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1,6-Dihydro-1,6-disilapentalene derivatives by 1,1-organoboration of triynes

Dedicated to: Professor Peter Jutzi on the occasion of his 60th birthday.

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Abstract

The triynes $R^1C{\equiv}C{-}SiMe_2{-}C{\equiv}C{-}SiMe_2{-}C{\equiv}CR^1$ [$R^1 = H$ (**3**), $SiMe_3$ (**4**) $SnMe_3$ (**5**)] were prepared, and their reactivity towards triorganoboranes R_3B **6** [R = Et (**a**), CH_2Ph (**b**), Ph (**c**), 2-thienyl (**d**)] was studied. In the case of **3**, decomposition was observed whereas the reaction of **4** and **5** with **6** affords the 1,6-dihydro-1,6-disilapentalene derivatives **7a**–**d** (from **4**) and **9a**, **c** (from **5**) in almost quantitative yield. This is the result of stereo- and regioselective intermolecular 1,1-organoboration in the first step of the reaction, followed by two consecutive intramolecular 1,1-vinylborations. The products were characterised by their ^1H-, ^{11}B-, ^{13}C-, ^{29}Si- and ^{119}Sn-NMR data. © 1998 Elsevier Science S.A. All rights reserved.

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

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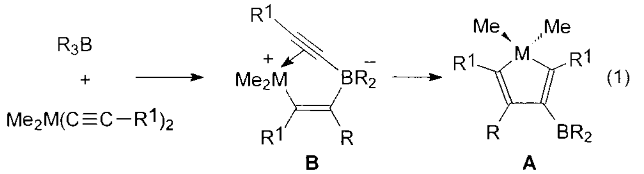
1. Introduction

Metalloles are attractive compounds for both organometallic and organic syntheses [1]. We have shown that numerous siloles [2], germoles [3], stannoles [4] or plumboles [5] of type **A** can be prepared by 1,1-organoboration [6] of diynes, in which the C≡C bonds are separated by Me_2M moieties (M = Si, Ge, Sn, Pb) as shown in Eq. (1).



In the case of M = Sn [7] and Pb [8], the crucial zwitterionic intermediates of type **B** have been isolated and fully characterised. We have now started to study the reactivity of cyclic and non-cyclic polyynes, with C≡C bonds separated by Me_2Si moieties, towards various triorganoboranes. The corresponding tin and lead compounds would also be of interest; however, these are much less stable owing to exchange reactions at the M−C≡ bonds. In this work, we report on the synthesis of the triynes **3-5** (Scheme 1) and their reactivity towards the triorganoboranes R_3B **6** [R = Et (**a**), CH_2Ph (**b**), Ph (**c**), 2-thienyl (**d**)].

2. Results and discussion

2.1. Synthesis of the triynes 3–5

Scheme 1 summarises the most convenient route to the triynes **3**–**5**. At first, bis(dimethylsilyl)ethyne **1** is

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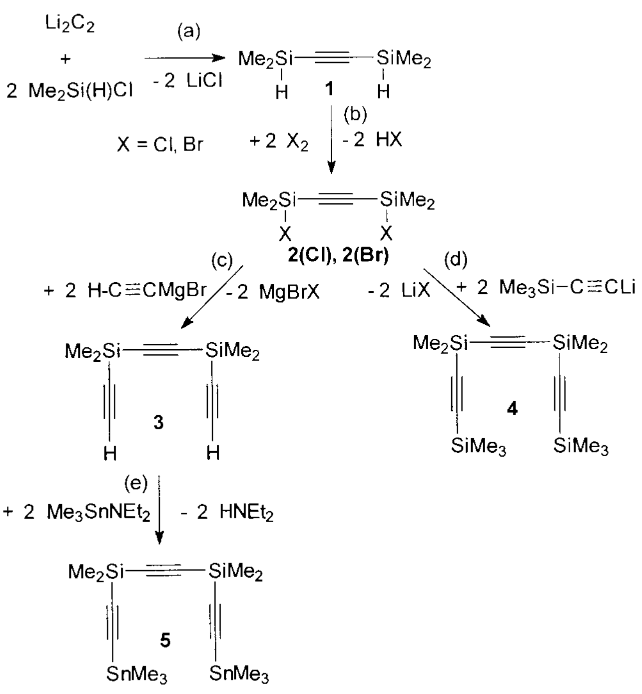
prepared [9] (step a) which is then treated with bromine to give **2** (step b). The reaction of **2** either with ethynyl magnesium bromide or trimethylsilylethynyl lithium leads to **3** (step c) and **4** (step d), respectively. As usual for terminal alkynes [10], the reaction of **3** with two equivalents of trimethyltin diethylamide affords **5** in almost quantitative yield. All compounds **1**–**5** are stable for years when kept under N_2 or Ar in the refrigerator.

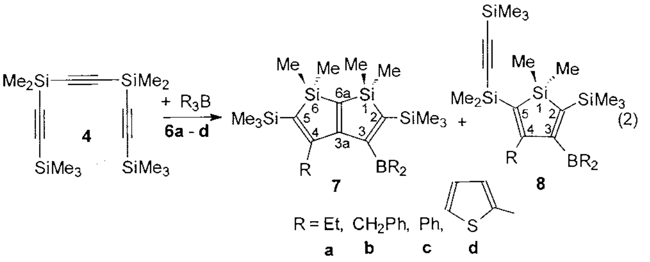


Scheme 1.

2.2. 1,1-Organoboration of the triynes 3–5

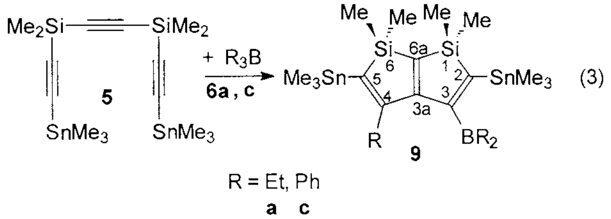
There was no reaction of **3** with R_3B **6a**–**d** at r.t. or in boiling hexane. The reaction started in boiling toluene, leading to a complex mixture of compounds which could not be identified so far. This is reminiscent of the reaction of $Me_2Si(C{\equiv}CH)_2$ with **6a** where the primarily formed silole is trapped, under the reaction conditions (boiling triethylborane; ca. 100°C), by various Diels–Alder cycloadditions [11].

