1. Introduction

There is a considerable interest in the synthesis of 1-silacyclobutene derivatives [1-7]. For the last few years we are dealing with the combination of 1,2-hydroboration and 1,1-organoborations and have applied this approach to the synthesis of several heterocycles including 1-silacyclobutene derivatives (A in Scheme 1) [8-12] and 4-silaspiro[3.3]hepta-1,5-diene derivatives (B in Scheme 1) [13]. The 1-silacyclobutene derivatives bear a variety of substituents at the silicon atom such as Si-Cl, Si-H, Si-Ph, Si-Me as well as at ring position 4 (Me, Bu, Ph). The synthetic approach adopted by our group has certain advantages, for instance, the reactions are highly selective and side reactions appear to be negligible [10]. The reaction has been fully explored and the mechanism is reasonably well understood.

Here we have extended our work [12] to study the hydroboration of trialkyn-1-ylsilanes Me-Si(C≡C-R)3 1 and Ph-Si(C≡C-R)3 2 [R= tBu(a), Ph(b), 4-Me-C₆H₄(c)]. These silanes were treated with one equivalent and two equivalents of 9-BBN, aiming for the synthesis of 1-silacyclobutene derivatives with exocyclic Si-alkenyl or Si-alkynyl functions. In addition to Si-Me or Si-Ph group in the starting silanes, the influence of Si-C≡C-R groups were investigated on the course of the 1,2-hydroboration reactions.

2. Experimental Procedure

All preparative work and handling of air sensitive chemicals were carried out by observing precautions to exclude oxygen and moisture. Dry solvents and oven-dried glassware were used throughout. Silanes 1, 2 [14-19] and 3b [20] were prepared following the literature.
procedure. Crystalline 9-borabicyclo[3.3.1]nonane (9-BBN), 3,3-dimethylbutyne, n-BuLi in hexane (1.6 m) were commercial products and were used as received. NMR spectra: Varian Inova 300 MHz and 400 MHz spectrometers (23±1°C), all equipped with multinuclear units, using C6D6 solutions, if not mentioned (ca. 10-15 % v/v) in 5 mm tubes. Chemical shifts are given with respect to SiMe4 [δ1H (C6D5H) = 7.15, δ13C (C6D6) = 128.0, δ29Si = 0 for SiMe4 with Ξ(29Si) = 19.867187 MHz], and δ11B = 0 for BF3·OEt2 with Ξ(11B) = 32.08397 MHz. 29Si NMR spectra were recorded using the refocused INEPT pulse sequence with 1H decoupling [21-24], based on 3J(29Si-C=C-1H) = 25-30 Hz or 3J(29Si-Me/Ph) = 7 Hz (after optimisation of the respective refocusing delays).

2.1. Preparation of trialkyn-1-ylsilanes 1 and 2.

The silane derivatives 1 and 2 were prepared following the literature procedure. They were purified by fractional distillation (R= n-Bu(a)) or recrystallization (R= Ph(b), 4-Me-C6H4(c)) and their structures were determined by NMR in solution and X-ray structural analysis in the solid state [18].

2.2. Hydroboration of trialkyn-1-ylsilanes 1 and 2 using 9-BBN.

A Schlenk tube was charged with a THF solution of silane 1a (0.45 g, 1.57 mmol) and crystals of 9-BBN (0.19 g, 1.56 mmol). The reaction mixture was stirred.
at room temperature for 12 h. After the reaction was complete, all volatile materials were removed under reduced pressure (≈ 10⁻² Torr) and the oily liquid left was identified as the mixture of silanes 5a and 8a (in the ratio of 8:2, respectively, ¹H NMR). The other silane derivatives (6b,c and 9b,c) were synthesized at high temperature (80 - 100°C) using toluene or benzene as the solvent. The reaction period lasted from 10 - 30 min. Compound 7b was prepared in a different way. A solution of alkenylsilane 3b (1.86 g, 5.37 mmol) in hexane (5 mL) was added to freshly prepared 3,3-dimethylbutynyl lithium at -78°C. The reaction mixture was slowly allowed to warm up to room temperature. Further stirring at room temperature for three hours was continued, all volatiles were removed in a vacuum, and solid materials mainly LiCl were separated. The oily product left was identified as 7b (Fig. 2) containing reasonable amount of 12b vide infra.

