Pages: 9





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Synthesis, Molecular Structure and Properties of a Ferrocene-Based Difluoropyrrolo-Oxaborole Derivative

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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(dipyrromethene) compound. The 2-ketopyrrole compound readily reacted with BF₃·Et₂O to produce the bis(difluoropyrrolo)-oxaborole compound, FBF, as a red/ brown solid which was characterised by X-ray crystallography. ⁵⁷Fe Mössbauer spectra for 2 and FBF were consistent with low-spin iron(II) (d⁶) ferrocene derivatives. A cyclic vol-

tammogram 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 2by 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 spectroscopic data.

Introduction

The incorporation of the chelating boron difluoride (BF₂) group into bidentate sites of flexible molecular species is a simple method to rigidify their structures.^[1] The structural modification can have a major effect, particularly on the excited state, and this is particularly true for dipyrromethene derivatives.^[2] The basic unit is flexible and excitedstate emission is not noticeably strong, which can be attributed to efficient internal conversion promoted by facile molecular distortion. In comparison, the BF₂ version which is more commonly known as borondipyrromethene (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 into which the BF2 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 dipyrromethane. 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

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have been discussed in the literature.^[5,6] In attempts to prepare a bis(Bodipy)ferrocene derivative we found that the bis(ketopyrrole) derivative 2 was produced instead^[7] and could be converted readily to the BF₂ adduct, FBF. Unlike some previous examples, the compound is nonfluorescent. Excited state quenching is highly probable because of the close proximity of the redox-active ferrocene to the difluoropyrrolo-oxaborole.

Results and Discussion

Synthesis

It has been established that, starting from ferrocenecarbaldehyde and pyrrole, the corresponding nonalkylated boron dipyrromethene (Bodipy) derivative can be prepared in reasonable yield.^[8] At first our interest was to see if the same reaction could be carried out by using 1,1'-ferrocenedicarbaldehyde instead. Several attempts to directly prepare the Bodipy derivative FBD1 failed (Scheme 1). The dipyrromethane derivative 1 is known^[9] and was prepared without much problem in 70% yield. All attempts in our hands to oxidise 1 and chelate two BF₂ groups to the dipyrromethene groups failed to yield any product which could be identified as the desired derivative. Unsubstituted pyrroles are prone to oxidation and so a change in the reagent to 3-ethyl-2,4dimethylpyrrole 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 diketone 2, and all our attempts to encourage this to react further with the pyrrole derivative and using Lewis acids were unsuccess-

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ful. However, compound 2 readily reacted with BF₃·Et₂O to afford FBF as a red/brown solid. The compound was characterised by NMR spectroscopy including ¹H, ¹³C, ¹¹B and ¹⁹F nuclei. From inspection of **FBF** we might expect, because of restricted rotation, that the two fluorine nuclei for each ketopyrrole 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 δ = -149.9 (broad) and -158.0 ppm (doublet, J = 26 Hz). In contrast, only a single broad peak at $\delta = 2.16$ ppm was observed in the ¹¹B NMR spectrum. The ESI-MS spectrum showed a peak at m/z = 485 corresponding to loss of BF₂ 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 $[M - F]^+$, m/z 533 $[M - BF_2+2H]^+$, m/z 513 $[M - BF_2+2H]^+$ $BF_3+H]^+$, m/z 485 [M - 2BF₂+3H] (see Supporting Information).



Scheme 1. Reagents and conditions: (i) pyrrole, TFA (ii) DDQ or *p*chloranyl or activated MnO₂ (iii) 3-ethyl-2,4-dimethylpyrrole, Et₃N, BF₃·OEt₂; POCl₃, 3-ethyl-2,4-dimethylpyrrole, Et₃N, BF₃·OEt₂ (iv) 3-ethyl-2,4-dimethylpyrrole (v) Et₃N, BF₃·OEt₂.

X-ray Crystallography

As part of characterisation of the final compound and precursors, single crystals were grown for compounds 1, 2 and FBF, and were subjected to X-ray diffraction analysis. The structures of 1 and 2 (Figure 1) confirmed 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 cylopentadienide (Cp) rings. The effect is to twist the pyrromethanone 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.

FULL PAPER



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

The compound **FBF** crystallises 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



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).

Pages: 9

www.eurjic.org

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 formed by the endocyclic N-B-O atoms. 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 and is 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.

Table 1. Selected bond lengths and angles for FBF.

