

1,1-Ethylboration of Di(alkyn-1-yl)silanes with Two and Three Si-H Functions. New Silacyclopentadienes

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The reaction of the di(alkyn-1-yl)silanes $\text{Me}_2\text{Si}(\text{C}\equiv\text{CSiMe}_2\text{H})_2$ **1a** and $\text{Me}(\text{H})\text{Si}(\text{C}\equiv\text{CSiMe}_2\text{H})_2$ **1b** with triethylborane was studied. In the case of **1a**, the 4-ethyl-3-diethylboryl-1,1-dimethyl-2,5-bis(dimethylsilyl)-1-sila-2,4-cyclopentadiene **2a** was the sole product. In the case of **1b**, the analogous silole **2b** was formed along with two other products which were identified as di(alkenyl)silanes **3b** and **4b**, in which different types of electron-deficient Si-H-B bridges could be detected. All products were characterised by consistent sets of solution NMR data (^1H , ^{11}B , ^{13}C and ^{29}Si NMR). The coupling constants $^1J(^{13}\text{C}, ^{13}\text{C})$ were measured for **2a** and calculated by using DFT methods (B3LYP/6-311+G(d,p) level of theory).

Key words: Alkynes, Boranes, Siloles, Si-H Activation, NMR

Introduction

Although 1,1-ethylboration of alkyn-1-ylsilanes is slow [1, 2], it can be induced by prolonged heating at 90–100 °C of the reaction mixtures, taking advantage of the relatively high thermal stability of the silanes. These reactions proceed by cleavage of the $\text{Si}-\text{C}\equiv$ bond via the short-lived zwitterionic intermediate **A**, leading in most cases to alkenes **B1**, in which the silyl and the boryl groups occupy *cis*-positions at the $\text{C}=\text{C}$ bond (Scheme 1) [1]. Clearly, the presence of two different terminal silyl groups (*e.g.*, $\text{R}^1 = \text{SiR}_3$) in the alkyne gives rise to the formation of isomers. Nevertheless, starting from di(alkyn-1-yl)silanes with terminal trimethylsilyl groups affords selectively the siloles **C** [1–5], and it had been suggested [1] that consecutive 1,1-deorganoboration and 1,1-organoboration reactions take place until the correct stereochemistry is present for the irreversible ring closure to give **C**.

Considering the importance of siloles [6, 7], optimised syntheses with a choice of numerous different substituents are desirable. In the present work, we have studied the 1,1-ethylboration of the di(alkyn-1-yl)silanes $\text{Me}_2\text{Si}(\text{C}\equiv\text{CSiMe}_2\text{H})_2$ **1a** and $\text{Me}(\text{H})\text{Si}(\text{C}\equiv\text{CSiMe}_2\text{H})_2$ **1b** with triethylborane, BET_3 , in order to find potential intermediates on the way to the siloles. These intermediates may be stabilised by

Table 1. ^{13}C and ^{29}Si NMR data^a of the di(alkyn-1-yl)silanes **1a** and **1b**.

	$\delta^{29}\text{Si}$	$\delta^{13}\text{C}(\text{Me})$	$\delta^{13}\text{C}$ [Si(C \equiv) ₂]	$\delta^{13}\text{C}$ ($\equiv\text{C}-\text{Si}$)
1a	–38.0 [1.8] (Me_2HSi), –41.4 [1.8] (Me_2Si)	–3.3 (56.2) 0.2 (61.8)	111.7 (89.5, 12.4)	112.5 (77.9, 15.2)
1b	–64.5 [1.7] (MeHSi), –38.3 [1.7] (Me_2Hsi)	–2.9 (57.0) –2.4 (61.6)	108.4 (92.7, 12.3)	114.7 (77.6, 15.8)

^a In C_6D_6 at 23 ± 1 °C; coupling constants [± 0.3 Hz]; $J(^{29}\text{Si}, ^{13}\text{C})$ are given in parentheses, $J(^{29}\text{Si}, ^{29}\text{Si})$ in brackets.

electron-deficient Si-H-B bridges for which unequivocal evidence has been provided recently [8, 9].

