Benniston AC, Sirbu D, Turta C, Probert MR, Clegg W.
Synthesis, Molecular Structure and Properties of a Ferrocene-based
Difluoropyrrolo-oxaborole Derivative.
European Journal of Inorganic Chemistry 2014, 2014(36), 6212-6219.

Copyright:

This is the peer reviewed version of the above article, which has been published in final form at <http://dx.doi.org/10.1002/ejic.201402752>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

Date deposited:

19/11/2014

Embargo release date:

02 December 2015

This work is licensed under a [Creative Commons Attribution-NonCommercial 3.0 Unported License](http://creativecommons.org/licenses/by-nc/3.0/)

Synthesis, Molecular Structure and Properties of a Ferrocene-based Difluoropyrrolo-oxaborole Derivative

Andrew C. Benniston,^{*,[a]} Dumitru Sirbu,^[b] Constantin Turta,^[b] Michael R. Probert^[c] and William Clegg^[c]

Abstract: Reaction of 1,1'-ferrocenedicarbonyl chloride with 3-ethyl-2,4-dimethylpyrrole in DCM produced the half-way product; namely, the ferrocene bis-2-ketopyrrole derivative **2** and not the expected bis-dipyrrromethene compound. The 2-ketopyrrole compound readily reacted with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to produce the *bis*-difluoropyrrolo-oxaborole compound, **FBF**, as a red/brown solid which was characterized by X-ray crystallography. ^{57}Fe Mössbauer spectra for **2** and **FBF** were consistent with low-spin iron(II) (d^6) ferrocene derivatives. A cyclic voltammogram for **2** in acetonitrile revealed a reversible wave at +0.31 V vs Fc^+/Fc (ferrocene-based) and an irreversible wave at -2.38 V vs Fc^+/Fc (ketopyrrole-based). The electrochemical behaviour is severely perturbed by the chelation of the BF_2 groups. Alterations to the electronic properties of **2** by formation of **FBF** are also evident in the absorption profiles. DFT calculations ((B3PW91, 6-31G(3df)) support the observed changes in the electrochemistry findings and the Mössbauer data.

Introduction

The incorporation of the chelating boron difluoride (BF_2) group into bidentate sites of flexible molecular species is a simple method to rigidify their structure.^[1] The structural modification can have a major effect, particularly for the excited state, and this is especially observed for dipyrrromethene derivatives.^[2] The basic unit is flexible and excited-state emission is not noticeably strong, and is attributed to efficient internal conversion promoted by facile molecular distortion. By comparison, the BF_2 version which is more commonly known as borondipyrrromethene (Bodipy) fluoresces strongly and quantum yields can easily reach unity in fluid solution.^[3] It is not surprising that over the past few years attention has turned to other potential organic groups where the BF_2 group could be introduced.^[4] It is noticeable that for the preparation of Bodipy derivatives the half-way product is the 2-ketopyrrole, which is rarely isolated since it reacts further to form the dipyrrromethane. Considering the N

(pyrrole) and O (ketone) atoms are arranged to facilitate formation of a five-membered ring adduct with BF_2 , it is surprising that only two examples are discussed in the literature.^[5,6] In attempts to prepare a bis-Bodipyferrocene derivative we found that the bis-ketopyrrole derivative **2** was produced instead,^[7] and could be converted readily to the BF_2 adduct, **FBF**. Unlike some previous examples the compound is non-fluorescent. Excited state quenching is highly probable because of the close proximity of the redox-active ferrocene to the difluoropyrrolo-oxaborole.

Scheme 1. Reagents and Conditions. (i) pyrrole, TFA (ii) DDQ or p-chloranil or activated MnO_2 (iii) 3-ethyl-2,4-dimethylpyrrole, Et_3N , $\text{BF}_3 \cdot \text{OEt}_2$; POCl_3 , 3-ethyl-2,4-dimethylpyrrole, Et_3N , $\text{BF}_3 \cdot \text{OEt}_2$ (iv) 3-ethyl-2,4-dimethylpyrrole (v) Et_3N , $\text{BF}_3 \cdot \text{OEt}_2$.

Results and Discussion

Synthesis

It is established that, starting from ferrocene carboxaldehyde and pyrrole, the corresponding unalkylated boron dipyrrromethene (Bodipy) derivative can be prepared in reasonable yield.^[8] At first our interest was to see if the same reaction could be carried out using 1,1'-ferrocenedicarbonyl chloride instead. Several attempts to prepare directly the Bodipy derivative **FBD1** failed (Scheme 1). The dipyrrromethane derivative **1** is known^[9] and was prepared without much problem in 70% yield. All attempts in our hands to oxidize **1** and chelate two BF_2 groups to the dipyrrromethene groups failed to yield any product which could be identified as the desired derivative. Unsubstituted pyrroles are prone to