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

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

⁵⁷Fe Mössbauer Spectroscopy

The Mössbauer spectra at 7 K 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) were 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 the 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 with that of 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 with that of **2** can be explained by the higher coplanarity of the electron-withdrawing substituents with the cyclopentadienyl rings, which ensures 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]

$$\ln f = -\frac{6E\gamma}{k\theta_{\rm D}^2}T\tag{1}$$

where $E\gamma$ is the recoil energy, k is Boltzmann's constant and θ_D^2 is the Debye temperature, which is a measure of the crystal hardness. Plots of $\ln(f_T/f_{7K})$ vs. T (Figure 4) are linear over the temperature range 80 K to 200 K and from the slopes the corresponding θ_D^2 values were calculated.



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

The θ_D^2 value for ferrocene was estimated at 173 K. As the relative absorption of **FBF** at room temperature has only a minor decrease compared with 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 that of the parent ferrocene. The calculated θ_D^2 value is about 139 K. The lower Debye temperature for **2** compared with ferrocene and **FBF** suggests there are weaker intermolecular interactions.

www.eurjic.org

Pages: 9

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

	Temp. [K]	Isomer shift $\delta [{ m mms}^{-1}]$	Quadrupole splitting $\Delta EQ \text{ [mm s}^{-1}\text{]}$	Relative Absorption $f_T/f_{7K}^{[c]}$
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	n.a.
	300	0.43	2.20	n.a.
DBF ^[b]	80	0.53	2.17	n.a.
Fc	7	0.54	2.40	_
	293	0.45	2.39	0.31

[a] Data taken from ref.^[11] [b] Data taken from ref.^[12] [c] n.a.: not available.



Figure 4. Plot of $\ln(f_T | f_{7K})$ vs. *T* for ferrocene (\bullet) and compound **2** (\blacksquare). 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.

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 of the ferrocene and compare this with 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 constructed from different starting geometries and the energy minimised (see Supporting Information). Bond lengths and angles were compared with those in 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 with that in **2** (+0.647). Because **FBF** is C_2 symmetric, the summation of Mulliken charges for carbon atoms at each Cp ring is 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 with 40.9° at the other Cp site. The corresponding dihedral angle for **FBF** is only 8° meaning any conjugation is maximised for this system but it also contains the electron-withdrawing BF₂ unit.



Figure 5. Mulliken charges on the atoms calculated by 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 the Mulliken charge at the ferrocene centre, the starting structure for **FBF** was again minimised by 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 kcalmol⁻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

Pages: 9



www.eurjic.org

reduced to +0.548 and the 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 oxidise than the uncomplexed version. In addition, we can also speculate that the electric field across the iron nucleus will decrease slightly for **FBF** compared with in compound **2**.

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

	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] $\Delta MC = MC_{FBF} - MC_2$. [c] $\Delta MC = MC_{opt} - MC_{unopt}$.

Electrochemistry and Absorption Spectroscopy

The redox behaviour of 2 and FBF was measured by using cyclic voltammetry in dry acetonitrile with 0.2 M TBATFB as the 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 pyrrolo-ketone group. There is also evidence 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 BF₂ 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 quasireversible waves can be observed at -1.54 and -1.84 V vs. Fc⁺/Fc. The shift to a 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 was noted that the ferrocene redox behaviour is irreversible in FBF, implying that a decomposition pathway is introduced for the ferrocenium ion. Considering that an electrophilic centre is created in close proximity to a polarised 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 that of FBF alone.



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.

The room-temperature electronic absorption spectra for 2 and FBF are shown in Figure 7. The spectrum of 2 consists of a band in the near-UV region at $\lambda_{max} = 271 \text{ nm}$ $(\varepsilon_{\rm max} = 1.7 \times 10^4 \,{\rm M}^{-1} \,{\rm cm}^{-1})$ and a moderately strong narrow band at $\lambda_{\text{max}} = 337 \text{ nm} (\varepsilon_{\text{max}} = 3.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$. According to DFT calculations (see Supporting Information) this band is likely associated with the HOMO-LUMO transition localised on the ketopyrrole unit and the calculated energy gap is 3.69 eV (336 nm). A much less intense broad band can also be observed in the visible region at λ_{max} = 462 nm ($\varepsilon_{max} = 1.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). This latter band was assigned to electronic transitions for the ferrocene group. Chelation with BF₂ changes the absorption profile entirely, resulting in a considerably broader but weaker band in the visible region at $\lambda_{\text{max}} = 407 \text{ nm} (\varepsilon_{\text{max}} = 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$ with a shoulder at 339 nm. The intensity of the band at $\lambda_{\text{max}} = 272 \text{ nm} (\varepsilon_{\text{max}} = 7.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1})$ is considerably less. 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 observable from FBF in fluid solution, in the solid state or when oxidised.^[15]



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

Pages: 9

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Spectroelectrochemistry

Perturbation of the UV/Vis spectra for 2 and FBF was monitored by 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 with a slight change in the band shape and a tail stretching to around 800 nm (Figure 8). There was a concomitant decrease in 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 oxidising 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).

