

# 1-Sila-[1]ferrocenophanes, structure and reactivity Ring-opening by reactions with boron halides

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Dedicated to Professor Hans Bock on the occasion of his 75th birthday

## Abstract

1-Sila-[1]ferrocenophanes (**1–5**) were studied with respect to their NMR spectroscopic parameters, in particular the coupling constants involving the carbon atom C(1) [ $^1J(^{13}\text{C}(1), ^{13}\text{C}(2,5))$ ,  $^1J(^{29}\text{Si}, ^{13}\text{C}(1))$  and  $^1J(^{57}\text{Fe}, ^{13}\text{C})$ ]. The disiloxane **6**, containing two 1-sila-[1]ferrocenophane units, possesses a linear Si–O–Si group, as shown by X-ray structural analysis, being different from the bent structure of the same compound that has been reported in the literature. Ring-opening reactions of the complexes **2–5** with some boron halides (PhBCl<sub>2</sub>, BCl<sub>3</sub>, BBr<sub>3</sub> and BI<sub>3</sub>) gave the ferrocene derivatives **7–12**, in which the cyclopentadienyl rings bear silyl and boryl groups, respectively. Two of these complexes (**9a** and **10**) were treated with lithium diethylamide in a 1:1 molar ratio, and in both cases selective substitution at the boron atom was observed (**13**, **14**). All products were characterised by their <sup>1</sup>H-, <sup>11</sup>B-, <sup>13</sup>C- and <sup>29</sup>Si-NMR data.

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## 1. Introduction

The severe distortion of the sandwich structure in [1]ferrocenophanes [1–3] is mirrored by their reactivity in ring-opening reactions [4–6], and also by unusual NMR parameters. For the investigation of such effects, 1-sila-[1]ferrocenophanes are particularly suited because they are readily accessible [3,4b,5a,4f], and can be stored for prolonged periods without decomposition. Our current interest in ferrocene derivatives containing heteroelements [7] prompted us to use the ring-opening reaction of 1-sila-[1]ferrocenophanes with boron halides for the synthesis of ferrocene derivatives bearing different substituents in 1,1'-positions. Although the principles of this particular ring-opening have been reported

recently for the [1]ferrocenophanes **1** and **2** [8], the general scope of the reaction with boron halides has not been explored. In the present work, we discuss the molecular structure of the disiloxane **6** containing two 1-sila-[1]ferrocenophane units, we report missing coupling constants [ $^1J(^{13}\text{C}, ^{13}\text{C})$ ,  $^nJ(^{29}\text{Si}, ^{13}\text{C})$  ( $n = 1, 2, 3$ ) and  $^1J(^{57}\text{Fe}, ^{13}\text{C})$ ] for some of the 1-sila-[1]ferrocenophanes **1–5** (Scheme 1), and we describe the reactions of **2–5** with some boron halides (BX<sub>3</sub> with X = Cl, Br, I, and PhBCl<sub>2</sub>) together with first attempts to make use of the ring-opened products.

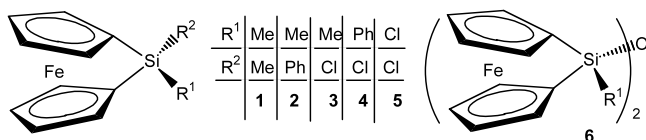
## 2. Results and discussion

### 2.1. Measurement of coupling constants for rare spin-1/2 nuclei in the 1-sila-[1]ferrocenophanes **1–5**

Although <sup>1</sup>H-, <sup>13</sup>C-, <sup>29</sup>Si- [9] and even <sup>57</sup>Fe-NMR data [10] of 1-sila-[1]ferrocenophanes have been reported,

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Scheme 1. 1-Sila-[1]ferrocenophanes studied by NMR spectroscopy, X-ray crystallography (6), and by ring-opening reactions (2–5) with boron halides.

coupling constants involving  $^{13}\text{C}$  such as  $^1J(^{13}\text{C}, ^{13}\text{C})$ ,  $^nJ(^{29}\text{Si}, ^{13}\text{C})$  ( $n = 1, 2, 3$ ) and  $^1J(^{57}\text{Fe}, ^{13}\text{C})$  are completely missing in the literature. These data are of interest with regard to the unusual bonding situation of the carbon atom C(1), as shown for example by the marked shift of the  $^{13}\text{C}(1)$  resonance to low frequencies, typical of [1]ferrocenophanes. In routine  $^{13}\text{C}$ -NMR spectra, the  $^{29}\text{Si}$  satellites belonging to the  $^{13}\text{C}(1)$  resonance are difficult to detect, since these  $^{13}\text{C}$  nuclei possess long relaxation times and usually give rise to notoriously weak signals. However, application of the refocused INEPT pulse sequence [11], based on coupling constants  $^nJ(^{13}\text{C}(1), ^1\text{H})$  ( $n = 2, 3$ ), permits to overcome signal-to-noise problems, as has been suggested for other ferrocene and metallocene derivatives [12]. Thus, various coupling constants can be determined, including  $^1J(^{13}\text{C}, ^{13}\text{C})$ , within reasonable time (see Fig. 1 and Table 1). The refocused INEPT pulse sequence, based on  $^1J(^{13}\text{C}, ^1\text{H})$  can also be successfully applied to enhance the intensities of the  $^{13}\text{C}(2, 3, 4, 5)$  NMR signals in order to facilitate the detection of satellites (see Fig. 2).

