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Synthesis of 4-silaspiro[3.4]octa-1,5-diene derivatives: hybrid spiro compounds

Ezzat Khan[a]*, Bernd Wrackmeyer[b], Rhett Kempe[b] and Germund Glatz[b]

Trialkynyl(vinyl)silanes CH_2=CH–Si(C≡C–R)$_3$ (R = Bu, Ph, *p*-tolyl) were prepared and treated with 9-borabicyclo[3.3.1]nonane (9-BBN). Consecutive 1,2-hydroboration and intramolecular 1,1-carboboration reactions (each requires different reaction conditions) were studied. 1,2-Hydroboration of the Si–vinyl group takes place at ambient temperature (23°C in tetrahydrofuran), followed by intramolecular 1,1-vinylboration to give 1-silacyclopent-2-ene derivatives, bearing still two alkynyl functions at the silicon atom. Further treatment with a second equivalent of 9-BBN affords 1-alkenyl-1-(alkynyl)-1-silacyclopent-2-ene derivatives. These undergo intramolecular 1,1-vinylboration to give 4-silaspiro[3.4]octa-1,5-dienes bearing the boryl groups at 2 and 6 positions. Protodeborylation of all new compounds (intermediates and final products) using acetic acid in slight excess afforded corresponding silanes including spirosilanes. All compounds were characterized using multinuclear NMR spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{29}Si) in solution state. Solid-state structures for one of the trialkynyl(vinyl)silanes (R = *p*-tolyl) and one of the 1-silacyclopent-2-ene derivatives (R = Ph) were confirmed using X-ray diffraction. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: alkynyl(vinyl)silanes; hydroboration; carboboration; protodeborylation; spirosilanes

Introduction

Considering the enormous attraction of tetraorganosilanes,[1,2] the class of spirosilanes has received scant attention, possibly as a result of somewhat tedious synthetic strategies and limited choice of substituent patterns. 1,1-Carboboration of dialkynyl- and tetraalkynylsilanes has been shown to open a convenient route to cyclic silanes, such as siloles or bisiloles,[3] although rather severe reaction conditions (heating for prolonged periods of time at 100–120°C) are required when for example trialkylboranes (BR_3; R = Me, Et) are used. This problem can be circumvented using more Lewis-acidic triorganoboranes such as $B(C_6F_5)_3$.[4] Another elegant way has been proposed by introducing the boryl group into the respective molecule via 1,2-hydroboration, hoping for intramolecular 1,1-carboboration under relatively mild reaction conditions in the next step.[5] Both processes, 1,2-hydroboration[6] and 1,1-carboboration,[3] are well known for their efficiency and high selectivity for reducing C–C multiple bonds of organosilane derivatives, in most cases. Exploiting these consecutive reactions, various silacycles have been reported.[3,7,8] 1,2-Hydroboration followed by intramolecular 1,1-carboboration provides perhaps the most convenient access to the formation of numerous spirosilanes. It has advantage over other methods,[9] such as to tolerate various substituents at different ring positions, allowing assembly of various ring systems around the silicon atom and leading to silacycles containing C–C unsaturated bonds.

We have reported the spirosilanes 4-silaspiro[3.3]hepta-1,5-dienes (**A**)[10] and 5-silaspiro[4.4]nona-1,6-dienes (**B**)[11] (Fig. 1) containing axially chiral silicon atoms. The reactions were carried out for a variety of substituents on ring carbons and it was concluded that the nature of R (alkyl, aryl, heteroaryl) does not affect the course of chemical reactions.[11]

In continuation of this work, a hybrid of **A** and **B** could be made accessible if appropriate functional groups are present in the starting silanes. Thus, an alkynylsilane bearing one vinyl group, available for 1,2-hydroboration, and three alkynyl functions for either intramolecular 1,1-carboboration or another 1,2-hydroboration was expected to lead finally to the desired spirosilanes containing a five- and a four-membered ring. Silanes with general structural formula (H_2C=CH)Si(C≡C–R)$_3$ (R = Bu, Ph, *p*-tolyl; **1a–c**) fulfil all the requirements for formation of the proposed hybrid spirosilanes. NMR spectroscopy, in particular ^{13}C NMR and ^{29}Si NMR, served to monitor the reactions, to detect intermediates and to characterize the products in solution. Some precursors were obtained as solid crystalline materials, for which crystal structures could be determined supporting the proposed reactions. Moreover, density functional theory calculations enabled a comparison of optimized gas-phase structures with experimental data, including NMR parameters.

Results and Discussion

Starting Materials

Trialkynyl(vinyl)silanes act as starting materials for the syntheses of the title compounds. They can be obtained by the reaction of alkynyl lithium reagents and trichloro(vinyl)silane (in 3:1 ratio) at −78°C.[12] They are colourless oily (**1a**), waxy (**1b**) or crystalline solids (**1c**), and can tolerate air, moisture and fairly high temperature

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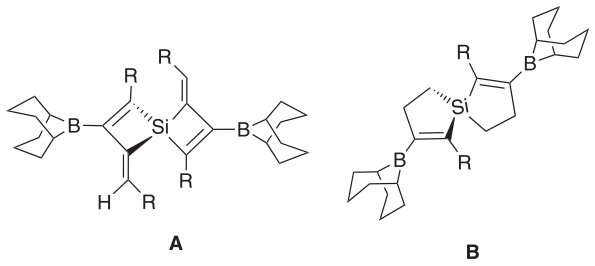


Figure 1. Spirosilanes (R = alkyl, aryl) obtained via consecutive 1,2-hydroboration and 1,1-carboboration reactions.

(>150°C). They were purified by fractional distillation (**1a**) or recrystallization (**1b** and **1c**) and were characterized using NMR spectroscopy in solution state, together with one example (**1c**) in solid state using X-ray diffraction (Experimental section; Table 1 and Fig. 2).

Although the structure solution of silane **1c** suffers from some sort of disorder, the structure can be solved without obstructions and connectivities (except C=C bond) can be established for atoms with the required accuracy. Apparently, there are weak intermolecular interactions between the vinyl unit and one of the alkynyl groups of a neighbouring molecule, one of the possible reasons for disorder. The geometry around the silicon atom is close to perfect tetrahedral. All C–Si–C angles are in the range 109.0–110.8°, except C13–Si1–C22 (106.7°). All other bond angles and bond lengths are within the expected range reported for alkynylsilanes as well as alkynylgermanes.[13] Interestingly, density functional theory calculations show the optimized gas-phase structure of **1c** with a preferred intramolecular orientation of the $-CH=CH_2$ group along the vector of one of the C≡C bonds (Fig. 3). The optimized structure of the parent compound $CH_2=CH-Si(C\equiv CH)_3$ also shows this particular structural feature. Since the calculated NMR parameters (see below) such as chemical shifts δ (^{13}C) and coupling constants $J(^{29}Si,^{13}C)$ are very similar for all three alkynyl groups, these interactions must be rather weak.

