Ruthenium(II) complexes with ferrocene-modified arene ligands: synthesis and electrochemistry

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Abstract

A series of arene–ruthenium complexes of the general formula [RuCl₂{η⁶-C₅H₅(CH₂)₂R}L] with R = OH, CH₂OH, OC(O)Fc, CH₂OC(O)Fc (Fc = ferrocenyl) and L = PPh₃, (diphenylphosphino)ferrocene, or bridging 1,1’-bis(diphenylphosphino)ferrocene, have been synthesized. Two synthetic pathways have been used for these ferrocene-modified arene–ruthenium complexes: (a) esterification of ferrocene carboxylic acid with 2-(cyclohexa-1,4-dienyl)ethanol, followed by condensation with RuCl₂·nH₂O to afford [RuCl₂{η⁶-C₅H₅(CH₂)₂OC(O)Fc}]₂, and (b) esterification between ferrocene carboxylic acid and [RuCl₂{η⁶-C₅H₅(CH₂)₂OH}L] to give [RuCl₂{η⁶-C₅H₅(CH₂)₂OC(O)Fc}L]. All new compounds have been characterized by NMR and IR spectroscopy as well as by mass spectrometry. The single-crystal X-ray structure analysis of [RuCl₂{η⁶-C₅H₅(CH₂)₂OH}L] shows that the presence of a CH₂CH₂CHOH side-arm allows [RuCl₂{η⁶-C₅H₅(CH₂)₂OH}L] to form an intramolecular hydrogen bond with a chlorine atom. The electrochemical behavior of selected representative compounds has been studied. Complexes with ferrocenylation side arms display the expected cyclic voltammograms, two independent reversible one-electron waves of the Ru(II)/Ru(III) and Fe(II)/Fe(III) redox couples. Introduction of a ferrocenylphosphine onto the ruthenium is reflected by an additional reversible, one-electron wave due to ferrocene/ferrocenium system which is, however, coupled with the Ru(II)/Ru(III) redox system.

Keywords: Arene ligands; Ferrocene derivatives; Phosphine ligands; Ruthenium; Electrochemistry

1. Introduction

Heteronuclear ruthenium complexes with ferrocene-containing ligands such as [Ru(NH₃)₅(NCFc)]²⁻, are known for more than 25 years [1]. However, arene–ruthenium complexes containing chelating bis(phosphinyl)ferrocene ligands have been reported for the first time by Bruce et al. [2]. Since then, other complexes containing ferrocene and arene–ruthenium units have been synthesized by either coordination to metal by a sulfdio, a phosphido or an amido ferrocenyl derivative (for recent examples see [3]), or reaction of terminal ferrocenyl alkynes with the metal center (for recent examples see [4]). Nevertheless, the functionalization of an η⁶-arene ligand by a ferrocenyl group has not received great attention, and examples of such compounds are still rare [5]. Among them we have to mention the work of Hidai and co-workers [6], who have synthesised a ruthenium complex containing a bidentate cyclopentadienyl-modified ferrocenyl phosphine ligand (Scheme 1). In this compound, the cyclopentadienyl moiety is tethered to a phosphine ferrocene derivative in four steps before being activated and finally coordinated to the ruthenium atom. This chiral-at-the-metal complex was used in asymmetric catalysis, but no electrochemical study was performed.

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In this paper, we used two different strategies in order to tether a ferrocenyl moiety to an arene ligand coordinated to a ruthenium atom. Both imply a classical esterification reaction, in which the esterification is done either prior to the coordination of the arene ligand (a), or after the arene coordination (b), as lined out in Scheme 2.

From these two complementary approaches, a wide variety of complexes can be synthesised. Starting from the dinuclear ruthenium complex \([\text{RuCl}_2\{\eta^6-C_6H_6(CH_2)_2OC(O)Fc}\}]_2\), route A, a phosphine ligand (L) can be introduced by cleavage of the chloro bridge, forming the corresponding \([\text{RuCl}_2\{\eta^6-C_6H_6(CH_2)_2OC(O)Fc}\}L\], where in route B, L is introduced prior to the esterification. The use of (diphenylphosphino)ferrocene (FcPPh2) or 1,1'-bis(diphenylphosphino)ferrocene (fc(PPh2)2) as the ligands allow us to introduce an other ferrocene moiety onto the ruthenium atom. This way, we can form heteronuclear complexes possessing as many as three different metallic cores, two different ferrocene centers and one ruthenium.

