

# New mono and dinuclear arene ruthenium chloro complexes containing ester substituents

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## Abstract

The dinuclear arene ruthenium complexes  $[\text{RuCl}_2\{\text{C}_6\text{H}_5(\text{CH}_2)_3\text{OCO-}p\text{-C}_6\text{H}_4\text{-OC}_8\text{H}_{17}\}]_2$  (**1**) and  $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COOCH}_2\text{CH}_3)_2\}]_2$  (**2**) have been obtained by dehydrogenation of the corresponding cyclohexadiene derivative with ruthenium chloride hydrate. The single-crystal X-ray structure analysis of **2** shows the arene ligands to be involved in slipped-parallel  $\pi$ - $\pi$  stacking interactions with neighbouring molecules, thus forming infinite chains along the *b*-axis. The dinuclear complexes **1** and **2** react with two equivalents of triphenylphosphine ( $\text{PPh}_3$ ) to give in excellent yield the corresponding mononuclear phosphine complexes  $[\text{RuCl}_2\{\text{C}_6\text{H}_5(\text{CH}_2)_3\text{OCO-}p\text{-C}_6\text{H}_4\text{-OC}_8\text{H}_{17}\}(\text{PPh}_3)]$  (**3**) and  $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COOCH}_2\text{CH}_3)_2\}(\text{PPh}_3)]$  (**4**), respectively. The single-crystal X-ray structure analysis of **4** reveals the formation of a dimer through two C-H...Cl interactions in the solid state.

*Keywords:* Arene ligands; Chloro bridges; Dinuclear complexes; Phosphine ligands; Ruthenium

## 1. Introduction

The introduction of functionalised arene ligands in arene ruthenium complexes has been motivated mainly by the possibility of using the functionalised side-chain as coordinating group: examples of chelating side-chains at arene ligands include amines [1], alcohols [2], arsines [3], carboxylic acids [4], thioethers [5], and phosphines [6]. However, few examples of functionalised arene ruthenium complexes with non-chelating side-chains are known, they have found applications in arene exchange [6a], electrochemistry [7], polymerisation [8], peptide labelling [4] or resolution of racemates [9]. Therefore, we were interested in the synthesis of mono- and di-functionalised arene ruthenium complexes containing ester substituents as potential entry to the synthesis of metal containing liquid crystals.

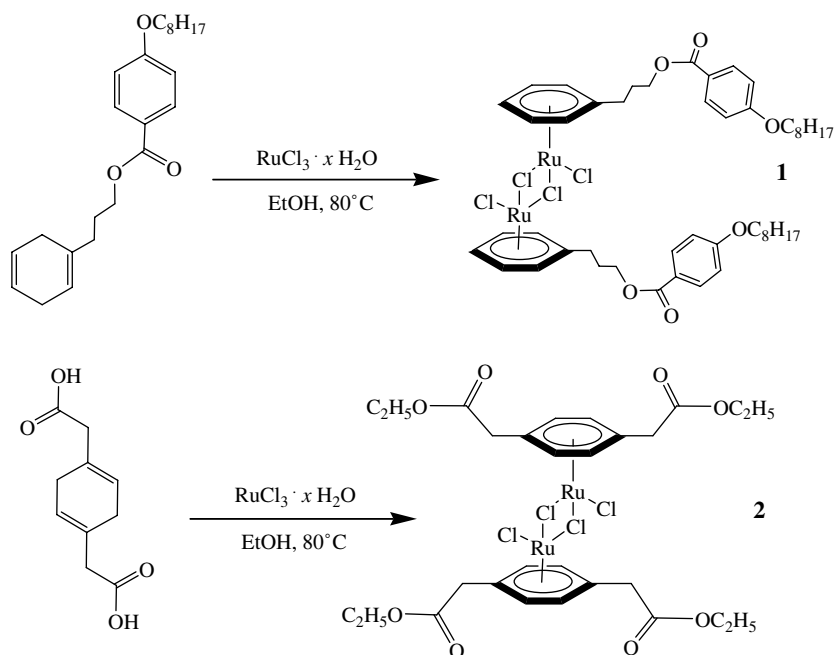
Herein, we report the synthesis and molecular structure of new functionalised dinuclear arene ruthenium complexes containing ester substituents  $[\text{RuCl}_2\{\text{C}_6\text{H}_5(\text{CH}_2)_3\text{OCO-}p\text{-C}_6\text{H}_4\text{-OC}_8\text{H}_{17}\}]_2$  (**1**) and  $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COOCH}_2\text{CH}_3)_2\}]_2$  (**2**), and their corresponding mononuclear triphenylphosphine derivatives  $[\text{RuCl}_2\{\text{C}_6\text{H}_5(\text{CH}_2)_3\text{OCO-}p\text{-C}_6\text{H}_4\text{-OC}_8\text{H}_{17}\}(\text{PPh}_3)]$  (**3**) and  $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COOCH}_2\text{CH}_3)_2\}(\text{PPh}_3)]$  (**4**), respectively. The potential mesomorphism properties of **1** and **3** are discussed, and the single-crystal X-ray structure analyses of **2** and **4** are presented.

