ELSEVIER

Journal of Organometallic Chemistry 577 (1999) 82–92

Journal of Organometallic Chemistry

1,1-Organoboration of tetraynes—routes to new siloles, stannoles and fused heterocycles

Bernd Wrackmeyer *, Gerald Kehr, Jürgen Süß, Elias Molla [1]

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

Received 4 August 1998

Abstract

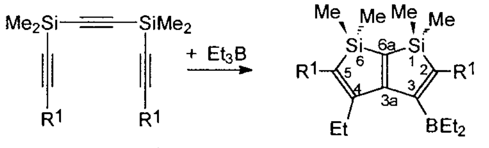
The tetraynes R^{1}C≡C–SiMe$_2$–C≡C–SiMe$_2$–C≡C···SiMe$_2$–C≡CR^2 [R^1 = R^2 = H (**1a**), SnMe$_3$ (**1b**), R^1 = SiMe$_3$, R^2 = H (**2a**), R^2 = SnMe$_3$ (**2b**)] and R^{1}C≡C–SiMe$_2$–C≡C–SnMe$_2$–C≡C–SiMe$_2$–C≡CR^1 [R^1 = H (**3a**), ^{n}Bu (**3b**), ^{t}Bu (**3c**), ^{i}Pent (**3d**), Ph (**3e**), SiMe$_3$ (**3f**)] were prepared, and their reactivity towards triethylborane Et$_3$B **4** was studied. In the cases of **1a** and **2a**, decomposition was observed whereas the reaction of the other tetraynes with Et$_3$B affords siloles, 1,6-dihydro-1,6-disilapentalenes, 1,6-dihydro-1,6-stannasilapentalenes, and tricyclic heterocycles. In several cases it proved possible to show the stepwise proceeding of the intramolecular 1,1-vinylboration, once the reaction had started with an intermolecular 1,1-ethylboration. Zwitterionic intermediates were detected in the case of the reaction of **3** with Et$_3$B. Characterisation of the products and intermediates was achieved by multinuclear NMR spectroscopy (^{1}H-, ^{13}C-, ^{11}B-, ^{13}C-, ^{29}Si-, ^{119}Sn-NMR). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Boron; Alkynes; 1,1-Organoboration; Siloles; Pentalenes; NMR

---

1. Introduction

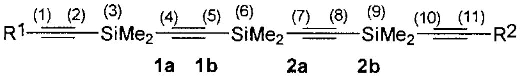
1,1-Organoboration of 1-alkynylsilanes or 1-alkynylstannanes has proved useful in the syntheses of numerous novel heterocyclic systems, not readily available by other methods [1]. Recently, we have shown that the 1,1-organoboration of certain triynes, in which the C≡C bonds are separated by Me$_2$Si moieties leads to 1,6-dihydro-1,6-disilapentalene derivatives **A** (Eq. (1)) [2]. The proposed intermediates were siloles and zwitterionic borate-like species, which however could not be detected or isolated by NMR spectroscopy.



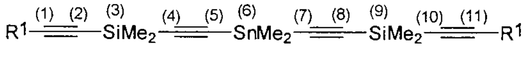
R^1 = SiMe$_3$, SnMe$_3$ **A**

(1)

Since it was known that the 1,1-organoboration of diynes of the type Me$_2$M(C≡CR^1)$_2$ can lead to metalloles [3] (M = Si [4], Ge [5], Sn [6], Pb [7]), the tetraynes of the type **1**–**3** appeared to be attractive starting materials for 1,1-organoboration reactions. Here we report on the synthesis of **1**–**3**, and on their reactivity towards triethylborane Et$_3$B **4**.



	1a	**1b**	**2a**	**2b**
R^1 =	H,	SnMe$_3$,	SiMe$_3$,	SiMe$_3$
R^2 =	H,	SnMe$_3$,	H,	SnMe$_3$



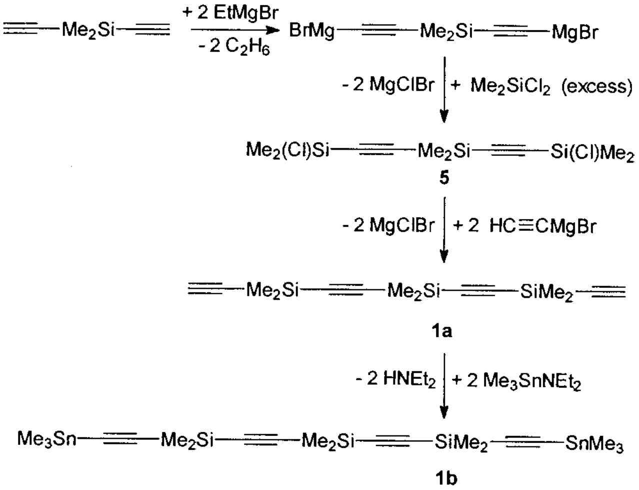
	3a	**3b**	**3c**	**3d**	**3e**	**3f**
R^1 =	H,	^{n}Bu,	^{t}Bu,	^{i}Pent,	Ph,	SiMe$_3$

---

* Corresponding author. Tel.: +49-921-552542; fax: +49-921-552157; e-mail: b.wrack@uni-bayreuth.de

[1] Alexander-von-Humboldt fellow; on leave from Jahangirnagar University, Department of Chemistry, Savar, Dhaka, Bangladesh.

PII: S0022-328X(98)01029-8

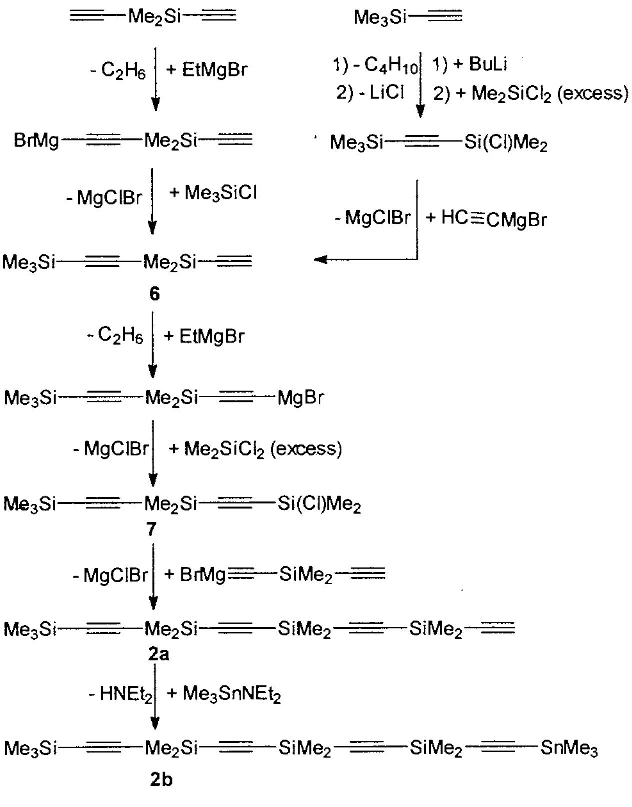


Scheme 1.

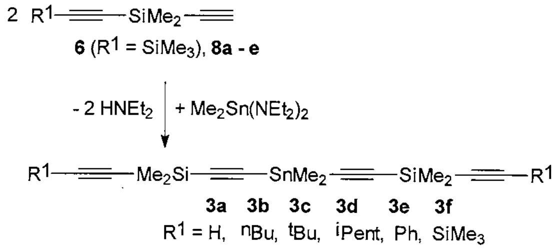
2. Results and discussion

2.1. Synthesis of the tetraynes 1–3

The most convenient route to the tetraynes **1a** and **1b** is shown in Scheme 1. The use of Grignard-derivatives is advisable [8] since we found that lithiation of the terminal alkynes was accompanied by numerous side reactions as a consequence of cleavage of Si–C≡ bonds. The step from **1a** to **1b** is a quantitative reaction, as for most terminal alkynes [9].



Scheme 2.



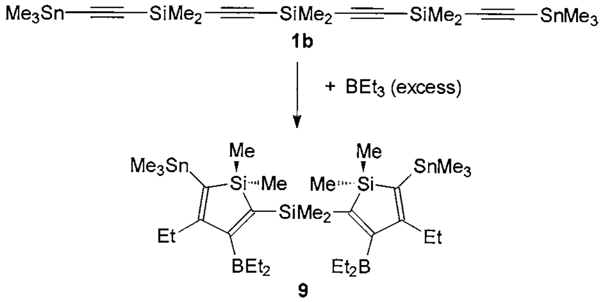
Scheme 3.