2. Results and discussion

2.1. Synthesis and characterisation

The dinuclear ruthenium complex \([\text{RuCl}_2\{\eta^6-C_6H_6(CH_2)_2OC(O)Fc}\}]_2\) [7] reacts with two equivalents of PPh3, FePPh2 or with one equivalent of fc(PPh2)2 in dichloromethane to give quantitatively the heteronuclear complexes \([\text{RuCl}_2\{\eta^6-C_6H_6(CH_2)_2OC(O)Fc\}-(PPh3)]\) \((1)\), \([\text{RuCl}_2\{\eta^6-C_6H_6(CH_2)_2OC(O)Fc\}-(FePPh2)]\) \((2)\) and the ferrocene bridged, pentanuclear complex \([\{\text{RuCl}_2\{\eta^6-C_6H_6(CH_2)_2OC(O)Fc\}\}_2(\mu-fc(PPh2)_2)\}]_2\) \((3)\), respectively (Scheme 3). The composition and structure of the products have been determined by \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR, infrared and mass spectrometry.

The formation of complexes 1, 2 and 3 is conveniently monitored by \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopy. The \(^{31}\text{P}\{^1\text{H}\}\) NMR of 1 shows a singlet at 28.6 ppm, the chemical shift being comparable to those observed for the analogous triphenylphosphate (\(\eta^6\)-arene)--ruthenium complexes.

\[\text{COOH}\] \[\text{OH}\] \[\text{RuCl}_3 \cdot n\text{H}_2\text{O}\] \[\text{Fe}\] \[\text{RuCl}_3 \cdot n\text{H}_2\text{O}\] \[\text{Fe}\] \[\text{RuCl}_3 \cdot n\text{H}_2\text{O}\] \[\text{Fe}\]
[RuCl₂(η⁶-C₆H₅Fc)(PPh₃)] [7], and [RuCl₂(η⁶-C₆Et₆) (PPh₃)] [8] which show signals at 28.6 and 24.0 ppm, respectively. The presence of an electron donating ferrocene moiety in 2 and 3 results in an upfield shift of the ³¹P{¹H} NMR signals by almost 10 ppm as compared to complex 1.

In a similar reaction pathway, the dinuclear ruthenium complex [RuCl₂{η⁶-C₆H₅(CH₂)₃OH}][Cl] [9] reacts with phosphine ligands in dichloromethane to give quantitatively [RuCl₂{η⁶-C₆H₅(CH₂)₃OH}(PPh₃)] (4), and the heteronuclear complexes [RuCl₂{η⁶-C₆H₅(CH₂)₃OH}(FePPh₃)] (5) and [{RuCl₂(η⁶-C₆H₅(CH₂)₃OH)}₂(μ-fc(PPh₃)₂)] (6), respectively (Scheme 4). Compounds 4, 5 and 6 have been characterized by NMR and IR spectroscopy, and by mass spectrometry. Complex 4 was first synthesised by Miyaki et al. [9] from the reaction of [Ru{η⁶-C₆H₅(CH₂)₃OH}Cl₂] with triphenylphosphine in CH₂CN. To study its electrochemical behavior, using a slightly different synthetic route, complex 4 was synthesized in excellent yield.

As for complexes 1 to 3, the formation of 4, 5 and 6 is best monitored by ³¹P{¹H} NMR spectroscopy. These complexes exhibit signals at 29.4, 21.4 and 20.9 ppm respectively. All attempts to crystallize complex 5 and 6 have failed, and only the single-crystal X-ray analysis of complex 4 was obtained, see Fig. 1.

The ruthenium atom possesses a pseudo-octahedral geometry, and the metrical parameters around the metallic core compare well with those of similar three-legged piano-stool [Ru(η⁶-arene)(PPh₃)Cl₂] complexes [10]. A distortion at the arene ligand is present, the Ru–C bond distance trans to the phosphorous atom, Ru(1)–C(1) 2.280(5) Å, is elongated as compared to the other Ru–C bonds [ranging between 2.170(4) and 2.249(5) Å]. In the solid state, an intramolecular hydrogen bond between the hydroxy function and a chlorido ligand is observed. The O–Cl distance of the hydrogen bond [O(1)–H···Cl(1)] is 3.121(5) Å with an angle of 159.2°. Complexes 4, as well as 5 and 6 contain a hydroxy function available for esterification by classical method [11].