Table 1. Data pertinent to the crystal structure determinations of **1c** and **5b**

	1c	5b
Formula	$C_{58}H_{48}B_2Si_2$	$C_{52}H_{40}Si_2$
Crystal	Colourless prism	Colourless prism
Dimensions (mm)	0.77 × 0.23 × 0.11	1.08 × 0.77 × 0.61
Crystal system	Monoclinic	Orthorhombic
Space group	C2	$Pca2_1$
Lattice parameters		
a (pm)	2019.9(2)	3551.7(4)
b (pm)	608.2(7)	1011.9(12)
c (pm)	1915.1(2)	1110.9(12)
$\alpha = \gamma$ (°)	90.0	90.00
β (°)	91.1(10)	126.478(10)
Z	2	4
Volume (Å^3)	2352.1(4)	3992.8(8)
F (000)	848	1520
Abs. coeff. μ (mm^{-1})	0.11	0.13
Diffractometer	STOE IPDS II, Mo Kα, λ = 71.069 pm, graphite monochromator	
Measuring range (°)	2.0–25.8	2.0–25.7
Reflections collected	4369	7072
Ind. reflections ($I > 2\sigma(I)$)	2736	3834
Data/restraint/parameters	2736/1/280	3834/1/487
wR_2/R_1 ($I > 2\sigma(I)$)	0.046/0.077	0.079/0.116
Max./min. residual electron density (×10^{-6} epm^{-3})	0.29/−0.17	0.25/−0.23

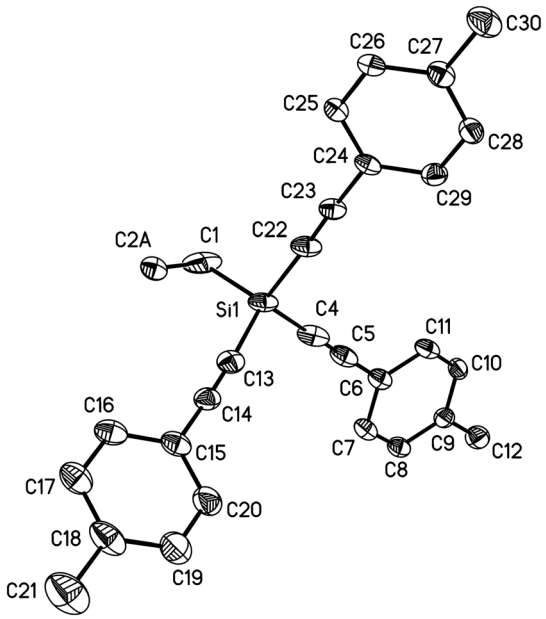


Figure 2. Molecular structure of **1c** (ORTEP plot ellipsoids drawn at 40% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and bond angles (°): C1–Si1 182.7(4), C4–C5 120.8(4), C4–Si1 180.9(4), C22–Si1 183.2(3); C2A–C1–Si1 132.0(6), C5–C4–Si1 177.6(3), C14–C13–Si1 173.9(2), C23–C22–Si1 175.8(3), C4–Si1–C13 110.6(14), C4–Si1–C1 110.8(18), C13–Si1–C1 109.7(2), C4–Si1–C22 110.0(14), C1–Si1–C22 109.0(15).

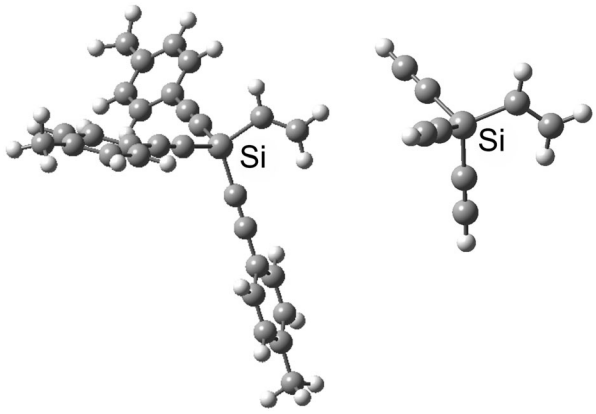
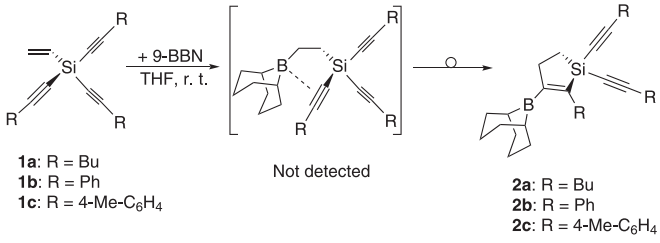


Figure 3. Calculated optimized gas-phase geometries (B3LYP/6-311 + G(d, p) level of theory) of **1c** and the parent compound $CH_2=CH-Si(C\equiv CH)_3$.

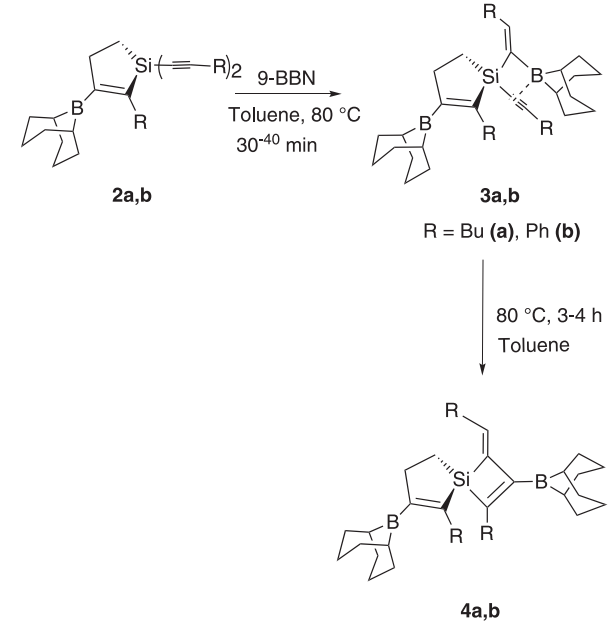
1,2-Hydroboration and 1,1-Carboboration

The presence of at least one $Si-CH=CH_2$ function, in addition to the Si–C≡C– units (**1a–c**), enhances the utility of these compounds. When treated with 9-borabicyclo[3.3.1]nonane (9-BBN),[14,15] such silanes react preferably at the $Si-CH=CH_2$ group via regioselective 1,2-hydroboration, even in the presence of three Si–C≡C– units (Scheme 1). After 1,2-hydroboration of the Si–vinyl group, the boryl group occupies a position favourable for intramolecular 1,1-vinylboration (intermediates in square brackets are not detected)



