

Synthesis and molecular structure of the trinuclear ruthenium cluster cations $[\text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})\text{C}_6\text{H}_5\}(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ and $[\text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})(\text{CH}_2)_3\text{C}_6\text{H}_5\}(\text{C}_6\text{Me}_6)_2(\text{O})]^+$

Ludovic Vieille-Petit, Bruno Therrien*, Georg Süss-Fink*

Institut de Chimie, Université de Neuchâtel, Case postale 2, CH-2007 Neuchâtel, Switzerland

Received 4 September 2003; accepted 13 September 2003

Available online 21 November 2003

Abstract

Benzoic acid 2-cyclohexa-1,4-dienyl ethyl ester (**1**), and 4-phenylbutyric acid 2-cyclohexa-1,4-dienyl ethyl ester (**2**) are prepared by reacting, respectively, benzoic acid and 4-phenylbutyric acid with 2-cyclohexa-1,4-dienyl ethanol. These dienyl ester derivatives react with $\text{RuCl}_3 \cdot n \text{H}_2\text{O}$ in refluxing ethanol to afford in good yield $[\text{Ru}\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})\text{C}_6\text{H}_5\}\text{Cl}_2]_2$ (**3**), and $[\text{Ru}\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})(\text{CH}_2)_3\text{C}_6\text{H}_5\}\text{Cl}_2]_2$ (**4**). The trinuclear arene–ruthenium cluster cations $[\text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})\text{C}_6\text{H}_5\}(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**5**), and $[\text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})(\text{CH}_2)_3\text{C}_6\text{H}_5\}(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**6**) are synthesised from the dinuclear precursor $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+$, and the mononuclear complexes $[\text{Ru}\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})\text{C}_6\text{H}_5\}(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Ru}\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})(\text{CH}_2)_3\text{C}_6\text{H}_5\}(\text{H}_2\text{O})_3]^{2+}$, accessible, respectively, from **3** and **4** in aqueous solution. The water-soluble trinuclear cluster cations **5**, and **6** possess a phenyl substituent attach to their side-arm which can act as a substrate for hydrogenation. The single-crystal X-ray structure analyses of **[5][PF₆]**, and **[6][PF₆]** have been determined.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Arene hydrogenation; Cluster catalysis; Intermolecular interactions; Ruthenium

1. Introduction

The complete characterisation of intermediary species involved in a catalytic cycle represents one of the most challenging task in organometallic chemistry. Recently, we have postulated that the water-soluble cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$, active catalyst in the hydrogenation of benzene to cyclohexane under biphasic conditions, to be involved in a catalytic mechanism in which the catalytic reaction occurs within a host–guest complex without prior coordination of the substrate [1,2]. This new catalytic phenomenon, for which we coined the term “supramolecular cluster catalysis”, relies entirely on weak intermolecular interactions between

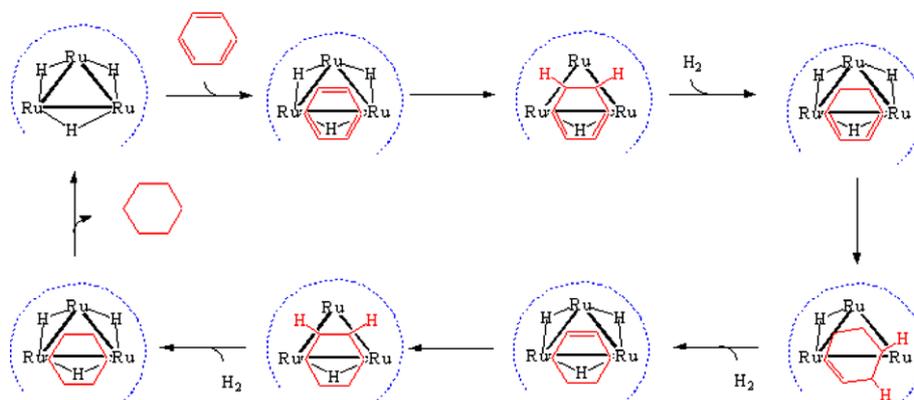
substrate and catalyst molecule, thus violating the mechanistic doctrine of organometallic catalysis [3–5].

The catalytic hydrogenation of benzene, taking place inside the hydrophobic pocket, is supposed to proceed stepwise via the formation of cyclohexadiene and cyclohexene, which are hydrogenated to give cyclohexane, see Scheme 1. High-pressure NMR studies of the hydrogenation of benzene to give cyclohexane, catalysed by the cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$, reveals that the cyclohexadiene and cyclohexene are hydrogenated more rapidly than benzene [6]. The hydrogenation reaction by supramolecular cluster catalysis using $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ under biphasic conditions works not only for benzene but also for not too bulky benzene derivatives [1,2].

