1,1-Organoboration of Di-1-alkynylsilanes with Alkynyl Groups of Different Reactivity: New Organometallic-Substituted Siloles

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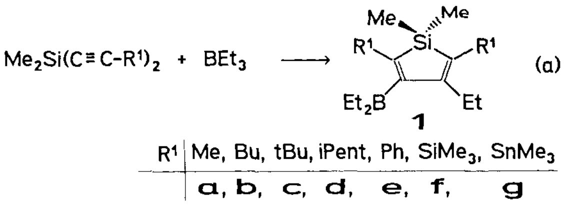
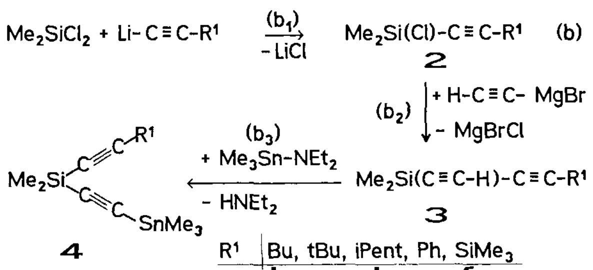
The synthesis of alkynyl[(trimethylstannyl)ethynyl]dimethylsilanes **4** [alkynyl $R^1-C\equiv C$: R^1 = Bu (**b**), *t*Bu (**c**), *i*Pent (**d**), Ph (**e**), $SiMe_3$ (**f**)] is reported. The intermolecular 1,1-ethyloboration of **4** with triethylborane takes place selectively at the $Sn-C\equiv$ bond to give first the alkenyl(alkynyl)dimethylsilanes **5** and **6**. There exists an equilibrium between **5** and **6**, and compound **6** has the suitable stereochemistry for the final intramolecular 1,1-vinyloboration to form the 4-(diethylboryl)-2-(trimethylstannyl)siloles **7**. Protodeborylation of **7** with water gives the 2-(trimethylstannyl)siloles **8**, and protodeborylation and protodestannylation with an excess of acetylacetone affords the siloles **9**. Multinuclear NMR (^{1}H-, ^{11}B-, ^{13}C-, ^{29}Si-, and ^{119}Sn-) serves for monitoring the reactions and for the characterization of the products.

The interest in metalloles[1] and particularly in siloles[1,2] is reflected by numerous attempts to synthesize these heterocycles by various multistep procedures[1,2]. Recently, we have shown that substituted siloles are readily accessible in high yield by 1,1-organoboration of di-1-alkynylsilanes[3,4]. If the substituents R^1 in Eq. (a) are alkyl, phenyl, or trimethylsilyl groups (**1a**–**f**)[3], the reaction conditions are rather harsh (90–100°C for up to 100 h in the presence of a large excess of triethylborane, Et_3B). In the case of $R^1 = SnMe_3$ (**1g**)[4], the reaction with Et_3B starts already at ca. –50°C, and it is essentially complete when the mixture is allowed to reach ambient temperature. This can be attributed to the labile $Sn-C\equiv$ bond which is much more readily cleaved than the $Si-C\equiv$ bond in the first step of the 1,1-organoboration. It has been assumed that the intermolecular 1,1-ethyloboration is followed by an *intramolecular* 1,1-vinyloboration leading to the silole ring. Considering the reaction conditions required for the synthesis of **1a**–**f**, it is conceivable that the intermolecular 1,1-ethyloboration is the rate-determining step.

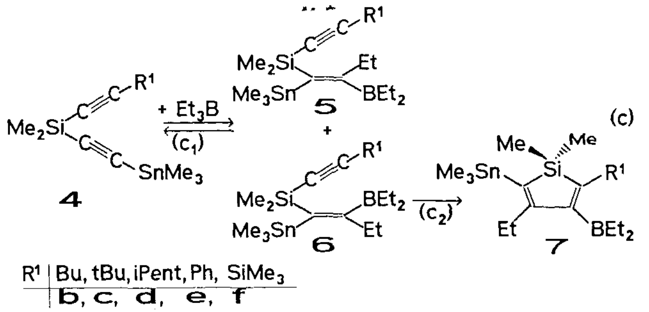
In order to shed more light on the reaction mechanism and also to increase the variety of siloles, we have prepared the new di-1-alkynyldimethylsilanes **4**, starting from the 1-alkynylchlorosilanes **2**[5] via the 1-alkynylethynylsilanes **3** which are converted into **4** by treatment with (diethylamino)trimethylstannane[6] [eq. (b)]. The $C\equiv C-SnMe_3$ group in the compounds **4** should be much more reactive towards Et_3B than the $C\equiv C-R^1$ moiety. Controlling the reaction between **4** and Et_3B by means of ^{1}H-, ^{11}B-, ^{13}C-, ^{29}Si, and ^{119}Sn-NMR analysis, we can compare the reaction conditions for inter- and intramolecular organoboration and can detect intermediates prior to the formation of siloles.





Results and Discussion

The compounds **4** are colorless, moisture-sensitive liquids (**4b**, **c**, **d**) or a solid (**4e**). The ^{13}C-, ^{29}Si-, and ^{119}Sn-NMR data of the alkyne derivatives **2**, **3**, and **4** are given in Table 1. Reactions of **4** with Et_3B are first carried out in toluene or CH_2Cl_2 in NMR tubes, monitored by NMR (see Figures 1



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and 2) between −78 and +25 °C [eq. (c)], and afterwards they are repeated on a preparative scale. Two types of intermediates (**5**, **6**) are identified by their characteristic NMR data. In all cases, the final products are the siloles **7**, which are isolated as air- and moisture-sensitive oily liquids. ^{13}C-, ^{29}Si-, and ^{119}Sn NMR data for **5**, **6**, and **7** are compiled in Table 2 and 3, respectively.

