

# 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  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{R}\}\text{L}]$  with  $\text{R} = \text{OH}, \text{CH}_2\text{OH}, \text{OC}(\text{O})\text{Fc}$ ,  $\text{CH}_2\text{OC}(\text{O})\text{Fc}$  ( $\text{Fc} = \text{ferrocenyl}$ ) and  $\text{L} = \text{PPh}_3$ , (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  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  to afford  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})\text{Fc}\}]_2$ , and (b) esterification between ferrocene carboxylic acid and  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}\text{L}]$  to give  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OC}(\text{O})\text{Fc}\}\text{L}]$ . 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  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}(\text{PPh}_3)]$  shows that the presence of a  $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  side-arm allows  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}(\text{PPh}_3)]$  to form an intramolecular hydrogen bond with a chlorine atom. The electrochemical behavior of selected representative compounds has been studied. Complexes with ferrocenylated side arms display the expected cyclic voltammograms, two *independent* reversible one-electron waves of the  $\text{Ru}(\text{II})/\text{Ru}(\text{III})$  and  $\text{Fe}(\text{II})/\text{Fe}(\text{III})$  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  $\text{Ru}(\text{II})/\text{Ru}(\text{III})$  redox system.

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

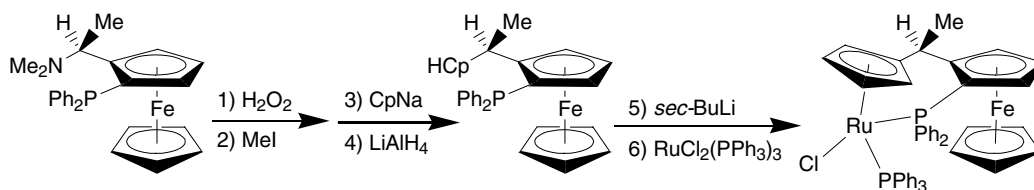
## 1. Introduction

Heteronuclear ruthenium complexes with ferrocene-containing ligands such as  $[\text{Ru}(\text{NH}_3)_5(\text{NCFc})]^{2+}$ , 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

sulfido, 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  $\eta^6$ -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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Scheme 1.

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.

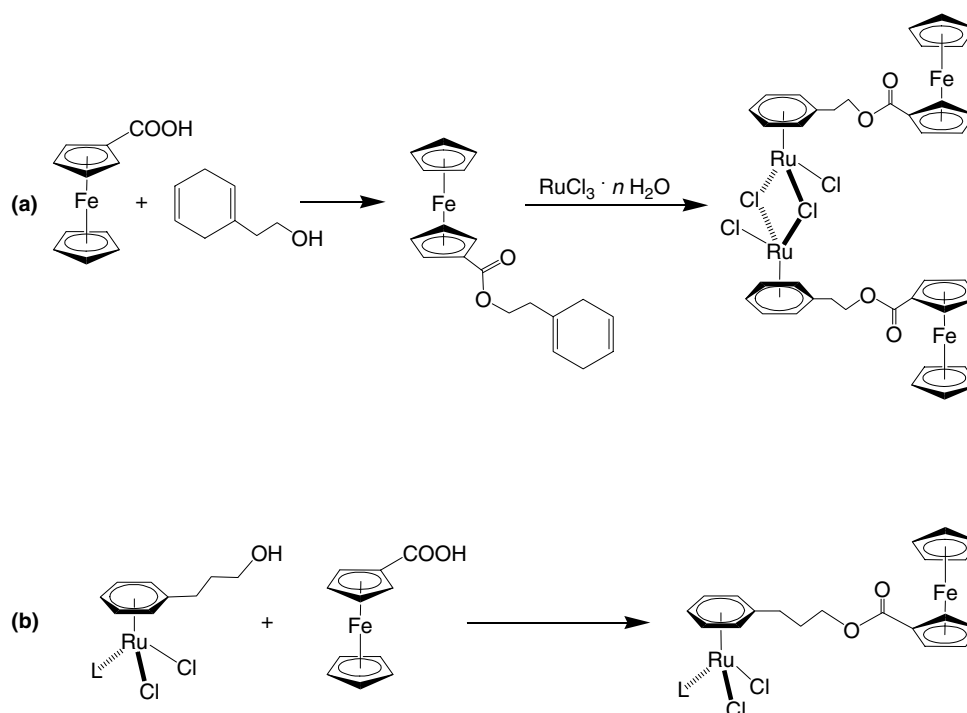
From these two complementary approaches, a wide variety of complexes can be synthesised. Starting from the dinuclear ruthenium complex  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{OC(O)Fc}\}]_2$ , route A, a phosphine ligand (L) can be introduced by cleavage of the chloro bridge, forming the corresponding  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{OC(O)Fc}\}\text{L}]$ , where in route B, L is introduced prior to the esterification. The use of (diphenylphosphino)ferrocene (FcPPh<sub>2</sub>) or 1,1'-bis(diphenylphosphino)ferrocene (fc(PPh<sub>2</sub>)<sub>2</sub>) as the ligands allow us to introduce another 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

