

## Synthesis and oxidation of hexafluoroisopropoxyborylferrocenes\*

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**Abstract:** The ferrocenylboranes (BOhfp)<sub>2</sub>Fc and 1,1'-(BOhfp)<sub>2</sub>Fc were prepared (Fc = ferrocenyl, Ohfp = (CF<sub>3</sub>)<sub>2</sub>CH-O); 1,1'-(BOhfp)<sub>2</sub>Fc was further oxidized giving [1,1'-(BOhfp)<sub>2</sub>Fc]<sup>+</sup>[Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> by oxidation of 1,1'-(BOhfp)<sub>2</sub>Fc with Ag<sup>+</sup>[Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> (R<sup>F</sup> = C(CF<sub>3</sub>)<sub>3</sub>). Their X-ray crystal structures were determined and give further information on the Fe–B interaction through the dip angles  $\alpha^*$ . In [1,1'-(BOhfp)<sub>2</sub>Fc]<sup>+</sup>[Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup>, this Fe–B interaction is enfeebled: the dip angles  $\alpha^*$  (0.3° and 5.4°) are significantly smaller than in (BOhfp)<sub>2</sub>Fc (7.8°) and 1,1'-(BOhfp)<sub>2</sub>Fc (8.0°), and the hexafluoroisopropoxy moieties are twisted out of the Cp plane by up to 66.1°. NMR and vibrational spectra support the crystal structure assignments.

**Keywords:** boron; crystallography; ferrocene; Lewis acids; oxidation.

### INTRODUCTION

Ferrocenylboranes were the subject of recent research and found widespread application in chemistry. The main advantage of the ferrocene backbone can be assigned to its electrochemical properties paired with the chemical and thermal inertness. Thus, ferrocenylboranes function, for example, as anion sensors for selective fluoride or hydrogen fluoride detection [1–4]. Owing to the relatively weak Lewis acidity of dialkoxyborylferrocenes, their fluoride binding is weak and recognition by NMR or electrochemical monitoring is possible even in the presence of other potentially competing anions. The ferrocenylborates on the basis of tris(1-pyrazolyl)borates can be assembled to heterooligometallic complexes and polymers to explore novel magnetic and conducting compounds [5–8]. Ferrocenylboranes linked via B–N bonds and bifunctional pyridine bases (4,4'-bipyridene or pyrazine) lead to charge-transfer polymers [9–11]. The charge-transfer interaction occurs between the ferrocene donor and the electron-poor B–N adduct bridge. In 1,3-dibora[3]ferrocenophanes, the two Cp rings of ferrocene are connected by a B–E–B (E = O, S, Se, Te, or NMe) fragment [12]. In these compounds, the Cp rings bent to the heteroelements and are exactly staggered, which is unusual for ferrocenophanes. The spontaneous formation of B–N bonds was amongst others exploited in electron sponges [13–15], which are composed of ferrocene and up to four 2,2'-bipyridylboronium moieties. Those stable multi-step redox systems are able to store up to nine electrons and the ligands are electronically communicating. Oligonuclear metallocene aggregates like [1.1]-diborataferrocenylphosphanes are capable of trapping Li ions [16]. In

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this redox-switchable Li scavenger, the ion is **not** coordinated by main-group Lewis bases. Bifunctional Lewis acids like Carpenters 1,1'-[B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub>Fc are highly electrophilic, also 1,2-bifunctional ferrocenylborane-based Lewis acids are known [17–19]. *Ansa*-ferrocenes take advantage of the self-assembly and reversible breaking of B–N or B–P Lewis acid–base pairs as interannular bridge. Thereby, the structure is switchable between a rigid *ansa*-structure and a flexible open-chain conformation by temperature or substitution pattern [20–23].

