Routes to Stannoles, Stannolenes and 1-Stanna-4-bora-2,5-cyclohexadienes – Crystal Structure of a Triorganotin Cation Stabilized by π-Coordination[1]

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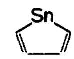
Di-1-alkynyltin compounds (**1**) react with triorganoboranes R_3B [**2a** (R = Et), **2b** (R = *i*Pr)] to give (η^2-alkynyl)tin compounds **3** (R = Et) and **4** (R = *i*Pr) in which a cationic three-coordinate tin centre is stabilized by intramolecular side-on coordination to the C≡C bond of an alkynylborate fragment. An X-ray analysis of **3e**, prepared from $Me_2Sn(C{\equiv}C\mathit{i}Pr)_2$ (**1e**) and Et_3B, proves the coordination of the tin atom to the C≡C bond as well as a weak B–C≡ bond. An important dynamic process, i.e. exchange of the alkynyl group between boron and tin, is shown by ^{11}B and ^{119}Sn NMR at variable temperature. Most of the intermediates **3** react with an excess of Et_3B by a second intramolecular 1,1-ethyloboration to dialkenyltin derivatives **7** which readily rearrange to the 3-stannolenes **8**. Without an excess of Et_3B, intramolecular 1,1-vinyloboration (leading to the stannoles **5**) competes with intramolecular 1,1-ethyloboration (leading to 1-stanna-4-bora-2,5-cyclohexadienes **9**). The latter route is preferred in the case of most of the intermediates **4** (intramolecular 1,1-isopropyloboration) and affords the six-membered rings **10** (R = *i*Pr). ^{11}B- and ^{13}C-NMR data indicate that the heterocycles **9** (R = Et) adopt a flatter conformation than **10** (R = *i*Pr).

Cyclic organotin compounds are versatile starting materials in organometallic synthesis[2]. Most routes to stannoles[3] (**A**), stannolenes[4] (**B**), and 1-stanna-4-bora-2,5-cyclohexadienes[5] (**C**) are limited to a particular pattern of substituents; in some cases the yield is rather low[3c] or frequently, multistep synthetic procedures are involved[5]. Organoboration of alkynyltin compounds[6,7] has opened an alternative way to these heterocycles. Previously, it has been shown that di-1-alkynyltin compounds **1a**, **b**, **g** react with trialkylboranes **2** to give derivatives of **A**, **B**, or **C**, depending on the nature of R and R^1[7], and that analogous reactions can also be carried out with other alkynylmetal compounds $L_nM(C{\equiv}C{-}R^1)_m$[6].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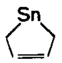
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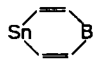

C

1 $Me_2Sn(C{\equiv}C{-}R^1)_2$

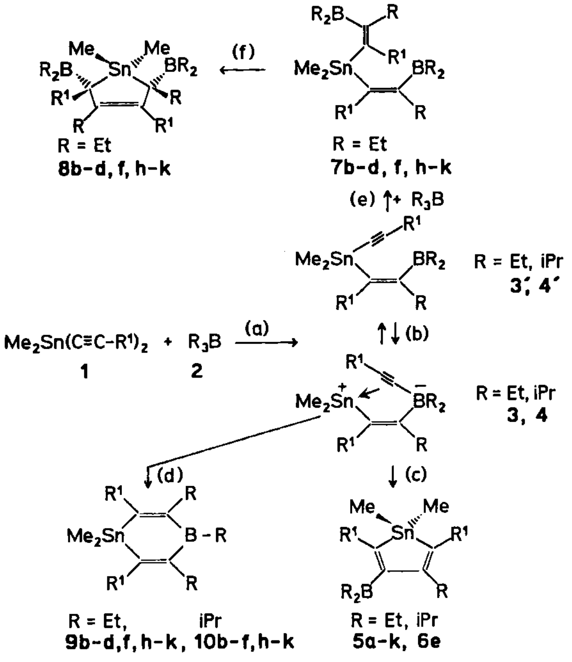
1	a	b	c	d	e	f	g	h	i	j	k
R^1	H	Me	Et	Pr	iPr	Bu	tBu	iPent	Oct	Ph	3-MeO-C_6H_4

BR_3

2	a	b
R	Et	iPr

It has been proposed that cleavage of the M–C≡ bond occurs, leading to an alkynylborate-like intermediate where the cationic metal fragment is side-on coordinated to the C≡C bond. For M = Pb [reaction between $Me_2Pb(C{\equiv}C{-}Me)_2$, **1b(Pb)**, and **2b**] such an intermediate has been isolated and fully characterized by multinuclear NMR and X-ray analysis[8]. Recently, the intermediacy of zwitterionic

Scheme 1. Organoboration of dialkynyldimethyltin compounds



	a	b	c	d	e	f	g	h	i	j	k
R^1	H	Me	Et	Pr	iPr	Bu	tBu	iPent	Oct	Ph	3-MeO-C_6H_4

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species with a diorganotin dication fragment[9,10] and various triorganotin cation fragments has been established by studying the organoboration of tetra-1-alkynyltin compounds[10]. However, so far the existence of stabilized triorganotin cations of the type **3** (R = Et) or **4** (R = *i*Pr) (see Scheme 1) as the result of the reaction between **1** and **2** has been claimed only on the basis of ^{11}B-NMR spectroscopic data for reaction solutions (reaction between **1g** and **2a**[7b]). In this paper we report on the synthesis and characterization, by X-ray analysis and multinuclear NMR, of the zwitterionic compounds **3** and **4**, on their dynamic character, their reactivity towards an excess of trialkylborane (to give the dialkenyltin derivatives **7**) and their rearrangement into the final products which are stannoles (**5**, **6**), stannolenes (**8**), and 1-stanna-4-bora-2,5-cyclohexadienes (**9**, **10**).

Results and Discussion

The di-1-alkynyltin compounds **1** (**1c–e**, **h–i**, and **k** have not been described in the literature) were prepared from the respective lithiated 1-alkynes and Me_2SnCl_2 (see Table 1 for ^{13}C- and ^{119}Sn-NMR data of the compounds **1**).

Table 1. ^{13}C- and ^{119}Sn-NMR data of dialkynyltin compounds **1a–k**[a,b,c]

Compound		δ ^{13}C				
No.	R¹	**Me₂**Sn	Sn-**C**≡	R¹-**C**≡	R¹	δ^{119}Sn
1a	H	-6.5 [502.7]	85.4 [585.0]	97.6 [122.0]		-153.8
1b	Me	-6.5 [498.0]	79.0 [633.0]	106.8 [133.9]	4.9 [11.8]	-156.0
1c	Et	-6.8 [497.0]	78.2 [640.9]	112.1 [132.4]	13.2, 13.5 [12.5] [7.1]	-156.7
1d[d]	Pr	-6.5 [497.3]	79.4 [636.7]	110.9 [133.0]	21.8, 21.9 [12.3] [6.9]	-155.3
1e	iPr	-6.5 [495.4]	77.9 [644.7]	116.3 [130.2]	21.3, 22.9 [12.0] [7.1]	-157.6
1f[e]	Bu	-6.6 [497.0]	79.1 [639.8]	110.9 [133.0]	19.5, 30.6 [12.0] [7.1]	-156.7
1g	tBu	-5.8 [496.6]	77.5 [637.8]	119.8 [125.8]	28.4, 31.2 [11.1] [3.7]	-157.6
1h[f]	iPent	-6.5 [497.0]	79.2 [638.7]	111.2 [132.4]	17.9, 37.6 [12.5] [6.6]	-155.3
1i[g]	Oct	-6.5 [496.5]	79.2 [640.9]	111.0 [133.0]	19.0, 31.6 [12.0] [< 5]	-156.4
1j[h]	Ph	-6.2 [497.0]	90.1 [602.0]	109.3 [126.2]	122.9, 131.9 [15.3] [7.6]	-147.6
1k[i]		-6.0 [499.7]	90.0 [598.4]	109.2 [125.3]	123.9, 116.5 [14.2] [7.1]	-147.0

[a] Ca. 20–40% in $CDCl_3$ at 26 ± 1°C. – [b] $^nJ(^{119}Sn,^{13}C)$ in Hz are given in [ ]. – [c] Data from literature for compounds **1a**[7a], **1b**[7c], **1g**[7b], **1j**[7g]. – [d] Other δ^{13}C values: 13.2 (CH_3). – [e] Other δ^{13}C values: 21.6 (CH_2), 13.3 (CH_3). – [f] Other δ^{13}C values: 27.0 (CH), 22.0 (CH_3). – [g] Other δ^{13}C values: 29.0, 28.9, 28.6, 28.6, 22.5 (CH_2), 13.9 (CH_3). – [h] Other δ^{13}C values: 128.1 (C-3), 128.3 (C-4). – [i] R¹ = 3-$MeOC_6H_4$; other δ^{13}C values: 159.1 (C-3), 115.3 (C-4), 129.2 (C-5), 124.5 [6.5] (C-6), 55.2 (OCH_3).

All reactions between **1** and **2** were at first carried out in NMR tubes in chloroform or in toluene and monitored by ^{119}Sn-NMR measurements in the temperature range between −78 and +25°C. Thus, the conditions for starting the reactions were determined and the formation of intermediates and final products could be observed. Afterwards, syntheses on a preparative scale were performed according to these conditions. With the exception of R¹ = H, the zwitterionic intermediates **3**, **4** could be detected in all cases. These compounds decompose very fast (e.g., **3b**, **c**, **d**) or slowly (0.5 to 6 h) in solution >0°C and must be stored at < −20°C if they are isolated as colorless solids. In the case of **3e**, crystals suitable for single-crystal X-ray analysis (vide infra) were obtained from pentane solution. All other compounds **3** and **4** were characterized by their consistent ^{1}H-, ^{11}B-, ^{13}C-, and ^{119}Sn-NMR data (see Experimental and Tables 2, 3).