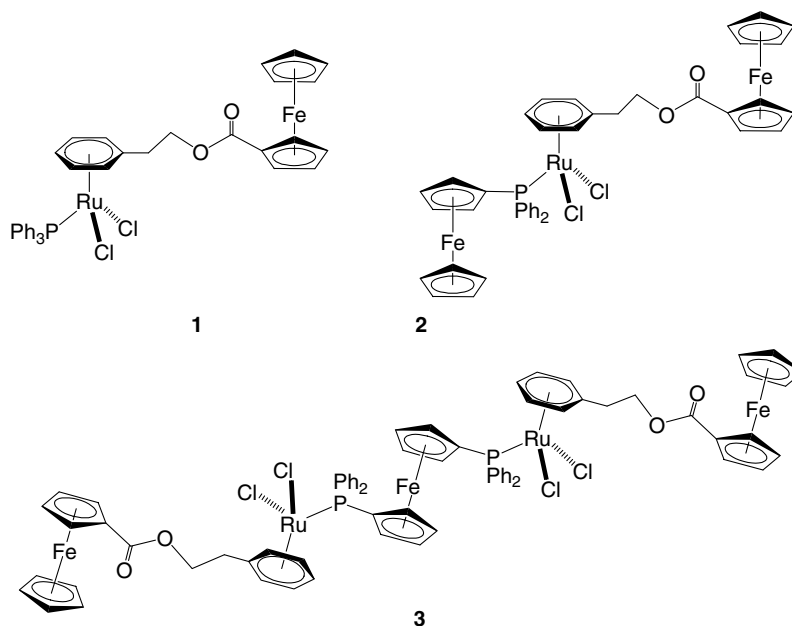
### 2.1. Synthesis and characterisation

The dinuclear ruthenium complex  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{O}(\text{CO})\text{Fc}\}]_2$  [7] reacts with two equivalents of PPh<sub>3</sub>, FcPPh<sub>2</sub> or with one equivalent of fc(PPh<sub>2</sub>)<sub>2</sub> in dichloromethane to give quantitatively the heteronuclear complexes  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{OC(O)Fc}\}\text{-}(\text{PPh}_3)]$  (1),  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{OC(O)Fc}\}\text{(FcPPh}_2)]$  (2) and the ferrocene bridged, pentanuclear complex  $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{OC(O)Fc})\}_2(\mu\text{-fc(PPh}_2)_2)]$  (3), respectively (Scheme 3). The composition and structure of the products have been determined by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR, infrared and mass spectrometry.

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



Scheme 2.



Scheme 3.

$[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{Fc})(\text{PPh}_3)]$  [7], and  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Et}_6)(\text{PPh}_3)]$  [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  $^{31}\text{P}\{^1\text{H}\}$  NMR signals by almost 10 ppm as compared to complex **1**.