In contrast to  $^1J(^{13}\text{C}(2), ^{13}\text{C}(3))$ , the magnitude of the coupling constants  $^1J(^{13}\text{C}(1), ^{13}\text{C}(2, 5))$ , determined for **1** (31.5 Hz) and **3** (32.1 Hz), is markedly reduced when compared with that of 1,1'-bis(trimethylsilyl)ferrocene [13] (36.3 Hz). In the case of **3**, all ring  $^{13}\text{C}$  resonances are different, and the magnitude of  $^1J(^{13}\text{C}(3), ^{13}\text{C}(4))$  could also be measured (46.0 Hz) which is almost identical with that of  $^1J(^{13}\text{C}(2), ^{13}\text{C}(3))$  (45.0 Hz) and  $^1J(^{13}\text{C}(4), ^{13}\text{C}(5))$  (45.2 Hz). Since the magnitude of  $^1J(^{29}\text{Si}, ^{13}\text{C}(1))$  (57.8 Hz) in **1** is also much smaller than in 1,1'-bis(trimethylsilyl)ferrocene [13] (73.6 Hz), the electron distribution around C(1) must be similar to that of  $\text{sp}^3$  hybridised carbon atoms. This is in agreement with the chemical shifts,  $\delta^{13}\text{C}(1)$ , and suggests a rather different bonding situation for C(1) when compared with the other carbon atoms of the cyclopentadienyl ring. On the other hand, the fact that the magnitude of  $^1J(^{57}\text{Fe}, ^{13}\text{C}(1))$  in 1-sila-[1]ferrocenophanes is not significantly different from that of  $^1J(^{57}\text{Fe}, ^{13}\text{C}(2, 3, 4, 5))$  or of  $^1J(^{57}\text{Fe}, ^{13}\text{C})$  in unstrained ferrocene derivatives [13, 14] seems to indicate that the nature of Fe–C(1) bonding has not changed much. However, this assumption is only valid if the sign of  $^1J(^{57}\text{Fe}, ^{13}\text{C}(1))$  in [1]ferrocenophanes is the same as in other ferrocenes, and experimental evidence on this respect is not available as yet. There is also the possibility of a compensation of counteracting influences, considering the complex relationship between magnitude and sign of coupling constants and the electronic structure, in particular if transition metal nuclei are involved.

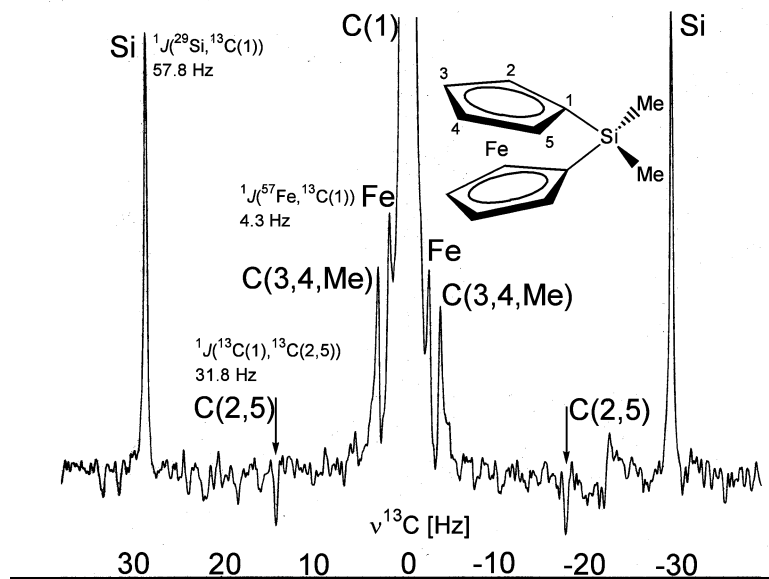


Fig. 1. 62.9 MHz  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of  $\text{Fe}(\text{C}_5\text{H}_4)_2[\text{SiMe}_2]$  (**1**)  $\text{CDCl}_3$  (ca. 5%), showing the  $^{13}\text{C}(1)$  resonance, recorded by using the refocused INEPT pulse sequence [11], based on  $^{2,3}J(^{13}\text{C}, ^1\text{H}) = 7.5$  Hz (result of 3000 transients; acquisition time 3.5 s; repetition time 3 s);  $^{29}\text{Si}$ ,  $^{57}\text{Fe}$  and  $^{13}\text{C}$  satellites are marked. Distortion of phase and wrong intensities for the  $^{13}\text{C}$  satellites arise because the effects of homonuclear decoupling are not refocused in the INEPT pulse sequence.

