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Combination of 1,2-Hydroboration and 1,1-Organoboration: A Convenient Route to 5-Silaspiro[4,4]nona-1,6-diene Derivatives

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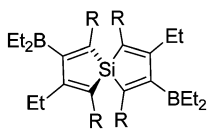
Keywords: Silanes / Spiro compounds / Hydroboration / Organoboration / NMR spectroscopy

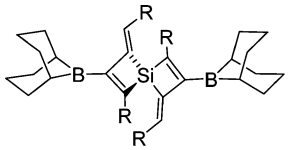
Dialkyn-1-yl(divinyl)silanes were prepared and their reactions with 9-borabicyclo[3.3.1]nonane (9-BBN) were studied. 1,2-Hydroboration takes place selectively at the vinyl group, followed by intramolecular 1,1-organoboration to form a 1-silacyclopent-2-ene ring. Repetition of this sequence affords, in essentially quantitative yield, 5-silaspiro[4,4]nona-1,6-diene derivatives bearing substituents in the 1,6-positions and 9-borabicyclo[3.3.1]nonyl groups in the 2,7-positions. Protodeborylation with an excess amount of acetic acid gives the respective spirosilanes bearing substituents only in the 1,6-positions. All new compounds were characterized by NMR spectroscopy in solution (^{1}H, ^{11}B, ^{13}C, ^{29}Si NMR) and for two examples of the spirosilanes by X-ray structural analysis in the solid state.

Introduction

In comparison to other tetraorganosilanes in general,[1,2] those with silicon in the center of a spiro structure are much less abundant.[3,4] There are few convenient routes towards spirosilanes, in particular if the rings contain C=C bonds or functional groups attached to carbon atoms. In addition to numerous saturated spirosilanes and a few examples of 5-silaspiro[4,4]nona-2,7-dienes,[3,4] previous work has shown that ethylboration of tetraalkyn-1-ylsilanes, $Si(C{\equiv}C\text{-}R)_4$, provides a straightforward route to 1,1-spirobisiloles **A**.[5–7] Recently, we characterized the first spirosilanes containing two four-membered rings **B** by using 1,2-hydroboration and 1,1-organoboration.[8] The combination of these stereo- and regioselective reactions is attractive in synthesis,[8–10] and in the present work further examples are given that are aimed at the synthesis and first structural characterization of the hitherto unknown 5-silaspiro[4,4]nona-1,6-diene derivatives.



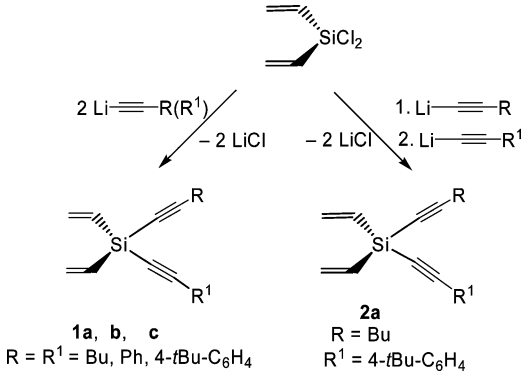
A



B

Results and Discussion

The strategy of combining 1,2-hydroboration and 1,1-organoboration for the synthesis of the title compounds requires silanes, in which the silicon atom bears two vinyl and two alkyn-1-yl groups, identical (**1**) or different (**2**). As shown in Scheme 1, silanes **1** or **2** are readily accessible. They are colorless liquids and stable towards air and moisture, and they are characterized by their typical NMR spectroscopic data sets (Table 1 and Figure 1).



Scheme 1. Synthesis of the starting dialkyn-1-yl(divinyl)silanes.

Silanes bearing a vinyl and an alkyn-1-yl group at the silicon atom react with 9-borabicyco[3.3.1]nonane (9-BBN) selectively by 1,2-hydroboration of the C=C bond, and the boron atom becomes linked to the terminal carbon atom of the vinyl group.[9] In comparison with other dialkylboranes, this is a unique property of 9-BBN, which prefers the terminal C=C bond over the C≡C bond.[11] The first intermediates from the 1,2-hydroboration (not detected) possess a favorable arrangement for *intramolecular* 1,1-alkylboration in the next step. The dashed line between boron and the alkynyl carbon atom (Scheme 2) indicates the interaction leading to cleavage of the Si–C≡ bond, formation of an alkyn-1-ylborate, and 1,1-alkylboration.[12] The alternative

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Table 1. ^{13}C and ^{29}Si NMR spectroscopic data[a] of dialkyn-1-yl-(divinyl)silanes **1a**–**c** and **2a**.