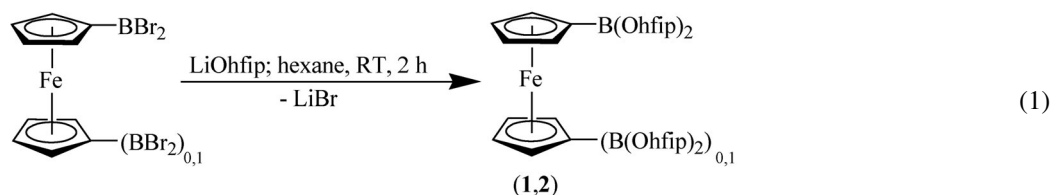
One of the reasons for this abundance of different ferrocene-based B compounds is the straightforward preparation of dibromoborylferrocene and 1,1'-bis(dibromoboryl)ferrocene [24–26], which are the basic synthesis modules for many ferrocenylboranes. Another intriguing aspect of ferrocenylborane-based chemistry is the still not well understood through-space B–Fe interaction, which was part of detailed investigations [27,28]. This interaction is linked to the bending of the boryl residue toward the Fe center: the  $\alpha^*$  dip angle ( $\alpha^* = 180^\circ - \alpha$ , with  $\alpha$  being the angle Cp(centroid)–C<sub>ipso</sub>–B) is used as an indicator for the Lewis acidity of the boryl moiety. The higher the borylation degree of the ferrocenylboranes, the smaller is  $\alpha^*$ . The introduction of  $\pi$ -donating residues or adduct formation effect the same. Ferrocenylboranes are redox-active and can be oxidized to the respective ferrocenium compounds that should exert higher Lewis acidity. The first structural analysis of a redox-switchable system was published only recently (2008) for 9-ferrocenyl-9-borafluorene [29]. Interestingly, the higher Lewis acidity of this compound is here accompanied by smaller values of the dip angle  $\alpha^*$ .

In this study we synthesized and characterized novel ferrocenylboranes and also studied their subsequent oxidation. To combine a decent stability with sufficient Lewis acidity, we chose the fluorinated alkoxide 1,1,1,3,3,3-hexafluoro-2-propoxy ligand (Ohfip) for the boryl residue. The Ohfip-ligand was proven to provide suitable Lewis acidity to an electron-deficient central atom, e.g., in the related B(Ohfip)<sub>3</sub>, as well as in monomeric Al[OC(CF<sub>3</sub>)<sub>3</sub>]<sub>3</sub> or dimeric Al<sub>2</sub>(Ohfip)<sub>6</sub> [30–34]. Carpenter and co-workers suggested that oxidation enhances the Lewis acidity of ferrocenylboranes, so that the B center in certain borylferrocenium compounds abstracts a fluoride from a [BF<sub>4</sub>]<sup>–</sup> counteranion [35]. To avoid this side reaction, we decided to use the silver salt of the perfluorinated alkoxyaluminate anion [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>–</sup> (R<sup>F</sup> = C(CF<sub>3</sub>)<sub>3</sub>) as an oxidant. The CF bonds of the latter are more resistant against fluoride ion abstraction [33]. Owing to its delocalized negative charge, the [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>–</sup>-anion belongs to the category of weakly coordinating anions (WCAs), which are ideal to investigate the crystal structures of the oxidized compounds due to the minimized interaction between the oppositely charged ions [36].

## RESULTS AND DISCUSSION

### Synthesis and NMR spectroscopic characterization

**1-(BOhfip)<sub>2</sub>Fc 1 and 1,1'-(BOhfip)<sub>2</sub>Fc 2:** The preparation of the bromoborylferrocene starting materials was realized by electrophilic substitution of ferrocene with borontribromide according to Siebert et al. [24–26]. First attempts to synthesize **2** from bromoborylferrocene and HO-hfip alcohol were not promising: however, we could characterize the desired compound as a byproduct. The main product of the reaction was ferrocene. We suggest that compound **2** was formed, but that the B–C bond was cleaved by the HBr released giving ferrocene and the volatile alkoxybromoborane Br-B(Ohfip)<sub>2</sub>. To prevent the formation of HBr, the alcohol was replaced by the alkoxide Li[Ohfip] [37]. The consecutively generated LiBr could be removed, and the clean products **1** and **2** were obtained in good yield (71 % **1**; 81 % **2**) after recrystallization from hexane or CH<sub>2</sub>Cl<sub>2</sub>, respectively (eq. 1).

