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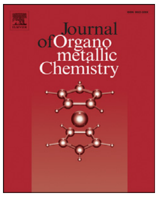

Electronic modification of redox active ferrocenyl termini and their influence on the electrontransfer properties of 2,5-diferrocenyl-*N*-phenyl-1*H*-pyrroles☆

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A series of 2,5-diferrocenyl-*N*-phenyl-1*H*-pyrroles of type 2,5-Fc_2-$^{c}C_4H_2NPh$ (Fc = $Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4R)$; **3a**, R = $^{c}C_4H_7O_2$; **3b**, H; **3c**, 3,5-$(CF_3)_2$-C_6H_3) was synthesized by Negishi *C,C* cross-coupling reactions to connect the heterocyclic unit with the redox active ferrocenyl moieties. The reaction of **3a** with *p*-toluene sulfonic acid gave **3d** (R = CHO). A subsequent cyanation reaction of **3d** produced **3e** (R = C≡N). Characterization of these molecules was performed by spectroscopic means and single crystal X-ray diffraction analysis (**3c**–**e**). It could be shown that the electronic properties of the 2,5-diferrocenyl-*N*-phenyl-1*H*-pyrroles is influenced by the substitution of electron withdrawing/donating functional groups in 1′-position of the ferrocenyls. The influence of the electronic nature of the substituents on the charge transfer character of the heterocyclic bridging system was investigated using electrochemical (cyclic and square-wave voltammetry) and spectroelectrochemical methodologies (*in situ* UV–Vis/NIR spectroscopy). The observed redox splittings $\Delta E^{\circ\prime}$ between the redox active ferrocenyls are 390 mV for **3a**, 485 mV for **3c**, 555 mV for **3d** and 600 mV for **3e** using $[N^nBu_4][B(C_6F_5)_4]$ as electrolyte. Furthermore, the electrochemistry studies were performed in $[N^nBu_4][PF_6]$ to determine changes of the electrostatic stabilization. The redox separation increases with increasing electron withdrawing ability of the ferrocenyl substituents in the order R = $^{c}C_4H_7O_2$ < H < 3,5-$(CF_3)_2$-C_6H_3 < CHO < C≡N, while the spectroelectrochemical studies reveal decreasing strength of the intramolecular electronic coupling between the iron atoms. All compounds show intense and broad absorptions in the NIR region and can be classified as strongly coupled class II systems according to Robin and Day.

Introduction

During the last decades, mixed-valent species have attracted considerable attention, in particular in the field of molecular electronics as they offer the possibility to act as model compounds for molecular wires, -switches, and other electronic building blocks [1–7]. Studies about charge transfer interactions are also helpful to understand electron transfer processes within complex natural processes such as the photosynthesis [8–12], but are not only beneficial to imitate selected charge transfer processes in nature to create molecular electronic materials [2,3,7,13–17]. Therefore, the investigation of charge transfer within molecules containing small conjugated backbones is a useful tool to understand the fundamentals of the design of such bridges and the modification of charge transfer in a controlled manner. Ferrocene is often used as redox active terminal group, due to its high thermal stability in the neutral and oxidized form as well as the excellent electrochemical reversibility of the ferrocene's Fe(II)/Fe(III) redox couple [4,18–20]. Within our research group a number of 2,5-diferrocenyl five-membered heterocycles including pyrroles [21,22], thiophenes [23], furans [24], phospholes [25] and siloles [26] have been synthesized to investigate the influence of the heteroatom on the charge transfer properties. It could be shown that the electronic interaction increases from thiophene over furan to pyrrole, whereas the electron transfer within phospholes and siloles is mediated mainly by the dienic system without a contribution of the

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☆ Dedicated to Prof. Dr. David Michael Mingos on the occasion of his 70th birthday.

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heteroatom [21–26]. Other examples for five-membered heterocycles are titanocenes [27] and zirkonocenes [28] (for reviews on five-membered heterocycles featuring redox active redox termini see Refs. [4,29]). Furthermore, within a series of 2,5-diferrocenyl-*N*-phenyl-1*H*-pyrroles, the electronic properties of the bridging system have been varied in a controlled manner by substitution of the phenyl group with selected electron withdrawing/donating substituents [30]. Beside the possibility of modifying the electronic properties of the π-conjugated bridge, the electronic character of the redox active termini can also be modified by attachment of electron-withdrawing or donating groups. Therefore, a series of diferrocenyl-functionalized thiophenes and ethylenedioxythio phenes with selected functional groups in 1′-position of the ferrocenyl substituent was synthesized and the electronic communication between the two ferrocenyls over the π-system was studied [31]. While electron-rich bridging systems seem to facilitate electron transfer, electron withdrawing groups at the ferrocenyl groups are beneficial.

In continuation of this work, we herein present a series of 2,5-diferrocenyl-*N*-phenyl-1*H*-pyrroles bearing electron withdrawing/donating groups at the ferrocenyl groups in 1′-position. The influence of the electronic nature of the substituents on the electrochemistry and charge transfer characteristics is reported as well.

Materials and methods

General data

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Tetrahydrofuran was purified by distillation from sodium/benzophenone ketyl. Hexane was purified with a MBRAUN SBS-800 purification system. Dichloromethane was purified by distillation from CaH_2. For column chromatography alumina with a particle size of 90 μm (standard, Merck KGaA) or silica with a particle size of 40–60 μm (230–400 mesh (ASTM), Fa. Macherey–Nagel) were used. As filtration support zeolite (Riedel de Häen) was applied.

