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Synthesis and molecular structure of the trinuclear ruthenium cluster cations $[H_3Ru_3(C_6H_6)(C_6H_2Me_4)_2(O)]^+$ and $[H_3Ru_3\{C_6H_5(CH_2)_2OH\}(C_6H_2Me_4)_2(O)]^+$

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Abstract

The trinuclear arene–ruthenium cluster cations $[H_3Ru_3(C_6H_6)(C_6H_2Me_4)_2(O)]^+$ (**2**) and $[H_3Ru_3\{C_6H_5(CH_2)_2OH\}(C_6H_2Me_4)_2(O)]^+$ (**3**) have been synthesised from the dinuclear precursor $[H_3Ru_2(C_6H_2Me_4)_2]^+$ (**1**) and the mononuclear complexes $[Ru(C_6H_6)(H_2O)_3]^{2+}$ and $[Ru\{C_6H_5(CH_2)_2OH\}(H_2O)_3]^{2+}$, isolated and characterised as the tetrafluoroborate salts. Cations **2** and **3** are analogues of the cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ which was found to catalyse the hydrogenation of benzene to give cyclohexane under biphasic conditions ('supramolecular cluster catalysis'). The single-crystal X-ray structure analyses of **2** and **3** have been determined. Unlike **[2]**$[BF_4]\cdot 3H_2O$, **[3]**$[PF_6]\cdot H_2O$ shows a dimeric structure in the solid state, thanks to hydrogen bonds between the hydroxo function of one molecule of **3**, a water molecule and the oxo cap of an other molecule of **3**.

Keywords: Cluster catalysis; Second sphere coordination; Arene hydrogenation; Biphasic catalysis

1. Introduction

In 1999 we found the water-soluble cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ (**4**) to catalyse the hydrogenation of benzene to give cyclohexane under biphasic conditions [1]. Experimental and modelling studies suggested catalysis by intact trinuclear ruthenium clusters, taking place inside the hydrophobic pocket spanned by the three arene ligands in **4** ('supramolecular cluster catalysis') [2]. Recently we were able to isolate the supramolecular catalyst–substrate host–guest complexes postulated for the hydroxyalkyl derivatives $[H_3Ru_3\{C_6H_5(CH_2)_2OH\}(C_6Me_6)_2(O)]^+$ (**5**) [3]. Searching for more active derivatives, we reasoned that replacing the two hexamethylbenzene in **4** and **5** with the less hindered 1,2,4,5-tetramethylbenzene (durene) should favour the insertion of the benzene host in the hydrophobic pocket, thus improving the catalytic activity. Herein we report the synthesis, characterisation, and catalytic activity of the water-soluble cluster cations $[H_3Ru_3(C_6H_6)(C_6H_2Me_4)_2(O)]^+$ (**2**) and $[H_3Ru_3\{C_6H_5(CH_2)_2OH\}(C_6H_2Me_4)_2(O)]^+$ (**3**). The single-crystal X-ray structure analysis of **[2]**$[BF_4]$ and **[3]**$[PF_6]$ have been performed, and the comparison with the hexamethylbenzene analogues is discussed.

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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. 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. Organic products were analysed by gas chromatography (GC) on a DANI

86.10 HT gas chromatograph using a CHROMPACK Carbowax WCOT fused silica column. The starting complexes $[Ru\{C_6H_5(CH_2)_2OH\}Cl_2]_2$ [3], $[Ru(C_6H_6)Cl_2]_2$ and $[Ru(C_6H_2Me_4)Cl_2]_2$ [4] were prepared according to published methods.

2.2. Syntheses

2.2.1. $[H_3Ru_2(C_6H_2Me_4)_2]^+$ (**1**)

A mixture of $[Ru(C_6H_2Me_4)Cl_2]_2$ (400 mg, 0.6 mmol) and Ag_2SO_4 (410 mg, 1.3 mmol) in water (40 ml) was stirred in the dark for 1 h. During this period the mixture was treated several times with ultrasound, until the orange solid was completely dissolved. The white precipitate (AgCl) was removed by filtration from the yellow solution containing $[Ru(C_6H_2Me_4)(H_2O)_3]^{2+}$. An aqueous solution containing $NaBH_4$ (86 mg, 2.3 mmol, 10 ml H_2O) was added dropwise to this yellow solution. The solution turned dark-red due to the formation of $[H_3Ru_2(C_6H_2Me_4)_2]^+$. After filtration, $[H_3Ru_2(C_6H_2Me_4)_2][BF_4]$ was precipitated from the aqueous solution by addition of an excess of $NaBF_4$. The green precipitate was centrifuged, dissolved in CH_2Cl_2, filtered on celite to eliminate the excess of $NaBF_4$ and purified on a silica-gel column (eluent: CH_2Cl_2/acetone 5:1). Yield: 180 mg (54%).