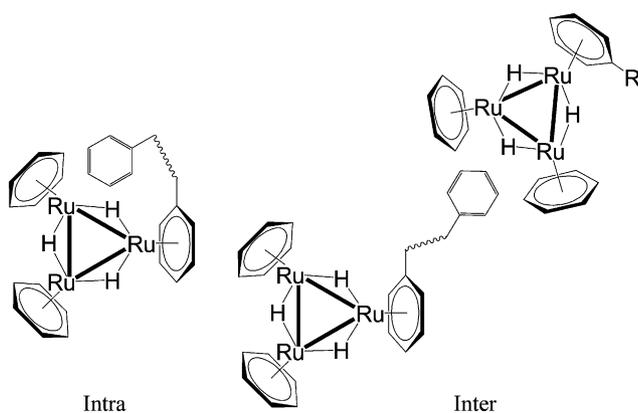
In this context, it was interesting to attach the aromatic substrate to the catalyst molecule and to check if the hydrogenation of the tethered phenyl group occurs by an intra- or inter-molecular process. Changing the length, and flexibility of the side-arm chain can allow the

* Corresponding authors. Tel.: +41-32-718-2499; fax: +41-32-718-2511.

E-mail addresses: bruno.therrien@unine.ch (B. Therrien), georg.suess-fink@unine.ch (G. Süss-Fink).



Scheme 1. Mechanism proposed for the hydrogenation of benzene within the hydrophobic pocket of cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$.



Scheme 2. Intra- and inter-molecular hydrogenation processes.

phenyl group to be hydrogenated via an intra- or inter-molecular processes, see Scheme 2.

Herein, we report the synthesis, characterisation, and hydrogenation activity of the water-soluble cluster cations $[H_3Ru_3\{C_6H_5(CH_2)_2OC(O)C_6H_5\}(C_6Me_6)_2(O)]^+$ (**5**), and $[H_3Ru_3\{C_6H_5(CH_2)_2OC(O)(CH_2)_3C_6H_5\}(C_6Me_6)_2(O)]^+$ (**6**) possessing a side-arm substituent on which is attached a terminal phenyl group. The single-crystal X-ray structure analyses of **[5][PF₆]**, and **[6][PF₆]** have been determined.

2. Experimental

2.1. General

All manipulations were carried out by routine under nitrogen atmosphere. De-ionised water and organic solvents were degassed and saturated with nitrogen prior to use. NMR spectra were recorded using a Varian Gemini 200 BB spectrometer and 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. The starting dinuclear dichloro complexes $[Ru(C_6Me_6)Cl_2]_2$ [7], and $[H_3Ru_2(C_6Me_6)_2]^+$ [8,9] were prepared according to published methods. 2-cyclohexa-1,4-dienyl ethanol was synthesised by sodium reduction of 2-phenyl ethanol in liquid ammonia [10].

2.2. Syntheses

2.2.1. Benzoic acid 2-cyclohexa-1,4-dienyl ethyl ester (**1**) and 4-phenylbutyric acid 2-cyclohexa-1,4-dienyl ethyl ester (**2**)

A solution of benzoic acid (1.25 g, 10.25 mmol) for **1** or 4-phenylbutyric acid (1.70 g, 10.48 mmol) for **2**, *N,N*-dicyclohexylcarbodiimide (3.30 g, 15.99 mmol), 4-(dimethylamino)pyridine (1 g, 8.18 mmol), 4-pyrrolidinopyridine (1.20 g, 8.10 mmol), and 2-cyclohexa-1,4-dienyl ethanol (1 g, 8.06 mmol) in CH_2Cl_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 concentrated under reduced pressure. A chromatogram of the residue was recorded on a silica gel column, eluting with hexane/acetone (10:1). The pure product was isolated from the first fraction, giving **1** or **2** as clear yellow oils. Yield: 1.71 g (93%) for **1**, 2.10 g (95%) for **2**.

Spectroscopic data for **1**: IR (solution in $CHCl_3$, cm^{-1}): $\nu = 1712$ (C=O ester). 1H NMR (200 MHz, $CDCl_3$): $\delta = 8.06$ (m, 2H, H_{ar}), 7.52 (m, 3H, H_{ar}), 5.74 (m, 2H, ethylenic H), 5.59 (m, 1H, ethylenic H), 4.44 (t, 2H, $-OCH_2CH_2-$, $^3J = 13.92$ Hz), 2.73 (m, 4H, $-C=C-CH_2-$), 2.46 (t, 2H, $-OCH_2CH_2-$, $^3J = 13.92$ Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 166.85$, 133.12, 131.40, 130.69, 129.83, 128.61, 124.42, 124.32, 121.28, 63.58, 36.83, 29.41, 27.06. MS (EI mode, acetone): $m/z = 228$ $[M]^+$. Anal. Calc. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.71; H, 6.98%.