The synthesis of **2** starts with the silane **6** which can be prepared readily by two routes as shown in Scheme 2. The silane **7** is obtained from **6** via its Grignard reagent, treated with an excess of Me_2SiCl_2. The triyne **2a** can then be obtained from the reaction of **7** with the mono-Grignard reagent prepared from $Me_2Si(C{\equiv}CH)_2$. Treatment of **2a** with one equivalent of $Me_3Sn{-}NEt_2$ affords **2b** in quantitative yield.

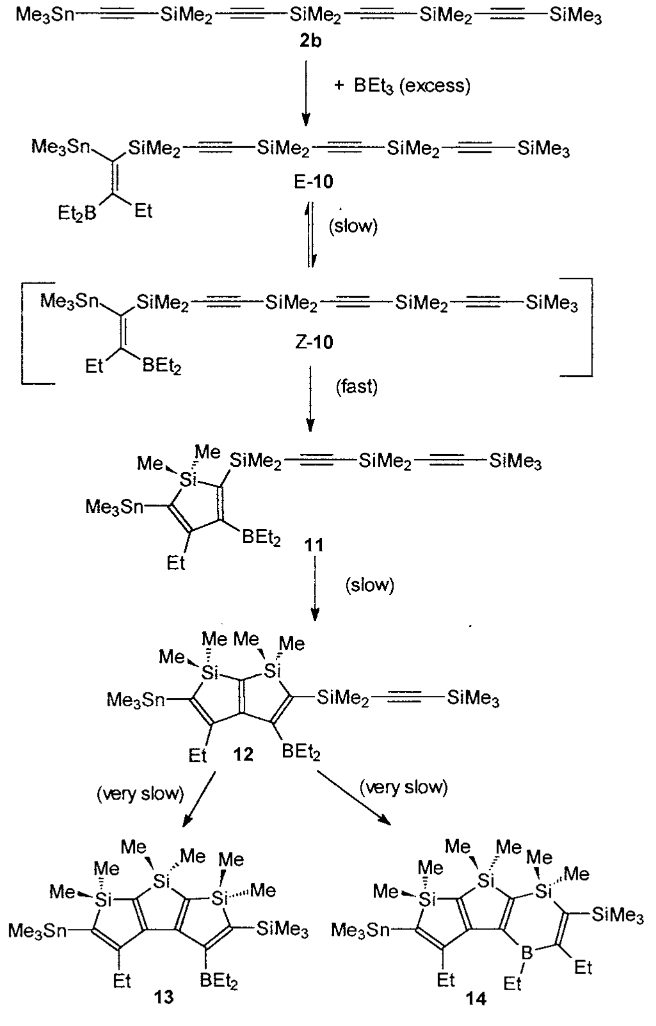
All compounds **3** are prepared, again in quantitative yield, from the reaction of two equivalents of the silanes **6** and **8** [2] with bis(diethylamino)dimethyltin (Scheme 3). The compounds **1a**, **2a**, **6** and **8** are stable towards air and water, whereas the tin compounds **1b**, **2b**, **3** and the silane **7** are sensitive to moisture.

2.2. 1,1-Organoboration of the tetraynes 1 and 2

It is well known that alkynylsilanes react with Et_3B **4** only after prolonged heating at $> 100°C$ [1,2,4]. A reaction between **1a** and **4** or **2a** and **4** started after some hours in boiling toluene, but led to a complex mixture of unidentified compounds, as had been observed previously for similar alkynes [2]. However, the Sn–C≡ bonds in **1b**, **2b** and **3** proved to be sufficiently reactive in order to start the intermolecular 1,1-ethylboration under mild reaction conditions. In the case of **1b**, the reaction with an excess of **4** was complete after warming to room temperature, and the bis(silolyl)silane **9** is formed selectively and quantitatively. The 1:1 reaction gave the same result, and the starting material **1b** was left. Therefore, Et_3B must have attacked **1b** more or less synchronously at both terminal Sn–C≡ bonds (Scheme 4).



Scheme 4.



Scheme 5.

Since the tetrayne **2b** possesses only one reactive Sn–C≡ bond, other products can be expected from its reaction with Et_3B **4**, as shown in Scheme 5. It is suggested that at first a mixture of non-cyclic products **10** is formed of which the *Z*-isomer (*Z*-**10**) cannot be detected, since it undergoes fast intramolecular 1,1-vinylboration to give the silole **11**. In contrast, the isomer *E*-**10** does not have the correct stereochemistry for intramolecular 1,1-vinylborations, and it has to rearrange by repeated steps of deorganoboration and organoboration to *Z*-**10**. The silole **11** can rearrange to the 1,6-dihydro-1,6-disilapentalene derivative **12**, as it has been reported for the 1,1-organoboration of triynes [2]. The ^{29}Si- and ^{119}Sn-NMR spectra of the reaction mixture show typical signals for the compounds *E*-**10** and **11** together with those for **12** (Fig. 1). This type of rearrangement is complete after 20 h at room temperature and pure **12** can be isolated by removing all volatile material at room temperature. The stereochemistry of **12** should be ideal for further intramolecular 1,1-organoboration reactions. However, it proved necessary to heat the sample for 72 h at 110°C in toluene in order to induce further reactions. These lead to a mixture of the new fused heterocycles **13** and **14**, in an approximately 3:2 ratio. The rather harsh reaction conditions are most likely due to steric repulsion between the ethyl and the diethylboryl group in **13**. The somewhat unexpected alternative formation of **14** (treatment of bis(1-alkynyl)silanes with Et_3B in general gives siloles [1,2,4]) can be explained in the same way, since steric repulsion is reduced for the six-membered ring which, according to its NMR data, is not planar.

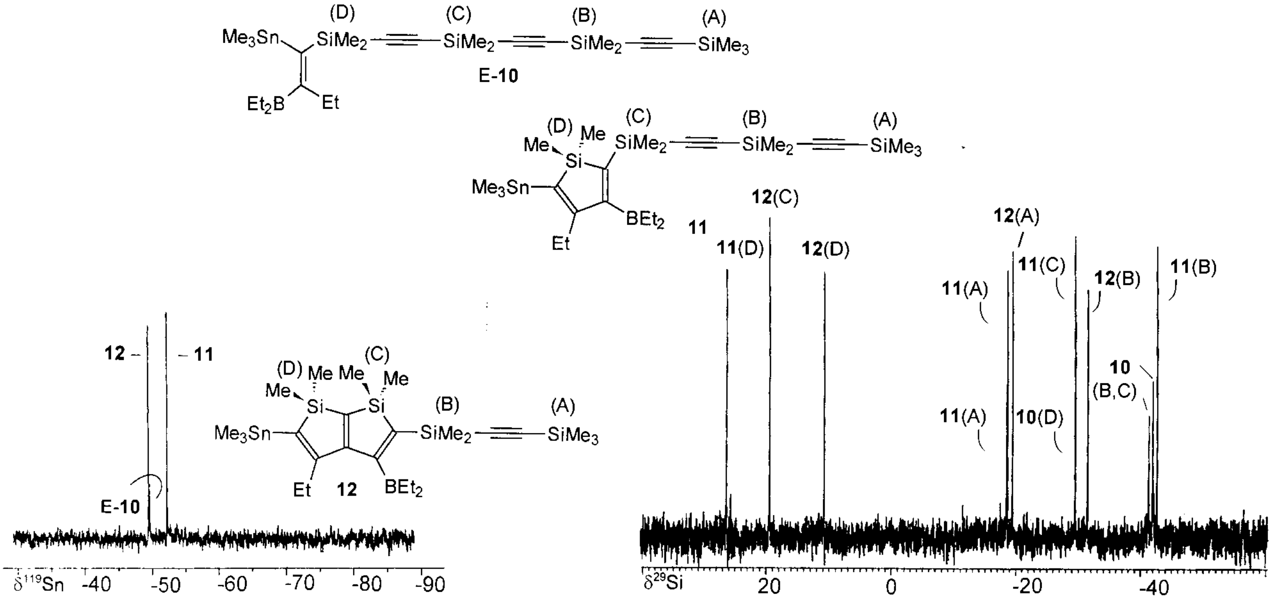
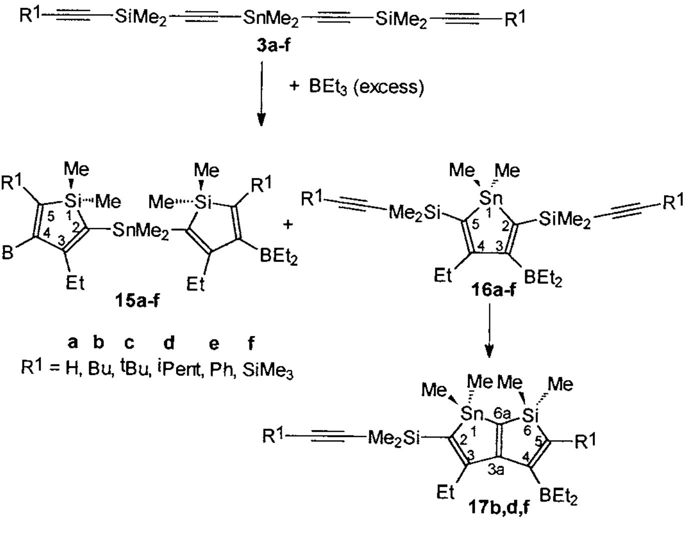


