

Electronically Intercommunicating Iron Centers in Di- and Tetraferrocenyl Pyrroles[§]

Alexander Hildebrandt, Dieter Schaarschmidt, and Heinrich Lang*

Lehrstuhl für Anorganische Chemie, Institut für Chemie, Fakultät für Naturwissenschaften, Technische Universität Chemnitz, Strasse der Nationen 62, 09111 Chemnitz, Germany

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Novel 2,5-diferrocenyl-1-phenyl-1*H*-pyrrole (**4**) and 2,3,4,5-tetraferrocenyl-1-phenyl-1*H*-pyrrole (**6**) have been prepared by a 2- or 4-fold Negishi cross-coupling reaction of 2,5-dibromo-1-phenyl-1*H*-pyrrole (**3**) and 2,3,4,5-tetrabromo-1-phenyl-1*H*-pyrrole (**5**), respectively, with FcZnCl (**2**) (Fc = Fe(η^5 -C₅H₄)(η^5 -C₅H₅)) in the presence of [(Ph₃P)₄Pd] as catalyst. The electronic and structural properties of **4** and **6** were investigated with UV-vis spectroscopy and single-crystal X-ray diffraction (**6**). Comparison of the appropriate bond distances in the pyrrole core system of **6** demonstrates considerable electron delocalization. Cyclic, square wave, and linear sweep voltammetry as well as in situ NIR spectro-electrochemistry highlight the electrochemical properties of both compounds. Molecules **4** and **6** display two (**4**) or four (**6**) electrochemically reversible one-electron transfer processes with remarkably high $\Delta E_{1/2}$ values and reduction potentials of $E^{0'} = -238$ and $E^{0'} = 212$ mV for **4** ($\Delta E_{1/2} = 450$ mV) and $E^{0'} = -280$, $E^{0'} = 51$, $E^{0'} = 323$, and $E^{0'} = 550$ mV for **6** ($\Delta E_{1/2} = 322$, 264, and 233 mV) using [NBu₄][B(C₆F₅)₄] as the supporting electrolyte. The pyrroles could be classified as class II systems according to Robin and Day. Additionally, **4**[**PF₆]_n (n = 1, 2)** were synthesized and studied, giving CV responses and NIR spectra identical to those obtained for **4** from electrochemical oxidations.

Introduction

Ferrocenyl-substituted aromatics and heteroaromatics have attracted rising attention during recent years because they can be regarded as model compounds for the investigation of metal-metal electronic communication. Moreover, these π -conjugated organometallics may be suitable for the design of novel electro-active materials.¹ The tendency of the iron centers in the mixed valence species to communicate through the aromatic bridging system has mostly been investigated by cyclovoltammetry (CV), whereas detailed spectro-electrochemical studies of these compounds were often neglected. However, the varying experimental conditions in those studies hinder the comparability of their results (e.g., the difference in the individual half-wave potentials $\Delta E_{1/2}$). Examples of those ferrocenyl-substituted aromatics and heteroaromatics were given by the hexaferrocenylbenzene of Volhardt,² which can be electrochemically oxidized in three redox waves with $\Delta E_{1/2}$ values of 130 and 250 mV, respectively, several substituted ferrocenyl thiophenes (2,5diferocenylthiophene and 3,4-diferrocenylthiophene)³ with less than 150 mV peak separation in the cylcovoltammetric studies, and diferrocenylpyridine,³ which exhibits nearly no observable metal-metal interaction, as the two ferrocenyl moieties were oxidized simultaneously. The highest $\Delta E_{1/2}$ values among symmetric ferrocenyl heteroaromatics have been reported in 1,3-di(ferrocenyl)benzo[b]thiophene (280 mV) and 1,3-di(ferrocenyl)benzo[b]selenophene (305 mV) by Sato and Ogawa.⁴ Winter and Kowalski synthesized azaferrocenes with heteroaromatics such as pyridine or thiophene as bridging units and studied their electro- and spectroelectrochemisty, resulting in higher $\Delta E_{1/2}$ values compared to the appropriate ferrocenyl derivatives.

Recently, we have reported on the synthesis and electrochemistry of supercrowded 2,3,4,5-tetraferrocenyl thiophene for the first time.⁶ Cyclic, square wave, and linear sweep voltammetry together with in situ NIR spectro-electrochemistry highlighted that this compound displays four electrochemically reversible one-electron transfer processes indicating

[§] Dedicated to Prof. Dr. Peter Klüfers on the occasion of his 60th birthday. *Corresponding author. E-mail: heinrich.lang@chemie.tu-chemnitz. de. Phone: +49 (0)371-531-21210. Fax: +49 (0)371-531-21219.