In agreement with previous results[7a], the reaction of **1a** with **2a** or **2b** affords selectively the stannoles **5a** or **6a**. If an excess of Et_3B (**2a**) is present, compounds **1b–k** react to

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

R¹ =	Me	Et	Pr	iPr	Bu	tBu	iPent	Oct	Ph	3-MeO-C₆H₄
	3b	**3c**	**3d**[d]	**3e**	**3f**[e]	**3g**	**3h**[f]	**3i**[g]	**3j**[h]	**3k**[i]
Temp. (K)	213	243	243	243	243	243	243	243	263	243
Me₂Sn	-1.8 [249.6]	0.3 [248.0]	-0.1 [248.0]	2.1 [240.9]	-0.3 [245.2]	3.5 [245.8]	-0.1 [249.6]	0.6 [246.3]	-2.3 [309.5]	-3.1 [323.7]
Sn-**C**=	129.3 [660.5]	139.4 [649.6]	137.7 [648.0]	146.8 [625.6]	138.0 [649.6]	148.1 [655.0]	139.9 [651.8]	138.2 [650.7]	137.7 [614.7]	137.3 [610.9]
B-**C**=	182.4 [br]	180.3 [br]	181.3 [br]	177.4 [br]	181.8 [br]	178.9 [br]	180.6 [br]	181.6 [br] [123.2]	177.9 [br]	175.5 [br]
B-**C**≡	108.2 [br] [74.0]	107.0 [br] [62.7]	108.2 [br]	106.1 [br] [79.6]	108.6 [br]	96.8 [br]	107.4 [br]	108.9 [br] [72.0]	109.1 (br)	103.6 (br)
B-C≡**C**	112.1 [45.8]	118.4 [45.8]	117.0 [45.2]	123.3 [48.0]	117.4 [46.3]	128.4 [n.o.]	117.1 [40.9]	117.4 [48.0]	115.0 (br)	113.7 (br)
BEt₂	18.5 [br]	18.0 [br]	18.3 [br]	17.9 [br]	18.4 [br]	20.0 [br]	18.1 [br]	19.8 [br]	19.5 [br]	20.0 [br]
	13.4	12.6	12.8	12.7	13.3	12.7	12.6	13.2	11.4	11.0
Et-C=	25.2 [128.6]	25.7 [139.5]	25.8 [139.5]	25.4 [136.5]	26.2 [140.6]	26.1 [166.8]	25.5 [139.4]	26.1 [139.5]	25.5 [109.5]	25.6 [104.6]
	14.6 [17.4]	14.4 [n.o.]	14.6 [17.4]	15.6 [16.3]	14.9 [16.3]	15.7	14.5	15.1	14.4	14.5
R¹-C=	19.1 [143.9]	25.5 [139.0]	34.9 [135.7]	31.5 [128.6]	32.9 [136.2]	39.2 [128.6]	30.6 [134.6]	33.2 [115.0]	144.2 [100.3]	145.9 [94.6]
		17.7 [46.9]	26.7 [43.1]	26.0 [26.2]	36.3 [42.0]	33.5 [45.8]	42.8 [39.8]	34.3 [41.4]	125.0 [14.2]	113.1 [27.8]
R¹-C≡	4.5	14.3 13.7	22.3 22.2	23.2 22.6	20.5 30.9	31.5 30.3	18.6 37.2	[g]	119.6	121.4
δ ^{119}Sn	189.1	201.5	199.6	215.4	194.8	160.2	197.7	200.8	11.6	31.2
δ ^{11}B	6.6[c]	-5.1	-3.1	-2.6	-5.0	0.5	-1.2	-1.8	33.3	30±5

[a] Ca. 20% in C_7D_8 (**3b–i**), in $CDCl_3$ (**3j,k**). – [b] $^nJ(^{119}Sn,^{13}C)$ in Hz are given in [ ], [br] denotes broad ^{13}C resonances of boron-bound carbon atoms; [n.o.] = not observed; (br) denotes broad ^{13}C resonance signals due to dynamic effects. – [c] δ^{11}B at 243 K. – [d] Other δ^{13}C values: 13.9, 13.1 (CH_3). – [e] Other δ^{13}C values: 22.2, 22.9 (CH_2), 13.9, 14.7 (CH_3). – [f] Other δ^{13} values: 26.9, 27.7 (CH), 21.8, 22.6 (CH_3). – [g] Other δ^{13}C values: 23.0, 23.1, 28.6–29.9, 32.1, 32.3 (CH_2), 14.3, 14.5 (CH_3). – [h] Other δ^{13}C values: 127.9, 128.1, 128.7, 130.5, 133.4 (CH). – [i] Other δ^{13}C values: 158.7, 158.9 (C), 109.4, 116.4, 117.4, 120.3, 125.6, 128.6, 129.7 (CH).

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

R^1 ■	Me **4b**	Et **4c**	Pr **4d**[c]	iPr **4e**	Bu **4f**[d]	iPent **4h**[e]	Oct **4i**[f]	Ph **4j**[g]	3-MeO-C$_6$H$_4$ **4k**[h]
Temp.(K)	263	263	298	298	298	298	298	263	243
Me$_2$Sn	-4.1[i] [286.6]	0.3 [239.8]	-0.3 [246.3]	2.7 [233.2]	-0.4 [244.1]	-0.3 [246.9]	-0.3 [245.2]	-3.1 [295.4]	-2.4 [292.1]
Sn-**C**=	129.4 [657.1]	141.2 [651.2]	139.4 [650.7]	149.3 [626.7]	139.5 [652.9]	139.1 [656.7]	139.5 [653.9]	138.6 [612.5]	138.4 [615.8]
B-**C**=	178.1 [br]	181.9 [br]	182.5 [br]	179.4 [br]	182.4 [br]	181.9 [br]	182.3 [br]	179.9 [br]	180.6 [br]
B-**C**≡	98.0 (br)	104.3 [br]	102.0 [br]	102.0 [br]	104.7 [br]	104.1 [br]	104.5 [br]	105.6 (br)	106.5 (br) [19.6]
B-C≡**C**	110.6 [n.o.]	119.9 [42.0]	118.7 [34.9]	127.0 [39.2]	118.9 [37.1]	118.8 [34.3]	118.9 [34.9]	116.3 (br)	116.2 (br)
BiPr$_2$	22.1 [br] 20.9 (br)	20.5 [br] 21.7	20.9 [br] 21.7 22.0	21.0 [br] 21.8	20.9 [br] 21.8 (br)	20.9 [br] 21.7 21.2	21.1 [br] 21.8	22.7 [br] 21.2	22.3 [br] 21.3
iPr-C=	31.9[j] [135.2] 21.5	32.8 [154.2] 21.7 [12.5]	32.6 [153.7] 22.0 [12.5]	33.0 [155.3] 22.6 [12.0]	32.6 [153.7] 22.0 [13.1]	32.6 [153.7] 22.0	32.7 [154.8] 22.0 [12.5]	34.0 [127.5] 23.1 [10.4]	34.0 [130.2] 23.1 [10.9]
R^1-C=	21.4 [129.7] 17.9	28.2 [134.1] 27.0 [45.8]	37.5 [126.4] 26.1 [28.3]	33.6 [122.1] 36.3 [43.6]	35.3 [128.6] 43.4 [42.5]	33.5 [126.4] 34.2 [44.7]	35.6 [127.5] 124.9 [19.6]	145.8 [92.6] 114.0 [28.9]	147.2 [96.5]
R^1-C≡	5.4	14.5 13.9	22.8 22.3	23.4 22.9	20.5 30.7	18.8 37.5	[f]	119.8	120.2
δ ^{119}Sn	68.2	183.5	167.0	193.8	164.3	161.9	165.3	72.6	84.5
δ ^{11}B	22.9[k]	4.5	6.6	1.5	6.6	5.1	8.7	26.4	15±5

[a] Ca. 20% in $CDCl_3$. — [b] $^nJ(^{119}Sn,^{13}C)$ 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. — [c] Other $\delta^{13}C$ values: 13.5, 13.9 (CH_3). — [d] Other $\delta^{13}C$ values: 21.9, 22.6 (CH_2), 13.3, 14.1 (CH_3). — [e] Other $\delta^{13}C$ values: 27.0, 28.3 (CH), 21.9, 22.6 (CH_3). — [f] Other $\delta^{13}C$ values: 20.8, 22.7, 22.8, 28.8, 29.0, 29.2, 29.4, 29.6, 29.7, 31.8, 32.0 (CH_2), 14.09, 14.11 (CH_3). — [g] Other $\delta^{13}C$ values: 128.1, 128.5, 128.8, 130.7, 133.6 (CH). — [h] Other $\delta^{13}C$ values: 158.7, 158.8 (C), 115.9 [6.6], 116.3, 118.1, 121.0 [28.3], 126.2, 129.0, 129.9 (CH). — [i] At 243 K: $^1J(^{119}Sn^{13}C)$ = 262.1 Hz. — [j] At 243 K: $^3J(^{119}Sn^{13}C) = 143.9$ Hz. — [k] At 243 K: $\delta^{11}B = 14.9$.

give at first the zwitterionic intermediates **3b**–**k**. Except for **3e** and **3g**, these react fast with an excess of **2a** to give the dialkenyltin derivatives **7** (for NMR data, see Table 4) which finally rearrange[7b,7g] to the stannolenes **8**. If there is no excess of Et_3B, intramolecular organoboration leads either to stannoles (**5**) or 1-stanna-4-bora-2,5-cyclohexadienes (**9**), or to mixtures of **5** and **9** (**5b**/**9b**: ca. 1:2; **5e**/**9e**: ca. 3.5/1; **5c**/**9c**, **5d**/**9d**, **5f**/**9f**, **5h**/**9h**, **5i**/**9i**, **5j**/**9j**, and **5k**/**9k**: all ca. 1:1). Triisopropylborane (**2b**) is less reactive than Et_3B and therefore compounds **4** do not react with an excess of **2b**. The intramolecular organoboration is preferred, leading in one case to a mixture of five- and six-membered heterocycles (**6e**/**10e**) or selectively to six-membered heterocycles (**10**). ^{11}B-, ^{13}C-, and ^{119}Sn-NMR data for stannoles **5**, **6**, stannolenes **8**, and 1-stanna-4-bora-2,5-cyclohexadienes **9**, **10** are listed in Tabes 5–8, respectively.