Spectroscopic data for **1**: ^{1}H NMR (200 MHz, acetone-d_6): δ =/5.96 (s, 4H, $C_6H_2Me_4$), 2.31 (s, 24H, $C_6H_2(CH_3)_4$), −/15.47 (s, 3H, Ru-hydride). $^{13}C\{^1H\}$ NMR (50 MHz, acetone-d_6): δ =/96.12, 86.73, 17.86. MS (ESI positive mode, acetone): m/z: 473 $[M]^+$. *Anal.* Calc. for $C_{20}H_{31}B_1F_4Ru_2$: C, 42.86; H, 5.58. Found: C, 42.35; H, 5.41%.

2.2.2. $[H_3Ru_3(C_6H_6)(C_6H_2Me_4)_2(O)]^+$ (**2**)

To a solution of [**1**][BF_4] (180 mg, 0.3 mmol) in acetone (50 ml) and water (30 ml), was added $[Ru(C_6H_6)Cl_2]_2$ (112 mg, 0.2 mmol). The mixture was stirred during 30 h at room temperature. The resulting red solution was evaporated to dryness, the residue was dissolved in CH_2Cl_2 and purified on silica-gel plates (eluent: CH_2Cl_2/acetone 2:1) to give pure [**2**][BF_4] as red–orange powder. Crystals suitable for X-ray analysis were obtained by an acetone/*n*-hexane solution. Yield: 104 mg (47%).

Spectroscopic data for **2**: ^{1}H NMR (400 MHz, acetone-d_6): δ =/5.71 (s, 6H, C_6H_6), 5.66 (s, 4H, $C_6H_2Me_4$), 2.22 (s, 24H, $C_6H_2(CH_3)_4$), −/18.55 (d, 2H, Ru-hydride, ^2J =/3.42 Hz), −/18.92 (t, 1H, Ru-Hydride, ^2J =/3.42 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, acetone-d_6): δ =/96.41, 95.53, 86.94, 86.80, 83.25, 18.05, 17.88. MS (ESI positive mode, acetone): m/z: 668 $[M]^+$. *Anal.* Calc. for $C_{26}H_{37}B_1F_4O_1Ru_3 \cdot H_2O$: C, 40.37; H, 5.08. Found: C, 40.52; H, 5.19%.

2.2.3. $[H_3Ru_3\{C_6H_5(CH_2)_2OH\}(C_6H_2Me_4)_2(O)]^+$ (**3**)

To a solution of [**1**][BF_4] (180 mg, 0.3 mmol) in acetone (50 ml) and water (30 ml), $[Ru\{C_6H_5(CH_2)_2OH\}Cl_2]_2$ (142 mg, 0.2 mmol) was added. The rest of the procedure is as described for **2**. [**3**][BF_4] was isolated as red–orange powder. Yield: 160 mg (67%). Crystals suitable for X-ray analysis were obtained by addition of KPF_6 to an acetone/*n*-hexane solution.

Spectroscopic data for **3**: ^{1}H NMR (400 MHz, acetone-d_6): δ =/6.17 (t, 1H, CH_2CH_2OH, ^3J =/7.03 Hz), 6.10 (m, 2H, C_6H_5), 5.72 (s, 4H, $C_6H_2Me_4$), 5.60 (m, 1H, C_6H_5), 5.39 (m, 2H, C_6H_5), 3.92 (m, 2H, CH_2CH_2OH), 2.56 (m, 2H, CH_2CH_2OH), 2.25 (s, 12H, $C_6(CH_3)_4$), 2.23 (s, 12 H, $C_6(CH_3)_4$), −/18.77 (d, 2H, Ru hydride, ^2J =/3.83 Hz), −/18.81 (t, 1H, Ru hydride, ^2J =/3.83 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, acetone-d_6): δ =/107.53, 96.48, 95.79, 86.89, 80.10, 77.30, 60.57, 36.81, 17.98, 17.87. MS (ESI positive mode, acetone): m/z: 712 $[M]^+$. *Anal.* Calc. for $C_{28}H_{41}B_1F_4O_2Ru_3 \cdot H_2O$: C, 41.13; H, 5.30. Found: C, 41.08; H, 4.98%.