Table 1. ^{13}C-, ^{29}Si-, and ^{119}Sn-NMR data[a] of thc alkyne derivatives **2**, **3**, and **4**

Comp.	δ^{13}C							δ^{29}Si	δ^{119}Sn
	Si-C≡	≡C-R^1	Sn-C≡ / H-C≡	Si-C≡C-Sn/ Si-C≡C-H	SiMe	SnMe	R^1		
2b[b]	81.2 (105.7)	110.3 (21.8)	-	-	4.0 (65.4)	-	22.1	-1.3	-
2c[c]	79.2 (105.7)	118.0 (20.7)	-	-	4.1 (65.4)	-	28.3	-0.7	-
2d[d]	81.1 (106.8)	110.4 (22.3)	-	-	4.1 (64.9)	-	18.0	-1.1	-
2e[e]	90.2 (102.5)	107.5 (20.7)	-	-	3.7 (65.4)	-	122.2	0.5	-
2f	108.9 (94.9) (12.7)	116.6 (16.6) (73.4)	-	-	3.7 (64.6)	-	-0.3 (56.7)	-1.9 -17.5	
3b[f]	81.0 (101.9)	109.1 (20.1)	94.2 (18.6)	87.3 (93.2)	0.5 (62.1)	-	22.1	-40.3	-
3c[g]	78.8 (101.4)	116.9 (19.1)	94.3 (18.5)	87.3 (93.2)	0.6 (62.7)	-	28.2	-40.2	-
3d[h]	80.8 (101.9)	109.1 (19.6)	94.2 (18.5)	87.8 (93.2)	0.5 (62.1)	-	18.1	-40.4	-
3e[i]	90.4 (97.0)	106.6 (19.6)	95.2 (17.4)	86.8 (94.8)	0.4 (62.1)	-	122.7	-39.0	-
3f	109.6 (91.0) (12.7)	115.6 (12.7) (79.2)	95.0 (18.6)	86.5 (93.9)	0.2 (62.6)	-	-0.3 (56.7)	-40.6 -18.2	-
4b[j]	81.9 (100.3)	108.3 (19.6)	113.9 (13.1) [391.8]	114.4 (88.2) [62.7]	1.1 (61.6)	-8.1 [402.2]	22.1	-43.5 [11.7]	-74.3
4c[k]	79.6 (99.7)	116.0 (19.1)	113.8 (13.6) [396.2]	114.5 (89.4) [63.2]	1.4 (61.6)	-7.9 [401.6]	28.2	-43.4 [11.7]	-74.8
4d[l]	81.8 (100.3)	108.4 (19.6)	113.9 (13.0) [395.6]	114.4 (89.4) [62.8]	1.2 (62.1)	-8.1 [402.2]	18.1	-43.5 [11.7]	-74.3
4e[m]	91.6 (97.3)	106.3 (18.5)	115.6 (13.6) [374.4]	113.7 (89.4) [58.8]	0.9 (62.1)	-8.2 [401.6]	123.3	-41.9 [11.0]	-73.1
4f	110.7 (89.0) (12.2)	114.6 (14.7) (77.3)	115.1 (13.7) [383.4]	113.4 (90.5) [61.1]	0.9 (61.4)	-8.1 [402.5]	-0.1 (56.2)	-43.8 -18.6	-73.4

[a] In C_6D_6 (ca. 20−30%) at 26 ± 1 °C; $J(^{29}Si^{13}C)$ in Hz in parentheses; $J(^{119}Sn^{13}C)$ and $J(^{119}Sn^{29}Si)$ in Hz in square brackets. Other $\delta^{13}C(R^1)$ data are given in footnotes [b] to [m]. — [b] $\delta^{13}(R^1) = 30.5, 19.6, 13.7$. — [c] $\delta^{13}C(R^1) = 30.7$. — [d] $\delta^{13}C(R^1) = 37.4, 27.5, 22.3$. — [e] $\delta^{13}C(R^1) = 132.3, 129.5, 128.6$. — [f] $\delta^{13}C(R^1) = 30.6, 19.7, 13.7$. — [g] $\delta^{13}C(R^1) = 30.8$. — [h] $\delta^{13}C(R^1) = 37.5, 27.4, 22.3$. — [i] $\delta^{13}C(R^1) = 132.2, 129.2, 128.6$. — [j] $\delta^{13}C(R^1) = 30.7, 19.8, 13.8$. — [k] $\delta^{13}C(R^1) = 31.0$. — [l] $\delta^{13}C(R^1) = 37.5, 27.3, 22.3$. — [m] $\delta^{13}C(R^1) = 132.4, 128.8, 128.4$.

Treatment of a hexane solution of the silole **7d** with an excess of water at 60 °C leads to protodeborylation, and pure **8d** (NMR: >95%) is obtained in high yield [eq. (d$_1$)]. In contrast, reactions of **7d** or **7e** with acetylacetone (Hacac) in a 1:1 ratio give mixtures of siloles whereas the reaction