Spectroscopic data for **2**: IR (solution in CHCl_3 , cm^{-1}): $\nu = 1732$ (C=O ester). ^1H NMR (200 MHz, acetone- d_6): $\delta = 7.35 - 7.19$ (m, 5H, H_{ar}), 5.73 (m, 2H, ethylenic H), 5.52 (m, 1H, ethylenic H), 4.20 (t, 2H, $-\text{OCH}_2\text{CH}_2-$), 2.72–2.64 (m, 6H, $\text{Ar}-\text{CH}_2\text{CH}_2\text{CH}_2-$ and $-\text{C}=\text{C}-\text{CH}_2-$), 2.39–2.29 (m, 4H, $-\text{OCH}_2\text{CH}_2-$ and $\text{Ar}-\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.98 (m, 2H, $\text{Ar}-\text{CH}_2\text{CH}_2\text{CH}_2-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3): $\delta = 173.75$, 141.72, 131.36, 126.24, 124.39, 124.30, 121.15, 62.81, 36.77, 35.39, 33.93, 29.31, 27.03, 26.83. MS (EI mode, acetone): $m/z = 270$ $[\text{M}]^+$. Anal. Calc. for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 79.96; H, 8.20. Found: C, 79.74; H, 8.13%.

2.2.2. $[\text{Ru}\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})\text{C}_6\text{H}_5\}\text{Cl}_2]_2$ (**3**)

To a solution of ruthenium trichloride hydrate (530 mg, 2.03 mmol) in ethanol (40 ml) was added **1** (1.70 g, 7.46 mmol) and the mixture was refluxed overnight. After cooling to room temperature, half of the volume was evaporated in vacuo. The orange precipitate was filtered, washed with ether, and dried to give pure $[\text{Ru}\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})\text{C}_6\text{H}_5\}\text{Cl}_2]_2$. Yield 750 mg (93%).

Spectroscopic data for **3**: IR (KBr, cm^{-1}): $\nu = 1717$ (C=O ester). ^1H NMR (200 MHz, $\text{dmsO}-d_6$): $\delta = 7.97$ (m, 4H, H_{ar}), 7.71–7.49 (m, 6H, H_{ar}), 6.08–5.95 (m, 8H, $\text{Ru}-\text{C}_6\text{H}_5$), 5.81 (m, 2H, $\text{Ru}-\text{C}_6\text{H}_5$), 4.59 (t, 4H, $-\text{OCH}_2\text{CH}_2-$, $^3J = 12.09$ Hz), 2.93 (t, 4H, $-\text{OCH}_2\text{CH}_2-$, $^3J = 12.09$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, $\text{dmsO}-d_6$): $\delta = 166.22$, 134.16, 129.93, 129.52, 125.34, 103.71, 89.22, 86.94, 84.88, 64.23, 32.83. MS (EI mode, dmsO): $m/z = 760.5$ $[\text{M}-\text{Cl}]^+$. Anal. Calc. for $\text{C}_{30}\text{H}_{28}\text{Cl}_4\text{O}_4\text{Ru}_2$: C, 45.24; H, 3.54. Found: C, 45.12; H, 3.49%.

2.2.3. $[\text{Ru}\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})(\text{CH}_2)_3\text{C}_6\text{H}_5\}\text{Cl}_2]_2$ (**4**)

To a solution of ruthenium trichloride hydrate (485 mg, 1.85 mmol) in ethanol (35 ml) was added **2** (1.90 g, 7.04 mmol) and the mixture was refluxed overnight. After cooling to room temperature, half of the volume was evaporated in vacuo. The orange precipitate was filtered, washed with ether, and dried to give pure $[\text{Ru}\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})(\text{CH}_2)_3\text{C}_6\text{H}_5\}\text{Cl}_2]_2$. Yield: 680 mg (83%).

Spectroscopic data for **4**: IR (KBr, cm^{-1}): $\nu = 1740$ (C=O ester). ^1H NMR (400 MHz, $\text{dmsO}-d_6$): $\delta = 7.28$ (m, 4H, H_{ar}), 7.17 (m, 6H, H_{ar}), 5.98 (m, 6H, $\text{Ru}-\text{C}_6\text{H}_5$), 5.77 (m, 4H, $\text{Ru}-\text{C}_6\text{H}_5$), 4.33 (t, 4H, $-\text{OCH}_2\text{CH}_2-$, $^3J = 6.27$ Hz), 2.77 (t, 4H, $-\text{OCH}_2\text{CH}_2-$, $^3J = 6.27$ Hz), 2.58 (t, 4H, $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2-$), 2.30 (t, 4H, $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.79 (m, 4H, $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{dmsO}-d_6$): $\delta = 173.20$, 142.17, 129.19, 126.73, 105.96, 103.90, 89.27, 86.90, 84.47, 63.31, 37.02, 33.69, 32.91, 26.99. MS (EI mode, dmsO): $m/z = 844.5$ $[\text{M}-\text{Cl}]^+$. Anal. Calc. for $\text{C}_{36}\text{H}_{40}\text{Cl}_4\text{O}_4\text{Ru}_2$: C, 49.10; H, 4.58. Found: C, 49.02; H, 4.53%.

