The Reactions of the Tri-μ-hydroxo-bis[η^6-*p*-cymeneosmium(II)] Cation with Aldehydes and Acids and the Homogeneously Catalysed Oxidation of Acetaldehyde and Propionaldehyde with Water. *X*-Ray Structure of [(p-$MeC_6H_4CHMe_2)_2Os_2(\mu$-$HCO_2)(\mu$-$OH)(\mu$-$H)][PF_6]$ †

Javier A. Cabeza, Arnold J. Smith, Harry Adams, and Peter M. Maitlis *
Department of Chemistry, University of Sheffield, Sheffield S3 7HF

Reaction of [(p-$MeC_6H_4CHMe_2)_2Os_2Cl_4$] with sodium hydroxide in water gave the tri-μ-hydroxo cation [(p-$MeC_6H_4CHMe_2)_2Os_2(\mu$-$OH)_3]^+$, isolated as PF_6 (**1a**) or BPh_4 (**1b**) salts. Complex (**1a**) reacted with formaldehyde, acetaldehyde, or propionaldehyde to give the complexes [(p-$MeC_6H_4CHMe_2)_2Os_2(\mu$-$RCO_2)(\mu$-$OH)(\mu$-$H)][PF_6]$ [R = H (**2a**), Me (**2b**), Et (**2c**)], and with cinnamaldehyde, benzaldehyde, or pivaldehyde to give the complexes [(p-$MeC_6H_4CHMe_2)_2Os_2(\mu$-$RCO_2)(\mu$-$OH)_2][PF_6]$ [R = *trans*-PhCH=CH (**3a**), Ph (**3b**), Bu^t (**3c**)]. Reaction of (**1a**) with carboxylic acids gave (**3**; R = *trans*-PhCH=CH, Ph, Me, or H). Complex (**1a**) catalysed the oxidation of acetaldehyde and propionaldehyde by water to the corresponding carboxylic acids; hydrogen was also produced. This reaction was slower but more selective than the previously reported ruthenium-catalysed reaction. The complexes have been characterised by microanalysis and i.r. and ^1H n.m.r. spectra. A single-crystal *X*-ray diffraction study on complex (**2a**) confirmed the proposed structure.

The tri-μ-hydroxo cations [$(C_5Me_5)_2M_2(\mu$-$OH)_3]^+$ (M = Rh or Ir)[1] have proved to be very versatile catalyst precursors for a number of catalytic reactions, [2,3] including the catalytic disproportionation of aldehydes into alcohols and acids in water.[3] The ratio of alcohol to acid produced by these catalysts was close to one, equation (1), whereas ruthenium-based catalysts gave hydrogen and more carboxylic acid, pointing to the existence of a second reaction, equation (2), wherein the aldehydes were oxidised by water to the corresponding acids (R = alkyl or aryl).

$$2R\text{-}CHO + H_2O \rightleftharpoons R\text{-}CO_2H + R\text{-}CH_2OH \quad (1)$$

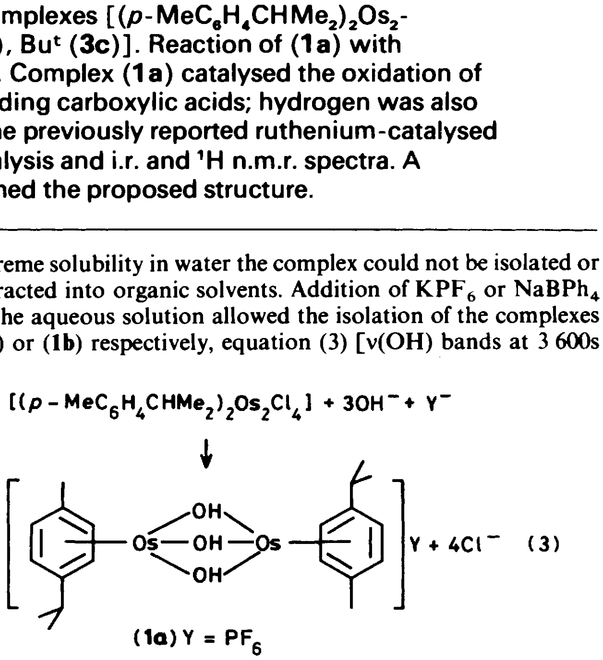
$$R\text{-}CHO + H_2O \rightleftharpoons R\text{-}CO_2H + H_2 \quad (2)$$

The use of *p*-cymene as protecting ligand has already allowed the development of a wide range of osmium chemistry.[4–6] We now report the synthesis of the cation [(p-$MeC_6H_4CHMe_2)_2Os_2(\mu$-$OH)_3]^+$ (**1**) and its stoicheiometric reactions with a number of aldehydes and acids in aqueous medium, as well as the homogeneous catalytic oxidation of acetaldehyde and propionaldehyde by water and the single-crystal *X*-ray structural determination of one of the isolated products, the μ-formato-μ-hydrido-μ-hydroxo complex (**2a**).

