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1,1-Ethylboration of alkyn-1-yl-chloro(methyl)silanes: alkenes with chloro(methyl)silyl and diethylboryl groups in cis positions

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The 1,1-ethylboration of alkyn-1-yl-chloro(methyl)silanes, $Me_2Si(Cl)-C{\equiv}C-R$ (1) and $Me(H)Si(Cl)-C{\equiv}C-R$ (2) [R = Bu (2a), CH_2NMe_2 (2b)] requires harsh reaction conditions (up to 20 days in boiling triethylborane), and leads to alkenes in which the boryl and silyl groups occupy cis ((*E*)-isomers: 3a, 3b, 5a, 5b) or trans positions ((*Z*)-isomers in smaller quantities: 4b and 6b). The alkenes are destabilized in the presence of SiH(Cl) and CH_2NMe_2 units (5b, 6b). NMR data indicate hyper-coordinated silicon by intramolecular N–Si coordination in 3b and 5b, by which, at the same time, weak Si–Cl–B bridges are favoured. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: alkynes; boranes; silanes; organoboration; NMR

INTRODUCTION

The application of alkynylsilanes in organometallic synthesis is important, since these compounds are readily accessible, and they possess at least one reactive $Si-C{\equiv}$bond in addition to the $C{\equiv}C$ bond itself and other potential functions at the silicon atom. 1,1-Organoboration[1] of alkyn-1-yl-trimethylsilanes with triethylborane (BEt_3) requires heating at 100 °C for several hours in order to give selectively and in high yield type-**A** alkenes, in which the silyl and boryl groups occupy cis positions at the C=C bond (Scheme 1).[2,3] Such reactions proceed via cleavage of the $Si-C{\equiv}$bond and an alkynylborate-like intermediate.[1] Other, more reactive triorganoboranes, such as triallylborane[4] or 1-boraadamantane,[5] react faster than BEt_3.[6,7] In contrast, it was found that the presence of a chloro function at silicon, e.g. in alkyn-1-yl-chloro(dimethyl)silanes, $Me_2Si(Cl)-C{\equiv}C-R$, appears to prevent 1,1-ethylboration, since no appreciable reaction was observed after heating the alkynes with BEt_3 at 100 °C for several hours.[8]

Alkenes bearing organometallic substituents at the C=C bond are attractive reagents for further transformations. Various methods have recently been reported for the preparation of alkenes with boryl and silyl substituents.[9–14] Considering the synthetic potential of alkenes of type **A**, in particular if one of the Si–Me groups can be replaced by the Si–Cl function, it appeared worthwhile to reinvestigate the reaction of alkyn-1-yl-chloro(methyl)silanes **1** and **2** (Scheme 2) with BEt_3, using harsher reaction conditions. The products could become useful synthons for heterocyclic chemistry, and their identification should be straightforward using multinuclear magnetic resonance spectroscopy (^1H, ^{11}B, ^{13}C, ^{29}Si NMR).

RESULTS AND DISCUSSION

Synthesis of the alkyn-1-yl-chloro(methyl)silanes 1 and2

The reaction of chlorosilanes, Me_2SiCl_2 or $Me(H)SiCl_2$, in five- to ten-fold excess, with the respective lithium reagent, $LiC{\equiv}C-Bu$ or $LiC{\equiv}C-CH_2NMe_2$, leads to the alkyn-1-yl-chloro(methyl)silanes **1** and **2** as described.[15–17]

Reactions of the alkyn-1-yl-chloro(methyl)silanes 1 and 2 with BEt_3

The reactions of **1a** and **1b** with BEt_3 as the solvent proceed extremely slowly. However, after 2–3 weeks at 110 °C (oil

