Et); 1.35 (br.), 1.03 (10H, BEt_2). – MS: *m/z* (%) = 584 (78) [M^+], 541 (100), 352 (18), 309 (26).

$C_{32}H_{58}B_2Sn$ (583.12)
Calcd. C 65.91 H 10.03 B 3.71 Sn 20.35
Found C 66.03 H 10.61 B 3.75 Sn 20.58

6d: Yield 3.6 g (78%); b.p. >180°C/10^{-3} Torr (decomposition). – ^{1}H NMR (in C_6D_6): δ [$^nJ(^{119}Sn,^1H)$] = 2.88 [80.2] (sept), 2.25 [90.1] (sept), 1.09 (d), 1.09 (d), 1.04 (d) (14H, 1,4-*i*Pr$_2$, assignment has not been carried out); 1.99, 1.98, 0.96 (t) (ABM$_3$, 5H, 3-Et); 1.33 (br.), 1.04 (10H, BEt$_2$). – MS: *M*/*z* (%) = 584 (100), 352 (20).

$C_{32}H_{58}B_2Sn$ (583.12)
Calcd. C 65.91 H 10.03 B 3.71 Sn 20.35
Found C 66.04 H 10.15 B 3.75 Sn 20.40

6e: Yield 3.6 g (70%); m.p. 180°C, colorless solid. – ^{1}H NMR (in C_6D_6): δ = 2.12, 1.92, 1.04 (t) (ABM$_3$, 5H, 4-Et); 1.50–1.35 (br.), 1.13 (t), 1.10 (t) (10H, BEt$_2$); 1.39 (s), 1.20 (s) (18H, *t*Bu).

$C_{36}H_{66}B_2Sn$ (639.23)
Calcd. C 67.64 H 10.41 B 3.38 Sn 18.57
Found C 68.21 H 10.82 B 3.40 Sn 18.55

(η^2-Alkyne)tin Compound **3e**: A solution of 3.2 g (7.2 mmol) of **1e** in 40 ml of toluene is cooled to –78°C, then 4.0 ml (28 mmol) of **2** is added, and the stirred mixture is slowly warmed to 10°C. After 0.5 h at 10°C (progress of the reaction monitored by NMR), the solvent and the excess of **2** are removed in vacuo. A colorless solid is left which is recrystallized from pentane at –78°C to give 3.0 g (78%) of pure **3e** (in solution and in the solid state, **3e** rearranges slowly to **3e″** at temperatures >10°C). – ^{1}H NMR (CD_2Cl_2, 245 K): δ = 2.12 (q), 0.96 (t) (5H, Et); 1.29 (s, 27H, ≡C*t*Bu); 1.22 (s, 9H, =C*t*Bu); 0.75 (t), 0.34 (m) (10H; BEt$_2$).

The other derivatives **3b**, **3c**, **3d** have proved too reactive for isolation. They are characterized by the multinuclear NMR data of the reaction solutions (see also Table 2).

3b: ^{1}H NMR (CD_2Cl_2, 245 K): δ = 2.40 (q), 1.22 (t) (≡CEt); 2.18 (m), 1.12 (t) [=C(Sn)Et]; 2.18 (m), 0.93 (t) [=C(B)Et]; 0.89 (m), 0.32 (m) (BEt$_2$).

3c: ^{1}H NMR (CD_2Cl_2, 233 K): δ = 2.55 (t), 2.39 (t), 1.64 (m), 1.54 (m), 1.15–0.95 (Pr); 2.12 (q), 0.95 (t) (Et); 0.84 (t), 0.40 (m) (BEt$_2$).

3d: ^{1}H NMR (CD_2Cl_2, 233 K): δ = 3.14 (sept), 1.10 (d) (=C*i*Pr); 2.77 (sept), 1.28 (d) (≡C*i*Pr); 2.01 (q), 0.92 (t) (Et); 0.76 (t), 0.37 (m) (BEt$_2$).

