Catalytic hydrogenation of aromatics under biphasic conditions: isolation and structural characterisation of the cluster intermediate $[(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)Ru_3(\mu_2\text{-}H)_2(\mu_2\text{-}OH)(\mu_3\text{-}O)]^+$

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Abstract

The water-soluble cluster cation $[(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ (**2**) catalyses the hydrogenation of benzene and benzene derivatives to give the corresponding cyclohexanes under biphasic conditions. The catalytic activity of **2** depends markedly on the substrate, an extremely high activity being observed for ethylbenzene. The cationic species present in the catalytic mixture of the ethylbenzene hydrogenation could be isolated as the tetrafluoroborate salt and characterised as the cation $[(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)Ru_3(\mu_2\text{-}H)_2(\mu_2\text{-}OH)(\mu_3\text{-}O)]^+$ (**3**). With **3** as the catalyst, the catalytic activity is also much higher for other benzene derivatives. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Water has become an attractive solvent for catalytic reactions, since the first industrial implementation of a biphasic propylene hydroformylation process catalysed by water-soluble rhodium phosphine complexes in a 100 000 t per year oxo plant (Ruhrchemie/Rhône–Poulenc) in 1984 proved to be successful [1]. As a consequence, aqueous-phase organometallic catalysis became a major issue of both applied and fundamental research [2]. Water is not only a cheap and environmentally friendly solvent, it also allows, in biphasic systems, the facile separation of the catalyst, remaining in the aqueous phase, from the products and the substrate being in the organic phase, thus overcoming the cardinal problem of homogeneous catalysis.

We have recently found that benzene and benzene derivatives are efficiently hydrogenated to the corresponding cyclohexanes under biphasic conditions, catalysed by benzene ruthenium complexes such as $(\eta^6\text{-}C_6H_6)_2Ru_2Cl_4$ [3], $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]Cl_2$ or $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]Cl_2$ [4], dissolved in water. In all cases, we were able to detect the trinuclear oxo-capped cation $[(\eta^6\text{-}C_6H_6)_3Ru_3(\mu_2\text{-}H)_2(\mu_2\text{-}Cl)(\mu_3\text{-}O)]^+$ (**1**) in the reaction mixture [3]. This cation, which we had isolated and characterised as the perchlorate salt [5], is considered to be the catalytically active species, since the isolated perchlorate salt of **1** is much more active in aqueous solution than any other benzene ruthenium precursor [3]. Unfortunately, under the catalytic conditions (hydrogen pressure), the trinuclear cluster cation **1** is not stable: it is converted into a mixture of the tetranuclear cluster cations $[(\eta^6\text{-arene})_4Ru_4H_4]^{2+}$ and $[(\eta^6\text{-arene})_4Ru_4H_6]^{2+}$.

Since the corresponding tetranuclear hydrido clusters are not accessible with the sterically hindered hexamethylbenzene ligand [6], we intended to design a cationic trinuclear oxo-capped cluster which is an active hydrogenation catalyst in aqueous solution, while being stable under hydrogen pressure (catalytic conditions). This aim was achieved by the synthesis of the mixed-ligand cluster cation $[(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ (**2**), accessible from $[(\eta^6\text{-}C_6H_6)_2Ru_3(H_2O)_3]^{2+}$ with $[(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_2\text{-}H)_3]^+$ in aqueous solution [7]. Cation **2** is indeed catalytically active for the hydrogenation of aromatic compounds under biphasic condi-

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tions and does not convert into a tetranuclear cluster; it is found intact at the end of the catalytic reaction [7].

To our surprise, we observed an unusually high catalytic activity of **2** for the hydrogenation of ethylbenzene to give ethylcyclohexane under biphasic conditions (110°C, 60 bar): A catalytic turnover of 850 cycles is achieved after just 15 min, whereas several hours are required for a similar turnover number of benzene, toluene, *n*- and *i*-propylbenzene. Only in the case of ethylbenzene could the cluster cation **2** not be recovered at the end of the catalytic reaction; it had changed into a more active species. We therefore decided to study in detail the reaction of **2** with ethylbenzene and hydrogen in water and to characterise the species formed.