5a: ¹H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 0.7, 0.9, 1.9 - 1.5, 2.6 (t, t, m, m, t, 27H, Bu), 1.4, 1.8 - 2.1 (m, 14H, 9-BBN), 7.0 (t, 1H, 3J(29Si,1H) = 7.2 Hz, =CH).

5b: ¹H NMR (400 MHz): δ = 0.4 (s, 3H, Si-Me), 1.2–2.2 (m, 14H, 9-BBN), 6.7 - 7.2, 7.5 (m, m, 15H, Ph), 8.0 (s, 1H, 3J(29Si,1H) = 18.8 Hz, =CH).

6a: ¹H NMR (400 MHz): δ = 0.7, 0.8, 1.9 - 1.5, 2.6 (t, t, m, m, t, 27H, Bu), 1.4 - 2.1 (m, 14H, 9-BBN), 7.2, 7.7 (m, m, 6H, Si-Ph, =CH).

6b: ¹H NMR (400 MHz): δ = 1.2 - 1.9 (m, 14H, 9-BBN), 6.6 - 7.9 (m, 20H, Si-Ph, Ph), 8.0 (s, 1H, 3J(29Si,1H) = 22.1 Hz, =CH).

6c: ¹H NMR (400 MHz): δ = 1.3 - 2.0 (m, 14H, 9-BBN), 1.9, 1.9, 2.0, 6.4 - 8.2 (s, s, s, m, 27H, Si-Ph, 4-Me-C₆H₄, =CH).

8a: ¹H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 0.7, 0.9, 1.9 - 1.5, 2.4 (t, t, m, m, 27H, nBu), 1.4, 1.8 - 2.1 (m, 28H, 9-BBN), 6.9 (t, 2H, 3J(29Si,1H) = 7.1 Hz, =CH).

8b: ¹H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 1.2–2.2 (m, 28H, 9-BBN), 6.7–7.2, 7.5 (m, m, 15H, Ph), 7.4 (s, 2H, =CH).

9b: ¹H NMR (C₆D₆): δ = 1.2–2.1 (m, 28H, 9-BBN), 6.8–7.3, 7.6, 8.2 (m, m, m, 22H, Si-Ph, Ph, =CH).

10b: ¹H NMR (400 MHz): δ = 0.2 (s, 3H, Si-Me), 1.6 - 1.9 (m, 14H, 9-BBN), 6.7 (s, 1H, 3J(29Si,1H) = 14.6 Hz, =CH), 6.6 - 7.1 (m, 15H, Ph).

11b: ¹H NMR (400 MHz): δ = 1.4-2.1 (m, 14H, 9-BBN), 6.8–8.2 (m, 21H, Si-Ph, Ph, =CH).

11c: ¹H NMR (400 MHz): δ = 1.4-2.1 (m, 14H, 9-BBN), 1.8, 1.8, 6.5–8.2 (s, s, m, 27H, 4-Me-C₆H₄, Si-Ph, =CH).

12b: ¹H NMR (400 MHz): δ = 1.0, 1.1 (s, s, 18H, 1H, 1H) = 7.2 Hz, =CH).

2.3. 1,1-Vinylboration of alkenyl(dialkyn-1-yl)silanes 5-7 and dialkenyl(alkyn-1-yl) silanes 8 and 9

The mixture containing silanes 5b and 8b was heated at 80-100°C in an NMR tube for 2-4 h in C₆D₆. The reaction was monitored by ²⁹Si{¹H} NMR spectroscopy to show the presence of 10b and 13b. They could be distinguished by their characteristic NMR data. The same experimental procedure was followed for the formation of 1-silacyclobutene derivatives 11b,c, 12b and 14b. A slight variation in the reaction time was observed, rearrangement of silanes 6, 7 and 9 took 24 h to afford heterocycles 11, 12 and 14, respectively.

10b: ¹H NMR (400 MHz): δ = 0.2 (s, 3H, Si-Me), 1.6 - 1.9 (m, 14H, 9-BBN), 6.7 (s, 1H, 3J(29Si,1H) = 14.6 Hz, =CH), 6.6 - 7.1 (m, 15H, Ph).

11b: ¹H NMR (400 MHz): δ = 1.4-2.1 (m, 14H, 9-BBN), 6.8–8.2 (m, 21H, Si-Ph, Ph, =CH).

11c: ¹H NMR (400 MHz): δ = 1.4-2.1 (m, 14H, 9-BBN), 1.8, 1.8, 6.5–8.2 (s, s, m, 27H, 4-Me-C₆H₄, Si-Ph, =CH).

