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Inorganica Chimica Acta 359 (2006) 2644–2649
Inorganica Chimica Acta
www.elsevier.com/locate/ica

A new precursor for organo-osmium complexes

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Received 31 August 2005; accepted 19 September 2005
Available online 9 March 2006

Dedicated in friendship and admiration to Brian James for his 70th birthday.

Abstract

The use of potassium osmate, $K_2[OsO_2(OH)_4]$, as a precursor for some cyclopentadienyl-osmium complexes is described. The X-ray structures of $OsBr(PPh_3)_2Cp$, OsCl(dppe)Cp and OsX(dppe)Cp* (X = Cl, Br) are reported.

Keywords: Cyclopentadienyl; Osmium; Phosphine; X-ray structures

1. Introduction

There is increasing interest in the organometallic chemistry of osmium as the nature of the differences from its lighter congenor ruthenium become more apparent. The usual precursor for these complexes is osmium(VIII) oxide, OsO_4, a pale yellow solid (m.p. 31 °C) which has an appreciable vapour pressure at ambient temperatures and which can cause severe physiological problems if appropriate care is not taken [1]. The use of dilute solutions for staining or other preparation of organic samples for histological study is well-known [2]. Conversion of OsO_4 to other starting materials has been documented in books of syntheses, tested procedures for the rather insoluble $(NH_4)_2[OsBr_6]$ (by direct reduction with conc. aqueous HBr) [3a] or $(NH_4)_2[OsCl_6]$ [by treatment with conc. HCl and Fe(II)] [3b] being examples.

The difficulty in reduction of OsO_4 directly by concentrated HCl has resulted in bromo-osmium complexes being generally prepared for use as precursors. The intermediate $H_2[OsBr_6]$ can be used for the synthesis of some cyclopentadienyl-osmium complexes, such as $OsBr(PPh_3)_2Cp$ [4] or $OsCp_2$ [5], the further reduction to osmium(II) being achieved with an excess of PPh_3 or zinc, respectively. The presence of iron(II) or (III) compounds limits the applicability of this route when cyclopentadienyl ligands are involved.

Recent changes to rules covering transport of hazardous materials by air have resulted in there being some reluctance to transport OsO_4 and other starting materials which are less problematical have been sought. One of these is so-called "potassium osmate" which is formulated as the tetrahydroxo-dioxo-osmate(VI), $K_2[OsO_2(OH)_4]$. Conversion of OsO_4 to this salt is effected in ethanolic KOH [6]. We have recently developed methods for entry into cyclopentadienyl-osmium chemistry from this material and present below one-pot syntheses of several common precursors.

2. Results and discussion

Potassium osmate is a brown solid which is soluble in hot concentrated HCl with reaction to form a yellow solution, but unlike OsO_4, insoluble in aromatic hydrocarbons (benzene and toluene), alcohols (MeOH, EtOH), dichloromethane or acetone. In order to reduce the osmium, we have heated it in refluxing concentrated HCl overnight. The excess of HCl was removed by distillation to give a brick-red solid, after which a solution of PPh_3 in aqueous *t*-butanol which had been degassed by argon was added to the residue. After heating at reflux point for 18 h, the resulting green solution was allowed to cool to give a green precipi-

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doi:10.1016/j.ica.2005.09.070

tate which was then collected, washed with ethanol and hexane and dried under reduced pressure to give $OsCl_2(PPh_3)_3$ in 99% yield. This compound has also been prepared directly from $(NH_4)_2[OsCl_6]$ and PPh_3 in *t*-butanol [7].

Introduction of a cyclopentadienyl group was accomplished by treating $OsCl_2(PPh_3)_3$ with LiCp in thf for 15 min. After removal of solvent, the residue was extracted with the minimum amount of benzene and filtered through a short silica column. Excess PPh_3 was eluted with hexane and the yellow $OsCl(PPh_3)_2Cp$ (**1-Os**) (76% yield) was washed off the column with 10% acetone–hexane. Ready exchange of PPh_3 for dppe was achieved by heating the two reactants in refluxing toluene overnight. Similar purification on a silica column afforded OsCl(dppe)Cp (**2-Os**) in 81% yield.