Fig. 1. 49.7 MHz ^{29}Si (refocused INEPT, ^1H decoupled) and 93.3 MHz $^{119}Sn\{^1H$-inverse gated$\}$ NMR spectra of the reaction mixture containing *E*-**10**, **11** and **12**. The assignment are indicated, based on changes of the intensities as the reaction proceeds towards **12**.



Scheme 6.

2.3. *1,1-Organoboration of the tetraynes 3*

Scheme 6 summarises the results of the 1,1-organoboration of the tetraynes **3**. After warming to room temperature, the reaction mixtures contain two new compounds **15** and **16** (approximate ratios: **15a**/**16a** = 1/3; **15b**/**16b** = 1/3; **15c**/**16c** = 1:2; **15d**/**16d** = 1:1; **15e**/**16e** = 1:2; **15f**/**16f** = 3:1). In the case of the stannoles **16**, intramolecular 1,1-vinylboration should lead to the 1,6-dihydro-1-stanna-6-sila-pentalene derivatives **17**. In contrast to the formation of **12** and other comparable 1,6-dihydro-1,6-disila-pentalenes [2], this rearrangement requires prolonged heating at > 140°C and is accompanied by decomposition of **15** as well as of **16**. However, **17b**, **d**, **f** could be identified with certainty by their typical NMR data (see also Fig. 2 for ^{29}Si- and ^{119}Sn-NMR spectra).

By monitoring the progress of the reactions of **3** with Et$_3$B **4** by ^{29}Si- and ^{119}Sn-NMR, it proved possible to identify various intermediates. Scheme 7 shows two routes to the bis(2-silolyl)tin derivatives **15**. NMR spectra indicate that the route via compounds **21**–**23** is preferred, since characteristic ^{29}Si- and ^{119}Sn-NMR signals of these intermediates could be observed (Fig. 3).

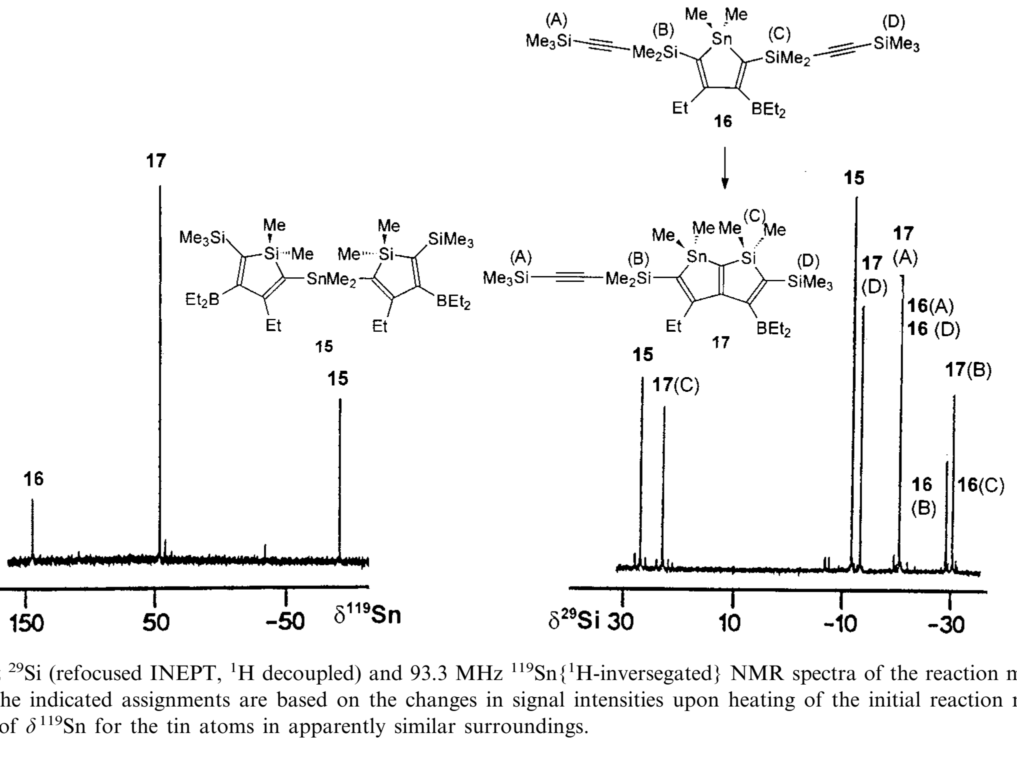
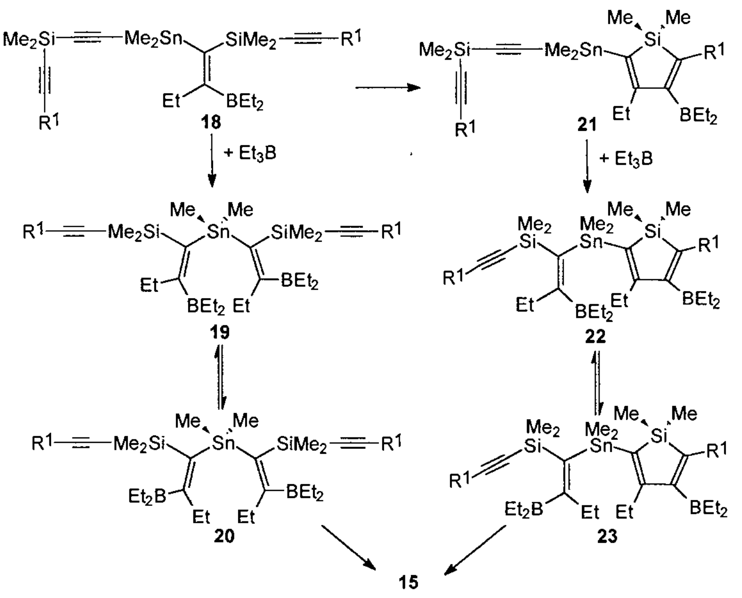


Fig. 2. 49.7 MHz ^{29}Si (refocused INEPT, ^{1}H decoupled) and 93.3 MHz ^{119}Sn{^{1}H-inversegated} NMR spectra of the reaction mixture containing **15**, **16** and **17**. The indicated assignments are based on the changes in signal intensities upon heating of the initial reaction mixture. Note the enormous range of δ^{119}Sn for the tin atoms in apparently similar surroundings.



Scheme 7.

The route to the stannoles **16** is depicted in Scheme 8. Although the intermediates **24** were not detected by NMR, the typical signals (e.g. at high frequency in the ^{119}Sn-NMR spectrum with δ^{119}Sn 188.8, and large magnitude of $|^2J(^{119}\text{Sn},^{29}\text{Si})| = 217.1$ Hz; see Fig. 3; δ^{11}B values around -10, typical of four-coordinate boron atoms [11]) for the zwitterionic intermediates **25a**, **25b** and **25f** were strong at -50°C. At room temperature these intermediates rearrange irreversibly to the stannoles **16**, in the same way as has been described previously [5,10].

