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1-Silacyclopent-2-enes and 1-silacyclohex-2-enes bearing functionally substituted silyl groups in 2-positions. Novel electron-deficient Si–H–B bridges

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The reactions of alkyn-1-yl(vinyl)silanes $R_2Si[C{\equiv}C\text{-}Si(H)Me_2]CH{=}CH_2$ [R = Me (1a), Ph (1b)], $Me_2Si[C{\equiv}C\text{-}Si(Br)Me_2]CH{=}CH_2$ (2a), and of alkyn-1-yl(allyl)silanes $R_2Si[C{\equiv}C\text{-}Si(H)Me_2]CH_2CH{=}CH_2$ (R = Me (3a), R = Ph (3b)] with 9-borabicyclo[3.3.1]nonane in a 1:1 ratio afford in high yield the 1-silacyclopent-2-ene derivatives 4a, b and 5a, and the 1-silacyclohex-2-ene derivatives 6a, b, respectively, all of which bear a functionally substituted silyl group in 2-position and the boryl group in 3-position. This is the result of selective intermolecular 1,2-hydroboration of the vinyl or allyl group, followed by intramolecular 1,1-organoboration of the alkynyl group. In the cases of 4a, b, potential electron-deficient Si–H–B bridges are absent or extremely weak, whereas in 6a,b the existence of Si–H–B bridges is evident from the NMR spectroscopic data (^1H, ^{11}B, ^{13}C and ^{29}Si NMR). The molecular structure of 4b was determined by X-ray analysis.

KEYWORDS: silanes; heterocycles; hydroboration; organoboration; NMR, multinuclear; X-Ray

INTRODUCTION

The presence of a vinyl or an allyl group bonded to the silicon atom in alkyn-1-ylsilanes offers attractive synthetic potential in 1,2-hydroboration[1–7] or 1,1-organoboration[8] reactions, in particular if these two types of reactions can be combined. Recently this was demonstrated by the straightforward synthesis of 1-silacyclopent-3-enes and 1-silacyclohex-2-enes.[9] It was shown that there is a choice of substituents R^1 in the Si–C≡C-R^1 unit (Scheme 1).

In this context, silyl groups R^1 with a Si–H or a Si–halogen function might be interesting candidates, considering further transformations and potential formation of Si–H–B[10–14] or Si–halogen–B bridges.[15] Although there is some interest in 1-silacyclopentenes[16–21] and 1-silacyclohexenes,[10,14] the convenient access to these heterocycles is limited so far to the hydroboration/organoboration method.[9] Therefore, the silanes **1**–**3** (Scheme 1) were prepared, and their reactivity towards 9-borabicyclo[3.3.1]nonane (9-BBN) was studied. It was expected, in analogy to previous results,[9] that 9-BBN would work as a hydroborating reagent in the first step of the reactions, followed by intramolecular 1,1-organoboration in the second step.

RESULTS AND DISCUSSION

Synthesis of the alkyn-1-yl(vinyl)silanes and the alkyn-1-yl(allyl)silanes

The alkyn-1-ylsilanes **1** and **3** were readily prepared from the respective silicon chlorides by treatment with the alkynyl Grignard reagent (Scheme 2). In the case of **1a**, the Si–H could be replaced with the Si–Br function in **2a** via the palladium-catalysed reaction of **1a** with allyl bromide.[22–24] The compound **2a** is a promising silane for further applications, since numerous other functions at the silicon atom can be introduced by taking advantage of the reactive Si–Br bond.

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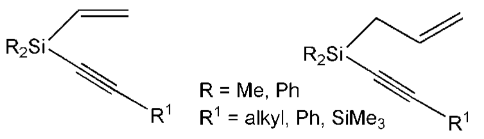
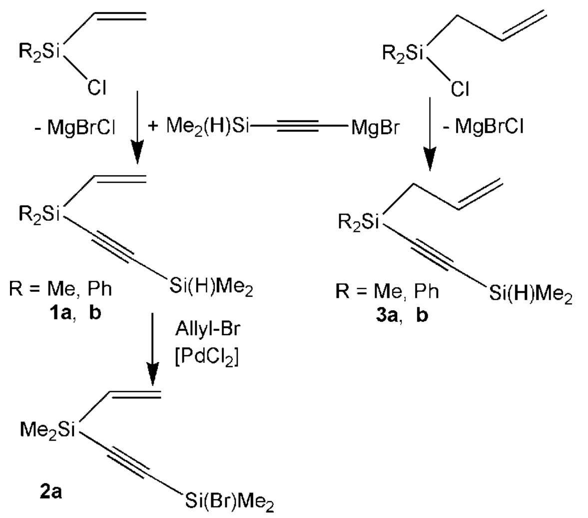
Hydroboration/organoboration of the alkyn-1-ylsilanes 1–3 with 9-BBN

The 1 : 1 reactions of **1**, **2** and **3** with 9-BBN (Scheme 3) led selectively to the 1-silacyclopent-2-enes **4** and **5**, and to the 1-silacyclohex-2-enes **6**, respectively, isolated as colourless oils or as a crystalline solid (**4b**). Gentle heating (50–60 °C) for several minutes was required to achieve complete conversion of the alkyne derivatives. As in previous studies,[9] where an intermediate of the type **9** had been identified, intermediates **7**, **8** or **9** were proposed here, but were not observed. The structures of the final products clearly indicate that 1,2-hydroboration took place in the expected way[1–7] in the first step, followed by 1,1-organoboration[8] in the second step of the reactions. Usually, intermolecular 1,1-organoboration of alkyn-1-ylsilanes requires rather harsh reaction conditions,[8,25] and the intramolecular 1,1-organoboration is known[26] to proceed under much milder reaction conditions. It is remarkable that neither the intermolecular 1,2-hydroboration nor the intramolecular 1,1-organoboration were affected by the presence of Si–H or Si–Br functions.