	$\delta^{13}C$ (Si-C≡)	$\delta^{13}C$ (≡C)	$\delta^{13}C$ (Si–HC=)	$\delta^{13}C$ (=CH_2)	$\delta^{29}Si$
1a[b]	78.6 [107.1]	110.4 [20.4]	133.9 [81.2]	135.2	–54.6
1b[c]	87.6 [105.1]	108.7 [20.0]	132.4 [82.1]	136.7	–52.7
1c[d]	87.2 [105.4]	109.0 [20.3]	132.9 [81.8]	136.4	–52.8
2a[e]	78.2 [108.1]	111.3 [20.3]	133.4 [81.7]	135.8	–53.7
	87.6 [104.3]	108.2 [20.0]			

[a] Measured in C_6D_6 at 296 ± 1 K, coupling constants [Hz] corresponding to $^1J(^{29}Si,^{13}C)$ and $^2J(^{29}Si,^{13}C)$ are given in square brackets. [b] Other ^{13}C data: δ = 30.8, 22.2, 19.9, 13.8 (Bu) ppm. [c] Other ^{13}C data: δ = 122.7, 132.4, 129.3, 128.5 (*i, o, p, m*, Ph) ppm. [d] Other ^{13}C data: δ = 120.1, 132.4, 125.5, 152.4, 34.7, 31.1 (*i, o, m, p*, C_{tert}, Me_3, 4-*t*BuC_6H_4) ppm. [e] See Figure 1; other ^{13}C data: δ = 13.7, 19.9, 22.1, 30.6 (Bu), 120.1, 132.3, 125.5, 152.3, 34.7, 31.2 (*i, o, m, p*, C_{tert}, Me_3, 4-*t*Bu-C_6H_4) ppm.

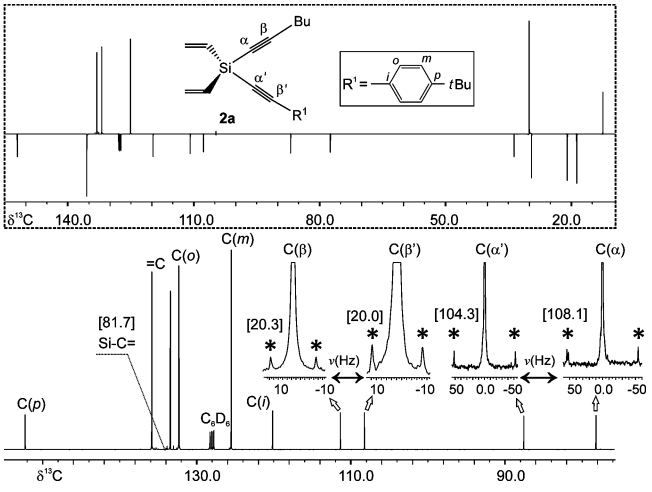
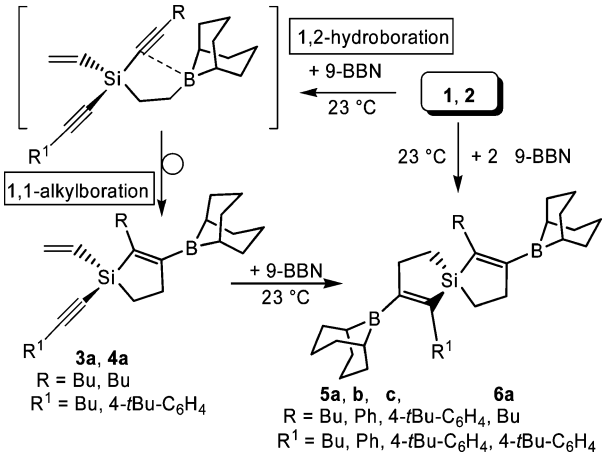


Figure 1. 100.5 MHz $^{13}C\{^1H\}$ NMR spectra of dialkyn-1-yl(divinyl)silane **2a** as obtained (Scheme 1) without further purification. Some ^{29}Si satellites are marked by asterisks, and the coupling constants $J(^{29}Si,^{13}C)$ are given in brackets. The insert shows the J-modulated spectrum.

enlargement of the 9-borabicyclo[3.3.1]nonane ring system[13] was not observed here. Usually, the *intermolecular* 1,1-organoboration of alkyn-1-ylsilanes requires harsh conditions and long reaction times.[12,14] However, the *intramolecular* 1,1-organoboration proceeds fast and more smoothly, in most cases studied so far.[8–10,15] This is shown by the reactions of **1** or **2** with 9-BBN either in an equimolar ratio or with two equivalents of 9-BBN (Scheme 2). If an equimolar amount of 9-BBN is used, monitoring of the reaction by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy (Table 2, Figure 2) enables 1-silacyclopent-2-enes **3** or **4** to be detected in mixtures with the respective starting silane **1** or **2** and spirosilanes **5** or **6**.

1-Silacyclopent-2-enes **3** or **4** can be converted into the title compounds by adding more 9-BBN, or the treatment of **1** or **2** with two equivalents of 9-BBN leads directly to the desired 5-silaspiro[4,4]nona-1,6-diene derivatives **5** or **6**. These spirosilanes are air sensitive, oily liquids (**5a**, **5c**) or crystalline compounds (**5b**, **6a**) that are formed in essentially quantitative yield. The consistent NMR spectroscopic



Scheme 2. Combination of 1,2-hydroboration and 1,1-organoboration. The intermediates shown in brackets were not detected. 1-Silacyclopent-2-enes **3a** and **4a** were identified in mixtures along with the starting silanes and the spirosilanes (see Figure 2).

Table 2. ^{11}B, ^{13}C, and ^{29}Si NMR spectroscopic data[a] for 1-silacyclopent-2-enes **3a** and **4a**.