The pentamethylcyclopentadienyl analogue was obtained in a one-pot procedure by adding a degassed solution of pentamethylcyclopentadiene in aqueous ethanol to the residue obtained after heating potassium osmate with conc. HCl. The mixture was heated at reflux point for 1 h before adding 1,5-cyclooctadiene and continued heating at reflux overnight. After this time, evaporation of the solvent, extraction with diethyl ether and further evaporation gave a residue [probably OsCl(cod)Cp*] which was treated directly with a solution of dppe in heptane. After heating at reflux point for 18 h, the yellow precipitate which separated was filtered off. Chromatography of the filtrate (silica gel) afforded a further amount of pure yellow OsCl(dppe)Cp* (**3-Os**) (combined yield 61%).

2.1. Molecular structures

In the course of this work, we determined the molecular structures of $OsBr(PPh_3)_2Cp$ (**4-Os**) (obtained by the previously reported route from $H_2[OsBr_6]$, PPh_3 and cyclopentadiene and crystallised from benzene/hexane), OsCl(dppe)Cp (**2-Os**) (obtained as described above and crystallised from dichloromethane/hexane), OsCl(dppe)Cp* (**3-Os**), and [obtained from $OsBr(PPh_3)_2Cp$ and dppe and crystallised from benzene/methanol]. An earlier structural determination was carried out on a mixture of OsX(dppe)Cp* (X = Br/Cl 82/18, **3/5-Os**), obtained when **5-Os** was crystallised from chloroform. These molecules are illustrated in Figs. 1–3 and selected bond distances are presented in Table 1, together with values previously reported for the ruthenium analogues. As can be seen, these are further examples of Group 8 complexes of the type MX(PP)Cp′, all having pseudo-octahedral geometry at the metal centre.

The structure of $OsBr(PPh_3)_2Cp$ (**4-Os**) as its dichloromethane solvate has been reported previously, together with the isomorphous and isostructural ruthenium compound **4-Ru** [8]. The present study, carried out on a solvent-free crystal, shows surprising and significant differences in the coordination geometry around the osmium centre. Thus, in the present study, the Os–P distances are longer by up to 15 standard deviations, while the Os–Br distance is also longer, by 0.04_1 Å. The increase in Os–C(cp) distances is less significant, average values being 2.21_8 and 2.17_7 Å. These changes result in a slight opening of the P–Os–P and P–Os–Br angles.

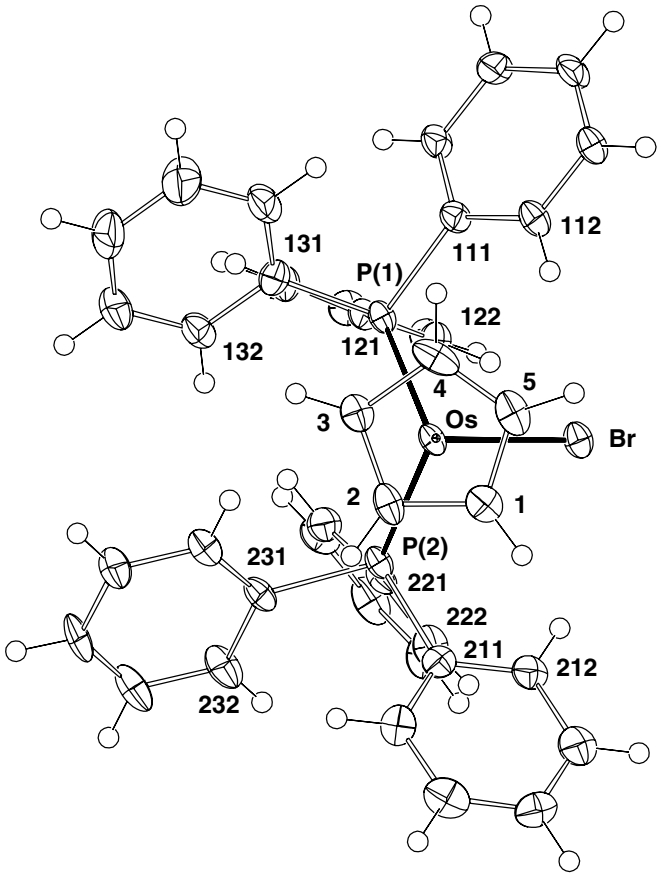
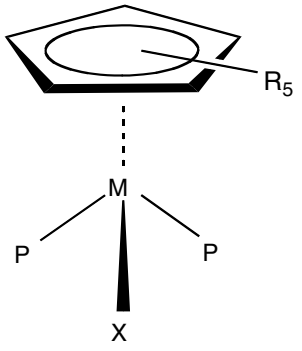


Fig. 1. Projection of a single molecule of $OsBr(PPh_3)_2Cp$ (**4-Os**) down the cp-centroid/metal atom vector.