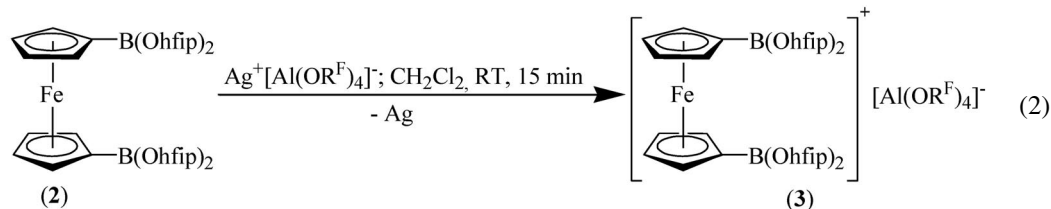


The  $^1\text{H}$  NMR resonances of **1** appear at 5.26 ppm (septet, Ohfip-substituent), 4.64 and 4.46 ppm (two signals of the AA'BB' spin system), and at 4.23 ppm (singlet, unsubstituted Cp). The corresponding integral ratios are consistent with the assigned molecular structure. The  $^{19}\text{F}$  NMR spectrum shows a doublet of the fluorinated alkoxy ligand at  $-75.4$  ppm. The signals of the Ohfip substituent are shifted ( $^1\text{H}$ : by 0.89 and 0.85 ppm,  $^{19}\text{F}$ : by 1.0 and 2.6 ppm) to higher field in both spectra compared to the alcohol and alkoxide, respectively. The  $^{11}\text{B}$  NMR signal of compound **1** occurs at 31.8 ppm ( $\Delta\nu_{1/2} = 208$  Hz).

Compound **2** exhibits two signal groups, a septet at 5.16 ppm and the multiplets of the substituted Cp rings at 4.45 and 4.60 ppm. To prove the molecular structure we consulted selected 2D NMR experiments. The nuclear Overhauser enhancement (NOE) in the  $^1\text{H}$ ,  $^1\text{H}$  NOESY NMR spectrum between the septet and the signal of the Cp ring at 4.45 proved the small spatial separation and that both signals belong to one molecule. Furthermore, it allowed the unambiguous assignment of the signal at 4.45 ppm to the protons of the Cp ring adjacent to the B substituent. Accordingly, the remaining signal is assigned to the other protons of the Cp ring. Via the cross-peaks of the  $^1\text{H}$ ,  $^{13}\text{C}$  HSQC experiment, it was possible to relate the proton signals to C resonances. The proton of the Ohfip ligand is directly bound to the C atom with the signal at 70.5 ppm. The signals of the ring protons at 4.45 and 4.60 ppm correlate to the C resonances at 74.7 and 75.0 ppm. The signals of the quaternary carbon atom are identified at 57.4 ppm by the correlation in the  $^1\text{H}$ ,  $^{13}\text{C}$  HMBC NMR spectrum, because, besides the characteristic shift to higher field, the  $^2J(^1\text{H}, ^{13}\text{C})$  cross-signals to the ring protons are observable. In the  $^{19}\text{F}$  NMR spectrum, a doublet at  $-75.5$  ppm and in the  $^{11}\text{B}$  NMR spectrum a singlet at 31.2 ppm were observed ( $\Delta\nu_{1/2} = 365$  Hz).

Also, vibrational spectra of **1** and **2** were recorded for completion and show the expected bands.

**Oxidation to [1,1'-(BOhfip)<sub>2</sub>Fc]<sup>+</sup>[Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> **3**:**  $\text{Ag}^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$  was applied as the simple to use oxidizing agent of choice (eq. 2), which was synthesized according to the procedure established in our group [33].