Table 1  
 $^{13}\text{C}$ - and  $^{29}\text{Si}$ -NMR data <sup>a</sup> of 1-sila-[1]ferrocenophanes (**1–5**) and of two 1,1'-bis(silyl)ferrocenes for comparison

Compound	$\delta^{13}\text{C}(1)$	$\delta^{13}\text{C}(2,5)$	$\delta^{13}\text{C}(3,4)$	$\delta^{13}\text{C}(\text{SiR})$	$\delta^{29}\text{Si}$
(1) $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{SiMe}_2$	32.9 [57.8] {4.3} 31.8	74.9 {5.0}	77.0 {3.9}	−3.5 [56.0]	−4.7
(2) $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{Si}(\text{Ph})\text{Me}$	32.1 [50.6] {4.4} 33.9	75.9, 76.0 {5.2} {5.2}	77.9, 78.0 {4.0} {4.0}	−2.5 [56.4] 135.7 [73.7] (i), 134.4 (o), 128.8 (m), 131.5 (p)	−7.7
(3) $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{Si}(\text{Cl})\text{Me}$	33.2 [73.4] {3.5}	73.3, 75.4 [8.7] {5.4} {4.8}	78.0, 78.3 {5.4} {4.8}	0.1 [62.3]	5.6
(4) $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{Si}(\text{Cl})\text{Ph}$	32.4 [77.0] {4.4}	74.6, 76.1 [8.2] [8.5] {4.9} {5.0}	78.2, 78.7 {5.4} {4.7}	132.1 (i), 133.9 (o), 128.5 (m), 131.9 (p)	− 13.9
(5) $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{SiCl}_2$	36.1 [99.1] {3.9}	74.8 [8.6] {4.9}	79.5 [6.7] {3.6}	−	−4.8
(6) $\{\text{Fe}(\text{C}_5\text{H}_4)_2\text{Si}(\text{Me})\}_2\text{O}$	38.4	74.0, 75.5	77.3, 77.9	−0.7	−
$\text{Fe}(\text{C}_5\text{H}_4-\text{SiMe}_3)_2$ <sup>b</sup>	72.7 [73.6]	73.3 [5.5] {4.8}	71.2 [4.4] { <sup>c</sup> }	0.2 [52.6]	−4.0
$\text{Fe}[\text{C}_5\text{H}_4-\text{Si}(\text{Cl})\text{Me}_2]_2$	69.0 [83.1] {5.2}	73.1 [6.7] {4.2}	72.3 {5.2}	2.7 [60.3]	23.2

<sup>a</sup> At  $23 \pm 1$  °C; coupling constants  $J(^{29}\text{Si}, ^{13}\text{C})$  in brackets, and  $^1J(^{57}\text{Fe}, ^{13}\text{C})$  in braces (all  $\pm 0.2$  Hz).

<sup>b</sup> Ref. [13], in  $[d_6]$ acetone;  $^1J(^{13}\text{C}(1), ^{13}\text{C}(2,5)) = 36.3$  Hz;  $^1J(^{13}\text{C}(2,5), ^{13}\text{C}(3,4)) = 44.8$  Hz.

<sup>c</sup> Ref. [13];  $^{57}\text{Fe}$  satellites overlap with  $^{29}\text{Si}$  satellites.

## 2.2. Formation and molecular structure of the disiloxane **6**

Hydrolysis of **3** under mild conditions with traces of water in chloroform gives in low yield the disiloxane **6**, in which the [1]ferrocenophane rings are still present. The formation of compound **6** in trace quantities has also been reported to take place in hexane solutions of **3**, and its molecular structure has been determined [15]. The complex isolated from hexane solutions shows a

bent arrangement of the Si–O–Si handle (angle Si–O–Si  $143.25(12)^\circ$ ). In contrast, the X-ray structural analysis carried out for crystals of **6**, isolated from solutions of **3** in chloroform, revealed a structure with a linear Si–O–Si unit as shown in Fig. 3. Being aware of the bent Si–O–Si bridge in **6** when it was crystallised from hexane and the data set was measured at low temperature, we solved and refined the crystal structure of our sample of **6** very carefully. However, there have been no hints pointing to a nonlinear Si–O–Si unit. The systematic