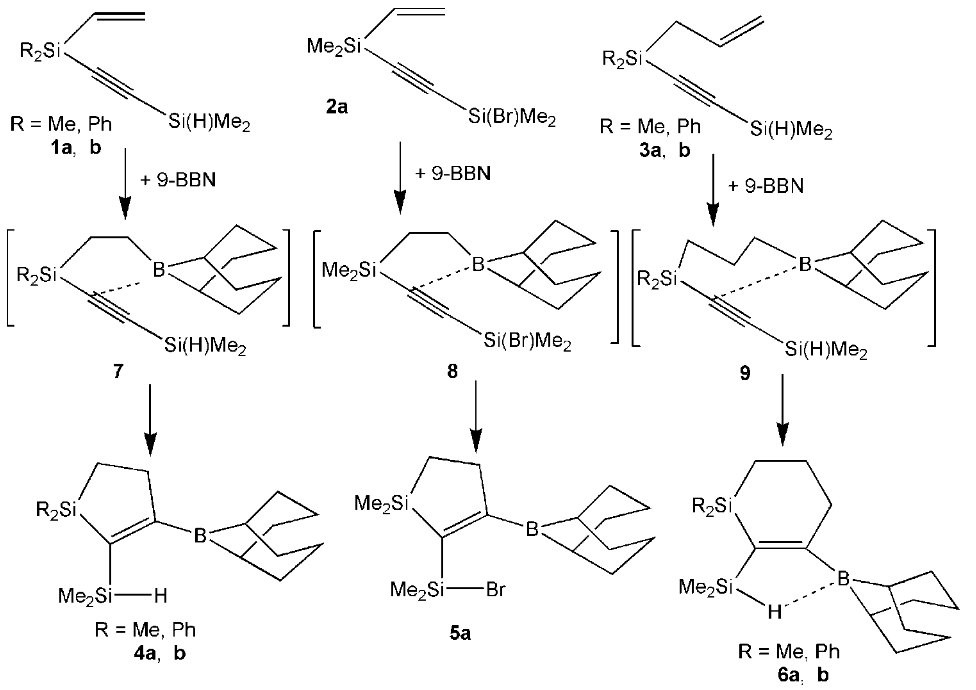


Scheme 1. Alkyn-1-yl(vinyl)- and alkyn-1-yl(allyl)silanes.

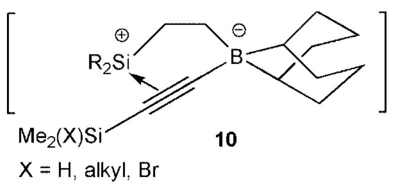
The intramolecular activation of the Si–C≡ bond by the neighbourhood to the electron deficient boron atom (indicated in Scheme 3 by dashed lines in the formulae for the intermediates **7–9**) is followed by cleavage of the Si–C≡ bond, formation of a zwitterionic borate-like intermediate of the type **10** (Scheme 4). Such intermediates have been structurally characterized,[8] when analogous reactions of alkyny-1-yltin[27] and -lead compounds[28] with triorganoboranes had been studied. In the present



Scheme 2. Synthesis of the alkyn-1-ylsilanes **1–3**.



Scheme 3. Hydroboration/organoboration of the alkny-1-ylsilanes to give 1-silacyclopent-2-enes **4, 5** or the 1-silacyclohex-2-enes **6**. In the structures of the proposed intermediates **7–9**, the activation of the Si–C≡ bonds by the boryl groups is indicated by dashed lines.



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Scheme 4. Proposed zwitterionic intermediate, immediate precursor of **4** or **5**.

case, fast rearrangement into the final products took place.

NMR spectroscopy

The proposed structures of the products **4, 5** and **6** in solution follows conclusively from the consistent set of NMR data (^{1}H, ^{11}B, ^{13}C, ^{29}Si NMR), as given in Table 1 and in the Experimental section.