Table 4. ^{13}C- and ^{119}Sn-NMR data of dialkenyltin compounds **7**[a,b]

R^1 =	Me **7b**	Et **7c**	Pr **7d**[c]	Bu **7f**[d]	iPent **7h**[e]	Oct **7i**[f]	Ph **7j**[g]	3-MeO-C$_6$H$_4$ **7k**[h]
Temp.(K)	213	243	243	243	243	243	298	298
Me$_2$Sn	-7.8 [300.8]	-6.4 [292.1]	-6.2 [292.1]	-6.0 [292.6]	-6.1 [292.1]	-6.5 [292.1]	-6.4 [310.0]	-6.3 [308.5]
Sn-**C**=	134.2 [512.8]	141.5 [501.4]	140.1 [503.3]	140.5 [503.5]	140.4 [504.6]	140.1 [502.5]	141.7 [489.5]	141.5 [490.7]
B-**C**=	163.2 [br] [65.4]	161.9 [br] [69.8]	162.5 [br]	162.5 [br] [68.1]	162.1 [br] [66.5]	161.9 [br] [68.7]	164.3 [br]	164.3 [br]
BEt$_2$	21.9 [br] 9.3	21.8 [br] 10.9	21.8 [br] 9.3	22.2 [br] 9.7	21.7 [br] 9.3	22.7 [br] 9.1	21.9 [br] 8.8	22.2 [br] 9.1
Et	23.1 [79.6] 13.7	22.6 [81.7] 14.6	22.9 [80.1] 14.5	23.2 [81.3] 14.9	22.9 [80.0] 14.5	22.7 [82.9] 14.4	25.2 [74.5] 14.0 [8.8]	25.2 [74.1] 14.4 [8.7]
R^1	20.0 [61.4]	27.2 [61.0] 15.6 [9.8]	36.6 [58.9] 24.4 [9.8]	34.7 [58.9] 33.8	40.2 [58.1] 32.5	34.3 [60.0]	146.4 [44.8] 127.8 [31.7]	147.7 [44.7] 120.5 [17.4]
δ ^{119}Sn	-86.6	-90.5	-89.5	-91.1	-88.2	-91.0	-96.8	-97.1

[a] Ca. 20% in C_7D_8. — [b] $^nJ(^{119}Sn,^{13}C)$ in Hz are given in [ ]; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms. — [c] Other $\delta^{13}C$ values: 14.4 (CH_3). — [d] Other $\delta^{13}C$ values: 23.8 (CH_2), 15.0 (CH_3). — [e] Other $\delta^{13}C$ values: 28.8 (CH), 22.7 (CH_3). — [f] Other $\delta^{13}C$ values: 23.1, 30.0, 30.3, 31.0, 32.4 (CH_2), 14.4 (CH_3). — [g] Other $\delta^{13}C$ values: 127.9 (data from literature[7g]). — [h] Other $\delta^{13}C$ values: 160.2 [6.5] (C-3), 129.2 (C-4), 110.6 [9.6] (C-5), 113.7 [17.4] (C-6), 54.6 (OCH_3).

NMR Spectra

All NMR data (Tables 2 to 8) support the proposed structures of the organoboration products. The ^{1}H-NMR spectra become rather complex for R^1 ≠ H, Me, in particular if mixtures have to be analyzed. ^{11}B-NMR spectra were indicative in the case of the compounds **3** and **4**, proving the presence of the tetra-coordinate boron atoms[8–11]. Otherwise, the ^{11}B resonance signals are very broad (>500 Hz) and $\delta^{11}B$ values are in the typical range ($\delta = +85 \pm 2$) for triorganoboranes. In the case of the stannolenes **8** and 1-stanna-4-bora-2,5-cyclohexadienes **9** and **10**, the ^{11}B nuclear shielding is somewhat increased ($\delta = +72 \pm 3$) with respect to that in **5**, **6**, and **7**.

^{119}Sn- (see Figure 1) and ^{13}C-NMR data (see Figure 2) provide valuable information on the compositon of mixtures, the structure, and the dynamic behavior of the various compounds. Therefore, the progress of the reactions can be monitored conveniently by ^{119}Sn-NMR measurements at variable temperature as shown in Figure 1. This reveals another important feature, namely the significant temperature dependence of ^{119}Sn nuclear shielding of the zwitterionic intermediates **3** and **4** (some instructive examples are given in Table 9). The changes in ^{119}Sn nuclear shielding with temperature can be attributed to the bridging alkynyl group being linked either to boron or to tin (**3'**, **4'**)

Table 5. ^{13}C- and ^{119}Sn-NMR data of stannoles **5** and **6e**[a,b]

R^1 =	H	Me	Et	Pr	iPr	iPr	Bu	tBu	iPent	Oct	Ph
	5a[c]	**5b**	**5c**[d]	**5d**[e]	**5e**[f]	**6e**[g]	**5f**[h]	**5g**[i]	**5h**[j]	**5i**[k]	**5j**[l]
Me$_2$Sn	-9.3 [329.7]	-9.5 [295.4]	-7.8 [291.0]	-8.1 [292.1]	-4.4 [283.4]	-5.7 [282.6]	-8.0 [292.3]	-4.4 [282.4]	-8.2 [291.1]	-8.1 [292.1]	-7.8 [312.8]
C-2	127.8 [410.4]	133.7 [437.3]	143.4 [427.2]	141.4 [424.0]	149.0 [414.7]	147.6 [408.1]	141.8 [426.2]	154.2 [421.9]	141.2 [427.2]	141.6 [425.1]	146.5 [413.0]
C-3	175.3 [br]	166.0 [br]	164.7 [br]	164.8 [br]	162.4 [br]	163.4 [br]	165.1 [br] [52.0]	161.6 [br]	164.8 [br] [52.9]	164.6 [br] [52.3]	160.3 [br]
C-4	162.7 [89.9]	153.0 [117.4]	151.6 [117.2]	151.7 [117.2]	149.5 [117.2]	152.6 [113.8]	151.9 [117.7]	151.7 [133.0]	151.6 [117.7]	151.5 [117.7]	154.5 [86.1]
C-5	121.0 [484.4]	132.8 [487.1]	142.6 [478.5]	140.3 [475.2]	148.2 [466.5]	149.6 [462.2]	140.7 [477.4]	150.9 [464.4]	140.4 [477.4]	140.4 [476.3]	142.2 [421.0]
BEt$_2$,	21.4 [br]	22.1 [br]	22.8 [br]	22.2 [br]	22.7 [br]	23.7 [br]	22.6 [br]	23.3 [br]	22.4 [br]	22.2 [br]	22.2 [br]
BiPr$_2$	9.2	8.9	9.6	9.0	9.3	19.4 19.5	9.3	10.6	9.0	9.0	9.4
Et,	30.9 [62.6]	25.1 [53.8]	26.5 [55.6]	25.9 [55.6]	26.2 [55.6]	38.7 [60.5]	26.4 [54.0]	27.8 [67.6]	26.2 [54.5]	26.0 [54.5]	25.3 [52.2]
iPr	13.2	13.8	14.7	14.1	15.2	23.3	14.5	16.4	14.3	14.2	14.6
R^1-C^2		17.4 [72.4]	29.2 [71.9]	37.6 [70.8]	35.2 [65.9]	34.8 [66.8]	35.6 [70.0]	38.2 [64.3]	33.4 [67.6]	35.5 [69.8]	
R^1-C^5		20.9 [n.o.]	25.5 [63.2]	34.0 [63.2]	30.9 [58.9]	32.8 [54.2]	32.0 [63.2]	37.5 [55.6]	29.8 [61.6]	31.9 [n.o.]	
δ ^{119}Sn	+19.5[m]	0.7	-4.5	-3.5	-6.6	+9.1	-4.1	+17.7	-3.7	-4.5	+14.6

[a] Ca. 20−40% in CD$_2$Cl$_2$ (**5a**), in CDCl$_3$ (**5d**, **5i**, **5j**, **6e**), in C$_7$D$_8$ (**5c**, **5e**, **5g**, **5h**), and in C$_6$D$_6$ (**5f**) at 26 ± 1 °C. — [b] $^nJ(^{119}$Sn,^{13}C) in Hz are given in [ ]; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms; [n.o.]: not observed. — [c] Data from ref.[7a]. — [d] Other δ^{13}C values: 18.5 [17.4], 18.3 (CH$_3$). — [e] Other δ^{13}C values: 26.8 [15.3], 26.6 [15.8], 14.1, 14.2 (CH$_3$). — [f] Other δ^{13}C values: 26.0, 26.1 (CH$_3$). — [g] Other δ^{13}C values: 25.8 [11.7], 26.1 [10.8] (CH$_3$). — [h] Other δ^{13}C values: 23.1, 23.2, 36.2 [15.3], 36.5 [14.2] (CH$_2$), 14.4, 14.5 (CH$_3$). — [i] Other δ^{13}C values: 34.0, 34.3 (CH$_3$). — [j] Other δ^{13}C values: 43.1 [14.2], 43.4 [14.2] (CH$_2$), 28.0, 28.1 (CH), 22.7 (CH$_3$). — [k] Other δ^{13}C values: 33.6 [14.2], 33.8 [14.2], 32.1, 28.7−29.9, 22.8 (CH$_2$), 14.2 (CH$_3$). — [l] Data from ref.[7g]. — [m] **6a**: δ^{119}Sn +32.1.

Table 6. ^{13}C- and ^{119}Sn-NMR data of stannolenes **8**[a,b]

R^1 =	Me	Et	Pr	Bu	iPent	Oct
	8b	**8c**[c]	**8d**[d]	**8f**[e]	**8h**[f]	**8i**[g]
Me$_2$Sn	-8.5 [270.8] -8.5 [246.9]	-6.2 [268.1] -6.7 [245.8]	-6.2 [270.3] -6.6 [245.8]	-6.1 [269.2] -6.5 [245.2]	-6.0 [269.2] -6.5 [244.1]	-6.1 [268.1] -6.5 [244.7]
Et-C=	145.3 [10.4]	143.7 [12.0]	144.1 [12.0]	144.2 [12.0]	144.1 [12.0]	144.1 [12.0]
R^1-C=	134.8 [12.0]	143.7 [12.0]	142.4 [11.4]	142.3 [11.4]	142.3 [12.0]	142.4 [11.4]
Et-C	72.6 [br] [n.o.]	73.1 [br] [52.9]	73.3 [br] [52.0]	73.2 [br] [52.3]	73.0 [br] [52.0]	73.2 [br] [52.3]
R^1-C	65.0 [br] [n.o.]	73.1 [br] [52.9]	72.4 [br] [53.0]	72.5 [br] [52.9]	72.4 [br] [50.0]	72.6 [br] [52.3]
BEt$_2$	15.7 [br] 8.6	15.3 [br] 9.0	15.3 [br] 9.0,9.0	15.4 [br] 9.0,9.1	15.3 [br] 9.0,9.1	15.4 [br] 9.0,9.1
Et-C=	29.3, 14.7 [63.2]	28.6, 14.4 [64.3]	28.7, 14.4 [65.4]	28.9, 14.5 [65.4]	29.0, 14.5 [66.5]	28.9, 14.5 [64.3]
R^1-C=	19.7 [65.4]	28.6, 14.4 [64.3]	38.9, 23.1 [63.2]	36.0, 32.2 [63.2]	33.7, 38.8 [62.1]	36.2, 32.1 [61.6]

