Fused Silacarbacycles Containing a Silole Unit: 1,2-Hydroboration and 1,1-Organoboration of Alkynyl(vinyl)silanes

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solid state.

SiMea

SiMe

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The reaction of various alkynyl(vinyl)silanes containing two alkynyl groups with 9-borabicyclo[3.3.1]nonane (9-BBN) proceeds by regioselective 1,2-hydroboration of the vinyl group in the first step, followed by two intramolecular 1,1-organoboration reactions to afford 1,6-disilapentalene derivatives, fused silacarbacycles with a silole unit. Similarly, the analo-

Introduction

Among silacarbacycles, the siloles^[1] deserve particular attention owing to the rich chemistry of their cyclic diene system and, more recently, to their attractive photophysical properties.^[2-5] Although numerous synthetic procedures have been developed for the synthesis of siloles,^[1] many of these methods are cumbersome multistep routes. Moreover, fused ring systems containing the silole unit are scarce.^[1,6] It turned out that 1,1-organoboration reactions of dialkvnylsilanes provide a versatile route to siloles.^[7,8] allowing in principle to introduce numerous different substituents at all ring positions.^[9,10] This includes even functional groups such as hydrogen and/or chlorine at silicon.^[11] Previously, we have shown that 1,1-organoboration of certain trivnes affords mainly 1,6-dihydro-1,6-disilapentalene derivatives^[12] (Scheme 1), along with side products, which could not be separated. Similar results were obtained with comparable tetraynes.^[13] However, rather harsh conditions are required in order to start the reactions in the case of alkynylsilanes (100 °C, several hours), and ring closure appeared to be slow and accompanied by side reactions. Molecular models suggested that steric repulsion between the ethyl and diethylboryl groups prevents a clean intramolecular reaction.

Therefore, we have started a new approach, in which intermolecular 1,2-hydroboration is combined with intramolecular 1,1-organoboration. This helps to introduce the boryl group into the molecule under relatively mild conditions, and it was hoped that the steric hindrance of further intramolecular reactions would be less severe. As a convenient and regioselective hydroborating reagent we have se-

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gous reaction of an alkynyl(allyl)silane gives a 1,7-disilaind-

ene derivative. The products were characterized by multi-

nuclear magnetic resonance (^{1}H , ^{11}B , ^{13}C and ^{29}Si NMR) in solution and in two cases by X-ray structural analysis in the

Scheme 1. Synthesis of a 1,6-dihydro-1,5-disilapentalene derivative by 1,1-organoboration of a 1,4,7,10-tetrasila-2,5,8-triyne.

lected 9-BBN [bis(9-borabicyclo[3.3.1]nonane)],^[14] and various alkynyl(vinyl)silanes 1-5 were used, all of which contained two C=C bonds (see Schemes 2 and 3).



Scheme 2. Reaction of 9-BBN with the alkynyl(vinyl)silanes 1. In the structures of the intermediates (not detected), the interaction of the electrophilic boron atom with the alkynyl carbon atom, indicated by a dashed line, is followed by cleavage of the Si–C(alkyne) bond, leading to a zwitterionic intermediate, which rearranges into the 1,1-organoboration product.^[7]

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Scheme 3. Reactions of the alkynylsilanes 2-4 with 9-BBN.

Results and Discussion

The synthesis and spectroscopic properties of the alkynyl(vinyl)silanes **1–5** used here have been reported elsewhere.^[15] In the course of the 1,2-hydroboration with 9-BBN, the vinyl group is preferred over the alkynyl group [Scheme 2 (a)]. In the next step, the neighbored Si–C(alkyne) bond is cleaved and 1,1-organoboration takes place [Scheme 2 (b); the intermediates shown in brackets indicate the mechanism of 1,1-orhganoboration^[7]]. These first two steps have already been used to prepare numerous silacyclopent-2-enes,^[16,17] and the reactions have been analyzed by theoretical methods.^[18] In the final step, this process is repeated with the remaining Si–C=C–R unit to give the products **6** containing the silole unit [Scheme 2 (c)]. The intramolecular activation of the Si–C(alkyne) bond [Scheme 2 (b), (c)] allows to conduct the reactions fast under milder conditions (100 ± 10 °C; 2–5 min) than shown in

Scheme 1. The methyl groups at the silicon atom bearing the vinyl group can be replaced by one or two phenyl groups, as shown for the alkynyl(vinyl)silanes 2–4, which react readily with 9-BBN to give the fused silacarbacycle 7–9 (Scheme 3).

