

# 1,3-Dibora-[3]ferrocenophanes; synthesis and characterization <sup>☆</sup>

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## Abstract

The first 1,3-dibora-2-aza-[3]ferrocenophanes (**1** and **2**) were obtained by cleavage of the Si–N bonds of heptamethyldisilazane using 1,1'-bis(dibromoboryl)ferrocene and 1,1'-bis[bromo(methyl)boryl]ferrocene respectively. Reactions between 1,1'-bis[dialkylamino(halogeno)boryl]ferrocenes and Li<sub>2</sub>E (E = O, S, Se, or Te) led to the first 1,3-dibora-2-chalcogena-[3]ferrocenophanes (**3a–3d**, and **4c**). The X-ray structure determination of 1,3-bis(diisopropylamino)-1,3-dibora-2-selena-[3]ferrocenophane (**4c**) (monoclinic; space group, *P*2<sub>1</sub>/*n*) reveals a staggered conformation and a slightly tilted arrangement (6.4°) of the cyclopentadienyl rings. The [3]ferrocenophanes were characterized by NMR spectroscopy in solution and in the solid state (**4c**: <sup>77</sup>Se CP MAS NMR).

**Keywords:** Boron; Iron; Diboraferrocenophanes; NMR, multinuclear; X-ray diffraction

## 1. Introduction

Ferrocenophanes are attractive compounds [1,2] essentially for two reasons. First, they are often found to be non-rigid systems in which the cyclopentadienyl rings and the bridge undergo coupled intramolecular movements, as shown by temperature-dependent <sup>1</sup>H NMR spectroscopy [3–5]. Second, there is a continuing search for interactions between the metallocene iron atom and external heteroelements which are part of the triatomic bridge [1,5–7]. The bridge connecting the two cyclopentadienyl rings may consist of a great variety of different elements, including both main group and transition metals [1,5,8–10]. Boron atoms in bridge positions are rare, although some 1,3-dichalcogena-2-bora-[3]ferrocenophanes, Fe(C<sub>5</sub>H<sub>4</sub>E)<sub>2</sub>BR (R = Ph, E = O [11]; R = NEt<sub>2</sub>, E = S [12], Se or Te [5]; R = alkyl, cyclohexyl, mesityl, N<sup>i</sup>Pr<sub>2</sub> or NEt<sup>i</sup>Pr, E = S [12]) have been described. However, ferrocenophanes with boron atoms linked directly to the cyclopentadienyl rings have not been prepared as yet. Such compounds are of additional interest since they contain two π systems –

at the cyclopentadienyl ring and at the boron centres – which are arranged perpendicular to each other. In the present work we report synthetic routes (Scheme 1) to the first 1,3-dibora-[3]ferrocenophanes (**1–4**) and on the characterization of 1,3-dibora-2-selena-[3]ferrocenophane (**4c**) by a single-crystal X-ray structure determination.

## 2. Results and discussion

### 2.1. Synthesis

1,1'-Bis(dibromoboryl)ferrocene (**5**) [13,14] serves as a convenient starting material for the synthesis of 1,3-dibora-[3]ferrocenophanes, as shown in Scheme 1. 1,3-Dibora-2-aza-[3]ferrocenophane (**1**) is formed directly if **5** is treated with heptamethyldisilazane. Compound **5** is also readily converted to 1,1'-bis[bromo(methyl)boryl]ferrocene (**6**) [13], and the subsequent reaction of **6** with heptamethyldisilazane affords **2**. Aminolysis of **5** with an excess of dimethylamine yields 1,1'-bis[bis(dimethylamino)boryl]ferrocene (**7**) [13] which exchanges two Me<sub>2</sub>N groups with two equivalents of BCl<sub>3</sub> to give 1,1'-bis[chloro(dimethylamino)boryl]ferrocene (**8**). Reactions between **8** and lithium chalcogenides Li<sub>2</sub>E (E = O, S, Se or Te) afford the 1,3-dibora-2-chalcogena-

<sup>☆</sup> Dedicated to Professor Peter Paetzold on the occasion of his 60th birthday

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that the different surroundings of the respective ring carbon atoms are averaged by motion of the cyclopentadienyl rings. At a lower temperature ( $-60^{\circ}\text{C}$ ), the C(2, 5) and C(3, 4) resonance signals become broader (whereas all other signals stay sharp) but the slow-exchange limit could not be reached. Chemical shifts  $\delta(^{77}\text{Se})$  are a sensitive structural probe [19], at least qualitatively with regard to structural changes. This is shown by the difference between  $\delta(^{77}\text{Se})$  of **4c** at  $-40^{\circ}\text{C}$  in solution (+4.3 ppm) and at room temperature in the solid state ( $^{77}\text{Se}$  CP MAS NMR:  $\delta = +41.1$  ppm) which also points towards structural changes in solution compared with the solid state.