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Scheme 1. Syntheses of Ferrocenyl Pyrroles 4 from 2 and 3 and 6 from 2 and 5^{*a*}



 a Conditions: (i) In tetrahydrofuran; (1) *t*-BuLi, -30 °C, 30 min; (2) [ZnCl₂·2thf]. (ii) In tetrahydrofuran, [Pd(PPh_3)_4] (1 mol %), 60 °C, 48 h.

significant electrostatic interaction among the four ferrocenyl units as oxidation progresses. Spectro-electrochemistry confirmed that positive charges are localized on the Fc⁺ groups in the mixed valent intermediates, as no charge transfer bands of significant strength could be detected. In continuation of this work we were interested in varying the heteroatom of the cyclic core system to modify the electronic properties and improve the electrochemical interaction between the terminal redox-active ferrocenyl functionalities. It is well known that polypyrroles are electro-active materials of high conductivity.⁷ For this reason we decided to use pyrroles as organic bridging units between ferrocenyl groups to decrease the energy gap between the redox-active groups and the connecting system itself. This prompted us to synthesize the title compounds 2,5-diferrocenyl- and 2,3,4,5-tetraferrocenyl-1-phenyl-1H-pyrrole, respectively, and to study their electrochemical properties.

Results and Discussion

Synthesis and Characterization. Treatment of ferrocenyl zinc chloride (2)^{8,9} with 2,5-dibromo-1-phenyl-1*H*-pyrrole (3) in the molar ratio of 3:1 in the presence of catalytic amounts of [Pd(PPh₃)₄] gave 2,5-diferrocenyl-1-phenyl-1*H*-pyrrole (4) (Scheme 1). An excess of 2 is required to reach complete conversion of the reactants. Under similar Negishi *C*,*C* cross-coupling conditions 2,3,4,5-tetrabromo-1-phenyl-1*H*-pyrrole (5) was reacted with FcZnCl (2) (Fc = Fe(η^5 -C₅H₄)(η^5 -C₅H₅)), yielding 2,3,4,5-tetraferrocenyl-1-phenyl-1*H*-pyrrole (6) (Scheme 1). After appropriate workup, this molecule could be obtained as an orange solid material in 68% yield (Experimental Section).

Pyrroles **4** and **6** are stable to air and moisture both in the solid state and in solution. They have been identified by elemental analysis, IR, UV–vis, and NMR (1 H, 13 C{ 1 H}) spectroscopy. ESI TOF mass spectrometry and single-crystal X-ray structure analysis (**6**) were additionally carried out.

The electrochemical behavior of both compounds (CV, LSV, SWV, NIR spectroscopy) was determined.

While the IR spectra of 4 and 6 are not very expressive, 1 H NMR spectroscopy shows some peculiarities. In 4 the two CH pyrrole protons appear at 6.33 ppm as a singlet, while for the cyclopentadienyl groups one singlet (C5H5) and two pseudotriplets with $J_{\rm HH} = 1.8$ Hz (C₅H₄) centered at 3.88 and 4.02 ppm are found as expected for AA'XX' spin systems. In 6, the four ferrocenyl units show a distinct signal pattern caused by the steric demand of the ferrocenyl groups (Figure 1). The signals for the α protons of cyclopentadienyl rings appear as very broad resonances, while those in β position occur as poorly resolved pseudotriplets with the expected coupling pattern (vide supra). The free rotation around the pyrrole-ferrocenyl carbon-carbon bond could be reduced by cooling NMR samples to -80 °C, resulting in the observation of eight individual signals for the protons of the C_5H_4 units (Figure 1). The exchange rates of those protons can be determined by line-shape-fitting of the NMR spectra at the appropriate temperatures. The activation parameters of the rotations around the pyrrole-ferrocenyl C,C bond could be quantified from the exchange rates in graphical analyses according to Eyring.¹⁰ The ferrocenyls in the 2 and 5 position exhibit an activation enthalpy of ΔH^{\ddagger} = 26.8 (±1.2) kJ·mol⁻¹ and an activation entropy of $\Delta S^{\ddagger} = -94.1$ (±4.5) J·mol⁻¹·K⁻¹; those in positions 3 and 4 have values of $\Delta H^{\ddagger} = 27.9$ (±1.5) kJ·mol⁻¹ and $\Delta S^{\ddagger} = -88.6$ (±5.6) J·mol⁻¹·K⁻¹, respectively.

Single crystals of $6 \cdot CHCl_3$ suitable for X-ray diffraction analysis could be obtained by diffusion of *n*-hexane into a chloroform solution containing **6** at 25 °C. The molecular structure of $6 \cdot CHCl_3$ in the solid state is shown in Figure 2. Important bond distances (Å), bond angles (deg), and torsion angles (deg) are summarized in the caption of Figure 2.

Compound **6**•**CHCl₃** crystallized in the triclinic space group $P\overline{1}$. The ferrocenyl substituents are rotated by 44.6(1)° (Fe1), 37.8(1)° (Fe2), 68.1(2)° (Fe3), and 18.3(1)° (Fe4) out of the plane of the pyrrole core.¹¹ The cyclopentadienyl ligands at the iron centers exhibit an almost eclipsed conformation (2–4°). As common for aromatic compounds the C₄N arrangement is planar (rms deviation 0.0244 Å). It is noteworthy that the C1–C2 bond length (1.400(3) Å), as a formal double bond, is elongated, when compared with localized C,C double bonds (1.34 Å). In addition, the C2–C3 bond (1.435(3) Å) is shorter than those for localized C,C single bonds (1.53 Å).¹² This behavior is already known for pyrroles,¹³ indicating strong electronic delocalization in the core system, which is significantly more pronounced than in the 2,3,4,5-tetraferrocenylthiophene.⁶

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Figure 1. (Left) Experimental ¹H NMR spectra of **6** in the range between 3.75 and 5.00 ppm; toluene- d_8 ; various temperatures. (Right) Simulated ¹H NMR spectra of **6** with different exchange rates (protons of ferrocenyls in 2,5 position/protons of ferrocenyls in 3,4 position).