Complexes 4, 5 and 6 react with ferrocenecarboxylic acid in dichloromethane, in the presence of condensation agents, N,N-dicyclohexylcarbodiimine,
Attempts to crystallize complexes 7, 8 and 9 were unsuccessful. The $^1$H and $^{31}$P($^1$H) NMR spectra of complexes 7, 8 and 9 show the expected signals, being in agreement with the structures proposed in Scheme 5.

Complexes 3, 6, 7 and 9 give rise to the expected molecular peaks $m/z$ at 1568, 1171, 783 and 1595, respectively, which in complexes 1, 4, 5 and 8 the fragments [M–Cl]$^+$ are observed as the most intense peaks. The loss of chlorine atoms have been previously observed for dichloro arene–ruthenium complexes [4c].

2.2. Electrochemistry

The representative and some model compounds (such as ligands and precursors) have been studied by voltammetry and cyclic voltammetry on platinum disc electrode. The relevant data are summarized in Table 1. As revealed by the separation of cyclvoltammetric peaks ($\Delta E_p$ 60–70 mV at 100 mV/s scan rate) and their intensity ratios ($i_{pa}/i_{pc}$) close to unity, the ferrocene/ferrocenium oxidations are in all cases one-electron, reversible redox processes. The nature of Ru-centered oxidations is generally more difficult to judge, as the respective waves are sometimes located at the onset of the base electrolyte decomposition. Nevertheless, where both counter peaks are clearly detectable, the $\delta E_p$ and ($i_{pa}/i_{pc}$) values also point to a normal one-electron, reversible processes.

The redox potential of the Ru$^{II/III}$ couples in complexes 4 and 5 are higher than those observed in the analogous complexes [RuCl$_2$(η$^6$-C$_6$H$_5$)(PPh$_3$)] ($E^0$; Ru: 0.48 V) and [RuCl$_2$(η$^6$-C$_6$H$_5$)(FcPPh$_2$)] ($E^0$; Fe: 0.03, Ru: 0.66 V) [4c], which corresponds to a lower electron donating ability of the η$^6$-arene ligand in 4 and
5. A shift of the Ru$^{II/III}$ redox potential to higher values upon replacing a simple triphenylphosphine with a ferrocenyl phosphine ligand also corresponds well to the mentioned pair and can be accounted for by the preceding oxidation which changes the strongly electron-donating ferrocene substituent at phosphorus into an electron-withdrawing ferrocenium, thus lowering the redox potential to higher values

6. The wave appears at the onset of base electrolyte decomposition; counterwave not clearly detectable.

Efficient compensation of P $\rightarrow$ Ru donation with P $\leftarrow$ Ru back bonding interactions [4c].

A formal introduction of a second ferrocenyl unit in this type of complexes to give ferrocene-carbonyl-modified compounds 1 and 2 is reflected by the presence of an additional, reversible ferrocene/ferrocenium wave, see Fig. 2. The wave appears at the same position for both compounds and is shifted by 30 mV cathodically from the oxidation of FcCO$_2$H. The ferrocenyl group is separated from the $\eta^6$-arene by a non-conjugated tether and behaves as an independent redox system while the ferrocene group within the coordinated phosphine part communicates with the ($\eta^6$-arene)$\rightarrow$ruthenium unit similarly as described for 5 and 6. The Ru$^{II/III}$ and Fe(phosphine)$^{II/III}$ potentials in the pairs of analogous complexes 4–1 and 5–2 differ only insignificantly.