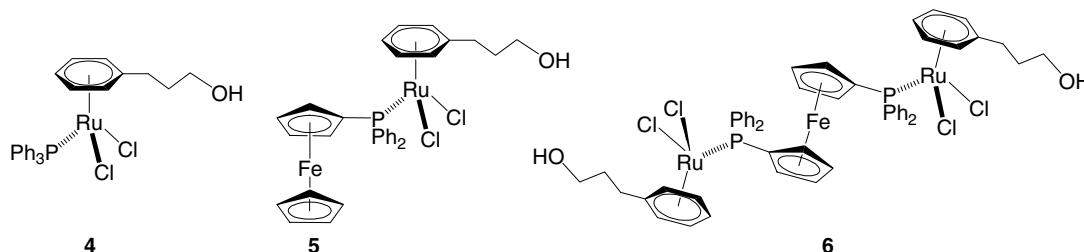
In a similar reaction pathway, the dinuclear ruthenium complex  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}]_2$  [9] reacts with phosphine ligands in dichloromethane to give quantitatively  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}(\text{PPh}_3)]$  (**4**), and the heteronuclear complexes  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}(\text{FcPPh}_2)]$  (**5**) and  $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH})\}_2(\mu\text{-fc}(\text{PPh}_2)_2)]$  (**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  $[\text{Ru}\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}\text{Cl}_2]_2$  with triphenylphosphine in  $\text{CH}_3\text{CN}$ . 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  $^{31}\text{P}\{^1\text{H}\}$  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  $[\text{Ru}(\eta^6\text{-arene})(\text{PPh}_3)\text{Cl}_2]$  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,



Scheme 4.

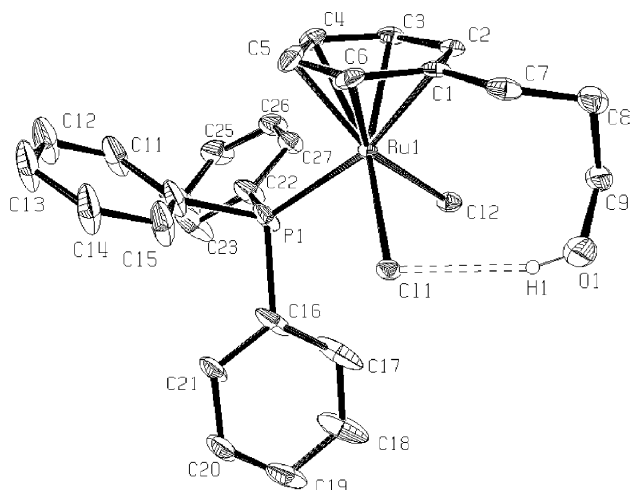


Fig. 1. ORTEP view of **4**, displacement ellipsoids are drawn at the 35% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1) 2.3446(14), Ru(1)–Cl(1) 2.4199(10), Ru(1)–Cl(2) 2.4105(12), Ru(1)–C(1) 2.280(5), Ru(1)–C(2) 2.249(5), Ru(1)–C(3) 2.170(4), Ru(1)–C(4) 2.176(5), Ru(1)–C(5) 2.193(6), Ru(1)–C(6) 2.171(5); P(1)–Ru(1)–Cl(1) 86.21(4), P(1)–Ru(1)–Cl(2) 88.84(6), Cl(1)–Ru(1)–Cl(2) 90.21(4).

4-(dimethyl-amino) pyridine, and 4-pyrrolidinopyridine to give the corresponding ferrocenoyl derivatives,  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OC(O)Fc}\}(\text{PPh}_3)]$  (**7**),  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OC(O)Fc}\}(\text{FcPPh}_2)]$  (**8**) and  $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OC(O)Fc})\}_2(\mu\text{-fc}(\text{PPh}_2)_2)]$  (**9**), see Scheme 5. These new complexes have been characterized unambiguously by NMR, IR and mass spectroscopy.

The infrared spectrum of **7**, **8** and **9** exhibit the characteristic  $\nu_{\text{CO}}$  absorption around  $1710\text{ cm}^{-1}$  of the ester function and a set of bands around  $1100$  and  $1000\text{ cm}^{-1}$  due to the presence of ferrocene moieties. All