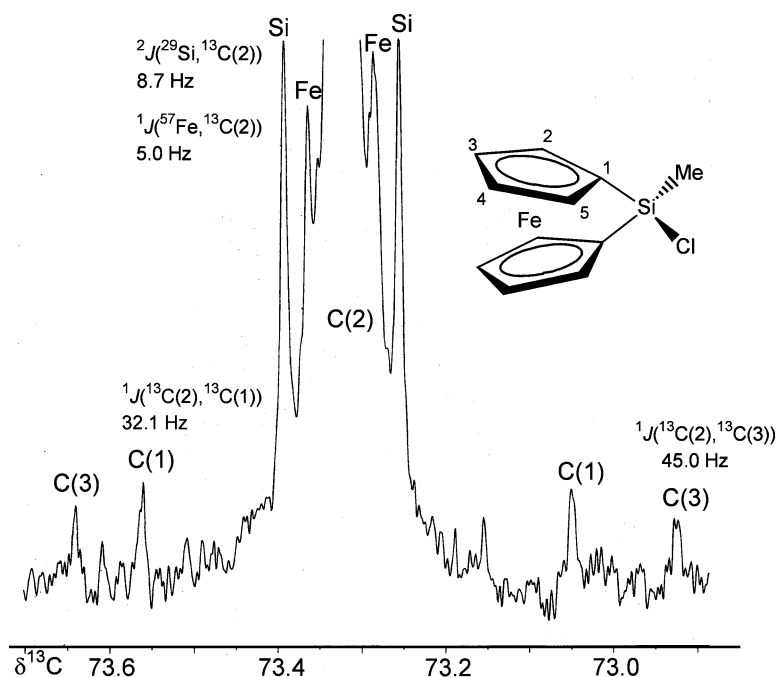


Fig. 2. 62.9 MHz  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of  $\text{Fe}(\text{C}_5\text{H}_4)_2[\text{Si}(\text{Cl})\text{Me}]$  (**3**) in  $\text{CDCl}_3$  (ca. 5%), showing the  $^{13}\text{C}(2)$  resonance, recorded by using the refocused INEPT pulse sequence [11], based on  $^1J(^{13}\text{C}, ^1\text{H}) = 175$  Hz (result of 3000 transients; acquisition time 3.5 s; repetition time 3 s);  $^{29}\text{Si}$ ,  $^{57}\text{Fe}$  and  $^{13}\text{C}$  satellites are marked.

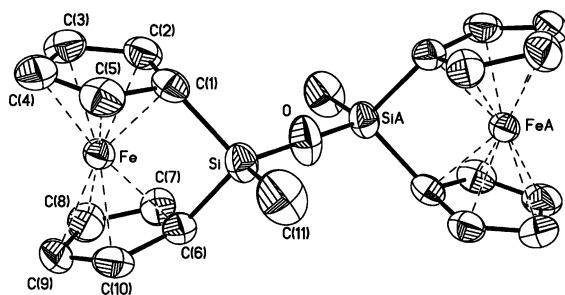


Fig. 3. ORTEP plot (50% probability; hydrogen atoms are omitted for clarity) of the molecular structure of the siloxane **6** (see Table 2).

extinctions reveal clearly the orthorhombic space group *Pccn*. The comparison with the published space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* [15] indicates that our sample is a completely different modification of **6**.

Important structural features of **6** are collected in Table 2 in order to compare with corresponding data of the isomer with the bent structure [15]. Most geometrical parameters concerning the [1]ferrocenophane units are similar for the two different crystalline phases of **6** except of the angle Si–O–Si. It is well known that this bond angle is very sensitive to subtle effects [16,17]. However, this appears to be the first case of a single disiloxane in which structural analyses have revealed a substantial difference in the bond angle Si–O–Si. A distantly related case concerns the molecular structures of diastereomers with bond angles Si–O–Si of 180 and 172.8(2)° [18]. The variation in the bond angle Si–O–Si has been the subject of numerous experimental and theoretical studies [19,20]. The present findings emphasize once more the extreme sensitivity of this parameter to apparently subtle, unintentional influences.

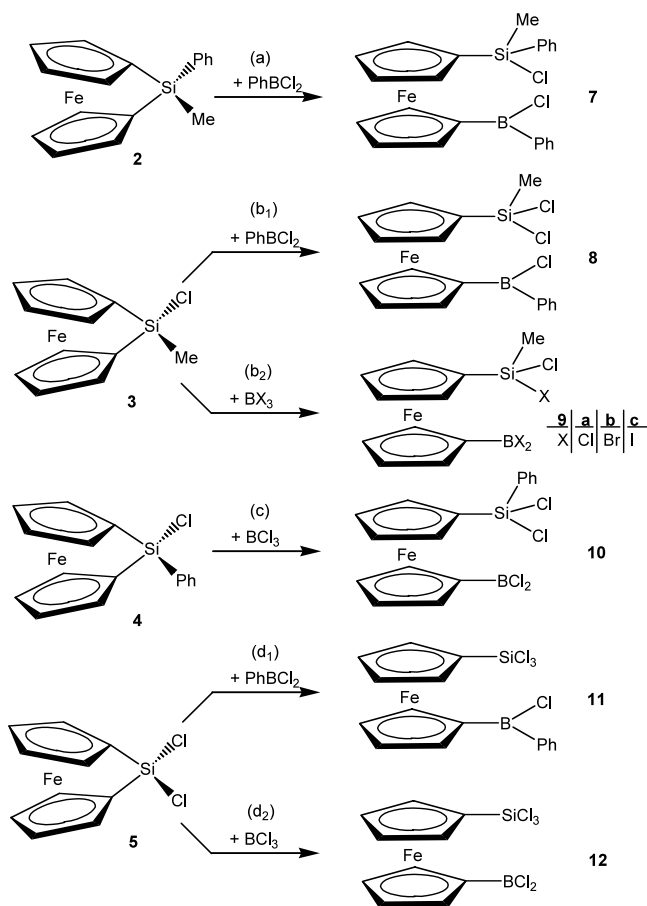
Table 2  
Selected geometrical data of the disiloxane **6** with linear and bent structure<sup>a</sup>

	Bond lengths (pm) (linear Si–O–Si)	Bond lengths (pm) (bent Si–O–Si)	Bond angles (°) (linear Si–O–Si)	Bond angles (°) (bent Si–O–Si)	
Si–O	160.59(11)	163.08(18) 163.77(19)	180	143.25(12)	Si–O–Si
Si–C(Me)	184.7(4)	185.1(3) 184.7(3)	95.78(17)	96.82(11)	C(1)–Si–C(6)
Si–C(1,6)(fc)	186.9(4)	188.2(3)	111.78(13)	111.18(11)	O–Si–C(1)
Fe–C(1,6))	186.2(4) 200.5(4) 200.2(4)	188.5(3) 201.0(2) 201.6(2)	109.47(14) 21.5	111.21(11) 19.7, 20.2	O–Si–C(6) $\alpha^b$
			35.5 (at C(1)) 32.6 (at C(6))	Not given	$\beta^c$

<sup>a</sup> Data for the bent structure taken from Ref. [15]; data collected at 173 K.