A part of this work has been communicated.[5,7]

Results and Discussion

Reaction of the *p*-cymeneosmium dimer [(p-$MeC_6H_4CHMe_2)_2Os_2Cl_4$][4] with excess sodium hydroxide in water (70 °C, 10 min) gave a yellow solution, presumably containing the chloride complex [(p-$MeC_6H_4CHMe_2)_2Os_2(\mu$-$OH)_3]Cl$, by analogy with the hexamethylbenzeneruthenium[8] and pentamethylcyclopentadienyl-rhodium and -iridium[1] systems. Owing to its extreme solubility in water the complex could not be isolated or extracted into organic solvents. Addition of KPF_6 or $NaBPh_4$ to the aqueous solution allowed the isolation of the complexes (**1a**) or (**1b**) respectively, equation (3) [ν(OH) bands at 3 600s and 3 570(sh) cm^{-1} for (**1a**) and 3 548s,br cm^{-1} for (**1b**), Table 1]. The formulation of (**1a**) and (**1b**) as dinuclear complexes is based on their conductance data [*B* values in the Onsager equation[9] ($\Lambda = \Lambda_0 - BC^{\frac{1}{2}}$); 369 for (**1a**) and 348 for (**1b**),‡ determined by measuring the conductivity of acetone solutions at different concentrations (*C*)] and by analogy to the ruthenium complex [(p-$MeC_6H_4CHMe_2)_2Ru_2(\mu$-$OH)_3]^+$.[8] By contrast, Stephenson and co-workers[8] found that the tetranuclear complex [$(C_6H_6)_4Os_4(\mu$-$OH)_4(\mu_4$-$O)][BPh_4]_2$ was obtained when the ligand is benzene instead of *p*-cymene.



(**1a**) Y = PF_6
(**1b**) Y = BPh_4

Reactions with Aldehydes.—When aqueous solutions of (**1a**) were reacted with excess formaldehyde, acetaldehyde, or propionaldehyde (60 °C, 2 h), yellow air-stable crystals of (**2a**), (**2b**), or (**2c**) respectively precipitated, equation (4). Their i.r. spectra (Table 1) clearly showed the presence of the hydroxy and carboxylate groups. Bridging hydrides were not evident in the i.r. spectra, but they were observed in the ^1H n.m.r. spectra

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† μ-Formato-μ-hydrido-μ-hydroxo-bis[η^6-*p*-cymeneosmium(II)] hexafluorophosphate.

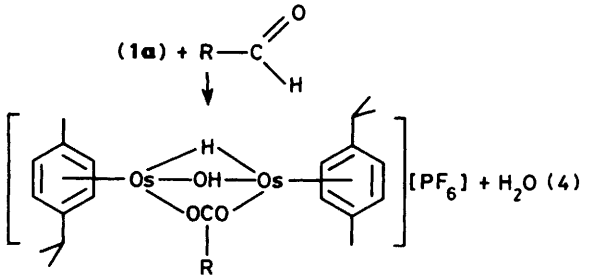
Supplementary data available (No. SUP 56488, 5 pp.): H-atom coordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

‡ Complex (**2a**), a 1:1 electrolyte, gave a *B* value of 306, and the complex [$(C_5Me_5)_4Rh_4(\mu$-$H)_4][BF_4]_2$,[10] a 1:2 electrolyte, gave a *B* value of 1 200.

Table 1. Analytical and i.r. data

Compound	Analysis[a] (%) C	Analysis[a] (%) H	I.r.[b] (cm^{-1}) ν(OH)	I.r.[b] (cm^{-1}) ν(CO$_2$)
(1a) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-OH})_3][\text{PF}_6]$	28.6 (28.4)	3.8 (3.7)	3 600s, 3 570(sh)	
(1b) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-OH})_3][\text{BPh}_4]$	52.5 (51.9)	5.4 (5.0)	3 548s,br	
(2a) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-HCO}_2)(\mu\text{-OH})(\mu\text{-H})][\text{PF}_6]$	29.5 (29.4)	3.9 (3.7)	3 530s	1 550s, 1 335s
(2b) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-MeCO}_2)(\mu\text{-OH})(\mu\text{-H})][\text{PF}_6]$	30.4 (30.3)	3.9 (3.8)	3 530s	1 548s, 1 448s
(2c) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-EtCO}_2)(\mu\text{-OH})(\mu\text{-H})][\text{PF}_6]$	31.3 (31.2)	4.0 (4.0)	3 540s	1 538s, 1 423s
(3a) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-PhCH=CHCO}_2)(\mu\text{-OH})_2][\text{PF}_6]$	36.2 (35.7)	3.9 (3.8)	3 593s	1 530s, 1 395s
(3b) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-PhCO}_2)(\mu\text{-OH})_2][\text{PF}_6]$	33.9 (34.2)	3.7 (3.7)	3 602s	1 537s, 1 398s
(3c) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-Bu}^t\text{CO}_2)(\mu\text{-OH})_2][\text{PF}_6]$	32.1 (32.3)	4.0 (4.2)	3 590s	1 545s, 1 417s
(3d) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-MeCO}_2)(\mu\text{-OH})_2][\text{PF}_6]$	29.7 (29.8)	3.6 (3.7)	3 580s	1 546s, 1 428s
(3e) $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-HCO}_2)(\mu\text{-OH})_2][\text{PF}_6]$	29.4 (28.9)	3.9 (3.6)	3 582s	1 558s, 1 350s