The 1,1'-bis[halogeno(dialkylamino)boryl]ferrocenes **8** and **9** have not been reported previously. The  $\delta(^{11}\text{B})$  data for these compounds (**8**,  $\delta = 36.7$  ppm; **9**,  $\delta = 35.2$  ppm) are typical of three-coordinated boron atoms surrounded by Cl,N,C or Br,N,C [20], and indicate that there are no intramolecular B–N–B bridges. The same conclusion follows from the consistent set of  $^1\text{H}$  and  $^{13}\text{C}$  NMR data.

### 3. Experimental details

All compounds were prepared and handled in an inert atmosphere (Ar) by using carefully dried glass-

ware and solvents. Boron halides  $\text{BBr}_3$  and  $\text{BCl}_3$ , dialkylamine and heptamethyldisilazane were commercial products. 1,1'-Bis(dibromoboryl)ferrocene (**5**) and 1,1'-bis[bis(dimethylamino)boryl]ferrocene (**7**) were prepared according to literature procedures [13,14].

NMR spectra were measured using JEOL FX 90Q, Bruker AC 300 ( $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$  and  $^{14}\text{N}$  NMR) and JEOL EX 270 ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) spectrometers. Chemical shifts are given with respect to  $\text{Me}_4\text{Si}$  ( $\delta(^1\text{H}(\text{C}_6\text{D}_5\text{H})) = 7.15$  ppm;  $\delta(^{13}\text{C}(\text{C}_6\text{D}_6)) = 128.0$  ppm) and external  $\text{Et}_2\text{O}-\text{BF}_3$  ( $\delta(^{11}\text{B}) = 0$  ppm;  $\Xi(^{11}\text{B}) = 32.083972$  MHz); neat  $\text{CH}_3\text{NO}_2$  ( $\delta(^{14}\text{N}) = 0$  ppm;  $\Xi(^{14}\text{N}) = 7.226455$  MHz).

#### 3.1. 1,3-Dibromo-2-methyl-1,3-dibora-2-aza-[3]ferrocenophane (**1**)

A solution of 0.79 g (4.51 mmol) heptamethyldisilazane in 5 ml of toluene was added in one portion at  $-78^{\circ}\text{C}$  to a solution of 2.38 g (4.53 mmol) of 1,1'-bis(dibromoboryl)ferrocene (**5**) in 100 ml of toluene. After stirring for 12 h, all volatile material was removed in vacuo. The residue was dissolved in 100 ml of hexane and heated to reflux for 2 h. The mixture was cooled to room temperature and side products were filtered off. The filtrate was dried in vacuo to give **1** as a brown solid (yield, 1.49 g (83%); melting point (m.p.),  $125-129^{\circ}\text{C}$  (decomposition)).

Table 2

Chemical shifts  $\delta(^{11}\text{B})$  and  $\delta(^{13}\text{C})$  ( $\delta(^1\text{H})$ ) of the 1,3-dibora-2-aza-[3]ferrocenophanes (**1** and **2**) and 1,3-dibora-2-chalcogena-[3]ferrocenophanes (**3a-d** and **4c**). All data for solutions in  $\text{C}_6\text{D}_6$  (around 5–15%) at  $25^{\circ}\text{C}$ , if not stated otherwise

Compound	$\delta(^{11}\text{B})$ (ppm)	$\delta(^{13}\text{C}(1))$ <sup>a</sup> (ppm)	$\delta(^{13}\text{C}(2,5))$ (ppm)	$\delta(^{13}\text{C}(3,4))$ (ppm)	$\delta(^{13}\text{C}(\text{NMe}))$ (ppm)	$\delta(^{13}\text{C}(\text{BNR}_2))$ (ppm)
<b>1</b> <sup>b</sup>	+44.9	74.5	77.8 <sup>c</sup> (4.04)	76.3 (4.11)	39.8 (3.21)	–
<b>2</b>	+54.7	78.6	75.2 (3.91)	73.2 (4.25)	35.4 (2.81)	7.8 (BMe) (0.82)
<b>3a</b>	+30.6	71.3	73.7 (4.18)	71.3 (4.23)	–	39.1, 36.3 (2.68), (2.83)
<b>3b</b>	+41.3	75.8	75.9 (4.22)	72.2 (4.26)	–	41.3, 41.0 (2.66), (2.96)
<b>3c</b>	+42.3	77.0	76.3 (4.24)	72.2 (4.26)	–	41.3, 42.8 (2.63), (2.96)
<b>3d</b>	+43.8	NO <sup>d</sup>	77.1 (4.26)	72.1 (4.26)	–	41.1, 46.5 (2.61), (2.92)
<b>4c</b> <sup>e</sup>	+41.8	78.8	76.1 <sup>f</sup> (4.35)	72.2 (4.28)	–	52.3, 47.6 <sup>g</sup> (4.35) <sup>h</sup> , (3.48)