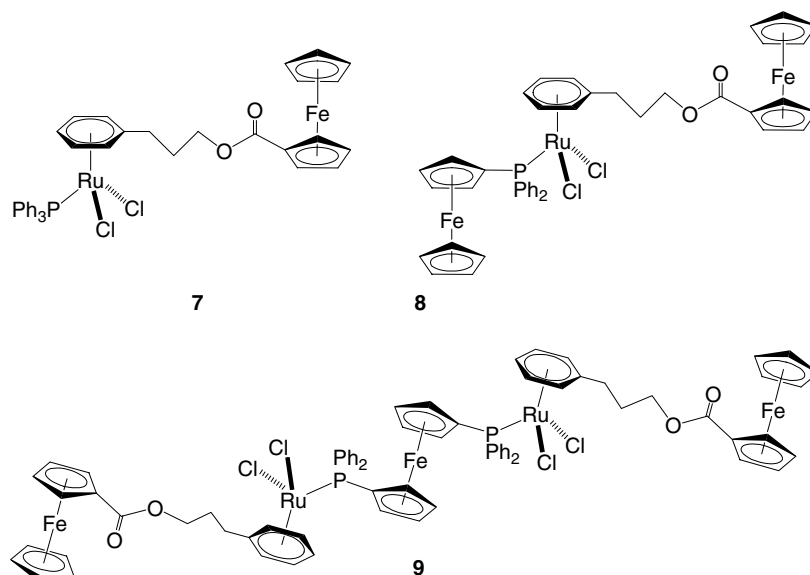
attempts to crystallize complexes **7**, **8** and **9** were unsuccessful. The  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of complexes **7**, **8** and **9** show the expected signals, being in agreement with the structures proposed in Scheme 5.

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  $[\text{M}-\text{Cl}]^+$  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 cyclovoltammetric 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  $\text{Ru}^{\text{II/III}}$  couples in complexes **4** and **5** are higher than those observed in the analogous complexes  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)(\text{PPh}_3)]$  ( $E^0$ ; Ru: 0.48 V) and  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)(\text{FcPPh}_2)]$  ( $E^0$ ; Fe: 0.03, Ru: 0.66 V) [4c], which corresponds to a lower electron donating ability of the  $\eta^6$ -arene ligand in **4** and



Scheme 5.

Table 1  
Cyclic voltammetric data<sup>a,b</sup>

Compound	Couple <sup>c</sup>	$E^0$ (V)	$\delta E_p$ (mV)
<b>1</b>	Fe <sup>C</sup>	0.23	60
	Ru	0.79	70
<b>2</b>	Fe <sup>P</sup>	0.11	60
	Fe <sup>C</sup>	0.23	60
<b>4</b>	Ru	0.90	70
	Ru	0.76	60
<b>5</b>	Fe <sup>P</sup>	0.10	70
	Ru	0.88	70
<b>6</b>	Fe <sup>P</sup>	0.10	70
	Ru	0.80–0.83 <sup>d,e</sup>	70
fc(C(O)O(CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>8</sub> ) <sub>2</sub> <sup>b</sup>	Fe	0.47	70
FcCO <sub>2</sub> H	Fe	0.26	60
fc(CO <sub>2</sub> H) <sub>2</sub> <sup>b</sup>	Fe	0.45 <sup>d</sup>	
FcPPh <sub>2</sub>	Fe	0.11	65
fc(PPh <sub>2</sub> ) <sub>2</sub>	Fe	0.18	60

<sup>a</sup>The potentials are given relative to internal ferrocene/ferrocenium  $E^0$  is redox potential determined by cyclic voltammetry as  $E^0 = 1/2(E_{pa} + E_{pc})$ , while  $\delta E_p$  stands for the separation of the cyclic voltammetric counter peaks,  $\Delta E_p = E_{pa} - E_{pc}$ .  $E_{pa}$  and  $E_{pc}$  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.

<sup>b</sup>Fc = ferrocenyl, fc = ferrocene-1,1'-diyl, fc(PPh<sub>2</sub>)<sub>2</sub> = 1,1'-bis(diphenylphosphino)ferrocene.

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

<sup>d</sup> $E_{pa}$  given.

<sup>e</sup>The wave appears at the onset of base electrolyte decomposition; counterwave not clearly detectable.