The ^{13}C NMR spectra, recorded with a sufficient signal-to-noise ratio for observing ^{29}Si satellite signals corresponding to the coupling constants $J(^{29}\text{Si},^{13}\text{C})$,[29,30] provide useful structural information (Fig. 1). The assignment of the ^{13}C NMR signals is further supported by the typically broad NMR signals for boron-bonded ^{13}C nuclei.[31]

The question for bridges of the type Si–H–B or Si-Br-B is best addressed by the ^{29}Si and ^{11}B NMR spectra. Electron-deficient Si–H–B bridges have been firmly established for numerous examples,[10–14] for which the stereochemistry is similar compared with that in **4** and **5**. Reliable qualitative information on such Si–H–B bridges is evident from the unusual isotope-induced chemical shift $^2\Delta^{10/11}\text{B}(^{29}\text{Si})$ which is readily observed in the ^{29}Si NMR spectra (Fig. 2). These effects are hardly visible in the case of **4**, whereas they are readily apparent for **6** (Fig. 2). This suggests that the steric repulsion between the geminal silyl groups is reduced in the five-member ring **4** when compared with the six-member ring **6**. In the latter, this repulsion forces the exocyclic silyl group to approach the boryl group, which appears to be one requisite for the Si–H–B bridge. The molecular structure of **4b** in the solid state (vide infra) is in agreement with this argument. The ^{11}B nuclear shielding in **6** is increased when compared with that in **5**, in agreement with the Si–H–B bridge in **6**. The NMR spectroscopic evidence is corroborated by the IR spectra which show the absorption for the stretching vibration of the Si–H bond in **4b** in the normal range ($\nu = 2083\ \text{cm}^{-1}$), whereas in the case of **6b**, this vibration is observed at considerably lower wave numbers ($\nu = 1919\ \text{cm}^{-1}$), typical for the Si–H–B bridge.

Table 1. ^{13}C and ^{29}Si NMR data[a] for the 1-silacyclopent-2-enes **4a, b** and **5a**, and the 1-silacyclohex-2-enes **6a, b**

	δ^{29}Si	δ^1H	$\delta^{13}\text{C}_{(\text{C}-2)}$	$\delta^{13}\text{C}_{(\text{C}-3)}$	$\delta^{13}\text{C}_{(\text{C}-4)}$	$\delta^{13}\text{C}_{(\text{C}-5)}$	$\delta^{13}\text{C}_{(\text{C}-6)}$
4a[b]	27.5 {11.3}	4.37 (178.0)	140.4 [47.9] (Si-1) [61.4]	190.5 (br)	39.0 [6.4], [12.0] (^{2}J or ^{3}J)	11.1 [51.8]	—
4b[c]	18.4 {10.6}	4.67 (177.8)	136.3 [45.2] (Si-1) [65.7]	195.3 (br)	39.3 [11.8], [10.1] (^2J or ^3J)	11.2 [54.0]	—
5a[d]	28.7 {14.4}	—	138.8 [47.5] (Si-1) [67.8]	193.3 (br)	40.2 [5.5], [13.6] (^2J or ^3J)	11.2 [51.9]	—
6a[e]	−16.2 {8.2} (+2.7ppb)	3.78 (160.1)	131.6 [53.1] (Si-1) [57.0]	191.0 (br)	35.8 [9.8] [11.6] (^3J, ^3J)	22.3 [<3] (^2J)	13.3 [51.2]
6b[f]	−23.8 {8.4}	3.57 (148.6)	127.3 [58.6], [56.7][g]	195.8 (br)	36.3 [9.6], [11.7] (^3J, ^3J)	21.8 [<3] (^2J)	11.6 [52.6]

[a] In C_6D_6 at 296 K (ca. 5%); chemical shifts δ^1H (±0.05 ppm), δ^{13}C (±0.1 ppm), δ^{29}Si (±0.1 ppm), δ^{11}B (±0.3 ppm); coupling constants $^1J(^{29}\text{Si},{}^1\text{H})$, $J(^{29}\text{Si},^{13}\text{C})$ and $^2J(^{29}\text{Si},^{29}\text{Si})$ are given ±0.3 Hz in parentheses, brackets and braces, respectively. ^{13}C NMR signals for boron-bonded carbon atoms are broad (br) owing to partially relaxed scalar $^{13}\text{C}-^{11}\text{B}$ spin–spin coupling.[29] Isotope-induced chemical shifts $^2\Delta^{10/11}\text{B}(^{29}\text{Si})$ are given in ppb (±0.5 ppb) with a negative sign for the shift of the signal for the heavy isotopomer to lower frequency.

[b] Other ^{13}C NMR data: $\delta = -0.8$ [51.0] (SiMe_2H), 0.7 [48.2] ($\text{Me}_2\text{Si-1}$), 24.2, 33.4 (br), 34.5 (BBN); $\delta^{11}\text{B} = 85.1$; other ^{29}Si NMR data: $\delta = -23.1$ {11.3} (SiMe_2H).

[c] Other ^{13}C NMR data: $\delta = -0.9$ [51.1] (SiMe_2H), 24.2, 33.4 (br), 34.7 (BBN), 137.1 [65.6], 136.1, 128.6, 130.1 (Ph: *i*, *o*, *m*, *p*); $\delta^{11}\text{B} = 86.0$; other ^{29}Si NMR data: $\delta = -20.6$ {10.6} [Me_2Si, $^2\Delta^{10/11}\text{B}(^{29}\text{Si}) = -11.0$ ppb].

[d] Other ^{13}C NMR data: $\delta = 0.6$ [49.0] ($\text{Me}_2\text{Si-1}$), 6.6 [55.3] (SiMe_2Br), 24.1, 33.6 (br), 35.6 (BBN); $\delta^{11}\text{B} = 86.4$; other ^{29}Si NMR data: $\delta = 13.4$ {14.4} (SiMe_2Br).