2.2.4. $[\text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})\text{C}_6\text{H}_5\}(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**5**)

To a solution of $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2][\text{BF}_4]$ (70 mg, 0.11 mmol) in acetone (20 ml), and H_2O (10 ml) was added **3** (64 mg, 0.08 mmol). The mixture was heated to 50 °C for 24 h in a closed pressure Schlenk tube. The resulting red solution was filtered through celite and evaporated to dryness; the residue was dissolved in CH_2Cl_2 (10 ml), and purified on silica-gel plates (eluent: $\text{CH}_2\text{Cl}_2/\text{acetone}$ 2:1) to give pure **[5][BF₄]** as red crystalline powder. Red crystals suitable for X-ray analysis were obtained from an acetone/*n*-hexane solution after addition of a small amount of KPF_6 . Yield: 45 mg (43%).

Spectroscopic data for **5**: IR (KBr, cm^{-1}): $\nu = 1716$ (C=O ester). ^1H NMR (400 MHz, acetone- d_6): $\delta = 8.06$ (m, 2H, H_{ar}), 7.69 (m, 1H, H_{ar}), 7.55 (m, 2H, H_{ar}), 5.93 (m, 2H, $\text{Ru}-\text{C}_6\text{H}_5$), 5.62 (m, 3H, $\text{Ru}-\text{C}_6\text{H}_5$), 4.78 (t, 2H, $-\text{OCH}_2\text{CH}_2-$, $^3J = 6.82$ Hz), 2.97 (t, 2H, $-\text{OCH}_2\text{CH}_2-$, $^3J = 6.82$ Hz), 2.32 (s, 36H, $\text{Ru}-\text{C}_6(\text{CH}_3)_6$), -19.20 (d, 2H, $\text{Ru}-\text{Hydride}$, $^2J = 3.84$ Hz), -19.88 (t, 1H, $\text{Ru}-\text{Hydride}$, $^2J = 3.84$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6): $\delta = 166.18$, 133.64, 130.58, 129.72, 129.05, 102.32, 95.13, 85.40, 80.60, 78.85, 64.88, 33.96, 17.54. MS (ESI mode, acetone): $m/z = 874$ $[\text{M} + 2\text{H}]^+$. Anal. Calc. for $\text{C}_{39}\text{H}_{53}\text{B}_1\text{F}_4\text{O}_3\text{Ru}_3$: C, 48.80; H, 5.57. Found: C, 48.64; H, 5.61%.

2.2.5. $[\text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OC}(\text{O})(\text{CH}_2)_3\text{C}_6\text{H}_5\}(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**6**)

To a solution of $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2][\text{BF}_4]$ (145 mg, 0.23 mmol) in acetone (30 ml), and H_2O (15 ml) was added **4** (132 mg, 0.15 mmol). The mixture was heated to 50 °C for 20 h in a closed pressure Schlenk tube. The resulting red solution was filtered through celite and evaporated to dryness; the residue was dissolved in CH_2Cl_2 (10 ml). After chromatography on silica-gel plates (eluent: $\text{CH}_2\text{Cl}_2/\text{acetone}$ 5:2), **[6][BF₄]** was isolated from the most important red fraction. Red crystals suitable for X-ray analysis were obtained from an acetone/*n*-hexane solution after addition of a small amount of KPF_6 . Yield: 46 mg (32%).

Spectroscopic data for **6**: IR (KBr, cm^{-1}): $\nu = 1739$ (C=O ester). ^1H NMR (400 MHz, acetone- d_6): $\delta = 7.31$ (m, 2H, H_{ar}), 7.21 (m, 3H, H_{ar}), 5.91 (m, 2H, $\text{Ru}-\text{C}_6\text{H}_5$), 5.53 (m, 3H, $\text{Ru}-\text{C}_6\text{H}_5$), 4.53 (t, 2H, $-\text{OCH}_2\text{CH}_2-$), 2.81 (t, 2H, $-\text{OCH}_2\text{CH}_2-$), 2.67 (t, 2H, $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2-$), 2.38 (t, 2H, $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2-$), 2.31 (s, 36H, $\text{Ru}-\text{C}_6(\text{CH}_3)_6$), 1.94 (m, 2H, $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2-$), -19.23 (d, 2H, $\text{Ru}-\text{Hydride}$, $^2J = 3.62$ Hz), -19.90 (t, 1H, $\text{Ru}-\text{Hydride}$, $^2J = 3.62$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, acetone- d_6): $\delta = 172.81$, 141.90, 129.46, 127.79, 126.25, 102.25, 94.94, 85.27, 80.26, 78.59, 63.77, 34.96, 33.74, 33.30, 26.88, 16.73. MS (ESI mode, acetone): $m/z = 915$ $[\text{M} + \text{H}]^+$. Anal. Calc. for $\text{C}_{42}\text{H}_{59}\text{B}_1\text{F}_4\text{O}_3\text{Ru}_3$: C, 50.35; H, 5.94. Found: C, 50.23; H, 5.82%.

