The Synthesis of Di- and Tetra-nuclear *p*-Cymene–Osmium Hydride Complexes; Characterisation by ^{1}H(^{187}Os) Reverse INEPT Two-dimensional Nuclear Magnetic Resonance Spectroscopy

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$[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{H})(\mu\text{-}\mathrm{Cl})\mathrm{Cl_2}]$ was formed from reaction of propan-2-ol with either $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2Cl_4}]$ (in the presence of $\mathrm{KPF_6}$ or $\mathrm{HPF_6}$ as catalyst) or $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{Cl})_3][\mathrm{PF_6}]$. The dinuclear trihydride $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{H})_3]^+$ (**5**) and the tetranuclear tetrahydride $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_4\mathrm{Os_4}(\mu\text{-}\mathrm{H})_4]^{2+}$ were obtained from reaction of $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{OH})_3]^+$ (**4**) with propan-2-ol, and the trihydride (**5**) was also prepared by reaction of (**4**) with formaldehyde. The chloro-acetate $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Os(O_2CMe)Cl}]$ gave a mixture of $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{H})(\mu\text{-}\mathrm{Cl})(\mu\text{-}\mathrm{O_2CMe})]^+$ and $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Os_2}(\mu\text{-}\mathrm{H})_2(\mu\text{-}\mathrm{O_2CMe})]^+$ (**13**); while the diacetate $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Os(O_2CMe)_2}]$ (**8a**) gave a mixture of (**13**), $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{H})(\mu\text{-}\mathrm{O_2CMe})_2]^+$ (**14**), and (**5**) on reaction with propan-2-ol at 80 °C. The bis(trifluoroacetate) $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Os(O_2CCF_3)_2}]$ reacted analogously with propan-2-ol to give a mixture of two neutral complexes, $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{H})(\mu\text{-}\mathrm{O_2CCF_3})(\mathrm{O_2CCF_3})_2]$ and $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{H})_2(\mathrm{O_2CCF_3})_2]$. In each reaction the proportions of each product depended on the time of reaction, longer times favouring more highly hydrided complexes. The new hydride complexes were characterised with the help of n.m.r. spectroscopy including ^{1}H(^{187}Os) reverse INEPT two-dimensional n.m.r. spectra. The diacetate (**8a**) underwent hydrolysis to give $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{OH})_2(\mu\text{-}\mathrm{O_2CMe})]^+$ and methanolysis to give $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{OMe})_3]^+$, and on work-up (**14**) was hydrolysed to $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{H})(\mu\text{-}\mathrm{OH})(\mu\text{-}\mathrm{O_2CMe})_2]$.

Although there have been many publications on the chemistry of arene–ruthenium hydride complexes,[1–3] rather little has appeared on the analogous osmium complexes.[4,5] The recent description of a high yield synthesis of $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2Cl_4}]$ ($p\text{-}\mathrm{MeC_6H_4CHMe_2}$ = 4-isopropyltoluene, *p*-cymene),[6,7] together with the observation that the arene–osmium bond is rather inert, has led us to undertake a more detailed examination of the chemistry of arene–osmium complexes. We here report on new hydride complexes; parts of this work have been communicated.[8,9]

Results and Discussion

$[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{H})(\mu\text{-}\mathrm{Cl})\mathrm{Cl_2}]$, (**2**).—The closely related μ-hydrido bis(pentamethylcyclopentadienyl)-rhodium and -iridium complexes could conveniently be prepared by reaction of the appropriate $[(\mathrm{C_5Me_5})_2\mathrm{M_2Cl_4}]$ with propan-2-ol.[10] This reaction was not successful when applied to $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2Cl_4}]$, (**1**). However, (**1**) did react with propan-2-ol in the presence of a large anion to give $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{H})(\mu\text{-}\mathrm{Cl})\mathrm{Cl_2}]$, (**2**); yields for various additives were: $\mathrm{Na_2SO_4}$ (23%), $\mathrm{KBF_4}$ (52%), $\mathrm{KPF_6}$ (93%), and $\mathrm{HPF_6}$ (100%). The role of the anion is probably to facilitate the formation of the cationic $[(p\text{-}\mathrm{MeC_6H_4CHMe_2})_2\mathrm{Os_2}(\mu\text{-}\mathrm{Cl})_3]^+$, (**3**), which is then attacked rather easily by the propanol.

In support of this suggestion, (**3**) was formed when (**1**) was treated with either $\mathrm{KPF_6}$ or $\mathrm{HPF_6}$ in non-alcoholic solvents; (**3**) also reacted easily and quantitatively with propan-2-ol to give (**2**). One possible explanation for the high reactivity of (**3**) is that an Os–Cl (bridge) bond can be opened more easily than a bridge or a terminal Os–Cl bond can be broken in (**1**), in order to create a vacant site at which the propanol can co-ordinate prior to reaction. Alternatively, and more plausibly, the charge on (**3**) may make it a better electrophile towards the propanol than is (**1**).