[a] Prof. A. C. Benniston
Molecular Photonics Laboratory, School of Chemistry
Newcastle University
Newcastle upon Tyne, NE1 7RU, UK
E-mail: a.c.benniston@ncl.ac.uk
[b] Prof. C. Turta and Mr D. Sirbu
Institute of Chemistry, Academy of Sciences of Moldova
Chisinau
Republic of Moldova
[c] Dr M. R. Probert and Prof. W. Clegg
Crystallography Laboratory, School of Chemistry,
Newcastle University
Newcastle upon Tyne, NE1 7RU, UK

oxidation and so a change in the reagent to 3-ethyl-2,4-dimethylpyrrole and reaction with 1,1'-ferrocenedicarbonyl chloride was attempted. Once again the desired product **FBD2** was not isolated. Instead of producing the dipyrromethene the reaction actually stopped at the di-ketone **2**, and all our attempts to react this further with the pyrrole derivative and using Lewis acids were unsuccessful. However, compound **2** readily reacted with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to afford **FBF** as a red/brown solid. The compound was characterized by NMR spectroscopy including ^1H , ^{13}C , ^{11}B and ^{19}F nuclei. From inspection of **FBF** we might expect, because of restricted rotation, that the two fluorine nuclei for each keto-pyrrole are inequivalent, resulting in F-F coupling. Typical J values are around 100 Hz for vicinal fluorines and 20 Hz for intramolecular through-space interactions.^[10] The actual spectrum consists of two signals at $\delta = -149.9$ (broad) and -158.0 (doublet, $J = 26$ Hz). By contrast only a single broad peak at $\delta = 2.16$ is observed in the ^{11}B NMR spectrum. The ESI-MS spectrum showed a peak at $m/z = 485$ corresponding to loss of BF_2 groups, while an ASAP/APCI-FTMS experiment resulted in a molecular ion peak at m/z 580 together with fragmentation patterns for sequential loss of BF_2 groups: m/z 561 $[\text{M}-\text{F}]^+$, m/z 533 $[\text{M}-\text{BF}_2+2\text{H}]^+$, m/z 513 $[\text{M}-\text{BF}_3+\text{H}]^+$, m/z 485 $[\text{M}-2\text{BF}_2+3\text{H}]^+$ (see Supporting Information).

Table 1. Selected bond lengths and angles for **FBF**.

Atoms	Bond Length/Å ^[b]	Atoms	Bond Angle/° ^[b]
C6-C7	1.396(3) (1.400)	N-C7-C6	107.44(19) (107.52)
C7-N	1.391(3) (1.385)	C7-C6-O	112.4(2) (113.16)
N-B	1.538(3) (1.560)	C6-O-B	110.90(18) (111.19)
O-B	1.509(3) (1.535)	O-B-N	99.26(18) (97.92)
O-C6	1.328(3) (1.304)	F1-B-F2	110.6(2) (112.95)
B-F2	1.373(3) (1.375)	F2-B-N	114.2(2) (112.48)
B-F1	1.383(3) (1.363)	F2-B-O	110.4(2) (108.69)
Fe-C5	2.036(2) (2.035)	F1-B-N	112.0(2) (113.22)
Fe-C (av) ^[a]	2.045 (2.041)	F1-B-O	109.9(2) (110.50)

[a] Average bond length calculated from the other four Fe-C bonds. [b] The first value in each case is crystallographically determined, and the second (in parentheses) is calculated using DFT (B3PW91) and the 6-31G(3df) basis set.

X-ray Crystallography

As part of characterization of the final compound and precursors, single crystals were grown for compounds **1**, **2** and **FBF** and were subjected to X-ray diffraction analysis. Structures for **1** and **2** (Figure 1) confirm their identity. Two points are worth noting about the structure of **2**. The first is the N-H...O intramolecular hydrogen bond between a pyrrole and ketone on the two cyclopentadienide (Cp) rings. The effect is to twist the pyrrromethanone groups out of conjugation with their Cp rings by different amounts (dihedral angles 48.5° and 30.3°); the other N-H...O hydrogen bond is intermolecular, linking the molecules in

chains. The second point is the incorporation of a chloroform solvent molecule.

Figure 1. Crystallographically determined molecular structures for **1** (A) and **2** (B).

Figure 2. Crystallographically determined molecular structure for **FBF** showing selected atom labelling (top) and a view showing the angle between the planes created to show the eclipsed arrangement (bottom).

The compound **FBF** crystallized in the orthorhombic space group *Pbcn*. The asymmetric unit comprises half the molecular structure, the Fe atom lying on a crystallographic twofold rotation axis. The structure for **FBF** is illustrated in Figure 2 and selected bond lengths and angles are collected in Table 1. The geometry at the boron centre is close to tetrahedral; the F-B-N bond angles are noticeably greater than the ideal 109.5° and the smallest angle is the endocyclic N-B-O. The bond lengths are quite similar to those found for the two other known literature structures containing the basic pyrroloxaborole ring.^[5,6] The C6-O bond length is certainly longer than expected for a formal double bond, consistent with a shift in electron density towards the boron centre. The two difluoropyrrolo-oxaborole groups are arranged head-to-tail and are partially eclipsed, which is more clearly seen in the lower picture of Figure 2. The angle between planes created using the two equivalent sets of Fe-C5-C6 atoms is 62.3°. The two cyclopentadienide rings for the ferrocene are almost eclipsed (7.9°). The torsion angle C1-C5-C6-O is only 8.0° meaning the Cp ring and the pyrroloxaborole group are almost coplanar.

Figure 3. ⁵⁷Fe Mössbauer spectra for **2** (top) and **FBF** (bottom) measured at 7K.