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 difluoropytrolo-oxaborole group. The alteration in the absorption profile was reversible. Applying a positive potential of +0.7 V and then +1.2 V resulted only in a decrease in the absorption profile at 400 nm. Considering that the oxidation wave for **FBF** is irreversible, the effect is likely due to compound degradation.



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 blue +1.2 V (blue).

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 (Scheme 2). 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 towards 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'-ferrocenedicarbaldehyde deactivates reaction at the other site.^[18]



Scheme 2.

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.

Pages: 9

www.eurjic.org

Experimental Section

General: ¹H, ¹³C and DEPT-135° NMR spectra, as well as 2D homo- (1H/1H COSY-45°) and heteronuclear (1H/13C HMQC and HMBC) correlation spectra were recorded by using 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 protonoated solvent. ¹¹B NMR spectrum are referenced relative to BF₃·OEt₂ ($\delta = 0.0$ ppm) as external reference. ¹⁹F NMR spectra are referenced relative to CF₃COOH (-76.55 ppm vs. CFCl₃) as external reference. FTIR spectra were recorded by using a Varian 800 FTIR spectrometer. Electronic absorption spectra were recorded by using a Hitachi U3310 spectrophotometer. The ⁵⁷Fe Mössbauer spectrum was acquired at room temperature (r.t.) by means of a conventional spectrometer in the constant-acceleration mode (MS4, Edina, USA) equipped with a 57Co source (3.7 GBq) in a rhodium matrix. Isomer shifts are given relative to α -Fe at room temp. 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)] by using a Princeton Applied Research Potentiostat model 263a. For spectroelectrochemical experiments, platinum was used as the working and counter electrodes and silver wire was used as a pseudoreference electrode.

Computational calculations were performed by 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 minimisation calculations were monitored by using Molden and run in parallel with frequency calculations to ensure that optimised 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'-ferrocenedicarbaldehyde,^[20] 1,1'-ferrocene dicarboxylic acid^[21] and 1,1'-ferrocene dicarbonyl dichloride^[22] were prepared by using modified literature methods.

1,1'-Ferrocene-Bis(2,2'-dipyrromethane) (1):^[16] A solution of 1,1'ferrocenedicarbaldehyde (0.5 g, 2.1 mmol) dissolved in pyrrole (10 mL, 144 mmol, 70 equiv.) was bubbled with Ar for 15 min. TFA (0.04 mL, 0.52 mmol, 0.25 equiv.) was added and the solution was stirred at room temp. under an Ar atmosphere. After 30 min, 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 ($3 \times 20 \text{ mL}$), separated and dried with anhydrous Na₂SO₄, filtered and the solvent removed in vacuo. The resultant 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. 1 H NMR (400 MHz, CDCl₃): δ = 7.85 (br. s, 4 H, NH), 6.64 (d, J = 1.5 Hz, 4 H, H2+H2'-pyrrole), 6.13 (dd, J = 5.7, 2.8 Hz, 4 H, H3+H3'-pyrrole), 5.94 (s, 4 H, H4+H4'-pyrrole), 5.00 (s, 2 H, Hmethane), 4.04 (s, 2 H, α -Cp), 3.95 (s, 2 H, β -Cp) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 133.5 (C5+C5'-pyrrole), 116.7 (C2+C2'pyrrole), 108.2 (C3+C3'-pyrrole), 106.4 (C4+C4'-pyrrole), 90.0 (Cp-ipso), 69.1 (β-Cp), 68.5 (α-Cp), 38.0 (C-methane) ppm.

1,1'-Ferrocene–Bis[2-(4-ethyl-3,5-dimethylpyrro)methanone] (2): $Fc(COCl)_2$ (310 mg, 1 mmol) was dissolved in dry DCM (12 mL) under an N₂ atmosphere and 3-ethyl-2,4-dimethylpyrrole (0.4 mL,

