

# Synthesis and Structures of New Borylferrocenes, and Structures of 2-Chalcogeno-bis(aminoboryl)[3]ferrocenophanes and 1,1'-Tris(dimethylaminoboryl)[3]ferrocenophane [1, 2]

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*In Memory of Professor Herbert Schumann*

**Keywords:** 1,1'-(Bromodiorganylaminoboryl)ferrocenes; 1,1'-Bis[bis(diorganylamino)boryl]ferrocenes; 1,1'-Tris(dimethylaminoboryl)[3]-ferrocenophane; 1,1'-[2-Chalcogeno-bis(1,3-diorganylaminoboryl)[3]ferrocenophanes; NMR spectroscopy; X-ray diffraction

**Abstract.** The reaction of  $\text{Br}_2\text{BCpFeCp}$  with  $(\text{Me}_3\text{Si})_2\text{S}$  affords the hexacyclic tris(ferrocenyl)trithia-triborane  $(\text{CpFeCp-BS})_3$ , whereas the tris(ferrocenyl)boroxine is obtained from  $\text{CpFeCpB}(\text{NMe}_2)_2$  and  $\text{H}_2\text{O}$  via the isolated intermediate  $[\text{CpFeCpBO}]_3\cdot\text{HNMe}_2$ . In this compound there are two ferrocenyl units in *trans*-orientation and a third one is bonded to an  $\text{O}_2\text{BNHMe}_2$  unit with formation of a tetracoordinated boron atom (We use the symbol Cp here not only for the  $\text{C}_5\text{H}_5$  unit but also for  $\text{C}_5\text{H}_4$  or  $\text{C}_5\text{H}_3$  units). The structures of several bromo(dialkylamino)borylferrocenes and the 1,1'-bis[bromo(dialkylamino)boryl]ferrocenes were determined. They show no Fe–B interaction.

The  $\text{Br}(\text{R}_2\text{N})\text{B}$  and the  $(\text{R}_2\text{N})_2\text{B}$  groups are increasingly twisted against their Cp planes. In case of  $1,1'-[\text{Br}(\text{iPr}_2\text{N})\text{BCp}]_2\text{Fe}$  the  $\text{CB}(\text{Br})\text{N}$  planes are twisted against the respective Cp planes by  $38.7$  and  $112.5^\circ$ , which brings the bromine atoms closer to the iron atom. This twisting is enhanced by an increase of the steric demands by the amino groups and is largest for  $(\text{iPr}_2\text{N}t\text{BuHNBCp})_2\text{Fe}$ . The structures of two 1,1'-chalcogeno-bis(diorganylaminoboryl)[3]ferrocenophanes  $X[(\text{R}_2\text{N})\text{BCp}]_2\text{Fe}$  ( $X = \text{O}, \text{S}; \text{R} = \text{Me}, \text{iPr}$ ) are reported as well as the new 1,1'-tris(dimethylaminoboryl)[3]ferrocenophane.

## Introduction

Since the detection of ferrocene [3–5] its chemistry has been extensively investigated [6, 7]. Due to its stability and its versatility it has become an important reagent in many areas of chemistry including material chemistry [8], catalysts [9] and polymer chemistry [10]. Planar-chiral ferrocenes, in general 1,2- and 1,3-disubstituted ferrocenes, are used in stereoselective syntheses, for instance for the synthesis of precursor molecules *en route* to (+)biotin [11] or to the herbicide (*S*)-metolachlor [12].

Meanwhile, a large number of monoborylated and 1,1'-diborylated ferrocenes are known as well as tri- and tetraborylated ferrocenes [13–21]. Siebert et al. [13], Wrackmeyer et al. [14, 18] and we [2, 20] have shown that the reaction of ferrocene, ruthenocene and osmocene with  $\text{BBr}_3$ , depending on the stoichiometry, produces the dibromoboryl metallocenes  $(\text{Br}_2\text{BCp})\text{MCp}$ ,  $(\text{Br}_2\text{BCp})_2\text{M}$ ,  $(\text{Br}_2\text{BCp})\text{M}[\text{Cp}(\text{BBr}_2)_2]$  and  $[(\text{Br}_2\text{B})_2\text{Cp}]_2\text{M}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ). All of these compounds show  $\text{BBr}_2$  groups that are bent in the direction towards the M

atom. This can be explained by  $\text{B}(\text{sp}^2)\text{-M}(\text{d}_{x^2-y^2}, \text{d}_{z^2})$  interactions. Meanwhile it is well known that this bending depends strongly on the Lewis acidity of the boryl  $\text{BX}_2$  substituent [19, 21].

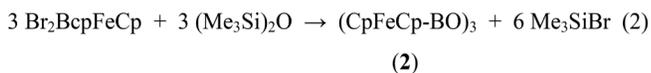
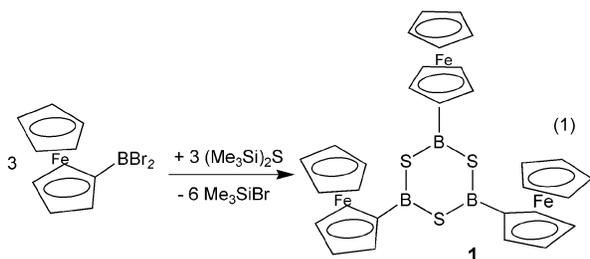
In this paper we describe the synthesis of a number of new boryl-substituted ferrocenes having weak Lewis acidic  $\text{BX}_2$  or  $\text{BXY}$  substituents ( $\text{OR}, \text{NR}_2$ ) as well as some boron substituted ferrocenophanes like the novel  $1,1'-\text{Fe}(\text{CpBNMe}_2)_2\text{BNMe}_2$ .

## Results

### Ferrocenyltrichalcogenotriboranes

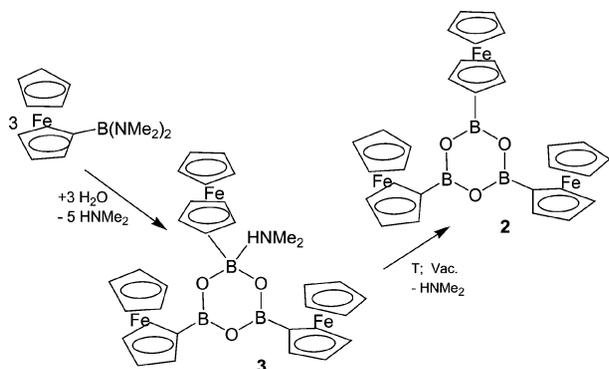
The first tri(ferrocenyl)trichalcogenotriborane,  $[\text{CpFeCp-BSe}]_2$  was obtained by the reaction of  $\text{CpFe}(\text{CpBBr}_2)$  with  $(\text{Me}_3\text{Si})_2\text{Se}$  in the presence of  $\text{NEt}_3$  and  $\text{CH}_2\text{Cl}_2$  [22]. Its crystal structure shows an almost planar  $\text{B}_3\text{Se}_3$  ring with  $\text{Se-B-Se}$  bond angles close to  $128.7$  and  $\text{B-Se-B}$  bond angles of  $111.3^\circ$ . We obtained the missing link between  $[\text{CpFeCpBSe}]_3$  and  $[\text{CpFeCpBO}]_3$  (**2**) the trithiatriborane  $[\text{CpFeCp-BS}]_3$  (**1**) by the reaction of  $\text{Br}_2\text{BCpFeCp}$  and  $(\text{Me}_3\text{Si})_2\text{S}$  in boiling hexane as shown in Equation (1). However, we obtained no crystals suitable for an X-ray determination of its molecular structure.

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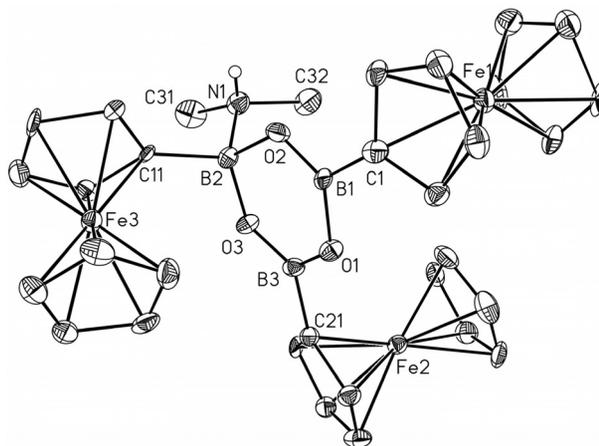
The known tris(ferrocenyl)boroxine  $[\text{CpFeCpBO}]_3$ , (**2**) was prepared from  $\text{CpFeCp-BCl}_2$  by hydrolysis to give the boronic acids  $\text{CpFeCp-B(OH)}_2$  which readily dehydrates to produce the six-membered boroxine **2** [23], whose crystal structure showed an almost planar ring system [24]. The ferrocene units stand all on one side of the ring.

We tried to prepare **2** from  $\text{CpFe}(\text{CpBBR}_2)$  and  $(\text{Me}_3\text{Si})_2\text{O}$  as shown in Equation (2). The cleavage of the Si–O bond proved to be very slow even under reflux condition. On the other hand, the hydrolysis of  $\text{CpFe}(\text{CpBBR}_2)$  with water or aqueous ethanol produced at room temperature only a green solid precipitate, which may consist of a ferrocenium salt. However, the hydrolysis of  $\text{CpFeCpB}(\text{NMe}_2)_2$  with water in THF at low temperature (starting at  $-60^\circ\text{C}$ ) was successful. As shown in Scheme 1, the first isolable product is the dark red 1:1 dimethylamine adduct **3** of tris(ferrocenyl)boroxine **2**. Several crystallisation steps were necessary to obtain the  $\text{Me}_2\text{NH}$  free compound **2** as an orange microcrystalline powder. The molecular structure of **3** could be determined by X-ray crystallography. It crystallises in the orthorhombic space group *Pna2* with one molecule of  $[\text{CpFeCpBO}]_3 \cdot \text{HNMe}_2$  and one molecule of benzene in the asymmetric unit. Its structure is depicted in Figure 1 and its packing in the unit cell in Figure 2. The non planar six-membered boroxine ring of **3** consists of two tricoordinated boron atoms and one tetracoordinated boron atom and three dicoordinated oxygen atoms. The B2–C bond of the tetracoordinated boron atom is slightly but significantly longer than the other two B–C bonds. Also, the B2–N1 bond is, as expected, longer than the B2–O bonds (for more data see Figure 1). The  $\text{FeCp}_2$  units are differently oriented to one another,

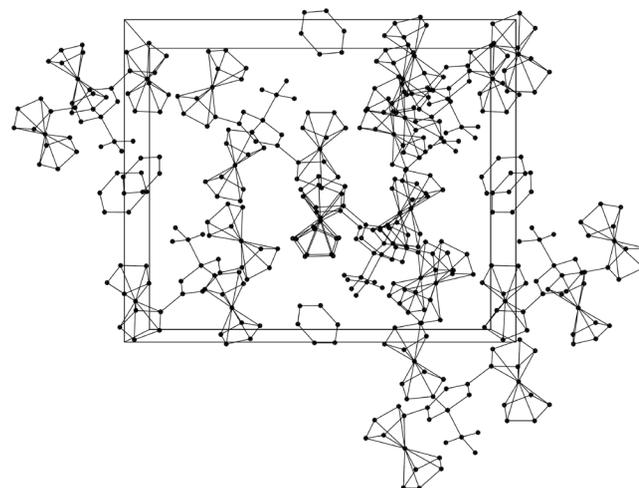


Scheme 1.

e.g. the  $\text{C}_5$  planes of C1 to C5 and C11 to C15 are oriented by  $61.6^\circ$  against each other, whereas the angle for the planes C1 to C5 against the plane of C21 to C25 is larger with  $73.4^\circ$  and the angle between the planes C11 to C15 and C21 to C25 adopt a twist angle of  $64.4^\circ$ .



**Figure 1.** The molecular structure of  $[\text{CpFeCp-BO}]_3\text{NHMe}_2$  (**3**). Thermal ellipsoids are shown on a 25 % probability scale. Selected bond lengths are given in Å and bond angles in deg. B1–O1 1.396(9), B1–O2 1.324(9), B2–O2 1.450(9), B2–O3 1.461(9), B3–O3 1.345(9), B3–O1 1.381(9), B1–C1 1.56(1), B2–C11 1.58(1), B3–C21 1.56(1), B2–N1 1.653(9), Fe1–C10 2.018(8), Fe1–C1 2.082(8), Fe2–C21 2.046(7), Fe3–C11 2.077(6), B1–C1 1.52(1), B2–C11 1.528(9), B3–C21 1.53(1), C–C 1.37(1) – 1.455(9). O1–B1–O2 123.3(7), O2–B2–O3 114.0(6), O3–B3–O1 122.5(6), B1–O1–B3 117.7(6), B2–O3–B3 119.7(6), B1–O2–B2 120.4(6). Twist angles: C1–C5/O1B1O2 103.1; C11–C15/O3BO2 46.1, C21–C25/O1B3O3 24.4.



**Figure 2.** Packing of  $[\text{CpFeCp-BO}]_3\text{NHMe}_2 \cdot \text{C}_6\text{H}_6$ . View down the *b* axis.

The B1O1B3 plane forms an angle of  $20.9^\circ$  with the O2B2O3 plane. Two of the  $\text{FeCp}_2$  units (at B1 and B3) are fixed at the  $\text{B}_3\text{O}_3$  ring in opposite directions. This arrangement reduces steric strain. Therefore, the two boroxine derivatives **2** and **3** are sterically different.