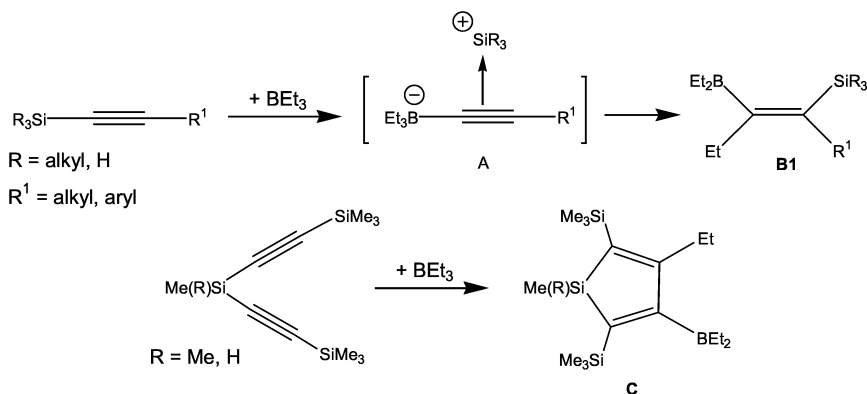
Results and Discussion

Synthesis

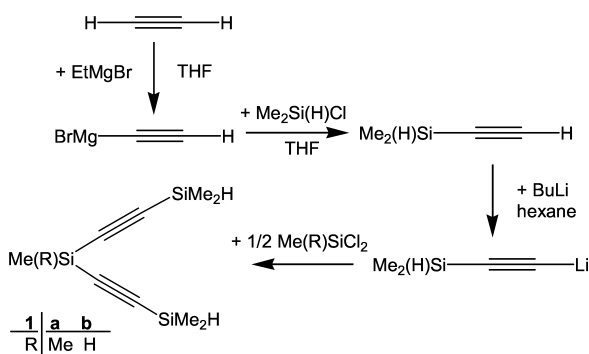
The di(alkyn-1-yl)silanes **1a** and **1b** were prepared as shown in Scheme 2. They are colourless, volatile liquids which can be readily separated from side products by condensation. The NMR data of **1a** and **1b** (Table 1) are comparable with those for analogous alkynes bearing terminal SiMe_3 groups [10].

Reactions of the di(alkyn-1-yl)silanes **1a** and **1b** with triethylborane

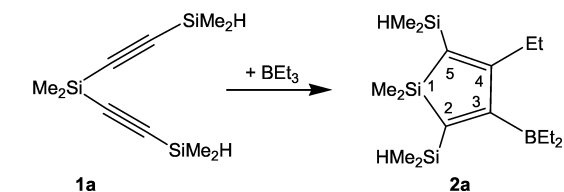
Both **1a** and **1b**, dissolved in benzene or toluene, do not react with an excess of BET_3 at room temperature. Heating of the reaction mixtures at 90–100 °C



Scheme 1. Mechanism of 1,1-organoboration and formation of 1-sila-2,4-cyclopentadienes.

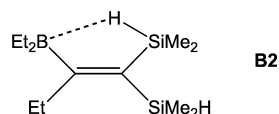


Scheme 2. Synthesis of the bis(dimethylsilylethynyl)methylsilanes.

Scheme 3. 1,1-Ethylboration of bis(dimethylsilylethynyl)dimethylsilane **1a** leading to the silole **2a**.

for several hours was necessary until the reactions were complete. In the case of **1a**, the silole **2a** was the sole product (Scheme 3), readily identified by its NMR parameters (*vide infra*).

Although the 2-SiMe₂H and the 3-BEt₂ groups in **2a** are in close neighbourhood, there appears to be no appreciable interaction of the Si-H function with the electron-deficient boron atom. In contrast, in alkenes such as **B2** [11], where a comparable substituent pattern at the C=C bond is present, the different steric requirements, most likely the stronger mutual steric repulsion of the silyl groups when compared with **2a**, enforce the formation of the Si-H-B bridge.



In contrast to **2a**, the analogous silole **2b** is formed as one of the major products ($\approx 60\%$) along with two other products, **3b** ($\approx 25\%$) and **4b** ($\approx 10\%$), as shown in Scheme 4. Once the starting compound **1b** had been consumed, further heating of the mixture containing **2b**, **3b** and **4b** at 90–100 °C for 15 h did not induce appreciable changes in the product distribution. It is conceivable that the first step, the intermolecular 1,1-ethylboration (Scheme 4a), leads to two isomers **B3** and **B4**, of which **B3** can rearrange by intramolecular 1,1-vinylboration to give the silole **2b** (Scheme 4b), analogous to **2a**. It can be concluded that in the reaction of **1a** with BEt₃ the second intermolecular 1,1-ethylboration is slow, whereas in the case of the reaction of **1b** with BEt₃, the second intermolecular 1,1-ethylboration competes with other reactions. Apparently, the SiMeH-group exerts less steric hindrance than the SiMe₂ group, and thus facilitates the intermolecular 1,1-ethylboration of the remaining C≡C-SiMe₂H unit in **B4** (Scheme 4c) to give the di(alkenyl)silanes **3b** and **4b**. The existence of an electron-deficient Si-H-B bridge in the intermediate **B4** can be assumed in analogy to that in **B2**. However, in the cases of **3b** and **4b**, NMR spectroscopy (*vide infra*) provides firm evidence for the presence of Si-H-B bridges.

NMR spectroscopic results

The ¹¹B, ¹³C and ²⁹Si NMR data of the siloles **2a,b** are given in Table 2, and the data for the

Table 2. ^{11}B , ^{13}C , and ^{29}Si NMR data^a of the silacyclopentadienes **2a** and **2b**.