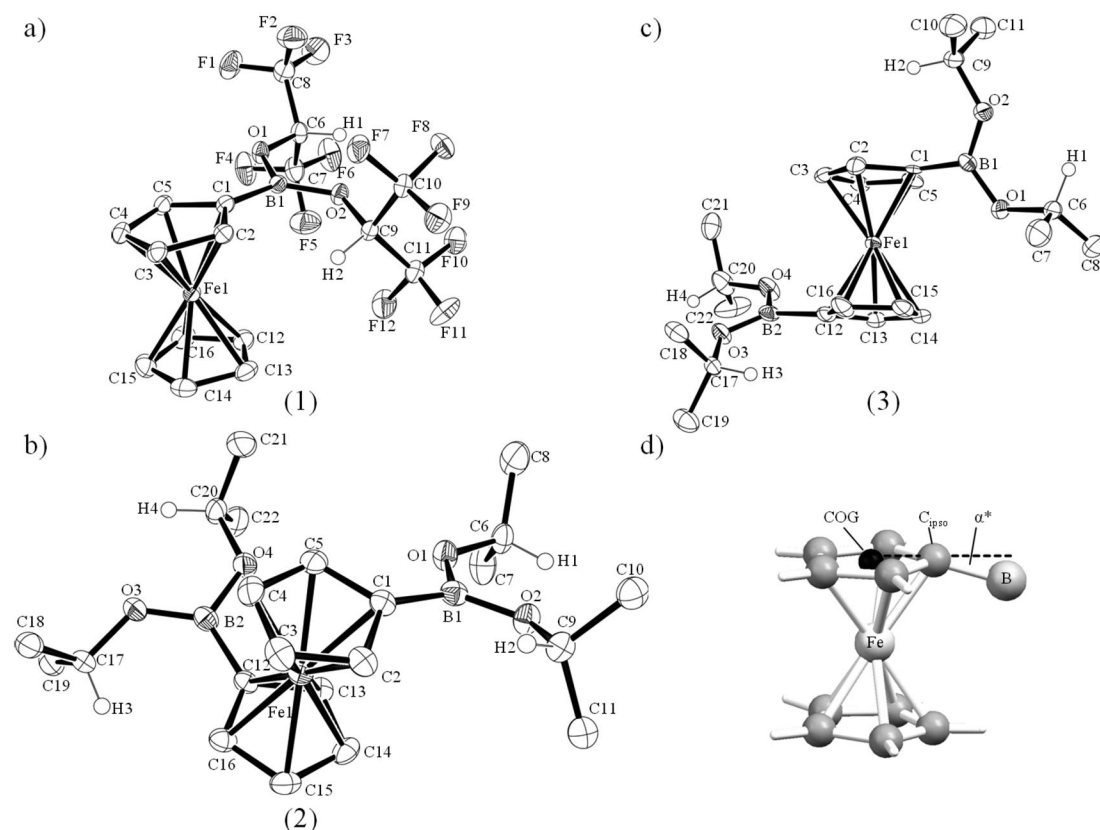


The claret-red ferrocenylboranes **1** and **2** were oxidized with  $\text{Ag}^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$  to deep blue ferrocenium derivatives. The concomitantly formed elemental Ag was filtered off, the crude product was washed and recrystallized from  $\text{CH}_2\text{Cl}_2$  at  $2^\circ\text{C}$  (91 % **3**). Owing to the paramagnetism of the oxidized compounds, the NMR spectra were not meaningful; however, vibrational spectra were recorded for completion and show the expected bands in agreement with the assigned molecular structures. From the vibrational data, we also expect the formation of the ferrocenium salt [1-(BOhfip)<sub>2</sub>Fc]<sup>+</sup>[Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> **4**, however, no crystals suitable for analysis could be grown hitherto.

### X-ray crystal structures

The proposed molecular structures of compounds **1–3** were confirmed by X-ray analysis of single crystals. A section of the structure of **1** (orthorhombic, *Pbca*) is shown in Fig. 1a, along with selected metrical data.

The dip angle  $\alpha^*$  of  $7.8^\circ$  is found in the expected range ( $\text{FcB}(\text{Me})_2 = 13.0^\circ$ ,  $\text{FcB}(\text{OH})(\text{Me}) = 10.8^\circ$ , and  $\text{FcB}(\text{OMe})_2 = 5.6^\circ$ ) [28]. The electron-withdrawing effect of the polyfluorinated groups on the B–O  $\pi$ -bonding is probably responsible for the increase of the dip angle  $\alpha^*$  of  $2.2^\circ$  if compared to  $\text{FcB}(\text{OMe})_2$ . The same trend is observed when studying the Fe–B distance of  $3.126(1)$  Å ( $\text{FcB}(\text{Me})_2 =$