[a] Calculated values in parentheses. [b] Nujol mulls.



(2a) R = H
(2b) R = Me
(2c) E = Et

as singlets at δ *ca.* −10.4 p.p.m. bearing satellites due to coupling to ^{187}Os (1.64% natural abundance) (Table 2). The presence of three different bridging ligands could also be seen in the *p*-cymene ^{1}H n.m.r. spectra which showed the aromatic protons (two AB systems) and isopropyl methyls (two doublets) to be diastereotopic. This particular pattern is always present when the metal to which the *p*-cymene is η^6-co-ordinated is a chiral centre.[4,11] The formulation of these complexes was also confirmed by the *X*-ray structure of (**2a**) (Figure).

By contrast, the reaction of acetaldehyde with $[(\text{C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-OH})_3]\text{Cl}$ gave, after addition of KPF$_6$, mixtures of $[(\text{C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-MeCO}_2)(\mu\text{-H})_2][\text{PF}_6]$, $[(\text{C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-MeCO}_2)_2(\mu\text{-H})][\text{PF}_6]$, and $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{MeCO}_2)_2]$[3] (longer reaction times giving less of the first and more of the second), while addition of acetaldehyde to $[(\text{C}_6\text{Me}_6)_2\text{Ru}_2(\mu\text{-OH})_3][\text{PF}_6]$ gave $[(\text{C}_6\text{Me}_6)_2\text{Ru}_2(\mu\text{-MeCO}_2)_3][\text{PF}_6]$.[3]

Complex (**2b**) was recovered unchanged after treatment with equimolar amounts of aqueous solutions of acetic or hexafluorophosphoric acids. This shows that osmium-hydride and -hydroxy ligands are much less sensitive to acids than their ruthenium or rhodium analogues.[3] In fact, (**1a**) reacted with excess acetic acid (see below) to give only $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-MeCO}_2)(\mu\text{-OH})_2][\text{PF}_6]$ (**3d**) where two hydroxy groups still remain in the complex.

When (**1a**) was reacted with the water-insoluble cinnamaldehyde, benzaldehyde, or pivaldehyde in acetone or aqueous acetone the complexes (**3a**), (**3b**), or (**3c**) were obtained and hydrogen was detected in the gas phase by gas chromatography, equation (5). Their i.r. spectra showed ν(OH) in the range 3 600—3 590 cm^{-1}, *ca.* 60 cm^{-1} higher than was observed for the mono-μ-hydroxo complexes (**2a**)—(**2c**). The ^{1}H n.m.r. spectra of (**3a**)—(**3c**) showed no hydride peaks and from the *p*-cymene patterns it was immediately evident that the osmiums were not chiral centres (Table 2).

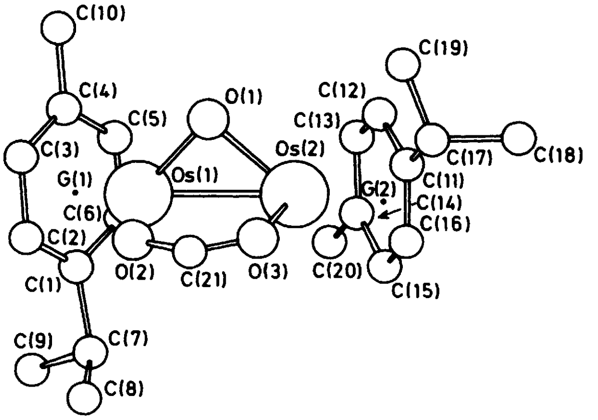
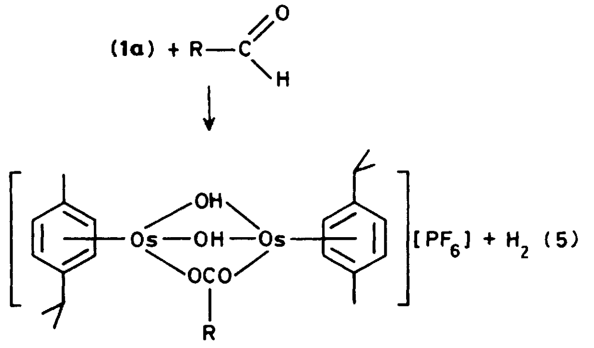


