Synthesis of 2- and 3-Stannolenes via Addition of Trimethyltin Alkoxides to 3-Diethylboryl-4-ethyl-1,1-dimethylstannole

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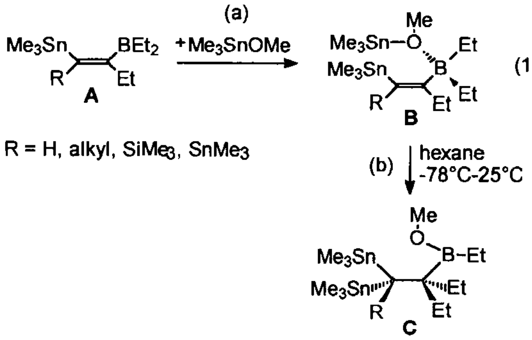
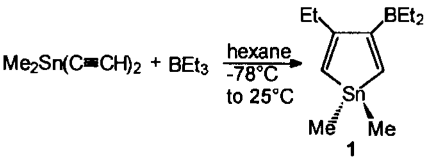
Trimethyltin alkoxides (**2**) react stereoselectively with 3-diethylboryl-4-ethyl-1,1-dimethylstannole (**1**) via addition of the Me_3Sn group to C(2) to the C(2)=C(3) bond and a 1,2 shift of an ethyl group from boron to C(3) to give the 2-stannolenes **3**. The molecular structure of **3f′** [R = (*S*)-2-Bu] was determined by single-crystal X-ray analysis, confirming the *cis* positions of the Et(RO)B and the Me_3Sn group. These 2-stannolenes **3** undergo, upon heating to ca. 80 °C, facile rearrangement by irreversible allylic migration of the Et(RO)B group to the 3-stannolenes **4** in which the *cis* positions of the boryl and the stannyl group are retained. All 2-stannolenes (in contrast to the 3-stannolenes) are readily deprotoborylated to give the 3-stannolene **5**. The structures of **3**, **4**, and **5** follow conclusively from ^{1}H-, ^{11}B-, ^{13}C-, and ^{119}Sn-NMR spectra. The negative sign of the geminal coupling constants ^2J(SnSn) was determined in the case of **3**, **4**, and **5** by 2D ^{119}Sn/^{1}H heteronuclear shift correlations.

There are only a few methods available for the synthesis of stannolenes[1,2], and in general, these routes are limited to a particular pattern of substituents. Considering the synthetic potential of cyclic organotin compounds in organic or organo-metallic synthesis[3,4], the straightforward synthesis of 2- or 3-stannolenes is an attractive object. Since we have found a convenient route to stannoles via 1,1-organoboration of diethynyltin compounds[5,6], these compounds could serve as starting materials. Recently, we have shown that the reactivity of alkenes is greatly modified if stannyl and boryl substituents are present[7–9]. The boryl group in **A** [eq. (1)] functions as an electrophilic anchor, attracting the nucleophilic site of a suitable reagent Nuc~~El such as MeO–$SnMe_3$ (**B**), and then either the =$CSnMe_3$ group or the C=C bond can be readily attacked by the electrophilic site. In this context, the reaction shown in eq. (1) is of particular interest, since in hexane addition to the C=C bond takes place exclusively to give **C**[8]. This attack at the C=C bond should place the boryl group and the entering Me_3Sn group in *cis* positions, and it should also work when the stannyl and boryl group in **A** are in *trans* positions.



(1)



(2)

$$Me_3SnNEt_2 + ROH \xrightarrow[-78°C \text{ to } -15°C]{\text{ether}} Me_3SnOR + HNEt_2 \quad (3)$$

2a - h

	a	b	c	d	e	f	f′	g	h
R=	Me	Et	nPr	iPr	nBu	(R/S)-2-Bu	(S)-2-Bu	chex	Bn

In this paper we report on the reaction of the stannole **1** with a series of trimethyltin alkoxides **2** in order to shed some light on the reaction mechanism outlined in eq. (1). The stannole **1** and the trimethyltin alkoxides **2** are readily available according to eq. (2) and (3).

Results and Discussion

The first step of the reaction between the stannole **1** and various trimethyltin alkoxides is essentially complete when the reaction mixtures, prepared at −78° in hexane, are allowed to reach ambient temperature [eq. (4a)]. The *tert*-butyl derivative **2k** does not react, even after prolonged heating at reflux. In all other cases, ^{119}Sn NMR data for the reaction solutions indicate the presence of organometallic-substituted stannolenes which were subsequently identified as the 2-stannolenes **3a–i**. Therefore, we assume that the mechanism for these reactions shown in eq. (4a) is analogous to that in eq. (1). All NMR data are consistent with a stereospecific reaction. In the case of **3f**, one of the dia-

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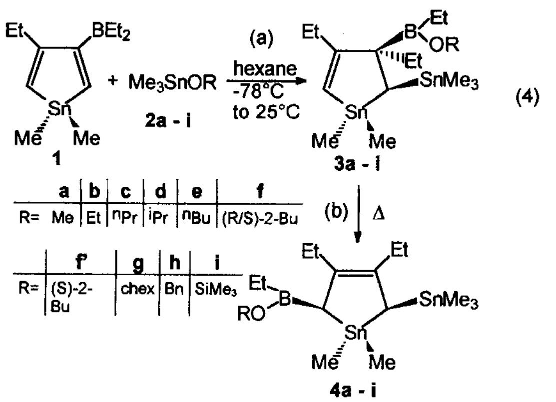
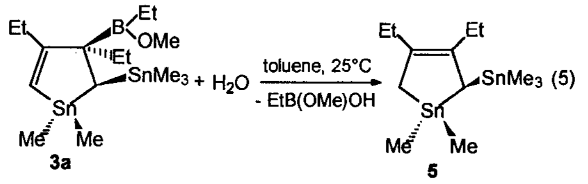
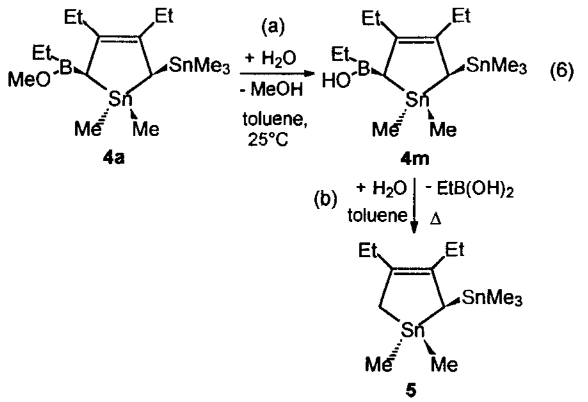
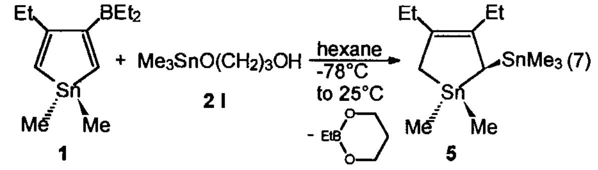


stereomers crystallizes (**3f'**), and the results of the X-ray analysis (vide infra) confirm the *cis* positions of the stannyl and the ethyl(alkoxy)boryl group. Heating of the compounds **3a–h** for a short time up to 80 °C in benzene solution induces an intramolecular rearrangement to the 3-stannolenes **4a–h** [eq. (4b)]. The trimethylsiloxy derivative (**3i**) is much more labile. The conversion of **3i** to **4i** takes place already at room temperature (90% after 12 h). The migration of the boryl group reminds of an irreversible allylic rearrangement. Only one isomer **4** is formed, with the boryl and the stannyl group in *cis* positions as shown by ^{1}H-NOE difference spectra. The proximity of the boryl- and stannyl group follows from the response of ^{1}H resonances of the boryl group when the ^{1}H(SnMe$_3$) transitions are saturated, whereas no effect is observed for the ^{1}H(5) NMR signal. The reaction between **1** and trimethyllead methoxide [**2a**(Pb)] proceeds in the same way to give first the 2-stannolene **3a**(Pb) and, after distillation, the 3-stannolene **4a**(Pb). However, the lead derivative is much less stable than the corresponding tin compound and always contains some impurities (ca. 5–10%) of other unidentified organolead compounds.





Interestingly, the compounds **3** are readily protodeborylated [eq. (5)] by water to give the 3-stannolene **5**; there was no NMR spectroscopic evidence for an intermediate with a 2-stannolene structure. In contrast, the protodeborylation of the compounds **4** with water takes place very slowly and affords first the boronic acid via cleavage of the BO bond [eq. (6)]. Compound **5** is also obtained when **1** reacts with the tin alkoxide **2l**. Then **3l** is only formed as an intermediate which readily rearranges to **5** accompanied by elimination of 2-ethyl-1,3,2-dioxaboracyclohexane [eq. (7)].



NMR Spectroscopic Results

^{13}C- and ^{119}Sn-NMR data of the trimethyltin alkoxides **2a–l** are given in Table 1. Tables 2, 3, and 4 list ^{11}B-, ^{13}C-, and ^{119}Sn-NMR data of the 2-stannolenes (**3**), 3-stannolenes **4**, and **5**, respectively. The consistent NMR data sets support the proposed structures of the compounds **3**, **4**, and **5**. The assignment of the ^{13}C resonances is straightforward, based on 2D ^{13}C/^{1}H heteronuclear shift correlations and also on the detection of $^{117/119}$Sn satellites owing to $^{n}J(^{117/119}\text{Sn},^{13}\text{C})$ (n = 1,2,3,4) and typical broad signals for boron-bonded ^{13}C nuclei[10,11b,11c] (see Figure 1).