2.3. Hydrogenation reactions

In a typical experiment, a solution of [5][BF₄] or [6][BF₄] (10 mg) in 10 ml of degassed water was placed in a 100 ml stainless-steel autoclave. After purging four times with hydrogen, the autoclave was pressurised with hydrogen (60 bar) and heated to 80 °C in an oil bath under vigorous stirring. After 3 days, the autoclave was placed in an ice-bath and the pressure released. The aqueous solution containing the cluster was evaporated to dryness under vacuum, and the residue was analysed by NMR and mass spectrometry.

2.4. X-ray crystallography

Crystals of [5][PF₆], and [6][PF₆] were mounted on a Stoe image plate diffraction system equipped with a ϕ circle goniometer, using Mo K α graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–200°, increment of 1.5° and 1.2°, $D_{\max} - D_{\min} = 12.45 - 0.81$ Å. The structures were solved by direct methods using the program SHELXS-97 [11]. The refinement and all further calculations were carried out using SHELXL-97 [12]. In [5][PF₆], and [6][PF₆], the hydrogen atoms have been included in calculated positions and treated as

Table 1
Crystallographic and selected experimental data of [5][PF₆] and [6][PF₆]

	[5][PF ₆] · acetone	[6][PF ₆]
Chemical formula	C ₄₂ H ₅₉ F ₆ O ₄ PRu ₃	C ₄₂ H ₅₉ F ₆ O ₃ PRu ₃
Formula weight	1076.07	1060.07
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Crystal colour and shape	red block	orange plate
Crystal size	0.48 × 0.45 × 0.40	0.25 × 0.25 × 0.08
<i>a</i> (Å)	11.884(1)	10.3849(9)
<i>b</i> (Å)	13.129(1)	14.286(1)
<i>c</i> (Å)	15.166(2)	14.890(1)
α (°)	89.14(1)	84.43(1)
β (°)	74.02(1)	74.50(1)
γ (°)	69.43(1)	84.39(1)
<i>V</i> (Å ³)	2120.9(4)	2112.7(3)
<i>Z</i>	2	2
<i>T</i> (K)	153(2)	293(2)
<i>D_c</i> (g cm ⁻³)	1.685	1.666
μ (mm ⁻¹)	1.159	1.160
Scan range (°)	4.04 < 2 θ < 51.84	4.20 < 2 θ < 51.76
Unique reflections	7683	7642
Reflections used	6261	5876
[<i>I</i> > 2 σ (<i>I</i>)]		
<i>R</i> _{int}	0.0460	0.0728
Final <i>R</i> indices	0.0309, <i>wR</i> ₂ 0.0761	0.0406, <i>wR</i> ₂ 0.1027
[<i>I</i> > 2 σ (<i>I</i>)]		
<i>R</i> indices (all data)	0.0411, <i>wR</i> ₂ 0.0801	0.0532, <i>wR</i> ₂ 0.1077
Goodness-of-fit	0.956	0.934
Maximum, Minimum	0.561, -0.465	0.803, -0.898
$\Delta\rho$ (e Å ⁻³)		

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. Figures were drawn with ORTEP [13].

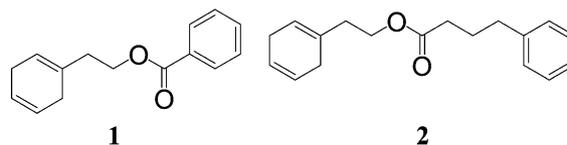
3. Results and discussion

Benzoic acid 2-cyclohexa-1,4-dienyl-ethyl ester (**1**), and 4-phenylbutyric acid 2-cyclohexa-1,4-dienyl-ethyl ester (**2**) are prepared by reacting, respectively, benzoic acid and 4-phenylbutyric acid with 2-cyclohexa-1,4-dienyl-ethanol (see Scheme 3).

