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Synthesis and structure of novel spirosilanes. Combination of 1,2-hydroboration and 1,1-organoboration

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The reaction of tetra(alkyn-1-yl)silanes Si(C≡C-R^1)$_4$ 1 [R^1 =^{t}Bu (a), Ph (b), C$_6$H$_4$-4-Me (c)] with 9-borabicyclo[3.3.1]nonane (9-BBN) in a 1 : 2 ratio affords the spirosilane derivatives 5a–c as a result of twofold intermolecular 1,2-hydroboration, followed by twofold intramolecular 1,1-organoboration. Intermediates 3a–c, in which two alkenyl- and two alkyn-1-yl groups are linked to silicon, were identified by NMR spectroscopy. The molecular structure of the spiro compound 5c was determined by X-ray analysis, and the solution-state structures of products and intermediates follow conclusively from the consistent NMR spectroscopic data sets (^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR). Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: boranes; silanes; alkynes; heterocycles; hydroboration; organoboration; NMR, multinuclear; X-ray

Introduction

Intermolecular 1,1-organoboration[1] of alkyn-1-ylsilanes is a slow reaction, requires prolonged times of heating at ≥100 °C, and its success depends on the respective substituents both on silicon and on the C≡C bond. However, introduction of the boryl group into the molecule by a different type of reaction opens the way to an intramolecular 1,1-organoboration if Si–C≡C-R^1 functions are available. This intramolecular process requires less harsh reaction conditions, as has been shown previously for the stepwise synthesis of siloles,[2] and by combining 1,2-hydroboration and 1,1-organoboration for the synthesis of 1-silacyclopent-2-ene[3,4] and 1-silacyclobutene derivatives.[5,6] The 1,2-hydroboration of alkyn-1-ylsilanes is particularly attractive in this context since it is highly regiospecific[7–9] if the alkyn-1-yl group bears a substituent other than hydrogen (Scheme 1). A bulky alkyl group at the C≡C bond, such as the ^{t}Bu group, or an aryl group, induces complete regiospecifity if 9-borabicyclo[3.3.1]nonane (9-BBN)[10,11] is used as hydroborating reagent. Intermediates of type **A** have already been detected in reaction solutions.[5] Although, the presence of a second alkyn-1-yl groups as in **A** invites a second 1,2-hydroboration, provided that there is sufficient 9-BBN available, the reactions can be controlled to allow for the desired intramolecular 1,1-organoboration leading to **B**. This rearrangement proceeds via a borate-like intermediate[1] as in **A**, in which the dashed line indicates an interaction of the electron-deficient boron atom with the alkynyl carbon atom attached to silicon. Cleavage of this Si–C(alkyne) bond and formation of the B–C(alkyne) leads to a borate and finally to **B**.[6]

In this work, we report that the reaction of tetra(alkyn-1-yl)silanes Si(C≡C-R^1)$_4$ **1** [R^1 = ^{t}Bu (**a**), Ph (**b**), C$_6$H$_4$-4-Me (**c**)] with 9-BBN affords finally spirosilanes by consecutive 1,2-hydroboration and 1,1-organoboration.

Results and Discussion

Tetra(alkyn-1-yl)silanes Si(C≡C-R^1)$_4$ **1** [R^1 =^{t} Bu (**a**), Ph (**b**), C$_6$H$_4$-4-Me (**c**)], serving as starting materials, are readily available[12,13] by the reaction of $SiCl_4$ with the respective lithium alkynides, which were used in slight excess.