**Fig. 1** (a–c) Molecular structures of **1**, **2**, and **3**; thermal ellipsoids are shown at the 50 % probability level. H atoms of the ferrocenyl moiety omitted for clarity. Selected atom distances [Å], angles [°] and interplanar angles [°]: (a) B1–C1 = 1.537(2), B1–O1 = 1.337(2), B1–O2 = 1.381(2), O1–C6 = 1.405(2), O2–C9 = 1.400(1), Fe1–B1 = 3.126(1), Fe1–O1 = 3.946, Fe1–O2 = 3.936; C1–B1–O1 = 115.2(1), C1–B1–O2 = 129.3(1), O1–B1–O1 = 115.5(1); BO<sub>2</sub>–Cp: 15.8; COG–Fe1–COG = 176.3 (COG: geometrical center of the plane defined by the five C atoms);  $\alpha^*$  = 7.8. (b) F atoms omitted for clarity: B1–C1 = 1.531(3), B1–O1 = 1.377(3), B1–O2 = 1.374(3), O1–C6 = 1.406(3), O2–C9 = 1.399(3), Fe1–B1 = 3.091; Fe1–O1 = 3.631, Fe1–O2 = 4.120; C1–B1–O1 = 117.0(2), C1–B1–O2 = 128.5(2); BO<sub>2</sub>–Cp: 17.2; COG–Fe1–COG = 179.9;  $\alpha^*$  = 8.0. (c) F atoms and the [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>–</sup> anion omitted for clarity: B1–C1 = 1.575(9), B2–C12 = 1.571(9), B1–O1 = 1.365(8), B1–O2 = 1.354(8), B2–O3 = 1.352(8), B2–O4 = 1.364(8), O1–C6 = 1.412(7), O2–C9 = 1.412(7), O3–C17 = 1.404(7), O4–C20 = 1.414(7), Fe1–B1 = 3.238; Fe1–B2 = 3.194, Fe1–O1 = 3.454, Fe1–O2 = 4.476, Fe1–O3 = 4.322, Fe1–O4 = 3.518; C1–B1–O1 = 117.0(5), C1–B1–O2 = 123.9(6), O1–B1–O2 = 119.0(5), C12–B2–O3 = 126.4(6), C12–B2–O4 = 115.1(6), O3–B2–O4 = 118.5(6); BO<sub>2</sub>–Cp: 66.1 (at B1), 36.9 (at B2); COG–Fe1–COG = 179.8;  $\alpha^*$  = 0.3 (at B1), 5.4 (at B2). (d) Definition of the dip angle  $\alpha^*$  and further geometric terms.

3.008(3) Å, FcB(OH)(Me) = 3.056(3) Å, and FcB(OMe)<sub>2</sub> = 3.179(3) Å [28]. The B atom is coordinated trigonal planar, the sum of angles about B1 is 360°, but both angles around the C<sub>ipso</sub>–C are significantly different: the C1–B1–O1 angle is compressed with 115.2(1)° compared to the wide C1–B1–O2 angle of 129.3(1)°. This effect occurs also in FcB(OH)<sub>2</sub> (118.2° and 123.9°), but is more pronounced in ferrocenyl alkoxides like FcB(OMe)<sub>2</sub> (e.g., 114.9° and 127.7°) [28,38]. The Ohfp moieties are twisted out of the plane defined by the five Cp carbons by 15.8°, respectively, as previously observed for ferrocenylboranes [39]. This pattern can be considered as a sign for a relatively weak Fe–B interaction.

Figure 1b shows the molecular structure of compound **2** (monoclinic, C2/c) together with selected structural data. The dip angles of 1,1'-ferrocenylboranes are usually smaller than the dip

angles of the corresponding mono-borylated ferrocenyls (e.g.,  $\text{FcBBr}_2/\text{Fc}(\text{BBr}_2)_2$   $\alpha^* = 18.3/9.1^\circ$  or  $\text{FcOMe}_2/\text{Fc}(\text{OMe}_2)_2$   $\alpha^* = 6.1/5.2^\circ$ ) [27,28,40]. In our case, the dip angle  $\alpha^*$  is  $8.0^\circ$  and therefore slightly larger than in compound **1**, which could result from the steric demand of the perfluorinated isopropoxy ligands or packing effects. Concomitantly, the Fe1-B1 distance is a bit shorter and the boron atoms are trigonal planar coordinated, with similar bond angles as compound **1**. Compared to the mono-borylated compound **1**, the Ohfip moieties are even more twisted ( $17.2^\circ$ ).