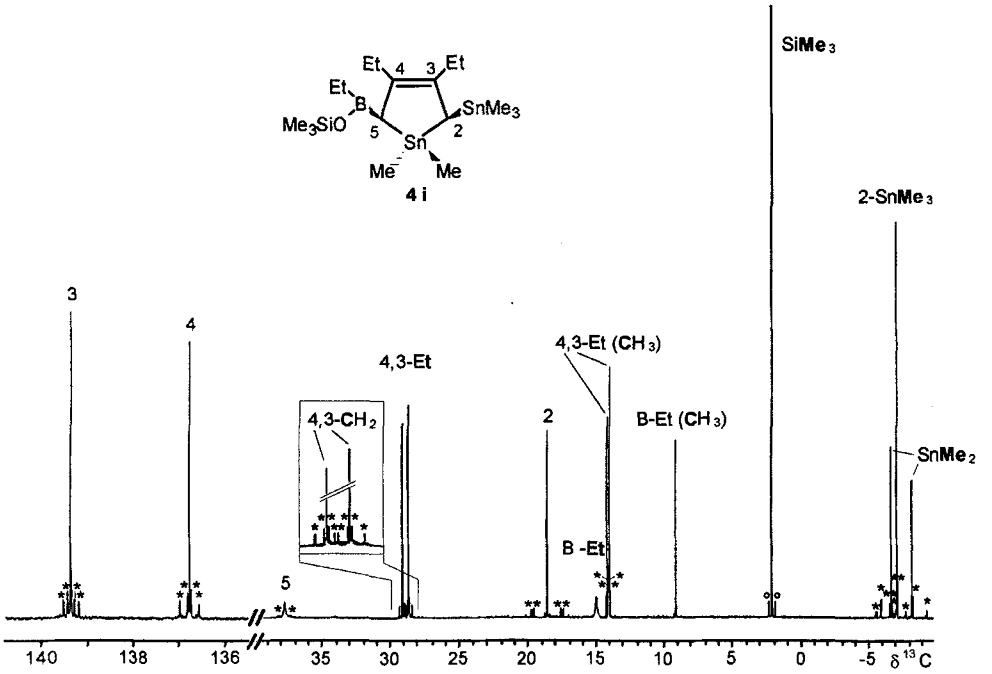
The ^{11}B nuclear shielding is almost identical for **3** and **4**, and the influence of different RO groups is small, as expected[11]. Similarly, δ^{13}C values except those of the EtB moiety of **3** and **4** are hardly affected by the groups R in the RO group. The same is true for the ^{119}Sn-^{13}C coupling constants. The most sensitive parameter appears to be the geminal coupling constant $^{2}J(^{119}\text{Sn}^{119}\text{Sn})$ in both **3** and **4**. There is a systematic relationship between the magnitude of $|^{2}J(^{119}\text{Sn},^{119}\text{Sn})|$ and the steric requirement of R. In the 2-stannolenes **3**, primary groups R (Me, Et *n*Pr, *n*Bu, Bz) cause $|^{2}J(^{119}\text{Sn},^{119}\text{Sn})|$ values between 33.2 to 25.8 Hz, whereas secondary groups R (*i*Pr, *s*Bu, *c*hex) cause $|^{2}J(^{119}\text{Sn}^{119}\text{Sn})|$ values between 12.2 and 14.0 Hz. For the 3-stannolenes, smaller $|^{2}J(^{119}\text{Sn},^{119}\text{Sn})|$ values (31.5 to 47.2 Hz) are observed for the primary alkyl groups R and larger values $|^{2}J(^{119}\text{Sn},^{119}\text{Sn})|$ (58.9 to 70.5 Hz) for secondary alkyl groups R. If R = SiMe$_3$, the $|^{2}J(^{119}\text{Sn},^{119}\text{Sn})|$ value for **3i** (22.4 Hz) comes close to the range for secondary groups R in the other compounds **3**, and for **4i** (72.7 Hz) it exceeds this range. The δ^{119}Sn values for compounds **3** show little variation with the different groups R. In the case of the compounds **4**, δ^{119}Sn(SnMe$_2$) data cover a range of 8.6 ppm and there is a linear correlation between δ^{119}Sn(SnMe$_2$) and the coupling constants $|^{2}J(^{119}\text{Sn},^{119}\text{Sn})|$ [$\delta^{119}\text{Sn}(1) = -0.2 \cdot |^{2}J(^{119}\text{Sn},^{119}\text{Sn})| + 87.6$; r = 0.976(9)]. All δ^{119}Sn(SnMe$_3$) values for **3**, **4**, and **5** are found in the typical range of alkyltrimethyltin compounds[12]. In the case of the δ^{119}Sn(SnMe$_2$) values, the usual deshielding effect, typical

Table 1. ^{13}C- and ^{119}Sn-NMR data[a] of trimethyltin alkoxides (**2**)

Com-pound	R	δ ^{13}C		δ ^{119}Sn
		Me$_3$Sn	**R**	**Me$_3$Sn**
2a	Me	-5.8 [398.0]	52.8	129.0
2b	Et	-3.1 [416.0]	58.1, 19.5	119.5
2c	^{n}Pr	-4.8 [n.m.]	66.8, 28.1,10.6	121.5
2d	^{i}Pr	-4.6 [395.1]	66.8 [25.1], 28.2 [17.4]	109.8
2e	^{n}Bu	-5.1 [395.8]	65.1, 37.4, 19.5, 14.2	122.8
2f	2-Bu	-4.6 [398.0]	72.0 [25.0], 34.5 [16.0], 25.8 [10.0], 10.7	115.3
2g	chex	-4.5 [393.2]	73.1, 38.6, 26.4, 24.8	110.3
2h	Bn	-5.0 [396.7]	68.5, 145.3, 128.4, 127.0, 126.9	130.0
2i[b]	SiMe$_3$	-2.9 [407.7]	3.6 (58.1)	121.0
2k	^{t}Bu	-2.6 [395.0]	71.2 [30.5], 34.0 [15.8]	91.0
2l[c]	(CH$_2$)$_3$OH	-4.6 [n.m.]	65.3, 35.2	143.5

[a] 50% in C_6D_6; 298 K; $^nJ(^{119}Sn, ^{13}C)$ in Hz are given in [ ]; n.m.: not measured. – [b] $^1J(^{29}Si, ^{13}C)$ in Hz are given in ( ); $\delta^{29}Si$ = 7.5. – [c] Saturated in $CDCl_3$.

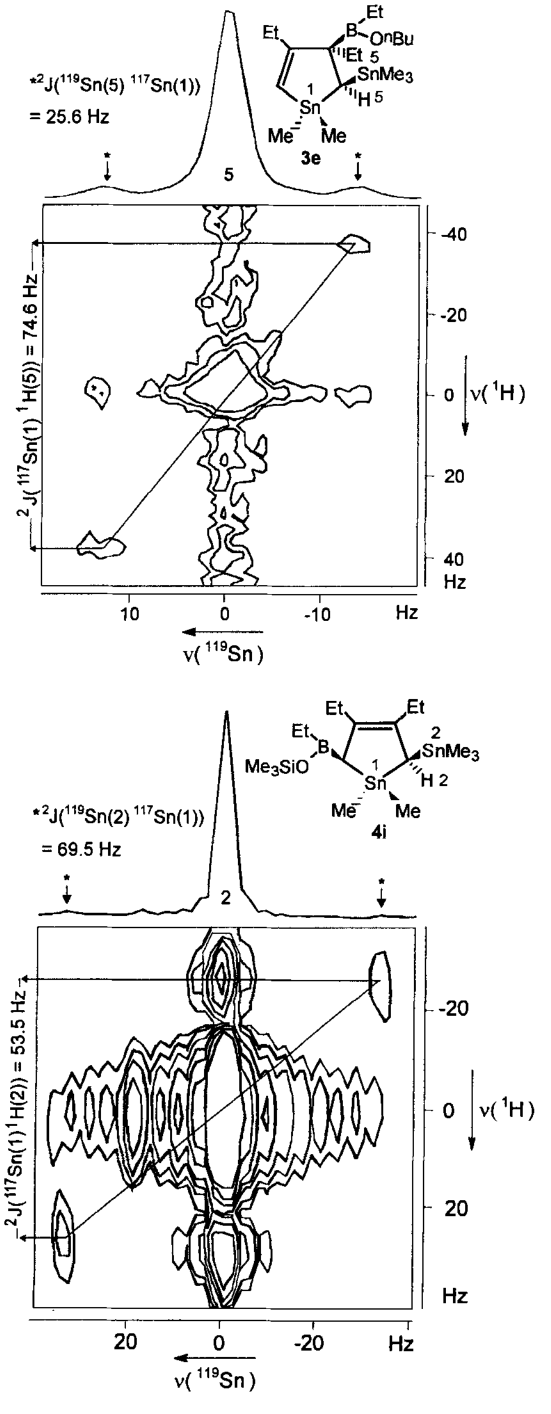
Figure 1. 75.5 MHz $^{13}C\{^1H\}$-NMR spectrum of the 3-stannolene derivative **4i** (≈ 20% in C_6D_6 at 25 ± 1 °C). The assignments are given and $^{117/119}Sn$ satellites according to $J(Sn^{13}C)$ are marked by asterisks; ^{29}Si satellites according to $^1J(^{29}Si^{13}C)$ for the Me$_3$Si group are marked by open circles. Note the typical broad ^{13}C resonances for the boron-bonded carbon atoms C(5) and BCH$_2$ of the BEt group



of the five-membered ring[12], becomes apparent. In general, the presence of a C=C bond adjacent to the tin atom leads to increased ^{119}Sn nuclear shielding by at least 40 ppm [e.g., compare $\delta^{119}Sn$ of the stannole **1** (δ = +19.5) with $\delta^{119}Sn$ of 2-stannolenes **3** (Table 2)]. This rule is not observed in the case of the compounds **3**, **4**, and **5**, since the ^{119}Sn nuclear shielding in the 2-stannolenes **3** is even slightly reduced [except for **3a**(Pb)] as compared with that in **4** or **5**. The low ^{119}Sn nuclear shielding in **3** may be an indication of a strained bonding situation which is relieved by the facile rearrangement to **4**.