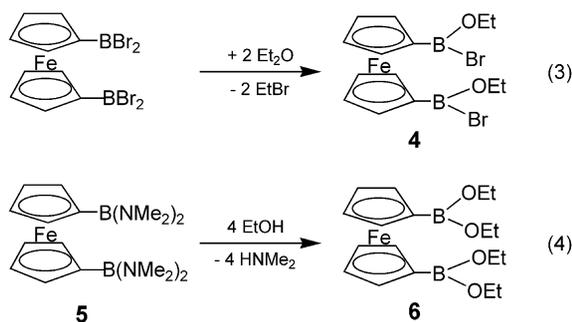
The  $^{11}\text{B}$  chemical shifts of **1**, **2**, and **3** correspond with other triorganyltrithiaboranes and triorganylboroxines [27]. The  $^{11}\text{B}$

resonance of **1** was observed at 57.5 ppm, which falls in the area of other cyclic  $RB(SR')_2$  systems ( $\delta^{11}\text{B}$  range from 61 to 58 ppm). Only one  $^{11}\text{B}$  NMR signal was observed for **2** at 31.6 ppm (range for boroxines  $(\text{RBO})_3 = 29$  to 34 ppm) [25].  $^{13}\text{C}$  NMR signals were observed at 70.0 ppm for the unsubstituted Cp rings, and those at 73.3 and 74.4 ppm are associated with the substituted Cp rings whose boron bonded carbon atom could not be localised. The dimethylamine adduct **3** showed only a broad  $^{11}\text{B}$  NMR signal at 24.6 ppm

### 1,1'-Bis(organyloxoboryl) Ferrocenes

Siebert et al. [13] and Wrackmeyer et al. [14, 18] early demonstrated that the dihalogenoborylferrocenes, particularly the dibromoborylferrocenes are excellent precursors for the synthesis of other borylferrocenes. For instance, the reaction of 1,1'-( $\text{Br}_2\text{BCp}$ ) $_2\text{Fe}$  with  $\text{SnMe}_4$  generates either 1,1'-( $\text{BrMeBCp}$ ) $_2\text{Fe}$  or 1,1'-( $\text{Me}_2\text{BCp}$ ) $_2\text{Fe}$  depending on stoichiometry and reaction conditions. Reactions with  $\text{AsF}_3$  or  $\text{AsCl}_3$  gives access to  $(\text{F}_2\text{BCp})_2\text{Fe}$  or  $(\text{Cl}_2\text{BCp})_2\text{Fe}$  whereas the reaction with secondary amines yields either  $[\text{Br}(\text{R}_2\text{N})\text{BCp}]_2\text{Fe}$  or  $[(\text{R}_2\text{N})_2\text{BCp}]_2\text{Fe}$ , depending on stoichiometry. Reactions between  $(\text{Br}_2\text{BCp})_2\text{Fe}$  and  $\text{Et}_2\text{O}$  leads to ether cleavage and formation of ethyloxoborylferrocenes [18]. However, we could not isolate  $[(\text{EtO})_2\text{BCp}]_2\text{Fe}$  as previously reported [18]. But we were able to isolate  $[\text{Br}(\text{EtO})\text{BCp}]_2\text{Fe}$  in 67.8 % yield as shown in Equation (3). This compound shows an  $^{11}\text{B}$  NMR signal at 38.9 ppm.

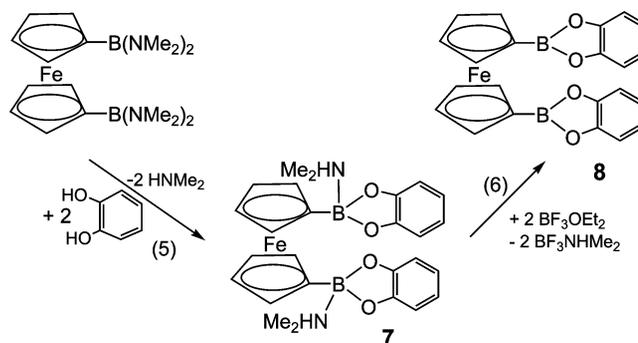
When the reaction of  $(\text{Br}_2\text{BCp})_2\text{Fe}$  with  $\text{Et}_2\text{O}$  was carried out at  $-30^\circ\text{C}$  or at room temperature, a mixture of bromo-(ethoxy)borylferrocenes  $\text{Br}_n(\text{EtO})_{4-n}\text{B}_2\text{Cp}_2\text{Fe}$  could be observed in the  $^{11}\text{B}$  NMR spectrum. However,  $[(\text{EtO})_2\text{BCp}]_2\text{Fe}$  (**6**) resulted at  $-30^\circ\text{C}$  as shown in Equation (4) by the solvolysis of  $[(\text{Me}_2\text{N})_2\text{BCp}]_2\text{Fe}$  with anhydrous ethanol. The orange-red crystals were isolated in 65 % yield,  $\delta^{11}\text{B} = 29.7$  ppm. At room temperature, a green precipitate formed from the two components, and in the filtrate an  $^{11}\text{B}$  NMR signal at 18.0 ppm shows the presence of  $\text{B}(\text{OEt})_3$ . The solid, most likely is a ferrocinium salt, but it was not characterised.



Reactions in analogy to Equation (4) provide an easy access to other organyloxoborylferrocenes. For instance, catechol reacts with **5** to produce bis(benzodioxaboryl)ferrocene, which was isolated as its bis(dimethylamine) adduct **8** (see Equation (5)). This compound crystallises in lemon yellow platelets, m. p,  $280^\circ\text{C}$ . Treatment of this solid with two equivalents of

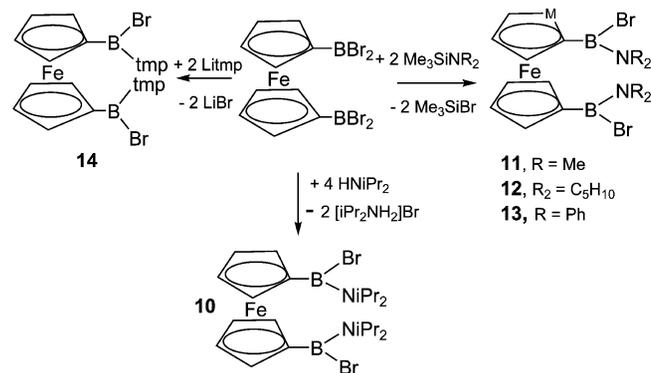
$\text{F}_3\text{B}\cdot\text{OEt}_2$  in diethyl ether suspension led to a solution of bis(benzodioxaboryl)ferrocene **9** as shown in Equation (6). It crystallises as thin orange platelets in 99 % yield,  $\delta^{11}\text{B} = 35.7$  ppm. The boron atom of **9** is significantly deshielded compared to **8** ( $\delta^{11}\text{B} = 29.7$  ppm).

Compound **9** is the thermodynamic trap of the reaction of  $[(\text{Me}_2\text{N})_2\text{BCp}]_2\text{Fe}$  (**7**) with catechol because the 1:1 reaction yielded a mixture of **8** and **9**, respectively. And **9** resulted also besides some byproducts by treatment of  $[\text{Br}(\text{Me}_2\text{N})\text{Cp}]_2\text{Fe}$  with dilithium catecholate in a 1:1 ratio instead of generating a catecholato bridge between the two boron atoms of  $[\text{Br}(\text{Me}_2\text{N})\text{Cp}]_2\text{Fe}$  by elimination of  $\text{LiBr}$ .

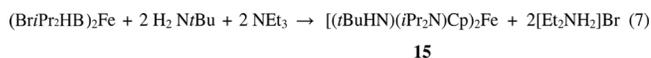


### Organylamino-borylferrocenes

The aminolysis of bis(dibromoboryl)ferrocene was first studied by Siebert et al. [13]. Its bromine atoms can be successively replaced by  $\text{R}_2\text{N}$  groups. Wrackmeyer et al. used the reaction of  $(i\text{Pr}_2\text{N})_2\text{BCl}$  with 1,1'-dilithiumferrocene to prepare 1,1'- $[(i\text{Pr}_2\text{N})_2\text{BCp}]_2\text{Fe}$  [18]. We used often reactions of trimethylsilyl diorganylamines with  $(\text{Br}_2\text{BCp})_2\text{Fe}$  for preparing 1,1'-(bromodiorganyl-aminoboryl) ferrocenes as shown in Scheme 2 because  $\text{Me}_3\text{SiBr}$  can be readily removed from the reaction mixture in vacuo.



Scheme 2.

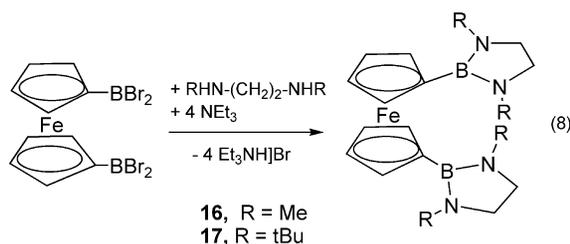


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However, for introducing bulky amino groups such as the 2,2,6,6-tetramethylpiperidino group (tmp) we could isolate the

corresponding bis(bromoaminoboryl)ferrocene (**14**) only when Litmp was reacted with  $(\text{Br}_2\text{BCp})_2\text{Fe}$ . On the other hand, we were surprised that 1,1'-bis(diisopropylamino-*tert*-butylamino-boryl)ferrocene (**15**) could be prepared from 1,1'-bis[bromo-bis(isopropylamino)boryl]-ferrocene and *tert*-butylamine in the presence of triethylamine in spite of the fact that this combination of amino groups is sterically quite demanding as shown in Eq.(7).

There is no steric hindrance to synthesise 1,1'-bis(*N,N*-dimethyl-1,3,2-diazaborolidyl)-ferrocene (**16**). This compound was first described by Herberhold et al. [27]. It was prepared from 1,3-dimethyl-2-chloro-1,3,2-diazaborolane and 1,1'-dilithiumferrocene. We obtained single crystals of **16** by aminolysis of  $(\text{Br}_2\text{BCp})_2\text{Fe}$  with  $\text{MeHN-CH}_2\text{CH}_2\text{NHMe}$  in the presence of  $\text{NEt}_3$  [Equation (8)] as well as the corresponding 1,1'-bis(*N,N*-di-*tert*-butylboryl-1,3,2-diazaborolidyl)ferrocene (**17**) and determined its crystal structures. These compounds are of interest as well as  $[(\text{isoPr}_2\text{N})\text{tert-BuNHBCp}]_2\text{Fe}$  (**15**) for studying the influence of bulky groups on the conformation of these compounds.

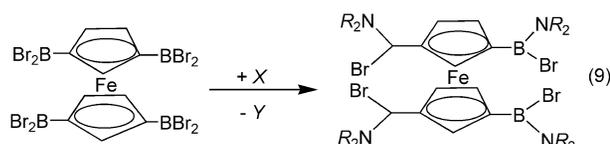


The shielding of the boron nuclei of compounds **10–17** correspond with noncyclic and cyclic bromo(dialkylamino)arylboranes and bis(diorganylamino)arylboranes [25]. Amongst the bromo(dialkylamino)borylferrocenes, compound **10** ( $\delta^{11}\text{B} = 35.4$  ppm) shows the best shielded boron nucleus, whereas the boron atoms of the tmp derivative **14** ( $\delta^{11}\text{B} = 42.9$  ppm) is less shielded due to its significantly twisted tetramethylpiperidino group. Hindered rotation about the B–N bond is observed for compounds **10** and **11**.

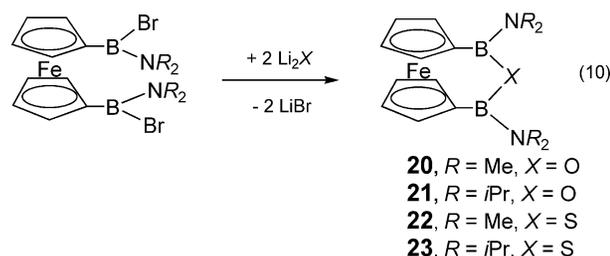
The analogous *N,N*-di-*tert*-butyl-2,3-dehydro-1*H*-1,3,2 diazaborolidinyl ferrocene compounds [26] are closely related to compounds **16** and **17** [26], but the  $^{11}\text{B}$  chemical shifts for the dehydro derivative show much better shielding of the boron atoms both for the monosubstituted ferrocene and 1,1'-disubstituted derivative (both with  $\delta^{11}\text{B} = 25.3$  ppm). It is interesting to note that the C2,5 atoms of **16** are about 2.9 ppm deshielded compared with the atoms C3,4, but for **17** the two resonances are 10 ppm apart. This is due to the observation that the two Cp rings are tilted against the CBN2 plane by 30.8 and 32.1 ppm in **16** but in **17** by of 43.9 and 75.9°, respectively. This affects also the  $^{13}\text{C}$  chemical shift of the C1 atoms.

In most cases the boron bonded carbon atoms are not observed in the  $^{13}\text{C}$  NMR spectra due to the large quadrupole moment of the boron atoms. But in case of **16** and **17** we could observe the  $^{13}\text{C}$  NMR signal for C1 after applying a large number of pulses within 11 hours or collecting the data at  $-70$  °C.  $^{13}\text{C}$  NMR signals for C-2,5 and C-3,4 are 73.98 and 71.06 ppm for **16** and its signal for C1 was found at 66.94 ppm ( $h_{1/2} =$

168 Hz). For **17** the chemical shifts are 79.01, 81.80 and 68.96, ppm for C-2,5, C-3,4 and C1, respectively. This deshielding of the ring carbon atoms particularly for **17** can be attributed to the strong twisting of the  $\text{BN}_2$  atom group which results also in longer B–C bonds [1.599, 1.594(6) Å] than found for **16** [1.569(4) Å]. On the other hand the B–N bond lengths are on the shorter side for **16** [1.410, 1.405(3) Å] compared to **17** [1.445 to 1.437(6) Å]. They correspond with those of the analogous 2,3-dihydro-1*H*-1,3,2-diazaborolylferrocenes [26].



**18**, R = Me, X = 4  $\text{Me}_3\text{SiNMe}_2$ , Y = 4  $\text{Me}_3\text{SiBr}$   
**19**, R = *iPr*, X = 4  $\text{iPr}_2\text{NH}$  + 4  $\text{Et}_3\text{N}$  Y = 4  $\text{Et}_3\text{NHBr}$



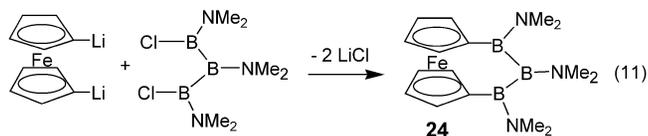
The boron nuclei of the tetrakis(bromodialkylaminoboryl)ferrocenes **18** and **19**, prepared according to Equation (9), are shielded with  $\delta^{11}\text{B} = 37.3$  and 36.5 ppm. This fits well with other bromo(amino)organylamines [25]. The structures of these compounds could be determined (see below). They are of interest because one can expect that two bromoaminoboryl groups bonded to a Cp ring will lead to steric crowding.

### Borylferrocenophanes

Borylgroup containing ferrocenophanes were first described by Herberhold et al. [27]. They reported i. a. the synthesis of  $X(\text{Me}_2\text{NBCp})_2\text{Fe}$  ( $X = \text{S}, \text{Se}, \text{Te}$ ) and of  $\text{Se}(\text{iPr}_2\text{NBCp})_2\text{Fe}$  by the reaction of  $[\text{Cl}(\text{R}_2\text{N})\text{BCp}]_2\text{Fe}$  with  $\text{Li}_2\text{X}$  ( $X = \text{S}, \text{Se}, \text{Te}$ ). They determined the molecular structure of  $\text{Se}(\text{iPr}_2\text{NBCp})_2\text{Fe}$ . We prepared the ferrocenophanes **20–23** (see Equation (10)) analogously and we could grow well shaped single crystals of **20** and **23** for the determination of their molecular structures.

We also prepared 1,1'-bis(dimethylaminoboryl)[3]ferrocenophane [2] and determined its structure. But we need not discuss it here as its synthesis and structure has already been adequately described by Herberhold et al. [28] and Braunschweig et al. [29]. Braunschweig and Manners et al. [30] also prepared and determined the structure of several aminoboryl[1] bridged ferrocenophanes,  $\text{R}_2\text{NB}(\text{Cp})_2\text{Fe}$  [30]. We extended the bridging boron atoms to three by preparing tris(dimethylaminoboryl)[3]ferrocenophane (**24**) according to Equation (11) by reacting  $(\text{LiCp})_2\text{Fe}$  [31] with the triborane derivative  $\text{Cl}(\text{Me}_2\text{N})\text{B}-\text{BNMe}_2-\text{B}(\text{NMe}_2)\text{Cl}$  [32]. Compound **24** crystal-

lises in orange-red platelets. So it is now possible to compare the influence of mono-, di- and triboryl substituents on the structure of boryl[ $\eta$ ]ferrocenophanes.