Figure 2. ORTEP diagram (50% probability level) of the molecular structure of **6** · **CHCl**₃ with the atom-numbering scheme. All hydrogen atoms and one molecule of chloroform have been omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): average D–Fe = 1.649, C1–C2 = 1.400(3), C2–C3 = 1.435(3), C3–C4 = 1.386(3), N1–C1 = 1.393(3), N1–C4 = 1.394(3), N1–C5 = 1.430(3), C1–C11 = 1.471(3), C2–C21 = 1.476(3), C3–C31 = 1.492(3), C4–C41 = 1.479(3); N1–C1–C2 = 107.3(2), C1–C2–C3 = 107.4(2), C1–N1–C4 = 109.6(2), C1–N1–C5 = 125.8(2), average D–Fe–D = 177.18; N1–C1–C2–C3 = 4.7(3), C6–C5–N1–C1 = -71.0(3), N1–C1–C11–C12 = 52.9(4), N1–C4–C41–C42 = -0.4(4), C1–C2–C21–C22 = -41.8(4), C4–C3–C31–C32 = 60.2(3) (D = denotes the centroids of C₅H₄ or C₅H₅).

Electrochemistry and Spectro-electrochemistry

The redox properties of **4** and **6** were studied by cyclovoltammetry (CV), square wave voltammetry (SWV), linear sweep voltammetry (LSV), and spectro-electrochemistry

Table 1. Cyclovoltammetric Data (potentials vs FcH/FcH⁺)^a

compd	$E^{0\prime}~(\mathrm{mV})$	$\Delta E_{\rm p} ({\rm mV})^b$	$\Delta E_{1/2} (\mathrm{mV})^c$
4, [NBu ₄][PF ₆] wave 1	-198	80	315
4, [NBu ₄][PF ₆] wave 2	117	85	
4, $[NBu_4][B(C_6F_5)_4]$ wave 1	-238	68	450
4 , $[NBu_4][B(C_6F_5)_4]$ wave 2	212	75	

^{*a*} Scan rate 100 mV·s⁻¹ at a glassy-carbon electrode of 0.5 mmol dm⁻³ solutions of **4** in dry dichloromethane containing 0.1 mol dm⁻³ of $[N(^{\prime\prime}Bu)_4][PF_6]$ or $[N(^{\prime\prime}Bu)_4][B(C_6F_5)_4]$ as supporting electrolyte at 25 °C. ^{*b*} ΔE_p = difference between oxidation and reduction potential. ^{*c*} $\Delta E_{1/2}$ = potential difference between two redox processes.

(NIR spectroscopy) in dry dichloromethane utilizing 0.1 mol dm⁻³ [N(^{*n*}Bu)₄][PF₆] and [N(^{*n*}Bu)₄][B(C₆F₅)₄], respectively, as supporting electrolyte. The data of the cyclovol-tammetric experiments were carried out at scan rates of 100 mV s⁻¹ and are summarized in Tables 1 (4) and 2 (6). All potentials are referenced to the FcH/FcH⁺ redox couple (Fc=Fe(η^5 -C₅H₄)(η^5 -C₅H₅)) as recommended by IUPAC.¹⁴

The cyclovoltamograms of **4** are shown in Figure 3, and those of **6** in Figure 6. Pyrrole **4** exhibits two diffusioncontrolled ferrocenyl-related redox events independent of the electrolyte used. Each of the two ferrocenyl substituents shows a reversible electrochemical behavior with ΔE_p values of 80 and 85 mV for electrolyte [N("Bu)₄][PF₆] and 68 and 75 mV for [N("Bu)₄][B(C₆F₅)₄]. Electrochemical reversibility is characterized by values of 59 mV.¹⁵ The use of dichloromethane and [N("Bu)₄][B(C₆F₅)₄] as solvent/supporting electrolyte results in a better resolution as compared with the system dichloromethane/[N("Bu)₄][PF₆], due to the lower ion-pairing capabilities (spherical diameter [PF₆]⁻, 3.3 Å;

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Figure 3. Voltammograms of dichloromethane solutions containing 0.5 mmol·L⁻¹ of **4** at 25 °C. (Left) Supporting electrolyte $[N(^{n}Bu)_{4}][PF_{6}]$; CV (scan rate: 100 mV·s⁻¹) and LSV (scan rate 1 mV·s⁻¹). (Right) Supporting electrolyte $[N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}]$; CV (scan rate: 100 mV·s⁻¹), and LSV (scan rate 1 mV·s⁻¹).



Figure 4. NIR spectra of 4 at rising potentials (bottom: -200 to 225 mV; top: 250 to 600 mV vs Ag/AgCl) at 25 °C, in dichloromethane, supporting electrolyte [N("Bu)₄][PF₆]. Arrows indicate increasing or decreasing absorptions.

