

1,2-Hydroboration and 1,1-Carboboration of Alkynyl(ferrocenyl)vinylsilanes. Novel Siloles

Bernd Wrackmeyer^a, Elena V. Klimkina^a, Wolfgang Milius^b, Christian Butterhof^a, and Kathrin Inzenhofer^a

^a Anorganische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany

^b Anorganische Chemie I, Universität Bayreuth, D-95440 Bayreuth, Germany

Reprint requests to Prof. Dr. B. Wrackmeyer. E-mail: b.wrack@uni-bayreuth.de

Z. Naturforsch. **2014**, *69b*, 1269 – 1289 / DOI: 10.5560/ZNB.2014-4099

Received May 7, 2014

Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

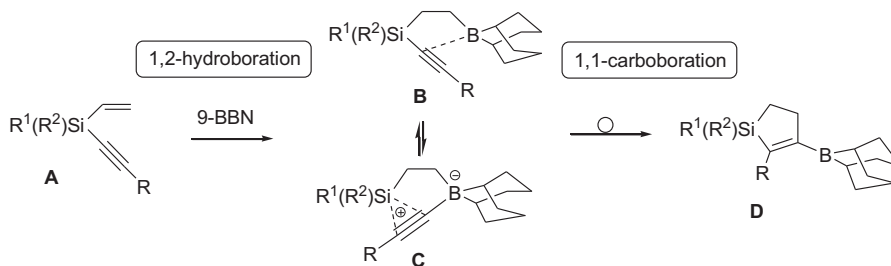
Alkynyl(ferrocenyl)vinylsilanes containing up to three alkynyl units were prepared and treated with 9-borabicyclo[3.3.1]nonane (9-BBN). All reactions proceeded in the beginning by regioselective 1,2-hydroboration of the vinyl group, with boron attached to the terminal carbon. This was followed by intra-molecular 1,1-carboboration, leading to fused silacarbacycles, depending on the number of C≡C bonds. Thus, new siloles and even fused siloles became available. The solution-state structures were revealed by multinuclear NMR techniques (¹H, ¹¹B, ¹³C, ²⁹Si NMR), complemented by calculated single-molecule structures and calculated NMR parameters at the B3LYP/6-311+G(d,p) level of theory. In one case, the solid-state structure of a bicyclic derivative was determined.

Key words: Hydroboration, 1,1-Carboboration, Ferrocenylsilanes, Siloles, NMR Spectroscopy, DFT Calculations, X-Ray Diffraction

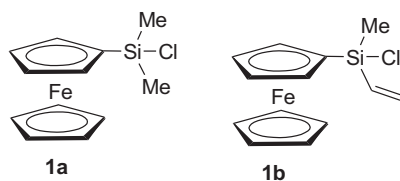
Introduction

The rich chemistry of organoboranes is well documented [1–4]. Among numerous applications 1,1-carboboration [5–9] can be used to build new C–C bonds. For this purpose, the reactivity of certain alkynes towards triorganoboranes is attractive, as has been shown for many alkynyltin compounds [5, 6, 8–12]. Although alkynylsilanes offer even greater synthetic potential, straightforward reactions with most triorganoboranes require harsh conditions and thermally robust triorganoboranes, *e. g.* triethylbo-

rane [5, 6, 13]. To circumvent this problem, highly electrophilic triorganoboranes can be used, such as B(C₆F₅)₃ [14–16] or strained triorganoboranes, such as 1-boraadamantane [17]. An interesting alternative is the intra-molecular 1,1-carboboration, which is expected to have a lower energy of activation when compared with the inter-molecular reaction. This means, the boryl group has first to be introduced by another method into the respective silane, and then the Si–C≡C unit, already present as in **A** (or to be generated), is ready for the intra-molecular 1,1-carboboration [18, 19]. The first step can be easily achieved by the well



Scheme 1. Principle steps of 1,2-hydroboration, followed by 1,1-carboboration. R¹ and R² can be various organyl groups, and R can contain further Si–C≡C units.



in which one or more silicon atoms bear ferrocenyl groups ($\text{Fc} = \eta^5\text{-C}_5\text{H}_5\text{-Fe-}\eta^5\text{-C}_5\text{H}_5$). For the latter purpose we have used chloro(ferrocenyl)silanes **1a**, **b** [21].

Results and Discussion

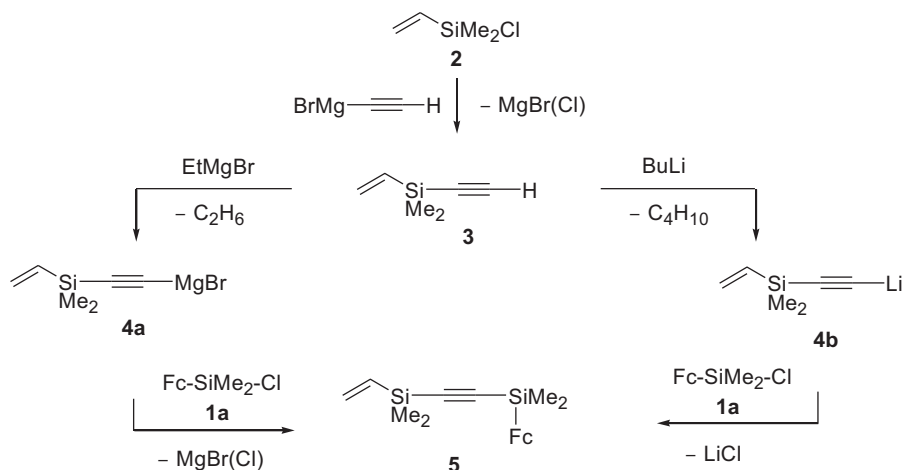
Synthesis of alkynylsilanes

known 1,2-hydroboration, preferably of a vinyl group (Scheme 1) to give **B**, in which the Si-C \equiv bond is activated by the electron-deficient boron. By cleavage of the Si-C \equiv bond the alkynyl group C \equiv C-R migrates to boron to give the zwitterionic intermediate **C** which finally rearranges to **D**. Depending on the nature of R, further reactions may follow.

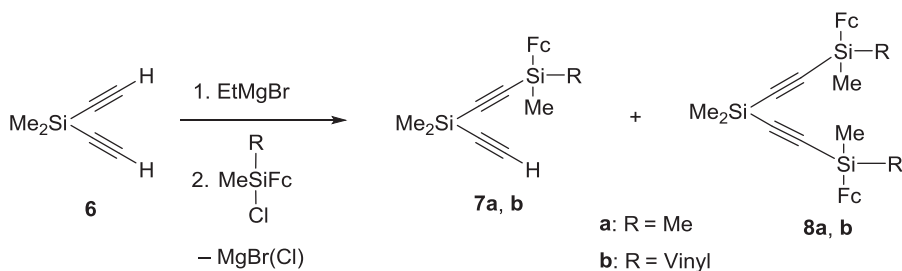
This has already been successfully demonstrated by the synthesis of some condensed siloles [20]. In the present work, we want to show the principles of combined 1,2-hydroboration and 1,1-carboration for a simple example, followed by attempts to extend this reaction sequence towards more complex silanes,

A simple and important starting material is ethynyl(vinyl)silane **3** [22], readily available, which can be converted into the alkynyl(vinyl)ferrocenylsilane **5** (Scheme 2).

Diethynyl(dimethyl)silane (**6**) is another useful starting material, since it can be mono-metallated using EtMgBr, and the reaction of the alkynyl Grignard reagent with **1a** or **1b** affords **7a** or **7b**. Unfortunately, the mono-metallation of **6** is accompanied by di-metallation, and therefore, compounds **8a** or **8b** are



Scheme 2. Synthesis of the alkynyl(dimethyl)vinylsilanes **3** and **5**.



Scheme 3. The conversion of diethynyl(dimethyl)silane (**6**) into various other alkynylsilanes taking advantage of the $\equiv\text{C-H}$ function(s).

Table 1. ^{13}C and ^{29}Si NMR spectroscopic data ^a of silanes **3**–**5**, **7**, **8**, **12**–**15**, **17a**, and **18**.




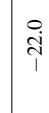
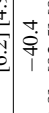
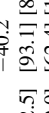

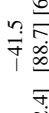
		$\delta^{29}\text{Si(A)}$	$\delta^{29}\text{Si(B)}$	$\delta^{29}\text{Si(C)}$	$\delta^{13}\text{C}$ Si-C(1)≡	$\delta^{13}\text{C}$ Si-C(2)≡	$\delta^{13}\text{C}$ Si-C(3)≡	$\delta^{13}\text{C}$ C(4)≡	$\delta^{13}\text{C}$ Fc	$\delta^{13}\text{C}$ CH=CH ₂	$\delta^{13}\text{C}$ Other
3		-25.2 [85.9] [72.3] [57.9] [16.0]	-	-	88.2 [86.2]	96.8 [16.0]	-	-	-	137.3 [72.1] 133.9	-1.2 [57.8] (SiMe ₂), 26.7, 68.5 (THF)
4a		-33.4	-	-	109.8	162.9 (br)	-	-	-	142.0, 130.9	0.8 (SiMe ₂), 26.7, 68.7 (THF)
5		-25.5 [79.9] [71.5] [57.6] [12.6]	-22.0 [80.4] [80.2] [58.2] [12.8] [6.2] [4.9]	-	112.1 [80.0] [12.7]	114.5 [80.4] [12.5]	-	-	68.2 [80.2] (C ¹), 71.4 [4.9] (C ^{3,4}), 133.4 73.4 [6.2] (C ^{2,5}), 69.1 (Cp)	136.7 [71.4] 133.4	-1.3 [57.7] (SiMe ₂) (Vin), 0.0 [58.2] (SiMe ₂) (Fc)
7a		-21.3 [80.4] [78.8] [58.2] [12.7] [6.3] [5.2]	-40.4 [92.5] [90.3] [62.3] [18.4] [15.0]	-	115.1 [78.9] [15.0]	109.5 [90.2] [12.6]	86.9 [92.8]	94.6 [18.2]	67.7 [80.4] (C ¹), 71.6 [5.2] (C ^{3,4}), 73.6 [6.4] (C ^{2,5}), 69.0 (Cp)	-	-0.3 [58.3] (SiMe ₂) (Fc), 0.3 [62.4] (SiMe ₂)
7b		-28.2 [82.7] [82.5] [74.1] [60.0] [13.0] [6.3] [5.1]	-40.2 [93.1] [89.6] [62.4] [18.2] [14.9]	-	113.0 [82.7] [14.9]	111.1 [89.6] [13.0]	86.8 [93.2]	94.7 [18.3]	65.8 [82.5] (C ¹), 71.8 [5.1] (C ^{3,4}), 71.9 [5.0] (C ^{3,4}), 73.8 [6.5] (C ^{2,5}), 73.9 [6.3] (C ^{2,5}), 69.1 (Cp)	135.6 [74.1] 134.4	-2.0 [60.0] (SiMe) (Fc), 0.3 [62.4] (SiMe ₂)
8a		-21.6	-42.2	-	115.1	110.5	-	-	67.9 [80.4] (C ¹), 71.6 (C ^{3,4}), 73.7 (C ^{2,5}), 69.1 (Cp)	-	-0.3 (SiMe ₂) (Fc), 0.3 (SiMe ₂)
8b		-28.0 [83.0] [82.4] [74.3] [59.8] [13.1] [6.2] [5.1]	-41.5 [88.7] [62.0] [14.6]	-	112.8 [83.0] [14.6]	111.5 [88.8] [13.1]	-	-	65.9 [82.5] (C ¹), 71.8 [5.1] (C ^{3,4}), 71.9 [5.0] (C ^{3,4}), 73.8 [6.3] (C ^{2,5}), 73.9 [6.2] (C ^{2,5}), 69.2 (Cp)	134.3 (=CH ₂), 135.7 [74.2] (=CH-)	-1.97 [60.0], -1.96 [60.0] (SiMe) (Fc), 0.5 [62.0] (SiMe ₂)

Table 1. Continued.