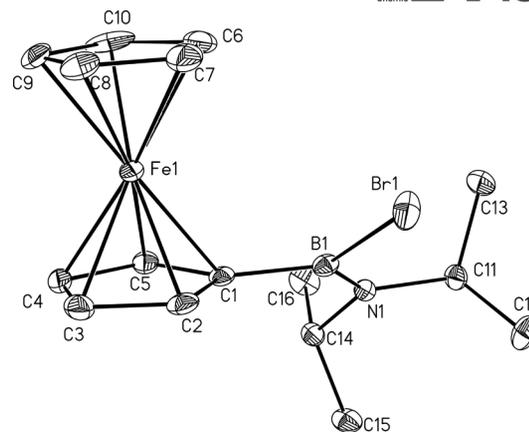
### X-ray Structural Studies

We determined the crystal structure of **3**, CpFe{CpBBr(NiPr<sub>2</sub>)}, **11**, **12**, **15**, **16**, **17**, **18**, **19**, **20**, **23** and **24** which are shown in Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, Figure 7, Figure 8, Figure 9, Figure 10, Figure 11, Figure 12, and Figure 13. Table 1 gives an overview of selected bonding parameters for the structures of the aminoborylferrocenes presented in this paper.

The bromo(diisopropylamino)borylferrocene (see Figure 3) crystallises in the monoclinic space group *P2<sub>1</sub>/n*. There are two independent molecules in the unit cell. Its Cp rings adopt an almost eclipsed position (12°) and the two Cp planes are tilted against each other by only 1.3°. The Fe–C distance to the boryl group carrying C1 atom is 2.063(4) Å. All other Fe–C bonds are significantly shorter, the shortest is the Fe1–C10 distance with 2.025(5) Å. There is no B···Fe interaction as demonstrated by an increase of the Fe···B distance from 2.855 (2.742 Å) in CpFeCpBBr<sub>2</sub> [18] to 3.235 Å in CpFe{CpBBr(NiPr<sub>2</sub>)}.

The C–C bonds are of different lengths, the longest ones are C1–C2 and C1–C5 [1.436(6) and 1.433(6) Å] whereas the shortest is the C3–C4 bond opposite to atom C1 with 1.402(8) Å. As expected, the tricoordinate boron atom has a planar environment with a B1–C1 bond length of 1.554(6) Å. The B1–N1 bond length is 1.374(6) Å, typical for a planar environment about the nitrogen atom and the presence of B–N  $\pi$ -bonding. The BBrN plane is twisted against its Cp plane by 22°.

Crystals of 1,1'-bis(bromodimethylaminoboryl)ferrocene (**11**) are orthorhombic, space group *Pbcn*, *Z* = 4. Its molecular



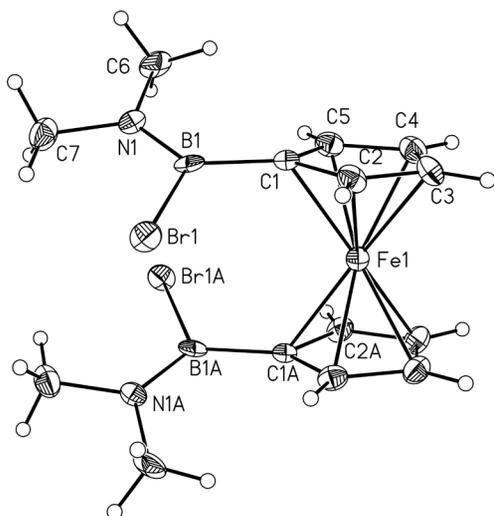
**Figure 3.** Molecular structure of CpFe{CpBBr(NiPr<sub>2</sub>)}. Thermal ellipsoids are shown on a 25 % probability scale. Selected bond lengths in Å and bond angles in deg. B1–Br1 1.994(5), B1–N1 1.374(6), B1–C1 1.554(6), Fe1–C1 2.063(4), Fe1–C2 2.032(4), Fe1–C3 2.042(5), Fe1–C4 2.047(5), Fe1–C5 2.043(4), Fe1–C6 2.032(5), Fe1–C7 2.039(5), Fe1–C8 2.044(9), Fe1–C9 2.033(4), Fe1–C10 2.025(5), Fe1···B1 3.235(6), C1–C2 1.436(6), C2–C3 1.407(7), C3–C4 1.402(8), C4–C5 1.435(7), C5–C1 1.433(6), C6–C7 1.369(9), C7–C8 1.372(8), C8–C9 1.382(8), C9–C10 1.406(8), C10–C6 1.445(9). – C1–C2–C3 108.9(4), C2–C3–C4 109.9(4), C3–C4–C5 107.6, C4–C5–C1 108.4(4), C5–C1–C2 106.4, C1–B1–N1 128.0(4), C1–B1–Br1 112.2(3), Br1–B1–N1 119.7(3). –Twist angle C1–C5/C6–C10 1.8°, deviation from eclipsed conformation 14°.

structure is depicted in Figure 4. The iron atom lies on a two-fold axis. Its Cp groups are tilted against each other by 2.7°, and their carbon atoms are present in an almost perfect eclipsed position. Its B1–C1 bonds are 2.56(1) Å. Amongst the Fe–C bonds the Fe–C1 bond is the longest [2.066(8) Å] compared to the short Fe–C5 bond of 2.027(8) Å, thus the iron atom is not located above the centre of the Cp rings. Also, the B–N bonds [1.39(1) Å] are typical for mono(amino)boranes. The BBrN plane is bent with respect to the C1C2C5 plane by 23.6°, and this brings the boron and bromine atoms closer to the iron atom (3.229 and 4.0665 Å, respectively).

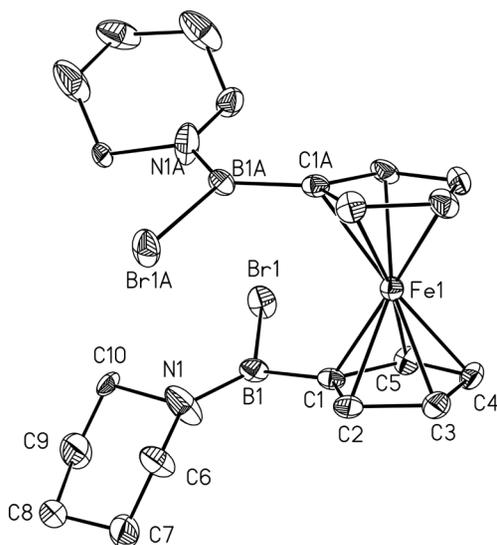
The orange-brown needles of 1,1'-bis(bromopiperidinoboryl)ferrocene, **12**, crystallise in the monoclinic space groups *C2/c* with *Z* = 4. Figure 5 presents its molecular structure for

**Table 1.** Selected bonding parameters of the molecular structures of monoboryl and bis(boryl) ferrocenes. Bond lengths and distances *d* are presented in Å, angles between planes in degree.

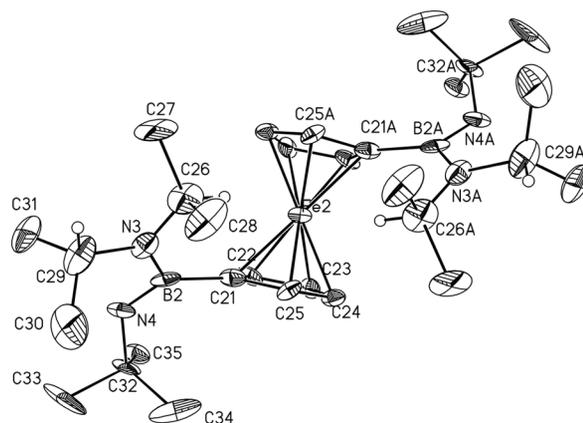
	<i>d</i> (B–C) / Å	<i>d</i> (B···Fe) / Å	<i>d</i> (B–N) / Å	C1–C5/C6–C10 / °	C1–C5/BNX / °	<i>d</i> (Fe···Br) / Å
(Br <sub>2</sub> Pr <sub>2</sub> NB)CpFeCp	1.554(6)	3.235	1.374(6)	1.8	37.7	3.849
(BrMe <sub>2</sub> NBCp) <sub>2</sub> Fe ( <b>11</b> )	1.56(1)	3.229	1.38(1)	2.7	23.8	4.065
(Br <sub>2</sub> Pr <sub>2</sub> NBCp) <sub>2</sub> Fe ( <b>10</b> )	1.57(2)	3.218	1.36(2)	10.8/12.0	38.6	4.112
(BrPipBCp) <sub>2</sub> Fe ( <b>12</b> )	1.56(2)	3.258	1.36(2)	3.5	22.4	4.075
( <i>i</i> Pr <sub>2</sub> N <sub>2</sub> BuNHBCp) <sub>2</sub> Fe ( <b>15</b> )	1.595(4)	3.441	1.461, 1.394	11.7	47.9	
(Me <sub>2</sub> N <sub>2</sub> C <sub>2</sub> H <sub>2</sub> B <sub>2</sub> Cp) <sub>2</sub> Fe ( <b>16</b> )	1.569(4)	3.288	1.405(4)	3.7	30.8, 32.1	
( <i>i</i> Bu <sub>2</sub> N <sub>2</sub> C <sub>2</sub> H <sub>2</sub> B <sub>2</sub> Cp) <sub>2</sub> Fe ( <b>17</b> )	1.604(5)	3.499	1.437(7)	12.6	43.9	
	1.593(8)	3.596	1.430(6)		76.9	
[(Me <sub>2</sub> NBrB) <sub>2</sub> Cp] <sub>2</sub> Fe ( <b>18</b> )	1.55(1), 1.57(1)	3.197, 3.232	1.37(1), 1.38(1)	2.7	24.0, 25.6	4.044, 4.045
[( <i>i</i> Pr <sub>2</sub> NBrB) <sub>2</sub> Cp] <sub>2</sub> Fe ( <b>19</b> )	1.578	3.274	1.345	3.4	142.1	3.886,
	1.527	3.222	1.420		147.2	3.892
	1.552	3.228	1.369		145.9	3.896
	1.553	3.315	1.375		142.5	3.955



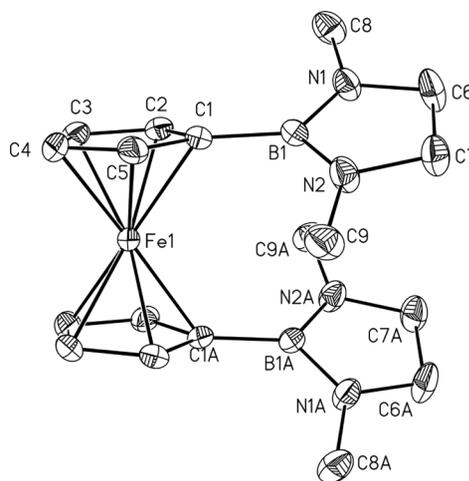
**Figure 4.** Molecular structure of  $[\text{Br}(\text{Me}_2\text{N})\text{BCp}]_2\text{Fe}$  (**11**). Thermal ellipsoids are shown on a 25 % probability scale. Selected bond lengths are given in Å and bond angles in deg. B1–C1 1.56(1), B1–N1 1.38(1), B1–Br1 1.968(9), N1–C6 1.47(1), N1–C7 1.45(1), C1–C2 1.44(1), C2–C3 1.34(1), C3–C4 1.43(1), C4–C5 1.40(1), C5–C1 1.43(1), Fe1–C1 2.066(8), Fe1–C2 2.044(8), Fe1–C3 2.051(9), Fe1–C4 2.051(9), Fe1–C5 2.027(8). N1–B1–Br1 117.9(7), N1–B1–C1 126.5(8), C1–B1–Br1 115.6(6), C6–N1–C7 110.9(7), C6–N1–B1 123.3(7), C7–N1–B1 125.7(8); Twist angles: C1–C5/B1N1Br1 23.8°, B1C1C2C5/C1–C5 0.5°, B1C1Fe1/B1AC1AFe1 16.5°, C6N1C7/C1B1Br1. Tilt angle Cp/ Cp': 2.7°.



**Figure 5.** Molecular structure of  $[\text{Br}(\text{pip})\text{BCp}]_2\text{Fe}$  (**12**). Only one orientation of the piperidine rings is shown. Thermal ellipsoids are presented on a 25 % probability scale. Selected bond lengths are given in Å and bond angles in deg. B1–C1 1.56(2), B1–N1 1.36(2), B1–Br1 1.96(1), C1–C2 1.44(1), C2–C3 1.40(1), C3–C4 1.30(1), C4–C5 1.43(1), C6–C7 1.36(2), C7–C8 1.51(2), C8–C9 1.51(2), C9–C10 1.39(2), Fe1–C1 2.066(9), Fe1–C2 2.040(9), Fe1–C3 2.05(1), Fe1–C4 2.054(9), Fe1–C5 2.040(9), C1–C2 1.44(1), C2–C3 1.40(1), C3–C4 1.40(1), C4–C5 1.43(1), C6–C7 1.36(2), C7–C8 1.51(2), C8–C9 1.51(2), C9–C10 1.39(2); N1–B1–Br1 117.1(8), C1–B1–Br1 114.9(7), N1–B1–C1 128.0(9), C2–C1–C5 105.4(8), C1–C2–C3 108.1(0), C2–C3–C4 110.6(9), C3–C4–C5 106.6(9), C4–C5–C1 109.3(8). Tilt angle: 3.5°. Twist angle: C1–C5/B1Br1N1 21.8°.

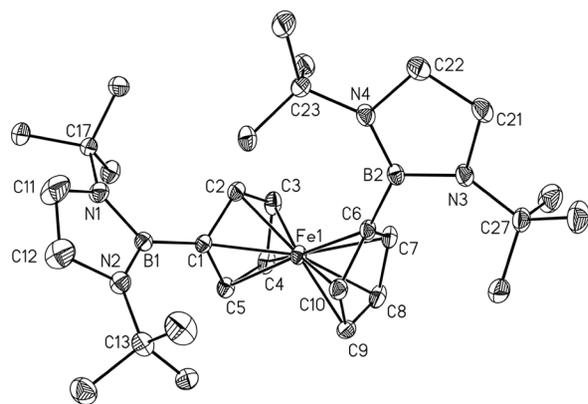


**Figure 6.** Molecular structure of  $[\text{iPr}_2\text{N}(\text{tBuNH})\text{BCp}]_2\text{Fe}$  (**15**). Only one of the two independent molecules in the unit cell is shown. Thermal ellipsoids are presented on a 25 % probability scale. Selected bond lengths are given in Å and bond angles in deg. B1–C1 1.61(1), B1–N1 1.476(8), B1–N2 1.40(1), C1–C2 1.46(1), C2–C3 1.44(1), C3–C4 1.43(2), C4–C5 1.40(1), C5–C1 1.39(2), Fe1–C1 2.109(6), Fe1–C2 2.112(8), Fe1–C3 2.082(8), Fe1–C4 2.039(9), Fe1–C5 2.032(7). N1–B1–N2 120.2(6), N1–B1–C1 115.1(7), C1–B1–N2 124.7(5), B1–C1–C5 126.0(7), B1–C1–C2 126.4(7), C2–C1–C5 105.7(8). Torsion angles: C2C1B1N1 126.0°, C5C1B1N1 –43.0°. Tilt angle: C1–C5/C1A–C5A 11.7°, C21–C25/C21A–C25A 1.7°.