⁵⁷Fe Mössbauer Spectroscopy

The Mössbauer spectra at 7K for **2** and **FBF** are shown in Figure 3 with relevant parameters presented in Table 2. For comparison purposes ferrocene (Fc), 1,1'-diacetylferrocene (DAF) and 1,1'-dibenzoylferrocene (DBF) are used as reference compounds. The isomer shift and large quadrupole splitting for the clear doublet are typical for low-spin iron (d⁶) ferrocene

derivatives. The values of isomer shifts for both **2** and **FBF** are similar to those found for the reference compounds.^[11,12] The relatively low quadrupole splittings for the diketones compared to Fc are typical for conjugated electron-withdrawing substituents which increase the symmetry of the electron environment on the iron nucleus by removing electron density from the cyclopentadienyl rings.^[13] The lower quadrupole splitting for **FBF** compared to **2** is explained by the higher coplanarity of the electron-withdrawing substituents with the cyclopentadienyl rings, which ensure better overlap of π orbitals and an additional withdrawing effect of the BF₂ group. The corollary is a reduction in electron density on the cyclopentadienyl rings, as supported by the DFT calculations, which results in a lower electric field gradient at the iron nucleus. The recoil-free fractions for **2** and **FBF** are highly temperature-dependent as seen from their relative absorption ratios f_T/f_{7K} . This effect was previously explained as the result of vibration for the examined atom in the crystal lattice. The logarithmic form of the relation between recoil-free absorption f of the γ rays and temperature T for a "thin" absorber is given by Equation 1.^[14]

$$\ln f = -\frac{6E_r}{k\theta_D^2}T \text{ Eq. 1}$$

where E_r is the recoil energy, k is Boltzmann's constant and θ_D is the Debye temperature, which is a measure of the crystal hardness. Plots of $\ln(f_T/f_{7K})$ versus T (Figure 4) are linear over the temperature range 80K to 200K and from the slopes the corresponding θ_D values were calculated.

The θ_D value for ferrocene was estimated at 173K. As the relative absorption of **FBF** at room temperature has only a minor decrease compared to the parent ferrocene it was taken as being a very close value. As can be seen from Figure 4 the slope for the relative absorption of **2** is greater than the parent ferrocene. The calculated θ_D value is about 139K. The lower Debye temperature for **2** compared to ferrocene and **FBF** suggests there are weaker intermolecular interactions.

Figure 4. Plot of $\ln(f_T/f_{7K})$ vs T for ferrocene (●) and compound **2** (■). Points between 8 and 200 K were least-squares fitted to a straight line ($r^2 > 0.99$). Dashed lines are shown as a continuation of the fitted lines.

Table 2. Experimental Mössbauer parameters for **2**, **FBF** and reference compounds.

Compound	Temp, K	Isomer Shift δ , mm/s	Quadrupole Splitting ΔE_Q , mm/s	Relative Absorption f/f_{7K}
2	7	0.54	2.28	-
	293	0.44	2.26	0.095
FBF	7	0.52	2.06	-
	300	0.44	2.03	0.27
DAF ^{[a],[b]}	77	0.53	2.15	na
	300	0.43	2.20	na
DBF ^[b]	80	0.53	2.17	na
Fc	7	0.54	2.40	-
	293	0.45	2.39	0.31

[a],[b] Data taken from references 11 and 12.

Molecular Modelling

A preliminary inspection of the molecular structure for **FBF** would suggest that the eclipsed conformer does not represent the energy minimum. Despite this our first goal was to establish the electron density on the Cp rings for the ferrocene and compare this to the uncomplexed derivative **2**. The main driver for finding such information was to explain the Mössbauer results. Since the latter relied on collecting data on solid crystalline samples, DFT calculations to elucidate Mulliken charges on selected atoms were performed directly on models generated from the X-ray structures for **FBF** and compound **2**. In order to determine firstly the best basis set, molecular models for **FBF** were compiled from different starting geometries and energy minimized (see Supporting Information). Bond lengths and angles were compared to the X-ray determined molecular structure. We found that DFT calculations using B3PW91 and the 6-31G (3df) basis set afforded structures for which Fe-C bond lengths for the ferrocene group were close to those found by X-ray analysis (Table 1). Other bond lengths were in reasonable agreement with the X-ray determined structures. Hence, Mulliken charges were calculated for the X-ray structures of **FBF** and **2** using DFT (B3PW91) and the 6-31G (3df) basis set (Figure 5). The first point to note is the increase in positive charge at the iron centre for **FBF** (+0.677) compared to **2** (+0.647). Because **FBF** is C_2 symmetric the summation of Mulliken charges for carbon atoms at each Cp ring are identical (-0.739) and less than values for the Cp rings in compound **2** (-0.850, -0.874). There appears to be a slight extra build-up of negative charge (-0.024) on the one Cp ring for compound **2**. It is clear from the structure that this Cp ring and the difluoropyrrolo-oxaborole are more conjugated since the dihedral angle is only 11.9° compared to 40.9° at the other Cp site. The corresponding dihedral angle for **FBF** is only 8°, meaning any conjugation is maximized for this system, but it also contains the electron-withdrawing BF_2 unit.

Figure 5. Mulliken charges on the atoms calculated using DFT (B3PW91) and the 6-31G(3df) basis set for X-ray determined structures of **FBF** (top) and **2**·CHCl₃ (bottom). The summation of the Mulliken charges (MC) for carbons only in each Cp ring of the ferrocene is also shown.