12		-28.7 [82.8] [75.2] [73.5] [59.2] [13.2] [1.7] {1.7}	-41.5 [89.6] [87.6] [62.0] [14.6] [14.6] {1.7}	-21.3 [80.3] [79.3] [58.2] {1.7}	111.3 [82.8] [14.5]	113.6 [87.6] [13.0]	110.0 [89.5] [12.5]	115.2 [79.2] [14.8]	67.9 [80.3] (C ¹), 71.7 [4.9] (C ^{3,4}), 73.7 [6.4] (C ^{2,5}), 69.1 (Cp)	134.7 [73.3] (=CH-), 135.5 (=CH ₂) -0.1 [58.2] (SiMe ₂)(Fc), 128.4 (C _m), 130.2 (C _p), 134.6 (C _o), 133.9 [75.2] (C _i)
13		-28.0 [83.2] [82.5] [74.0] [60.0] [13.2] [6.4] [5.1] {1.7}	-41.8 [89.4] [88.5] [62.0] [14.7] × 2 {1.7}	-17.7 [75.0] [56.3] [12.2] {1.7}	112.6 [83.2] [14.7]	111.8 [88.4] [13.1]	109.9 [89.4] [12.1]	115.9 [75.0] [14.7]	66.0 [82.5] (C ¹), 71.8 [5.0] (C ^{3,4}), 71.9 [4.9] (C ^{3,4}), 73.8 [6.4] (C ^{2,5}), 74.0 [6.0] (C ^{2,5}), 69.2 (Cp)	134.4 (=CH ₂), 135.8 [74.1] (=CH-) (SiMe ₂)(Vim), 0.0 [56.3] (SiMe ₃), 0.6 [61.9] (SiMe ₂)
14		-27.8 [83.6] [82.4] [74.0] [60.0] [14.4] × 2	-40.9 [89.2] [86.8] [62.2] [14.4] × 2	-29.7 [76.7] [5.5]	113.2 [83.3] [14.4]	111.2 [89.3] [12.9]	115.8 [86.8] [12.6]	110.0 [86.5] [14.2]	65.9 [82.6] (C ¹), 71.8 [4.5] (C ^{3,4}), 72.0 [4.7] (C ^{3,4}), 73.8 [6.3] (C ^{2,5}), 74.0 [6.1] (C ^{2,5}), 69.3 (Cp)	134.4 (=CH ₂), 135.8 [74.6] (=CH-) (SiMe ₂)(Vim), 0.4 [62.2] (SiMe ₂), 128.5 [6.1] (C _m), 130.6 (C _p), 133.4 [76.8] (C _i), 135.9 [5.2] (C _o)
15		-24.8 [78.4] [71.7] [57.8] [12.5] [6.1] [5.3]	-41.8 [88.9] [61.9] [14.7]	-21.4 [80.3] [79.2] [58.1] [12.5] [6.1] [5.3]	113.4 [78.3] [14.5]	111.3 [89.0] [12.5]	110.1 [88.5] [12.5]	114.9 [79.3] [14.7]	67.9 [80.2] (C ¹), 71.6 [5.4] (C ^{3,4}), 73.6 [6.1] (C ^{2,5}), 69.1 (Cp)	133.7 (=CH ₂), 136.3 [71.7] (=CH-) (SiMe ₂)(Vim), 0.5 [61.9] (SiMe ₂), -0.2 [58.4] (SiMe ₂)(Fc)
17a		-27.4	-	-	111.6	160.3 (br)	-	-	71.4 (C ^{3,4}), 74.3 (C ^{2,5}), 69.4 (Cp), n.o. (C ¹)	2.4 [58.0] (SiMe ₂)(Fc), 26.7, 68.9 (THF)
18^b		-32.6 [77.0]	-41.4 [62.0] [15.2]	-40.7 [62.2] [14.7]	109.7 [86.0] [14.0]	115.1 [87.1] [13.1]	112.0 [87.7] [14.5]	111.0 [88.3] [14.9]	67.9 [80.5] (C ¹), 71.7 (C ^{3,4}), 73.7 (C ^{2,5}), 69.2 (Cp)	132.8 [75.6] (=CH-), 137.7 (=CH ₂) -0.1 [58.2] (SiMe ₂)(Fc), 0.3 [62.0] (SiMe ₂), 0.5 [62.3] (SiMe ₂), 133.3 [77.0], 135.5, 128.5, 130.5 (Ph: i, o, m, p)

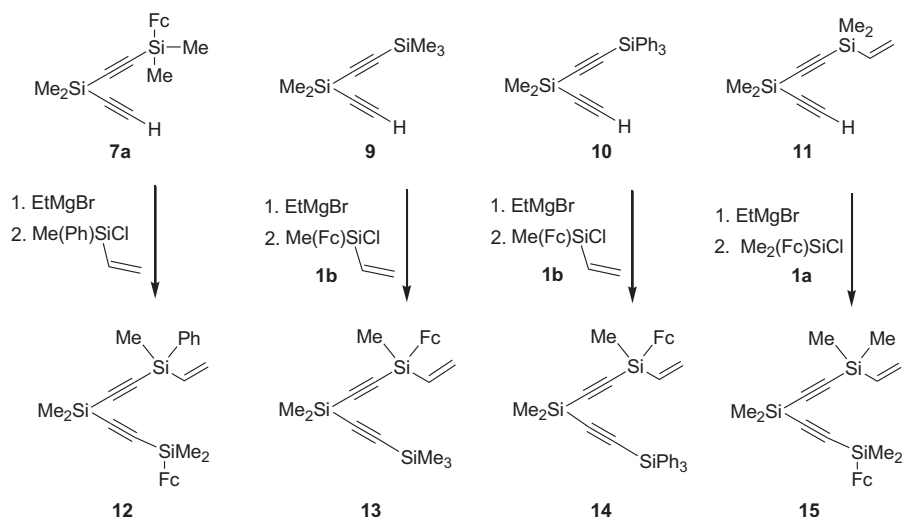
^a In CD₂Cl₂ and in C₆D₆ (for **18**) at 296 K; ⁿJ(²⁹Si, ¹³C) coupling constants [±0.5 Hz] are given in brackets; ³J(²⁹Si, ²⁹Si) coupling constants [±0.3 Hz] are given in braces; ^b other ²⁹Si NMR data: δ = -21.4 (FcSiMe₂) [57.8], other ¹³C NMR data: δ = 109.8 [90.0] [12.0] (C(5)≡); 115.3 [79.1] [14.5] (FcSi-C(5)≡).

present in mixtures with **7a** or **7b** (Scheme 3). Compounds **7a** and **7b** were purified by sublimation.

Similar strategies have been used to prepare **9**, **10** and **11** [23], and metallation of **7a**, **9**, **10**, **11** with EtMgBr, followed by treatment with the appropriate chlorosilane affords alkynylsilanes **12–15** containing

the ferrocenyl unit linked to one of the terminal silicon atoms (Scheme 4) (Fig. 1). All proposed structures of the new alkynylsilanes follow from a consistent set of NMR data (Table 1).

One example for further extension of the chain is **18**, containing now three C≡C units in addition to the



Scheme 4. The conversion of ethynyl(silylethynyl)silanes **7a** and **9–11** into alkynyl(vinyl)silanes **12–15**.

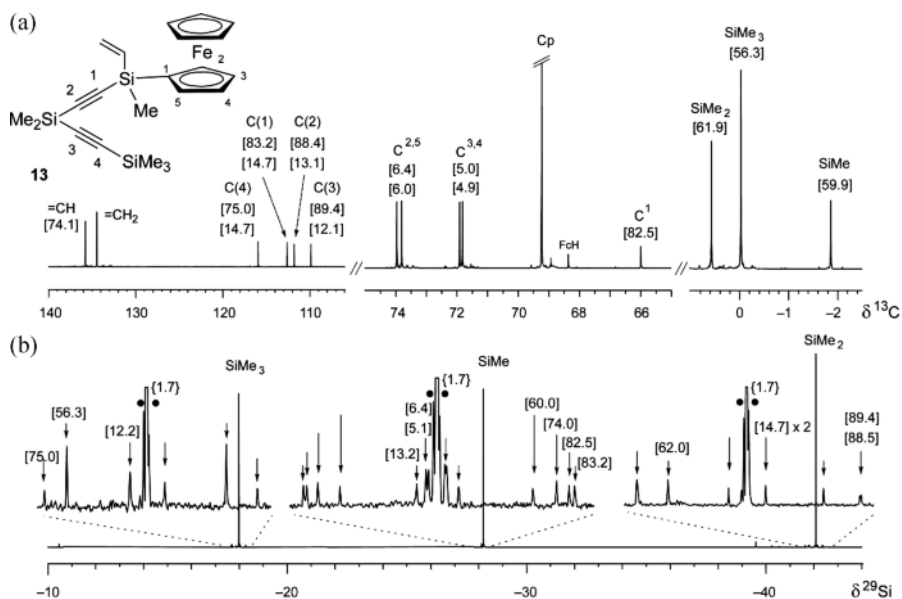
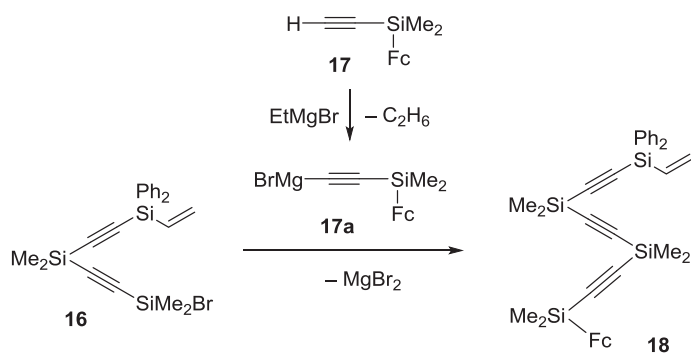
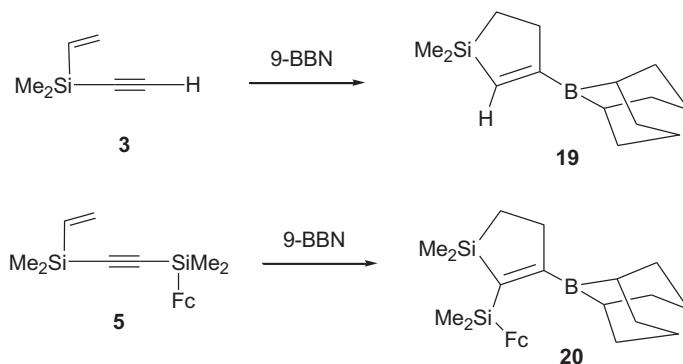


Fig. 1. Trimethylsilylethynyl[ferrocenyl(methyl)(vinyl)silylethynyl]dimethylsilane (**13**). a) 125.8 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2 , at 23°C ; coupling constants $^nJ(^{29}\text{Si}, ^{13}\text{C})$ are given in brackets); b) 99.4 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (refocused INEPT [24, 25]; in CD_2Cl_2 , at 23°C). The ^{13}C satellites for $^nJ(^{29}\text{Si}, ^{13}\text{C})$ are marked by arrows and given in brackets, the ^{29}Si satellites for $^3J(^{29}\text{Si}, ^{29}\text{Si})$ are marked by filled circles and given in braces.

Scheme 5. Synthesis of **18**, containing one vinyl and three alkynyl units.

Scheme 6. Synthesis of 1-silacyclopent-2-enes by 1,2-hydroboration and intramolecular 1,1-vinylboration.

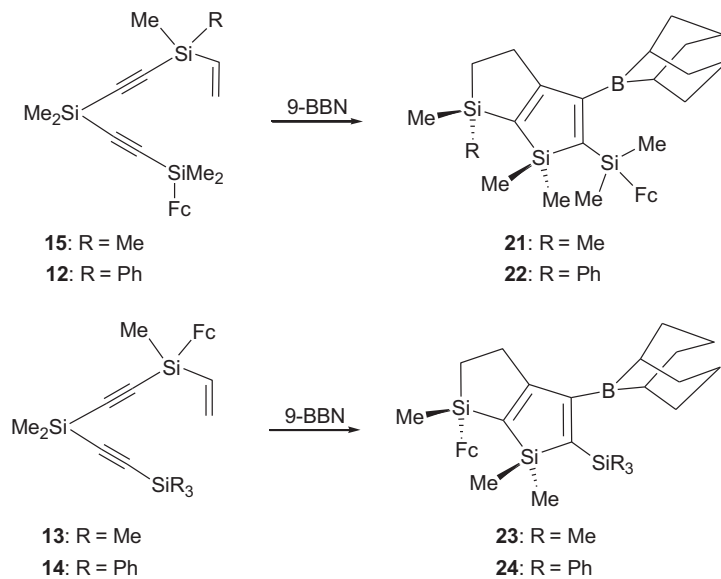
Scheme 7. Reactions of the alkynyl(vinyl)silanes **12**–**15** with 9-BBN.

Table 2. Continued.

