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Dinuclear ruthenium sawhorse-type complexes containing carboxylato bridges and ferrocenyl substituents: Synthesis and electrochemistry

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Abstract

The ferrocenyl-containing diruthenium complexes $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2L_2]$ (Fc = ferrocenyl, fc = ferrocen-1,1′-diyl; **1**: $L = NC_5H_4\text{–}COOC_6H_4\text{–}OC_{10}H_{21}$, **2**: $L = NC_5H_4\text{–}COOC_6H_4\text{–}OC_{16}H_{33}$, **3**: $L = NC_5H_4\text{–}OOC\text{–}fc\text{–}C_{12}H_{25}$) and $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOC_6H_5)_2(NC_5H_4\text{–}OOC\text{–}fc\text{–}C_{12}H_{25})_2]$ (**4**) have been synthesized from $Ru_3(CO)_{12}$, ferrocene carboxylic or benzoic acid and the corresponding pyridine derivative. The synthesis of the new pyridine derivative $NC_5H_4\text{–}OOC\text{–}fc\text{–}C_{12}H_{25}$ used for the preparation of **3** and **4** is also reported. Complexes **1**–**4** posses a so-called sawhorse structure consisting of the $Ru_2(CO)_4$ backbone and two bridging carboxylato ligands, while the coordination sphere around the ruthenium atoms is completed by the pyridine-derived ligands bonded in the axial positions. The electrochemical behavior of **1**–**4** and their known analogues $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2L_2]$ (**5**: $L = NC_5H_5$, **6**: $L = P(C_6H_5)_3$, **7**: $L = NC_5H_4\text{–}OOCFc$) has been studied by voltammetry on rotating disc electrode and by cyclic voltammetry.

Keywords: Carboxylato bridges; Dinuclear complexes; Ruthenium; Ferrocene; Electrochemistry

1. Introduction

Sawhorse-type ruthenium complexes are well-known since 1969, when Lewis and co-workers reported the formation of $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCR)_2]_n$ polymers by refluxing $Ru_3(CO)_{12}$ in the corresponding carboxylic acid and their depolymerisation in coordinating solvents to give dinuclear complexes of the type $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCR)_2L_2]$, L being acetonitrile, pyridine or another two-electron donor [1]. These dinuclear complexes have been shown later, by a single-crystal X-ray structure analysis of $[Ru_2(CO)_4(\mu_2\text{-}\eta_2\text{-}OOCBu^n)_2PBu^t_3)_2]$ to have a $Ru_2(CO)_4$ backbone in a sawhorse-type arrangement with two symmetrical $\mu_2\text{-}\eta^2$-carboxylato bridges and two axial (phosphine) ligands [2]. In the meantime, a considerable number of such sawhorse-type diruthenium complexes with carboxylato [3], carboxamido [4], phosphinato [5], sulfonato [6], pyrazolato [7] or oximato [8] bridges have been reported. We have found that complexes of the type $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOC_6H_5)_2L_2]$, where L represents pyridine ligands substituted with long aliphatic chains, exhibit mesomorphic properties, forming nematic liquid crystals in a temperature range of 150–225 °C [9].

Bearing this in mind, we synthesized the ferrocenecarboxylato derivatives **1** and **2** as well as the analogous complexes **3** and **4** containing additional ferrocenyl substituents in the pyridine ligands. Unfortunately, light-polarised microscopy shows **1**–**4** to have no mesomorphic properties. On the other hand, the presence of chemically

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different ferrocenyl substituents makes **1**–**4** interesting substrates for electrochemical studies. Herein, we report the synthesis and characterization of **1**–**4** and that of the new pyridine ligand NC_5H_4–OOC–fc–$C_{12}H_{25}$, as well as the electrochemistry of **1**–**4** and their analogues $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2L_2]$ (Fc = ferrocenyl, fc = ferrocen-1,1′-diyl; **5**: L = NC_5H_5, **6**: L = $P(C_6H_5)_3$, **7**: L = NC_5H_4–OOCFc) [10].