1-Stannacyclopenta-2,4-diene **3e″**: Keeping a solution of 0.50 g (0.92 mmol) of **3e** in CH_2Cl_2 at ambient temperature for 3 d causes rearrangement to **3e″** (≥95%) [and unidentified products (≤5%)]. – MS: *m*/*z* (%) = 541 (4) [M$^+$], 379 (78), 81 (100). – ^{1}H NMR (CD_2Cl_2): δ = 1.89 (q), 1.04 (t) (5H, Et); 1.40 (s), 1.22 (s) (18H, *t*Bu); 1.40–1.35 (br.), 1.07 (10H, BEt$_2$); 1.10 (s, 18H, *t*Bu).

Bis(η^2-alkyne)tin Compound **4a**: Compound **2** (4.00 ml, 28.0 mmol) is added to a stirred solution of 3.20 g (11.6 mmol) of **1a** 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 **2** are removed in vacuo (10^{-3} Torr). A solid yellowish residue remains which is recrystallized from pentane at –78°C to give 3.80 g (69%) of pure **4a**[6]; m.p. >20°C (decomposition). – ^{1}H NMR (C_7D_8, 243 K): δ [$^nJ(^{119}Sn,^1H)$] = 2.22 (q), 0.96 (t) (10H, =CEt); 1.81 [107.6] (s, 6H, =CMe); 1.42 [7.3] (s, 6H, ≡CMe); 1.10 (t), 0.80 (br.) (20H, BEt$_2$); (CD_2Cl_2, 233 K): δ [$J(^{119}Sn,^1H)$] = 2.20 [6.8] (s, 6H, ≡CMe); 2.14 (q), 0.93 (t) (10H, =CEt); 2.08 [108.5] (s, 6H, =CMe); 0.73 (t), 0.34 (m) (2H, BEt$_2$).

All other compounds **4b–e** are identified in the reaction mixtures (see also Table 3) and are present as mixtures together with their precursors or the respective products **5** and/or **6**.

4b: ^{1}H NMR (CD_2Cl_2, 233 K): δ = 2.60 (q), 1.22 (t) (≡CEt); 2.40 (q), 1.23 (t) [=C(Sn)Et]; 2.18 (m), 0.99 (t) [=C(B)Et]; 0.80 (m), 0.52 (m) (BEt$_2$).

4c: ^{1}H NMR (CD_2Cl_2, 233 K). δ = 233 K): δ = 2.72 (m), 2.55 (t), 2.30 (m), 1.64 (m), 1.15–0.95 (Pr); 2.19 (q), 1.05 (t) (Et); 0.69 (t), 0.53 (m), 0.26 (m) (BEt$_2$).

4d: ^{1}H NMR (CD_2Cl_2, 233 K): δ = 3.38 (sept), 1.25 (d), 1.21 (d) (=C*i*Pr); 2.79 (sept), 1.36 (d) (≡C*i*Pr); 2.22 (q), 2.15 (q), 1.01 (t) (Et); 0.72 (t), 0.56 (m), 0.22 (m) (BEt$_2$).

Sodium Diethyl[(E)-1-ethyl-2-(trimethylstannyl)-1-propen-1-yl]-(propynyl)borate (**8**): After cooling 0.97 g (3.20 mmol) of (*E*)-diethyl[(*E*)-1-ethyl-2-(trimethylstannyl)-1-propen-1-yl]borane[17] to –78°C, 0.20 g (3.20 mmol) of sodium propynide is added in one portion. The mixture is slowly warmed to room temperature and stirred for 1 h; 1.16 g (100%) of pure **8** is obtained as a viscous yellow oil. – ^{1}H NMR (THF/[D$_8$]THF, 298 K): δ [$^nJ(^{119}Sn^1H)$] = 2.05 (q), 0.78 (t) (5H, =CEt); 1.78 [63.7] {s, 3H, =C(Sn)Me}; 1.62 (s, 3H, ≡CMe); 0.67 (t), 0.11 (m), –0.12 (m) (10H, BEt$_2$); 0.01 [49.0] (s, 9H, SnMe$_3$).

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[152/92]