Instrumentation

Infrared spectra were recorded with a FT-Nicolet IR 200 equipment. The ^1H NMR spectra were recorded with a Bruker Avance III 500 spectrometer operating at 500.303 MHz in the Fourier transform mode; the $^{13}C\{^1H\}$ NMR spectra were recorded at 125.800 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent as reference signal (^1H NMR: δ ($CDCl_3$) = 7.26 ppm; $^{13}C\{^1H\}$ NMR: δ ($CDCl_3$) = 77.16 ppm). The melting points were determined with a Gallenkamp MFB 595 010 M melting point apparatus. Elemental analyses were performed with a Thermo FlashEA 1112 Series instrument. High resolution mass spectra were recorded using a micrOTOF QII Bruker Daltonite workstation. UV–vis spectra were recorded with a THERMO Genesys 6 spectrometer.

X-ray diffraction

Data were collected with an Oxford Gemini S diffractometer at 110 K (**3c**), 100 K (**3e**) and 298 K (**3d**) using Mo K_α ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods and refined by full-matrix least square procedures on F^2 [32,33]. All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions. Graphics of the molecular structures have been created by using ORTEP [34].

Crystal Data for **3c**: $C_{46}H_{29}F_{12}Fe_2N$, M_r = 935.40 g mol^{-1}, monoclinic, $I2/a$, $\lambda = 0.71073$ Å, a = 15.966(5) Å, b = 11.505(5) Å, c = 20.160(5) Å, V = 3691(2) Å^3, Z = 4, ρ_{calcd} = 1.683 g m^{-3}, μ = 0.885 mm^{-1}, T = 110 K, θ range 3.05–25.99°, 9001 reflections collected, 3592 independent reflections (R_{int} = 0.0362), R_1 = 0.1011, wR_2 = 0.2050 ($I > 2\sigma(I)$).

Crystal Data for **3d**: $C_{32}H_{25}Fe_2NO_2$, M_r = 567.23 g mol^{-1}, orthorhombic, $P2_12_12_1$, λ = 0.71073 Å, a = 7.4624(4) Å, b = 10.8241(7) Å, c = 31.111(3) Å, V = 2512.9(3) Å^3, Z = 4, ρ_{calcd} = 1.499 g m^{-3}, μ = 1.186 mm^{-1}, T = 298(2) K, θ range 3.03–25.24°, 7251 reflections collected, 3849 independent reflections (R_{int} = 0.0743), R_1 = 0.0523, wR_2 = 0.1235 ($I > 2\sigma(I)$), absolute structure parameter [35] = −0.01(3).

Crystal Data for **3e**: $C_{32}H_{23}Fe_2N_3$, M_r = 561.23 g mol^{-1}, monoclinic, $P2_1/n$, λ = 0.71073 Å, a = 7.2651(3) Å, b = 20.0798(8) Å, c = 16.5610(5) Å, V = 2413.53(16) Å^3, Z = 4, ρ_{calcd} = 1.545 g m^{-3}, μ = 1.230 mm^{-1}, T = 100 K, θ range 2.98–26.00°, 10967 reflections collected, 4703 independent reflections (R_{int} = 0.0354), R_1 = 0.0332, wR_2 = 0.0727 ($I > 2\sigma(I)$).

Electrochemistry

Electrochemical measurements on 1.0 mmol L^{-1} solutions of the analytes in anhydrous, 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 Radiometer Voltalab PGZ 100 electrochemical workstation combinated with a personal computer. A three electrode cell, which utilized a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm^2) 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 a 1 μm and then with a 1/4 μm diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of 0.01 mol L^{-1} $[AgNO_3]$ and 0.1 mol L^{-1} $[N^nBu_4][B(C_6F_5)_4]$ or $[N^nBu_4][PF_6]$ in acetonitrile in a Luggin capillary with a Vycor tip. This Luggin capillary was inserted into a second Luggin capillary with a Vycor tip filled with a 0.1 mol L^{-1} $[N^nBu_4][B(C_6F_5)_4]$ or $[N^nBu_4][PF_6]$ solution in dichloromethane [36]. 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 [37]. When decamethylferrocene was used as an internal standard, the experimentally measured potentials were converted into E *vs* FcH/FcH$^+$ by addition of −0.61 V for $[N^nBu_4][B(C_6F_5)_4]$ or −0.54 V for $[N^nBu_4][PF_6]$ as electrolyte [38]. Data were then manipulated on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH$^+$ couple to $\Delta E^{\circ\prime} = 0$ mV. Ferrocene itself showed a redox potential of 220 mV *vs* Ag/Ag$^+$ (ΔE_p = 61 mV) within the measurements [39,40]. The cyclic voltammograms, which are depicted in Fig. 4, were taken after typically two scans and are considered to be steady state cyclic voltammograms in which the signal pattern differs not from the initial sweep.

Spectroelectrochemistry

UV–Vis/NIR measurements were carried out in an OTTLE (= optically thin layer electrochemistry) cell with quartz windows similar to that described previously [41] in dry dichloromethane solutions containing 2.0 mmol L^{-1} analyte and 0.1 mol L^{-1} of $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte using a Varian Cary 5000 spectrophotometer at 25 °C. The working electrode Pt-mesh,

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