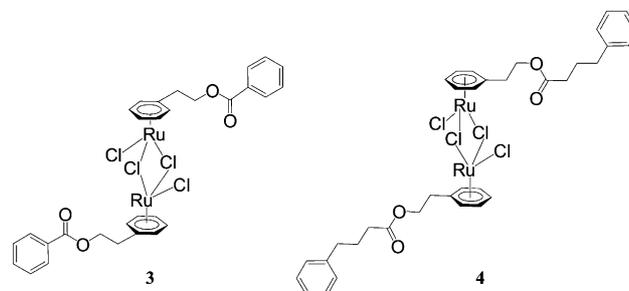
The infrared spectra of **1** and **2** exhibit the characteristic ν_{CO} absorption of the ester function at 1712 and 1732 cm⁻¹, respectively. In the ¹³C{¹H} NMR spectrum, **1** and **2** give rise to a characteristic signal at 167 and 174 ppm corresponding to the CO of the ester function. The dienyl function of **1** and **2** reacts with RuCl₃ · *n* H₂O in refluxing ethanol to afford in good yield [Ru{C₆H₅(CH₂)₂OC(O)C₆H₅}Cl₂]₂ (**3**), and [Ru{C₆H₅(CH₂)₂OC(O)(CH₂)₃C₆H₅}Cl₂]₂ (**4**) (see Scheme 4).

The complexation of the dienyl ester derivatives **1** and **2** to a ruthenium atom in an η^6 -fashion is conveniently monitored by ¹H NMR spectroscopy: the coordinated arene gives rise to a set of signals between 5–6 ppm corresponding to the arene protons.

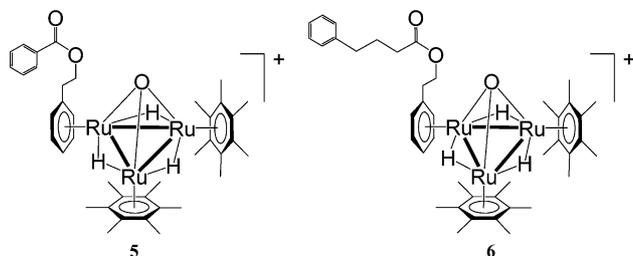
The trinuclear cations [H₃Ru₃{C₆H₅(CH₂)₂OC(O)C₆H₅}(C₆Me₆)₂(O)]⁺ (**5**), and [H₃Ru₃{C₆H₅(CH₂)₂OC(O)(CH₂)₃C₆H₅}(C₆Me₆)₂(O)]⁺ (**6**) have been synthesised in solution (acetone/water) from [Ru{C₆H₅(CH₂)₂OC(O)C₆H₅}(H₂O)₃]²⁺, and [Ru{C₆H₅(CH₂)₂OC(O)(CH₂)₃C₆H₅}(H₂O)₃]²⁺, and from the known dinuclear precursor [H₃Ru₂(C₆Me₆)]⁺ [8,9], see Scheme 5. The ¹H



Scheme 3.



Scheme 4.



Scheme 5.

NMR spectra of **5** and **6** give rise to two hydride signals, a triplet ($\delta = -19.88$ ppm for **5** and -19.90 ppm for **6**) and a doublet ($\delta = -19.20$ ppm for **5** and -19.23 ppm for **6**) integrating for 1 and 2 protons, respectively, and a characteristic singlet at 2.3 ppm for the methyl groups of the hexamethylbenzene ligands, the rest of the signals correspond to the protons of the phenylester–arene–ruthenium moiety.

Clusters **5** and **6**, which possess a phenyl substituent at the end of a tethered side-arm, have been tested in various hydrogenation reaction conditions (60 bar of H_2 , 50–110 °C, 12–72 h) to generate the corresponding cyclohexyl derivatives $[H_3Ru_3\{C_6H_5(CH_2)_2OC(O)C_6H_{11}\}(C_6Me_6)_2(O)]^+$, and $[H_3Ru_3\{C_6H_5(CH_2)_2OC(O)(CH_2)_3C_6H_{11}\}(C_6Me_6)_2(O)]^+$. A modelling study had suggested that, in the case of **5**, the phenyl can be only hydrogenated in the hydrophobic pocket of a neighbouring molecule, whereas in **6** a longer and more flexible chain could as well allow the phenyl substituent to be incorporated into its own hydrophobic pocket, suggesting a possible auto-hydrogenation mechanism, see Scheme 2.

However, compounds $[5][BF_4]$ and $[6][BF_4]$ turned out to be inactive for the hydrogenation of the phenylester group in water, they show partial decomposition without hydrogenation under the conditions; 50–110 °C under 60 bar H_2 during 12–72 h. It appears that mono- and di-nuclear species, among which, we identified by NMR spectroscopy $[H_3Ru_2(C_6Me_6)_2]^+$, are formed during the hydrogenation reaction. The fate of the phenylester–arene–ruthenium moiety is unclear, no decomposition products containing a phenylester group have been identified so far by 1H NMR and mass spectrometry. To gain further insight on the instability of **5** and **6** under hydrogenation conditions, X-ray structure analyses of $[5][PF_6]$ and $[6][PF_6]$ have been performed.

The molecular structure of **5** is shown in Fig. 1. The metal core consists of three ruthenium atoms capped by a μ^3 -oxo ligand. The three hydrido ligands bridging the three ruthenium–ruthenium single bonds were located from a difference Fourier map and their positions fixed. Selected bond lengths and angles are listed in Table 2.