2. Results and discussion

The reaction of $[(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ (**2**) with ethylbenzene under hydrogen pressure in aqueous solution results in the formation of the trinuclear cluster $[(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)Ru_3(\mu_2\text{-}H)_2(\mu_2\text{-}OH)(\mu_3\text{-}O)]^+$ (**3**) according to Scheme 1. The reaction is carried out at room temperature in neutral solution (pH 6–7) over a period of 2 h. Cation **3** crystallises from acetone as the tetrafluoroborate salt.
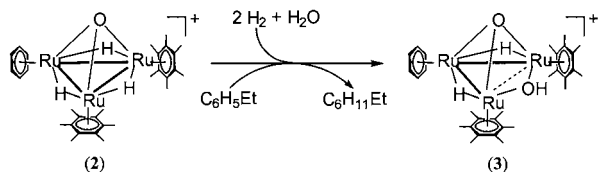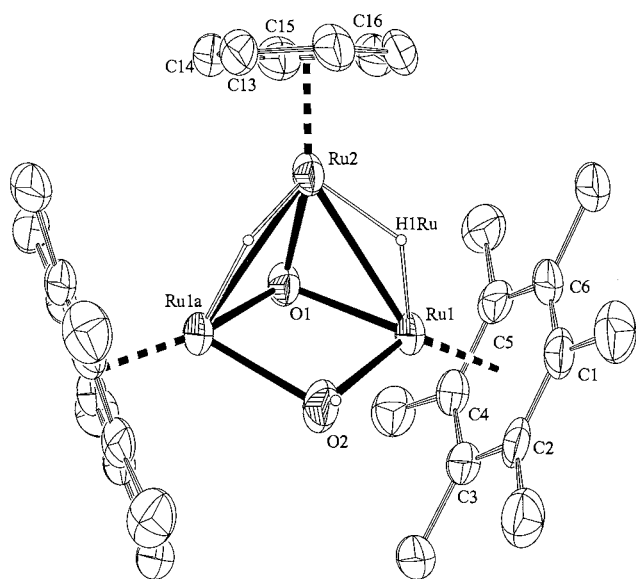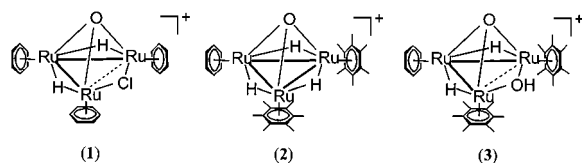

Scheme 1.

Fig. 1. Molecular structure of cation **3**.

Table 1
Selected bond lengths (Å) and angles (°) for **3**

Interatomic distances	
Ru(1)–Ru(2)	2.780(1)
Ru(2)–Ru(1a)	2.780(1)
Ru(1)···Ru(1a)	3.196(1)
Ru(1)–O(1)	2.041(4)
Ru(1)–O(2)	2.086(5)
Ru(1a)–O(1)	2.041(4)
Ru(1a)–O2(1)	2.086(5)
Ru(1)–H(1)	1.78(8)
Ru(2)–H(1)	1.72(8)
O(2)–H	0.77(9)
Ru(1)–C(1)	2.215(6)
Ru(1)–C(2)	2.194(6)
Ru(1)–C(3)	2.204(6)
Ru(1)–C(4)	2.192(6)
Ru(1)–C(5)	2.196(6)
Ru(1)–C(6)	2.206(6)
Ru(2)–C(13)	2.227(10)
Ru(2)–C(14)	2.223(7)
Ru(2)–C(15)	2.190(6)
Ru(2)–C(16)	2.223(9)
Hydrogen bond	
O(1)···O(1W)	2.71(1)
Bond angles	
Ru(1a)–Ru(2)–Ru(1)	70.17(3)
Ru(1a)–O(1)–Ru(1)	103.1(3)
Ru(1a)–O2(1)–Ru(1)	100.0(3)
Ru(1)–O(1)–Ru(2)	86.6(2)
Ru(1a)–O(1)–Ru(2)	86.6(2)

The product is characterised by NMR and IR spectroscopy, mass spectroscopy, micro-analysis, and by a single-crystal X-ray structure analysis. In the ^{1}H-NMR spectrum in D_2O, **3** gives rise to a singlet ($\delta = 5.83$ ppm) for the hydroxo ligand, a singlet ($\delta = 5.37$ ppm) for the benzene ligand and a singlet ($\delta = 2.03$ ppm) for the two equivalent hexamethylbenzene ligands; the two equivalent hydrido ligands appear as a singlet ($\delta = -13.56$ ppm) in the high-field region. In the electrospray mass spectrum, the molecular peak is observed at m/z 744 with the expected Ru_3 isotope pattern (calculated for ^{102}Ru: 743). The ν(O–H) absorption is observed in the infrared spectrum at 3413 cm^{-1} (KBr).