The reasons for these changes is not obvious; the presence of the solvent molecule in a unit cell of otherwise similar volume creating steric pressure or other interactions on the complex may be relevant, but the difference may also reflect the caution needed in using results derivative of r.t. data without libration correction for quantitative purposes.



	X	PP	C_5R_5
1-M	Cl	$(PPh_3)_2$	Cp
2-M	Cl	dppe	Cp
3-M	Cl	dppe	Cp*
4-M	Br	$(PPh_3)_2$	Cp
5-M	Br	dppe	Cp*

M = Fe, Ru, Os

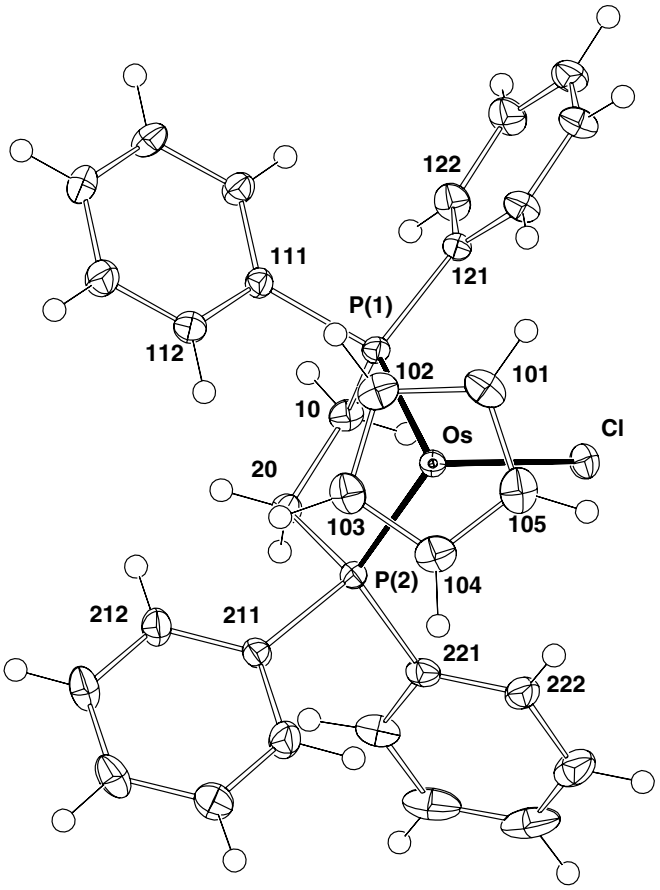


Fig. 2. Projection of a single molecule of OsCl(dppe)Cp (**2-Os**) down the cp-centroid/metal atom vector.