	$\delta^{13}C$ (C-2)	$\delta^{13}C$ (C-3)	$\delta^{13}C$ (C-4)	$\delta^{13}C$(C-5)	$\delta^{29}Si$	$\delta^{11}B$
3a[b]	146.8 [67.5]	169.2 (br.)	34.1	10.4 [60.3]	–11.8	85.6
4a[c]	146.1 [69.4]	174.6 (br.)	35.0	10.9 [59.9]	–10.9	86.0

[a] Measured in C_6D_6 at 23 °C, (br.) indicates that the ^{13}C NMR signal is broadened owing to partially relaxed ^{11}B–^{13}C spin–spin coupling[20]; coupling constants [Hz] corresponding to $^1J(^{13}C,^{29}Si)$ are given in square brackets. [b] See Figure 3; other ^{13}C data: δ $[J(^{29}Si,^{13}C)]$ = 136.3 [69.9, =CH], 134.3 (=CH_2), 110.7 [16.3, C≡], 80.9 [89.6, Si–C≡], 31.0, 22.3, 20.1, 13.8 (≡C-Bu), 33.7, 32.9, 23.5, 14.4 [(C-2)–Bu], 34.0, 34.0, 32.5 (br.), 23.6 (BBN) ppm. [c] See Figure 2 for the ^{29}Si NMR spectrum; other ^{13}C data: δ [J ($^{29}Si,^{13}C$)] = 34.5, 34.6, 32.5 (br.), 23.6 (BBN), 109.3 [16.2, ≡C], 90.4 [87.8, Si–C≡] ppm; other carbon atoms are without assignment.

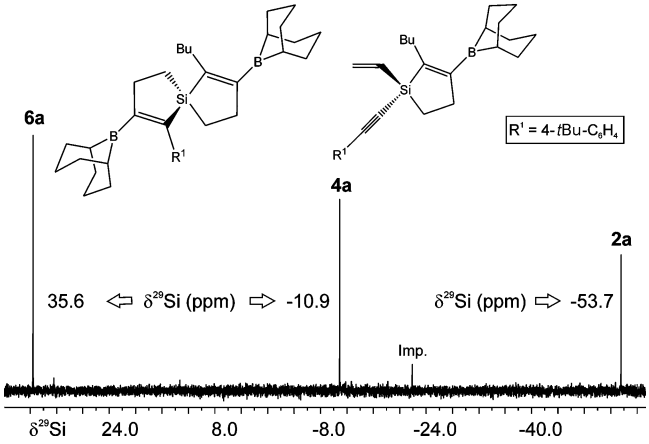


Figure 2. $^{29}Si\{^1H\}$ NMR 59.6 MHz spectrum (refocused INEPT[18]) of the reaction mixture containing the starting silane **2a**, 1-silacyclopent-2-ene **4a** and spiro-silane **5a**.

data sets (Table 3) are in complete agreement with the proposed structures. The structure in solution is confirmed by the molecular structure of **5b** in the solid state, as shown by X-ray analysis (vide infra).

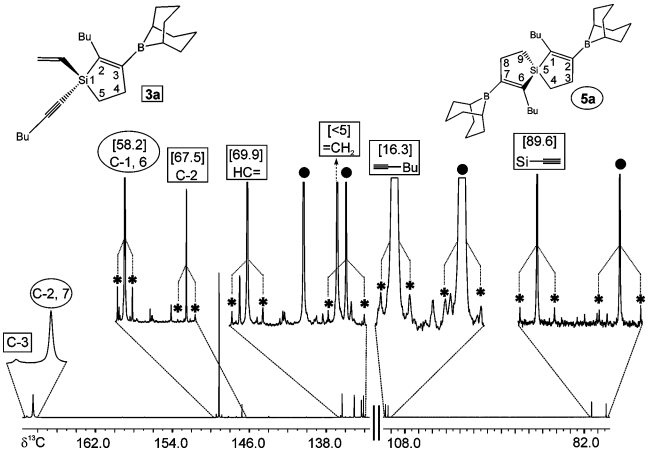


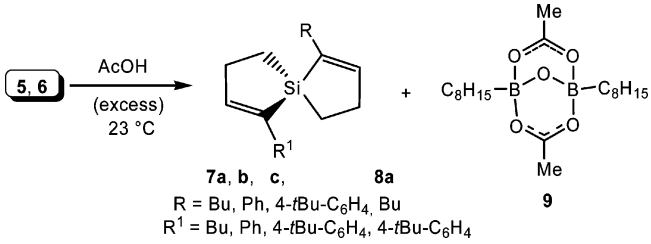
Figure 3. Part of the 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture containing starting material **2a** (marked by filled circles), 1-silacyclopent-2-ene derivative **3a** (marked by squares), and spirosilane **5a** (marked by circles). ^{29}Si satellites are marked by asterisks.

Table 3. ^{11}B, ^{13}C, and ^{29}Si NMR spectroscopic data[a] for 5-sila-[4,4]spirononа-1,5-diene derivatives **5**–**8**.

