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Synthesis and molecular structure of trinuclear mixed-metal cluster cations containing arene and hydrido ligands

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Ruthenium and Osmium Chemistry Topical Issue

Abstract

The mixed-metal trinuclear cluster cations $[H_3Ru_2(C_6Me_6)_2Os(C_6H_6)(O)]^+$ (**1**), $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2Os(p\text{-}MeC_6H_4{}^i\text{-}Pr)(O)]^+$ (**2**) and $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2Os(C_6H_6)(O)]^+$ (**3**) have been synthesised from the corresponding dinuclear precursors $[H_3Ru_2(\text{arene})_2]^+$ and the corresponding mononuclear complexes $[Os(\text{arene})(H_2O)_3]^{2+}$, isolated and characterised as the tetrafluoroborate and hexafluorophosphate salts. The cations **1**, **2** and **3** are heteronuclear analogues of the cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ that possesses a homonuclear metallic core. The single-crystal X-ray structure analyses of [**1**][BF_4], [**2**][PF_6] and [**3**][PF_6] reveal an equiangular metal triangle despite the presence of an osmium atom in the metallic core.

Keywords: Arene ligand; Cluster; Hydride; Osmium; Ruthenium

1. Introduction

Recently, we have developed a straightforward route to assemble trinuclear arene ruthenium complexes [1,2]. This strategy has been employed to synthesise clusters with different auxiliary groups such as ferrocenyl units [3], chiral substituents [4,5], or polymerisable side-chains [6]. Arene ruthenium clusters have an interesting catalytic potential for hydrogenation reactions and other processes [7–10].

However, mixed arene ruthenium/osmium clusters have not been reported so far. Therefore, we used this elegant method to synthesise mixed trinuclear arene Ru_2Os complexes. The molecular structures of these mixed-metal cluster cations have been determined by single-crystal X-ray structure analysis of the salts $[H_3Ru_2(C_6Me_6)_2Os(C_6H_6)(O)][BF_4]$ ([**1**][BF_4]), $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2Os(p\text{-}MeC_6H_4{}^iPr)(O)][PF_6]$ ([**2**][PF_6]) and $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2Os(C_6H_6)(O)][PF_6]$ ([**3**][PF_6]).

2. Experimental

2.1. General remarks

All reactions were carried out by standard Schlenk technique under argon atmosphere. Bidistilled water and organic solvents were degassed and saturated with argon prior to use. NMR spectra were recorded using a Bruker 400 MHz spectrometer. Electro-spray mass spectra were obtained in positive-ion mode with a LCQ Finnigan mass spectrometer. Infrared spectra were recorded using a Perkin–Elmer Spectrum One spectrophotometer. Microanalyses were performed by the Laboratory of Organic Chemistry, ETH Zurich

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

Complex	[**1**][BF_4]	[**2**][PF_6]	[**3**][PF_6] · 0.5acetone
Chemical formula	$C_{30}H_{45}BF_4OOsRu_2$	$C_{30}H_{45}F_6OOsPRu_2$	$C_{27.5}H_{40}F_6O_{1.5}OsPRu_2$
Formula weight	900.81	958.97	931.91
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	*Pccb*	$P2_12_12_1$	*C*2/*c*
Crystal colour and shape	red block	orange plate	orange block
Crystal size	0.4 × 0.2 × 0.2	0.3 × 0.3 × 0.1	0.5 × 0.5 × 0.45
a (Å)	14.1467(10)	17.5322(18)	14.342(3)
b (Å)	15.7572(19)	17.3448(12)	15.403(3)
c (Å)	16.8100(12)	10.9961(7)	27.467(5)
β (°)			97.48(3)
V ($Å^3$)	3747.2(6)	3343.8(5)	6016(2)
Z	4	4	8
T (K)	153(2)	153(2)	173(2)
D_{calc} (g cm^{-3})	1.597	1.905	2.058
μ (mm^{-1})	4.216	4.785	5.318
Scan range (°)	$5.50 < 2\theta < 51.94$	$4.38 < 2\theta < 51.84$	$4.04 < 2\theta < 51.86$
Unique reflections	3487	6463	5832
Reflections used [$I > 2\sigma(I)$]	2300	5981	4656
R_{int}	0.0699	0.0371	0.0534
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.1082$, $wR_2 = 0.2249$	$R_1 = 0.0238$, $wR_2 = 0.0597$	$R_1 = 0.0284$, $wR_2 = 0.0656$
R indices (all data)	$R_1 = 0.1346$, $wR_2 = 0.2336$	$R_1 = 0.0272$, $wR_2 = 0.0642$	$R_1 = 0.0388$, $wR_2 = 0.0633$
Goodness-of-fit	1.119	1.083	0.922
Maximum and minimum $\Delta\rho$ (e $Å^{-3}$)	3.314 and −4.003	1.391 and −0.568	1.500 and −0.871

(Switzerland). The starting compounds $[H_3Ru_2(C_6Me_6)_2][BF_4]$ [11,12], $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2][BF_4]$ [13], $[(C_6H_6)_2Os_2Cl_4]$ [14] and $[(p\text{-}MeC_6H_4{}^iPr)_2Os_2Cl_4]$ [15] were prepared according to published methods.