To delve more into the effect of conjugation on Mulliken charge at the ferrocene centre the starting structure for **FBF** was minimized, again using DFT (B3PW91) and the 6-31G (3df) basis set. The results from these calculations are deemed to better represent a solution phase structure. The refined structure (see Supporting Information) is some 216 kcal mol⁻¹ lower in energy and the dihedral angle is increased to 20.8°. As a result of the decrease in conjugation the Mulliken charge at the iron is reduced to +0.548 and charge on each Cp ring is increased to -0.936. The same calculation performed on **2** is rather similar in that there is a build-up of negative charge at the Cp rings and a reduction of charge at the iron centre. A summary of the results is collected in Table 3. From inspection of the results it is possible to predict that the iron(II) centre in the ferrocene for **FBF** will be harder to oxidize than the uncomplexed version. In addition, we can also speculate that the electric field across the

iron nucleus will decrease slightly for **FBF** compared to compound **2**.

Table 3. Collection of Mulliken Charges (MC) for selected atoms and groups.

Compound	2	FBF	
MC (Fe)			$\Delta MC^{[b]}$
opt structure	+0.530 (-0.117) ^[c]	+0.548 (-0.129) ^[c]	+0.018
unopt structure	+0.647	+0.677	+0.03
MC (Cp) ^[a]			$\Delta MC^{[b]}$
opt structure	-1.103/-1.107	-0.936 (-0.197) ^[c]	+0.167/+0.171
unopt structure	-0.850/-0.874	-0.739	+0.111/+0.135

[a] cyclopentadienide ring, [b] $\Delta MC = MC_{\text{FBF}} - MC_2$, [c] $\Delta MC = MC_{\text{opt}} - MC_{\text{unopt}}$

Figure 6. Cyclic voltammogram recorded for **2** in acetonitrile containing 0.2 M TBATFB vs Fc^+/Fc . The dashed line shows the additional irreversible oxidation peak when the potential window is increased.

Electrochemistry and Absorption Spectroscopy

The redox behaviour of **2** and **FBF** were measured by cyclic voltammetry in dry acetonitrile using 0.2 M TBATFB as background electrolyte. The cyclic voltammogram of **2** (Figure 6) revealed a reversible wave at +0.31 V vs Fc^+/Fc , associated with the ferrocene site redox, and an irreversible wave at -2.38 V vs Fc^+/Fc . The reduction wave must be associated with the pyrroloketone group. There is also sign of an additional irreversible process present at potentials greater than +1 V; cycling to such a potential also removes the reversibility of the ferrocene couple. Complexation of **2** with BF_2 causes a series of changes to the redox behaviour of **FBF** (see Supporting Information). The redox potential for the ferrocene is anodically shifted to +0.66 V vs Fc^+/Fc , and two quasi-reversible waves are observed at -1.54 and -1.84 V vs Fc^+/Fc . The shift to more positive potential for the ferrocene unit is consistent with the electron-withdrawing effect of the pyrrolo-oxaborole substituents and fully supported by the DFT calculations. It is noted that the ferrocene redox behaviour is irreversible in **FBF**, implying that a decomposition pathway is introduced for the ferrocenium ion. Considering an electrophilic centre is created in close proximity to a polarized B-F bond, nucleophilic attack of a fluorine atom at the ferrocenium is one possible breakdown mechanism. To support this idea NaBr was added to a solution of **2** in MeCN, which resulted in

complete loss of reversibility of the ferrocene couple (see Supporting Information). Additionally, the irreversible anodic wave shifts to a lower potential, affording a very similar voltammogram to **FBF** alone.

The room-temperature electronic absorption spectra for **2** and **FBF** are shown in Figure 7. The spectrum of **2** comprises a band in the near-UV region at $\lambda_{\text{max}} = 271 \text{ nm}$ ($\epsilon_{\text{max}} = 1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and a moderately strong narrow band at $\lambda_{\text{max}} = 337 \text{ nm}$ ($\epsilon_{\text{max}} = 3.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). According to DFT calculations (see Supporting Information) this band is likely associated with the HOMO-LUMO transition localized on the ketopyrrole unit; the calculated energy gap is 3.69 eV (336 nm). A much less intense broad band is also observed in the visible region at $\lambda_{\text{max}} = 462 \text{ nm}$ ($\epsilon_{\text{max}} = 1.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). This latter band is assigned to electronic transitions for the ferrocene group. Chelation with BF_2 changes the absorption profile entirely, resulting in a considerably broader but weaker band in the visible region at $\lambda_{\text{max}} = 407 \text{ nm}$ ($\epsilon_{\text{max}} = 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) with a shoulder at 339 nm. The intensity of the band at $\lambda_{\text{max}} = 272 \text{ nm}$ ($\epsilon_{\text{max}} = 7.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) is considerably less intense. Both these absorption bands are consistent with the spectrum of previous difluoropyrrolo-oxaborole derivatives.^[5,6] Also prominent in the spectrum is a broad featureless band in the region 500–650 nm, which must arise from the perturbed ferrocene group. No room-temperature fluorescence is observed from **FBF** in fluid solution, in the solid state or when oxidized.^[15]

Figure 7. Room-temperature UV-Vis absorption spectra for **2** (red) and **FBF** (blue) in acetonitrile.

Spectroelectrochemistry

Perturbation of the UV-Vis spectra for **2** and **FBF** was monitored using an optically transparent thin-layer electrode (OTTLE) and the spectroelectrochemistry method by application of negative and positive potentials. Application of a negative potential of -1.8 V to the working electrode for a solution of **2** in acetonitrile produced a small increase in the ferrocene-based region around 460 nm, coupled to a slight change in the band shape and a tail stretching to around 800 nm (Figure 8). There was a concomitant decrease to the high-energy side of the spectrum which is consistent with ketopyrrole reduction. The tail is likely

from a weak charge-transfer transition. The original spectrum could not be reproduced by application of an oxidizing potential. Oxidation of the ferrocene unit at +0.7 V for **2** resulted in an expected red-shift for the visible absorption band because of ferrocenium ion formation. The most notable effect is the change to the high-energy absorption band which is actually replaced by a broader feature located around 400 nm (Figure 8 insert). Again we might expect to observe some charge-transfer character because of electron donation from the ketopyrrole to the ferrocenium ion. The original spectrum was restored by application of a reducing potential.