	$\delta^{13}C$ (C-1, 6)	$\delta^{13}C$ (C-2, 7)	$\delta^{13}C$ (C-3, 8)	$\delta^{13}C$ (C-4, 9)	δ ^{29}Si	δ ^{11}B
5a[b]	149.1 [58.2]	168.5 (br.)	34.3	9.4 [50.8]	34.9	85.6
5b[c]	149.7 [58.9]	173.5 (br.)	35.2	9.3 [51.8]	33.2	86.0
5c[d]	149.6 [59.3]	173.0 (br.)	34.5	9.3 [52.5]	35.8	87.0
6a[e]	150.0 [58.2]	172.4 (br.)	34.6	10.4 [49.9]	35.6	86.4
	148.8 [58.9]	169.0 (br.)	34.9	8.8 [52.3]		
7a[f]	143.3 [59.8]	147.7 [11.5]	30.4	8.5 [51.1]	28.5	–
7b[g]	141.0 [60.8]	148.0 [11.2]	29.8	6.6 [51.7]	29.9	–
7c[h]	142.3 [61.8]	148.3 [11.2]	31.2	8.0 [52.1]	29.8	–
8a[i]	143.8 [60.6]	148.2 [11.9]	31.0	8.4 [50.2]	29.2	–
	141.7 [60.3]	147.7 [10.8]	30.6	8.2 [51.8]		

[a] Measured in C_6D_6 at 23 °C, (br.) indicates that the ^{13}C NMR signal is broadened owing to partially relaxed ^{11}B–^{13}C spin–spin coupling[20]; coupling constants [±0.4 Hz] corresponding to $^1J(^{29}Si,^{13}C)$ and $^2J(^{29}Si,^{13}C)$ are given in square brackets. [b] Other ^{13}C data: δ = 33.9, 33.9, 32.4 (br.), 23.7 (9-BBN), 33.8, 33.2, 23.7, 14.4 (Bu) ppm. [c] Other ^{13}C data: δ [$J(^{29}Si,^{13}C)$] = 34.3, 34.8, 32.7 (br.), 23.7 (9-BBN), 143.7 [6.3], 128.4, 128.2, 126.4 (*i, o, m, p*, Ph) ppm. [d] Other ^{13}C data: δ [$J(^{29}Si,^{13}C)$] = 34.9, 34.4, 32.7 (br.), 23.8 (9-BBN), 140.9 [6.7], 128.2, 125.3, 149.1, 35.2, 31.5 (*i, o, m, p*, C_{tert}, Me_3, 4-*t*Bu-C_6H_4) ppm. [e] Other ^{13}C data: δ [$J(^{29}Si,^{13}C)$] = 33.9, 33.8, 32.7 (br.), 32.5 (br.), 23.8, 23.7 (9-BBN), 34.6, 33.4, 23.9, 14.4 (Bu), 141.1 [6.3], 128.2, 125.1, 148.9, 34.1, 31.7 (*i, o, m, p*, C_{tert}, Me_3, 4-*t*Bu-C_6H_4) ppm. [f] See Figure 4 for the ^{29}Si NMR spectrum; other ^{13}C data: δ [$J(^{29}Si,^{13}C)$] = 31.9 [5.9], 25.3, 23.0, 14.2 (Bu) ppm. [g] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 138.9 [5.5], 127.5, 125.5, 125.5 (*i, o, m, p*, Ph) ppm. [h] Other ^{13}C data: δ [$J(^{29}Si,^{13}C)$] = 137.5 [5.3], 126.7, 125.9, 149.5, 34.4, 31.4 (*i, o, m, p*, C_{tert}, Me_3, 4-*t*Bu-C_6H_4) ppm. [i] Other ^{13}C data: δ [$J(^{29}Si,^{13}C)$] = 32.2, 31.1, 23.0, 14.1 (Bu), 137.6 [5.2], 126.6, 125.7, 149.3, 32.9, 31.5 (*i, o, m, p*, C_{tert}, Me_3, 4-*t*Bu-C_6H_4) ppm.

Because spirosilanes **5** and **6** possess reactive B–C bonds, they invite further transformations. The protodeborylation is a typical reaction that is frequently performed after generating the desired organic compound. In these cases, in general, little attention is paid to the fate of the boryl group. We have shown that protodeborylation of diethyl(organo)-boranes or 9-organo-9-borabicyclo[3.3.1]nonanes with an excess amount of acetic acid can lead directly to bicyclic boron–oxygen compounds.[16] Therefore, it was of interest to prove this point in the case of spirosilanes **5** and **6** (Scheme 3).



Scheme 3. Protodeborylation of spirosilanes **5** and **6** by using an excess amount of acetic acid.

The protodeborylation of **5** and **6** affords 1,6-disubstituted 5-silaspiro[4,4]nona-1,6-dienes **7** and **8** in essentially quantitative yield along with the bicyclic boron–oxygen compound **9**. The latter compound was characterized previously both in solution (NMR spectroscopy) and in the solid state (X-ray structural analysis).[16] The NMR spectra and melting point of **9** are identical to those already reported. Spirosilanes **7** and **8** are obtained in pure state, readily characterized by their NMR spectroscopic data (Table 3; Figure 4) and in one case (**7b**) by X-ray structural analysis (vide infra). The information from the ^{29}Si NMR spectrum on the coupling constants $J(^{29}Si,^{13}C)$ (Figure 4) is frequently more readily obtained and complementary to the results from ^{13}C NMR measurements (Table 3).