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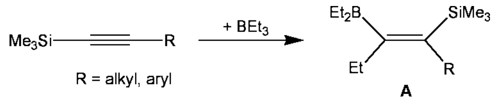
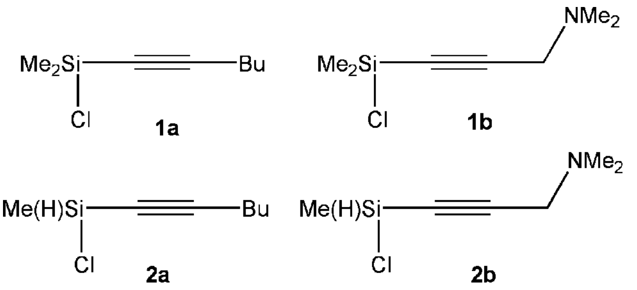


Scheme 1. 1,1-Ethylboration of alkyn-1-yl-trimethylsilanes.



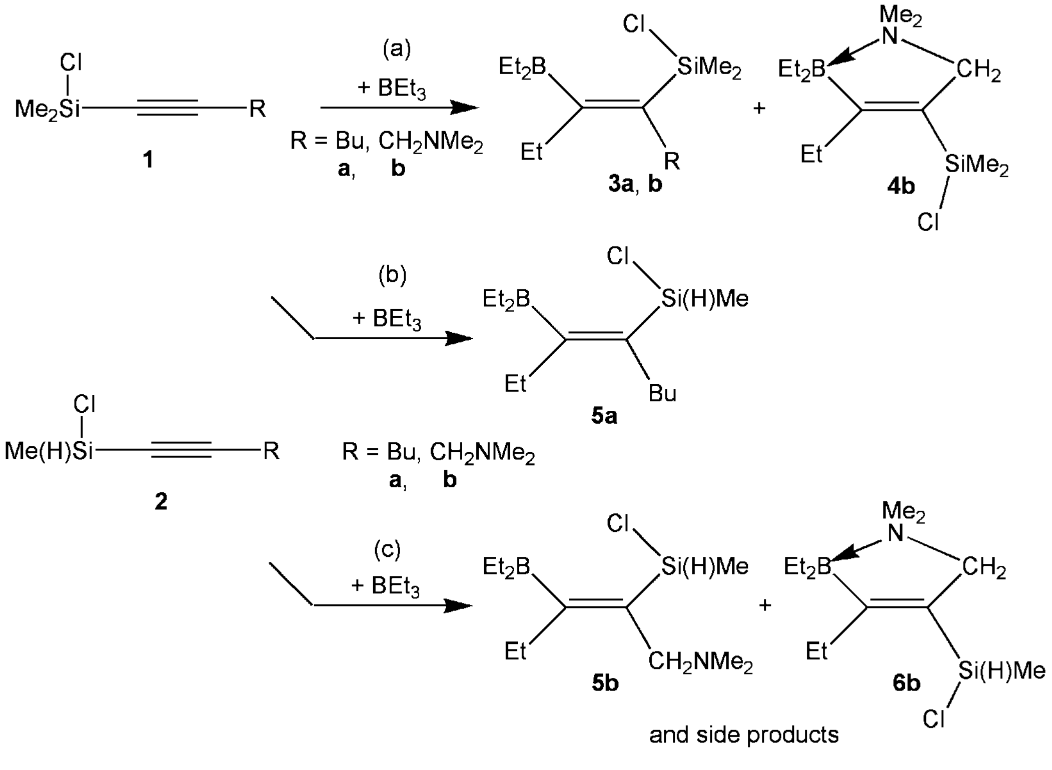
Scheme 2. Alkyn-1-yl-chloro(methyl)silanes studied for 1,1-ethylboration.