The reaction of **4** with **6a**–**d** started also in boiling toluene and was complete after 48 h. The mixtures of products consist to more than 85% of the 1,6-dihydro-1,5-disilapentalene derivatives **7a**–**d** and less than 15% of the silole derivatives **8a**–**d**, Eq. 2, as shown by repeated experiments.



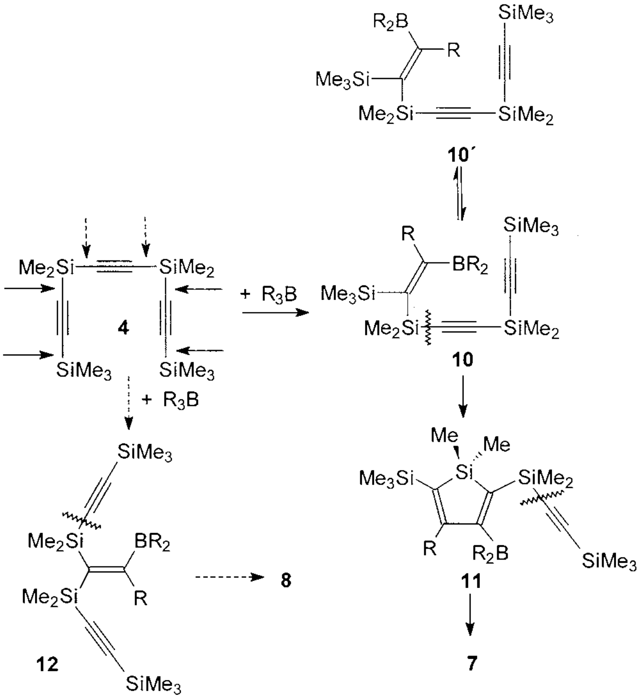
(2)

In contrast, the analogous reaction of **5** with **6a**,**c** starts already below room temperature and is complete after 1 h at r.t.. It leads selectively to the 1,5-dihydro-1,5-disilapentalene derivatives **9a**,**c** (Eq. 3).

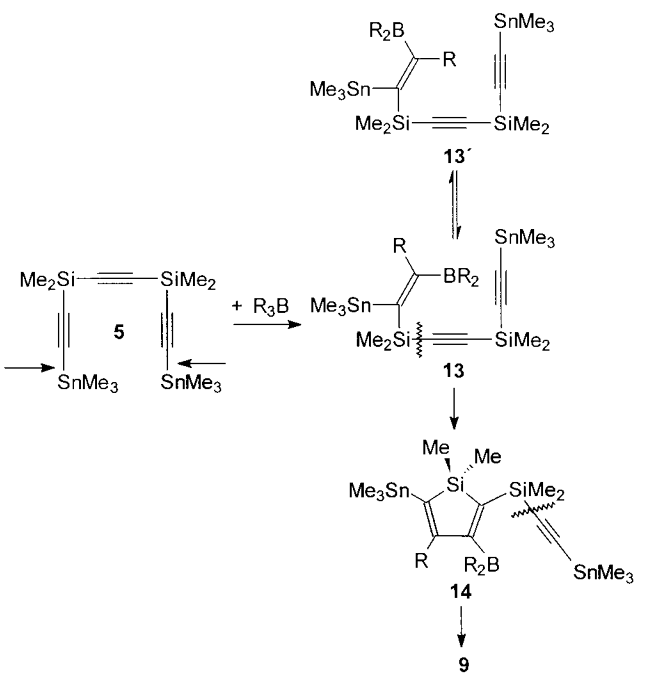


(3)

The reaction mechanism of 1,1-organoboration is well established [6]. In Scheme 2 it is shown that the intermolecular 1,1-organoboration can start with the cleavage of the Si–C≡ bonds in **4** in several places. Cleavage of the Si–C≡ bonds indicated by drawn arrows leads to intermediates **10**, **10′**, and **11**, of which the latter finally rearranges to the major product **7**. The equilibrium between **10** and **10′** (as the result of 1,1-deorganoboration and 1,1-organoboration) is important, since **10′** cannot undergo further intramolecular 1,1-organoboration reactions. The alternative attack of R_3B at Si–C≡ bonds marked by broken arrows leads to the siloles **8** via the intermediates **12**. This route corresponds closely to that described previously [2] for the



Scheme 2.



Scheme 3.

synthesis of siloles by 1,1-organoboration. It is evident from the product distribution **7**/**8** > 4/1 that the cleavage of the Si–C≡ bonds marked by drawn arrows is preferred not only for statistical reasons (2/1).

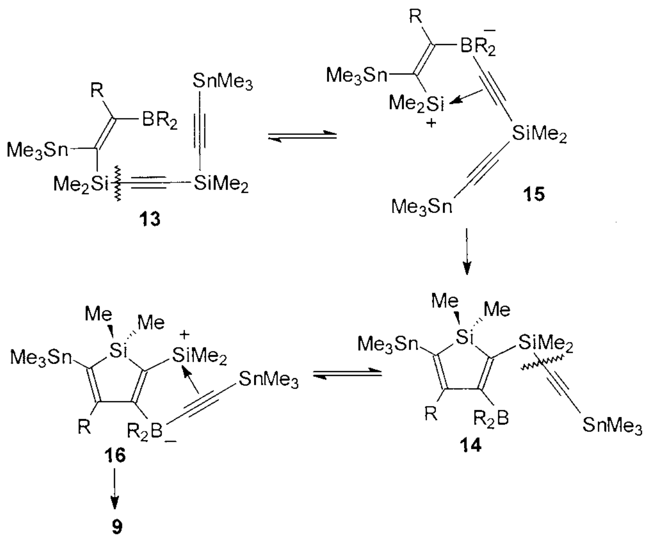
In the case of **5**, the greater reactivity of the Sn–C≡ bond, as compared with the Si–C≡ bond, controls the course of the reaction. This corresponds to the results of 1,1-organoboration of diynes of the type $Me_2Si(C{\equiv}CSnMe_3)C{\equiv}CR^1$) ($R^1$ = alkyl, aryl, etc.) [12]. It is shown in Scheme 3 that the intermolecular 1,1-organoboration starts exclusively by attack at one of the Sn–C≡ bonds (drawn arrows) leading to the intermediates **13** and **13′** which are in equilibrium with each other (in the same way as **10** and **10′**). Two consecutive intramolecular 1,1-vinyloborations lead selectively, via the silole **14**, to the 1,6-dihydro-1,6-disilapentalenes **9**.