It is necessary to know the absolute sign of $^2J(^{119}Sn,^{119}Sn)$ in the compounds **3**, **4**, and **5** in order to analyze the trends of the $^2J(^{119}Sn,^{119}Sn)$ values and to confirm the J/δ correlation. A negative sign of scalar ^{119}Sn-^{119}Sn coupling constants across sp^3 hybridized carbon atoms has been determined previously[13,14]. However, there are numerous examples with small $|^2J(^{119}Sn,^{119}Sn)|$ values[15] of unknown sign. From 2D $^{119}Sn/^1H$ HETCOR experiments (see Figure 2) performed for **3**, **4**, and **5**, it follows that the sign of $^2J(Sn,Sn)$ is negative in these compounds.

Figure 2. Contour plots of the 186.5 MHz two-dimensional (2D) ^{119}Sn/^{1}H heteronuclear shift correlations of the 2-stannolene derivative **3e** (Figure 2a) and the 3-stannolene **4i** (Figure 2b). The ^{117}Sn satellites in F_2 [ν(^{119}Sn)] are marked by asterisks. Their cross peaks with the corresponding ^{117}Sn satellites in F_1 [ν(^{1}H)] reveal a positive tilt[19] indicating that the signs of the reduced coupling constants $^{2}K(^{117}\mathrm{Sn}^{1}\mathrm{H}(5))$ (**3e**) or $^{2}K(^{117}\mathrm{Sn}^{1}\mathrm{H}(2))$ (**4i**) and $^{2}K(^{119}\mathrm{Sn}^{117}\mathrm{Sn})$ are alike. Since $^{2}K(\mathrm{Sn}^{1}\mathrm{H})$ is known to be negative[20], it follows that $^{2}K(^{119}\mathrm{Sn}^{117}\mathrm{Sn}) < 0$ and also $^{2}J(^{119}\mathrm{Sn}^{117}\mathrm{Sn}) < 0$

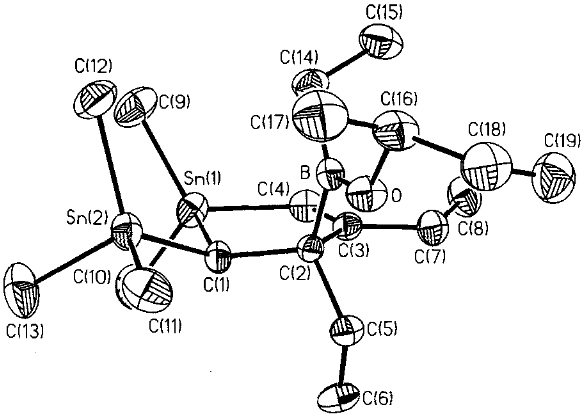


X-Ray Analysis of 3f′

Table 5 contains experimental data[16], and the molecular structure of **3f′** is depicted in Figure 3, with selected bond lengths and angles in the legend.

The best plane of the heterocycle is formed by the atoms Sn(1), C(2), C(3) and C(4). Atom C(1) is shifted by 11.3° out of this plane. The environment of the Sn(1) atom corresponds to a strongly distorted tetrahedron with a small endocyclic bond angle C(1)−Sn−C(4) = 85.2(1)°. The exocyclic bond angle C(9)−Sn−C(10) = 108.5(2)° should be related to the magnitude of $|^{1}J(^{119}\mathrm{Sn}^{13}\mathrm{C}_{\mathrm{Me}})|$[17]. However, the proposed correlation between $|^{1}J(^{119}\mathrm{Sn}^{13}\mathrm{C}_{\mathrm{Me}})|$ and the bond angle $\mathrm{C_{Me}{-}Sn{-}C_{Me}}$[17] is not well fulfilled as has been found for other examples[9a,9d,18]. The environment of the boron atom is exactly trigonal planar. All bond distances are in the expected order of magnitude. The position of the boryl group with respect to the C=C bond does not give an indication of the facile thermally induced rearrangement of **3** to **4**.

Figure 3. Molecular structure of the 2-stannolene derivative **3f′**. Selected bond lengths [pm] and angles [°]: Sn(1)−C(1) 215.6(3), Sn(1)−C(4) 210.7(4), Sn(1)−C(9) 214.7(6), Sn(1)−C(10) 214.9(5), Sn(2)−C(1) 216.2(4), Sn(2)−C(11) 213.5(5), Sn(2)−C(12) 215.3(5), Sn(2)−C(13) 214.1(6), O−B 136.0(4), B−C(2) 159.9(5), C(1)−C(2) 156.9(5), C(2)−C(3) 154.2(5), C(3)−C(4) 133.6(5), C(1)−Sn(1)−C(4) 85.2(1), C(1)−Sn(1)−C(9) 118.7(2), C(4)−Sn(1)−C(9) 115.3(2), C(1)−Sn(1)−C(10) 111.4(2), C(4)−Sn(1)−C(10) 116.4(2), C(9)−Sn(1)−C(10) 108.5(2), O−B−C(2) 115.4(3), Sn(1)−C(1)−Sn(2) 114.7(2), Sn(1)−C(1)−C(2) 106.9(2), Sn(2)−C(1)−C(2) 123.9(2), B−C(2)−C(1) 107.8(3), B−C(2)−C(3) 106.3(3), C(1)−C(2)−C(3) 112.6(3), C(2)−C(3)−C(4) 122.3(3), Sn(1)−C(4)−C(3) 111.7(3)



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Experimental

All compounds were handled under Ar by using carefully dried glassware and solvents. − The trimethyltin(IV) alkoxides **2a−h**, **k**[21a], hexamethylsilastannoxane **2i**[21b] and trimethyllead(IV) methoxide **2a**(Pb)[21c] were prepared by literature methods. − Deuterated solvents were stored over molecular sieves and saturated with Ar. − ^{1}H/^{13}C-NMR: Jeol JNM-EX270E, Bruker AC 300, Bruker AM 500 (270.67 MHz/67.94 MHz, 300.13 MHz/75.5 MHz, and 500.13 MHz/125.8 MHz, respectively); ^{11}B-NMR: Jeol FX90Q (28.7 MHz), $\mathrm{Et_2O \cdot BF_3}$ as external standard; ^{119}Sn-NMR: Bruker AC 300 (111.9 MHz), $\mathrm{SnMe_4}$ as external standard; ^{207}Pb-NMR: Jeol FX90Q (18.7 MHz), $\mathrm{PbMe_4}$ as external standard. − MS: EI-MS (70 eV) VARIAN MAT CH 7. − Elemental analyses

Table 2. ^{13}C- and ^{119}Sn-NMR data[a] of 2-stannolenes (**3a**–**3i**)

Compound	**3a**	**3b**	**3c**	**3d**[b]	**3e**	**3f**[c]	**3g**	**3h**	**3i**	**3a**(Pb)
R	**Me**	**Et**	**^{n}Pr**	**^{i}Pr**	**^{n}Bu**	**(S)-2-Bu**	**chex**	**Bn**	**SiMe$_3$**	**Me**
C(5)	14.1 [350.4][d] [256.6][e]	13.3 [344.4] [251.8]	13.1 [341.1] [250.7]	13.1 [346.6] [249.6]	13.0 [340.2] [240.4]	13.2 [340.8] [248.0]	13.2 [343.3] [248.4]	13.1 [336.5] [250.4]	13.0 [n.o.] [n.o.]	23.0 [279.6] {244.1}
C(4)	55.4 (br)	55.3 (br)	55.4 (br)	55.4[f] (br)	55.3[g] (br)	55.8 (br)	55.8 (br)	55.3 (br)	55.7 (br)	56.6 (br)
C(3)	170.6 [79.7][d] [62.7][e]	171.0 [82.8] [62.1]	171.0 [82.8] [61.0]	170.7 [79.6] [62.7]	171.0 [82.2] [60.6]	171.0 [82.2] [64.6]	171.2 [86.1] [64.6]	170.8 [82.2] [60.6]	171.3 [86.1] [58.7]	171.1 [80.9] {103.5}
C(2)	123.4 [445.3] [20.3]	122.7 [450.1] [19.6]	122.4 [452.3] [19.6]	122.6 [448.5] [19.6]	122.3 [452.9] [18.6]	122.7 [446.3] [20.3]	122.8 [448.0] [19.6]	122.8 [450.0] [19.6]	122.5 [452.9] [16.6]	123.8 [445.8] {33.2}
Me^1	-6.8[h] [330.0]	-6.7 [327.0]	-6.8 [325.9]	-6.7 [323.7]	-6.8 [324.8]	-6.7 [321.7]	-6.6 [322.8]	-6.9 [n.o.]	-6.8 [n.o.]	-6.6[i] [336.8]
Me^1	-6.3 [302.8] [6.8]	-6.1 [304.1] [7.6]	-6.1 [304.6] [7.1]	-6.3 [305.2] [n.o.]	-6.1 [303.2] [7.8]	-6.0 [306.4] [7.6]	-6.0 [307.1] [n.o.]	-6.0 [305.2] [9.8]	-6.0 [n.o.] [n.o.]	-6.3 [303.0] {17.4}
Me$_3$Sn	-7.0 [311.4] [9.6]	-6.9 [311.7] [9.8]	-7.0 [311.2] [9.3]	-7.0 [310.6] [9.8]	-6.9 [309.1] [9.8]	-6.8 [310.3] [9.6]	-6.8 [309.1] [9.8]	-7.0 [306.0] [9.8]	-6.9 [313.0] [9.8]	-1.0[k] {167.8} [8.7]
Et^4	28.5[l] [49.8][d] 13.2	28.4 [49.0] 13.1	28.4 [46.9] 13.0	28.4 [48.0] 12.7	28.4 [46.9] 13.0	28.4 [49.6] 12.8	28.5 [47.1] 12.9	28.5 [47.0] 12.9	29.0 [n.o.] 12.3	28.4[m] [46.0] 13.1[n]
Et^3	28.8 [80.2][d] 8.1	28.9 [81.7] 8.0	29.0 [80.7] 7.9	28.4 [80.1] 7.8	29.0 [82.2] 7.9	28.6 [81.4] 7.9	28.7 [84.1] 8.0	29.1 [82.2] 7.9	29.0 [80.2] 7.8	29.0 [79.9] 8.2
B-Et	8.3 (br) 8.0	8.7 (br) 8.7	8.8 (br) 8.6	8.8 (br) 9.7	8.8 (br) 8.6	9.2 (br) 10.0	9.2 (br) 10.1	8.9 (br) 8.3	14.9 (br) 9.4	8.4 (br) 8.2
B-OR[o]	53.4	61.4	67.4	67.6	65.6	72.8	73.2	67.7	2.0	53.4
δ^{119}Sn [p]	83.9 16.4 [33.2]	86.1 15.4 [27.1]	87.1 15.8 [25.8]	87.4 15.4 [14.0]	87.1 15.6 [26.8]	89.7 16.2 [12.9]	87.5 15.3 [13.9]	87.1 15.8 [29.2]	92.8 18.1 [22.4]	84.5[q] {< 10}