bath), the reactions afford selectively (>96% purity) the desired alkenes **3a** and **3b** along with a small amount (<5%) of the (Z)-isomer **4b** (Scheme 3a). The 1,1-ethylboration of **2a** and **2b** is already complete after 2–3 days under the same conditions. In the case of **2a**, clean formation of the alkene **5a** is observed (Scheme 3b); however, a 3 : 1 mixture of **5b** and **6b** (Scheme 3c) and several unidentified side products is obtained when starting from **2b**. Attempts to purify this mixture by fractional distillation lead to extensive decomposition. In contrast, the compounds **3a, 5a**, and the mixtures containing **3b** and **4b** could be isolated by distillation. The isolated products are colourless oils, sensitive to traces of oxygen and moisture, readily soluble in all inert organic solvents, and they can be stored in a refrigerator for prolonged periods. In all reactions of the propargylamine derivatives **1b** and **2b**, the ^{11}B NMR spectra of the reaction mixtures show intermolecular N–B coordination, since the ^{11}B NMR signal of the excess of BEt$_3$ is shifted to low frequencies. This shift depends on the excess of BEt$_3$ relative to the alkyne; therefore, fast exchange between free and coordinated BEt$_3$ takes place.

The reduced stability of the alkenes **5b** amd **6b**, in particular when compared with **3b** and **4b**, indicates that the presence of the Si–H and Si–Cl functions together with an amino function in close proximity within the same molecule is unfavourable. It is conceivable that elimination of HCl leads to unsaturated, highly reactive species. Although this is an interesting aspect, it prevents the straightforward synthesis of the desired alkenes.

NMR spectroscopic results

The pattern of substituents at the C=C bond in the alkenes **3–6** is consistent with the ^{1}H, ^{13}C, ^{11}B and ^{29}Si NMR data set (Table 1). The mutual positions of the substituents follow from the results of appropriate one-dimensional ^{1}H/^{1}H NOE experiments;[18,19] in the case of the isomers **4b** and **6b**, the



Scheme 3. 1,1-Ethylboration of the alkyn-1-yl-chloro(methyl)silanes; formation of the alkenylsilanes **3–6**.

Table 1. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of the alkenes **3**–**6**, and of **A** (R = Bu) and **7a**[22] for comparison

	3a	**3b**	**5a**	**5b**	**A**[b] (R = Bu)	**7a**	**4b**[c]	**6b**
δ^{13}C(SiC=)	131.9 (80.2)	133.7 (86.6)	131.4 (80.0)	133.6 (94.3)	135.0 (70.0)	133.4 (71.1)	122.0 (80.2)	122.9 (80.6)
δ^{13}C(BC=)	167.0 (br)	167.3 (br)	170.0 (br)	169.5 (br)	161.8 (br)	166.5 (br)	186.4 (br)	190.1 (br)
δ^{13}C(SiMe)	2.8 (56.0)	3.8 (60.3)	1.1 (55.8)	1.9 (63.7)	0.0 (50.2)	−2.1 (49.4)	0.7 (57.1)	1.4 (59.0)
δ^{13}C(BEt$_2$)	20.4 (br) 9.8	19.5 (br) 10.1	21.9(br) 9.7	20.2 (br) 10.5	21.5 (br) 9.8	21.5 (br) 10.5	11.0	14.2 (br) 11.1
δ^{13}C(R)	33.0, 29.4, 22.3, 13.1	45.1, 59.4 (7.4)	33.2, 29.1, 22.7, 13.3	45.9 60.1 (4.7)	32.7, 29.5, 22.6, 13.4	34.0, 30.2, 24.1, 14.8	45.5, 46.8 71.3	44.3, 44.2, 70.7 (12.3)
δ^{13}C(Et)	23.0 (9.1), 13.8	23.2 (9.9), 13.4	23.5, 14.2	24.7 (11.5), 13.2	23.5, 14.7	23.5 (8.8), 14.2	26.1	25.0 (8.0), 15.0
δ^{11}B	78.5	73.3	82.5	74.5	83.0	78.9	5.7	5.9
δ^{29}Si	21.1	15.8	3.9 [208.0]	−21.2 [246.8]	−6.5	−14.6 [168.8]	13.9	−9.7 Q[227.0]

[a] Measured in D_6D_6 at 23 °C; coupling constants $J(^{29}Si, ^{13}C)$ (±0.3 Hz) are given in parentheses and $^1J(^{29}Si, ^1H)$ in brackets [±0.3 Hz]; (br) denotes ^{13}C NMR signals of carbon atoms linked to boron.

