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New Oxo–Ruthenium and Oxo–Osmium Pyridine Complexes, and Use of the Former as Catalysts for Oxidation of Alcohols

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The new complexes *trans*-$[RuO_2(py)_4]^{2+}$, *trans*-$[OsO_2(py)_3(H_2O)]^{2+}$, *trans*-$[MO_2(py)_2X_2]$ (M = Ru or Os; X = Cl or Br, py = pyridine) and *trans*-$[Ru_2O_6(py)_4]$ are reported. Both *trans*-$[RuO_2(py)_4]^{2+}$ and *trans*-$[Ru_2O_6(py)_4]$ in CH_2Cl_2 are efficient oxidants for primary alcohols to aldehydes and secondary alcohols to ketones, and function catalytically, with *N*-methylmorpholine *N*-oxide (mmo) or $[NBu^n_4][IO_4]$ as co-oxidants. A simple preparation of *trans*-$[Ru(py)_4Cl_2]$ and the isolation of $[OsO_4{\cdot}L]$, $[OsO_2L_2(O_2C_2H_4)]$, and $[OsO_2L_2(O_2C_6H_{10})]$ (L = pyridine *N*-oxide) are also reported. Complexes were characterised by Raman, i.r. and ^1H n.m.r. spectroscopy.

Many oxo–osmium complexes with pyridine (py) are known {*e.g.*, $[OsO_4{\cdot}py]$,[2–4] *trans*-$[Os_2O_6(py)_4]$[2,4] and a wide variety of 'osmyl' complexes of the type *trans*-$[OsO_2(py)_2L_2]$[2,5]}; a number have been characterised by *X*-ray methods, *e.g.*, *trans*-$[Os_2O_6(py)_4]{\cdot}6H_2O$[6] and $[OsO_2(py)_2(m\text{-}O\text{–}C_6H_4\text{–}CO_2)]$.[7] There are, however, far fewer oxo–ruthenium–pyridine complexes; apart from the recently reported *trans*-$[RuO_2(py)_2(RCO_2)_2]$,[8] $[RuO_2(py)_2Cl_2]$,[9] and the ill defined '$RuO_4(py)_2$'[10,11] or '$RuO_2(OH)_2(py)_2$'.[4,12] In recent work we have shown that some oxo–ruthenium-(VII)[13,14] and -(VI)[1,15,16] complexes can function as efficient oxidants for alcohols, so it is likely that oxo–ruthenium(VI)–pyridine species will be of interest from this standpoint. We report here some new complexes of this type, present evidence that '$[RuO_4(py)_2]$' is in fact $[Ru_2O_6(py)_4]$, and show that these complexes are indeed efficient oxidants. We have also synthesised osmium(VI) analogues of these complexes and report results of our endeavours to isolate pyridine *N*-oxide analogues of the pyridine complexes.

Results and Discussion

Preparation of Pyridine Complexes.—*trans*-$[RuO_2(py)_4]^{2+}$, *trans*-$[OsO_2(py)_3(H_2O)]^{2+}$, *trans*-$[MO_2(py)_2X_2]$ (M = Ru or Os, X = Cl or Br). Careful addition of HBF_4 or HPF_6 to an aqueous solution of *trans*-$[RuO_3(OH)_2]^{2-}$ in aqueous basic solution, in the presence of pyridine (py), yields yellow crystals of *trans*-$[RuO_2(py)_4][BF_4]_2$ or *trans*-$[RuO_2(py)_4][PF_6]_2$. An analogous procedure, but using *trans*-$K_2[OsO_2(OH)_4]$, pyridine, and HBF_4, yields *trans*-$[OsO_2(py)_3(H_2O)][BF_4]_2$. Earlier we reported the isolation of *trans*-$[RuO_2(py)_2Cl_2]$;[9] we now give improved preparations for this complex and report the isolation of the bromo analogue by treatment of an aqueous basic solution of *trans*-$[RuO_3(OH)_2]^{2-}$ with HX. The new osmium analogues are prepared by reaction of *trans*-$K_2[OsO_2(OH)_4]$ with pyridine, followed by addition of HX.

It seems likely, in view of the basic similarity of preparative methods and of the analytical data, that the '$[Hpy]_2[OsO_3Cl_2(H_2O)]$' species of Scagliarini and Masetti-Zannini,[17] later formulated by us as $[Hpy]_2[OsO_2(OH)_2Cl_2]$,[18] is, in fact, $[OsO_2(py)_2Cl_2]$.

