

X-ray crystallographic study of two dinuclear triply-bridged *p*-cymene osmium complexes

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Abstract

The single crystal X-ray structure analyses of $[\text{Os}_2(p\text{-cymene})_2(\mu\text{-H})_3]\text{PF}_6$ (**[1]**PF₆) and $[\text{Os}_2(p\text{-cymene})_2(\mu\text{-Cl})_3]\text{PF}_6$ (**[2]**PF₆) are presented. The two triple bridged arene osmium complexes show the metal to be in an octahedral geometry, where the *p*-cymene ligand is facially coordinated and where the bridging ligands (Cl or H) occupy the remaining three coordination sites. In the dinuclear trihydrido complex a strong metal–metal interaction is observed. This is not the case for the trichloro complex where a large metal–metal distance indicates no metal–metal bonding.

Keywords: Arene ligand; Bridging ligand; Crystal packing; Hydride; Osmium

1. Introduction

Arene osmium complexes are relatively scarce as compared to the rich arene ruthenium chemistry. Likewise, the number of structural studies of arene osmium complexes is much smaller than that of the arene ruthenium analogues. Thus, a search in the Cambridge structural database reveals a 10–1 ratio for structures possessing an η^6 -arene ruthenium moiety compared to η^6 -arene osmium [1]. Therefore, all structurally characterised arene osmium compounds contribute to the systematics of the metrical parameters of arene osmium derivatives.

Herein we report the single-crystal structure analyses of two dinuclear arene osmium complexes, $[\text{Os}_2(p\text{-cymene})_2(\mu\text{-H})_3]\text{PF}_6$ and $[\text{Os}_2(p\text{-cymene})_2(\mu\text{-Cl})_3]\text{PF}_6$. The results show that the dinuclear trihydrido complex possesses a strong metal–metal interaction, whereas the trichloro analogue displays no metal–metal interaction.

2. Experimental section

2.1. General remarks

$[\text{Os}_2(p\text{-cymene})_2(\mu\text{-H})_3]\text{PF}_6$ and $[\text{Os}_2(p\text{-cymene})_2(\mu\text{-Cl})_3]\text{PF}_6$ were prepared according to published methods [2].

2.2. Crystallisations

Preparation of **[1]**PF₆: in a test tube, 1 mL of chloroform is added to an acetone solution (3 mL) of $[\text{Os}_2(p\text{-cymene})_2(\mu\text{-H})_3]\text{PF}_6$ (1 mg). The solution is left at room temperature overnight, the test tube being slightly open, until small orange plates are observed.

Preparation of **[2]**PF₆: in a test tube, 1 mL of chloroform is added to an acetone solution (3 mL) of $[\text{Os}_2(p\text{-cymene})_2(\mu\text{-Cl})_3]\text{PF}_6$ (1 mg). The solution is left at room temperature for several days, the test tube being slightly open, until yellow plates are observed.

2.3. X-ray crystallographic study

Crystals of **[1]**PF₆, and **[2]**PF₆ were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ

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Table 1
Crystallographic and selected experimental data for [1]PF₆ and [2]PF₆

	[1]PF ₆	[2]PF ₆
Chemical formula	C ₂₀ H ₃₁ F ₆ POs ₂	C ₂₀ H ₂₈ Cl ₃ F ₆ POs ₂
Formula weight	796.82	900.14
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P2₁/n</i>	<i>Pccn</i>
Crystal colour and shape	Orange plate	Yellow plate
Crystal size	0.28 × 0.22 × 0.12	0.35 × 0.25 × 0.08
<i>a</i> (Å)	10.1948(9)	10.984(1)
<i>b</i> (Å)	9.5725(6)	13.460(1)
<i>c</i> (Å)	23.832(2)	16.835(2)
<i>B</i> (°)	92.769(10)	
<i>V</i> (Å ³)	2323.1(3)	2489.2(4)
<i>Z</i>	4	4
<i>T</i> (K)	153(2)	153(2)
<i>D_c</i> (g cm ⁻³)	2.278	2.402
<i>μ</i> (mm ⁻¹)	11.049	10.638
Scan range (°)	4.28 < 2θ < 51.74	4.84 < 2θ < 51.74
Unique reflections	4330	2370
Reflections used [<i>I</i> > 2σ(<i>I</i>)]	3572	1423
<i>R_{int}</i>	0.0620	0.1080
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0299, <i>wR</i> ₂ 0.0707	0.0530, <i>wR</i> ₂ 0.1324
<i>R</i> indices (all data)	0.0383, <i>wR</i> ₂ 0.0772	0.0978, <i>wR</i> ₂ 0.1464
Goodness-of-fit	0.981	0.931
Max, min Δρ/e (Å ⁻³)	1.404, -1.789	2.937, -1.576

circle goniometer, using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–200°, increment of 0.9 and 0.7°, respectively, 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 [3]. The refinement and all further calculations were carried out