2. Results and discussion

2.1. Synthesis and characterization

Dodecacarbonyltriruthenium reacts with ferrocene carboxylic acid or with benzoic acid in refluxing tetrahydrofuran to give, in the presence of the corresponding pyridine derivative, the dinuclear complexes $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2L_2]$ (**1**: L = NC_5H_4–$COOC_6H_4$–$OC_{10}H_{21}$, **2**: L = NC_5H_4–$COOC_6H_4$–$OC_{16}H_{33}$, **3**: L = NC_5H_4–OOC–fc–$C_{12}H_{25}$) or $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOC_6H_5)_2(NC_5H_4\text{–}OOC\text{–fc–}C_{12}H_{25})_2]$ (**4**), respectively. Complexes **1**–**4** are obtained as air-stable orange or yellow powders, which have been unambiguously characterized by their IR, NMR and MS data as well as by correct micro-analytical data (see Section 3).

The new ferrocenyl-containing diruthenium complexes **1**–**4** as well as the known complexes $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2(NC_5H_5)_2]$ (**5**), $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2(P(C_6H_5)_3)_2]$ (**6**), $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2(NC_5H_4\text{–}OOCFc)_2]$ (**7**) [10] have been electrochemically studied by cyclic voltammetry at a rotating platinum disc electrode (RDE) and by cyclic voltammetry at a stationary platinum disc electrode in dichloromethane solutions.

2.2. Electrochemistry

The redox behavior of the ferrocenecarboxylato-bridged complexes **5** and **6** (Table 1) is similar as far as both compounds undergo two narrow-separated, reversible one-electron oxidations, which can be assigned to the oxidation of the ferrocene units, and a one-electron irreversible oxidation of the diruthenium core. These redox steps, however, are observed in different order: **6** becomes oxidized first at the Ru_2 unit and then at the ferrocene units, whereas **5** undergoes first ferrocene/ferrocenium oxidations, followed by the irreversible, Ru_2-centered oxidation at a potential markedly higher than that for **6** and associated with some chemical complications (probably adsorption) that are reflected by an