 $[B(C_6F_5)_4]^-$, 10 Å),¹⁶ and, hence, in a superior quality of the electrochemical data for multiredox processes with positively charged analytes.¹⁷ LSV confirmed two individual one-electron processes for the oxidation of the ferrocenyls. The advantage of using $[N(^nBu)_4][B(C_6F_5)_4]$ as electrolyte results in a significantly higher separation of the redox potentials $([N(^nBu)_4][PF_6], \Delta E_{1/2} = 315 \text{ mV}; [N(^nBu)_4][B(C_6F_5)_4], \Delta E_{1/2} = 450 \text{ mV})$ (Table 1). Despite similar geometries and therefore similar electrostatic interactions, the obtained $\Delta E_{1/2}$ values for pyrrole **4** are remarkably higher when compared with analogous species measured under the same conditions, i.e., 2,5-diferrocenylthiophene (($[N(^nBu)_4][PF_6], \Delta E_{1/2} = 152 \text{ mV}$;

 $[N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}], \Delta E_{1/2} = 260 \text{ mV})$, pointing to significant electronic communication in the pyrrole derivative. This was proven by in situ UV-vis-NIR spectroscopy (vide infra). On the basis of the full reversibility of the CV waves, the oxidized complexes $4[\mathbf{PF}_6]_n$ (n = 1, 2) were considered as accessible synthetic targets. According to a well-established procedure,¹⁸ complex 4 was reacted with 1 equiv of [FcH][PF₆] in tetrahydrofuran at -20 °C. The initial dark red solution immediately turned dark green, and after completion of the reaction, addition of *n*-hexane allowed the precipitation of $4[PF_6]$. As the redox potential of the redox couple $4^+/4^{2+}$ is more positive than that of the ferrocene/ ferrocenium couple, the dication 4[PF₆]₂ was prepared by reacting **4** with two stoichiometric amounts of $[AgPF_6]$ in tetrahydrofuran at -20 °C.¹⁸ Excellent yields of spectroscopically pure materials were obtained by partial precipitation and vacuum drying. Both cationic complexes gave CV responses identical to that obtained for 4 (Experimental Section).

The spectro-electrochemical studies were conducted by stepwise increase of the potential from -500 to 1200 mV vs Ag/AgCl in an OTTLE cell (OTTLE = optically transparent thin-layer electrode) containing dichloromethane solutions of 4 (1.0 mmol dm⁻³) and [N(ⁿBu)₄][PF₆] (0.1 mol dm⁻³). This procedure allows the generation of 4⁺ and 4²⁺ from neutral 4. Compound 4 does not contain any absorption in the NIR range. In contrast, the spectra of the monooxidized species 4[PF₆] show an absorption characteristic for mixed valence systems (= MV) Fe(II)/Fe(III) (Figure 4). The isolated mono- and dioxidized compounds 4[PF₆] and 4[PF₆]

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Figure 5. Deconvolution of NIR absorptions of $4[PF_6]$ using three Gaussian-shaped bands determined by spectro-electrochemistry in an OTTLE cell: experimental data (solid line); Gaussian-shaped absorptions (dashed line).





possess the same characteristics as the in situ generated species.

Deconvolution of the NIR absorption was achieved using three distinct overlapping transitions with Gaussian shapes (Figure 5). The fits are good enough to allow an almost exact overlay of the sum of the spectral components with the experimental spectra. Two bands were found at 4820 and 4250 cm⁻¹, respectively. The most intense absortion ($\varepsilon_{max} =$ 4200 $L \cdot mol^{-1} \cdot cm^{-1}$) at 4820 cm⁻¹ showed a characteristic peak width at half-height for IVCT bands (2369 cm⁻¹),¹⁹ while the band at 4250 cm^{-1} might be attributed to a ligandto-metal charge transfer absorption.^{20b} A third broad Gaussian-shaped band represents the baseline correction. It is noteworthy that the NIR transitions of the MV complex 4[PF₆] differ from 2,5-diferrocenylthiophene, for which no IVCT absorptions are found between 800 and 2800 nm, indicating the superior electron transfer properties of the pyrrole molecule. As expected, the double-oxidized species 4[PF₆]₂ exhibits no IVCT band.

Depending on the electrolyte, tetraferrocenyl-pyrrole **6** exhibits three ([N("Bu)₄][PF₆]) or four ([N("Bu)₄][B(C₆F₅)₄]) separate reversible oxidation processes. Using the classical hexafluorophosphate anion as supporting electrolyte leads to two one-electron processes at -226 mV ($\Delta E_p = 72 \text{ mV}$) and -26 mV ($\Delta E_p = 72 \text{ mV}$) and one two-electron

Table 2. Cyclovoltammetric Data (potentials vs FcH/FcH^+)^{*a*}

-	-		
compd	$E^{0\prime}$ (mV)	$\Delta E_{\rm p} ({\rm mV})^b$	$\Delta E_{1/2} (\mathrm{mV})^c$
6, [NBu ₄][PF ₆] wave 1 6, [NBu ₄][PF ₆] wave 2	$-226 \\ -26$	72 72	200
6 , [NBu ₄][PF ₆] wave 3	134	104	160
6 , [NBu ₄][B(C ₆ F ₅) ₄] wave 1 6 , [NBu ₄][B(C ₆ F ₅) ₄] wave 2	$-280 \\ 51$	62 63	322
6 , $[NBu_4][B(C_6F_5)_4]$ wave 3	323	62	264
6 , $[NBu_4][B(C_6F_5)_4]$ wave 4	550	61	233