Scheme 1. 1,2-Hydroboration of trialkynyl(vinyl)silane derivatives **1a–c** at ambient temperature. Intramolecular activation of the Si–C≡ bond is indicated by the dashed line.

to afford 1-silacyclopent-2-ene derivatives **2a–c** (*ca* 1 h reaction time at room temperature). The silanes **2a–c** as shown in Scheme 1 (see also Figs 4 and 5) possess two alkynyl functional groups which can react further with another equivalent of 9-BBN. However, this second 1,2-hydroboration takes place much more slowly (*ca* 24 h at 23°C and less than 5% conversion can be observed) to afford intermediates **3a** and **3b** (Scheme 2). The same mixture, after heating to 80°C in toluene for several minutes, shows considerable progress in the second 1,2-hydroboration reaction (>80%, NMR spectroscopy). Intermediates **3a** and **3b** are stable at room temperature, and ring closure to **4** is negligible or not observed even after four days at room temperature. This is a positive aspect of such



Scheme 2. 1,2-Hydroboration, followed by intramolecular 1,1-carboboration, of 1-silacyclopent-2-ene derivatives **2a** and **2b** using 9-BBN as hydroborating reagent.

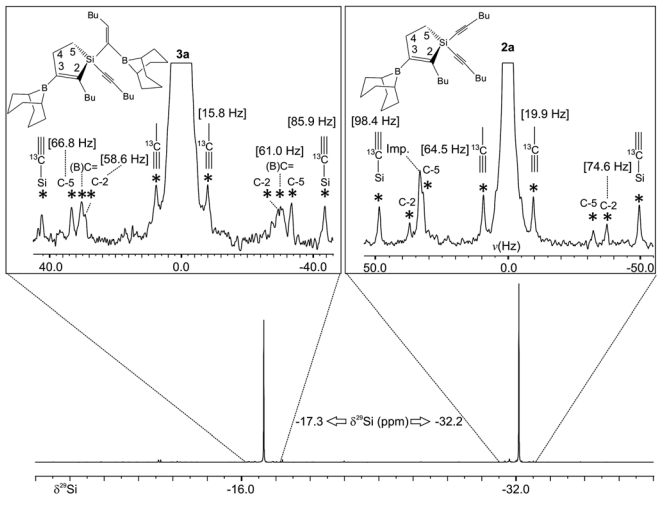


Figure 4. 59.6 MHz $^{29}Si\{^{1}H\}$ NMR spectra of a mixture containing **2a** and **3a**. Expansions are given for both the signals showing ^{13}C satellites, marked by asterisks, corresponding to coupling constants $^{1/2}J(^{29}Si, ^{13}C)$, given in square brackets.

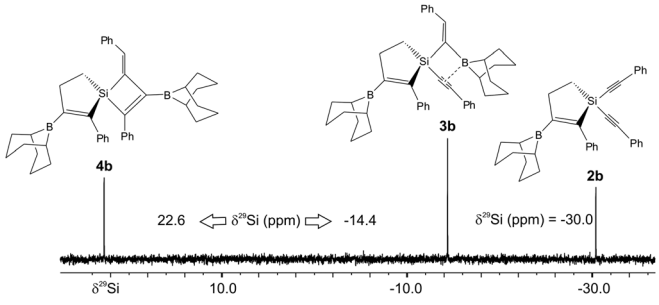


Figure 5. 59.6 MHz $^{29}Si\{^{1}H\}$ NMR spectra (refocused INEPT) of reaction mixture containing 1-silacyclopent-2-ene derivatives **2b**, **3b** and spirosilane **4b**.

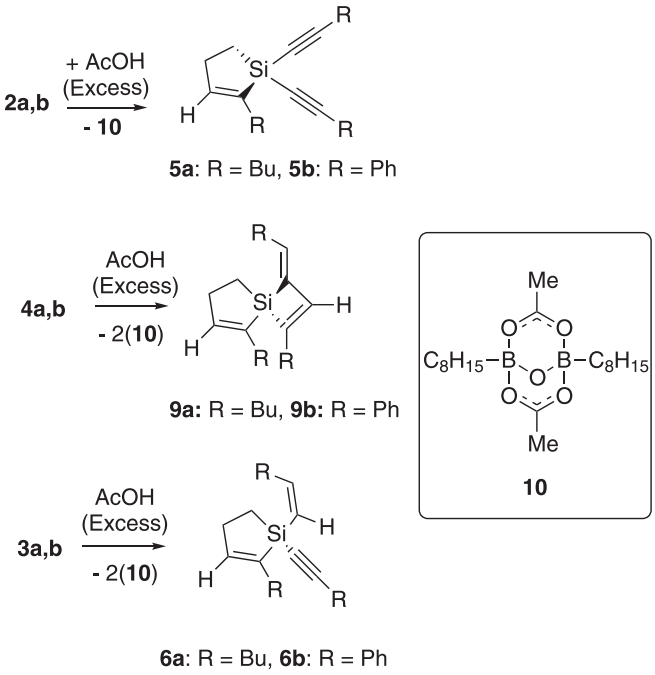
intermediates as they can be characterized in solution state using NMR spectroscopy (Fig. 4) and it is helpful in understanding the reaction pathway (Schemes 1 and 2). The dashed line between boron atom and alkynyl group in **3** indicates Si–C≡ bond activation leading to Si–C≡ bond cleavage. Heating of intermediates **3a** and **3b** at 80°C for 1 to 6 h is required for intramolecular rearrangement into **4a** and **4b**. These desired hybrid spirosilanes (Scheme 2) are formed almost quantitatively (>90%, from NMR spectra). Clearly, ^{29}Si NMR spectroscopy serves as a powerful tool for monitoring the progress of the reactions since all silanes shown in the schemes possess distinct chemical shifts δ (^{29}Si) (Figs 4 and 5).

Protodeborylation

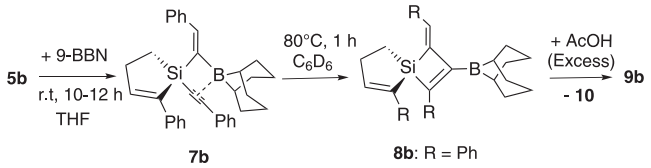
The presence of a diorganoboryl group invites further chemistry. Compounds containing this group may be converted into hydrolysis or oxidation products and most importantly into Suzuki-type coupling products.[16] Compounds **2**, **3** and **4** bear boryl substituents, which can be replaced simply by hydrogen by treating these compounds with an excess of acetic acid. Since all other functions show sufficient stability in the presence of acetic acid, the boryl group can easily be removed (Scheme 3). The resulting bicyclic boron compound **10** is isolated following a literature procedure,[17] and the desired boron-free pure compounds are obtained as viscous oils or crystalline material (**9b**) (Scheme 4).