Figure 8. Main: Electronic absorption spectra for **2** in acetonitrile showing starting spectrum (black) and after reduction (blue). Insert: Absorption spectra before (black) and after oxidation (red).

Figure 9. Main: Electronic absorption spectra for **FBF** in acetonitrile at the start (black) and after reduction at -1.2 V (red) and -1.6 V (blue). Insert: Absorption spectra before (black) and after oxidation at +0.7 V (red) and +1.2 V (blue).

Similar spectroelectrochemistry experiments performed using **FBF** in acetonitrile are shown in Figure 9. Application of a

reduction potential at -1.2 V resulted in a very noticeable band-narrowing and a blue shift by 5 nm together with an increase in peak intensity. Further reduction at -1.6 V followed the same trend and can be explained by electron addition to the second difluoropyrrolo-oxaborole group. The alteration to the absorption profile was reversible. Applying a positive potential of +0.7 V and then +1.2 V resulted only in a decrease of the absorption profile at 400 nm. Considering that the oxidation wave for **FBF** is irreversible the effect is likely due to compound degradation.

Conclusions

Although mono-Bodipy ferrocene derivatives are known^[16] it would appear that the bis derivative may be more difficult to achieve, especially using the conventional approaches toward Bodipy synthesis (Chart 1). The failure to obtain the compound is surprising considering that the dipyrromethane precursor **1** (Scheme 1) was used by Butenschön *et al.*^[17] to prepare a bis-porphyrin derivative. A steric argument for failure does not therefore seem to be valid. The deactivation of the dipyrromethane toward oxidation by the presence of a second group on the other Cp ring seems to be the only feasible explanation. Certainly we have seen that oxidation of one aldehyde group in 1,1'-ferrocene dicarboxyaldehyde deactivates reaction at the other site.^[18]

Chart 1

Unfortunately the poor irreversible electrochemistry witnessed for the pyrroloxaborole derivative **FBF** does preclude its use as a useful redox reporter. On the other hand compound **2** may be more suitable by using the chelating properties of the ketopyrrole group, and the binding of groups with nucleophilic character. Noting that the absorption profile for **FBF** stretches well into the red region, the compound may have more application as a dark-state energy transfer quencher for fluorophores which emit between 500 and 600 nm.

Experimental Section

¹H-, ¹³C- and DEPT-135° NMR spectra, as well as two-dimensional homo- (¹H/¹H COSY-45°) and heteronuclear (¹H/¹³C HMQC and HMBC) correlation spectra were recorded with Jeol ECS-400 MHz and Bruker Avance-III 400 MHz spectrometers. Chemical shifts for ¹H- and ¹³C-NMR spectra are referenced relative to the residual protiated solvent. ¹¹B-NMR spectrum are referenced relative to BF₃·OEt₂ (δ 0.0) as external reference. ¹⁹F-NMR spectrum are referenced relative to CF₃COOH (-76.55 ppm vs CFCl₃) as external reference. FT-infrared spectra were recorded with a Varian 800 FT-IR spectrometer. Electronic absorption spectra were recorded using a Hitachi U3310 spectrophotometer. The ⁵⁷Fe-Mössbauer spectrum was acquired at room temperature (RT) using a conventional spectrometer in the constant-acceleration mode (MS4,

Edina, USA) equipped with a ^{57}Co source (3.7 GBq) in a rhodium matrix. Isomer shifts are given relative to $\alpha\text{-Fe}$ at RT. The spectrum was fitted using the Mössbauer Fitting Program (Edina). The cyclic voltammetry experiments were conducted in a three-electrode system (working electrode – glassy carbon, counter electrode – platinum, reference electrode – Ag/AgCl/NaCl (3M)) using Princeton Applied Research Potentiostat model 263a. For spectroelectrochemical experiments platinum was used as working and counter electrodes and silver wire was used as a pseudoreference electrode.

Computational calculations were performed using a 32-bit version of Gaussian09^[19] on a quadruple-core Intel Xeon system with 4GB RAM. The calculations were run in parallel, fully utilising the multi-core processor. Energy minimization calculations were monitored using Molden and run in parallel with frequency calculations to ensure optimized geometries represented local minima.

Synthesis

All chemicals were purchased from commercial sources and used as received unless otherwise stated. Basic solvents for synthesis were dried using literature methods. Solvents for spectroscopic investigations were of the highest purity available. 1,1'-ferrocene dicarboxaldehyde,^[20] 1,1'-ferrocene dicarboxylic acid^[21] and 1,1'-ferrocene dicarbonyl dichloride^[22] were prepared by using modified literature methods.