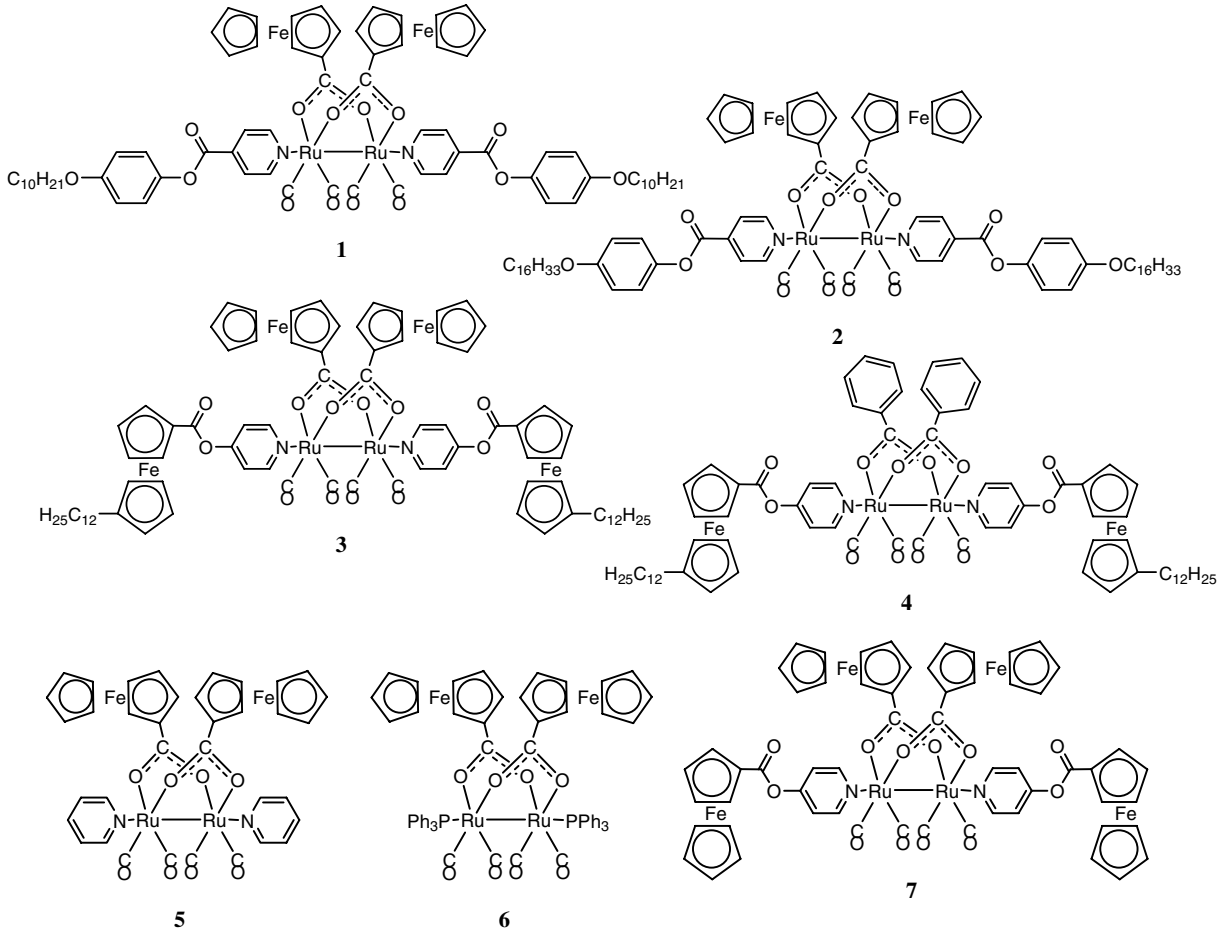

Table 1
Summary of cyclic voltammetric data[a]

Compound	E_{pa}	E_{pc}	Assignment[b]
1	+0.16		Ru
	(+0.30)	+0.23	Fc
	+0.38	(+0.30)	Fc
2	(+0.16)	+0.09	Fc
	+0.22	(+0.15)	Fc
	+0.66		Ru
	+0.84		follow-up process
3	(+0.17)	(+0.09)	Fc
	(+0.23)	(+0.13)	Fc
	+0.35	+0.24	Fc[d]
	+0.65		Ru or follow-up
4	(+0.18)	+0.11	Fc
	(+0.17)	+0.23	Fc
	+0.77		Ru
	+0.86[c]		follow-up process
5	(+0.18)	+0.11	Fc
	(+0.17)	+0.24	Fc
	+0.86[c]		Ru + follow-up process
6	(+0.18)	(+0.11)	Fc
	+0.28	+0.18	Fc
	+0.78		Ru
7	+0.32	+0.24	Fc[e]
	+0.59		Ru

[a] Cyclic voltammograms were recorded at platinum disc electrode on ca. 5×10^{-4} M dichloromethane solutions containing 0.1 M Bu_4NPF_6 as the supporting electrolyte at room temperature. The potentials are given relative to ferrocene/ferrocenium reference. E_{pa} and E_{pc} denote the anodic and cathodic peak potentials, respectively. Only E_{pa} values are given for irreversible oxidations. The quoted values were obtained at the scan rate of 100 mV/s. Brackets indicate where peaks are observed only as more or less resolved shoulders.

[b] Fc and Ru denote ferrocene- and Ru_2-centered oxidations, respectively.

[c] Broad wave.

[d] Probably bielectronic process. The counterwave is associated with desorption.

[e] Bielectronic process.