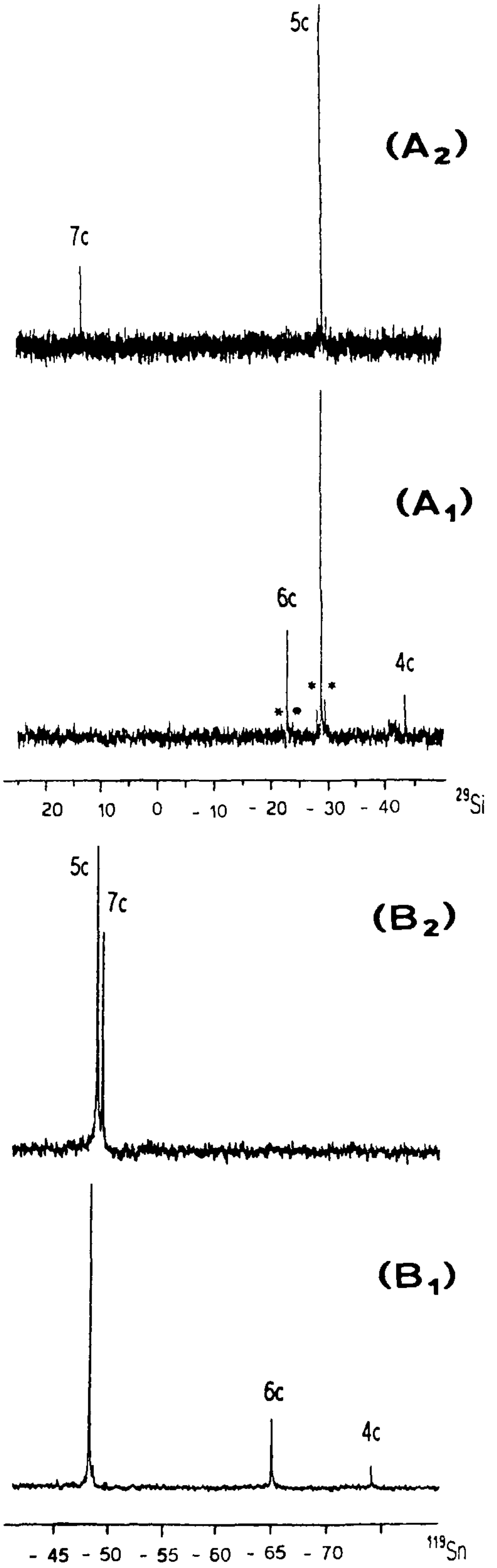


Figure 1. The reaction between the di-1-alkynyldimethylsilane **4c** and Et_3B in CD_2Cl_2, monitored by ^{29}Si- (refocused INEPT pulse sequence with CPD-^{1}H decoupling) and ^{119}Sn-NMR (inverse-gated ^{1}H decoupling) spectroscopy (δ scale). — (A_1) 59.6-MHz ^{29}Si-NMR spectrum at −40 °C. — (A_2) 59.6-MHz ^{29}Si-NMR spectrum at −40 °C, after warming the reaction solution to 0 °C for 2 min. — (B_1) 111.9-MHz ^{119}Sn-NMR spectrum corresponding to (A_1). — (B_2) 111.9-MHz ^{119}Sn-NMR spectrum corresponding to (A_2)

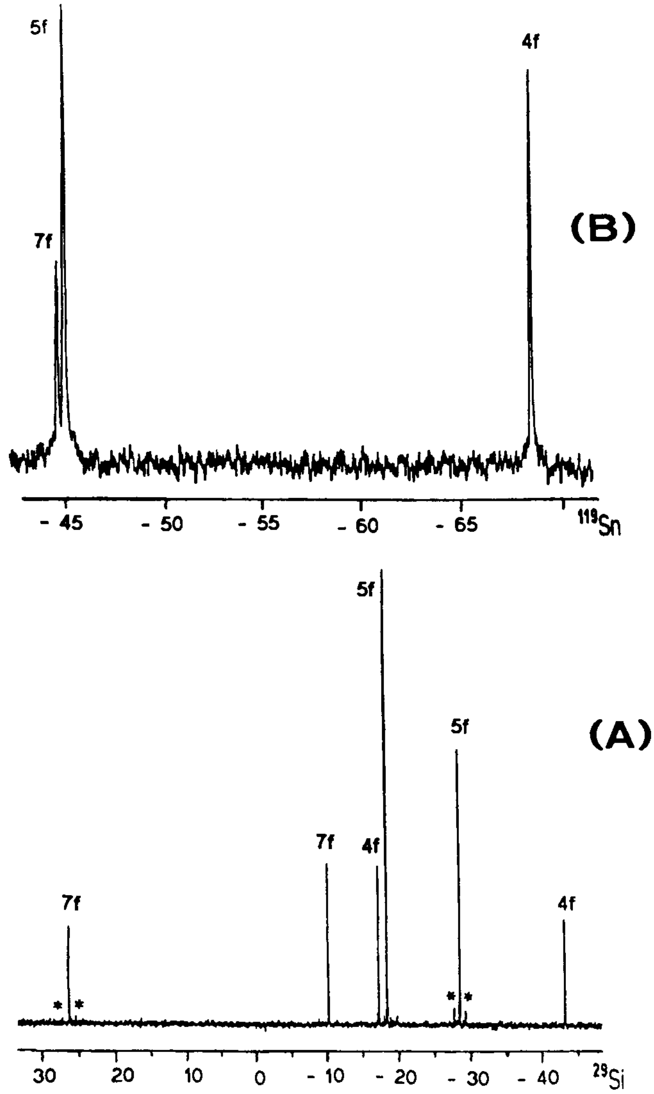
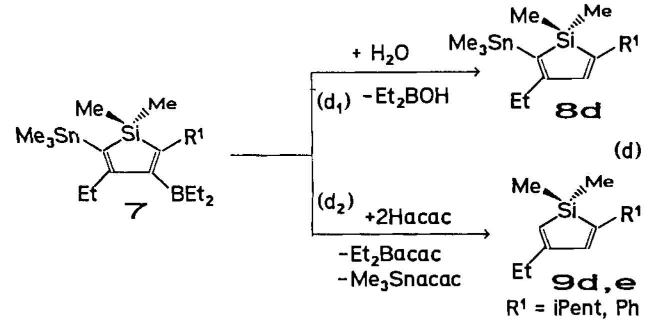
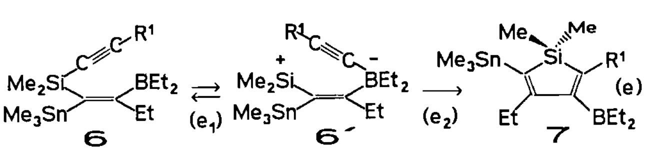


Figure 2. The reaction between the di-1-alkynyldimethylsilane **4f** and Et_3B in CD_2Cl_2, monitored by ^{29}Si- (refocused NEPT pulse sequence with CPD-^1H decoupling) and ^{119}Sn-NMR (inverse gated ^1H decoupling) spectroscopy (δ scale). The alkene derivative **6f** is not detected owing to its low concentration. Obviously, **6f** is much more reactive than **6c** (see Figure 1). – (A) 59.6-MHz ^{29}Si-NMR spectrum at –40°C after warming to 0°C for 2 min; each product is characterized by two ^{29}Si-NMR signals and by $^{117/119}Sn$ satellites according to $^2J(Sn^{29}Si)$ (see **5f**, **7f**). – (B) 111.9-MHz ^{119}Sn-NMR spectrum corresponding to (A)

with an excess of Hacac affords the siloles **9** again in high yield [eq. (d_2)]. These protodeborylations are representative of all siloles **7**.

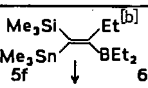
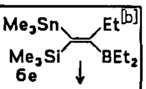


The intermolecular 1,1-ethyloboration [eq. (c_1)] is a reversible reaction[7]. Therefore, the intermediates **5** and **6** are in an equilibrium with each other. The irreversible ring closure [eq. (c_2)] shifts this equilibrium towards **6** and finally towards **7**. Only compound **6** has the proper stereochemistry for rearrangement into the silole **7** by intramolecular 1,1-vinyloboration [eq. (e)].