NMR Spectroscopic Studies for Structural Elucidation

Although typical ^{11}B chemical shifts[18] of compounds **2**, **3** and **4** (Experimental section) reveal the presence of three-coordinate boron atoms linked to three carbons, much more additional proof for the solution-state structures is required. As already pointed out, ^{29}Si NMR spectra are helpful (Figs 3 and 4), in particular if the signal-to-noise ratio enables assignment of ^{13}C satellites corresponding to coupling constants $^{n}J(^{29}Si, ^{13}C)$ ($n = 1, 2$) (Figs 3 and 5).



Scheme 3. Protodeborylation of synthesized compounds at various stages.



Scheme 4. Synthesis of **7b** and **8b** using **5b** as precursor. Protodeborylation of **8b** leads to the formation of **9b**.

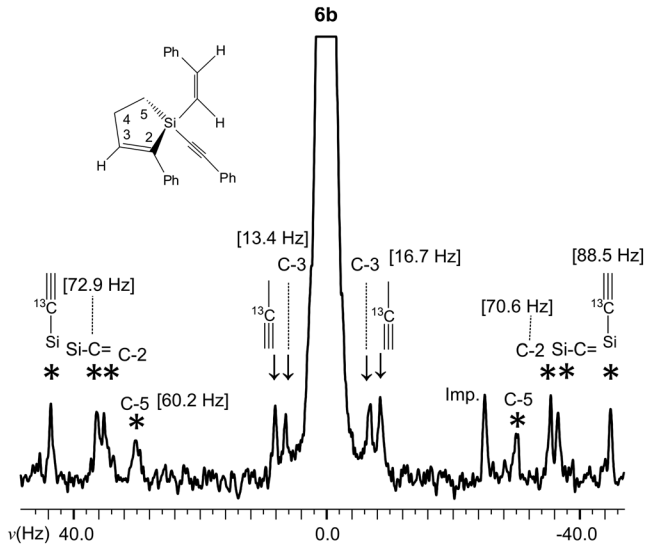


Figure 6. Expansion of 59.6 MHz $^{29}Si\{^{1}H\}$ NMR spectrum of **6b**, showing ^{13}C satellites, marked by asterisks, corresponding to coupling constants $^{1/2}J(^{29}Si,^{13}C)$, given in square brackets.

The latter information is complemented by ^{13}C NMR spectra showing the ^{29}Si Satellites for relevant signals, together with characteristic ^{13}C chemical shifts (Fig. 6), and in the case of the boryl-substituted derivatives by typically broadened ^{13}C NMR signals of carbon atoms linked to boron.[19,20]

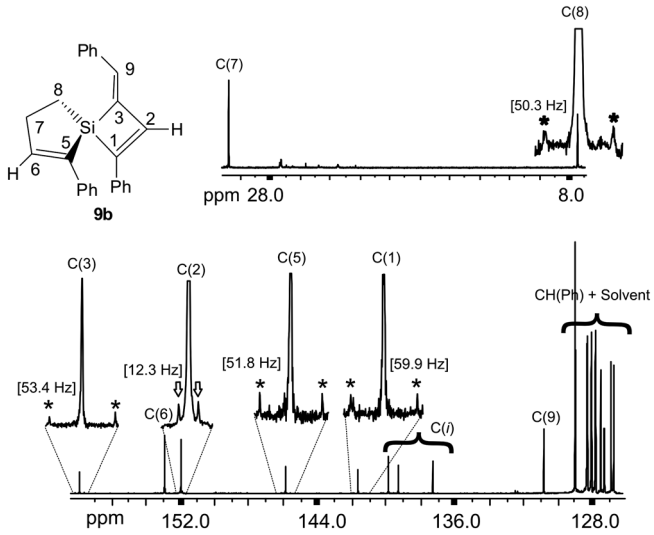


Figure 7. 100.5 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **9b**. Aliphatic (upper trace) and olefinic (lower trace) expansions are given for carbons showing ^{29}Si coupling satellites, marked by asterisks and arrows corresponding to $^{1}J(^{29}Si,^{13}C)$ and $^{2}J(^{29}Si,^{13}C)$, respectively. The values of corresponding coupling constants are given in square brackets.

Calculations of ^{29}Si chemical shifts[20,21] based on optimized gas-phase geometries reflect the experimental data, showing the increased ^{29}Si magnetic shielding with increasing number of alkynyl groups and the typical deshielding in five-membered rings,[20] in contrast to comparable non-cyclic derivatives or four-membered rings. The structural dependence of coupling constants $^{n}J(^{29}Si,^{13}C)$ is also noteworthy, and the experimental data (Figs 4, 6 and 7) are reasonably well reproduced by the calculated values (Fig. 8).

X-ray Diffraction Study of 5b

The molecular structure of **5b**[21] is shown in Fig. 9, together with selected bond lengths and angles. Relevant data for crystal structure determination and refinement are listed in Table 1. In a molecule of **5b**, all atoms of the principal plane (1-silacyclopent-2-ene) deviate from planarity. The C^2–Ph (C21–C26) plane is twisted by an angle of 10.6° and the Ph rings attached to ≡C– atoms (C3–C8 and C11–C16) form angles of 82.0° and 97.0°, respectively, with the principal plane. The endocyclic C–Si–C angle is expectedly smaller (∠C17–Si1–C20 = 94.9°) than the excocyclic angles (∠C1–Si1–C17 = 109.8°, ∠C1–Si1–C9 = 106.8° and ∠C9–Si1–C17 = 116.8°). The surroundings of silicon atom are distorted tetrahedral, and all bond lengths and angles of 1-silacyclopent-2-ene ring are well comparable with analogous structures containing the same ring system.[7,8] Bond lengths of C18–C19 and C17=C18 are slightly shorter than the analogous bonds in 9-BBN-substituted derivatives.[7,8] The elongation of these bonds in the latter case can be traced to hyperconjugation involving the empty p_z orbital of the boron and C–C σ-bonds.[22–24] The C≡C bond lengths (120.8(8) pm) in **5b** are identical to those in **1c**.

Conclusions

Hybrid spirosilanes, 4-silaspiro[3.4]octa-1,5-dienes, bearing boryl groups and R substituents (R = Bu, Ph) are accessible in high yield

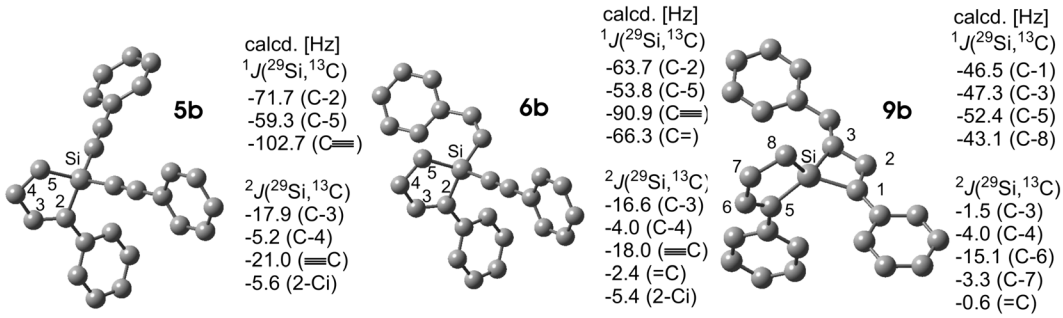


Figure 8. Calculated coupling constants $^nJ(^{29}Si,^{13}C)$ ($n = 1$, 2) based on optimized gas-phase geometries (B3LYP/6-311 + G(d,p) level of theory). For experimental data, see Figs 4, 6 and 7.