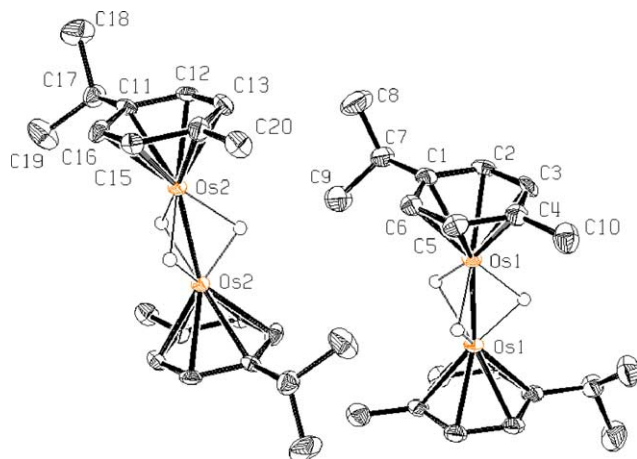


Fig. 1. ORTEP drawing of **1** showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and PF₆ anions are omitted for clarity. Selected bond lengths (Å): Os(1)–Os(1)ⁱ 2.4708(4), Os(2)–Os(2)ⁱⁱ 2.4710(5), C(1)–Os(1) 2.218(6), C(2)–Os(1) 2.202(6), C(3)–Os(1) 2.209(6), C(4)–Os(1) 2.232(6), C(5)–Os(1) 2.208(6), C(6)–Os(1) 2.192(6), C(11)–Os(2) 2.207(6), C(12)–Os(2) 2.191(6), C(13)–Os(2) 2.200(6), C(14)–Os(2) 2.224(6), C(15)–Os(2) 2.206(6), C(16)–Os(2) 2.200(6). Symmetry code: (i) 0.5 – *x*, *y*, 0.5 – *z*; (ii) 1 – *x*, –*y*, 1 – *z*.

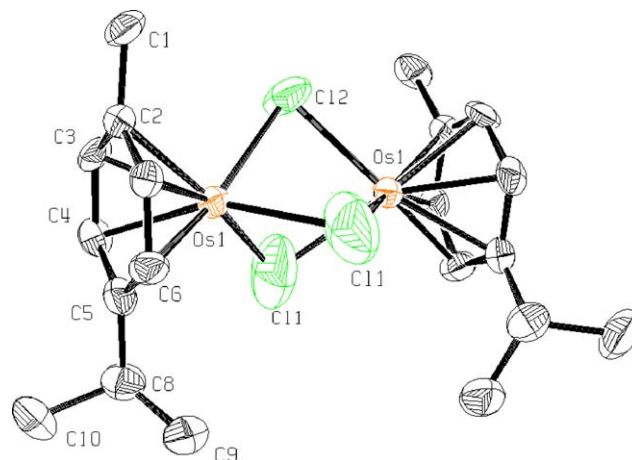


Fig. 2. ORTEP drawing of **2** showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and PF₆ molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Os(1)–Os(1)ⁱ 3.236(1), Os(1)–Cl(1) 2.422(4), Os(1)–Cl(2) 2.470(9), C(2)–Os(1) 2.202(15), C(3)–Os(1) 2.165(14), C(4)–Os(1) 2.178(14), C(5)–Os(1) 2.196(15), C(6)–Os(1) 2.153(13), C(7)–Os(1) 2.147(15); Cl(1)–Os(1)–Cl(2) 81.5(2), Cl(1)–Os(1)–Cl(1)ⁱ 80.3(3), Os(1)–Cl(1)–Os(1)ⁱ 83.8(2), Os(1)–Cl(2)–Os(1)ⁱ 82.8(3). Symmetry code: (i) 0.5 – *x*, –0.5 – *y*, *z*.

using SHELXL-97 [4]. In **1**, the hydrido ligands were located from Fourier difference maps and fixed at their positions whereas the remaining H-atoms of complex **1** and those of compound **2** were included in calculated positions and treated as riding atoms using the SHELXL default parameters. In both cases the non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2 . In one independent molecule of complex **1**, the hydrido ligands were disordered over two positions and were treated with partial occupancy factors of 0.5. In complex **2**, the residual electron densities greater than $2e \text{ \AA}^{-3}$ are both observed around the osmium atom at less than 1 Å. Crystallographic details are summarised in Table 1. Figs. 1 and 2 were drawn with ORTEP [5] and Fig. 3 with MERCURY [6].