## 2. Results and discussion

Two different strategies are used to form functionalised dinuclear arene ruthenium complexes containing ester substituents. Both imply an esterification reaction, in which the esterification is done either prior to the coordination of the arene ligand (**1**), or simultaneously with the coordination of the arene ligand (**2**), see Scheme 1. The dinuclear arene ruthenium complex  $[\text{RuCl}_2\{\text{C}_6\text{H}_5(\text{CH}_2)_3\text{OCO-}p\text{-C}_6\text{H}_4\text{-OC}_8\text{H}_{17}\}]_2$  (**1**) is synthesised by standard dehydrogenation

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of the appropriate cyclohexadiene with  $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$  in refluxing alcohol [10]. 3-(Cyclohexa-1,4-dienyl)propyl-4-(octyloxy)benzoate is prepared by standard esterification method [11] from 3-(cyclohexa-1,4-dienyl)propan-1-ol [2b] and 4-(octyloxy)benzoic acid.

By contrast,  $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COOCH}_2\text{CH}_3)_2\}]_2$  (**2**) is obtained by treatment of cyclohexa-1,4-diene-1,4-dicarboxylic acid with  $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$  in refluxing ethanol. The carboxylic acid functions react with the solvent to form the corresponding di-ester derivative. This particular behaviour has been previously observed during the reaction of cyclohexa-1,4-dienecarboxylic acid with  $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$  in refluxing ethanol, affording the dinuclear complex  $[\text{RuCl}_2(\text{C}_6\text{H}_5\text{CH}_2\text{COOCH}_2\text{CH}_3)_2]$  [4]. Compounds **1** and **2** are air-stable orange solids, which have been unambiguously characterised by  $^1\text{H}$  NMR, infrared and mass spectrometry.

The single-crystal X-ray structure analysis of **2** shows the ruthenium atoms to be in a distorted octahedral geometry, surrounded by the diethyl 2,2'-(1,4-phenylene)diacetate ligand, a terminal chlorine atom and two bridging chlorine atoms. Selected bond lengths and bond angles are given in the caption of Fig. 1. The tethered arms point away from the aromatic plane and the metrical parameters around the metallic cores compare well with those of similar dinuclear arene ruthenium  $[\text{RuCl}_2(\text{arene})]_2$  complexes [6a,12]. The OCO bond angles of the two carboxylate pendants [ $123.9(4)^\circ$  and  $124.3(4)^\circ$ ] differ only slightly from those observed in other functionalised arene ruthenium complexes with ester substituents [6a,6i,8b,13].

The packing arrangement in the crystal is quite interesting. Despite the presence of two side-arms, slipped-parallel  $\pi$ -stacking interactions are observed involving the phenyl