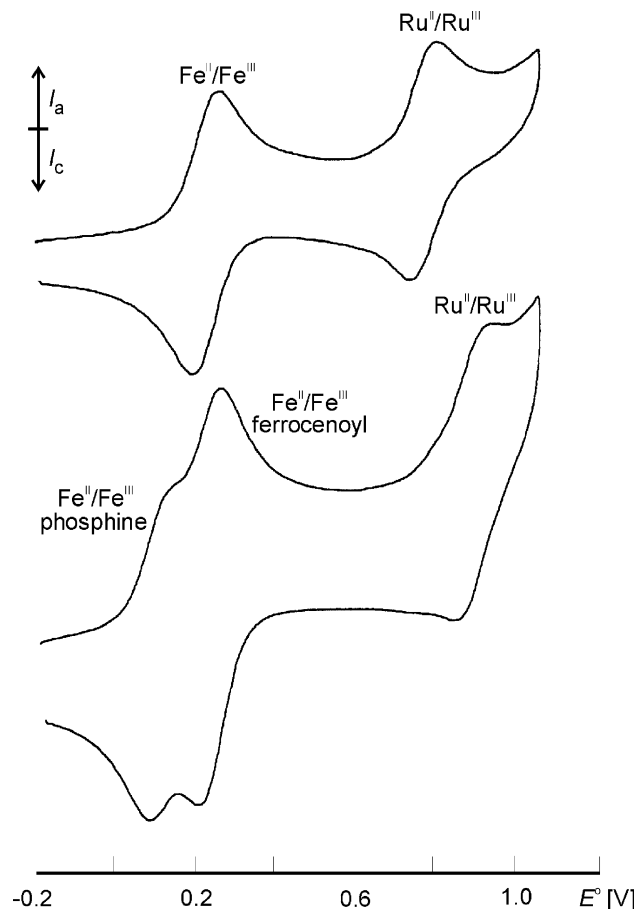


Fig. 2. Cyclic voltammograms of complexes **1** (top) and **2** (bottom).

**5.** A shift of the Ru<sup>II/III</sup> 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 electron density at the ruthenium center and making the Ru-oxidation more difficult. However, the mutual difference of the Ru<sup>II/III</sup> potential is notably lower in the present case (0.12 V) than for the mentioned  $\eta^6$ -C<sub>6</sub>Me<sub>6</sub> complexes (0.18 V).

The presence of a ferrocenyl phosphine in **5** and **6** is naturally reflected by an additional wave due to the ferrocene/ferrocenium couple. Similarly to [RuCl<sub>2</sub>( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)(FcPPh<sub>2</sub>)], the ferrocene/ferrocenium redox potentials in **5** and **6** are nearly identical with those in the corresponding uncoordinated phosphines, which contrasts with the expected behavior that an electron density decrease at phosphorus, due to the coordination to ruthenium, would be relayed further onto the ferrocene unit and result into an increase of its oxidation potential. As it is apparent that the ferrocene and ( $\eta^6$ -arene)-ruthenium units communicate electronically (see above), the negligible potential shift is probably a result of an

efficient compensation of P → Ru donation with P ← 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<sub>2</sub>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)-ruthenium unit similarly as described for **5** and **6**. The Ru<sup>II/III</sup> and Fe(phosphine)<sup>II/III</sup> potentials in the pairs of analogous complexes **4-1** and **5-2** differ only insignificantly.

### 3. Experimental

#### 3.1. General

All manipulations were carried out using freshly distilled CH<sub>2</sub>Cl<sub>2</sub>. NMR spectra were recorded on a

Varian 200 MHz spectrometer. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer (4000–400  $\text{cm}^{-1}$ ). 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  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{O}(\text{CO})\text{Fc}\}]_2$  [7] and  $[\text{Ru}\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}\text{Cl}_2]$  [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 přístroje, 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.  $4 \times 10^{-4}$  M of the analyte and 0.1 M  $\text{Bu}_4\text{NPF}_6$  (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  $\text{min}^{-1}$ ) at a scan rate of 20 mV/s. The potentials are given in volts relative to the redox potential of the internal ferrocene/ferrocenium standard.

## 3.2. Syntheses

3.2.1.  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{O}(\text{CO})\text{Fc}\}L]$  (**1**:  $L = \text{PPh}_3$ , **2**:  $L = \text{FcPPh}_2$ ) and  $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})\text{Fc})\}_2(\mu\text{-fc}(\text{PPh}_2)_2)]$  (**3**)

