



The synthesis and electrochemistry of 2,5-dimethylazaferrocenes with heteroaryl bridges

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ABSTRACT

We report on the synthesis of complexes having two equivalent redox active 2,5-dimethylazaferrocenyl entities connected by heteroaryl (heteroaryl = thiophenyl, bithiophenyl and pyridyl) bridges. The new compounds have been investigated by various electrochemical techniques including cyclic voltammetry (CV), differential pulse voltammetry (DPV) and square wave voltammetry (SW) and were found to exhibit two consecutive reversible or partially reversible one-electron oxidations. Comproportionation constants (K_c) calculated from $\Delta E_{1/2}$ values indicate that the thermodynamic stability of their monoxidized forms exceeds those of analogous ferrocenes. In this paper we also report the X-ray crystal structure and UV–Vis spectroelectrochemistry of parent 2,5-dimethylazaferrocene.

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1. Introduction

Homo- and heterobinuclear complexes with π -conjugated bridges have attracted considerable attention during recent years because they serve as simple models for investigating metal–metal electronic communication [1]. There is also an increasing awareness that such metal capped π -conjugated systems will play a role in the design of new generations of electronic materials [2]. Ferrocenes, due to the high stabilities of their neutral and oxidized forms, have been extensively explored as electroactive end-groups in that area of research [3]. Compounds with two ferrocenyl units can be divided into two subclasses. The first class is represented by complexes in which the ferrocenyl fragments are equivalent by symmetry. The second one comprises complexes with non-equivalent ferrocenyl sites which is mostly imposed by a low symmetry of the bridging heterocycle(s). 2,5-Di(ferrocenyl)-thiophene (**1**) [4], 3,4-di(ferrocenyl)thiophene (**2**) [4], 2,6-di(ferrocenyl)pyridine (**3**) [4], 1,3-di(ferrocenyl)benzo[*b*]thiophene (**4**) [5], 1,3-di(ferrocenyl)benzo[*b*]selenophene (**5**) [5], 5,5'-di(ferrocenyl)-3,3'-dimethoxy-2,2':5',2'':5'':2'''-quaterthiophene (**6**) [6], *cis/trans* di(ferrocenyl)-tetrathiafulvalene (**7**) [7] and 5,5'-di(ferro-

nyl)-2,2'-bis(thiazole) (**8**) [8] (Fig. 1) are representative examples of the first class of complexes.

Derivatives of class two are represented by 2,3-di(ferrocenyl)benzo[*b*]thiophene (**9**) [5], 2,5-di(ferrocenyl)thiazole (**10**) [8,9] and 2,5-di(ferrocenyl)oxazole (**11**) [10] (Fig. 2).

The degree of interactions between the iron centers in the mixed-valent states of **1–5** has been mostly investigated by cyclic voltammetry (CV). Unfortunately, the different experimental conditions applied hamper a straightforward comparison of the difference between the individual half-wave potentials, $\Delta E_{1/2}$, of **1–5** and of the comproportionation constants (K_c) derived thereof via Eq. (1) [11]. In Eq. (1), F is the Faraday constant, n the number of transferred electrons and $\Delta E_{1/2}$ the difference of half-wave potentials. Nevertheless, the highest $\Delta E_{1/2}$ values of 280 mV and 305 mV have been reported for **4** and **5**, respectively, corresponding to $K_c = 5.4 \times 10^4$ for **4** and $K_c = 1.4 \times 10^5$ for **5** [5]. Lower degrees of electronic interactions between the iron centers have been detected (by means of CV technique) for **1** ($\Delta E_{1/2} = 150$ mV, $K_c = 340$), **2** ($\Delta E_{1/2} = 140$ mV, $K_c = 230$) along with negligible interactions in the case of **3** (one two-electron redox wave, $\Delta E_{1/2} \approx 0$ mV) [4]. Extensive studies by Tárrega and Molina [8–10] on unsymmetrical di(ferrocenyl) substituted heteroarenes suggest the presence of electronic iron–iron interactions in **10** and **11** ($\Delta E_{1/2} = 140$ mV, $K_c = 2.32 \times 10^2$ in each case) but not in **8** (one two-electron redox wave, $\Delta E_{1/2} \approx 0$ mV). These interactions can be efficiently modulated by protonating the bridging ligands [8–10]. Moreover, complex **10** showed dual optical and redox sensor activities toward Zn^{2+} , Cd^{2+} , Hg^{2+} , Ni^{2+} and Pb^{2+} cations [8]. These results clearly shown that utilization of ferrocenyl fragments as

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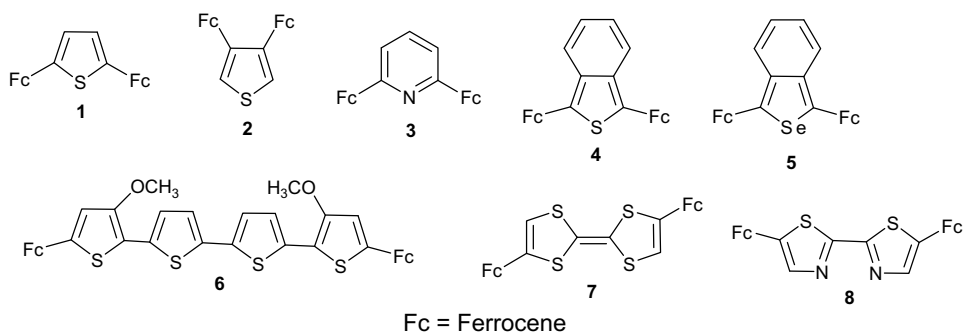


Fig. 1. Symmetrical heteroaryl bridged diferrocenes.