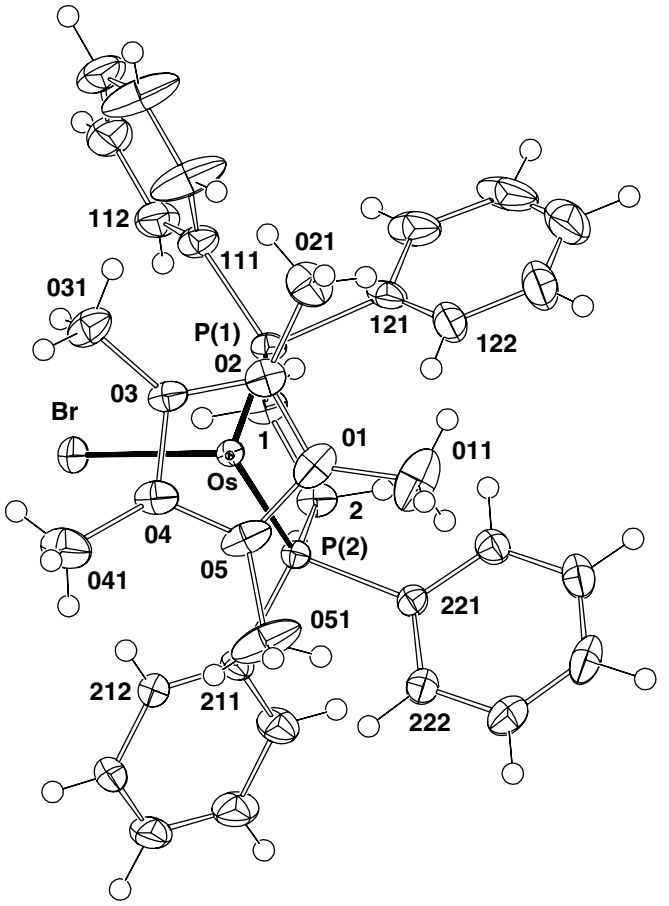


Fig. 3. Projection of a single molecule of OsBr(dppe)Cp* (**5-Os**) down the cp-centroid/metal atom vector.

As expected, the similarity of the covalent radii of ruthenium and osmium (Ru: 1.26, Os 1.28 Å) [9] results in there being essentially no differences in the M–P and M–Cl bond lengths in MCl(dppe)Cp and MX(dppe)Cp*, with the exception of the Os–Br and Ru–Cl bonds in the latter, which differ by 0.13 Å (cf. the difference in covalent radii of Cl and Br, 0.15 Å). The M–C(cp) distances are somewhat shorter than the M–C(cp*) separations on account of the increased bulk of the latter ligand. Significant differences are found in the P–M–X angle pair between the PPh_3 and dppe complexes, contingent on the effects of the Ru–P–C–C–P ring constraint in the latter.

2.2. Electrochemistry

It was of interest to compare the ease of oxidation of these complexes, together with several analogous compounds. Cyclic voltammograms were measured and showed one or two oxidation processes, the potentials of which are summarised in Table 2. Several comparisons can be made, the most pertinent being the change in a series of MCl(dppe)Cp′ as the Group is descended. For both Cp and Cp* compounds, the ease of oxidation M(II)/M(III) increases as Fe > Os > Ru, with the Cp* derivatives being more easily oxidised than the Cp compounds by ca. 280 (Fe), 220 (Ru) or 210 mV (Os), as expected when the more strongly electron-donating Cp* ligand replaces Cp. The dppe complexes are more readily oxidised than the bis-PPh_3 analogues, while replacement of Cl by Br results in an increase of oxidation potential of ca. 25 mV. Irreversible second oxidations, assigned to M(III)/M(IV), were found for four of the compounds, although somewhat surprisingly, not for some of the Cp* complexes.

3. Conclusions

We have described useful routes into selected organo-osmium precursors from a more readily available source of osmium, namely $K_2[OsO_2(OH)_4]\cdot 2H_2O$. Reliable and improved routes into the complexes OsX(PP)Cp′ (X = Cl, Cp′ = Cp PP = $(PPh_3)_2$, dppe; X = Cl, Cp′ = Cp*, PP = dppe) are also reported.

4. Experimental

4.1. General

All reactions were carried out under dry argon, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under argon and degassed before use.

