

Hydroboration of 1-alkynyl(chloro)silanes—new synthons in heterocyclic chemistry

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Abstract

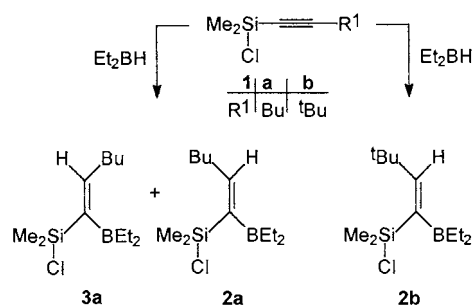
The 1-alkynyl(chloro)dimethylsilanes $R^1C\equiv C(Cl)SiMe_2$ [**1a** ($R^1 = Bu$), **1b** ($R^1 = tBu$)] react with tetraethylborane(6) to give the (Z)-1-chlorodimethylsilyl-1-diethylboryl-alkenes **2a,b**. These alkenes react with N- or C-lithiated azoles (pyrazole, thiazole) by LiCl elimination and formation of the novel five-membered heterocycles **4a**, **5b** and **6b**. In **5b** and **6b**, derived from thiazole and 4-methyl-thiazole, zwitterionic structures result which can be regarded as borane adducts of carbenes. All new compounds were characterised by ¹H-, ¹¹B-, ¹³C-, ^{14/15}N- and ²⁹Si-NMR spectroscopy © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Hydroboration of 1-alkynylsilanes has been described under various conditions [1], using dialkylboranes such as the dimer of 9-borabicyclo[3.3.1]nonane, (9-H-9-BBN)₂, tetraethylborane(6), Et₂BH [2],¹ borane-tetrahydrofuran, BH₃–THF in THF [3a,4], or pentaborane(9) B₅H₉ [3]. In some cases, carboranes are formed as final products [3,5,6]; however, in general 1,2-dihydroboration occurs first, leading to alkenylboranes and, in the presence of an excess of the borane reagent, also to diborylated alkanes [6,7]. The stereochemistry is defined: in most cases, the boron atom moves to the carbon atom bearing the silyl substituent. Exceptions are known for ethynylsilanes and also for

1-propynylsilanes if tetraethylborane(6) is used as the hydroborating reagent [1,8]. Scant attention has been paid to 1-alkynylsilanes which bear an additional functional group. We have now studied the reaction of the 1-alkynyl(chloro)dimethylsilanes **1a** and **1b** (Scheme 1) with Et₂BH. As a first attempt to explore the potential of the products thus obtained in heterocyclic synthesis, the reactions with N- and C-lithiated azoles were studied.



Scheme 1.

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¹ The formula Et₂BH is used for simplicity: tetraethylborane(6) is usually obtained and used as a mixture with triethylborane and small amounts of other ethyldiboranes(6).

Table 1
 ^{11}B , ^{13}C and ^{29}Si -NMR data ^a of the alkenes **2**, **3**

	2a (R ¹ = Bu)	3a (R ¹ = Bu)	2b (R ¹ = ^t Bu)
$\delta^{13}\text{C}(\text{R}^1\text{CH}=\)$	145.6	155.1	152.5
$\delta^{13}\text{C}(\text{BC}(\text{Si})=)$	156.5 (br)	n.o.	149.0 (br)
$\delta^{13}\text{C}(\text{SiMe})$	3.8	4.7	5.2
$\delta^{13}\text{C}(\text{BR}_2)$	21.5 (br), 8.1	21.5 (br), 9.1	21.6 (br), 9.4
$\delta^{13}\text{C}(\text{R}^1)$	35.4, 31.9, 22.8, 14.2	35.2, 31.8, 22.7, 14.1	36.6, 30.4
$\delta^{29}\text{Si}$	14.7	16.2	15.7
$\delta^{11}\text{B}$	84.0	84.0	82.0

^a Measured in C_6D_6 at 20°C. Abbreviations: n.o. means not observed; (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{13}C - ^{11}B coupling.