3 mmol) was added. The solution was stirred under $N_{\rm 2}$ at room temp. in the dark for 15 h after which time TLC analysis indicated no starting material was left. Solvents were removed in vacuo and the resultant solid was dissolved in DCM and chromatographed on SiO₂ 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, CDCl₃): δ = 10.20 (s, 2 H, NH), 4.72 (ap t, J = 1.9 Hz, 4 H, H-Cp), 4.51 (ap t, J = 1.9 Hz, 4 H, H-Cp), 2.43 (q, J = 7.5 Hz, 4 H, CH₂-ethyl), 2.37 (s, 6 H, CH₃-5-methyl), 2.27 (s, 6 H, CH₃-3-methyl), 1.09 (t, J = 7.5 Hz, 6 H, CH₃ethyl) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 185.28 (C=O), 132.25 (C5-pyrrol), 129.31 (C3-pyrrol), 127.18 (C2-pyrrol), 125.35 (C4-pyrrol), 84.55 (C-Cp-*ipso*), 72.72 + 71.34 (C-Cpα+β), 17.26 (CH₂-ethyl), 15.34 (CH₃-ethyl), 11.66 (CH₃-3,5-methyl) ppm. FTIR: $\tilde{v} = 650$ (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) cm⁻¹. HRMS (ESI, m/z): found [M + H]⁺ 485.1875, calcd. for C₂₈H₃₃FeN₂O₂: 485.1891. C₂₈H₃₂FeN₂O₂ (484.42): calcd. C 69.42, H 6.66, N 5.78; found C 69.15, H 6.83, N 5.61.

1,1'-Ferrocene-Bis[2-(4-ethyl-3,5-dimethylpyrro)methanoneborondifluoride] (FBF): Fc(COCl)₂ (200 mg, 0.65 mmol) was dissolved in dry DCM (10 mL) under an N2 atmosphere and 3-ethyl-2,4dimethylpyrrole (0.27 mL, 2.0 mmol) was added. The solution was stirred under N₂ at room temp. in the dark for 15 h after which time TLC analysis indicated no starting material was left. Et₃N (1.5 mL) and BF₃·OEt₂ (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 removed in vacuo and the resultant solid dissolved 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, CDCl₃): δ = 5.16 (ap t, J = 1.9 Hz, 4 H, H-Cp), 4.88 (ap t, J = 1.9 Hz, 4 H, H-Cp), 2.34 (q, J = 7.6 Hz, 4 H, CH₂-ethyl), 2.31 (s, 6 H, CH₃-5-methyl), 2.18 (s, 6 H, CH₃-3-methyl) 1.04 (t, J = 7.6 Hz, 2 H) ppm. ¹³C NMR (101 MHz, CDCl₃): 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-Cpa+β), 73.37 (C-Cp-ipso), 17.66 (CH2-ethyl), 14.70 (CH₃-ethyl), 12.62 (CH₃-3-methyl), 12.54 (CH₃-5-methyl) ppm. FTIR: $\tilde{v} = 663$ (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) cm⁻¹. C₂₈H₃₀B₂F₄FeN₂O₂ (580.02): calcd. C 57.98, H 5.21, N 4.83; found C 57.70, H 5.45, N 4.62. HRMS (ASAP/APCI-FTMS, m/z): found $580.1769 [M]^+$, $561.1792 [M - F]^+$, $533.1862 [M - BF_2 + 2H]^+$, 513.1807 $[M - BF_3 + H]^+$, 485.1881 $[M - 2BF_2 + 3H]^+$, calcd. for $C_{28}H_{30}B_2F_4FeN_2O_2$: 580.1784. HRMS (ESI, *m/z*): found [M – $2BF_2 + 3H^{+}_{2} + 485.1887$, calcd. for $C_{28}H_{33}FeN_2O_2$: 485.1891.

X-ray Crystallography: Single-crystal diffraction data were collected on an Agilent Technologies Gemini A Ultra diffractometer at 150 K using Mo- K_{α} 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 (for 1), -1015719 (for 2) and -1015720 (for FBF) contain the supplementary crystallographic data for this paper.

Pages: 9

www.eurjic.org

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

	1	2	FBF
Formula	$\mathrm{C}_{28}\mathrm{H}_{26}\mathrm{FeN}_4$	C ₂₈ H ₃₂ FeN ₂ O ₂ · CHCl ₃	$C_{28}H_{30}B_2F_4FeN_2O_2$
$M_{ m r}$	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)
Ζ	4	8	4
Unique data,	4987, 317	8756, 349	3134, 181
parameters			
$R (F, F^2 > 2\sigma)$	0.0322	0.0393	0.0427
$R_{\rm w}$ (F^2 , all data)	0.0817	0.0986	0.1097

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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FULL PAPER

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Pages: 9

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Ferrocene-Based Heterocycles

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Synthesis, Molecular Structure and Properties of a Ferrocene-Based Difluoropyrrolo-Oxaborole Derivative

Keywords: Sandwich complexes / Boron heterocycles / Moessbauer spectroscopy / Electrochemistry



Reaction of 1,1'-ferrocenedicarbonyl chloride with 3-ethyl-2,4-dimethylpyrrole produces the bis(ketopyrrole) compound.



Chelation of BF_2 to the ketopyrrole units forms the difluoropyrrolo-oxaborole.