^{*a*} Scan rate 100 mV·s⁻¹ at a glassy-carbon electrode of 0.5 mmol dm⁻³ solutions of **6** in dry dichloromethane containing 0.1 mol dm⁻³ of $[N("Bu)_4][PF_6]$ or $[N("Bu)_4][B(C_6F_5)_4]$ as supporting electrolyte at 25 °C. ^{*b*} ΔE_p = difference between oxidation and reduction potential. ^{*c*} $\Delta E_{1/2}$ = potential difference between two redox processes.

process at 134 mV, which is less reversible ($\Delta E_p = 104 \text{ mV}$). This two-electron process could be resolved by using the advanced supporting electrolyte $[N("Bu)_4][B(C_6F_5)_4]$.^{16,17} The electrochemical data of **6** are summarized in Table 2. The differences in the potentials of the first and second redox couple of 200 mV ($[N("Bu)_4][PF_6]$) or 322 mV ($[N("Bu)_4]-[B(C_6F_5)_4]$) are lower than those in pyrrole **4**, due to its increased steric demand and therefore the decreased tendency of the cyclopentadienyls to be coplanar with the pyrrole core system. The $\Delta E_{1/2}$ values are higher than those for the appropriate isostructural thiophene derivative,⁶ which indicates stronger electronic interaction among the ferrocenyl moieties in **6**.

In situ NIR measurements of 6 were performed in an OTTLE cell containing a dichlormethane solution of 0.1 $\operatorname{mol} \cdot L^{-1} [N(^{n}\operatorname{Bu})_{4}][B(\tilde{C}_{6}F_{5})_{4}] \text{ and } 0.1 \operatorname{mmol} \cdot L^{-1} \text{ of } 6 \text{ in a}$ potential range between -500 and 1500 mV vs Ag/AgCl. While the potential is increased stepwise (the step length differs from 25 to 100 mV), **6** is oxidized to 6^+ , 6^{2+} , 6^{3+} , and finally 6^{4+} . Upon raising the potential from -500 to 200 mV, oxidation of pyrrole 6 occurs and the extinction of NIR bands increases. In situ formed $6[B(C_6F_5)_4]$ evinces a strong broad band between 1500 and 2500 nm, similar to that observed in $4[PF_6]$ as well as a sharp absorption in the UVvis part of the spectra at 663 nm, which most probably can be assigned to a ligand-to-metal charge transfer transition (Figure 7).²⁰ Further increase of the potential to 525 mV leads to the in situ formation of $6[B(C_6F_5)_4]_2$. As this oxidation takes place, the extinction of the NIR absorptions decreases. The LMCT band in the UV-vis region is shifted hypsochromically to 607 nm (Figure 7). Compounds 6[B- $(C_6F_5)_4]_3$ and $6[B(C_6F_5)_4]_4$ could be in situ generated by increasing the potentials to 800 and 1100 mV, respectively. During these oxidation processes no NIR absorption could be observed, and therefore, they are not depicted in Figure 7. UV-vis absorptions could be found at 818 nm for 6^{3+} and 782 nm for **6**⁴⁺.

Deconvolution of the NIR data of $6[B(C_6F_5)_4]$ was performed using three Gaussian-shaped overlapping absorptions (Figure 8). The sum of the Gaussian functions closely matches the measured spectrum. The IVCT band can be

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Figure 6. Voltamograms of dichloromethane solutions containing 0.5 mmol·L⁻¹ of **6** at 25 °C. (Left) Supporting electrolyte $[N(^{n}Bu)_{4}][PF_{6}]$; CV (scan rate: 100 mV·s⁻¹). (Right) Supporting electrolyte $[N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}]$; CV (scan rate: 100 mV·s⁻¹) and LSV (scan rate 1 mV·s⁻¹).



Figure 7. NIR spectra of 6 at rising potentials (bottom: oxidation of 6 to 6^+ , -500 to 200 mV; top: oxidation of 6^+ to 6^{2+} , 250 to 525 mV vs Ag/AgCl) at 25 °C, in dichloromethane, supporting electrolyte [N("Bu)₄][B(C₆F₅)₄]. Arrows indicate increasing or decreasing absorptions.

observed at 4752 cm^{-1} possessing an extinction of $\varepsilon_{\text{max}} = 4900 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and a bandwidth at half-height of 2719 cm⁻¹.

Band shape analyses for both pyrrole compounds were performed according to the Hush model for symmetric



Figure 8. Deconvolution of NIR absorptions of $6[B(C_6F_5)_4]$ using three Gaussian-shaped bands determined by spectroelectrochemistry in an OTTLE cell.

mixed valence species (eqs 1 and 2)²¹ and the classification criterion of Brunschwig, Creutz and Sutin.²²

$$(\Delta \nu_{1/2})_{\text{theo}} = (2310\nu_{\text{max}})^{1/2}$$
(1)

$$\Gamma = 1 - ((\Delta \nu_{1/2}) / (\Delta \nu_{1/2})_{\text{theo}})$$
(2)

Theoretical bandwidth at half-height could be calculated as 3341 cm⁻¹ for $\mathbf{4}^+$ and 3313 cm⁻¹ for $\mathbf{6}^+$. Therefore, Γ values of 0.31 ($\mathbf{4}^+$) and 0.18 ($\mathbf{6}^+$) could be determined. According to this classification 2,5-diferrocenyl-1-phenyl-1*H*-pyrrole ($\mathbf{4}$) and 2,3,4,5-tetraferrocenyl-1-phenyl-1*H*-pyrrole ($\mathbf{6}$) can be assigned as class II systems. The Hush theory is a two-state model; however, in $\mathbf{6}^+$ three iron(II) centers and

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one iron(III) ion are present. This system is much more complicated, and the use of Hush's formula may be inadequate, as more than one IVCT process could appear in a close range and, therefore, the bandwidth at half-height could be enlarged.