2.2. Syntheses

Preparation of $[H_3Ru_2(C_6Me_6)_2Os(C_6H_6)(O)][BF_4]$ ([**1**][BF_4]): In a 100 mL pressure Schlenk tube, $[H_3Ru_2(C_6Me_6)_2][BF_4]$ (61.5 mg, 0.100 mmol) and $[(C_6H_6)_2Os_2Cl_4]$ (37.3 mg, 0.055 mmol) were dissolved in degassed acetone (15 mL) and water (10 mL). The tube was sealed and the mixture was stirred at room temperature for 48 h. During this period, the colour of the solution changed from deep-brown to orange-red. After filtration, the volume of the mixture was reduced to 10 mL in vacuo, KPF_6 (18.4 mg, 0.10 mmol) was added under vigorous stirring and the orange-brown suspension was filtered. The residue was purified by preparative thin-layer chromatography on silica (eluent acetone/dichloromethane 1:2). The orange-red band was recovered and extracted with acetone. Yield: 28%. Single crystals suitable for X-ray analysis were obtained, over a 24 h period, after addition of KBF_4 and slow diffusion of ether in an acetone solution containing [**1**][PF_6].

Spectroscopic data for [**1**][BF_4]: ^1H NMR (400 MHz, acetone-d_6): $\delta = 5.68$ (s, 6H, C_6H_6), 2.30 (s, 36H, $C_6(CH_3)_6$), −19.11 (t, 1H, Ru-hydride, $^2J = 3.5$ Hz), −19.39 (d, 2H, Ru–Os-hydride, $^2J = 3.5$ Hz). IR (KBr pellets) ν (cm^{-1}): 3431 (s), 3130 (s), 1631 (m), 1400 (s), 840 (vs), 558 (s). MS (ESI positive mode, acetone): *m*/*z*: 813 $[M]^+$. *Anal.* Calc. for $C_{30}H_{45}F_6OOsPRu_2 \cdot 2H_2O$: C, 36.21; H, 4.96. Found: C, 36.41; H, 4.67%.

Preparation of $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2Os(p\text{-}MeC_6H_4{}^iPr)(O)][PF_6]$ ([**2**][PF_6]): Starting from $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2][PF_6]$ (61.9 mg, 0.100 mmol) and $[(p\text{-}MeC_6H_4{}^iPr)_2Os_2Cl_4]$ (43.5 mg, 0.055 mmol) and using a work-up analogous to that for [**1**][PF_6], the yield was 24%. Orange-red X-ray quality crystals were obtained by slow diffusion of ether into an acetone solution of [**2**][PF_6].

Spectroscopic data for [**2**][PF_6]: ^1H NMR (400 MHz, acetone-d_6): $\delta = 5.79$ (d, 2H, $p\text{-}MeC_6H_4{}^iPr$, $^3J = 5.6$ Hz), 5.60 (s, 4H, $C_6H_2(CH_3)_4$), 5.55 (d, 2H, $p\text{-}MeC_6H_4{}^iPr$, $^3J = 5.6$ Hz), 2.50 (sept, 1H, $p\text{-}MeC_6H_4CH(CH_3)_2$, $^3J = 6.9$ Hz), 2.30 (s, 3H, $p\text{-}CH_3C_6H_4{}^iPr$), 2.23 (s, 12H, $C_6H_2(CH_3)_4$), 2.22 (s, 12H, $C_6H_2(CH_3)_4$), 1.29 (d, 6H, $p\text{-}MeC_6H_4CH(CH_3)_2$, $^3J = 6.9$ Hz), −18.06 (t, 1H, Ru-hydride, $^3J = 3.8$ Hz), −19.13 (d, 2H, Ru–Os-hydride, $^2J = 3.8$ Hz). IR (KBr pellets) ν (cm^{-1}): 3430 (s), 3129 (s), 2963 (m), 2921 (m), 1631 (w), 1455 (m), 1400 (s), 1029 (m), 839 (vs), 558 (s). MS (ESI positive mode, acetone): *m*/*z*: 813 $[M]^+$. *Anal.* Calc. for $C_{30}H_{45}F_6OOsPRu_2 \cdot 2H_2O$: C, 36.21; H, 4.96. Found: C, 35.79; H, 4.68%.