Table 6 (*Continued*)

R^1 =	Me	Et	Pr	Bu	iPent	Oct
	8b	**8c**[c]	**8d**[d]	**8f**[e]	**8h**[f]	**8i**[g]
Et-C	24.6 [29.4] 14.7 [25.1]	27.1 [27.9] 16.0 [45.8]	27.1 [27.8] 16.0 [45.8]	26.8 [27.2] 15.9 [42.5]	26.4 [27.8] 15.8 [40.9]	26.8 [28.3] 15.9 [42.5]
R^1-C	19.7 [29.4]	27.1 [27.9] 16.0 [45.8]	37.6 [27.3] 24.8 [44.7]	35.1 [27.2] 34.0 [45.2]	33.4 [27.8] 40.9 [45.8]	35.4 [28.3] 31.8 [45.8]
δ^{119}Sn	55.0	54.0	55.9	54.4	55.9	54.4

[a] Ca. 20−40% in CDCl$_3$ at 26 ± 1 °C. — [b] $^nJ(^{119}$Sn,^{13}C) in Hz are given in [ ]; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms. — [c] ^{13}C-INADEQUATE: $^1J(^{13}$C-2,^{13}C-3) = 41.1, $^1J(^{13}$C-2,^{13}C$_{CH_2}$) = 33.3, $^1J(^{13}$C-3,^{13}C$_{CH_2}$) = 44.1, $^1J(^{13}$C,^{13}C)$_{EtC^2}$ = 34.7, $^1J(^{13}$C,^{13}C)$_{EtC^3}$ = 39.7, $^1J(^{13}$C,^{13}C)$_{BEt}$ = 31.2 Hz. — [d] Other δ^{13}C values: 15.1, 15.4 (CH$_3$). — [e] Other δ^{13}C values: 24.0, 24.2 (CH$_2$), 14.1, 14.2 (CH$_3$). — [f] Other δ^{13}C values: 29.5 (CH), 22.6, 22.7, 22.9 (CH$_3$). — [g] Other δ^{13}C values: 22.9, 29.5, 29.6, 29.69, 29.74, 29.9, 30.9, 31.2, 32.1 (CH$_2$), 14.2 (CH$_3$).

Table 7. ^{13}C- and ^{119}Sn-NMR data of 1-stanna-4-bora-2,5-cyclohexadienes **9**[a,b]

R^1 =	Me	Et	Pr	Bu	i Pent	Oct	Ph	3-C$_6$H$_4$OMe
	9b	**9c**	**9d**[c]	**9f**[d]	**9h**[e]	**9i**[f]	**9j**[g]	**9k**[h]
Me$_2$Sn	−10.6 [318.9]	7.8 [315.0]	-8.3 [315.0]	-8.0 [337.0]	-8.2 [315.0]	-8.2 [316.1]	-9.1 [342.7]	-7.8 [313.9]
C-2,6	149.0 [473.4]	155.3 [467.6]	152.9 [463.2]	153.2 [467.0]	153.0 [468.1]	153.2 [468.1]	153.1 [431.7]	152.8 [430.5]
C-3,5	162.7 [br]	164.7 [br]	162.2 [br]	162.3 [br] [40.0]	161.9 [br] [38.1]	161.9 [br] [39.8]	163.3 [br]	162.9 [br]
BEt	16.2 [br] 8.6	17.0 [br] 9.6	16.5 [br] 8.7	16.8 [br] 9.4	16.6 [br] 9.2	16.4 [br] 9.0	16.7 [br] 8.7	16.6 [br] 8.7
Et-C^{3,5}	23.2 [61.6] 15.0 [9.8]	23.9 [64.3] 16.0 [n.o.]	23.6 [n.o.] 15.5 [9.8]	23.9 [63.2] 15.9 [9.0]	23.7 [64.3] 15.8 [9.8]	23.6 [63.2] 15.6 [10.4]	25.6 [54.7] 15.6 [8.3]	25.7 [56.7] [h]
R^1-C^{2,6}	20.2 [54.8]	27.7 [50.7] 16.2	36.1 [50.1] 24.0 [14.2]	34.1 [50.0] 33.6 [14.2]	32.1 [50.1] 40.4 [12.5]	34.1 [48.5] 30.9 [13.6]	145.4 [39.4]	[h]
δ ^{119}Sn	-136.5	-139.4	-139.1	-139.9	-139.4	-140.2	-132.0	-130.6

[a] Ca. 20−40% in CDCl$_3$ (**9b**, **9d**, **9i**, **9k**), in C$_7$D$_8$ (**9c**, **9h**), in C$_6$D$_6$ (**9f**) at 26 ± 1 °C. — [b] $^nJ(^{119}$Sn,^{13}C) in Hz are given in [ ]; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms; [n.o.]: not observed. — [c] Other δ^{13}C values: 13.9 (CH$_3$). — [d] Other δ^{13}C values: 23.0 (CH$_2$), 14.4 (CH$_3$). — [e] Other δ^{13}C values: 28.2 (CH), 22.7 (CH$_3$). — [f] Other δ^{13}C values: 22.8, 29.5, 29.6, 29.7, 29.8, 32.0 (CH$_2$), 14.2 (CH$_3$). — [g] Data from ref.[7g]. — [h] Other ^{13}C resonances not assigned because of severe overlap with signals for **7k** and **8k**.

as shown in Scheme 1 (b). At higher temperature, contributions from the presence of **3′** or **4′** in the equilibrium become increasingly important. This is also evident from reduced ^{11}B nuclear shielding at higher temperature [see Table 2 (**3b**, **3j**, **3k**) and Table 3 (**4b**, **4j**, **4k**)]. The temperature range for NMR studies is rather limited owing to the

Table 8. ^{13}C- and ^{119}Sn-NMR data of 1-stanna-4-bora-2,5-cyclohexadienes **10**[a,b]

R^1 =	Me **10b**[c]	Et **10c**	Pr **10d**[d]	iPr **10e**[e]	Bu **10f**[f]	iPent **10h**[g]	Oct **10i**[h]	Ph **10j**[i]	3-C_6H_4OMe **10k**[j]
Me_2Sn	-9.9 [314.3]	-9.3 (br) -5.7 (br)	-10.0 (br) -5.6 (br)	-3.9 (br) -1.8 (br)	-9.4 (br) -5.2 (br)	-9.8 (br) -5.5 (br)	-9.9 (br) -5.6 (br)	-8.7 [337.0]	-8.5 [337.9]
C-2,6	137.3 [465.6]	145.0 [452.9]	142.9 [451.2]	150.1 [445.1]	143.3 [453.4]	142.7 [451.8]	143.0 [451.2]	142.8 [416.0]	142.4 [413.1]
C-3,5	169.0 [br]	167.2 [br]	168.1 [br] [35.0]	165.9 [br]	168.5 [br] [39.2]	167.7 [br] [39.0]	167.9 [br] [38.1]	170.1 [br]	170.0 [br] [29.4]
B **iPr**	25.2 [br] 20.7	25.1 [br] 21.0	25.4 [br] 20.9	25.4 [br] 21.1	26.1 [br] 21.6	25.6 [br] 21.1	25.5 [br] 21.0	26.2 [br] 21.0	26.1 [br] 20.9
iPr-$C^{3,5}$	30.8 [70.8] 22.7 [7.1]	31.0 [71.4] 23.5 [7.0]	30.8 [71.4] 23.4 (br)	31.0 [70.4] [e]	31.5 [71.9] 24.0 (br)	30.9 [71.9] 23.5 (br)	30.9 [71.9] 23.4 (br)	32.4 [63.5] 23.7 [8.0]	32.4 [63.2] 23.7 [6.0]
R^1-$C^{2,6}$	20.6 [53.3]	27.6 [46.9] 16.2 [16.4]	36.4 [44.7] 24.8 [15.3]	32.8 [41.1] [e]	34.7 [45.2] 34.7 [15.3]	32.3 [44.7] 41.3 [13.6]	34.3 [44.7] 31.8 [14.7]	146.2 [34.2] 126.6 [18.3]	147.6 [34.9] 112.2 [18.5]
$\delta^{119}Sn$	-121.0	-122.6	-122.4	-145.3	-122.6	-122.1	-121.9	-117.1	-116.7

[a] Ca. 20–40% in $CDCl_3$ at 26 ± 1°C. – [b] $^nJ(^{119}Sn,^{13}C)$ 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. – [c] Data from ref.[7c]. – [d] Other $\delta^{13}C$ values: 14.0 (CH_3). – [e] Other signals are not assigned owing to overlap with signals from **6e**. – [f] Other $\delta^{13}C$ values: 23.3 (CH_2), 14.8 (CH_3). – [g] Other $\delta^{13}C$ values: 28.2 (CH), 22.5 (br), 22.43, 22.36 (CH_3). – [h] Other $\delta^{13}C$ values: 22.8, 29.5, 29.7, 29.8, 32.1 (CH_2), 14.2 (CH_3). – [i] Other $\delta^{13}C$ values: 128.0 (*m*), 124.5 (*p*) (CH) (data from ref.[7g]). – [j] Other $\delta^{13}C$ values: 159.3 [6.5] (C-3), 109.6 (C-4), 119.1 [17.4] (C-5), 128.9 [6.5] (C-6), 54.9 (OCH_3).

Table 9. Temperature dependence of ^{119}Sn nuclear shielding of the zwitterionic compounds **3** and **4** in $CDCl_3$

	3b	**3d**	**3e**	**3j**	**4b**	**4c**	**4j**
R^1 =	Me	Pr	iPr	Ph	Me	Et	Ph
R =	Et	Et	Et	Et	iPr	iPr	iPr
Temp. (K)				δ ^{119}Sn			
208	146.5	211.1	218.3	128.4	153.7	193.1	138.8
223	104.6	202.7	216.1	93.9	134.3	191.4	124.6
243	47.7	187.8	212.4	49.6	102.1	188.0	99.7
263	2.5	167.5	207.4	11.6	68.2	183.5	72.6
283	-34.2	137.7	199.8	-22.4	29.6	176.0	41.5

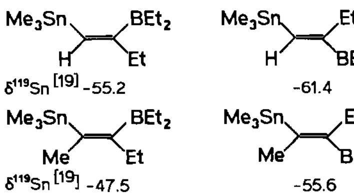
reactivity of the compounds **3** and **4**. The $\delta^{119}Sn$ data in Table 9 show that the equilibrium in Schme 1 (b) is shifted more to the side of **3** if R^1 = *i*Pr (**3e**). In general, it appears that the compounds **4** are more stable than **3** with respect to the formation of **4'** and **3'**. Interestingly, the compounds **3** and **4** are destabilized if R^1 = Ph or 3-$MeOC_6H_4$.