To a solution of  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{O}(\text{CO})\text{Fc}\}]_2$  (200 mg, 0.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) was added L ( $\text{PPh}_3$  (114 mg, 0.43 mmol),  $\text{FcPPh}_2$  (155 mg, 0.42 mmol),  $\text{fc}(\text{PPh}_2)_2$  (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,  $\text{cm}^{-1}$ ):  $\nu(\text{CH})$  3060 (w), 2923 (w);  $\nu(\text{CO})$  1698 (s); Fc 1095 (m), 999 (w);  $\text{PPh}_3$  526 (s).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.83$  (m, 6H,  $\text{PPh}_3$ ), 7.44 (m, 9H,  $\text{PPh}_3$ ), 5.22 (m, 5H,  $\text{C}_6\text{H}_5$ ), 4.74 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.55 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.43 (m, 2H,  $-\text{OCH}_2\text{CH}_2-$ ), 4.15 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.07 (m, 2H,  $-\text{OCH}_2\text{C}(\text{H}_2)-$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 28.6$  ppm. MS (EI mode,  $\text{CHCl}_3$ ):  $m/z = 733$  [M–Cl]. Anal. Calc. for  $\text{C}_{37}\text{H}_{33}\text{Cl}_2\text{Fe}_1\text{O}_2\text{P}_1\text{Ru}_1$ : C, 57.83; H, 4.33. Found: C, 58.07; H, 4.38%.

### 3.2.3. Spectroscopic data 2

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CH})$  3062 (w), 2925 (m);  $\nu(\text{CO})$  1710 (s); Fc 1106 (w), 1001 (m);  $\text{PPh}_2$  486 (w).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.76$  (m, 4H,  $\text{PPh}_2$ ), 7.36 (m, 6H,  $\text{PPh}_2$ ), 5.15 (m, 5H,  $\text{C}_6\text{H}_5$ ), 4.64 (s, 2H,  $\text{C}_5\text{H}_4$ ), 4.42 (s, 4H,  $\text{C}_5\text{H}_4$ ), 4.38 (m, 2H,  $-\text{OCH}_2\text{CH}_2-$ ), 4.31 (s, 2H,  $\text{C}_5\text{H}_4$ ), 4.01 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.79 (s, 5H,  $\text{C}_5\text{H}_5$ ), 2.88 (m, 2H,  $-\text{OCH}_2\text{CH}_2-$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 20.9$  ppm. MS (EI mode,  $\text{CHCl}_3$ ):  $m/z = 899$  [M+Na]. Anal. Calc. for  $\text{C}_{41}\text{H}_{37}\text{Cl}_2\text{Fe}_2\text{O}_2\text{P}_1\text{Ru}_1$ : C, 56.19; H, 4.26. Found: C, 56.02; H, 4.38%.

### 3.2.4. Spectroscopic data 3

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CH})$  3053 (w), 2924 (m);  $\nu(\text{CO})$  1709 (s); Fc 1096 (w), 1027 (m);  $\text{PPh}_2$  485 (w).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.89$  (m, 8H,  $\text{PPh}_2$ ), 6.99 (m, 12H,  $\text{PPh}_2$ ), 4.80 (m, 10H,  $\text{C}_6\text{H}_5$ ), 4.78 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.70 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.33 (m, 4H,  $-\text{OCH}_2\text{CH}_2-$ ), 4.26 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.02 (m, 4H,  $\text{C}_5\text{H}_4$ ), 3.93 (s, 10H,  $\text{C}_5\text{H}_5$ ), 2.84 (m, 4H,  $-\text{OCH}_2\text{C}(\text{H}_2)-$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 25.5$  ppm. MS (EI mode,  $\text{CHCl}_3$ ):  $m/z = 1568$  [M]. Anal. Calc. for  $\text{C}_{72}\text{H}_{64}\text{Cl}_4\text{Fe}_3\text{O}_4\text{P}_2\text{Ru}_2$ : C, 55.19; H, 4.12. Found: C, 55.32; H, 4.60%.

3.2.5.  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}(L)]$  (**4**:  $L = \text{PPh}_3$ , **5**:  $L = \text{FcPPh}_2$ ) and  $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH})\}_2(\mu\text{-fc}(\text{PPh}_2)_2)]$  (**6**)