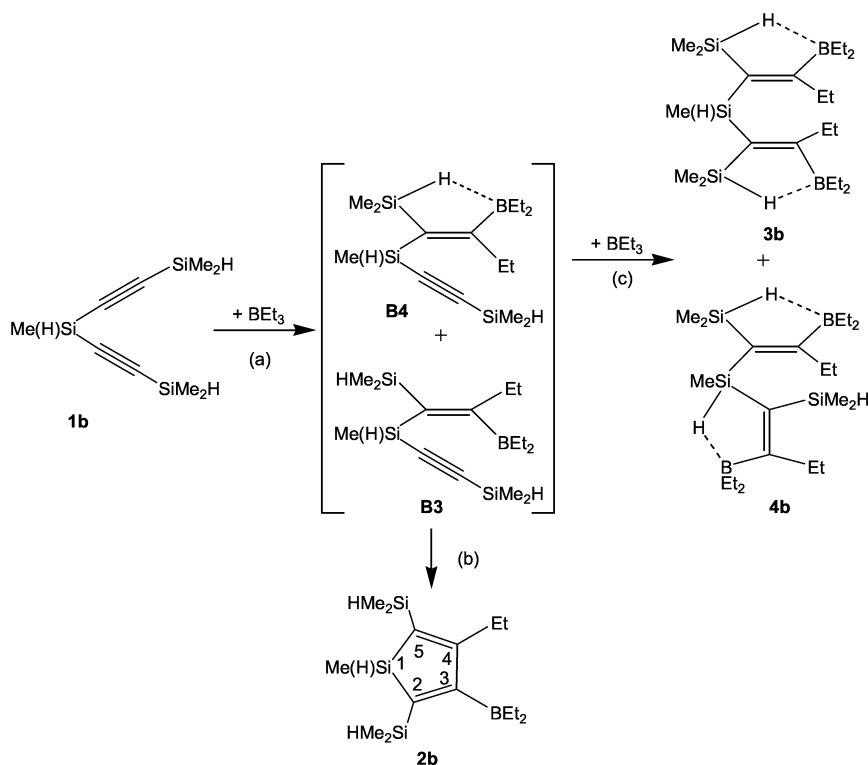
	$\delta^{29}\text{Si}$	$\delta^{11}\text{B}$	$\delta^{13}\text{C}^2$	$\delta^{13}\text{C}^3$	$\delta^{13}\text{C}^4$	$\delta^{13}\text{C}^5$	$\delta^{13}\text{C}(1\text{-Me})$	$\delta^{13}\text{C}(2,5\text{-SiMe}_2)$	$\delta^{13}\text{C}(\text{BEt}_2)$	$\delta^{13}\text{C}(4\text{-Et})$
2a	26.7 (Si^1) [11.7] (2-Si) [10.9] (5-Si)	-24.8 86.9	-29.0 (63.0, 45.9 ^b)	143.6 (br)	187.5 (12.4 ^c , 7.7 ^d)	172.1 (62.7, 50.7 ^b)	137.1 (48.0)	-1.7 -1.5 (51.3)	-1.4 (51.3)	23.1 (br), 30.5 (9.3), 15.6
2b	3.9 (Si^1) [11.8] (2-Si) -28.7 [10.9] (5-Si)	-24.7 86.8	(64.2, 45.7 ^b)	141.5 (br)	189.3 (12.3 ^c , 7.9 ^d)	173.8 (62.6, 50.7 ^b)	132.7 (47.3)	-4.4 -1.4 (51.4)	-1.3 (51.4) -0.9 (51.6) -0.8 (51.6)	23.2 (br), 30.5 (8.8), 15.6

^a In C_6D_6 at 23 ± 1 °C; coupling constants [± 0.3 Hz] $J(^{29}\text{Si}, ^{13}\text{C})$ are given in parentheses, $J(^{29}\text{Si}, ^{29}\text{Si})$ in brackets; (br) denotes the broad ^{13}C NMR signal for a carbon atom linked to boron; ^b $^1J(^{29}\text{Si}^1, ^{13}\text{C})$; ^c $^3J(^{29}\text{Si}(2), ^{13}\text{C}^4)$; ^d $^{2,3}J(^{29}\text{Si}^1, ^{13}\text{C}^4)$; $^2J(^{29}\text{Si}(5), ^{13}\text{C}^4)$ is not resolved.

Table 3. ^{11}B , ^{13}C , and ^{29}Si NMR data^a of the di(alkenyl)silanes **3b** and **4b**.

	$\delta^{29}\text{Si}$	$\delta^{11}\text{B}$	$\delta^{13}\text{C}(\text{Si}_2)=$	$\delta^{13}\text{C}(\text{B})=$	$\delta^{13}\text{C}(\text{SiMe})$	$\delta^{13}\text{C}(\text{SiMe}_2)$	$\delta^{13}\text{C}(\text{BEt}_2)$	$\delta^{13}\text{C}(\text{Et})$
3b	-7.2 [10.7], -47.6 [10.7]	76.0	135.4 (63.4, 51.2 ^b)	192.2 (br)	-0.8 (47.6)	-0.6 (51.8) -0.5 (51.8)	21.2 (br), 10.9	33.1 (10.8), 13.8
4b ^c	-0.3 [10.4] ^d , -23.5 [10.6], -30.7 [10.8]	76.0	131.2, 133.0	192.2, 195.7	-0.7	-0.6, -0.2, 0.0, 0.3	20.2 (br), 20.6 (br), 10.6, 11.3	31.8, 32.5, 13.9, 14.4

^a In C_6D_6 at 23 ± 1 °C; coupling constants [± 0.3 Hz] $J(^{29}\text{Si}, ^{13}\text{C})$ are given in parentheses, $J(^{29}\text{Si}, ^{29}\text{Si})$ in brackets; (br) denotes the broad ^{13}C NMR signal for a carbon atom linked to boron; ^b $^1J(^{29}\text{Si}_{\text{H,Me}}, ^{13}\text{C}^2)$; ^c Minor component in the mixture; assignment of ^{13}C NMR data is not complete; ^d see Fig. 2.