Figure. A view of the dinuclear cation in (**2a**) with the atomic numbering scheme (hydrogen atoms omitted for clarity)

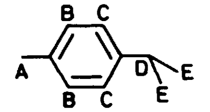


(3a) R = *trans*-PhCH=CH
(3b) R = Ph
(3c) R = Bu^t

Reactions with Acids.—Addition of excess cinnamic, benzoic, or acetic acid to an acetone solution of (**1a**) gave deeper yellow solutions, from which the di-μ-hydroxo-μ-carboxylate complexes (**3a**), (**3b**), and (**3d**) were isolated, equation (6). They were characterised by their i.r. and ^{1}H n.m.r. spectra.

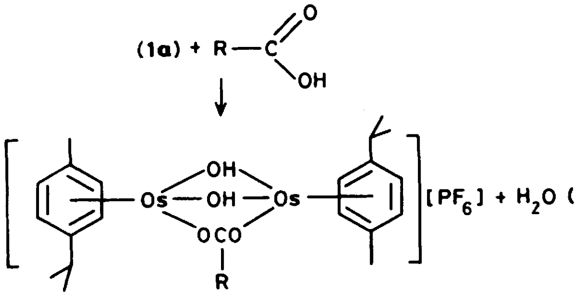
Only one hydroxy group of (**1a**) was replaced by carboxylate, even in the presence of a large excess of carboxylic acid. However, the formate complex (**3e**) could only be prepared pure when a 1 : 1 ratio of formic acid to (**1a**) was used. Reaction of excess formic acid with (**1a**) in acetone or dichloromethane at 20 °C gave a mixture of (**3e**) and a presumably dinuclear compound with three different bridges (^{1}H n.m.r.) which could

Table 2. ^{1}H N.m.r. data[a] (δ/p.p.m.)



Compound	A	B + C	D	E	R–CO$_2$	OH	Hydride[b]
(1a)[c]	2.18 (s)	6.03 (d, 6.0), 5.78 (d, 6.0)	2.54 (sp, 7.0)	1.25 (d, 7.0)		2.32 (s)	
(1b)[d,e]	2.24 (s)	5.99 (d, 5.9), 5.81 (d, 5.9)	2.55 (sp, 7.0)	1.26 (d, 7.0)		2.82 (s)	
(2a)[c]	2.60 (s)	6.00 (d, 5.9), 5.84 (d, 5.9), 5.75 (d, 6.1), 5.72 (d, 6.1)	2.82 (sp, 7.0)	1.36 (d, 7.0), 1.34 (d, 7.0)	6.32 (s, 1 H)	5.10 (s)	−10.34 [66.5]
(2b)[c]	2.57 (s)	5.96 (d, 5.8), 5.78 (d, 5.6), 5.71 (d, 5.6), 5.67 (d, 5.8)	2.80 (sp, 7.0)	1.34 (d, 7.0), 1.33 (d, 7.0)	1.92 (s, 3 H)	4.90 (s)	−10.39 [66.5]
(2c)[c]	2.56 (s)	5.99 (d, 5.5), 5.77 (d, 5.7), 5.73 (d, 5.7), 5.66 (d, 5.5)	2.78 (sp, 7.0),	1.33 (d, 7.0), 1.32 (d, 7.0)	2.19 (q, 7.6, 2 H), 0.89 (t, 7.6, 3 H)	4.93 (s)	−10.37 [66.8]
(3a)[c]	2.22 (s)	6.00 (d, 6.2), 5.73 (d, 6.2)	2.70 (sp, 7.0)	1.31 (d, 7.0)	7.52 (d, 15.7, 1 H), 7.49 (m, 2 H), 7.37 (m, 3 H), 6.26 (d, 15.7, 1 H)	4.20 (s, br)	
(3b)[f]	2.33 (s)	6.06 (d, 5.4), 5.08 (d, 5.4)	2.86 (sp, 7.0)	1.34 (d, 7.0)	8.11 (dd, 7.6, 1.2, 2 H), 7.59 (tt, 7.0, 1.2, 1 H), 7.46 (dd, 7.6, 7.0, 2 H)	6.07 (s)	
(3c)[c]	2.19 (s)	5.94 (d, 5.8), 5.67 (d, 5.8)	2.65 (sp, 7.0)	1.29 (d, 7.0)	1.13 (s, 9 H)	4.18 (s,br)	
(3d)[c]	2.22 (s)	5.94 (d, 5.7), 5.71 (d, 5.7)	2.69 (sp, 7.0)	1.30 (d, 7.0)	1.92 (s, 3 H)	4.25 (s,br)	
(3e)[f]	2.22 (s)	5.96 (d, 5.5), 5.73 (d, 5.5)	2.74 (sp, 7.0)	1.30 (d, 7.0)	8.52 (s, 1 H)	6.20 (s)	

[a] Multiplicity and J(H–H)/Hz in parentheses. [b] Singlets with satellites, $J(^{187}\text{Os}-^{1}\text{H})$/Hz in square brackets. [c] In CDCl$_3$. [d] In CD$_3$NO$_2$. [e] BPh$_4$: 7.34 (m, 8 H), 7.00 (t, 6.0, 8 H), 6.83 (t, 6.0, 4 H). [f] In (CD$_3$)$_2$CO.