To a solution of  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}]_2$  (300 mg, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) was added L ( $\text{PPh}_3$  (265 mg, 1.01 mmol),  $\text{FcPPh}_2$  (378 mg, 1.02 mmol),  $\text{fc}(\text{PPh}_2)_2$  (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,  $\text{cm}^{-1}$ ):  $\nu(\text{OH})$  3182 (s, br);  $\nu(\text{CH})$  3059 (w), 2927 (w); Fc 1093 (m), 999 (w);  $\text{PPh}_3$  527 (w).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.73$  (m, 6H,  $\text{PPh}_3$ ), 7.40 (m, 9H,  $\text{PPh}_3$ ), 5.35 (m, 2H,  $\text{C}_6\text{H}_5$ ), 5.13 (m, 2H,  $\text{C}_6\text{H}_5$ ), 4.52 (m, 1H,  $\text{C}_6\text{H}_5$ ), 3.77 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 2.79 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 1.96 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 29.4$  ppm. MS (ESI, positive mode, acetone):  $m/z = 535$  [M–Cl]. Anal. Calc. for  $\text{C}_{27}\text{H}_{27}\text{Cl}_2\text{O}_1\text{P}_1\text{Ru}_1$ : C, 56.8; H, 4.77. Found: C, 57.00; H, 4.70%.

### 3.2.7. Spectroscopic data 5

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{OH})$  3431 (s, br);  $\nu(\text{CH})$  3056 (w), 2931 (w); Fc 1097 (s), 1027 (m);  $\text{PPh}_2$  487 (m).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.79$  (m, 4H,  $\text{PPh}_2$ ), 7.41 (m, 6H,  $\text{PPh}_2$ ), 5.21 (m, 2H,  $\text{C}_6\text{H}_5$ ), 5.07 (m, 3H,  $\text{C}_6\text{H}_5$ ), 4.55 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.38 (m, 2H,  $\text{C}_5\text{H}_4$ ), 3.95 (s, 5H,  $\text{C}_5\text{H}_5$ ),

3.75 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 2.70 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 1.91 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 21.4$  ppm. MS (ESI, positive mode, acetone):  $m/z = 643$  [M–Cl]. Anal. Calc. for  $\text{C}_{31}\text{H}_{31}\text{Cl}_2\text{Fe}_1\text{O}_1\text{P}_1\text{Ru}_1$ : C, 54.87; H, 4.60. Found: C, 54.95; H, 4.69%.

### 3.2.8. Spectroscopic data 6

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{OH})$  3416 (s, br);  $\nu(\text{CH})$  3055 (w), 2923 (w); Fc 1095 (m), 1027 (m);  $\text{PPh}_2$  490 (w).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.58$  (m, 8H,  $\text{PPh}_2$ ), 7.44 (m, 12H,  $\text{PPh}_2$ ), 5.98 (t, 2H,  $\text{C}_6\text{H}_5$ ), 5.75 (d, 4H,  $\text{C}_6\text{H}_5$ ), 5.27 (m, 4H,  $\text{C}_5\text{H}_4$ ), 5.17 (d, 4H,  $\text{C}_6\text{H}_5$ ), 4.50 (m, 4H,  $\text{C}_5\text{H}_4$ ), 3.43 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 2.36 (t, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 1.63 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 20.9$  ppm. MS (ESI, positive mode, acetone):  $m/z = 1171$  [M]. Anal. Calc. for  $\text{C}_{52}\text{H}_{52}\text{Cl}_4\text{Fe}_1\text{O}_2\text{P}_2\text{Ru}_2$ : C, 53.35; H, 4.48. Found: C, 53.42; H, 4.55%.

### 3.2.9. $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OC}(\text{O})\text{Fc}\}(L)]$ (7: $L = \text{PPh}_3$ , 8: $L = \text{FcPPh}_2$ ) and $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OC}(\text{O})\text{Fc})\}_2(\mu\text{-fc}(\text{PPh}_2)_2)]$ (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  $[\text{RuCl}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}(L)]$  (0.4 mmol of 4 and 5; 0.2 mmol of 6) in  $\text{CH}_2\text{Cl}_2$  (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,  $\text{cm}^{-1}$ ):  $\nu(\text{CH})$  3057 (w), 2927 (w);  $\nu(\text{CO})$  1708 (s); Fc 1096 (m), 1002 (w);  $\text{PPh}_3$  529 (s).  $\delta = 7.87$  (m, 6H,  $\text{PPh}_3$ ), 7.50 (m, 9H,  $\text{PPh}_3$ ), 5.25 (m, 5H,  $\text{C}_6\text{H}_5$ ), 4.69 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.53 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.23 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ), 4.11 (s, 5H,  $\text{C}_5\text{H}_5$ ), 2.95 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ), 1.78 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 28.3$  ppm. MS (EI mode,  $\text{CHCl}_3$ ):  $m/z = 783$  [M]. Anal. Calc. for  $\text{C}_{38}\text{H}_{35}\text{Cl}_2\text{Fe}_1\text{O}_2\text{P}_1\text{Ru}_1$ : C, 58.33; H, 4.51. Found: C, 58.56; H, 4.78%.