### Table 1

Cyclovoltammetric data.$^a$,$^b$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Couple</th>
<th>$E^0$ (V)</th>
<th>$\delta E_p$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe$^C$</td>
<td>0.23</td>
<td>60</td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td>0.79</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>Fe$^a$</td>
<td>0.11</td>
<td>60</td>
</tr>
<tr>
<td>Fe$^C$</td>
<td></td>
<td>0.23</td>
<td>60</td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td>0.90</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>Ru</td>
<td>0.76</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>Fe$^e$</td>
<td>0.10</td>
<td>70</td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td>0.88</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>Fe$^e$</td>
<td>0.10</td>
<td>70</td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td>0.80–0.83$^d$</td>
<td>70</td>
</tr>
</tbody>
</table>

$^a$The potentials are given relative to internal ferrocene/ferrocenium $E^0$ is redox potential determined by cyclic voltammetry as $E^0 = 1/2(E_p + E_c)$, while $\delta E_p$ stands for the separation of the cyclovoltammetric counter peaks, $E_p = E_p - E_c$. $E_p$ and $E_c$ are the anodic and cathodic peak potentials, respectively. $E^0$ values are identical with the respective half-wave potentials ($E_{1/2}$) determined by voltammetry. For conditions see Section 3.

$^b$Fe = ferrocenyl, Fc = ferrocene-1,1'-diyl, fc(PPh$_3$)$_2$ = 1,1'-bis(dipheny1phosphino)ferrocene.

$^c$Fe$^{II/III}$ or Ru$^{II/III}$ redox couples. For compounds having more ferrocenyl groups, indexes P and C indicate ferrocene/ferrocenium couples in the phosphine and carboxyl part, respectively.

$^d$ $E_p$ given.

$^e$ The wave appears at the onset of base electrolyte decomposition; counterwave not clearly detectable.

Fig. 2. Cyclic voltamograms of complexes 1 (top) and 2 (bottom).
Varian 200 MHz spectrometer. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer (4000–400 cm⁻¹). Microanalyses were carried out 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. The starting dinuclear dichloro complexes [RuCl₂{η⁶-C₆H₅(CH₂)₃O(CO)Fc}]₂ [7] and [Ru{η⁶-C₆H₅(CH₂)₃OH}Cl₂]₂ [9] were prepared according to the published methods. All other reagents were purchased (Fluka or Aldrich) and used as received.

Electrochemical measurements were carried out with a multipurpose polarograph PA3 interfaced to an XY Recorder 4103 (both by Laboratorní prístroje, Prague) at room temperature using a standard three-electrode system: platinum disc working, platinum wire auxiliary, and Ag/AgCl (1 M KCl) reference electrode. The analyzed solutions contained ca. 4 × 10⁻⁴ M of the analyte and 0.1 M Bu₄NPF₆ (Fluka, puriss for electrochemistry) dissolved in dichloromethane (Merck p.a., used without further purification) and were purged with argon. Cyclic voltammograms were recorded on stationary disc electrode at 100 mV/s while the voltammograms were measured with rotating electrode (1000 min⁻¹) at a scan rate of 20 mV/s. The potentials are given in volts relative to the redox potential of the internal ferrocene/ferroceenium standard.

3.2. Syntheses

3.2.1. [RuCl₂{η⁶-C₆H₅(CH₂)₃O(CO)Fc}]₂/L] (1) = L = PPh₃, 2: L = FePPh₃ and [RuCl₂{η⁶-C₆H₅(CH₂)₃O(CO)Fc}]₂/L] (2)

To a solution of [RuCl₂{η⁶-C₆H₅(CH₂)₃O(CO)Fc}]₂ (200 mg, 0.2 mmol) in CH₂Cl₂ (20 ml) was added L (PPh₃ (114 mg, 0.43 mmol), FePPh₃ (155 mg, 0.42 mmol), fcpPPh₃ (116 mg, 0.21 mmol)), and the mixture was stirred for 24 h. The orange-brown precipitate was filtered through celite to eliminate insoluble degradation materials. The solution is evaporated and the solid dried under vacuum to give the product. Yield 153 mg (50%) for 1: Yield 122 mg (35%) for 2: Yield 151 mg (48%) for 3.

3.2.2. Spectroscopic data 1

IR (KBr, cm⁻¹): ν(CH) 3060 (w), 2923 (w); ν(CO) 1710 (s); Fe 1106 (w), 1001 (m); PPh₃ 486 (w). ¹H NMR (200 MHz, CDCl₃, ppm): δ = 7.76 (m, 4H, PPh₃), 7.36 (m, 6H, PPh₃), 5.15 (m, 5H, C₅H₅), 6.44 (s, 2H, C₅H₅), 4.42 (s, 4H, C₅H₅), 4.38 (m, 2H, –OCH₂CH₂ –), 4.31 (s, 2H, C₅H₅), 4.01 (s, 5H, C₅H₅), 3.79 (s, 5H, C₅H₅), 2.88 (m, 2H, –OCH₂CH₂ –). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ = 20.9 ppm. MS (EI mode, CHCl₃): ml/z = 899 [M + Na]. Anal. Calc. for C₅H₅Cl₂Fe₂O₂P: Ru₃: C, 56.19; H, 4.26. Found: C, 56.02; H, 4.38%.