Scheme 4. 1,1-Ethylboration of bis(dimethylsilyl)ethynylmethylsilane **1b** leading to the silole **2b** and to the di(alkenyl)silanes **3b** and **4b** which contain electron-deficient Si-H-B bridges.

di(alkenyl)silanes **3b** and **4b** in Table 3. The siloles show a typical pattern of ^{13}C NMR signals in the olefinic region, three sharp ($\text{C}^{2,4,5}$) and one broad

(C^3), accompanied by ^{29}Si satellites corresponding to $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^{2,3}J(^{29}\text{Si}, ^{13}\text{C})$ [2–5]. The olefinic region of the ^{13}C NMR spectrum for the mixture con-

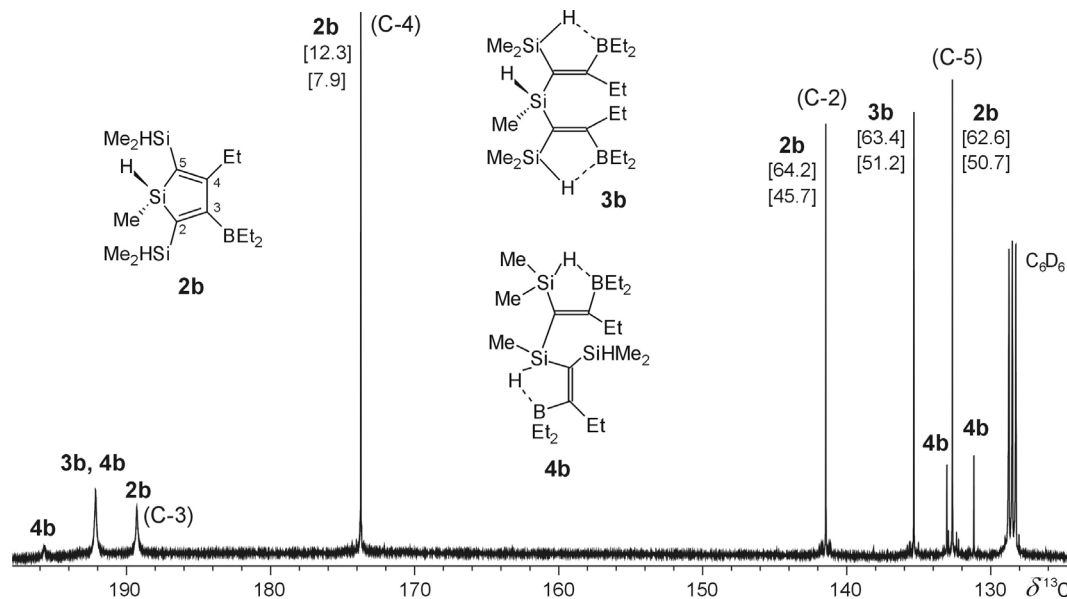


Fig. 1. 100.6 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the mixture containing **2b**, **3b** and **4b**, showing the range for olefinic carbons. Coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ [Hz] are given in brackets. Note the broad ^{13}C NMR signals for the carbon atoms linked to boron.