### 3.2.11. Spectroscopic data 8

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CH})$  3066 (w), 2920 (m);  $\nu(\text{CO})$  1706 (s); Fc 1111 (w), 1008 (m);  $\text{PPh}_2$  478 (w).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.82$  (m, 4H,  $\text{PPh}_2$ ), 7.40 (m, 6H,  $\text{PPh}_2$ ), 5.17 (m, 5H,  $\text{C}_6\text{H}_5$ ), 4.67 (s, 2H,  $\text{C}_5\text{H}_4$ ),

4.44 (s, 4H,  $\text{C}_5\text{H}_4$ ), 4.34 (s, 2H,  $\text{C}_5\text{H}_4$ ), 4.18 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ), 4.03 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.84 (s, 5H,  $\text{C}_5\text{H}_5$ ), 2.91 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ), 1.83 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 29.5$  ppm. MS (EI mode,  $\text{CHCl}_3$ ):  $m/z = 855$  [M–Cl]. Anal. Calc. for  $\text{C}_{42}\text{H}_{39}\text{Cl}_2\text{Fe}_2\text{O}_2\text{P}_1\text{Ru}_1$ : C, 56.66; H, 4.42. Found: C, 56.32; H, 4.35%.

### 3.2.12. Spectroscopic data 9

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CH})$  3057 (w), 2927 (w);  $\nu(\text{CO})$  1708 (s); Fc 1095 (m), 1019 (m);  $\text{PPh}_2$  468 (m).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.87$  (m, 8H,  $\text{PPh}_2$ ), 7.03 (m, 12H,  $\text{PPh}_2$ ), 4.82 (m, 10H,  $\text{C}_6\text{H}_5$ ), 4.79 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.65 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.28 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ), 4.24 (m, 4H,  $\text{C}_5\text{H}_4$ ), 3.99 (m, 4H,  $\text{C}_5\text{H}_4$ ), 3.94 (s, 10H,  $\text{C}_5\text{H}_5$ ), 2.99 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ), 1.79 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 29.7$  ppm. MS (EI mode,  $\text{CHCl}_3$ ):  $m/z = 1595$  [M]. Anal. Calc. for  $\text{C}_{74}\text{H}_{68}\text{Cl}_4\text{Fe}_3\text{O}_4\text{P}_2\text{Ru}_2$ : C, 55.73; H, 4.30. Found: C, 55.42; H, 4.12%.

## 3.3. Structure determinations

X-ray data for [4]:  $\text{C}_{27}\text{H}_{27}\text{Cl}_2\text{OPRu}$ ,  $M = 570.43$  g/mol, monoclinic,  $P2_1/c$  (no. 14),  $a = 16.7409(8)$ ,  $b = 7.8989(3)$ ,  $c = 18.0745(10)$  Å,  $\beta = 93.469(6)^\circ$ ,  $U = 2385.7(2)$  Å<sup>3</sup>,  $T = 153$  K,  $Z = 4$ ,  $\mu$  (Mo  $K\alpha$ ) =  $0.967$  mm<sup>-1</sup>, 4622 reflections measured, 3145 unique ( $R_{\text{int}} = 0.0370$ ) which were used in all calculations. The final  $wR(F^2)$  was 0.1168 (all data). The data were measured using a Stoe Image Plate Diffraction system equipped with a  $\phi$  circle, using Mo  $K\alpha$  graphite monochromated radiation ( $\lambda = 0.71073$  Å) with  $\phi$  range 0–180°, increment of 0.7°, 3 min per frame,  $2\theta$  range from 2.0° to 26°,  $D_{\text{max}} - D_{\text{min}} = 12.45 - 0.81$  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  $F^2$ . Fig. 2 was drawn with ORTEP [14].

## 4. Supplementary material

CCDC-216104 4 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](http://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](mailto:deposit@ccdc.cam.ac.uk)].

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