

1,1-Ethylboration of Diethynyl(dimethyl)silane: Formation of a Silole Followed by [4+2]Cycloadditions to 7-Silanorbornadienes and 7-Silanorbornenes

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Diethynyl(dimethyl)silane, $\text{Me}_2\text{Si}(\text{C}\equiv\text{C}-\text{H})_2$ **2**, reacts with triethylborane, Et_3B **1**, by 1,1-ethylboration to give a silole, 3-diethylboryl-1,1-dimethyl-sila-2,4-cyclopentadiene **3**, as a short-lived intermediate which reacts further with **2** or dimerises via [4+2]cycloadditions to the 7-silanorbornadiene **4** or the 7-silanorbornene derivatives **5**, respectively. Since the silole **3** was not detected by NMR, the analogous reactions were studied using 1-alkynyl(ethynyl)-dimethylsilanes, $\text{Me}_2\text{Si}(\text{C}\equiv\text{C}-\text{H})\text{C}\equiv\text{C}-\text{R}$ **6** [$\text{R} = \text{Bu}$ (**a**), ${}^i\text{Pent}$ (**b**), ${}^t\text{Bu}$ (**c**)]. In these cases, 1,1-ethylboration gave the siloles **7a,b,c** and **7'a,b**, now detected in the reaction solutions, and also 7-silanorbornadienes as [4+2]cycloaddition products. Major products were identified, and the progress of the reactions was monitored by NMR spectroscopy (^1H , ^{11}B , ^{13}C and ^{29}Si NMR).

Introduction

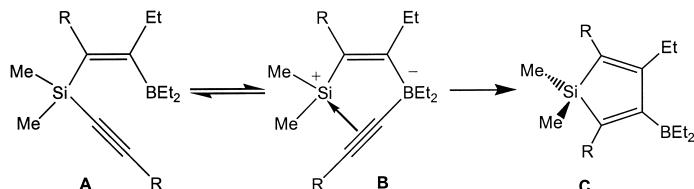
Reactions of bis(1-alkynyl)silanes with triorganoboranes have been shown to offer efficient routes to sila-2,4-cyclopentadienes (siloles) [1 - 3]. Indeed, this method appears more versatile than most other related preparative pathways [4]. Although silanes with a large variety of alkynyl groups, identical or different, linked to silicon have been studied in 1,1-organoboration reactions, ethynylsilanes have not received much attention so far, since complex mixtures of products were formed which were difficult to analyse [5]. Preliminary experiments with diethynyl(dimethyl)silane, $\text{Me}_2\text{Si}(\text{C}\equiv\text{C}-\text{H})_2$ **2**, and triethylborane, Et_3B **1**, did not produce a silole [5]. Therefore, we have reinvestigated in more detail this reaction, using in particular ^{29}Si NMR spectroscopy. For comparison, the reactions of 1-alkynyl(ethynyl)dimethylsilanes, $\text{Me}_2\text{Si}(\text{C}\equiv\text{C}-\text{H})\text{C}\equiv\text{C}-\text{R}$ [$\text{R} = \text{Bu}$ (**6a**), ${}^i\text{Pent}$ (**6b**), ${}^t\text{Bu}$ (**6c**)], with **1** are also discussed.

Results and Discussion

General

Bis(1-alkynyl)silanes usually react with triorganoboranes by cleavage of one of the Si-C \equiv bonds and 1,1-organoboration to give intermediates **A** in equilibrium with **B**, and the latter can rearrange by an intramolecular vinylboration to the silole **D** (Scheme 1; the reaction of triethylborane is shown). Zwitterionic intermediates of type **B** have been characterised for the lead and tin analogues [6, 7]. In the case of alkynylsilanes, the rather harsh reaction conditions (*ca.* 100 °C for several days) which are required to induce the intermolecular 1,1-organoboration leading to **A**, prevent in general the isolation or even the detection of intermediates of type **A** or **B**.

Thus, the success of the silole synthesis (**D**) depends on the stability of the siloles under the reaction conditions. Apparently this stability is rather



Scheme 1.

low for R = H, since in the reaction mixtures containing triethylborane **1** and $\text{Me}_2\text{Si}(\text{C}\equiv\text{C}-\text{H})_2$ **2**, a silole **3** could not be detected. In contrast, the corresponding stannole **3Sn** can be isolated [8], since the 1,1-ethylboration of $\text{Me}_2\text{Sn}(\text{C}\equiv\text{C}-\text{H})_2$ is already complete at -20°C .