A section of the molecular structure of compound **3** is shown in Fig. 1c; relevant metric parameters are included. The non-interacting counterion  $[\text{Al}(\text{OR}^{\text{F}})_4]^-$  was omitted of clarity. There are two different dip angles  $\alpha^*$  in the oxidized species of compound **2**, in fact  $5.4^\circ$  (at B2) and  $0.3^\circ$  (at B1). As expected, the dip angles decrease and along with them the Fe–B interaction, since the trivalent cationic Fe atom is not able to contribute as much electron density to the Lewis acid B centers as the neutral divalent atom in **1** and **2**. Especially, the smaller dip angle of  $0.3^\circ$  at B1 indicates that the interaction is almost turned off by oxidation. Furthermore, this angle is one of the smallest dip angles ever measured in ferrocenyl boranes. The B atoms are still trigonal planar coordinated, but the Ohfip moieties are twisted out of the Cp ring plane by  $36.9^\circ$  at B2 and actually by  $66.1^\circ$  at B1, which means that the  $p_z$ -orbital of the respective B atoms is not able to interact with the Fe-based orbitals. These results show that the Fe–B stabilization is overcompensated by the steric aspect of the bulky perfluorinated ligands, which prefer to avoid the Cp ring protons or the second  $\text{B}(\text{Ohfip})_2$  residue.

By comparing the neutral species **1** and **2** with the oxidized species **3**, (Table 1) it follows that in **3** the C–B distance increase while the B–O distances decrease, caused by the changed electronic environment. To relieve the electron deficiency of the B atom in **3**, the B–O  $\pi$ -interaction becomes more important. The huge difference of the interplanar angles upon oxidation shows that the influence of the sterically demanding Ohfip moieties increases and therewith overcompensates the  $\text{C}_{\text{ipso}}\text{-B}$   $\pi$ -interaction. The resulting Fe–B distances and  $\alpha^*$  angles indicate only a residual and weak Fe–B interaction in **3**. It would be possible that the origin of the twisting result from a Coulomb interaction between Fe1 and O1 ( $d_{\text{Fe1-O1}} = 3.454 \text{ \AA}$ ), the affected B–O bond is not significantly longer, but in contrast the B–O bond, which is facing away from Fe1, is longer than its counterpart.

**Table 1** Bond distances  $d$  [ $\text{\AA}$ ], interplanar angles [ $^\circ$ ] and dip angles [ $^\circ$ ] of **1**, **2**, and **3** (average values in parentheses).

	$d_{\text{CB}}$	$d_{\text{BO}}$	$d_{\text{FeB}}$	$\text{BO}_2\text{-Cp-plane}$	$\alpha^*$
<b>1</b>	1.537 (1.537)	1.377–1381 (1.379)	3.126	15.8	7.8
<b>2</b>	1.531 (1.531)	1.374–1.376 (1.375)	3.091	17.2	8.0
<b>3</b>	1.571–1.574 (1.573)	1.353–1.365 (1.359)	3.238 (B1), 3.194 (B2)	66.1 (B1), 36.9 (B2)	0.3 (B1), 5.4 (B2)

## CONCLUSION

In this paper, we report the straightforward synthesis and characterization of 1-(BOhfip)<sub>2</sub>Fc **1** and 1,1'-(BOhfip)<sub>2</sub>Fc **2** and the subsequent oxidation of **2** with  $\text{Ag}^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$  to the ferrocenium derivative  $[1,1'-(\text{BOhfip})_2\text{Fc}]^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$  **3**. Furthermore, the crystal structures of **1** and **2** and even the rare crystal structure of the oxidized ferrocenylborane **3** were obtained. It appears that we could also oxidize **1** with  $\text{Ag}^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ , however, here we did not obtain a crystal structure proof. It could be shown that the dip angles  $\alpha^*$  strongly decrease upon oxidation and the Fe–B interaction is enfeebled. In addition, the Ohfip moieties twist out of the Cp plane to minimize steric interactions with the Cp ring protons or the second  $\text{B}(\text{OR}^{\text{F}})_2$  residue. The systematic application of **2** and **3** as Lewis acid catalysts in an inverse electron-demanding Diels–Alder reaction of 1,2-diazenes is currently under investigation.