Preparation of $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2Os(C_6H_6)(O)][PF_6]$ ([**3**][PF_6]): Starting from $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2][PF_6]$ (61.9 mg, 0.100 mmol) and $[(C_6H_6)_2Os_2Cl_4]$ (37.3 mg, 0.055 mmol) and using a work-up analogous to that for [**1**][PF_6], the yield was 26%. Orange X-ray quality crystals were obtained by slow diffusion of ether into an acetone solution of [**3**][PF_6].

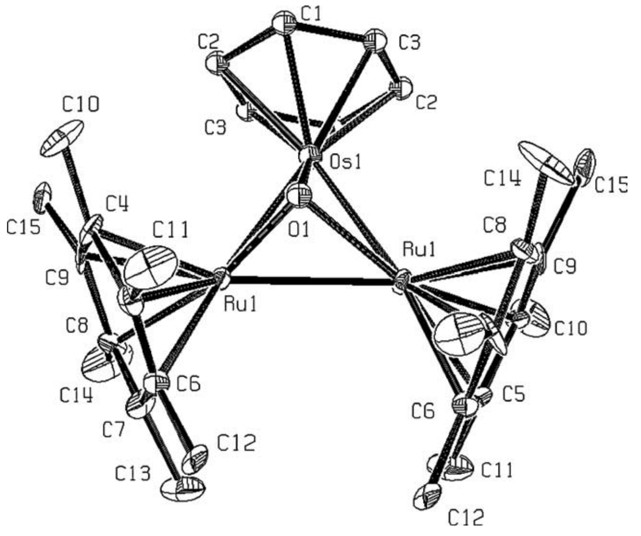


Fig. 1. ORTEP drawing of cation **1** at the 25% probability level. Hydrogen atoms and tetrafluoroborate molecule are omitted for clarity.

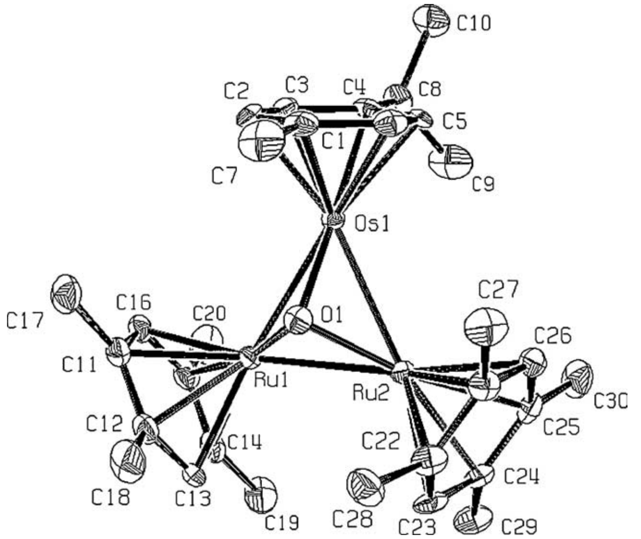


Fig. 2. ORTEP drawing of cation **2** at the 35% probability level. Hydrogen atoms and hexafluorophosphate molecule are omitted for clarity.

Spectroscopic data for [**3**][PF_6]: ^1H NMR (400 MHz, acetone-d_6): $\delta = 5.68$ (s, 6H, $C_6\mathit{H}_6$), 5.61 (s, 4H, $C_6\mathit{H}_2(CH_3)_4$), 2.22 (s, 12H, $C_6H_2(C\mathit{H}_3)_4$), 2.21 (s, 12H, $C_6H_2(C\mathit{H}_3)_4$), −18.08 (t, 1H, Ru-hydride, $^2J = 3.7$ Hz), −18.93 (d, 2H, Ru–Os-hydride, $^2J = 3.7$ Hz). IR (KBr pellets) ν (cm^{-1}): 3430 (s), 3129 (s), 2984 (m), 2920 (m), 1634 (w), 1448 (m), 1399 (s), 1386 (s), 1026 (m), 840 (vs), 558 (s). MS (ESI positive mode, acetone): *m*/*z*: 758 $[M]^+$. *Anal.* Calc. for $C_{26}H_{37}F_6OOsPRu_2 \cdot H_2O$: C, 33.91; H, 4.27. Found: C, 33.82; H, 4.11%.