[a] 50% in C_6D_6; 298 K; $^nJ(^{119}Sn, ^{13}C)$ in Hz are given in [ ]; $^nJ(^{207}Pb, ^{13}C)$ in Hz are given in { }; (br) denotes broad ^{13}C resonances of boron-bonded carbon atoms; n.o.: not observed. – [b] 30% in [D$_8$]toluene. – [c] The NMR data correspond to the (4*S*)(5*S*)(*S*)-diastereomer. The δ^{13}C values of the (4*R*)(5*R*)(*S*)-diastereomer are slightly different; $\delta^{119}Sn_{(Sn-1)} = 86.7$; $\delta^{119}Sn_{(SnMe_3)} = 16.1$; $^2J(^{119}Sn, ^{119}Sn) = 12.2$ Hz. – [d] $^nJ(^{119}Sn\text{-}1, ^{13}C)$. – [e] $^nJ(^{119}Sn_{(SnMe_3)}, ^{13}C)$. – [f] $^2J(^{119}Sn, ^{13}C) = 8.0$ Hz, 243 K. – [g] $^2J(^{119}Sn, ^{13}C) = 18.2$ Hz, 248 K. – [h] $^3J(^{119}Sn, ^{13}C) = 13.0$ Hz. – [i] $^3J(^{207}Pb, ^{13}C) = 2.7$ Hz. – [k] *Me*$_3$Pb-group. – [l] $^3J(^{119}Sn_{(SnMe_3)}, ^{13}C) = 24.8$ Hz. – [m] $^3J(^{207}Pb, ^{13}C) = 11.0$ Hz. – [n] $^4J(^{207}Pb, ^{13}C) = 8.5$ Hz. – [o] Other δ^{13}C (**R**) = 17.4 (**3b**), 25.2, 10.7 (**3c**), 25.1, 24.6 (**3d**), 34.1, 19.5, 14.1 (**3e**), 31.4, 22.1, 10.1 (**3f**), 31.8, 22.4, 10.1 (**3f'**), 35.3, 34.9, 25.9, 23.8 (**3g**), 139.8, 128.5, 126.4 (**3h**); $\delta^{29}Si = 9.0$, $^1J(^{29}Si, ^{13}C) = 60.3$ Hz (**3i**). – [p] First row: $\delta^{119}Sn_{(Sn-1)}$; second row: $\delta^{119}Sn_{(SnMe_3)}$; $^2J(^{119}Sn, ^{119}Sn)$ in Hz are given in [ ]. – [q] $^2J(^{207}Pb, ^{119}Sn)$ in Hz are given in { }; $\delta^{207}Pb = 78.4$.

were carried out by Dornis & Kolbe, Mülheim, and Pascher, Remagen.

3-Trimethylstannoxypropan-1-ol (**2l**). 1,3-Propandiole (0.104 g, 1.37 mmol) was added to a solution of 0.550 g (1.37 mmol) of 1,3-bis(trimethylstannoxy)propane in 20 ml of diethyl ether at ambient temp. After stirring overnight 0.46 g (70%) of the white, solid product **2l** was isolated by decanting, washing with 5 ml of diethyl ether and drying in vacuo (see Table 1 for ^{119}Sn- and ^{13}C-NMR data). – ^{1}H-NMR ($CDCl_3$): $\delta[^nJ(^{119}Sn, ^1H)] = 0.47$ [57.1] (s, 9H, Me$_3$Sn); 1.80 (m, 2H, CH$_2$); 3.92 (t, 4H, OCH$_2$).

3,4-Diethyl-4-(ethylorganoxyboryl)-1,1-dimethyl-5-trimethylstannyl-2-stannolene (**3a–i**), *3,4-Diethyl-5-(ethylorganoxyboryl)-1,1-dimethyl-1-trimethylstannyl-3-stannolene* (**4a–i**). – *General Procedure:* A solution of 4.0 mmol of the trimethyltin(IV) alkoxide (**2a–i**) in 10 ml of hexane was cooled to −78 °C, and a freshly prepared solution of 4.0 mmol of 3-diethylboryl-1,1-dimethyl-4-

Table 3. ^{13}C- and ^{119}Sn-NMR data[a] of 3-stannolenes (**4a**–**4i**)

Compound	**4a**	**4b**	**4c**	**4d**[b]	**4e**	**4f**[c]	**4g**	**4h**[b]	**4i**	**4a**(Pb)
R	**Me**	**Et**	**^{n}Pr**	**^{i}Pr**	**^{n}Bu**	**(S)-2-Bu**	**chex**	**Bn**	**SiMe$_3$**	**Me**
C(2)	18.5 [307.4][d] [264.5][e]	18.5 [306.3] [261.6]	18.5 [306.3] [260.5]	18.5 [306.3] [261.6]	18.5 [306.3] [260.5]	18.6 [306.3] [259.4]	18.4 [305.7] [259.9]	18.5 [304.1] [260.5]	18.5 [305.7] [257.8]	27.1 [293.2] {204.0}
C(3)	139.1 [45.2][e] [17.0][d]	139.1 [43.6] [17.4]	139.2 [49.0] [17.4]	138.9 [43.6] [18.5]	139.2 [43.6] [18.0]	139.5 [41.4] [19.1]	139.3 [42.0] [19.6]	139.4 [43.6] [17.4]	139.4 [41.4] [18.5]	140.6 {88.8} [22.3]
C(4)	136.1 [53.2][e] [11.3][d]	136.4 [53.4] [10.9]	136.6 [54.0] [n.o.]	136.5 [53.4] [10.9]	136.6 [53.4] [11.4]	136.9 [53.4] [11.8]	136.9 [53.4] [12.0]	136.1 [53.4] [10.9]	136.8 [53.4] [10.9]	136.8 {107.4} [9.8]
C(5)	34.6 (br)	34.4 (br)	34.2 (br)	33.7 (br)	34.1 (br)	33.6 (br)	33.8 (br)	34.4 (br)	37.8[f] (br)	34.8 (br)
Me^1	-8.3 [297.3]	-8.2 [300.8]	-8.2 [300.8]	-8.4 [302.5]	-8.3 [301.9]	-8.0 [303.0]	-8.1 [303.5]	-8.4 [303.0]	-8.2 [303.0]	-6.8[g] [306.3]
Me^1	-6.8 [247.7] [24.9]	-6.8 [275.7] [22.9]	-6.8 [276.8] [22.9]	-7.0 [275.7] [22.9]	-6.8 [276.8] [22.9]	-6.8 [267.0] [n.o.]	-6.9 [277.9] [20.7]	-6.9 [279.0] [22.9]	-6.7 [282.3] [20.7]	-6.5 [270.3] {51.2}
Me$_3$Sn	-7.1 [308.5] [9.5]	-7.1 [308.4] [9.8]	-7.1 [308.0] [9.8]	-7.2 [308.4] [9.8]	-7.1 [308.4] [9.8]	-7.1 [308.4] [9.8]	-7.1 [308.4] [9.3]	-7.3 [308.4] [9.4]	-7.1 [309.0] [9.7]	0.2[h] {137.3} [8.8]
Et^3	28.5 [n.o.][d] [14.7][e] 13.9 [9.5][e]	28.6 [73.0] [15.4] 13.9 [8.7]	28.6 [71.9] [14.2] 14.0 [8.7]	28.4 [73.0] [15.8] 13.7 [8.7]	28.6 [73.0] [15.3] 13.9 [9.8]	28.6 [n.o.] [16.3] 14.0 [n.o.]	28.7 [73.0] [16.3] 13.9 [8.7]	28.5 [73.0] [15.3] 13.8 [8.7]	28.7 [73.0] [16.3] 13.9 [8.7]	28.1 [n.o.] {27.2} 13.9 {20.7}
Et^4	29.0 [n.o.][d] [11.3][e] 14.1 [9.5][e]	29.1 [56.6] [10.9] 14.1 [18.1]	29.0 [56.7] [10.9] 14.1 [n.o.]	28.8 [57.9] [10.9] 13.9 [17.4]	29.0 [56.7] [10.9] 14.1 [13.1]	29.1 [n.o.] [10.9] 14.1 [n.o.]	29.0 [57.8] [10.9] 14.1 [17.4]	28.9 [56.8] [10.9] 13.9 [16.3]	29.1 [57.8] [10.9] 14.0 [16.3]	28.9 [53.4] {26.2} 14.3 {43.6}
B-**Et**	11.4 (br) 9.0	11.6 (br) 9.1	11.8 (br) 9.0	11.4 (br) 8.9	11.9 (br) 9.0	11.9 (br) 8.9	11.9 (br) 9.1	12.1 (br) 8.7	14.9 (br) 9.1	11.4 (br) 8.9
B-O**R**[i]	52.2	60.3	66.5	66.3	64.6	71.7	72.5	66.7	2.0	52.2
δ^{119}Sn [k]	82.4 12.6 [31.5]	79.1 13.1 [38.6]	78.0 13.0 [46.5]	75.4 13.2 [58.9]	78.0 13.0 [47.2]	73.9 12.7 [66.8]	74.2 12.4 [70.5]	79.3 13.4 [44.3]	73.8 11.7 [72.7]	85.7[l] {95.4}