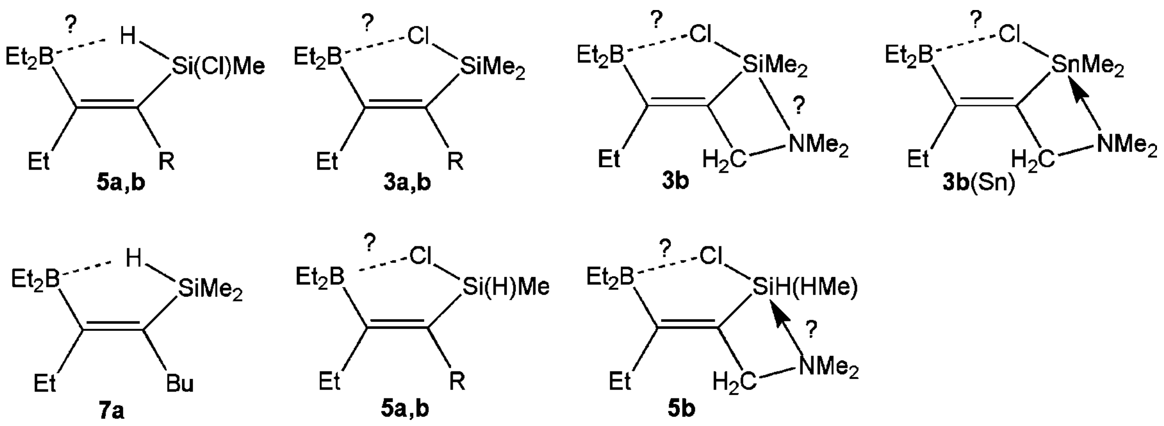
[b] The concentration of this isomer in the mixture with **3b** was too low for complete unambiguous assignments of ^{13}C NMR signals.

[c] In $CDCl_3$.

intramolecular coordinative N–B bond is confirmed by the ^{11}B NMR signals at low frequency (δ^{11}B 5.7, 5.9), typical of tetracoordinate boron atoms.[20]

Further intramolecular interactions are conceivable for the alkenes **3** and **5**, as shown in Scheme 4. Electron-deficient Si–H–B bridges in related molecules have been described recently.[21–24] They are readily identified owing to the unusually large isotope-induced chemical shifts $^2\Delta^{10/11}B(^{29}Si)$ in the ^{29}Si NMR spectra. Such effects are not observed in the ^{29}Si NMR spectra of **5a** or **5b**. Since this effect is readily observed in the case of **7a**,[22] it is concluded that the presence of the Si–Cl function in **5a** and **5b** reduces the hydride character of the Si–H function and prevents the boron-induced activation of this bond. The possibility of weak Si–Cl–B bridges, in particular in the cases of **3b** and **5b**, cannot be ruled out, since the ^{11}B nuclear shielding is slightly increased by up to 10 ppm when compared with that in alkenes of type **A**. This bridge may become stronger if there is a coordinative N–Si bond in the alkenes **3b** and **5b**. Such an interaction is clearly evident in the case of the tin analogue **3b**(Sn),[25] where the increase in ^{119}Sn nuclear shielding and changes in the magnitude of the coupling constants $^1J(^{119}Sn, ^{13}C)$ reflect the increase in the coordination number of the tin atom.[26,27] Indeed, the comparison of the respective data in Table 1 (δ^{29}Si and $^1J(^{29}Si, ^{13}C)$) indicates that the mean coordination number of the silicon atom in **3b** and **5b** is >4. The ^{29}Si nuclear shielding is increased (e.g. see **3a**/**3b** and **5a**/**5b**), although this shielding effect would be balanced to some extent by Si–Cl–B bridges. Even more significant are the changes in the magnitude of $^1J(^{29}Si, ^{13}C)$ or $^1J(^{29}Si, ^1H)$. The N–Si coordination is expected to enforce distorted trigonal bipyramidal surroundings of the silicon atom, where the Si–Me, Si–H and the Si–C=moieties prefer equatorial positions. Therefore, the magnitude of $^1J(^{29}Si, ^{13}C)$ in **3b** and **5b** is larger than in comparable compounds **3a** and **5a**. Similarly, there is a striking change in the magnitude of $^1J(^{29}Si, ^1H)$ in going from **5a** (208.0 Hz) to **5b** (246.8 Hz). These structural features would also be favourable for the formation of Si–Cl–B bridges in **3b** and **5b**, since the boron, chlorine and silicon atoms and the two olefinic carbon atoms can be easily arranged in one plane. Indeed, the ^{11}B nuclear shielding is somewhat increased in **3b** and **5b** when compared with that in **3a** and **5a**.