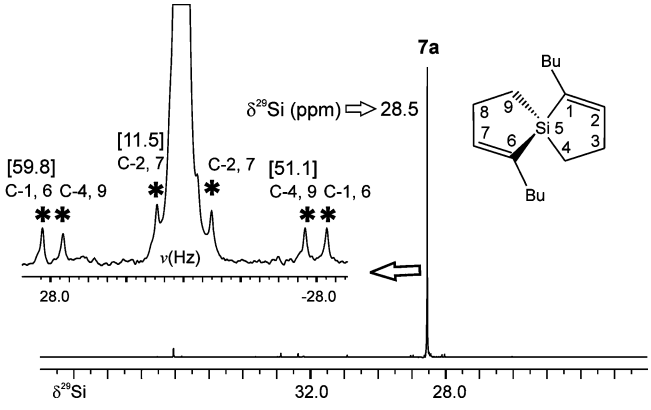


Figure 4. 59.6 MHz $^{29}Si\{^1H\}$ NMR spectrum (refocused INEPT[18]) of 1,6-dibutyl-5-silaspiro[4.4]nona-1,6-diene **7a**. Satellites marked by asterisks correspond to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$.

X-ray Structure Analysis of Spirosilanes 5b and 7b

The molecular structures of 5-silaspiro[4.4]nona-1,6-diene derivatives **5b** and **7b** are shown in Figure 5 and 6, respectively. Selected structural parameters are given in Table 4. All the bond lengths and angles are comparable to those reported for simple 1-silacyclopent-2-enes.[9] The five-membered rings are almost planar [mean deviations for **5b**: 9.3 (Si1, C1–4) and 1.8 pm (Si1, C11–14); for **7b**: 5.1 pm]. The planes of the five-membered rings are oriented almost

perpendicular to each other (**5b**: 84.9°; **7b**: 94.1°). The CBC planes of 9-BBN in **5b** are twisted by 52.2° (C21–B1–C25) and 55.4° (C29–B2–C33) against the respective ring planes. The surroundings of the boron atoms in **5b** are trigonal planar within the experimental error. Expectedly, the endocyclic bond angles are acute (e.g., in **5b**: ∠C1–Si1–C4 93.00° and ∠C11–Si1–C14 93.4°) in contrast to the exocyclic bond angles (e.g., in **5b**: ∠C1–Si1–C14 121.3°, ∠C1–Si1–C11 111.5°, ∠C4–Si1–C14 119.3°, and ∠C4–Si1–C11 120.5°). The structure of **7b** compares well to that of its immediate precursor **5b**. The changes in most of the bond lengths are either minor or negligible within experimental error. The C2–C3 and C3–C4 bond lengths in **7b** are slightly shorter than the respective bonds in **5b** by 2.4 and 1.8 pm, respectively. Elongation of these bonds in **5b** can be explained by invoking the concept of hyperconjugation, which involves the p_z orbital of the boron atom and C–C σ bonds.[17] Comparison of bond angles of **7b** with those of **5b** shows an increase of 3.8° in ∠C4–C3–C2 and a decrease in ∠C3–C2–C1 by 1.8°. Intermolecular interactions were negligible in both **5b** and **7b**.

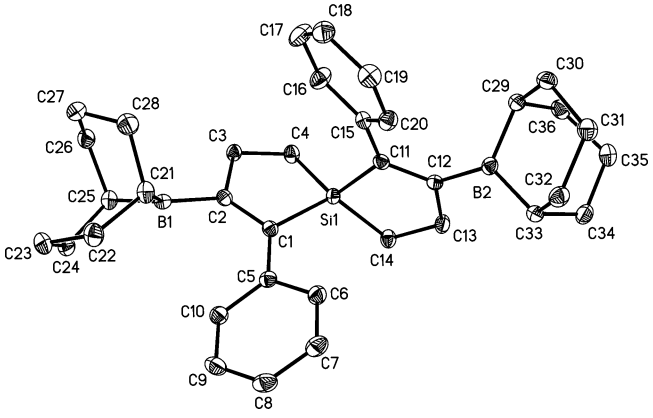


Figure 5. Molecular structure of 2,7-bis[9-(9-borabicyclo[3.3.1]-nonyl)]-1,6-diphenyl-5-silaspiro[4.4]nona-1,6-diene (**5b**; ORTEP plot, 40% probability level, hydrogen atoms are omitted for clarity). Selected structural parameters are listed in Table 5.

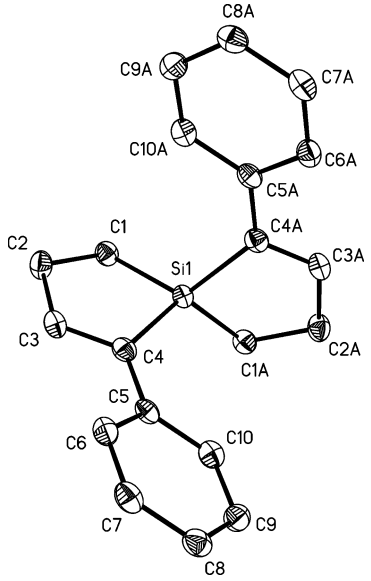


Figure 6. Molecular structure of 1,6-diphenyl-5-silaspiro[4.4]nona-1,6-diene (**7b**; ORTEP plot, 50% probability; hydrogen atoms are omitted for clarity). Selected structural parameters are listed in Table 5.

Table 4. Selected bond lengths [pm] and angles [°] for spirosilanes **5b** and **7b**.