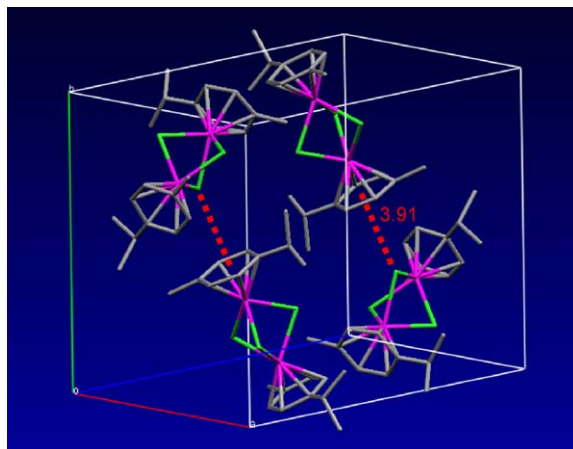
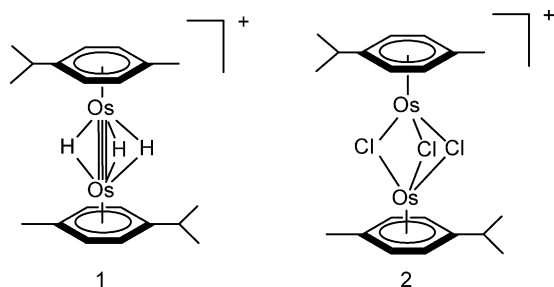


Fig. 3. Crystal packing of **2** showing the chlorine–benzene distances.



Scheme 1.

CCDC-254151 **[1]**PF₆ and 254152 **[2]**PF₆ 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: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussion

In 1981, the synthesis of the dinuclear complex [Os(*p*-cymene)Cl₂]₂ opened the door to the formation of *p*-cymene osmium derivatives [7]. From this dinuclear arene osmium compound, a variety of complexes were synthesised [2,8–19], among them the cationic species [Os₂(*p*-cymene)₂(μ-H)₃]⁺ (**1**) and [Os₂(*p*-cymene)₂(μ-Cl)₃]⁺ (**2**), see Scheme 1.

The two compounds were identified based on spectroscopic evidence, NMR, infrared, and mass spectroscopy [2]. However, they were not structurally characterised. Recently, we have been using these compounds in our laboratory and in order to rationalise the reactivity of **1** and **2**, single-crystal X-ray structure analysis was performed. In both compounds, the *p*-cymene rings can be considered planar with the isopropyl groups bending towards the osmium. The molecular structure and the atomic numbering scheme of **1** are presented in Fig. 1.

Two independent half-molecules are observed in the crystal packing of **1**. The short Os–Os distances of 2.4708(4) and 2.4710(5) Å are attributed to a metal–metal triple bond. The values are comparable to the mesitylene analogue [Os₂(C₆H₃Me₃)₂(μ-H)₃] (2.4741(2) Å) [20]. In both dimeric molecules the two benzene rings of the *p*-cymene moieties are in a perfect eclipsed conformation.

In complex **2**, the two halves of the dimeric complex are related by symmetry and are joined by three chlorine ligands bridging the two osmium atoms, see Fig. 2. Each osmium atom is coordinated to an η⁶-*p*-cymene ligand. The average bond angle for the bridging chloro ligands is 83.3(3)° compare to 84–86° in the ruthenium analogues [Ru₂(*p*-cymene)₂(μ-Cl)₃]⁺ [21], [Ru₂(C₆H₆)₂(μ-Cl)₃]⁺ and [Ru₂(C₆H₅Me)₂(μ-Cl)₃]⁺ [22]. This slightly difference in bridging angles is due to a shorter Os–Os distance in **2** (3.236(1) Å) compared to those found in [Ru₂(*p*-cymene)₂(μ-Cl)₃]⁺

(3.282(3) Å), [Ru₂(C₆H₆)₂(μ-Cl)₃]⁺ (3.285(1) Å) and [Ru₂(C₆H₅Me)₂(μ-Cl)₃]⁺ (3.275(1) Å). The bridging Os–Cl distances are shorter than the one observed in [Os(*p*-cymene)Cl₂]₂ [23].

In the crystal packing, one chlorine atom is oriented towards the benzene ring of the *p*-cymene ligand, see Fig. 3. The distance between the chlorine atom and the centroid of the benzene ring of the *p*-cymene ligand is 3.91 Å. Otherwise; there is no meaningful interaction between the dinuclear cation and the PF₆ anion, other than normal coulombic attractions.

Acknowledgements

This work was supported by the Swiss National Science Foundation (grant no. 20-61227-00). We thank Professor H. Stoeckli-Evans for access to X-ray facilities.

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