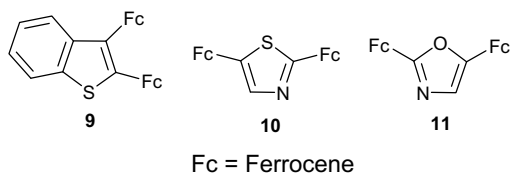


Fig. 2. Unsymmetrical heteroaryl bridged diferrocenes.

capping groups in heteroaryl bridged dinuclear complexes provides access to their corresponding thermodynamically stable mixed-valence monoxidized forms that exhibit fair levels of Fe(II)–Fe(III) electronic interactions

$$K_c = \exp\left[\frac{n \cdot F}{R \cdot T} \cdot \Delta E_{1/2}\right] \quad (1)$$

The synthesis of novel bridged metallocenes with a high degree of electron delocalization in their mixed-valence state(s) presents a continuous scientific challenge. With this in mind we here report on the synthesis and electrochemical characterization of the three novel 2,5-dimethylazaferrocenyl substituted derivatives 2,5-di(1'-(2,5-dimethylazaferrocenyl))thiophene (**12**), 2,6-di(1'-(2,5-dimethylazaferrocenyl))pyridine (**13**) and 5,5'-di(1'-(2,5-dimethylazaferrocenyl))-2,2'-bithiophene (**14**). Complexes **12** and **13** are close relatives of compounds **1** and **3**. The rationale for introduction of 2,5-dimethylazaferrocene was to investigate the degree of electronic interactions mediated by thiophenyl, bithiophenyl and pyridyl bridges when connected to end-groups with a higher redox potential than that of ferrocene [13].

In this paper we also report the X-ray crystal structure of parent 2,5-dimethylazaferrocene (**15**) along with the UV–Vis spectroelectrochemical characterization of its associated radical cation.

2. Results and discussion

2.1. Synthesis of **12**, **13** and **14**

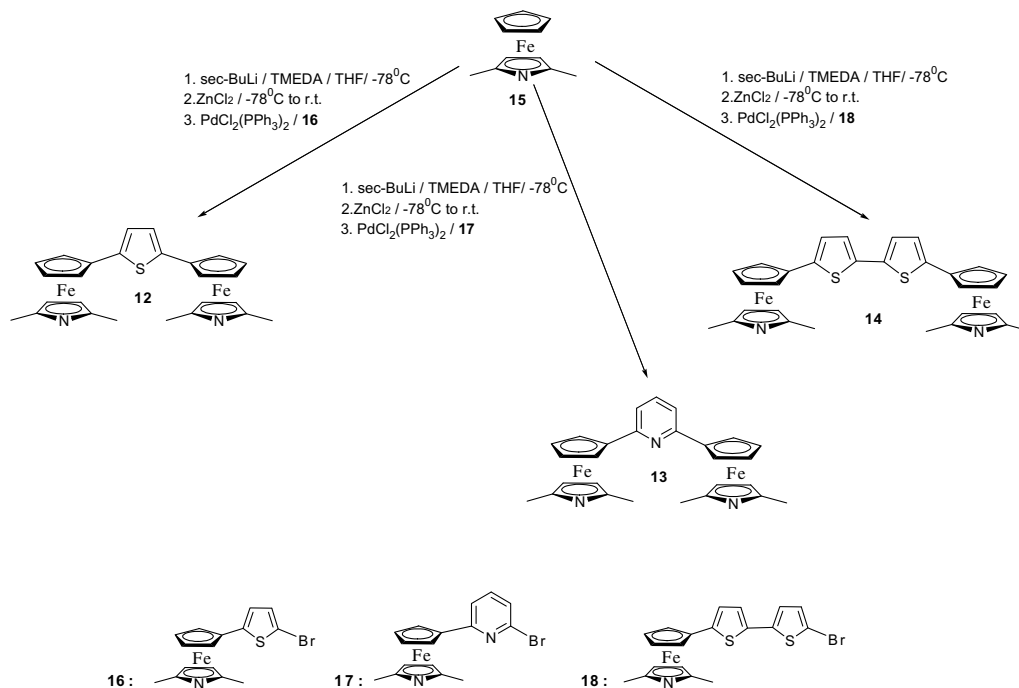
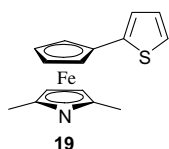
Several preparative strategies have successfully been applied to the synthesis of symmetrical heteroaryl bridged diferrocenes. Complexes **4** and **5** were obtained by three step linear syntheses [5]. The final steps involve formation of the benzo[*b*]thiophene and benzo[*b*]selenophene bridging fragments by the ring-closure of *ortho* diferrocenoylbenzene with Lawesson's reagent or selenating reagents. A simpler strategy toward the synthesis of complex **1** comprises the thermolysis of ethynylferrocene in the presence of mononuclear metal carbonyls and elemental sulfur in benzene solution [12]. However, the most straightforward and universal approach is represented by palladium catalyzed cross-coupling reactions of ferrocenylzinc chloride and dihaloheteroarenes. Based on this methodology, complexes **1**, **2**, **3**, **6**, **7** and **9** have been obtained

[4–7]. We have already reported that 2,5-dimethylazaferrocenyl-zinc chloride undergoes palladium catalyzed cross-coupling reactions with dibromoheteroarenes to yield 1'-heteroaryl-2,5-dimethylazaferrocenes [13]. As a logical continuation of this study we applied this type of cross-coupling reactions toward the preparation of symmetrical heteroaryl bridged dinuclear azaferrocenyl complexes.

The synthetic route for the preparation of compounds **12**, **13** and **14** is outlined in Scheme 1 and involves lithiation of 2,5-dimethylazaferrocene (**15**) [14] followed by addition of ZnCl₂. In the next step a catalytic amount of PdCl₂(PPh₃)₂ in THF and the appropriate reactive 1'-heteroaryl-2,5-dimethylazaferrocenes **16** [13], **17** [13] or **18** were successively added at room temperature to the stirring reaction mixtures.

