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

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Abstract

The ferrocenyl-containing diruthenium complexes [Ru₂(CO)₄(μ₂-η²-OOCFc)₂L₂] (Fc = ferrocenyl, fc = ferrocen-1,1′-diyl; 1: L = NC₅H₄–COOC₅H₄–OC₅H₄₂₁, 2: L = NC₅H₄–COOC₅H₄–OC₅H₄₃₃, 3: L = NC₅H₄–OOC–fc–C₅H₅₂₁, 4: L = NC₅H₄–OOC–fc–C₅H₅₃₃) have been synthesized from Ru₂(CO)₁₂, ferrocene carboxylic or benzoic acid and the corresponding pyridine derivative. The synthesis of the new pyridine derivative NC₅H₄–OOC–fc–C₅H₅₂₅ used for the preparation of 3 and 4 is also reported. Complexes 1–4 posses a so-called sawhorse structure consisting of the Ru₂(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 [Ru₂(CO)₄(μ₂-η²-OOCFc)₂L₂] (5: L = NC₅H₄, 6: L = P(C₅H₅)₃, 7: L = NC₅H₄–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 [Ru₂(CO)₄(μ₂-η²-OOCR)₂]ₙ polymers by refluxing Ru₂(CO)₁₂ in the corresponding carboxylic acid and their depolymerisation in coordinating solvents to give dinuclear complexes of the type [Ru₂(CO)₄(μ₂-η²-OOCR)₂L₂], 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 [Ru₂(CO)₄(μ₂-η²-OOCBu⁺)₂PBu′₂]₂ to have a Ru₂(CO)₄ backbone in a sawhorse-type arrangement with two symmetrical μ₂-η²-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 [Ru₂(CO)₄(μ₂-η²-OOC₅H₄₅₃₃)₂L₂], 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 ferrocencarboxylato 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...
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 NC₆H₄–OCOC₂H₅, as well as the electrochemistry of 1–4 and their analogues [Ru₂(CO)₄(μ₂-η²-OCOC₂H₅)L₂] (Fc = ferrocenylium, fc = ferrocen-1,1′-diyl; 5: L = NC₆H₅, 6: L = P(C₆H₅)₃, 7: L = NC₆H₄–OCOC₂H₅) [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 [Ru₂(CO)₄(μ₂-η²-OCOC₂H₅)L₂] (1: L = NC₆H₄–OCOC₂H₅–OC₂H₅–C₂H₅, 2: L = NC₆H₄–COOC₆H₄–OC₁₂H₂₅, 3: L = NC₆H₄–OCOC₂H₅–OC₁₂H₂₅, 5: L = NC₆H₄–OCOC₂H₅–OC₂H₅–C₂H₅) or [Ru₂(CO)₄(μ₂-η²-OCOC₂H₅)L₂][NC₆H₄–OCOC₂H₅–C₂H₅(μ₂-η²-OOCFc)]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 [Ru₂(CO)₄(μ₂-η²-OCOC₂H₅)L₂][NC₆H₄–OC₆H₅(μ₂-η²-OOCFc)]₂ (5), [Ru₂(CO)₄(μ₂-η²-OCOC₂H₅)L₂][P(C₆H₅)₃]₂ (6), [Ru₂(CO)₄(μ₂-η²-OCOC₂H₅)L₂][NC₆H₄–OCOC₂H₅]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 Ru₂ unit and then at the ferrocene units, whereas 5 undergoes first ferrocene/ferrocenium oxidations, followed by the irreversible, Ru₂-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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{pa}$</th>
<th>$E_{pc}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+0.16</td>
<td>+0.23</td>
<td>Ru</td>
</tr>
<tr>
<td></td>
<td>(+0.30)</td>
<td>(+0.30)</td>
<td>Fc</td>
</tr>
<tr>
<td>2</td>
<td>+0.16</td>
<td>+0.09</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>+0.22</td>
<td>(+0.15)</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>+0.66</td>
<td>Ru</td>
<td>follow-up process</td>
</tr>
<tr>
<td></td>
<td>+0.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(+0.17)</td>
<td>(+0.09)</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>(+0.23)</td>
<td>(+0.13)</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>+0.35</td>
<td>+0.24</td>
<td>Fc^d</td>
</tr>
<tr>
<td></td>
<td>+0.65</td>
<td>Ru or follow-up</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(+0.18)</td>
<td>+0.11</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>(+0.17)</td>
<td>+0.23</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>+0.77</td>
<td>Ru</td>
<td>follow-up process</td>
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<tr>
<td></td>
<td>+0.86^e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(+0.18)</td>
<td>+0.11</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>(+0.17)</td>
<td>+0.24</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>+0.86^e</td>
<td>Ru + follow-up process</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(+0.18)</td>
<td>(+0.11)</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>-0.28</td>
<td>+0.18</td>
<td>Fc</td>
</tr>
<tr>
<td></td>
<td>+0.78</td>
<td>Ru</td>
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</tr>
<tr>
<td>7</td>
<td>+0.32</td>
<td>+0.24</td>
<td>Fc^e</td>
</tr>
<tr>
<td></td>
<td>+0.59</td>
<td>Ru</td>
<td></td>
</tr>
</tbody>
</table>

^a Cyclic voltammograms were recorded at platinum disc electrode on ca. $5 \times 10^{-4}$ M dichloromethane solutions containing 0.1 M Bu$_4$NPF$_6$ 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.