Relevant ^{13}C resonances of all compounds are readily assigned on the basis of $^{117/119}Sn$ satellites due to the coupling constants $J(^{117/119}Sn,^{13}C)$, or broadened signals owing to partially relaxed scalar ^{13}C-^{11}B coupling (see Figure 2), and in most cases by 2D $^{13}C/^1H$ heteronuclear shift correlations. The latter experiments are also useful with regard to the comparison of relative signs of coupling constants[12,13]. Thus, in the case of **5a** all signs of coupling constants $^1J(^{119}Sn,^{13}C_{Me})$ and $^1J(^{119}Sn,^{13}C_{C=})$ were shown to be negative [reduced coupling constants $^1K > 0$; relative to $^2K(^{119}Sn,^1H_{Me})$ (<0[14]) and $^2K(^{119}Sn,^1H_{C=})$ (>0[15])].

If the interconversion of **3** or **4** into **3'** or **4'** is fast as compared to the NMR time scale both ^{13}C-NMR signals of the bridging alkynyl group become broad; in the case of **4** ⇄ **4'**, the diastereotopic character of the methyl groups in the iPr_2B moiety is lost in the fast exchange limit (e.g., **4b** at 263 K or **4f**, **4i** at 298 K, **4j** at 263 K and **4k** even at 243 K). The unsymmetrical bonding situation at the tin atom in compounds **3** and **4** is reflected by the rather small coupling constants $|^1J(^{119}Sn,^{13}C_{Me})|$ (<250 Hz in most cases) and the rather large values $|^1J(^{119}Sn,^{13}C_{C\equiv})|$ (635 ± 20 Hz). A negative sign of $^1J(^{119}Sn,^{13}C_{Me})$ [reduced coupling constant $^1K(^{119}Sn,^{13}C_{Me}) > 0$, as expected[13]] was determined by 2D $^{13}C/^1H$ heteronuclear shift correlations [relative to $^2K(^{119}Sn,^1H_{Me})$ (<0[14])]. All values $|J(^{119}Sn,^{13}C_{C\equiv})|$ in **3** and **4** are small (<80 Hz) and can be of either sign[10]. However, the presence of this coupling indicates bonding between the tin atom and the alkynyl group, since the alternative coupling pathway across 4 or 5 bonds would not lead to substantial scalar ^{119}Sn-^{13}C coupling.

The $\delta^{13}C$ data in the olefinic range of the stannoles **5** and **6** (Table 5) are fully in accord (except for **5a**) with the *or*-conformation (the C_2B plane lies perpendicular to the C=C–B plane) of the R_2B group[16] with respect to the stannole ring (see especially the good agreement between $\delta^{13}C$ data for **5e** and **6e**). In the case of **5a**, the difference in the $\delta^{13}C$-2,5 values (6.8 ppm) must be attributed to CB(pp)π interactions causing deshielding of the ^{13}C-2 nucleus. The direction and magnitude of all other substituent-induced changes in the olefinic $\delta^{13}C$ values of **5** are in the expected order.

The $\delta^{119}Sn$ data of the stannoles **5** and **6e** change unpredictably with the substituents R^1. Thus, replacement of R^1 = H by a methyl group in monoalkenyltin compounds leads to deshielding of the ^{119}Sn nuclei, irrespective of the *cis* or *trans* position of Me_3Sn and Et_2B group. In contrast, ^{119}Sn nuclear shielding in **5** increases by 18.8 ppm if R^1 = H is replaced by a methyl group. Fairly constant $\delta^{119}Sn$ values are observed for R^1 = Et, Pr, *i*Pr, Bu, *i*Pent, and Oct ($\delta^{119}Sn = +5 \pm 1.6$). If R^1 = *t*Bu (**5g**) or Ph (**5j**) again deshielding is observed. A difference in the $\delta^{119}Sn$ values for **5e** and **6e** ($\Delta^{119}Sn = 15.7$) is also observed, in the same direction as for **5a** and **6a**[7a] ($\Delta^{119}Sn = 12.1$). It has been shown that ^{119}Sn nuclei become extremely deshielded if R^1 = $SiMe_3$ ($\delta^{119}Sn = +133.5$ if R = Et[7d]). Therefore, it appears that in the case of stannoles the usual substituent-induced shifts



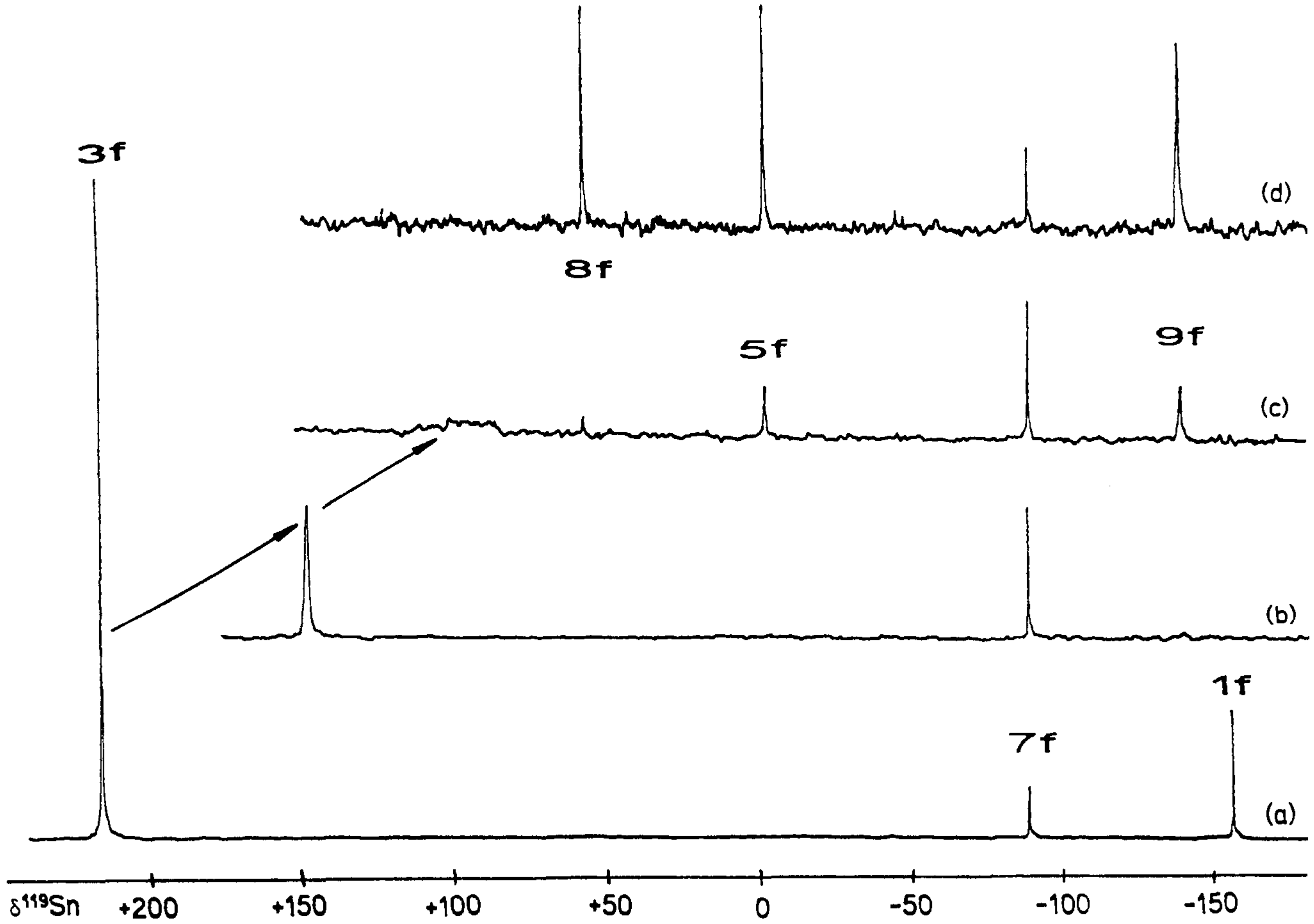
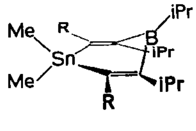


Figure 1. 33.3 MHz ^{119}Sn{^{1}H inverse gated)-NMR spectrum (NOE-suppressed) of a reaction solution of **1f** and **2a** (ratio 1:1.4), showing that the progress of the organoboration can be readily monitored; the assignment of the ^{119}Sn resonances is based on their change in intensity as a function of time and corresponding changes in the ^{1}H-, ^{11}B- and ^{13}C-NMR spectra; note the temperature dependence of the ^{119}Sn-NMR signal of **3f**. – (a) Spectrum taken after mixing the components at $-70\,°C$. – (b) The same spectrum as in (a) after 1 h at 10°C. – (c) The same spectrum as in (b) after 2 h at 25°C. – (d) The same spectrum as in (c) after 12 h at 25°C

known for δ^{119}Sn values are not valid because of a specific effect related to the stannole system. A dominating part is played by the +I effect of the substituents R^1 and also – to a smaller extent – of the R_2B group.

The ^{13}C(SnMe) resonances of many 1-stanna-4-bora-2,5-cyclohexadienes **10** are broad [except e.g. **10b**: $\Delta G_c^{\ddagger}(-30\,°C) = 53 \pm 1$ kJ/mol] and split into two signals already at ambient temperature, in contrast to a single sharp ^{13}C(SnMe) signal for comparable compounds **9**. This indicates that compounds **10**, on steric grounds, readily adopt a non-planar ring structure, e.g. a chair or a half-chair conformation, whereas a close to planar six-membered ring is favored in the case of compounds **9**.The ^{11}B nuclear shielding of **10** ($\delta^{11}B = +73.5 \pm 1$) is slightly reduced as compared to **9** ($\delta^{11}B = +70.0 \pm 1$). This also suggests that CB(pp)π interactions in **10** are weaker than in **9**, and it is conceivable that the boron atom is shifted out of the plane formed by the C=C bonds and possibly the tin atom (see structure **D**).