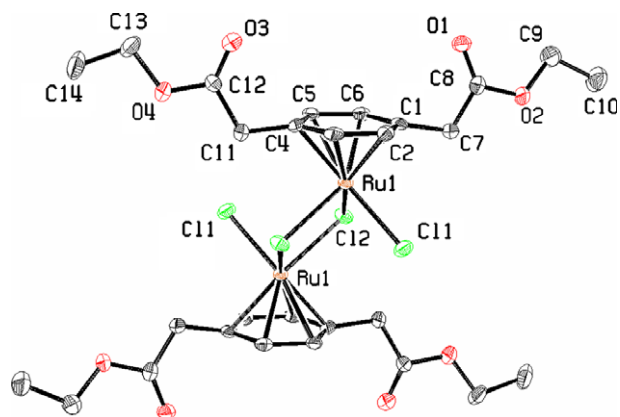


Fig. 1. ORTEP drawing of  $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COOCH}_2\text{CH}_3)_2\}]_2$  (**2**), displacement ellipsoids are drawn at the 50% probability level and the hydrogen atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ):  $\text{Ru}(1)\text{-Ru}(1)^i$  3.662(1),  $\text{Ru}(1)\text{-Cl}(1)$  2.4070(11),  $\text{Ru}(1)\text{-Cl}(2)$  2.4427(12),  $\text{Ru}(1)\text{-Cl}(2)^i$  2.4305(9);  $\text{Ru}(1)\text{-Cl}(2)\text{-Ru}(1)^i$  97.43(4),  $\text{Cl}(1)\text{-Ru}(1)\text{-Cl}(2)$  86.59(4),  $\text{C}(1)\text{-C}(7)\text{-C}(8)$  114.7(3),  $\text{C}(4)\text{-C}(11)\text{-C}(12)$  113.0(3) ( $i = -x, -y, 1-z$ ).

rings of the arene ligands. The  $\pi$ -stacking interacting systems form a series of one-dimensional supramolecular multimers along the  $b$ -axis, see Fig. 2. The distance observed between the  $\pi$ - $\pi$  interacting systems (centroid $\cdots$ centroid 4.21  $\text{\AA}$ ) is slightly longer than the theoretical value calculated for this stacking mode [14].

The dinuclear ruthenium complexes **1** and **2** react with two equivalents of  $\text{PPh}_3$  in dichloromethane to give in excellent yield the mononuclear triphenylphosphine complexes  $[\text{RuCl}_2\{\text{C}_6\text{H}_5(\text{CH}_2)_3\text{OCO}\text{-}p\text{-C}_6\text{H}_4\text{-OC}_8\text{H}_{17}\}(\text{PPh}_3)]$  (**3**) and  $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COOCH}_2\text{CH}_3)_2\}(\text{PPh}_3)]$  (**4**), respectively (Scheme 2). The composition and structure

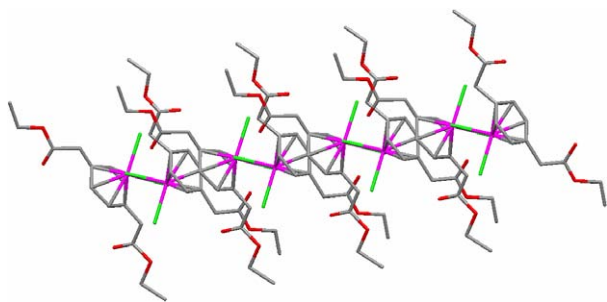


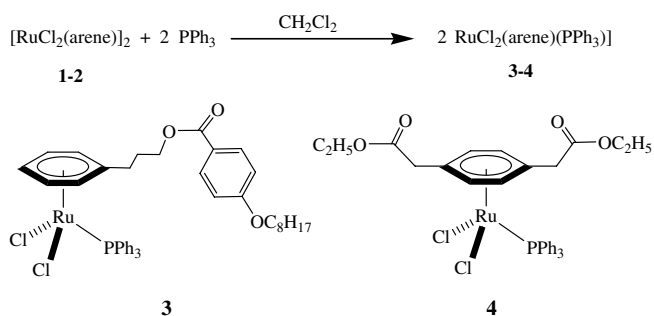
Fig. 2. Part of an infinite chain of **2** along the *b*-axis.

of the products have been determined by  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$  NMR, infrared and mass spectrometry.

The formation of complexes **3** and **4** is conveniently monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Each  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows singlets at 28.7 and 24.2 ppm, respectively, the chemical shift being comparable to those observed for the analogous triphenylphosphine arene ruthenium complexes  $[\text{RuCl}_2(\text{C}_6\text{H}_5\text{Fc})(\text{PPh}_3)]$  (Fc = ferrocene carboxylic acid phenethyl ester) [13] and  $[\text{RuCl}_2(\text{C}_6\text{Et}_6)(\text{PPh}_3)]$  [15] which show signals at 28.6 and 24.0 ppm, respectively. Compound **4** is an orange air-stable crystalline substance, the single-crystal X-ray analysis of which shows the expected molecular structure, see Fig. 3.

Two neighbouring molecules form in the solid state a weak hydrogen-bonded dimer, see Fig. 4. The Cl–C distances of the hydrogen bonds are, respectively, 3.393(9) and 3.613(9) Å, with C–H $\cdots$ Cl angles of 159.0° and 134.3°. The total distance between the two ruthenium atoms is 5.547(2) Å.