2.4. NMR spectroscopic results

The NMR data given in the Tables 1–6 are fully consistent with the proposed structures of the tetraynes and their 1,1-organoboration products. The advantageous application of NMR spectroscopy is documented also in the Figs. 1–4. Fig. 4 shows typical examples of 2D heteronuclear shift correlations (HETCOR), in this case by ^{1}H detection, which help to establish the connectivity of ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn nuclei in the starting materials as well as in the products. As in previous

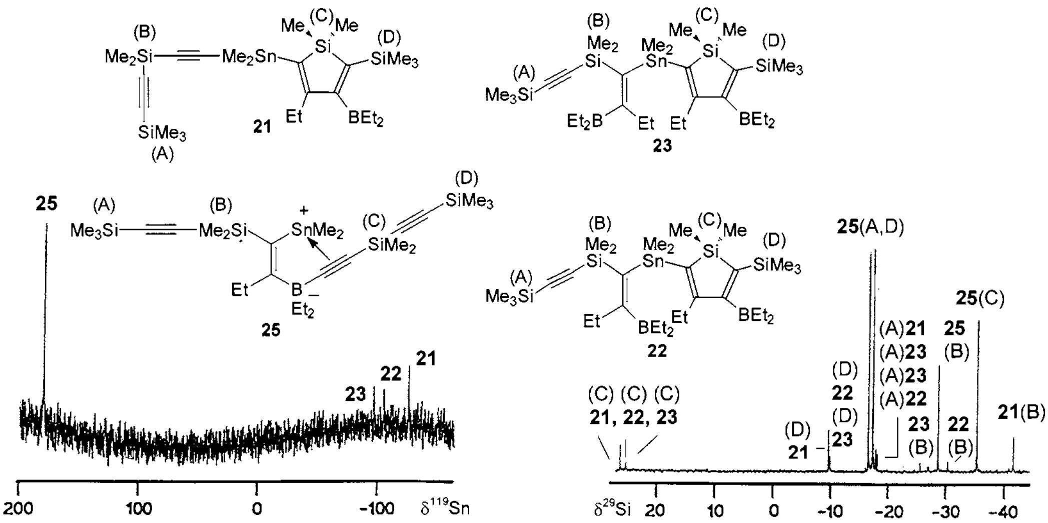
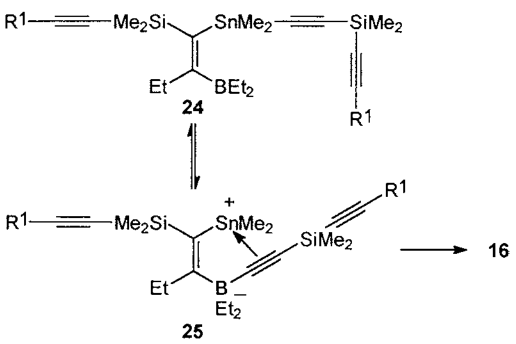


Fig. 3. 59.5 MHz ^{29}Si (refocused INEPT, ^{1}H decoupled) and 111.9 MHz ^{119}Sn{^{1}H-inversegated} NMR spectra of the reaction mixture containing various intermediates of the reaction of **3f** with Et$_3$B. The indicated assignments are based on intensity changes as the reaction proceeds as well as on ^{13}C-NMR data, measured from parallel measurements.



Scheme 8.

work in this field [1], the measurement of coupling constants $J(^{29}Si, ^{13}C)$, $J(^{119}Sn, ^{13}C)$ from the corresponding satellites in the ^{13}C-NMR spectra, and the observation of broadened ^{13}C-NMR signals, typical of boron-bonded carbon atoms [12,13], are particularly helpful for structural assignments. In the case of ^{13}C-NMR spectra, the refocused INEPT pulse sequence [14], based on coupling constants $^{3}J(^{13}C, ^{1}H(MeSi))$, proved very useful, since it was possible to identify the relevant ^{13}C signals of quaternary carbon atoms together with satellite signals, and to circumvent the problem of long relaxation times. The sensitivity of ^{29}Si nuclear shielding to the ring size [15] is demonstrated in the cases of the compounds **13** and **14**: in the six-membered ring in **14**, the ^{29}Si nuclear shielding is increased by 32.4 ppm with respect to the five-membered ring in **13**.

3. Conclusions

1,1-Organoboration reactions of tetraynes with $SiMe_2$ or $SnMe_2$ moieties separating the C≡C bonds

Table 1
^{13}C, ^{29}Si and ^{119}Sn NMR data[a] of the tetraynes **1** and **2**

	1a ($CDCl_3$) $R^1 = R^2 = H$	**1b** ($CDCl_3$) $R^1 = R^2 = SnMe_3$	**2a** ($CDCl_3$) $R^1 = SiMe_3$; $R^2 = H$	**2b** (C_7D_8) $R^1 = SiMe_3$, $R^2 = SnMe_3$
$\delta^{13}C$ C(1)	94.8 (19.0)	115.9 (13.4) [359.4]	115.6 (15.0) (75.3)	115.6 (15.5) (76.0)
$\delta^{13}C$ C(2)	86.4 (94.3)	112.8 (89.1) [55.8]	109.2 (89.0) (12.5)	109.7 (90.4) (12.3)
$\delta^{13}C$ C(4)	110.8 (89.3, 15.0)	111.7 (87.3) (15.0) [2.3]	111.5 (88.0) (14.0)	111.5 (88.8) (14.8) [2.0]
$\delta^{13}C$ C(5)	111.0 (88.8, 15.0)	110.4 (89.0) (14.5)	110.4 (88.7) (14.8)	111.1 (88.9) (15.0)
$\delta^{13}C$ C(7)	111.0 (88.8, 15.0)	110.4 (89.0) (14.5)	111.2 (88.0) (15.0)	110.5 (89.6) (14.7)
$\delta^{13}C$ C(8)	110.8 (89.3, 15.0)	111.7 (87.3) (15.0) [2.3]	110.4 (88.5) (14.8)	112.3 (87.9) (15.0) [2.5]
$\delta^{13}C$ C(10)	86.4 (94.3)	112.8 (89.1) [55.8]	86.4 (93.7)	113.0 (90.6) [60.2]
$\delta^{13}C$ C(11)	94.8 (19.0)	115.9 (13.4) [359.4]	94.4 (18.3)	115.8 (13.7) [377.3]
$\delta^{13}C$ Me(3,6,9)	0.0, −0.1, 0.0 (62.0) (62.8) (62.0)	0.5, 0.1, 0.5 (61.5) (62.0) (61.5)	0.0, 0.1, 0.2 (62.0) (82.0) (61.5)	0.0, −0.2, 0.4 (61.8) (63.0) (62.0)
$\delta^{13}C$ R^1, R^2		−7.6 [402.5]	0.24 (56.0)	−8.4 [402.0]
$\delta^{29}Si$ Si(3,6,9)	−40.0, −41.0, −40.0	−43.0, −41.3, −43.0 [11.2]	−41.7, −41.0, −39.9 (2.0) (2.0) (2.0)	−41.9, −41.4, −43.2 (2.0) (2.0) [14.3]
$\delta^{119}Sn$ ($R^{1,2}$)		−70.9		−74.2
$\delta^{29}Si(R^1)$			−18.0 (2.0)	−18.5 (2.0)

[a] Samples with 15–40% (v/v) at 25°C; $^{n}J(^{29}Si, ^{13}C)$ (±0.3 Hz) are given in parentheses; $^{n}J(^{119}Sn, X)$ ($X = ^{29}Si, ^{13}C$) [±0.5 Hz] are given in brackets.