Suitable crystals of the tetrafluoroborate salt of **3** were obtained from acetone upon slow evaporation of the solvent. A single-crystal X-ray structure analysis was performed with one of the orange block-shaped crystals. The tetragonal crystal contains eight formula units and eight water molecules per unit cell; half of the cation, half of the anion and half of the water molecule per asymmetric unit. The tetrafluoroborate anion is strongly disordered. The structure of **3** is depicted in Fig. 1; selected bond lengths and angle are given in Table 1.

Scheme 2.
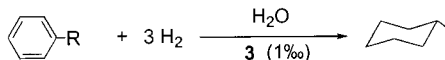
Scheme 3.

The cluster cation **3** consists of an isosceles triangle of three ruthenium atoms being capped by a μ_3-oxo ligand. The two hydrido ligands bridging the two ruthenium–ruthenium bonds could be localised and fully refined. The third ruthenium–ruthenium distance Ru(1)–Ru(1a) is too long [3.196(1) Å] for a metal–metal bond, but this open edge is bridged by a μ_2-hydroxo ligand. The molecular arrangement of **3** shows an almost perfect C_s symmetry. The oxo ligand is mirror-symmetrically coordinated to the Ru$_3$ triangle, two ruthenium–oxygen distances being longer [Ru(1)–O(1), Ru(1a)–O(1): 2.041(4) Å] in comparison with the third ruthenium–oxygen bond in the mirror plane [Ru(2)–O(1): 2.014(6) Å]. The water molecule is hydrogen-bonded to the μ_3-oxo ligand [O⋯O distance 2.757(9) Å] and cannot be removed in vacuo. Cluster **3** is an analogue of the chloro derivative **1** [5] found in the catalytic arene hydrogenation by Ru$_2$(η^6-C$_6$Me$_4$)$_3$Cl$_4$ in water [3] (Scheme 2).

Cluster **3** was indeed found to be a very active catalyst: it catalyses the hydrogenation of benzene and various benzene derivatives in aqueous solution to give the corresponding cyclohexane derivatives with higher turnover numbers than the other arene ruthenium derivatives. The reaction proceeds under hydrogen pressure (60 bar) at 110°C with vigorous stirring of the

biphasic system (Scheme 3). Cation **3** can be recovered unchanged as the tetrafluoroborate salt after a catalytic run from the aqueous phase.

With benzene, the reaction is almost complete within 15 min, corresponding to a catalytic turnover frequency of 5466 h^{-1}. The activity is much higher than that reported for the other catalysts in the homogeneous phase, viz. [(η^6-C$_6$Me$_6$)Ru$_2$(μ_2-H)(μ_2-Cl)$_2$]Cl$_2$: 241 h^{-1} [8], (η^5-C$_5$H$_5$)$_2$Rh$_2$Cl$_4$: 23 h^{-1} [9], (η^3-C$_3$H$_5$)Co[(P(OMe)$_3$)$_3$]$_3$: 0.7 h^{-1} [10]. The catalytic activity of **3** decreases in the case of substituted benzene derivatives (Table 2). Toluene is hydrogenated more slowly than benzene, presumably due to the steric hindrance of the alkyl substituent, which, however, is counterbalanced by the increased electronic density of the aromatic cycle. Unfortunately, the hydrogenation of functionalised benzene derivatives is not very selective: Cyclohexylbenzene and biphenyl give the same product, the catalytic turnover frequency being 1000 h^{-1}.

Table 3 shows the influence of methyl substitution in the aromatic cycle on the hydrogenation capacity. Surprisingly, the more sterically hindered *ortho*-xylene is more easily hydrogenated than the less hindered *meta*- and *para*-xylenes. 1,2,4,5-Tetramethylbenzene is not hydrogenated all. Table 4 shows the catalytic activities of cation **3** and cation **2**. Cation **3** is up to 50 times faster than cation **2**. We suppose **3** to be the catalyst precursor, although we could detect **3** only in the case of ethylbenzene hydrogenation.