The thermal behaviour of **1** and **3** has been studied in view of possible mesomorphic properties. However, both complexes decompose without apparition of liquid crystalline phases. The orange compound **1** decomposes at 205 °C to give a black solid. In the case of **3**, the decomposition occurs at lower temperature (155 °C) and is accompanied by the emergence of dark red bubbles in a liquid phase, suggesting cleavage of the tethered ester chain and formation of a ruthenium compound which is then soaked in the organic liquid phase.



Scheme 2.

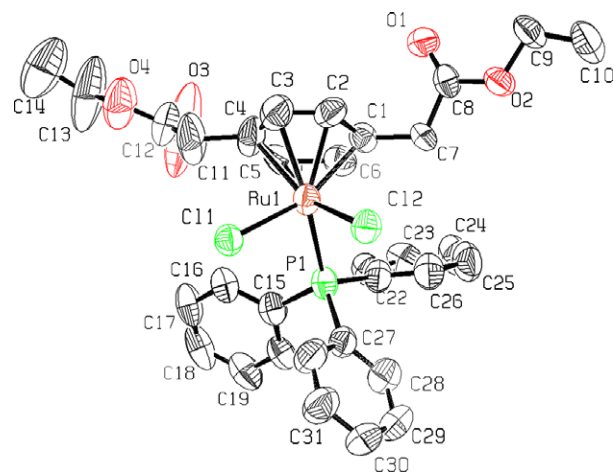


Fig. 3. ORTEP drawing of  $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COOCH}_2\text{CH}_3)_2\}(\text{PPh}_3)]$  (**4**), displacement ellipsoids are drawn at the 50% probability level and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ru(1)–Cl(1) 2.4110(16), Ru(1)–Cl(2) 2.4037(19), Ru(1)–P(1) 2.354(2); Cl(1)–Ru(1)–Cl(2) 89.33(6), P(1)–Ru(1)–Cl(1) 88.37(7), P(1)–Ru(1)–Cl(2) 86.99(7), C(1)–C(7)–C(8) 113.0(6), C(4)–C(11)–C(12) 120.8(9).

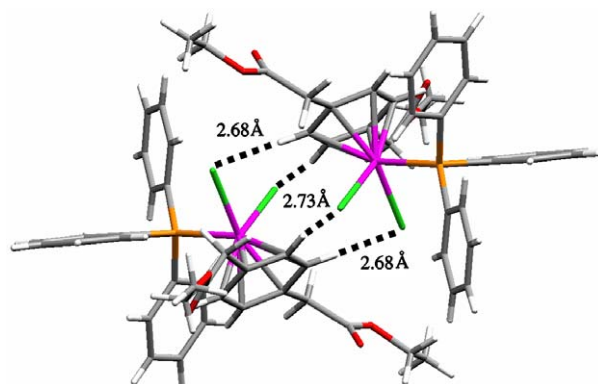


Fig. 4. Hydrogen-bonded network between two symmetry related molecules of **4**.

### 3. Experimental

#### 3.1. General

All organic solvents were degassed and saturated with nitrogen prior to use. 4-(Octyloxy)benzoic acid was purchased from Acros Organics and ruthenium chloride hydrate was generously given by Johnson Matthey. 3-(Cyclohexa-1,4-dienyl)propan-1-ol [2b] and cyclohexa-1,4-diene-1,4-dicarboxylic acid [16] were prepared according to published methods. NMR spectra were recorded on a Varian 200 MHz spectrometer. IR spectra were recorded on a Perkin–Elmer 1720X FT-IR spectrometer (4000–400  $\text{cm}^{-1}$ ). 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.

### 3.2. Syntheses

#### 3.2.1. Synthesis of 3-(cyclohexa-1,4-dienyl)propyl-4-(octyloxy)benzoate

A solution of 4-(octyloxy)benzoic acid (1.8 g, 7.2 mmol), *N,N*-dicyclohexylcarbodiimide (2.24 g, 10.9 mmol), 4-(dimethylamino)pyridine (1.32 g, 10.8 mmol) and (cyclohexa-1,4-dienyl)propan-1-ol (1.0 g, 7.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (80 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 filtrate was concentrated under reduced pressure. A chromatogram of the residue was recorded on a silica gel column, eluting with hexane/ $\text{CH}_2\text{Cl}_2$  (1:1). The pure product was isolated from the first fraction, giving 3-(cyclohexa-1,4-dienyl)propyl-4-(octyloxy)benzoate as a white solid. Yield: 2.54 g (95%).