23		12.4 [71.6] [60.1] [52.8] [52.0] {13.7} [7.4]	17.3 [57.2] [48.7] × 2 [43.6] [13.8] {9.5}	-11.5 [61.6] [51.0] [11.2] [9.5]	14.2 [51.9]	36.5 [8.6]	182.4 [11.2] [10.1] [7.4]	179.2 (br)	157.7 [61.5] [43.6]	140.2 [60.1] [57.3]	70.9 [71.6] (C ¹), 71.1 [4.4] (C ^{3,4}), 71.6 [4.4] (C ^{3,4}), 73.4 [5.6] (C ^{2,5}), 74.0 [5.6] (C ^{2,5}), 68.6 (Cp)	-2.6 [48.6] [Si(6)Me, trans to Fc], -2.5 [48.8] [Si(6)Me, cis to Fc], -1.1 [52.9] (SiMeFc), 2.8 [51.0] (SiMe ₃)	23.5, 32.7 (br), 34.39, 34.43
24		11.9 [52.9] {13.5}	18.5 [48.7] {13.7} {10.6}	-21.7	14.0	36.8	181.0	184.6 (br)	146.2	143.1	70.6 (C ¹), 71.0 (C ^{3,4}), 71.5 (C ^{3,4}), 73.3 (C ^{2,5}), 73.9 (C ^{2,5}), 68.5 (Cp)	-3.4 [Si(6)Me], -3.3 [Si(6)Me], -1.5 (SiMeFc), 127.0 (C _m), 129.6 (C _p), 136.9 (C _o), 137.2 (C _i)	23.1, 32.4 (br), 33.91, 33.93
25		14.0 [71.4] [60.4] [52.6] [52.2] {13.5}	8.0 [59.3] [58.6] [50.3] × 2 {13.5}	-	13.7 [52.1]	35.2 [7.5]	182.6 [6.4]	169.8 (br)	151.7 [58.6] [7.7]	136.6 [60.5] [59.2]	71.1 [71.3] (C ¹), 71.0 [4.3] (C ^{3,4}), 71.5 [4.3] (C ^{3,4}), 73.9 [5.5] (C ^{2,5}), 74.0 [5.5] (C ^{2,5}), 68.5 (Cp)	-4.1 [50.2] [Si(6)Me trans to Fc], -3.9 [50.4] [Si(6)Me cis to Fc], -1.1 [52.7] (SiMeFc)	23.7, 32.9 (br), 34.28, 34.40
26 +		15.1 {14.2}, 15.3 {14.2}	23.2 {14.2}; 23.7 {14.2}	-	14.4 [52.7], 14.9 [52.2]	35.6 [8.9], 35.7 [8.9]	190.2 [6.4], 190.9 [6.4]	51.2 (br), 51.4 (br)	32.6 (br), 33.1 (br)	134.0 [59.2], 134.6 [59.2]	71.1 [70.6] (C ¹), 71.7 [70.6] (C ¹), 70.9 × 2 (C ^{3,4}), 71.4 × 2 (C ^{3,4}), 73.3, 73.4, 73.7, 73.9 (C ^{2,5}), 68.49, 68.52 (Cp)	26: -0.5 [52.2], (SiMeFc), 2.57 [50.2] [Si(6)Me trans to Fc], 2.61 [48.8] [Si(6)Me cis to Fc], 26': -1.0 [52.0] (SiMeFc), 2.70 [50.1] × 2 [Si(6)Me]	23.7, 23.64, 23.99, 24.0, 29.7 (br), 29.8 (br), 31.3 (br), 31.4 (br), 34.60, 34.67, 34.74, 34.83, 33.6, 34.1

26 : 26' = 1 : 1

Table 2. Continued.

27^b		13.2	19.2 [49.7] {13.4} {10.3}	-30.7 [56.2] [12.2] × 2 {10.3} {1.6}	13.3	35.1	184.3	180.5 (br)	154.5	138.9	68.2 (C ¹), 71.6 (C ^{3,4}), 73.7 (C ^{2,5}), 68.9 (Cp)	-2.2 [49.3] [Si(6)Me ₂], -0.9 [SiMe ₂], 0.1 [58.2] (SiMe ₂ Fc), 128.4 (C _m), 129.8 (C _p), 135.6 (C _o), 137.4 (C _i), 114.9 (C≡), 116.2 (C≡),	23.6, 32.6 (br), 34.4
28^c		13.2	17.2 [49.8] {13.8} {11.8}	4.7 [51.4] {13.9} {8.8}	12.8 [52.2]	34.4 [8.8]	179.9 [9.8] [6.2]	177.2 (br)	159.8 [62.5] [43.1]	142.9 [61.8] [55.1]	71.2 (C ^{3,4}), 73.5 (C ¹), 75.1 (C ^{2,5}), 68.8 (Cp)	-3.4 [51.3] [Si(7)Me ₂], -2.8 [49.8] [Si(6)Me ₂], 1.1 [53.4] (SiMe ₂ Fc), 128.1 [5.0] (C _m), 129.5 (C _p), 135.1 [3.6] (C _o), 137.6 [67.9] (C _i), 177.4 [9.9] [5.0] (C(3b)), 153.1 [56.8] × 2 (C(6a))	23.3, 31.6 (br), 35.2

^a In CD₂Cl₂ or in [D₈]toluene (for **21** and **27**) at 296 K; ⁿJ(²⁹Si, ¹³C) coupling constants [±0.5 Hz] are given in brackets; ²J(²⁹Si, ²⁹Si) coupling constants [±0.5 Hz] are given in braces; ^b other ²⁹Si NMR data: δ = -22.6 (FcSiMe₂) {1.6} [4.6] [6.2] [12.9] [58.4] [79.4] [81.6]; ^c other ²⁹Si NMR data: δ = -15.3 (FcSiMe₂) [4.3] [8.8] [11.7] [53.5] [62.6] [71.8].

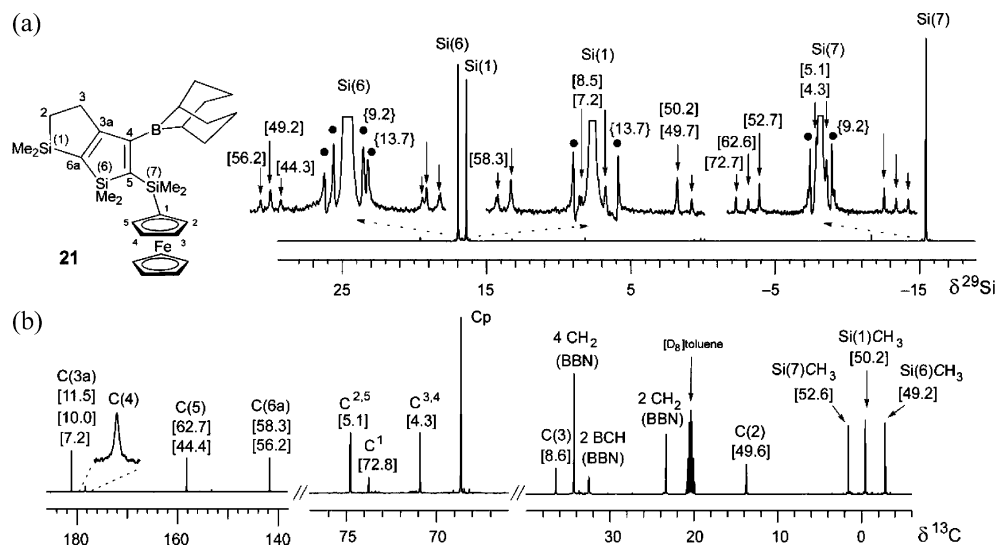


Fig. 2. 4-(9-Borabicyclo[3.3.1]non-9-yl)-5-dimethyl(ferrocenyl)silyl-1,1,6,6-tetramethyl-1,2,3,6-tetrahydro-1,6-disilapentane (**21**). a) 125.8 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2 , at 23°C; coupling constants $^nJ(^{29}\text{Si}, ^{13}\text{C})$ are given in brackets); b) 99.4 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (refocused INEPT [24, 25]; in CD_2Cl_2 , at 23°C). The ^{13}C satellites for $^nJ(^{29}\text{Si}, ^{13}\text{C})$ are marked by arrows and given in brackets, the ^{29}Si satellites for $^2J(^{29}\text{Si}, ^{29}\text{Si})$ are marked by filled circles and given in braces.

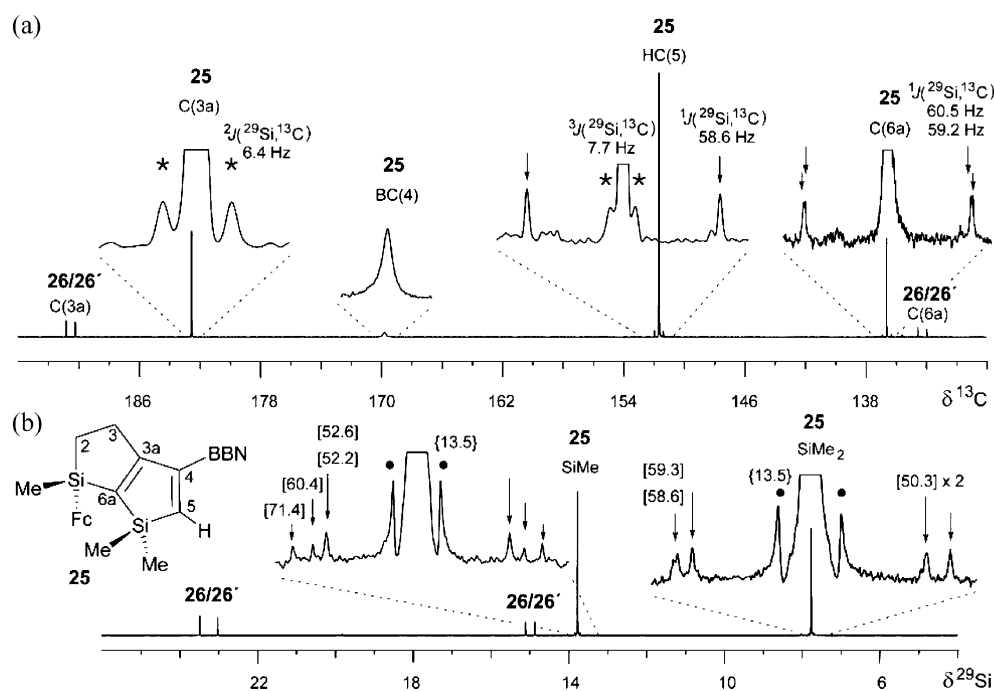
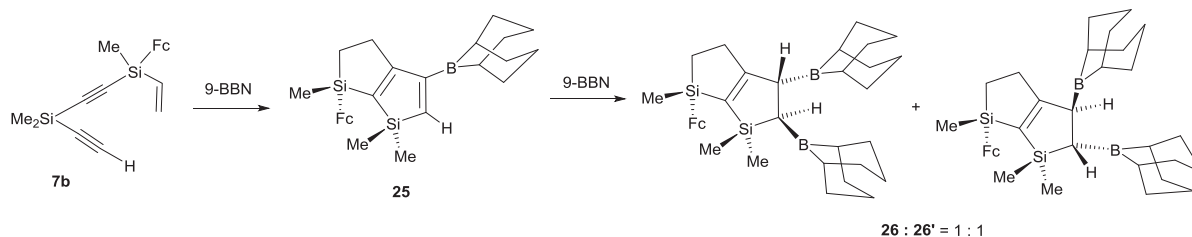


Fig. 3. The reaction mixture of **25** and **26/26'**. a) 100.5 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the region for the olefinic carbon atoms (in CD_2Cl_2 , at 23°C); b) 99.4 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (refocused INEPT [24, 25]; in CD_2Cl_2 , at 23°C). The ^{13}C satellites for $^1J(^{29}\text{Si}, ^{13}\text{C})$ are marked by arrows and given in brackets, the ^{29}Si satellites for $^2J(^{29}\text{Si}, ^{29}\text{Si})$ are marked by filled circles and given in braces.

Scheme 8. Reaction of the ethynyl(vinylsilylethynyl)silane **7b** with one and two equivalents of 9-BBN.Table 3. Experimental and calculated $\delta^{13}\text{C}$ and $\delta^{29}\text{Si}$ NMR chemical shifts and coupling constants of silanes **20**, **21** and **25**.