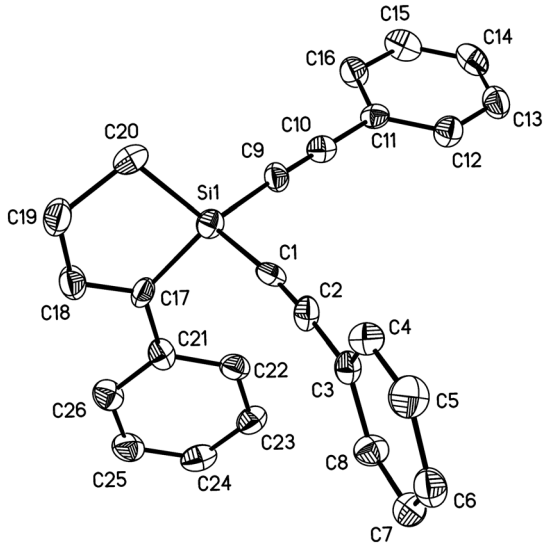


Figure 9. Molecular structure of **5b** (ORTEP plot, ellipsoids drawn at 40% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and bond angles (°): C1–C2 120.8(8), C9–C10 121.2(8), C1–Si1 182.7(7), C17–C18 132.8(8), C17–Si1 184.2(7), C18–C19 150.8(8), C19–C20 155.0(8), C20–Si1 185.5(6); C2–C1–Si1 173.4(6), C1–C2–C3 176.5(7), C10–C9–Si1 176.3(6), C18–C17–Si1 107.0(5), C17–C18–C19 120.1(6), C18–C19–C20 109.4(5), C19–C20–Si1 102.7(4), C9–Si1–C1 106.8(3), C1–Si1–C17 109.8(3), C17–Si1–C20 94.9(3).

by combining consecutive intermolecular 1,2-hydroboration and intramolecular 1,1-carboboration reactions. So far the combination of these processes appears to open the only access to such spirosilanes. Protodeboylation of precursors and final products was successfully carried out under ambient reaction conditions. All precursors and spirosilanes are sufficiently stable in acetic acid solution and no side reactions/products were observed. Solution-state NMR data served for structural assignments of precursors, intermediates and final products, confirmed by calculated optimized gas-phase structures and calculated NMR parameters.

Experimental

General

All manipulations were performed observing precautions to exclude traces of air and moisture in Schlenk-type glassware. Carefully dried solvents and oven-dried glassware were used throughout. BuLi in hexane (1.6 M), trichloro(vinyl)silane, ethynylbenzene, 1-ethynyl-4-methylbenzene, 1-hexyne, glacial acetic acid and 9-BBN were used as commercial products without further purification. Mass spectra: FOCUS DSQ (Thermo) mass spectrometer; the *m/z* data refer to the isotopes ^1H, ^{11}B, ^{12}C, ^{28}Si (**5b** only). 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 relative 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 ppm for ^{13}C and ^{29}Si, and ±0.4 ppm for ^{11}B; coupling constants are given to ±0.4 Hz for $J(^{29}Si,^{13}C)$. ^{29}Si NMR spectra were measured using the refocused INEPT pulse sequence,[25] based on $^3J(^{29}Si,^1H)$ (15–25 Hz) after optimizing the delay times in the pulse sequence. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

All quantum-chemical calculations were carried out using the Gaussian 09 program package.[26] Optimized geometries at the B3LYP/6-311 + G(d.p) level of theory[27] were found to be minima by the absence of imaginary frequencies. NMR parameters were calculated[28,29] at the same level of theory. Calculated nuclear magnetic shielding constants $\sigma^{11}B$ were converted by $\delta^{11}B$ (calcd) = $\sigma(^{11}B) - \sigma(^{11}B, B_2H_6)$, with $\sigma(^{11}B, B_2H_6) = +84.1$ ($\delta^{11}B$ (B_2H_6) = 18 and $\delta^{11}B$ (BF_3–OEt_2) = 0), and calculated $\sigma(^{29}Si)$ were converted to chemical shifts $\delta^{29}Si$ by $\delta^{29}Si$ (calcd) = $\sigma(^{29}Si, TMS) - \sigma(^{29}Si)$, with $\sigma(^{29}Si, TMS) = +340.1$ and $\delta^{29}Si$ (TMS) = 0.

Syntheses of Trialkynyl(vinyl)silanes 1a and 1b

A freshly prepared suspension of hexyn-1-yllithium (25.0 mmol) in hexane (60.0 ml) was cooled to −78°C and trichloro(vinyl)silane (8.3 mmol, 1.3 ml) was slowly added. The reaction mixture was warmed to room temperature and stirring was continued for 12 h (overnight). Insoluble materials were separated and all readily volatile materials were removed under reduced pressure. The colourless oily residue was identified as a mixture of **1a** and $Si(Cl)(CH{=}CH_2)(C{\equiv}C{-}Bu)_2$. The silane $Si(CH{=}CH_2)(C{\equiv}C{-}Bu)_2Cl$ ($\delta^{29}Si = -46.3$; b.p. = 150–155°C/6.5×10^{-1} mbar) was separated by fractional distillation and a pure sample of **1a** was obtained and characterized using multinuclear NMR spectroscopy (^1H, ^{13}C and ^{29}Si). The same synthetic pathway was followed for the synthesis of **1b**, except purification of the reaction mixture. The residual solid (LiCl including **1b**) was washed with toluene, all volatiles were removed *in vacuo* and **1b** (*ca* 85%) was obtained as a waxy solid. The solid was washed two to three times with pentane and all lighter fractions and impurities were isolated, to give pure **1b** (98%, NMR spectra). Preparation and experimental work up for **1c** were exactly the same as for **1a** and **1b**. The silane

$Si(Cl)(CH{=}CH_2)(C{\equiv}C\text{–}4\text{-}Me\text{–}C_6H_4)_2$ was washed with hexane and the remaining solid residue was dissolved in THF. Needle-like colourless crystals appeared after 3–4 days. A single crystal of suitable dimensions was selected and studied using X-ray diffraction.