2.3. Catalytic runs

In a typical experiment, a solution of [**2**][BF_4] or [**3**][BF_4] (8 mg) in 10 ml of degassed water was placed in a 100 ml stainless-steel autoclave, and the substrate benzene was added with a 1/1000 ratio catalyst/substrate. 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. After 30 min, the autoclave was placed in an ice-bath and the pressure released. The two-phase system was separated by decanting. The aqueous phase containing the catalyst was evaporated to dryness under vacuum, and the residue was analysed by NMR and mass spectrometry. The organic phase containing cyclohexane and benzene was analysed by NMR spectroscopy and GC.

2.4. X-ray crystallography

Crystals of [**2**][BF_4], and [**3**][PF_6] were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation (λ =/0.71073 Å) with ϕ range 0–200°, increment of 1.2 and 1.3°, D_{max}–D_{min} =/12.45–0.81 Å. The structures were solved by direct methods using the program SHELXS-97 [5]. The refinement and all further calculations were carried out using SHELXL-97 [6]. In [**2**][BF_4], and [**3**][PF_6] 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

Table 1
Crystallographic and selected experimental data of [**2**][BF_4], and [**3**][PF_6]

	[**2**][BF_4]·(H_2O)$_3$	[**3**][PF_6]·H_2O
Chemical formula	$C_{26}H_{43}BF_4O_4Ru_3$	$C_{28}H_{43}F_6O_3PRu_3$
Formula weight	809.62	875.80
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Crystal colour and shape	orange rod	red block
Crystal size	$0.35 \times 0.20 \times 0.15$	$0.40 \times 0.30 \times 0.25$
a (Å)	10.625(1)	10.6312(8)
b (Å)	17.285(2)	18.240(1)
c (Å)	16.368(2)	15.972(1)
α (°)	90	90
β (°)	102.96(1)	96.438(9)
γ (°)	90	90
V (Å^3)	2929.6(5)	3077.6(4)
Z	4	4
T (K)	153(2)	153(2)
D_{calc} (g cm^{-3})	1.836	1.890
μ (mm^{-1})	1.582	1.571
Scan range (°)	$3.90 < 2\theta < 51.70$	$4.40 < 2\theta < 51.80$
Unique reflections	5650	5944
Reflections used [$I > 2\sigma(I)$]	4162	5287
R_{int}	0.0448	0.0262
Final R indices [$I > 2\sigma(I)$]	0.0359, wR_2 0.0916	0.0228, wR_2 0.0568
R indices (all data)	0.0527, wR_2 0.0964	0.0270, wR_2 0.0581
Goodness-of-fit	0.991	1.027
Max, Min $\Delta\rho$ e (Å^{-3})	1.163, −0.712	1.055, −0.729

summarised in Table 1. Fig. 1 was drawn with ORTEP [7] and Fig. 2 with the program POV-RAY [8].

3. Results and discussion

The trinuclear cations $[H_3Ru_3(C_6H_6)(C_6H_2Me_4)_2(O)]^+$ (**2**) and $[H_3Ru_3\{C_6H_5(CH_2)_2OH\}(C_6H_2Me_4)_2(O)]^+$ (**3**) have been synthesised in solution (acetone/water) from $[Ru\{C_6H_5(CH_2)_2OH\}(H_2O)_3]^{2+}$ [3], and $[Ru(C_6H_6)(H_2O)_3]^{2+}$ [9], and from the known dinuclear precursor $[H_3Ru_2(C_6H_2Me_4)]^+$ (**1**), obtained by a different synthetic route than previously reported [10] (Scheme 1). The dinuclear durene complex **1**, accessible by $[Ru(C_6H_2Me_4)(H_2O)_3]^{2+}$ and $NaBH_4$ in aqueous solution, is isolated as the tetrafluoroborate salt and purified by column chromatography. The compound is stable for days under an inert atmosphere, but decomposes slowly in air or in solution.

The ^{1}H NMR spectrum of **2** shows a triplet ($\delta = -18.92$ ppm) and a doublet ($\delta = -18.55$ ppm) in the hydrides region, a singlet ($\delta = 2.22$ ppm) for the methyl groups of the durene, a singlet ($\delta = 5.66$ ppm) for the protons of the durene ligand, and a singlet ($\delta = 5.71$ ppm) for the aromatic protons of the benzene ligands. The ^{1}H NMR spectrum of **3** shows a triplet and a doublet for the hydrido ligands ($\delta = -18.81$ and -18.77 ppm), multiplets at 2.56 and 3.92 ppm for the CH_2 groups, a series of multiplets at 5.39, 5.60 and 6.10 ppm for the aromatic protons of the phenylethanol, a singlet at 5.72 ppm for the aromatic protons of the durene ligands, a triplet at 6.17 ppm for the OH; surprisingly the methylene protons of the durene ligands give rise to two singlets at 2.23 and 2.25 ppm, respectively, suggesting a rigid structure of **3** even in solution.