	20	20 (calcd.)	21	21 (BMe ₂) (calcd.) ^a	25	25 (calcd.)
$\delta^{29}\text{Si}$ (Si(1))	29.1	35.1	16.7	22.0	14.0	16.9
$\{^2J(^{29}\text{Si}, ^{29}\text{Si})\}$	{10.2}	{+11.3}	{13.7}	{+13.2}	{13.5}	{+12.8}
$\delta^{29}\text{Si}$ (Si(6))	-13.7	-12.0	17.3	22.4	8.0	11.3
$\delta^{29}\text{Si}$ (Si(7))	-	-	-15.0	-12.6	-	-
$\{^2J(^{29}\text{Si}, ^{29}\text{Si})\}$			{9.2}	{+11.5}		
$\delta^{13}\text{C}$ (C(2))	10.2	9.7	13.7	13.1	13.7	13.5
$[^1J(^{29}\text{Si}, ^{13}\text{C})]$	[50.8]	[-44.7]	[49.6]	[-43.5]	[52.1]	[-45.9]
$\delta^{13}\text{C}$ (C(3))	39.5	41.4	36.4	45.5	35.2	36.4
$[^2J(^{29}\text{Si}, ^{13}\text{C})]$	[6.4]	[-7.8]	[8.6]	[-3.4]	[7.5]	[-4.0]
$[^3J(^{29}\text{Si}, ^{13}\text{C})]$	[11.3]	[-11.7]		[-8.6]		
$\delta^{13}\text{C}$ (C(3a))	-	-	181.1	185.9	182.6	188.9
$[^2J(^{29}\text{Si}(1), ^{13}\text{C})]$			[7.2]	[-8.6]	[6.4]	[-7.8]
$[^2J(^{29}\text{Si}(6), ^{13}\text{C})]$			[10.2]	[-11.5]		
$[^3J(^{29}\text{Si}(7), ^{13}\text{C})]$			[11.5]	[-11.5]		
$\delta^{13}\text{C}$ (C(4))	187.0	195.7	178.3	188.9	169.8	174.9
$[^2J(^{29}\text{Si}, ^{13}\text{C})]$		[-1.7] (Si(1))		[-1.9] (Si(6))		[-5.0] (Si(6))
$[^2J(^{29}\text{Si}, ^{13}\text{C})]$		[+5.1] (Si(6))		[-4.7] (Si(7))		-
$[^3J(^{29}\text{Si}, ^{13}\text{C})]$		-		[-7.9] (Si(1))		[-7.8] (Si(1))
$\delta^{13}\text{C}$ (C(5))	142.7	145.5	158.2	158.3	151.7	163.9
$[^1J(^{29}\text{Si}(6), ^{13}\text{C})]$	[61.9]	[-57.4]	[44.4]	[-39.4]	[58.6]	[-51.3]
$[^1J(^{29}\text{Si}, ^{13}\text{C})]$	[48.0]	[-40.9]	[62.7]	[-58.5]	[7.7] (³ J)	[-1.4] (³ J)
$\delta^{13}\text{C}$ (C(6a))	-	-	141.7	146.8	136.6	143.4
$[^1J(^{29}\text{Si}(1), ^{13}\text{C})]$			[58.3]	[-52.9]	[60.5]	[-55.8]
$[^1J(^{29}\text{Si}(6), ^{13}\text{C})]$			[56.2]	[-52.1]	[59.2]	[-54.0]
$\delta^{13}\text{C}$ (Si(1)Me)	0.2	-1.8 [-41.4],	-0.4	-2.7 [-43.5],	-1.1 [52.7]	-4.6 [-46.3]
$[^1J(^{29}\text{Si}, ^{13}\text{C})]$	[48.2]	-2.0 [-42.0]	[50.2]	-2.1 [-45.3]		
$\delta^{13}\text{C}$ (Si(6)Me)	1.2	2.4 [-44.3],	-2.8	-3.3 [-43.0],	-4.1 [50.2]	-6.0 [-44.5]
$[^1J(^{29}\text{Si}, ^{13}\text{C})]$	[52.5]	-0.8 [-48.0]	[49.2]	-4.5 [-42.1]	-3.9 [50.4]	-6.3 [-44.7]
					(<i>trans</i> to Fc),	(<i>trans</i> to Fc),
					(<i>cis</i> to Fc)	(<i>cis</i> to Fc)
$\delta^{13}\text{C}$ (Si(7)Me)	-	-	1.6	0.1 [-44.8],	-	-
$[^1J(^{29}\text{Si}, ^{13}\text{C})]$			[52.6]	0.8 [-48.3]		
$\delta^{13}\text{C}$ (Fc(C ¹))	73.6	78.2	73.8	78.6	71.1	75.0
$[^1J(^{29}\text{Si}, ^{13}\text{C})]$	[71.6]	[-66.2]	[72.8]	[-66.9]	[71.3]	[-67.0]
$\delta^{13}\text{C}$ (Fc(C ^{2,5}))	74.2	76.6 [-6.0],	74.8	76.6 [-6.0],	73.9 [5.5]	76.5 [-6.0]
$[^2J(^{29}\text{Si}, ^{13}\text{C})]$	[5.4]	77.1 [-5.8]	[5.1]	76.7 [-5.7]	74.0 [5.5]	76.4 [-6.0]
$\delta^{13}\text{C}$ (Fc(C ^{3,4}))	71.0	71.9 [-4.4],	70.9	71.2 [-4.4]	71.0 [4.3]	72.6 [-4.4]
$[^3J(^{29}\text{Si}, ^{13}\text{C})]$	[4.2]	71.1 [-4.2]	[4.3]	71.8 [-4.3]	71.5 [4.3]	73.7 [-4.5]
$\delta^{13}\text{C}$ (Fc(Cp))	68.6	70.6	68.7	70.7	68.5	70.3

^a The calculations were carried out for the BMe₂ derivative.

Si-CH=CH₂ function (Scheme 5). Although there are viable alternatives, we have obtained **18**, starting from **16** [23] and **17** [21].

Reactions with 9-borabicyclo[3.3.1]nonane (9-BBN)

The reactions of alkyne-silanes **3** and **5** with 9-BBN (Scheme 6) were considered first to demonstrate the principal route as a first step to siloles irrespective of the presence of the ferrocenyl group. Both **19** and **20** are formed almost quantitatively under mild reaction conditions and can be readily identified by their characteristic NMR data (Table 2). Calculated structures (see below) suggest that the arrangement of the 9-BBN unit in **19** is favorable for CB(pp) π interactions, in contrast to the situation in **20**. This is supported by the increased ¹¹B nuclear shielding in **19** ($\delta^{11}\text{B} = 78.3$ ppm), when compared with that in **20** ($\delta^{11}\text{B} = 87.8$ ppm). Intermediates of type **B** or **C** (Scheme 1) were not detected. ²⁹Si NMR spectra [26] measured for reaction solutions provide first important information on the products, and final structural assignments follow from ¹³C NMR spectra and from ²⁹Si satellites for coupling constants $^nJ(^{29}\text{Si}, ^{13}\text{C})$. Frequently, the observation of ¹³C satellites in ²⁹Si NMR spectra is very useful and confirms and complements this information (see *e. g.* Figs. 2, 3, and 5).

The presence of an additional Si-C \equiv C function as in **12**–**15** allows for a second intramolecular 1,1-vinylboration, by which another five-membered ring is formed. This reaction sequence proceeds selectively and quantitatively (Scheme 7). The NMR spectra of the products **21**–**24** strongly support the suggested solution-state structures (Table 2), and crystalline material of **21** turned out to be suitable for X-ray diffraction structure analysis (see below).

The reaction sequence of 9-BBN with **7b** (Scheme 8) leads to the expected silole derivative **25**. Because of the ethynyl group in **7b**, **25** contains a Si-CH= function, and the reduced steric hindrance allows 1,2-hydroboration with a second equivalent of 9-BBN to take place, by which the stereoisomers **26** and **26'** are formed in a 1:1 ratio. This is readily seen in the ²⁹Si NMR spectra (Fig. 3B), even if one attempts to observe a 1:1 ratio of **7b**/9-BBN.

The silole **25** served as an example to demonstrate applications of 1D ¹H-¹H NOE difference experiments (Fig. 4) to visualize the spatial proximity of ¹H nuclei. This allows to assign the three different ¹H(SiMe)

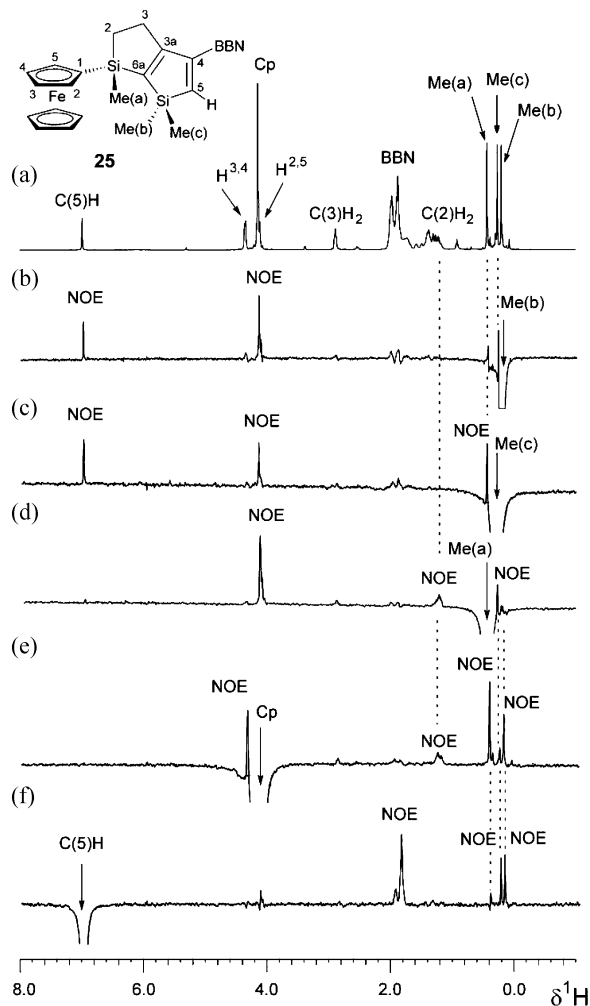


Fig. 4. 400 MHz ¹H/¹H NOE difference spectra of 4-(9-borabicyclo[3.3.1]non-9-yl)-1-ferrocenyl-1,6,6-trimethyl-1,2,3,6-tetrahydro-disilapentalene (**25**) (gradient enhanced [27]; in CD₂Cl₂; at 23°C; relaxation delay 1.5 s; mixing time 0.6 s). The irradiated transitions are marked by arrows; the resulting intensities arising from NOE are indicated. a) Normal ¹H NMR spectrum; b) irradiation: ¹H(Me(b)); response: ¹H(Cp) and ¹H(C(5)H); c) irradiation: ¹H(Me(c)); response: ¹H(Me(a)), ¹H(Cp) and ¹H(C(5)H); d) irradiation: ¹H(Me(a)); response: ¹H(Me(c)), ¹H(C(2)H₂) and ¹H(Cp); e) irradiation: ¹H(Cp); response: ¹H(Me(b)), ¹H(Me(a)), ¹H(C(2)H₂) and ¹H^{3,4}; f) irradiation: ¹H(C(5)H); response: ¹H(Me(b)), ¹H(Me(c)) and ¹H(BBN).

NMR signals, the ¹H(2) and ¹H(3) multiplets, and the neighborhood of =C¹H to the 9-BBN unit.

In the case of **18**, one vinyl and three alkynyl units are present. The reaction with 9-BBN (Scheme 9) pro-

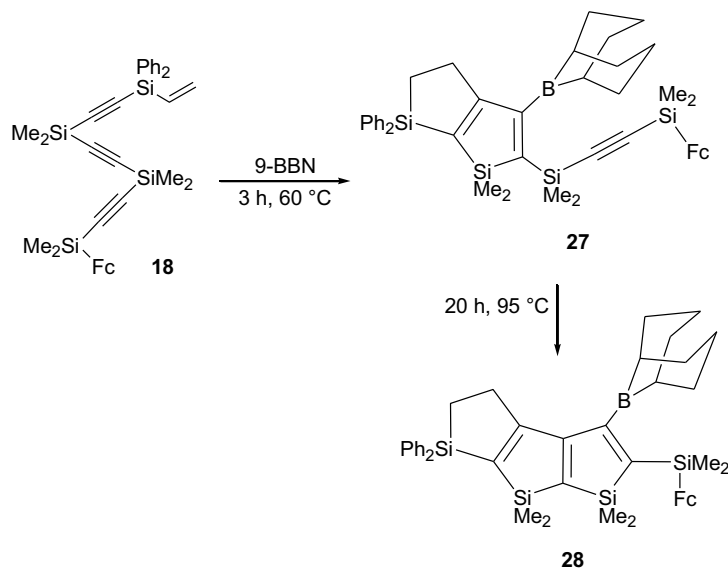
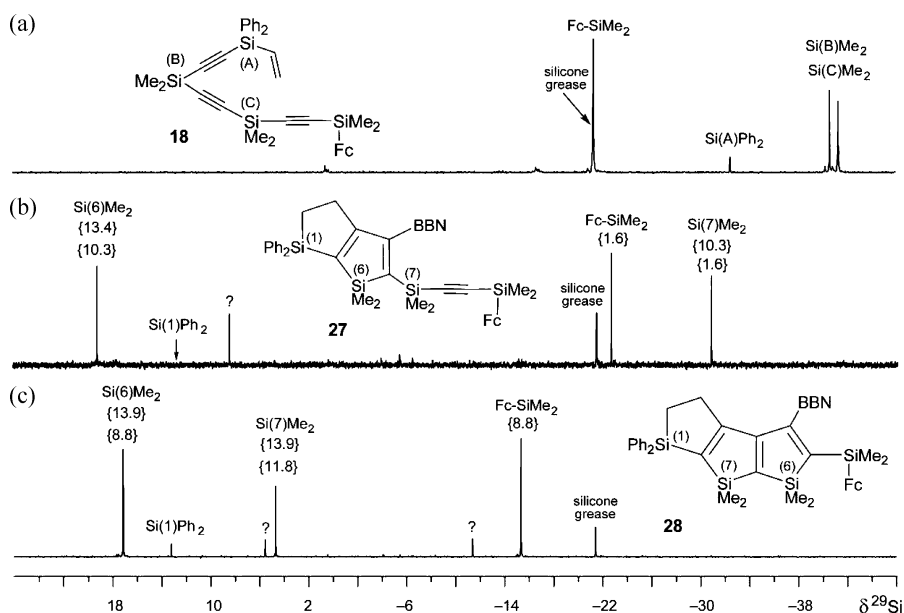
Scheme 9. Synthesis of compound **28**.

Fig. 5. 79.4 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra (refocused INEPT [24, 25], optimized for $^{29}\text{SiMe}_2$). a) $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **18** (in C_6D_6 , at 23°C); b) $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **27** (in $[\text{D}_8]\text{toluene}$, at 23°C); c) $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **28** (in CD_2Cl_2 , at 23°C). Question marks indicate unidentified products.

ceeds fast towards the silole derivative **27** which still possesses a suitable exocyclic $\text{Si}-\text{C}\equiv\text{C}$ function for the third ring closure to give **28**. Fig. 5 shows that ^{29}Si NMR spectra help to monitor the reaction. It should be

noted that the INEPT pulse sequence was optimized for $\text{Si}-\text{Me}$ groups, and therefore the intensity of the $^{29}\text{SiPh}_2$ NMR signal is small. It was not possible to obtain highly purified starting material **18**, and the ^{29}Si

NMR spectra of the product **28** show unidentified signals for impurities in addition to silicone grease.