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 $\Delta E_p$ 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 ferrocencarboxylic 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
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. Dodecamethylnitiniruthenium [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(µ₂-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 [Ru₂(CO)₄(µ₂-η⁷-COOCF₅)]₂(NCS₄H₄-COO-C₂H₄-OCH₂(OH)₃)₂(1): Yield 90% (209 mg, 0.14 mmol). ¹H NMR (400 MHz, CDCCl₃): 9.15 (d, 4H, Hₚyr, J = 6 Hz), 8.26 (d, 4H, Hₚyr, J = 6 Hz), 6.98–7.23 (m, 8H, H₂ar), 4.60 (s, 4H, HCP), 4.23 (s, 4H, HCP), 4.10 (s, 10H, Hₚyr), 4.01 (t, 4H, OCH₂, J = 6.5 Hz), 1.84 (q, 4H, CH₂, J = 7 Hz), 1.32–1.50 (m, 28H, CH₃), 0.92 (t, 6H, CH₃, J = 6 Hz). ¹³C NMR (100 MHz, CDCCl₃): 104.45 (4C, CO), 184.32 (2C, COO), 163.86 (2C, COO), 157.81 (2C, CO–C₁₀H₂₁), 153.21 (4C, NC), 144.07 (2C, CO–C), 138.50 (2C, C–COO), 124.89 (4C, NCH₂CH₂), 122.48 (4C, COOCCH₂H), 115.70 (4C, COOCCH₂CH₂), 75.47 (2C, C–COO), 70.85–70.55–70.00 (12C, CCP), 68.91 (2C, OCH₂), 32.32–29.99–29.81–29.75–29.67–26.46 (14C, CH₂), 23.11 (2C, CH₃CH₂), 14.55 (2C, CH₃), ESI-MS: 1485.2 [M+2H]⁺. IR (CaF₂, THF): ν(COO) 2027.2 (vs), 1972.3 (m), 1942.2 (vs), ν(COO) 1559.7 (s) cm⁻¹. Anal. Calc. for C₇₀H₁₆8Fe₂N₂O₁₄Ru₂ (1483.19) C, 56.66, H, 5.27, N, 1.80. Found: C, 56.69, H, 5.16, N, 1.89%.

Data for [Ru₂(CO)₄(µ₂-η⁷-COOCF₅)]₂(NCS₄H₄-COO-C₂H₄-OCH₂(OH)₃)₂(2): Yield 90% (232 mg, 0.14 mmol). ¹H NMR (400 MHz, CDCCl₃): 9.15 (d, 4H, Hₚyr, J = 5 Hz), 8.27 (d, 4H, Hₚyr, J = 5 Hz), 7.23 (d, 4H, Hₚyr, J = 9 Hz), 7.01 (d, 4H, Hₚyr, 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, OCH₂, J = 6.5 Hz), 1.85 (q, 4H, CH₂, J = 7 Hz), 1.31–1.51 (m, 52H, CH₂), 0.92 (t, 6H, CH₃, J = 6.6 Hz). ¹³C NMR (100 MHz, CDCCl₃): 204.45 (4C, CO), 184.33 (2C, COO), 163.85 (2C, COO), 157.83 (2C, CO–C₁₀H₂₁), 153.21 (4C, NC), 144.10 (2C, COO–C), 138.52 (2C, C–COO), 124.89 (4C, NCH₂CH₂), 122.47 (4C, COOCCH₂H), 115.70 (4C, COOCCH₂CH₂), 75.47 (2C, C–COO), 70.86–70.57–70.00 (18C, CCP), 68.92 (2C, OCH₂), 32.35–32.00–30.13–30.03–29.83–29.80–26.47–26.03 (24C, CH₂), 23.12 (2C, CH₂CH₂), 14.55 (2C, CH₃), ESI-MS: 1652.6 [M+H]⁺. IR (CaF₂, THF): ν(COO) 2022.9 (vs), 1973.0 (m), 1942.3 (vs), ν(COO) 1557.1 (s) cm⁻¹. Anal. Calc. for C₇₂H₁₇₀Fe₂N₂O₁₄Ru₂ (1651.51) C, 59.64, H, 6.10. Found: C, 59.88, H, 6.43%.