The structures of the final products leave no doubt about the intermediacy of zwitterionic species such as **15** (analogous to **B**) shown in Scheme 4, the immediate precursor to **14**, which rearranges to **9** via a similar intermediate **16**. However, the lifetime of these species, in which a formally positively charged tri-coordinate silicon atom is stabilised by side-on coordination to the C≡C bond, is too short, in contrast with similar zwitterionic tin and lead derivatives [7,8]

2.3. NMR-Spectroscopic results

The NMR data of the 1-alkynylsilanes **1**–**5** are given in the Section 3. The structures of the 1,6-dihydro-1,6-disilapentalene derivatives **7a**–**d** and **9a**,**c** are proposed on the consistent set of ^1H (Section 3), ^{13}C-, ^{29}Si- and ^{119}Sn-NMR data (Table 1). This is also true for the siloles **8a**–**d** (Table 2) which are formed as minor products, and for which comparable sets of NMR data already exist [2]. The ^{11}B chemical shifts of the compounds **7**–**9** (footnote 'b' in Tables 1 and 2) are not particularly diagnostic, except for the fact that the data are in agreement with boron atoms in trigonal planar surroundings, typical of triorganoboranes [13].

^{29}Si-NMR (Fig. 1), and in the case of the reactions of **5**, also ^{119}Sn-NMR spectroscopy proved extremely valuable for monitoring the progress of the reactions. As can be seen from the data in the Tables 1 and 2, the formation of the new products is readily evident, since there is no overlap with NMR signals of the starting materials. There is little variation of the $\delta^{29}Si$ values of **7** and **9**. The ^{29}Si shielding is markedly increased with respect to corresponding siloles (see Table 2), and the $^{29}Si(1)$ nuclear shielding in the boryl-substituted ring is 8–9 ppm less than that of $^{29}Si(6)$. Further evidence of the ring formation comes from the observation of satellites due to geminal coupling constants $^2J(^{29}Si,^{29}Si)$ or $^2J(^{119}Sn,^{29}Si)$. The $^{29}Si(1)$-NMR signal is broader than that of Si(6) which is caused by unresolved $^{29}Si(1)-^{11}B$ coupling across three bonds. This effect is much more pronounced in the case of ^{119}Sn-NMR signals as shown for **9a** in Fig. 1. The assignment of the ^{119}Sn-NMR signals is straightforward because of the different line widths. The broader line belongs to the 2-$SnMe_3$ group because of a partially relaxed $^{119}Sn-^{11}B$ coupling [$|^3J(^{119}Sn,^{11}B)|$ 50–60 Hz], as the result of scalar relaxation of the second kind [14,15]. The broadening is much smaller or negligible for the ^{119}Sn-NMR signal of the 5-$SnMe_3$ group [$|^5J(^{119}Sn,^{11}B)| < 10$ Hz]. Compound **9a** is also a good example for coupling across conjugated π systems, considering the magnitude of $|^6J(^{119}Sn,^{119}Sn)| = 56.0$ Hz (Fig. 2).



Scheme 4.

Table 1
^{13}C-, ^{29}Si- and ^{119}Sn-NMR data[a, b] of the 1,6-dihydro-1,6-disilapentalene derivatives **7a**–**d** and **9a**, **c**

	δ^{13}C						δ^{29}Si				δ^{119}Sn	
	=C(2)	=C(3)	=C(3a)	=C(4)	=C(5)	=C(6a)	Si(1)	2-Si	5-Si	Si(6)	2-Sn	5-Sn
7a[c]	148.8 (43.9) (62.0)	180.0 br.	180.0 (n.o.)	168.6 (9.6)	144.7 (46.7) (62.9)	149.5 (58.2) (58.2)	19.0 (8.7) (14.0)	−11.8 (8.7)	−10.9 (8.7)	11.8 (8.7) (14.0)		
7b[d]	151.1 (42.8) (61.7)	178.1 br.	180.5 (7.7) (9.8) (11.2)	162.5 (3.9) (9.8)	148.7 (47.0) (61.0)	148.2 (56.8) (58.6)	19.4 (9.5) (13.8)	−12.1 (9.5)	−11.0 (8.0)	11.7 (8.0) (13.8)		
7c[e]	156.7 (43.7) (60.9)	179.2 br.	180.3 (n.o.)	166.9 (n.o.)	151.4 (45.4) (60.9)	148.6 (57.4) (57.4)	17.8 (9.5) (13.6)	−11.4 (9.5)	−10.3 (8.2)	10.9 (8.2) (13.6)		
7d[f]	158.8 (42.1) (61.0)	174.8 br.	180.9 (n.o.)	157.8 (n.m.)	157.7 (44.6) (59.9)	147.7 (56.6) (57.8)	18.1 (9.7) (13.8)	−10.3 (9.7)	−9.9 (7.8)	10.9 (7.8) (13.8)		
9a[g]	149.0 [380.2] [9.4] (44.4)	181.0 br.	178.7 [85.2]	168.0 [2.2]	147.4 [378.5] [9.4] (49.1)	148.2 [10.8] [7.6] (57.0) (59.0)	19.3 [98.6] [9.6]			10.9 [83.2] [14.6]	−56.6 [56.0]	−53.3 [56.0]
9c[h]	160.9 [378.0] [8.5] (43.0)	179.3 br.	179.3 [n.m.]	167.5 [n.m.]	155.1 [378.7] [8.9] (46.8)	147.9 [11.4] [7.8] (68.6) (77.8)	18.3 [95.8] [1.8]			10.6 [82.5] [0.8]	−59.5 [n.o.]	−51.9 [n.o.]

[a] 15–40% (v/v) at 25°C in [D8]toluene; $^{n}J(^{29}\text{Si}, ^{13}\text{C})$ in Hz (± 0.5 Hz) are given in parentheses; $^{n}J(^{119}\text{Sn}, \text{X})$ ($\text{X} = {}^{29}\text{Si}, {}^{13}\text{C}$) in Hz ($\pm 0.5$ Hz) are given in brackets; br., broad resonances due to $^{1}J(^{13}\text{C}, ^{11}\text{B})$; n.o., not observed; n.m., not measured; {br}, broad resonaces due to dynamic effects.