The compounds **6–9** are obtained in essentially quantitative yield as faintly yellow air-sensitive oils or solids, and the proposed structures are fully supported by ¹H, ¹¹B, ¹³C and ²⁹Si NMR spectroscopic data sets (Exp. Sect. and Table 1). Furthermore, the molecular structure of **6c** could be determined by X-ray diffraction (vide infra). The progress of the reactions is most conveniently monitored by ²⁹Si NMR spectroscopy, which, together with ¹³C NMR spectroscopy, also serves to assign the structure of the final products. In the ²⁹Si NMR spectra, the signals typical of alkynylsilanes at low frequency^[15,19,20] are replaced by ²⁹Si NMR signals at much higher frequencies, typical of the cyclic structures.^[20] Particularly helpful for the structural as-

Table 1. Selected ¹³C and ²⁹Si NMR spectroscopic data^[a] of disilapentalenes 6, 7, 8 and 9.

	δ^{29} Si(1)	δ^{29} Si(6)	$\delta^{13}C(2)$	$\delta^{13}C(3)$	$\delta^{13}C(3a)$	$\delta^{13}C(4)$	$\delta^{13}C(5)$	δ^{13} C(6a)	
6a ^[b]	18.4	8.0	13.3	35.2	181.8	169.9	151.5	137.6	
	{13.6}	{13.6}	[50.1]	[8.3]	[6.4], [6.1]	br.	[58.4]	$2 \times [58.8]$	
6b ^[c]	18.2	8.6	13.6	36.9	182.2	163.8	164.2	136.4	
	{13.1}	{13.1}	[50.1]	[8.1]	[6.1]	br.	[57.9]	$2 \times [59.0]$	
6c ^[d]	17.0	-3.4	13.8	38.0	184.5	182.3	148.0	137.6	
	{13.4}	{13.4}	[49.2]	[8.9]	[6.4]	br.	[63.9]	$2 \times [60.4]$	
6d ^[e]	16.8	16.7	14.2	36.4	181.9	181.3	153.5	141.9	
	{10.8}	{10.8}	[49.8]	[8.7]	[11.7], [9.3], [7.0]	br.	[62.1], [44.7]	$2 \times [58.1]$	
6e ^[f]	16.8	19.0	14.2	36.9	181.0	182.7	151.9	144.0	
	{13.6}	{13.6}	[50.0]	[8.7]	[13.7], [8.9], [7.2]	br.	[69.1], [44.3]	$2 \times [57.0]$	
-[-]		{11.9}			100 1			100 6	
7 ^[g]	11.7	19.5	13.0	36.9	183.6	182.0	152.5	139.6	
	{13.1}	{13.1}	[51.9]	[8.3]	[13.8], [8.8], [7.5]	br.	[68.8], [44.7]	[60.9], [57.5]	
8 ^[h]	12.4	17.4	14.0	36.8	183.7	179.0	158.4	139.0	
	{13.5}	{13.5} {9.5}	[50.8]	[8.6]	[11.1], [9.7], [7.2]	br.	[61.5], [43.6]	[60.2], [57.2]	
9 ^[i]	12.1	18.9	13.8	37.1	182.2	184.5	147.2	141.9	
	{13.2}	$\{13.2\}$ $\{9.9\}$	[50.9]	[8.3]	[12.1], [9.4], [7.4]	br.	[67.8], [46.5]	[59.6], [56.0]	