Cations **2** and **3** are found to be catalytically active for the hydrogenation of benzene under biphasic conditions, they show a catalytic activity of 1790 and 1150 h^{-1} (TOF), respectively, for a catalyst/substrate ratio 1:1000, at 110 °C under 60 bar H_2 during 30 min. However, clusters **2** and **3** are unstable under these conditions, giving a mixture of mono-, di- and tetranuclear species, among which, we identified by mass spectrometry as well as NMR spectroscopy

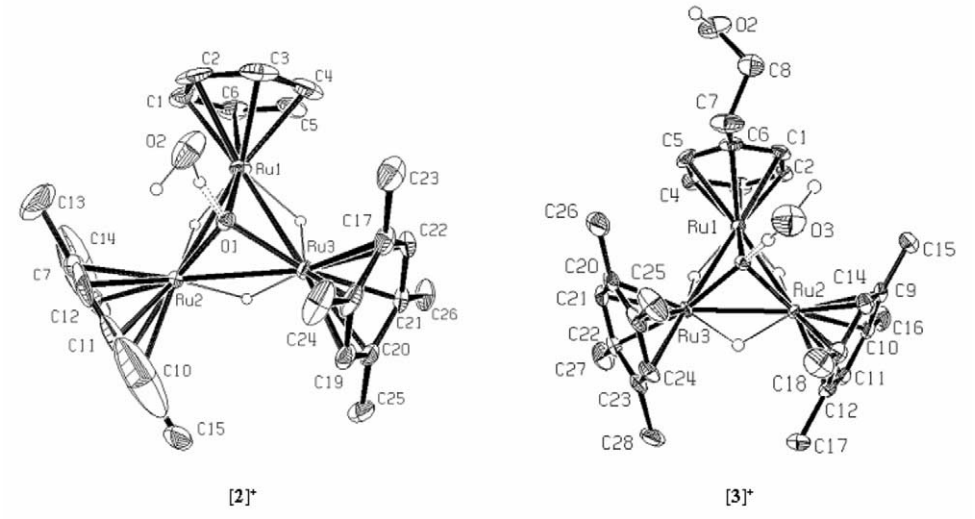


Fig. 1. Molecular structure of cations **2** and **3** at 35% probability level, H atoms and anions omitted for clarity.

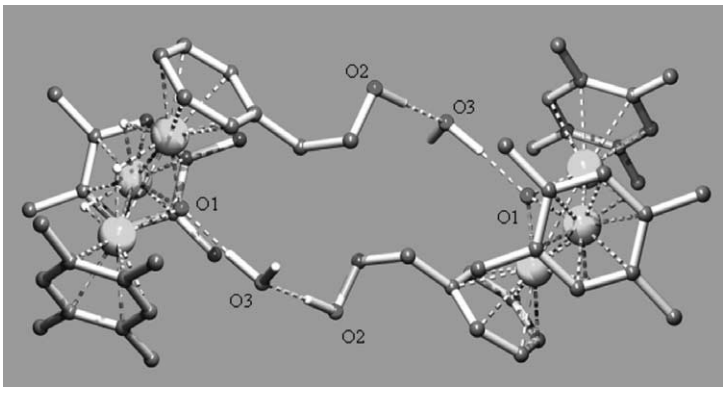


Fig. 2. Dimeric structure of **3** showing the intramolecular hydrogen bonds.