Preparation of 1,1'-Ferrocene bis(2,2'-dipyrromethane) 1^[16]

A solution of 1,1'-ferrocene dicarboxaldehyde (0.5 g, 2.1 mmol) dissolved in 10 mL (144 mmol, 70 eq) of pyrrole was bubbled with Ar for 15 mins. TFA (0.04 mL, 0.52 mmol, 0.25 eq) was added and the solution was stirred at RT under an Ar atmosphere. After 30 mins aqueous NaOH (0.1 M, 6 mL) was added to stop the reaction. The mixture was poured into water (30 mL) and extracted with ethyl acetate (30 mL). The collected organic layer was washed with distilled water (3 x 20 mL), separated and dried over anhydrous Na_2SO_4 , filtered and solvent removed *in vacuo*. The obtained crude product was purified by chromatography on silica-gel using a petroleum ether (40 – 60 °C) : ethyl acetate (6:1) mixture as eluent, collecting the first brown band. The solvent was removed *in vacuo* to give 0.7 g (yield 71%) of the product as a yellow crystalline solid.

^1H -NMR (400 MHz, CDCl_3): δ 7.85 (br s, 4H, NH), 6.64 (d, J = 1.5 Hz, 4H, H2+H2'-pyrrole), 6.13 (dd, J = 5.7, 2.8 Hz, 4H, H3+H3'-pyrrole), 5.94 (s, 4H, H4+H4'-pyrrole), 5.00 (s, 2H, H-methane), 4.04 (s, 2H, $\alpha\text{-Cp}$), 3.95 (s, 2H, $\beta\text{-Cp}$). ^{13}C NMR (101 MHz, CDCl_3): δ 133.5 (C5+C5'-pyrrole), 116.7 (C2+C2'-pyrrole), 108.2 (C3+C3'-pyrrole), 106.4 (C4+C4'-pyrrole), 90.0 (Cpippo), 69.1 ($\beta\text{-Cp}$), 68.5 ($\alpha\text{-Cp}$), 38.0 (C-methane).

Preparation of 1,1'-Ferrocene bis(2-(4-ethyl-3,5-dimethylpyrro)methanone) 2

$\text{Fc}(\text{COCl})_2$ (310 mg, 1 mmol) was dissolved in dry DCM (12 mL) under a N_2 atmosphere and 3-ethyl-2,4-dimethylpyrrole (0.4 mL, 3 mmol) was added. The solution was stirred under N_2 at RT in the dark for 15 h after which time TLC analysis indicated no starting material was left. Solvents were reduced *in vacuo* and the resulting solid was redissolved in DCM and chromatographed on SiO_2 using a DCM-MeOH (1%) mixture as eluent, in order to obtain 305 mg (yield 63 %) of product as a yellow microcrystalline solid.

^1H NMR (400 MHz, CDCl_3): δ 10.20 (s, NH, 2H), 4.72 (ap t, H-Cp, J = 1.9 Hz, 4H), 4.51 (ap t, H-Cp, J = 1.9 Hz, 4H), 2.43 (q, $\text{CH}_2\text{-ethyl}$, J = 7.5 Hz, 4H), 2.37 (s, $\text{CH}_3\text{-5-methyl}$, 6H), 2.27 (s, $\text{CH}_3\text{-3-methyl}$, 6H), 1.09 (t, $\text{CH}_3\text{-ethyl}$, J = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 185.28 (C=O), 132.25 (C5-pyrrol), 129.31 (C3-pyrrol), 127.18 (C2-pyrrol), 125.35 (C4-pyrrol), 84.55 (C-Cpippo), 72.72 + 71.34 (C-Cp α + β), 17.26 ($\text{CH}_2\text{-ethyl}$), 15.34 ($\text{CH}_3\text{-ethyl}$), 11.66 ($\text{CH}_3\text{-3,5-methyl}$). FTIR (cm^{-1}): 650 (w), 733 (w), 769 (m), 786 (m), 825 (w), 859 (m), 973 (m), 1027 (w), 1043 (w), 1106 (m), 1141 (w), 1206 (w), 1235 (w), 1284 (s), 1328 (m), 1377 (s), 1423 (s), 1450 (s), 1486 (vs), 1568 (s), 2867 (w), 2926 (w), 2960 (w), 3203 (w, br).

HRMS (ESI, m/z): found $[\text{M}+\text{H}]^+$ 485.1875, calcd for $\text{C}_{28}\text{H}_{33}\text{FeN}_2\text{O}_2$: 485.1891. Elemental analysis found: C 69.15, H 6.83, N 5.61, calcd for $\text{C}_{28}\text{H}_{32}\text{FeN}_2\text{O}_2$: C 69.42, H 6.66, N 5.78.

Preparation of 1,1'-Ferrocene bis(2-(4-ethyl-3,5-dimethylpyrro)methanoneborondifluoride) FBF

$\text{Fc}(\text{COCl})_2$ (200 mg, 0.65 mmol) was dissolved in dry DCM (10 mL) under a N_2 atmosphere and 3-ethyl-2,4-dimethylpyrrole (0.27 mL, 2.0 mmol) was added. The solution was stirred under N_2 at RT in the dark for 15 h after which time TLC analysis indicated no starting material was left. Et_3N (1.5 mL) and $\text{BF}_3\cdot\text{OEt}_2$ (2 mL) were added and the reaction mixture was stirred for a further 3 h until TLC analysis showed no intermediate product remained. The solvents were reduced *in vacuo* and the resulting solid redissolved in DCM and chromatographed in darkness on SiO_2 using a DCM-petroleum ether (1:1) mixture as eluent, in order to obtain 40 mg (yield 11 %) of the product as a red-brown solid.