Table 2
^{13}C-, ^{29}Si- and ^{119}Sn-NMR data[a] of the tetraynes **3a**–**f**

	3a	**3b**	**3c**	**3d**	**3e**	**3f**
$R^1 =$	H	Bu	^{t}Bu	$^{i}Pent$	Ph	$SiMe_3$
$\delta^{13}C$ C(1, 11)	94.9 (19.7)	108.5 (20.7)	116.9 (18.9)	109.0 (20.2)	106.5 (19.5)	114.8 (78.0) (13.9)
$\delta^{13}C$ C(2, 10)	86.7 (94.3)	86.7(94.3)	79.5 (99.9)	81.5 (100.3)	91.0 (97.1)	110.3 (89.8) (12.2)
$\delta^{13}C$ C(4, 8)	114.4 (88.6) [88.5]	115.5 (88.5) [88.4]	115.7 (88.0) [88.0]	115.8 (87.7) [91.8]	114.9 (87.6) [87.6]	115.2 (88.5) [88.0]
$\delta^{13}C$ C(5, 7)	111.7 (13.8) [525.7]	110.0 (13.6) [540.2]	110.7 (13.0) [536.4]	110.3 (13.6) [548.8]	111.4 (13.6) [529.0]	112.8 (13.6) [528.3]
$\delta^{13}C$ Me(3,6,9)	(62.0) −8.9 [491.2]	0.8 (62.2)−6.7 [499.5]	(62.1) −6.9 [490.5]	(62.2) −6.6 [490.4]	(62.1) −6.7 [490.0]	0.8 (61.4) −6.7 [490.6]
$\delta^{13}C$ R^1, R^2		23.4, 32., 21.1, 15.2	28.3, 30.7	18.3, 37.7, 27.6, 22.5	123.0, 132.2, 129.0, 128.5	−0.2 (56.2)
$\delta^{29}Si$ Si(3,9)	−40.9 [13.2]	−42.9 [14.6]	−41.2 [13.2]	−42,5 [13.9]	−41.1 [13.2]	−43.0 [12.5]
$\delta^{119}Sn$ Sn(6)	−164.5	−166.4	−165.4	−166.0	−164.8	−164.1

[a] In C_6D_6, 15–40% (v/v) at 25°C; $^{n}J(^{29}Si, ^{13}C)$ (±0.3 Hz) are given in parentheses; $^{n}J(^{119}Sn, X)$ ($X = ^{29}Si, ^{13}C$) [±0.5 Hz] are given in brackets.

Table 3
^{119}Sn-, ^{29}Si- and ^{13}C-NMR data[a] of the bis[2-sillolyl]dimethylstannanes **15a–f** and the bis[2-silolyl]dimethylsilane **9**

	δ^{13}C				δ^{29}Si	δ^{119}Sn
	C(2)	C(3)	C(4)	C(5)	Si(1)	
15a[b] R^1 = H	137.1 [385.2] (53.1)	171.2	181.0 Broad	135.5 [17.8] (60.1)	16.4 [104.9]	−103.4
15b[c] R^1 = Bu	135.1 [401.5] (53.8)	171.1 [7.3]	166.3 Broad	150.0 [21.5] (59.6)	13.3 [106.9]	−105.0
15c[d] R^1 = ^{t}Bu	135.6 [395.6] (52.3)	169.9 [8.7]	162.4 Broad	160.0 [19.1] (59.9)	13.2 [106.9]	−106.2
15d[e] R^1 = ^{i}Pent	135.0 [401.9] (54.0)	170.9 [8.0]	166.0 Broad	149.9 [22.0] (59.4)	13.4 [107.7]	−104.8
15e[f] R^1 = Ph	137.9 [374.9] (51.9)	171.5 [6.5]	168.0 Broad	152.0 [22.9] (59.9)	14.4 [104.4]	−104.3
15f[g] R^1 = SiMe$_3$	142.1 [382.9] (50.3)	170.6 [3.9] (11.8)	184.1 Broad	146.8 [14.8] (60.8)	25.7 [110.6] (10.9)	−102.6
9[h]	146.5 [14.0] (44.0) (64.5)	183.8 [72 ± 2] Broad	169.9 [3.7] (8.9) (11.7)	141.2 [381.5] (51.3)	25.0[i] [107.0] (10.0)	−50.0

[a] In C_6D_6, **9** in C_7D_8, 15–40% (v/v) at 25°C; $^nJ(^{29}Si, ^{13}C)$ ($\pm$0.3 Hz) are given in parentheses; $^nJ(^{119}Sn, X)$ (X = ^{29}Si, ^{13}C) [$\pm$0.5 Hz] are given in brackets; broad denotes broad signals due to partiallyrelaxed scalar ^{13}C–^{11}B coupling. $\delta^{11}B(C_6D_6) = 87.0 \pm 0.5$.

[b] δ^{13}C(**15a**) = 33.4 [50.0], 14.6 [9.0] (Et); 22.8 broad, 9.2 (BEt$_2$); −3.6 (47.2) (SiMe$_2$), −7.5 [340.2] (SnMe$_2$).

[c] δ^{13}C(**15b**) = 33.8, 32.6, 23.5, 14.2 (Bu); 33.6 [52.6], 14.8 [9.2] (Et); 22.7 broad, 9.2 (BEt$_2$); −2.8 (47.8) (SiMe$_2$); −7.1 [338.4] (SnMe$_2$).

[d] δ^{13}C(**15c**) = 36.4, 32.8 (^{t}Bu); 32.8 [49.7], 15.8 [8.7] (Et); 22.3 broad, 9.7 (BEt$_2$); −1.1 (47.4) (SiMe$_2$); −6.5 [339.0] (SnMe$_2$).

[e] δ^{13}C(**15d**) = 40.9, 30.6, 28.7, 22.9 (^{i}Pent); 33.5 [49.9], 14.8 [9.2] (Et); 22.6 broad, 9.3 (BEt$_2$); −2.7 (47.8) (SiMe$_2$); −7.9 [338.8] (SnMe$_2$).

[f] δ^{13}C(**15e**) = 142.4, 128.7, 127.5, 126.2 (Ph); 33.4 [47.9], 15.1 [8.8] (Et); 22.3 broad, 9.7 (BEt$_2$); −2.8 (48.0) (SiMe$_2$); −7.0 [342.8] (SnMe$_2$).

[g] δ^{13}C(**15f**) = 32.6 [48.2], 15.7 [8.8] (Et); 23.0 broad, 9.8 (BEt$_2$); (51.2) (SiMe$_3$); −2.2 (47.2) (SiMe$_2$); −6.9 [344.6] (SnMe$_2$).δ^{29}Si(SiMe$_3$) = −10.9.

[h] δ^{13}C(**9**) = 31.5 [46.0], 15.5 [8.8] (Et); 22.1 broad, 7.8 (BEt$_2$); 2.2 (50.5) (SiMe$_2$); −2.2 [2.3] (47.6) (SiMe$_2$ (silolyl)); −8.6 [338.2] (SnMe$_3$).

[i] δ^{29}Si (SiMe$_2$) = −21.4 (10.0).

proceed stepwise, and rather harsh reaction conditions are required to make use of all four C≡C bonds. In several cases it was possible to identify intermediates, even those with a zwitterionic structure, in which a triorganostannyl cation is co-ordinated by an alkynyl group belonging to an alkynylborate anion. It became clear that the 1,1-organoboration of polyynes with more than four C≡C bonds will probably not lead to pure products, since the 1,1-organoboration of the tetrayne **2b** afforded in the last step a mixture of two fused heterocycles **13** and **14**.

4. Experimental

4.1. General

All compounds were handled in an atmosphere of dry argon, observing all precautions to exclude oxygen and moisture when boranes were used. Carefully dried solvents were used for syntheses and preparation of the samples for NMR measurements. Starting materials were either available as commercial products and used without further purification (chlorosilanes, *n*-butyl lithium (1.6 M in hexane), Et_3B) or prepared as described (HC≡CMgBr in THF [16], $Me_3Sn{-}NEt_2$, $Me_2Sn(NEt_2)_2$ [17]). Electron impact (EI) mass spectra: Finnigan MAT 8500 with direct inlet. IR spectra: Perkin Elmer 983 G spectrometer. NMR measurements: Bruker ARX 250 or DRX 500 [^{1}H-, ^{11}B-, ^{13}C-, ^{29}Si-NMR (refocused INEPT [14] based on $^2J(^{29}Si, ^1H) = 7$ Hz), ^{119}Sn-NMR (inverse gated ^{1}H decoupled or refocused INEPT [14] based on $^2J(^{119}Sn, ^1H) = 50–60$ Hz)]. Chemical shifts are given with respect to Me_4Si [δ^1H ($CHCl_3/CDCl_3$) = 7.24, (C_6D_5H) = 7.14, ($C_6D_5CD_2H$) = 2.03; δ^{13}C ($CDCl_3$) = 77.0, (C_6D_6) = 128.0, ($C_6D_5\mathit{C}D_3$) = 20.4; δ^{29}Si = 0 for $\Xi(^{29}Si) = 19.867184$ MHz], BF_3OEt_2 [$\delta^{11}B = 0$; $\Xi(^{11}B) = 32.083971$ MHz], and Me_4Sn [$\delta^{119}Sn = 0$ for $\Xi(^{119}Sn) = 37.290665$ MHz].