## EXPERIMENTAL SECTION

**General:** Due to the air and moisture sensitivity of most materials, all manipulations were undertaken with vacuum and Schlenk techniques as well as in a glove box with an Ar atmosphere ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 1$  ppm). The solvents were dried by using conventional drying agents and directly distilled. NMR spectra were obtained in  $d_2$ -methylene chloride at room temperature on a BRUKER AVANCE II<sup>+</sup> 400 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are given with respect to TMS,  $^{19}\text{F}$  NMR spectra to fluorotrichloromethane, and  $^{11}\text{B}$  NMR spectra to the boron-trifluoride-diethyl-ether-complex. IR spectra were recorded on a ZnSe or Diamond ATR unit on a Nicolet Magna IR Spectrometer with  $1\text{ cm}^{-1}$  resolution or on a Diamond ATR unit ( $200\text{--}30\,000\text{ cm}^{-1}$ ) on a BRUKER alpha Fourier transform-infrared (FT-IR) spectrometer with a resolution of  $4\text{ cm}^{-1}$ . Raman spectra were obtained on a BRUKER VERTEX 70 spectrometer with a BRUKER RAM II Raman unit in sealed melting-point capillaries. Data collections for X-ray structure determinations were performed on a Rigaku Spider image plate or a BRUKER APEX II Quazar CCD diffractometer at 100 and 110 K, respectively, with Mo radiation. The single crystals were mounted in perfluoroether oil on a MiTeGen Micromount<sup>TM</sup>. Dibromoborylferrocene, 1,1'-bis(dibromoboryl)ferrocene,  $\text{Ag}^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ , and LiOhfip were synthesized according to the established procedures [24–26,33,37].

**Preparation of compound 1:** Dibromoborylferrocene (1.342 g, 3.78 mmol) and LiOhfip (1.314 g, 7.55 mmol) were placed on one side of a special two-flask fritplate vessel with J. Young valves and dissolved in hexane (70 mL). An orange solution over colorless precipitate formed and was left stirring for 2 h. The mixture was filtered to the other side of the vessel, the solvent was removed in vacuo, and the solid was placed in a clean two-flask fritplate vessel with J. Young valves and dissolved in hexane (50 mL). After recrystallization of the product at  $-40\text{ }^\circ\text{C}$ , the excess filtrate was poured to the other side of the vessel and the residual solvent was removed in vacuo. Compound **1** was obtained on the starting side of the vessel (1.419 g, 2.68 mmol, 71 %).  $^1\text{H}$  NMR (400.17 MHz):  $\delta = 4.21$  (s, 5H, Cp), 4.44 (m, 4H BCCH), 4.62 (m, 4H, BCCHCH), 5.23 (sept., 4H, CB(Ohfip)<sub>2</sub>), 5.32 (t, CHDCl<sub>2</sub>).  $^{19}\text{F}$  (376.54 MHz):  $\delta = -75.4$  (d, 12F CF<sub>3</sub>).  $^{11}\text{B}$  (128.39 MHz):  $\delta = 31.5$  (br). IR (Diamond ATR, corrected):  $\tilde{\nu} = 483$  (s), 503 (w), 522 (vw), 627 (vw), 674 (w), 687 (s), 697 (w), 742 (w), 754 (vw), 818 (w), 834 (m), 865 (m), 872 (m), 891 (w), 903 (m), 1001 (w), 1024 (w), 1038 (w), 1066 (w), 1103 (vs), 1192 (vs), 1218 (s), 1258 (s), 1281 (m), 1305 (m), 1337 (w), 1365 (w), 1381 (w), 1461 (w), 2958 (vw), 3108 (vw), 3203 (vw)  $\text{cm}^{-1}$ . Raman:  $\tilde{\nu} = 75, 131, 223, 256, 277, 316, 389, 433, 485, 597, 628, 676, 688, 700, 754, 836, 865, 892, 1002, 1024, 1041, 1054, 1068, 1081, 1106, 1180, 1197, 1211, 1290, 1322, 1353, 1380, 1398, 1411, 1461, 2960, 2981, 3108, 3118\text{ cm}^{-1}$ .