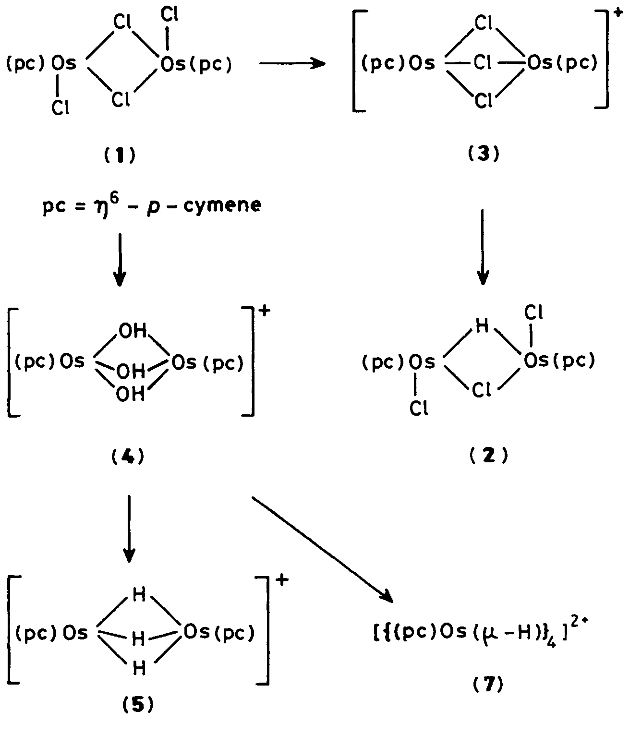


Table 1. Analytical, i.r., and mass spectral data

	Compound	Analysis (%)[a] C	Analysis (%)[a] H	I.r. (cm^{-1})[b]	M.s. (*m/e*)[c]
(2)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})(\mu\text{-Cl})\text{Cl}_2]$	31.4	4.2	OsCl: 286s, 270(sh)	756, M^+
		(31.8)	(3.9)		
(3)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-Cl})_3][\text{PF}_6]$	26.8	2.8	OsCl: 265s	
		(26.8)	(2.7)		
(5)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})_3][\text{PF}_6]$	30.3	4.2		655, M^+
		(30.2)	(3.9)		
(7)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Os}_4(\mu\text{-H})_4][\text{BF}_4]_2$	32.2	4.2		
		(32.6)	(3.8)		
(8a)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})_2]$	37.4	4.7	CO_2: 1 546s br, 1 417s br	444, M^+
		(38.0)	(4.6)		
(10)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-OMe})_3][\text{PF}_6]$	31.1	4.3		
		(31.1)	(4.2)		
(11a)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})\text{Cl}]$	34.5	3.7	CO_2: 1 519s, 1 480s, 1 388s	420, M^+
		(34.4)	(4.1)	OsCl: 282s	
(11b)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CCF}_3)\text{Cl}]$	30.5	3.2	CO_2: 1 695s, 1 400s	474, M^+
		(30.5)	(3.0)	OsCl: 280s	
(12)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})(\mu\text{-Cl})(\mu\text{-O}_2\text{CMe})][\text{PF}_6]$	29.4	3.8	CO_2: 1 520s, 1 435s	
		(29.7)	(3.6)	OsCl: 267m	
(13)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})_2(\mu\text{-O}_2\text{CMe})][\text{PF}_6]$	30.1	3.7	CO_2: 1 532s, 1 442s	
		(30.9)	(3.9)		
(15)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})(\mu\text{-OH})(\mu\text{-O}_2\text{CMe})_2]$	36.3	4.7	CO_2: 1 550s vbr, 1 420s br	766, $(M - \text{H}_2\text{O})^+$
		(36.7)	(4.7)	OH: 3 508m br	

[a] Calculated values in parentheses. [b] Nujol mull. [c] Strongest peak in the isotopic group of ions.

Complex (**2**) was characterised spectroscopically (Tables 1 and 2). The mass spectrum [electron impact (e.i.) mode] showed a group of molecular ion peaks around *m/e* 756, with intensities in agreement with simulated spectra based on Os, Cl, and C isotopes. The hydride signal in the ^{1}H n.m.r. spectrum was a singlet (δ −12.73) with satellites arising from coupling to ^{187}Os [$I = \frac{1}{2}$, 1.64% abundant, J(Os–H) 60.8 Hz]. The spectrum also showed pairs of lines for the *p*-cymene Me_2CH and the ring proton resonances, showing them to be diastereotopic; the osmium is therefore bound to four different ligands. Confirmation was obtained from the ^{187}Os n.m.r. [by ^{1}H(^{187}Os) reverse INEPT two-dimensional spectroscopy, see below] signal at δ −2 037 p.p.m. which was a doublet, indicating that the osmiums were equivalent and bound to one (bridging) hydrogen.