Hydroboration of tetra(alkyn-1-yl)silanes 1 with 9-BBN

The reaction of **1** with 9-BBN shown in Scheme 2 in a 1 : 2 ratio affords selectively the alkene derivatives **3a–c** (see e.g. Fig. 1). Compounds **2**, precursors of **3**, were not observed in the reaction mixtures. Heating of the compounds **3** induces rearrangements via intramolecular 1,1-organoboration. In the case of **4c**, the intermediate in which the first four-membered ring had been formed was detected by ^{29}Si NMR (Fig. 2). The final rearrangement leads to the spirosilanes **5a–c** (see e.g. Fig. 3). The reactions can be conveniently monitored by ^{29}Si NMR spectroscopy since products and intermediates possess distinct chemical shifts δ^{29}Si (see Figs 1 and 2, and Tables 1 and 2). The boryl groups in **5** can be smoothly removed by protodeborylation using an excess of acetic acid,[14] as shown for the case **6c**. The spirosilanes **5** are air-sensitive waxy solids (**5a**) or crystalline solids (**5b, c**), of which **5c** could be crystallized to give single crystals suitable for an X-ray structural analysis.

NMR spectroscopic results

The ^{11}B, ^{13}C and ^{29}Si NMR data of the compounds **3** are listed in Table 1, and those of the spirosilanes in Table 2. ^{1}H NMR data are given in the Experimental section. The data set is fully consistent

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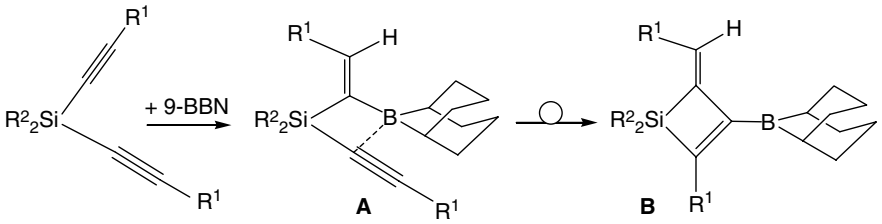
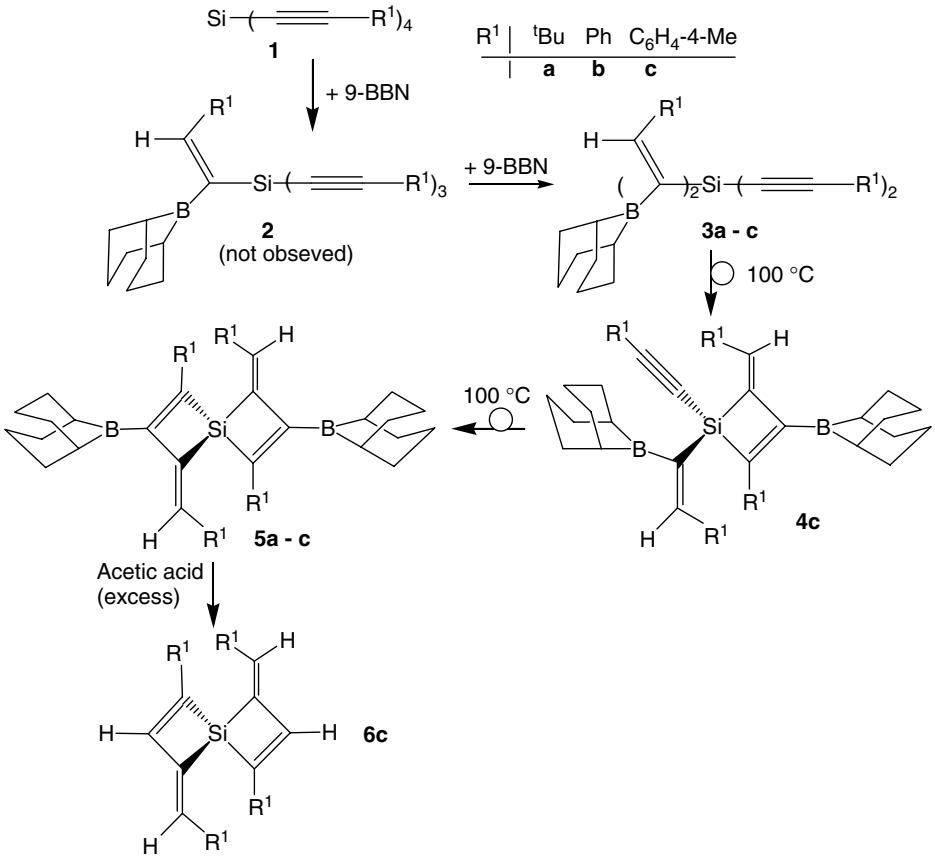


Scheme 1. 1,2-hydroboration, followed by 1,1-vinylboration of dialkyn-1-yl(diorgano)silanes.