12b: ¹H NMR (400 MHz): δ = 1.0, 1.1 (s, s, 18H, 1H, 1H) = 7.2 Hz, =CH).
3. Results and Discussion

Trialkyn-1-ylsilanes were prepared following the reported synthetic procedure. They were purified and structurally characterized using modern analytical techniques (NMR and X-ray structural analysis) [18]. These silanes are useful synths for further transformations, and they can be converted into alkenylsilanes ([5,6,8,9] and various 1-substituted 1-silacyclobutene derivatives ([10,11,13,14]). The trihexyn-1-yl(methyl)silane 1a was treated with 9-BBN in 1:1 molar ratio. The reaction proceeded selectively at room temperature and afforded a mixture of products 5a and 8a (Scheme 2). These silanes were accompanied by some rearranged products (respective 1-silacyclobutene derivatives, vide infra) at the same temperature. Owing to more than two fractions in the mixture it was not easy to assign correctly all signals in the NMR spectra (13C and 1H). The 29Si NMR spectroscopy proved to be a powerful technique for proposing the structures of various intermediates and final products (Figs. 1, 2). All the related compounds e.g. 5b, 8b and 1-silacyclobutene derivatives, 10b,13b possess characteristic 29Si chemical shifts and they could readily be identified in the mixtures. The same reaction was carried out for silane 2 with one equivalent of 9-BBN. It was observed that the 1,2-hydroboration takes place less readily when compared with silane 1. Thus, silane derivatives 6a-c were formed in almost quantitative yield (≈ 95%) along with a very small amount of 9b,c (≈ 5%). The 29Si NMR did not show even traces of 1-silacyclobutenes at this stage of the reaction. The

Table 1. 1H, 13C and 29Si NMR data[a] of alkenyl(dialkyn-1-yl)silanes

| R1 | δ(13C (BC=)) | δ(13C (C=)) | δ(29Si) | δ(11B) |
|----|--------------|-------------|---------|--------|
| Bu | 144.2-22.0   | 83.3 [99.5] | 108.6 [19.5] | -54.1 | 82.3 |
| Ph | 146.5-21.0   | 92.4 [98.6] | 107.5 [18.6] | -51.1 | 86.4 |
| Me | 141.2-19.0   | 91.2 [101.2] | 108.3 [18.8] | -55.8 | 82.7 |
| Bu | 143.8-17.0   | 90.8 [102.8] | 108.7 [20.0] | -55.2 | 84.3 |
| Ph | 152.8-15.0   | 90.3 [102.9] | 108.8 [19.5] | -55.2 | 84.5 |
| 4-Me-C6H4 | 144.2-13.0 | 87.8 [104.6] | 108.9 [19.2] | -61.4 | 85.6 |
| Bu | 148.1-11.0   | 85.8        | 108.8     | -41.1 | 82.7 |
| Ph | 149.5-10.0   | 96.3 [85.5] | 108.8 [15.8] | -39.4 | 86.4 |
| 4-Me-C6H4 | 143.9-9.0   | 85.8        | 108.6 [16.3] | -29.1 | 84.0 |

[a] Measured in C6D6, coupling constants J(29Si,13C) [± 0.4 Hz] are given in square brackets, superscript ‘br’ denotes a broad 13C resonance signal [29,30].

Scheme 2. Reaction of trialkyn-1-ylsilanes with 9-BBN as hydroboration reagent.
product distribution in the mixture depends upon various factors, e.g. reaction temperature and nature of the groups R and R'. It was concluded that the Si-Ph group reduces the reactivity, hence, allowing for quantitative hydroboration of only one Si-C≡C- bond in the presence of one equivalent of 9-BBN. The same was true for reaction of silane 2 with two equivalents of 9-BBN.

Alkenyl silane 3b and its analogues are useful synthons for further transformations [9,20]. The chlorosilane 3b was treated with Li-C≡C-tBu at –78°C according to literature procedure. The reaction mixture contained alkyn-1-ylsilane 7b precursor of 12b and some unidentified side products (Scheme 3). Although the chlorosilane, 4b was not detected but can be proposed as an immediate precursor of 7b, Scheme 3. In the reaction mixture there were no indications of borate-like intermediates (11B NMR) [9].