[e] Other ^{13}C NMR data: $\delta = -0.8$ [49.2] (SiMe_2H), 0.7 [50.4] ($\text{Me}_2\text{Si-1}$), 24.7, 32.1 (br), 35.6; $\delta^{11}\text{B} = 75.9$; other ^{29}Si NMR data: $\delta = -4.8$ {8.2} [SiMe_2H, $^2\Delta^{10/11}\text{B}(^{29}\text{Si}) = -67.0$ ppb].

[f] Other ^{13}C NMR data: $\delta = -1.1$ [50.0] (SiMe_2H), 24.9, 31.5 (br), 35.7 (BBN), 138.1 [67.1], 136.4 [3.8], 128.6 [4.9]; 130.0 (Ph: *i*, *o*, *m*, *p*); $\delta^{11}\text{B} = 70.8$; other ^{29}Si NMR data: $\delta = 2.0$ {8.4} [SiMe_2H, $^2\Delta^{10/11}\text{B}(^{29}\text{Si}) = -79.0$ ppb].

[g] No assignment for coupling with ^{29}Si-1 or $^{29}\text{Si}(\text{SiMe}_2\text{H})$.

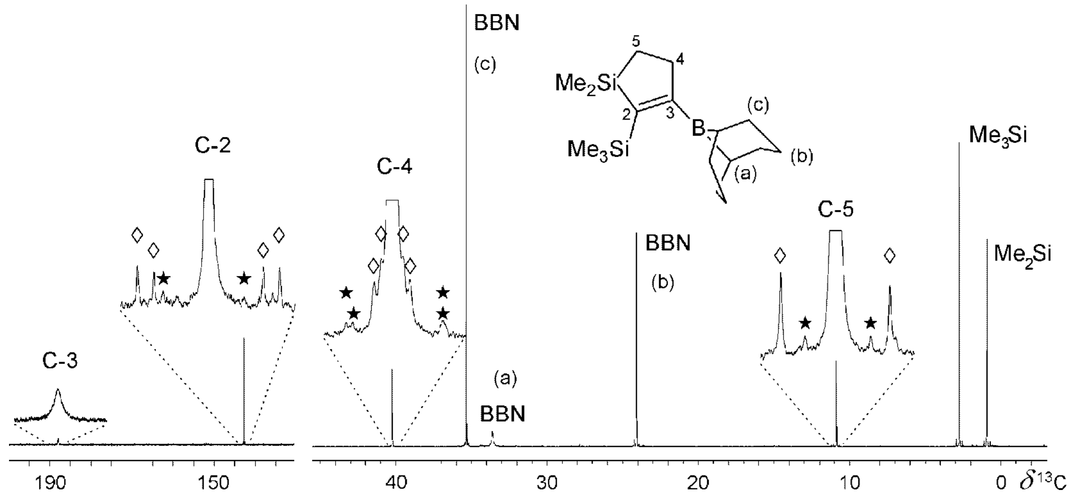

Figure 1. The 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the 1-silacyclopent-2-ene **5a** in C_6D_6 (5%). Note the broad ^{13}C NMR signals of carbon atoms bonded to boron.[31] Si satellites are marked by diamonds. Impurities are marked by asterisks.