Reaction of Diethynyl(dimethyl)silane **2** with triethylborane **1**

In the reaction of **2** with **1** at 80°C , depending on reaction time, two major compounds were formed, and their NMR spectra could be analysed to propose a 7-silanorbornadiene derivative **4** and a 7-silanorbornene derivative **5** as the results of [4+2]cycloadditions of **3** either with **2** or with a second molecule of **3**, respectively (Scheme 2).

In the presence of a large excess of **2**, the 7-silanorbornadiene **4** is the main product after 8 d at 80°C . Isomers **4'** and **5'** (structures not assigned) are also formed. Their concentration ($< 10\%$) was too low to allow for a complete assignment of all NMR data. Although alkynylsilanes are known to be weak dienophiles [9], the reactivity of the silole **3** is high enough to produce preferably the [4+2]cycloaddition product **4** provided there is an excess of **2**. If the concentration of **2** decreases, dimerisation of **3**, in yet another [4+2]cycloaddition, to **5** becomes competitive. This is graphically depicted in Fig. 1. The NMR data of the main products (Scheme 3) are in support of the proposed structures. Although, the NMR spectra indicate some decomposition, especially after 15 d at 80°C , the steady increase in

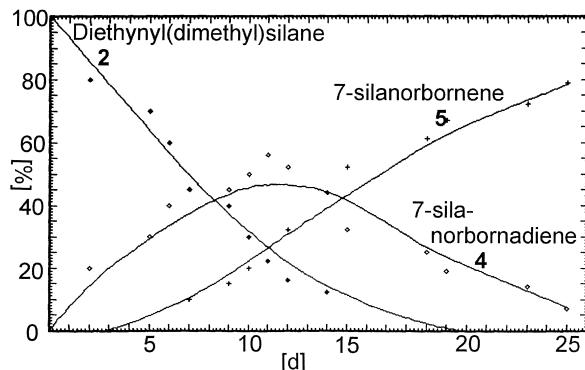
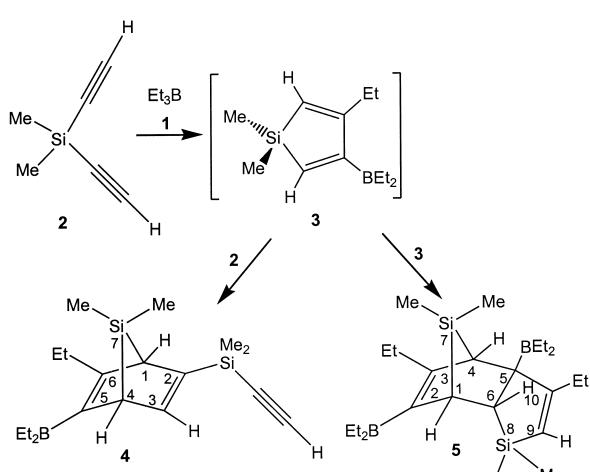


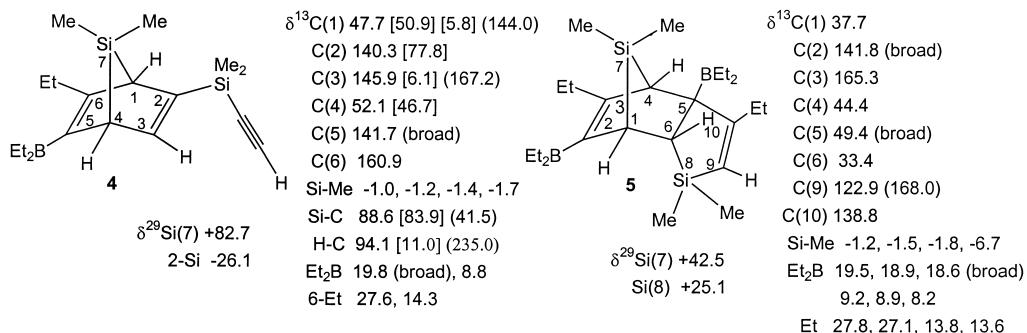
Fig. 1. Changes in the concentration of **2**, **4** and **5** as a function of reaction time at 80°C , starting with a 3:1 molar ratio of Et_3B (**1**) / $\text{Me}_2\text{Si}(\text{C}\equiv\text{C}-\text{H})_2$ (**2**). The data are derived from ^{29}Si NMR spectra recorded by ^1H decoupled INEPT (refocused) experiments. The errors in these experiments with respect to quantitative analysis are believed to be similar for the compounds **2**, **4** and **5**. The addition of the concentrations in % does not sum up to 100%, since the intensities of signals of the minor isomers ($< 10\%$) and of decomposition products are not included.

the concentration of **5** points towards a *retro*-Diels-Alder reaction of **4** and a dimerisation of **3** to **5**. It appears that in the course of the dimerisation the boryl-substituted double bond in **3** is much more reactive than the other one. This is in agreement with the behaviour of alkenylboranes and alkenes as dienophiles in Diels-Alder reactions [10]. The *endo*-isomer is usually preferred [11], and the diethylboryl groups in **5** prefer positions distant to each other.