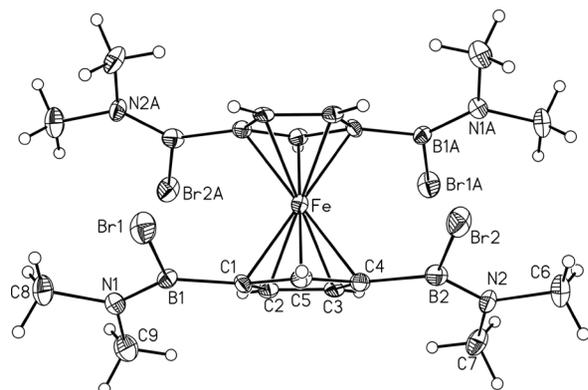


**Figure 7.** Molecular structure of 1,1'-bis(dimethyldiazaborolidinyl)ferrocene (**16**). Selected bond lengths in Å and bond angles in deg. B1–C1 1.569(4), B1–N1 1.410(3), B1–N2 1.405(3), C1–C2 1.432(4), C1–C5 1.424(3), C2–C3 1.413(3), C4–C5 1.420(4), C3–C4 1.404(4), N1–C8 1.428(3), N2–C9 1.435(3), Fe1–C1 2.076(2), Fe1–C2 2.055(2), Fe1–C3 2.040(2), Fe1–C4 2.033(2), Fe1–C5 2.040(2), Fe1···B 3.288; C1–B1–N1 124.9(2), C1–B1–N2 126.9(2), N1–B1–N2 108.1(2), B1–C1–C2 127.3(2), B1–C1–C5 126.5(2), C1–C2–C3 109.0(2), C1–C5–C4 108.6(2), C2–C3–C4 107.9(3), C5–C4–C3 108.3(2). Twist angles: C1 to C5/B1N1N2 149.0, Fe1–C1–B1/Fe1C(1A)B(1A) 15.5, C1–C5/C1A–C5A 4.8°. Tilt angle; 3.7.

one of the two site disordered piperidino group. The iron atom is sitting on a  $C_2$  axis. The BBrN planes are twisted against the  $C_5$  plane by  $21.6^\circ$  whereas the two Cp rings are tilted against each other by  $3.3^\circ$ . The bond C3–C4 is the shortest C–C bond [1.40(1) Å], the longest ones are those to atoms C1

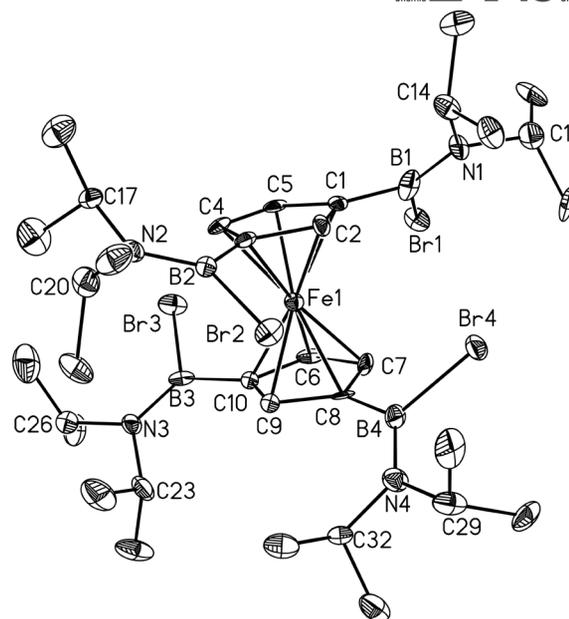


**Figure 8.** Molecular structure of 1,1'-bis(di-*n*-butyldiazaborolidinyl)ferrocene (**17**). Thermal ellipsoids are shown on a 25 % probability scale. Selected bond lengths in Å and bond angles in deg. B1–C1 1.599(5), B1–N1 1.445(6), C1–N2 1.435(6), B2–C6 1.594(6), B2–N3 1.437(5), B2–N4 1.432(6), C1–C2 1.423(6), C2–C3 1.412(5), C3–C4 1.412(7), C4–C5 1.418(6), C1–C5 1.433(5), C6–C7 1.438(6), C7–C8 1.320(6), C8–C9 1.412(7), C9–C10 1.416(6), C6–C10 1.423(6), Fe1–C1 2.136(3), Fe1–C2 2.041(3), Fe1–C3 2.042(4), Fe1–C4 2.042(4), Fe1–C5 2.075(4), Fe1–C6 2.156(4), Fe1–C7 2.055(4), Fe1–C8 2.028(4), Fe1–C9 2.032(4), Fe1–C10 2.076(4). C1–B1–N1 120.8(3), C1–B1–N2 131.8(4), C6–B2–N3 120.4(3), C6–B2–N4 131.3(4), N1–B1–N2 107.3(3), N2–B2–N4 108.2(3), B1–C1–C2 121.8(2), C1–C2–C3 110.8(2), C2–C3–C4 106.8(4), C3–C4–C5 108.3(3), C4–C5–C1 109.2(4), B2–C6–C7 122.3(3), C6–C7–C8 109.4(4), C7–C8–C9 1107(6)(4), C8–C9–C10 107.7(4), C9–C10–C6 110.1(4). Tilt angle: 12.6, Twist angles; C1–C5/B1N1N2 131.8, C6 to C19/B2N3N4 103.3, B1 N1N2/B 2N3N4 88.8.



**Figure 9.** Molecular structure of 1,1',3,3'-tetrakis(bromodimethylaminoboryl)ferrocene (**18**). Only one of the two independent molecules in the unit cell is shown. Thermal ellipsoids are presented on a 25 % probability scale. Selected bond lengths are given in Å and bond angles in deg. B1–Br1 1.982(9), B1–N1 1.37(1), B1–C1 1.55(1), B2–Br2 1.978(9), B2–N2 1.38(1), B2–C4 1.57(1), Fe–C1 2.062(8), Fe–C2 2.035(9), Fe–C3 2.054(7), Fe–C4 2.071(7), Fe–C5 2.026(7). C1–B1–N1 127.7(8), C1–B1–Br1 115.3(6), N1–B1–Br1 117.0(6), C4–B2–N2 125.3(9), C4–B2–Br2 115.7(6), N2–B2–Br2 119.0(7), B1–C1–Fe 123.8(6), B1–C1–C2 126.7(7), B1–C1–C5 128.6(7), B2–C4–Fe 124.4(6), B2–C4–C3 128.3(7), B2–C4–C5 126.7(7). Tilt angle: 2.7°. Twist angle: C1–C5/B1Br1N 24.5, C1–C5/B2N2Br2 25.6.

and C5. This stands in contrast to compound **11** where the C3–C4 bond is longer than the adjacent C2–C3 and C4–C5 bonds. This difference may be caused by the larger steric requirement

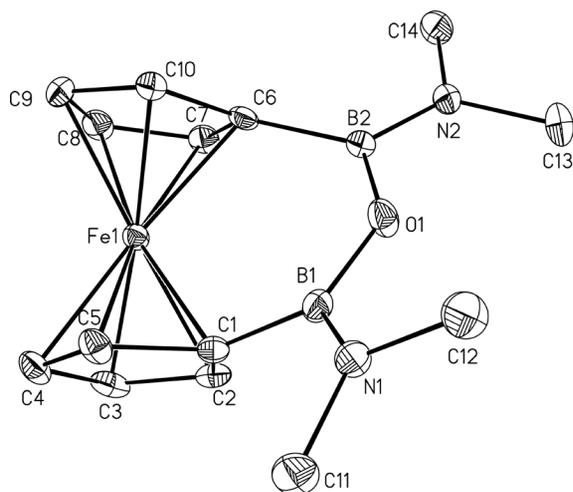


**Figure 10.** Molecular structure of 1,1',3,3'-tetrakis(bromodiisopropylaminoboryl)ferrocene (**19**). Only one of the two independent molecules in the unit cell is shown. Thermal ellipsoids are presented on a 25 % probability scale. Selected bond lengths are given in Å and bond angles in deg. B1–Br1 2.00(2), B1–N1.33(2), B1–C1 1.59(2), B2–Br2 1.99(2), B2–N2 1.41(2), B2–C3 1.53(2), B3–Br3 1.98(2), B3–N3 1.37(2), B3–C10 1.56(2), B4–Br4 1.99(2), B4–N4 1.38(2), B4–C8 1.55(2), Fe1–C1 2.09(1), Fe1–C2 2.05(1), Fe1–C3 2.098(2), Fe1–C4 2.06(1), Fe1–C5 2.04(1), Fe1–C6 2.01(1), Fe1–C7 2.03(1), Fe1–C8 2.09(1), Fe1–C9 2.05(1), Fe1–C10 2.07(1). C1–B1–Br1 112.4(13), C1–B1–N1 125.9(16), N1–B1–Br1 112.4(13), C3–B2–Br2 113.0(10), C3–B2–N2 128.4(13), N2–B2–Br2 118.6(119); C10–B3–Br3 113.8(10), C10–B3–N3 126.5(12), Br3–B3–N3 119.6(11), C8–B4–Br4 120.0(11), C8–B4–N4 127.5(14), Br4–B4–N4 120.0(11), Fe1–C1–B1 126.1(11), Fe1–C3–B2 126.4(10), Fe1–C10–B3 125.5(10), Fe1–C8–B4 130.4(11). Tilt angle C1–C5/C6–C10 3.4. Twist angle: C1–C5/B1N1Br1 142.1, C1–C5/B2N2Br2 147.2, C6–C19/B3N3Br3 145.8, C6–C10/B4N4Br4 142.5.

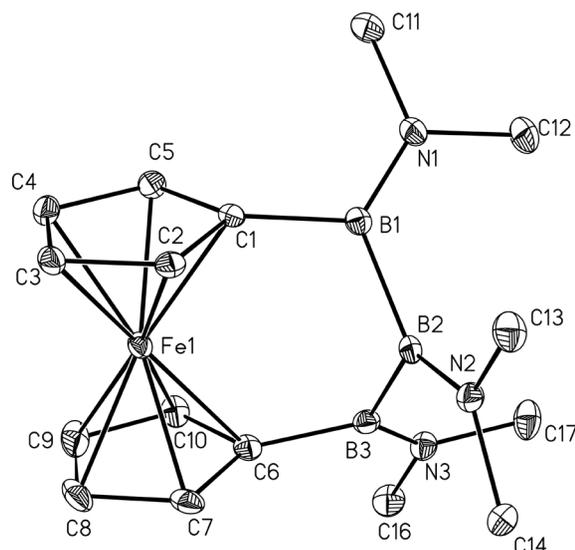
of the piperidino group compared to the dimethylamino group. The B–N bond length of 1.36(1) Å is typical for B–N  $\pi$ -bonding, the N1C6C10 plane is bent against the B1N1Br1 plane by 12°.

Compound **15** is monoclinic, space group  $C2/c$ . There are two independent molecules in the asymmetric unit. Only one molecule is shown in Figure 6. The iron atoms are located on a  $C_2$  axis. Its B–C bonds are comparatively long [1.61(1) for B1–C1 and 1.56(1) Å for B2–C2]. Astonishingly, the two B–N bonds at the boron atoms are quite different: 1.45(1) and 1.48(1) Å to the *tert*-butylamino groups at B1 and B2. 1.39(1) and 1.40(1) were found for the BN bonds to the isopropylamino group. The tilt angle for C1–C5/C1A–C5A (10.2°) is much larger compared with the angle of only 1.7° for C21–C26/C21A–C26A. Both features are also typical for the derivatives **16** and **17**.

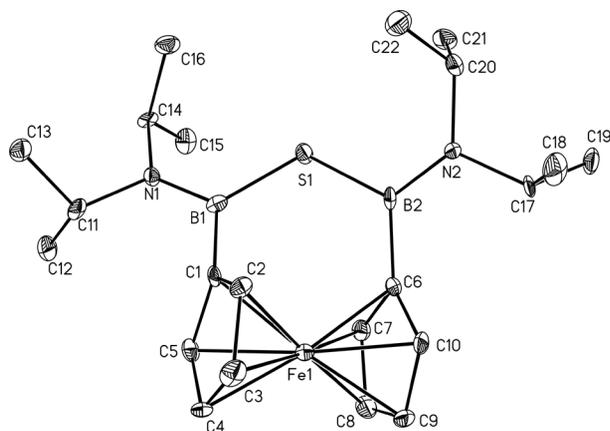
The 1,1'-bis(dimethyldiazaborolidinyl)ferrocene (**16**) crystallises in the orthorhombic space group  $P2_12_12$ . The asymmetric unit contains only half a molecule. Its iron atom resides on a twofold axis. The Cp rings are almost eclipsed and they form



**Figure 11.** Molecular structure of 2-oxo-1,3-[bis(dimethylaminoboryl)][3]-ferrocenophane (**20**). Thermal ellipsoids are drawn on a 25 % probability scale. Bond lengths in Å, bond angles in deg. B1–O1 1.384(4), B2–O1 1.386(4), B1–N1 1.397(4), B2–N2 1.394(4), B1–C1 1.580(4), B2–C6 1.580(4), C1–C2 1.4534(4), C2–C3 1.419(4), C3–C4 1.416(5), C4–C5 1.426(4), C5–C1 1.433(4), C6–C7 1.432(4), C7–C8 1.422(4), C8–C9 1.401(5), C9–C10 1.436(4), C10–C6 1.434(4), Fe1–C1 2.028(3), Fe1–C2 2.022(3), Fe1–C3 2.044(3), Fe1–C4 2.065(3), Fe1–C5 2.047(3), Fe1–C6 2.021(3), Fe1–C7 2.041(3), Fe1–C8 2.066(3), Fe1–C9 2.056(3), Fe1–C10 2.014(3). B1–O1–B2 131.8(2), C1–B1–N1 121.7(3), C1–B1–O1 121.2(2), N1–B1–O1 117.2(3), C6–B2–N2 122.2(3), C6–B2–O1 120.7(2), N2–B2–O1 117.1(2), B1–C1–C2 128.3(3), C1–C2–C3 109.3(3), C2–C3–C4 108.2(3), C3–C4–C5 107.4(3), C4–C5–C1 109.4(3), C6–C7–C8 109.5(3), C7–C8–C9 108.0(3), C8–C9–C10 108.1(3), C9–C10–C6 108.7(2). Tilt angle C1–C5/C6–C10 9.0.