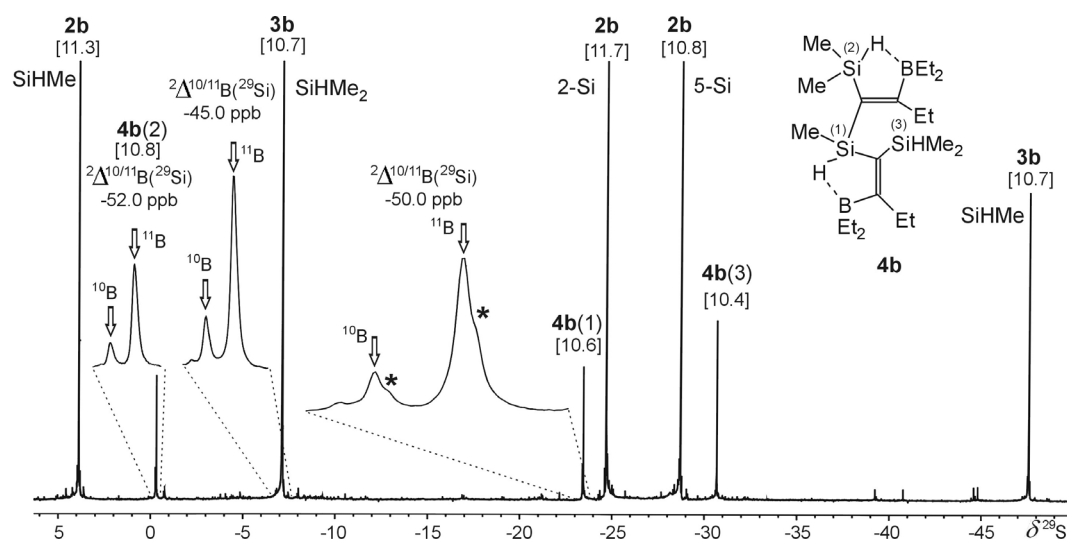


Fig. 2. 79.5 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the mixture containing **2b**, **3b** and **4b** (refocused INEPT, based on $^1J(^{29}\text{Si}, ^1\text{H}) = 180$ Hz). Coupling constants $^2J(^{29}\text{Si}, ^{29}\text{Si})$ [Hz] are given in brackets. Note the large negative isotope-induced chemical shifts $^2\Delta^{10/11}\text{B}(^{29}\text{Si})$ which are typical of electron-deficient Si-H-B bridges. Some of the signals show a small isotope-induced chemical shift $^3\Delta^{10/11}\text{B}(^{29}\text{Si}) = +7 \pm 1$ ppb as indicated for the expanded signal **4b(1)** by asterisks.

taining **2b**, **3b** and **4b** is shown in Fig. 1. The information on $^1J(^{29}\text{Si}, ^{13}\text{C})$ is also available from the ^{13}C satellites in the ^{29}Si NMR spectra. The silicon atom in 1-position of **2b** is a chiral centre and therefore, the methyl groups in the 2,5-SiMe₂H groups are di-

astereotopic and give rise to four different $^{13}\text{C}(\text{SiMe}_2)$ signals.

In the case of **2a**, the ^{13}C satellites were also measured and the assignment of ^{13}C NMR signals on the basis of $^1J(^{13}\text{C}, ^{13}\text{C})$ completed (see Scheme 5).

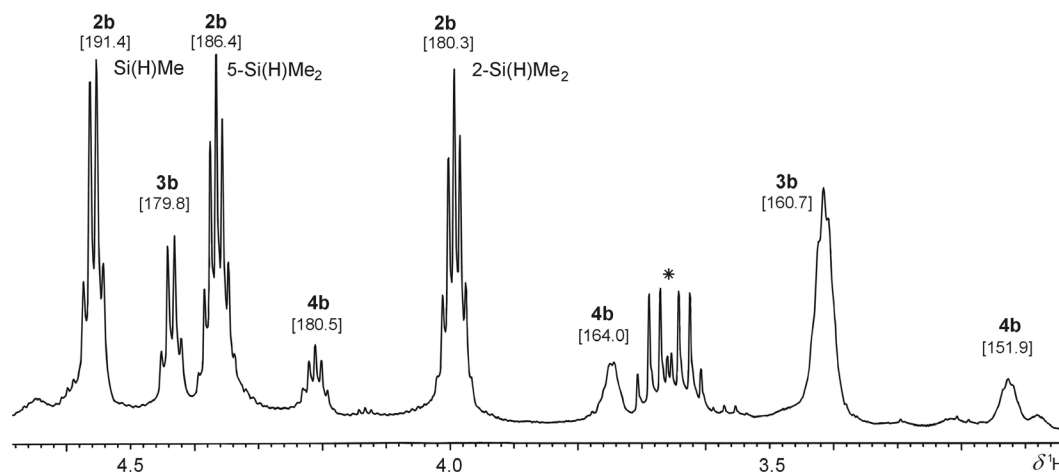
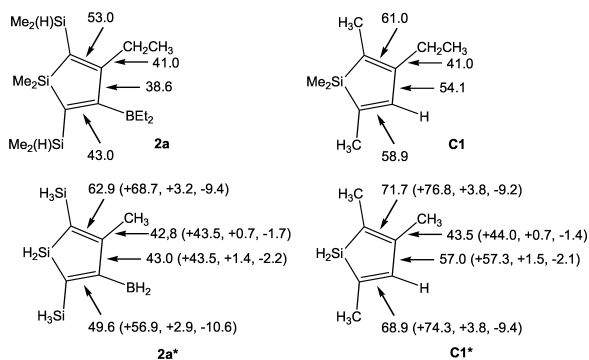


Fig. 3. 400 MHz ^1H NMR spectrum of the reaction mixture containing **2b**, **3b** and **4b**, showing the range of the Si-H functions. Coupling constants $^1J(^{29}\text{Si}, ^1\text{H})$ [Hz] are given in brackets. The $^1\text{H}(\text{Si-H})$ signals for Si-H-B moieties are broad and shifted to lower frequencies with respect to those for simple Si-H functions. The asterisk indicates impurities which contain OCH_2 units due to oxidation.



Scheme 5. Experimental coupling constants $^1J(^{13}\text{C}, ^{13}\text{C})$ in **2a** and **C1** [27] for comparison, and calculated [B3LYP/6-311+G(d,p)] coupling constants for **2a*** and **C1***. The calculated data in parentheses refer to the Fermi contact (FC), spin-dipole (SD) and the paramagnetic spin-orbital term (PSO), respectively.