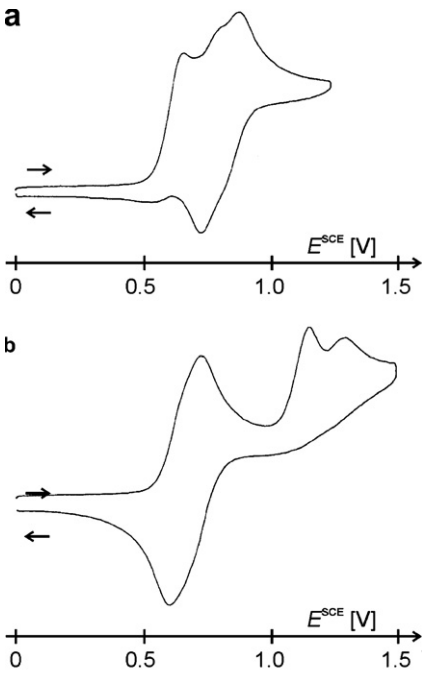

Fig. 1. Cyclic voltammograms of **6** (a) and **5** (b) as recorded at 100 mV s^{-1} scan rate on platinum disc electrode for ca. 5×10^{-4} M analyte solutions in dichloromethane containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. The potentials are given relative to ferrocene/ferrocenium.

additional wave at ca. + 0.84 V versus ferrocene/ferrocenium (see Fig. 1).

The observed shift towards less positive potentials of the core oxidation upon replacement of pyridine (complex **5**) with PPh_3 (complex **6**) is in accordance with the donor ability of these ligands: The phosphine as a stronger base (donor) can be expected to increase the electron density at the Ru_2 core, thus facilitating the oxidation. However, the variation of the redox potential of the Ru_2-centered oxidation as a function of the axial ligands is not that simple. As observed for **6**, a lowering of the Ru_2-centered oxidation potential (or an increase in the donating ability of the ligand) can shift the Ru_2-wave negatively, so that it even precedes the oxidation of the ferrocene unit. In such case, however, the first oxidation has to influence the following one by making any subsequent electron removal more difficult. This leads to a discontinuity in the changes of the redox potentials. It is also noteworthy that the close separation of the individual ferrocene/ferrocenium processes (about 50 mV) points to a rather limited electronic communication between the ferrocencarboxylato bridges.

The redox response of the pyridinecarboxylic esters **1** and **2** is very similar to that of **5**. Upon raising the external potential, the compounds first undergo two narrow spaced oxidations at the ferrocene units, followed by an irreversible oxidation at the bimetallic core. In accordance with very similar structures that differ only by the length of the peripheral alkyl chain the corresponding waves are found at nearly identical potentials.

Moving the ferrocencarboxylic unit to the periphery as in **4** has only a slight effect on the overall appearance of the cyclic voltammogram, with the exception that the distant ferrocene units are oxidized *independently*, thus giving rise to a reversible ferrocene/ferrocenium wave with ΔE_p characteristic for one-electron process and a height corresponding to the two-electron exchanged. Similarly to **5**, the ferrocene oxidation is followed by an irreversible oxidation at more positive potentials that shifts even further anodically upon repeated scanning (Fig. 2).

The redox response of complexes that combine Ru-bonded and pyridine ester ferrocenecarboxylic units is rather complex. In the case of **7**, a poorly resolved system of three waves followed by a well-separated irreversible wave with E_{pa} + 0.65 V is observed. These redox processes are further complicated by pronounced adsorption phenomena. The analogous compound alkylated at the lateral ferrocene units, **3**, shows a similar voltammogram (Fig. 2). The first wave is resolved only very poorly and followed by an irreversible wave at a potential higher than for **7**. In the whole series, an increase of the molecular weight results in lowering of the diffusion coefficients which is in turn

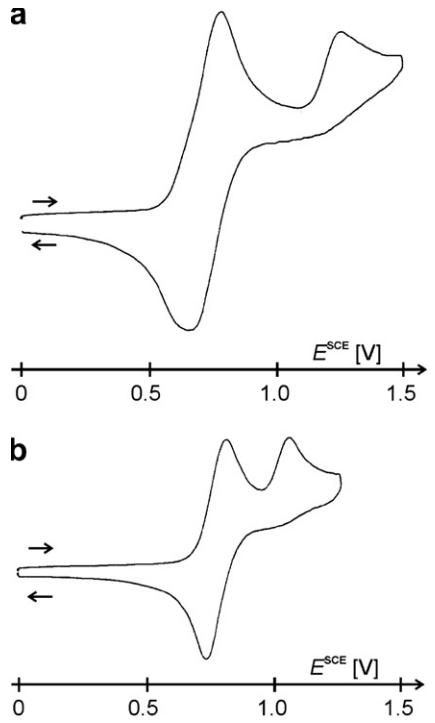

Fig. 2. Cyclic voltammograms of **3** (a) and **4** (b) as obtained at scan rate 100 mV s^{-1} on platinum disc electrode for ca. 5×10^{-4} M analyte solutions in dichloromethane containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. The potentials are given relative to ferrocene/ferrocenium.

reflected by a significant lowering of the peak and limiting currents.