Scheme 2. Twofold 1,2-hydroboration, followed by twofold 1,1-vinylboration of tetraalkyn-1-ylsilanes.

with the proposed structures. The chemical shifts δ^{11}B are found within a small range, typical of three-coordinate boron atoms in triorganoboranes with few or negligible BC(pp)π interactions.[15] Therefore, it can be assumed that the orientation of the BC_2 plane of the 9-BBN unit is preferably perpendicular to the four-membered ring. ^{29}Si NMR spectra[16,17] measured using $^{1}H \rightarrow {}^{29}Si$ polarization transfer from the olefinic protons, e.g. via INEPT pulse sequences,[18,19] serve for assigning intermediates and products. This assignment is supported by observing the respective ^{13}C satellite signals (see Fig. 1). The ^{13}C NMR spectra provide a wealth of information on the structures by characteristic chemical shifts δ^{13}C, coupling constants $J(^{29}Si,^{13}C)$ and the broadened ^{13}C NMR signals for carbon atoms linked directly to ^{11}B nuclei (as a result of partially relaxed scalar $^{13}C-{}^{11}B$ spin–spin coupling[20]). As can be deduced from the ^{11}B NMR spectra, the boryl group prefers an orientation perpendicular to the four-membered ring, evident by the ^{13}C(9-BBN) signals, typical of restricted rotation about the C(3)–B bond (Fig. 3).

X-ray structural analysis of 5c

The molecular structure of **5c** is shown in Fig. 4 as the first example of structural characterization of this type of molecule. Although the crystals studied were non-meroedric twins, the structure could be determined without doubt to confirm the molecular connectivity and to obtain relevant structural parameters. Intermolecular interactions appear to be negligible. The endocyclic bond angles are typically small (∠C1Si1C11 = 75.9 and C18Si1C28 = 74.8°) in contrast to the exocyclic bond angles [∠C1Si1C18 130.8(3), C11SiC18 124.2(3), C1Si1C28 124.9(3), C11Si1C18 125.2(3), C11Si1C28 135.8(3)]. The endocyclic bond angles and all other angles and bond lengths in the ring systems agree with those previously reported for a related monocyclic silane.[6] Similarly, the BC_2 planes of the 9-BBN groups are significantly twisted against the ring planes of the spirosilane (∠56.1 and 55.3°), in agreement with the solution-state NMR data.

Table 1. ^{13}C, ^{29}Si and ^{11}B NMR data[a] of the dialkenyl(dialkyn-1-yl)silanes **3**

	$\delta^{13}C$(BC=)	$\delta^{13}C$(=C)	$\delta^{13}C$(BBN)	$\delta^{13}C$(≡C)	$\delta^{13}C$(Si–C>)	$\delta^{29}Si$	$\delta^{11}B$
3a[b]	146.1 (br) [72.4]	161.4	35.1, 31.8 (br), 23.9	118.1 [18.3]	84.1 [100.6]	−65.7	82.7
3b[c]	146.1 (br)	153.5	34.8, 31.9 (br), 23.8	109.8 [19.3]	93.3 [99.1]	−62.8	84.3
3c[d]	145.3 (br) [71.2]	153.7	34.8, 34.4, 31.8 (br), 23.8	109.3 [18.9]	92.9 [99.5]	−62.9	85.0