$[Ru_2O_6(py)_4]$. Koda's procedure[10] for making '$[RuO_4(py)_2]$' gave, in our hands, ill defined products with variable analyses. We find that direct reaction of RuO_4 vapour with a pyridine–water mixture, slow addition of $[Hpy]Cl$ to an aqueous solution of *trans*-$[RuO_3(OH)_2]^{2-}$ in base, or careful addition of HBF_4 to aqueous *trans*-$[RuO_3(OH)_2]^{2-}$ in base with pyridine gives a dark red powder which consistently analysed as $RuO_3{\cdot}2py$. Evidence for the dimeric formulation is given below.

trans-$[Ru(py)_4Cl_2]$. Although a number of methods for the preparation of *cis*-$[Ru(py)_4Cl_2]$[19] and its *trans* isomer[19–24] have been reported, they either involve multi-stage preparations or unusual starting materials. We find that a simple method of producing the *trans* isomer in high yield is the reaction of pyridine with freshly reduced, commercial ruthenium trichloride.

Vibrational and ^1H N.M.R. Data: Structures of the Complexes.—Although we were unable to obtain crystals of any of the new complexes in a form suitable for *X*-ray analysis, the combined use of Raman, infrared, and ^1H n.m.r. data allows us to assign structures to them with reasonable certainty. These spectroscopic data are listed in Table 1.

A *trans* arrangement of oxo ligands in *trans*-$[RuO_2(py)_4]^{2+}$, *trans*-$[OsO_2(py)_3(H_2O)]^{2+}$, and $[MO_2(py)_2X_2]$ is suggested by the vibrational spectra. They show, in addition to bands attributable to co-ordinated pyridine modes, strong Raman bands near 830 cm^{-1} (Ru) and 890 cm^{-1} (Os) which we assign to the symmetric stretch $\nu_{sym.}(MO_2)$ of a *trans* O=M=O ('osmyl') moiety. These bands do not appear in the i.r., but in the i.r. there are strong absorptions, absent in the Raman, near 840 cm^{-1} which we assign to the asymmetric stretch $\nu_{asym.}(MO_2)$ of the osmyl unit. Similar bands at similar wavenumbers have been observed in many authenticated 'osmyl' complexes containing *trans* O=Os=O units;[18] data for 'ruthenyl' species containing *trans* O=Ru=O units are much more sparse, but similar Raman and i.r. bands have been observed in *trans*-$NaK_5[RuO_2(HIO_6)_2]{\cdot}8H_2O$[1] and in *trans*-$[RuO_2(NH_3)_4]Cl_2$.[9] A similar situation is observed for $[MO_2(py)_2X_2]$, for which the Raman and i.r. spectra also suggest a *trans* arrangement of halogeno ligands. A *trans* arrangements of pyridine ligands is also suggested in $[MO_2(py)_2X_2]$ from the relative simplicity of the i.r. bands due to co-ordinated pyridine; it has been observed that in *cis*-$[Ir(py)_2Cl_4]$ these are more complex in profile than in *trans*-$[Ir(py)_2Cl_4]$, and the same is the case for *cis*- and *trans*-$[Pt(py)_2Cl_2]$.[25]

The ^1H n.m.r. spectra of $[MO_2(py)_2X_2]$ and $[M_2O_6(py)_4]$ show only one set of signals (a doublet from $H^{2,6}$, a triplet from H^4 and a triplet from $H^{3,5}$);[11] all the pyridine ligands will be equivalent in a *trans* configuration, rather than the two sets of