3.2.3. Spectroscopic data 2

IR (KBr, cm⁻¹): ν(CH) 3062 (w), 2925 (m); ν(CO) 1710 (s); Fe 1106 (w), 1001 (m); PPh₃ 486 (w). ¹H NMR (200 MHz, CDCl₃, ppm): δ = 7.76 (m, 4H, PPh₃), 7.36 (m, 6H, PPh₃), 5.15 (m, 5H, C₅H₅), 6.44 (s, 2H, C₅H₅), 4.42 (s, 4H, C₅H₅), 4.38 (m, 2H, –OCH₂CH₂ –), 4.31 (s, 2H, C₅H₅), 4.01 (s, 5H, C₅H₅), 3.79 (s, 5H, C₅H₅), 2.88 (m, 2H, –OCH₂CH₂ –). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ = 20.9 ppm. MS (EI mode, CHCl₃): ml/z = 899 [M + Na]. Anal. Calc. for C₅H₅Cl₂Fe₂O₂P: Ru₃: C, 56.19; H, 4.26. Found: C, 56.02; H, 4.38%.

3.2.4. Spectroscopic data 3

IR (KBr, cm⁻¹): ν(CH) 3053 (w), 2924 (m); ν(CO) 1709 (s); Fe 1096 (w), 1027 (m); PPh₃ 485 (w). ¹H NMR (200 MHz, CDCl₃, ppm): δ = 7.89 (m, 8H, PPh₃), 6.99 (m, 12H, PPh₃), 4.80 (m, 10H, C₅H₅), 4.78 (m, 4H, C₅H₅), 4.70 (m, 4H, C₅H₅), 4.33 (m, 4H, –OCH₂CH₂ –), 4.26 (m, 4H, C₅H₅), 4.02 (m, 4H, C₅H₅), 3.93 (s, 10H, C₅H₅), 2.84 (m, 4H, –OCH₂C H₅ –). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ = 25.5 ppm. MS (EI mode, CHCl₃): ml/z = 1568 [M]. Anal. Calc. for C₅H₅Cl₂Fe₂O₂P: Ru₃: C, 55.19; H, 4.12. Found: C, 55.32; H, 4.60%.

3.2.5. [RuCl₂{η⁶-C₆H₅(CH₂)₅O}]₂(L) (4) = L = PPh₃, 5: L = FePPh₃ and [RuCl₂{η⁶-C₆H₅(CH₂)₅O}]₂(μ-fc/PPh₃) (6)

To a solution of [RuCl₂{η⁶-C₆H₅(CH₂)₅O}]₂ (300 mg, 0.5 mmol) in CH₂Cl₂ (20 ml) was added L (PPh₃ (265 mg, 1.01 mmol), FePPh₃ (378 mg, 1.02 mmol), fcPPh₃ (283 mg, 0.51 mmol)), and the mixture was stirred overnight. The orange-brown precipitate was filtered through celite to eliminate insoluble degradation materials. The solution is evaporated and the solid dried under vacuum to give the product. Yield 465 mg (81%) for 4: Yield 520 mg (75%) for 5: Yield 220 mg (38%) for 6.

3.2.6. Spectroscopic data 4

IR (KBr, cm⁻¹): ν(OH) 3182 (s, br); ν(CH) 3059 (w), 2927 (w); Fe 1093 (m), 999 (w); PPh₃ 527 (w). ¹H NMR (200 MHz, CDCl₃): δ = 7.73 (m, 6H, PPh₃), 7.40 (m, 9H, PPh₃), 5.35 (m, 2H, C₅H₅), 5.13 (m, 2H, C₅H₅), 4.52 (m, 1H, C₅H₅), 3.77 (m, 2H, –CH₂CH₂CH₂OH), 2.79 (m, 2H, –CH₂CH₂CH₂OH), 1.96 (m, 2H, –CH₂CH₂ CH₂OH). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ = 29.4 ppm. MS (ESI, positive mode, acetone): ml/z = 535 [M – Cl]. Anal. Calc. for C₂₇H₂₇Cl₂O₃P₂: Ru₃: C, 56.8; H, 4.77. Found: C, 57.00; H, 4.70%.