Conclusion

We have shown that novel 2,5-diferrocenyl-1-phenyl-1Hpyrrole (4) and 2,3,4,5-tetraferrocenyl-1-phenyl-1*H*-pyrrole (6) are accessible in a straightforward synthesis methodology. As proven by dynamic NMR spectroscopy, the perferrocenylated pyrrole (6) evinces rotation barriers in solution even at room temperature, due to the sterical demand of the four ferrocenyl groups. Comparison of the C,C double bond and the single bond length in the pyrrole core system of 6, determined by single-crystal X-ray diffraction, indicates considerable electron delocalization. Organometallics 4 and 6 display two (4) or four (6) electrochemically reversible oneelectron processes with formal reduction potentials of $E^{0'}$ = -238 and $E^{0\prime} = 212$ mV for **4** and $E^{0\prime} = -280$, $E^{0\prime} = 51$, $E^{0\prime} =$ 323, and $E^{0'} = 550 \text{ mV}$ for **6** using $[N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}]$ as supporting electrolyte. With $\Delta E_{1/2}$ values of 315 mV $([N(^{n}Bu)_{4}][PF_{6}])$ and 450 mV $([N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}])$ the 2,5diferrocenyl-1-phenyl-1H-pyrrole (4) exhibits to the best of our knowledge the largest separation of the oxidation potentials among ferrocenyl aromatics or heteroaromatics ever described in literature. Most probably this increased intermetallic communication, when compared to other ferrocenyl heteroaromatics, can be explained by the decreasing of the energy gap between the ferrocenyl moieties and the heterocyclic core system and the increased delocalization in the C₄N unit itself. Spectro-electrochemical studies confirmed electronic communication between the ferrocenyl moieties in the monocations through the C₄N core of both compounds. This delimits the title compounds from the appropriate thiophene systems,⁶ where the interaction between the ferrocenyl functionalities is mainly attributed to electrostatic effects. The pyrroles could be classified as class II systems according to Robin and Day²³ by band shape analyses of the IVCT absorptions.

Experimental Section

General Conditions. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, toluene, *n*-hexane, and *n*-pentane were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride.

Instruments. Infrared spectra were recorded with a FT-Nicolet IR 200. The ¹H NMR spectra were recorded with a Bruker Avance III 500 spectrometer operating at 500.303 MHz in the Fourier transform mode; the ¹³C{¹H} NMR spectra were recorded at 125.800 MHz. Chemical shifts are reported in δ (parts per million) downfield from tetramethylsilane with the solvent as reference signal (¹H NMR: CHCl₃, δ 7.26; ¹³C{¹H} NMR: CDCl₃, δ 77.00). The melting points of analytically pure samples (sealed off in nitrogen-purged capillaries) were determined using a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed using a Thermo FLASHEA 1112 Series instrument. Spectro-electrochemical measurements were carried out in an OTTLE cell similar to

that described previously^{24,6} from dichloromethane solutions containing 0.1 mol·L of $[N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}]$ or $[N(^{n}Bu)_{4}][PF_{6}]$ as supporting electrolyte using a Varian Cary spectrometer. High-resolution mass spectra were recorded using a micrOTOF QII Bruker Daltonite workstation.

Reagents. 2,5-Dibromo-1-phenyl-1*H*-pyrrole,²⁵ 2,3,4,5-tetrabromo-1-phenyl-1*H*-pyrrole,²⁵ and $[N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}]^{26}$ were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