^1H NMR (400 MHz, CDCl_3): δ 5.16 (ap t, H-Cp, J = 1.9 Hz, 4H), 4.88 (ap t, H-Cp, J = 1.9 Hz, 4H), 2.34 (q, $\text{CH}_2\text{-ethyl}$, J = 7.6 Hz, 4H), 2.31 (s, $\text{CH}_3\text{-5-methyl}$, 6H), 2.18 (s, $\text{CH}_3\text{-3-methyl}$, 6H) 1.04 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 175.84 (C=O), 151.21 (C5-pyrrol), 136.01 (C4-pyrrol), 132.38 (C3-pyrrol), 131.98 (C2-pyrrol), 76.47 + 74.37 (C-Cp α + β), 73.37 (C-Cpippo), 17.66 ($\text{CH}_2\text{-ethyl}$), 14.70 ($\text{CH}_3\text{-ethyl}$), 12.62 ($\text{CH}_3\text{-3-methyl}$), 12.54 ($\text{CH}_3\text{-5-methyl}$). FTIR (cm^{-1}): 663 (w), 748 (w), 801 (w), 829 (w), 886 (w), 973 (m), 996 (m), 1025 (s), 1054 (s), 1097 (s), 1134 (m), 1166 (s), 1261 (w), 1307 (m), 1362 (m), 1383 (w), 1401 (w), 1451 (w), 1490 (w), 1589 (s), 1682 (w), 2874 (w), 2930 (w), 2967 (w). Elemental analysis found: C 57.70, H 5.45, N 4.62, calcd for $\text{C}_{28}\text{H}_{30}\text{B}_2\text{F}_4\text{FeN}_2\text{O}_2$: C 57.98, H 5.21, N 4.83. HRMS (ASAP/APCI-FTMS, m/z): found 580.1769 $[\text{M}]^+$, 561.1792 $[\text{M}-\text{F}]^+$, 533.1862 $[\text{M}-\text{BF}_2+2\text{H}]^+$, 513.1807 $[\text{M}-\text{BF}_3+\text{H}]^+$, 485.1881 $[\text{M}-2\text{BF}_2+3\text{H}]^+$, calcd for $\text{C}_{28}\text{H}_{30}\text{B}_2\text{F}_4\text{FeN}_2\text{O}_2$: 580.1784. HRMS (ESI, m/z): found $[\text{M}-2\text{BF}_2+3\text{H}]^+$ 485.1887, calcd for $\text{C}_{28}\text{H}_{33}\text{FeN}_2\text{O}_2$: 485.1891.

X-ray crystallography

Single-crystal diffraction data were collected on an Agilent Technologies Gemini A Ultra diffractometer at 150 K using $\text{MoK}\alpha$ radiation (for **1**) and on a Crystal Logic kappa diffractometer and Rigaku Saturn 724+ CCD detector at 100 K using synchrotron radiation (for **2** and **FBF**). Full details are given in the Supporting Information and limited data for all structures are collected in Table 4. All the structures are fully ordered. CCDC-1015718–1015720 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystallographic data for **1**, **2**, and **FBF**

Compound	1	2	FBF
Formula	$\text{C}_{28}\text{H}_{26}\text{FeN}_4$	$\text{C}_{28}\text{H}_{32}\text{FeN}_2\text{O}_2\cdot\text{CHCl}_3$	$\text{C}_{28}\text{H}_{30}\text{B}_2\text{F}_4\text{FeN}_2\text{O}_2$
M_r	474.4	603.8	580.0
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	$Pbca$	$Pbcn$
a (Å)	8.8878(4)	20.174(4)	14.561(6)
b (Å)	13.6514(5)	13.240(3)	11.950(5)
c (Å)	18.5142(7)	21.343(5)	14.581(6)
β (°)	97.310(4)		
V (Å ³)	2228.09(16)	5701(2)	2537.2(18)
Z	4	8	4
Unique data,	4987, 317	8756, 349	3134, 181
params			
R (F , $F^2 > 2\sigma$)	0.0322	0.0393	0.0427
R_w (F^2 , all data)	0.0817	0.0986	0.1097

Acknowledgements

We thank Newcastle University for financial support and FP7-PEOPLE-2009-IRSES grant (246902) for funding to cover the exchange of researchers. Dumitru Sirbu thanks the World Federation of Scientists for a Scholarship in the framework of the National Scholarship Programme and the Alexander von Humboldt Foundation. The EPSRC UK National Mass Spectrometry Facility at Swansea University