<sup>a</sup> The  $^{13}\text{C}(1)$  NMR signals are readily observed at low temperatures ("quadrupolar decoupling" of  $^{11}\text{B}$ ): solutions in toluene- $d_8$  measured at  $-60^{\circ}\text{C}$ .

<sup>b</sup>  $\delta(^{14}\text{N})$ ,  $-245.0$  ppm.

<sup>c</sup>  $^{13}\text{C}-^{13}\text{C}$  INADEQUATE:  $^1J(^{13}\text{C}(1), ^{13}\text{C}(2)) = 39.7$  Hz;  $^1J(^{13}\text{C}(2), ^{13}\text{C}(3)) = 46.0$  Hz.

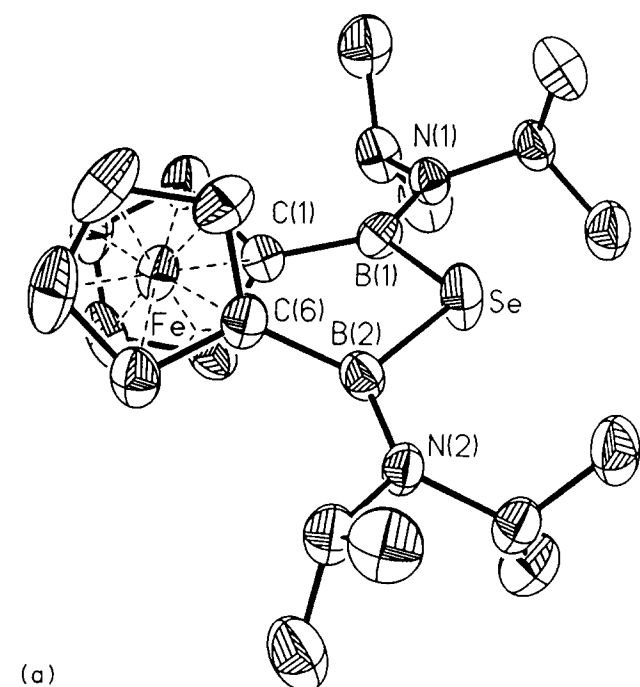
<sup>d</sup> NO, not observed.

<sup>e</sup>  $\delta(^{77}\text{Se})$  in toluene- $d_8$  at  $-40^{\circ}\text{C}$ : +4.3; in the solid state at  $25^{\circ}\text{C}$  ( $^{77}\text{Se}$  CP MAS NMR): +41.1.

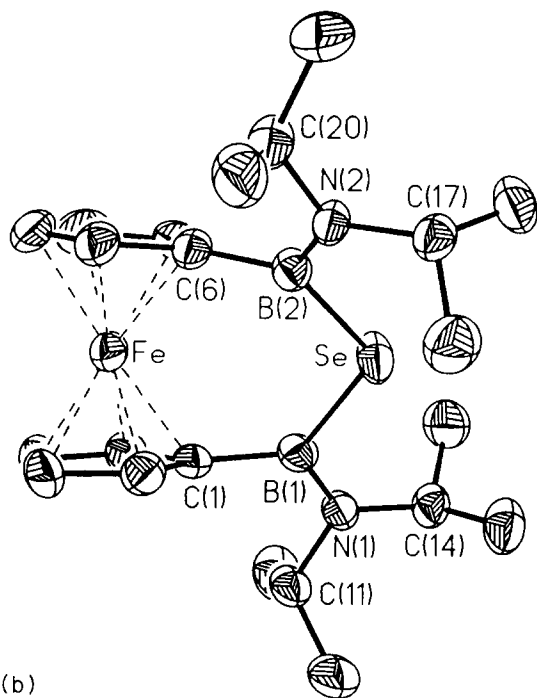
<sup>f</sup>  $^{13}\text{C}-^{13}\text{C}$  INADEQUATE:  $^1J(^{13}\text{C}(1), ^{13}\text{C}(2)) = 39.2$  Hz;  $^1J(^{13}\text{C}(2), ^{13}\text{C}(3)) = 45.3$  Hz.