The precise role of the cluster cation [(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ_2-H)$_2$(μ_2-OH)(μ_3-O)]$^+$ (**3**) in the catalytic hydrogenation of benzene and benzene derivatives is not clear. In the case of the hydrogenation of ethylbenzene, no substitution of a benzene or a hexamethylbenzene ligand by the ethylbenzene substrate is observed; **3** is recovered unchanged. This means that the aromatic substrate is not coordinated (by substitution) to one of the ruthenium atoms during the catalytic

Table 2
Hydrogenation of benzene and monosubstituted derivatives under biphasic conditions[a]

Substrate	Product	Yield (%)[b]	Time (h)	TON[c]	TOF (h^{-1})[d]
Benzene	Cyclohexane	91.1	0.25	911	5466
Toluene	Methylcyclohexane	92.3	0.33	923	2769
Ethylbenzene	Ethylcyclohexane	85.3	0.25	853	3413
Propylbenzene	Propylcyclohexane	97.1	0.33	971	2913
Isopropylbenzene	Isopropylcyclohexane	100.0	0.33	1000	3000
Cyclohexylbenzene	Bicyclohexyl	100.0	1.0	1000	1000
Biphenyl[e]	Bicyclohexyl	100.0	1.0	1000	1000

[a] Conditions: catalyst [(η^6-C$_6$H$_6$)(η^6-C$_6$Me$_6$)$_2$Ru$_3$(μ_2-H)$_2$(μ_2-OH)(μ_3-O)][BF$_4$] (cation **3**) (0.01 mmol), 5 ml H$_2$O, catalyst/substrate ratio 1/1000, temperature 110°C, hydrogen pressure 60 bar, stirred at 900 min^{-1}.
[b] Measured by GC.
[c] Catalytic turnover number: moles of substrate transformed per mole of catalyst.
[d] Catalytic turnover frequency: moles of substrate transformed per mole of catalyst per hour.
[e] Substrate dissolved in cyclohexane (10 ml).

Table 3
Hydrogenation of di-,tri- and tetra-substituted derivatives under biphasic conditions[a]

Substrate	Product	Yield (%)[b]	Time (h)	TON[c]	TOF (h^{-1})[d]
o-Xylene	trans-1,2-Dimethylcyclohexane	10.0	0.25	875	3736
	cis-1,2-Dimethylcyclohexane	77.5			
m-Xylene	trans-1,3-Dimethylcyclohexane	78.1	0.33	974	2922
	cis-1,3-Dimethylcyclohexane	18.1			
p-Xylene	trans-1,4-Dimethylcyclohexane	26.5	0.33	880	2640
	cis-1,4-Dimethylcyclohexane	69.5			
1,3,5-Trimethylbenzene	trans,trans-1,3,5-Trimethylcyclohexane	60.6	0.5	760	1520
	cis,cis-1,3,5-Trimethylcyclohexane	13.5			
1,2,4,5-Tetramethylbenzene[e]	trans,trans,trans-1,2,4,5-Tetramethylcyclohexane	0.0	3	0	0
	cis,cis,cis-1,2,4,5-Tetramethylcyclohexane	0.0			

[a] Conditions: catalyst [(η^6-C$_6$H$_6$)(η^6-C$_6$Me$_6$)$_2$Ru$_3$(μ_2-H)$_2$(μ_2-OH)(μ_3-O)][BF$_4$] (cation **3**) (0.01 mmol), 5 ml H$_2$O, catalyst/substrate ratio 1/1000, temperature 110°C, hydrogen pressure 60 bar, stirred at 900 min^{-1}.
[b] Measured by GC.
[c] Catalytic turnover number: moles of substrate transformed per mole of catalyst.
[d] Catalytic turnover frequency: moles of substrate transformed per mole of catalyst per hour.
[e] Substrate dissolved in cyclohexane (10 ml).