2. Results and discussion

2.1. Hydroboration of 1-alkynyl(chloro)dimethylsilanes **1a,b** with Et_2BH

The 1-alkynyl(chloro)dimethylsilanes, $\text{R}^1\text{C}\equiv\text{CSiMe}_2\text{-Cl}$ (**1**), can be prepared by the reaction of dichloro-dimethylsilane in excess with lithium alkynides $\text{LiC}\equiv\text{CR}^1$ [9,10]. When we studied the reaction of **1a** (R¹ = Bu) with Et_2BH , we always found two products **2a** and **3a** in the final reaction mixture, which were present in a non-constant ratio (ca. 2:1 to 4:1; **2a** always in excess) in repeated experiments. The analogous reaction of **1b** (R¹ = ^tBu) proceeded much more slowly, and gave only one product **2b**. The results are summarised in Scheme 1.

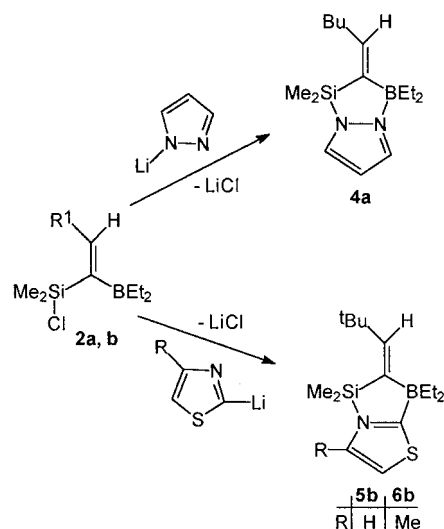
There is no hint in the literature on *trans*-1,2-hydroboration. The most likely explanation for the formation of **3a** involves 2-fold hydroboration of **1a**, followed by dehydroboration which can lead to either **2a** or **3a**. ^{29}Si -NMR spectra of the reaction mixtures show the two signals for **2a** and **2b** and a weak signal at $\delta^{29}\text{Si} = 27.4$, which could arise from the product of 2-fold hydroboration, $\text{Me}_2\text{Si}(\text{Cl})\text{C}(\text{BEt}_2)_2(\text{CH}_2)_4\text{CH}_3$. This implies that the hydroboration of **2a** takes place faster than that of **1a** which is conceivable. Apparently, the chloro-substituent at the silicon atom reduces the reactivity of **1** towards hydroborating agents (corresponding 1-alkynyl(trimethyl)silanes react fast with Et_2BH already below 0°C). The formation of products such as **3a** should be suppressed if R¹ is a more bulky group preventing a second hydroboration. This is confirmed by the selective formation of **2b** which however requires a reaction time of 4 days at room temperature or heating at 65°C for 4 h. The NMR data (Table 1) proves the proposed substituent pattern at the C=C bond in **2** and **3**. The positions of the substituents in **2a,b** and **3a** were also confirmed by 1D $^1\text{H}/^1\text{H}$ -NOE difference spectra or by 2D $^1\text{H}/^1\text{H}$ -NOESY experiments.

2.2. Reactions of the 1-silyl-1-diethylboryl-alkenes **2** with *N*- and *C*-lithiated azoles

The alkenes **2** contain two electrophilic centres, namely the silyl and the boryl group. The results of their reactions with *N*- and *C*-lithiated azoles, containing two nucleophilic centres each, are summarised in Scheme 2. The reaction of **2a** (containing a small amount of **3a**) with *N*-pyrazolyl lithium leads straightforwardly to **4a**, as expected. A product arising from the presence of **3a** could not be detected after crystallisation from pentane. The reactions of **2b** with two *C*-lithiated thiazoles proceeded in the same way, and the products **5b** and **6b** were isolated, each possessing a somewhat unexpected zwitterionic structure (NMR data are listed in Table 2).