As is evident from Scheme 3 and Fig. 1, ^{29}Si NMR spectra are particularly instructive for monitoring the reaction between **1** and **2**, and also for the determination of the product distribution. ^{11}B NMR spectra can be readily obtained from the reaction mixtures; however their diagnostic value is low, since only a single broad signal ($\delta^{11}\text{B}$ 87 ± 2) underneath of the fairly sharp ^{11}B NMR signal for Et_3B can be observed. When **2** starts to react with **1**, the ^{29}Si NMR signal for **2** ($\delta^{29}\text{Si}$ -38.9) becomes weaker and at first two other ^{29}Si NMR signals start to grow, at $\delta^{29}\text{Si}$ -26.1 and $+82.7$. The former signal is in the range expected for alkenyl(alkynyl)dimethylsilanes [12], whereas the latter one is typical of the 7-silanorbornadiene structure, where the ^{29}Si nucleus becomes extremely deshielded [13] when compared with other tetraorganosilanes. This deshielding is related to



Scheme 2.

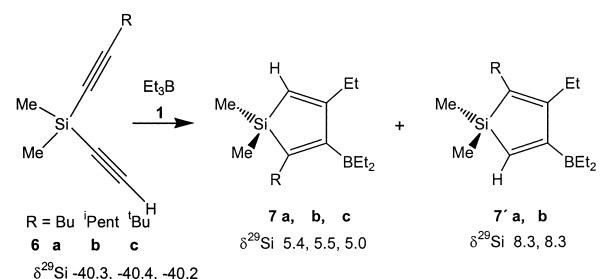


Scheme 3. ^{13}C and ^{29}Si NMR data of **4** and **5**; coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ are given in brackets and $J(^{13}\text{C}, ^1\text{H})$ in parentheses; (broad) denotes the broadened ^{13}C NMR signal of a carbon atom linked to boron.

the unique electronic structure of 7-silanorbornadienes [14]. After several days, an increasing amount of the 7-silanorbornene derivative **5** is formed, giving rise to two new ^{29}Si NMR signals, one at $\delta^{29}\text{Si}$ 42.5 (Si-7) and the other one at $\delta^{29}\text{Si}$ 25.1 in the typical range for sila-2-cyclopentenes with two methyl groups attached to silicon [15].

*Reactions of 1-alkynyl(ethynyl)dimethylsilanes **6** with triethylborane **1***

Since the intermediacy of the silole **3** could only be assumed, the reactions of **1** with 1-alkynyl-(ethynyl)dimethylsilanes, $\text{Me}_2\text{Si}(\text{C}\equiv\text{C}-\text{H})\text{C}\equiv\text{C}-\text{R}$ **6**, were also studied. These reactions afford complex mixtures if $\text{R} = \text{Bu}$ (**6a**) or $^i\text{Pent}$ (**6b**), since two siloles **7a,b** and **7'a,b** (molar ratio *ca.* 3:2) are formed first (Scheme 4). Then, [4+2]cycloadditions of the siloles with the alkynes **6a** and **6b**, respectively, lead to 7-silanorbornadienes. This becomes evident from the ^{29}Si NMR spectra which show the signals for the siloles **7** and **7'** (see Scheme 4) and 7-silanorbornadienes [$\delta^{29}\text{Si}$ -27.9 , $+77.2$; -28.8 , $+72.6$ ($\text{R} = \text{Bu}$), and -27.8 , $+80.3$, -28.8 , $+77.1$ ($\text{R} = ^i\text{Pent}$)]. Therefore, the proposed mechanism for the reaction of **2** with **1** is confirmed. The silole **3** must be the important intermediate. After more than 8 d of heating at $100\text{ }^\circ\text{C}$, numerous signals appear, some of which may be assigned to dimerisation products similar to **5** [e. g., $\delta^{29}\text{Si}(7) +38.4$, $+44.0$ ($\text{R} = \text{Bu}$), and $+38.5$, $+44.1$ ($\text{R} = ^i\text{Pent}$)]. In the case of **6c** ($\text{R} = ^i\text{Bu}$), the formation of the silole **7c** is preferred, since the $\text{Si}-\text{C}\equiv\text{C}-^i\text{Bu}$ unit is much less reactive than the $\text{Si}-\text{C}\equiv\text{C}-\text{H}$ unit, and according to the ^{29}Si NMR spectra only a small amount of a 7-silanorbornadiene (<20%) ($\delta^{29}\text{Si} -27.4$, $+71.1$) is



Scheme 4.

present in the reaction solution after 8 d at 100 °C. Clearly, the steric demand of a ^tBu group in 2-position at the silole ring does not favour further [4+2]-cycloadditions.