Table 4
Comparison of catalytic turnover frequencies of cations **2**[a] and **3**[a]

Substrate	Product	2		3		TOF(**3**)/TOF(**2**)
		Time (h)	TOF (h^{-1})[b]	Time (h)	TOF (h^{-1})[b]	
Benzene	Cyclohexane	3.5	289	0.25	5466	18.9
Toluene	Methylcyclohexane	2.2	440	0.33	2769	6.3
Ethylbenzene	Ethylcyclohexane			0.25	3413	
Propylbenzene	Propylcyclohexane	8.0	117	0.33	2913	24.9
Isopropylbenzene	Isopropylcyclohexane	14.0	71	0.33	3000	42.3
Cyclohexylbenzene	Bicyclohexyl	2.0	500	1.0	1000	2.0
Biphenyl[c]	Bicyclohexyl	14.5	74	1.0	1000	13.5
o-Xylene	trans-1,2-Dimethylcyclohexane	14.0	71	0.25	3736	52.6
	cis-1,2-Dimethylcyclohexane					
m-Xylene	trans-1,3-Dimethylcyclohexane	3.0	232	0.33	2922	12.6
	cis-1,3-Dimethylcyclohexane					
p-Xylene	trans-1,4-Dimethylcyclohexane	2.0	396	0.33	2640	6.7
	cis-1,4-Dimethylcyclohexane					
1,3,5-Trimethylbenzene	trans,trans-1,3,5-Trimethylcyclohexane	14.0	71	0.5	1520	21.4
	cis,cis-1,3,5-Trimethylcyclohexane					

[a] Catalyst (cation **2** or **3**) as tetrafluoroborate salt (0.01 mmol), catalyst/substrate ratio 1/1000, temperature 110°C, hydrogen pressure 60 bar, stirred at 900 min^{-1}.
[b] Catalytic turnover frequency: moles of substrate transformed per mole of catalyst per hour.
[c] Substrate dissolved in cyclohexane (10 ml).

process; it seems that it is only loosely bound to the open triangular face of the triruthenium framework, opposite to the oxo cap, a phenomenon that may be explained by interactions between the aromatic ligands and the aromatic substrate in aqueous solution. Similar phenomena are observed in inclusion complexes of benzene–ruthenium units and cyclodextrines [11].

3. Experimental

3.1. General

All manipulations were carried out by routine under nitrogen atmosphere, using Standard Schlenk techniques, although the compounds are not air-sensitive. The twice-distilled water was degassed and saturated

with nitrogen prior to use. The NMR spectra were recorded on a Varian Gemini 200 BB instrument; the treatment of the spectra was performed using a SUN Varian station. The IR spectra were recorded on a Perkin–Elmer FT-IR 1720 X spectrometer (4000–400 cm^{-1}) as KBr pellets. Micro-analytical data were obtained from the Service de Microchimie, Université de Genève. Electron mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer using acetone as the mobile phase. The organic phase containing products and substrate was analysed by gas chromatography (GC) on a DANI 86.10 HT gas chromatograph using a CHROMPACK Carbowax WCOT fused silica column. The starting cation [(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ$_2$-H)$_3$(μ$_3$-O)]$^+$ (**2**) [7] was synthesised from (η^6-C$_6$Me$_6$)$_2$Ru$_2$Cl$_4$ [12] and (η^6-C$_6$H$_6$)$_2$Ru$_2$Cl$_4$ [13] according to published methods.

3.2. Synthesis of [(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ$_2$-H)$_2$(μ$_2$-OH)(μ$_3$-O)]$^+$ (3)

[(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ$_2$-H)$_3$(μ$_3$-O)][BF$_4$] (cation **2**) (16 mg, 1.93×10^{-2} mmol) was dissolved in 5 ml of

Table 5
Crystallographic and selected experimental data for **3**

Compound	[(η^6-C$_6$H$_6$)(η^6-C$_6$Me$_6$)$_2$Ru$_3$(μ$_2$-H)$_2$-(μ$_2$-OH)(μ$_3$-O)][BF$_4$]·H$_2$O
Empirical formula	C$_{30}$H$_{47}$B$_1$F$_4$O$_3$Ru$_3$ (cation **3**)
Crystal colour	Orange
Crystal shape	Block
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.15$
M_r (g mol^{-1})	845.70
Crystal system	Tetragonal
Space group	$I4/m$
a (Å)	18.2490(9)
b (Å)	18.2490(9)
c (Å)	20.2191(10)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	6733.6(6)
Z	8
D_c (g cm^{-3})	1.668
μ (Mo–K$_\alpha$) (mm^{-1})	1.379
$F(000)$	3392
θ scan-range (°)	1.65–26.05
T (K)	153(2)
Reflections measured	26 603
Independent reflections	3355
Reflections observed [$I > 2\sigma(I)$]	2580
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0501$, $wR_2 = 0.1467$
R indices (all data)[a]	$R_1 = 0.0643$, $wR_2 = 0.1551$
Goodness of fit	1.030
Maximum Δ/σ	0.001
Residual density: maximum, minimum $\Delta\rho$ (e$^-$ Å^{-3})	$+1.539$, -2.789