The mechanism of this process has been demonstrated by the syntheses of stannoles[8] or plumboles[9] and zwitterionic compounds analogous to **6'**, containing a cationic triorganotin[8] or triorganolead fragment[10], have already been isolated and fully characterized. The rearrangement of **6** to **7** is a smooth reaction which takes place between 0°C and ambient temperature. Although it has not been possible to detect **6'**, NMR data (vide infra) suggest an interaction between the boron atom and the $C{\equiv}C{-}R^1$ group in **6**. The comparatively mild reaction conditions required for the intramolecular 1,1-vinyloboration [eq. (c_2), (e)] prove that the harsh conditions used for the synthesis of **1** [eq. (a)] are due to the intermolecular 1,1-ethyloboration. Once the boryl

Table 2. ^{13}C-, ^{29}Si-, and ^{119}Sn-NMR data[a] of the alkenyl(alkynyl)dimethylsilanes **5**, **6** and of two alkenes[b] for comparison

	5b	5c	5e	5f		6b	6c	6e	
Si-C≡	86.5	83.8	96.1	115.7 [11.4]	-	87.5	82.6	94.6	-
R^1-C≡	109.1	115.9	105.9	114.5	-	112.2	117.3	108.2	-
$^{Si}_{Sn}$C=	136.3	135.2 [359.7]	133.8	133.9 [356.4]	138.7	138.1	136.3	136.1	140.3 [304.6]
B-C=	186.2	185.6	187.0	187.0	185.4	185.0	183.5	184.9	181.8
MeSi	3.5	3.0 (53.4) [12.0]	2.4 (53.4) [12.0]	2.5 (53.5) [12.0]	3.0 (50.7) [12.4]	0.9	1.6	1.0	1.6 (50.7) [11.6]
MeSn	-5.0 [318.0]	-5.8 [309.5]	-6.0 [318.8]	-5.5 [316.1]	-5.3 [305.2]	-5.4	-5.7 [314.8]	-6.1	-4.9 [302.7]
R^1	22.5[c]	28.1[d]	123.5[e]	-0.2	-	22.5[f]	28.3[g]	123.0[h]	-
Et-C=	33.3, 14.6	32.5, 14.4	33.3, 14.4	33.0,[i] 14.5[j]	32.1, 14.4	35.9, 15.1	35.0, 14.4	35.6, 14.8	34.8, 14.4
EtB	23.1, 10.0	21.8, 9.4	22.1, 9.5	21.9 9.4	21.7, 9.5	23.1, 11.0	22.0, 10.0	21.0, 10.3	21.7, 9.5
$\delta^{29}Si$	-29.4 [88.5]	-28.8 [89.2]	-27.8 [92.6]	-29.4 [93.0]	-9.6 [93.0]	-21.1	-22.9 [120.6]	-19.8	-7.1 [92.1]
$\delta^{119}Sn$	-47.5	-47.6	-45.1	-45.1	-51.8	-64.3	-64.6	-64.7	-66.4

[a] Compounds **5b** and **6b** in $[D_8]$toluene, **5e** and **6e** in CD_2Cl_2; the concentration of the compounds **6** is always much lower than that of **5**. Coupling constants $J(^{29}Si^{13}C)$ in Hz are given in parentheses, $J(^{119}Sn^{13}C)$ and $J(^{119}Sn^{29}Si)$ in Hz in square brackets. – [b] B. Wrackmeyer, *Polyhedron* **1986**, *11*, 1709–1721. – [c] $\delta^{13}C(R^1)$ = 31.6, 20.7, 14.0. – [d] $\delta^{13}C(R^1)$ = 30.7. – [e] $\delta^{13}C(R^1)$ = 131.9, 128.7, 128.6. – [f] $\delta^{13}C(R^1)$ = 31.6, 20.7, 14.1. – [g] $\delta^{13}C(R^1)$ = 30.2. – [h] $\delta^{13}C(R^1)$ = 132.3, 129.4, 127.5. – [i] $^3J(^{119}Sn^{13}C)$ = 124.3 Hz. – [j] $^4J(^{119}Sn^{13}C)$ = 9.3 Hz.

group is part of the molecule and the stereochemistry is proper, the cleavage of the Si–C≡ bond readily takes place.

NMR Spectroscopic Results

The NMR data of **2** (Table 1) are fully in accord with the values for other alkynylsilanes[11]. Similarly, the expected[11] changes of chemical shifts and coupling constants are induced by the introduction of the ethynyl group (**3**) or the (trimethylstannyl)ethynyl group into **4** (Table 1).

In order to classify differences between NMR data of the intermediates **5** and **6**, the data for the corresponding Me_3Si derivatives are particularly useful (see Table 2). On the basis of these data, nothing unusual can be deduced from the ^{13}C-NMR signals of olefinic and aliphatic carbon atoms in **5** and **6**. Also the fairly large change in the $\delta^{119}Sn$ values appears to be in the normal range. However, the change in the $\delta^{29}Si$ values is more than three times larger between **5** and **6** ($\Delta^{29}Si$ ca. 8 ppm) than expected ($\Delta^{29}Si$ ca. 2.5 ppm for the Me_3Si derivatives). There is also a deshielding of ca. 3 ppm of the alkynyl $^{13}C(R^1)$ nucleus. In the case of **6c**, the value of the geminal coupling constant $|\,^2J(^{119}Sn^{29}Si)\,|$ (120.6 Hz) is $\approx$30 Hz larger than in the case of **5** or in the Me_3Si derivatives. This, together with the ^{29}Si deshielding in **6** as compared to **5**, indicates a weak interaction between the alkynyl group and the boron atom in the *cis*-position. In the zwitterionic tin compounds[8] (analogous to **6′**), the same trend in ^{13}C and ^{119}Sn shielding and in $^2J(^{119}Sn^{29}Si)$ is observed, although the effects are much more pronounced owing to the transfer of the alkynyl group to the boron atom.