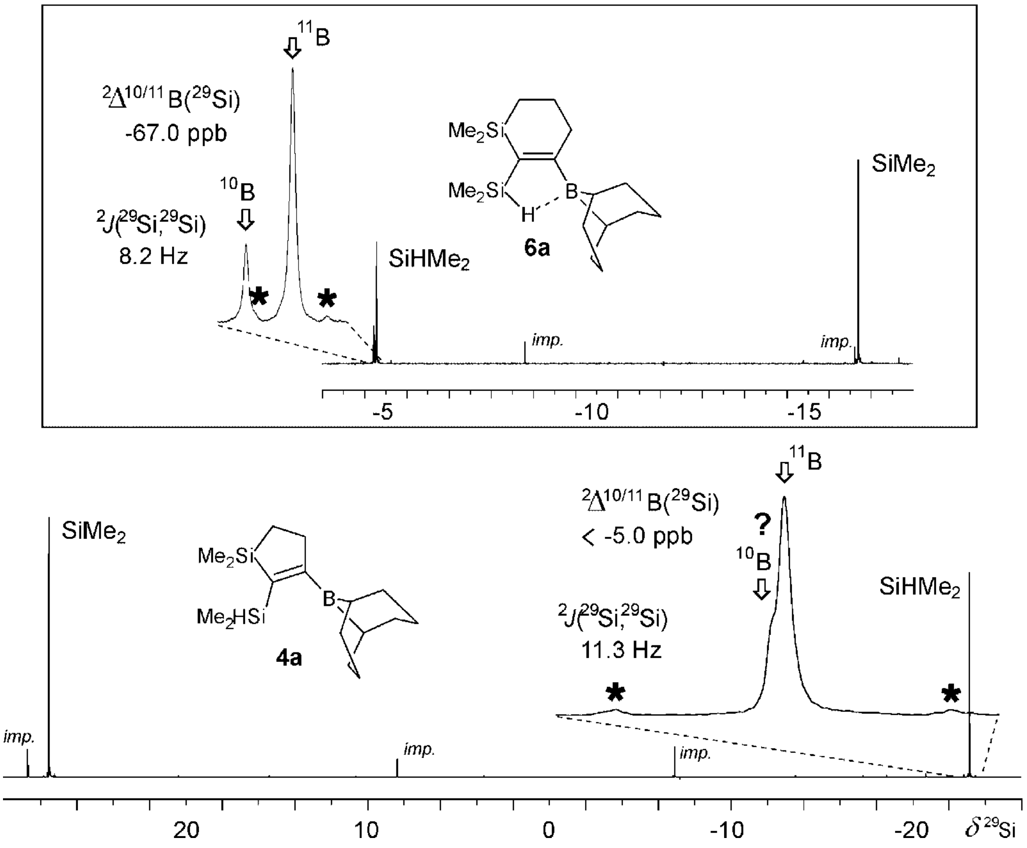

Figure 2. The 99.6 MHz $^{29}Si\{^1H\}$ NMR spectra of **4a** (lower trace) and **6a** (insert), both recorded using the refocused INEPT pulse sequence[38,39] with delays based on $^2J(^{29}Si,^1H_{Me}) = 7$ Hz. Note the marked difference in ^{29}Si nuclear shielding for the ^{29}Si-1 nuclei with typical deshielding for the five-member ring.[27,28] There is also a marked difference for the $\delta^{29}Si(SiMe_2H)$ values, since in **6a** the Si–H–B bridge is present (see the characteristic isotope-induced chemical shift $^2\Delta^{10/11}B(^{29}Si)$[11–14]), whereas such a bridge does not play a role in the case of **5a** [see the expansion of the $^{29}Si(SiH)$ NMR signal of **4a**]. ^{29}Si satellites are marked by asterisks and diamonds, respectively (for other data see Table 1).

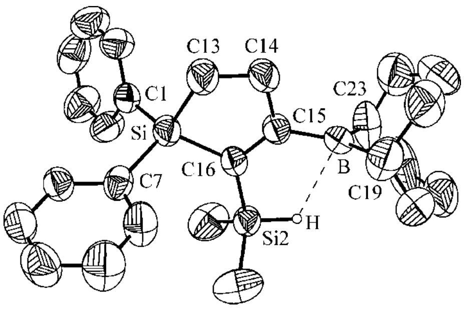

Figure 3. ORTEP plot (50%) of the molecular structure of the 1-silacyclopent-2-ene **4b** (except for the Si–H group, H atoms have been omitted). Selected bond lengths (pm) and angles (deg): Si1–C1, 187.2(4); Si1–C7, 186.8(4); Si1–C13, 187.6(4); Si1–C16, 187.7(3); C13–C14, 151.0(5); C14–C15, 152.0(5); C15–C16, 137.4(4); B–C15, 157.4(5); Si2–H, 133; B–H, 265; C1–Si1–C7, 108.2(2); C13–Si1–C16, 93.4(2); Si1–C13–C14, 105.0(3); C14–C15–C16, 118.0(2); Si1–C16–C15, 108.3(3); Si2–C16–C15, 120.4(2); Si1–C16–Si2, 131.3(2).

Any appreciable coordinative Br–B bonding in **5** should be mirrored by increased ^{11}B nuclear magnetic shielding,[15] which is not the case.

Crystal structure of the 1-silacyclopent-2-ene 4b

The molecular structure of **4b** is shown in Fig. 3. The five-member ring is almost planar (mean deviation 90 pm), and the endocyclic bond angle at the silicon atom is small [93.4(2)°], as expected.[9] Since the surroundings of the boron atom are trigonal planar within experimental error, any coordinate interactions involving the boron atom must be absent or extremely weak. However, the BC_2 plane of the 9-BBN unit is strongly twisted against the SiC_4 plane [71.9(2)°], and the Si–H bond is oriented into the direction of the boron atom (mean deviation of the plane B–C15–C16–Si2–H: 50 pm). Although the determination of the Si–H and B–H distances is associated with a considerable experimental error, the large B–H distance (265 pm) rules out B–H bonding. With the exception of the C14–C15 bond [152.0(5) pm], all other bond lengths and angles are found in the expected range. The elongation of the C14–C15 bond can be explained by the effect of hyperconjugation[32,33] involving this C–C σ bond and the formally empty boron p_z orbital,[34,35] in agreement with the arrangement of the 9-BBN group.

CONCLUSIONS

The combination of 1,2-hydroboration and 1,1-organoboration is an efficient strategy in the synthesis of novel heterocycles such as 1-silacyclopent-2-enes and 1-silacyclohex-2-enes, and it is shown that this method tolerates functional groups with Si–Br or Si–H bonds in 2-positions. The application of multinuclear NMR spectroscopy is valuable beyond measuring routine NMR data, since it allows one to distinguish between the absence or presence of electron-deficient Si–H–B bridges.