[a] In C₆D₆ or in CD₂Cl₂ (**6a**, **7**, **8**, **9**) at 296 K. ${}^{n}J({}^{29}Si, {}^{13}C)$ coupling constants [±0.5 Hz] are given in brackets; ${}^{2}J({}^{29}Si, {}^{29}Si)$ coupling constants {±0.3 Hz} are given in braces. [b] Other ${}^{13}C$ NMR spectroscopic data: $\delta = -4.1$ [50.2], -0.2 [50.2] (SiMe₂); 23.7, 31.9 (br.), 34.4 (BBN) ppm. [c] Other ${}^{13}C$ NMR spectroscopic data: $\delta = -3.7$ [49.7], 0.4 [50.2] (SiMe₂); 24.0, 33.6 (br.), 34.4 (BBN); 126.7, 127.9, 128.8, 144.0 [5.9] [1.8] (Ph) ppm. [d] Other ${}^{13}C$ NMR spectroscopic data: $\delta = -3.7$ [49.7], 0.5 [49.6] (SiMe₂); 23.2 (br.), 24.0, 25.3, 31.7, 35.5 (BBN); 49.1 (NMe₂); 69.1 (CH₂N) ppm. [e] Other ${}^{13}C$ NMR spectroscopic data: $\delta = -2.4$ [48.5], -0.9 [51.3], 0.2 [50.2] (SiMe₂); 24.2, 33.0 (br.), 34.1 (BBN) ppm. Other ${}^{29}Si$ NMR spectroscopic data: $\delta = -25.6$ (SiMe₂H) {10.2} ppm. [f] Other ${}^{13}C$ NMR spectroscopic data: $\delta = -2.4$ [48.5], -0.9 [51.3], 0.2 [50.2] (SiMe₂); 24.2, 33.0 (br.), 34.1 (BBN) ppm. Other ${}^{29}Si$ NMR spectroscopic data: $\delta = -25.6$ (SiMe₂H) {10.2} ppm. [f] Other ${}^{13}C$ NMR spectroscopic data: $\delta = -2.4$ [48.5], -0.9 [51.3], 0.2 [50.2] (SiMe₂); 24.2, 33.0 (br.), 34.1 (BBN) ppm. Other ${}^{29}Si$ NMR spectroscopic data: $\delta = -2.3$ [49.6], -0.1 [50.7] (SiMe₂); 7.7 [56.0] (SiMe₂Br); 23.7, 33.0 (br.), 34.8 (BBN) ppm. Other ${}^{29}Si$ NMR spectroscopic data: $\delta = 10.7$ (SiMe₂Br) {11.9} ppm. [g] Other ${}^{13}C$ NMR spectroscopic data: $\delta = -2.2$ [50.1] [Si(2)Me₂]; 7.4 [56.0] (SiMe₂Br); 23.4, 32.9 (br.), 34.7 (BBN); 128.3 [5.5], 129.8, 135.4, 137.1 [68.2] (Ph) ppm. Other ${}^{29}Si$ NMR spectroscopic data: $\delta = 9.8$ (SiMe₂Br) {13.3} ppm. [h] Other ${}^{13}C$ NMR spectroscopic data: $\delta = -2.7$ [48.8] [Si(6)Me, *trans* to Ph]; -2.4 [49.1] [Si(6)Me, *cis* to Ph]; -2.2 [52.1] [Si(1)Me]; 2.9 [51.0] (SiMe₃); 23.6, 32.8 (br.), 34.5, 34.6 (BBN); 128.2 [5.1], 129.4, 134.4, 139.9 [65.5] (Ph) ppm. Other ${}^{29}Si$ NMR spectroscopic data: $\delta = -3.3$ [49.6] [Si(6)Me

signment is the observation of ²⁹Si satellites in the ²⁹Si NMR spectra, corresponding to the coupling constants ² $J(^{29}\text{Si},^{29}\text{Si})$ (see Figure 1), as well as in the ¹³C NMR spectra, corresponding to ${}^{n}J(^{29}\text{Si},^{13}\text{C})$ (n = 1,2; see Figures 1 and 2). In ¹³C NMR spectra, the broadened signals, owing to partially relaxed ¹³C-¹¹B spin-spin coupling,^[21] lend further support to the assignment. The δ^{11} B data are in the typical region of triorganoboranes without significant

 $CB(pp)\pi$ interactions.^[22] In the case of **6c**, the intramolecular N–B coordination is clearly evident by $\delta^{11}B = 8.9$ ppm, in the range characteristic for tetracoordinate boron atoms.^[22]

The synthetic method introduced here can be extended to different ring sizes (Scheme 4). When an allyl group is present at one silicon atom as in 5, the analogous reaction sequence as for 1-4 leads to the fused silacarbacycle 10



Figure 1. Bottom: 99.4 MHz ²⁹Si{¹H} NMR spectrum (refocused INEPT; in C₆D₆ at 296 K) of the reaction solution containing the bicyclic compound **6e**. Coupling constants ²J(²⁹Si,²⁹Si) are given in braces. The phase distortion of the ²⁹Si satellite signals is typical of homonuclear coupling, since this magnetization is not refocused in the course of the pulse sequence. Top: 128.5 MHz ¹³C{¹H} NMR spectrum of the region for the olefinic carbon atoms showing expansions for the ²⁹Si satellites [coupling constants "J(²⁹Si,¹³C) are given in brackets]. In the case of ¹³C-6a, the ²⁹Si satellites overlap. A signal from an impurity is marked by an asterisk.