[b] $\delta^{11}\text{B(BEt}_2) = 87 \pm 1$; $\delta^{11}\text{B[B(CH}_2\text{Ph)}_2] = 83 \pm 2$; $\delta^{11}\text{B(BPh}_2) = 71.0 \pm 2$; δ^{11}B[B(2-thienyl)2] = 60 ± 2.

[c] δ^{13}C (**7a**) = 29.6, 16.7 (Et); 22.0 br., 9.8 (BEt$_2$); 2.2 (50.5), 1.6 (51.5) ((Me$_3$Si(2,5)); −2.5 (48.6) (Me$_2$Si(1)); −3.0 (48.6) (Me$_2$Si(6)).

[d] δ^{13}C (**7b**) = 140.7, 128.7, 128.6, 126.5, 42.2 (Ph–CH$_2$); 140.6, 129.1, 128.1, 124.7, 38.3 br. (B(Ph–CH$_2$)$_2$); 2.5 (Me$_3$Si(2)); 0.7 ((Me$_3$Si(5)); −3.1 (Me$_2$Si(1)); −3.5 (Me$_2$Si(6)).

[e] δ^{13}C (**7c**) = 141.0 br., 138.7, 131.2, 127.2 (BPh$_2$); 141.9, 130.5, 127.6, 127.2 (Ph), 1.7 (51.7) (Me$_3$Si(2)); 0.7 (51.3) ((Me$_3$Si(5)); −2.7 (Me$_2$Si(1)); −3.3 (Me$_2$Si(6)).

[f] δ^{13}C (**7d**) = n.o., 146.1 {br}, 135.6 {br}, 128.0 {br} (B(2-thienyl)); 143.0 {br}, 140.9 {br}, 135.7 {br}, 128.4 {br} (B(2-thienyl)); 142.8, 130.0, 127.0, 125.8 (C(3)(2-thienyl)); 1.7 (51.7) (Me$_3$Si(5)); 0.6 (52.1) ((Me$_3$Si(2)); −2.6 (49.2) {br} (Me$_2$Si(1)); −3.1/−3.5 {br} (Me$_2$Si(6)).

[g] δ^{13}C (**9a**) = 31.1 [44.8], 16.5 [8.6] (Et); 21.6 br., 9.6 (BEt$_2$); −3.3 [2.2] (48.8), −3.6 [2.2] (48.8) (Me$_2$Si(1,6)); −7.5 [332.6], −8.1 [333.4] (Me$_3$Sn(2,5)).

[h] δ^{13}C (**9c**) = 141.8 br., 138.6, 131.2, 127.3 (BPh$_2$); 144.1 [35.9], 129.3, 128.3, 127.1 (Ph); −3.3 [2.9] (n.o.) (Me$_2$Si(6)); −3.8 [2.0] (40.7) (Me$_2$Si(1)); −7.5 [336.9], −8.4 [343.8] (Me$_3$Sn(2,5)).

Table 2
^{13}C- and ^{29}Si-NMR data[a,b] of the silole derivatives **8a–d**

	δ^{13}C				δ^{29}Si			
	=C(2)	=C(3)	=C(4)	=C(5)	Si(1)	2-Si	5-Si	SiMe$_3$
8a[c]	147.5 (n.m.)	179.2 br.	171.6 (n.o.)	133.6 (n.m.)	28.2	−11.4	−30.9	−19.5
8b[d]	151.0 (43.9) (61.7)	182.5 br.	167.0 (n.o.)	138.6 (n.m.)	27.7	−11.2	−30.6	−19.4
8c[e]	155.1 (n.m.)	181.5 br.	171.4 (n.o.)	(n.m.)	29.5	−9.8	−29.6	−19.5
8d[f]	155.8 (n.m.)	179.0 br.	163.0 (n.o.)	144.5 (n.m.)	28.3	−9.4	−29.7	−19.5

[a] 15–40% (v/v) at 25°C in [D8] toluene; $^{n}J(^{29}\mathrm{Si},^{13}\mathrm{C})$ in Hz (± 0.5 Hz) are given in parentheses; br., broad resonances due to $^{1}J(^{13}\mathrm{C},^{11}\mathrm{B})$; n.o., not observed; n.m., not measured; n.a., not assigned.

[b] $\delta^{11}\mathrm{B}(\mathrm{BEt_2}) = 87 \pm 1$; $\delta^{11}\mathrm{B}[\mathrm{B(CH_2Ph)_2}] = 83 \pm 2$; $\delta^{11}\mathrm{B}(\mathrm{BPh_2}) = 71.0 \pm 2$ δ^{11}B[B(2-thienyl)$_2$] $= 60 \pm 2$.

[c] δ^{13}C(**8a**) = 114.5, 113.9 (C≡C); 29.8, 15.1 (Et); 22.4 br., 9.2 (BEt$_2$);. −0.1 (SiMe$_3$); −1.8 (MeSi(1)).

[d] δ^{13}C(**8b**) = 140.4, 129.2, 128.2, 124.9, 39.4 br. (B(Ph–CH$_2$)$_2$); 138.8, 129.4, 128.3, 126.9, 42.3 (Ph–CH$_2$); 114.6, 114.1 (C≡C); 2.0 (2-SiMe); 0.8 (5-SiMe). −0.3 (SiMe$_3$); −2.6 (MeSi(1)).

[e] δ^{13}C(**8c**) = 144.2, n.a.(Ph); 141.9 br., 138.1, 131.6, 127.7 (BPh$_2$); 115.2, 114.3 (C≡C); 2.0 (2-SiMe); 0.8 (5-SiMe). −0.3 (SiMe$_3$); −2.6 (MeSi(1)).

[f] δ^{13}C(**8d**) = 144.7 br., 141.8, 136.5, 129.0 (B(2-thienyl)); 144.7 br., 141.7, 137.1, 128.9 (B(2-thienyl)); 144.8, 127.3, 126.0, 124.7 (2-thienyl); 115.0, 114.5 (CC); 1.4 (5-SiMe); 0.9 (2-SiMe). −0.1 (55.4) (SiMe$_3$); −2.0 (MeSi(1)).