NMR parameters and DFT calculations

The gas-phase structures of most starting alkynylsilanes and products were optimized by calculations

at the B3LYP/6-311+G(d,p) level of theory [28–32], and NMR parameters (chemical shifts [33] $\delta^{13}\text{C}$, $\delta^{29}\text{Si}$ and coupling constants $^nJ(^{29}\text{Si},^{13}\text{C})$ [34–36]) were calculated at the same level. Three examples (**20**, **21**, **25**) for NMR parameters are given in Table 3, showing reasonable agreement with experimental data, as in related previous work [21, 26, 37], given

Table 4. Selected bond lengths (pm) and angles (deg) of the silacarbacycles **21**, **21** (BMe₂) (calcd.).

	21	21 (BMe ₂) (calcd.) ^a
Si(1)–C(1)	191.2(5)	190.8
Si(1)–C(4)	184.8(6)	186.8
Si(2)–C(4)	185.9(6)	186.5
Si(2)–C(6)	187.8(7)	191.0
Si(3)–C(1)	187.3(5)	188.4
Si(3)–C(13)	187.3(6)	189.4
C(1)–C(2)	137.9(7)	137.0
C(2)–C(3)	152.3(7)	151.2
C(3)–C(4)	136.4(8)	136.0
C(3)–C(5)	151.5(7)	152.3
C(5)–C(6)	153.1(9)	155.3
Si(1)–C(7)	186.1(7)	189.3
Si(1)–C(8)	185.1(7)	189.0
Si(2)–C(9)	185.1(8)	189.0
Si(2)–C(10)	185.4(9)	189.2
Si(3)–C(11)	186.5(6)	189.5
Si(3)–C(12)	185.0(7)	189.4
B–C(2)	157.6(8)	157.5
B–C(23)	158.2(9)	157.7
B–C(27)	156.6(9)	157.4
C(1)–Si(1)–C(4)	93.7(2)	93.5
C(4)–Si(2)–C(6)	93.3(3)	93.7
C(7)–Si(1)–C(8)	110.0(3)	108.8
C(9)–Si(2)–C(10)	109.2(4)	108.5
C(1)–Si(3)–C(13)	107.0(2)	116.0
C(11)–Si(2)–C(12)	110.3(3)	106.6
C(1)–Si(3)–C(11)	111.1(3)	112.7
C(1)–Si(3)–C(12)	113.8(3)	108.5
C(11)–Si(3)–C(13)	108.3(3)	106.9
C(12)–Si(3)–C(13)	106.1(3)	105.6
Si(1)–C(1)–C(2)	106.5(4)	106.3
Si(1)–C(4)–C(3)	106.9(4)	106.2
Si(2)–C(4)–C(3)	108.8(4)	109.2
Si(2)–C(6)–C(5)	105.9(4)	105.3
Si(3)–C(1)–C(2)	130.5(4)	127.5
C(1)–C(2)–C(3)	114.5(5)	115.4
C(2)–C(3)–C(4)	118.3(5)	118.5
C(2)–C(3)–C(5)	122.8(5)	121.9
C(4)–C(3)–C(5)	118.9(5)	119.6
C(3)–C(5)–C(6)	110.0(5)	110.2
Si(1)–C(4)–Si(2)	144.3(3)	144.6
Si(1)–C(1)–Si(3)	123.0(3)	126.1
C(1)–C(2)–B	127.1(5)	126.8
C(3)–C(2)–B	118.2(4)	117.7
C(2)–B–C(23)	123.5(5)	119.8
C(2)–B–C(27)	126.4(6)	120.8
C(23)–B–C(27)	110.1(5)	119.3

Table 4. Continued.

C ₅ / Si (β) ^b	2.6 (bent away from Fe)
C ₅ / C ₅ (twist) (τ) ^b	4.4
C ₅ -Fe-C ₅ (γ) ^b	177.4
C(1)–Si(1)–C(4)–C(3)–C(2) Δ (pm) ^c	1.7
C(4)–Si(2)–C(6)–C(5)–C(3) Δ (pm) ^c	7.9
C(2)–B–C(23)–C(27) Δ (pm) ^c	0.7
C(1)–Si(1)–C(4)–C(3)–C(2) / C(2)–B–C(23)–C(27)	64.6

^a The calculations were carried out for the BMe₂ derivative; ^b the definition of the angles β , γ and τ is given in ref. [38]; ^c mean deviation from plane.

Table 5. Crystallographic data of the silacarbacycle **21**.

21	
Empirical formula	C ₃₀ H ₄₅ BFeSi ₃
Crystal color and shape	yellow-orange needle
Dimensions, mm ³	0.26 × 0.14 × 0.12
Temperature, K	293(2)
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>Lattice parameters</i>	
<i>a</i> , pm	669.70(13)
<i>b</i> , pm	1498.1(3)
<i>c</i> , pm	1675.9(3)
α , deg	68.95(3)
β , deg	81.61(3)
γ , deg	86.06(3)
<i>Z</i>	2
Absorption coefficient μ , mm ⁻¹	0.6
Diffractometer	Stoe IPDS I (MoK α , λ = 71.073 pm), graphite monochromator
Measuring range ϑ , deg	2.28 – 26.05
Reflections collected	10920
Independent reflections [<i>I</i> > 2 σ (<i>I</i>)]	2318
Absorption correction	numerical
Max. / min. transmission	0.8621 / 0.7322
Refined parameters	316
wR2 / <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.174 / 0.076
Max. / min. residual electron density, e pm ⁻³ × 10 ⁻⁶	0.84 / -0.28

for shortcomings in the theoretical model. Importantly, $\delta^{29}\text{Si}$ data are approximately predicted, both for ²⁹Si in the cycles and in substituents, and as well as for ²*J*(²⁹Si, ²⁹Si). In Table 4, the experimental structural parameters of **21** are compared with calculated data.

X-Ray structure studies of the silacarbacycle 21

The molecular structure of **21** is shown in Fig. 6, and relevant structural parameters are given in Table 4.

Intermolecular interactions appear to be negligible. The half-saturated five-membered ring is almost planar (mean deviation 7.9 pm), and the silole ring can be regarded as planar (mean deviation 1.7 pm). Expectedly, there are acute endocyclic bond angles C(4)–Si(2)–C(6) (93.7(2)°) and C(2)–Si(1)–C(4) (93.3(3)°). All other bond lengths and angles are in the usual range. The surroundings of the boron atom are trigonal planar within the experimental error, and the plane B,C(23),C(27) is twisted by 64.7° against the plane of the silole ring. The Cp rings of the ferrocenyl group

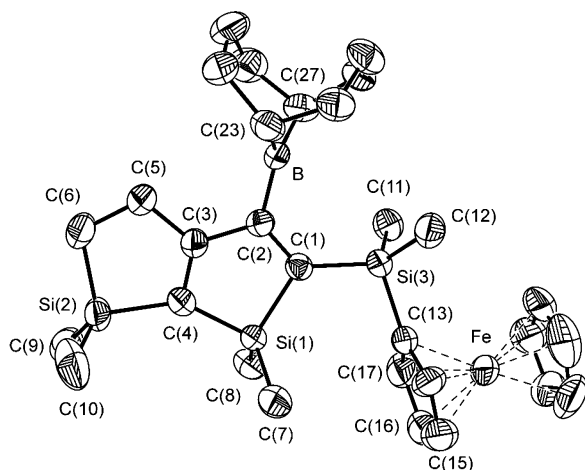


Fig. 6. Molecular structure of the silacarbacycle **21** in the solid state (ORTEP plot with 40% probability ellipsoids; hydrogen atoms have been omitted for clarity; for selected distances and angles see Table 4).

adopt their usual almost parallel and eclipsed arrangement (see Table 4 for details).

Conclusions

Combined consecutive 1,2-hydroboration and 1,1-carboboration reactions applied to appropriate alkynyl(vinyl)silanes offer attractive synthetic potential for the synthesis of fused silacarbacycles which otherwise are hardly accessible. A limiting factor for the number of fused cycles appears to be solely the purity of the starting silane. The solution-state structures can be revealed by NMR methods, in particular ^{13}C and ^{29}Si NMR spectroscopy, when spectra are recorded to allow for the observation of ^{29}Si and ^{13}C satellites. Such measurements are complemented by quantum-chemical calculations of NMR parameters, using the optimized calculated single-molecule geometries.

Experimental

Starting materials and measurements

All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The deuterated solvent CD_2Cl_2 was distilled over CaH_2 in an atmosphere of argon. All other solvents were distilled from Na metal in an atmosphere of argon. Silicon halides, ethynylmagnesium bromide

(0.5 M in THF), $n\text{BuLi}$ (1.6 M in hexane), EtMgBr (1 M in THF), and 9-BBN were commercial products and were used as received. $\text{FcSiMe}_2(\text{Cl})$ **1a** [21], $\text{Me}(\text{Fc})(\text{Vin})\text{SiCl}$ **1b** [21], $\text{FcSiMe}_2(\text{C}\equiv\text{CH})$ **17** [21], silylethynylsilanes **9–11**, and **16** [23] were prepared following literature procedures. NMR measurements: Bruker DRX 500: ^1H , ^{13}C , and ^{29}Si NMR [refocused INEPT [24, 25] based on $^{2,3}J(^{29}\text{Si}, ^1\text{H}) = 25$ Hz (Si–vinyl), 7 Hz (Si–Me) or 4–5 Hz (Si–Ph)]; Varian INOVA 400: ^1H , ^{13}C , ^{29}Si NMR; chemical shifts (ppm) are given relative to Me_4Si [$\delta(^1\text{H}(\text{C}_6\text{D}_5\text{H})) = 7.15$, $(\text{CHDCl}_2) = 5.31$, $(\text{C}_6\text{D}_5\text{CD}_2\text{H}) = 2.08$ (± 0.01); $\delta(^{13}\text{C}(\text{C}_6\text{D}_6)) = 128.2$, $(\text{CD}_2\text{Cl}_2) = 53.8$, $(\text{C}_6\text{D}_5\text{CD}_3) = 20.4$ (± 0.1); $\delta(^{29}\text{Si}) = 0$ (± 0.1) for $\Xi(^{29}\text{Si}) = 19.867184$ MHz]; external $\text{BF}_3\text{-OEt}_2$ [$\delta(^{11}\text{B}) = 0$ (± 0.3) for $\Xi(^{11}\text{B}) = 32.083971$ MHz]. Assignments in ^1H and ^{13}C NMR spectra were confirmed by 2D $^1\text{H}/^{13}\text{C}$ HSQC [39] and in some cases by gradient enhanced $^1\text{H}-^1\text{H}$ NOE difference experiments [27]. EI-MS spectra: Finnigan MAT 8500 spectrometer (ionization energy 70 eV) with direct inlet. The m/z data refer to the isotopes ^1H , ^{11}B , ^{12}C , ^{28}Si , and ^{56}Fe . Melting points (uncorrected) were determined using a Büchi 510 apparatus.

All quantum-chemical calculations were carried out using the GAUSSIAN 09 program package [40]. The calculated nuclear shielding constants were converted into chemical shifts $\delta^{13}\text{C}$ and $\delta^{29}\text{Si}$, using the calculated shielding constants for SiMe_4 with $\sigma(^{13}\text{C}) = 181.0$ and $\sigma(^{29}\text{Si}) = 340.1$, respectively.

Dimethyl(ethynyl)(vinyl)silane (3)

To the solution of the ethynylmagnesium bromide (200 mL, 0.5 M in THF, 100 mmol) the equimolar amount of $\text{Me}_2(\text{Vin})\text{SiCl}$ (11.4 g, 13.0 mL, 94.5 mmol) was added dropwise at -78°C . The reaction mixture was allowed to reach ambient temperature and kept stirring for 24 h. The silane **3** was removed from the reaction mixture together with THF at reduced pressure (10–0.01 Torr), and kept as solution in THF. ^1H NMR (500.13 MHz, THF, 23°C): $\delta = 0.24$ (s, 6H, CH_3), 1.80 (CH_2 , THF), 2.86 (s, 1H, $\equiv\text{CH}$, $^1J(^{13}\text{C}, ^1\text{H}) = 237.7$ Hz), 3.65 (OCH_2 , THF), 5.89 (dd, 1H, $=\text{CH}_2$ -*trans*, $^3J(\text{H},\text{H}) = 20.0$ Hz, $^2J(\text{H},\text{H}) = 4.0$ Hz), 6.02 (dd, 1H, $=\text{CH}_2$ -*cis*, $^3J(\text{H},\text{H}) = 14.9$ Hz, $^2J(\text{H},\text{H}) = 4.0$ Hz), 6.14 (dd, 1H, $=\text{CH}-$, $^3J(\text{H},\text{H}) = 20.0$ Hz, $^3J(\text{H},\text{H}) = 14.9$ Hz).