Figure 2. 125.8 MHz ${}^{13}C{}^{1}H$ NMR spectrum (296 K) of the bicyclic compound **6b**. Coupling constants ${}^{n}J({}^{29}Si, {}^{13}C)$ are given in brackets (the relative intensities of the ${}^{29}Si$ satellites in the cases of C-3a, C-6a correspond to coupling with two ${}^{29}Si$ nuclei).

(Scheme 4). Compound 10 possesses similar properties as **6–9**, is clearly identified by its NMR spectroscopic data set (Exp. Sect.), and its molecular structure was determined by X-ray diffraction (vide infra).



Scheme 4.

First attempts to remove the boryl group by protodeborylation showed that all compounds 6-10 react only slowly with methanol, in particular with the Me₃Si group in neighborhood to the boryl group. However, the silole ring remains unchanged (Scheme 5), as indicated by the NMR spectroscopic data for 11 (Exp. Sect.).



Scheme 5. Slow methanolysis of 10.



Figure 3. Molecular structure (ORTEP plot with 40% probability; hydrogen atoms have been omitted for clarity) of the disilapentalene derivative 6c. Selected bond lengths [pm] and angles [°]: Sil-C4 185.3(3), Si1-C1 186.2(3), Si2-C4 185.6(3), Si2-C6 187.2(3), N-C11 150.3(4), N-B 176.8(4), B-C14 161.8(4), B-C18 163.0(4), B-C2 167.2(4), C1-C2 135.8(4), C1-C11 149.0(4), C2-C3 152.8(4), C3-C4 136.8(4), C3-C5 152.5(4), C5-C6 154.0(4); C4-Si1-C1 91.27(13), C7-Si1-C8 108.60(15), C4-Si2-C6 93.52(14), C9-Si2-C10 108.83(17), C13-N-C12 107.7(3), C13-N-B 108.8(2), C12-N-B 122.1(2), C11-N-B 103.0(2), C14-B-C18 104.8(2), C14-B-C2 122.7(2), C18–B–C2 113.3(2), C14–B–N 111.3(2), C18–B–N 111.0(2), C2–B–N 93.4(2), C2–C1–C11 113.5(3), C2–C1–Si1 111.9(2), C11-C1-Si1 133.6(2), C1-C2-C3 110.7(2), C1-C2-B 111.3(2), C3-C2-B 138.0(2), C4-C3-C5 116.8(2), C4-C3-C2 118.1(3), C5-C3-C2 125.1(2), C3-C4-Si1 107.6(2), C3-C4-Si2 110.3(2), Si1-C4-Si2 142.05(17), C3-C5-C6 110.8(3), C5-C6-Si2 105.7(2), C1–C11–N 106.0(2); B–C2–C1–C11 144.3(2).

X-ray Structural Analyses of the Fused Silacarbacycles 6c and 10

The molecular structures of the silacarbacycles 6c (Figure 3) and 10 (Figure 4) show the almost planar silole ring (major deviation from planarity 2.6 pm for 6c and 1.8 pm for 10) fused to a saturated nonplanar five- and six-membered ring, respectively. In the case of 6c, another nonplanar ring is present due to N-B coordination, in agreement with NMR spectroscopic data in solution. Intermolecular interactions appear to be negligible for both, 6c and 10. The structural parameters are in close agreement with those found for the few examples obtained by 1,1-organoboration reactions,^[8,11] although the C-C bond lengths appear to be slightly elongated, when compared with data for other siloles.^[1,23] This can be caused by the various organometallic substituents at the C=C bonds. Most notably are the typically acute endocyclic bond angles in the silole units of 6c [91.3(1)°] and 10 [94.0(5)°]. In the half-saturated part of the silacarbacycle of 6c, the endocyclic C4-Si2-C6 angle is slightly wider [93.5(1)°],^[24] and in 10, the endocyclic angles at Si1 [94.0(5)°] and Si2 [104.2(6)°] are expectedly quite different, since Si2 is part of a six-membered ring. The surroundings of the boron atom in **6c** correspond to a distorted tetrahedron, whereas the boron atom in 10 pos-