**Figure 13.** Molecular structure of 1,2,3-(tris(dimethylaminoboryl))[3]-ferrocenophane (**24**). Thermal ellipsoids are drawn on a 25 % probability scale. Bond lengths in Å, bond angles in deg. B1–B2 1.708(3), B2–B3 1.709(3), C1–B1 1.577(3), B1–N1 1.395(3), C6–B3 1.581(3), B3–N3 1.398(3), C1–C2 1.432(3), C2–C3 1.426(2), C3–C4 1.414(3), C4–C5 1.427(3), C5–C1 1.443(2), C6–C7 1.431(3), C7–C8 1.423(3), C8–C9 1.419(4), C9–C10 1.425(3), C10–C6 1.443(3); Fe1–C1 2.076(1), Fe1–C2 2.033(1), Fe1–C3 2.041(2), Fe1–C4 2.467(2), Fe1–C5 1.053(2), Fe1–C6 2.071(2), Fe1–C7 2.036(2), Fe1–C8 2.040(2), Fe1–C9 2.504(2), Fe1–C10 2.052(2). B1–B2–B3 111.8(1), C1–B1–N1 120.5(2), C1–B1–B2 113.3(2), B1–B2–B3 111.8(2), B1–B2–N2 124.4(2), C6–B3–B2 114.2(2), C6–B3–N3 119.9(2), B3–B2–N2 122.8(2), B1–C1–C2 124.2(2), C1–C2–C3 109.7(2), C2–C3–C4 107.7(2), C3–C4–C5 107.9(2), C4–C5–C1 109.3(3). Tilt angle: 1.9°.



**Figure 12.** Molecular structure of 2-thio-1,3-[bis(diisopropylaminoboryl)][3]ferrocenophane (**23**). Thermal ellipsoids are drawn on a 25 % probability scale. Bond lengths in Å, bond angles in deg. B1–S1 1.863(9), B2–S1 1.877(8), B1–N1 1.41(1), B2–N2 1.10(1), B1–C1 1.58(1), B2–C6 1.56(1), N1–C11 1.502(9), N1–C14 1.484(8), N2–C17 1.498(8), N2–C20 1.495(9), C1–C2 1.422(9), C2–C3 1.42(1), C3–C4 1.39(1), C4–C5 1.42(1), C5–C1 1.42(1), C6–C7 1.42(1), C7–C8 1.42(1), C8–C9 1.42(1), C9–C10 1.41(1), C10–C6 1.44(1). B1–S1–B2 112.4(4), C1–B1–N1 120.5(7), C1–B1–S1 121.2(8), S1–B1–N1 118.1(5), C6–B2–S1 118.5(5), C6–B2–N2 123.6(6), S1–B2–N2 117.8(8), B1–C1–C2 129.8(7), C1–C2–C3 109.6(7), C2–C3–C4 107.7(7), C3–C4–C5 107.9(7), C4–C5–C1 109.6(7). Tilt angle: C1–C5/C6–C10 9.0.

a twist angle with the BN<sub>2</sub> plane of 31.6°. Its B–C bonds are longer than in bromodialkylaminoborylferrocenes. Another feature is that the B–N bonds are on the longer side with 1.410(3) and 1.405(3) Å. This is typical for bis(amino)-borane systems. The B1 atom is slightly moved above the C1–C5 plane by 0.042 Å. These features are also observed for compound **17** which crystallises in the triclinic system, space group  $P\bar{1}$ . The tilting of the Cp ring planes is comparatively large with 13.2° (see Figure 7 and Figure 8). The steric effect of the *t*Bu group is, therefore, rather drastic which becomes evident also by the torsion of its BN<sub>2</sub> planes against the Cp planes by 43.9° and 76.9°. The BN<sub>2</sub>C<sub>2</sub> rings are bent upwards and downwards, respectively. Atom B1 is 0.332 Å above the C1–C5 plane, whereas atom B2 is 0.530 Å below the C6–C10 plane.

Steric effects are significant in the 1,1',3,3'-tetrakis(bromodialkylaminoboryl)ferrocenes **18** and **19**. Compound **18** crystallises monoclinically in space group  $P2_1/n$  with  $Z = 2$  (see Figure 9). That there are only two molecules of **18** in the unit cell is due to the fact that the iron atom is located on an inversion centre. This has also the consequence that the carbon atoms of the Cp rings are present in a staggered conformation. The Cp rings are oriented almost parallel to one another, and the BNBr planes include a twist angle with their respective Cp planes of 24.0 and 25.6°. This strong twisting brings the bro-

mine atoms closer to the iron atom (see Table 1). The torsion angles C2–C1–B1–Br1 of  $-154.2^\circ$  and C3–C4–B2–Br2 of  $153.1^\circ$  show that the boron atoms are bent slightly underneath the Cp planes by  $0.065\text{Å}$ . The boron and nitrogen atoms reside in a planar environment and the B–N bond lengths with values of  $1.37(1)$  and  $1.38(1)\text{Å}$  are in agreement with B–N  $\pi$ -bonding.

The molecular structure of **19** (Figure 10) is similar to **18**. The two Cp rings are bent against each other by  $3.5^\circ$ . But the BNBr planes include now a larger twist angle with its Cp ring of  $38.7^\circ$  (B1N1Br1) and  $145.9^\circ$  (B2N2Br2). This generates an angle of  $112.5^\circ$  between the B1N1Br1 and B2N2 Br2 planes. The C<sub>2</sub>N1 plane forms an angle with the C1B1Br1 plane of  $11.3^\circ$ , the other three C<sub>2</sub>N units are bent against the respective CBBr planes by  $9.4$ ,  $6.8$  and  $4.5^\circ$ .

Compound **20**, the oxadiborylferrocenophane crystallises monoclinically, space group  $P2_1$  with  $Z = 2$  (see Figure 11). The tilting of its two Cp rings is  $9.8^\circ$ , and the B1–O1–B2 unit is not perpendicularly oriented to the two Cp rings as shown by the angle C1–C5/N1–B1–O1 of  $57.2^\circ$  and C 6–C10/N2–B2–O1 of  $55.7^\circ$ . The torsion angle B1–C1–C6–B2 is  $27.3^\circ$  whereas the torsion angles of C1–B1–O1–B2, C11–N1–B1–O1 and C13–N2–B2–O1 are  $17.7$ ,  $-173.1$  and  $2.6^\circ$ . Fe1–C distances are short for Fe1–C1 ( $2.028\text{Å}$ ) and Fe1–C6 ( $2.021\text{Å}$ ), but the Fe1–C10 bond is even shorter with  $2.014\text{Å}$ . Both Fe1–B distances are  $3.077\text{Å}$ . Actually, the O1 atom is not much more apart from the iron atom with  $3.371\text{Å}$ . It should be noted that the B–O bond lengths are  $1.384(4)$  (O1) and  $1.386(4)$  (O2) Å, and the B1–O1–B2 bond angle is  $131.8(2)^\circ$ . This indicates that the B–O bond may have some weak  $\pi$ -bond character.

The orange thiadiborylferrocenophane **23** crystallises also monoclinically but in space group  $P2_1/n$  with  $Z = 4$  (see Figure 12). The two Cp rings are tilted by  $7.5^\circ$ , and the bending of the planes C1–C5 against the N1–B1–S1 plane is  $61.5^\circ$  and of C6–C10 against N2–B2–S1 is  $42.4^\circ$ . The planes N1B1C1 and N2B2C6 enclose an angle of  $39.0^\circ$ . The torsion angle B1–C1–C6–B2 was determined as  $35.2^\circ$ . Other torsion angles are C1–B1–C6–B2 =  $35.2^\circ$ , S1–B1–N1–C1 =  $171.8^\circ$ , B2–S1–B1–C1 =  $4.6^\circ$ , and B1–S1–B2–C6 =  $37.4^\circ$ . The Fe1–B1 and Fe1–B2 distances are  $3.174$  and  $3.141\text{Å}$ , and the Fe1 distance to S1 is  $3.759\text{Å}$ . Amongst the Fe–C bond lengths those to atoms C2 and C7 ( $2.03$  and  $2.02\text{Å}$ ) are shorter than to the boron bonded atoms C1 and C6 (both  $2.036\text{Å}$ ). The B1–C1 and B2–C6 bond lengths are  $1.58(1)$  and  $1.56(1)\text{Å}$ . The Fe1⋯B1 distance is  $3.17$  and the Fe1⋯B2 distance is  $3.14\text{Å}$ . These are shorter than for the other dialkylaminoborylferrocenes. It should be noted that the B1–S1–B2 bond angle of  $112.5^\circ$  is quite open for a dicoordinated sulfur atom.

The tris(dimethylaminoboryl)[3]ferrocenophane **24** crystallises monoclinically, space group  $P2_1/n$ , with  $Z = 4$ . The “long” triboryl group has the effect that the tilt angle between the two Cp rings is now only  $1.9^\circ$ . These rings are present in an eclipsed conformation as shown by a torsion angle B1C1C6B3 of only  $1.6^\circ$ . The N1B1B2 plane is twisted against the Cp1–5 ring by  $54.3^\circ$  and the N3B3B2 plane against the Cp6–10 ring by  $121.8^\circ$ . An almost perpendicular arrangement is observed for the three Me<sub>2</sub>NB planes as shown by torsion angles for N3–B3–N2–N2 ( $-84.5^\circ$ ), N1–B1–B2–N2 ( $88.0^\circ$ ), N2–B2–N3–

B3 ( $84.5^\circ$ ). Almost coplanar are the atoms C1–N1–B1–B2 as shown by a torsion angle of  $175.6^\circ$  and for C16–N3–B3–B2 with  $178.6^\circ$ . The Fe–C bond lengths span a range from  $2.02$  to  $2.64\text{Å}$ , the shortest bonds are to atoms C2 and C7 (both  $2.020\text{Å}$ ). The Fe1–B distance to atom B1 is  $3.174\text{Å}$ , to atom B3  $3.155\text{Å}$  and to atom B2  $3.401\text{Å}$ . The B–B bond lengths are  $1.708(3)$  for B1–B2 and  $1.709(3)$  for B2–B3. They are typical for electron precise triboranes [30]. The substituents at the boron and nitrogen atoms are present in a planar environment. The N1–B1–B2 bond angle is quite open with  $125.84(1)^\circ$ , the N1–B1–C1 bond angle corresponds with  $120.5(2)^\circ$  to a trigonal planar environment, whereas the C1–B1–B2 angle is rather acute with  $113.3(2)^\circ$ . Additional data are listed in Figure 13.

## Discussion and Conclusion

Amongst the interesting species of borylated ferrocenes are those where the FeCp<sub>2</sub> molecule is attached to a six-membered B<sub>3</sub>X<sub>3</sub> ring (X = Se, S, O). The tris(ferrocenyl)selenaborane ring [CpFeCpBSe]<sub>3</sub> (**1**) was the first of this kind whose structure had been determined by X-ray crystallography. The ring system is planar, and its Cp rings are present in an eclipsed configuration [14]. Unfortunately, we could not get single crystals of the corresponding triferrocenylthiaboroxine **1**. However, Wagner et al. [24] solved the structure of triferrocenylboroxine **2**, which has an almost planar B<sub>3</sub>O<sub>3</sub> ring with B–O bond lengths of  $1.379$  to  $1.389\text{Å}$ . Its B–O–B bond angles are slightly larger than  $120^\circ$  and the O–B–O bond angles consequently a bit smaller than  $120^\circ$  ( $119.4$ – $119.7^\circ$ ). The Cp<sub>2</sub>Fe units are placed only one side of the B<sub>3</sub>O<sub>3</sub> ring, and the Cp groups of the Cp<sub>2</sub>Fe units are present in the eclipsed configuration. In contrast, the adduct (CpFeCp)BO<sub>3</sub>·HNMe<sub>2</sub> (**3**) a precursor of **2**, shows a half chair conformation with two tricoordinate boron atoms and one tetracoordinated boron atom. This arrangement induces a staggered conformation for the Cp ring at the tetracoordinated boron atom and an eclipsed conformation for the FeCp<sub>2</sub> group at the tricoordinated ring boron atom. The B–C bond lengths of **3** are comparatively long [ $1.56(1)$  and  $1.57(1)\text{Å}$ ], in contrast to **2**, where the three B–C bond lengths are shorter ( $1.524$ ,  $1.532$  and  $1.532\text{Å}$ ) [24]. The B–C bond length difference in **3** between the tricoordinate boron atoms and the Cp rings is  $0.02\text{Å}$  compared with the longer B–C bond to the tetracoordinated B2 atom [ $1.58(1)\text{Å}$ ]. This rather small difference indicates that B–C  $\pi$ -bonding can be neglected. The B–C bond lengths can be compared with those of (PhBO)<sub>3</sub> ( $1.544$ ,  $1.544$  and  $1.549\text{Å}$ ) [29], which are slightly shorter than in **2** but close to those of (EtBO)<sub>3</sub> ( $1.563$  to  $1.568\text{Å}$ ) [30].

In compounds **16** and **17** the Cp rings adopt eclipsed positions as well as in **11**, **12**, **18** and **19** due to the C<sub>2</sub> symmetry of the molecules. As the steric requirement of the amino groups increase we can notice a lengthening of the B–C bonds. The longest one was observed for compounds **15** and **17**. As far as we are aware these are the longest B–C bonds of borylferrocenes. The diazaborolidinyl rings of **16** are twisted by  $30.8$  and  $32.1^\circ$  against its Cp rings, whereas the BN<sub>2</sub> units of **17** are even stronger twisted with  $43.0^\circ$  (Cp1) and  $76.9^\circ$  (Cp6) in the

opposite direction, i.e. there is an angle of 86.6° between the two diazaborolidinyl rings. The boron atoms of **16** are located slightly above the Cp rings as has also been observed for the dehydrodiazaborolidylferrocene [26] but the boron atoms of **17** are significantly located above and below their Cp rings. This is due to the stronger disturbance of symmetry by the di-*tert*-butyldiazaborolidinyl group of compound **17**. This is mirrored by the Fe–C distances. Their average length is 2.068 Å, which are longer than in ferrocene itself (2.052 Å). Their structures can be compared with the unsaturated mono- and bis(bis(*tert*-butyl-dehydrodiazaborolidyl)ferrocenes [26]. Their Cp rings are twisted by 9.8° for the monosubstituted ferrocene CpFeCpB(N<sub>2</sub>C<sub>4</sub>tBu<sub>2</sub>H<sub>2</sub>), and by 12.9° for the disubstituted derivative Fe(CpBN<sub>2</sub>C<sub>4</sub>tBu<sub>2</sub>H<sub>2</sub>)<sub>2</sub> in contrast to the almost coplanar Cp rings in **18** and **19**. However, the strongest twisting of the Cp planes against each other is observed for bis(diisopropyl-*tert*-butyl-boryl)ferrocene, **15**. These results clearly show that the conformation of the boryl-substituted ferrocenes is strongly influenced by steric effects.