Synthesis of 2,5-Diferrocenyl-1-phenyl-1*H*-pyrrole (4). To 920 mg (5 mmol) of ferrocene and 56 mg (0.5 mmol) of KO^tBu dissolved in 20 mL of tetrahydrofuran was added 4.6 mL (7.5 mmol) of a 1.6 M solution of tert-butyllithium in n-pentane at -30 °C. After 1 h of stirring, 2.2 g (8 mmol) of dry [ZnCl₂·2thf] was added. The solution was kept for 1 h at -30 °C and an additional hour at 25 °C. Afterward, 35 mg (0.03 mmol) of [Pd(PPh₃)₄] and 500 mg (1.66 mmol) of 2,5-dibromo-1-phenyl-1H-pyrrole were added in a single portion, and the reaction solution was stirred for 48 h at 60 °C. After evaporation of all volatiles, the precipitate was dissolved in 200 mL of dichloromethane and washed three times with 100 mL portions of water. The organic phase was dried over MgSO4, and the solvent was evaporated to dryness in an oil-pump vacuum. The remaining solid was purified by column chromatography on alumina using an *n*-hexane-toluene mixture of ratio 1:1 (v/v) as eluent. All volatiles were removed under reduced pressure. Compound 4 was obtained as an orange solid. Yield: 526 mg (1.03 mmol, 62% based on 3.) Anal. Calcd for $C_{30}H_{25}Fe_2N$ (511.22): C, 70.48; H, 4.93; N, 2.74. Found; C, 70.52; H, 5.01; N, 2.69. Mp: 238 °C. IR data (KBr): 3089 m, 2923 w, 1597 w, 1498 s,1417 s, 1328 w, 1105 m, 1001 s, 819 s, 766 s. ¹H NMR (CDCl₃, δ): 3.88 $(pt, J_{HH} = 1.8 Hz, 4H, C_5H_4), 4.02 (s, 10 H, C_5H_5), 4.07 (pt, J_{HH})$ $\begin{array}{l} = 1.8 \text{ Hz}, 4\text{H}, \text{ C}_5\text{H}_4), 6.33 \text{ (s, 2H, C}_4\text{H}_2\text{N}), 7.30-7.35 \text{ (m, 2H, C}_6\text{H}_5), 7.46-7.54 \text{ (m, 3H, C}_6\text{H}_5). \ ^{13}\text{C}\{^1\text{H}\} \text{ NMR (CDCl}_3, \delta): \end{array}$ 66.81 (C₅H₄), 67.60 (C₅H₄), 69.56 (C₅H₅), 77.37 (C*i*-C₅H₄), 79.28 (Ci-C₄H₂N), 108.16 (C₄H₂N), 128.78 (C₆H₅), 128.88 (C_6H_5) , 130.08 (C_6H_5) , 140.23 $(C_i-C_6H_5)$. HR-ESI-MS [m/z]: 511.0680 [M]⁺

Synthesis of 4[PF₆]. A 300 mg (0.58 mmol) amount of 4 was dissolved in 10 mL of dry tetrahydrofuran, and 194 mg (0.58 mmol) of FcH[PF₆] was added at -20 °C in a single portion. After 1 h of stirring the reaction mixture was allowed to warm to 25 °C, and stirring was continued for an additional 2 h. After evaporation of all volatiles, the dark green solid was washed three times with 50 mL portions of *n*-hexane. The remaining solid was dried in the oil-pump vacuum. Complex 4[PF₆] could be isolated as a dark green solid. Yield: 364 mg (0.55 mmol, 95% based on 4). Mp: 256 °C (dec). Anal. Calcd for C₃₀H₂₅F₆Fe₂NP (656.18): C, 54.91; H, 3.81; N, 2.13. Found: C, 53.47; H, 3.91; N, 1.83. IR data (KBr): 3110 w, 2922 m, 2855 w, 1510 s, 1406 s, 1380 w, 1308 m, 1246 m, 1182 m, 844 s, 822 s. HR-ESI-MS [*m*/*z*]: 511.0680 [M – PF₆]⁺.

Synthesis of $4[PF_6]_2$. A 200 mg (0.39 mmol) amount of 4 was dissolved in 10 mL of tetrahydrofuran, and 197 mg (0.78 mmol) of $[AgPF_6]$ was added at -20 °C in a single portion. After stirring the reaction solution for 1 h at this temperature, it was allowed to warm to 25 °C, and stirring was continued for an additional 2 h. The dark solution was filtered from the in situ formed silver particles through Celite. After evaporation of all volatiles the residue was washed three times with 50 mL portions of *n*-hexane. The remaining dark violet solid was dried in an oilpump vacuum. Yield: 302 mg (0.37 mmol, 95% based on 4). Mp: 232 °C (dec). Anal. Calcd for $C_{30}H_{25}F_{12}Fe_2NP_2$ (801.14): C, 44.98; H, 3.15; N, 1.75. Found: C, 46.03; H, 3.46; N, 1.69. IR data (KBr): 2924 s, 2853 m, 1655 m, 1637 m, 1527 w, 1495 m,

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1461 w, 1261, w, 1109 s, 845 s. HR-ESI-MS [m/z]: 255.5345 $[M - 2 \cdot PF_6]^{2+}$.