5b			
C1–C2	135.8(2)	C11–C12	135.2(2)
C2–C3	152.6(2)	C12–C13	152.3(2)
C3–C4	154.2(2)	C13–C14	153.9(2)
C1–C5	147.2(2)	C11–C15	147.4(2)
C1–Si1	186.7(1)	C11–Si1	187.2(1)
C4–Si1	187.7(1)	C14–Si1	187.3(1)
C2–B1	155.8(2)	C12–B2	156.0(2)
Si1–C1–C2	110.0(1)	Si1–C11–C12	111.1(1)
C1–C2–C3	116.6(1)	C11–C12–C13	116.6(1)
C2–C3–C4	111.7(1)	C12–C13–C14	112.4(1)
C3–C4–Si1	104.90(9)	C13–C14–Si1	106.3(2)
C1–Si1–C4	93.00(6)	C11–Si1–C14	93.4(1)
C1–Si1–C11	111.5(1)	C4–Si1–C14	119.3(1)
C1–Si1–C14	121.3(1)	C4–Si1–C11	120.5(1)
7b			
C3–C4	134.0(2)	C4–C5	147.6(2)
C2–C3	150.2(2)	C4–Si1	187.9(2)
C1–C2	154.4(2)	C1–Si1	187.3(2)
Si1–C4–C3	108.2(1)	C4–Si1–C4A	113.7(1)
C4–C3–C2	120.4(1)	C4–Si1–C1A	120.4(1)
C3–C2–C1	109.8(1)	C1–Si1–C1A	117.2(1)
C2–C1–Si1	105.6(1)	C1–Si1–C4A	120.4(1)
C1–Si1–C4	93.34(1)		

Conclusions

The consecutive combination of 1,2-hydroboration and 1,1-organoboration has opened an efficient route to 5-silaspiro[4,4]nona-1,6-dienes and is promising for further applications. The new spirosilanes were characterized in solution by multinuclear NMR and for two examples in the solid state by X-ray structural analysis.

Experimental Section

General: All preparative work as well as handling of the samples was carried out by observing precautions to exclude trace amounts of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. BuLi in hexane (1.6 M), dichloro(divinyl)silane, ethynylbenzene, 1-hexyne, 1-ethynyl-4-*tert*-butylbenzene, glacial acetic acid, and 9-borabicyclo[3.3.1]nonane were used as commercial products without further purification. Mass spectra: FOCUS DSQ (Thermo) mass spectrometer; the *m*/*z* data refer to the isotopes ^{1}H, ^{11}B, ^{12}C, ^{28}Si. NMR measurements in C_6D_6 (concentration ca. 5–10%) with samples in 5 mm tubes at 23 ± 1 °C: Varian Inova 300 and 400 MHz spectrometers for ^{1}H, ^{11}B, ^{13}C, and ^{29}Si NMR; chemical shifts are given relative to Me_4Si [$\delta^{1}H$ (C_6D_5H) = 7.15 ppm; $\delta^{13}C$ (C_6D_6) = 128.0 ppm; $\delta^{29}Si$ = 0 ppm for $\Xi(^{29}Si)$ = 19.867184 MHz]; external $BF_3{\cdot}OEt_2$ [$\delta^{11}B$ = 0 ppm for $\Xi(^{11}B)$ = 32.083971 MHz]. Chemical shifts are given to ±0.1 for ^{13}C and ^{29}Si, and ±0.4 ppm for ^{11}B; coupling constants are given ±0.4 Hz for $J(^{29}Si,^{13}C)$. ^{29}Si NMR spectra were measured by using

the refocused INEPT pulse sequence,[18] based on $^{3}J(^{29}Si,^{1}H_{HC=}) = 20–25$ Hz or $^{2,3}J(^{29}Si,^{1}H) = 8–12$ Hz after optimizing the delay times in the pulse sequence. The melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus.

General Procedure for the Synthesis of Dialkyn-1-yl(divinyl)silanes 1a–c and 2a: To a freshly prepared suspension of hexyn-1-yllithium (25 mmol) in hexane (50 mL) cooled to –78 °C was added dichloro(divinyl)silane (12.5 mmol, 2 mL) in one portion. The reaction mixture was warmed to room temperature and stirring was continued for 4–5 h. Insoluble materials were filtered off, and all readily volatile materials were removed in vacuo. The colorless oily residue was identified as the mixture of **1a** and $Si(CH=CH_2)_2(C\equiv C–Bu)Cl$ as the side product. These compounds could be separated by fractional distillation to give both pure **1a** and the chlorosilane. The latter, $Si(CH=CH_2)_2(C\equiv C–Bu)Cl$ (3.8 g, 19.2 mmol), was added to a freshly prepared suspension of 4-*tert*-butylphenylethynyllithium (19.2· mmol) in hexane (60 mL), following identical reaction conditions, and silane **2a** was obtained as an oil (>99% from ^{1}H NMR; see also Figure 1). The same preparative method was adopted for the preparation of dialkyn-1-yl(divinyl)silanes **1b** and **1c**.

1a: ^{1}H NMR (400 MHz): δ = 0.7, 1.3, 2.0 (t, m, t, 18 H, Bu), 6.0 (m, 6 H, Si-vinyl) ppm.

1b: ^{1}H NMR (400 MHz): δ = 6.0 [t, $^{3}J(^{1}H,^{1}H)$ = 8.8 Hz, 2 H, =CH], 6.2 (d, 4 H, $=CH_2$), 6.9, 7.3 (m, m, 10 H, Ph) ppm.