<sup>g</sup>  $\delta(^{13}\text{C})$  ( $\delta(^1\text{H})$ ) values for Me groups: 24.3 (1.63), 22.4 (0.91) ppm.

<sup>h</sup> Assigned by  $^{13}\text{C}-^1\text{H}$  HETCOR.



(a)



(b)

Fig. 1. Molecular structure of 1,3-bis(diisopropylamino)-1,3-dibora-2-selena-[3]ferrocenophane (**4c**). (a) View showing the staggered conformation of the cyclopentadienyl rings. (b) View showing the orientation of the 1,3-dibora-2-selena bridge. Selected bond lengths and angles are as follows: B(1)–N(1), 139.2(6) pm; B(2)–N(2), 137.8(6) pm; Se–B(1), 199.9(4) pm; Se–B(2), 201.7(4) pm; B(1)–C(1), 157.6(6) pm; B(2)–C(6), 156.8(6) pm; C(1)–B(1)–Se, 119.8(3)°; Se–B(1)–N(1), 118.7(3)°; N(1)–B(1)–C(1), 121.4(3)°; C(6)–B(2)–Se, 116.5(3)°; Se–B(2)–N(2), 118.6(3)°; N(2)–B(2)–C(6), 124.5(4)°; B(1)–Se–B(2), 110.2(2)°; C(3)–C(2)–C(1)–B(1), 2.5°; C(8)–C(7)–C(6)–B(2), 2.4°; B(1)–C(1)–Fe/B(2)–C(6)–Fe, 36.0°.

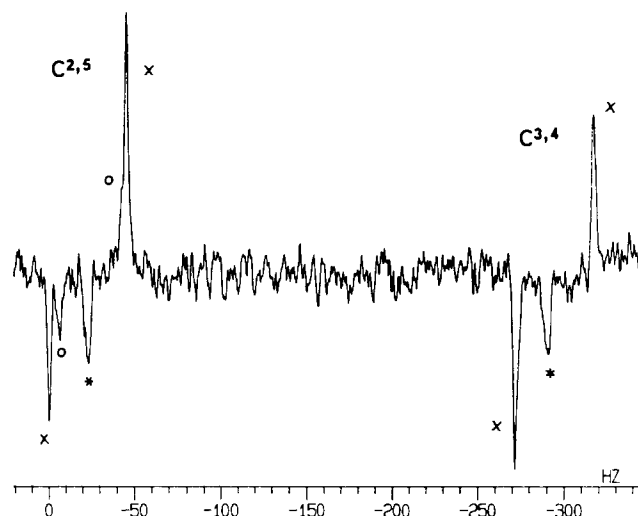


Fig. 2. 67.9 MHz INADEQUATE  $^{13}\text{C}$  NMR spectrum of 1,3-bis(diisopropylamino)-1,3-dibora-2-selena-[3]ferrocenophane (**4c**) in  $\text{C}_6\text{D}_6$  at 25°C: x,  $^1J(^{13}\text{C}(2), ^{13}\text{C}(1)) = 39.2$  Hz; o,  $^1J(^{13}\text{C}(2), ^{13}\text{C}(3)) = 45.3$  Hz; \*, = residual signals of  $^{13}\text{C}$ ,  $^{12}\text{C}$  isotopomers.

### 3.2. 1,2,3-Trimethyl-1,3-dibora-2-aza-[3]ferrocenophane (**2**)

A solution of 0.35 g (2.00 mmol) of heptamethyldisilazane in 5 ml of toluene was added dropwise at 110°C to a solution of 0.79 g (2.00 mmol) of 1,1'-bis[bromo(methyl)boryl]ferrocene (**6**) in 20 ml of toluene. After heating for reflux for further 3 h, all volatile material was removed in vacuo, and **2** was isolated as a brown oil (yield, 0.35 g (66%); more than 95% pure according to  $^1\text{H}$  NMR).

### 3.3. 1,3-Bis(dimethylamino)-1,3-dibora-2-thia-[3]ferrocenophane (**3b**)

At room temperature, 1.3 ml of a THF solution of  $\text{Li}_2\text{S}$  (1 M) [21] were added to a solution of 0.48 g (1.32 mmol) of 1,1'-bis[chloro(dimethylamino)boryl]ferrocene (**8**) in 5 ml of tetrahydrofuran (THF). The mixture was stirred for 2 h; then hexane was added and the precipitated  $\text{LiCl}$  was filtered off. Removal of the solvent gave **3b** as a yellow powder (yield 0.30 g (69%); m.p., 105–107°C).