[a] 50% in C_6D_6; 298 K; $^nJ(^{119}Sn, ^{13}C)$ in Hz are given in [ ]; $^nJ(^{207}Pb, ^{13}C)$ in Hz are given in { }; (br) denotes broad ^{13}C resonances of boron-bonded carbon atoms; n.o.: not observed. – [b] 30% in [D$_8$]toluene. – [c] The NMR data correspond to the (2*S*)(5*S*)(*S*)-diastereomer. The δ^{13}C values of the (2*R*)(5*R*)(*S*)-diastereomer are slightly different; $\delta^{119}Sn_{(Sn\text{-}1)} = 74.6$; $\delta^{119}Sn_{(SnMe_3)} = 12.8$; $^2J(^{119}Sn, ^{119}Sn) = 66.8$ Hz. – [d] $^nJ(^{119}Sn\text{-}1, ^{13}C)$. – [e] $^nJ(^{119}Sn_{(SnMe_3)}, ^{13}C)$. – [f] $^1J(^{119}Sn, ^{13}C) = 117.1$ Hz. – [g] $^3J(^{207}Pb, ^{13}C) = 5.4$ Hz. – [h] *Me*$_3$Pb-group. – [i] Other δ^{13}C (**R**) = 17.8 (**4b**), 25.4, 10.8 (**4c**), 25.0, 24.9 (**4d**), 34.4, 19.6, 14.2 (**4e**), 31.9, 22.8, 10.4 (**4f**), 31.8, 23.0, 10.6 (**4f′**), 34.9, 26.1, 24.4, 24.1 (**4g**), 128.3, 127.1, 126.6 (**4h**); $\delta^{29}Si = 9.0$, $^1J(^{29}Si, ^{13}C) = 60.0$ Hz (**4i**). – [k] First row: $\delta^{119}Sn_{(Sn\text{-}1)}$; second row: $\delta^{119}Sn_{(SnMe_3)}$; $^2J(^{119}Sn, ^{119}Sn)$ in Hz are given in [ ]. – [l] $^2J(^{207}Pb, ^{119}Sn)$ in Hz are given in { }; $\delta^{207}Pb = 76.7$.

ethylstannole (**1**)[5] in 10 ml of hexane was added. The stirred mixture was warmed to ambient temp. The solvent was removed in vacuo leaving the yellowish, oily products **3a**–**i** in 89–97% yield (see Table 2 for ^{119}Sn- and ^{13}C-NMR data). The colorless, liquid products **4a**–**i** were obtained by distillation at 5 · 10^{-5} Torr or heating over 80°C for about 1 h (see Table 3 for ^{119}Sn- and ^{13}C-NMR data).

3a: Yield 1.18 g (95%). – ^{1}H-NMR (C_6D_6): δ [$^nJ(^{119}Sn, ^1H)$] = 0.07 [50.3] (s, 9H, Me_3Sn); 0.22 (s, 6H, 1-Me); 0.64 (s, 1H, 5-H); 0.77 (t, 3H, CH_3); 0.99 (q, 2H, BCH_2); 1.07 (t, 3H, CH_3); 1.50 (m,

Table 4. ^{13}C- and ^{119}Sn-NMR data[a] of 3,4-diethyl-2-trimethylstannyl-3-stannolene (**5**)

δ^{13}C									δ^{119}Sn	
C(2)	**C(3)**	**C(4)**	**C(5)**	**Me^1**	**Me^1**	**SnMe$_3$**	**Et^3**	**Et^4**	**Sn(1)**	**SnMe$_3$**
17.5 [295.4] [250.7]	140.9 [50.1] [16.3]	133.5 [54.5] [19.6]	18.7 [324.8] [10.4]	-8.6 [304.1] [< 3]	-9.3 [293.2] [24.0]	-7.8 [305.2] [8.7]	27.9 [59.4] [13.6] 13.9[b]	28.6 [57.7] [13.1] 13.9[b]	67.2 [29.3]	14.4 [29.3]

[a] 50% in C_6D_6; 298 K; ^nJ(^{119}Sn, ^{13}C) in Hz are given in [ ]; ^2J(^{119}Sn, ^{119}Sn) in Hz is given in [ ]. – [b] ^nJ(^{119}Sn, ^{13}C) = 10.9 Hz.

Table 5. Data for the X-ray analysis of compound **3f′**

Formula: $C_{19}H_{41}BOSn_2$. – Molecular mass: 533.7. – Crystal size: 0.22 × 0.22 × 0.30 mm^3. – Crystal colour: colourless. – Crystal system: Monoclinic. – Space group: $P2_1$. – Lattice parameters: a = 946.4(2) pm, b = 1304.8(3) pm, c = 1010.6(2) pm, β = 103.47(3)°. – Volume [pm^3 · 10^6]: 1213.7(4). – Z: 2. – Absorption coefficient [mm^{-1}]: 2.06. – Diffractometer: Siemens P4. – Radiation: Mo-K_α, λ = 71.073 pm, graphite-monochromated. – Temperature [K]: 173. – 2θ range: 2°–55°. – Reflections collected: 3710. – Independent and observed reflections: 3284 (R_{int} = 1.14%; $F > 0.0 \cdot \sigma(F)$). – Structure solution: SHELXTL-PLUS Direct Methodes. – Number of parameters refined: 209. – Absorption correction: Semi-empirical (Ψ-scans). – Min./max. transmission factor: 0.2403/0.3284. – R/wR-Value: 0.0207/0.0190 [$w^{-1} = \sigma^2(F)$]. – Max./min residual electron density [e · pm^{-3}] · 10^{-6}: 0.33/–0.19.

1 H, 4-CH$_2$); 1.82 (m, 1 H, 3-CH$_2$); 2.07 (m, 1 H, 3-CH$_2$); 2.07 (m, 1 H, 4-CH$_2$); 3.38 (s, 3 H, OCH$_3$); 6.36 [130.6] (s, 1 H, 2-H).

3b: Yield 1.58 g (92%). – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] 0.08 [50.8] (s, 9 H, Me$_3$Sn); 0.25 [52.9] (s, 3 H, 1-Me); 0.28 [55.1] (s, 3 H, 1-Me); 0.65 [78.7] (s, 1 H, 5-H); 0.74 (t, 3 H, CH$_3$); 0.77 (t, 3 H, CH$_3$); 0.99 (q, 2 H, BCH$_2$); 1.06 (t, 3 H, CH$_3$); 1.08 (t, 3 H, CH$_3$); 1.51 (m, 1 H, 4-CH$_2$); 1.78 (m, 1 H, 3-CH$_2$); 2.08 (m, 1 H, 3-CH$_2$); 2.08 (m, 1 H, 4-CH$_2$); 3.72 (q, 2 H, OCH$_2$); 6.36 [133.8] (s, 1 H, 2-H).

3c: Yield 1.86 g (89%). – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] = 0.10 [49.9] (s, 9 H, Me$_3$Sn); 0.25 [50.6] (s, 3 H, 1-Me); 0.29 [55.0] (s, 3 H, 1-Me); 0.67 [78.4] (s, 1 H, 5-H); 0.77 (t, 3 H, CH$_3$); 0.79 (t, 3 H, CH$_3$); 0.82 (t, 3 H, CH$_3$); 1.03 (q, 2 H, BCH$_2$); 1.09 (t, 3 H, CH$_3$); 1.42 (m, 2 H, CH$_2$); 1.55 (m, 1 H, 4-CH$_2$); 1.81 (m, 1 H, 3-CH$_2$); 2.07 (m, 1 H, 3-CH$_2$); 2.10 (m, 1 H, 4-CH$_2$); 3.65 (t, 2 H, OCH$_2$); 6.36 [133.6] (s, 1 H, 2-H).