1a. Yield 86%. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.7$, 1.2, 1.9 (t, m, t, 27H, Bu), 5.9 (m, 1H, =CH), 6.0 (m, 1H, =CH), 6.3 (m, 1H, HC=). ^{13}C NMR (100.5 MHz): δ [J(^{29}Si,^{13}C)] = 13.6, 19.9, 22.1, 30.5 (Bu), 79.0 [116.6 Hz] (Si–*C*≡), 109.7 [23.0 Hz] (≡*C*), 133.9 [87.7 Hz] (Si–*C*=), 135.2 (=*C*). ^{29}Si NMR (59.6 MHz): $\delta = -73.9$.

1b. Yield 85%. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 6.1$ (dd, 1H, J(^{1}H,^{1}H) = 13.5, 4.2 Hz, $=CH_2$), 6.5 (dd, 1H, J(^{1}H,^{1}H) = 20.1, 13.5 Hz, HC=), 6.6 (dd, 1H, J(^{1}H,^{1}H) = 20.1, 4.2 Hz, $=CH_2$), 6.8–6.9, 7.3–7.4 (m, m, 15H, Ph). ^{13}C NMR (100.5 MHz): δ [J(^{29}Si,^{13}C)] = 87.2 [116.4 Hz] (Si–*C*≡), 108.2 [23.0 Hz] (≡*C*), 132.0 [89.6 Hz] (Si–*C*=), 137.1 (=*C*), 122.5, 132.6, 128.4, 129.4 (Ph). ^{29}Si NMR (59.6 MHz): $\delta = -71.2$.

1c. Yield 85%; m. p. 108–110°C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.5$, 6.6, 6.7 (m, m, m, 3H, $Si\text{–}C_2H_3$), 2.6 (s, Me), 7.4, 7.7 (m, m, 12H, 4-Me–C_6H_4). ^{13}C NMR (100.5 MHz): δ [J(^{29}Si,^{13}C)] = 85.7 [116.4 Hz] (Si–*C*≡), 107.5 [22.9 Hz] (≡*C*)], 21.5 (Me), 119.1, 132.2, 129.9, 139.5 (4-Me–C_6H_4). ^{29}Si NMR (59.6 MHz): $\delta = -71.8$.

Syntheses of 1,1-(Dialkyn-1-yl)-1-silacyclopent-2-ene Derivatives 2a–c, 3a,b and 4a,b

A Schlenk tube was charged with a solution of **1a** (1.6 g, 5.4 mmol) in THF (10 ml) and one equivalent of 9-BBN (0.58 g, 5.4 mmol). The reaction mixture was stirred at room temperature for 30–40 min, and all volatile materials were removed under reduced pressure. The reaction afforded pure **2a** (>90%, NMR spectroscopy) which was used for further transformations. Important NMR data were collected for **2a** and it was dissolved in 5 ml of toluene and one further equivalent of 9-BBN (0.58 g, 5.4 mmol) was added. The reaction mixture was heated to 80°C for *ca* 4 h to give **3a**, followed by intramolecular 1,1-carboboration to afford **4a**. The procedure for the preparation of silanes **3b** and **4b** was exactly the same.

2a. ^{1}H NMR (300 MHz): $\delta = 0.7$, 1.0, 1.2–1.4, 2.0, 2.6 (t, t, m, m, m, 27H, Bu), 1.2 (m, 2H, C^5H_2), 2.5 (m, 2H, C^4H_2), 1.3, 1.8–2.0 (m, 14H, BBN). ^{13}C NMR: δ [J(^{29}Si,^{13}C)] = 146.0 [74.6 Hz] (C^2), 169.3-br (C^3), 34.6 (C^4), 11.9 [64.5 Hz] (C^5), 13.7, 20.1, 22.2, 30.8 (≡C–*Bu*), 14.5, 23.8, 34.5, 34.1 (C^2–*Bu*), 23.5, 32.2-br, 33.8 (9-BBN), 81.5 [98.4 Hz] (Si–*C*≡), 109.8 [19.9 Hz] (≡C). ^{29}Si NMR: $\delta = -32.2$. ^{11}B NMR: $\delta = 85.1$.

2b. ^{1}H NMR (300 MHz): $\delta = 1.3$, 1.6–1.8 (m, m, 14H, 9-BBN), 1.5 (dd, 2H, C^5H_2), 2.9 (dd, 2H, C^4H_2), 6.8–6.9, 7.0–7.2, 7.3, 7.6 (m, m, m, m, 15H, Ph). ^{13}C NMR: δ [J(^{29}Si,^{13}C)] = 144.5 [77.8 Hz] (C^2), 175.50-br (C^3), 34.9 (C^4), 12.3 [64.8 Hz] (C^5), 34.5, 32.4-br, 23.5 (9-BBN), 90.0 [98.7 Hz] (Si-*C*≡), 108.5 [19.3 Hz] (≡C), 142.0, 128.9, 128.5, 126.9 (C^2-*Ph*), 123.0, 132.5, 128.4, 129.1 (2 × ≡C-*Ph*). ^{29}Si NMR: $\delta = -30.3$. ^{11}B NMR: $\delta = 85.1$.

2c. ^{1}H NMR (400 MHz): $\delta = 1.1$, 1.5–1.9 (m, m, 14H, 9-BBN), 0.8 (m, 2H, C^5H_2), 2.6 (m, 2H, C^4H_2), 1.6 (s, Me), 1.8 (s, Me), 6.4, 6.7, 7.0, 7.3 (m, m, m, m, 12H, 4-Me–C_6H_4). ^{13}C NMR: δ [J(^{29}Si,^{13}C)] = 144.9 [75.9 Hz] (C^2), 174.2-br (C^3), 34.9 (C^4), 12.5 [64.9 Hz] (C^5), 23.6, 32.3-br, 34.6 (9-BBN), 89.6 [99.6 Hz] (Si–*C*≡), 108.7 [19.1 Hz] (≡C), 21.3 (Me), 120.2, 132.4, 129.2, 139.1 (2 × ≡C–(4-Me–C_6H_4)), 21.1 (Me), 136.2, 132.6, 129.0, 140.3 (C^2–(4-Me–C_6H_4)). ^{29}Si NMR: $\delta = -30.5$. ^{11}B NMR: $\delta = 84.3$.