Dimethyl(vinyl)silylethynyl(dimethyl)(ferrocenyl)silane (5)

Method A

A THF solution of EtMgBr (0.74 mL, 1 M in THF, 0.74 mmol) was added dropwise to a solution of **3** (2.0 mL, 0.37 M in THF, 0.74 mmol) at 0°C . The reaction solution of **4a** was stirred for 20 h at r. t. and for 4 h at 55°C . Then, a solution of $\text{FcSiMe}_2(\text{Cl})$ (**1a**) (165 mg, 0.59 mmol) in THF

(0.5 mL) was added dropwise. The reaction mixture was kept stirring for 20 h at r. t. and heated for 3 d at 55°C. The progress of the reaction was monitored by ^1H and ^{29}Si NMR spectroscopy. The solvent was removed *in vacuo* to leave an oily solid. The solid was extracted twice with portions of hexane (10 mL). Insoluble materials were filtered off, and hexane was removed *in vacuo* to give **5** as an orange-yellow oil (0.170 g; 82% calculated on **1a**).

4a: ^1H NMR (500.13 MHz, THF, 23°C): δ = 0.04 (s, 6H, CH_3), 1.80 (CH₂, THF), 3.68 (OCH₂, THF), 5.80 (m, 2H, =CH₂), 6.09 (m, 1H, =CH-).

5: ^1H NMR (399.8 MHz, CD₂Cl₂, 23°C): δ = 0.29 (s, 6H, FcSiCH₃), 0.40 (s, 6H, (vinyl)SiCH₃), 4.19 (s, 5H, Cp), 4.20 (m, 2H, H^{2,5}), 4.38 (m, 2H, H^{3,4}), 5.90 (dd, 1H, =CH₂-*trans*, $^3J(\text{H,H})$ = 20.3 Hz, $^2J(\text{H,H})$ = 4.0 Hz), 6.06 (dd, 1H, =CH₂-*cis*, $^3J(\text{H,H})$ = 14.6 Hz, $^2J(\text{H,H})$ = 4.0 Hz), 6.19 (dd, 1H, =CH-, $^3J(\text{H,H})$ = 20.3 Hz, $^3J(\text{H,H})$ = 14.6 Hz).

Method B

A solution of $n\text{BuLi}$ (0.29 mL, 1.6 M in hexane, 0.48 mmol) in hexane was added dropwise to a solution of **3** (1.3 mL, 0.37 M in THF, 0.48 mmol) in THF at -78°C. The reaction solution of **4b** was stirred for 30 min at r. t. and added dropwise to the solution of FcSiMe₂(Cl) (**1a**) (133 mg, 0.48 mmol) in THF (15 mL). The reaction mixture was kept stirring for 20 h at r. t. (the progress of the reaction was monitored by ^1H and ^{29}Si NMR spectroscopy). The solvent was removed *in vacuo*, and the remaining oil was dissolved in hexane. Insoluble materials were filtered off, and hexane was removed *in vacuo* to give 159 mg of the mixture containing **5** (90%) together with an unidentified side product (10%) as an orange-yellow oil.

Ethynyl[*dimethyl(ferrocenyl)silylethynyl*] dimethylsilane (**7a**)

A THF solution of EtMgBr (1.59 mL, 1 M in THF, 1.59 mmol) was added dropwise to a solution of **6** (2.06 mL, 0.777 M in THF, 1.60 mmol) in THF at r. t. The solution became yellow (**6(MgBr)**), was stirred for additional 1.5 h at r. t. and cooled to 0°C. Then, the solution of FcSiMe₂(Cl) (**1a**) (0.40 mg, 1.44 mmol) in THF (5 mL) was added dropwise. The reaction mixture was kept stirring for 20 h at r. t. and heated for 20 h at 50–60°C. The progress of the reaction was monitored by ^1H and ^{29}Si NMR spectroscopy. The solvent was removed *in vacuo*, and the resulting solid was extracted with portions of hexane (30 mL) and toluene (15 mL). After filtration the solvents were removed *in vacuo* to give a mixture containing **7a** (ca. 95%) and **8a** (ca. 5%) (from ^{29}Si NMR spectroscopy). The mixture was heated to 70–80°C in a vacuum (8×10^{-3} Torr) for 1–2 h to sublime off the product **7a** as an orange-yellow oil (312 mg; 62% calculated on **1a**). **7a**: ^1H NMR (500.13 MHz, CD₂Cl₂,

23°C): δ = 0.43 (s, 6H, SiCH₃, $^2J(^{29}\text{Si},^1\text{H})$ = 7.6 Hz), 0.45 (s, 6H, FcSiCH₃, $^2J(^{29}\text{Si},^1\text{H})$ = 7.1 Hz), 2.57 (s, 1H, $\equiv\text{CH}$, $^1J(^{13}\text{C},^1\text{H})$ = 238.9 Hz), 4.24 (s, 5H, Cp), 4.25 (m, 2H, H^{2,5}), 4.43 (m, 2H, H^{3,4}), 5.99 (dd, 1H, =CH₂-*trans*, $^3J(\text{H,H})$ = 20.1 Hz, $^2J(\text{H,H})$ = 3.8 Hz), 6.06 (dd, 1H, =CH₂-*cis*, $^3J(\text{H,H})$ = 14.6 Hz, $^2J(\text{H,H})$ = 4.0 Hz), 6.19 (dd, 1H, =CH-, $^3J(\text{H,H})$ = 20.3 Hz, $^3J(\text{H,H})$ = 14.6 Hz).

Ethynyl[*ferrocenyl(methyl)(vinyl)silylethynyl*] dimethylsilane (**7b**)

The synthesis was carried out as described for **7a**, starting from a THF solution of **6** (3 mL, 0.777 M in THF, 2.33 mmol), EtMgBr (2.2 mL, 1 M in THF, 2.2 mmol) and Me(Fc)Si(Vin)Cl (579 mg, 1.99 mmol). The reaction mixture was kept stirring for 20 h at r. t. and heated for 4 h at 45°C. The resulting mixture contained **7b** together with **8b** (20–25%) (from ^{13}C NMR spectroscopy). The residue was condensed *in vacuo* (80–90°C/ 8×10^{-3} Torr) to give 323 mg (45%) of **7b** as an orange-red oil. The residue contained **8b** (200 mg).

7b: ^1H NMR (500.13 MHz, CD₂Cl₂, 23°C): δ = 0.42 (s, 6H, SiCH₃, $^2J(^{29}\text{Si},^1\text{H})$ = 7.6 Hz), 0.50 (s, 3H, FcSiCH₃, $^2J(^{29}\text{Si},^1\text{H})$ = 7.3 Hz), 2.56 (s, 1H, $\equiv\text{CH}$, $^1J(^{13}\text{C},^1\text{H})$ = 239.1 Hz), 4.20, 4.22 (m, m, 1H, 1H, H^{2,5}), 4.22 (s, 5H, Cp), 4.42 (m, 2H, H^{3,4}), 5.97 (dd, 1H, =CH₂-*trans*, $^3J(\text{H,H})$ = 19.9 Hz, $^2J(\text{H,H})$ = 3.6 Hz), $^3J(^{29}\text{Si},^1\text{H})$ = 9.0 Hz), 6.13 (dd, 1H, =CH₂-*cis*, $^3J(\text{H,H})$ = 14.7 Hz, $^2J(\text{H,H})$ = 3.6 Hz), 6.28 (dd, 1H, =CH-, $^3J(\text{H,H})$ = 19.9 Hz, $^3J(\text{H,H})$ = 14.7 Hz).

8b: ^1H NMR (500.13 MHz, CD₂Cl₂, 23°C): δ = 0.45 (s, 6H, SiCH₃, $^2J(^{29}\text{Si},^1\text{H})$ = 7.6 Hz), 0.49 (s, 6H, FcSiCH₃, $^2J(^{29}\text{Si},^1\text{H})$ = 7.2 Hz), 4.20, 4.23 (m, m, 2H, 2H, H^{2,5}), 4.23 (s, 10H, Cp), 4.40 (m, 4H, H^{3,4}), 5.97 (dd, 2H, =CH₂-*trans*, $^3J(\text{H,H})$ = 20.0 Hz, $^2J(\text{H,H})$ = 3.8 Hz), 6.11 (dd, 2H, =CH₂-*cis*, $^3J(\text{H,H})$ = 14.5 Hz, $^2J(\text{H,H})$ = 3.8 Hz), 6.27 (dd, 2H, =CH-, $^3J(\text{H,H})$ = 20.0 Hz, $^3J(\text{H,H})$ = 14.5 Hz).

Dimethyl(ferrocenyl)silylethynyl[*methyl(phenyl)(vinyl)*] silylethynyl]dimethylsilane (**12**)

A THF solution of EtMgBr (0.61 mL, 0.61 mmol, 1 M in THF) was added dropwise to a solution of **7a** (212 mg, 0.61 mmol) in THF (3 mL). The reaction mixture was stirred for 1.5 h and cooled to 0°C. Then, a THF solution of Me(Ph)(Vin)SiCl (111 mg, 0.11 mL, 0.61 mmol) was added dropwise. The reaction mixture was stirred for 20 h at r. t. and heated for 1 h at 45°C. Then, the volatile materials were removed *in vacuo*, and the resulting solid was extracted with hexane (15 mL). Insoluble materials were filtered off, and hexane was removed *in vacuo*. The oily residue was heated to 50–60°C in a vacuum (8×10^{-3} Torr) for 1–2 h to sublime off impurities. The residue was dissolved in pentane (30 mL), insoluble materials were filtered off,

and pentane was removed *in vacuo* to give 210 mg (70%) of **12** as an orange oil. – ^1H NMR (500.13 MHz, CD_2Cl_2 , 23°C): $\delta = 0.42$ (s, 6H, SiCH_3), 0.42 (s, 6H, SiCH_3), 0.52 (s, 3H, FcSiCH_3 , $^2J(^{29}\text{Si}, ^1\text{H}) = 7.1$ Hz), 4.20 (s, 5H, Cp), 4.22 (m, 2H, $\text{H}^{2,5}$), 4.38 (m, 2H, $\text{H}^{3,4}$), 5.97 (dd, 1H, $=\text{CH}_2$ -*trans*, $^3J(\text{H},\text{H}) = 19.6$ Hz, $^2J(\text{H},\text{H}) = 4.2$ Hz), 6.17 (dd, 1H, $=\text{CH}_2$ -*cis*, $^3J(\text{H},\text{H}) = 14.5$ Hz, $^2J(\text{H},\text{H}) = 4.2$ Hz), 6.27 (dd, 1H, $=\text{CH}-$, $^3J(\text{H},\text{H}) = 19.6$ Hz, $^3J(\text{H},\text{H}) = 14.5$ Hz), 7.40 (m, 3H, Ph), 7.65 (m, 2H, Ph-*o*).

Trimethylsilylethynyl[ferrocenyl(methyl)(vinyl)silylethynyl]dimethylsilane (13)

A THF solution of EtMgBr (1.34 mL, 1 M in THF, 1.34 mmol) was added dropwise to a solution of **9** (243 mg, 1.35 mmol) in THF (1.5 mL). The reaction mixture was stirred for 1.5 h and cooled to 0°C . A solution of $\text{Me}(\text{Fc})(\text{Vin})\text{SiCl}$ (**1b**) (360 mg, 1.24 mmol) in THF (2 mL) was added dropwise. The reaction mixture was stirred for 20 h at r.t. and heated for 8 h at 45°C . THF was removed *in vacuo*, and the resulting solid was extracted with portions of hexane (30 mL) and toluene (15 mL). Insoluble materials were filtered off, and the volatile materials were removed *in vacuo* (8×10^{-3} Torr, 5 h at 40 – 50°C) to give 373 mg (69%) of **13** as an orange oil. – ^1H NMR (500.13 MHz, CD_2Cl_2 , 23°C): $\delta = 0.18$ (s, 9H, SiCH_3 , $^2J(^{29}\text{Si}, ^1\text{H}) = 7.1$ Hz), 0.37 (s, 6H, SiCH_3 , $^2J(^{29}\text{Si}, ^1\text{H}) = 7.5$ Hz), 0.47 (s, 3H, FcSiCH_3 , $^2J(^{29}\text{Si}, ^1\text{H}) = 7.1$ Hz), 4.18, 4.20 (m, m, 1H, 1H, $\text{H}^{2,5}$), 4.21 (s, 5H, Cp), 4.39 (m, 2H, $\text{H}^{3,4}$), 5.94 (dd, 1H, $=\text{CH}_2$ -*trans*, $^3J(\text{H},\text{H}) = 20.0$ Hz, $^2J(\text{H},\text{H}) = 3.8$ Hz), 6.10 (dd, 1H, $=\text{CH}_2$ -*cis*, $^3J(\text{H},\text{H}) = 14.5$ Hz, $^2J(\text{H},\text{H}) = 3.8$ Hz), 6.26 (dd, 1H, $=\text{CH}-$, $^3J(\text{H},\text{H}) = 20.0$ Hz, $^3J(\text{H},\text{H}) = 14.5$ Hz).