3d: Yield 1.87 g (90%). – ^{1}H-NMR ([D$_8$]toluene): δ [^nJ(^{119}Sn, ^{1}H)] = 0.01 [50.5] (s, 9 H, Me$_3$Sn); 0.15 (s, 3 H, 1-Me); 0.23 (s, 3 H, 1-Me); 0.57 (s, 1 H, 5-H); 0.63 (t, 3 H, CH$_3$); 0.70 (t, 3 H, CH$_3$); 0.87 (q, 2 H, BCH$_2$); 1.00 (t, 3 H, CH$_3$); 1.03 (d, 3 H, CH$_3$); 1.04 (d, 3 H, CH$_3$); 1.38 (m, 1 H, 4-CH$_2$); 1.70 (m, 1 H, 3-^{3}CH$_2$); 1.95 (m, 1 H, 3-CH$_2$); 2.00 (m, 1 H, 4-CH$_2$); 4.20 (m, 1 H, OCH); 6.26 [133.7] (s, 1 H, 2-H).

3e: Yield 1.92 g (90%). – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] = 0.11 [50.4] (s, 9 H, Me$_3$Sn); 0.26 (s, 3 H, 1-Me); 0.31 (s, 3 H, 1-Me); 0.68 [78.1] (s, 1 H, 5-H); 0.75 (t, 3 H, CH$_3$); 0.80 (t, 3 H, CH$_3$); 0.85 (t, 3 H, CH$_3$); 1.00 (q, 2 H, BCH$_2$); 1.10 (t, 3 H, CH$_3$); 1.31 (m, 2 H, CH$_2$); 1.44 (m, 2 H, CH$_2$); 1.54 (m, 1 H, 4-CH$_2$); 1.80 (m, 1 H, 3-CH$_2$); 2.10 (m, 1 H, 3-CH$_2$); 2.10 (m, 1 H, 4-CH$_2$); 3.72 (t, 2 H, OCH$_2$); 6.40 [131.5] (s, 1 H, 2-H).

3f′: Yield 1.91 g (89%). – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] = 0.10 [51.4] (s, 9 H, Me$_3$Sn); 0.23 (s, 3 H, 1-Me); 0.32 (s, 3 H, 1-Me); 0.68 (s, 1 H, 5-H); 0.76 (t, 3 H, CH$_3$); 0.79 (t, 3 H, CH$_3$); 0.81 (t, 3 H, CH$_3$); 1.00 (q, 2 H, BCH$_2$); 1.07 (d, 3 H, CH$_3$); 1.08 (t, 3 H, CH$_3$); 1.43 (m, 2 H, CH$_2$); 1.47 (m, 1 H, 4-CH$_2$); 1.80 (m, 1 H, 3-CH$_2$); 2.10 (m, 1 H, 3-CH$_2$); 2.10 (m, 1 H, 4-CH$_2$); 4.04 (m, 1 H, OCH); 6.36 [130.8] (s, 1 H, 2-H).

3g: Yield 2.07 g (92%). – ^{1}H-NMR (C_6D_6): [^nJ(^{119}Sn, ^{1}H)] = 0.14 [50.8] (s, 9 H, Me$_3$Sn); 0.28 (s, 3 H, 1-Me); 0.36 [54.7] (s, 3 H, 1-Me); 0.74 (s, 1 H, 5-H); 0.79 (t, 3 H, CH$_3$); 0.80 (t, 3 H, CH$_3$); 0.99 (q, 2 H, BCH$_2$); 1.12 (t, 3 H, CH$_3$); 1.18 (m, 2 H, CH$_2$); 1.38 (m, 4 H, CH$_2$); 1.48 (m, 1 H, 4-CH$_2$); 1.65 (m, 4 H, CH$_2$); 1.82 (m, 1 H, 3-CH$_2$); 2.14 (m, 1 H, 3-CH$_2$); 2.14 (m, 1 H, 4-CH$_2$); 4.00 (m, 1 H, OCH); 6.40 [133.5] (s, 1 H, 2-H).

3h: Yield 1.93 g (85%). – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] = 0.06 [49.6] (s, 9 H, Me$_3$Sn); 0.21 (s, 3 H, 1-Me); 0.23 (s, 3 H, 1-Me); 0.66 (s, 1 H, 5-H); 0.71 (t, 3 H, CH$_3$); 0.74 (t, 3 H, CH$_3$); 0.96 (q, 2 H, BCH$_2$); 1.04 (t, 3 H, CH$_3$); 1.42 (m, 1 H, 4-CH$_2$); 1.74 (m, 1 H, 3-CH$_2$); 2.05 (m, 1 H, 3-CH$_2$); 2.12 (m, 1 H, 4-CH$_2$); 4.78 (s, 2 H, OCH$_2$); 6.38 [134.2] (s, 1 H, 2-H); 7.02–7.15 (m, 5 H, Ph).

3i: Yield 2.20 g (90%). – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] = 0.13 (s, 9 H, Me$_3$Sn); 0.18 (s, 9 H, Me$_3$Si); 0.26 (s, 3 H, 1-Me); 0.32 (s, 3 H, 1-Me); 0.64 [77.9] (s, 1 H, 5-H); 0.74 (t, 3 H, CH$_3$); 0.82 (t, 3 H, CH$_3$); 1.00 (q, 2 H, BCH$_2$); 1.08 (t, 3 H, CH$_3$); 1.32 (m, 1 H, 4-CH$_2$); 1.70 (m, 1 H, 3-CH$_2$); 2.06 (m, 1 H, 3-CH$_2$); 2.06 (m, 1 H, 4-CH$_2$); 6.35 [133.4] (s, 1 H, 2-H).

3a(Pb): Yield 2.24 g (97%). – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] {^nJ(^{207}Pb, ^{1}H)} = 0.25 [53.0] (s, 3 H, 1-Me); 0.29 [55.3] (s, 3 H, 1-Me); 0.73 {51.6} (s, 9 H, Me$_3$Pb); 0.6–0.9 (t, 3 H, CH$_3$); 0.6–0.9 (t, 3 H, CH$_3$); 0.90 (q, 2 H, BCH$_2$); 1.08 (t, 3 H, CH$_3$); 1.43 {86.3} (s, 1 H, 5-H); 1.50 (m, 1 H, 4-CH$_2$); 1.80 (m, 1 H, 3-CH$_2$); 2.05 (m, 1 H, 3-CH$_2$); 2.10 (m, 1 H, 4-CH$_2$); 3.37 (s, 3 H, OCH$_3$); 6.43 [132.0] (s, 1 H, 2-H).

4a: b.p. 110°C/10^{-3} Torr. – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] = 0.16 [50.8] (s, 9 H, Me$_3$Sn); 0.22 [56.4] (s, 3 H, 1-Me); 0.24 [52.1] (s, 3 H, 1-Me); 0.80 (m, 2 H, BCH$_2$); 0.90–1.10 (3 × t, 9 H, 3 × CH$_3$); 1.77 [78.5] [55.1] (s, 1 H, 2-H); 1.84 (m, 1 H, 3-CH$_2$); 2.08 (m, 1 H, 4-CH$_2$); 2.22 (m, 1 H, 4-CH$_2$); 2.29 [23.9] (s, 1 H, 5-H); 2.47 (m, 1 H, 3-CH$_2$); 3.35 (s, 3 H, OCH$_3$). – MS: m/z (%) = 494 (3) [M$^+$], 423 (1.5) [M$^+$ – EtBOMe], 329 (41) [M$^+$ – Me$_3$Sn], 297 (28) [M$^+$ – Me$_3$Sn – MeOH], 179 (100) [$C_{11}H_{20}BO^+$], 71 (45) [EtBOMe$^+$]. – $C_{16}H_{35}BOSn_2$ (491.6): calcd. C 39.09, H 7.18, B 2.20, Sn 48.28; found C 39.05, H 6.95, B 2.16, Sn 48.28.

4b: b.p. 99°C/5 · 10^{-5} Torr. – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] = 0.13 [50.8] (s, 9 H, Me$_3$Sn); 0.22 [55.1] (s, 3 H, 1-Me); 0.23 (s, 3 H, 1-Me); 0.77 (m, 2 H, BCH$_2$); 0.97–1.01 (3 × t, 9 H, 3 × CH$_3$); 1.09 (t, 3 H, CH$_3$); 1.78 [70.8] [55.5] (s, 1 H, 2-H); 1.83 (m, 1 H, 3-CH$_2$); 2.07 (m, 1 H, 4-CH$_2$); 2.24 (m, 1 H, 4-CH$_2$); 2.30 [23.3] (s, 1 H, 5-H); 2.46 (m, 1 H, 3-CH$_2$); 3.68 (m, 2 H, OCH$_2$). – $C_{17}H_{37}BOSn_2$ (505.7): calcd. C 40.38, H 7.38, B 2.14, Sn 46.94; found C 41.38, H 7.72, B 2.11, Sn 48.64.

4c: b.p. 105°C/5 · 10^{-5} Torr. – ^{1}H-NMR (C_6D_6): δ [^nJ(^{119}Sn, ^{1}H)] = 0.13 [50.8] (s, 9 H, Me$_3$Sn); 0.22 (s, 3 H, 1-Me); 0.23 [52.5] (s, 3 H, 1-Me); 0.80 (m, 2 H, BCH$_2$); 0.84 (t, 3 H, CH$_3$); 0.93–1.02 (3 × t, 9 H, 3 × CH$_3$); 1.48 (m, 2 H, CH$_2$); 1.77 [79.0] [54.6] (s, 1 H, 2-H); 1.81 (m, 1 H, 3-CH$_2$); 2.02 (m, 1 H, 4-CH$_2$); 2.25 (m, 1 H, 4-CH$_2$); 2.42 (m, 1 H, 3-CH$_2$); 2.31 [26.0] (s, 1 H, 5-H); 3.60 (m, 2 H, OCH$_2$). – MS: m/z (%): 522 (4) [M$^+$], 479 (5) [M$^+$ – nPr], 423

(10) [M$^+$ − nPr − EtBO], 357 (52) [M$^+$ − Me$_3$Sn], 297 (71) [M$^+$ − Me$_3$Sn − nPrOH], 207 (100) [M$^+$ − Me$_3$Sn − Me$_2$Sn], 165 (74) [M$^+$ − Me$_3$Sn − Me$_2$Sn − C$_3$H$_6$], 57 (47) [EtBOH$^+$].