In order to increase the yields, an excess of the readily available 2,5-dimethylazaferrocene was used. It is worth to point out that the bromo-substituted bithiophene derivative **18** is another example of a new 1'-heteroaryl-2,5-dimethylazaferrocene that was obtained in the course of this work. It was therefore characterized by various spectroscopic techniques and by elemental analysis (see Section 4). Analytically pure samples of **12** and **14** have been obtained after standard workup and crystallization from *n*-hexane with 58% and 73% isolated yields. The pyridine derivative **13** has been isolated as orange-red viscous solid in a 61% yield. All newly synthesized compounds are fairly thermally and air stable. Interestingly, in case of the reaction with **16** we were able to isolate, besides the expected **12**, trace amounts of the bithiophene complex **14** and of debrominated **19** (Fig 3). Similar side reactions were seemingly encountered in the reactions with **17** and **18**. In those cases we also observed upon column chromatography additional small, broad and weakly colored fractions. The ¹H NMR spectra of these fractions indicated the presence of complex mixtures of still unseparated products.

The structures of **12**, **13** and **14** were confirmed by spectroscopic methods and elemental analyses. The ¹H NMR spectrum of **12** shows a singlet at 6.96 ppm for the two equivalent thieryl ring protons, two four protons singlets at 4.50 ppm and 4.31 ppm for the substituted cyclopentadienyl ligands, a singlet at 4.27 ppm for the β-pyrrolyl protons and a singlet at 2.12 ppm from the four α-pyrrolyl methyl groups. The ¹H NMR spectrum of **13** exhibits a low-field one proton triplet at 7.59 ppm and a two protons doublet at 7.30 ppm. This pattern clearly indicates the presence of a symmetrical 2,6-disubstituted pyridine ring. The two triplets of the cyclopentadienyl ligands' protons appear at 4.93 ppm and 4.40 ppm, along with a four protons singlet at 4.24 ppm for the β-pyrrolyl protons and a singlet at 2.03 ppm from the four α-pyrrolyl methyl groups. The ¹H NMR spectrum of **14** shows two doublets at 7.03 ppm and 6.99 ppm for the two pairs of non-equivalent thieryl protons, two four protons singlets at 4.51 ppm and 4.33 ppm for the substituted cyclopentadienyl ligands, a

Scheme 1. Synthesis of compounds **12**, **13** and **14**.Fig. 3. The structure of byproduct **19**.

singlet at 4.29 ppm for the β -pyrrolyl protons and a singlet at 2.14 ppm from the four α -pyrrolyl methyl groups.

2.2. Electrochemical studies of **12**, **13**, **14** and **18**

One important incentive for preparing heteroaryl bridged dinuclear 2,5-dimethylazaferrocenes **12**, **13** and **14** was to investigate their electrochemical behavior, especially with respect to electronic communication between the iron centers. It was of particular interest to compare the thermodynamic stabilities (K_c values, Eq. (1)) of their mixed-valent radical cations to those of the analogous ferrocenes **1** and **3** and to that of the closely related **8**.

Electrochemical studies on the heteroaryl bridged 2,5-dimethylazaferrocene derivatives **12**, **13** and **14** and on the azaferrocenyl substituted bithiophene **18** were conducted in CH₂Cl₂/NBu₄PF₆ (0.2 M) at 293 K. The choice of this supporting electrolyte follows our recent observation [13] that the 0/+ couple of parent 2,5-dimethylazaferrocene is considerably more reversible in this electrolyte when compared to CH₂Cl₂/NBu₄ClO₄ [15]. Under these conditions, all heteroaryl bridged 2,5-dimethylazaferrocenes displayed two consecutive closely to moderately spaced one-electron oxidations. While the radical cations appear to be stable on the voltammetric time-scale, dioxidized **12**²⁺ and **13**²⁺ are not. Overall reversibility coefficients as they were calculated by the ratio of the total cathodic reverse and the anodic forward currents $i_{p,rev}/i_{p,forw}$ are 0.9 in the case of **12** and 0.85 for **13** at $v = 0.1$ V/s but steadily increase to approach 1.0 as the sweep rate is increased to 1.0 V/s (**12**) or 2.0 V/s (**13**) or upon cooling. No such complications were observed for **14**.

As it is apparent from the cyclic voltammograms and square wave voltammograms in Fig. 4 and the data in Table 1, the splitting of half-wave potentials, $\Delta E_{1/2}$, and K_c values increase in the order **13** < **14** < **12**. In lieu of a direct measure of the degree of electronic coupling, e.g. by the analysis of electronic intervalence charge transfer bands of the associated radical cations (vide infra), it is not clear whether this trend also mirrors an increase of “communication” across the bridge. While there are several examples of such correlations between $\Delta E_{1/2}$ (K_c) and the electronic coupling element V_{AB} (or a parameter directly related to V_{AB}) [16,17] in the literature, [18] there are also adverse cases where such correlations do not exist [19]. We nevertheless note that the $\Delta E_{1/2}$ values of **12** and **13** (and consequently their K_c values) are consistently larger than those of the analogous ferrocene derivatives **1** and **3**. One may speculate that this arises from the lower energy gap between the azaferrocene based “redox orbitals” and those of the respective bridge. Thus, 2,5-dimethylazaferrocene is oxidized 170 mV positive of the Cp₂Fe^{0/+} couple. Bridge centered, irreversible oxidations are observed at higher potentials, mostly as two-electron waves. Upon increasing the sweep rate, the peak currents of the bridge-based oxidations decrease and approach the one-electron limit but they remain chemically irreversible. The loss of the cathodic reverse peak(s) associated with the first two oxidations after scanning through the bridge oxidation and the distortion of successive voltammograms signals electrode fouling. This required thorough wiping of the electrode after passing through the bridge-based oxidation.