Figure 4. Molecular structure (ORTEP plot with 40% probability; hydrogen atoms have been omitted for clarity) of the disilaindene derivative **10**. Selected bond lengths [pm] and angles [°]: Si1–C4 186.5(12), Si1–C1 188.4(12), Si2–C4 186.2(12), Si2–C7 187.5(11), Si3–C1 185.2(13), B–C26 155.1(17), B–C2 155.2(16), B–C22 161.8(17), C1–C2 138.0(15), C2–C3 152.5(15), C3–C4 137.7(13), C3–C5 151.1(13), C5–C6 151.4(14), C6–C7 153.2(16); C8–Si1–C9 108.6(6), C4–Si1–C1 94.0(5), C10–Si2–C16 108.1(5), C4–Si2–C7 104.2(5), C26–B–C2 127.1(11), C26–B–C22 107.8(10), C2–B–C22 125.0(11), C2–C1–Si3 131.4(10), C2–C1–Si1 106.4(9), Si3–C1–Si1 122.2(7), C1–C2–C3 116.1(10), C1–C2–B 126.5(11), C3–C2–B 117.5(10), C4–C3–C5 124.6(10), C4–C3–C2 116.3(10), C5–C3–C2 119.1(9), C3–C4–Si2 120.7(8), C3–C4–Si1 107.0(8), Si2–C4–Si1 132.1(6), C3–C5–C6 116.4(8), C5–C6–C7 111.6(10), C6–C7–Si2 107.9(9).

sesses trigonal-planar surroundings within the experimental error. In 10, the BC_2 plane of the BBN unit forms an angle of 66.5° with the plane of the silole ring.

Conclusions

1,2-Hydroboration followed by intramolecular 1,1-organoboration provides a useful route to fused silacarbacycles, containing a silole unit. The synthetic potential of this method becomes evident by inspecting the range of potential substituents at the C=C bond in the starting alkynyl(vinyl)silanes 1–4. This enables further transformations of the bicyclic compounds reported here. Moreover, the alkynyl(vinyl)silanes 1-4 can be modified to contain three, four or more $C \equiv C$ bonds separated by silicon atoms. As will be reported in forthcoming publications, such alkynyl(vinyl)silanes can be converted by cascade reactions into fused siloles containing two, three or more silole units, depending on the number of $C \equiv C$ bonds in the starting alkynyl(vinyl)silanes. The steric hindrance, which prevented such an approach in previous work,^[13] appears to be of minor importance if the first step, 1,2-hydroboartion, leads to a silacyclopent-2-ene derivative.

Experimental Section

General and Starting Materials: All compounds were handled under dry argon to exclude air and moisture, and carefully dried solvents and oven-dried glassware were used throughout. 9-BBN (Aldrich) was used as received. The synthesis of the alkynylsilanes 1-5 is described elsewhere.^[15] NMR measurements at 23 °C in 5 mm (o.d.) tubes in C_6D_6 , if not mentioned otherwise (concentration 5– 10%): Bruker ARX 250, DRX 500 and Varian Inova 400 [¹H, ¹¹B, ¹³C, ²⁹Si NMR (refocused INEPT^[25] based on ²J(²⁹Si, ¹H_{Me}) \approx 7 Hz or ${}^{3}J({}^{29}\text{Si},{}^{1}\text{H}_{Ph}) \approx 4-5$ Hz)]. Chemical shifts are given relative to Me₄Si $[\delta^{1}H(C_{6}D_{5}H) = 7.15 \text{ ppm}, \delta^{1}H(CHDCl_{2}) = 5.33 (\pm 0.01)$ ppm; $\delta^{13}C(C_6D_6) = 128.0$ ppm, $\delta^{13}C(CD_2Cl_2) = 53.8 (\pm 0.05)$ ppm; δ^{29} Si = 0 ± 0.01 ppm for Ξ (²⁹Si) = 19.867184 MHz] and BF₃-OEt₂ $[\delta^{11}B = 0 \pm 0.3 \text{ ppm for } \Xi^{(11}B) = 32.083971 \text{ MHz}]$. Assignments in ¹H and ¹³C NMR spectra were confirmed by 2D ¹H/¹³C HSQC^[26] and in some cases by gradient-enhanced ¹H-¹H NOE difference experiments.^[27] EI-MS spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70 eV) with direct inlet, the m/z data refer to the isotopes 1H, 12C, 11B, 14N, 28Si. Elemental analyses were performed with a Vario Elementar EL III. Melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus.