Table 1
Selected bond distances (Å) and angles (°) in MX(PP)Cp′

Complex	**1-Ru**[a]	**1-Os**[b]	**2-Ru**[c]	**2-Os**	**3-Ru**[d]	**3-Os**
MX	RuCl	OsCl	RuCl	OsCl	RuCl	OsCl
PP	$(PPh_3)_2$	$(PPh_3)_2$	dppe	dppe	dppe	dppe
Cp′	Cp	Cp	Cp	Cp	Cp*	Cp*
Solvate	CH_2Cl_2	CH_2Cl_2	$CHCl_3$	CH_2Cl_2		
Bond distances (Å)						
M–P(1)	2.323(1)	2.320(2)	2.2688(7)	2.2705(7)	2.2882(5)	2.2714(9)
M–P(2)	2.329(1)	2.319(2)	2.2863(7)	2.2797(7)	2.2812(5)	2.2694(8)
M–X	2.448(1)	2.460(2)	2.4466(7) [Cl]	2.4488(8) [Cl]	2.4532(5) [Cl]	2.4437(9) [Cl]
M–C(Cp)	2.159–2.218(3)	2.183–2.235(6)	2.169–2.227(4)	2.172–2.243(4)	2.219–2.252(2)	2.214–2.250(4)
(av.)	2.20(1)	2.21(2)	2.20(3)	2.22(5)	2.24(1)	2.230(14)
Bond angles (°)						
P(1)–M–P(2)	103.79(3)	103.23(6)	83.48(2)	83.43(3)	82.15(2)	82.12(3)
P(1)–M–X	88.29(3)	88.44(6) [Cl]	83.04(3) [Cl]	84.00(3) [Cl]	81.93(2) [Cl]	82.22(3) [Cl]
P(2)–M–X	89.15(3)	89.77(5) [Cl]	93.28(3) [Cl]	93.33(3) [Cl]	90.93(2) [Cl]	90.74(3) [Cl]

Complex	**4-Ru**[e]	**4-Os**	**4-Os**[e]	**5-Os**	**3/5-Os**
MX	RuBr	OsBr	OsBr	OsBr	Os(Br/Cl)
PP	$(PPh_3)_2$	$(PPh_3)_2$	$(PPh_3)_2$	dppe	dppe
Cp′	Cp	Cp	Cp	Cp*	Cp*
Solvate	CH_2Cl_2		CH_2Cl_2		
Bond distances (Å)					
M–P(1)	2.323(2)	2.327(2)	2.290(2)	2.2870(6)	2.2851(5)
M–P(2)	2.329(2)	2.318(2)	2.297(2)	2.2780(7)	2.2781(5)
M–X	2.5683(8) [Br]	2.585(1) [Br]	2.5438(9) [Br]	2.5818(4) [Br]	2.5708(3) [Br/Cl]
M–C(Cp)	2.172–2.220(5)	2.19–2.24(1)	2.150–2.197(6)	2.229–2.260(3)	2.228–2.261(2)
(av.)	2.20(2)	2.22(2)	2.18(2)	2.242(13)	2.240(14)
Bond angles (°)					
P(1)–M–P(2)	103.18(5)	104.28(8)	103.13(7)	82.11(2)	82.13(2)
P(1)–M–X	88.36(4) [Br]	89.50(6) [Br]	88.45(5) [Br]	82.39(2) [Br]	82.42(1) [Br/Cl]
P(2)–M–X	90.77(4) [Br]	90.94(6) [Br]	90.48(5) [Br]	91.84(2) [Br]	91.95(1) [Br/Cl]

[a] Ref. [11].
[b] Ref. [8a].
[c] Ref. [12].
[d] Ref. [13].
[e] Ref. [8b].

Table 2
Electrochemical data for MCl(dppe)Cp′ (M = Fe, Ru, Os; Cp′ = Cp, Cp*)

	Complex	E_1	E_2
2-Fe	FeCl(dppe)Cp	+0.04	+0.68
3-Fe	FeCl(dppe)Cp*	−0.24	
1-Ru	$RuCl(PPh_3)_2Cp$	+0.595	
	$RuCl(PPh_3)_2Cp^*$	+0.385	
	RuCl(dppm)Cp*	+0.245	
2-Ru	RuCl(dppe)Cp	+0.46	
3-Ru	RuCl(dppe)Cp*	+0.28	+1.37
4-Os	$OsBr(PPh_3)_2Cp$	+0.490	
2-Os	OsCl(dppe)Cp	+0.38	+1.18
3-Os	OsCl(dppe)Cp*	+0.17	+1.19
5-Os	OsBr(dppe)Cp*	+0.195	

Conditions: 0.1 M $[NBu_4]PF_6/CH_2Cl_2$, scan rate 100 mV s^{-1}, 293 K, Pt electrodes.

4.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 MHz). Samples were dissolved in $CDCl_3$ or C_6D_6 contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Finnegan LCQ spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas.

4.3. Reagents

Potassium osmate was obtained from Johnson Matthey and used as received.