3a. ^{1}H NMR (300 MHz): $\delta = 0.8$, 0.9, 1.0, 1.2–1.5, 2.4–2.9 (t, t, t, m, m, Bu, C^4H_2, C^5H_2), 1.4, 1.7–2.1 (m, m, 28H, 9-BBN), 7.0 (t, 1H, ^3J(^{1}H,^{1}H) = 7.2 Hz, =CH). ^{13}C NMR: δ [J(^{29}Si,^{13}C)] = 148.7 [66.7 Hz] (C^2), 168.0 (br, C^3), 34.1 (C^4), 12.5 [58.6 Hz] (C^5), 13.7, 20.2, 22.3, 30.8 (≡C–*Bu*), 14.3, 14.4, 23.1, 23.8, 32.1, 33.7, 33.3, 35.0 (C^2–*Bu*, =C–*Bu*), 23.5, 23.8, 31.5-br, 32.2-br, 33.7, 33.8, 34.5, 34.6 (2 × 9-BBN), 85.0 [85.7 Hz] (Si–*C*≡), 110.0 [15.6 Hz] (C≡), 146.1 (br, B–C=), 158.5 (=CH). ^{29}Si NMR: $\delta = -17.2$. ^{11}B NMR: $\delta = 84.8$.

3b. ^{1}H NMR (300 MHz): $\delta = 1.2$ (m, 2H, C^5H_2), 2.9 (m, 2H, C^4H_2), 1.3–2.1 (m, 14H, 9-BBN), 6.8–7.5 (m, 15H, Ph), 8.0 (s, 1H, ^3J(^{29}Si,^{1}H) = 17.8 Hz, =CH). ^{13}C NMR: δ [J(^{29}Si,^{13}C)] = 147.9 [68.3 Hz] (C^2), 173.7-br (C^3), 33.6 (C^4), 12.5 [58.8 Hz] (C^5), 23.6, 23.8, 31.9-br, 32.3-br, 34.3, 34.5, 34.7, 34.8 (2 × 9-BBN), 94.5 [85.6 Hz] (Si–*C*≡), 108.7 [15.9 Hz] (≡C), 123.8, 125.7, 126.4, 128.1, 128.1, 128.4, 128.6, 129.3, 129.6, 132.1, 140.7, 142.8 (3 × Ph), 148.2-br (B–*C*=), 154.6 (=CH). ^{29}Si NMR: $\delta = -14.4$. ^{11}B NMR: $\delta = 87.3$.

4a. ^{1}H NMR (300 MHz): $\delta = 0.9$, 0.9, 1.2–1.6, 1.8–2.1, 2.5, 2.8 (t, t, m, m, m, m, protons not assigned, Bu, 9-BBN, C^4H_2, C^5H_2), 6.0 (t, 1H, ^3J(^{1}H,^{1}H) = 6.8 Hz, =CH). ^{13}C NMR: δ [J(^{29}Si,^{13}C)] = 168.0 [49.3] (C^1), 177.6-br (C^2), 148.8 [50.5] (C^3), 147.9 [55.9] (C^5), 170.7-br (C^6), 33.5 (C^7), 9.9 [46.4] (C^8), 127.5 (=CH), 14.3, 14.4, 14.4, 23.0, 23.2, 23.5, 32.6, 32.9, 33.2, 33.9, 34.1, 34.6 (3 × Bu), 23.6, 23.6, 31.4-br, 32.5-br, 33.8, 33.4, 33.4 (2 × 9-BBN). ^{29}Si NMR: $\delta = 22.7$. ^{11}B NMR: $\delta = 84.7$.

4b. ^{1}H NMR (400 MHz): $\delta = 1.3$ (m, 2H, C^8H_2), 2.9 (m, 2H, C^7H_2), 1.4, 1.6–2.0 (m, m, 28H, 9-BBN), 6.9–7.2, 7.4 (m, m, 16H, =CH, Ph). ^{13}C NMR: δ [J(^{29}Si,^{13}C)] = 163.2 [51.1] (C^1), 180.1-br (C^2), 150.9 [49.6] (C^3), 147.3 [57.5] (C^5), 177.5-br (C^6), 33.8 (C^7), 9.5 [48.2] (C^8), 132.4 (=CH), 23.6, 23.7, 32.3-br, 32.9-br, 34.2, 34.3, 34.6, 34.8 (2 × 9-BBN), 142.5 [6.5], 140.6 [6.8], 139.9, 128.9, 128.6, 128.5, 128.4, 128.2, 127.1, 126.9, 126.7 (3 × Ph). ^{29}Si NMR: $\delta = 22.6$. ^{11}B NMR: $\delta = 88.1$.

Protodeborylation of 1-Silacyclopent-2-ene Derivatives 2, 3 and spirosilanes 4a,b

A solution of **2a** (1.26 g, 3.0 mmol) in pentane (10 ml) was mixed with an excess of acetic acid (2 ml) at 23°C. The reaction mixture was stirred for 40–60 min. All readily volatile materials were removed under reduced pressure. The oily residue left was dissolved in pentane and the solution was kept at −35°C. Most of the fairly insoluble boron–oxygen compound **10** settled and was separated. The solvent and other readily volatile material were evaporated. The mixture containing 5a and trace amount of 10 was heated to 80°C under reduced pressure (10^{-2} torr) for 1 h. Pure **5a** was obtained as a colourless viscous oil. The protodeborylation reactions of silanes **2b**, **3a**,**b** and **4a**,**b** with acetic acid were carried out under identical reaction conditions.

The silane **5b** was taken up into a Schlenk tube and was dissolved in 2–3 ml of diethylether. After 24 h, colourless crystals of **5b** suitable for X-ray single-crystal analysis were obtained at 273 K, and a single crystal of appropriate dimensions was selected at room temperature for X-ray diffraction.

5a. Yield 50%. ^{1}H NMR (300 MHz): $\delta = 0.7$, 0.9, 1.2–1.3, 2.0, 2.4 (t, m, m, t, m, 27H, Bu), 1.1 (m, 2H, C^5H_2), 2.3 (m, 2H, C^4H_2), 6.3 (m, 1H, C^3H). ^{13}C NMR: δ [J(^{29}Si,^{13}C)] = 142.2 [75.1 Hz] (C^2), 148.3 [15.5 Hz] (C^3), 32.3 (C^4), 11.2 [63.7 Hz] (C^5), 13.6, 19.9, 22.2, 30.7 (2 × ≡C–*Bu*), 14.3, 23.1, 30.2, 32.5 (C^2–*Bu*), 81.0 [100.0 Hz] (Si–*C*≡), 109.8 [19.2 Hz] (≡C). ^{29}Si NMR: $\delta = -34.5$.