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})_3][\text{PF}_6]$, (**5**).—When the tri-μ-hydroxo-diosmium complex $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-OH})_3]^+$ (**4**) as a hexafluorophosphate salt was treated with propan-2-ol, the colour of the solution changed from yellow to red (80 °C, 2 h) and a dark insoluble solid precipitated; the starting material had all reacted within 4 h. The ^{1}H n.m.r. spectrum of the dark solid showed it to be composed of three different hydrides, while the solution showed that only one single complex, identified as the tri-μ-hydride (**5**) [δ −14.87, J(Os–H) 83.3 Hz; the integral showed 1.5 hydrides per *p*-cymene] was present. The complex was confirmed as a trihydride by its fast atom bombardment (f.a.b.). mass spectrum (molecular ion at *m/e* 655 corresponding to $^{12}\text{C}_{20}\text{H}_{31}{}^{192}\text{Os}_2{}^+$), and in particular by its ^{187}Os n.m.r. spectrum [by ^{1}H(^{187}Os) reverse INEPT two-dimensional spectroscopy, see below], a 1:1:1:1 quartet (with separation 84 Hz) at δ −2 526 p.p.m., showing the osmiums to be equivalent and coupled to three equivalent hydrides. This complex is presumably isostructural with the $[(\text{C}_5\text{Me}_5)_2\text{Ir}_2(\mu\text{-H})_3]^+$ cation.[10,11]

Another way to prepare the trihydride (**5**) (45%) is by prolonged reaction (72 h, 60 °C) of the tri-μ-hydroxy complex (**4**) with formaldehyde; by contrast, when that reaction was carried out for short times (2 h, 60 °C), the product was $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-HCO}_2)(\mu\text{-OH})(\mu\text{-H})][\text{PF}_6]$ (**6**).[12]

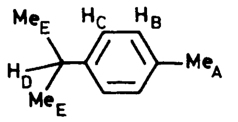
The trihydride (**5**) did not react with acetic acid (in CDCl_3, 24 h, 35 °C); it gave the tri-μ-chloro complex (**3**) quantitatively with CCl_4.

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Os}_4(\mu\text{-H})_4][\text{BF}_4]_2$ (**7**).—A rather different reaction occurred when the tetrafluoroborate salt of the tri-μ-hydroxo complex (**4**) was refluxed (40 h) in propan-2-ol. In that case the (red) solution contained (**5**) (80%, by n.m.r. integration) and two other (unidentified) hydrides. The dark solid, insoluble in propan-2-ol, gave a deep brown solution on extraction with dichloromethane which contained a single complex, shown to be the tetranuclear tetrahydride dication (**7**).

The identification of this material as (**7**) rests largely on the n.m.r. spectra. The ^{1}H n.m.r. spectrum shows one set of *p*-cymene resonances and one hydride [δ −11.15, J(Os–H) 36 Hz] with intensity ratios such that there was one hydride for each *p*-cymene. The ^{187}Os n.m.r. spectrum [by ^{1}H(^{187}Os) reverse INEPT two-dimensional spectroscopy, see below] was a quintet (δ −2 171 p.p.m.) with separation 36 Hz. This indicates that the complex is fluxional since evidently all the four hydrides and the four osmiums appear equivalent and the ^{187}Os atoms couple equally to each of the four hydrides. It is not known whether (**7**) is isostructural with the isoelectronic (58 electron) $[(\text{C}_5\text{Me}_5)_4\text{Rh}_4(\mu\text{-H})_4]^{2+}$. That dication has a skeleton with four long and two short metal–metal bonds and the four hydrides bridge the four faces of the distorted Rh_4 tetrahedron.[13] However, in that complex the hydrides are quite rigid and the ^{1}H n.m.r. solution spectrum is exactly that expected from the solid-state structure. Since tetranuclear 58 electron clusters would be expected to be paramagnetic if they were of strict T_d symmetry,[14] it seems likely that complex (**7**), which is diamagnetic, is also distorted in a similar fashion to $[(\text{C}_5\text{Me}_5)_4\text{Rh}_4(\mu\text{-H})_4]^{2+}$.