The magnitude of $^1J(^{13}\text{C}=^{13}\text{C})$ [13] becomes markedly smaller with increasing number of organometallic substituents at the $\text{C}=\text{C}$ bond. This is also reflected by calculations of the coupling constants [14–16] for **2a*** using DFT methods at the B3LYP/6-311+G(d,p) level of theory (Scheme 5). Given for the slightly different substituent patterns, the agreement between experimental and calculated coupling constants is acceptable. Apparently, the organometallic groups take influence on the Fermi contact term (FC), leaving non-contact interactions such as the paramagnetic spin-orbital (PSO) and the spin-dipole term (SD) almost unaffected. As can be seen from the calculations, the

PSO contributions are significant for double bonds [15] and small for single bonds, and SD contributions play a minor role. Since these contributions to spin-spin coupling are not available by experiments, the calculations provide valuable additional information. Some differences between experimental and calculated data for **2a** and **2a*** can result from the geometry optimised for **2a***, where the BH_2 plane is coplanar with the SiC_4 plane. In the case of **2a**, it can be expected for steric reasons that the BEt_2 group prefers a conformation in which the BC_2 plane is orthogonal with respect to the SiC_4 plane. Such a conformation favours σ - π (hyperconjugative) electron delocalisation involving the boron p_z orbital. This reduces the σ electron density in adjacent $\text{C}-\text{C}$ bonds which leads to smaller values of the coupling constants $^1J(^{13}\text{C}, ^{13}\text{C})$ [17]. The calculations also predict that the magnitude of $^2J(^{29}\text{Si}(5), ^{13}\text{C}^4)$ should be much smaller than that of $^{2,3}J(^{29}\text{Si}(1), ^{13}\text{C}^4)$ and $^3J(^{29}\text{Si}(2), ^{13}\text{C}^4)$, in agreement with the experimental data (see Table 2).

The ^{29}Si NMR signals of the siloles **2a, b** and the di(alkenyl)silanes **3b** and **4b** are accompanied by ^{29}Si satellites due to $^2J(^{29}\text{Si}, ^{29}\text{Si})$ in the order of 10 Hz, typical of two-bond coupling across an sp^2 hybridised carbon atom. The tilt of relevant cross peaks [18] in 2D $^{29}\text{Si}/^1\text{H}$ and $^{13}\text{C}/^1\text{H}$ HETCOR experiments [19] reveal that the sign of $^2J(^{29}\text{Si}, ^{29}\text{Si})$ in **2a** is positive, and this most likely applies also to **2b** and the di(alkenyl)silanes **3b** and **4b**. The positive sign of

${}^2J({}^{29}\text{Si}, {}^{29}\text{Si})$ is also predicted by the calculations carried out for **2a*** (Scheme 5).

The mixture containing the silole **2b** and the di(alkenyl)silanes **3b** and **4b** is of particular interest for NMR spectroscopic studies. The ${}^{29}\text{Si}$ NMR spectrum (Fig. 2) shows the expected eight signals, of which three are split due to a pronounced isotope-induced chemical shift ${}^2\Delta^{10/11}\text{B}({}^{29}\text{Si})$, typical of the Si-H-B bridge [8, 9, 11, 12]. The ${}^1\text{H}/{}^{29}\text{Si}$ heteronuclear shift correlations prove that these ${}^{29}\text{Si}$ nuclei are attached to ${}^1\text{H}$ nuclei which have broadened ${}^1\text{H}$ resonances, shifted markedly to lower frequencies when compared with the other ${}^1\text{H}(\text{Si})$ NMR signals (Fig. 3).

The presence of the Si-H-B bridge is reflected by slightly increased shielding of the ${}^{11}\text{B}$ nuclei relative to analogous ${}^{11}\text{B}$ nuclei in trigonal-planar surroundings. Furthermore, the ${}^{29}\text{Si}$ nuclei become markedly deshielded (Table 3 and Fig. 2), and the loss of electron density in the Si-H bond is also reflected by the smaller magnitude of the coupling constants ${}^1J({}^{29}\text{Si}, {}^1\text{H})$ (Tables 2 and 3, and Fig. 3).

Conclusions

The intermolecular 1,1-ethylboration of ethynylsilanes bearing silyl groups with Si-H functions on both alkynyl carbon atoms (*e.g.* in **1b**) is apparently rather fast. This leads to a situation where, under the reaction conditions, intermolecular and intramolecular 1,1-organoboration compete with each other. Furthermore, equilibria between 1,1-organoboration and 1,1-deorganoboration, which usually help to achieve the final irreversible ring-closure (*e.g.* in the case of **2a**), cannot be reached so easily because electron-deficient Si-H-B bridges seem to enhance the stability of the respective alkene derivatives (*e.g.* **3b** and **4b**). However, the clean formation of **2a** shows that siloles with silyl groups in 2,5-positions, bearing Si-H functions, are accessible, where the reactivity of Si-H bonds invites for further transformations.