5b. Yield 65%; m.p. 84–86°C. ^{1}H NMR (300 MHz): $\delta = 1.3$ (t, 2H, ^3J(^{1}H,^{1}H) = 6.8 Hz, C^5H_2), 2.4 (m, 2H, C^4H_2), 7.1 (t, 1H, ^3J(^{1}H,^{1}H) = 7.3 Hz, C^2H), 6.9, 7.2, 7.4, 7.9 (m, m, m, m, 15H, Ph). ^{13}C NMR: δ [J(^{29}Si,^{13}C)] = 139.9 [76.8 Hz] (C^2), 150.0 [14.8 Hz] (C^3), 31.0 (C^4), 10.8 [58.9 Hz] (C^5), 89.6 [100.2 Hz] (Si–*C*≡), 108.5 [19.5 Hz] (≡C), 122.9, 132.4, 128.4, 129.1 (2 × ≡C–*Ph*), 138.7 [5.2 Hz], 129.0, 127.6, 127.3 (C^2–*Ph*). ^{29}Si NMR: $\delta = -32.5$. GC-MS: $t_R = 26.98$ min; *m/z* (%) = 360.1 (42) [M^+], 282.1 (6) [$M^+ - C_6H_6$], 258.0 (100) [$M^+ - C_8H_6$], 229.0 (22) [$M^+ - C_{10}H_{11}$], 180.0 (52) [$M^+ - C_{14}H_{12}$],

129.0 (72) [$M^+ - C_{18}H_{15}$].

6a. Yield 59%. ^{1}H NMR (300 MHz): δ = 0.8, 0.9, 0.9, 1.2–1.4, 2.1, 2.2–2.4 (t, t, t, m, t, m, 31H, Bu, C^4H_2, C^5H_2), 5.7 (d, 1H, $^3J(^1H,^1H)$ = 13.8 Hz, =C(Si)H), 6.3 (m, 1H, C^3H), 6.4 (dt, 1H, $^3J(^1H,^1H)$ = 7.5, 13.8 Hz, H(Bu)C=). ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 143.4 [68.9 Hz] (C^2), 147.2 [13.6 Hz] (C^3), 32.2 (C^4), 11.2 [58.7 Hz] (C^5), 13.8, 20.1, 22.2, 30.6 (≡C–*Bu*), 14.3, 14.3, 22.9, 23.2, 31.0, 32.4, 32.8 [5.4 Hz], 33.7 (2 × Bu), 83.0 [88.9 Hz] (Si–*C*≡), 109.6 [17.1 Hz] (≡C), 125.2 [73.0 Hz] (Si–*C*=), 151.9 (=*C*–Bu). ^{29}Si NMR: δ = −21.6.

6b. Yield 55%. ^{1}H NMR (300 MHz): δ = 0.9 (m, 2H, C^5H_2), 2.2 (m, 2H, C^4H_2), 5.8 (d, 1H, $^3J(^1H,^1H)$ = 14.8 Hz, =CH), 6.5–7.2, 7.4, 7.6 (m, m, m, 17H, =CH, C^3H, Ph). ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 141.9 [70.6 Hz] (C^2), 148.9 [13.4 Hz] (C^3), 31.1 (C^4), 10.1 [60.2 Hz] (C^5), 92.1 [88.5 Hz] (Si–*C*≡), 108.4 [16.7 Hz] (≡C), 139.6, 139.4 [5.6 Hz], 132.3, 129.3, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 127.3, 123.3 (3 × Ph), 126.4 [72.9 Hz] (Si–*C*=), 149.7 (=*C*–Bu). ^{29}Si NMR: δ = −18.5.

9b. Yield 56%. ^{1}H NMR (300 MHz): δ = 0.9, 1.2 (m, m, 2H, C^8H_2), 2.6 (m, 2H, C^7H_2), 6.9–7.2, 7.4, 7.5 (m, m, m, 17H, Ph, C^6H, =CH), 7.8 (s, 1H, $^3J(^{29}Si,^1H)$ = 20.1 Hz, C^2H). ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 141.6 [59.9] (C^1), 153.0 [4.7] (C^2), 157.9 [53.4] (C^3), 145.9 [51.8] (C^5), 152.0 [12.3] (C^6), 30.8 (C^7), 7.3 [50.3] (C^8), 130.8 (=CH), 139.9, 139.3, 137.3, 129.0, 128.9, 128.9, 128.3, 127.5, 127.3, 127.2, 126.8, 126.7 (3 × Ph). ^{29}Si NMR: δ = 19.7.

Hydroboration of 5b to Afford 7b and 8b Followed by Protodeborylation

Silane **5b** (0.90 g, 2.50 mM) was dissolved in toluene (5 ml) and an equimolar amount of 9-BBN (0.305 g, 2.50 mM) was added. The mixture was heated to 80–100°C for 30 min. The progress of the reaction was monitored using ^{29}Si NMR spectroscopy, showing the formation of **7b**, and heating was continued for further 1–2 h. During this time intramolecular 1,1-carboboration took place to give **8b**. This product was subjected to protodeborylation under the aforementioned conditions and **9b** was obtained (see above).

7b. ^{1}H NMR (400 MHz): δ = 1.2, 1.4 (m, m, 2H, C^5H_2), 2.5, 2.6 (m, m, 2H, C^4H_2), 1.2, 1.7–2.0 (m, 14H, 9-BBN), 6.8, 7.0, 7.1, 7.3, 7.5 (m, m, m, m, m, 15H, Ph), 8.1 (s, 1H, $^3J(^{29}Si,^1H)$ = 17.8 Hz, =CH). ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 142.8 [69.5 Hz] (C^2), 148.1 [13.1 Hz] (C^3), 31.4 (C^4), 12.4 [57.7 Hz] (C^5), 23.6, 32.9-br, 34.3, 35.0 (9-BBN), 93.4 [86.8 Hz] (Si–*C*≡), 108.4 [16.1 Hz] (C≡), 123.7, 126.9, 127.5, 128.0, 128.3, 128.6, 128.6, 128.6, 129.7, 132.2, 139.5, 140.5 (3 × Ph), 148.0-br (B–*C*=), 155.3 (=C). ^{29}Si NMR: δ = −17.9. ^{11}B NMR: δ = 84.8.

8b. Yield 89%. ^{1}H NMR (300 MHz): δ = 1.4, 1.7–2.2 (m, m, 14H, BBN), 1.2 (m, 2H, CH_2), 2.6 (m, 2H, CH_2), 6.9–7.2, 7.4, 7.6 (m, m, m, arylic protons, =CH). ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 157.9 [53.4] (C^1), 153.0-br (C^2), 145.9 [51.9] (C^3), 141.6 [60.4] (C^5), 152.0 [13.3]-br (C^6), 30.9 (C^7), 7.4 [49.9] (C^8), 139.8, 139.3 [5.7], 137.3, 130.8, 129.0, 129.0, 128.9, 128.6, 128.3, 127.5, 127.3, 127.2, 126.7 (3 × Ph and =CH). ^{29}Si NMR: δ = 16.8. ^{11}B NMR: δ = 85.7.

X-ray Structure Determination

Details pertinent to the crystal structure determinations are listed in Table 1. Crystals of suitable dimensions were selected (in perfluorinated oil[30] at room temperature), and the data collections were carried out at 133(2) K (**1c**, **2b**) using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit. Structure solutions and refinements were accomplished using SIR97,[31] SHELXL-97[32] and WinGX.[33]

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