The silole ring gives rise to typical ^{13}C resonances of the olefinic carbon atoms. The substituent distribution becomes readily apparent from $\delta^{13}C$ values, ^{29}Si and $^{117/119}Sn$ satellites owing to coupling constants $J(^{29}Si^{13}C)$ and $J(^{119}Sn^{13}C)$, respectively, and from broadened ^{13}C resonances as the result of partially relaxed scalar ^{13}C-^{11}B spin-spin coupling (see Figure 3). In principle, the same criteria can be used for the assignment as for other siloles[3] or stannoles[4,7,8]. Similarly, the structure of the siloles **8** and **9** can be deduced straightforwardly from consistent NMR data. The $\delta^{29}Si$ values of the siloles **7b** to **7e** and **8d** cover only a small range between +11.4 (**8d**) to +14.7 (**7b**, **e**). The $\delta^{29}Si$ value of **8d** (+11.4) shows that the boryl group exerts only a slight influence on the ^{29}Si shielding. However, the presence of an additional Me_3Si group (**7f**: $\delta^{29}Si = +25.9$) leads to deshielding, whereas the absence of the Me_3Sn group (**9d**, **e**: $\delta^{29}Si = +4.5$, $+6.0$) gives rise to increased ^{29}Si nuclear shielding. Similar trends of ^{119}Sn nuclear shielding have been observed in corresponding stannoles[7].

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Experimental

All compounds were handled under N_2 by using carefully dried glassware and solvents. Deuterated solvents were stored under N_2 over molecular sieves. Starting materials such as solutions of butyllithium (1.6 M) in hexane (Aldrich), Me_2SiCl_2 (Merck), and the starting alkynes (Aldrich, Farchan Lab.) were commercial products. (Diethylamino)trimethylstannane[12] and triethylborane[13] were prepared according to literature procedures.

Elemental analyses: Dornis & Kolbe, Mülheim a.d. Ruhr, and Mikroanalytisches Labor Pascher, Remagen. – IR: Perkin-Elmer 983. – MS: EI-MS (70 eV), Varian MAT CH-7 with direct inlet. – $^1H/^{13}C$ NMR: Bruker AC 300 (300.13/75.5 MHz), Jeol JNM-EX 270E (270.67/67.94 MHz), Jeol FX 90Q (89.56/22.50 MHz). – ^{11}B

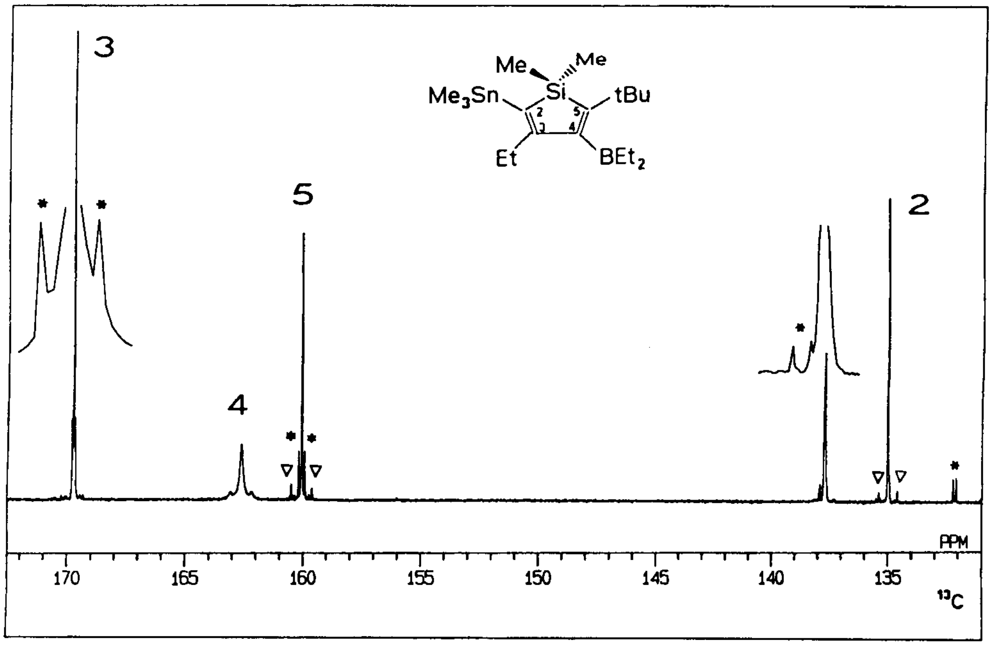

Figure 3. 67.94-MHz $^{13}C\{^1H\}$-NMR spectrum (δ scale) of the silole **7c** (in [D_8]toluene, 26 ± 1 °C) showing the region for olefinic ^{13}C nuclei. The assignments are based on the $^{117/119}Sn$ (*) and ^{29}Si satellites (△) and on the broad ^{13}C-4 NMR signal, indicating the bond to the quadrupolar nuclei $^{10/11}B$

Table 3. ^{13}C-, ^{29}Si-, and ^{119}Sn-NMR data[a] of the 4-(diethylboryl)-2-(trimethylstannyl)siloles **7** and of the deborylated siloles **8** and **9**

	7b	7c	7d	7e	7f	8d	9d	9e
C-2	133.8 (53.9) [405.4]	134.6 (53.4) [402.2]	133.9 (54.5) [406.5]	137.1 (53.4) [392.4]	141.1 (51.8) [383.4]	132.5 (52.8) [410.8]	118.8 (68.5)	121.2 (68.5)
C-3	170.6 [6.6]	169.4 [4.4]	170.7 [6.5]	171.1 [5.0]	169.9 [9.0]	169.4 [3.9]	162.1 (6.0)	162.1 (5.8)
C-4)	166.1	162.3	166.1	168.7	184.0	142.6 (11.7) [80.2]	142.0 (8.8)	141.3 (8.8)
C-5	149.7 (60.0) [20.9]	159.7 (62.1) [18.5]	149.8 (60.5) [20.7]	151.8 (58.6) [20.7]	146.3 (44.0) (63.1) [14.2]	153.9 (59.6) [15.6]	149.9 (60.8)	146.5 (62.1)
MeSi	-3.2 (47.8)	-1.1 (47.4)	-2.8 (48.0)	-3.0 (48.6)	-2.4 (47.4)	-3.7 (48.4)	-4.2 (49.4)	-3.5 (50.4)
MeSn	-8.2 [336.7]	-7.7 [336.2]	-7.9 [336.8]	-8.0 [337.9]	-8.0 [338.4]	-8.2 [338.4]	-	-
R^1-C^5	32.5[c]	32.9 36.9	30.7[d]	142.4[e]	1.6 (50.9)	30.9[g]	30.9[h]	139.4[i]
Et-C^3	33.1 [50.7] 15.0 [9.2]	32.5 [50.1] 16.2 [8.7]	33.3 [50.1] 15.2 [8.7]	33.0 [49.0] 15.4 [8.7]	32.0 [45.8] 15.9 [8.8]	33.0 [49.8] 14.3 [8.8]	29.1 12.2	29.2 12.4
EtB	22..5 9.1	22.4 10.2	22.7 9.3	22.3 9.7	22.7 9.5	- -	- -	- -
δ^{29}Si	+14.7 [106.4]	+13.5 [99.6]	+13.6 [104.0]	+14.7 [99.6]	+25.9[f] [106.2]	+11.4 [93.8]	+4.5	+6.0
δ^{119}Sn	-47.8	-50.8	-50.8	-50.6	-48.7	-50.8	-	-