Experimental Section

All preparative work and the handling of the compounds were carried out in an atmosphere of dry Ar, observing all conditions to exclude traces of oxygen and moisture. All solvents were freshly distilled, and oven-dried glass ware was used. Triethylborane, BuLi in hexane (1.6 M), and chlorosilanes were commercial products, and were used without further purification. Ethynyl(dimethyl)silane was prepared following literature procedures [20, 21]. The compound **1a** has

been described before [22], made by different procedures. The purity of **1a** and **1b** was checked by ${}^1\text{H}$, ${}^{13}\text{C}$ and ${}^{29}\text{Si}$ NMR spectroscopy in solution (Table 1). NMR measurements: Bruker ARX 250, Bruker DRX 500 and Varian Inova 400 NMR spectrometers, all equipped with multinuclear units. Chemical shifts are given with respect to Me_4Si [$\delta^1\text{H}$ ($\text{C}_6\text{D}_5\text{H}$) = 7.15; $\delta^{13}\text{C}$ (C_6D_6) = 128.0; $\delta^{29}\text{Si}$ = 0 for $\Xi({}^{29}\text{Si})$ = 19.867184 MHz]; to external $\text{BF}_3\text{-OEt}_2$ with $\delta^{11}\text{B}$ = 0 for $\Xi({}^{11}\text{B})$ = 32.083971 MHz. The 1D ${}^{29}\text{Si}$ NMR spectra were measured by using the refocused INEPT pulse sequence [23], based on ${}^1J({}^{29}\text{Si}, {}^1\text{H})$ and on ${}^2J({}^{29}\text{Si}, {}^1\text{H}_{\text{Me}})$. Gradient-enhanced 2D ${}^1\text{H}/{}^{29}\text{Si}$ HSQC [24] and 1D gradient-enhanced ${}^1\text{H}/{}^1\text{H}$ NOE spectra [25] served for the assignment of ${}^1\text{H}$ and ${}^{29}\text{Si}$ NMR signals. EI-MS spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70 eV) with direct inlet; the m/z data refer to the isotopes ${}^1\text{H}$, ${}^{12}\text{C}$, ${}^{11}\text{B}$, ${}^{28}\text{Si}$. IR spectra: Perkin Elmer, Spectrum 2000 FTIR. All calculations were carried out using the Gaussian 03 program package [26], and the optimised structure of **2a*** (Scheme 5) was identified as a true minimum by calculation of the harmonic frequencies.

Bis(dimethylsilylethynyl)dimethylsilane (1a) and bis(dimethylsilylethynyl)methylsilane (1b)

The THF solution of ethynyl(dimethyl)silane (1 M; 25 ml) was cooled to -78°C , and BuLi in hexane (1.6 M; 15.6 ml) was added. The mixture was warmed to room temperature, stirred for 2 h, and cooled again to -78°C . Then the respective chlorosilane (12.5 mmol) was added dropwise, and, after warming to room temperature, the mixture was heated at reflux for 1 h. Insoluble materials were filtered off, and the solvents were removed in a vacuum (30 Torr) by gentle heating in a water bath (40°C). A heterogenous residue was left, and volatile materials were collected as colourless liquids in a trap (-78°C) at 10^{-1} Torr. The yield was between 25 and 35% in repeated experiments both for **1a** and **1b**. **1a**: ${}^1\text{H}$ NMR: δ = 0.02 (d, 12H, SiHMe_2 , ${}^3J({}^1\text{H}, {}^1\text{H})$ = 3.9 Hz); 0.21 (s, 6H, SiMe_2); 4.11 (sp, 2H, SiH, ${}^3J({}^1\text{H}, {}^1\text{H})$ = 3.9 Hz, ${}^1J({}^{29}\text{Si}, {}^1\text{H})$ = 202.4 Hz). IR: $\nu(\text{Si-H})$ = 2143 cm^{-1} . **1b**: ${}^1\text{H}$ NMR: δ = 0.01 (d, 12H, SiHMe_2 , ${}^3J({}^1\text{H}, {}^1\text{H})$ = 3.9 Hz); 0.17 (d, 3H, SiHMe , ${}^3J({}^1\text{H}, {}^1\text{H})$ = 3.9 Hz); 4.07 (sp, 2H, SiH, ${}^3J({}^1\text{H}, {}^1\text{H})$ = 3.9 Hz, ${}^1J({}^{29}\text{Si}, {}^1\text{H})$ = 201.7 Hz); 4.33 (q, 1H, SiH, ${}^3J({}^1\text{H}, {}^1\text{H})$ = 3.9 Hz, ${}^1J({}^{29}\text{Si}, {}^1\text{H})$ = 223.0 Hz). IR: $\nu(\text{Si-H})$ = 2145, 2156 cm^{-1} .