Conclusions

The results from this study indicate that siloles obtained from 1,1-organoborations of di(1-alkynyl)dimethylsilanes are reasonably stable under the reaction conditions (*ca.* 100 °C for several days), provided there are two organyl groups in 2,5-positions [1a]. If only one of the organyl groups is replaced by hydrogen as in **7** or **7'**, the siloles are present in the reaction solutions, but they undergo [4+2]cycloadditions with the respective alkynylsilane, or they dimerise slowly in the absence of alkyne. If there are hydrogen atoms in 2,5-positions, the corresponding silole **3** cannot be detected under the reaction conditions (80 °C), and a 7-silanorbornadiene- **4** and / or a 7-silanorbornene derivative **5** are the major products.

Experimental Section

All preparative work and handling of the compounds was carried out in an inert atmosphere of nitrogen or

argon. Solvents were carefully dried and glassware was used oven-dried. Triethylborane (Schering) was used as a commercial product, and the silanes **3** [16] and **6** [2a, 16] were prepared following the literature procedures. NMR measurements: Bruker AC 300 and Bruker ARX 250 [^1H , ^{11}B , ^{13}C NMR, and ^{29}Si NMR (refocused INEPT [17])]. Chemical shifts are given with respect to Me_3Si [$\delta^1\text{H}$ ($\text{C}_6\text{D}_5\text{H}$) 7.15; $\delta^1\text{H}$ ($\text{C}_6\text{D}_5\text{CD}_2\text{H}$) 2.03; $\delta^{13}\text{C}$ (C_6D_6) 128.0; $\delta^{13}\text{C}$ (C_7D_8 ; CD_3) 20.4; $\delta^{29}\text{Si} = 0$ for $\Xi(^{29}\text{Si}) = 19.867184$ MHz], $\text{BF}_3\text{-Et}_2\text{O}$ [$\delta^{11}\text{B} = 0$; $\Xi(^{11}\text{B}) = 32.083971$ MHz].

*1,1-Ethylboration of the alkynylsilanes **3** and **6** (general procedure):* Mixtures of triethylborane **1** and the respective alkynylsilane **3** or **6** (scale: 5 to 10 mmol; molar ratio ca. 3:1) were prepared at room temperature without a solvent, and heated at 80 °C (**3**, if the temperature is raised to 100 °C, decomposition becomes dominant) or 100 °C (**6**; the rate of the reaction is very slow at 80 °C) for several days (see e. g. Fig. 1). The same mixtures were also sealed in NMR tubes, together with a small amount of [D_8]toluene, kept under the same conditions, and the progress of the reactions was monitored by ^{29}Si NMR spectroscopy. A mixture containing **1** and **2** in a 1 : 8 molar ratio, heated at 80 °C for 6 d, was analysed by ^{29}Si

NMR to contain mainly (90 %) the excess of **2** and the 7-silanorbornadiene **4**. After removing all volatile material *in vacuo* (**1** and **2**), colourless or yellowish oils were left and analysed by NMR. The same compounds (in the same ratio) were present as in the reaction solutions. Attempts to separate **4** by fractional distillation under reduced pressure led to decomposition. Decomposition of the reaction mixtures containing **1**, **2**, **4** and **5** or **1**, **6**, **7**, **7'** and [4+2]cycloaddition products was also observed by chromatography on silica or Al_2O_3 (elution with hexane gave only **2**). **4:** ^1H NMR (500.13 MHz, C_7D_8): $\delta = 0.04$, 0.05, 0.24, 0.26 (4xs, 12H, SiMe), 1.15, 1.00 (m, t, 10H, BEt_2), 2.40, 0.95 (m, t, 5H, 6-Et), 2.10 (s, 1H, $\equiv\text{CH}$), 3.06 (broad, s, 1-H), 6.88 (m, 1H, C-3-H), 3.07 (dd, $J(\text{H},\text{H})$ 1.5 and 2.7 Hz, 1H, C-4-H). **7c:** $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta = 131.9$ (C-2), 162.2 (broad) (C-3), 146.3 (C-4), 119.5 (C-5), 32.8, 31.3 (2- $t\text{Bu}$), 20.0 (broad), 9.9 (BEt_2), 28.5, 12.3 (4-Et), -1.7 (SiMe₂).

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