It is also of interest to compare the half-wave potentials of derivatives **18/14** that only differ with respect to the 5'-substituent at the second thiophene ring (Br for **18** but 2,5-dimethyl-1'-azaferrocenyl for **14**). Compound **18** exhibits a reversible one-electron oxidation at +0.190 V and an irreversible bridge oxidation at 0.85 V. The half-wave potential of the **18/18**⁺ couple is thus exactly midway between that of the two one-electron, azaferrocenyl based oxidations at +0.142 and +0.242 V of **14**. Reasons that could account for the cathodic shift of the first oxidation wave of **14** when compared to **18** are the lesser electron withdrawing effect of the 2,5-dimethyl-azaferrocenyl substituent with respect to the

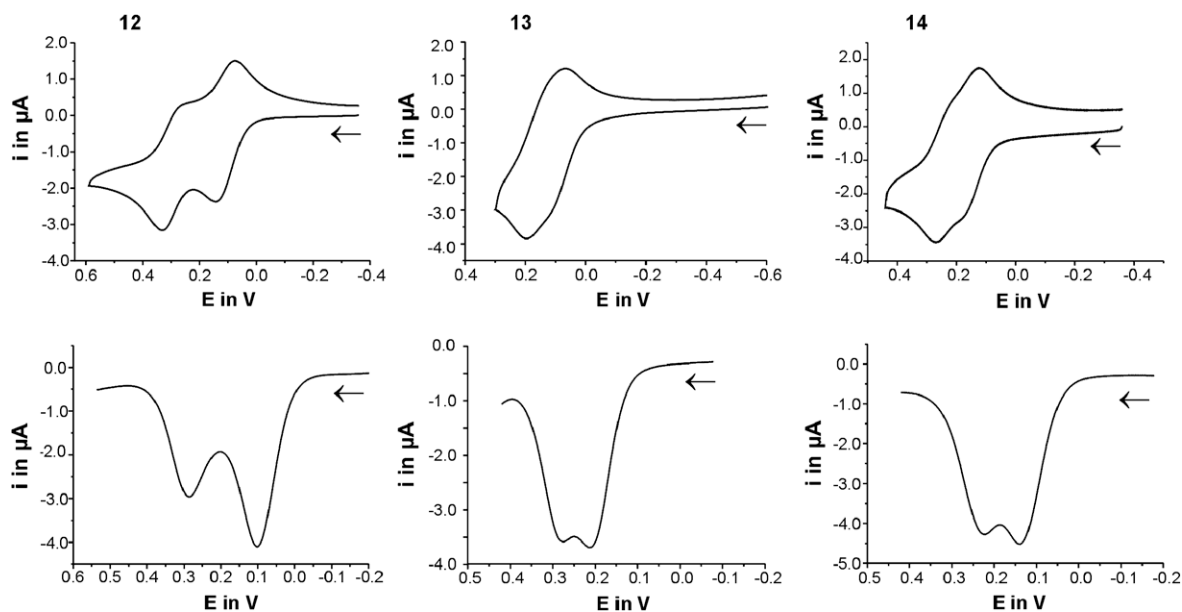


Fig. 4. Cyclic (upper row) and square wave voltammograms (lower row) of compounds **12** (left), **13** (middle) and **14** (right) in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ at $T = 293\text{ K}$.

Table 1

Voltammetric data for compounds **12**, **13** and **14**, their bromo-substituted precursors **16**, **17** and **18** and of parent 2,5-dimethylazaferrocene **15**

| Compound | $E_{1/2}^{0/+}$ [V] | $E_{1/2}^{+/2+}$ | $\Delta E_{1/2}$ [V] | K_c | i_p , bridge ^a |
|------------------------|---------------------|-------------------|----------------------|--------------------|-----------------------------|
| 12 | 0.127 (± 2) | 0.313 (± 2) | 0.185 (± 4) | 1540 (± 240) | 0.85 (± 5) |
| 13 | 0.193 (± 3) | 0.273 (± 3) | 0.080 (± 6) | 24 (± 5) | 0.92 (± 5) |
| 14 | 0.142 (± 3) | 0.242 (± 2) | 0.100 (± 3) | 55 (± 5) | 0.73 (± 5) |
| 18 ^b | 0.190 (± 2) | n. a. | n. a. | n. a. | 0.85 (± 5) |
| 15 ^b | 0.170 (± 2) | n. a. | n. a. | n. a. | 1.02 (± 5) |
| 16 ^b | 0.215 (± 2) | n. a. | n. a. | n. a. | 0.88 (± 5) |
| 17 ^b | 0.265 (± 2) | n. a. | n. a. | n. a. | 1.03 (± 5) |

^a Peak potential of an irreversible process at 293 K and $v = 0.1\text{ V/s}$.

^b Data taken from Ref. [13].

bromide, a gain of thermodynamic stabilization for the mixed-valent radical cation **14**⁺ by “electronic communication” which is not available for **18**⁺, or a mélange of both. Whichever the reason is, the cathodic shift of the **14/14**⁺ couple with respect to **18/18**⁺ signals conjugation between the bithiophene and the azaferrocenyl subunits of **14** and **18**. An even larger shift is observed for **12/16** with a single thiophene ring as the intervening bridge. For pair **13/17** with the weakly conjugating 2,6-pyridinediyl bridge the shift is consequently smaller.

In order to directly probe for electronic interactions between the individual azaferrocenyl entities we attempted to record UV–Vis–NIR spectra of the intermediate radical cation of thiophenyl bridged **12**⁺ with the largest comproportionation constant of this series. Repeated attempts to electrogenerate and characterize **12**⁺ inside our OTTE cell were, however, not met by success and inevitably led to rapid filming of the working electrode. Obviously, oxidized **12** electropolymerizes rapidly. This is a well-known behavior of thiophenes [20–22].

The radical cation of parent **15**, in contrast, could be unambiguously identified by this technique. Neutral **15** absorbs at 495, 436 and 330 nm. These bands relate to the $^1A_{1g} \rightarrow ^1E_{1g}(a)$, $^1A_{1g} \rightarrow ^1E_{2g}$ and $^1A_{1g} \rightarrow ^1E_{1g}(b)$ absorptions that are observed at 458, 436 and 330 nm for parent ferrocene and at higher energies for methyl substituted derivatives [23]. Upon oxidation these bands red-shift to 735, 697 and 570 nm. **15**⁺ thus absorbs at lower energy than poly-2,5-bis-(2-thiophene)-1',2',3',4',5'-pentamethylazaferrocene ($\lambda_{\text{max}} = 662\text{ nm}$) [22] and parent ferrocenium (641

and 631 nm), but at similar energy as the 1,1'-dimethylferrocenium ion (711, 702 nm) [24]. Even under the conditions of spectroelectrochemistry, **15**⁺ is only short-lived and is subject to polymerization upon which the radical cation bands disappear while a red film forms on the working electrode. The extinction coefficients provided in Fig. 5 are therefore just a lower estimate. Attempts to record the ESR spectrum of electrogenerated **15**⁺, however, failed even when the electrolysis was performed at $-20\text{ }^\circ\text{C}$ and when the probe was cooled to 4 K.