**Preparation of compound 2:** 1,1'-Bis(dibromoboryl)ferrocene (1.440 g, 2.74 mmol) and LiOhfip (2.011 g, 11.56 mmol) were mixed in the glovebox, weighed into one side of a special two-flask fritplate vessel with J. Young valves and dissolved in CS<sub>2</sub> (80 mL). The mixture was stirred at room temperature for 2 h and then washed two times with CS<sub>2</sub>. The residual solvent was removed and the product extracted with CH<sub>2</sub>Cl<sub>2</sub>. Upon removal of the solvent from this extracted filtrate, microcrystalline compound **2** was obtained in good yield (1.962 g, 2.24 mmol, 81 %). Crystals suitable for X-ray diffraction (XRD) were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> at  $2\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR (400.17 MHz):  $\delta = 4.47$  (m, 4H BCCH), 4.62 (m, 4H, BCCHCH), 5.17 (sept., 4H, CB(Ohfip)<sub>2</sub>), 5.32 (t, CHDCl<sub>2</sub>).  $^{19}\text{F}$  (376.54 MHz):  $\delta = -75.1$  (d, 24F CF<sub>3</sub>).  $^{11}\text{B}$  (128.39 MHz):  $\delta = 31.4$  (br).  $^{13}\text{C}$  (100.62 MHz):  $\delta = 53.5$  (m, CD<sub>2</sub>Cl<sub>2</sub>), 57.4 (m, BCCH<sub>2</sub>CH<sub>2</sub>), 70.5 (m, OCH(CF<sub>3</sub>)<sub>2</sub>), 74.7 (m, BCCH<sub>2</sub>CH<sub>2</sub>), 75.0 (m, BCCH<sub>2</sub>CH<sub>2</sub>), 120.8 (m, OCH(CF<sub>3</sub>)<sub>2</sub>). IR (ZnSe ATR, corrected):  $\tilde{\nu} = 673$  (m), 690 (vs), 741 (m), 810 (w), 820 (w), 844 (w), 864 (w), 874 (m), 904 (w), 1024 (w), 1038 (w), 1103 (vs), 1196 (vs), 1226 (s), 1263 (vs), 1284 (s), 1325 (w), 1336 (m), 1363 (w), 1380 (m), 1462 (w), 2852 (vw), 2920 (vw), 2964 (vw)  $\text{cm}^{-1}$ . Raman:  $\tilde{\nu} = 131, 206, 298, 325, 333, 345, 401, 451, 474, 626, 673, 700, 755, 838, 865, 875, 892, 1024, 1039, 1064, 1081, 1108, 1182, 1197, 1276, 1290, 1311, 1326, 1340, 1382, 1398, 1459, 1471, 1496, 2971, 3122\text{ cm}^{-1}$ .

**Preparation of compound 3:** Compound **2** (0.400 g, 0.458 mmol) and  $\text{Ag}^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$  (0.488 g, 0.458 mol) were mixed in the glovebox and weighed into one side of a special two-flask fritplate vessel with J. Young valves and dissolved in  $\text{CH}_2\text{Cl}_2$  (15 mL). The blue solution was stirred at room temperature for 15 min and filtered and washed once with  $\text{CH}_2\text{Cl}_2$  (2 mL). The solvent was removed, and compound **3** was obtained in good yield (0.771 g, 0.421 mmol, 91 %). Crystals were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$  at 2 °C. IR (Diamond ATR, corrected):  $\tilde{\nu} = 445$  (m), 481 (vw), 536 (m), 560 (w), 692 (s), 726 (vs), 744 (w), 755 (w), 828 (w), 867 (s), 906 (m), 968 (vs), 1040 (vw), 1094 (s), 1111 (vs), 1197 (vs), 1240 (s), 1265 (s), 1352 (w), 1373 (m), 1421 (vs), 1468 (vw), 2239 (vw), 2361 (vw), 2857 (vw), 2920 (vw)  $\text{cm}^{-1}$ . Raman:  $\tilde{\nu} = 79, 167, 235, 293, 322, 500, 560, 746, 797, 856, 885, 1063, 1104, 1179, 1278, 1386, 1459, 1488, 1504, 1990, 2063, 2094, 2329, 2688, 2758, 2846, 2938, 3125$   $\text{cm}^{-1}$ .

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