4d: ^{1}H-NMR [D$_8$]toluene: δ [^nJ(^{119}Sn, ^{1}H)] = −0.03 (s, 9H, Me$_3$Sn); 0.12 (s, 3H, 1-Me); 0.13 (s, 3H, 1-Me); 0.67 (m, 2H, BCH$_2$); 0.80−0.90 (3 × t, 9H, 3 × CH$_3$); 0.98 (d, 3H, CH$_3$); 1.00 (d, 3H, CH$_3$); 1.69 [79.8] [53.5] (s, 1H, 2-H); 1.71 (m, 1H, 3-CH$_2$); 1.93 (m, 1H, 4-CH$_2$); 2.13 (m, 1H, 4-CH$_2$); 2.18 (m, 1H, 3-CH$_2$); 2.18 [26.3] (s, 1H, 5-H); 4.09 (m, 1H, OCH). − MS: m/z (%): 522 (2) [M$^+$], 357 (63) [M$^+$ − Me$_3$Sn], 297 (72) [M$^+$ − Me$_3$Sn − iPrOH], 207 (70) [M$^+$ − Me$_3$Sn − Me$_2$Sn], 165 (100) [M$^+$ − Me$_3$Sn − Me$_2$Sn − C$_3$H$_6$].

4e: b.p. 100°C/5 · 10^{-5} Torr. − ^{1}H-NMR (C$_6$D$_6$): δ [^nJ(^{119}Sn, ^{1}H)] = 0.15 [51.2] (s, 9H, Me$_3$Sn); 0.24 (s, 3H, 1-Me); 0.24 (s, 3H, 1-Me); 0.75 (m, 2H, BCH$_2$); 0.85 (t, 3H, CH$_3$); 0.98−1.01 (3 × t, 9H, 3 × CH$_3$); 1.32 (m, 2H, CH$_2$); 1.47 (m, 2H, CH$_2$); 1.79 [79.9] [55.1] (s, 1H, 2-H); 1.85 (m, 1H, 3-CH$_2$); 2.04 (m, 1H, 4-CH$_2$); 2.27 (m, 1H, 4-CH$_2$); 2.35 [24.8] (s, 1H, 5-H); 2.45 (m, 1H, 3-CH$_2$); 3.67 (m, 1H, OCH$_2$). − MS: m/z (%): 536 (2) [M$^+$], 423 (10) [M$^+$ − EtBOnBu], 371 (63) [M$^+$ − Me$_3$Sn], 297 (82) [M$^+$ − Me$_3$Sn − nBuOH], 221 (88) [M$^+$ − Me$_3$Sn − Me$_2$Sn], 165 (100) [Me$_3$Sn$^+$], 109 (45) [C$_8$H$_{13}^+$], 57 (45) [EtBOH$^+$]. − C$_{19}$H$_{41}$BOSn$_2$ (533.7): calcd. C 42.76, H 7.74; found C 40.97, H 7.52.

4f′: − ^{1}H-NMR (C$_6$D$_6$): δ [^nJ(^{119}Sn, ^{1}H)] = 0.13 (s, 9H, Me$_3$Sn); 0.23 (s, 3H, 1-Me); 0.25 (s, 3H, 1-Me); 0.80 (m, 2H, BCH$_2$); 0.83 (t, 3H, CH$_3$); 0.94−1.03 (3 × t, 9H, 3 × CH$_3$); 1.10 (d, 3H, CH$_3$); 1.41 (m, 2H, CH$_2$); 1.80 (s, 1H, 2-H); 1.83 (m, 1H, 3-CH$_2$); 1.92 (m, 1H, 4-CH$_2$); 2.30 (m, 1H, 4-CH$_2$); 2.32 (s, 1H, 5-H); 2.43 (m, 1H, 3-CH$_2$); 3.94 (m, 1H, OCH).

4g: b.p. 103°C/5 · 10^{-5} Torr. − ^{1}H-NMR (C$_6$D$_6$): δ [^nJ(^{119}Sn, ^{1}H)] = 0.20 (s, 9H, Me$_3$Sn); 0.29 (s, 6H, 1-Me); 0.79 (m, 2H, BCH$_2$); 1.00−1.11 (3 × t, 9H, 3 × CH$_3$); 1.20 (m, 2H, CH$_2$); 1.42 (m, 4H, 2 × CH$_2$); 1.71 (m, 4H, 2 × CH$_2$); 1.86 (s, 1H, 2-H); 1.90 (m, 1H, 3-CH$_2$); 2.12 (m, 1H, 4-CH$_2$); 2.32 (m, 1H, 4-CH$_2$); 2.40 (s, 1H, 5-H); 2.48 (m, 1H, 3-CH$_2$); 4.09 (m, 4H, OCH).

4h: b.p. 113°C/5 · 10^{-5} Torr. − ^{1}H-NMR ([D$_8$]toluene): δ [^nJ(^{119}Sn, ^{1}H)] = 0.03 [50.8] (s, 9H, Me$_3$Sn); 0.10 (s, 3H, 1-Me); 0.11 (s, 3H, 1-Me); 0.80 (m, 2H, BCH$_2$); 0.83−1.00 (3 × t, 9H, 3 × CH$_3$); 1.69 [79.2] [53.9] (s, 1H, 2-H); 1.77 (m, 1H, 3-CH$_2$); 1.93 (m, 1H, 4-CH$_2$); 2.22 (m, 1H, 4-CH$_2$); 2.30 [25.9] (s, 1H, 5-H); 2.36 (m, 1H, 3-CH$_2$); 4.70 (s, 2H, OCH$_2$); 6.97−7.15 (m, 5H, Ph).

4i: ^{1}H-NMR (C$_6$D$_6$): δ [^nJ(^{119}Sn, ^{1}H)] {^nJ(^{29}Si, ^{1}H)} = 0.14 [50.8] (s, 9H, Me$_3$Sn); 0.16 {6.4} (s, 9H, SiMe$_3$); 0.25 [52.5] (s, 3H, 1-Me); 0.26 [52.5] (s, 3H, 1-Me); 0.80 (m, 2H, BCH$_2$); 0.94−1.04 (3 × t, 9H, 3 × CH$_3$); 1.79 [81.0] [56.0] (s, 1H, 2-H); 1.87 (m, 1H, 3-CH$_2$); 2.04 (m, 1H, 4-CH$_2$); 2.28 (m, 1H, 4-CH$_2$); 2.42 (m, 1H, 3-CH$_2$); 2.41 [23.9] (s, 1H, 5-H). − MS: m/z (%): 552 (2) [M$^+$], 387 (57) [M$^+$ − Me$_3$Sn], 297 (66) [M$^+$ − Me$_3$Sn − Me$_3$SiOH], 237 (72) [M$^+$ − Me$_3$Sn − Me$_2$Sn], 165 (33) [Me$_3$Sn$^+$], 129 (100) [EtBOSiMe$_3^+$]. − C$_{18}$H$_{41}$BOSiSn$_2$ (549.8): calcd. C 39.32, H 7.52; found C 39.11, H 7.69.

4a(Pb): b.p. 107°C/5 · 10^{-5} Torr. − ^{1}H-NMR (C$_6$D$_6$): δ [^nJ(^{119}Sn, ^{1}H)] {^nJ(^{207}Pb, ^{1}H)} = 0.22 [52.1] (s, 6H, 1-Me); 0.80 {49.9} (s, 9H, Me$_3$Pb); 0.80 (m, 2H, BCH$_2$); 0.97−1.03 (3 × t, 9H, 3 × CH$_3$); 1.81 {20.0} (m, 1H, 3-CH$_2$); 2.14 {24.4} (m, 1H, 4-CH$_2$); 2.20 (m, 1H, 4-CH$_2$); 2.30 (s, 1H, 5-H); 2.44 {9.0} (m, 1H, 3-CH$_2$); 2.49 [37.2] {90.5} (s, 1H, 2-H); 3.34 (s, 3H, OCH$_3$).

3,4-Diethyl-1,1-dimethyl-1-trimethylstannyl-3-stannolene (**5**): A solution of 0.48 g (2.0 mmol) of **2l** in 10 ml of hexane was cooled to −78°C, and a freshly prepared solution of 0.59 g (2.0 mmol) of **1** in 20 ml of hexane was added. The stirred mixture was warmed to ambient temp. The solvent was removed in vacuo and the slightly yellow residue was purified by distillation, giving 0.8 g (95%) of **5** as a colorless liquid (53°C/5 · 10^{-5} Torr) (see Table 4 for ^{119}Sn- and ^{13}C-NMR data). − ^{1}H-NMR (C$_6$D$_6$): δ [^nJ(^{119}Sn, ^{1}H)] = 0.12 [50.8] (s, 9H, Me$_3$Sn); 0.15 [52.5] [1.5] (s, 3H, 1-Me); 0.27 [53.3] (s, 3H, 1-Me); 1.01 (t, 3H, CH$_3$); 1.04 (t, 3H, CH$_3$); 1.48 [49.2] (d, 1H, 5-H$_2$); 1.67 [72.0] [47.8] (s, 1H, 2-H); 1.77 (m, 1H, 3-CH$_2$); 1.83 [49.2] (d, 1H, 5-H$_2$); 2.09 (m, 1H, 4-CH$_2$); 2.29 (m, 1H, 4-CH$_2$); 2.47 (m, 1H, 3-CH$_2$). − MS: m/z (%): 424 (4) [M$^+$], 259 (100) [M$^+$ − Me$_3$Sn], 165 (18) [Me$_3$Sn$^+$], 135 (16) [MeSn$^+$], 109 (75) [M$^+$ − Me$_3$Sn − Me$_2$Sn]. − C$_{13}$H$_{28}$Sn$_2$ (421.7): calcd. C 37.02, H 6.69; found C 36.95, H 6.76.