Reaction of the Alkynylsilanes 1–5 with 9-BBN (General Procedure): To a solution of the respective alkynylsilane **1a–e**, **2**, **4** or **5** (300– 500 mg, 1.5–2.0 mmol) in benzene or toluene (2–3 mL) an equimolar amount of 9-BBN was added in one portion, and the mixture was rapidly heated up to 90–110 °C. After 2–5 min, when the crystalline 9-BBN was dissolved, the reaction was complete. Volatile materials were removed in vacuo to give slightly yellowish oils or solids. The NMR spectroscopic analysis of the products thus formed showed an almost quantitative transformation of the alkynyl(vinyl)silanes into the fused silacarbacycles, and the products were found to be pure (95–98%). The compounds **6c** and **10** were crystallized from hexane to yield single crystals suitable for X-ray analysis. **4-(9-Borabicyclo[3.3.1]non-9-yl)-1,1,6,6-tetramethyl-1***H***,2***H***,3***H***,6***H***,1,6-disilapentalene (6a):** ¹H NMR (500.13 MHz, CD₂Cl₂, 296 K): δ = 0.18 (s, 6 H, SiMe₂), 0.21 (s, 6 H, SiMe₂), 1.00 (m, 2 H, CH₂Si), 1.35, 1.8–2.0 (m, 14 H, BBN), 2.80 (m, 2 H, CH₂), 6.95 [s, ²*J*(²⁹Si,¹H) = 14.9 Hz, 1 H, =CH] ppm. ¹¹B NMR (160.5 MHz): δ = 80.6 ppm.

4-(9-Borabicyclo[3.3.1]non-9-yl)-1,1,6,6-tetramethyl-5-phenyl-1*H***,2***H***,3***H***,6***H***-1,6-disilapentalene (6b):** ¹H NMR (500.13 MHz, C₆D₆, 296 K): δ = 0.42 (s, 6 H, SiMe₂), 0.47 (s, 6 H, SiMe₂), 1.16 (m, 2 H, CH₂Si), 1.4–2.1 (m, 14 H, BBN), 2.96 (m, 2 H, CH₂), 7.14 (m, 1 H, Ph-*p*), 7.20 (m, 2 H, Ph-*o*), 7.25 (m, 2 H, Ph-*m*) ppm. ¹¹B NMR (160.5 MHz): δ = 83.1 ppm. EI-MS for C₂₄H₃₅BSi₂: *m/z* (%) = 390 (4) [M⁺], 270 (45) [M⁺ – BBN(C₈H₁₄B)], 255 (100) [M⁺ – BBN(C₈H₁₄B) – Me].

4-(9-Borabicyclo]3.3.1]non-9-yl)-5-[(dimethylamino)methyl]-1,1,6,6-tetramethyl-1*H***,2***H***,3***H***,6***H***,-6-disilapentalene (6c):** M.p. 54–58 °C. ¹H NMR (500.13 MHz C₆D₆, 296 K): $\delta = 0.33$ (s, 6 H, SiMe₂), 0.38 (s, 6 H, SiMe₂), 1.11 (br. s, 2 H, BBN), 1.17 (m, 2 H, CH₂Si), 1.9–2.6 (m, 12 H, BBN), 2.19 (s, 6 H, NMe₂), 3.13 (s, 2 H, CH₂N), 3.28 (s, 2 H, CH₂) ppm. ¹¹B NMR (160.5 MHz): $\delta = 8.9$ ppm. EI-MS (70 eV) for C₂₁H₃₈BNSi₂: *m/z* (%) = 371 (100) [M⁺]. C₂₁H₃₈BNSi₂ (371.24): calcd. C 67.94, H 10.26, N 3.77; found C 65.95, H 10.48, N 3.70; formation of carbides leads to a low C value.

4-(9-Borabicyclo[3.3.1]non-9-yl)-5-(dimethylsilyl)-1,1,6,6-tetramethyl-1*H***,2***H***,3***H***,6***H***-1,6-disilapentalene (6d): ¹H NMR (500.13 MHz, C₆D₆, 296 K): \delta = 0.33 (s, 6 H, SiMe₂), 0.36 [d, ³***J***(H,H) = 3.6 Hz, 6 H, SiHMe₂], 0.37 (s, 6 H, SiMe₂), 1.15 (m, 2 H, CH₂Si), 1.6–2.3 (m, 14 H, BBN), 2.82 (m, 2 H, CH₂), 4.77 [sept, ³***J***(H,H) = 3.6, ¹***J***(²⁹Si,¹H) = 182.8 Hz, 1 H, SiH] ppm. ¹¹B NMR (160.5 MHz): \delta = 79.8 ppm. EI-MS (70 eV) for C₂₀H₃₇BSi₃:** *m/z* **(%) = 372 (86) [M⁺], 252 (100) [M⁺ – BBN(C₈H₁₄B)].**