[a] Measured in C_6D_6 at 23 °C; coupling constants $J(^{29}Si,^{13}C)$ [±0.3 Hz] are given in square brackets; (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar $^{13}C-^{11}B$ spin–spin coupling.[20] [b] Other ^{13}C data: δ (ppm) = 37.7, 30.8, 30.5, 28.5 (=C–^{t}Bu, ≡C–^{t}Bu). [c] Other ^{13}C NMR data: δ (ppm) = 140.1, 137.9, 132.5, 132.2, 130.8, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 125.7, 123.7 (Ph carbons with out assignment). [d] Other ^{13}C NMR data: δ (ppm) = 138.8, 138.4, 137.6, 132.4, 132.1, 131.0, 129.3, 129.1, 128.5, 120.9, 21.4, 21.3 (*p*-tolyl).

Table 2. ^{13}C, ^{29}Si and ^{11}B NMR data[a] of the spirosilanes **5** and **6**

	$\delta^{13}C$(C-2)	$\delta^{13}C$(C-3)	$\delta^{13}C$(C-4)	$\delta^{13}C$(=CH)	$\delta^{29}Si$	$\delta^{11}B$
5a[b]	171.4 [49.3]	178.0 (br)	144.6 [47.4]	141.4 [12.1]	−2.4	87.1
5b[c]	163.7 [49.2]	181.3 (br)	148.8 [48.3]	139.8	−0.9	88.0
5c[d]	163.2 [49.4]	180.0 (br)	148.0 [48.1]	132.3	−0.9	87.4
6c[e]	142.9 [50.8]	153.2 [16.7]	157.5 [51.8]	132.2, 132.4	−5.6	–

[a] Measured in C_6D_6 at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C-^{11}B scalar coupling;[20] Coupling constants $^1J(^{29}Si,^{13}C)$ are given in square brackets. [b] Other ^{13}C data: $\delta J[^{29}Si,^{13}C]$ = 35.8 [4.1], 35.1 [5.2], 32.3, 29.9 (^{t}Bu), 34.41, 34.37, 32.5 (br), 23.7 (BBN). [c] Other ^{13}C data: δ (ppm) = 139.2 (*i*), 129.3 (*i*), 128.7 (*o*), 132.8 (*o*), 127.6 (*p*), 128.8 (*p*), 127.3 (*m*), 128.3 (*m*) (C2-Ph, =C–Ph), 34.4, 34.2, 32.4 (br), 23.5 (BBN). [d] Other ^{13}C data: $\delta J[^{29}Si,^{13}C]$ = 137.3 [*i*, 4.2] 136.6 [*i*, 4.7], 129.6, 129.5, 128.5, 127.3, 137.5 (*p*), 137.0 (*p*), 21.2 (Me), 21.1 (Me) (*p*-tolyl), 34.5, 34.3, 32.4(br), 23.7 (BBN). [e] Other ^{13}C data: δ (ppm) = 138.4, 137.2, 136.6, 134.2, 129.8, 129.7, 129.1, 129.0, 127.6, 127.0, 21.3, 21.1 (*p*-tolyl).