Triphenylsilylethynyl[ferrocenyl(methyl)(vinyl)silylethynyl]dimethylsilane (14)

A THF solution of EtMgBr (0.61 mL, 1 M in THF, 0.61 mmol) was added dropwise to a solution of **10** (224 mg, 0.61 mmol) in THF (5 mL). The reaction mixture was stirred for 2 h and cooled to 0°C . A solution of $\text{Me}(\text{Fc})(\text{Vin})\text{SiCl}$ (**1b**) (168 mg, 0.58 mmol) in THF (2 mL) was added dropwise. The reaction mixture was stirred for 20 h at r.t. and heated for 20 h at 45°C . Then, the volatile materials were removed *in vacuo*, and the resulting solid was extracted with hexane (30 mL). Insoluble materials were filtered off, and hexane was removed *in vacuo*. The oily residue was heated *in vacuo* (140 – $150^\circ\text{C}/2 \times 10^{-3}$ Torr) for 1–2 h to remove impurities. The residue was dissolved in pentane (30 mL), insoluble materials were filtered off, and pentane was removed *in vacuo* to give 223 mg (62%) of **14** as an orange oil. – ^1H NMR (500.13 MHz, CD_2Cl_2 , 23°C): $\delta = 0.48$ (s, 6H, SiCH_3), 0.49 (s, 3H, FcSiCH_3), 4.14, 4.22 (m, m, 1H, 1H, $\text{H}^{2,5}$), 4.19 (s,

5H, Cp), 4.38 (m, 2H, $\text{H}^{3,4}$), 5.97 (dd, 1H, $=\text{CH}_2$ -*trans*, $^3J(\text{H},\text{H}) = 20.0$ Hz, $^2J(\text{H},\text{H}) = 3.8$ Hz), 6.11 (dd, 1H, $=\text{CH}_2$ -*cis*, $^3J(\text{H},\text{H}) = 14.5$ Hz, $^2J(\text{H},\text{H}) = 3.8$ Hz), 6.28 (dd, 1H, $=\text{CH}-$, $^3J(\text{H},\text{H}) = 20.0$ Hz, $^3J(\text{H},\text{H}) = 14.5$ Hz), 7.40 (m, 6H, Ph-*m*), 7.46 (m, 3H, Ph-*p*), 7.67 (m, 6H, Ph-*o*).

Dimethyl(ferrocenyl)silylethynyl[dimethyl(vinyl)silylethynyl]dimethylsilane (15)

A THF solution of EtMgBr (0.92 mL, 1 M in THF, 0.92 mmol) was added dropwise to a solution of **11** (178 mg, 0.93 mmol) in THF (1.5 mL). The reaction mixture was stirred for 1.5 h and cooled to 0°C . A solution of $\text{Me}_2\text{Si}(\text{Fc})\text{Cl}$ (**1a**) (246 mg, 0.88 mmol) in THF (2 mL) was added dropwise. The reaction mixture was stirred for 20 h at r.t. and heated for 20 h at 45°C . THF was removed *in vacuo*, and the resulting solid was extracted with portions of hexane (30 mL) and toluene (15 mL). Insoluble materials were filtered off, and the volatile materials were removed *in vacuo* (8×10^{-3} Torr, 2 h) to give 275 mg (72%) of **15** as an orange oil. – ^1H NMR (500.13 MHz, CD_2Cl_2 , 23°C): $\delta = 0.24$ (s, 6H, (vinyl) SiCH_3 , $^2J(^{29}\text{Si}, ^1\text{H}) = 7.5$ Hz), 0.36 (s, 6H, SiCH_3 , $^2J(^{29}\text{Si}, ^1\text{H}) = 7.6$ Hz), 0.39 (s, 6H, FcSiCH_3 , $^2J(^{29}\text{Si}, ^1\text{H}) = 7.1$ Hz), 4.19 (m, 2H, $\text{H}^{2,5}$), 4.20 (s, 5H, Cp), 4.37 (m, 2H, $\text{H}^{3,4}$), 5.87 (dd, 1H, $=\text{CH}_2$ -*trans*, $^3J(\text{H},\text{H}) = 19.6$ Hz, $^2J(\text{H},\text{H}) = 4.5$ Hz), 6.03 (dd, 1H, $=\text{CH}_2$ -*cis*, $^3J(\text{H},\text{H}) = 14.6$ Hz, $^2J(\text{H},\text{H}) = 4.3$ Hz), 6.14 (dd, 1H, $=\text{CH}-$, $^3J(\text{H},\text{H}) = 19.6$ Hz, $^3J(\text{H},\text{H}) = 14.6$ Hz).

Dimethyl(ferrocenyl)silylethynyl[[diphenyl(vinyl)silylethynyl](dimethyl)silylethynyl]dimethylsilane (18)

A THF solution of EtMgBr (0.64 mL, 1 M in THF, 0.64 mmol) was added dropwise to a solution of **17** (171 mg, 0.64 mmol) in THF (5 mL). The reaction solution of **17a** was stirred for 20 h at r.t. Then, the solution of **16** (290 mg, 0.64 mmol) in hexane (1 mL) was added dropwise. The reaction mixture was kept stirring for 2 h at r.t. The solvent was removed *in vacuo* to leave an oily solid. The solid was extracted twice with portions of hexane (10 mL). Insoluble materials were filtered off, and hexane was removed *in vacuo*. The oily residue was heated *in vacuo* (140 – $150^\circ\text{C}/2 \times 10^{-3}$ Torr) for 1–2 h to remove impurities. The residue was dissolved in pentane (30 mL), insoluble materials were filtered off, and pentane was removed *in vacuo* to give 294 mg (72%) of **18** as an orange-yellow oil.

17a: ^1H NMR (500.13 MHz, THF, 23°C): $\delta = 0.21$ (s, 6H, CH_3), 1.80 (CH_2 , THF), 3.71 (OCH_2 , THF), 4.12 (m, 2H, $\text{H}^{2,5}$), 4.16 (s, 5H, Cp), 4.23 (m, 2H, $\text{H}^{3,4}$).

18: ^1H NMR (500.13 MHz, C_6D_6 , 23°C): $\delta = 0.25$ (s, 6H, SiCH_3), 0.30 (s, 6H, SiCH_3), 0.34 (s, 6H, SiCH_3), 4.13 (m, 2H, $\text{H}^{2,5}$), 4.16 (s, 5H, Cp), 4.20 (m, 2H, $\text{H}^{3,4}$), 6.07 (m, 2H, $=\text{CH}_2$), 6.37 (m, 1H, $=\text{CH}-$), 7.16 (m, 3H, Ph), 7.75 (m, 2H, Ph-*o*).

3-(9-Borabicyclo[3.3.1]non-9-yl)-1-silacyclopent-2-ene (19)

To a THF solution of **3** (2.97 mL, 0.37 M in THF, 0.55 mmol) the equimolar amount of 9-BBN (135 mg) was added in one portion. The reaction solution was stirred for 20 h at r.t. Then, the solvent was removed *in vacuo* to give **19** as a colorless oil. – ¹H NMR (500.13 MHz, CD₂Cl₂, 23°C): δ = 0.18 (s, 6H, SiCH₃), 0.81 (t, ³J(¹H,¹H) = 6.7 Hz, 2H, CH₂Si), 1.25 (m, 2H, BCH), 1.73 (m, 4H, BBN), 1.89 (m, 8H, BBN), 2.76 (td, 2H, C(3)H₂, ³J(¹H,¹H) = 6.7 Hz, ⁴J(¹H,¹H) = 1.8 Hz), 6.91 (t, 1H, =CHSi, ⁴J(¹H,¹H) = 1.8 Hz). – ¹¹B NMR (160.5 MHz, CD₂Cl₂, 23°C): δ = 78.3.

Reaction of the alkynylsilanes 5, 12–15 with 9-BBN (general procedure)

To the solution of the respective alkynylsilane **5**, **12–15** (150–300 mg, 0.2–0.4 mmol) in CD₂Cl₂ (0.6 mL) the equimolar amount of 9-BBN was added in one portion. The reaction mixture was kept stirring at r.t. or heated at 40–50°C. The progress of the reactions was monitored by ²⁹Si NMR spectroscopy. 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%).

3-(9-Borabicyclo[3.3.1]non-9-yl)-2-dimethyl(ferrocenyl)silyl-1-silacyclopent-2-ene (20)

To a solution of **5** (150 mg, 0.43 mmol) in CD₂Cl₂ (0.6 mL) the equimolar amount of 9-BBN (50 mg) was added in one portion. The progress of the reaction was monitored by ²⁹Si NMR spectroscopy. After 20 h at r.t., the reaction was complete, and the solution contained **20** (ca. 95%). – ¹H NMR (500.13 MHz, CD₂Cl₂, 23°C): δ = –0.06 (s, 6H, SiCH₃), 0.42 (s, 6H, FcSiCH₃), 0.59 (m, 2H, CH₂Si, ³J(¹H,¹H) = 6.9 Hz), 1.53 (m, 2H, BCH), 1.89 (m, 4H, BBN), 2.04 (m, 8H, BBN), 2.75 (m, 2H, C(3)H₂, ³J(¹H,¹H) = 6.9 Hz), 4.14 (s, 5H, Cp), 4.16 (m, 2H, H^{2,5}), 4.36 (m, 2H, H^{3,4}). – ¹¹B NMR (160.5 MHz, CD₂Cl₂, 23°C): δ = 87.8.

4-(9-Borabicyclo[3.3.1]non-9-yl)-5-dimethyl(ferrocenyl)silyl-1,1,6,6-tetramethyl-1,2,3,6-tetrahydro-1,6-disilapentalene (21)

To a solution of **15** (190 mg, 0.44 mmol) in CD₂Cl₂ (0.6 mL) the equimolar amount of 9-BBN (53 mg) was added in one portion. The progress of the reaction was monitored by ²⁹Si NMR spectroscopy. After 24 h at r.t., the reaction was complete, and the solvent was removed *in vacuo* to give 229 mg of **21**. Yellow-orange single crystals of **21** suitable for X-ray diffraction grew from hexane solutions after

2 weeks at –30°C (m. p. 165–175°C). – ¹H NMR (500.13 MHz, [D₈]toluene, 23°C): δ = 0.10 (s, 6H, Si(6)CH₃), 0.22 (s, 6H, Si(1)CH₃), 0.59 (s, 6H, FcSiCH₃), 1.08 (m, 2H, CH₂Si), 1.52 (m, 2H, BBN), 1.76 (m, 2H, BBN), 1.97 (m, 4H, BBN), 2.13 (m, 6H, BBN), 2.75 (m, 2H, C(3)H₂), 4.01 (s, 5H, Cp), 4.10 (m, 2H, H^{2,5}), 4.20 (m, 2H, H^{3,4}). – ¹¹B NMR (160.5 MHz, [D₈]toluene, 23°C): δ = 89.7. – MS (ESI, 70 eV) for C₃₀H₄₅BFeSi₃ (556.6): *m/z*(%) = 574 (5) [M+H₂O]⁺, 556 (100) [M]⁺, 448 (50) [M–C₈H₁₂]⁺, 436 (95) [MH–BC₈H₁₄]⁺, 421 (4), 380 (15), 333 (5), 280 (5), 243 (30), 210 (15).

4-(9-Borabicyclo[3.3.1]non-9-yl)-5-dimethyl(ferrocenyl)silyl-1,6,6-trimethyl-1-phenyl-1,2,3,6-tetrahydro-1,6-disilapentalene (22)

The synthesis was carried out as described for **21**, starting from **12** (190 mg, 0.38 mmol) and 9-BBN (47 mg). After 24 h at r.t. and 7 h at 45°C, the reaction was complete. – ¹H NMR (500.13 MHz, CD₂Cl₂, 23°C): δ = –0.15 (s, 3H, Si(6)CH₃ *cis* to Ph), –0.03 (s, 3H, Si(6)CH₃ *trans* to Ph), 0.45 (s, 3H, Si(1)CH₃), 0.56 (s, 3H, FcSiCH₃), 0.57 (s, 3H, FcSiCH₃), 1.23 (m, 1H, C(2)HSi(1) *trans* to Ph), 1.28 (m, 1H, C(2)HSi(1) *cis* to Ph), 1.66 (m, 2H, BBN), 1.77 (m, 2H, BBN), 1.92 (m, 2H, BBN), 2.09 (m, 4H, BBN), 2.21 (m, 4H, BBN), 2.80 (m, 2H, C(3)H₂), 4.17 (s, 5H, Cp), 4.22 (m, 2H, H^{2,5}), 4.40 (m, 2H, H^{3,4}), 7.33 (m, 3H, Ph), 7.50 (m, 2H, Ph-*o*). – ¹¹B NMR (160.5 MHz, CD₂Cl₂, 23°C): δ = 88.3.

4-(9-Borabicyclo[3.3.1]non-9-yl)-5-trimethylsilyl-1-ferrocenyl-1,6,6-trimethyl-1,2,3,6-tetrahydro-1,6-disilapentalene (23)

The synthesis was carried out as described for **21**, starting from **13** (373 mg, 0.86 mmol) and 9-BBN (104 mg). After 24 h at r.t., the reaction was complete. – ¹H NMR (500.13 MHz, CD₂Cl₂, 23°C): δ = 0.26 (s, 3H, Si(6)CH₃ *cis* to Fc), 0.27 (s, 9H, Si(CH₃)₃), 0.35 (s, 3H, Si(6)CH₃ *trans* to Fc), 0.47 (s, 3H, FcSiCH₃), 1.28 (m, 1H, C(2)HSi(1) *cis* to Fc), 1.35 (m, 1H, C(2)HSi(1) *trans* to Fc), 1.66 (m, 2H, BBN), 1.75 (m, 2H, BBN), 1.91 (m, 2H, BBN), 2.09 (m, 4H, BBN), 2.18 (m, 4H, BBN), 2.80 (m, 2H, C(3)H₂), 4.13, 4.17 (m, m, 1H, 1H, H^{2,5}), 4.17 (s, 5H, Cp), 4.37, 4.39 (m, m, 1H, 1H, H^{3,4}). – ¹¹B NMR (160.5 MHz, CD₂Cl₂, 23°C): δ = 86.4.