Table 4
^{119}Sn-, ^{29}Si- and ^{13}C-NMR data[a] of the stannole derivatives **16a–f**

	δ^{13}C				δ^{29}Si		δ^{119}Sn
	=C(2)	=C(3)	=C(4)	=C(5)	Si(2)	Si(5)	
16a[b]	142.2	183.7	168.7	135.6	-26.9	-25.8	136.5
$R^1 = H$	[200.5]	Broad	[86.5]	[274.9]	[102.5]	[107.5]	
	(71.1)		(11.8)	(72.3)			
16b[c]	143.7	183.1	168.1	137.9	-27.6	-28.4	132.6
$R^1 = Bu$	[200.5]	Broad	[89.5]	[272.9]	[104.7]	[114.3]	
	(72.4)		(12.7)	(72.3)			
16c[d]	143.1	183.1	168.1	137.7	-27.6	-28.4	133.6
$R^1 = {}^tBu$	[201.6]	Broad	[87.8]	[271.4]	[108.4]	[112.8]	
	(72.1)		(13.1)	(74.1)			
16d[e]	143.5	182.8	167.8	137.7	-27.7	-28.5	132.4
$R^1 = {}^iPent$	[201.1]	Broad	[89.5]	[275.7]	[106.9]	[117.2]	
	(72.6)		(13.0)	(71.5)			
16e[f]	143.1	183.7	168.7	137.4	-26.1	-27.2	134.8
$R^1 = Ph$	[199.5]	Broad	[94.8]	[271.9]	[108.4]	[115.7]	
	(70.9)		(11.6)	(70.5)			
16f[g]	142.6	183.1	168.7	137.3	-27.3	-28.4	134.4
$R^1 = SiMe_3$	[200.8]	Broad	[87.6]	[276.6]	[102.6]	[112.8]	
	(66.4)		(12.8)	(71.9)			

[a] In C_6D_6, 15–40% (v/v) at 25°C; $^nJ(^{29}Si, ^{13}C)$ (± 0.3 Hz) are given in parentheses; $^nJ(^{119}Sn, X)$ ($X = {}^{29}Si, {}^{13}C$) [± 0.5 Hz] are given in brackets; broad denotes broad signals due to partially relaxed scalar ^{13}C–^{11}B coupling. $\delta^{11}B = 87.0 \pm 0.4$.

[b] $\delta^{13}C$(**16a**) = 32.0 [85.6], 16.6 [9.0] (Et); 23.1 broad, 9.9 (BEt_2).

[c] $\delta^{13}C$(**16b**) = 31.9 [87.0], 16.1 [9.9] (Et); 22.9 broad, 9.7 (BEt_2).

[d] $\delta^{13}C$(**16c**) = 31.8 [87.4], 16.2 [9.8] (Et); 22.8 broad, 10.1 (BEt_2).

[e] $\delta^{13}C$(**16d**) = 31.8 [87.0], 16.2 [9.7] (Et); 22.6 broad, 9.7 (BEt_2).

[f] $\delta^{13}C$(**16e**) = 32.0 [88.3], 16.2 [8.8] (Et); 22.9 broad, 9.8 (BEt_2).

[g] $\delta^{13}C$(**16f**) = 32.1 [85.6], 16.1 [9.9] (Et); 23.2 broad, 9.6 (BEt_2); $\delta^{29}Si$ ($SiMe_3$) = -19.0, -19.1.

4.2. *3,6,9-Hexamethyl-3,6,9-trisila-undeca-1,4,7,10-tetrayne* ***1a***

A solution of EtMgBr (19 mmol) in THF (20 ml) was added to a saturated solution of acetylene in THF (50 ml) over a period of 40 min. The reaction mixture was stirred for an additional 2 h at room temperature and gave a solution of HC≡CMgBr which was then cooled to 5°C. A solution of compound **5** (1.89 g, 6.45 mmol) in THF (10 ml) was added dropwise, and the reaction mixture was allowed to warm up to room temperature and was kept stirring for 10 h. The reaction mixture was hydrolysed with an aqueous NH_4Cl solution (80 ml). After repeated extraction of the aqueous phase with pentane, the pentane extracts were combined and dried with Na_2SO_4. Insoluble material was filtered off, and the solvent was removed in vacuo and 1.69 g (98%) of the pure compound **1a** was left as a colourless solid. IR (in hexane): $\nu(C\equiv C) = 2043$ cm^{-1}, $\nu(\equiv C{-}H) = 3277$, 3295 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta^1H = 0.27$ (s, 6H, $SiMe_2$), 0.28 (s, 12H, $SiMe_2$), 2.42 (s, 2H, ≡CH).

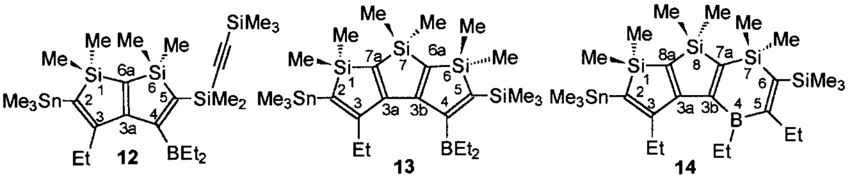
4.3. *3,6,9-Hexamethyl-1,11-bis(trimethylstannyl)-3,6,9-trisila-undeca-1,4,7,10-tetrayne* ***1b***

Me_3SnNEt_2 (0.57 g; 2.42 mmol) was added to a solution of **1a** in hexane (10 ml) at room temperature. The reaction mixture was stirred for 3 h. Removal of all volatile material in vacuo left the pure compound **1b** as a colourless oil (0.63 g, 87%). ^{1}H-NMR ($CDCl_3$) δ^1H [$^nJ(^{119}Sn\,^1H)$]: 0.27 [60.8] (s, 18H, $SnMe_3$), 0.30 (s, 12H, $SiMe_2$), 0.31 (s, 6H, $SiMe_2$).

4.4. *3,6,9-Hexamethyl-11-trimethylsilyl-3,6,9-trisila-undeca-1,4,7,10-tetrayne* ***2a***

A solution of EtMgBr (4.16 mmol) in THF (5 ml) was added dropwise to a solution of diethynyldimethylsilane, $Me_2Si(C\equiv CH)_2$, (0.44 g; 4.04 mmol) in THF (5 ml) over a period of 50 min. The solution became yellow and was stirred additionally for 1.5 h. This solution was then added dropwise to a solution of compound **7** (1.10 g; 4.04 mmol) in THF (5 ml) over 15 min. The reaction mixture was stirred overnight, and then the solvent was removed, after which an oily solid was left. The solid was extracted twice with portions of pentane (30 ml) and filtered. Removal of solvent in vacuo gave solid **2a** (1.37 g, 98%). IR (hexane): $\nu(C\equiv C) = 2043$ cm^{-1}, $\nu(\equiv C{-}H) = 3296$ cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ^1H [$^nJ(^{29}Si\,^1H)$]: 0.15 (7.6) (s, 9H, $SiMe_3$), 0.30 (7.6) (s, 6H, $SiMe_2$), 0.31 (s, 6H, $SiMe_2$), 0.33 (7.0) (s, 6H, $SiMe_2$), 2.43 (s, 1H, ≡CH).