[a] In C_6D_6 at 26 ± 1 °C (ca. 20–30%); coupling constants $J(^{29}Si^{13}C)$ are given in Hz in parentheses and $J(^{119}Sn^{13}C)$ in Hz in square brackets. – [b] From Ref.[4]; the numbering of the ring carbon atoms has been changed for better comparison with **7**. – [c] $\delta^{13}C(R^1)$ = 33.7, 23.3, 14.1. – [c] $\delta^{13}C(R^1)$ = 40.9, 28.7, 22.9. – [e] $\delta^{13}C(R^1)$ = 128.7, 127.5, 126.2. – [f] $\delta^{29}Si(SiMe_3)$ = –11.1. – [g] $\delta^{13}C(R^1)$ = 39.3, 28.2, 22.7. – [h] $\delta^{13}C(R^1)$ = 39.2, 28.1, 22.6. – [i] $\delta^{13}C(R^1)$ = 129.0 (*m*), 127.1 (*p*), 126.8 (*o*).

NMR: Jeol FX 90Q (28.70 MHz), $Et_2O \cdot BF_3$ as external reference [$\Xi(^{11}B)$ = 32.083791 MHz]. – ^{29}Si/^{119}Sn NMR: Bruker AC 300 (59.60/111.92 MHz), Jeol FX 90Q (17.76/33.34 MHz), $SiMe_4$ and $SnMe_4$ as external references [$\Xi(^{29}Si)$ = 19.867184 MHz; $\Xi(^{119}Sn)$ = 37.290665 MHz].

1-Alkynylchlorosilanes **2**. *General Procedure:* A freshly prepared suspension of 0.2 mol of the respective lithiated alkyne in 200 ml of hexane is added dropwise at room temp. to 73 ml (0.6 mol) of Me_2SiCl_2. The mixture is refluxed for 5 h and filtered. After removal of the solvent and excess Me_2SiCl_2 in vacuo (15 Torr), the residue is purified by fractional distillation to give the pure products in 44–55% yield.

2b: Yield 15.4 g (44%); b.p. 80 °C/15 Torr. – IR (hexane): ν(C≡C) = 2182 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$) = 0.36 (7.2) [s, 6H, $SiMe_2$]; 2.01 [t, 2H, CH_2]; 1.24 [m, 2H, CH_2]; 1.23 [m, 2H, CH_2]; 0.76 [t, 3H, Me].

2c: Yield 19.2 g (55%); b.p. 55 °C/15 Torr. – IR (hexane): ν(C≡C) = 2160 cm^{-1}. – ^{1}H NMR (C_6D): δ ($J(^{29}Si^1H)$) = 0.35 (7.7) [s, 6H, $SiMe_2$]; 1.06 [s, 9H, Me]. – $C_8H_{15}ClSi$ (174.8): calcd. C 54.99, H 8.65; found C 56.84, H 8.95.

2d: Yield 20.4 g (54%); b.p. 87 °C/15 Torr. – IR (hexane): ν(C≡C) = 2182 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$) = 0.36 (7.5) [s, 6H, $SiMe_2$]; 2.01 [t, 2H, CH_2]; 1.22 [m, 2H, CH_2]; 1.50 [m, 1H, CH]; 0.72 [d, 6H, Me].

2e: Yield 19.1 g (49%); b.p. 55 °C/5 · 10^3 Torr. – IR (hexane): ν(C≡C) = 2165 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$) = 0.47 (7.2) [s, 6H, $SiMe_2$]; 6.99 [m, 3H, CH]; 7.38 [m, 2H, CH].

2f: Yield 21.0 g (55%); b.p. 58 °C/15 Torr. – IR (hexane): ν(C≡C) = 2112 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$) = 0.34 (7.7) [s, 6H, $SiMe_2$]; 0.05 (6.8) [s, 9H, $SiMe_3$]. – MS, *m/z* (%): 190 (15) [M$^+$], 175 (100), 97 (10), 93 (8), 73 (5).

1-Alkynylethynylsilanes **3**. – *General Procedure:* 140 mmol of the respective 1-alkynylchlorosilane is added slowly at 5 °C to a freshly prepared solution of 175 mmol of ethinylmagnesium bromide[14] in 1 l of THF. After stirring for 15 h at room temp. the mixture is hydrolyzed by adding a 1 M NH_4Cl solution. After the addition of 100 ml of pentane, the organic layer is separated. The water/THF phase is extracted five times with 30 ml of pentane each. The combined organic layers are then dried with sodium sulfate. After removal of the solvent in vacuo (15 Torr) the residue is purified by fractional distillation to give the pure products in 59–85% yield.

3b: Yield 13.5 g (59%); b.p. 92 °C/15 Torr. – IR (hexane): ν(≡C–H) = 3296; ν(C≡C) = 2181, 2041 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$) = 0.19 (7.5) [s, 6H, $SiMe_2$]; 1.98 [t, 2H, CH_2]; 1.25 [m, 2H, CH_2]; 1.24 [m, 2H, CH_2]; 0.71 [t, 3H, Me]; 2.19 [s, 1H, CH]. – MS, *m/z* (%): 164 (1) [M$^+$], 149 (100), 122 (40), 83 (75), 53 (28), 43 (39). – $C_{10}H_{16}Si$ (164.3): calcd. C 73.09, H 9.81; found C 72.99, H 9.85.