μ-*Hydrido*-μ-*carboxylato-diosmium Complexes*.—Reaction of (**1**) with two equivalents of a silver carboxylate gave the

Table 2. N.m.r. data (δ/p.p.m.)[a]



Compound	^{1}H N.m.r.[b]						^{187}Os N.m.r.[c]
	A	B + C	D	E	Hydride	Others	
(2)[d]	2.41 (s)	6.07 (d, 5.5) 5.93 (d, 5.5) 5.81 (d, 5.5) 5.55 (d, 5.5)	2.87 (spt, 7.0)	1.40 (d, 7.0) 1.39 (d, 7.0)	−12.73 (ss, 60.8)		−2 037 (d, 61)
(3)[e]	2.32	6.80 (6.2) 6.60 (6.2)	2.72 (7.0)	1.31 (7.0)			
(5)[f]	2.50	5.84 (6.0) 5.80 (6.0)	2.51 (7.0)	1.29 (7.0)	−14.87 (83.3)		−2 526 (q, 84)
(7)[e]	2.35	6.92 (6.2) 5.96 (6.2)	2.96 (7.0)	1.54 (7.0)	−11.15 (36.0)		−2 171(qnt,36)
(8a)[f]	2.28	6.40 (5.4) 6.14 (5.4)	2.69 (7.0)	1.32 (7.0)		O_2CMe 1.96 (s)	
(8b)[d,g]	2.20	6.48 (5.3) 6.22 (5.3)	2.68 (7.0)	1.30 (7.0)			
(10)[d]	2.32	5.93 (5.3) 5.76 (5.3)	2.65 (7.0)	1.29 (7.0)		OMe 4.75 (s)	
(11a)[d]	2.34	6.28 (5.7) 6.02 (5.7)	2.78 (7.0)	1.36 (7.0)		O_2CMe 1.92 (s)	
(11b)[d,g]	2.12	6.42 (5.4) 6.16 (5.4)	2.61 (7.0)	1.32 (7.0)			
(12)[d]	2.27	6.69 (5.4) 6.32 (5.4) 6.08 (5.4) 5.82 (5.4)	2.65 (7.0)	1.28 (7.0) 1.27 (7.0)	−9.57 (66.3)	O_2CMe 1.98 (s)	−1 951 (d, 66)
(13)[d]	2.44	6.33 (5.4) 6.16 (5.4)	2.58 (7.0)	1.29 (7.0)	−13.73 (75.6)	O_2CMe 2.38 (s)	−1 185 (t, 76)
(14)[d]	2.08	6.34 (5.5) 6.05 (5.5)	2.51 (7.0)	1.18 (7.0)	−9.59 (64.2)	O_2CMe 2.06 (s)	
(15)[f]	2.51	5.99 (5.4) 5.78 (5.2) 5.68 (5.4) 5.63 (5.4)	2.79 (7.0)	1.33 (7.0) 1.32 (7.0)	−10.42 (66.0)	O_2CMe 1.89 (s) 1.85 (s)	
(16)[d,g]	2.52	6.07 (5.4) 5.85 5.75 (5.4)	2.77 (7.0)	1.33 (7.0) 1.32 (7.0)	−10.33 (66.0)		
(17)[d,g]	2.47	6.48 (5.7) 6.29 (5.7)	2.60 (7.0)	1.30 (7.0)	−13.71 (76.5)		

[a] Multiplicity and coupling constant (Hz) in parentheses; s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, spt = septet, ss = singlet with satellites. [b] Relative to $SiMe_4$. Multiplicities for A, B + C, D, E, and hydride are s, d, spt, d, and ss throughout. [c] Relative to OsO_4. [d] In $CDCl_3$. [e] In $(CD_3)_2CO$. [f] In CD_2Cl_2. [g] ^{19}F Resonances (CF_3) at −74.5 (**8b**), −74.7 (**11b**), −72.9 and −76.3 (**16**), −75.0 (**17**) relative to $CFCl_3$.