4.4. Preparation of $OsCl_2(PPh_3)_3$

A solution of $K_2[OsO_2(OH)_4]$ (2.00 g, 5.43 mmol) in conc. HCl (300 ml) was heated at reflux point for 18 h.

The excess HCl was evaporated and a degassed solution of PPh_3 (10.0 g, 38.13 mmol) in *t*-butanol (420 ml) and water (150 ml) was added to the solid residue. After heating a reflux point for 18 h, after which time a green suspension had formed, the mixture was cooled and the precipitate filtered off, washed with EtOH and hexane and dried in vacuum to give $OsCl_2(PPh_3)_3$ (5.63 g, 99%).

4.5. Preparation of $OsCl(PPh_3)_2Cp$ (**1-Os**)

Thf (50 ml) was added to a solid mixture of LiCp (30 mg, 0.45 mmol; from LiBu and C_5H_6 in hexane, followed by filtration of the white LiCp and drying) and $OsCl_2(PPh_3)_3$ (468 mg, 0.45 mmol) and the solution was stirred for 15 min. After removal of solvent under vaccum, the residue was taken up in a minimum amount of benzene and chromatographed (silica gel). Hexane removed PPh_3 and 10% acetone–hexane eluted yellow $OsCl(PPh_3)_2Cp$ (**1-Os**) (234 mg, 76%). ^{1}H NMR ($CDCl_3$): δ 4.37 (s, 5H, Cp), 7.15–7.39 (m, 30H, Ph). ^{3}P NMR ($CDCl_3$): δ −1.20 (s, PPh_3). ES-MS (positive ion, MeOH, *m*/*z*): 781, $[M-Cl]^+$; 519, $[Os(PPh_3)Cp]^+$.

4.6. Preparation of OsCl(dppe)Cp (**2-Os**)

A solution of $OsCl(PPh_3)_2Cp$ (1.8 g, 2.2 mmol) and dppe (964 mg, 2.42 mmol) in toluene (100 ml) was heated at reflux point for 18 h. The mixture was filtered and the filtrate was chromatographed on silica gel, washing off displaced PPh_3 with hexane and eluting the product with 10% acetone–hexane to give yellow OsCl(dppe)Cp (**2-Os**) (1.23 g, 81%). *Anal.* Calc. for ($C_{36}H_{39}ClOsP_2 \cdot CH_2Cl_2$): C, 49.65; H, 4.04. Found: C, 49.63; H, 4.10%. *M*, 690. IR (nujol): 1306w, 1180w, 1095s, 1026w, 998w, 791m, 749m, 696s, 671w cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.17, 2.38 (2 × m, 2 × 2H, CH_2), 4.52 (s, 5H, Cp), 6.84–8.02 (m, 20H, Ph). ^{13}C NMR (C_6D_6): δ 29.12–30.44 (m, CH_2), 75.75 [t, *J*(CP) 2.5 Hz, Cp], 128.07–143.56 (m, Ph). ^{31}P NMR (C_6D_6): δ 46.6. ES-MS (positive ion, MeOH, *m*/*z*): 655, $[M-Cl]^+$.

4.7. Preparation of OsCl(dppe)Cp* (**3-Os**)

A solution of $K_2[OsO_4(OH)_2]$ (138 mg, 0.42 mmol) in conc. HCl (20 ml) was heated at reflux point for 18 h. The excess HCl was distilled off before adding a degassed solution of pentamethylcyclopentadiene (0.1 ml, 0.62 mmol) in aqueous ethanol (2 + 15 ml). This mixture was heated under reflux for 1 h, 1,5-cyclooctadiene (0.26 ml, 2.10 mmol) was added and the mixture heated a further 18 h. After removal of solvent, the residue was extracted with Et_2O and the filtered solution was again evaporated. After addition of dppe (182 mg, 0.46 mmol) in heptane (20 ml) and heating under reflux for 18 h, the yellow precipitate which had separated was filtered off (176 mg). The filtrate was then chromatographed (silica gel column, eluted with 1% acetone–hexane) to give a further amount of pure yellow OsCl(dppe)Cp* (**3-Os**) (total yield 192 mg, 61%). *Anal.* Calc. for ($C_{41}H_{49}ClOsP_2 \cdot CH_2Cl_2$): C, 56.95; H, 5.18; *M*, 760. Found: C, 56.83; H, 5.23%. *M*, 760. IR (nujol, cm^{-1}): 1306w, 1155w, 1094s, 1027m, 867w, 788m, 693s, 668vs, 646w. ^{1}H NMR (C_6D_6): δ 1.57 (s, 15H, C_5Me_5), 1.97–2.09, 2.49–2.59 (2 × m, 2 × 2H, CH_2), 7.05–7.82 (m, 20H, Ph). ^{13}C NMR (C_6D_6): δ 10.18 (s, C_5 Me_5), 30.63–31.24 (m, CH_2), 86.10 [t, *J*(CP) = 2.6 Hz, C_5Me_5, 127.77–140.78 (m, Ph). ^{31}P NMR (C_6D_6): δ 43.1. ES-MS (positive ion, MeOH): 760, M^+; 725, $[M-Cl]^+$.