3. Experimental

3.1. General comments

All manipulations were carried out by routine under nitrogen atmosphere. Organic solvents were degassed and saturated with nitrogen prior to use. All reagents were purchased either from Aldrich or Fluka and used as received. NMR spectra were recorded on a Bruker 400 MHz spectrometer. IR spectra were recorded on a Perkin–Elmer 1720X FT-IR spectrometer (4000–400 cm^{-1}). Microanalyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland). Electro-spray mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer. Dodecacarbonyltriruthenium [11] was prepared according to published method and 1-(pyridyloxy)carbonyl-1′-dodecylferrocene was obtained by analogy using the method reported by Donnio et al. [12] for 1-(pyridyloxy)carbonyl-1′-tetradecylferrocene.

3.2. Synthesis of complexes *1–4*

A solution of $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and the appropriate carboxylic acid (0.47 mmol) in dry tetrahydrofuran (40 ml) was heated at 120 °C in a pressure Schlenk tube for 12 h. Then the solvent was evaporated to give a yellow-brown residue, which was dissolved in tetrahydrofuran, and the appropriate ligand (0.47 mmol) was added. The solution was stirred at room temperature for 2–3 h, the solution was evaporated and the product isolated from the residue by crystallization from a tetrahydrofuran/hexane mixture. In order to improve the purity, the raw product was subjected to a thin-layer chromatography on silica gel using dichloromethane as eluent and obtained as an orange or yellow powder.

Data for $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2(NC_5H_4\text{–}COO\text{-}C_6H_4\text{–}OC_{10}H_{21})_2]$ (**1**): Yield 90% (209 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 9.15 (d, 4H, H_{pyr}, $J = 6$ Hz), 8.26 (d, 4H, H_{pyr}, $J = 6$ Hz), 6.98–7.23 (m, 8H, H_{ar}), 4.60 (s, 4H, HCp), 4.23 (s, 4H, HCp), 4.10 (s, 10H, HCp), 4.01 (t, 4H, OCH_2, $J = 6{,}5$ Hz), 1.84 (q, 4H, CH_2, $J = 7$ Hz), 1.32–1.50 (m, 28H, CH_2), 0.92 (t, 6H, CH_3, $J = 6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 204.45 (4C, CO), 184.32 (2C, COO), 163.86 (2C, COO), 157.81 (2C, *C*O–$C_{10}H_{21}$), 153.21 (4C, N*C*), 144.07 (2C, COO–*C*), 138.50 (2C, *C*–COO), 124.89 (4C, $NCH_2\mathit{CH_2}$), 122.48 (4C, $COOCH\mathit{CH_2}$), 115.70 (4C, $COOCHCH_2\mathit{CH}$), 75.47 (2C, *C*–COO), 70.85–70.55–70.00 (12C, CCp), 68.91 (2C, $O\mathit{CH_2}$), 32.32–29.99–29.81–29.75–29.67–26.46 (14C, CH_2), 23.11 (2C, $\mathit{CH_2}$–CH_3), 14.55 (2C, CH_3). ESI-MS: 1485.2 $[M+2H]^+$. IR (CaF_2, THF): $\nu_{(CO)}$ 2022.7 (vs), 1972.3 (m), 1942.2 (vs), $\nu_{(OCO)}$ 1559.7 (s) cm^{-1}. *Anal.* Calc. for $C_{70}H_{76}Fe_2N_2O_{14}Ru_2$ (1483.19) C, 56.66, H, 5.27, N, 1.80. Found: C, 56.69, H, 5.16, N, 1.89%.