1c: ^{1}H NMR (400 MHz): δ = 1.1, 7.1, 7.3 (s, m, m, 26 H, 4-*t*Bu-C_6H_4), 6.1 (dd, 2 H, =CH-Si), 6.3 (m, 4 H, $H_2C=$) ppm.

2a: ^{1}H NMR (400 MHz): δ = 0.6, 1.2, 1.9 (t, m, t, 9 H, Bu), 6.0 (dd, 2 H, =CH-Si), 6.2 (m, 4 H, $H_2C=$), 1.0, 7.0, 7.3 (s, m, m, 13 H, 4-*t*Bu-C_6H_4) ppm.

Syntheses of 1-Silacyclopent-2-ene Derivatives 3a and 4a and 2,7-Bis[9-(9-borabicyclo[3.3.1]nonyl)]-1,6-(*R*,R[1])-5-silaspiro[4.4]nona-1,6-dienes 5a–c and 6a: To a Schlenk tube charged with a solution of **1a** (1.6 g, 6.6 mmol) was added 9-BBN (0.82 g, 6.6 mmol, 1 equiv.) in THF (10 mL). The reaction mixture was stirred at room temperature for 2–4 h, and all volatile materials were then removed under reduced pressure. A small part of the oily residue was dissolved in C_6D_6 and analyzed by NMR spectroscopy. The reaction afforded a mixture of **1a** (starting silane), **3a** and **5a**. A further equivalent of 9-BBN (0.82 g, 6.6 mmol) was added by using the same conditions to give pure **5a**. The procedure for the preparation of spirosilanes **5b**, **5c**, and **6a** was exactly the same. The solvent (THF) from spirosilane **5b** was completely evaporated, and the remaining solid was dissolved in pentane (3 mL). The solution was kept at room temperature. Single crystals suitable for X-ray structure analysis appeared within 1–2 h. All soluble impurities were filtered off, and a single crystal of appropriate dimensions was selected and studied by X-ray analysis at low temperature (133 K).

3a: ^{1}H NMR (400 MHz): δ = 0.7, 0.8, 1.5, 2.0, 2.1 (t, t, m, t, t, 18 H, Bu), 6.0–6.2 (m, 3 H, $CH=CH_2$) ppm. Other signals were not assigned due to overlap with signals belonging to other compounds in the mixture.

5a: ^{1}H NMR (400 MHz): δ = 1.3–1.9 (m, 28 H, 9-BBN), 0.9, 1.3, 2.4 (t, m, t, 18 H, Bu), 0.9, 1.0 (m, m, 4 H, $C^{4,9}H_2$), 2.7 (m, 4 H, $C^{3,8}H_2$) ppm.

5b: Yield (after recrystallization from pentane): 93%. M.p. 104–106 °C. ^{1}H NMR (400 MHz): δ = 1.4–1.9 (m, 28 H, 9-BBN), 1.1 [ddd, $^{2}J(^{1}H,^{1}H)$ = 15.5 Hz, $^{3}J(^{1}H,^{1}H)$ = 5.3, 9.3 Hz, 1 H, $C^{4,9}H_2$], 1.2 [ddd, $^{2}J(^{1}H,^{1}H)$ = 15.5 Hz, $^{3}J(^{1}H,^{1}H)$ = 3.7, 9.1 Hz, 1 H, $C^{4,9}H_2$], 2.8 [ddd, $^{2}J(^{1}H,^{1}H)$ = 18.2 Hz, $^{3}J(^{1}H,^{1}H)$ = 5.3, 9.3 Hz, 1 H, $C^{3,8}H_2$], 2.9 [ddd, $^{2}J(^{1}H,^{1}H)$ = 18.2 Hz, $^{3}J(^{1}H,^{1}H)$ = 3.7, 9.1 Hz, 1 H, $C^{3,8}H_2$], 7.2, 7.1, 7.0 (m, m, m, 10 H, Ph) ppm.

5c: ^{1}H NMR (400 MHz): δ = 1.4–1.9 (m, 28 H, 9-BBN), 1.1 (m, 4 H, $C^{4,9}H_2$), 2.8 (m, 4 H, $C^{3,8}H_2$), 1.2, 7.1, 7.2 (s, m, m, 26 H, 4-*t*Bu-C_6H_4) ppm.

6a: ^{1}H NMR (400 MHz): δ = 1.3–1.9 (m, 28 H, 9-BBN), 0.8, 1.5, 2.7 (t, m, t, 9 H, Bu), 1.3 (m, 4 H, $C^{4,9}H_2$), 2.9 (m, 4 H, $C^{3,8}H_2$), 1.2, 7.1, 7.2 (s, m, m, 13 H, 4-*t*Bu-C_6H_4) ppm.

Protodeborylation of Spirosilanes 5 and 6: A solution of **5a** (1.2 g, 2.5 mmol) in pentane (10 mL) was mixed with an excess amount of acetic acid (2.0 mL) at 23 °C. The reaction mixture was stirred for 40–60 min. Then, all the readily volatile materials were removed under reduced pressure. The oily residue left was dissolved in pentane, and the solution was kept at –35 °C. Boron–oxygen compound **9** precipitated and was separated. Pure spirosilane **7a** was

Table 5. Data pertinent to the crystal structure determinations of **5b** and **7b**.