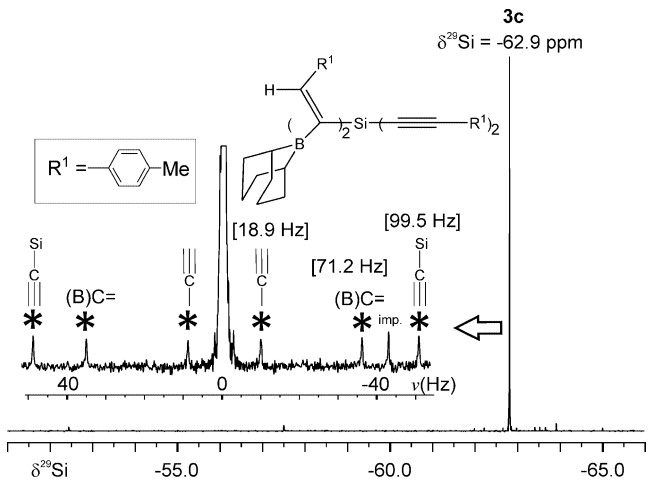


Figure 1. $^{29}Si\{^1H\}$ NMR spectra, 59.6 MHz (refocused INEPT), of the intermediate **3c**; expansion of the signal shows ^{13}C satellites, marked by asterisks, corresponding to $^1J(^{29}Si,^{13}C)$ and $^2J(^{29}Si,^{13}C)$; further ^{13}C satellites are visible, close to the parent peak, which arise from $^nJ(^{29}Si,^{13}C)$ ($n \geq 2$), with a coupling of 4.9 and 2.1 Hz.

DFT calculations of the model compound 5M

The gas phase geometry of the model compound **5M** (Fig. 5) has been optimized at the B3LYP/6-311+G(d,p) level of theory.[21–25] The principle structural features correspond closely to those of **5c**. The twist angle (34°) of the Me_2B groups against the ring planes is smaller than in **5c** as the result of reduced steric interactions in the model compound.

Conclusions

The stepwise synthesis of the racemic mixtures of the novel spirosilanes reported here is of interest with respect to formation of axially chiral spirosilanes which are unknown so far for two four-membered rings.[26,27] The B–C=and the C=C bonds in **5** and **6** invite further transformations, e.g. by selective oxidation or asymmetric hydrogenation, respectively.

Experimental

Starting materials and measurements

All preparations and handling of samples were carried out under an inert atmosphere (Ar), and carefully oven-dried glassware and dry solvents were used throughout. BuLi in hexane (1.6 M), $SiCl_4$, 3,3-dimethyl-1-butyne, ethynylbenzene, *p*-tolylethynyl, glacial acetic acid and 9-borabicyclo[3.3.1]nonane were commercial products. The tetra(alkyn-1-yl)silanes **1a–c**[12,13,28] were prepared following the literature procedure.

Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet; the *m/z* data refer to the isotopes ^1H, ^{11}B, ^{12}C, ^{28}Si. NMR measurements in C_6D_6 (concentration *ca* 10–15%) with samples in 5 mm tubes at 23 ± 1 °C: Varian Inova 300 and 400 MHz spectrometers for ^1H, ^{11}B, ^{13}C, and ^{29}Si NMR; 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 $\Xi(^{29}Si)$ = 19.867184 MHz]; external BF_3-OEt_2 [$\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 MHz]. Chemical shifts are given to ±0.1 for ^{13}C and ^{29}Si, and ±0.2 ppm for ^{11}B; coupling constants are given ±0.3 Hz for $J(^{29}Si,^{13}C)$. ^{29}Si NMR spectra were measured by using the refocused INEPT pulse sequence,[18,19] based on $^3J(^{29}Si,^1H_{HC=})$ or $^3J(^{29}Si,^1H_{C(3)H})$ (*ca* 20 Hz). The melting point (m.p., uncorrected) was determined using a Büchi 510 melting point apparatus. DFT calculations were carried out using the Gaussian 03 program package.[29]