(6)

(3a) R = *trans*-PhCH=CH
(3b) R = Ph
(3d) R = Me
(3e) R = H

not be separated. The formate complex **(3e)** was stable towards loss of CO$_2$ and was recovered unchanged from hot acetone (60 °C for 24 h).

Catalytic Reactions.—When the reactions of **(1a)** with acetaldehyde or propionaldehyde in water were analysed after long reaction times, it was noted that free acetic or propionic acids and hydrogen were produced (Table 3). Only traces of ethanol or n-propyl alcohol could be detected by g.c.–m.s.*

In this case the oxidation reaction defined by equation (2) predominated to an even greater extent than for the reactions catalysed by areneruthenium complexes,[3] but although **(1a)** showed a greater selectivity for oxidation, the turnover numbers (mol of product per mol of catalyst) were lower than those obtained with ruthenium catalysts.

Turnovers were raised by higher temperatures or by addition of base (Table 4), but acetaldehyde was always oxidised faster than propionaldehyde. The amounts of aldol condensation products were negligible, and under neutral conditions they were not even detected.

When water was used as solvent a fine crystalline yellow solid, characterised as the dinuclear complexes **(2b)** or **(2c)**, was formed after the first hours of reaction; the use of 1,4-dioxane as co-solvent avoided the formation of that precipitate, but its influence on the rates was very small. No specific investigations of the mechanism of the osmium-catalysed reaction were undertaken and we presume that it proceeds by a path analogous to that which has been proposed for the ruthenium-catalysed reactions.[3,†]

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* Control experiments showed that the total amount of alcohol in the samples was *less* than *ca.* 0.009 mmol (representing a turnover of 0.5), which is the lowest limit for quantification in the conditions under which the catalytic reactions were carried out.

† *Note added in proof*: **(1)** (0.04 mmol) also catalysed the transfer of hydrogen from formaldehyde (10 mmol) to acetaldehyde (10 mmol) giving ethanol (3.8 mmol); a little acetic acid (0.05 mmol) and a trace of formic acid were also formed (in water, 96 h, 60 °C). Propionaldehyde was reduced similarly but acetone was not.

Table 3. Results for the oxidation of acetaldehyde and propionaldehyde to the corresponding acids with water and (**1a**) under neutral conditions[a]

				Acid	
Aldehyde	Solvent	Time (h)	Temp. (°C)	mmol	t.n.[b]
MeCHO	water	96	20	0.43	24
MeCHO	water–dioxane (2:1)	96	20	0.66	37
MeCHO	water	72	60	0.85	48
MeCHO	water–dioxane (2:1)	72	60	0.93	52
EtCHO	water	72	60	0.39	22
EtCHO	water–dioxane (2:1)	72	60	0.51	29

[a] Conditions: aldehyde 0.5 cm^3, solvent 3 cm^3, catalyst 15 mg. Prior to g.c. analyses the samples were quenched with 1 mol dm^{-3} hydrochloric acid (1 cm^3). [b] Turnover number.

Table 4. Results for the oxidation of acetaldehyde and propionaldehyde to the corresponding acids with water and (**1a**) under basic conditions[a]

				Acid	
Aldehyde	Solvent	Time (h)	Temp. (°C)	mmol	t.n.[b]
MeCHO	water	96	20	1.31	74
MeCHO	water–dioxane (2:1)	96	20	1.25	70
MeCHO	water	72	60	1.38	78
MeCHO	water–dioxane (2:1)	72	60	1.76	99
EtCHO	water	72	60	0.65	36
EtCHO	water–dioxane (2:1)	72	60	0.92	52

[a] Conditions: aldehyde 0.5 cm^3, solvent 3 cm^3, Na_2CO_3 10 mg, catalyst 15 mg. Prior to g.c. analyses the samples were quenched with 1 mol dm^{-3} hydrochloric acid (1 cm^3). [b] Turnover number.