Broad ^{13}C-NMR signals owing to partially relaxed ^{13}C–^{11}B coupling across one bond help to assign the ^{13}C-NMR spectra, together with ^{29}Si and $^{119/117}$Sn satellites (in **9**). A typical example taking advantage of ^{13}C–Si–C–^{1}H coupling is shown in Fig. 3. Further assignments are based on 2D ^{1}H/^{1}H COSY and 2D ^{13}C/^{1}H heteronuclear shift correlations, based either on $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ and $^{n}J(^{13}\mathrm{C},^{1}\mathrm{H})$ ($n > 1$).

2.4. Conclusions

1,1-Organoboration of polyynes appears to be a promising method for the synthesis of novel fused heterocyclic compounds, as shown here in the case of triynes for the first time. The 1,6-dihydro-1,6-disilapentalene derivatives should be useful in further transformations. Their synthesis can be improved and the substitution pattern can be modified by developing stepwise procedures, taking advantage of the results presented in this work.

3. Experimental

All compounds were handled in an atmosphere of dry argon, and carefully dried solvents were used for syntheses and preparation of the samples for NMR measurements. Starting materials were either used as commercial products without further purification (Me$_2$Si(H)Cl, *n*-butyl lithium 1.6 M in hexane, Et$_3$B) or prepared as described (HC≡CMgBr in THF [16], Ph$_3$B [17], tri(2-thienyl)borane [18]). 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 [19] based on $^{2}J(^{29}\mathrm{Si},^{1}\mathrm{H}) = 7$ Hz), ^{119}Sn-NMR (inverse gated ^{1}H decoupled or by refocused INEPT [19] based on $^{2}J(^{119}\mathrm{Sn},^{1}\mathrm{H}) = 50–60$ Hz)]. Chemical shifts are given with respect to Me$_4$Si [δ^{1}H (CHCl$_3$/CDCl$_3$) = 7.24, (C$_6$D$_5$H) = 7.14, (C$_6$D$_5$CD$_2$H) = 2.03; δ^{13}C (CDCl$_3$) = 77.0, (C$_6$D$_6$) = 128.0, (C$_6$D$_5$*C*D$_3$) = 20.4; δ^{29}Si = 0 for $\Xi(^{29}\mathrm{Si}) = 19.867184$ MHz], BF$_3$OEt$_2$ [δ^{11}B = 0; $\Xi(^{11}\mathrm{B}) = 32.083971$ MHz], and Me$_4$Sn [δ^{119}Sn = 0 for Ξ (^{119}Sn) = 37.290665 MHz].

3.1. Bis(dimethylsilyl)ethyne ***1***

A slow stream of acetylene was bubbled into a solution of *n*-BuLi in hexane (250 ml, 1.6 M) at r.t. for 1 h. The excess of acetylene was removed from the white suspension thus formed by heating at reflux for 15 min. Then the suspension was cooled to 0°C, and Me$_2$SiHCl (50 g, 530 mmol) was added dropwise during 1 h. The reaction mixture was heated at 70°C for 12 h, and insoluble material was filtered off. Fractional distillation gave 10.4 g (37%) of the product **1** as a colourless liquid (b.p. 95°C /760 Torr). ^{1}H-NMR (C$_6$D$_6$): δ^{1}H ($^{n}J(^{29}\mathrm{Si},^{1}\mathrm{H})$) {$^{n}J(^{1}\mathrm{H},^{1}\mathrm{H})$} = 0.09 (7.3) {3.8} d, 12H, Me$_2$Si, 4.24 (202.5) {3.8} sept, 2H, HSi; ^{13}C-NMR (C$_6$D$_6$): δ^{13}C ($J(^{29}\mathrm{Si},^{13}\mathrm{C})$) = −3.2 (56.1) Me$_2$Si, 112.8 (78.8, 12.6); ^{29}Si-NMR (C$_6$D$_6$): δ^{29}Si = −38.4.

3.2. Bis(bromodimethylsilyl)ethyne ***2(Br)***

A solution of Br$_2$ (19.36 g, 6.20 ml, 122.53 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added dropwise to a cooled