The structures of **5b** and **6b** follow unambiguously from their ^{13}C -NMR spectra. In the range for the olefinic carbon atoms, there are three sharp and two broad signals (for the boron-bonded carbon atoms [11]), whereas the other isomer (with Si-C and B-N bonds) would require only one broad but four sharp signals. The broad ^{13}C resonance signal of the thiazole ring is found at rather high frequency. This indicates a considerable contribution of a canonic structure in which the carbon atom bears the formally positive charge. As shown in Scheme 3, both types of heterocycles can be described by canonic structures with greater (A) or smaller (B) separation of charge. In the case of **4a**, type B is expected to be dominant, whereas more balanced contributions of A and B can be predicted for **5b** and **6b**. The structure B for **5b** and **6b** corresponds exactly to that of a carbene-borane adduct [12].

The nitrogen chemical shifts of **4–6** are in the expected range. In **4a**, one of the lone pairs of electrons is needed to keep up the 6 π electron count of the heteroaromatic system, and the other one is engaged in



Scheme 2.

Table 2

¹¹B, ¹³C, ^{14/15}N, ²⁹Si-NMR data of the heterocycles **4–6**^a

	4a (R ¹ = Bu)	5b (R = ^t Bu, R ¹ = H)	6b (R = Me, R ¹ = ^t Bu)
δ ¹³ C(R ¹ CH=)	146.2	157.9	157.7 [4.5]
δ ¹³ C(BC(Si)=)	50.0 (br) [61.9]	142.1(br) [67.3]	142.5 (br) [68.2] (46.0)
δ ¹³ C(NC)	131.7, 134.9	132.2 (NCR)	143.4 (NCR)
δ ¹³ C(=C)=(SCN)	110.0	123.3/219.3 (br)	118.0/221.2 (br) (66.0)
δ ¹³ C(SiMe)	0.3 [53.4]	2.3 [53.7]	1.8 [53.3]
δ ¹³ C(BR ₂)	20.0(br), 11.0	21.2 (br), 11.5	21.0 (br), 11.7 (55.0)
δ ¹³ C(R ¹)	33.9, 33.9, 22.9, 14.5	36.9, 30.4	36.4, 30.4, 13.9 (R = Me)
δ ²⁹ Si	14.8	22.1	22.4
δ ¹¹ B	2.1	−7.6	−4.5
δ ^{14/15} N	−155.4 ¹⁵ N–Si, −115.0 ¹⁵ N–B	−138.0 ¹⁴ N–Si	−138.5 ¹⁴ N–Si

^a Measured in CDCl₃ at 20°C. Abbreviations: n.o. means not observed; (br) denotes a broad ¹³C resonance signal as the result of partially relaxed scalar ¹³C–¹¹B coupling. Coupling constants *J*(²⁹Si,¹³C) are given in brackets [± 0.2 Hz] and ¹*J*(¹³C,¹¹B) in parentheses (± 5 Hz).

coordinative bonding. This means that one ¹⁵N resonance remains in the region typical of pyrrole type nitrogen atoms [13], whereas the other one is shifted to lower frequency compared to azine (pyridine) type ni-trogen atoms [13]. Irrespective of the relative contribution of A or B to the structures of **5b** and **6b**, the nitrogen nuclear shielding must be increased with respect to thiazole itself (δN = −81.8), since the nature of the lone pair of electrons at the nitrogen atom has changed. Indeed, the nitrogen nuclear shielding in **5b** and **6b** increases by 56 ppm with respect to thiazole.

²⁹Si-NMR spectra of all compounds are readily recorded as shown in Fig. 1 for the example of **4a**. This enables one to measure the coupling constant ¹*J*(²⁹Si,¹³C_{C=C}) which is not available from the relevant ¹³C-NMR signal, since this is broad and of low intensity.