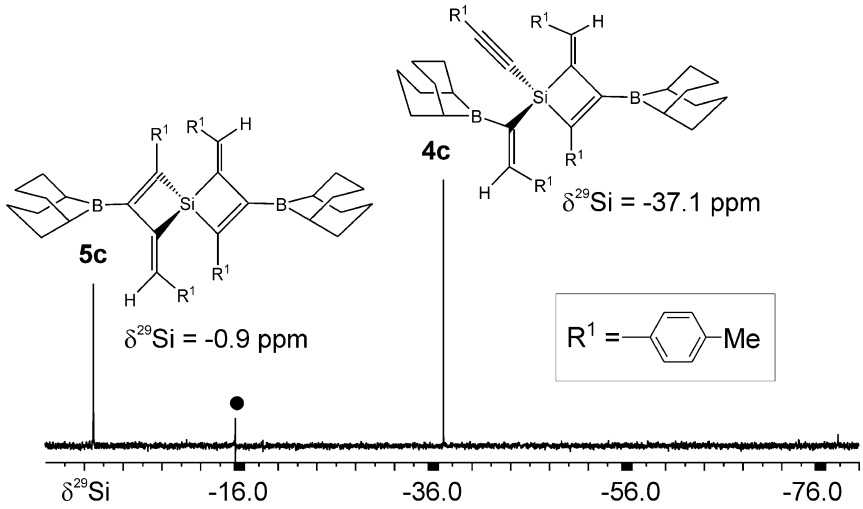


Figure 2. $^{29}Si\{^1H\}$ NMR spectra, 59.6 MHz (refocused INEPT), showing the intermediate **4c** and final product **5c** (an artefact is marked by a solid circle).

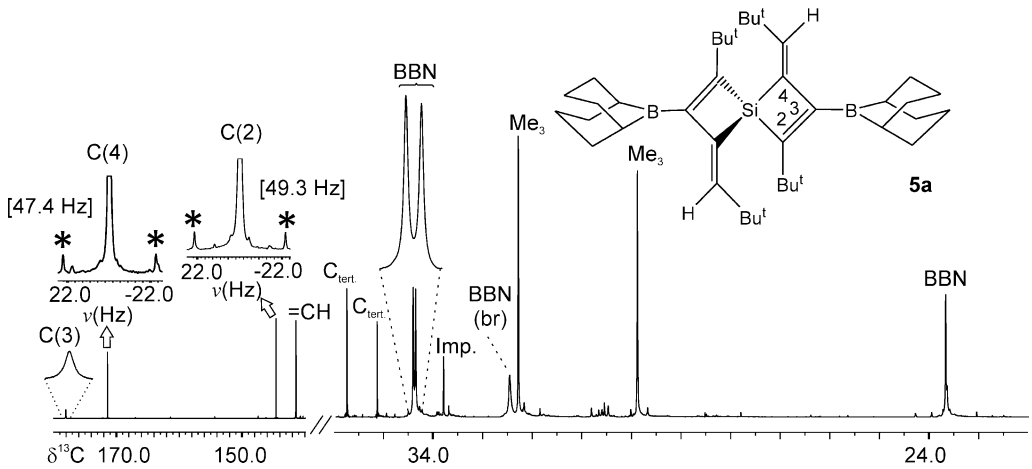


Figure 3. $^{13}C\{^1H\}$ NMR spectra, 100.5 MHz, of the spirosilane **5a** [*ca* 15% (v/v) solution in C_6D_6]. The ^{29}Si satellites for corresponding carbon signals in the expanded regions are marked by asterisks. Note the typically broad signal[20] of the carbon atom C-3 linked to boron.

Hydroboration of 1a–c with two equivalents of 9-BBN to give first 3a–c and finally 5a–c