D



These assumptions should be corroborated by δ^{13}C values of the olefinic carbon atoms in **9** and **10**, in particular of the olefinic carbon atom in β-position with respect to the three-coordinate boron atom, by comparing data for non-cyclic and cyclic compounds. It has been shown that ^{13}C nuclear shielding of these carbon atoms is very sensitive towards potential CB(pp)π interactions[16,17]. Since the compounds analogous to **7** with R = *i*Pr are not observed in the reaction mixtures, data for the corresponding monoalkenyl tin derivatives (vide infra) serve for comparison. A comparison of the δ^{13}C(SnC=) data shows that in the non-cyclic compounds the BR_2 moieties prefer the *or*-conformation as expected[16]. In the cyclic compounds **10** any CB(pp)π interactions are still weak, since the ^{13}C(Sn–C=) nuclear shielding is reduced only by ca. 6 ppm or less. In contrast, the shielding of the ^{13}C(SnC=) nuclei is much stronger reduced (ca. 15.5 ppm) in compounds **9**. This again suggests a more flattened ring in **9** as compared to **10**. The coupling constants $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}_{C=})$ appear to be rather insensitive to differing ring structures, although they are indicative of the ring closure (see data for compounds **7** and **9**). The smaller values $|\,^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}_{C=})\,|$ for **9** as compared to **7** (ca. 40 Hz

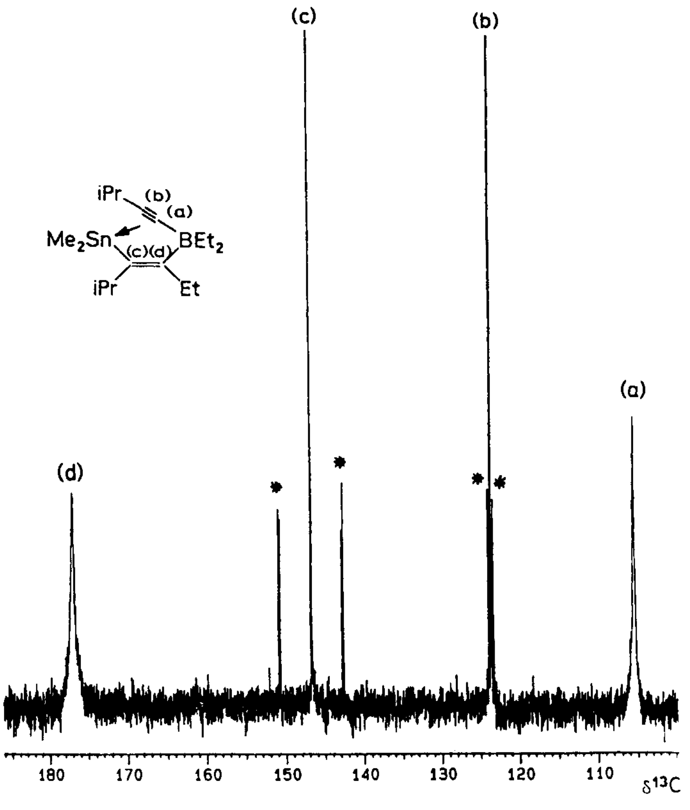


Figure 2. 75.5 MHz $^{13}C\{^1H\}$-NMR spectrum of the zwitterionic compound **3e** (at −30°C, in $CDCl_3$) showing the range of the olefinic and alkynyl ^{13}C resonances [plotted at increased gain in order to show the broad signals and the $^{117/119}Sn$ satellites (*)]. The two broad ^{13}C resonances for the boron-bound carbon atoms are readily identified, and the two other signals are assigned on the basis of their greatly differing coupling constants $|\,^1J(^{119}Sn,^{13}C_{C=})\,|$

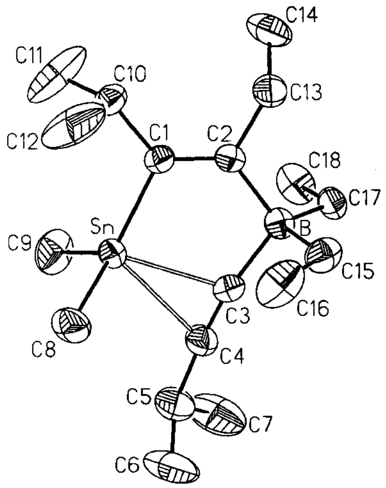
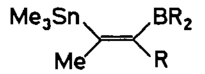


Figure 3. Molecular structure fo **3e**. Selected bond distances [Å] and bond angles [°]: Sn–C1 2.116(4), Sn–C3 2.339(4), Sn–C(4) 2.523(5), Sn–C(8) 2.128(5), Sn–C9 2.136(5), B–C2 1.616(6), B–C3 1.651(6), C1–C2 1.334(6), C1–C10 1.529(6), C3–C4 1.213(6), C4–C5 1.483(7); C1–Sn–C3 84.2(2), C1–Sn–C4 112.6(2), C3–Sn–C4 28.6(1), C1–Sn–C8 118.1(2), C1–Sn–C9 119.1(2), C8–Sn–C9 113.9(2), C2–B–C3 110.1(3), Sn–C1–C2 114.5(3), B–C2–C1 125.2(4), Sn–C3–B 105.5(2), B–C3–C4 170.1(4), C3–C4–C5 174.0(5), C3–Sn–C8 107.3(2), C4–Sn–C8 95.7(2), C3–Sn–C9 108.6(2), C4–Sn–C9 90.9(2)

difference) can be ascribed to the enforced small endocyclic bond angles C–Sn–C in **9**. The $\delta^{119}Sn$ values of **9** and **10** also indicate structural differences between the six-membered rings. Thus, the order of the $\delta^{119}Sn$ values found for the monoalkenyl tin compounds is reversed for **9** and **10**. In the case of **10e**, the $\delta^{119}Sn$ value ($\delta = -145.3$) is markedly different from the $\delta^{119}Sn$ values for the other compounds **10**. This can be attributed to further twisting of the ring in order to reduce steric interactions between the isopropyl groups in the 2,3,4,5,6 positions. $\Delta^{119}Sn$ values of the order of ca. 100 ppm or less were observed also for saturated five- and six-membered cyclic tin compounds[18], the ^{119}Sn nuclei being always deshielded in the five-membered rings.

Compound:			**7b**	**9b**	**10b**
R =	Et	iPr	Et	Et	iPr
$\delta^{13}C$ (Sn-C=) $^1J(^{119}Sn,^{13}C)$ [Hz]	133.6 [536.0]	131.2 [535.9]	134.2 [512.8]	149.0 [473.4]	137.3 [465.6]
$\delta^{13}C$ (B-C=)	163.0	165.0	163.2	162.7	169.0
$\delta^{119}Sn$	-47.5	-54.2	-86.6	-136.5	-121.0

X-Ray Analysis of 3e

Experimental data are given in Table 10[20] and atomic coordinates together with equivalent isotropic displacement coefficients are given in Table 11. The molecular structure of **3e** is depicted in Figure 3, and important bond lengths and bond angles are given in the legend to Figure 3.

The atoms Sn, C1, C2, B, C3, C4, and C5 lie in one plane. As for other compounds with alkynyl groups as bridging ligands between main group elements[21], the nature of the C≡C bond seems to be hardly affected by the asymmetric side-on coordination [$d_{C3C4} = 121.3(6)$ pm and the bond angles BC3C4 (170.1(4)°) and C3C4C5 (174.0(5)°) differ little from 180°]. The surrounding of the tin atom is pyramidal (sum of relevant bond angles 351.1°) with respect to the C1,C8,C9 plane, the tin atom being oriented towards the C≡C bond. Interestingly, the B–C3 bond [$d_{BC3} = 165.1(3)$ pm] is the longest B–C bond in **3e**, although the C3 atom is formally sp-hybridized. This suggests that the electron-deficient tin atom also participates in the electron density

Table 10. Data for the X-ray analysis of compound **3e**[a]

Formula $C_{18}H_{35}BSn$; molecular mass 381.0; crystal size $0.51 \times 0.37 \times 0.29$ mm³; space group *P*bca; **Z** = 8; a = 1352.5, b = 1566.1, c = 1929.0 pm; $\alpha = \beta = \gamma = 90^0$; V = 4086 (1)·$10^{-30}$ m³; ρ (calc.) = 1.196 gcm^{-3}; μ = 1.24 mm^{-1}; radiation Mo K_α; λ = 71.069 pm; temperature 190 K; 2Θ: $3 \leq 2\Theta \leq 55^0$; number of independent reflections 3595; observed reflections 2763 [$F_0 \geq 4\sigma(F)$]; R = 0.0410; R_W = 0.0456 [$w^{-1} = (\sigma^2(F_0) + 0.002F_0^2)$]; residual electron density: −0.43 eÅ^{-3} (min.), 1.01 eÅ^{-3} (max)

[a] Crystals of **3e** are destroyed on cooling below 190 K, probably as a result of a phase transition.

of this σ bond, a prerequisite of the equilibrium in Scheme 1 (b). All other bond lengths and bond angles are in the expected range. In a comparable zwitterionic lead compound[8], the surrounding of the lead atom is almost trigonal-planar (sum of relevant bond angles 356.7°) and the B–C3 bond is slightly shorter than the other B–C bonds. The bond angles BC17C18 (115.9°) and BC15C16 (116.9°) are similar to those in BEt_4^- [22].

Table 11. Atomic coordinates (· 10^4) and equivalent isotropic displacement coefficients [$Å^2 \cdot 10^3$]. * Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Sn	1568(1)	6882(1)	3206(1)	31(1)*
B	-73(3)	7534(3)	4280(2)	32(1)*
C(1)	809(4)	8061(3)	3148(2)	32(1)*
C(2)	177(3)	8202(2)	3666(2)	30(1)*
C(3)	671(3)	6700(3)	4233(2)	32(1)*
C(4)	1183(4)	6070(3)	4303(2)	40(1)*
C(5)	1774(5)	5299(4)	4467(3)	62(2)*
C(6)	1287(6)	4501(4)	4231(3)	89(3)*
C(7)	2040(6)	5308(4)	5219(3)	84(3)*
C(8)	1135(5)	5890(3)	2517(3)	55(2)*
C(9)	3109(4)	6881(4)	3450(4)	61(2)*
C(10)	1033(4)	8631(3)	2523(2)	41(2)*
C(11)	2094(5)	8876(6)	2469(4)	104(3)*
C(12)	690(8)	8210(5)	1866(3)	100(4)*
C(13)	-394(4)	9037(3)	3686(3)	45(2)*
C(14)	212(5)	9787(3)	3964(3)	63(2)*
C(15)	-1190(4)	7175(4)	4189(3)	48(2)*
C(16)	-1417(4)	6701(5)	3527(3)	69(2)*
C(17)	101(4)	7929(3)	5053(2)	40(1)*
C(18)	1159(4)	8159(3)	5233(3)	52(2)*

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Experimental

All compounds were handled under N_2 by using carefully dried glassware and solvents. Deuterated solvents were stored over molecular sieves and saturated with N_2. Starting materials such as solutions of butyllithium (1.6 M) in hexane (Aldrich) and most terminal alkynes were commercial products. Me_2SnCl_2 was prepared from Me_4Sn and $SnCl_4$ and purified by recrystallization from hexane. – Elemental analyses: Dornis & Kolbe, Mülheim, and Pascher, Remagen. – IR: Perkin-Elmer 983. – MS: EI-MS (70 eV), Varian MAT CH-7 with direct inlet. – $^{1}H/^{13}C$ NMR: Bruker AC 300 (300.13/75.5 MHz), Bruker AM 500 (500.13/125.8 MHz), Jeol JNM-EX 270E (270.67/67.94 MHz). – ^{11}B NMR: Bruker AC 300 (96.3 MHz) and Jeol FX 90Q (28.7 MHz), $Et_2O \cdot BF_3$ as external standard. – ^{119}Sn NMR: Bruker AC 300 (111.9 MHz) and Jeol FX 90Q (33.3 MHz), $SnMe_4$ as external standard.