The first 2,1,3-chalcogeno-bis(dimethylaminoboryl)[3]ferrocenophanes, X(Me<sub>2</sub>NBCp)<sub>2</sub>Fe (X = O, S, Se, Te) were reported by Herberhold et al. in 1995 [27]. They determined only the structure of Se(*i*Pr<sub>2</sub>NBCp)<sub>2</sub>Fe. We now add the structure of two more species, O(Me<sub>2</sub>NBCp)<sub>2</sub>Fe and S(*i*Pr<sub>2</sub>NBCp)<sub>2</sub>Fe. Three features are of interest: the dependence of the angle between the Cp ring depending on the size of the chalcogen atom, the bending angle between a Cp ring and the B(NR<sub>2</sub>)X group and finally the angle B–X–B. In case of the oxo compound **20**, the Cp rings are tilted by 8.2°, in case of the sulfur compound by 7.5°, and in case of the selenium compound by 2.4°. The angle between the Cp rings and the B(NR<sub>2</sub>)X groups are 57.3° for **20**, 58.9° for Cp1–5/B1NMe<sub>2</sub>(S) for **23**. The B–O–B bond angle is 131.8°, the B–S–B bond angle 112.4° and the B–Se–B angle 110.2°. There is, therefore, a considerable widening of the B–X–B bond angle for all these compounds particularly compared with the respective dialkylderivatives R<sub>2</sub>BX.

The structure of the triborylferrocenophane allows a comparison with the monoboryl- and diboryl-ferrocenophanes. The most intriguing molecules are those of the monoboryl species. Tilt angles of 31.2 to 32.4° were observed for Me<sub>2</sub>NB(Cp)<sub>2</sub>Fe, (Me<sub>3</sub>Si)<sub>2</sub>NB(Cp)<sub>2</sub>Fe, *t*Bu(Me<sub>3</sub>Si)NB(Cp)<sub>2</sub>Fe, *i*Pr<sub>2</sub>NB(Cp)<sub>2</sub>Fe [31]. In case of 1,2-bis(dimethylaminodiboryl)-[2]ferrocenophane [32] the tilt angle is only 11.1°, and this angle is even further reduced to 2.6° in **24**. Moreover, in case of compound **24** the B–B–B bonds angle is 111.8° which is smaller than for most triborane derivatives, and the N–B–B–N torsion angles of 88.0° and –84.5° show, that they are similar to those of (Me<sub>2</sub>N)<sub>2</sub>B–BNMe<sub>2</sub>–B(NMe<sub>2</sub>)<sub>2</sub> [33]. There is no doubt, that all these borylferrocenophanes offer a wide field for interesting research.

## Experimental Section

All reactions were performed in an atmosphere of nitrogen or argon using the Schlenk techniques. Solvents were made anhydrous before use by the usual methods (drying with CaH<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, LiAlH<sub>4</sub>, or potas-

sium/benzophenone). Amines were either distilled before use or recrystallised from an anhydrous solvent. Borylated ferrocene starting materials were prepared by literature procedures [13–21]. NMR: Jeol L 60 (<sup>1</sup>H), Jeol GSX 270 (<sup>1</sup>H), Jeol EX 400 (<sup>13</sup>C, <sup>11</sup>B) with SiMe<sub>4</sub> or BF<sub>3</sub>OEt<sub>2</sub> as standards. IR: Nicolet 520-FT-IR spectrometer, usually in nujol/hostafilon oil; X-ray: Siemens R3m/V or P4 diffractometer, Mo-K<sub>α</sub> radiation, graphite mono-chromator, scintillation counter or area detector. In most cases the melting of the compounds was accompanied by decomposition.

**2,4,6-Triferrocenyl-1,3,5,2,4,6-trithiatriborine (1):** A solution of (Me<sub>3</sub>Si)<sub>2</sub>S (1.0 mL, 5.98 mmol) in hexane (10 mL) was slowly added to an ice cooled solution of dibromoborylferrocene (2.13 g, 5.98 mmol) in hexane (30 mL). Even after keeping the mixture at reflux for 3 h, the compounds had not reacted quantitatively. In spite of this, all volatile products were removed in vacuo. The residue was afterwards treated with hot benzene (50 mL) leaving 310 mg of an undissolved solid. The residue of the filtrate, after removing the benzene, was afterwards crystallised from pentane at –30 °C to produce 1.67 g (41 %) of red-brown microcrystalline crystals of **1**, m.p. 158–160 °C. C<sub>30</sub>H<sub>27</sub>B<sub>3</sub>S<sub>3</sub>Fe<sub>3</sub> (683.73): calcd. C 52.7, H 3.99; found C 51.0, H 3.58 %. NMR in CDCl<sub>3</sub>: <sup>1</sup>H: δ = 4.14 (s, 15 H, Cp), 4.72 (t, <sup>3</sup>J(H,H) = 1.46 Hz, 6 H, Cp-subst.), 4.83, (t, <sup>3</sup>J(<sup>1</sup>H<sup>1</sup>H) = 1.47 Hz, 6 H, Cp subst.). <sup>13</sup>C: δ = 70.2 (Cp unsubst.), 74.0 (Cp subst.), 74.7 (Cp subst.), CB not obsv. <sup>11</sup>B (C<sub>6</sub>D<sub>6</sub>): δ = 57.5 (br). IR: ν = 3091 m, 2924 st, 1434 vst, 1376 st, 1244 vst, 1003 vst, 819 vst, 763 st, 677 vst, 495 st, 479 st, 441 cm<sup>–1</sup>.

**Tris(ferrocenyl)boroxine-Dimethylamine (3) and Tris(ferrocenyl)boroxine (2):** To a THF solution (10 mL) of (Me<sub>2</sub>N)<sub>2</sub>BCpFeCp (690 mg, 2.40 mmol) was added a 0.5 M solution of water in THF (5 mL) at –60 °C. The mixture was stirred until it has reached ambient temperature. Under these conditions dimethylamine developed readily. After stirring the solution for 12 h a broad <sup>11</sup>B NMR signal at 24.6 ppm for **3** with a shoulder at lower field was observed. Compound **2** was isolated from part of the THF solution which was kept at reflux for 1 week. This resulted in a shift of the <sup>11</sup>B NMR signal to 31 ppm besides a weak signal at δ = 25 ppm. Afterwards, all volatiles were removed in vacuo. Crystallisation of the solid residue from toluene (30 mL) gave as a first fraction tiny crystals of orange coloured **3** whose structure was determined by X-ray crystallography. Three further crystallisations yielded crystals of **2**. Yield: 1.27 g (67 %), m.p. 236–238 °C. C<sub>30</sub>H<sub>27</sub>O<sub>3</sub>B<sub>3</sub>Fe (633.55): calcd. C 56.7, H 4.29; found C 56.5, H 5.04 %. NMR of **2** (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H: δ = 4.12 (s, 15 H, unsub. Cp), 4.38 (pseudotrip., <sup>3</sup>J(H,H) = 1.47 and 1.95 Hz resp., 6 H), 4.81 (pseudotrip., <sup>3</sup>J(H,H) = 1.46 and 1.96 Hz, 6 H). <sup>13</sup>C: δ = 70.0, 73.1, 74.4, CB (not obs.). <sup>11</sup>B: δ = 31.6, (br). IR: ν = 3228 w, 3088 w, 2927 m, 1462 st, 1311 vst, 1106 st, 1024 m, 823 st, 729 st, 650 m, 427 vst, 482 st cm<sup>–1</sup>.

**1,1'-Bis(brom-ethoxyboryl)ferrocene (4):** [13c]: At –70 °C, a solution of (Br<sub>2</sub>BCp)<sub>2</sub>Fe (4.35 g, 4.28 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added to a solution of diethyl ether (640 mg, 8.56 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solution was allowed to attain room temperature within 4 h. Afterwards, all volatile materials were removed in vacuo. The residue was dissolved in pentane (15 mL). At –78 °C a red-brown precipitate formed (2.65 g, 62 %). This material transformed into an oil at room temperature from which crystals of **4** separated on standing for two weeks, m.p. 140–145 °C. C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>BB<sub>2</sub>Fe (355.57): calcd. C 36.9, H 3.98, found C 36.7, H 4.26 %. NMR (in C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H: δ = 1.07 (t, <sup>3</sup>J(H,H) = 7.32 Hz, 6 H, Me), 4.07 (q, <sup>3</sup>J(H,H) = 7.32 Hz, 4 H, CH<sub>2</sub>), 4.32 (pseudotrip., <sup>3</sup>J(H,H) = 1.47, 1.97 Hz, 4 H, Cp). <sup>13</sup>C: δ = 16.8 (Me), 65.7 (CH<sub>2</sub>), 74.8 (C-3,4), 76.1 (C-5), CB not found. <sup>11</sup>B: δ = 38.9. IR: ν = 3099 w, 2982 st, 2931 m, 1484 vst, 1755 vst, 1379

vst, 1229 vst, sh, 1220 st, 1098 m, 936 m, 772 st, 653 m, 479 st  $\text{cm}^{-1}$ .  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{BBr}_2\text{Fe}$  (355.57): calcd. C 36.9, H 3.98, found C 36.7, H 4.26.

**1,1'-Bis(diethoxyboryl)ferrocene (6):** [13c]:  $[(\text{Me}_2\text{N})_2\text{BCp}]_2\text{Fe}$ , **5** (2.72 g, 7.12 mmol), was dissolved in hexane (15 mL) and a solution of ethanol (1.68 mL, 28.5 mmol) diluted with hexane (5 mL) was added dropwise at  $-60^\circ\text{C}$  whilst stirring. At  $-30^\circ\text{C}$  compound **6** separated as an orange red crystalline powder. Yield: 1.79 g (65 %), m.p.  $140^\circ\text{C}$ .  $\text{C}_{18}\text{H}_{28}\text{O}_4\text{B}_2\text{Fe}$  (385.89), calcd. C 56.0, H 7.31; found C 55.0, H 6.82 %. **NMR** (in  $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ :  $\delta = 1.27$  (t,  $^3J(\text{H,H}) = 6.84$  Hz, 12 H, Me), 4.07 (q,  $^3J(\text{H,H}) = 6.84$  Hz, 8 H,  $\text{CH}_2$ ), 4.30 (t,  $^3J(\text{H,H}) = 1.47$ , 1.95 Hz, 4 H, Cp), 4.36 (t,  $^3J(\text{H,H}) = 1.47$ , 1.95 Hz, 4 H, Cp).  $^{13}\text{C}$ :  $\delta = 17.6$  (Me), 59.4 ( $\text{CH}_2$ ), 72.1 (C-3,4), 74.7 (C-2,5), CB (not detect.).  $^{11}\text{B}$ :  $\delta = 29.7$ .

**1,1'-Bis(catecholoboryl)ferrocene (9):** To a solution of  $[(\text{Me}_2\text{N})_2\text{BCp}]_2\text{Fe}$  (890 mg, 2.41 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) was dropped a solution of 1,2-dihydroxybenzene (530 mg, 4.82 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL). A yellow precipitate formed quickly which proved to be **8** (1.02 g, 68 %), m.p.  $280^\circ\text{C}$  (dec.). To a stirred suspension of this adduct (280 mg, 0.55 mmol) in diethyl ether (15 mL) was added  $\text{BF}_3\cdot\text{OEt}_2$  (160 mg, 1.1 mmol). This resulted in a slow change of the yellow colour to orange whilst the precipitate went into solution. After removal of all volatiles the residue was crystallised from diethyl ether at  $-30^\circ\text{C}$ . Yield of **9**: 230 mg (99 %), m.p.  $181^\circ\text{C}$ , orange crystals.  $\text{C}_{22}\text{H}_{16}\text{O}_4\text{B}_2\text{Fe}$  (424.85), **(9)**: calcd. C 62.62, H 3.80; found C 62.2, H 3.84 %. **NMR** (in  $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ :  $\delta = 4.15$  (t,  $^3J(\text{H,H}) = 1.46$ , 1.96 Hz, 4 H, Cp), 3.66 (t,  $^3J(\text{H,H}) = 1.46$ , 1.96 Hz, 4 H, Cp), 6.78 (m, 6 H, H-3,3',6,6'), 6.96 (m, 4 H, H-4,4',5,5').  $^{13}\text{C}$ :  $\delta = 73.8$  (C-3,4), 74.9 (C-2,5), CB (no found), 112.5 (C-3,3',6,6'), 122.6 (C-4,4',5,5'), 149.0 (C-1,1',2,2').  $^{11}\text{B}$ :  $\delta = 35.7$ . **IR**:  $\nu = 3038$  w, 1512 m, 1501 st, 1489 st, 1479 vst, 1387 st, 1322 st, 1312 st, 1238 st, 1132 m, 1115 st, 899 m, 811 m, 744 vst, 689 m, 499 m, 427  $\text{m cm}^{-1}$ .

**1,1'-Bis(bromodiisopropylaminoboryl)ferrocene (10):** [18, 27]: To an ice cold stirred solution of  $(\text{Br}_2\text{BCp})_2\text{Fe}$  (3.78 g, 7.20 mmol) in hexane (60 mL) was slowly added a solution of diisopropylamine (4.06 mL, 28.9 mmol). A suspension formed. At room temperature the solid  $[\text{iPr}_2\text{NH}_2]\text{Br}$  was removed by filtration. (3.06 g, 16.8 mmol) and the solution reduced to 20 mL in vacuo. After cooling to  $-30^\circ\text{C}$  2.77 g (68 %) of orange brown crystals of **10** separated, m.p.  $151\text{--}152^\circ\text{C}$ .

**1,1'-Bis(bromodimethylamino)borylferrocene (11):** A solution of 1,1-bis(dibromoboryl)-ferrocene (3.25 g, 9.14 mmol) in hexane (25 mL) was cooled to  $-50^\circ\text{C}$ . Whilst stirring, a solution of  $\text{Me}_2\text{NSiMe}_3$  (2.88 mL, 2.13 g, 18.2 mmol), in hexane (50 mL) was added. After the mixture had attained room temperature another portion of pure  $\text{Me}_2\text{NSiMe}_3$  (0.50 mL) was added. Afterwards, after 1 h, all volatiles were removed in vacuo. Crystallisation of the residue from hexane at  $-78^\circ\text{C}$  produced 1.78 g (98 %) of red crystals of **11**, m.p.  $46^\circ\text{C}$ .  $\delta^{11}\text{B}$  ( $\text{C}_6\text{D}_6$ ) = 33.4 ppm. For further data see [27].

**1,1'-Bis(bromopiperidinoboryl)ferrocene (12):** Prepared according to **11** from  $\text{Me}_3\text{Si}(\text{NC}_5\text{H}_{10})$  (1.54 g, 9.78 mmol) and  $(\text{Br}_2\text{BCp})_2\text{Fe}$  (2.70 g, 4.89 mmol) in hexane (29 mL). Red crystals of **12**, yield: 80 %. m.p.  $76\text{--}78^\circ\text{C}$   $\text{C}_{20}\text{H}_{28}\text{N}_2\text{B}_2\text{Br}_2\text{Fe}$  (533.81): calcd. C 46.50, H 5.78, N 5.25; found: C 46.32, H 5.64, N 5.12 %. **NMR** (in  $\text{CDCl}_3$ ):  $^1\text{H}$ :  $\delta = 1.57$  (m, 8 H,  $\text{CH}_2$ , H-2,4), 1.68 (m, 4 H,  $\text{CH}_2$ , H-3), 3.50 (t,  $^3J(\text{H,H}) = 5.3$  Hz, 4 H,  $\text{CH}_2$ ), 3.60 (t,  $^3J(\text{H,H}) = 5.3$  Hz, 4 H,  $\text{CH}_2$ ), 4.38 (pseudotr.,  $^3J(\text{H,H}) = 1.46$ , 1.96 Hz, 4 H, H-2,5), 4.41 (pseudotr. 5,  $^3J(\text{H,H}) = 1.46$ , 1.96 Hz).  $^{13}\text{C}$ :  $\delta = 25.4$  (pip C3), 28.0, 28.3 (pip, C2, C4), 50.9, 52.5 (pip, C1, C5), 73.6 (C-3,4), 77.3 (C-2,5), CB (not found).  $^{11}\text{B}$ :  $\delta = 36.1$  (br). **IR**:  $\nu = 2995$  w, 2932 m, 2852 st, 1496 vst,

1490 vst, 1265 vst, 1210 vst, sh, 1110 m, 927 m, 767 st, 653 m. 464  $\text{m cm}^{-1}$ .