<sup>b</sup> The angle  $\alpha$  describes the angle between the least-square planes of the cyclopentadienyl rings.

<sup>c</sup> The angle  $\beta$  describes the deviation of the C(1)–Si and C(6)–Si bond vectors from the respective cyclopentadienyl ring plane.



Scheme 2. Ring-opening reactions of the 1-sila-[1]ferrocenophanes (**2**–**6**) with some boron halides.

### 2.3. Reactions of the 1-sila-[1]ferrocenophanes **2**–**5** with boron halides

The results of the ring-opening reactions are summarised in Scheme 2. The reactions proceed smoothly

under mild conditions, and afford the pure products **7–12** in quantitative yield. In the case of  $\text{BBr}_3$  and  $\text{BI}_3$  (Scheme 2, b<sub>2</sub>), cooling to  $-78^\circ\text{C}$  is required before the boron halides are added in order to suppress side reactions. In all cases studied,  $^{11}\text{B}$ - and  $^{29}\text{Si}$ -NMR spectra of the reaction solutions give the desired information on the progress of the reactions and on the number of products. The compounds **7–12** are extremely sensitive towards traces of moisture. However, they could be characterised by the consistent set of  $^1\text{H}$ - (experimental),  $^{11}\text{B}$ -,  $^{13}\text{C}$ -, and  $^{29}\text{Si}$ -NMR data (Table 3). Typically, the presence of a chiral centre gives rise to eight  $^{13}\text{C}$ H signals of the cyclopentadienyl rings (Fig. 4). In some cases (e.g. **9a,c**), the assignments in Table 3 were confirmed by 2D  $^1\text{H}/^1\text{H}$  NOESY experiments [21] which indicate the spatial proximity of the  $^1\text{H}^{2,5}$  nuclei to the organic substituent at silicon.

#### 2.4. Substitution of a B–Cl function in **9a** and **10** by the diethylamino group

Further use of the ring-opened products such as **7–12** depends a great deal on the functional groups at the boron atom. In the cases of **9**, **10** or **12**, the replacement of one of the B–Cl functions by a B-dialkylamino function is desirable, since the stabilising effect of the amino group is expected to help later on in selective reactions of the remaining B–Cl function. Considering the presence of Si–Cl functions in these molecules, one

aspect of further transformations concerns the synthesis of [*n*]ferrocenophanes ( $n \geq 2$ ). Therefore, we have studied the reaction of both **9a** and **10** with lithium diethylamide. As shown in Scheme 3 and by the NMR data in Table 3, this reaction leads selectively to the compounds **13** and **14**, in which the Si–Cl bonds are unchanged. The  $^{13}\text{C}$ -NMR data of the  $\text{NEt}_2$  group indicates that there is restricted rotation about the B–N bond as in many other aminoboranes [22].

### 3. Conclusions

The relatively small magnitude of the coupling constants  $^1J(^{29}\text{Si}, ^{13}\text{C}(1))$  and  $^1J(^{13}\text{C}(1)\text{C}(2))$  in 1-sila-[1]ferrocenophanes such as **1–5** mirrors the changes in the bonding situation for carbon atom C(1) when compared with the other cyclopentadienyl carbon atoms. The molecular structure of the disiloxane **6** in the solid state appears to be affected by extremely subtle influences such as the solvent from which the crystals are grown. It appears that all boron halides can be used for ring-opening reactions with 1-sila-[1]ferrocenophanes bearing alkyl-, aryl- or chloro-substituents at silicon. The 1-silyl-1'-boryl-substituted ferrocenes **7–12** invite for further transformations, and in this context the selective substitution of one B–Cl against a B– $\text{NEt}_2$  function was demonstrated in the cases of **13** and **14**.

Table 3  
 $^{11}\text{B}$ -,  $^{13}\text{C}$ - and  $^{29}\text{Si}$ -NMR data <sup>a</sup> of the 1-silyl-1'-boryl-ferrocenes (**7–14**)