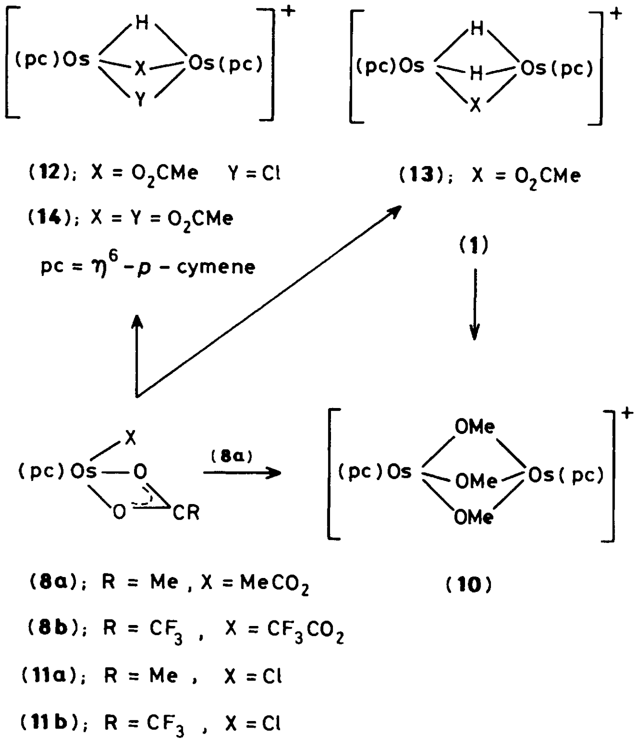
hygroscopic carboxylates, $[(p\text{-}MeC_6H_4CHMe_2)Os(O_2CR)_2]$ (**8a**, R = Me; **8b**, R = CF_3). Molecular weight measurements (e.i. mass spectra and osmometry) showed them to be mononuclear. The n.m.r. spectra showed only one type of carboxylate group even at −80 °C indicating rapid exchange; we presume that in the solid state one carboxylate is mono- and the other bi-dentate, as in $[(arene)Ru(O_2CR)_2]$ (R = alkyl).[15] Complex (**8a**) reacted with water to give the known di-μ-hydroxo-μ-acetate complex $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)][PF_6]$ (**9**),[12] and with methanol to give the tri-μ-methoxo complex $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}OMe)_3][PF_6]$ (**10**), in both cases after the addition of KPF_6.

When complex (**1**) was treated with only one equivalent of silver carboxylate the monochloro-monocarboxylates $[(p\text{-}MeC_6H_4CHMe_2)Os(O_2CR)Cl]$, (**11a**, R = Me; **11b**, R = CF_3), containing bidentate carboxylate, were obtained.

Reaction of the chloro-acetate (**11a**) with propan-2-ol (80 °C, 19 h) gave a complex identified as the μ-hydrido-μ-chloro-μ-acetate $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}O_2CMe)][PF_6]$ (**12**) (79%), together with some of the di-μ-hydrido-μ-acetate $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)][PF_6]$ (**13**), after addition of KPF_6. On longer reaction (80 °C, 30 h) the proportion of (**13**) increased (to 35%) and that of (**12**) dropped (to 65%).

The identity of (**12**) was immediately apparent from the ^{1}H n.m.r. spectrum since it showed the *p*-cymene hydrogens to be diastereotopic; thus each osmium is again a chiral centre with four different ligands (H, Cl, *p*-cymene, and acetate). The spectrum also showed the integrations expected for a ratio of *p*-cymene:hydride:acetate of 2:1:1. The hydride signal at δ −9.57 [*J*(Os–H) 66.3 Hz] permitted the detection of the ^{187}Os chemical shift of −1 951 p.p.m. as a 1:1 doublet separated by 66 Hz.

Reaction of the diacetate (**8a**) with propan-2-ol (80 °C) gave three complexes, the ratios of which depended on the reaction time. A 2:3 ratio of the monohydride-diacetate



$[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$ (**14**) and the dihydride-monoacetate $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]^+$ (**13**), was obtained after 4 h. By contrast, more of the dihydride-monoacetate (**13**) (85% by n.m.r.) was obtained after 16 h; after still longer reaction times significant amounts of the tri-μ-hydride (**5**) were found. Thus the effect of increasing the reaction time was to increase the number of μ-hydrides present; similar observations have previously been reported for the pentamethylcyclopentadienyl-rhodium and -iridium complexes.[10] The dihydride-monoacetate (**13**) was characterised by ^1H and ^{187}Os n.m.r. spectroscopy [by $^1H(^{187}Os)$ reverse INEPT two-dimensional spectrosopy]. The hydride is at δ −13.73 [*J*(Os–H) 75.6 Hz] and ^{187}Os at δ −1 185 p.p.m. as a 1:0:1 triplet with the outer lines separated by 152 Hz.

The hydrido-diacetate complex (**14**) proved troublesome to isolate pure. On attempted purification by column chromatography on alumina of the crude product from a 3-h reaction of (**8a**) with propan-2-ol, hygroscopic crystals of the μ-hydroxy-μ-hydrido-diacetato complex $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}O_2CMe)_2]$ (**15**), analogous to (**6**),[12] were isolated. The ^1H n.m.r. spectrum of (**15**) again showed diastereotopic *p*-cymenes, indicative of the presence of four different ligands on each osmium. The same chromatogram gave, on further elution and addition of KPF_6, complex (**13**). Thus we can conclude that one carboxylate is readily hydrolysed but the second one is much less labile. A rather similar situation has been observed for arene ruthenium carboxylates.[2]

The trifluoroacetate complex (**8b**) also reacted rather analogously with propan-2-ol to give a mixture of two materials, identified as mono- and dihydrido-complexes; again longer reaction times gave more of the latter (60:40 after 3 h/80 °C; 35:65 after 6 h). The complexes could not be separated but were identified from their ^1H and ^{19}F n.m.r. spectra as $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}H)(\mu\text{-}O_2CCF_3)(O_2CCF_3)_2]$,(**16**), and $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}H)_2(O_2CCF_3)_2]$, (**17**). The monohydride was assigned a neutral structure, with one bridging trifluoroacetate and two terminal ones, since each osmium was again a chiral centre (diastereotopic *p*-cymenes).