3.2.7. Spectroscopic data 5

IR (KBr, cm⁻¹): ν(CH) 3431 (s, br); ν(CH) 3056 (w), 2931 (w); Fe 1097 (s), 1027 (m); PPh₃ 487 (m). ¹H NMR (200 MHz, CDCl₃): δ = 7.79 (m, 4H, PPh₃), 7.41 (m, 6H, PPh₃), 5.21 (m, 2H, C₅H₅), 5.07 (m, 3H, C₅H₅), 4.55 (m, 2H, C₅H₅), 4.38 (m, 2H, C₅H₅), 3.95 (s, 5H, C₅H₅),
3.75 (m, 2H, –CH₂CH₂CH₂OH), 2.70 (m, 2H, –CH₂CH₂CH₂OH), 1.91 (m, 2H, –CH₂CH₂CH₂OH). ¹³P [¹H] NMR (81 MHz, CDCl₃): δ = 21.4 ppm. MS (ESI, positive mode, acetone): m/z = 643 [M–Cl]. Anal. Calc. for C₃H₃Cl₂Fe₂O₂P: Ru₁: C, 54.87; H, 4.60. Found: C, 54.95; H, 4.69%.

3.2.8. Spectroscopic data 6
IR (KBr, cm⁻¹): ν(OH) 3416 (s, br); ν(CH) 3055 (w), 2923 (w); Fe 1095 (m), 1027 (m); PPh₂ 490 (w). ¹H NMR (200 MHz, CDCl₃): δ = 7.58 (m, 8H, PPh₂), 7.44 (m, 12H, PPh₂), 5.98 (t, 2H, C₆H₅), 5.75 (d, 4H, C₆H₅), 5.27 (m, 4H, C₆H₅), 5.17 (d, 4H, C₆H₅), 4.50 (m, 4H, C₆H₅), 3.43 (m, 4H, –CH₂CH₂CH₂OH), 1.63 (m, 4H, –CH₂CH₂CH₂OH). ³¹P [¹H] NMR (81 MHz, CDCl₃): δ = 20.9 ppm. MS (ESI, positive mode, acetone): m/z = 1171 [M]. Anal. Calc. for C₃H₃Cl₂Fe₂O₂P: Ru₂: C, 53.35; H, 4.48. Found: C, 53.42; H, 4.55%.

3.2.9. [RuCl₂(η⁶-C₆H₅(CH₃)₂OC(O)Fc)(L)] (7: L = PPh₃, 8: L = Fe₂PPh₃) and [RuCl₂(η⁶-C₆H₅(CH₃)₃OC(O)Fc)(L)] [μ-fc (PPh₂)] (9)
A solution of ferrocene carboxylic acid (100 mg, 0.43 mmol), N,N-dicyclohexylcarbodiimide (93 mg, 0.45 mmol), 4-(dimethylamino)pyridine (37 mg, 0.3 mmol), 4-pyrrolidinopyridine (45 mg, 0.3 mmol), and [RuCl₂(η⁶-C₆H₅(CH₃)₂OC(O)Fc)] (0.4 mmol of 4 and 5; 0.2 mmol of 6) in CH₂Cl₂ (20 ml) was stirred under nitrogen at room temperature during 3 days. The resulting solution was filtered through celite to remove N,N-dicyclohexylurea, and the solid dried under vacuum to give the product. Yield 135 mg (43%) for 7: Yield 188 mg (53%) for 8: Yield 88 mg (28%) for 9.