2.3. X-ray crystallographic study

Crystals of [**1**][BF_4], [**2**][PF_6] and [**3**][PF_6] were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle, using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–100°, increment of, respectively, 1.4°, 1.2° and 0.8°, 2θ range from 2.0° to 26°, D_{max}–D_{min} = 12.45–0.81 Å. The structures were solved by direct methods using the program SHELXS-97 [16]. The refinement and all further calculations were carried out using SHELXL-97 [17]. In [**1**][BF_4], the hydrido ligands were not located from Fourier difference maps and they were generated at their positions, whereas in [**2**][PF_6] and [**3**][PF_6] they were located and fixed. In all cases, the other 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. In complexes [**1**][BF_4] and [**3**][PF_6], the residual electron densities greater than 1 e $Å^{-3}$ are observed around the ruthenium and osmium atoms at less than 1 Å. Crystallographic details are summarised in Table 1. Figs. 1–3 were drawn with ORTEP [18].

3. Results and discussion

The trinuclear cations $[H_3Ru_2(C_6Me_6)_2Os(C_6H_6)(O)]^+$ (**1**), $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2Os(p\text{-}MeC_6H_4{}^i\text{-}Pr)(O)]^+$ (**2**) and $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)_2Os(C_6H_6)(O)]^+$ (**3**) have been synthesised in solution (acetone/water) from the triaqua complexes $[Os(C_6H_6)(H_2O)_3]^{2+}$ and $[Os(p\text{-}MeC_6H_4{}^iPr)(H_2O)_3]^{2+}$ formed in situ from the corresponding dichloride dimers, and from the known dinuclear precursors $[H_3Ru_2(C_6Me_6)]^+$ [11,12] and $[H_3Ru_2(1,2,4,5\text{-}C_6H_2Me_4)]^+$ [13], see Scheme 1.

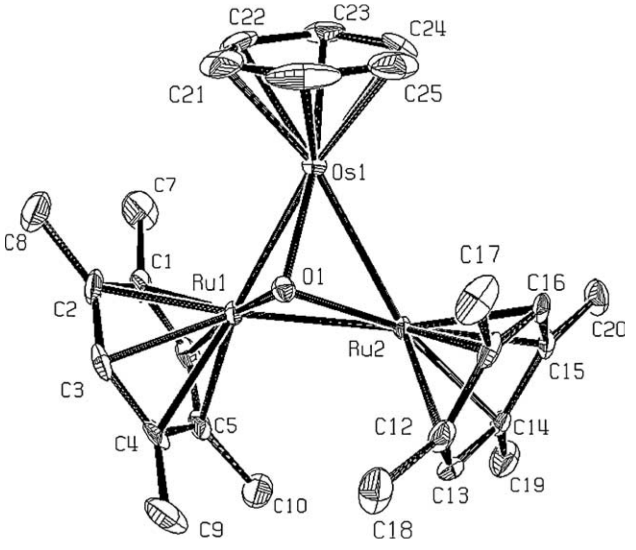
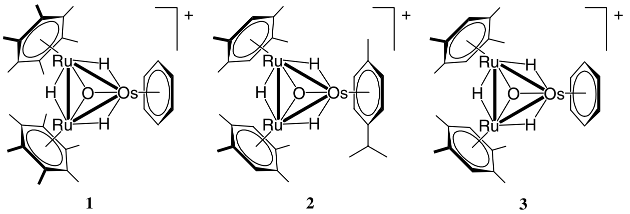


Fig. 3. ORTEP drawing of cation **3** at the 35% probability level. Hydrogen atoms, acetone and hexafluorophosphate molecule are omitted for clarity.

The ^1H NMR spectra of [**1**][BF_4], [**2**][PF_6] and [**3**][PF_6] give rise to two characteristic hydride signals, a triplet ($\delta = -19.11$ ppm for **1**, -18.06 ppm for **2** and -18.08 ppm for **3**) and a doublet ($\delta = -19.39$ ppm for **1**, -19.13 ppm for **2** and -18.93 ppm for **3**) integrating for 1 and 2 protons, respectively, the rest of the signals correspond to the protons of the arene-metal moieties.

$$[H_3Ru_2(\text{arene})_2]^+ + [(\text{arene}')Os(H_2O)_3]^{2+} \rightarrow [H_3Ru_2(\text{arene})_2Os(\text{arene}')(O)]^+ + 2H_2O + 2H^+$$

The X-ray structure analyses of [**1**][BF_4], [**2**][PF_6] and [**3**][PF_6] have been performed. Poor quality crystals of [**1**][BF_4] have been obtained, and for comparison only, its molecular structure is presented, see Fig. 1. The molecular structures of cations **2** and **3** are shown in Figs. 2 and 3, respectively. Interestingly, despite the replacement of one ruthenium by an osmium atom, the metrical parameters around the metallic framework compare well with those of the trinuclear ruthenium cluster cations, $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ (**4**) [10], see Table 2.