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.00 (d, 2H), 6.93 (d, 2H), 5.74 (m, 2H), 5.51 (m, 1H), 4.32 (t, 2H), 4.03 (t, 2H), 2.68 (m, 4H), 2.15 (m, 2H), 1.83 (m, 4H), 1.42 (m, 10H), 0.92 (t, 3H); IR (KBr):  $\nu_{(\text{OCO})}$  1716.5  $\text{s cm}^{-1}$ ; ESI-MS: 369.1  $[\text{M}+\text{H}]^+$ . Anal. Calc. for  $\text{C}_{24}\text{H}_{34}\text{O}_3$  (368.51): C, 76.77; H, 9.13. Found: C, 77.20; H, 8.95%.

#### 3.2.2. Synthesis of $[\text{RuCl}_2\{\text{C}_6\text{H}_5(\text{CH}_2)_3\text{OCO}-p\text{-C}_6\text{H}_4\text{-OC}_8\text{H}_{17}\}_2]$ (**1**)

To a solution of ruthenium trichloride hydrate (1.2 g, 4.9 mmol) in ethanol (40 mL) was added 3-(cyclohexa-1,4-dienyl)propyl-4-(octyloxy)benzoate (18.0 g, 49.0 mmol), and the mixture was refluxed for 12 h. The orange precipitate was filtered, washed with ether, and dried under vacuum to give **1**. Yield: 2.44 g (93%).

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.93 (d, 2H), 6.92 (d, 2H), 5.65 (m, 3H), 5.43 (d, 2H), 4.34 (t, 2H), 4.03 (t, 2H), 2.78 (q, 2H), 2.12 (q, 2H), 1.34 (m, 12H), 0.92 (t, 3H); IR (KBr):  $\nu_{(\text{OCO})}$  1715.0  $\text{s cm}^{-1}$ ; ESI-MS: 1047.2  $[\text{M}-\text{Cl}]^+$ . Anal. Calc. for  $\text{C}_{48}\text{H}_{64}\text{Cl}_4\text{O}_6\text{Ru}_2$  (1081.0): C, 53.33; H, 5.97. Found: C, 53.48; H, 6.15%.

#### 3.2.3. Synthesis of $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COO}-\text{CH}_2\text{CH}_3)_2\}_2]$ (**2**)

To a solution of ruthenium trichloride hydrate (1.0 g, 4.1 mmol) in ethanol (40 mL) was added cyclohexa-1,4-diene-1,4-dicarboxylic acid (6.80 g, 40 mmol), and the mixture was refluxed overnight. The orange precipitate was filtered, washed with ether, and dried under vacuum to give **2**. Yield: 1.55 g (90%).

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.50 (s, 8H), 4.17 (q, 8H), 3.69 (s, 8H), 1.28 (t, 12H); IR (KBr):  $\nu_{(\text{OCO})}$  1728.2  $\text{s cm}^{-1}$ ; ESI-MS: 809.0  $[\text{M}-\text{Cl}]^+$ . Anal. Calc. for  $\text{C}_{28}\text{H}_{36}\text{Cl}_4\text{O}_8\text{Ru}_2$  (844.5): C, 39.82; H, 4.30. Found: C, 39.53; H, 4.45%.

#### 3.2.4. Synthesis of $[\text{RuCl}_2\{\text{C}_6\text{H}_5(\text{CH}_2)_3\text{OCO}-p\text{-C}_6\text{H}_4\text{-OC}_8\text{H}_{17}\}(\text{PPh}_3)]$ (**3**)

To a solution of **1** (110 mg, 0.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was added  $\text{PPh}_3$  (55 mg, 0.21 mmol), and the mix-