2.3. X-Ray diffraction study of 2,5-dimethylazaferrocene (**15**)

2,5-Dimethylazaferrocene (**15**) was first synthesized in 1964 by Pauson et al. [25]. Along with azaferrocene **20** (Fig. 6) it is the simplest heteroferrocene.

To the best of our knowledge, no X-ray crystal structures have been reported for either **15** or **20** up to now. 2,5-Dimethylazaferro-

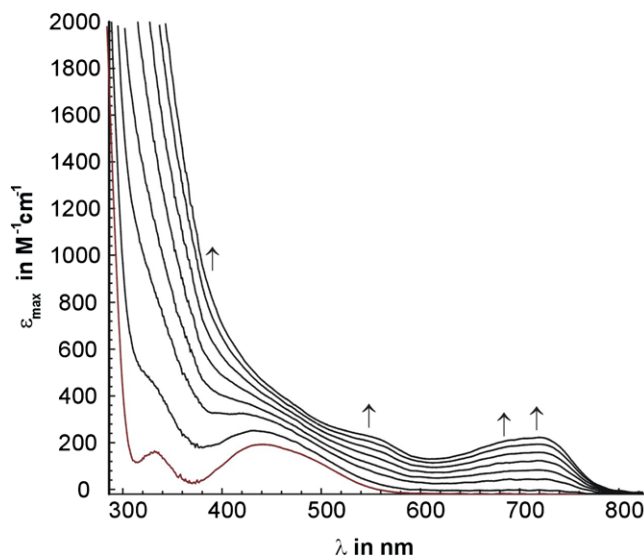


Fig. 5. UV–Vis–NIR spectroelectrochemistry on 2,5-dimethylazaferrocene in $\text{C}_4\text{H}_4\text{Cl}_2\text{-1,2}/\text{NBu}_4\text{PF}_6$.

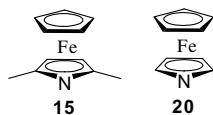


Fig. 6. The structures of 2,5-dimethylazaferrocene **15** and azaferrocene **20**.

cene (**15**) reportedly forms an oil at room temperature [25,26]. We now have found that after careful removal of residual solvent in a freeze/pump procedure **15** forms crystals which do not melt at room temperature for hours under vacuum. This initial observation led, after several attempts, to crystals suitable for X-ray diffraction analysis. It is, however, important to underline that selection of the best crystals and their manipulation were carried out at low temperatures. Compound **15** crystallizes in the orthorhombic space group *Pbca*. Data pertaining to the data collection and structure refinement are collected in Table 2. Table 3 provides a selection of the most important interatomic distances and bond angles. A plot of an individual molecule of **15** is displayed in Fig. 7.

The iron atom is sandwiched between a π -bonded 2,5-dimethylpyrrole and a π -bonded cyclopentadienyl ring with distances of 1.652 Å to the centroid of the pyrrole ($\text{Pyr}_{\text{centr}}$) and 1.657 Å to the centroid of the cyclopentadienyl ring (Cp_{centr}). Interestingly the DFT/B3LYP calculations on azaferrocene **20** predict the reverse tendency with a longer distance of 1.659 Å for $\text{Fe}-\text{Pyr}_{\text{centr}}$ and shorter one of 1.653 Å for $\text{Fe}-\text{Cp}_{\text{centr}}$ [27]. The two $\text{Fe}\cdots$ ring centroid vectors in **15** subtend an angle of 177.9° at the iron atom. In the crystal **15** adopts a geometry intermediate between staggered and eclipsed. The average $\text{C}(\text{Cp})-\text{Cp}_{\text{centr}}-\text{Pyr}_{\text{centr}}-\text{C}/\text{N}(\text{Pyr})$ angle is 17.9°. Each of the two rings in **15** is planar within 0.004 Å and their planes are inclined toward each other by 2.9°. There remains the question whether this inclination reflects the known tendency of the pyrrole ligand to undergo a haptotropic $\eta^5 \rightarrow \eta^1$ shift [28]. The distance between the perpendicular projection of the iron atom on the Pyr ring plane and the Pyr centroid is 0.024 Å in **15**. The analogous distance for the iron atom and the Cp ring is 0.016 Å.

In the solid state molecules of **15** are stabilized by weak interactions only and exhibit a hierarchic pattern of organization. At the simplest level, molecules of **15** form infinite layers along the

Table 2
Crystal data and structure refinement for **15**

| Compound | 15 |
|---|---|
| Empirical formula | $\text{C}_{11}\text{H}_{13}\text{FeN}$ |
| Formula weight | 215.07 |
| Temperature (K) | 123(1) |
| Wavelength | 1.54184 Å/Cu K_{α} |
| Crystal system, space group | Orthorhombic, <i>Pbca</i> |
| Unit cell dimensions | |
| <i>a</i> (Å) | 12.3490(2) |
| <i>b</i> (Å) | 7.95460(10) |
| <i>c</i> (Å) | 19.1921(3) |
| Volume, <i>Z</i> | 1885.27(5) Å ³ , 4 |
| Density (calculated) (mg/m ³) | 1.515 |
| Absorption coefficient (mm ⁻¹) | 12.378 |
| <i>F</i> (000) | 896 |
| Crystal color/morphology | Orange-brown stick |
| Crystal size (mm) | 0.47 × 0.22 × 0.16 |
| θ range for data collection (°) | 5.84–66.68 |
| Index ranges | −14 ≤ <i>h</i> ≤ 14, −9 ≤ <i>k</i> ≤ 8, −22 ≤ <i>l</i> ≤ 22 |
| Refns collected/unique [<i>R</i> _{int}] | 7170/1642 [0.0428] |
| Refns observed [<i>I</i> > 2σ(<i>I</i>)] | 1343 |
| Absorption correction | Semi-empirical from equivalents |
| Data/restraints/parameters | 1642/0/118 |
| Goodness-of-fit on <i>F</i> ² | 1.102 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0406, <i>wR</i> ₂ = 0.1175 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0490, <i>wR</i> ₂ = 0.1230 |
| Largest difference peak, hole (e Å ⁻³) | 0.613, −0.555 |