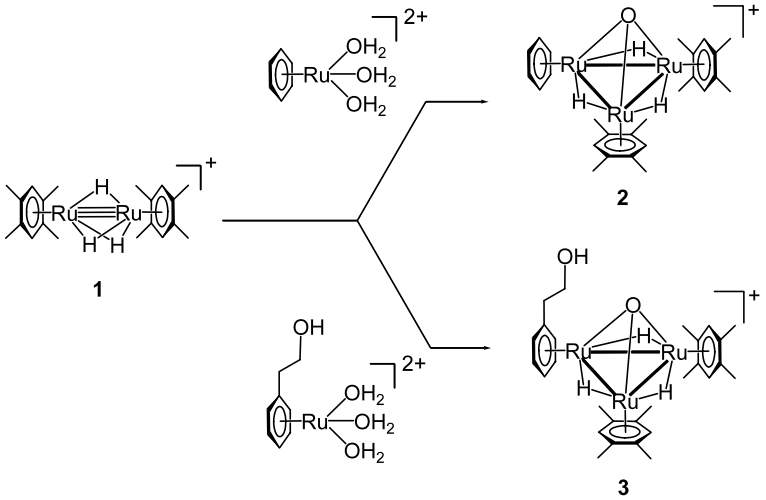
$[H_4Ru_4(C_6H_6)(C_6H_2Me_4)_3]^{2+}$ and $[H_4Ru_4\{C_6H_5(CH_2)_2OH\}(C_6H_2Me_4)_3]^{2+}$. Under milder conditions (catalyst/substrate ratio 1:1000, 90 °C, 60 bar H_2, 2 h) the catalytic activity of **2** and **3** is reduced by a factor of three (410 and 460 h^{-1} TOF), but decomposition is still observed. It is known that tetranuclear species such as $[H_4Ru_4(C_6H_6)_4]^{2+}$ are catalytically active for the hydrogenation of benzene (376 h^{-1} TOF) [11]. In order to rationalise the stability of **2** and **3** a single-crystal X-ray structure analyses was performed.

The molecular structures of **2** and **3** are shown in Fig. 1. For comparison, selected bond lengths and angles of the hexamethylbenzene analoguous derivatives **4** and **5** are listed with those of complexes **2** and **3** in Table 2. In all cases, the metal core consists of three ruthenium atoms, with Ru–Ru distances being in accordance with a metal–metal single bond. The three ruthenium atoms are capped by a μ_3-oxo ligand which is almost symmetrically coordinated. In complexes **2** and **3** the durene ligands adopt a staggered configuration, to minimise the contacts between the methyl groups, the closest C–C (methyl–methyl) distances being 3.86 and 3.99 Å.

Table 2
Selected bond lengths (Å) and angles (°) for **[2]**[BF_4], **[3]**[PF_6], **[4]**[BF_4], and **[5]**[PF_6]

	[2][BF_4]	**[3]**[PF_6]	**[4]**[BF_4]	**[5]**[PF_6]
Interatomic distances				
O(1)–Ru(1)	2.005(7)	2.004(2)	2.008(3)	2.007(3)
O(1)–Ru(2)	1.999(6)	2.004(2)	2.003(3)	2.002(2)
O(1)–Ru(3)	2.000(7)	2.004(2)	1.999(3)	2.002(3)
Ru(1)–Ru(2)	2.730(1)	2.7654(3)	2.7442(6)	2.7463(5)
Ru(1)–Ru(3)	2.752(1)	2.7330(3)	2.7450(6)	2.7535(5)
Ru(2)–Ru(3)	2.771(1)	2.7697(3)	2.7992(6)	2.8090(5)
Angles				
Ru(1)–Ru(2)–Ru(3)	60.02(3)	59.177(8)	59.35(2)	59.41(1)
Ru(1)–Ru(3)–Ru(2)	59.24(3)	60.333(7)	59.32(2)	59.16(1)
Ru(2)–Ru(1)–Ru(3)	60.74(3)	60.490(9)	61.32(2)	61.43(1)

Interestingly, cluster **3** shows a dimeric structure in the solid state thanks to intermolecular hydrogen bonds between the oxo cap of one molecule, a water molecule, and the hydroxo function of an other molecule, see Fig. 2. The angle forms by the three oxygen atoms [O(1)···O(3)···O(2)] involved in the hydrogen bond



Scheme 1.

network is 128.2°. The O¬O distances are, respectively, 2.779(3) Å for O(1)¬O(3) and 2.795(4) Å for O(2)¬O(3). Unlike **3**, cation **2** shows only one single hydrogen bond between the oxo cap and one water molecule. The O¬O distance of the hydrogen bond [O(2)¬H···O(1)] is 2.732(6) Å with an angle of 169.9°.

In order to compare the size of the hydrophobic pocket in the different cluster cations, we calculated the area formed by the three centroids of the arene ligands. As expected, the smallest area is observed in cation **2** (13.88 $Å^2$), **2** possesses the less substituted arene ligands, two durenes and one benzene. Clusters **3** and **4** show intermediate values (13.96 and 14.07 $Å^2$), while the largest area is observed for complex **5** (14.08 $Å^2$), who possesses two hexamethylbenzenes and one phenylethanol.

4. Supplementary material

Full tables of atomic parameters, bond lengths and angles are deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 210520 for [**2**][BF_4], and 210521 for [**3**][PF_6]. Copies of this data may be obtained free of charge from The Director, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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