Data for $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2(NC_5H_4\text{–}COO\text{-}C_6H_4\text{–}OC_{16}H_{33})_2]$ (**2**): Yield 90% (232 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 9.15 (d, 4H, H_{pyr}, $J = 5$ Hz), 8.27 (d, 4H, H_{pyr}, $J = 5$ Hz), 7.23 (d, 4H, H_{ar}, $J = 9$ Hz), 7.01 (d, 4H, H_{ar}, $J = 9$ Hz), 4.61 (t, 4H, HCp, $J = 1.8$ Hz), 4.23 (t, 4H, HCp, $J = 1.8$ Hz), 4.11 (s, 10H, HCp), 4.04 (t, 4H, OCH_2, $J = 6.5$ Hz), 1.85 (q, 4H, CH_2, $J = 7$ Hz), 1.31–1.51 (m, 52H, CH_2), 0.92 (t, 6H, CH_3, $J = 6.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 204.45 (4C, CO), 184.33 (2C, COO), 163.85 (2C, COO), 157.83 (2C, *C*O–$C_{16}H_{33}$), 153.21 (4C, N*C*), 144.10 (2C, COO–*C*), 138.52 (2C, *C*–COO), 124.89 (4C, $NCH_2\mathit{CH_2}$), 122.47 (4C, $COOCH\mathit{CH_2}$), 115.70 (4C, $COOCHCH_2\mathit{CH}$), 75.47 (2C, *C*–COO), 70.86–70.57–70.00 (18C, CCp), 68.92 (2C, $O\mathit{CH_2}$), 32.35–32.00–30.13–30.03–29.83–29.80–29.68–26.47–26.03 (24C, CH_2), 23.12 (2C, $\mathit{CH_2}$–CH_3), 14.55 (2C, CH_3). ESI-MS: 1652.6 $[M+H]^+$. IR (CaF_2, THF): $\nu_{(CO)}$ 2022.9 (vs), 1973.0 (m), 1942.3 (vs), $\nu_{(OCO)}$ 1557.1 (s) cm^{-1}. *Anal.* Calc. for $C_{82}H_{100}Fe_2N_2O_{14}Ru_2$ (1651.51) C, 59.64, H, 6.10. Found: C, 59.88, H, 6.43%.

Data for $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOCFc)_2(NC_5H_4\text{–}OOC\text{–}fc\text{–}C_{12}H_{25})_2]$ (**3**): Yield 83% (225 mg, 0.13 mmol). NMR ^{1}H 400 MHz ($CDCl_3$): 8.97 (d, 4H, H_{pyr}, $J = 5.4$ Hz), 7.50 (d, 4H, H_{pyr}, $J = 5.4$ Hz), 4.97 (t, 4H, HCp, $J = 1.8$ Hz), 4.64 (t, 4H, HCp, $J = 1.6$ Hz), 4.58 (t, 4H, HCp, $J = 1.8$ Hz), 4.27–4.23 (m, 12H, HCp), 4.13 (s, 10H, HCp), 2.38 (t, 4H, $CH_2\mathit{CH_2}$Cp, $J = 8$ Hz), 1.55–1.30 (m, 40H, CH_2), 0.92 (t, 6H, CH_3, $J = 7$ Hz). NMR ^{13}C

100 MHz ($CDCl_3$): 204.96 (4C, CO), 184.11 (2C, COO), 169.43 (2C, COO), 159.21 (2C, C_{pyr}), 153.87 (4C, C_{pyr}), 118.11 (4C, C_{pyr}), 92.18 (2C, CCp), 75.8–73.71–71.71–70.68–70.64–70.60–70.01–69.82–69.30 (18C, CCp), 34.4–32.–31.6–30.1–30.07–29.9–29.8–29.3–26.1–25.4–23.1 (22C, CCp), 14.56 (2C, CH_3). ESI-MS: 1747.25 $[M+Na]^+$. IR (CaF_2, $CHCl_3$): $\nu_{(CO)}$ 2021 (vs), 1970 (m), 1939 (vs), $\nu_{(OCO)}$ 1558 (s) cm^{-1}. *Anal.* Calc. for $C_{82}H_{92}Fe_4N_2O_{12}Ru_2$ (1723.13) C, 57.16; H, 5.38; N, 1.63. Found: C, 58.20; H, 5.81; N, 1.68% $C_{82}H_{92}Fe_4N_2O_{12}Ru_2 \cdot C_6H_{14}$.