The change in the coordination number of the silicon atom should also be mirrored by isotope-induced chemical shifts $^1\Delta^{12/13}C(^{29}Si)$, which can be measured accurately (±0.3 ppb; positive sign indicates that the signal of the heavier isotopomer is shifted to higher frequency) from the ^{13}C satellites in the ^{29}Si NMR spectra (Fig. 1). Thus, in the case of **3a**, both methyl and olefinic ^{13}C nuclei cause a positive shift (+1.4 ppb and +0.7 ppb respectively), whereas in the case of **3b**, for which all other NMR data suggest an increase in the coordination number of silicon, the isotope-induced shift caused by the methyl ^{13}C is less positive (+0.6 ppb) and that caused by the olefinic ^{13}C is negative



Scheme 4. Potential Si–H–B, Si–Cl–B bridges and N–Si coordination.

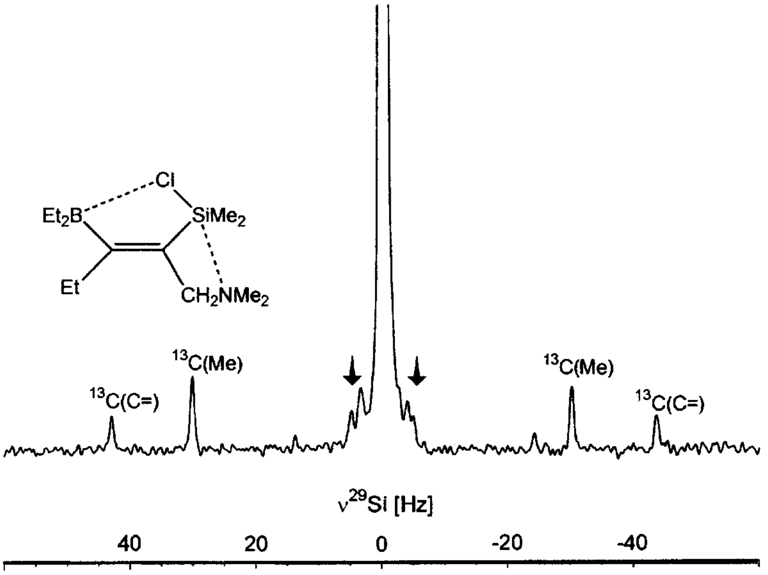


Figure 1. 49.7 MHz ^{29}Si{^{1}H} NMR spectrum (refocused INEPT[28]) of the alkenylsilane **3b** (10% v/v in C_6D_6; result of 512 transients; acquisition time 4 s; repetition time 5 s; FT after zero-filling without line broadening). The ^{13}C satellites (see text for isotope-induced chemical shifts $^1\Delta^{12/13}$C(^{29}Si)) are assigned; those marked with arrows belong to ^2J(^{29}Si, ^{13}C) = 7.4 Hz and ^3J(^{29}Si, ^{13}C) = 9.9 Hz.