Compound $\text{Fe}(\text{C}_5\text{H}_4\text{-R})(\text{C}_5\text{H}_4\text{-R}')$	$\delta^{13}\text{C}(1)$	$\delta^{13}\text{C}(2,5)$	$\delta^{13}\text{C}(3,4)$	$\delta^{13}\text{C}(\text{SiR})$ (BPh)	$\delta^{29}\text{Si}$	$\delta^{11}\text{B}$
( <b>7</b> ) R = Si(Me)(Ph)Cl R' = B(Ph)Cl	69.3 n.m. (br)	74.6, 74.8 76.1, 76.6	73.7, 73.8 77.1, 77.2	0.5 <sup>b</sup>	13.3	55.4
( <b>8</b> ) R = Si(Me)Cl <sub>2</sub> R' = B(Ph)Cl	68.6 [100.6] n.m. (br)	74.5 77.6	74.6 77.8	6.0 [72.9] 136.2 (i), 136.8 (o), 128.1 (m), 135.1 (p)	18.0	55.4
( <b>9a</b> ) R = Si(Me)Cl <sub>2</sub> R' = BCl <sub>2</sub>	68.2 [99.6] 69.9 (br) <sup>c</sup>	74.96 [8.1] 76.8	74.98 78.1	6.5 [72.8]	22.2	51.4
( <b>9b</b> ) R = Si(Me)(Cl)Br R' = BBr <sub>2</sub>	70.4 69.7 (br) <sup>c</sup>	75.3, 75.4 77.8, 77.9	75.8, 75.8 79.3, 79.3	8.2 [70.1]	16.9	49.1
( <b>9c</b> ) R = Si(Me)(Cl)I R' = BI <sub>2</sub>	72.0 68.2 (br) <sup>c</sup>	75.5, 75.8 79.6, 79.7	76.7, 76.8 80.6, 80.6	10.8 [66.5]	−4.2	29.8
( <b>10</b> ) R = Si(Ph)Cl <sub>2</sub> R = BCl <sub>2</sub>	68.9 n.m. (br)	75.2 76.9	75.5 78.4	132.9 (i), 132.3 (o), 128.3 (m), 131.7 (p)	10.3	52.0
( <b>11</b> ) R = SiCl <sub>3</sub> R' = B(Ph)Cl	69.8 n.m. (br)	74.6 77.9	75.0 78.2	136.2 (i), 136.7 (o), 128.1 (m), 134.9 (p)	2.2	54.6
( <b>12</b> ) R = SiCl <sub>3</sub> R' = BCl <sub>2</sub>	68.2 [127.8] 69.8 (br) <sup>c</sup>	75.0 [10.1] 77.3	75.5 [7.3] 78.6	–	2.0	52.6
( <b>13</b> ) R = Si(Me)Cl <sub>2</sub> R' = B(NEt <sub>2</sub> )Cl	66.9 [101.8] 68.5 (br) <sup>c</sup>	73.2 73.9	73.7 75.9	8.5 [72.8] 43.5, 44.2; 15.0, 15.6	22.5	36.5
( <b>14</b> ) R = Si(Ph)Cl <sub>2</sub> R' = B(NEt <sub>2</sub> )Cl	65.7 n.m. (br)	73.5 74.4	74.1 76.3	133.7 (i), 133.4 (o), 128.2 (m), 131.4 (p) 43.5, 44.2, 15.2, 15.8	11.0	36.4

<sup>a</sup> At  $23 \pm 1^\circ\text{C}$ ; coupling constants  $J(^{29}\text{Si}, ^{13}\text{C})$  in brackets ( $\pm 0.2$  Hz); n.m., not measured; (br) denotes the broad  $^{13}\text{C}$ -NMR signal of a carbon atom linked to boron [25].

<sup>b</sup>  $^{13}\text{C}$  (SiPh, BPh) = 127.5, 127.6, 131.5, 130.6, 132.9, 134.3, 135.2, 135.0 (without assignment).

<sup>c</sup> Measured at 235 K.

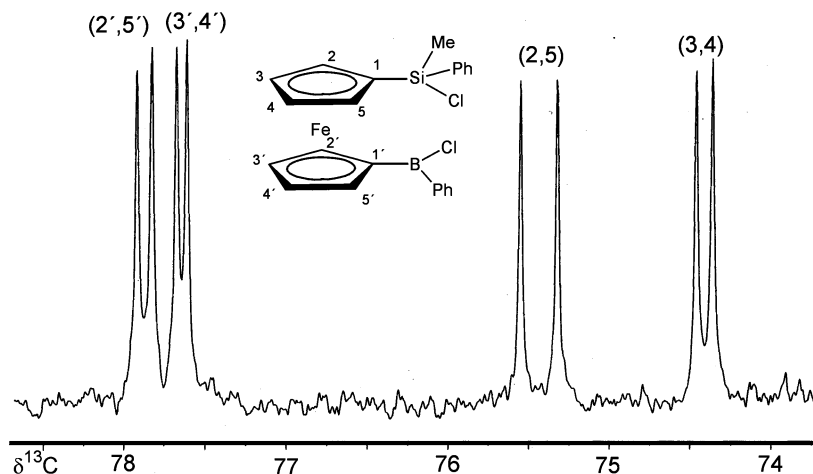
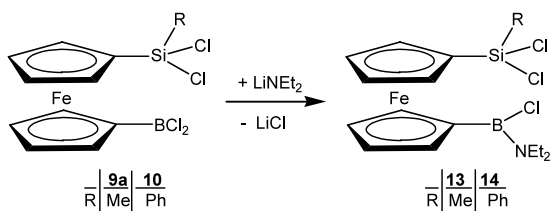


Fig. 4. 62.9 MHz  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the ring-opened product **7**, showing the range of the  $^{13}\text{C}$ (cyclopentadienyl) resonances. The silicon is a chiral centre, and therefore, all  $^{13}\text{C}$ H signals are different.