The ab initio calculations (6-31G* [14]) carried out for the parent compound of **5b** or **6b** and its isomer (with N–B and C–Si bonds) show that the isomer with C–B and N–Si bonds, corresponding to **5b** and **6b**, is slightly more stable (although the difference of 1.8 kcal mol^{−1} is not significant). The calculated (GIAO [14]) ¹¹B, ¹³C and ¹⁵N isotropic magnetic shieldings based on the 6-31G* optimised geometry are in reasonable agreement with the experimental data, considering the different substituent pattern.

3. Conclusions

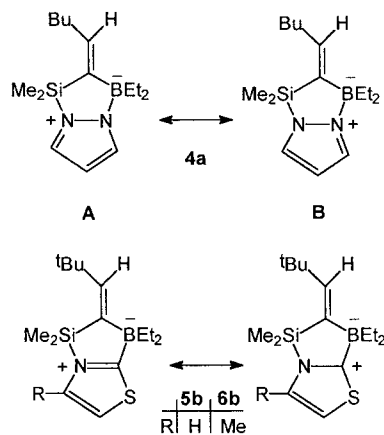
The new alkenes bearing a chlorosilyl and a diethylboryl group in geminal positions at the C=C bond are readily accessible, and possess considerable potential in heterocyclic chemistry. They are attractive starting materials for further transformations, in particular in reactions with reagents in which two nucleophilic centres are present.

4. Experimental

4.1. Starting materials and measurements

The preparative work and all handling of samples was carried out under an inert atmosphere (Ar or N₂), using carefully dried glass ware and dry solvents. BuLi (1.6 M) in hexane, pyrazole, thiazole, 4-methyl-thiazole, 1-hexyne, 3,3-dimethyl-1-butyne, Me₂SiCl₂ and Et₃B were commercial products. The 1-alkynyl(chloro)-dimethylsilanes **1a,b** [6,7], and the reagent Et₂BH [2] were prepared as described and the hydride concentration (1.17%) was determined by ¹¹B-NMR spectroscopy [15].

NMR spectra were recorded by using ARX 250 and DRX 500 instruments, equipped with multinuclear units and variable temperature control. If not mentioned otherwise, samples dissolved in C₆D₆ (10–20%) in 5 mm (o.d.) tubes were measured at 25 ± 1°C. Chemical shifts are given with respect to solvent signals (δ¹H (C₆D₅H) = 7.15; δ¹³C (C₆D₆) = 128.0; (CDCl₃) = 77.0) and external references (δ¹¹B (BF₃OEt₂) = 0, Ξ¹¹B = 32.083971 MHz; δ¹⁵N (MeNO₂, neat) = 0, Ξ¹⁵N =



Scheme 3.