EXPERIMENTAL

General

The preparative work and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Solvents were carefully dried and distilled in an argon atmosphere, and oven-dried glassware was used throughout. A solution of ethynyl(dimethyl)silane in THF was prepared as described[36,37] and used for the reaction with EtMgBr in order to obtain the alkynyl Grignard reagent. Other starting materials were commercially available (allyl bromide, palladium dichloride, chlorosilanes, 9-BBN) and were used without further purification. NMR measurements (see Table 1 for accuracy of the data; Bruker ARX 250, DRX 500 and Varian Inova 400): ^{1}H, ^{13}C ^{11}B, ^{29}Si NMR [refocused INEPT[38,39] based on or $^{1}J(^{29}\text{Si},^{1}\text{H}) = 200$ Hz or $^{2,3}J(^{29}\text{Si},^{1}\text{H}) = 7$ Hz]. Chemical shifts are given relative to Me_4Si [δ^{1}H (C_6D_5H) = 7.15; δ^{13}C (C_6D_6) = 128.0; $\delta^{29}\text{Si} = 0$ for $\Xi(^{29}\text{Si}) = 19.867184$ MHz; $\delta^{11}\text{B} = 0$ for external BF_3-OEt_2 with $\Xi(^{11}\text{B}) = 32.083971$ MHz]. FTIR: Perkin Elmer 1600 and Perkin Elmer Spectrum One. EI-MS spectra: Finnigan MAT 8500 spectrometer (ionization energy 70eV) with direct inlet; the m/z data refer to the isotopes ^{1}H, ^{12}C, ^{11}B, ^{28}Si. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

Preparation of alkyn-1-ylsilanes 1 and 3

To the solution of the $Me_2(H)Si{-}C{\equiv}C{-}MgBr$ (30 mmol) in THF [150 ml; freshly prepared by treatment of the THF solution of $Me_2(H)Si{-}C{\equiv}C{-}H$ with C_2H_5MgBr at RT] the equimolar amount of the dimethyl(vinyl)-, diphenyl(vinyl), allyl(dimethyl)- or allyl(diphenyl)chlorosilane was added at 0 °C. The mixture was kept stirring for 1 h at room temperature, then THF was removed *in vacuo* and the oily residue was dissolved in pentane. Insoluble materials were filtered off, pentane was removed *in vacuo* and fractional distillation at reduced pressure gave the silanes **1** and **3** as colourless liquids.

1a

Yield 69%, b.p. = 67–69 °C/15 Torr; ^{1}H NMR (400 MHz, 296 K): $\delta = 0.18$ (s, 6H, $SiMe_2$), 0.19 [d, 6H, $SiMe_2H$, $^{3}J(^{1}\text{H},^{1}\text{H}) = 3.8$ Hz], 4.07 [sp, 1H, SiH, $^{3}J(^{1}\text{H},^{1}\text{H}) = 3.8$ Hz, $^{1}J(^{29}\text{Si},^{1}\text{H}) = 201.8$ Hz], 5.80 [dd, 1H, $=CH_2$, $^{2}J(^{1}\text{H},^{1}\text{H}) = 4.1$ Hz, $^{3}J(^{1}\text{H},^{1}\text{H})_{trans} = 19.5$ Hz], 5.99 [dd, 1H, $=CH_2$, $^{2}J(^{1}\text{H},^{1}\text{H}) = 4.1$ Hz, $^{3}J(^{1}\text{H},^{1}\text{H})_{cis} = 14.5$ Hz], 6.09 [dd, 1H, =CH, $^{3}J(^{1}\text{H},^{1}\text{H}) = 14.5$ Hz, 19.5 Hz]; ^{13}C NMR (100.5 MHz, 296 K): δ [$J(^{29}\text{Si},^{13}\text{C})$] = −3.1 [56.1] [7.4] ($SiMe_2H$), −1.7 [57.5] ($SiMe_2$), 111.8 [78.6] [12.9] (HSi–C≡), 113.3 [79.0] [12.6]

(Me_2Si–C≡), 133.2 (=CH_2), 136.0 [71.7] (CH=); ^{29}Si NMR (79.4 MHz, 296 K): $\delta = -38.5$ ($SiHMe_2$), −32.8 ($SiMe_2$). IR (toluene): $\nu = 2140.4$ cm^{-1} (Si–H).

1b

Yield 81%, b.p. = 102–108 °C/6 × 10^{-2} Torr; ^1H NMR (400 MHz, 296K): $\delta = 0.02$ [d, 6H, $SiMe_2H$, $^3J(^1H,^1H) = 3.9$ Hz], 4.27 [sp, 1H, SiH, $^3J(^1H,^1H) = 3.9$ Hz, $^1J(^{29}Si,^1H) = 203.5$ Hz], 6.0 (m, 2H, =CH_2), 6.35 [dd, 1H, =CH-, $^3J(^1H,^1H)_{trans} = 19.8$ Hz, $^3J(^1H,^1H)_{cis} = 14.8$ Hz], 7.1 (m, 6H, Ph), 7.7 (m, 4H, Ph); ^{13}C NMR (100.5 MHz, 296 K): δ [$J(^{29}Si,^{13}C)$] = −2.7 [55.4] (Me_2*Si*), 110.9 [87.2] [12.4] (≡C-$SiPh_2$), 116.5 [77.4] [13.2] (≡C–$SiMe_2$), 133.8 [77.1], 136.1, 128.9, 130.8 (Ph: *i*, *o*, *m*, *p*), 133.6 [75.5] (=CH–), 137.6 (=CH_2); ^{29}Si NMR (79.4 MHz, 296 K): δ {$^3J(^{29}Si,^{29}Si)$} = −38.3 {1.6} (Me_2Si), −3.7 {1.6} (Ph_2Si). IR (toluene): $\nu = 2037.6$ cm^{-1} (C≡C), 2139.4 cm^{-1} (Si–H). EI-MS: *m/z* (%): 292 (100) [M^+], 277 (38) [M^+-CH_3].