3c: Yield 15.1 g (68%); b.p. 60 °C/15 Torr. – IR (hexane): ν(≡C–H) = 3297; ν(C≡C) = 2160, 2041 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$) = 0.18 (7.7) [s, 6H, $SiMe_2$]; 1.05 [s, 9H, Me]; 2.20 [s, 1H, CH]. – MS, *m/z* (%): 164 (40) [M$^+$], 149 (100), 107 (100), 83 (80), 53 (25), 43 (28). – $C_8H_{15}ClSi$ (164.3): calcd. C 73.09, H 9.81; found C 73.03, H 9.91.

3d: Yield 16.4 g (66%); b.p. 95 °C/15 Torr. – IR (hexane): ν(≡C–H) = 3297; ν(C≡C) = 2181, 2042 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$) = 0.17 (7.7) [s, 6H, $SiMe_2$]; 2.00 [t, 2H, CH_2]; 1.20 [m, 2H, CH_2]; 1.50 [m, 1H, CH]; 0.70 [d, 6H, Me]; 2.21 [s, 1H, CH]. – MS, *m/z* (%): 178 (1) [M$^+$], 163 (80), 122 (40), 83 (100), 53 (18), 43 (20).

3e: Yield 21.9 g (85%); b.p. 115 °C/15 Torr. – IR (hexane): ν(≡C–H) = 3296; ν(C≡C) = 2165, 2042 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$) = 0.29 (7.7) [s, 6H, $SiMe_2$]; 7.00 [m, 3H, CH]; 7.33 [m, 2H, CH]; 2.17 [s, 1H, CH]. – MS, *m/z* (%): 184 (45) [M$^+$], 169 (100), 53 (5), 43 (3).

3f: Yield 18.4 g (73%); b.p. 65 °C/15 Torr. – IR (hexane): ν(≡C–H) = 3294; ν(C≡C) = 2111, 2041 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$) = 0.21 (7.7) [s, 6H, $SiMe_2$]; 0.05 (6.8) [s, 9H, $SiMe_3$]; 2.11 [s, 1H, CH]. – MS, *m/z* (%): 180 (10) [M$^+$], 165 (100), 83 (5), 73 (5).

1-Alkynyl[(trimethylstannyl)ethynyl]silanes **4**. *General Procedure:* 15 mmol of the respective ethynylsilane **3** is added at room temp. to 15 mmol of (diethylamino)trimethylstannane. After stirring the solution for 1 h, volatile materials (diethylamine) are removed in vacuo (5 · 10^{-3} Torr).

4b: Yield 4.7 g (96%). – IR (hexane): ν(C≡C) = 2180, 2042, 2089 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$), [$J(^{119}Sn^1H)$] = 0.19 (7.0) [s, 6H, $SiMe_2$]; 0.06 [60.4] [s, 9H, $SnMe_3$]; 1.95 [t, 2H, CH_2]; 1.22 [m, 2H, CH_2]; 1.23 [m, 2H, CH_2]; 0.68 [t, 3H, Me]. – MS, *m/z* (%): 313 (55) [M$^+$ – CH_2], 271 (15), 165 (100), 135 (22), 133 (28), 120 (8), 57 (16).

4c: Yield 4.6 g (94%). – IR (hexane): ν(C≡C) = 2158, 2042, 2089 cm^{-1}. – ^{1}H NMR (C_6D_6): δ ($J(^{29}Si^1H)$), [$J(^{119}Sn^1H)$] = 0.17 (7.5) [s, 6H, $SiMe_2$]; 0.01 [60.2] [s, 9H, $SnMe_3$]; 1.01 [s, 9H, Me]. – MS, *m/z* (%): 327 (20) [M$^+$], 313 (100), 165 (38), 163 (55), 133 (22), 57

(18), 43 (20). – C$_{13}$H$_{24}$SiSn (327.1): calcd. C 47.73, H 7.40; found C 48.08, H 8.11.

4d: Yield 4.8 g (93%). – IR (hexane): ν(C≡C) = 2180, 2042, 2089 cm^{-1}. – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)), [J(^{119}Sn^{1}H)] = 0.21 (7.4) [s, 6H, SiMe$_2$]; 0.03 [60.4] [s, 9H, SnMe$_3$]; 1.96 [t, 2H, CH$_2$]; 1.17 [m, 2H, CH$_2$]; 1.48 [m, 1H, CH]; 0.67 [d, 6H, Me]. – MS, *m/z* (%): 327 (100) [M$^+$ – Me], 177 (10), 135 (18), 43 (8).

4e: Yield 5.1 g (98%); m.p. 67°C. – IR (hexane): ν(C≡C) = 2164, 2043, 2090 cm^{-1}. – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)), [J(^{119}Sn^{1}H)] = 0.42 (7.2) [s, 6H, SiMe$_2$]; 0.07 [60.6] [s, 9H, SnMe$_3$]; 6.94 [m, 3H, CH]; 7.38 [m, 2H, CH]. – MS, *m/z* (%): 347 (8) [M$^+$], 333 (100), 303 (15), 183 (35), 159 (10). – C$_{17}$H$_{20}$SiSn (347.1): calcd. C 51.90, H 5.81; found C 52.19, H 5.91.

4f: Yield 4.9 g (96%); m.p. 40°C. – IR (hexane): ν(C≡C) = 2110, 2043, 2089 cm^{-1}. – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)), [J(^{119}Sn^{1}H)] = 0.22 (6.8) [s, 6H, SiMe$_2$]; 0.00 [59.8] [s, 9H, SnMe$_3$]; –0.01 (6.8) [s, 9H, SiMe$_3$]. – MS, *m/z* (%): 344 (1) [M$^+$], 329 (100), 299 (25), 179 (25), 165 (100), 135 (30), 97 (15), 73 (20), 43 (20).

4-(Diethylboryl)-2-(trimethylstannyl)siloles **7**. *General Procedure:* At –78°C 80 mmol of BEt$_3$, is added to a solution of 20 mmol of the respective [(trimethylstannyl)ethinyl]silane **4** in 20 ml of toluene. After stirring the solution for 1 h at room temp., the solvent and excess BEt$_3$ is removed in vacuo (5 · 10^{-3} Torr). Attempts at distillation of the compounds **7** lead mainly to decomposition (> 70°C/10^{-3} Torr).