Table 1  
Crystallographic and selected experimental data of **2** and **4**

Compound	<b>2</b>	<b>4</b>
Chemical formula	$\text{C}_{28}\text{H}_{36}\text{Cl}_4\text{O}_8\text{Ru}_2$	$\text{C}_{32}\text{H}_{33}\text{Cl}_2\text{O}_4\text{PRu}$
Formula weight	844.51	684.52
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal colour and shape	orange and rod	yellow and rod
Crystal size (mm)	$0.45 \times 0.18 \times 0.10$	$0.60 \times 0.40 \times 0.12$
$a$ (Å)	6.3280(12)	10.4018(13)
$b$ (Å)	10.684(2)	12.1841(15)
$c$ (Å)	13.170(3)	13.2542(17)
$\alpha$ (°)	67.41(2)	83.032(15)
$\beta$ (°)	77.33(3)	71.654(14)
$\gamma$ (°)	77.50(2)	70.984(14)
$V$ (Å <sup>3</sup> )	793.4(3)	1507.1(3)
$Z$	1	2
$T$ (K)	173(2)	173(2)
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.768	1.508
$\mu$ ( $\text{mm}^{-1}$ )	1.336	0.786
Scan range (°)	$4.18 < 2\theta < 52.08$	$4.34 < 2\theta < 52.20$
Unique reflections	2899	5527
Reflections used	2329	2309
$[I > 2\sigma(I)]$		
$R_{\text{int}}$	0.0563	0.0903
Final $R$ indices	$R_1 = 0.0294$ ,	$R_1 = 0.0518$ ,
$[I > 2\sigma(I)]$	$wR_2 = 0.0616$	$wR_2 = 0.1126$
$R$ indices (all data)	$R_1 = 0.0464$ ,	$R_1 = 0.1311$ ,
	$wR_2 = 0.0698$	$wR_2 = 0.1341$
Goodness-of-fit	1.014	0.759
Maximum and minimum $\Delta\rho$ ( $\text{e Å}^{-3}$ )	0.718 and $-1.043$	0.480 and $-1.030$

ture was stirred for 5 h. The orange solution was filtered through Celite to eliminate insoluble degradation materials. The solution was evaporated and the solid dried under vacuum to give **3**. Yield: 132 mg (82%).

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.97 (d, 2H), 7.80 (m, 6H), 7.39 (m, 9H), 6.93 (d, 2H), 5.31 (d, 2H), 5.21 (dd, 2H), 4.62 (t, 1H), 4.37 (t, 2H), 4.04 (t, 2H), 2.84 (t, 2H), 2.16 (q, 2H), 1.82 (q, 2H), 1.34 (m, 10H), 0.92 (t, 3H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 28.7; IR (KBr):  $\nu_{(\text{OCO})}$  1699.3  $\text{s cm}^{-1}$ ; ESI-MS: 825.1  $[\text{M}+\text{Na}]^+$ . Anal. Calc. for  $\text{C}_{42}\text{H}_{47}\text{Cl}_2\text{O}_3\text{PRu}$  (802.8): C, 62.84; H, 5.90. Found: C, 63.21; H, 6.14%.

#### 3.2.5. Synthesis of $[\text{RuCl}_2\{p\text{-C}_6\text{H}_4(\text{CH}_2\text{COO}-\text{CH}_2\text{CH}_3)_2\}(\text{PPh}_3)]$ (**4**)

To a solution of **2** (1.0 g, 1.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added  $\text{PPh}_3$  (650 mg, 2.5 mmol), and the mixture was stirred for 6 h. The orange solution was filtered through Celite to eliminate insoluble degradation materials. The solution was evaporated and the solid dried under vacuum to give **4**. Yield: 1.1 g (67%).

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.81 (m, 6H), 7.42 (m, 9H), 5.26 (s, 4H), 4.16 (q, 4H), 3.30 (s, 4H), 1.28 (t, 6H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 24.2; IR (KBr):  $\nu_{(\text{OCO})}$  1726.5  $\text{s cm}^{-1}$ ; ESI-MS: 706.9  $[\text{M}+\text{Na}]^+$ , 649.0  $[\text{M}-\text{Cl}]^+$ . Anal. Calc. for  $\text{C}_{32}\text{H}_{33}\text{Cl}_2\text{O}_4\text{PRu}$  (684.5): C, 56.15; H, 4.86. Found: C, 55.88; H, 4.73%.

### 3.3. X-ray crystallography

Single-crystals of **2** and **4** were mounted on a Stoe Image Plate Diffraction system equipped with a  $\phi$  circle goniometer, using Mo K $\alpha$  graphite monochromated radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with  $\phi$  range 0–200°,  $D_{\text{max}}-D_{\text{min}} = 12.45-0.81 \text{ \AA}$ , increment of 1.8° and 1.2°, respectively. The structures were solved by direct methods using the program SHELXS-97 [17]. The refinement and all further calculations were carried out using SHELXL-97 [18]. In all compounds the hydrogen atoms have been included in calculated positions and treated as riding atoms using the SHELXL default parameters. All non-H atoms were refined anisotropically, using weighted full-matrix least-square on  $F^2$ . Crystallographic details are summarised in Table 1. Figs. 1 and 3 are drawn with ORTEP [19] and Figs. 2 and 4 with MERCURY [20].

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### Appendix A. Supplementary data

CCDC 607156 (**2**) and 607157 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2006.06.006](https://doi.org/10.1016/j.ica.2006.06.006).

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