In the crystal structure of $[5][PF_6] \cdot$ acetone, two η^6 - $C_6H_5\{(CH_2)_2OCOC_6H_5\}$ arene ligands of two neigh-

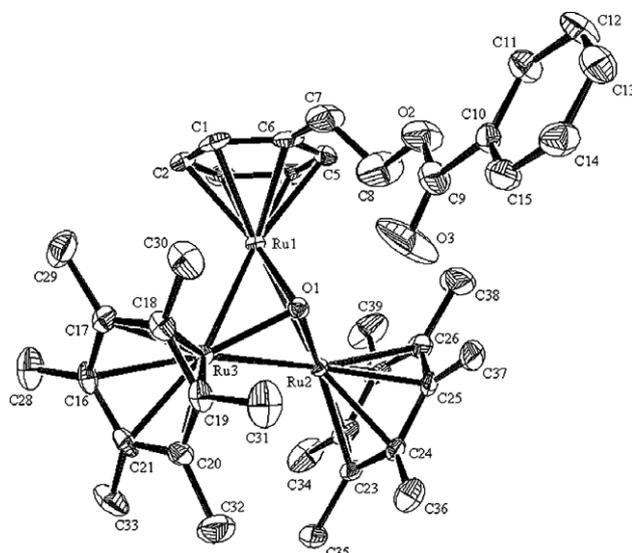


Fig. 1. ORTEP drawing of cation **5**, displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms acetone molecule, and hexafluorophosphate anion are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for $[5][PF_6]$ and $[6][PF_6]$

	$[5][PF_6]$	$[6][PF_6]$
<i>Interatomic distances</i>		
O(1)–Ru(1)	2.007(2)	2.002(3)
O(1)–Ru(2)	2.000(2)	1.993(3)
O(1)–Ru(3)	2.002(2)	1.984(3)
Ru(1)–Ru(2)	2.7473(5)	2.7470(5)
Ru(1)–Ru(3)	2.7489(6)	2.7374(5)
Ru(2)–Ru(3)	2.7791(5)	2.7922(6)
<i>Angles</i>		
Ru(1)–Ru(2)–Ru(3)	59.655(13)	59.225(14)
Ru(1)–Ru(3)–Ru(2)	59.598(13)	59.565(13)
Ru(2)–Ru(1)–Ru(3)	60.748(14)	61.210(15)
Ru(1)–O(1)–Ru(2)	86.58(9)	86.89(11)
Ru(1)–O(1)–Ru(3)	86.58(8)	86.73(12)
Ru(2)–O(1)–Ru(3)	87.95(9)	89.18(11)

bouring molecules form a strong π stacking interactions in a parallel mode, see Fig. 2. The carbon–carbon distances [3.379(5), 3.373(5), and 3.358(5) Å] are in good agreement with the theoretical value calculated for this kind of π stacking [3.77 Å] [14].

The molecular structure of **6** is shown in Fig. 3. The ruthenium atoms possess a pseudo-octahedral geometry, and the metrical parameters around the metallic framework compare well with those of similar $[H_3Ru_3(\eta^6\text{-arene})_3(O)]^+$ tri-nuclear ruthenium cluster cations [15–23]. As in $[5][PF_6]$, the metal core consists of three ruthenium atoms capped by a μ^3 -oxo ligand. Selected bond lengths and angles are listed in Table 2.

In the crystal structure, the phenylester moiety shows no interaction with the triruthenium framework. An intramolecular hydrogen contact is observed between

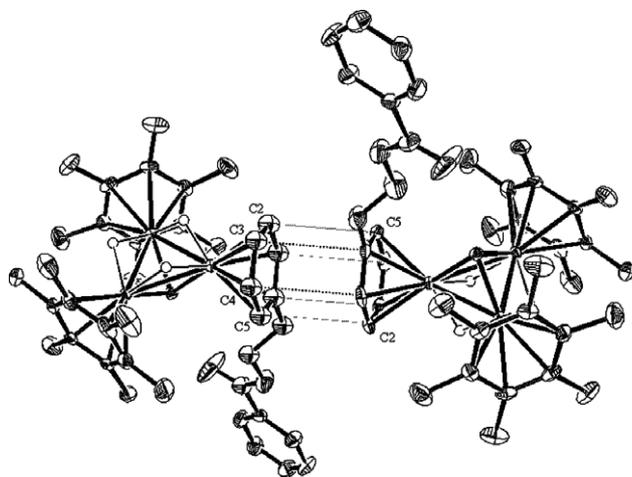


Fig. 2. π interactions in **5**.