(−5.1 ppb). Although, a quantitative treatment of isotope-induced chemical shifts is difficult,[33] these data appear to become a further sensitive NMR parameter, as has been shown by ^{29}Si NMR for compounds containing the Si–H–B bridge[21–24] and also for $^1\Delta^{12/13}$C(^{119}Sn) determined by ^{119}Sn NMR spectroscopy for various organotin compounds.[34–36]

CONCLUSIONS

Alkyn-1-yl-chloro(methyl)silanes can be converted by 1,1-ethylboration into alkenes with (*E*) configuration, in which the chloro(methyl)silyl and the boryl group are in cis positions at the C=C double bond. These alkenes can become useful synthons in heterocyclic synthesis. The stereoselectivity of the 1,1-ethylboration is lost to some extent if there is both an Si–H function and a dimethylaminopropargyl group in the starting alkyne. For the respective (*E*)-alkenes containing the CH_2NMe_2 group, NMR data indicate weak intramolecular N–Si coordination together with Si–Cl–B bridging, and for the (*Z*)-alkenes the ^{11}B NMR data suggest strong intramolecular N–B coordination.

EXPERIMENTAL

The preparative work and handling of samples for NMR measurements were carried out by observing necessary precautions to exclude traces of oxygen and moisture. Otherwise, non-selective oxidation of the B–C bonds and hydrolysis of the Si–Cl functions take place. Solvents were dried by standard methods. The chlorosilanes, 1-hexyne, *N*,*N*-dimethylpropargyl amine, and butyllithium in hexane (1.6 M) were used as commercial products without further purification. The alkyne derivatives **1** and **2** were prepared following literature procedures.[15–17,37]

NMR spectra were recorded at 23 °C on Bruker ARX 250 or DRX 500 spectrometers, both equipped with multinuclear units, using C_6D_6 solutions if not mentioned otherwise (*ca* 5–10% v/v) in 5 mm tubes. Chemical shifts are given with respect to Me_4Si (δ^1H (C_6D_5H) = 7.15, $\delta^{13}C$ (C_6D_6) = 128.0), $\delta^{29}Si = 0$ for Me_4Si with Ξ (^{29}Si) = 19.867187 MHz, and $\delta^{11}B = 0$ for BF_3–OEt_2 with Ξ (^{11}B) = 32.083971 MHz. All values ^3J(H, H) in the products are 7.3 ± 0.5 Hz, if not mentioned otherwise. ^{29}Si NMR spectra were recorded using the refocused INEPT pulse sequence with ^1H decoupling.[28–32] Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet. IR spectra: Perkin–Elmer Spectrum 2000 FTIR.

(*E*)-3-Diethylboryl-4-[chloro(dimethyl)silyl]-3-hexene

3a

Hexyn-1-yl-chloro(dimethyl)silane (**1a**; 2.5 g, 14.3 mmol) was dissolved in BEt_3 (6 ml) and the mixture was heated at 110 °C (oil bath) for 20 days until ^{29}Si NMR spectra showed that the alkyne had been consumed. The excess of BEt_3 was removed in a vacuum, and the residue was distilled under reduced pressure to give pure **3a** (b.p. 60–62 °C/2.5×10^{-3} Torr; 3.7 g, yield 95%). The compound **3b** (b.p. 70–74 °C; yield 95%) was prepared in the same way starting from **1b**. It contained a small amount (<5%) of the (*Z*)-isomer **4b**.