Starting materials: The dialkylnyltin compounds **1a**[23], **1b**[24], **1f**[25], **1g**[24], **1j**[23], triethylborane (**2a**)[26], triisopropylborane (**2b**)[27], and 1-ethynyl-3-methoxybenzene[28] were prepared according to literature procedures.

Dialkynylstannanes (**1**). *General Procedure:* A freshly prepared suspension of 85 mmol of the respective lithiated alkyne in 100 ml of toluene is stirred at −78 °C, and 8.3 g (38 mmol) of Me_2SnCl_2 is added in one portion. The mixture is warmed to room temp., stirred for 12 h, and filtered. After removal of the solvent in vacuo (0.1 Torr), the residue is purified either by fractional distillation, by sublimation, or by recrystallization to give a pure product in 62–89% yield (see Table 1 for ^{119}Sn- and ^{13}C-NMR data).

1c: Yield 6.0 g (62%); b.p. 34 °C/0.1 Torr. – IR ($CHCl_3$): $\tilde{\nu}$ = 2152 cm^{-1} (C≡C). – ^{1}H NMR ($CDCl_3$): δ [$^{n}J(^{119}Sn,^{1}H)$] = 0.18 [66.8] [s, 6H, $Sn(CH_3)_2$]; 0.93 (t, 6H, CH_3); 2.03 (q, 4H, CH_2). – $C_{10}H_{16}Sn$ (254.95): calcd. C 47.11, H 6.33; found C 47.24, H 6.41.

1d: Yield 9.6 g (89%); m.p. 52 °C. – IR ($CHCl_3$): $\tilde{\nu}$ = 2151 cm^{-1} (C≡C). – ^{1}H NMR ($CDCl_3$): δ [$^{n}J(^{119}Sn,^{1}H)$] = 0.28 [68.5] [s, 6H, $Sn(CH_3)_2$]; 2.09 (t, 4H, CH_2); 1.41 (m, 8H, CH_2); 0.86 (t, 6H, CH_3). – MS, *m/z* (%): 269 (42) [M – 15], 202 (6), 135 (6), 120 (4), 69 (56), 57 (68), 43 (100).

1e: Yield 7.0 g (65%); m.p. 35 °C. – IR ($CHCl_3$): $\tilde{\nu}$ = 2150 cm^{-1} (C≡C). – ^{1}H NMR ($CDCl_3$): δ [$^{n}J(^{119}Sn,^{1}H)$] = 0.29 [68.3] [s, 6H, $Sn(CH_3)_2$]; 1.08 (d, 12H, CH_3); 2.48 (m, 2H, CH). – MS; *m/z* (%): 269 (57) [M^+ – 15], 187 (46), 135 (28), 120 (28), 97 (41), 83 (45), 71 (65), 67 (67), 57 (100), 43 (72). – $C_{12}H_{20}Sn$ (283.0): calcd. C 50.93, H 7.12; found C 50.47, H 7.12.

1h: Yield 9.3 g (72%); b.p. 57 °C/0.2 Torr. – IR ($CHCl_3$): $\tilde{\nu}$ = 2155, 2243 cm^{-1} (C≡C). – ^{1}H NMR ($CDCl_3$): δ [$^{n}J(^{119}Sn,^{1}H)$] = 0.29 [68.5] [s, 6H, $Sn(CH_3)_2$]; 2.13 (t, 4H, CH_2), 1.33 (m, 4H, CH_2); 1.58 (m, 2H, CH); 0.79 (d, 12H, CH_3). – MS, *m/z* (%): 325 (100) [M^+ – 15], 135 (5). – $C_{16}H_{28}Sn$ (339.1): calcd. C 56.67, H 8.32, Sn 35.01; found C 57.05, H 8.55, Sn 34.49.

1i: Yield 13.8 g (86%); b.p. 131 °C/0.1 Torr. – IR ($CHCl_3$): $\tilde{\nu}$ = 2155 cm^{-1} (C≡C). – ^{1}H NMR ($CDCl_3$): δ [$^{n}J(^{119}Sn,^{1}H)$] = 0.29 [65.3] [s, 6H, $(Sn(CH_3)_2$]; 2.12 (t, 4H, CH_2); 1.40 (m), 1.18 (m) (24H, CH_2); 0.79 (t, 6H, CH_3). – MS, *m/z* (%): 409 (100) [M^+ – 15], 287 (15), 137 (10), 135 (21), 120 (9), 95 (17), 81 (24), 71 (18), 57 (23), 43 (20). – $C_{22}H_{40}Sn$ (423.3): calcd. C 62.43, H 9.52, Sn 28.05; found C 64.12, H 10.20, Sn 25.62.

1k: Yield 9.8 g (63%); m.p. 71–73 °C. – IR ($CHCl_3$): $\tilde{\nu}$ = 2139, 2253 cm^{-1} (C≡C). – ^{1}H NMR ($CDCl_3$): δ [$^{n}J(^{119}Sn,^{1}H)$] = 0.62 [68.7] [s, 6H, $(Sn(CH_3)_2$]; 3.77 (s, 6H, OCH_3); 6.8–7.3 (m, 8H, CH). – MS, *m/z* (%): 412 (8) [M^+], 397 (100), 262 (31), 251 (19), 219 (9), 176 (10), 151 (9), 132 (30), 120 (38), 102 (15), 89 (14), 63 (18), 43 (10).

Stannoles **5**, **6** *and 1-Stanna-4-bora-2,5-cyclohexadienes* **9**, **10**. *General Procedure:* A solution of 4 mmol of **1b–k** in 10 ml of CH_2Cl_2 is cooled to −78 °C and 4 mmol of **2** is added in one portion; the mixture is warmed to room temp. and stirred for 15 h. After removal of the solvent in vacuo, the remaining oils are purified by distillation ($5 \cdot 10^{-2}$ Torr) (see Tables 6, 7, and 9 for ^{119}Sn- and ^{13}C-NMR data).

Mixtures of compounds **5b/8b/9b**, **5c/9c**, **5d/9d**, **5f/9f**, **5h/9h**, **5i/9i**, **5j/8j/9j**, **5k/8k/9k**, and **6e/10e** are obtained. The compounds **5a**[7a], **5g**[7d], **5j**[7g], **9j**[7g], **10b**[7c], **10j**[7g] have already been described.

5e: Yield 1.0 g (68%); b.p. 83 °C/$5 \cdot 10^{-2}$ Torr. – ^{1}H NMR ($CDCl_3$): δ [$^{n}J(^{119}Sn,^{1}H)$] = 0.35 [53.8] [s, 6H, $Sn(CH_3)_2$]; 1.35 (q), 0.94 (t) (10H, BEt_2); 2.30 (m), 0.94 (d) (7H, *i*Pr); 2.10 (m), 0.89 (d) (7H, *i*Pr); 1.90 (q), 0.89 (t) (5H, Et). – MS, *m/z* (%): 382 (68) [M^+], 283 (42), 203 (100), 217 (43), 135 (52), 133 (48), 69 (39). – $C_{18}H_{35}BSn$ (381.0): calcd. C 56.75, H 9.26; found C 54.86, H 9.07.

10c: Yield 1.3 g (84%); b.p. 92 °C/$5 \cdot 10^{-2}$ Torr. – ^{1}H NMR ($CDCl_3$): δ [$^{n}J(^{119}Sn,^{1}H)$] = 0.23 [52.2] [s, 6H, $Sn(CH_3)_2$]; 1.70 (m), 0.99 (d) (7H, B*i*Pr); 2.88 (m), 1.19 (d) (14H, *i*Pr); 2.28 (m br), 1.04 (t) (10H Et). – MS, *m/z* (%): 396 (11) [M^+], 357 (29), 335 (24), 247 (47), 151 (52), 135 (53), 71 (62), 55 (81), 43 (100).

10d: Yield 1.0 g (59%); b.p. 102 °C/$5 \cdot 10^{-2}$ Torr. – ^{1}H NMR ($CDCl_3$): δ [$^{n}J(^{119}Sn,^{1}H)$] = 0.20 [52.1] [s, 6H, $Sn(CH_3)_2$]; 1.68 (m), 1.0 (d) (7H, B*i*Pr); 2.89 (m), 1.19 (d) (14H, *i*Pr); 2.62 (m br), 2.28 (m br), 1.43 (m), 0.94 (t) (14H, Pr). – MS, *m/z* (%): 424 (22) [M^+], 381 (41), 259 (63), 231 (94), 135 (84), 69 (100), 43 (85), 41 (99). – $C_{21}H_{41}BSn$ (423.1): calcd. C 59.62, H 9.77; found C 59.52, H 9.72.

10f: Yield 1.1 g (59%); b.p. 108 °C/5 · 10^{-2} Torr. – ^{1}H NMR (CDCl$_3$): δ $^{n}J(^{119}$Sn,^{1}H)] = 0.02 [51.2] [s, 6H, Sn(CH$_3$)$_2$]; 1.68 (m), 0.98 (d) (7H, B*i*Pr); 2.89 (m), 1.20 (d) (14H, *i*Pr); 2.35 (m br), 1.35 (m br), 0.96 (t) (18H, Bu). – MS, *m/z* (%): 452 (23) [M^{+}], 409 (75), 387 (94), 275 (73), 245 (63), 151 (34), 135 (68), 113 (100), 71 (69), 41 (79). – C$_{23}$H$_{45}$BSn (451.1): calcd. C 61.24, H 10.05; found C 61.05, H 10.65.