References

- [1] a) H. Zhang, C. Huo, K. Ye, P. Zhang, W. Tian, Y. Wang, *Inorg. Chem.* **2006**, 45, 2788–2794; b) Y. Kubota, Y. Ozaki, K. Funabiki, M. Matsui, *J. Org. Chem.* **2013**, 78, 7058–7067; c) W. Li, W. Lin, J. Wang, X. Guan, *Org. Lett.* **2013**, 15, 1768–1771; d) D. Frath, J. Massue, G. Ulrich, R. Ziessel, *Angew. Chem. Int. Ed.* **2014**, 53, 2290–2310.
- [2] a) M. J. Kwak, Y. Kim, *Bull. Korean Chem. Soc.* **2009**, 30, 2865–2866; b) S. H. Choi, K. Kim, J. Lee, Y. Do, D. G. Churchill, *J. Chem. Crystallogr.* **2007**, 37, 315–331.
- [3] J. Karolin, L. B.-A. Johansson, L. Strandberg, T. Ny, *J. Am. Chem. Soc.* **1994**, 116, 7801–7806.
- [4] a) G. Zhang, J. Lu, S. Michal, C. L. Fraser, *J. Am. Chem. Soc.* **2010**, 132, 2160–2162; b) S. Xu, R. E. Evans, T. Liu, G. Zhang, J. N. Demas, C. O. Trindle, C. L. Fraser, *Inorg. Chem.* **2013**, 52, 3597–3610; c) G. Bai, C. Yu, C. Cheng, E. Hao, Y. Wei, X. Mu, L. Jiao, *Org. Biomol. Chem.* **2014**, 12, 1618–1626; d) D. Frath, A. Poirer, G. Ulrich, A. D. Nicola, R. Ziessel, *Chem. Commun.* **2013**, 49, 4908–4910; e) F. Montalbano, N. R. Candeias, L. F. Veiros, V. Andre, M. T. Duarte, M. R. Bronze, R. Moreira, P. M. P. Gois, *Org. Lett.* **2012**, 14, 988–991; f) C. Glotzbach, U. Kauscher, J. Voskuhl, N. S. Kehr, M. C. A. Stuart, R. Fröhlich, H. J. Galla, B. J. Ravoo, K. Nagura, S. Saito, S. Yamaguchi, E. U. Würthwein, *J. Org. Chem.* **2013**, 78, 4410–4418.
- [5] M. Broering, R. Krueger, C. Kleeberg, *Z. Anorg. Allg. Chem.* **2008**, 634, 1555–1559.
- [6] J. Chen, A. Burghart, C.-W. Wan, L. Thai, C. Ortiz, J. Reibenspies, K. Burgess, *Tetrahedron Lett.* **2000**, 41, 2303–2307.
- [7] For examples of ferrocene-pyrrole derivatives see: a) J. L. Sessler, R. S. Zimmerman, G. J. Kirkovits, A. Gebauer, M. Scherer, *J. Organomet. Chem.* **2001**, 637–639, 343–348; b) M. Scherer, J. L. Sessler, A. Gebauer, V. Lynch, *Chem. Commun.* **1998**, 85–86; c) M. Scherer, J. L. Sessler, M. Moini, A. Gebauer, V. Lynch, *Chem. Eur. J.* **1998**, 4, 152–158; d) S. Ramakrishnan, A. Srinivasan, *Org. Lett.* **2007**, 9, 4769–4772; e) S. Ramakrishnan, K. S. Anju, A. P. Thomas, K. C. Gowri Sreedevi, P. S. Salini, M. G. Derry Holaday, E. Suresh, A. Srinivasan, *Organometallics*, **2012**, 31, 4166–4173; f) S. J. Coles, G. Denuault, P. A. Gale, P. N. Horton, M. B. Hursthouse, M. E. Light, C. N. Warriner, *Polyhedron*, **2003**, 22, 699–709.
- [8] M. Rajeswara Rao, K. V. Pavan Kumar, M. Ravikanth, *J. Organomet. Chem.* **2010**, 695, 863–869.
- [9] B. Koszarna, H. Butenschön, D. T. Gryko, *Org. Biomol. Chem.* **2005**, 3, 2640–2645.
- [10] X. Xie, Y. Yuan, R. Krüger, *M. Bröring Mag. Res. Chem.* **2009**, 47, 1024–1030.
- [11] M. L. Good, J. Buttone, D. Foyt, *Ann. N.Y. Acad. Sci.* **1974**, 239, 193–207.
- [12] G. Neshvad, R. M. G. Roberts, J. Silver, *J. Organomet. Chem.* **1982**, 236, 349–358.
- [13] M. C. Clemance, R. M. G. Roberts, J. Silver, *J. Organomet. Chem.* **1983**, 241, 219–222.

is also thanked for collecting mass spectra of compounds. We thank Diamond Light Source for access to synchrotron facilities (beamline I19).

Keywords: Ferrocene • Electrochemistry • Difluoropyrrolo-oxaborole • Mössbauer • Absorption

- [14] R. H. Herber, in: R.H. Herber (Ed.), *Chemical Mössbauer Spectroscopy*, Plenum Press, New York, **1984**, 199–216.
- [15] For examples of switching fluorescence on/off by redox changes see: a) P. V. Solntsev, J. R. Sabin, S. J. Dammer, N. N. Gerasimchuk, V. N. Nemykin, *Chem. Commun.* **2010**, 46, 6581–6583; b) P. Zhu, C. Zhu, Y. Zhao, Q. Wei, Y. Chen, *Adv. Mater. Res.* **2009**, 79–82, 1703–1706.
- [16] X. Yin, Y. Li, Y. Zhu, X. Jing, Y. Li, D. Zhu, *Dalton Trans.* **2010**, 39, 9929–9935.
- [17] B. Koszarna, H. Butenschön, D. T. Gryko, *Org. Biomol. Chem.* **2005**, 3, 2640–2645.
- [18] A. C. Benniston, D. Sirbu, C. Turta, M. R. Probert, W. Clegg, *Tetrahedron Lett.* **2014**, 55, 3777–3780.
- [19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [20] F. G. R. Fröhlich, A. A. Zabelinskaja-Mackova, H. M. Fechter, H. Griengl, *Tetrahedron Asymmetry*, **2003**, 355–362.
- [21] C. G. Rodríguez-Cendejas, L. S. Liebeskind, E. Peña-Cabrera, *Archive for Organic Chemistry*, 2005, 250–265.
- [22] T. Ikeda, S. Shinkai, K. Sada, M. Takeuchi, *Tetrahedron Lett.* **2009**, 50, 2006–2009.