Table 5
^{13}C-, ^{29}Si- and ^{119}Sn-NMR data[a] of the fused heterocycles **12**–**14**



	12[b]	**13**[c]	**14**[d]
δ^{13}C(2)	147.8 (49.0) [378.8]	148.0 (49.0) [382.7]	147.4 (49.7) [382.2]
δ^{13}C(3)	168.1	168.0	168.6 [10.3]
δ^{13}C(3a)	179.0 [82.9]	174.2 [87.1]	177.8 (8.6)(8.6) [88.8]
δ^{13}C(3b)		175.6 [10.3]	183.1 broad
δ^{13}C(4)	181.9 broad	181.2 broad	
δ^{13}C(5)	143.9[e] (43.8)(69.7) [8.9]	153.4[e] (42.5) (61.6)	184.8 broad
δ^{13}C(6)			148.4 (53.1)(53.1) [1.6]
δ^{13}C(6a)	150.5[e] (56.1)(58.8) [11.8]	153.9 (57.0)(57.0) [8.4]	
δ^{13}C(7a)		156.9 (56.5)(57.3) [11.0]	163.7[e] (42.6)(56.9) [8.4]
δ^{13}C(8a)			149.3 (56.1)(59.9) [11.8]
δ^{13}C(1-Me)	−3.6 (50.2) {2.6]	−3.8 (50.0)	−3.8 (50.0), −3.6 (50.0)
δ^{13}C(6-Me)	−2.6 (49.5)	−2.6 (49.1)	
δ^{13}C(7-Me)		−3.7 (50.0)	0.2 (51.7), 1.3 (50.0)
δ^{13}C(8-Me)			−2.9 (49.1), −2.8 (50.0)
δ^{13}C(EtB)	22.1 broad, 9.8	18.0 broad, 9.7	20.8 broad, 9.7
δ^{13}C(3-Et)	31.3 [45.0], 16.7 [8.4]	32.6 [50.0], 15.7 [8.6]	30.8 [46.6], 16.7 [9.5]
δ^{13}C(5-Et)			32.2 (10.3)(10.3), 15.2
δ^{13}C(2-SnMe$_3$)	−8.0 [337.2]	−8.3 [338.0]	−8.2 [338.0]
δ^{29}Si(1)	10.8 (13.6) [85.0]	6.3 (11.7) [83.2]	9.9 (13.8) [88.0]
δ^{29}Si(6,7,8)	19.4 (10.9)(13.6) [1.8]	Si(6): 12.9 (8.7)(13.2) [4.6] Si(7):1.1 (11.7)(13.2) [2.8]	Si(7): −19.5 (8.6)(8.6) [4.0] Si(8): 16.4 (8.6)(13.8) [2.5]
δ^{119}Sn	−49.8	−53.8	−52.8

[a] In C_7D_8, 15–40% (v/v) at 25°C; $^nJ(^{29}Si, ^{13}C)$ (± 0.3 Hz) are given in parentheses; $^nJ(^{119}Sn, X)$ (X = ^{29}Si, ^{13}C) [± 0.5 Hz] are given in brackets; broad denotes broad signals due to partially relaxed scalar ^{13}C–^{11}B coupling. The numbering scheme of **14** was selected for better comparison.

[b] $\delta^{11}B = 86.5$; $\delta^{13}C = 2.3$ (56.6) 5-SiMe$_2$, 0.1 (56.1) *Me*$_3$Si–C≡, 114.8 (77.5) (12.3) ≡*C*–SiMe$_2$, 115.3 (77.8) (12.1) ≡*C*–SiMe$_3$; $\delta^{29}Si = -31.5$ (10.9) (1.6) [5.7] 6-SiMe$_2$, −19.4 (1.6) Me$_3$Si–C≡.

[c] $\delta^{11}B = 86.5$.

[d] $\delta^{11}B = 72.0$.

[e] The larger value belongs to coupling with the exocyclic ^{29}Si nucleus.

4.5. 3,6,9-Hexamethyl-1-trimethylstannyl-11-trimethylsilyl-3,6,9-trisila-undeca-1,4,7,10-tetrayne *2b*

As described for **1b**, treatment of **2a** with one equivalent of Me$_3$SnNEt$_2$ afforded compound **2b** in 89% yield as a colourless solid. ^{1}H-NMR(C_7D_8): δ^1H [$^nJ(^{119}Sn\,^1H)$]: 0.00 [60.7] (s, 9H, SnMe$_3$), 0.01 (s, 9H, SiMe$_3$), 0.11 (s, 6H, SiMe$_2$), 0.17 (s, 6H, SiMe$_2$), 0.22 (s, 6H, SiMe$_2$).

4.6. 3,6,9-Hexamethyl-3,9-disila-6-stanna-undeca-1,4,7,10-tetrayne *3a*

Bis(diethylamino)dimethyltin, Me$_2$Sn(NEt$_2$)$_2$ (0.48.g; 2.02 mmol) in diethylether (20 ml) was added to a dilute solution of diethynyldimethylsilane, Me$_2$Si(C≡CH)$_2$, (0.44 g; 4.04 mmol) in diethylether (50 ml). After stirring the mixture for 2 h, all volatile material was removed in vacuo. Compound **3a** (91%) was left as a colourless solid. IR (hexane): ν(C≡C) = 2037, 2041, 2092 cm^{-1}, ν(≡C–H) = 3289 cm^{-1}. ^{1}H-NMR (C_6D_6) δ^1H ($^nJ(^{29}Si\,^1H)$) [$^nJ(^{119}Sn\,^1H)$]: 0.06 [69.0] (s, 6H, SnMe$_2$), 0.18 (7.2) (s, 12H, SiMe$_2$), 2.20 (s, 2H, ≡CH). EI-MS: *m*/*z* (%) = 363 (5) [M$^+$], 348 (100), 255 (20), 225 (10), 165 (40), 135 (25), 43 (10).

4.7. 3,6,9-Hexamethyl-1,11-bis(trimethylsilyl)-3,9-disila-6-stanna-undeca-1,4,7,10-tetrayne *3f*

In the same way as described for **3a**, the silane **6** reacted with Me$_2$Sn(NEt$_2$)$_2$ in 2:1 molar ratio to give compound **3f** as a colourless solid in 95% yield. IR (hexane): ν(C≡C) = 2037, 2092, 2110 cm^{-1}; ^{1}H-NMR (C_6D_6) δ^1H ($^nJ(^{29}Si\,^1H)$) [$^nJ(^{119}Sn\,^1H)$]: 0.02 (6.8) (s, 18H, SiMe$_3$), 0.05 [69.0] (s, 6H, SnMe$_2$), 0.24 (7.0) (s, 12H, SiMe$_2$). EI-MS: *m*/*z* (%) = 508 (5) [M$^+$], 493 (100), 327 (25), 297 (40), 181 (15), 135 (25), 73 (10), 43 (15). The compounds **3b**–**e** were prepared in the same

Table 6
^{13}C-, ^{29}Si- and ^{119}Sn-NMR data[a] of the 1,6-dihydro-1-stanna-6-sila-pentalene derivatives **17b**, **d**, **f**

	17b (R^1 = ^{n}Bu)	**17d** (R^1 = ^{i}pent)	**17f** (R^1 = SiMe$_3$)
δ^{13}C(2)	142.5 [274.8] (72.0)	142.4 [273.1] (71.7)	142.2 [274.7] (70.7)
δ^{13}C(3)	166.7	166.7	167.0
δ^{13}C(3a)	177.8 [69.4]	177.8	178.3 [74.0]
δ^{13}C(4)	163.6 broad	163.0 broad	181.8 broad [85.0]
δ^{13}C(5)	151.0 [10.0]	150.9 [10.4]	146.7 [5.0]
δ^{13}C(6a)	143.7 [322.8]	143.6 [324.2] (60.0)	152.3 [308.4] (57.8)
δ^{13}C(Me$_2$Sn(1))	−8.0 [337.0]	−8.0 [323.1]	−8.2 [328.5]
δ^{13}C(Me$_2$Si(6))	−3.1	−3.0	−2.9 (47.4)
δ^{13}C(Me$_2$Si-2)	2.4	2.2	1.7
δ^{13}C(Et-3)	30.9, 16.8	30.6, 17.0	29.5, 17.0
δ^{13}C(Et$_2$B)	22.3 broad, 9.3	22.4 broad, 9.3	22.7 broad, 9.5
δ^{13}C(≡CSi)	85.6	85.5	113.7
δ^{13}C(≡CR^1)	108.0	107.9	114.9
δ^{13}C(R^1)	22.3, 31.0, 20.1, 13.8; 32.7, 33,6, 23.5, 14.3	18.4, 37.9, 27.5, 22.7; 28.8, 40.9, 28.6, 23.0	1.5, 1.4
δ^{29}Si(Si(6))	10.7	10.8	21.8 [121.3] (9.4)[b]
δ^{29}Si (2-Si)	−28.5	−28.5	−28.7 [83.6]
δ^{119}Sn (Sn(6))	42.3	42.1	37.4

[a] In C$_6$D$_6$, 15–40% (v/v) at 25°C; $^nJ(^{29}$Si, ^{13}C) (±0.3 Hz) are given in parentheses; $^nJ(^{119}$Sn, X) (X = ^{29}Si, ^{13}C) [±0.5 Hz] are given in brackets; broad denotes broad signals due to partially relaxed scalar ^{13}C–^{11}B coupling.