10h: Yield 1.4 g (72%); b.p. 105 °C/5 · 10^{-2} Torr. – ^{1}H NMR (CDCl$_3$) (relevant data): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.19 [52.3] [s, 6H, Sn(CH$_3$)$_2$]; 2.89 (m), 1.17 (d) (14H, *i*Pr). – MS, *m/z* (%): 498 (13) [M^{+}], 413 (38), 345 (100), 289 (76), 151 (49), 135 (40), 95 (53), 69 (81), 57 (63), 43 (99). – C$_{25}$H$_{49}$BSn (479.2): calcd. C 62.66, H 10.31, B 2.26, Sn 24.77; found C 63.15, H 11.40, B 3.86, Sn 21.68.

10i: Yield 1.6 g (95%); decomp. 200 °C/5 · 10^{-2} Torr. – ^{1}H NMR (CDCl$_3$) (relevant data): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.21 [52.3] [s, 6H, Sn(CH$_3$)$_2$]; 2.89 (m), 1.19 (d) (14H, *i*Pr); 1.70 (m), 0.99 (d) (7H, B*i*Pr). – MS, *m/z* (%): 443 (55) [M^{+} – 121], 401 (33), 331 (64), 236 (35), 205 (35), 181 (32), 151 (36), 135 (31), 113 (37), 97 (33), 83 (45), 69 (89), 55 (100).

10k: Yield 1.5 g (93%); decomp. 200 °C/5 · 10^{-2} Torr. – ^{1}H NMR (CDCl$_3$) (relevant data): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.07 [53.1] [s, 6H, Sn(CH$_3$)$_2$]. – MS, *m/z* (%): 483 (24) [M^{+} – 69], 404 (36), 321 (41), 306 (45), 175 (95), 159 (100), 135 (89), 121 (52), 57 (40), 43 (52).

Stannolenes **8**. *General Procedure:* A solution of 4 mmol of **1** in 10 ml of CH$_2$Cl$_2$ is cooled to –78 °C and 9 mmol of **2b** is added in one portion; the mixture is warmed to room temp. and stirred for 15 h. Solvents and traces of excess of **2b** are removed in vacuo between 25 and 60 °C (see Tables 4, 6 for ^{119}Sn- and ^{13}C-NMR data). The dialkenyltin compounds **7** as precursors of the compounds **8** have not been isolated. They are characterized by multinuclear NMR data of the reaction solutions (see Table 4). The compounds **8b**[7c] and **8j**[7g] have already been described.

8c: Yield 1.5 g (83%); b.p. 92 °C/5 · 10^{-2} Torr. – ^{1}H NMR (CDCl$_3$): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.31 [47.5], (s, 3H, SnCH$_3$), 0.17 [49.0] (s, 3H, SnCH$_3$); 2.09 [30] (m, 2H, CH$_2$C), 2.35 [95] (m, 2H, CH$_2$C) [$^{2}J(^{1}$H^{1}H) = 15 Hz]; 1.07 [2.5] (m, 6H, C*H*$_3$CH$_2$C); 2.27 [1.5] (m, 4H, CH$_2$C=), 1.12 (m, 6H, C*H*$_3$CH$_2$C=), 1.15 (m, 8H, BCH$_2$), 1.01 (m, 12H, BCH$_2$C*H*$_3$). – MS, *m/z* (%): 452 (8) [M^{+}], 302 (26), 273 (81), 203 (100), 175 (39), 135 (16), 69 (36), 41 (40). – C$_{22}$H$_{46}$B$_2$Sn (450.9): calcd. C 58.60, H 10.28; found C 58.74, H 10.27.

8d: Yield 1.4 g (74%); b.p. 95 °C/5 · 10^{-2} Torr. – ^{1}H NMR (CDCl$_3$) (relevant data): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.26 [47.4] (s, 3H, SnCH$_3$), 0.12 [49.3] (s, 3H, SnCH$_3$); 2.11 (m), 1.45 (m), 1.06 (m), 0.96 (m). – MS, *m/z* (%): 480 (12) [M^{+}], 330 (42), 301 (100), 231 (97), 165 (63), 135 (15), 69 (43), 55 (57), 41 (49). – C$_{24}$H$_{50}$B$_2$Sn (479.0): calcd. C 60.18, H 10.52, B 4.51,Sn 24.78; found C 59.22, H 10.85, B 4.52, Sn 25.32.

8f: Yield 1.0 g (51%); b.p. 97 °C/5 · 10^{-2} Torr. – ^{1}H NMR (CDCl$_3$) (relevant data): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.30 [47.0] (s, 3H, SnCH$_3$), 0.16 [49.1] (s, 3H, SnCH$_3$); 2.32 (m), 2.26 (m), 1.39 (m), 1.11 (m), 1.00 (m). – MS, *m/z* (%): 508 (10) [M^{+}], 410 (16), 359 (39), 329 (72), 259 (99), 231 (71), 135 (38), 85 (50), 69 (67), 57 (100), 41 (79). – C$_{26}$H$_{54}$B$_2$Sn (507.0): calcd. C 61.59, H 10.73, B 4.26, Sn 23.41; found C 62.43, H 11.45, B 3.98, Sn 22.19.

8h: Yield 1.0 g (48%); b.p. 79 °C/5 · 10^{-2} Torr. – ^{1}H NMR (CDCl$_3$) (relevant data): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.27 [47.2] (s, 3H, SnCH$_3$), 0.12 [49.1] (s, 3H, SnCH$_3$); 2.12 (m), 1.50 (m), 1.29 (m), 1.06 (m), 1.02 (d), 0.93 (d), 0.93 (m). – MS, *m/z* (%): 536 (11) [M^{+}], 386 (30), 357 (88), 287 (67), 237 (56), 195 (55), 135 (31), 81 (41), 69 (87), 57 (100), 43 (71).

8i: Yield 0.88 g (35%); b.p. 108 °C/5 · 10^{-2} Torr. – ^{1}H NMR (CDCl$_3$) (relevant data): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.28 [46.5] (s, 3H, SnCH$_3$), 0.14 [49.5] (s, 3H, SnCH$_3$); 2.14 (m), 1.32 (m), 1.08 (m), 0.96 (m). – MS, *m/z* (%): 620 (8) [M^{+}], 470 (35), 441 (100), 400 (18), 371 (84), 321 (59), 237 (60), 135 (12), 69 (47), 57 (44), 41 (31).

(η^{2}-Alkyne)tin Compounds **3**, **4**. *General Procedure:* A solution of 10 mmol of **1** in 6 ml of CH$_2$Cl$_2$ is cooled to –78 °C and 10 mmol of **2a** or **2b** is added (see Tables 2 and 3).

3b: ^{1}H NMR (C$_7$D$_8$/–30 °C): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.22 [48.7] [s, 6H, Sn(CH$_3$)$_2$]; 0.78 (q), 1.05 (t) (10H, BEt$_2$); 2.17 (q), 1.04 (t) (5H,Et); 1.78 [88.6] (s, 3H,CH$_3$); 1.17 (s, 3H, ≡CCH$_3$).

3c: ^{1}H NMR (C$_7$D$_8$/–30 °C): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.35 [47.1] [s, 6H, Sn(CH$_3$)$_2$]; 0.48 (q), 0.84 (t) (10H, BEt$_2$); 1.98 (q), 0.9 (t) (5H,Et); 2.25 (q), 0.8 (t) [5H,(Sn)Et]; 1.76 (q), 0.72 (t) (5H, ≡CEt).

3d: The reaction solution of **1d** and **2a** is stored at –78 °C for 14 d. After removal of the solvent in vacuo at –50 °C **3d** is recrystallized from pentane to give a 71% yield. – ^{1}H NMR (C$_7$D$_8$/–30 °C): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.34 [46.1] [s, 6H, Sn(CH$_3$)$_2$]; 0.69 (q), 1.03 (t) (10H, BEt$_2$); 2.14 (q), 0.97 (t) (5H,Et); 2.30 (t), 1.13 (m), 0.86 (t) (7H,Pr); 1.60 (t), 1.07 (m), 0.67 (t) (7H, ≡CPr).

3e: The solution of **1e** and **2a** is warmed to –30 °C for 90 min. After removal of the solvent at –30 °C in vacuo and recrystallization from pentane **3e** is obtained in 83% yield. – ^{1}H NMR (CDCl$_3$/–30 °C): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.70 [42.5] [s, 6H, Sn(CH$_3$)$_2$]; 0.25 (q), 0.70 (q) (10H, BEt$_2$); 1.92 (q), 0.87 (t) (5H,Et); 3.11 (m), 0.94 (d) (7H,*i*Pr); 2.60 (m), 1.23 (d) (7H, ≡C*i*Pr).

4b: ^{1}H NMR (CDCl$_3$/–10 °C): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.45 [49.9] [s, 6H, Sn(CH$_3$)$_2$]; 0.9 (m), 0.84 (d) (7H, B*i*Pr$_2$); 2.53 (m), 1.06 (d) (7H,*i*Pr); 1.98 [90.1] (s, 3H,CH$_3$); 1.99 (s, 3H, ≡CCH$_3$).

4c: The reaction solution of **1e** and **2b** is first warmed to room temp. for 15 min and then cooled to –10 °C for 1.5 h. After removal of the solvent at –10 °C in vacuo, **4e** is recrystallized from pentane to give a 77% yield. – ^{1}H NMR (CDCl$_3$/–30 °C): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.66 [46.3] [s, 6H, Sn(CH$_3$)$_2$]; 0.71 (m), 0.80 (d) (7H, B*i*Pr$_2$); 2.51 (m), 1.09 (d) (7H,*i*Pr); 2.55 (q), 1.00 (t) (5H,Et); 2.38 (q), 1.23 (t), (5H, ≡CEt).

4e: ^{1}H NMR (CDCl$_3$/25 °C): δ [$^{n}J(^{119}$Sn,^{1}H)] = 0.71 [45.5] [s, 6H, Sn(CH$_3$)$_2$]; 0.78 (m), 0.85 (d), 0.82 (d) (14H, B*i*Pr$_2$), 2.52 (m), 1.12 (d) (7H, =C*i*Pr); 3.45 (m), 0.99 (d) [7H,(Sn)*i*Pr]; 2.64 (m), 1.27 (d) (7H, ≡C*i*Pr).

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