3a: ^1H NMR (C_6D_6; 250.1 MHz): $\delta = 0.42$ (s, 6H, $SiMe_2$), 2.02, 1.00 (q, t, 2H, 3H, =C–Et), 2.17, 1.32, 0.95 (m, m, t, 2H, 4H, 3H, =C–Bu), 1.34, 1.00 (m, t, 4H, 6H, BEt_2). EI-MS, *m/z* (%): 243 (100) [$M^+ - 30$], 154 (38) [$M^+ - 120$], 139 (78) [$M^+ - 134$], 125 (38) [$M^+ - 148$], 93 (10) [$M^+ - 180$]. **3b**: ^1H NMR (C_6D_6; 250.1 MHz): $\delta = 0.46$ (s, 6H, $SiMe_2$), 1.85, 0.86 (q, t, 2H, 3H, =C–Et), 2.88 (s, 2H, =C–CH_2N), 1.95 (s, 6H, NMe_2), 1.32, 1.07 (m, t, 4H, 6H, BEt_2). **4b**: ^1H NMR (C_6D_6; 250.1 MHz): $\delta = 0.35$ (s, 6H, $SiMe_2$), 3.17 (s, 2H, =C–CH_2N), 2.10 (s, 6H, NMe_2); all other signals overlap with those for **3b**.

(*E*)-3-Diethylboryl-4-[chloro(methyl)silyl]-3-hexene

5a

Hexyn-1-yl-chloro(methyl)silane (**2a**; 4 g, 20.8 mmol) was dissolved in BEt_3 (9.5 ml) and the mixture was heated at 105 °C (oil bath) for 65 h. The ^{29}Si NMR spectra showed that the alkyne had been consumed. After removing the excess of BEt_3 in a vacuum the oily residue was distilled under reduced pressure to give the pure product **5a** (b.p. 66–70 °C/5×10^{-3} Torr; 4.9 g, yield 90%). The analogous treatment of **2b** gave a crude reaction mixture that contained the alkene **5b**, its (*Z*)-isomer **6b** in a ratio of about 3 : 1, and several unidentified side products. The attempts to separate the mixture by fractional distillation led to extensive decomposition.

5a: ^1H NMR (C_6D_6; 250.1 MHz): $\delta = 0.40$ (d, 3H, SiMe, ^3J(H, H) = 3.7 Hz), 2.01, 0.82 (q, t, 2H, 3H, =C–Et), 2.20, 1.34, 0.89 (m, m, t, 2H, 4H, 3H, =C–Bu), 1.22, 0.99 (m, t, 4H, 6H, BEt_2), 4.50 (q, 1H, SiH, ^3J(H, H) = 3.7 Hz, ^1J(^{29}Si, ^1H) = 208.0 Hz). EI-MS, *m/z* (%): 229 (100) [$M^+ - 30$], 173 (36) [$M^+ - 86$], 153 (42) [$M^+ - 106$], 69 (43) [$M^+ - 190$], 55 (25) [$M^+ - 204$]. IR: ν(Si–H) 2142 cm^{-1}.

5b: ^1H NMR (C_6D_6; 250.1 MHz): $\delta = 0.42$ (d, 3H, SiMe, ^3J(H, H) = 2.8 Hz), 1.83, 0.84 (q, t, 2H, 3H, =C–Et), 2.93 (s, 2H, =C–CH_2N), 2.08 (s, 6H, NMe_2), 1.12, 0.94 (m, t, 4H, 6H, BEt_2), 4.80 (q, 1H, SiH, ^3J(H, H) = 2.8 Hz, ^1J(^{29}Si, ^1H) = 246.8 Hz). **6b**: ^1H NMR (C_6D_6; 250.1 MHz): $\delta = 0.38$ (d, 3H, SiMe, ^3J(H, H) = 2.5 Hz), 2.23 (q, 2H, =C–CH_2), 3.17 (s, 2H, =C–CH_2N), 2.06 (s, 6H, NMe_2), 5.14 (q, 1H, SiH, ^3J(H, H) = 2.5 Hz, ^1J(^{29}Si, ^1H) = 227.0 Hz); all other signals overlap with those for **5b**.

Acknowledgements

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