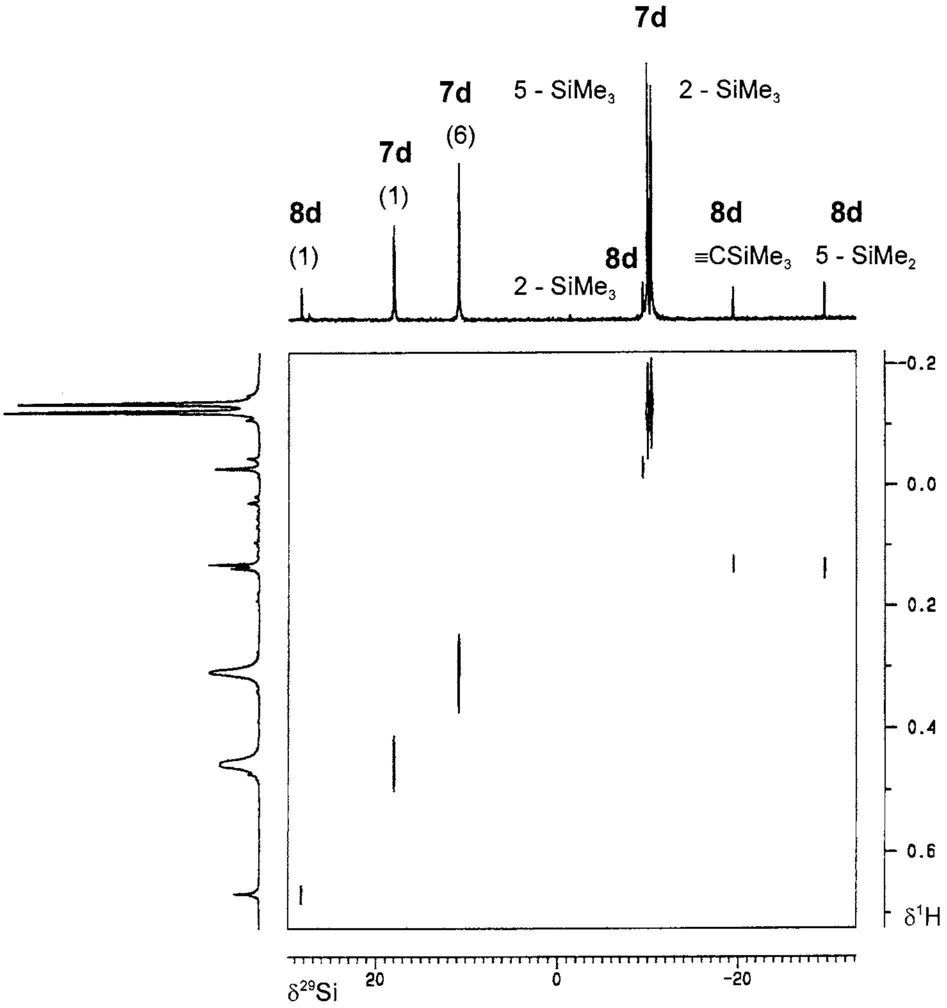


Fig. 1. Contourplot of the 49.7 MHz 2D ^{29}Si/^{1}H heteronuclear shift correlation of the reaction mixture containing **7d** and **8d**. The assignment of the ^{29}Si-NMR signals is indicated. The broad ^{1}H(SiMe$_2$) resonances are due to hindered rotation about the C(3)–B bond.

(10°C) solution of compound **1** (8.70 g, 61.26 mmol) in CH_2Cl_2 (50 ml) until colour of Br_2 did not disappear. The reaction mixture was allowed to reach r.t. and stirring was continued for 1 h. After removing of all volatile material at 25°C/15 Torr an oily liquid was left. Fractional distillation of this oil gave 11.55 g (63.5%) of **2(Br)** (b.p. 100°C/15 Torr) as a colourless liquid which solidifies after some time. ^{1}H-NMR (C6D6): δ^{1}H ($^{n}J(^{29}Si,^{1}H)$) = 0.46 (7.3) s, Me$_2$Si); ^{13}C-NMR (C_6D_6): δ^{13}C ($J(^{29}Si,^{13}C)$) = 4.2 (64.1) Me$_2$Si, 111.1 (89.6, 14.8) C≡C; ^{29}Si-NMR (C_6D_6): δ^{29}Si = −7.9.

3.3. *Bis(chlorodimethylsilyl)ethyne **2(Cl)***

A saturated solution of Cl_2 in CCl_4 (150 ml) was added dropwise to a cooled solution 0°C) of compound **1** (6.39 g, 45 mmol) in CCl_4 (50 ml) until a pale yellow colour persisted. The reaction mixture was then stirred at r.t. for 3 h. Fractional distillation gave 4.17 g (44%) of **2(Cl)** as a colourless liquid (b.p. 72°C/15 Torr). ul^{1}H-NMR (C_6D_6): δ^{1}H ($^{n}J(^{29}Si,^{1}H)$) = 0.31 (7.7) s, Me$_2$Si; ^{13}C-NMR (C_6D_6): δ^{13}C ($J(^{29}Si,^{13}C)$) = 3.2 (66.0) Me$_2$Si, 111.1 (91.6, 14.8) C≡C; ^{29}Si-NMR (C_6D_6): δ^{29}Si = −0.4.

3.4. *Bis(ethynyl-dimethylsilyl)ethyne **3***

A solution of compound **2** (2.91 g, 9.77 mmol) in tetrahydrofuran (10 ml) was added dropwise to a freshly prepared solution of HC≡CMgBr (29 mmol) in tetrahydrofuran (75 ml) at 5°C. The reaction mixture was allowed to attain r.t. and stirred overnight. The reaction mixture was hydrolysed with an aqueous NH_4Cl solution (80 ml). The aqueous layer was extracted 10 times with 25 ml portions of pentane. The pentane extracts were combined, dried over Na_2SO_4 and filtered. The solvent was removed at 15 Torr at r.t.. A colourless oil was left, identified as **3** (1.2 g, 64%). IR (hexane): ν(C≡C) = 2043 cm^{-1}, ν(≡C–H) = 3278, 3295 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ^{1}H ($^{n}J(^{29}Si,^{1}H)$) = 0.28 (7.5) s, 12H, Me$_2$Si, 2.42 s, 2H, ≡CH; ^{13}C-NMR ($CDCl_3$): δ^{13}C ($J(^{29}Si,^{13}C)$) = −0.2 (62.2) MeSi, 110.6 (88.8,

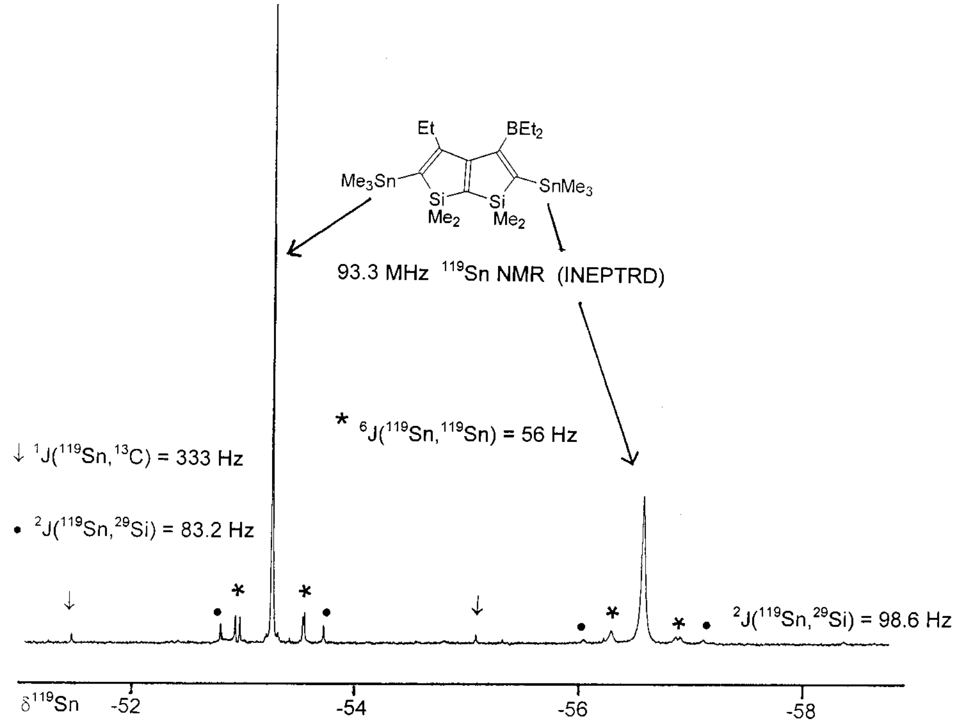


Fig. 2. 93.3 MHz ^{119}Sn{^{1}H}-NMR spectrum of **9a** recorded by the refocused INEPT pulse sequence based on $^2J(^{119}\mathrm{Sn},^1\mathrm{H}) = 52$ Hz. The broad ^{119}Sn(2-SnMe$_3$)resonance is the result of partially relaxed scalar ^{119}Sn–C≡C–^{11}B coupling (see text).