Scheme 3. Reactions of the 1-silyl-1'-dichloroboryl-ferrocenes **9a** and **10** with lithium diethylamide.

## 4. Experimental

### 4.1. General

All preparative work and handling of the compounds were carried out in an atmosphere of argon, using oven-dried glassware, and carefully dried solvents (hexane and toluene). The 1-sila-[1]ferrocenophanes **1–3** and **5** [3,4b,5a,4f] were prepared by literature methods, using dilithiated ferrocene  $\text{fcLi}_2(\text{tmeda})$  [23]. The chlorosilanes, ferrocene, butyl lithium (1.6 M in hexane), and the boron halides were used as commercial products without further purification.

NMR spectra ( $^1\text{H}$ -,  $^{11}\text{B}$ -,  $^{13}\text{C}$ -,  $^{29}\text{Si}$ -NMR): Bruker ARX 250 spectrometer; pulse lengths for the INEPT experiments [11,24] ( $^{13}\text{C}$ - and  $^{29}\text{Si}$ -NMR) were carefully calibrated, and the decoupler power and offset were optimised in order to achieve signals as sharp as possible and to avoid dielectric heating of the samples. The careful preparation of the samples for these experiments was controlled by observing highly resolved  $^1\text{H}$ -NMR spectra. This guaranteed the best results in  $^{13}\text{C}$ -NMR spectra using INEPT experiments. Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet; the  $m/z$  data refer to the isotopes  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{12}\text{C}$ ,  $^{28}\text{Si}$ ,  $^{56}\text{Fe}$ . Melting points (m.p.) (uncorrected): Büchi 510 melting point apparatus.

### 4.2. 1,1-Chloro(phenyl)-1-sila-[1]ferrocenophane (**4**)

Trichloro(phenyl)silane (1.5 ml, 9.4 mmol), dissolved in hexane (50 ml) was added dropwise at  $-78^\circ\text{C}$  to a suspension of  $\text{fcLi}_2(\text{tmeda})$  (2.7 g, 8.6 mmol) in hexane (100 ml). The reaction mixture was kept stirring for 12 h, then  $\text{Na}_2\text{SO}_4$  (3 g) was added, and all insoluble material was filtered off. The solvent was almost completely removed in vacuo, the remaining concentrated solution was cooled to  $-80^\circ\text{C}$ , and **4** precipitated as an orange crystalline product (1.8 g; 66%; m.p.  $79^\circ\text{C}$ ):  $^1\text{H}$ -NMR (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 3.83, 4.36, 4.43, 4.47$  (all m, 8H,  $\text{C}_5\text{H}_4$ ), 7.17–7.26, 7.97–8.0 (m, m, 3H, 2H, SiPh).

### 4.3. Isolation of the disiloxane derivative **6**

Hydrolysis of 0.05 g (0.1 mmol)  $\text{fc}[\text{SiMeCl}]$  **3** in  $\text{CHCl}_3$  (5 ml) containing traces of water gave, after partial slow evaporation of the solvent and storage for several days at  $-30^\circ\text{C}$ , a red crystalline product in a low yield, m.p.  $150^\circ\text{C}$  (decomp.) **6**:  $^1\text{H}$ -NMR (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.56, 4.52, 4.32, 4.03$  (all m, 16H,  $\text{C}_5\text{H}_4$ ), 0.68 (s, 6H, SiMe).

### 4.4. Synthesis of the compounds **7–12**

#### 4.4.1. General procedure

The respective 1-sila-[1]ferrocenophane (3 mmol) was dissolved in hexane (40 ml), and the solution was added dropwise at  $0^\circ\text{C}$  to a solution of the respective boron chloride ( $\text{BCl}_3$ ,  $\text{PhBCl}_2$ ; 15 mmol) in hexane (40 ml). After stirring the reaction mixture at room temperature (r.t.) for 3 h, the volatile materials were removed in vacuo. The residue was taken up in hexane, the solution filtered over  $\text{Na}_2\text{SO}_4$ , and then hexane was removed to leave the pure ( $^1\text{H}$ -NMR: >95%) products. The compounds **9b** and **9c** were obtained in a similar way, except that  $\text{BBr}_3$  or  $\text{BI}_3$  (5 mmol) dissolved in hexane



(120 ml) were added very slowly under vigorous stirring to a cold ( $-78\text{ }^{\circ}\text{C}$ ) solution of **3** (5 mmol) in hexane (100 ml).

Compound **7**: red oil; yield 80%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.23, 4.30, 4.43, 4.69, 4.73, 4.77, 4.82$  (all m, 8H,  $\text{C}_5\text{H}_4$ ), 0.75 (s, 3H, SiMe), 7.38–7.63, 8.03–8.07 (m, m, 10H, SiPh, BPh).

Compound **8**: red oil; yield 98%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.94, 4.85, 4.51, 4.36$  (all m, 8H,  $\text{C}_5\text{H}_4$ ), 0.87 (s, 3H, SiMe), 7.49–7.73, 8.10–8.23 (m, m, 3H, 2H, BPh).