*Hydrolysis of **3**:* To a solution of 1.69 g (3.44 mmol) of **3a** in 60 ml of toluene 0.062 g (3.44 mmol) of H$_2$O was added and the mixture was stirred for 1 h at ambient temp. After removal of the solvent in vacuo, the slightly yellow, oily product was purified by distillation at 5 · 10^{-5} Torr, giving 1.38 g (95%) of **5** as a colorless liquid.

*Hydrolysis of **4** at Ambient Temperature:* Water (0.018 g, 1.0 mmol) was added to a solution of 0.49 g (1.0 mmol) of **4a** in 0.4 ml of [D$_8$]toluene in a NMR tube. The progress of the hydrolysis was followed by NMR spectroscopy. After a few days at ambient temp. the products 3,4-diethyl-5-[ethyl(hydroxy)boryl]-1,1-dimethyl-1-trimethylstannyl-3-stannolene **4m** and methanol were identified. − ^{1}H-NMR ([D$_8$]toluene): δ [^nJ(^{119}Sn, ^{1}H)] = 0.10 [50.9] (s, 9H, Me$_3$Sn); 0.18 [n.o.] (s, 3H, 1-Me); 0.25 [n.o.] (s, 3H, 1-Me); 0.8 (m, 2H, BCH$_2$); 0.8−1.0 (3 × t, 9H, 3 × CH$_3$); 1.65 [n.o.] [n.o.] (s, 1H, 2-H); 1.48 (m, 1H, 3-CH$_2$); 1.77 (m, 1H, 4-CH$_2$); 2.03 (m, 1H, 4-CH$_2$); 2.23 [23.9] (s, 1H, 5-H); 2.42 (m, 1H, 3-CH$_2$). − ^{13}C-NMR: δ [^nJ(^{119}Sn, ^{13}C)] = 17.9 [295.3] [256.3] (C-2); 142.0 [45.0] [15.7] (C-3); 135.4 [50.9] [11.8] (C-4); 35.5 (br) (C-5); −8.0 [300.3] (1-Me); −6.9 [n.o.] (1-Me); −7.3 [311.0] [9.8] (Me$_3$Sn); 28.4, 13.9 (3-Et); 28.6, 14.2 (4-Et); 13.0 (br), 8.7 (B-Et). − ^{119}Sn-NMR: δ [^2J(^{119}Sn, ^{119}Sn)] = 85.6 [40.0] (SnMe$_2$); 12.4 [40.0] (SnMe$_3$). − ^{11}B-NMR: δ = 53.5.

*Hydrolysis of **4** at Higher Temperature:* A solution of 0.49 g (1.0 mmol) of **4a** in 20 ml of toluene together with 0.018 g (1.0 mmol) of H$_2$O was heated at reflux for 0.5 h. After removal of the solvent in vacuo the yellowish residue was examined by NMR spectroscopy and **4m** as well as the deborylated compound **5** were identified.

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[1] [1a] R. Marx, W. P. Neumann, K. Hilner, *Tetrahedron Lett.* **1984**, *25*, 625−628. − [1b] H. Gruetzmacher, S. Freitag, R. Herbst-Irmer, G. M. Sheldrick, *Angew. Chem.* **1992**, *104*, 459−461; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 437−438. − [1c] M. Weidenbruch, A. Schaefer, H. Kilian, S. Pohl, W. Saak, H. Marsmann, *Chem. Ber.* **1992**, *125*, 563−566.

[2] [2a] L. Kilian, B. Wrackmeyer, *J. Organomet. Chem.* **1978**, *153*, 153−164. − [2b] S. Kerschl, B. Wrackmeyer, *Z. Naturforsch., Teil B*, **1984**, *39*, 1037−1041. − [2c] B. Wrackmeyer, K. Horchler, *Z. Naturforsch., Teil B*, **1990**, *45*, 437−446. − [2d] B. Wrackmeyer, S. Kundler, R. Boese, *Chem. Ber.* **1993**, *126*, 1361−1370. − [2e] B. Wrackmeyer, S. Kundler, W. Milius, R. Boese, *Chem. Ber.* **1994**, *127*, 333−342. − [2f] B. Wrackmeyer, G. Kehr, D. Wettinger, *Inorg. Chim. Acta* **1994**, *220*, 161−173.

[3] [3a] A. J. Ashe III, P. Shu, *J. Am. Chem. Soc.* **1971**, *93*, 1804−1805. − [3b] J. J. Eisch, J. E. Galle, *J. Am. Chem. Soc.* **1975**, *97*, 4436−4437. − [3c] G. E. Herberich, B. Buller, B. Hessner, W. Oschmann, *J. Organomet. Chem.* **1980**, *195*, 253−259. − [3d] H.-O. Berger, H. Nöth, B. Wrackmeyer, *Chem. Ber.* **1979**, *112*, 2866−2883.

[4] M. Pereyre, J.-P. Quintard, A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, **1987**.

[5] L. Killian, B. Wrackmeyer, *J. Organomet. Chem.* **1977**, *132*, 213−221.

[6] B. Wrackmeyer, in *Organometallic Syntheses* (Eds.: R. B. King, J. J. Eisch), vol. 4, Elsevier, New York, **1988**, pp. 563−566.

[7] B. Wrackmeyer, K. Wagner, *Chem. Ber.* **1989**, *122*, 857−860.

[8] B. Wrackmeyer, K. Wagner, *Chem. Ber.* **1991**, *124*, 503−508.

[9] [9a] B. Wrackmeyer, S. M. Frank, M. Herberhold, A. Simon, H. Borrmann, *Chem. Ber.* **1991**, *121*, 691–697. – [9b] B. Wrackmeyer, K. Wagner, R. Boese, *Chem. Ber.* **1993**, *126*, 595–599. – [9c] B. Wrackmeyer, A. Ariza-Castolo, *Phosphorus, Sulfur, Silicon* **1994**, *90*, 121–129. – [9d] B. Wrackmeyer, S. Kerschl, H. E. Maisel, W. Milius, *J. Organomet. Chem.* **1995**, *490*, 197–202.

[10] B. Wrackmeyer, *Progr. NMR Spectrosc.* **1979**, *12*, 227–259.

[11] [11a] H. Nöth, B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds* in *NMR – Basic Principles and Progress*, vol. 14 (Eds.; P. Diehl, E. Fluck, R. Kosfeld), Springer, Berlin, **1978**. – [11b] B. Wrackmeyer, R. Köster in *Houben-Weyl, Methoden der Organischen Chemie*, vol. 13/3c (Ed.: R. Köster), Thieme, Stuttgart, **1984**, pp. 377–611. – [11c] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61–203.

[12] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73–186.

[13] [13a] W. Biffar, T. Gasparis-Ebeling, H. Nöth, W. Storch, B. Wrackmeyer, *J. Magn. Reson.* **1981**, *44*, 54–61. – [13b] B. Wrackmeyer, *J. Magn. Reson.* **1984**, *59*, 141–145.

[14] B. Wrackmeyer, H. Zhou, *Spectrochim. Acta, Part A* **1991**, *47A*, 849–856.

[15] [15a] T. N. Mitchell, A. Amamria, B. Fabisch, H. G. Kuivila, T. J. Karol, K. Swami, *J. Organomet. Chem.* **1983**, *259*, 157–164. – [15b] T. N. Mitchell, M. El-Behairy, *J. Organomet. Chem.* **1979**, *172*, 293–298.

[16] Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-401648, the names of the authors, and the journal citation.

[17] T. Lockhart, W. F. Manders, *J. Am. Chem. Soc.* **1987**, *109*, 7015–7921.

[18] [18a] B. Wrackmeyer, K. Wagner, A. Sebald, L. H. Merwin, R. Boese, *Magn. Reson. Chem.* **1991**, *29*, S3–S10. – [18b] B. Wrackmeyer, H. E. Maisel, W. Milius, *Z. Naturforsch., Teil B,* **1995**, *50*, in the press.

[19] A. Bax, R. Freeman, *J. Magn. Reson.* **1981**, *45*, 177–181.

[20] [20a] W. McFarlane, *J. Chem. Soc. (A),* **1967**, 528–530. – [20b] J. D. Kennedy, W. McFarlane, *J. Chem. Soc., Chem. Commun.* **1974**, 983–984.

[21] [21a] E. Amberger, M.-R. Kula, J. Lorberth, *Angew. Chem.* **1964**, *76*, 145–146. – [21b] H. Schmidbaur, H. Hussek, *J. Organomet. Chem.* **1964**, *1*, 244–256. – [21c] R. J. Puddephat, G. H. Thistlethwaite, *J. Chem. Soc. Dalton Trans.* **1972**, 570–572.

[95022]