Data for $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOC_6H_5)_2(NC_5H_4\text{–}OOC\text{–}fc\text{–}C_{12}H_{25})_2]$ (**4**): Yield 73% (173 mg, 0.11 mmol). NMR ^1H 400 MHz ($CDCl_3$): 9.00 (dd, 4H, H_{pyr}, $J = 5.3$ Hz, $J = 1.4$ Hz), 7.94 (d, 4H, H_{pyr}, $J = 7.4$ Hz), 7.53–7.32 (m, 10H, HPh), 4.97 (t, 4H, HCp, $J = 1.8$ Hz), 4.58 (t, 4H, HCp, $J = 1.8$ Hz), 4.26 (m, 8H, HCp), 2.37 (t, 4H, CH_2Cp, $J = 7.4$ Hz), 1.54 (m, 4H, CH_2CH_2Cp), 1.32–1.26 (m, 18H, $-(CH_2)-$), 0.91 (t, 6H, CH_3, $J = 7$ Hz). NMR ^{13}C 100 MHz ($CDCl_3$): 204.5 (4C, CO), 179.1 (2C, COO–), 169.4 (*C*OO–$_{pyr}$), 159.3 (OC_{pyr}), 153.9 (C_{pyr}), 133.8 (C_{pyr}), 132.0 (4C, C_{ar}), 130.1 (4C, C_{ar}), 128.3 (2C, C_{ar}), 118.3 (2C, C_{pyr}), 92.2 (2C, CCp), 69.8, 70.6, 71.7, 73.7 (8C, CCp), 23.1, 29.2, 29.8, 29.9, 30.06, 30.1, 31.6, 32.3 (22C, CH_2), 14.6 (2C, CH_3). ESI-MS: 1531.3 $[M+Na+H]^+$. IR (CaF_2, $CHCl_3$): $\nu_{(CO)}$ 2025 (vs), 1974 (m), 1941 (vs), $\nu_{(OCO)}$ 1559 (s) cm^{-1}. *Anal.* Calc. for $C_{74}H_{84}Fe_2N_2O_{12}Ru_2$(1507.3) C, 58.97; H, 5.62; N, 1.96. Found: C, 59.33; H, 5.89; N, 1.94%.

3.3. Synthesis of 1-carboxy-1′-dodecylferrocene

1-Carboxy-1′-dodecylferrocene was synthesized similarly to its known tetradecyl analogue [12]. A solution of 1-carbomethoxy-1′-dodecylferrocene (450 mg, 1.1 mmol) and KOH (367 mg, 6.6 mmol) in ethanol (25 mL) was stirred under reflux for 4 h. The solution was cooled to room temperature and poured onto a stirred ice/water mixture. Concentrated HCl was added slowly to acidified pH. The solid which precipitated was recovered by filtration and washed thoroughly with water. Purification of the residue by column chromatography (CH_2Cl_2) gave pure 1-carboxy-1′-dodecylferrocene as a red powder (357 mg, 0.90 mmol). Yield 79%. ESI-MS: $[M-H]^-$ 397; $[2\times M-H]^-$ 794.9; $[2\times M-H+Na]^-$ 817.3. NMR ^1H 400 MHz ($CDCl_3$): 4.80 (s, 2H, HCp), 4.43 (s, 2H, HCp), 4.15 (s, 4H, HCp), 2.30 (t, 2H, Cp–CH_2, $J = 7$ Hz), 1.28 (m, 20H, $-(CH_2)_{10}-$), 0.90 (t, 3H, CH_3, $J = 6$ Hz). NMR ^{13}C 100 MHz ($CDCl_3$): 179.0 (1C, *C*OO), 91.7 (1C, CCp), 72.9 (1C, CCp), 69.7, 70.4, 70.6, 71.5 (8C, CCp), 23.1, 28.7, 29.8, 29.9, 30.08, 30.1, 30.12, 31.5, 32.4 (11C, CH_2), 14.6 (1C, CH_3). IR (CaF_2, $CHCl_3$): 1674 $\nu_{(COO)}$, 1478 $\nu_{(CC)}$, 1274 $\nu_{(CO)}$.