**1,1'-Bis(bromodiphenylaminoboryl)ferrocene (13):** Prepared in analogy to **12** from  $(\text{Br}_2\text{BCp})_2\text{Fe}$  (2.58 g, 4.67 mmol) and  $\text{Me}_3\text{SiNPh}_2$  (2.24 g, 9.32 mmol) in hexane (20 mL). Red crystals. Yield of **13**: 62 %; m.p.  $80\text{--}85^\circ\text{C}$ .  $\text{C}_{34}\text{H}_{28}\text{N}_2\text{Br}_2\text{B}_2\text{Fe}$  (702.03): calcd. C 58.17, H 4.02, N 3.99; found C 56.95, H 3.92, N 3.82 %. **NMR** ( $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ :  $\delta = 4.10$  (br, 4 H, H-2,5), 4.32 (br, 4 H, H-3,4), 6.94 (m, 12 H, Ph, H-2,4,6), 7.03 (m, 8 H, Ph, H-3,5).  $^{13}\text{C}$ :  $\delta = 74.4$ , (C-3,4), 77.4 (C-2,5), CB(not found), 126.2 (Ph, C-4) 128.2, 129.0 (Ph, C-2,6, C-3,5), 148.5 (Ph, C-1).  $^{11}\text{B}$ :  $\delta = 39.9$ . **IR**:  $\nu = 3062$  w, 1587 m, 1443 st, 1387 st, 1245 st, sh, 1061 m, 945 m, 838 m, 774 m, 696 st, 502 m, 484  $\text{m cm}^{-1}$ .

**1,1'-Bis(bromo-tetramethylpiperidino-boryl)ferrocene (14):** A solution of  $(\text{Br}_2\text{BCp})_2\text{Fe}$  (4.02 g, 7.61 mmol) in hexane (30 mL) was cooled to  $-78^\circ\text{C}$ . Afterwards, a solution prepared from  $\text{tmpH}$  (2.59 mL, 2.15 g, 15.2 mmol) and  $\text{Li}^t\text{Bu}$  (9.97 mL, 1.56 m) was slowly added. After stirring for 3 d, the solvent was removed in vacuo. The residue on crystallisation from pentane (20 mL) yielded 3.76 g (77 %) of orange microcrystals of **14**; m.p.  $151^\circ\text{C}$ . **NMR** ( $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ :  $\delta = 1.44\text{--}1.46$  (m, 12 H, H-2,3,4), 1.51 (s, 24 H, Me), 4.57 (t,  $^3J(\text{H,H}) = 1.96$  Hz, 4 H, H-2,5), 4.66 (t,  $^3J(\text{H,H}) = 1.96$  Hz, 4H, H-3,4).  $^{13}\text{C}$ :  $\delta = 15.1$  (C3), 33.2 (C6,7,8,9), 36.5 (C2,4), 56.5 (C1,5), 74.9 (C3,4), 77.3 (C2,5), CB not obs.  $^{11}\text{B}$ :  $\delta = 42.9$ . **IR**:  $\nu = 3004$  w, 2943 st, 1439 st, sh, 1385 vst, 1244 m, 1049 st, 966 st, 827 m, 650 m, 505 m, 466  $\text{m cm}^{-1}$ .

**1,1'-Bis(diisopropylamino-tert-butylamino)borylferrocene (15):** A solution of 1,1'-bis(bromo-diisopropylaminoboryl)ferrocene (1.04 g, 1.84 mmol) in hexane (15 mL) was cooled to  $-15^\circ\text{C}$ . Afterwards, a mixture of *tert*-butylamine (0.19 mL, 1.84 mmol) and triethylamine (0.51 mL, 3.68 mmol) in hexane (10 mL), was added slowly whilst stirring. Stirring was continued at room temperature for 21 h. The insoluble  $[\text{Et}_3\text{NH}]\text{Br}$  was removed by filtration and the hexane from the filtrate in vacuo. The remaining solid was afterwards crystallised from hexane (30 mL) at  $-30^\circ\text{C}$  to give orange-red crystals of **15**. Yield: 420 mg, 42 %, m.p.  $155^\circ\text{C}$ .  $\text{C}_{30}\text{H}_{56}\text{N}_4\text{B}_2\text{Fe}$  (550.27): calcd. C 65.48, H 10.26, N 10.18; found C 64.60, H 9.54, N 9.73 %. **IR**:  $\nu = 3105$  w, 3083 w, 2966 vst, 1487 st, 1386 m, 1277 vst, 1233 st, 1224 m, 821 m, 617 m, 510  $\text{w cm}^{-1}$ .

**1,1'-Bis[1,3-dimethyl-1,3,2-diazaborolidinyl]ferrocene (16):** [14c]: To a solution of  $\text{Fe}(\text{CpBBr}_2)_2$  (1.11 g, 2.10 mmol) in benzene (40 mL) was added whilst stirring a solution of *N,N'*-dimethylethylene-diamine (0.45 mL, 4.2 mmol) and triethylamine (1.17 mL, 8.4 mmol) in benzene (15 mL) at  $0^\circ\text{C}$ . Stirring was continued until the suspension attained room temperature. Afterwards, the precipitate (1.45 g, 7.97 mmol) of  $[\text{Et}_3\text{NH}]\text{Br}$  was removed by filtration, followed by removal of the solvent from the filtrate in vacuo. The red crystalline residue was recrystallised by adding hexane (25 mL) at  $-30^\circ\text{C}$ . Yield: 650 mg, 71 %, m.p.  $83^\circ\text{C}$ .  $\text{C}_{18}\text{H}_{28}\text{N}_4\text{B}_2\text{Fe}$  (378.06), calcd. C 57.19, H 7.47, N 14.83; found C 56.32, H 7.23, N 14.77 %. **IR**:  $\nu = 3104$  m, 3083 m, 2857 vst, 1501 vst, 1402 vst, 1288 st, 1214 s, 821 st, sh, 670 m, 502 st, 478  $\text{m cm}^{-1}$ .

**1,1'-Bis(1,3-di-tert-butyl-1,3,2-diazaborolidinyl)ferrocene (17):** In analogy to **16**, a solution of *N,N'*-di-tert-butylethylenediamine (1.88 mL, 10.7 mmol) and triethylamine (2.98 mL, 21.5 mmol) in hexane was slowly added to a stirred solution of  $(\text{Br}_2\text{BCp})_2\text{Fe}$  (2.81 g, 5.35 mmol) in hexane (40 mL) at  $5^\circ\text{C}$ . The suspension that formed was stirred for 1 h. Afterwards, the precipitate of  $[\text{Et}_3\text{NH}]\text{Br}$  (3.92 g, 21.5 mmol) was removed by filtration and 50 % of the solvent of the

filtrate was evaporated in vacuo. From the remaining solution separated at  $-30\text{ }^{\circ}\text{C}$  red crystals of **17**, m.p.  $148\text{ }^{\circ}\text{C}$ . Yield: 2.28 g, 78 %.  $\text{C}_{30}\text{H}_{52}\text{N}_4\text{B}_2\text{Fe}$  (546.24): calcd. C 65.92, H 9.59, N 10.26; found: C 65.97, H 9.51, N 10.02 %. IR:  $\nu = 3094\text{ w}, 3081\text{ w}, 2967\text{ st}, 1473\text{ m}, 1394\text{ vst}, 1265\text{ vst}, \text{br}, 1232\text{ vst}, \text{br}, 821\text{ m}, 672\text{ w}, 497\text{ m}, 470\text{ w cm}^{-1}$ .

**1,3,1',3'-Tetrakis(bromodimethylaminoboryl)ferrocene (18):** A solution of 1,1',3,3'-tetra(dibromoboryl)ferrocene [20] (8.98 g, 10.4 mmol) in hexane (75 mL) was cooled to  $-50\text{ }^{\circ}\text{C}$ . Whilst stirring a solution of  $\text{Me}_3\text{SiNMe}_2$  (86.59 mL, 4.88 g, 41.6 mmol) in hexane (25 mL) was added slowly. After the addition the mixture was allowed to attain ambient temperature. All volatile material (hexane and  $\text{Me}_3\text{SiBr}$ ) was evaporated in vacuo. The residue was afterwards dissolved in hexane (ca. 50 mL), the turbid solution filtered and the filtrate kept at  $-30\text{ }^{\circ}\text{C}$ . Within 4 days red crystals had separated which were isolated by filtration and dried in vacuo. Yield of **18**: 5.06 g, 67.5 %, m.p.  $160\text{--}162\text{ }^{\circ}\text{C}$ . NMR ( $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ :  $\delta = 2.68$  (s, 12 H, Me), 2.85 (s, 12 H, Me), 4.92 (d,  $^3J(\text{H,H}) = 0.98\text{ Hz}$ , 4 H, H4,5), 4.99 (t,  $^3J(\text{H,H}) = 1.46\text{ Hz}$ , 2 H, H2).  $^{13}\text{C}$ :  $\delta = 41.2$  (Me), 43.1 (Me), 82.5 (C4,5), 86.6 ppm (C2), CB (not obs.).  $^{11}\text{B}$ :  $\delta = 37.3$  (br). IR (nujol, hostafon):  $\nu = 2954\text{ st}, 2932\text{ st}, 2872\text{ st}, 1518\text{ st}, 1461\text{ st}, 1255\text{ m}, 875\text{ m}, 847\text{ m}, 651\text{ st}, 538\text{ m}, 492\text{ m cm}^{-1}$ .

**1,3,1',3'-Tetrakis(bromodiisopropylaminoboryl)ferrocene (19):** To a stirred solution of 1,1',3,3'- $[(\text{Br}_2\text{B})_2\text{Cp}]_2\text{Fe}$  (1.16 g, 1.34 mmol) in benzene (50 mL) was added at  $0\text{ }^{\circ}\text{C}$  a solution containing  $i\text{Pr}_2\text{NH}$  (0.75 mL, 5.36 mmol) and  $\text{Et}_3\text{N}$  (0.74 mL, 5.36 mmol) in benzene (20 mL). After stirring for 2 h, the insoluble material was removed by filtration and benzene evaporated from the filtrate. The residue was

dissolved in hexane (30 mL). After filtration the filtrate was kept at  $-30\text{ }^{\circ}\text{C}$ . 320 mg of orange crystals (yield: 25 %), separated within a few days. m.p.  $200\text{ }^{\circ}\text{C}$ (dec.).  $\text{C}_{36}\text{H}_{62}\text{N}_4\text{B}_4\text{Br}_4\text{Fe}$  (945.6): calcd. C 43.2, H 6.61, N 5.93; found C 43.2, H 7.07, N 5.21 %. NMR ( $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ :  $\delta = 0.92$  (d,  $^3J(\text{H,H}) = 6.84\text{ Hz}$ , 12 H, Me), 1.04 (d,  $^3J(\text{H,H}) = 6.84\text{ Hz}$ , 12 H, Me), 1.57 (d,  $^3J(\text{H,H}) = 6.84\text{ Hz}$ , 12 H, Me), 1.60 (d,  $^3J(\text{H,H}) = 6.84\text{ Hz}$ , 12 H, Me), 3.31 (sept., br., 4 H, CH), 4.53 (sept. ( $^3J(\text{H,H}) = 6.84\text{ Hz}$ , 4 H, CH), 5.02 (d,  $^4J(\text{H,H}) = 1.46\text{ Hz}$ , 4 H, H4,5), 5.04 (t., br. 2 H, H2).  $^{13}\text{C}$ :  $\delta = 21.5$  (Me), 22.0 (Me), 23.9 (Me), 24.1 (Me), 47.7 (CH), 52.6 (CH), 81.7 (C-4,5), 86.1 ppm (C2), CB (not obs.).  $^{11}\text{B}$ :  $\delta = 36.5$  ppm. IR (nujol, hostafon):  $\nu = 3027\text{ w}, 2970\text{ st}, \text{sh}, 2931\text{ m}, 1470\text{ vst}, 1367\text{ st}, 1330\text{ vst}, 1188\text{ m}, 1137\text{ st}, 1092\text{ st}, 1005\text{ st}, 778\text{ m}, 756\text{ m}, 503\text{ w cm}^{-1}$ .

**1,1'-(Bis(dimethylaminoboryl)-2-oxo[3]-ferrocenophane (20):** To a solution of  $(\text{BrMe}_2\text{NBCp})_2\text{Fe}$  (780 mg, 1.08 mmol) in THF (20 mL) was added  $\text{Li}_2\text{O}$  (65 mg, 2.16 mmol). The suspension was stirred overnight. Afterwards, the solvent was removed in vacuo and the residue treated with hexane (50 mL). After 630 mg insoluble LiBr were separated by filtration 270 mg of an orange powder was recovered by evaporation of the solvent. The residue was crystallised from hot hexane/dichloroethane (1:1). Yield: 100 mg (21 %) of **20**, m.p.  $198\text{--}200\text{ }^{\circ}\text{C}$ .  $\text{C}_{18}\text{H}_{30}\text{N}_4\text{O}_2\text{B}_4\text{Fe}$ , calcd. C 49.9, H 6.97, N 12.9; found C 50.6, H 7.70, N 13.0 %. NMR ( $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ :  $\delta = 2.80$  (br., 24 H, Me), 4.38 (d,  $^4J(\text{H,H}) = 0.98\text{ Hz}$ , 4 H, H3,4), 4.50 (t,  $^4J(\text{H,H}) = 0.98\text{ Hz}$ , 2 H, H2,5);  $\delta^{13}\text{C} = 36.3$  (Me), 39.1 (Me), 83.0 (C3,4), 85.4 (C2,5) C1 (not obs.).  $^{11}\text{B}$ :  $\delta = 31.1$ , br.

**1,1'-(Bis(diisopropylaminoboryl)-2-oxo[3]-ferrocenophane (21):** To a solution of 1,1'-bis(diisopropylamino-bromoboryl)ferrocene (1.15 g,

**Table 2.** Crystallographic data and data related to data collection and structures solution for compounds **9–12** and **15–17**.