Table 1. Analytical, vibrational, and ^{1}H n.m.r. data of the complexes

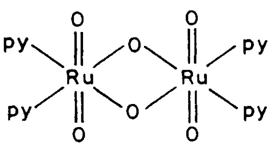
	Analysis/%^{a}				ν/cm$^{-1\,b}$				δ^c				
Compound	C	H	N	X = Cl or Br	*A*	*B*	*C*	*D*	H^{2,6}	H^{3,5}	H^4	Other signals	Solvent
trans-$[RuO_2(py)_4]$-$[PF_6]_2 \cdot H_2O$	31.1 (31.7)	2.6 (2.9)	7.3 (7.4)		*821*	obsc.	275w						
trans-$[RuO_2(py)_4]$ $[BF_4]_2 \cdot H_2O$	36.9 (37.5)	3.1 (3.4)	8.6 (8.7)		*818*s	840s	275w						
trans-$[OsO_2(py)_3$-$(H_2O)][BF_4]_2 \cdot H_2O$	26.5 (26.9)	2.4 (2.8)	6.2 (6.3)		*899*s	848s	282m		8.77 (br) [8.35 (t)]	7.79 (t) [7.54 (t)]	8.18 (t) [7.14 (t)]		$(CD_3)_2SO$
trans-$[RuO_2(py)_2$-$Cl_2] \cdot H_2O$	31.1 (31.5)	2.9 (3.2)	7.2 (7.4)	19.4 (18.7)	*836*s	837s		330s	8.57 (d)	7.38 (t)	7.79 (t)		$(CD_3)_2SO$
trans-$[RuO_2(py)_2$-$Br_2]$	26.6 (26.6)	2.1 (2.2)	6.2 (6.2)	34.5 (35.5)	*835*s	840s	275w	*221*w	8.57 (d)	7.39 (t)	7.80 (t)		$(CD_3)_2SO$
trans-$[OsO_2(py)_2$-$Cl_2]$	25.8 (26.6)	2.2 (2.2)	6.0 (6.2)	15.2 (15.7)	*902*s	855s	260w *315*w	328s *323*m	8.73 (d)	7.82 (t)	8.25 (t)		$(CD_3)_2SO$
trans-$[OsO_2(py)_2$-$Br_2]$	22.0 (22.2)	1.9 (1.9)	5.0 (5.2)	29.8 (29.6)	*900*s	858s	282w	*208*w	8.72 (d)	7.82 (t)	8.23 (t)		$(CD_3)_2SO$
trans-$[Ru_2O_6(py)_4]$	38.5 (39.1)	3.2 (3.3)	8.9 (9.1)	*d*	*810*m	815s	307m		8.66 (d) [7.56 (d)]	7.36 (t) [7.26 (t)]	7.78 (t) [7.65 (t)]		CD_2Cl_2
trans-$[Os_2O_6(py)_4] \cdot$ $2H_2O$	29.2 (29.0)	2.5 (2.9)	6.8 (6.8)		*888*s, *898*s	835s	308m		8.73 (d) [8.50 (d)]	7.69 (t) [7.44 (t)]	8.12 (t) [7.86 (t)]		D_2O
trans-$[Ru(py)_4Cl_2]$	48.9 (49.2)	4.1 (4.1)	11.3 (11.5)	14.5 (14.6)				340m	8.57 (d) [8.66 (d)]	7.06 (t) [7.29 (t)]	7.60 (t) [7.70 (t)]		$CDCl_3$
trans-$[Ru(py)_4Br_2]$	41.6 (41.6)	3.4 (3.5)	9.8 (9.7)	27.5 (27.7)				*245*w	8.71 (d)	7.07 (t)	7.63 (t)		$CDCl_3$
								E					
$OsO_4 \cdot$pyo	17.2 (17.2)	1.3 (1.4)	3.9 (4.0)		*933*s *962*	917s 837s	367w 376w	1 230s 825s	8.28 (d) [8.25 (d)]	 [7.43 (t)]	7.66 (m) [7.32]		$(CD_3)_2CO$
trans-$[OsO_2(pyo)_2$-$(O_2C_6H_{10})]$	35.8 (36.5)	3.7 (3.8)	5.2 (5.3)		*890*s	848s	325w	1 233s 825s	8.34 (d) [8.23 (q)]		7.35(m) [7.33 (m)]	δ(CH) 4.68br 4.97br	$CDCl_3$
trans-$[OsO_2(pyo)_2$-$(O_2C_2H_4)]$	30.3 (30.5)	3.0 (3.0)	5.9 (5.9)		*878*s	830s	322m 272m	1 195s 843s	8.36 (q) [8.02 (d)]		7.54 (t) [7.18 (m)]	$\delta(CH_2)$ 3.40 (s)	$(CD_3)_2SO$

A = $\nu_{sym.}(MO_2)$; *B* = $\nu_{asym.}(MO_2)$; *C* = $\delta_{asym}(MO_2)$; *D* = ν(MX); *E* = ν(N–O), δ(N–O). ^{a} Calculated values in parentheses. ^{b} Raman bands italic, other bands infrared. ^{c} δ values of py or pyo in the stated solvent in parentheses. ^{d} Found for Ru = 32.2%. Calc. = 32.9%.

signals which would be expected for a *cis* structure. The shifts are comparable with those found for *trans*-$[Ru(py)_4Cl_2]$.[19,26]

The Raman and i.r. spectra of $[Ru_2O_6(py)_4]$ are similar in profile to those of $[Os_2O_6(py)_4]$, *trans*-$[RuO_2(py)_4]^{2+}$, and *trans*-$[MO_2(py)_2X_2]$; non-coincident Raman and i.r. bands near 815 cm^{-1} are assigned to $\nu_{sym.}(RuO_2)$ and $\nu_{asym.}(RuO_2)$. The ^{1}H n.m.r. spectra of the complexes are very similar to those of $[Os_2O_6(py)_4]$ and to other metal–pyridine complexes in Table 1.