Table 5. Selected distances (Å) and angles (°)*

Co-ordination sphere of the osmium atoms			
Os(1)–Os(2)	2.766(1)		
Os(1)–O(1)	2.060(10)	Os(2)–O(1)	2.055(9)
Os(1)–O(2)	2.101(10)	Os(2)–O(3)	2.078(10)
Os(1)–G(1)	1.649(6)	Os(2)–G(2)	1.621(6)
Os(1)–C(1)	2.169(19)	Os(2)–C(11)	2.169(19)
Os(1)–C(2)	2.128(20)	Os(2)–C(12)	2.076(15)
Os(1)–C(3)	2.149(19)	Os(2)–C(13)	2.149(15)
Os(1)–C(4)	2.192(19)	Os(2)–C(14)	2.181(15)
Os(1)–C(5)	2.168(16)	Os(2)–C(15)	2.188(15)
Os(1)–C(6)	2.131(16)	Os(2)–C(16)	2.148(17)
Os(1)–O(1)–Os(2)	84.5(3)		
Os(1)–O(2)–C(21)	124.6(10)	Os(2)–O(3)–C(21)	122.9(10)
Os(1)–Os(2)–G(2)	146.9(2)	Os(2)–Os(1)–G(1)	147.8(2)
Formate ligand			
C(21)–O(2)	1.234(21)	O(2)–C(21)–O(3)	127.8(14)
C(21)–O(3)	1.221(23)		
p-Cymene ligands			
C(1)–C(2)	1.377(25)	C(11)–C(12)	1.440(22)
C(1)–C(6)	1.375(22)	C(11)–C(16)	1.421(22)
C(1)–C(7)	1.564(30)	C(11)–C(17)	1.492(27)
C(2)–C(3)	1.441(24)	C(12)–C(13)	1.408(23)
C(3)–C(4)	1.316(25)	C(13)–C(14)	1.394(22)
C(4)–C(5)	1.394(28)	C(14)–C(15)	1.448(22)
C(4)–C(10)	1.457(30)	C(14)–C(20)	1.483(24)
C(5)–C(6)	1.429(28)	C(15)–C(16)	1.387(25)
C(7)–C(8)	1.430(31)	C(17)–C(18)	1.497(32)
C(7)–C(9)	1.576(32)	C(17)–C(19)	1.497(28)

* G = Centroid of the *p*-cymene ring.

X-Ray Crystal Structure of (**2a**).—A single-crystal *X*-ray diffraction study of (**2a**) confirmed the expected structure (Figure); selected distances and angles are given in Table 5. Each osmium is η^6-co-ordinated to one *p*-cymene ring [Os(1)–C (mean) 2.156 and Os(2)–C (mean) 2.152 Å, the distances to the centroids (G) of the rings being Os(1)–G(1) 1.649(6) and Os(2)–G(2) 1.621(6) Å] and σ-bonded to one oxygen of a bridging formate [Os(1)–O(2) 2.101(10) and Os(2)–O(3) 2.078(10) Å] and to a bridging hydroxy group [Os(1)–O(1) 2.060(10) and Os(2)–O(1) 2.055(9) Å]. The bridging hydride could not be observed but its approximate position is evident from the gap in the osmium co-ordination spheres. The proximity of the metals to each other [2.766(1) Å] indicates some metal–metal interaction.

As in [$(p\text{-MeC}_6H_4CHMe_2)_2Os_2Cl_4$][12] and in [$(p\text{-MeC}_6H_4CHMe_2)RuCl(pyrazine)_2$][$PF_6$][13] the *p*-cymene rings in (**2a**) are planar [maximum deviations of the carbon atoms from the mean planes 0.016(2) Å for ring (1) and 0.009(2) Å for ring (2)]. This is in contrast to the *p*-cymene in the complex [$(p\text{-MeC}_6H_4CHMe_2)RuCl_2(PMe_2Ph)$] which adopts a boat conformation.[14] The methyl and isopropyl substituents in (**2a**) are bent [deviations from the ring planes 0.056(2) Å for C(7), 0.086(2) Å for C(10), and 0.075(1) Å for C(20) towards, and 0.014(2) Å for C(17) away from the osmium]. Both the methyl and isopropyl groups are usually bent towards the metal.[12–16]

Due to the three different bridges the two *p*-cymene rings are not parallel [dihedral angle 64.7(4)°]; the two rings are eclipsed, and twisted with respect to each other by an angle of approximately 120°.

The two osmium atoms and the formate ligand are approximately coplanar [maximum deviation 0.021(1) Å]; this plane is at an angle of 83° to the plane which contains the osmium atoms and the bridging oxygen of the hydroxy group. The Os–OH distances are normal,[8] but the angle Os(1)–O(1)–Os(2) is rather acute [84.5(3)°], presumably due to the short metal–metal distance caused by the presence of the bridging hydride.[17] The anion is unexceptional, but the O(1) ··· F(6) distance of 2.79 Å may indicate H-bonding to the hydroxy group.