3.1. 1-Silacyclobutene derivatives

The alkenyl(di-alkyn-1-yl)silanes 5-7 and dialkenyl(alkyn-1-yl)silanes 8, 9 were heated at 80 –120°C for several hours (Experimental section) in an NMR tube. The progress of the reaction was constantly monitored by 29Si NMR. The intramolecular 1,1-vinylboration leads to 1-(alkyn-1-yl)-1-silacyclobutenes 10-12 and 1-(alkenyl)-1-silacyclobutenes 13, 14. In the case of C≡C-tBu group, the 1,1-vinylboration was extremely slow even at elevated temperature and therefore, no data was collected. Moreover the silanes were stable at that temperature and they did not show marked decomposition as has been reported for R = SiMe₃ and R' = Me groups [12]. No reaction with threefold 1,2-hydroboration was observed. The 1-silacyclobutene heterocycles achieved in these reactions are oily liquids and could readily be identified from their characteristic NMR data (11B, 13C, 1H and 29Si).

3.2. NMR spectroscopic studies

The NMR spectroscopic data (11B, 13C and 29Si) for silanes 5 - 9 are listed in Table 1 and the respective 1H NMR data are collected in the Experimental section. The NMR data set is consistent with the proposed structures and the data show close resemblance to the reported alkenylsilane derivatives [11,26-28]. Structural assignments were readily based on coupling constants J(29Si,13C) especially for the Si-C≡C- unit and the broad 13C (BC-) NMR signal [29,30]. The coupling constants...
(29Si,13C) in 13C NMR spectra could be confirmed by observing 13C satellite signals in the respective 29Si NMR spectra. The 29Si NMR is the only access to the coupling constant value 1J(29Si,13C(B)) as can be seen in Figs. 1 and 2. In the mixtures, it can be deduced that all compounds possess distinct 29Si chemical shifts and the reaction mechanism and various intermediates could be proposed (Fig. 1). These facts make the mechanism of the reaction well understandable, the data listed in Table 1 are quite sufficient for structural elucidation of the title compounds in solution state.

The NMR data (11B, 13C and 29Si) of 1-silacyclobutene derivatives are listed in Table 2. The NMR data set is consistent with the proposed structures. The 29Si NMR spectroscopy serves as the main tool for assignments. The data obtained mainly for the four-membered ring (1-silacyclobutene) are well comparable with that of 1-silacyclobutenes [9] and analogous spiroisilane derivatives [13]. In 13C NMR spectra, the substituents on the silicon atom Si-(B)C=C and Si-C≡C- can be readily assigned, based on 29Si satellites for the 13C(Si-C≡C) signals, whereas a sharp 13C(=CH) and a broad 13C(B-C≡) signal [29,30] at high frequency are characteristic of the exocyclic Si-C(B)=C group. Other NMR data are within the expected range.

4. Conclusions
The process of 1,2-hydroboration and 1,1-organoboration can be applied separately to the synthesis of a large number of organometallic compounds. The reaction in which 1,2-hydroboration is followed by 1,1-vinylboration have proved to be a facile route for the synthesis of 1-silacyclobutene derivatives. Here, further new examples can be contributed to this class of silicon heterocycles. The synthetic route is preferred over other methods [1-7] owing to its simplicity and efficiency. The variety of functional groups on silicon atom is of prime importance. The groups considered in this study such as Si-C≡C and Si-C(B)=C can be used for further reactions.

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Table 2. 11B, 13C and 29Si NMR data[a] for 1-silacyclobutene derivatives 10 - 14.

| Compound | δ 13C (C-2) | δ 13C (C-3) | δ 13C (C-4) | δ 13C (=) | δ 29Si | δ 11B |
|----------|-------------|-------------|-------------|-----------|-------|-------|
| 10b      | 147.2 [57.3] | 177.4°      | 161.4 [59.4]| 132.4     | -18.1 | 88.2  |
| 11b      | 146.0 [58.3] | 181.6°      | 160.2 [60.0]| 138.9     | -23.5 | 85.8  |
| 11c      | 145.4 [58.2] | 180.7°      | 160.1 [60.2]| 139.6     | -24.0 | 87.9  |
| 12b      | 146.0 [56.5] | 179.5°      | 170.1 [59.6]| n.a.      | -24.8 | 87.3  |
| 13b      | 151.3 [52.7] | 178.8°      | 168.2 [52.1]| 137.8     | -1.6  | 88.2  |
| 14b      | 150.7 [n.o. ]| 180.4°      | 164.9 [n.o.]| 139.8     | -11.2 | 85.8  |

[a] Measured in C6D6 at 23 °C, some coupling constants 1J(29Si,13C) are given in square brackets, ‘n.a.’ means not assigned and ‘n.o.’ means not observed, due to signals crowded, superscript ‘br’ denotes a broad 13C resonance signal as a result of partially relaxed scalar 13C-11B coupling [29,30].