Table 3
Selected bond lengths (Å) and bond angles (°) for compound **15**

| 15 | |
|------------------|----------|
| Fe(1)–N(1) | 2.032(2) |
| Fe(1)–C(1) | 2.024(3) |
| Fe(1)–C(2) | 2.020(3) |
| Fe(1)–C(3) | 2.057(3) |
| Fe(1)–C(4) | 2.064(4) |
| Fe(1)–C(7) | 2.053(4) |
| Fe(1)–C(8) | 2.060(3) |
| Fe(1)–C(9) | 2.048(3) |
| Fe(1)–C(10) | 2.043(3) |
| Fe(1)–C(11) | 2.047(3) |
| N(1)–C(1) | 1.394(4) |
| N(1)–C(2) | 1.381(4) |
| C(1)–C(4) | 1.426(5) |
| C(2)–C(3) | 1.417(4) |
| C(3)–C(4) | 1.410(5) |
| C(2)–C(6) | 1.502(5) |
| C(7)–C(8) | 1.426(5) |
| C(8)–C(9) | 1.413(4) |
| C(9)–C(10) | 1.417(4) |
| C(10)–C(11) | 1.422(4) |
| C(7)–C(11) | 1.417(5) |
| C(1)–N(1)–C(2) | 106.3(2) |
| C(2)–C(3)–C(4) | 106.8(3) |
| C(4)–C(1)–C(5) | 127.6(3) |
| C(9)–C(10)–C(11) | 107.9(3) |
| C(7)–C(8)–C(9) | 107.4(3) |

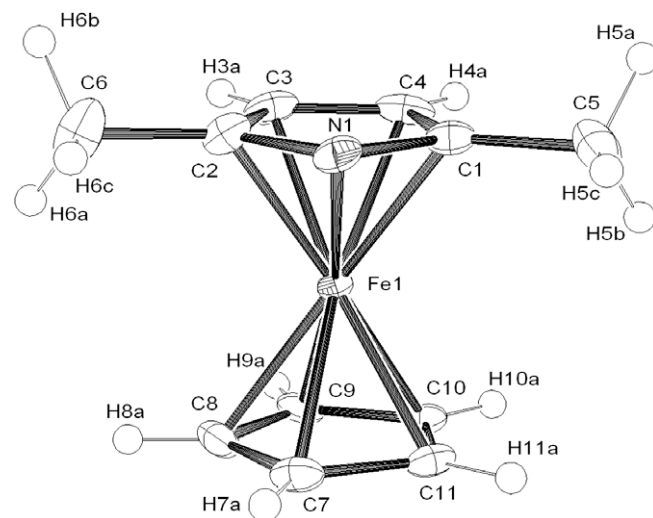


Fig. 7. ORTEP plot of the molecular structure of complex **15** in the crystal. Ellipsoids are drawn on a 50% probability level.

crystallographic *ac* plane. The layers are stabilized by intermolecular $\text{CH}\cdots\text{C}$ contacts of 2.763 Å between cyclopentadienyl proton H(8A) and carbon atom C(10) of the partner molecules' cyclopentadienyl ring. Additional stabilization is generated by intermolecular $\text{H}\cdots\text{H}$ contacts of 2.204 Å between methyl group proton H(6B) and methyl group proton H(5B). Within each layer the pyrrole nitrogen N(1) and carbon C(2) atoms both form weak (2.583 Å and 2.630 Å) intermolecular contacts with the same methyl group proton H(5A). The layers are held together by $\text{H}\cdots\text{H}$ intermolecular contacts of 2.315 Å between methyl group proton H(6C) and methyl group proton H(5C) from the second parallel layer. The bilayers that are generated in this manner are again held together by weak $\text{H}\cdots\text{H}$ contacts with the strongest such interaction between cyclopentadienyl proton H(9A) and methyl group proton H(6B) with a distance of 2.514 Å. One can assume that this relatively weak bilayer stabilization accounts for the oily character of **15** at room

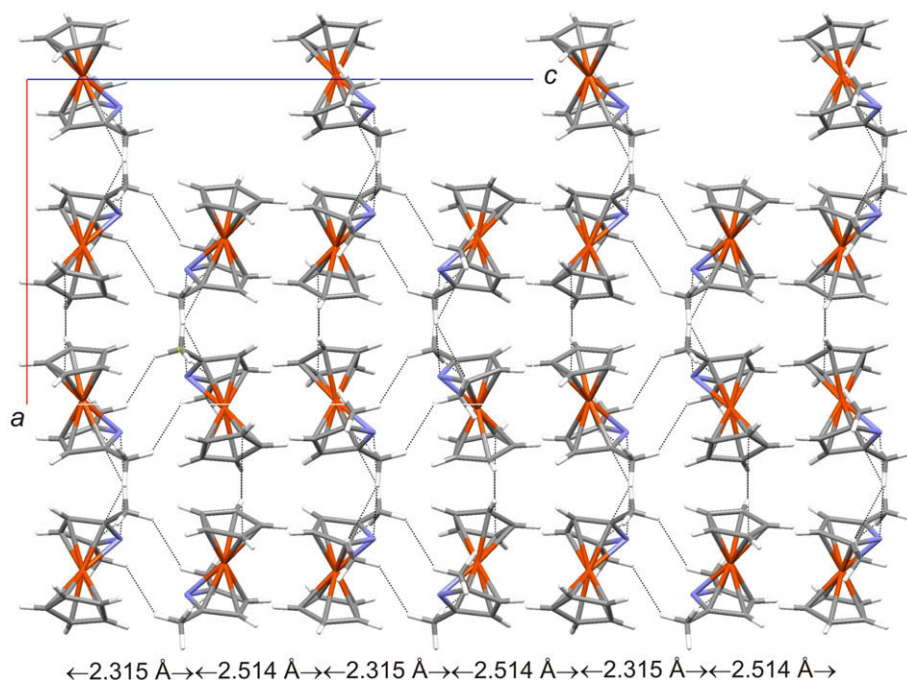


Fig. 8. Perpendicular projection of layers formed by molecules of **15** on the crystallographic *ac* plane. Weak intermolecular contacts within bilayers are marked by dashed lines.

temperature. The perpendicular projection of layers on crystallographic *ac* plane is shown in Fig. 8.