N.M.R. Spectra of Osmium Comlexes; ^{187}Os *N.M.R.*—A most useful tool for structural studies is the ^{187}Os n.m.r. Direct observation is extremely difficult, but indirect observation, *via* the ^{187}Os satellites of the ^1H n.m.r. spectrum ['$^1H(^{187}Os)$ reverse INEPT two-dimensional spectroscopy'] is considerably easier. This involves finding the ^{187}Os frequency range by the use of the echo type pulse sequence (1) [$\tau = \frac{1}{2}J(^{187}Os\text{–}^1H)$],

$$\frac{\pi}{2}(H)\text{-}\tau\text{-}\pi(H)\pi(Os)\text{-}\tau\text{-}AQT(H) \qquad (1)$$

which, when the π(Os) pulse is applied nearby on resonance, gives an inversion of the osmium satellites in the proton spectrum leaving the rest of the spectrum unchanged (*AQT* = acquisition time).

The spectra were measured on a Bruker AM 300 spectrometer with proton observation (5-mm tube) through the decoupling coil of a multinuclear 10-mm VSP probe. The ^{187}Os pulsing was achieved *via* the normal observing coil tuned to the ^{187}Os frequency range. The ^{187}Os pulses were generated with a broad-band BSV 3 decoupler and a frequency synthesizer with computer controlled phase shift capabilities [$\frac{\pi}{2}(^1H)$ 27 μs, $\frac{\pi}{2}(^{187}Os)$ 53 μs giving an effective spectral width of *ca.* ± 2.5 kHz in each dimension]. Typical parameters used were: relaxation delay, 1 s; ^1H sweep width, 500 Hz; ^{187}Os sweep width, 4 000 Hz; 256 data points in each dimension, zero-filled to 512 data points before transforming. Each experiment took *ca.* 7 h. Osmium chemical shifts are referenced to molten OsO_4 at Ξ 2.282 343 MHz; the errors are ±2 p.p.m.

The accurate determination of the ^{187}Os frequency was achieved by two-dimensional n.m.r. spectroscopy using the pulse sequence shown by (2), where D_1 is a relaxation delay, D_2 is $1/[2J(^{187}Os, {}^1H)]$, and D_3 is the variable delay to produce the second dimension. This is the pulse sequence previously described, but without decoupling.[16]

INEPT intensities are well described in the literature;[17] thus a 'quintet', as for complex (**7**), is observed as a multiplet of relative intensities −1:−1:0:1:1. In this work these spectra have been turned into magnitude spectra in order to produce a more conventional appearance, *i.e.* each point is $\sqrt{II^*}$ to remove phasing problems. The resultant observed is a spectrum of relative intensity 1:1:0:1:1. By exact analogy, the multiplicities observed were those expected for the other complexes described, *i.e.* 1:1 for the mono-μ-hydrides (**2**) and (**12**), 1:1:1:1 for the tri-μ-hydride (**5**), and 1:0:1 for the di-μ-hydride (**13**).

Our data also suggest some correlation between the number of μ-hydrido ligands, their ^1H chemical shifts and their *J*(Os–H). In general, shifts of *ca.* δ −10, −13.5, and −14.8 appear characteristic of mono-, di-, and tri-μ-hydrides respectively. The corresponding *J*(Os–H) are close to 66, 75, and 83 Hz respectively.

$$\begin{array}{llllllll} ^1H & (D_1\text{-}\frac{\pi}{2}\text{-}D_2\text{-}\pi\text{-}D_2\text{-} & \frac{\pi}{2}\text{-}D_3\text{-}\pi\text{-}D_3\text{-} & \frac{\pi}{2}\text{-}D_2\text{-}\pi\text{-}D_2\text{-acquire})_n & & & & (2) \\ ^{187}Os & (\quad \pi & \frac{\pi}{2} & \frac{\pi}{2} \quad \pi &) & & & \end{array}$$

Experimental

All experiments were carried out under a protective blanket of nitrogen; typical reactions are described below. Microanalytical data (University of Sheffield Microanalytical Service), i.r. and far-i.r. spectra (PE-157G and PE-180), n.m.r. spectra (PE R-12B, PE R-34, Bruker AM 250, AM 300, and WH 400), and mass spectra (e.i. on Kratos MS-25; f.a.b. on Kratos MS-80) are collected in Tables 1 and 2.