15.0) Si–C≡C–Si, 94.6 (18.3) ≡CH, 86.1 (94.3) ≡CSiMe$_2$; ^{29}Si-NMR (CDCl$_3$): $\delta^{29}\mathrm{Si} = -7.9$.

3.5. *Bis(trimethylsilylethynyl-dimethylsilyl)ethyne **4***

A solution of *n*-BuLi in hexane (1.6 M, 17 cm^3, 27.2 mmol) was added dropwise to a stirred solution of Me$_3$SiC≡CH (3.5 g; 5 ml; 35.71 mmol) in hexane (40 ml) at 0°C over 20 min. As soon as the white suspension had reached r.t. a solution of compound **2** (3.70 g, 12.41 mmol) in hexane (20 ml) was added and stirring was continued for 15 min.. After heating at reflux for 5 h pentane (100 cm^3) was added and insoluble material was filtered off. Removal of all volatile material left a colourless solid identified as the pure compound **4** (3.87 g; 93%). IR (hexane): = ν(C≡C) = 2113 cm^{-1}; ^{1}H-NMR (C$_6$D$_6$): δ^1H ($^nJ(^{29}\mathrm{Si},^1\mathrm{H})$ = 0.05 (7.2) s, 18H, Me$_3$Si, 0.24 (7.6) s, 12H, Me$_2$Si; ^{13}C-NMR (C$_6$D$_6$): δ^{13}C ($J(^{29}\mathrm{Si},^{13}\mathrm{C})$) = 0.1 (61.0) Me$_2$Si, −0.4 [56.1] Me$_3$Si, 111.6 (88.6, 14.8) Si–C≡C–Si, 115.8 (75.8, 14.8) ≡CSiMe$_3$, 109.8 (90.6, 11.8) ≡CSiMe$_2$; ^{29}Si-NMR (CDCl$_3$): δ^{29}Si = −42.7 SiMe$_2$, -18.2 SiMe$_3$. EI MS (70 eV): m/z (%) = 334 (40) [M$^+$], 319 (40), 231 (55), 73 (100).

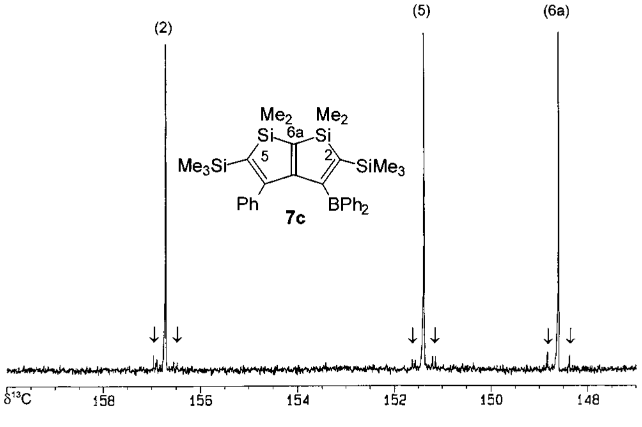


Fig. 3. Part of the 125.8 MHz ^{13}C{^{1}H}-NMR spectrum of **7c** recorded by the refocused INEPT pulse sequence based on $^3J(^{13}\mathrm{C},\mathrm{Si},\mathrm{C},^1\mathrm{H}) = 1.8$ Hz. This selects the ^{13}C(2,5,6a) resonances [^{29}Si satellites are marked by arrows: $^1J(^{29}\mathrm{Si}(1),\ ^{13}\mathrm{C}(2)) = 60.9$ Hz; $^1J(^{29}\mathrm{Si}(2\text{-}\mathrm{Si}),\ ^{13}\mathrm{C}(2)) = 43.7$ Hz; $^1J(^{29}\mathrm{Si}(6),^{13}\mathrm{C}(5)) = 60.9$ Hz; $^1J(^{29}\mathrm{Si}(5\text{-}\mathrm{Si})) = 45.4$ Hz; $^1J(^{29}\mathrm{Si}(1),^{13}\mathrm{C}(6a)) = 57.4$ Hz; $^1J(^{29}\mathrm{Si}(6),^{13}\mathrm{C}(6a)) = 57.4$ Hz]. The complete assignment rests on corresponding 2D ^{13}C/^{1}H and ^{29}Si/^{1}H heteronuclear shift correlations.

3.6. *Bis(trimethylstannylethynyl-dimethylsilyl)ethyne **5***

Me$_3$SnNEt$_2$ (0.57 g; 0.44 ml, 2.42 mmol) was added to a solution of compound **3** (0.23 g; 1.20 mmol) in hexane (10 ml) at r.t.. The reaction mixture was stirred for 3 h, and after removal of all volatile material the pure compound **5** (0.56 g; 90%) was left as colourless solid. ^{1}H-NMR ([D$_8$]toluene): δ^1H ($^nJ(^{29}\mathrm{Si},^1\mathrm{H})$) [$^nJ(^{119}\mathrm{Sn},^1\mathrm{H})$] = −0.01 [59.8] s, 18H, Me$_3$Sn, 0.17 (8.2) s, 12H, Me$_2$Si. ^{13}C-NMR ([D$_8$]toluene): δ^{13}C

($J(^{29}Si,^{13}C)$) [$J(^{119}Sn,^{13}C] = -0.3$ (61.4) Me_2Si, -8.3 [402.2] Me_3Sn, 111.3 (88.0, 14.6) [2.0] Si–C≡C–Si, 115.3 (14.0) [379.9] $\equiv CSnMe_3$, 113.0 (90.3) [60.7] $\equiv CSiMe_2$; ^{29}Si-NMR ([D_8]Toluene): $\delta^{29}Si$ [$J(^{119}Sn,^{29}Si] = -43.4$ [11.4]; ^{119}Sn-NMR ([D_8]Toluene) $\delta^{119}Sn = -74.5$.