Experimental

[$(p\text{-MeC}_6H_4CHMe_2)_2Os_2Cl_4$] was prepared as previously described.[4] Microanalyses (carried out by the Sheffield University Microanalytical Service), i.r. spectra (recorded on a PE-157G spectrophotometer as Nujol mulls), and ^1H n.m.r. spectra (Bruker AM250, at 22 °C) are collected in Tables 1 and 2. G.c. analyses were run on a Carlo-Erba gas chromatograph (Poropak-Q column at 170 °C, flame detector) and g.c.–m.s. analyses were obtained using a Kratos MS25 mass spectrometer. Hydrogen from the catalytic reactions was detected using a FM gas chromatograph (9-ft molecular sieve column at 20 °C, catharometer detector).

[$(p\text{-MeC}_6H_4CHMe_2)_2Os_2(\mu\text{-OH})_3$]Y [Y = PF_6 (**1a**) *or* BPh_4 (**1b**)].—[$(p\text{-MeC}_6H_4CHMe_2)_2Os_2Cl_4$] (300 mg, 0.38 mmol) was suspended in a solution of NaOH (150 mg, 3.75 mmol) in water (15 cm^3); on warming (70 °C, 10 min) the orange solid dissolved to give a pale yellow solution (A). KPF_6 (200 mg, 1.1 mmol) was then added and after stirring (10 min) the solution was filtered and extracted with dichloromethane (3 × 5 cm^3). The combined extracts were dried (anhydrous Na_2SO_4) and filtered; hexane (5 cm^3) was added and the solution concentrated (to *ca.* 3 cm^3) to give very pale yellow crystals of (**1a**) (272 mg, 85%).

Table 6. Atom co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
Os(1)	4 446(1)	1 460(1)	1 294(1)
Os(2)	2 238(1)	2 442(1)	1 738(1)
C(1)	5 730(18)	2 505(19)	806(6)
C(2)	6 443(19)	1 424(17)	1 052(7)
C(3)	5 816(19)	123(17)	969(7)
C(4)	4 553(19)	−104(19)	699(7)
C(5)	3 837(21)	995(22)	451(7)
C(6)	4 406(16)	2 309(18)	521(6)
C(7)	6 238(21)	3 985(23)	869(7)
C(8)	7 048(30)	4 266(31)	1 383(11)
C(9)	6 999(27)	4 163(21)	372(8)
C(10)	3 978(28)	−1 448(22)	674(9)
C(11)	430(19)	2 581(16)	2 135(7)
C(12)	132(16)	1 932(15)	1 622(6)
C(13)	382(17)	2 488(16)	1 138(7)
C(14)	1 009(16)	3 740(15)	1 147(6)
C(15)	1 328(18)	4 442(15)	1 652(7)
C(16)	1 063(18)	3 854(15)	2 119(7)
C(17)	140(22)	2 000(18)	2 646(8)
C(18)	−1 184(25)	2 611(20)	2 764(9)
C(19)	−6(31)	515(21)	2 637(11)
C(20)	1 385(21)	4 360(16)	660(6)
C(21)	4 858(20)	1 915(17)	2 471(6)
O(1)	2 971(10)	541(9)	1 666(3)
O(2)	5 428(11)	1 536(11)	2 098(4)
O(3)	3 647(12)	2 278(10)	2 451(4)
P(1)	−505(7)	−1 736(4)	861(2)
F(1)	−1 069(16)	−384(12)	608(6)
F(2)	−118(23)	−3 077(15)	1 117(7)
F(3)	−1 058(17)	−1 276(12)	1 387(5)
F(4)	89(18)	−2 153(16)	350(6)
F(5)	−1 914(20)	−2 355(14)	612(8)
F(6)	854(15)	−995(20)	1 073(8)

The tetraphenylborate salt (**1b**) was prepared as yellowish white plate-like crystals (320 mg, 83%) by adding an excess of $NaBPh_4$ to the pale yellow aqueous solution (A) described above.

$[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}HCO_2)(\mu\text{-}OH)(\mu\text{-}H)][PF_6]$ (**2a**).—Aqueous formaldehyde (0.5 cm^3, 40% w/w) was added to a solution of (**1a**) (150 mg, 0.18 mmol) in water (5 cm^3). The solution was stirred (60 °C, 2 h) to give yellow crystals which were filtered off, washed with water and diethyl ether, and dried (105 mg, 60%).

Compounds (**2b**) and (**2c**) were prepared similarly from the appropriate aldehydes in 58 and 40% yields respectively.

$[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}PhCH{=}CHCO_2)(\mu\text{-}OH)_2][PF_6]$ (**3a**).—Cinnamaldehyde (0.2 cm^3) was added to a solution of (**1a**) (140 mg, 0.17 mmol) in acetone (10 cm^3). After stirring (55 °C, 18 h) the solution was evaporated to dryness to leave an oil. Addition of hexane (10 cm^3) with vigorous stirring gave a pale grey powder which after crystallisation from dichloromethane–hexane gave pale yellow crystals of (**3a**) (70 mg, 44%).