[b] δ^{29}Si(5-SiMe$_3$) = −12.8 (9.4); δ^{29}Si (≡C–SiMe$_3$) = −19.5.

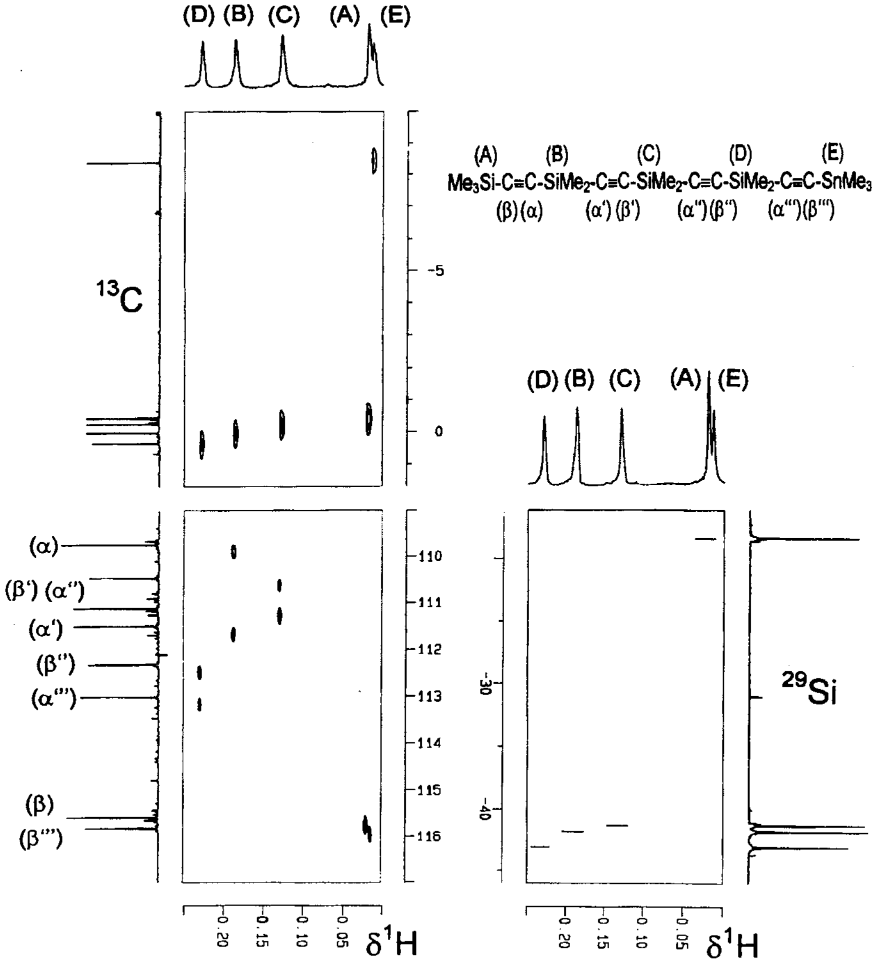


Fig. 4. Contour plots of the 500 MHz 2D (HMQC) ^{1}H/^{13}C and ^{1}H/^{29}Si experiments for **2b** which establish the connectivity of the respective resonance signals as indicated.

way from the corresponding silanes [18] and were obtained as colourless oily liquids.

4.8. Organoboration reactions with triethylborane ***4*** *(general procedure)*

All reactions were carried out first on a small scale (< 1 mmol) in NMR tubes. The alkynes were dissolved in benzene (C_6D_6) or toluene (C_7D_8), cooled at $-78°C$ and the desired amount (excess or stoichiometric amount) of triethylborane was injected in one portion. The progress of the reactions was monitored mainly by ^{29}Si- and ^{119}Sn-NMR (see Figs. 1–3). The same results were obtained when the reactions were carried out on a larger scale (> 2 mmol) in order to attempt distillation of the mixtures or to obtain products selectively by thermally induced rearrangements. This did not give pure products, and in many cases, decomposition occurred, leading to even more complex mixtures. Attempts to separate the mixtures on silica or Al_2O_3 have not been successful as yet, since the organoboration products decomposed, and elution with various polar and non-polar solvents did not give an appreciable amount of defined products. The products **9** and **12** were obtained quantitatively in high purity (^{1}H-NMR) just by removing all volatile material. In the case of the mixtures containing **15**/**16** all NMR spectra indicate there are no further impurities.

Acknowledgements

We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. E.M. thanks the Alexander-von-Humboldt Stiftung for a fellowship.

References

[1] B. Wrackmeyer, Coord. Chem. Rev. 145 (1995) 125–156, and literature cited therein.

[2] B. Wrackmeyer, G. Kehr, J. Süß, E. Molla, J. Organomet. Chem. 562 (1998) 207.

[3] J. Dubac, A. Laporterie, G. Manuel, Chem. Rev. 90 (1990) 215.

[4] (a) R. Köster, G. Seidel, J. Süß, B. Wrackmeyer, Chem. Ber. 126 (1993) 1107. (b) B. Wrackmeyer, H.E. Maisel, J. Süß, W. Milius, Z. Naturforsch. Teil B 51b (1996) 1320.

[5] B. Wrackmeyer, J. Organomet. Chem. 310 (1986) 151.

[6] (a) L. Killian, B. Wrackmeyer, J. Organomet. Chem. 132 (1977) 213. (b) L. Killian, B. Wrackmeyer, J. Organomet. Chem. 148 (1978) 137. (c) B. Wrackmeyer, J. Organomet. Chem. 364 (1989) 331. (d) B. Wrackmeyer, U. Klaus, W. Milius, E. Klaus, T. Schaller, J. Organomet. Chem. 517 (1996) 235.

[7] B. Wrackmeyer, K. Horchler, J. Organomet. Chem. 399 (1990) 1.

[8] O.G. Yarosh, L.V. Zhilitskaya, V.Yu. Yitskovski, A.I. Albanov, M.G. Voronkov, Metallorg. Khim. 2 (1989) 629.

[9] K. Jones, M.F. Lappert, Organomet. Chem. Rev. 1 (1966) 67.

[10] (a) B. Wrackmeyer, K. Horchler von Locquenghien, S. Kundler, J. Organomet. Chem. 503 (1995) 289. (b) B. Wrackmeyer, S. Kundler, R. Boese, Chem. Ber. 126 (1993) 1361.

[11] H. Nöth, B. Wrackmeyer, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), Nuclear Magnetic Resonance Spectroscopy of Boron Compounds in NMR-Basic Principles and Progress, vol. 14, Springer, Berlin, 1978.

[12] B. Wrackmeyer, Annu. Rep. NMR Spectrosc. 20 (1988) 61.

[13] A. Abragam, The Principles of Nuclear Magnetism, Ch. 8, Oxford University Press, Oxford, 1961.

[14] (a) G.A. Morris, R. Freeman, J. Am. Chem. Soc. 101 (1979) 760. (b) G.A. Morris, J. Am. Chem. Soc. 102 (1980) 428. (c) D.P. Burum, R.R. Ernst, J. Magn. Reson. 39 (1980) 163.

[15] E. Kupce, E. Lukevics, in: E. Buncel, J.R. Jones (Eds.), Isotopes in the Physical and Biomedical Sciences, Elsevier, New York, 1991, pp. 213–295, and literature cited therein.

[16] E.R.H. Jones, L. Skattebol, M. Whiting, Org. Synth. 39 (1959) 56.

[17] K. Jones, M.F. Lappert, J. Chem. Soc. (1965) 1944.

[18] B. Wrackmeyer, G. Kehr, J. Süß, Chem. Ber. 126 (1993) 2221.