[a] $R_1 = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$, $wR_2 = [\Sigma \, w(F_o^2 - F_c^2)^2 / \Sigma \, (wF_o^4)]^{1/2}$.

twice-distilled water. To this solution, placed in a 100 ml stainless steel autoclave, 1.225 ml of ethylbenzene were added. After purging four times with hydrogen, the autoclave was pressurised with hydrogen (60 bar) and held at room temperature under vigorous stirring of the reaction mixture (900 rpm). After 2 h the pressure was released. The two-phase system was separated by decanting. The yellow aqueous phase was evaporated to dryness; the residue was dissolved in acetone, and crystallisation at $-20°C$ gave [(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ$_2$-H)$_2$(μ$_2$-OH)(μ$_3$-O)][BF$_4$] (cation **3**). Yield 7 mg (8.27×10^{-3} mmol, 43%). Anal. Found: C, 42.86; H, 5.70. Calc. for C$_{30}$H$_{45}$B$_1$F$_4$O$_2$Ru$_3$·H$_2$O: C, 42.61; H, 5.60%. IR(cm^{-1}): 3413 (w), v(O–H); 3011 (w), v(C–H$_{ar}$); 2930 (s), 2853 (m), v(C–H); 1438 (m), 1385 (m), v(C=C); 1084 (br, vs), v(BF$_4$).

3.3. X-ray structure determination of complex 3

An orange crystal of [(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ$_2$-H)$_2$(μ$_2$-OH)(μ$_3$-O)][BF$_4$] (cation **3**) was mounted on a Stoe imaging plate diffractometer system (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite monochromator. Data collection was performed at $-120°C$ using Mo–K$_\alpha$ radiation ($\lambda = 0.710\,73$ Å). 200 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 200°$ and with the crystal oscillating through 1° in φ. The resolution range was D_{min}–D_{max} 12.45–0.81 Å. The structure was solved by Patterson methods using SHELXS-97 [14]. Refinement was done by full-matrix least squares on F^2 with SHELXL-97 [15]. The compound crystallises in the tetragonal system (centrosymmetric space group $I4/m$) with half a molecule of **3** as well as half a water molecule and half of an extremely disordered BF$_4^-$ anion per asymmetric unit. The B–F distances in the distorted BF$_4^-$ anion were constrained to their theoretical values [16]. The hydrogen atoms attached to the water molecule were derived from Fourier difference maps and constrained to their theoretical values [16]. The positions of the hydride H1–Ru and the hydroxide H atom were also found as electron density peaks and refined while the remaining hydrogen atoms of the organic ligand were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms (except F3, F3a, F4, F4a and F4b atoms, which were isotropically refined) were refined with anisotropic displacement parameters. Selected bond lengths and bond angles are listed in Table 1. Crystallographic details for compound **3** are summarised in Table 5. The figure was drawn with PLATON/PLUTON [17].

3.4. Catalytic runs

In a typical experiment, a solution of 0.01 mmol of [(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ$_2$-H)$_2$(μ$_2$-OH)(μ$_3$-O)][BF$_4$]

(cation **3**) in 5 ml of twice-distilled water was placed in a 100 ml stainless steel autoclave, and 10 mmol of the organic substrate was added. After purging four times with hydrogen, the autoclave was pressurised with hydrogen (60 bar) and heated to 110°C in an oil bath under vigorous stirring of the reaction mixture (900 rpm). After the reaction time indicated in Tables 3 and 4, the autoclave was cooled with ice water to room temperature, and the pressure was released. The two-phase system was separated by decanting; the aqueous phase was evaporated to dryness, the residue dissolved in D_2O and analysed by NMR spectroscopy. The organic phase containing the products and substrate was analysed by GC and NMR spectroscopy.

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 number: **3** CCDC 146719.

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