*3.7. Preparation of the 1,6-dihydro-1,6-disilapentalene (**7**)/silole (**8**) mixtures:1,1-organoboration of **4** with BEt$_3$ (**6a**), B(CH2Ph)$_3$ (**6b**), BPh$_3$ (**6c**) or B(2-thienyl)$_3$ (**6d**). (general procedure)*

To a solution of **4** (94 mg; 2.81 mmol) in toluene (20 ml) Et_3B (**6a**) (2.19 ml, 15 mmol) was added in one portion at r.t., and the reaction mixture was heated at 120°C for 90 h. The progress of the reaction was monitored by ^{29}Si-NMR spectroscopy. After removal of the solvent and excess of **6a** under high vacuum a residual yellowish oil was left and identified as a mixture containing 90% of **7a** and 10% of **8a**. The mixtures of **7b**/**8b** (120°C for 50 h; yellowish oil), **7c**/**8c** (120°C for 65 h; white solid), **7d**/**8d** (120°C for 96 h; white solid) were obtained in the same way. In the case of **7c**/**8c**, repeated recristallisation from pentane leads to pure samples of **7c** (see Fig. 3).

7a: ^1H-NMR: $\delta^1H = 2.01$, 0.88 5H, 4-Et; 1.37, 0.92 10H, BEt_2; 0.22, 0.19 12H, $Me_2Si(1,6)$; 0.15, 0.11 18H, 2,5-Me_3Si.

7b: ^1H-NMR: $\delta^1H = 7.22$–6.89 4-CH_2*Ph* and B(CH_2*Ph*)$_2$; 3.62 2H, 4-CH_2; 3.05, 2.71 ($^2J(^1H,^1H) =$ 17.0 Hz) 4H, BCH_2; 0.36, 0.27 12H, $Me_2Si(1,6)$; 0.33, 0.06 18H, 2,5-Me_3Si.

7c: ^1H-NMR: $\delta^1H = 7.66$, 7.21, 7.12 10H, BPh_2; 6.69, 6.68, 6.47 5H, 4-Ph; 0.56 6H, $Me_2Si(1)$; 0.48 6H, $Me_2Si(6)$; -0.22 9H, 5-Me_3Si; -0.27 9H, 2-Me_3Si.

7d: ^1H-NMR: $\delta^1H = 7.62$, 7.28, 7.20, 6.77, 6.74 6H, B(2-thienyl)$_2$; 6.41, 6.18, 5.97 4-(2-thienyl); 0.46 broad, 6H, $Me_2Si(1)$; 0.31 broad, 6H, $Me_2Si(6)$; -0.12 9H, 5-Me_3Si; -0.14 9H, 2-Me_3Si.

8a: ^1H-NMR: $\delta^1H = 2.25$, 0.88 5H, 4-Et); 1.43, 0.92 10H, BEt2; 0.32, 0.29 12H, $Me_2Si(1)$ and 5-$SiMe_2$; 0.08, 0.04 18H, 2-Me_3Si and $\equiv$C–$SiMe_3$.

8b: ^1H-NMR: $\delta^1H = 7.22$–6.89 4-CH_2*Ph*, B(CH_2*Ph*)$_2$; 3.72 2H, 4-CH_2); 2.81, 2.42 ($^2J(^1H,^1H) =$ 15.8 Hz) 4H, BCH_2; 0.52 6H, $Me_2Si(1)$; 0.28 6H, 5-Me_2Si; 0.22 9H, 2-Me_3Si; 0.14 9H, $\equiv$C–$SiMe_3$.

8c: ^1H-NMR: $\delta^1H = 7.60$, 7.15, 7.09 10H, BPh_2; 7.08, 6.61, 6.42 5H, 4-Ph; 0.74 6H, $Me_2Si(1)$; 0.25 6H, 5-Me_2Si; 0.18 9H, $\equiv$C–$SiMe_3$; 0.00 9H, 2-Me_3Si.

8d: ^1H-NMR: $\delta^1H = 7.75$, 7.74, 7.39, 7.29, 6.96, 6.83 6H, B(2-thienyl)2; 6.49, 6.39, 6.22 4-(2-thienyl); 0.67 6H, $Me_2Si(1)$; 0.14 6H, 5-Me_2Si; 0.13 9H, $\equiv$C-$SiMe_3$; -0.03 9H, 2-Me_3Si.

*3.8. Preparation of the 1,6-dihydro-1,6-disilapentalenes **9a** and **9c**:1,1-organo-boration of **5** with Et$_3$B or Ph$_3$B (general procedure)*

Et_3B (**6a**) (23 ml, 0.16 mmol) was added in one portion to a solution of **5** (80 mg; 0.16 mmol) in toluene (5 ml) and stirred for 3 h. Then the reaction mixture was allowed to attain r.t.. The ^{29}Si-NMR spectrum showed the complete conversion of the starting material to **9a**. Removal of all volatile material left **9a** as a colourless oil in quantitative yield. A similar reaction of the triyne **5** with Ph_3B (**6c**) gave **9c** as a colourless solid contaminated by a small amount of Me_3Sn–Ph as the result of an exchange reaction.

9a: ^1H-NMR: δ^1H [$J(^{119}Sn,^1H)] = 2.09$, 0.95 5H, 4-Et; 1.43, 0.96 10H, BEt_2; 0.25, 0.25 12H, $Me_2Si(1,6)$; 0.29 [53.2], 0.25 [53.2] 18H, 2,5-Me_3Sn.

9c: ^1H-NMR: δ^1H [$J(^{119}Sn,^1H)] = 7.41$, 7.08, 6.99 10H, BPh_2; 7.25, 7.08, 6.99 5H, 4-Ph); 0.47 6H, $Me_2Si(6)$; 0.34 6H, $Me_2Si(1)$; -0.17 [53.5], -0.26 [53.5] 18H, 2,5-Me_3Sn.

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