3.4. Synthesis of 1-(4-pyridyloxy)carbonyl-1′-dodecylferrocene NC_5H_4–OOC–fc–$C_{12}H_{25}$

In a pressure Schlenk tube, 1-carboxy-1′-dodecylferrocene (577 mg, 1.45 mmol), *N*,*N*′-dicyclohexylcarbodiimide (460 mg, 2.23 mmol), 4-dimethylaminopyridine (136 mg, 1.12 mmol), 4-pyrrolidinopyridine (83 mg, 0.56 mmol) and 4-hydroxypyridine (212 mg, 2.23 mmol) were introduced together with anhydrous dichloromethane (30 mL). The solution was stirred under nitrogen in the dark at room temperature for 48 h. Then the red solution was slowly filtered through Celite in order to eliminate the dicyclohexylurea. The product was obtained as an orange powder from the filtrate after column chromatography on silica gel using dichloromethane as eluent (442 mg, 0.93 mmol). Yield 64%. ESI-MS: 476 $[M+H]^+$; 477 $[M+2H]^+$. NMR ^1H 400 MHz (CD_3OD): 8.58 (d, 2H, H_{pyr}, $J = 5$ Hz), 7.37 (d, 2H, H_{pyr}, $J = 5$ Hz), 4.85 (s, 2H, HCp), 4.56 (s, 2H, HCp), 4.20 (s, 4H, HCp), 2.30 (t, 2H, Cp–CH_2, $J = 7.6$ Hz), 1.47 (m, 2H, $-(CH_2)-$), 1.25 (m, 18H, $-(CH_2)_9-$), 0.88 (m, 3H, CH_3). NMR ^{13}C 100 MHz (CD_3OD): 170.6 (1C, *C*OO), 160.0 (1C, COO_{-pyr}), 151.9 (2C, C_{pyr}), 118.8 (2C, C_{pyr}), 92.8 (1C, CCp), 70.4, 71.3, 72.3, 74.3 (8C, CCp), 23.7, 29.7, 30.4, 30.5, 30.6, 30.7, 30.8, 32.1, 33.1, 49.3 (12C, CH_2), 14.5 (1C, CH_3). *Anal.* Calc. for $C_{28}H_{37}FeNO_2$ (475.44) C, 70.73, H, 7.84, N, 2.95. Found: C, 70.82, H, 7.83, N, 2.84%.

3.5. Electrochemistry

Electrochemical measurements were carried out with a multipurpose polarograph PA3 interfaced to a Model 4103 XY recorded (both Laboratorní přístroje, Prague) at room temperature using a standard three-electrode cell: rotating (RDE) or stationary platinum disc (1 mm diameter) working electrode, platinum wire auxiliary electrode, and saturated calomel electrode (SCE) reference electrode, separated from the analyzed solution by a salt bridge filled with 0.1 M Bu_4NPF_6 in dichloromethane. The samples were dissolved in dichloromethane (Merck p.a.) to give ca. 5×10^{-4} M concentration of the analyte and 0.1 M Bu_4NPF_6 (supporting electrolyte; Fluka, purissimum for electrochemistry). The samples were deaerated with argon prior to the measurement and then kept under an argon blanket. Cyclic voltammograms were recorded at stationary platinum disc electrode (scan rates 50–500 mV/s), whereas the voltammograms were obtained at rotating disc electrode (500 rpm, scan rates 10–100 mV/s). Redox potentials were given relative to the ferrocene/ferrocenium reference ($E^{\circ\prime} = 0.41$ V versus SCE under the experiment conditions).

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