7b: Yield 8.5 g (100%). – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)), [J(^{119}Sn^{1}H)] = 0.21 (6.6) [s, 6H, SiMe$_2$]; 0.21 [53.4] [s, 9H, SnMe$_3$]; 2.11 [t, 2H, CH$_2$]; 1.38 [m, 2H, CH$_2$]; 1.15 [m, 2H, CH$_2$]; 0.89 [t, 3H, Me]; 2.14 [q, 2H, Et]; 0.94 [t, 3H, Et]; 1.31 [q, 4H, BEt]; 1.01 [t, 6H, BEt]. – MS, *m/z* (%): 426 (10) [M$^+$], 411 (100), 369 (10), 261 (5), 165 (12), 135 (8).

7c: Yield 8.5 g (100%). – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)), [J(^{119}Sn^{1}H)] = 0.20 (6.4) [s, 6H, SiMe$_2$]; 0.13 [53.1] [s, 9H, SnMe$_3$]; 1.00 [s, 9H, Me]; 1.93 [q, 2H, Et]; 0.93 [t, 3H, Et]; 1.36 [q, 4H, BEt]; 0.98 [t, 6H, BEt]. – MS, *m/z* (%): 426 (20) [M$^+$], 411 (100), 261 (16), 165 (10), 135 (8), 41 (8). – C$_{19}$H$_{39}$BSiSn (425.1): calcd. C 53.68, H 9.25; found C 52.99, H 9.48.

7d: Yield 8.8 g (100%). – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)), [J(^{119}Sn^{1}H)] = 0.14 (6.4) [s, 6H, SiMe$_2$]; 0.13 [53.4] [s, 9H, SnMe$_3$]; 2.00 [t, 2H, CH$_2$]; 1.27 [m, 2H, CH$_2$]; 1.46 [m, 1H, CH]; 0.82 [d, 6H, Me]; 2.08 [q, 2H, Et]; 0.89 [t, 3H, Et]; 1.31 [q, 4H, BEt]; 0.94 [t, 6H, BEt]. – MS, *m/z* (%): 440 (20) [M$^+$], 425 (100), 371 (5), 165 (15), 135 (10), 43 (5), 41 (10). – C$_{20}$H$_{41}$BSiSn (439.1): calcd. C 54.70, H 9.41; found C 54.43, H 9.56.

7e: Yield 8.9 g (100%). – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)), [J(^{119}Sn^{1}H)] = 0.31 (6.4) [s, 6H, SiMe$_2$]; 0.26 [53.4] [s, 9H, SnMe$_3$]; 6.99 [m, 3H, CH]; 7.11 [m, 2H, CH]; 2.25 [q, 2H, Et]; 0.96 [t, 3H, Et]; 1.37 [q, 4H, BEt]; 0.97 [t, 6H, BEt]. – MS, *m/z* (%): 446 (25) [M$^+$], 431 (100), 377 (4), 165 (8), 135 (6), 41 (4). – C$_{21}$H$_{35}$BSiSn (445.1): calcd. C 56.67, H 7.93; found C 56.48, H 8.15.

7f: Yield 8.7 g (100%). – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)), [J(^{119}Sn^{1}H)] = 0.23 (6.7) [s, 6H, SiMe$_2$]; 0.20 [53.0] [s, 9H, SnMe$_3$]; 0.09 (6.7) [s, 9H, SiMe$_3$]; 2.11 [q, 2H, Et]; 0.93 [t, 3H, Et]; 1.36 [q, 4H, BEt]; 0.99 [t, 6H, BEt].

Protodeborylation of **7d** *with an Excess of Water:* 140 mmol of H$_2$O is added to a solution of 9.2 mmol of **7d** in 50 ml of hexane. After stirring the mixture at 60°C for 15 h the organic layer is separated and dried with sodium sulfate. The solvent is removed in vacuo (15 Torr). The obtained residue is the pure product **8d** (93% yield). Attempts at distillation of compound **8d** lead to decomposition (> 70°C/10^{-3} Torr). – Yield 3.2 g (93%). – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)), [J(^{119}Sn^{1}H)] = 0.20 (6.4) [s, 6H, SiMe$_2$]; 0.22 [53.9] [s, 9H, SnMe$_3$]; 2.37 [t, 2H, CH$_2$]; 1.36 [m, 2H, CH$_2$]; 1.62 [m, 1H, CH]; 0.99 [d, 6H, Me]; 2.24 [q, 2H, Et]; 1.03 [t, 3H, Et]; 6.51 [15.4] [s, 1H, CH]. – MS, *m/z* (%): 373 (15) [M$^+$], 357 (30), 331 (20), 329 (25), 299 (20), 165 (100), 135 (25), 57 (40), 43 (40).

Protodeborylation of **7d** *and* **7e** *with an Excess of Hacac: General Procedure:* 35 mmol of Hacac is added to a solution of 7 mmol of the respective silole **7** in 50 ml of hexane. After stirring at room temp. for 6 d the mixture is poured into water. The product is separated with the organic layer from the water-soluble byproducts. The organic layer is dried with Na$_2$SO$_4$. After removed of the solvent in vacuo (15 Torr) fractional distillation of the residue gives the pure products **9** in 85–90% yield.

9d: Yield 1.2 g (85%), b.p. 30°C/5 · 10^{-3} Torr. – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)) = 0.21 (7.0) [s, 6H, SiMe$_2$]; 2.33 [t, 2H, CH$_2$]; 1.38 [m, 2H, CH$_2$]; 1.53 [m, 1H, CH]; 0.89 [d, 6H, Me]; 2.18 [q, 2H, Et]; 1.06 [t, 3H, Et]; 5.57 [s, 1H, SiCH=]; 6.41 [s, 1H, CH=]. – C$_{13}$H$_{24}$Si (208.4): calcd. C 74.92, H 11.61; found C 74.74, H11.48.

9e: Yield 1.4 g (90%), b.p. 50°C/5 · 10^{-3} Torr. – ^{1}H NMR (C$_6$D$_6$): δ (J(^{29}Si^{1}H)) = 0.10 (6.8) [s, 6H, SiMe$_2$]; 7.00 [m, 3H, Ph]; 7.21 [m, 2H, Ph]; 2.03 [q, 2H, Et]; 0.88 [t, 3H, Et]; 5.49 [s, 1H, SiCH=]; 6.77 [s, 1H, CH=].

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