Compound **9a**: red oil; yield 93%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.85, 4.61, 4.51, 4.36$  (all m, 8H,  $\text{C}_5\text{H}_4$ ), 0.97 (s, 3H, SiMe).  $\text{C}_{11}\text{H}_{11}\text{BCl}_4\text{FeSi}$ ; EI-MS:  $m/e = 380$  [42%,  $\text{M}^+$ ].

Compound **9b**: dark red oil; yield 60%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.97, 4.62, 4.55, 4.38$  (all m, 8H,  $\text{C}_5\text{H}_4$ ), 1.12 (a, 3H, SiMe).  $\text{C}_{11}\text{H}_{11}\text{BBR}_3\text{ClFeSi}$ ; EI-MS:  $m/e = 513$  [100%,  $\text{M}^+$ ].

Compound **9c**: dark red oil; yield 66%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.65, 4.66, 4.21, 4.04, 3.98$  (all m, 8H,  $\text{C}_5\text{H}_4$ ), 0.89 (s, 3H, SiMe).  $\text{C}_{11}\text{H}_{11}\text{BClFeI}_3\text{Si}$ ; EI-MS:  $m/e = 653$  [4%,  $\text{M}^+$ ].

Compound **10**: red oil; yield 88.5%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.73, 4.60, 4.48, 4.39$  (all m, 8H,  $\text{C}_5\text{H}_4$ ), 7.38–7.49, 7.72–7.76 (m, m, 3H, 2H, SiPh).

Compound **11**: red oil; yield 97%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.80, 4.75, 4.40, 4.29$  (all m, 8H,  $\text{C}_5\text{H}_4$ ), 7.32–7.56, 7.95–8.06 (m, m, 3H, 2H, BPh).

Compound **12**: red oil; yield 89.1%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.78, 4.66, 4.57, 4.46$  (all m, 8H,  $\text{C}_5\text{H}_4$ ).

#### 4.5. Synthesis of the compounds **13**, **14**

##### 4.5.1. General procedure

A suspension of lithium diethylamide (10 mmol) in toluene (40 ml) was added dropwise at  $0\text{ }^{\circ}\text{C}$  to a solution of **9a** or **10** (10 mmol) in toluene (70 ml). The reaction mixture was kept stirring for 4 h at r.t., then  $\text{Na}_2\text{SO}_4$  (2 g) was added, and insoluble materials were filtered off. Evaporation of the toluene in vacuo left the products as viscous orange oils.

Compound **13**: yield 96.5%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.47, 4.44, 4.29$  (m, m, m, 4H, 2H, 2H,  $\text{C}_5\text{H}_4$ ), 1.00 (s, 3H, SiMe), 3.27–3.39, 1.03–1.23 (m, m, 4H, 6H,  $\text{NEt}_2$ ).  $\text{C}_{15}\text{H}_{21}\text{BCl}_3\text{FeNSi}$ ; EI-MS:  $m/e = 416$  [100%,  $\text{M}^+$ ].

Compound **14**: yield 92.9%;  $^1\text{H-NMR}$  (250.1 MHz;  $\text{CDCl}_3$ ):  $\delta^1\text{H} = 4.48, 4.37$  (m, m, 5H, 3H,  $\text{C}_5\text{H}_4$ ), 7.40–7.53, 7.75–7.81 (m, m, 3H, 2H, SiPh), 3.24–3.34, 1.14–1.22 (m, m, 4H, 6H,  $\text{NEt}_2$ ).  $\text{C}_{20}\text{H}_{23}\text{BCl}_3\text{FeNSi}$ ; EI-MS:  $m/e = 478$  [100%,  $\text{M}^+$ ].

#### 4.6. Crystal structure determination of **6**

The reflection intensities were collected on a Siemens P4 diffractometer (Mo- $\text{K}_\alpha$ -radiation,  $\lambda = 71.073\text{ pm}$ , graphite monochromated). Structure solution and refinement were carried out using the program package SHELXTL-PLUS V.5.1. Measuring temperature for the structure determination was 296 K. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms are on calculated positions. All hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

Compound **6**:  $\text{C}_{22}\text{H}_{22}\text{Fe}_2\text{OSi}_2$ , a red plate with dimensions  $0.18 \times 0.15 \times 0.08\text{ mm}$  crystallised in the orthorhombic space group *Pccn* with the lattice parameters  $a = 11.2485(7)$ ,  $b = 24.1939(14)$ ,  $c = 7.2724(5)\text{ pm}$ ,  $V = 1979.1(2)\text{ } 10^6\text{ pm}^3$ ,  $Z = 4$ ,  $\mu = 1.596\text{ mm}^{-1}$ ; 2333 reflections collected in the range  $3 \leq 2\theta \leq 50^\circ$ , 1732 reflections independent, 1311 assigned as observed [ $I > 2\sigma(I)$ ], full-matrix least-squares refinement against  $F^2$  with 125 parameters converged at  $R_1/wR_2$ -values of 0.039/0.088; empirical absorption correction ( $\Psi$ -scans) resulted in min./max. transmission factors of 0.388/0.462; the max./min. residual electron density was  $0.31/-0.32\text{ } 10^{-6}\text{ e pm}^{-3}$ .

#### 5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 208088 for compound **6**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax (internat.): +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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