4-(9-Borabicyclo[3.3.1]non-9-yl)-5-(bromodimethylsilyl)-1,1,6,6-tetramethyl-1*H***,2***H***,3***H***,6***H***-1,6-disilapentalene (6e): M.p. 68–72 °C. ¹H NMR (500.13 MHz, C₆D₆, 296 K): \delta = 0.32 (s, 6 H, SiMe₂), 0.47 (s, 6 H, SiMe₂), 0.83 (s, 6 H, SiBrMe₂), 1.13 (m, 2 H, CH₂Si), 1.61 (m, 2 H, BBN), 1.83 (2 H, BBN), 2.0–2.1 (m, 6 H, BBN), 2.23 (m, 4 H, BBN), 2.79 (m, 2 H, CH₂) ppm. ¹¹B NMR (160.5 MHz): \delta = 87.4 ppm.**

4-(9-Borabicyclo[3.3.1]non-9-yl)-5-(bromodimethylsilyl)-6,6-dimethyl-1,1-diphenyl-1*H***,2***H***,3***H***,6***H***-1,6-disilapentalene (7): ¹H NMR (500.13 MHz, CD₂Cl₂, 296 K): \delta = 0.39 (s, 6 H, SiMe₂), 0.86 (s, 6 H, SiBrMe₂), 1.67 (m, 2 H, CH₂Si), 1.7–2.3 (m, 14 H, BBN), 2.98 (m, 2 H, CH₂), 7.45 (m, 6 H, Ph), 7.64 (m, 4 H, Ph) ppm. ¹¹B NMR (160.5 MHz): \delta = 82.4 ppm.**

4-(9-Borabicyclo]3.3.1]non-9-yl)-1,6,6-trimethyl-1-phenyl-5-(trimethylsilyl)-1*H*,2*H*,3*H*,6*H*-1,6-disilapentalene (8): ¹H NMR (500.13 MHz, CD₂Cl₂, 296 K): δ = 0.10 [s, 3 H, Si(6)Me, *cis* to Ph], 0.15 (s, 9 H, SiMe₃), 0.21 [s, 3 H, Si(6)Me, *trans* to Ph], 0.41 [s, 3 H, Si(1)Me], 1.14 (m, 1 H, CH₂Si, *trans* to Ph), 1.23 (m, 1 H, CH₂Si, *cis* to Ph), 1.5–2.1 (m, 14 H, BBN), 2.72–2.79 (m, 2 H, CH₂), 7.24 (m, 3 H, Ph), 7.44 (m, 2 H, Ph) ppm. ¹¹B NMR (160.5 MHz): δ = 87.1 ppm.

4-(9-Borabicyclo]3.3.1]non-9-yl)-1,6,6-trimethyl-1-phenyl-5-(triphenylsilyl)-1*H*,2*H*,3*H*,6*H*-1,6-disilapentalene (9): ¹H NMR (500.13 MHz, CD₂Cl₂, 296 K): $\delta = -0.22$ [s, 3 H, Si(6)Me, *trans* to Ph], -0.09 [s, 3 H, Si(6)Me, *cis* to Ph], 0.55 [s, 3 H, Si(1)Me], 1.12 (m, 2 H, CH₂Si), 1.3–1.9 (m, 14 H, BBN), 2.89 (m, 2 H, CH₂), 7.36–7.48 (m, 11 H, Ph), 7.61 (m, 2 H, Ph), 7.73 (m, 7 H, Ph) ppm. ¹¹B NMR (160.5 MHz): $\delta = 89.0$ ppm.

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Table 2. Crystallographic data for the bicyclic compounds 6c a	and	11	1	(
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	6c	10	
Empirical formula	C ₂₁ H ₃₈ BNSi ₂	C ₃₂ H ₅₄ BSi ₃	
Crystal	colorless prism	colorless prism	
Size [mm]	$0.25 \times 0.19 \times 0.18$	$0.28 \times 0.20 \times 0.18$	
Crystal system	monoclinic	monoclinic	
Space group	$P2_1/n$	$P2_{1}/c$	
Lattice parameters			
a [pm]	1106.0(2)	1207.6(2)	
b [pm]	1287.7(3)	1885.3(4)	
c [pm]	1673.1(3)	2833.3(6)	
β [°]	108.13(3)	99.18(3)	
Ζ	4	8	
Absorption coefficient μ [mm ⁻¹]	0.161	0.167	
Diffractometer	STOE IPDS I (Mo- K_{α} , $\lambda = 71.073$ pm), graphite monochromator		
Measuring range θ [°]	1.96-26.01	2.02–26.11	
Reflections collected	15521	42086	
Independent reflections $[I > 2\sigma(I)]$	2140	2343	
Absorption correction ^[a]	none	none	
Refined parameters	226	649	
$wR_2/R_1 [I > 2\sigma(I)]$	0.1182/0.0546	0.1032/0.0488	
Max./min. residual electron density [10 ⁻⁶ e pm ⁻³]	0.334/-0.149	0.209/-0.133	

[a] Absorption corrections did not improve the parameter set.