A Schlenk tube was charged with tetrakis(*tert*-butylethynyl)silane (0.26 g, 0.74 mmol) and two equivalents of 9-BBN (0.1862 g, 1.48 mmol) were added as a solid in one portion. The reaction mixture was heated in toluene at 80–100 °C. The progress in the reaction was monitored by ^{29}Si NMR. After 20 min when twofold hydroboration was completed, all volatiles were removed under reduced pressure. The intermediate **3a**, in a sealed NMR tube, was heated at the same temperatrue for 3–4 h, using C_6D_6 as the solvent. During this time the intermediate **3a** was converted into the final product, spiro compound **5a.** The same synthetic procedure gave **3b** and**3c** and the corresponding spirosilanes **5b** and **5c**. The heating period for complete conversion of **3b** and **3c** into **5b** and **5c** was comparitively long (8–10 h). **3a**: ^1H NMR (400 MHz; C_6D_6): δ = 6.7 [s, 1H, $^3J(^{29}Si,^1H)$ = 21.6 Hz, =CH], 1.6–2.1 (m, 28H, BBN), 1.8–2.1 (m, 14H, BBN), 1.3, 1.1 (s, s, 9H, 9H, ≡C-^{t}Bu, =C-^{t}Bu); **3b**: ^1H NMR (400 MHz; C_6D_6): δ = 7.4 [s, 1H, =CH, $^3J(^{29}Si,^1H)$ = 19.4 Hz], 6.6–7.2, 7.3 (m, d, Ph), 1.2–2.0 (m, 14H, 14H, BBN, BBN); **3c**: ^1H NMR (400 MHz: C_6D_6): δ = 1.4–2.3 (m, 14H, 14H, BBN, BBN) 7.7 [s, 2H, =CH, =CH, $^3J(^{29}Si,^1H)$ = 19.7 Hz], 7.6, 7.3, 7.0, 6.7, 1.7, 2.1 (m, m, m, m, s, s, 14H, tolyl); **5a**: ^1H NMR (400 MHz; C_6D_6): δ = 1.17, 1.22 (s, s, 36H, ^{t}Bu), 1.5, 2.2 (m, 28H, 9-BBN), 5.9 [s, 2H, $^3J(^{29}Si,^1H)$ = 18.2 Hz, =CH]; **5b**:^1H NMR (400 MHz; C_6D_6): δ = 1.6–2.3 (m, 14 + 14H, 9-BBN, 9-BBN), 7.5 (s, 2H, =CH), 6.9–7.8 (m, 20H, Ph); EI-MS: *m/z* (%) = 676 (1) [M^+], 555 (13) [M^+-$C_8H_{13}B$], 436 (100) [M^+-$C_{16}H_{26}B_2$], 359 (5) [M^+-$C_{22}H_{31}B_2$]; **5c** (m. p. 230 °C; yield after recrystallization from hexane = 39%): ^1H NMR (400 MHz; C_6D_6): δ = 7.6, 7.3, 6.9, 6.8, 2.0, 1.9 (m, m, m, m, s, s, 14H, tolyl), 7.4 [s, 2H, $^3J(^{29}Si,^1H)$ = 17.3 Hz, =CH], 1.6–2.3 (m, 28H, 9-BBN).

Protodeborylation reaction of 5c

To a solution of **5c** in pentane (5 ml), glacial acetic acid was added in slight excess. The reaction mixture was stirred at room temperature for 1 h, the boron compound[14] was separated at low temperature as a solid. From the solution all volatile materials were removed in a vacuum and **6c** was obtained as colourless waxy solid. **6c**:^1H NMR (400 MHz; C_6D_6): δ = 1.9, 1.8, 6.7, 6.8, 7.3, 7.4 (s, s, d, d, d, d, 28H, *p*-tolyl), 7.1 [s, 2H, $^3J(^{29}Si,^1H)$ = 17.3 Hz, =CH], 8.1 [s, 2H, $^3J(^{29}Si,^1H)$ = 22.3 Hz, C3-H].