Table 3
Crystal data and refinement details

Complex	**2-Os**	**3-Os**	**4-Os**	**5-Os**	**3/5-Os**
Formula	$C_{31}H_{29}ClOsP_2 \cdot CH_2Cl_2$	$C_{36}H_{39}ClOsP_2$	$C_{41}H_{35}BrOsP_2$	$C_{36}H_{39}BrOsP_3$	$C_{36}H_{39}Br_{0.822}Cl_{0.178}OsP_2$
MW	774.12	759.31	859.78	803.76	795.89
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	28.292(2)	11.070(2)	14.416(3)	11.167(1)	11.1573(9)
b (Å)	10.8530(7)	17.773(2)	11.208(3)	17.764(2)	17.774(2)
c (Å)	19.716(1)	16.7070(9)	11.779(3)	16.792(2)	16.782(1)
α (°)			70.305(3)		
β (°)	107.432(2)	109.136(1)	84.699(3)	109.387(2)	109.379(2)
γ (°)			67.021(3)		
V (Å^3)	5776	3105	1648	3142	3140
ρ_c	1.78_0	1.62_4	1.73_2	1.69_9	1.68_4
Z	8	4	2	4	4
$2\theta_{max}$ (°)	68	58	58	75	75
μ(Mo Kα) (mm^{-1})	4.8	4.3	5.2	5.5	5.2
$T_{min/max}$	0.78	0.87	0.60	0.77	0.68
Crystal dimensions (mm^3)	0.22 × 0.20 × 0.15	0.26 × 0.22 × 0.18	0.12 × 0.05 × 0.04	0.12 × 0.10 × 0.08	0.13 × 0.10 × 0.09
N_{tot}	48865	28892	16264	61533	62129
N (R_{int})	11775 (0.040)	7847 (0.023)	8069 (0.061)	16020 (0.054)	16196 (0.029)
N_o	9056	7000	6452	10876	12874
R	0.032	0.024	0.053	0.030	0.034
R_w (n_w)	0.0038 (4)	0.048 (1.4)	0.061 (6)	0.024 (4)	0.028 (2)

4.8. Structure determinations

Full spheres of diffraction data were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full-matrix least-squares refinements. All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_h$ being constrained at estimates. Conventional residuals R, R_w on $|F|$ are quoted [weights: $(\sigma^2(F) + 0.000n_wF^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [10]. Pertinent data are recorded in Tables 1 and 3.

4.9. Variata

3-Os, **5-Os** and **3/5-Os** were isomorphous and refined in the same cell and coordinate setting, the halide in the latter being modelled as a Br/Cl composite, Br site occupancy 0.822(2) with Cl complementary **3-Os** was refined on F^2.

4-Os is isomorphous with the previously determined Ru/Cl analogue [11] and was refined in the same cell and coordinate setting.

5. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC Nos. 282442–282444, 298959, 298960. Copies of this information may be obtained free of charge from The Director, CCDC, 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.

Acknowledgements

We thank ARC for support of this work, Johnson Matthey plc, Reading, for a generous loan of potassium osmate, and Ms. K.A. Kramarczuk who supplied samples of $OsBr(PPh_3)_2Cp$ and $OsBr(dppe)Cp^*$.

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