3a

Yield 79%, b.p. = 76–80 °C/15 Torr; ^1H NMR (400 MHz, 296 K): $\delta = 0.01$ (s, 6H, $SiMe_2$), 0.04 [d, 6H, $SiMe_2H$, $^3J(^1H,^1H) = 3.8$ Hz], 2.10 [dt, 2H, CH_2, $^3J(^1H,^1H) = 7.8$ Hz, $^4J(^1H,^1H) = 1.0$ Hz, $^2J(^{29}Si,^1H) = 8.9$ Hz], 4.11 [sp, 1H, SiH, $^3J(^1H,^1H) = 3.8$ Hz, $^1J(^{29}Si,^1H) = 201.3$ Hz], 4.8–4.9 (m, 2H, =CH_2), 5.90 [ddt, 1H, =CH–, $^3J(^1H,^1H)_{trans} = 16.7$ Hz, $^3J(^1H,^1H)_{cis} = 9.9$ Hz, $^3J(^1H,^1H) = 7.8$ Hz]; ^{13}C NMR (100.5 MHz, 296 K): δ [$J(^{29}Si,^{13}C)$] = −3.0 [56.1] ($SiHMe_2$), −2.2 [55.8] ($SiMe_2$), 21.6 [53.6], 134.8, 115.9 [5.6] (CH_2–CH=CH_2), 112.3 [84.9] [12.6] (≡C–$SiMe_2$All), 116.1 [77.0] [14.0] (≡C–$SiHMe_2$); ^{29}Si NMR (79.4 MHz, 296 K): δ {$^3J(^{29}Si,^{29}Si)$} = −38.8 {1.8} (Me_2HSi), −32.0 {1.8} (Ph_2Si).

3b

Yield 85%, b.p. = 114–116 °C/6 × 10^{-2} Torr; ^1H NMR (400 MHz, 296 K): $\delta = 0.05$ (d, 6H, Me_2Si, $^3J(^1H,^1H) = 3.8$ Hz), 2.06 [dt, 2H, CH_2, $^3J(^1H,^1H) = 7.7$ Hz, $^4J(^1H,^1H) = 1.1$ Hz, $^2J(^{29}Si,^1H) = 9.0$ Hz], 4.28 [sp, 1H, SiH, $^3J(^1H,^1H) = 3.8$ Hz, $^1J(^{29}Si,^1H) = 203.0$ Hz], 4.8–4.9 (m, 2H, =CH_2), 5.85 [ddt, 1H, =CH–, $^3J(^1H,^1H) = 16.9$ Hz, $^3J(^1H,^1H) = 9.9$ Hz, $^3J(^1H,^1H) = 7.7$ Hz], 7.1 (m, 6H, Ph), 7.7 (m, 4H, Ph); ^{13}C NMR (100.5 MHz, 296 K): δ [$J(^{29}Si,^{13}C)$] = −2.7 [55.8] ($SiMe_2$), 22.7 [54.9], 133.5, 116.1 [5.4] (CH_2–CH=CH_2), 111.4 [85.3] [12.5] (≡C–Si–All), 116.3 [77.4] [12.7] (≡C–$SiHMe_2$), 134.0 [75.5], 135.8 [4.0], 128.1 [5.8], 130.7 (Ph: *i*, *o*, *m*, *p*); ^{29}Si NMR (79.4 MHz, 296 K): δ {$^2J(^{29}Si,^{29}Si)$} = −38.3 {1.7} (Me_2HSi), −27.4 {1.7} (Ph_2Si). IR (toluene): $\nu = 2140$ cm^{-1} (Si–H). EI-MS: *m/z* (%): 306 (8) [M^+], 265 (100) [M^+-C_3H_5].