$[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}PhCO_2)(\mu\text{-}OH)_2][PF_6]$ (**3b**).—A solution containing benzaldehyde (0.2 cm^3) and complex (**1a**) (150 mg, 0.180 mmol) in water–acetone (5 cm^3, 3 : 1) was stirred (55 °C, 2 h) and then evaporated to dryness to leave a brown-yellow oil; this was washed with water and diethyl ether and crystallised from acetone–diethyl ether to give pale yellowish grey crystals of (**3b**) (70 mg, 42%).

Complex (**3c**) was prepared similarly from pivaldehyde in 44% yield.

$[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}HCO_2)(\mu\text{-}OH)_2][PF_6]$ (**3e**).—Formic acid (6.5 μl, 0.17 mmol) was slowly added to a solution of complex (**1a**) (140 mg, 0.17 mmol) in dichloromethane (10 cm^3); the solution was stirred (20 °C, 10 min) and then worked-up to give very pale yellow crystals of (**3e**) (140 mg, 93%).

Complexes (**3a**), (**3b**), and (**3d**) were prepared similarly from the appropriate acids in 80, 85, and 85% yields respectively.

Catalytic Experiments.—The reactions were carried out in 5-cm^3 flasks, under argon, sealed by Suba-seals. Results are summarised in Tables 3 and 4. In a typical run, a solution containing propionaldehyde (0.5 cm^3), water (3 cm^3), Na_2CO_3 (10 mg), and (**1a**) (15 mg) was stirred in a thermostatted bath at 60 °C for 72 h. After cooling (to 20 °C) the presence of hydrogen in the gas phase was confirmed by g.c.; hydrochloric acid (1 cm^3, 1 mol dm^{-3}) was injected into the flask and the components of the liquid phase were analysed by g.c.–m.s.

Crystal Structure Determination of (**2a**).—*X*-Ray quality crystals of (**2a**) were grown by slow diffusion of diethyl ether through a concentrated dichloromethane solution.

Crystal data. $C_{21}H_{31}F_6O_3Os_2P$, $M = 856.85$, monoclinic, space group $P2_1/n$, $a = 9.961(12)$, $b = 10.038(8)$, $c = 25.372(31)$ Å, $\beta = 99.84(10)°$, $U = 2\,500$ Å^3, $Z = 4$, $D_c = 2.28$ g cm^{-3}, $F(000) = 1\,607.5$, Mo-K_α radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu = 105.9$ cm^{-1}.

Unit-cell parameters were obtained from a least-squares fit of the setting angles of 25 well-centred reflections. *X*-Ray reflection data in the range $3.5 \leqslant 2\theta \leqslant 50°$ were collected on a Nicolet R3M four-circle automatic diffractometer from a laminar crystal measuring approximately 0.35 × 0.25 × 0.07 mm. 3 235 Independent reflections with $I \geqslant 3\sigma(I)$ were obtained and corrected for Lorentz and polarisation effects. An empirical absorption correction based on ψ-scans of 10 reflections was also applied. The maximum and minimum transmission factors obtained were 1.000 and 0.159.

The structure was solved by Patterson and difference-Fourier methods and refined by cascade blocked-diagonal matrix least squares with weights $w_i = 1/[\sigma^2(F_i) + 0.000\,59F_i^2]$ to a final *R* value of 0.0587. All the non-hydrogen atoms were refined with independent positional and anisotropic thermal vibration parameters. Sufficient hydrogen atoms were located from a low-angle difference Fourier synthesis to define approximate torsion angles for all the methyl groups. All hydrogen atoms were constrained to ride on the adjacent heavy atom with calculated bond lengths and angles; the hydrogen (isotropic) vibration parameters were fixed at 1.2 times the U_{eq} values for their respective neighbours. All the hydrogen atoms bonded to carbon were included in the structure factor calculations.

The parameter shifts obtained on the final cycle of refinement were, in all cases, less than 0.02 of the corresponding estimated standard deviations. A final difference Fourier synthesis showed no peak higher than 1.7 e Å^{-3} and none which could be interpreted as an atom. The final analysis of variance against $\sin\theta$ and against $|F|$ showed no unusual features; neither did the normal probability plot. The SHELXTL suite of crystallographic programs[18] was used throughout. Selected bond lengths and angles are given in Table 5; atomic co-ordinates are in Table 6.

Acknowledgements

We thank the S.E.R.C. for supporting this work, the Spanish Ministry of Education for an award (to J. A. C.), the Royal Society for grants towards the purchase of the diffractometer, and Dr. B. F. Taylor for n.m.r. spectra.

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Received 2nd September 1985; *Paper* 5/1416