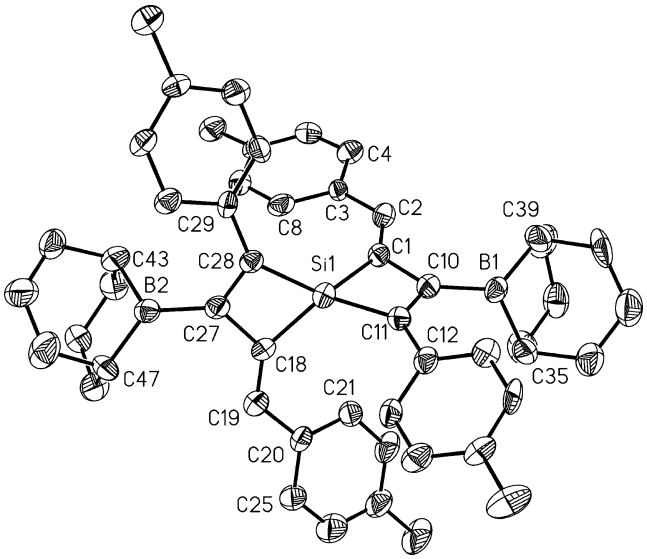


Figure 4. Molecular structure of the spirosilane, **5c**. ORTEP plot (drawn on 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and bond angles (deg): C1–C2 134.5(7), C1–C10 149.8(10), C1–Si1 185.3(7), C2–C3 144.1(9), C10–C11 138.4(8), C10–B1 158.8(10), C11–C12 145.4(10), C11–Si1 184.7(8), C35–B1 158.2(9), C39–B1 154.8(9), C2–C1–C10 127.8(7), C2–C1–Si1 144.0(6), C10–C1–Si1 88.1(4), C1–C2–C3 126.7(7), C11–C10–C1 104.0(6), C11–C10–B1 128.6(7), C1–C10–B1 126.8(6), C10–C11–C12 128.7(8), C10–C11–Si1 91.9(5), C12–C11–Si1 139.1(7), C39–B1–C35 110.5(6), C11–Si1–C1 75.8(4), C1–Si1–C18 130.8(3), C1–Si1–C28 124.9(3), C11–Si1–C18 125.2(3), C11–Si1–C28 135.8(3).

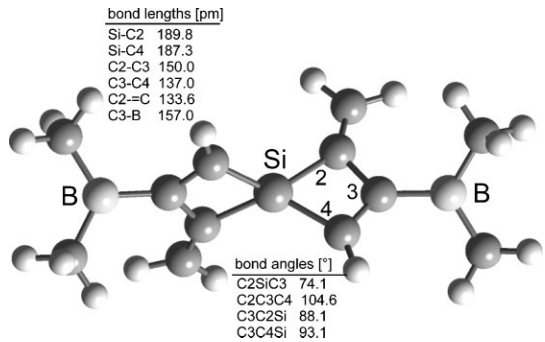


Figure 5. Optimized [B3LYP/6-311 + G(d,p)] gas phase geometry of the model compound **5M**.

X-Ray structural analysis of 5c

The X-ray crystal structural analysis of **5c** was carried out for a single crystal (selected in perfluorinated oil[30] at room temperature) at 273(2) K using a STOE IPDS II system (wavelength: $\lambda = 0.71069$ Å), equipped with an Oxford Cryostream low-temperature unit. The crystals were found to be non-meroedric twins. Therefore, strong reflex overlapping caused the observed low completeness. Thus, the structure determination is less than optimal, although the structure could be solved unambiguously. Formula weight: 732.69. Crystal system: monoclinic. Space group: P21/c. Unit cell dimensions: $a = 18.425(3)$ Å, $b = 19.610(2)$ Å, $c = 11.7318(11)$ Å, $\beta = 92.863(10)^\circ$. Volume $V = 4233.6(8)$ Å^3. $Z = 4$. Absorption coefficient $\mu = 0.090$ mm^{-1}. $F(000)$: 1576. Crystal size: $0.27 \times 0.25 \times 0.23$ mm. Theta range for data collection: 2.02–25.68°. Index ranges: $-21 \leq h \leq 22$, $-23 \leq k \leq 23$, $-11 \leq l \leq 11$. Reflections collected: 15 719. Independent reflections: 3781 [R(int) = 0.1125]. Data/restraints/parameters: 3781/0/496. Goodness-of-fit on F^2: 0.885. Final R indices [$F^2 > 2\sigma(F^2)$]: $R1 = 0.$ 0.062, $wR2 = 0.100$, R indices (all data): $R1 = 0.0182$, $wR2 = 0.129$. Largest difference peak and hole: 0.128 and -0.124 e · Å^{-3}. (Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 676 491. These data can obtained free of charge from the Cambridge Crystallographic Data Centre, via www.ccdc.cam.ac.uk/data_request/cif.) Structure solution and refinement were accomplished using SIR97,[31] SHELXL-97[32] and WinGX.[33]

Acknowledgments

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