	5b	**7b**
Formula	$C_{36}H_{46}B_2Si$	$C_{20}H_{20}Si$
Crystal	colorless prism	colorless prism
Dimensions [mm]	$0.47\times0.36\times0.35$	$1.08\times0.77\times0.61$
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
Lattice parameters		
a [pm]	996.9(9)	2094.6(2)
b [pm]	1248.3(9)	572.3(10)
c [pm]	1369.0(10)	1552.5(2)
α [°]	113.5(5)	90.00
β [°]	104.9(6)	126.478(10)
γ [°]	91.6(6)	90.00
Z	2	4
Absorption coefficient μ [mm^{-1}]	0.103	0.148
Diffractometer	STOE IPDS II, Mo-K_α, λ = 71.069 pm, graphite monochromator	
Measuring range [°]	1.7–25.7	2.4–24.6
Reflections collected	20118	8274
Independent reflections [$I>2\sigma(I)$]	4759	1180
Absorption correction	none	none
Refined parameters	352	136
wR_2/R_1 [$I>2\sigma(I)$]	0.110/0.040	0.095/0.035
Max./min. Residual electron density [epm$^{-3}\times10^{-6}$]	0.380/–0.302	0.216/–0.387

obtained as a colorless oil. The protodeborylation of silanes **7b**, **7c**, and **8a** was carried out under the same reaction conditions except that **9** was separated by different way. The mixture of respective spirosilanes (**7b**, **7c**, and **8a**) and **9** was heated at 120 °C (oil bath) under reduced pressure (10^{-2} Torr) for ca. 2 h. This led to the accumulation of boron–oxygen compound, **9** along the walls of the Schlenk tube. The colorless oil containing mainly the corresponding spirosilane was dissolved in pentane (2–3 mL) and introduced into another Schlenk tube. Crystallization proceeded in the case of **7b** (X-ray analysis) and **7c**, and crystals suitable for single X-ray crystal analysis were grown after 5 and 20 d, respectively.

7a: ^{1}H NMR (400 MHz): δ = 1.0 (m, 4 H, $C^{4,9}H_2$), 2.4 (m, 4 H, $C^{3,8}H_2$), 0.9, 1.6, 2.2 (t, m, t, 18 H, Bu), 6.4 [m, 2 H, ($C^{2,7}$H)] ppm.

7b: Yield (after recrystallization from hexane): 63%. M.p. 51–52 °C. ^{1}H NMR (400 MHz): δ = 0.8 [ddd, $^2J(^1H,^1H)$ = 15.7 Hz, $^3J(^1H,^1H)$ = 4.4, 9.5 Hz, 2 H, $C^{4,9}H_2$], 1.1 [ddd, $^2J(^1H,^1H)$ = 15.7 Hz, $^3J(^1H,^1H)$ = 4.1, 9.4 Hz, 2 H, $C^{4,9}H_2$], 2.4 [m, $^2J(^1H,^1H)$ = 19.0 Hz, 2 H, $C^{3,8}H_2$], 2.5 [m, $^2J(^1H,^1H)$ = 19.0 Hz, 2 H, $C^{3,8}H_2$], 6.9, 7.4 (m, m, 10 H, Ph), 7.1 (m, 2 H, $C^{2,7}$H) ppm. GC–MS: t_R = 22.01 min; *m*/*z* (%) = 288.06 (41) $[M]^+$, 134.3 (21) $[M - C_{12}H_{10}]^+$, 132.2 (72) $[M - C_{12}H_{12}]^+$, 158.0 (90) $[M - C_{10}H_{10}]^+$, 105.0 (100) $[M - C_{12}H_{14}Si]^+$.

7c: Yield (recovered after recrystallization from pentane): 20%. M.p. 64–65 °C. ^{1}H NMR (400 MHz): δ = 0.9, 1.2 (m, m, 4 H, $C^{4,9}H_2$), 2.5–2.6 (m, 4 H, $C^{3,8}H_2$), 7.1 [t, $^3J(^1H,^1H)$ = 3.1 Hz, $^3J(^{29}Si,^1H)$ = 13.9 Hz, 2 H, $C^{2,7}$H], 1.2, 7.2, 7.5 (s, m, m, 26 H, 4-*t*Bu-C_6H_4) ppm.

8a: ^{1}H NMR (400 MHz): δ = 0.9 (m, 4 H, $C^{4,9}H_2$), 2.5 (m, 4 H, $C^{3,8}H_2$), 0.8, 1.4, 2.3 (t, m, t, 9 H, Bu), 7.0 (t, 1 H, C^2H), 6.5 (m, 1 H, C^7H), 1.2, 7.2, 7.4 (s, m, m, 13 H, 4-*t*Bu-C_6H_4). GC–MS: t_R = 26.2 min; *m*/*z* (%) = 400.11 (20) $[M]^+$, 384.20 (13) $[M - CH_3]^+$, 343.20 (42) $[M - C_4H_9]^+$, 287.01 (8) $[M - C_8H_{18}]^+$, 56.99 (100) $[Si(CH_2)_2]^+$ or $[C_4H_8]^+$.

Crystal Structure Determination of Spirosilanes 5b and 6b: Details pertinent to the crystal structure determinations are listed in Table 5.[19] Crystals of appropriate size were selected (in perfluorinated oil[21] at room temperature), and the data collections were carried out at 133 K by using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit. Structure solutions and refinements were accomplished by using SIR97,[22] SHELXL-97,[23] and WinGX.[24]

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