Scheme 1.

In all cases, the metal core consists of two ruthenium atoms and one osmium, with metal–metal distances being in accordance with a metal–metal single bond. The three metals are capped by a μ_3-oxo ligand which is almost symmetrically coordinated. The Ru–Os distances are slightly longer than the Ru–Ru distances. However, the triangle formed by the three metal centres remains almost equiangular with the three angles at nearly 60°. In **2**, the *p*-cymene ring can be considered planar with the isopropyl group bent towards the osmium atom, while the two durene ligands adopt an eclipsed configuration.

In the crystal packing of [**2**][PF_6], the hexafluorophosphate anions are closely surrounded by four cations of **2**. A series of C–H···F contacts are observed, the H···F distances ranging from 2.33 to 2.67 Å. These values compare well with those observed for other systems with C–H···F interactions [19].

In the crystal packing of [**3**][PF_6], an acetone molecule, situated on a centre of symmetry, forms a hydrogen-bonded network with the μ_3-oxo ligand of two neighbour-

Table 2
Selected bond lengths (Å) and angles (°) for [**1**][BF_4], [**2**][PF_6], [**3**][PF_6], and [**4**][BF_4]

	[**1**][BF_4]	[**2**][PF_6]	[**3**][PF_6]		[**4**][BF_4] [10]
Interatomic distances (Å)					
O(1)–Ru(1)	2.04(3)	2.005(4)	2.004(3)	O(1)–Ru(1)	1.999(3)
O(1)–Os(1)	1.87(2)	2.003(4)	2.012(3)	O(1)–Ru(2)	2.003(3)
O(1)–Ru(2)	2.04(3)	2.004(4)	1.997(3)	O(1)–Ru(3)	2.008(3)
Ru(1)–Ru(2)	2.781(3)	2.7487(6)	2.7656(7)	Ru(1)–Ru(2)	2.7992(6)
Ru(1)–Os(1)	2.758(2)	2.7693(5)	2.7678(7)	Ru(1)–Ru(3)	2.7450(6)
Ru(2)–Os(1)	2.758(2)	2.7619(5)	2.7464(6)	Ru(2)–Ru(3)	2.7442(6)
Bond angles (°)					
Ru(1)–Ru(2)–Os(1)	59.72(3)	60.34(2)	60.28(2)	Ru(1)–Ru(2)–Ru(3)	59.35(2)
Ru(1)–Os(1)–Ru(2)	60.56(6)	59.60(1)	60.20(1)	Ru(1)–Ru(3)–Ru(2)	61.32(2)
Ru(2)–Ru(1)–Os(1)	59.72(3)	60.07(2)	59.52(2)	Ru(2)–Ru(1)–Ru(3)	59.33(2)

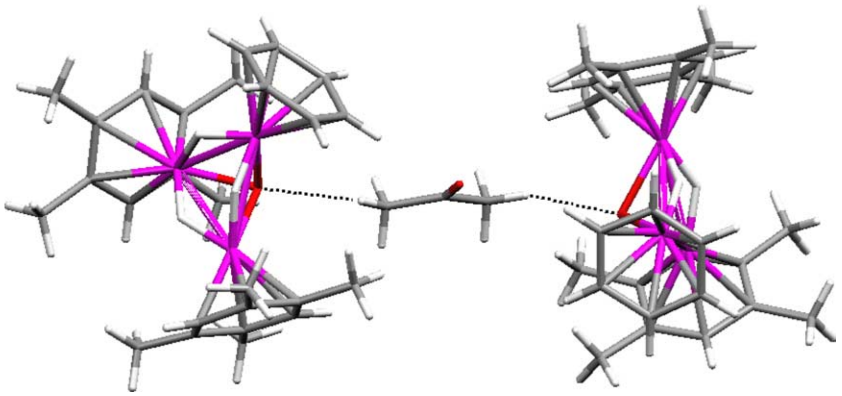


Fig. 4. Hydrogen-bonded system forms between two cations of **3** and an acetone molecule [20].

ing cluster cations, see Fig. 4. Thus, a weak μ_3-oxo–acetone–μ_3-oxo hydrogen-bonded system is obtained. The C–O distance of the hydrogen bond is 3.230(8) Å with a C–H···O angle of 134.3°. The total distance between the two bridged μ_3-oxo ligands is 8.91(1) Å.

4. Supplementary material

CCDC Nos. 219497 [**1**][BF_4], 219498 [**2**][PF_6] and 269570 [**3**][PF_6] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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].

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