3-(9-Borabicyclo[3.3.1]non-9-yl)-1,1-dimethyl-7,7-diphenyl-2-(trimethylsilyl)-1*H***,***4H***,***5H***,***6H***,***7H***-1,7-disilaindene (10): M.p. 91–94 °C. ¹H NMR (500.13 MHz, C₆D₆, 296 K): \delta = 0.22 (s, 6 H, SiMe₂), 0.39 (s, 9 H, SiMe₃), 1.27 (m, 2 H, CH₂-6), 1.67 (m, 2 H, CH₂-5), 1.9–2.3 (m, 14 H, BBN), 2.71 (m, 2 H, CH₂-4), 7.3 (m, 6 H, Ph), 7.7 (m, 4 H, Ph) ppm. ¹³C NMR (125.8 MHz): \delta [^{***n***}J(²⁹Si,¹³C)] = -1.3 [48.2] (SiMe₂), 3.6 [51.0] (SiMe₃), 11.4 [53.2] (C-6), 22.7 (C-5), 23.8 (BBN), 33.1 (br., BBN), 34.9 (BBN), 39.4 [6.5] (C-4), 128.5 (Ph), 130.0 (Ph), 130.8 [61.4] [52.6] (C-7a), 136.4 [3.8] (Ph), 137.6 [68.7] (Ph), 153.9 [62.1] [43.1] (C-2), 174.4 [11.6] [7.8 Hz] (C-3a), 183.8 (br., C-3) ppm. ¹¹B NMR (160.5 MHz): \delta = 82.0 ppm. ²⁹Si NMR (99.6 MHz): \delta [^2J(^{29}Si,^{29}Si)] = -18.2 [9.0] (SiPh₂), -11.7 [9.6] (SiMe₃), 27.6 [9.6] [9.0 Hz] (SiMe₂) ppm.**

Methanolysis of 10: To the solution of the disilaindene derivative 10 (0.26 g, 0.5 mmol) in C_6D_6 (0.7 mL) a tenfold excess of methanol was added. The mixture was kept at room temp. for 10 h and then heated at 60–70 °C for 8 h. All volatiles were removed in vacuo, and pure (¹H NMR) 11 was left as a yellowish oil.

1,1-Dimethyl-7,7-diphenyl-2-(trimethylsilyl)-1*H***,4***H***,5***H***,6***H***,7***H***-1,7disilaindene (11): ¹H NMR (500.13 MHz, C₆D₆, 296 K): \delta = 0.16 (s, 6 H, SiMe₂), 0.29 (s, 9 H, SiMe₃), 1.00 (m, 2 H, CH₂-6), 1.6– 2.3 (m, 16 H, BBN, CH₂-5), 2.48 (m, 2 H, CH₂-4), 7.20 [s, 1 H, CH, {}^{3}J({}^{29}\text{Si},{}^{1}\text{H}) = 17.7 Hz], 7.3 (m, 6 H, Ph), 7.8 (m, 4 H, Ph) ppm. {}^{13}\text{C} NMR (125.8 MHz): \delta [{}^{n}J({}^{29}\text{Si},{}^{13}\text{C})] = -2.2 [49.0] (SiMe₂), 0.1 [51.9] (SiMe₃), 11.0 [53.5] (C-6), 21.8 (C-5), 34.9 [7.8] (C-4), 128.5 (Ph), 130.0 (Ph), 131.4 [61.6] [53.2] (C-7a), 136.3 [3.8] (Ph), 137.7 [68.6] (Ph), 152.4 [60.1] [46.3] (C-2), 158.2 [8.5] [4.3] (C-3), 171.8 [9.4] [5.5 Hz] (C-3a) ppm. ²⁹Si NMR (99.6 MHz): \delta [{}^{2}J({}^{29}\text{Si},{}^{29}\text{Si})] = -18.7 [8.5] (SiPh₂), -7.4 [9.8] (SiMe₃), 21.8 [9.8] [8.5 Hz] (SiMe₂) ppm.**

Crystal Structure Determinations of the Silacarbacycle 6c and 10: Structure solution and refinement were carried out with the program package SHELXTL-PLUS V.5.1.^[28] Details pertinent to the crystal structure determinations are listed in Table 2. Crystals of appropriate size were sealed under argon in Lindemann capillaries, and the data collections were carried out at 20 °C.^[29]

Acknowledgments

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