### 3.4. 1,3-Bis(dimethylamino)-1,3-dibora-2-selena-[3]ferrocenophane (**3c**)

By use of the same procedure, the reaction of 1,1'-bis[chloro(dimethylamino)boryl]ferrocene (**8**) (0.51 g, 1.40 mmol) in 5 ml of THF and 1.4 ml of a THF solution of  $\text{Li}_2\text{Se}$  (1 M) [21] afforded **3c** (yield, 0.35 g (65%)) which decomposed above 75–80°C. Electron impact (EI) mass spectroscopy (MS): (70 eV): 374 ( $\text{M}^+$ , 100%); 330 ( $\text{M}^+ - \text{NMe}_2$ , 9%).

The compounds **3a** and **3d** were prepared in an analogous manner but were not isolated in the pure crystalline state.

### 3.5. 1,3-Bis(diisopropylamino)-1,3-dibora-2-selena-[3]ferrocenophane (**4c**)

A THF solution (0.9 ml) of  $\text{Li}_2\text{Se}$  (1 M) [21] was slowly added to a solution of 0.51 g (0.9 mmol) of 1,1'-bis[bromo(diisopropylamino)boryl]ferrocene (**9**) in 10 ml of THF at 0°C. After stirring for 2 h at room temperature, the THF was removed in vacuo. Then the residue was taken up in hexane and LiBr was filtered off. Compound **4c** crystallized from hexane at –20°C (yield, 0.28 g (64%); m.p., 153–154°C). EI MS (70 eV): 486 ( $\text{M}^+$ , 100%); 386 ( $\text{M}^+ - \text{N}^i\text{Pr}_2$ , 10%).

### 3.6. 1,1'-Bis[chloro(dimethylamino)boryl]ferrocene (**8**)

A solution of 1.50 g (3.93 mmol) of 1,1'-bis[bis(dimethylamino)boryl]ferrocene (**7**) in 20 ml of hexane was cooled to –20°C, and 8 ml of  $\text{BCl}_3$ -hexane (1 M) were added dropwise. The solution was stirred for 2 h at room temperature. Then the solvent was removed in vacuo, whereby **8** was left as a red crystalline solid (yield 1.10 g (76%); m.p., 77–80°C). EI MS (70 eV): 364 ( $\text{M}^+$ , 100%); 320 ( $\text{M}^+ - \text{NMe}_2$ , 7%); 44 ( $\text{NMe}_2^+$ , 44%).  $^1\text{H}$  NMR:  $\delta$  4.32 (H(2, 5)), 4.50 (H(3, 4)), 2.73, 2.58 ( $\text{NMe}_2$ ) ppm.  $^{13}\text{C}$  NMR;  $\delta$  76.2 (C(2, 5)), 72.8 (C(3, 4)), 69.7 (C(1)), 40.8, 40.5 ( $\text{NMe}_2$ ) ppm.  $\delta^{11}\text{B}$  NMR: 36.7 ppm.

### 3.7. 1,1'-Bis[bromo(diisopropylamino)boryl]ferrocene (**9**)

At –40°C, 2.42 g (24.0 mmol) of diisopropylamine were added dropwise to a solution of 1.50 g (2.85 mmol) of **5** in 30 ml of toluene. After warming to room temperature and stirring for 4 h, the hydrobromide  $\text{H}_2\text{N}^i\text{Pr}_2\text{Br}$  was filtered off. Compound **9** crystallized from hexane as a red solid (yield, 1.05 g (65%); m.p., 80–82°C). EI MS (70 eV): 566 ( $\text{M}^+$ , 8%), 44 ( $\text{H}_2\text{CMe}_2^+$ , 100%).  $^1\text{H}$  NMR:  $\delta$  4.31(H(2, 5)), 4.38(H(3, 4)), 4.28, 3.20 (NCH), 1.43, 0.90 ( $\text{NCCH}_3$ ) ppm.  $^{13}\text{C}$  NMR:  $\delta$  76.7 (C(2, 5)), 73.4 (C(3, 4)), 73.8(C(1)), 52.1, 47.2 (NCH), 23.9, 22.9 ( $\text{NCCH}_3$ ) ppm.  $^{11}\text{B}$  NMR:  $\delta$  35.2 ppm.

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