References
[1] T. Takahashi, Z. Xi, Y. Obora, N. Suzuki, J. Am. Chem. Soc. 117, 2665 (1995)
[2] M. Horacek, N. Bazyakina, P. Stepnicka, R. Gyepest, I. Cisarova, S. Bredeau, P. Meunier, J. Kubista, K. Mach, J. Organomet. Chem. 628, 30 (2001)
[3] A.C. Dema, C.M. Lukehart, A.T. McPhail, D.R. McPhail, J. Am. Chem. Soc. 112, 7229 (1990)
[4] J. Mohseni-Ala, N. Auner, Inorg. Chim. Acta 359, 4673 (2006)
[5] K.C. Jin, V.T. Dang, Y. Ikee, T. Yamada, S. Sano, M. Shiro, Y. Nagao, Heterocycles 70, 71 (2006)
[6] N. Auner, C.R. Heikenwälder, C. Wagner, Organometallics 12, 4135 (1993)
[7] G.T. Burns, T.J. Barton, J. Am. Chem. Soc. 105, 2006 (1983)
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[8] B. Wrackmeyer, H.E. Maisel, E. Molla, A. Motalib, A. Badshah, M.H. Bhatti, S. Ali, Appl. Organomet. Chem. 17, 465 (2003)
[9] B. Wrackmeyer, E. Khan, R. Kempe, Appl. Organomet. Chem. 21, 39 (2007)
[10] B. Wrackmeyer, E. Khan, S. Bayer, K. Shahid, Z. Naturforsch. 62b, 1174 (2007)
[11] E. Khan, S. Bayer, B. Wrackmeyer, Z. Naturforsch. 64b, 47 (2009)
[12] E. Khan, B. Wrackmeyer, Turk. J. Chem. (In press)
[13] B. Wrackmeyer, E. Khan, R. Kempe, Appl. Organomet. Chem. 22, 383 (2008)
[14] W.E. Davidsohn, M.C. Henry, Chem. Rev. 67, 73 (1976)
[15] L. Brandsma, Preparative Acetylenic Chemistry, 2nd edition (Elsevier, Amsterdam, 1988)
[16] L. Brandsma, Synthesis of Acetylenes, Allenes, Cumulenes – Methods and Techniques (Elsevier, Amsterdam, 2004)
[17] B. Wrackmeyer, E. Khan, A. Badshah, E. Molla, P. Thoma, O.L. Tok, W. Milius, R. Kempe, J. Senker, Z. Naturforsch. 65b, 119 (2010)
[18] B. Wrackmeyer, E. Khan, S. Bayer, O.L. Tok, E.V. Klimkina, W. Milius, R. Kempe, Z. Naturforsch. 65b, 725 (2010)

[19] E. Khan, B. Wrackmeyer, R. Kempe, Eur. J. Inorg. Chem. 5367 (2008)
[20] E. Khan, R. Kempe, B. Wrackmeyer, Appl. Organomet. Chem. 23, 204 (2009)
[21] G.A. Morris, R. Freeman, J. Am. Chem. Soc. 101, 760 (1979)
[22] G.A. Morris, J. Am. Chem. Soc. 102, 428 (1980)
[23] G.A. Morris, J. Magn. Reson. 41, 185 (1980)
[24] D.P. Burum, R.R. Ernst, J. Magn. Reson. 39, 163 (1980)
[25] B. Wrackmeyer, E. Khan, R. Kempe, Z. Anorg. Allg. Chem. 633, 453 (2007)
[26] B. Wrackmeyer, H. E. Maisel, W. Milius, M.H. Bhatti, S. Ali, J. Organomet. Chem. 669, 72 (2003)
[27] B. Wrackmeyer, E. Khan, W. Milius, Z. Naturforsch. 63b, 1267 (2008)
[28] B. Wrackmeyer, E. Khan, R. Kempe, Z. Naturforsch. 62b, 75 (2007)
[29] B. Wrackmeyer, Progr. NMR Spectrosc. 12, 227 (1979)
[30] B. Wrackmeyer, Annu. Rep. NMR Spectrosc. 20, 61 (1988)