Synthesis of 2,3,4,5-Tetraferrocenyl-1-phenyl-1*H*-pyrrole (6). To 1.22 g (6.54 mmol) of ferrocene and 112 mg (1 mmol) of KO^tBu dissolved in 30 mL of tetrahydrofuran was added 6.1 mL (9.81 mmol) of a 1.6 M solution of tert-butyllithium in n-pentane at -30 °C. After 1 h of stirring, 4.2 g (15 mmol) of dry $[ZnCl_2 \cdot 2thf]$ was added. The solution was kept for 1 h at -30 °C and an additional hour at 25 °C. Afterward, 70 mg (0.06 mmol) of [Pd(PPh₃)₄] and 500 mg (1.09 mmol) of 2,3,4,5-tetrabromo-1-phenyl-1H-pyrrole were added in a single portion, and the reaction solution was stirred for 48 h at 60 °C. After evaporation of all volatiles, the precipitate was dissolved in 200 mL of dichloromethane and washed three times with 100 mL portions of water. The organic phase was dried over MgSO₄, and the solvent was evaporated to dryness in an oil-pump vacuum. The remaining solid was purified by column chromatography on alumina eluting with a *n*-hexane-toluene mixture of ratio 1:1 (v/v). All volatiles were removed under reduced pressure. Compound 6 was obtained as an orange crystalline material. Yield: 634 mg (1.03 mmol, 68% based on 5). Anal. Calcd for C₅₀H₄₁Fe₄N (879.25): C, 68.30; H, 4.70; N, 1.59. Found: C, 67.92; H, 4.81; N, 1.52. Mp: 182 °C. IR data (KBr): 3083 w, 2922 m, 2851 w, 1653 m, 1498 m, 1409 m, 1104 s, 1037 m, 1001 s, 817 vs, 736 m. ¹H NMR (CDCl₃, δ): 3.80 (s, 10H, C₅H₅), 3.95 (s, 10H, C₅H₅), 4.07 (bs, 4H C₅H₄), 4.10 (pt, $J_{\rm HH} = 1.8$ Hz, 4H, C_5H_4), 4.19 (pt, $J_{HH} = 1.8$ Hz, 4H, C_5H_4), 4.60 (bs, 4H, C_5H_4). ¹³C{¹H} NMR (CDCl₃, δ): 66.43 (C₅H₄), 67.13 (C₅H₄), 69.00 (C₅H₄), 69.54 (C₅H₄), 70.24 (Ci-C₅H₄) 70.76 (C₅H₄), 72.43 (C5H4), 80.40 (Ci-C5H4), 84.63 (C4N), 122.59 (C4N), 128.31 (C₆H₅), 129.05 (C₆H₅), 132.09 (C₆H₅), 140.40 (C_i-C₆H₅). ESI-MS [m/z]: 879.0651[M]⁺.

Electrochemistry. Measurements on 1.0 mmol·L⁻¹ solutions of **4** and **6** in dry, air-free dichloromethane containing 0.1 mol·L⁻¹ of $[N(^nBu)_4][B(C_6F_5)_4]$ or $[N(^nBu)_4][PF_6]$ as supporting electrolyte were conducted under a blanket of purified argon at 25 °C utilizing a Voltalap PGZ 100 radiometer electrochemical workstation interfaced with a personal computer. A threeelectrode cell, which utilized a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm²), and an Ag/ Ag⁺ (0.01 mol·L⁻¹[AgNO_3]) reference electrode, mounted on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with 1 μ m and then 1/4 μ m diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of

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0.01 mol·L⁻¹ [AgNO₃] and 0.1 mol·L⁻¹ [N(^{n}Bu)₄][B(C₆F₅)₄] in acetonitrile, in a Luggin capillary with a Vycor tip. This Luggin capillary was inserted into a second Luggin capillary with Vicor tip filled with a 0.1 mol·L⁻¹ [N(^{n}Bu)₄][B(C₆F₅)₄] solution in acetonitrile. Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 5 mV. Experimentally potentials were referenced against an Ag/Ag⁺ reference electrode, but results are presented referenced against ferrocene as an internal standard, as required by IUPAC.¹⁴ To achieve this, since the ferrocene couple FcH/FcH⁺ interferes with the ferrocenyl signals of 4 and 6, each experiment was first performed in the absence of any internal standard and then repeated in the presence of $< 1 \text{ mmol} \cdot \text{L}^{-1}$ decamethylferrocene (Fc*). A separate experiment containing only ferrocene and decamethylferrocene was also performed. Data were then manipulated on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH⁺ couple to 0.0 V. Under our conditions the Fc^*/Fc^{*+} couple was at -619 mV vs FcH/FcH^+ , $\Delta E_p = 60$ mV, while the FcH/FcH⁺ couple itself was at 220 mV vs Ag/Ag⁺, ΔE_{p} $= 61 \text{ mV.}^{27}$

Crystal data for 6·CHCl₃: C₅₁H₄₂Cl₃Fe₄N, $M_r = 998.61$ g·mol⁻¹, triclinic, $P\overline{1}$, $\lambda = 0.71073$ Å, a = 11.5111(6) Å, b = 11.9216(5) Å, c = 15.8448(11) Å, $\alpha = 84.922(4)^\circ$, $\beta = 76.734(5)^\circ$, $\gamma = 70.897(4)^\circ$, V = 1999.61(19) Å³, Z = 2, $\rho_{calcd} = 1.659$ g·cm⁻³, $\mu = 1.663$ mm⁻¹, T = 100 K, θ range = $3.02-26.00^\circ$, reflections collected 14 970, independent 7824 ($R_{int} = 0.0288$), $R_1 = 0.0325$, w $R_2 = 0.0656$ [$I > 2\sigma(I$)]. Single crystals of 6·CHCl₃ were obtained by diffusion of *n*-hexane into a chloroform solution containing 6 at 25 °C. Data were collected with an Oxford Gemini S diffractometer, with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) using oil-coated shock-cooled crystals. The structure was solved by direct methods and refined by full-matrix least-squares procedures on $F^{2.28}$

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Supporting Information Available: Crystallographic data of 6 as CIF files are available free of charge via the Internet at http:// pubs.acs.org. Crystallographic data of 6 are also available from the Cambridge Crystallographic Database as file no. CCDC 792152.

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