3. Conclusions

Dinuclear 2,5-dimethylazaferrocene derivatives **12**, **14** and **13** having heteroaryl (thiophenyl, bithiophenyl, pyridyl) bridges have been readily prepared by palladium catalyzed cross-coupling reactions of 2,5-dimethylazaferrocenezinc chloride with the respective bromo-substituted heteroarene precursor. Electrochemical studies reveal that each of these complexes undergoes two consecutive one-electron oxidations to the modestly stable respective dication. The thermodynamic stabilities of the intermediate mixed-valent radical cations increase in the order 2,6-pyridyl bridged **13** < 5,5'-bithiophenyl bridged **14** < 2,5-thiophenyl bridged **12** and follow the expected trend. The K_c values of the radical cations are notably larger than for analogous ferrocenes, possibly as a result of the lower energy gap between the end-group and bridge-based oxidations. Parent 2,5-dimethylazaferrocene was also investigated by X-ray crystallography and exhibits a close to symmetrical binding of the iron to the two different rings. Weak intermolecular forces between individual molecules of **15** explain its oily character and previous failures to obtain crystals of this molecule. The associated azaferrocenium ion **15**⁺ proved to be sufficiently stable to be characterized by optical spectroscopy. Bands are shifted to lower energy when compared to the ferrocenium ion but are at similar energy as in 1,1'-dimethylferrocenium salts.

4. Experimental

4.1. General remarks

All preparations were carried out using standard Schlenk techniques. Chromatographic separations were carried out using silica gel 60 (Merck, 230–400 mesh ASTM). Tetrahydrofuran was distilled over sodium benzophenone ketyl. Other solvents were of reagent grade and were used without prior purification. 2,5-

Dimethylazaferrocene was prepared according to the literature procedure [26]. All other chemicals were purchased from Aldrich Chemical Co. NMR spectra were recorded on a Bruker AV300 spectrometer. Chemical shifts are reported in δ (ppm) using residual CHCl_3 (^1H δ 7.26 ppm) and CDHCl_2 (^1H δ 5.32 ppm) as the reference. Mass spectra were recorded using EI methods on a Finnigan MAT 710A spectrometer. Microanalyses were determined by Analytical Services of the University of Regensburg.

Electrochemical work was performed on a BAS CV50 potentiostat in a home-built vacuum tight one-compartment cell using Pt or glassy carbon disk electrodes from BAS as the working electrode, a platinum spiral as the counter electrode and a silver spiral as a pseudo-reference electrode. Each of the spiral-shaped electrodes is welded to Vycon wire and sealed into a glass tube. Counter and reference electrodes are introduced into the cell by appropriate fittings in the side-wall and sealed via a Quickfit screw. CH_2Cl_2 for electrochemical use was of Burdick&Jackson brand (Fluka) and was distilled from CaH_2 , deoxygenated by saturation with argon and briefly stored over molecular sieves. Potential calibration was performed by adding ferrocene or decamethylferrocene ($E_{1/2} = -0.545$ V versus $\text{Cp}_2\text{Fe}^{0/+}$) as an internal standard to the analyte solution. The amount of the reference system was adjusted until the peak currents of the respective standard were comparable to those of the analyte. Potentials are given against the ferrocene/ferrocenium couple. The splittings of half-wave potentials were directly taken from the CVs, square wave and differential pulse voltammograms (**12**) or by deconvolution of the overlapping peaks in square wave and differential pulse voltammetry (**13**, **14**). $\Delta E_{1/2}$ values were independently calculated from the CV peak potential separations and forward wave half-widths by the method of Richardson and Taube [11]. Values obtained from different methods were identical within ± 6 mV.

4.1.1. Synthesis of 1'-(5-(5'-bromo-2,2'-bithiophenyl))-2,5-dimethylazaferrocene (**18**)

Sec-BuLi (1.4 M in cyclohexane, 1.3 ml, 1.8 mmol) was added to an argon-saturated THF (12 ml) solution of 2,5-dimethylazaferro-

cene (263 mg, 1.22 mmol) and TMEDA (95 μ l, 0.06 mmol) at -78 °C. After the mixture was stirred for 1.5 h at -78 °C, $ZnCl_2$ (240 mg, 1.76 mmol) was added and the reacting mixture was warmed to room temperature and stirred for 1.5 h. Then, to the reacting mixture a suspension of $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol) in THF (2 ml) and a solution of 5,5'-dibromo-2,2'-bithiophene (454 mg, 1.40 mmol) in THF (3 ml) were added. The reaction mixture was stirred at room temperature for 2 h and then poured onto water. After workup, compound **18** was purified by column chromatography on silica gel by eluting with ethyl acetate and crystallized from *n*-hexane. Yield: 250 mg (45%).

1H NMR (300 MHz, $CDCl_3$): δ 6.97 (d, 3H, $^3J_{HH} = 3.6$ Hz, H thienyl), 6.90 (d, 1H, $^3J_{HH} = 3.8$ Hz, H thienyl), 4.50 (s, 2H, Cp), 4.33 (s, 2H, Cp), 4.29 (s, 2H, β -pyrrolyl), 2.11 (s, 6H, CH_3). HRMS (EI, 70 eV): 456.9261 (Calc. for $C_{19}H_{16}BrFeNS_2$: 456.9257). Anal. Calc. for $C_{19}H_{16}BrFeNS_2$: C, 49.90; H, 3.53; N, 3.06; S, 13.99. Found: C, 50.35; H, 3.69; N, 2.96; S, 13.88%.