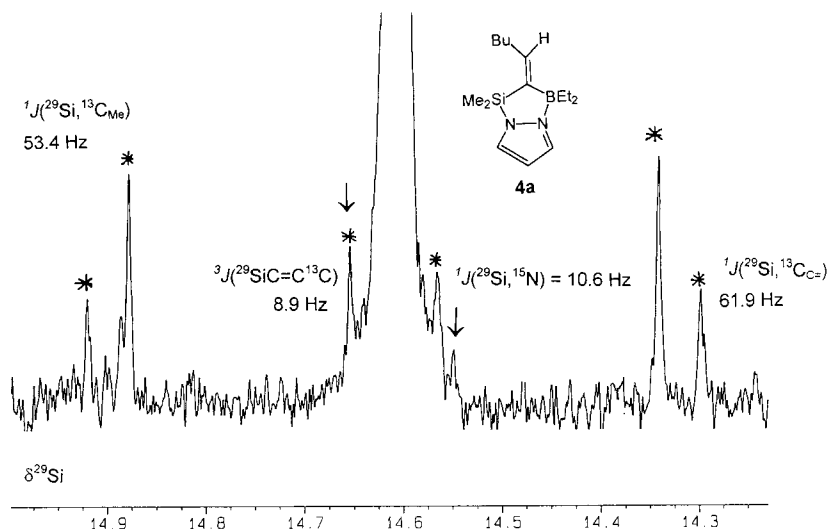


Fig. 1. ^{29}Si -NMR spectrum (99.4 MHz) of **4a** (5% in $[\text{D}_8]$ toluene, $22 = 1^\circ\text{C}$) recorded by the refocused INEPT pulse sequence [16] with ^1H decoupling (result of 800 transients, acquisition time 4 s; repetition delay 5 s). The ^{13}C satellites (isotope induced shifts $^1\Delta^{12/13}\text{C}(^{29}\text{Si}) = +1.5$ ppb (SiMe), $+0.5$ ppb (SiC=)) are marked by asterisks and the ^{15}N satellites (isotope induced shifts $^1\Delta^{14/15}\text{N}(^{29}\text{Si}) = -6.9$ ppb) by arrows. One of the ^{15}N satellites overlaps with the ^{13}C satellite corresponding to $^3J(^{29}\text{SiC}=\text{C}^{13}\text{C})$.

10.136767 MHz; $\delta^{14}\text{N}$ (MeNO₂, neat) = 0, $\Xi^{14}\text{N} = 7.226324$ MHz; $\delta^{29}\text{Si}$ (Me₄Si) = 0, $\Xi^{29}\text{Si} = 19.867184$ MHz). ^{15}N -NMR spectra were recorded by the refocused INEPT pulse sequence with ^1H decoupling [16], taking advantage of the scalar coupling $^{15}\text{N}-^1\text{H}$ (across two and three bonds with a magnitude of ca. 7 Hz). All ^{29}Si -NMR spectra were measured using the same technique, based on $^2J(^{29}\text{Si}, ^1\text{H}_{\text{Me}})$ and $^3J(^{29}\text{SiC}=\text{C}^1\text{H})$. Isotope induced chemical shifts $^1\Delta^{12/13}\text{C}(^{29}\text{Si})$ and $^1\Delta^{14/15}\text{N}(^{29}\text{Si})$ (see Fig. 1) are given with a negative sign if the signal of the heavy isotopomer is shifted to low frequency with respect to the lighter isotopomer.

4.2. (Z)-1-Chloro(dimethyl)silyl-1-diethylboryl-hex-1-ene **2a**

The reagent Et₂BH [2,13] (hydride concentration 1.17%) was cooled to -78°C and 1-hexenyl(chloro)dimethylsilane **1a** (1.50 g; 8.60 mmol) was added in one portion. The reaction mixture was stirred at -78°C for 45 min and then warmed up to room temperature, and kept stirring for 20 h. After removing all readily volatile material, a colourless, oily liquid remained which was identified as a mixture of **2a** in excess, and **3a** (in repeated experiments the ratio was not constant). **2a** ^1H -NMR (250 MHz; C₆D₆): $\delta^1\text{H} = 0.47$ (s, 6H, Me₂Si); 2.08 (t,d, 2H, CH₂C=); 5.77 (t, 1H, H-C=); various overlapping multiplets for the other ^1H resonances. **3a** ^1H -NMR (250 MHz; C₆D₆): $\delta^1\text{H} = 0.54$ (s, 6H, Me₂Si); 2.26 (t,d, 2H, CH₂C=); 6.40 (t, 1H, H-C=); various overlapping multiplets for the other ^1H resonances.

4.3. (Z)-1-Chloro(dimethyl)silyl-diethylboryl-3,3-dimethyl-but-1-ene **2b**

Compound **2b** is prepared in the same way as **2a**. However, the reaction takes a longer time for completion. The mixture was either kept at room temperature for 4 days or heated at 65°C for 4 h. After removing all readily volatile material **2b** was left in quantitative yield as a colourless, oily liquid. ^1H -NMR (250 MHz; C₆D₆): $\delta^1\text{H} = 0.57$ (s, 6H, Me₂Si); 0.97 (s, 9H, 'Bu); 1.33, 1.07 (q, t, 10H, Et₂B); 5.61 (s, 1H, H-C=; $^3J(^{29}\text{Si}, ^1\text{H}) = 23.8$ Hz).