Synthesis of bromo(dimethyl)silylethynyl (dimethyl)vinylsilane 2a

The mixture of the silicon hydride **1a** (typically 10–30 mmol) together with a 1.2-molar excess of allyl bromide (typically 12–36 mmol) and $PdCl_2$ (3 mol%) was heated for 1 h at 70 °C. Insoluble materials were filtered off, unreacted allyl bromide was removed at reduced pressure, and the residue was distilled *in vacuo* to give the bromosilane **2a** as a colourless liquid (84%; b.p. = 91–93 °C/15 Torr). ^1H NMR (400 MHz, 296 K): $\delta = 0.29$ (s, 6H, Me_2Si), 0.63 (s, 6H, Me_2SiBr), 5.96 [dd, 1H, =CH_2, $^3J(^1H,^1H)_{trans} = 20.0$ Hz, $^2J(^1H,^1H) = 3.7$ Hz], 6.05 [dd, 1H, =CH_2, $^3J(^1H,^1H)_{cis} = 14.5$ Hz, $^2J(^1H,^1H) = 3.7$ Hz]m 6.18 [dd, 1H, =CH–, $^3J(^1H,^1H) = 20.0$ Hz, 14.5 Hz]; ^{13}C NMR (100.5 MHz, 296 K): δ [$J(^{29}Si,^{13}C)$] = −1.3 [57.9] (Me_2Si), 4.8 [63.2] (Me_2SiBr), 110.2 [92.4] [12.3] (≡C-$SiBrMe_2$), 115.9 [77.1] [16.1] (≡C–$SiMe_2$), 134.5 [10.4] (=CH_2), 136.0 [72.1] (=CH–); ^{29}Si NMR (79.4 MHz, 296 K): δ {$^3J(^{29}Si,^{29}Si)$} = −24.5 {1.8} (Me_2Si), −8.7 {1.8} (Me_2SiBr).

Reaction of the silanes 1a,b, 2a and 3a,b with 9-borabicyclo[3.3.1]nonane (9-BBN)

General procedure

To the solution/suspension of 9-BBN (4–5 mmol) in benzene (3 mL) the equimolar amount of the respective silane was added, and the mixture was heated at reflux for 1 min. Then the solvent was removed *in vacuo* and the oily residue was distilled under reduced pressure to give colourless oils in essentially quantitative yield or recrystallized from hexane to give white solids in 70–80% yield.

4a

Boiling point = 92–98 °C/6 × 10^{-2} Torr; ^1H NMR (400 MHz, 296 K): $\delta = 0.08$ [d, 6H, $SiMe_2H$, $^3J(^1H,^1H) = 3.8$ Hz], 0.09 (s, 6H, $SiMe_2$), 0.60 (m, 2H, CH_2Si), 1.64, 1.80 (m, m, 2H, 12H, BBN), 2.64 (m, 2H, CH_2).

4b

Melting point = 114–121 °C; ^1H NMR (400 MHz, 296 K): $\delta = 0.19$ [d, 6H, $SiMe_2H$, $^3J(^1H,^1H) = 3.7$ Hz], 1.33 (m, 2H, CH_2Si), 1.60, 1.95, 2.11 (m, m, m, 2H, 4H, 8H, BBN), 2.98 (m, 2H, CH_2), 7.33 (m, 6H, Ph), 7.78 (m, 4H, Ph). IR (toluene): $\nu = 2083$ cm^{-1} (Si–H). EI-MS: *m/z* (%): 414 (1) [M^+], 292 (100) [M^+-(BBN–H)].

5a

^1H NMR (400 MHz, 296 K): $\delta = 0.37$ (s, 6H, $SiMe_2$), 0.75 (s, 6H, $SiMe_2Br$), 0.83 (m, 2H, CH_2Si), 1.6–2.3 (m, 14H, BBN), 2.88 (m, 2H, CH_2).

6a

Boiling point = 105–110 °C/6 × 10^{-2} Torr; ^1H NMR (400 MHz, 296 K): $\delta = 0.03$ (s, 6H, $SiMe_2$), 0.11 [d, 6H, $SiMe_2H$, $^3J(^1H,^1H) = 3.3$ Hz], 0.58 (m, 2H, 6-CH_2), 1.4–2.0 (m, 16H, BBN, 5-CH_2), 2.13 (m, 2H, 4-CH_2).

6b

^1H NMR (400 MHz, 296 K): $\delta = -0.14$ [d, 6H, $SiMe_2$, $^3J(^1H,^1H) = 3.1$ Hz], 1.07 (m, 2H, 6-CH_2), 1.6, 2.0 (m, m, 2H, 12H, BBN), 1.80 (m, 2H, 4-CH_2), 2.35 (m, 2H, 4-CH_2), 7.1 (m, 6H, Ph), 7.6 (m, 4H, Ph). IR (toluene): $\nu = 1919$ cm^{-1} (Si–H). EI-MS: *m/z* (%): 428 (42) [M^+].

X-Ray structural analysis of the 1-silacyclopent-2-ene 4b

The X-ray crystal structural analysis of **4b** was carried out at 293(2) K using a STOE IPDS I system with Mo Kα radiation so that $\theta_{max} = 28.1°$ for a crystal $0.08 \times 0.18 \times 0.26$ mm^3. $M = 414.53$, Triclinic space group: $P\bar{1}$. Unit cell dimensions: $a = 8.2735(17)$, $b = 11.478(2)$, $c = 14.024(3)$ pm, $\alpha = 94.81(3)$, $\beta = 100.60(3)$, $\gamma = 109.31(3)$ °, $V = 1220.4(4)$ nm^3, $Z = 2$, $\mu = 0.155$ mm^{-1}, $F(000) = 448$. Reflections collected = 10 640, independent reflections = 5488 ($R_{int} = 0.064$) and 2079 with $I > 2\sigma(I)$. Final R indices (observed data): $R = 0.063$, $wR = 0.135$; (all data): $R = 0.161$, $wR = 0.169$. CCDC deposition no. = 277 933.

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