3.2.10. Spectroscopic data 7
IR (KBr, cm⁻¹): ν(CH) 3057 (w), 2927 (w); ν(CO) 1708 (s); Fe 1095 (m), 1002 (w); PPh₂ 529 (s). δ = 7.87 (m, 6H, PPh₃), 7.50 (m, 9H, PPh₂), 5.25 (m, 5H, C₆H₅), 4.69 (m, 2H, C₆H₅), 4.53 (m, 2H, C₆H₅), 4.23 (m, 2H, –CH₂CH₂CH₂O–), 4.11 (s, 5H, C₆H₅), 2.95 (m, 2H, –CH₂CH₂CH₂O–), 1.78 (m, 2H, –CH₂CH₂CH₂O–). ³¹P [¹H] NMR (81 MHz, CDCl₃): δ = 28.3 ppm. MS (EI mode, CHCl₃): m/z = 783 [M]. Anal. Calc. for C₃H₃Cl₂Fe₂O₂P: Ru: C, 58.33; H, 4.51. Found: C, 58.56; H, 4.78%.

3.2.11. Spectroscopic data 8
IR (KBr, cm⁻¹): ν(CH) 3066 (w), 2920 (m); ν(CO) 1706 (s); Fe 1111 (w), 1008 (m); PPh₂ 478 (w). ¹H NMR (200 MHz, CDCl₃, ppm): δ = 7.82 (m, 4H, PPh₂), 7.40 (m, 6H, PPh₂), 5.17 (m, 5H, C₆H₅), 4.67 (s, 2H, C₆H₅), 4.44 (s, 4H, C₆H₅), 4.34 (s, 2H, C₆H₅), 4.18 (m, 2H, –CH₂CH₂CH₂O–), 4.03 (s, 5H, C₆H₅), 3.84 (s, 5H, C₆H₅), 2.91 (m, 2H, –CH₂CH₂CH₂O–), 1.83 (m, 2H, –CH₂CH₂CH₂O–). ³¹P [¹H] NMR (81 MHz, CDCl₃): δ = 29.5 ppm. MS (EI mode, CHCl₃): m/z = 855 [M–Cl]. Anal. Calc. for C₃H₃Cl₂Fe₂O₂P: Ru: C, 56.66; H, 4.42. Found: C, 56.32; H, 4.35%.

3.2.12. Spectroscopic data 9
IR (KBr, cm⁻¹): ν(CH) 3057 (w), 2927 (w); ν(CO) 1708 (s); Fe 1095 (m), 1019 (m); PPh₂ 468 (m). ¹H NMR (200 MHz, CDCl₃, ppm): δ = 7.87 (m, 8H, PPh₂), 7.03 (m, 12H, PPh₂), 4.82 (m, 10H, C₆H₅), 4.79 (m, 4H, C₆H₅), 4.65 (m, 4H, C₆H₅), 4.28 (m, 4H, –CH₂CH₂CH₂O–), 4.24 (m, 4H, C₆H₅), 3.99 (m, 4H, C₆H₅), 3.94 (s, 10H, C₆H₅), 2.99 (m, 4H, –CH₂CH₂CH₂O–), 1.79 (m, 4H, –CH₂CH₂CH₂O–). ³¹P [¹H] NMR (81 MHz, CDCl₃): δ = 29.7 ppm. MS (EI mode, CHCl₃): m/z = 1595 [M]. Anal. Calc. for C₃H₃Cl₂Fe₂O₂P: Ru₂: C, 55.73; H, 4.30. Found: C, 55.42; H, 4.12%.

3.3. Structure determinations
X-ray data for [4]: C₇₅H₇₅Cl₂OPRu, M = 570.43 g/mol, monoclinic, P2₁/c (no. 14), a = 16.7409(8), b = 7.8989(3), c = 18.0745(10) Å, β = 93.469(6)°, U = 2385.7(2) Å², T = 153 K, Z = 4, μ (Mo Kα) = 0.967 mm⁻¹, 4622 reflections measured, 3145 unique (R_m = 0.0370) which were used in all calculations. The final wR(F²) was 0.1168 (all data). The data were measured using a Stoe Image Plate Diffraction system equipped with a φ circle, using Mo Kα graphite monochromated radiation (λ = 0.71073 Å) with φ range 0–180°, increment of 0.7°, 3 min per frame, 2θ range from 2.0° to 26°, D_max – D_min = 12.45 – 0.81 Å. The structure was solved by direct methods using the program SHELXS-97 [12]. The refinement and all further calculations were carried out using SHELXL-97 [13]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F². Fig. 2 was drawn with ORTEP [14].

4. Supplementary material
CCDC-216104 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk.
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