4.4. 2-[(Z)-1-hexenyldiene]-1,3-dihydro-1,1-dimethyl-3,3-diethyl-1-sila-3-borata-4a,6a-diaza-pentalene **4a**

A solution of BuLi (8.58 mmol) in hexane (10 ml) was cooled to -78°C , and pyrazole (0.584 g; 8.58 mmol) was added. This mixture was kept stirring at -78°C for 3 h, and then at room temperature for 5 h. After cooling the mixture again to -78°C , the alkene **2a** (2.1 g; 8.6 mmol) was added in one portion. The mixture was warmed to room temperature, kept stirring for 2 h, and insoluble material was filtered off and washed with pentane. A colourless precipitate was obtained, when most of the solvent was removed in vacuo. Recrystallisation from pentane at -78°C gave pure **4a** (1.30 g; 55%) as colourless crystals (m.p. $116-118^\circ\text{C}$). ^1H -NMR (250 MHz; C₆D₆): $\delta^1\text{H} = 0.27$ (s, 6H, Me₂Si); 2.15 (t,d, 2H, CH₂C=); 6.52 (t, $^3J(^1\text{H}, ^1\text{H}(\text{CH}_2)) = 7.5$ Hz, 1H, H-C=); 5.87 (t, $^3J(^1\text{H}, ^1\text{H}) = 2.5$ Hz, 1H, H-C); 6.70 (d, $^3J(^1\text{H}, ^1\text{H}) = 2.5$ Hz, 1H, HCN); 7.23 (d,

$^3J(^1\text{H},^1\text{H}) = 2.5$ Hz, 1H, HCN); various overlapping multiplets for the other ^1H resonances.

4.5. 2-[(Z)-1-(3,3-Dimethyl)butenylidene]-1,3-dihydro-1,1-dimethyl-3,3-diethyl-1-sila-3-borata-4-thia-6a-aza-pentalene **5b**

A solution of BuLi (5.87 mmol) in ether (20 ml) was prepared and cooled to -78°C . After addition of thiazole the reaction mixture was kept stirring at -78°C for 12 h. Compound **2b** (1.43 g; 5.86 mmol) was added at -78°C . Then the mixture was warmed to room temperature, most of the solvent was removed, pentane (10 ml) was added, and insoluble material was filtered off. Removing pentane in vacuo left a pale, yellow solid which was recrystallised from pentane at -78°C to give 1.12 g (66%) of **5b** as colourless crystals (m.p. $57\text{--}58^\circ\text{C}$). $^1\text{H-NMR}$ (250 MHz; CDCl_3): $\delta^1\text{H} = 0.63$ (s, 6H, Me_2Si); $0.93\text{--}1.10$ (m, 10H, Et_2B); 1.12 (s, 9H, ^tBu); 6.41 (s, 1H, $\text{H-C}=\text{C}$); 7.49 (d, $^3J(^1\text{H},^1\text{H}) = 4.2$ Hz, HCN); 7.63 (d, $^3J(^1\text{H},^1\text{H}) = 4.2$ Hz, HCS).

Compound **6b** was isolated in the same way as described for **5b**. Compound **6b** was obtained in 76% yield as colourless crystals (m.p. $102\text{--}105^\circ\text{C}$). $^1\text{H-NMR}$ (250 MHz; C_6D_6): $\delta^1\text{H} = 0.41$ (s, 6H, Me_2Si); $1.00\text{--}1.13$ (m, 10H, Et_2B); 1.40 (s, 9H, ^tBu); 6.72 (s, 1H, $\text{H-C}=\text{C}$); 1.69 (d, $^4J(^1\text{H},^1\text{H}) = 1.8$ Hz, 3H, Me); 5.93 (q, $^4J(^1\text{H},^1\text{H}) = 1.8\text{Hz}$, 1H, HCS).

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