Compound	3-C <sub>6</sub> H <sub>6</sub>	9	10	11	12	15	16	17
Formula	C <sub>38</sub> H <sub>40</sub> NO <sub>3</sub> B <sub>3</sub> Fe <sub>3</sub>	C <sub>16</sub> H <sub>23</sub> NBBBrFe	C <sub>22</sub> H <sub>36</sub> N <sub>2</sub> B <sub>2</sub> Br <sub>2</sub> Fe	C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> BBBr <sub>2</sub> Fe	C <sub>20</sub> H <sub>28</sub> N <sub>2</sub> B <sub>2</sub> Br <sub>2</sub> Fe	C <sub>30</sub> H <sub>54</sub> B <sub>2</sub> N <sub>4</sub> Fe	C <sub>18</sub> H <sub>28</sub> N <sub>4</sub> B <sub>2</sub> Fe	C <sub>30</sub> H <sub>52</sub> N <sub>4</sub> B <sub>2</sub> Fe
M <sub>r</sub>	758.69	375.92	565.82	453.61	533.73	548.24	377.91	546.23
Crystal size / mm	0.6 × 0.5 × 0.5	0.5 × 0.3 × 0.3	0.6 × 0.6 × 0.4	0.36 × 0.2 × 0.2	0.30 × 0.30 × 0.2	0.3 × 0.35 × 0.6	0.65 × 0.3 × 0.28	0.4 × 0.32 × 0.18
Crystal system	orthorhombic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	triclinic
Space group	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>Pbcn</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> $\bar{1}$
<i>a</i> / Å	15.992(4)	6.003(1)	7.90(1)	13.889(2)	19.824(7)	23.133(8)	11.717(3)	10.76(1)
<i>b</i> / Å	19.515(2)	19.702(5)	11.69(1)	9.868(2)	10.329(3)	8.987(23)	8.093(2)	12.09(1)
<i>c</i> / Å	11.061(2)	13.936(6)	14.03(2)	12.275(2)	11.585(4)	18.858(7)	9.8892(2)	13.45(1)
$\alpha$ / deg	90	90	83.00(9)	90	90	90	90	109.44(1)
$\beta$ / deg	90	91.41(3)	89.3(1)	90	114.97(3)	123.89(1)	90	91.22(2)
$\gamma$ / deg	90	90	83.3(1)	90	90	90	90	112.46(1)
<i>V</i> / Å <sup>3</sup>	3452(1)	1647.7(9)	1278(3)	1682.4(5)	2150(1)	3254.4(9)	938.0(4)	1503(3)
<i>Z</i>	4	4	2	4	4	4	2	2
<i>D</i> <sub>calc.</sub> / g cm <sup>-3</sup>	1.460	1.515	1.471	1.791	1.649	1.119	1.338	1.207
$\mu$ (Mo- <i>K</i> $\alpha$ ) / mm <sup>-1</sup>	1.283	3.329	3.728	5.639	4.425	0.487	0.812	0.527
<i>F</i> (000)	2568	768	576	896	1072	1192	400	592
Temp / K	273	193	273	203	193	273	293	293
$2\theta$ range	3.3–50.0	3.56–48.06	2.44–46.1	5.06–47.98	4.54–50.06	3.72–48.00	5.38–50.00	3.26–50.00
Index range	$-19 \leq h \leq 1$ $-1 \leq k \leq 23$ $-13 \leq l \leq 8$	$-6 \leq h \leq 6$ $-5 \leq k \leq 22$ $-15 \leq l \leq 3$	$-8 \leq h \leq 8$ $-12 \leq k \leq 12$ $0 < l \leq 3$	$-11 \leq h \leq 2$ $0 \leq k \leq 14$ $-1 \leq l \leq 15$	$-23 \leq h < 0$ $-12 \leq k \leq 0$ $-12 \leq l \leq 12$	$1 \leq h \leq 26$ $-10 \leq k \leq 10$ $-21 \leq l \leq 18$	$-13 \leq h \leq 13$ $-1 \leq k \leq 9$ $-1 \leq l \leq 11$	$0 \leq h \leq 12$ $-13 \leq k \leq 12$ $-15 \leq l \leq 15$
Refl. measured	5501	2640	3706	1864	1911	5347	2384	5372
Refl. unique	5081	2542	3541	1286	1853	4251	1658	4271
<i>R</i> <sub>int</sub>	0.0478	0.055	0.02543	0.0299	0.0776	0.0496	0.0148	0.0681
Param. refined	433	181	270	98	131	345	116	345
<i>R</i> 1 ( <i>G</i> $\sigma$ <i>F</i> )	0.0438	0.0556	0.1114	0.0414	0.0675	0.1011	0.0270	0.0712
GOF ( <i>F</i> <sup>2</sup> )	1.066	1.038	0.2888	0.854	0.1357	1.053	1.061	1.029
$\Delta\rho$ (max/min) / e $\cdot$ Å <sup>-3</sup>	0.388/–0.429	0.553/–0.496	0.217/–0.117	0.480/–0.391	0.896/–0.642	0.066/–0.482	0.321/–0.216	0.75/–0.43

1.22 mmol) in THF (40 mL), was added Li<sub>2</sub>O powder (73 mg, 2.44 mmol). After stirring the suspension for 23 h the solvent was evaporated from the filtrate whose residue was dissolved in hexane (40 mL). The insoluble part (420 mg, 4.84 mmol LiBr, 99 %) was separated by filtration. 50 % of the hexane was afterwards evaporated in vacuo, and the remaining solution cooled to -30 °C. **21** separated as a microcrystalline yellow-orange powder, m.p. 150–155 °C which contained about 5 % impurities. C<sub>34</sub>H<sub>62</sub>N<sub>4</sub>O<sub>2</sub>B<sub>4</sub>Fe (657.98): calcd. C 62.10, H 9.50, N 8.51; found; C 61.3, H 9.03, N 7.93 %. **NMR** (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H: δ = 1.03 (d, <sup>3</sup>J(H,H) Hz, Me), 1.21 (d, <sup>3</sup>J(H,H) = 6.83 Hz, 12 H, Me), 1.47 (d, <sup>3</sup>J(H,H) = 6.84 Hz, 12 H, Me), 1.55 (d, <sup>3</sup>J(H,H) = 6.83 Hz, 12 H, Me), 3.30 (sept., <sup>3</sup>J(H,H) = 6.83 Hz, 4 H, CH), 3.29 (sept, <sup>3</sup>J(H,H) = 6.84 Hz, 4 H, CH), 4.58 (br., 4 H, H<sub>4,5</sub>), 4.65 (br., 2 H, 2 H). <sup>13</sup>C: δ = 22.9 (Me), 23.1 (Me), 24.3 (Me), 25.2 (Me), 44.4 (CH), 49.4 (CH), 82.6 (C-4,5), 84.8 (C-2), CB (not obs.). <sup>11</sup>B: δ = 29.4, br.

**1,1'-Bis(dimethylaminoboryl)-2-thia[3]-ferrocenophane (22):** 1,1'-(BrMe<sub>2</sub>NBCp)<sub>2</sub>Fe (1.21 g, 1.68 mmol) was dissolved in THF (15 mL). Whilst stirring a suspension of Li<sub>2</sub>S (154 mg, 3.56 mmol) in THF (10 mL) was added. Stirring was continued for 12 h. This resulted in an orange colored suspension. The slightly yellow solid (1.0 g) was afterwards removed by filtration. After the hexane was evaporated in vacuo 0.23 g (31 %) of **22** were left as an orange powder whose <sup>1</sup>H NMR spectrum showed that it consisted of 85 % of **22** and 15 % of impurities. Crystallisation from hexane improved the purity, but no analytically pure **22** was obtained. C<sub>18</sub>H<sub>30</sub>N<sub>4</sub>B<sub>4</sub>N<sub>4</sub>S<sub>2</sub>Fe (465.67); calcd. C 46.40, H 6.49, N 12.0; found C 45.3, H 6.43, N 11.20 %. **NMR** (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H: δ = 2.66 (s, 12 H, Me), 2.96 (s, 12 H, Me), 4.47 (br., 4 H, H<sub>4,5</sub>), 4.50 (br., 2 H, H<sub>2</sub>); <sup>13</sup>C: δ = 41.1 (Me), 41.4 (Me), 79.7 (C<sub>4,5</sub>), 84.2 (C-2), CB (not obs.); <sup>11</sup>B: δ = 40.2 (br). **IR** (nujol/hostafon): ν = 3006 w, 2927 vst, 1506 vst, 1391 vst, 1210 st, 1106 st, 971 m, 892 m, 799 w, 531 m, 455 w cm<sup>-1</sup>.

**1,1'-Bis(diisopropylaminoboryl)-2-thia[3]-ferrocenophane (23):** To a solution of (BriPr<sub>2</sub>NBCp)<sub>2</sub>Fe (1.61 g, 1.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added Li<sub>2</sub>S (160 mg, 3.48 mmol) and 15-crown-5 (1.35 mL, 6.8 mmol). After stirring for 2 h the <sup>11</sup>B NMR signal has shifted from 36.5 to 40.1 ppm. After removing the solvent in vacuo the residue was treated with hexane (70 mL). Insoluble material was removed by filtration and the filtrate reduced in volume by appr. 50 %. The resulting solution was afterwards kept at -30 °C for crystallisation. Yield: 850 mg of yellow orange needles, m.p. 249 °C (dec.). C<sub>34</sub>H<sub>62</sub>N<sub>4</sub>N<sub>4</sub>B<sub>4</sub>S<sub>2</sub>Fe (690.10: calcd. C 59.2, H 9.06, N 8.12; found C 58.2, H 8.93, N 8.08) %. **NMR** (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H: δ = 0.95 (d, <sup>3</sup>J(H,H)) 6.84 Hz, 12 H, Me), 0.96 (d, <sup>3</sup>J(H,H)) 6.84 Hz, 12 H, Me), 1.69 (d, <sup>3</sup>J(H,H) = 6.84 Hz, 12 H, Me), 1.72 (d, <sup>3</sup>J(H,H)) 6.84 Hz, 12 H, Me), 3.36 (sept., <sup>3</sup>J(H,H) = 6.84 Hz, 4 H, CH), 3.48 (sept. <sup>3</sup>J(H,H)) 6.84 Hz, 4 H, CH), 4.54 (br. 2 H, H<sub>2</sub>), 4.62 (br., 4 H, H<sub>4,5</sub>). <sup>13</sup>C: δ = 22.2 (Me), 22.3 (Me), 24.4 (Me), 24.6 (Me), 46.3 (CH), 52.6 (CH), 80.7 (C-4,5), 85.1 (C<sub>2</sub>), CB (not obs.). <sup>11</sup>B: δ = 40.2 (br); **IR** (Nujol, hostafon): ν = 3091 w, 3067 w, 2967 st, 2864 m, 1472 st, 1459 st, 1365 st, 1314 vst, 1299 vst, 1193 st, 1187 st, 1098 st,sh, 1013 st, 961 m, 874 m, 859 m, 800 st, 533 st, 532 m, 505 m cm<sup>-1</sup>.

**1,1'-(Tris(dimethylaminoboryl)[3]-ferrocenophane (24):** In analogy to the preparation of **19** a solution of 1,3-dichloro-1,2,3-tris(dimethylamino)triborane [33] (4.5 mmol) in Et<sub>2</sub>O (10 mL) was added to a THF solution of 1,1-dilithiumferrocene [34] (4.5 mmol). After stirring overnight the solid was removed from the red-orange solution. Afterwards, the solvents were evaporated. Crystallisation of the residue from hexane at -30 °C yielded 3.5 mmol of **24**. Only its crystal structure was determined.

## X-ray Structure Determinations

Samples were covered with perfluoroether oil and a crystal selected at -30 °C under a blanket of nitrogen. The selected crystal was afterwards transferred on the tip of a glass fibre, which was attached to a small copper tube. The tube was mounted on the head of the diffractometer (Siemens P4 equipped with scintillation counter or an area detector) which was in most cases cooled by a cold stream of nitrogen (-80 °C). Data collection was performed with graphite monochromated Mo-K<sub>α</sub> radiation. The unit cell dimensions were calculated by using the reflections collected on 5 sets of 10 frames each at different θ and ω angles, or from the positions of the reflections on a set of up to 10 exposures on photographic plates. Data were collected with the area detector by using the hemisphere mode or with the scintillation counter in the ω/2θ mode. The programs SAINT and SMART were used for data reduction [35], and the structures solved by using the SHELXTL or SHELX93 data programmes [36]. A survey of the crystallographic data and data referring to data collection and structure solution is presented in Table 2 and Table 3. Further data referring to the structure solution can be obtained from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data\_request by citing the CCDC numbers 772990–773001. The piperidino compound **12** showed a disordered piperidine ring with two six membered ring chair conformation. Their positions were refined with a site occupation factor of 0.5. Compound (tBuNH*i*Pr<sub>2</sub>NBCp)<sub>2</sub>Fe proved to be twinned and refinement took care of this. Absorption correction was performed for most data sets of the bromoboryl ferrocenes.

**Table 3.** Crystallographic data and data related to data collection and structures solution for compounds **20**, **23** and **24**.

Compound	<b>20</b>	<b>23</b>	<b>24</b>
Chem. formula	C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> B <sub>2</sub> Fe	C <sub>22</sub> H <sub>36</sub> N <sub>2</sub> B <sub>2</sub> FeNS	C <sub>16</sub> H <sub>26</sub> B <sub>3</sub> FeN <sub>3</sub>
Form wght.	309.79	438.06	348.68
Crystal size /mm	0.2 × 0.3 × 0.3	0.3 × 0.25 × 0.1	0.3 × 0.3 × 0.3
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 <sub>1</sub>	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n
a /Å	9.561(2)	5.961(1)	8.758(2)
b /Å	7.522(1)	11.949(5)	13.120(3)
c /Å	10.299(2)	32.00(1)	15.899(5)
α /°	90	90	90
β /°	94.49(2)	92.7(2)	90.98(1)
γ /°	90	90	90
V /Å <sup>3</sup>	738.4(2)	2277(1)	1826.6(8)
Z	2	4	4
D(calcd) /Mg·m <sup>-3</sup>	1.393	1.278	1.268
μ /mm <sup>-1</sup>	1.015	0.764	0.825
F(000)	324	036	736
Index range	-11 ≤ h ≤ 11 -8 ≤ k ≤ 8 -12 ≤ l ≤ 12	0 ≤ h ≤ 6 -1 ≤ k ≤ 13 -36 ≤ l ≤ 36	-9 ≤ h ≤ 10 -13 ≤ k ≤ 13 -20 ≤ l ≤ 20
2θ /°	54.74	48.04	55.50
Temp /K	222	208	163(1)
Refl. collected	4258	4308	6829
Refl. unique	2606	3524	3333
Refl. observed (4σ)	2484	3522	2996
R (int.)	0.0445	0.081	0.0486
No. variables	185	361	312
Wght. scheme <sup>1</sup> x/y	0.0381/0.0798	0.0778/0.00	0.0174/1.2762
GOOF	1.073	0.976	1.065
Final R(4σ)	0.0309	0.0643	0.0302
Final wR2	0.0758	0.130	0.0716
Larg. res. peak /e·Å <sup>3</sup>	0.406	0.507/-0.376	0.310

$$* w^{-1} = s^2 F_o^2 + (xP)^2 + yP; P = (F_o^2 + 2F_c^2)/3$$

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