Preparations.—$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})(\mu\text{-Cl})\text{Cl}_2]$ (**2**). *Method 1.* Complex (**1**) (200 mg, 0.25 mmol) and KPF_6 (292 mg, 1.58 mmol) were suspended in propan-2-ol (10 cm^3) and stirred (4 h, 80 °C) to give a bright orange solution. The solvent was evaporated to dryness and the residue extracted with dichloromethane (2 × 5 cm^3) and filtered. Concentration to *ca.* 1 cm^3 and addition of pentane (3 cm^3) gave red-orange crystals (179 mg, 93%).

Method 2. Complex (**3**) (210 mg, 0.23 mmol) was suspended in propan-2-ol (10 cm^3) and then stirred (4 h, 80 °C) to give a bright orange solution which was worked-up as above (143 mg, 82%).

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-Cl})_3][\text{PF}_6]$ (**3**). *Method 1.* Aqueous HPF_6 (0.5 cm^3, 60% w/w) was added to a dichloromethane solution (10 cm^3) of complex (**1**) (200 mg, 0.25 mmol). The colour immediately changed from red-orange to yellow. The dichloromethane layer was extracted with water (4 × 10 cm^3) to remove the excess of HPF_6 and dried (Na_2SO_4). Evaporation to dryness and addition of diethyl ether gave yellow crystals (202 mg, 90%).

Method 2. Carbon tetrachloride (2 cm^3) was added to a chloroform (10 cm^3) solution of complex (**2**) (100 mg, 0.12 mmol) and the solution stirred (3 d, 20 °C). Evaporation to dryness and addition of diethyl ether gave yellow crystals (96 mg, 89%).

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})_3][\text{PF}_6]$ (**5**). *Method 1.* Complex $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-OH})_3][\text{PF}_6]$, (**4**), (220 mg, 0.26 mmol) was refluxed (4 h) in propan-2-ol (20 cm^3). The colour of the solution changed from pale yellow to red-brown. The solvent was evaporated *in vacuo*, the residue extracted with chloroform (10 cm^3) and filtered to give a red solution plus a black insoluble residue. The red solution was concentrated to *ca.* 1 cm^3 and diethyl ether (5 cm^3) was added to give red needles (155 mg, 75%). Shorter reaction times gave some unreacted starting material, whilst longer reaction times produced higher amounts of the black chloroform-insoluble solid.

Method 2. Complex $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-OH})_3][\text{PF}_6]$ (**4**) (22 mg, 0.26 mmol) was added to an aqueous solution of formaldehyde (5 cm^3, 40% w/w) and the resulting pale yellow solution was stirred (3 d, 60 °C). By this time the solution was red with red crystals in suspension. The flask was left to stand (20 °C, 24 h) to give red needles (114 mg, 45%).

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Os}_4(\mu\text{-H})_4][\text{BF}_4]_2$ (**7**). Complex $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-OH})_3][\text{BF}_4]$ (**4**) (130 mg, 0.16 mmol) was refluxed (40 h) in propan-2-ol (15 cm^3). The reaction mixture was evaporated to dryness and the residue extracted with warm (40 °C) propan-2-ol to give a red solution and a black insoluble solid. After filtration, the black solid was extracted in the filter with dichloromethane to give a dark brown solution which was evaporated to dryness to give dark brown, nearly black, crystals (46 mg, 38%).

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})\text{Cl}]$ (**11a**). $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2\text{Cl}_4]$ (400 mg, 0.51 mmol) was treated with $\text{Ag}(\text{O}_2\text{CMe})$ (169 mg, 1.01 mmol) in benzene (20 cm^3). After stirring (24 h, 20 °C) the precipitated AgCl was filtered off, and the yellow solution was evaporated to dryness to give an oil. Addition of pentane led to the crystallisation of a yellow solid (352 mg, 83%).

Complex $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CCF}_3)\text{Cl}]$ (**11b**) was prepared similarly from $\text{Ag}(\text{O}_2\text{CCF}_3)$ and $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2\text{Cl}_4]$ in 88% yield.

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})_2]$ (**8a**). $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2\text{Cl}_4]$ (450 mg, 0.57 mmol) was added to a suspension of $\text{Ag}(\text{O}_2\text{CMe})$ (380.3 mg, 2.28 mmol) in benzene (20 cm^3). After stirring (24 h, 20 °C) the precipitated AgCl was filtered off and the yellow solution was worked-up as above to give complex (**8a**) (479 mg, 95%) as a very hygroscopic yellow solid.