4.1.2. Synthesis of 2,5-di(1'-(2,5-dimethylazaferrocenyl))thiophene (**12**)

Sec-BuLi (1.4 M in cyclohexane, 0.8 ml, 1.12 mmol) was added to an argon-saturated THF (12 ml) solution of 2,5-dimethylazaferrocene (158 mg, 0.73 mmol) and TMEDA (70 μ l) at -78 °C. After the mixture was stirred for 1.5 h at -78 °C, $ZnCl_2$ (148 mg, 1.08 mmol) was added and the reacting mixture was warmed to room temperature and stirred for 1.5 h. Then, a suspension of $PdCl_2(PPh_3)_2$ (26 mg, 0.04 mmol) in THF (1.5 ml) and a solution of 1'-(2-bromothiophen-5-yl)-2,5-dimethylazaferrocene (**16**) (70 mg, 0.18 mmol) in THF (2 ml) were added. The reaction mixture was stirred at room temperature for 2 h and then poured onto water. After workup, complex **12** was purified by column chromatography on silica gel by eluting with ethyl acetate-methanol (50:2) mixture and crystallized from *n*-hexane. Yield: 53 mg (58%).

1H NMR (300 MHz, $CDCl_3$): δ 6.96 (s, 2H, H thienyl), 4.50 (s, 4H, Cp), 4.31 (s, 4H, Cp), 4.27 (s, 4H, β -pyrrolyl), 2.12 (s, 12H, CH_3). MS (EI, 70 eV): m/z 510.0 (M^+), 416.0 ($M^+ - C_6H_8N$), 94.0 (C_6H_8N). HRMS: m/z 510.0513 (Calc. for $C_{26}H_{26}Fe_2N_2S$: 510.0515). Anal. Calc. for $C_{26}H_{26}Fe_2N_2S$: C, 61.17; H, 5.14; N, 5.49; S, 6.27. Found: C, 60.83; H, 5.38; N, 5.32; S, 6.03%.

1'-(thien-2-yl)-2,5-dimethylazaferrocene (**19**): 1H NMR (300 MHz, $CDCl_3$): δ 7.18 (d, 1H, $^3J_{HH} = 4.7$ Hz, H thienyl), 7.08 (d, 1H, $^3J_{HH} = 2.8$ Hz, H thienyl), 6.97 (dd, 1H, $^3J_{HH} = 4.7$ Hz, $^3J_{HH} = 2.8$ Hz, H thienyl), 4.50 (s, 2H, Cp), 4.29 (s, 2H, Cp), 4.24 (s, 2H, β -pyrrolyl), 2.07 (s, 6H, CH_3). MS (EI, 70 eV): m/z 296.9 (M^+).

4.1.3. Synthesis of 2,6-di(1'-(2,5-dimethylazaferrocenyl))pyridine (**13**)

The synthesis was performed as in Section 4.1.2., but with 1'-(2-bromopyridin-6-yl)-2,5-dimethylazaferrocene (**17**) (60 mg, 0.16 mmol). Yield: 49 mg (61%).

1H NMR (300 MHz, CD_2Cl_2): δ 7.59 (t, 1H, $^3J_{HH} = 7.7$ Hz, H pyridinyl), 7.30 (d, 2H, $^3J_{HH} = 7.7$ Hz, H pyridinyl), 4.93 (pseudo-t, 4H, $J = 1.6$ Hz, Cp), 4.40 (pseudo-t, 4H, $J = 1.6$ Hz, Cp), 4.24 (s, 4H, β -pyrrolyl), 2.03 (s, 12H, CH_3). 1H NMR (300 MHz, $CDCl_3$): δ 7.56 (t, 1H, $^3J_{HH} = 7.7$ Hz, H pyridinyl), 7.29 (d, 1H shielded by solvent signal, H pyridinyl), 4.95 (s, 4H, Cp), 4.41 (s, 4H, Cp), 4.23 (s, 4H, β -pyrrolyl), 2.06 (s, 12H, CH_3). MS (EI, 70 eV): m/z 505.0 (M^+), 411.0 ($M^+ - C_6H_8N$), 94.0 (C_6H_8N). HRMS: m/z 505.0895 (Calc. for $C_{27}H_{27}Fe_2N_3$: 505.0904). Anal. Calc. for $C_{27}H_{27}Fe_2N_3 \times 2H_2O$: C, 59.88; H, 5.77; N, 7.76. Found: C, 59.20; H, 5.33; N, 7.49%.

4.1.4. Synthesis of 5,5'-di(1'-(2,5-dimethylazaferrocenyl))-2,2'-bithiophene (**14**)

The synthesis was performed as in Section 4.1.2. but with 1'-(5-(5'-bromo-2,2'-bithiophenyl))-2,5-dimethylazaferrocene (**18**) (60 mg, 0.13 mmol). Yield: 56 mg (73%).

1H NMR (300 MHz, $CDCl_3$): δ 7.03 (d, 2H, $^3J_{HH} = 3.5$ Hz, H thienyl), 6.99 (d, 2H, $^3J_{HH} = 3.5$ Hz, H thienyl), 4.51 (s, 4H, Cp), 4.33 (s, 4H, Cp), 4.29 (s, 4H, β -pyrrolyl), 2.14 (s, 12H, CH_3). MS (EI, 70 eV): m/z 591.7 (M^+), 295.9 ($M^+ - C_{15}H_{14}NSFe$). HRMS: m/z = 592.0387 (Calc. for $C_{30}H_{28}Fe_2N_2S_2$: 592.0393). Anal. Calc. for $C_{30}H_{28}Fe_2N_2S_2$: C, 60.81; H, 4.77; N, 4.73; S, 10.80. Found: C, 60.79; H, 4.92; N, 4.36; S, 10.74%.

5. Crystal structure determination

Diffraction data for crystals of compound **15** was collected with an Oxford Diffraction Gemini Ultra CCD diffractometer [29] with multilayer optics and Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The structures were solved by direct methods (SIR-97) [30] and refined by full-matrix least-squares on F^2 (SHELXL-97) [31]. H atoms were calculated geometrically and a riding model was applied during the refinement process. Packing diagrams were generated with the MERCURY program [32].

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Appendix A. Supplementary material

CCDC 690769 contains 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.003.

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