4-Ethyl-2-diethylboryl-1,1-dimethyl-2,5-bis(dimethylsilyl)-1-sila-2,4-cyclopentadiene (2a)

The di(alkyn-1-yl)dimethylsilane **1a** (0.3 g, 13 mmol) was added to triethylborane (1 ml, 80 mmol), and the mixture was heated at 100°C for 12 h, after which ${}^{29}\text{Si}$ NMR spectra indicated that all starting material **1a** had been consumed. After removing all readily volatile material (ex-

cess of BEt_3), a colourless oil was left which was identified as pure **2a**, formed in quantitative yield. Attempted distillation led to decomposition. ^1H NMR: $\delta = 0.11$ (d, 6H, Me_2HSi , $^3J(^1\text{H}, ^1\text{H}) = 3.7$ Hz); 0.16 (d, 6H, Me_2HSi , $^3J(^1\text{H}, ^1\text{H}) = 3.9$ Hz); 0.19 (s, 6H, Me_2Si); 0.9–1.1 and 1.3–1.4 (m, 13H, Et_2B , Et); 2.23 (q, 2H, Et); 4.18 (sp, 1H, SiH, $^3J(^1\text{H}, ^1\text{H}) = 3.7$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 179.6$ Hz); 4.59 (sp, 1H, SiH, $^3J(^1\text{H}, ^1\text{H}) = 3.9$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 186.0$ Hz). IR: $\nu(\text{Si-H}) = 2103$ cm^{-1} . EI-MS: m/z (%): 322 (57) [M^+], 293 (100) [$\text{M}^+ - \text{C}_2\text{H}_5$].

1,1-Ethylboration of bis(dimethylethynyl)methylsilane (1b) with triethylborane

The reaction of **1b** with triethylborane was carried out in the same way as described for **1a**. When the ^{29}Si NMR spectrum of the reaction mixture indicated that **1b** was consumed and several products were formed, the mixture was heated for another 15 h in order to induce further changes in the product distribution. However, no significant changes were observed. The main components of the mixture were identified as the silole **2b** ($\approx 60\%$), and the di(alkenyl)silanes **3b** ($\approx 25\%$) and **4b** ($\approx 10\%$), of which **4b** was the minor product, along with $\approx 5\%$ of unidentified materials. **2b**: Relevant ^1H NMR data: $\delta = 0.00$ (d, 6H, Me_2Si , $^3J(^1\text{H}, ^1\text{H}) = 3.6$ Hz); 0.06 (d, 6H, Me_2Si , $^3J(^1\text{H}, ^1\text{H}) = 3.8$ Hz); 0.11; (d, 3H, MeSi, $^3J(^1\text{H}, ^1\text{H}) = 4.3$ Hz); 0.8–1.1 (m, 13H, Et_2B ,

Et); 2.2 (m, 2H, Et); 4.0 (sp, 1H, 2-SiHMe₂, $^3J(^1\text{H}, ^1\text{H}) = 3.6$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 180.3$ Hz); 4.37 (sp, 1H, 5-SiHMe₂, $^3J(^1\text{H}, ^1\text{H}) = 3.8$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 186.4$ Hz); 4.56 (q, 1H, SiHMe, $^3J(^1\text{H}, ^1\text{H}) = 4.3$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 191.4$ Hz). EI-MS: m/z (%): 308 (68) [M^+], 279 (100) [$\text{M}^+ - \text{C}_2\text{H}_5$].

3b: Relevant ^1H NMR data: $\delta = 0.10$ (d, 3H, MeSi, $^3J(^1\text{H}, ^1\text{H}) = 3.5$ Hz); 0.15 (d, 6H, Me_2Si , $^3J(^1\text{H}, ^1\text{H}) = 4.5$ Hz); 0.8–1.1 (m, 13H, Et_2B , Et); 2.2 (m, 2H, Et); 3.42 (sp, 2H, SiHMe₂, $^3J(^1\text{H}, ^1\text{H}) = 3.5$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 160.7$ Hz); 4.44 (q, 1H, SiHMe, $^3J(^1\text{H}, ^1\text{H}) = 4.5$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 179.8$ Hz). EI-MS: m/z (%): 377 (17) [$\text{M}^+ - \text{C}_2\text{H}_5$], 336 (64) [$\text{M}^+ - (\text{C}_2\text{H}_5)_2\text{BH}$].

4b: Relevant ^1H NMR data: $\delta = 0.09$ (d, 6H, Me_2Si , $^3J(^1\text{H}, ^1\text{H}) = 3.8$ Hz); 0.12 (d, 6H, Me_2Si , $^3J(^1\text{H}, ^1\text{H}) = 3.4$ Hz); 0.17 (d, 3H, MeSi, $^3J(^1\text{H}, ^1\text{H}) = 3.2$ Hz); 0.8–1.1 (m, 13H, Et_2B , Et); 2.2 (m, 2H, Et); 3.13 (sp, 1H, SiHMe₂, $^3J(^1\text{H}, ^1\text{H}) = 3.4$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 151.9$ Hz); 3.75 (q, 1H, SiHMe, $^3J(^1\text{H}, ^1\text{H}) = 3.2$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 164.0$ Hz); 4.21 (sp, 1H, SiHMe₂, $^3J(^1\text{H}, ^1\text{H}) = 3.8$ Hz, $^1J(^{29}\text{Si}, ^1\text{H}) = 180.5$ Hz).

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