4-(9-Borabicyclo[3.3.1]non-9-yl)-5-triphenylsilyl-1-ferrocenyl-1,6,6-trimethyl-1,2,3,6-tetrahydro-1,6-disilapentalene (24)

The synthesis was carried out as described for **21**, starting from **14** (150 mg, 0.24 mmol) and 9-BBN (30 mg). After 20 h at 50°C, the reaction was complete. – ¹H NMR (500.13 MHz, CD₂Cl₂, 23°C): δ = –0.29 (s, 3H, Si(6)CH₃), –0.22

(s, 3H, Si(6)CH₃), 0.39 (s, 3H, FcSiCH₃), 1.01 (m, 2H, BBN), (m, 6H, BBN, C(2)H₂Si), 1.54 (m, 8H, BBN), 2.74 (m, 2H, C(3)H₂), 4.09 (m, 2H, H^{2,5}), 4.10 (s, 5H, Cp), 4.31, 4.33 (m, m, 1H, 1H, H^{3,4}), 7.31 (m, 6H, Ph-*m*), 7.35 (m, 3H, Ph-*p*), 7.60 (m, 6H, Ph-*o*). – ¹¹B NMR (160.5 MHz, CD₂Cl₂, 23°C): δ = 88.1.

4-(9-Borabicyclo[3.3.1]non-9-yl)-1-ferrocenyl-1,6,6-trimethyl-1,2,3,6-tetrahydro-disilapentalene (25) and 4,5-bis(9-borabicyclo[3.3.1]non-9-yl)-1-ferrocenyl-1,6,6-trimethyl-1,2,3,4,5,6-hexahydro-1,6-disilapentalenes 26 and 26'

To a solution of **7b** (162 mg, 0.45 mmol) in CD₂Cl₂ (0.6 mL) the equimolar amount of 9-BBN (55 mg) was added in one portion. The progress of the reaction was monitored by ²⁹Si NMR spectroscopy. After 24 h at r. t. and 4 h at 45°C, the reaction mixture contained **25** (ca. 90%) and **26/26'** (ca. 10%). The second equimolar amount of 9-BBN was added to the reaction mixture. After 2 h at 45°C, the reaction mixture contained **26/26'** (ca. 95%).

25: ¹H NMR (399.8 MHz, CD₂Cl₂, 23°C): δ = 0.21 (s, 3H, Si(6)CH₃ *cis* to Fc), 0.27 (s, 3H, Si(6)CH₃ *trans* to Fc), 0.44 (s, 3H, FcSiCH₃), 1.22 (m, 1H, C(2)HSi), 1.30 (m, 1H, C(2)HSi), 1.65–2.05 (m, 14H, BBN), 2.89 (m, 2H, C(3)H₂), 4.12, 4.14 (m, m, 1H, 1H, H^{2,5}), 4.16 (s, 5H, Cp), 4.35, 4.37 (m, m, 1H, 1H, H^{3,4}), 7.0 (s, 1H, =CHSi(6)), ²J(²⁹Si, ¹H) = 14.4 Hz, ¹J(¹³C, ¹H) = 152.5 Hz). – ¹¹B NMR (160.5 MHz, CD₂Cl₂, 23°C): δ = 88.1.

26 + 26': ¹H NMR (399.8 MHz, CD₂Cl₂, 23°C): δ = 0.59 (**26**: s, 3H, Si(6)CH₃ *cis* to Fc), 0.17 (**26'**: s, 3H, Si(6)CH₃ *trans* to Fc), 0.28 (**26'**: s, 3H, Si(6)CH₃ *cis* to Fc), 0.29 (**26**: s, 3H, Si(6)CH₃ *trans* to Fc), 0.37 (**26**: s, 3H, FcSiCH₃), 0.41 (**26'**: s, 3H, FcSiCH₃), 1.16, 1.17 (m, m, 2H, 2H, C(2)H₂Si), 1.39 (m, 2H, BBN), 1.48 (m, 2H, BBN), 1.57 (m, 2H, BBN), 1.65, 1.68 (m, m, 1H, 1H, C(5)HSi), 1.70–2.00 (m, 50H, BBN), 2.52 (m, 4H, C(3)H₂), 2.36 (m, 2H, C(4)H), 4.06, 4.08, 4.09, 4.12 (m, m, m, m, 1H, 1H, 1H, 1H, H^{2,5}), 4.12, 4.13 (s, s, 5H, 5H, Cp), 4.32, 4.34 (m, m, 2H, 2H, H^{3,4}). – ¹¹B NMR (160.5 MHz, CD₂Cl₂, 23°C): δ = 81.4, 88.0.

4-(9-Borabicyclo[3.3.1]non-9-yl)-5-dimethyl[dimethyl(ferrocenyl)silylethynyl]silyl-6,6-dimethyl-1,1-diphenyl-1,2,3,6-tetrahydro-1,6-disilapentalene (27) and 4-(9-borabicyclo[3.3.1]non-9-yl)-5-dimethyl(ferrocenyl)silyl-1,1-diphenyl-6,6,7,7-tetramethyl-2,3,6,7-tetrahydro-1H-1,6,7-trisilacyclopenta[a]pentalene (28)

To a solution of **18** (413 mg, 0.64 mmol) in C₆D₆ (0.6 mL) the equimolar amount of 9-BBN (55 mg) was added in one portion. The progress of the reaction was monitored by ²⁹Si NMR spectroscopy. After 3 h at 60°C, the reaction mixture contained **27** (ca. 85%) together with several unidentified side products (ca. 15%). After 20 h at 95°C, the reaction mixture contained **28** (ca. 85%) together with several unidentified side products (ca. 15%).

27: ¹H NMR (500.13 MHz, [D₈]toluene, 23°C): δ = 0.38 (s, 6H, SiCH₃), 0.42 (s, 6H, SiCH₃), 0.49 (s, 6H, SiCH₃), 1.09 (m, 2H, C(2)H₂Si), 1.45–2.25 (m, 14H, BBN), 2.88 (m, 2H, C(3)H₂), 4.08 (s, 5H, Cp), 4.11 (m, 2H, H^{2,5}), 4.16 (m, 2H, H^{3,4}), 7.18 (m, 6H, Ph), 7.57 (m, 4H, Ph). – ¹¹B NMR (160.5 MHz, CD₂Cl₂, 23°C): δ = 86.7.

28: ¹H NMR (399.8 MHz, CD₂Cl₂, 23°C): δ = –0.18 (s, 6H, Si(6)CH₃), 0.08 (s, 6H, Si(7)CH₃), 0.61 (s, 6H, FcSiCH₃), 0.90 (m, 2H, C(2)H₂Si), 1.29 (m, 2H, BBN), 1.51 (m, 2H, BBN), 1.68 (m, 2H, BBN), 2.06 (m, 8H, BBN), 2.73 (m, 2H, C(3)H₂), 4.14 (s, 5H, Cp), 4.22 (m, 2H, H^{2,5}), 4.40 (m, 2H, H^{3,4}), 7.34 (m, 6H, Ph), 7.50 (m, 4H, Ph). – ¹¹B NMR (160.5 MHz, CD₂Cl₂, 23°C): δ = 86.2.

Crystal structure determination of **21**

The structure solutions and refinement was carried out with the program package SHELXTL-PLUS V.5.1 [41]. Details pertinent to the crystal structure determination are listed in Table 5. A crystal of appropriate size was sealed under argon in a Lindemann capillary, and the data collection was carried out at 293 K [42].

Acknowledgement

Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

- [1] N. S. Hosmane (Ed.), *Boron Science: New Technologies and Applications*, CRC Press, Boca Raton, FL **2011**.
- [2] H. C. Brown, M. Zaidlewicz, *Organic Syntheses via Boranes*, Vol. 2, Aldrich Chemical Co., Milwaukee, **2001**.
- [3] D. S. Matteson, *Stereodirected Synthesis with Organoboranes*, Springer, Berlin, Heidelberg, **1995**.
- [4] A. Pelter, K. Smith, H. C. Brown, *Borane Reagents*, Academic Press, New York, **1988**.
- [5] B. Wrackmeyer, *Coord. Chem. Rev.* **1995**, *145*, 125–156.
- [6] B. Wrackmeyer, *Heteroatom. Chem.* **2006**, *17*, 188–208.
- [7] G. Kehr, G. Erker, *Chem. Commun.* **2012**, *48*, 1839–1850.

- [8] B. Wrackmeyer, P. Thoma, S. Marx, G. Glatz, R. Kempe, *Z. Anorg. Allg. Chem.* **2013**, 639, 1205–1213.
- [9] B. Wrackmeyer, P. Thoma, W. Milius, *Z. Naturforsch.* **2013**, 68b, 493–502.
- [10] B. Wrackmeyer, B. H. Kenner-Hofmann, W. Milius, P. Thoma, O. L. Tok, M. Herberhold, *Eur. J. Inorg. Chem.* **2006**, 101–108.
- [11] B. Wrackmeyer, A. Pedall, W. Milius, O. L. Tok, Yu. N. Bubnov, *J. Organomet. Chem.* **2002**, 649, 232–245.
- [12] B. Wrackmeyer, P. Thoma, S. Marx, T. Bauer, R. Kempe, *Eur. J. Inorg. Chem.* **2014**, 2103–2112.
- [13] R. Köster, G. Seidel, J. Süß, B. Wrackmeyer, *Chem. Ber.* **1993**, 126, 1107–1114.
- [14] R. Liedtke, M. Harhausen, R. Fröhlich, G. Kehr, G. Erker, *Org. Lett.* **2012**, 14, 1448–1451.
- [15] R. L. Melen, *Chem. Commun.* **2014**, 50, 1161–1174.
- [16] G. Fang, G. Kehr, G. D. Constantin, G. Erker, *J. Am. Chem. Soc.* **2014**, 136, 68–71.
- [17] B. Wrackmeyer, W. Milius, E. V. Klimkina, Yu. N. Bubnov, *Chem. Eur. J.* **2001**, 7, 775–782.
- [18] B. Wrackmeyer, E. Khan, R. Kempe, *Appl. Organomet. Chem.* **2008**, 22, 383–388.
- [19] E. Khan, B. Wrackmeyer, R. Kempe, *Eur. J. Inorg. Chem.* **2008**, 5367–5372.
- [20] B. Wrackmeyer, O. L. Tok, E. V. Klimkina, W. Milius, *Eur. J. Inorg. Chem.* **2010**, 2276–2282.
- [21] B. Wrackmeyer, E. V. Klimkina, *Z. Naturforsch.* **2014**, 69b, 704–714.
- [22] T. K. Gar, A. A. Buyakov, A. V. Kisin, V. F. Mironov, *Zh. Obshch. Khim.* **1971**, 41, 1589–1594.
- [23] B. Wrackmeyer, E. Khan, S. Bayer, O. L. Tok, E. V. Klimkina, W. Milius, R. Kempe, *Z. Naturforsch.* **2010**, 65b, 725–744.
- [24] G. A. Morris, R. Freeman, *J. Am. Chem. Soc.* **1979**, 101, 760–761.
- [25] G. A. Morris, *J. Am. Chem. Soc.* **1980**, 102, 428–429.
- [26] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **2006**, 57, 1–49.
- [27] K. Stott, J. Keeler, Q. N. Van, A. J. Shaka, *J. Magn. Reson.* **1997**, 125, 302–324.
- [28] A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648–5652.
- [29] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 41, 785–789.
- [30] P. J. Stevens, F. J. Devlin, C. F. Chabrowski, M. J. Frisch, *J. Phys. Chem.* **1994**, 98, 11623–11627.
- [31] D. McLean, D. G. S. Chandler, *J. Chem. Phys.* **1980**, 72, 5639–5648.
- [32] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, 72, 650–654.
- [33] K. Wollinski, J. F. Hinton, P. J. Pulay, *J. Am. Chem. Soc.* **1990**, 112, 8251–8260.
- [34] T. Helgaker, M. Jaszunski, M. Pecul, *Progr. NMR Spectrosc.* **2008**, 53, 249–268.
- [35] R. H. Contreras, V. Barone, J. C. Facelli, J. E. Peralta, *Annu. Rep. NMR Spectrosc.* **2003**, 51, 167–260.
- [36] R. H. Contreras, J. R. Cheeseman, M. J. Frisch, G. E. Scuseria, *Chem. Phys. Lett.* **2003**, 375, 452–458.
- [37] E. Khan, B. Wrackmeyer, *Appl. Organomet. Chem.* **2014**, 28, 280–285.
- [38] M. Herberhold, *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1837–1839.
- [39] T. Parella, *J. Magn. Reson.* **2004**, 167, 266–272.
- [40] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, GAUSSIAN 09 (revision A.02), Gaussian, Inc., Wallingford CT (USA), **2010**.
- [41] G. M. Sheldrick, SHELXS/L-97 (release 97-2), Program for Crystal Structure Analysis, Universität Göttingen, Göttingen (Germany) **1998**.
- [42] CCDC 996894 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.