Data for [Ru₂(CO)₄(µ₂-η⁷-COOCF₅)]₂(NCS₄H₄-OOC-fc-C₂H₅₂)₂ (3): Yield 83% (225 mg, 0.13 mmol). NMR ¹H 400 MHz (CDCCl₃): 8.97 (d, 4H, Hₚyr, J = 5.4 Hz), 7.50 (d, 4H, Hₚyr, 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, CH₂CH₂CP, J = 8 Hz), 1.55–1.30 (m, 40H, CH₂), 0.92 (t, 6H, CH₃, J = 7 Hz). NMR ¹³C
100 MHz (CDCl₃): 204.96 (4C, CO), 184.11 (2C, COO), 169.43 (2C, COO), 159.21 (2C, Cₚ₋), 153.87 (4C, Cₚ₋), 118.11 (4C, Cₚ₋), 92.18 (2C, CCP), 75.8–73.71–71.71–70.68–70.64–70.60–70.01–69.82–69.30 (18C, CCP), 34.4–32.31.6–30.1–30.07–29.98–29.83–29.61–25.4–23.1 (22C, CCP), 14.56 (2C, CH₃). ESI-MS: 1747.25 [M+Na⁺]. IR (CaF₂, CHCl₃): ν(ν(O)) = 2021 (vs), 1970 (m), 1899 (vs), ν(CO) 1558 (s) cm⁻¹. Anal. Calc. for C₃₈H₃₂Fe₂N₂O₄Ru₂ (1723.13) C, 57.16; H, 5.38; N, 1.63. Found: C, 58.20; H, 5.81; N, 1.68% C₃₈H₃₂Fe₂N₂O₄Ru₂ · C₄H₁₄.

Data for [Ru₂(CO)₄(dpy]-OC/c₅H₅)s[N(C₅H₄–OOC–fc–C₁₂H₂₅)] (4): Yield 73% (173 mg, 0.11 mmol). NMR ¹H 400 MHz (CDCl₃): 9.00 (dd, 4H, Hₚ₋, J = 5.3 Hz, J = 1.4 Hz), 7.94 (d, 4H, Hₚ₋, 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, CH₂CP, J = 7.4 Hz), 1.54 (m, 4H, CH₂CH₂CH₂CH₂), 1.32–1.26 (m, 18H, (CH₂)₃), 0.91 (t, 6H, CH₃, J = 7 Hz). NMR ¹³C 100 MHz (CDCl₃): 204.5 (4C, CO), 179.1 (2C, COO−), 169.4 (COO−pyr), 159.3 (OCpyr), 153.9 (Cpyr), 133.8 (Cpyr), 132.0 (4C, Cαr), 130.1 (4C, Cαr), 128.3 (2C, Cαr), 118.3 (2C, Cpyr), 92.2 (2C, CCP), 69.8, 70.6, 71.7, 73.7 (8C, CCP), 23.1, 29.2, 29.8, 29.9, 30.06, 31.1, 31.6, 32.3 (22C, CH₃), 14.6 (2C, CH₃). ESI-MS: 1531.3 [M+Na⁺]. IR (CaF₂, CHCl₃): ν(ν(CO)) = 2025 (vs), 1974 (m), 1941 (vs), ν(ν(CO)) = 1559 (s) cm⁻¹. Anal.Calc. for C₃₂H₃₁Fe₂N₂O₄Ru₂: 75.87; H, 5.62; N, 1.96. Found: C, 59.33; H, 5.89; N, 1.94%.

3.3. Synthesis of 1-carboxy-1’-dodecylferroocene

1-Carboxy-1’-dodecylferroocene was synthesized similarly to its known tetradecyl analogue [12]. A solution of 1-carboxymethoxy-1’-dodecylferroocene (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 acidify pH. The solid which precipitated was recovered by filtration and washed thoroughly with water. Purification of the residue by column chromatography (CH₂Cl₂) gave pure 1-carboxy-1’-dodecylferroocene as a red powder (357 mg, 0.90 mmol). Yield 79%. ESI-MS: [M–H]⁻ 397; [2×M–H]⁻ 794.9; [2×M–H+Na⁺] 817.3. NMR ¹H 400 MHz (CDCl₃): 4.80 (s, 2H, HCP), 4.43 (s, 2H, HCP), 4.15 (s, 2H, HCP, 2.30 (t, 2H, C₂H₂), J = 7 Hz), 1.28 (m, 20H, -(CH₂)₃), 0.90 (t, 3H, CH₃, J = 6 Hz). NMR ¹³C 100 MHz (CDCl₃): 179.0 (1C, COO), 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, CH₂), 14.6 (1C, CH₃). IR (CaF₂, CHCl₃): 1674 ν(ν(CO)), 1478 ν(CO), 1274 ν(CC).
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