The bis(trifluoroacetato) complex (**8b**) was obtained similarly from $\text{Ag}(\text{O}_2\text{CCF}_3)$ as a hygroscopic yellow oil.

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-OMe})_3]\text{PF}_6$ (**10**). *Method 1.* $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})_2]$ (**8a**) (100 mg, 0.23 mmol) was dissolved in methanol (10 cm^3) and the yellow solution was stirred (10 min, 20 °C). KPF_6 (100 mg, 0.61 mmol) was added and the suspension evaporated to dryness. The residue was extracted with dichloromethane and filtered. Evaporation to dryness and addition of diethyl ether (5 cm^3) gave pale yellow crystals of (**10**) (78 mg, 76%).

Method 2. $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2\text{Cl}_4]$ (200 mg, 0.25 mmol) was added to a solution of NaOMe in methanol (prepared *in situ* from 69 mg of sodium in 10 cm^3 of methanol). After stirring (10 min, 20 °C) NH_4PF_6 (200 mg, 1.28 mmol) was added and the suspension was evaporated to dryness. The residue was extracted with dichloromethane and filtered. The solution was washed with water (2 × 5 cm^3), dried (Na_2SO_4), and evaporated to dryness to give an oil. Addition of diethyl ether gave pale yellow crystals of complex (**10**) (111 mg, 50%).

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})(\mu\text{-Cl})(\mu\text{-O}_2\text{CMe})][\text{PF}_6]$ (**12**). $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})\text{Cl}]$ (**11a**) (200 mg, 0.48 mmol) and KPF_6 (200 mg, 1.08 mmol) were refluxed in propan-2-ol (20 cm^3, 19 h). The suspension was evaporated to dryness to leave a greenish yellow residue which was extracted with dichloromethane and filtered through a column (3 × 15 cm) of Kieselguhr to give a yellow solution. Concentration to *ca.* 1 cm^3 and addition of diethyl ether gave yellow crystals of complex (**12**) (167 mg, 79%).

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})_2(\mu\text{-O}_2\text{CMe})][\text{PF}_6]$ (**13**). $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})_2]$ (**8a**) (200 mg, 0.45 mmol) and KPF_6 (200 mg, 1.0 mmol) were refluxed in propan-2-ol (20 cm^3, 16 h). The suspension was worked up as for complex (**12**) to give complex (**13**) after two recrystallisations from dichloromethane–diethyl ether (26 mg, 13%).

$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-H})(\mu\text{-OH})(\mu\text{-O}_2\text{CMe})_2]$ (**15**). $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})_2]$ (**8a**) (300 mg, 0.68 mmol) was refluxed in propan-2-ol (20 cm^3, 3 h). The solution was evaporated to dryness, the residue dissolved in dichloromethane (2 cm^3) and chromatographed on a column (3 × 20 cm^3) of neutral alumina. Elution with dichloromethane–propan-2-ol (6:1) afforded a yellow band, which on evaporation to dryness and addition of pentane gave yellow, very hygroscopic crystals of complex (**15**) (112 mg, 42%). Further elution of the column with dichloromethane–propan-2-ol (3:1) afforded a second yellow band. The solution was treated with KPF_6 (100 mg, 0.54 mmol) and worked-up to give complex (**13**) (30 mg, 10%).

Reaction of $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})_2]$ (**8a**) *with Water.*—$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CMe})_2]$ (200 mg, 0.45 mmol) was dissolved in water (5 cm^3). After stirring (30 min, 20 °C) KPF_6 (200 mg, 1.08 mmol) was added and the pale yellow solution extracted with dichloromethane (3 × 5 cm^3). The solution was dried (Na_2SO_4), evaporated to dryness, and the residue crystallised from pentane to give pale yellow crystals of the known $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CMe})][\text{PF}_6]$ (**9**) (128 mg, 64%).

Reaction of $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{O}_2\text{CCF}_3)_2]$ (**8b**) *with Propan-2-ol.*—$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Os}_2\text{Cl}_4]$ (400 mg, 0.51 mmol) was treated with $\text{Ag}(\text{O}_2\text{CCF}_3)$ (453 mg, 2.05 mmol) in benzene to give, after working up as for **(11a)**, complex **(8b)** as a yellow oil. The oil was dissolved in propan-2-ol (10 cm^3) and after stirring (3 h, 80 °C) the solution was evaporated to dryness. The residue was analysed by ^1H and $^{19}F-\{^1H\}$ n.m.r. spectroscopy and was a mixture of 60% $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}H)(\mu\text{-}O_2CCF_3)(O_2CCF_3)_2]$ **(16)** and 40% $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2(\mu\text{-}H)_2(O_2CCF_3)_2]$ **(17)**.

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