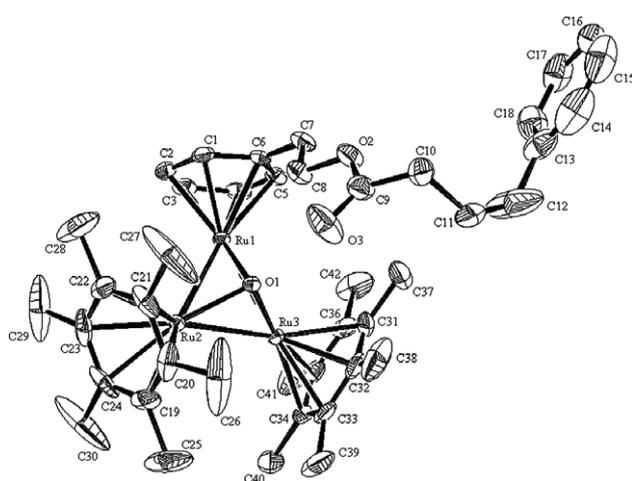


Fig. 3. ORTEP drawing of cation **6**, displacement ellipsoids are drawn at the 25% probability level. Hydrogen atoms, and hexafluorophosphate anion are omitted for clarity.

the C(8) H atom and the μ^3 -O(1), C–O distance 3.112(6) Å with a C–H \cdots O angle of 144°. As in the crystal structure of [5][PF₆]·acetone, two η^6 -C₆H₅{(CH₂)₂OC(CH₂)₃C₆H₅} arene ligands of two neighbouring molecules are forming a π stacking interaction in a parallel mode, carbon–carbon distances 3.520(7), 3.553(7), and 3.556(7) Å.

4. Supplementary material

Full tables of atomic parameters, bond lengths, and angles are deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ,

UK, deposition numbers: [5][PF₆] 218286, [6][PF₆] 218287.

Acknowledgements

The authors are grateful to the Fonds National Suisse de la Recherche Scientifique for financial support. A generous loan of ruthenium chloride hydrate from the Johnson Matthey Technology Centre is gratefully acknowledged.

References

- [1] G. Süss-Fink, M. Faure, T.R. Ward, *Angew. Chem.* 114 (2002) 105.
- [2] G. Süss-Fink, M. Faure, T.R. Ward, *Angew. Chem. Int. Ed.* 41 (2002) 99.
- [3] S. Bhaduri, D. Mukesh, *Homogeneous Catalysis*, Wiley-Interscience, New York, 2000.
- [4] B. Cornils, W.A. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 1996.
- [5] G.W. Parshall, S.D. Ittel, *Homogeneous Catalysis*, Wiley-Interscience, New York, 1992.
- [6] G. Laurency, M. Faure, L. Vieille-Petit, G. Süss-Fink, T.R. Ward, *Adv. Synth. Catal.* 344 (2002) 1073.
- [7] M.A. Bennett, T.-N. Huang, T.W. Matheson, A.K. Smith, *Inorg. Synth.* 21 (1982) 74.
- [8] M.A. Bennett, J.P. Ennett, K.I. Gell, *J. Organomet. Chem.* 233 (1982) C17.
- [9] M.A. Bennett, J.P. Ennett, *Inorg. Chim. Acta* 583 (1992) 198.
- [10] M.E. Kuehne, B.F. Lambert, *Org. Synth.* 5 (1973) 400.
- [11] G.M. Sheldrick, *Acta Cryst.* A46 (1990) 467.
- [12] G.M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, 1999.
- [13] L.J. Farrugia, *J. Appl. Cryst.* 30 (1997) 565.
- [14] S. Tsuzuki, K. Honda, T. Uchamaru, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* 124 (2002) 104.
- [15] H. Suzuki, T. Kakigano, M. Igarashi, A. Usui, K. Noda, M. Oshima, M. Tanaka, Y. Moro-oka, *Chem. Lett.* (1993) 1707.
- [16] G. Meister, G. Rheinwald, H. Stöckli-Evans, G. Süss-Fink, *J. Chem. Soc., Dalton Trans.* (1994) 3215.
- [17] M. Faure, M. Jahncke, A. Neels, H. Stöckli-Evans, G. Süss-Fink, *Polyhedron* 18 (1999) 2679.
- [18] M. Faure, A. Tesouro Vallina, H. Stöckli-Evans, G. Süss-Fink, *J. Organomet. Chem.* 621 (2001) 103.
- [19] L. Vieille-Petit, B. Therrien, G. Süss-Fink, *Inorg. Chim. Acta.* (2003) in press.
- [20] L. Vieille-Petit, B. Therrien, G. Süss-Fink, *Acta Cryst.* E59 (2003) m669.
- [21] L. Vieille-Petit, B. Therrien, G. Süss-Fink, *Eur. J. Inorg. Chem.* (2003) 3707.
- [22] L. Vieille-Petit, B. Therrien, G. Süss-Fink, *Inorg. Chim. Acta.* (2003) in press.
- [23] L. Vieille-Petit, B. Therrien, G. Süss-Fink, T.R. Ward, *J. Organomet. Chem.* 684 (2003) 117.