In view of these spectroscopic data and the analyses, the formulation $[Ru_2O_6(py)_4]$ is proposed rather than $[RuO_2(OH)_2(py)_2]$, which we had suggested earlier[4] for this complex. The possibility of the complex containing co-ordinated pyridine *N*-oxide (L), *e.g.* as $RuO_3 \cdot py \cdot L$, $Ru_2O_6(py)_nL_{4-n}$, *etc.*, is unlikely because no bands attributable to N–O stretches[27] are observed in the i.r. spectra of the complex. We find that all the i.r. bands, with the exception of those assigned to $\nu_{sym.}(RuO_2)$, $\nu_{asym.}(RuO_2)$, and $\delta(RuO_2)$ modes, are shifted to lower wavenumber in $[Ru_2O_6(C_5D_5N)_4]$ (C_5D_5N = $[^2H_5]$pyridine). We propose that the structure is as shown in the diagram below,



analogous to that established by *X*-ray methods[6] for $[Os_2O_6(py)_4]$. The i.r. bands at 635 and 595 cm^{-1}, little effected by deuteriation of the pyridine, may arise from asymmetric vibrations of the Ru_2O_2 bridge: similar modes are observed in $[Os_2O_6(py)_4]$[3,6] at 650 and 600 cm^{-1}.

The i.r., Raman, and ^{1}H n.m.r. spectra of *trans*-$[Ru(py)_4X_2]$ (X = Cl or Br) are close to those reported in the literature;[19,26] in the i.r. spectra of *trans*-$[Ru(C_5D_5N)_4Cl_2]$ the band assigned to $\nu_{asym.}(RuCl_2)$ at 340 cm^{-1} in the non-deuteriated complex shifts to 330 cm^{-1}.

Electronic spectra for these oxo–ruthenium(VI) and oxo–osmium(VI) species are listed in the Experimental section; the ruthenium species all show bands near 400 nm, typical[28,29] of the *trans*-dioxo–ruthenium(VI) moiety. Cyclic voltammetry of the complexes gave rather ill defined reduction waves; only in the case of *trans*-$[RuO_2(py)_2Cl_2]$ dissolved in dimethyl sulphoxide (dmso), with $[NBu^n_4]PF_6$ as supporting electrolyte, were well defined waves observed. There were four reduction waves of which the first was reversible ($E_{\frac{1}{2}} = +0.66$ V, ΔE = 65 mV *vs.* Ag–AgCl electrode) corresponding to Ru^{VI}–Ru^{V}; the others were irreversible ($E = +0.25$ V, $E_3 = +0.04$, $E_4 = -0.18$ V) probably arising from Ru^{V}–Ru^{IV}, Ru^{IV}–Ru^{III}, and Ru^{III}–Ru^{II} respectively.

Oxidations and Some Reactions of the Complexes.—We find that solutions of *trans*-$[RuO_2(py)_4][BF_4]_2$ or $[Ru_2O_6(py)_4]$ in dichloromethane are effective oxidants of primary alcohols to aldehydes and of secondary alcohols to ketones, being similar in

Table 2. Stoicheiometric and catalytic oxidations of *trans*-$[Ru_2O_6(py)_4]$ or *trans*-$[RuO_2(py)_4][BF_4]_2{\cdot}H_2O$

				Catalytic[b]					
		Stoicheiometric[b]		Co-oxidant: mmo			$[NBu^n_4][IO_4]$		
Alcohol	Product[a]	Yield (%)	Time (h)	Yield (%)	Time (h)	Turnover	Yield (%)	Time (h)	Turnover
Benzyl	A	99	3	99	2	120			
		(97)	(3)	(93)	(2)	(70)			
o-Chlorobenzyl	A	98	3	98	2	120			
		(96)	(3)	(96)	(2)	(70)			
p-Methoxybenzyl	A	99	3	99	2	120	80	3	100
		(99)	(4)	(99)	(2)	(75)	(98)	(10)	(50)
Piperonyl	A	96	3	99	2	133	99	2	133
		(98)	(3)	(99)	(2.5)	(70)	(56)	(3)	(50)
Cinnamyl	A	92	2	76	2.5	120			
		(85)	(3)	(97)	(2.5)	(70)	(65)	(3)	(50)
α-Tetralol[c]	K	86	4	94	2.5	70			
		(94)	(4)	(94)	(2.5)	(50)	(54)	(3.5)	(50)
Benzohydrol[d]	K			75	1.5	100			
				(92)	(2)	(70)	(85)	(3)	(50)
3-Cyclohexene-1-methanol	A			43	2.5	100			
				(54)	(2)	(50)			
Geraniol	A			55	2.5	70			
				(91)	(3)	(50)			
Cyclohexanol	K			82	3.5	70			
				(75)	(3)	(50)	(25)	(3)	(50)
Benzoin				58	2.5	70			
				(46)	(2.5)	(50)			

[a] A = Corresponding aldehyde, K = corresponding ketone. [b] Figures in parentheses refer to *trans*-$[RuO_2(py)_4][BF_4]_2{\cdot}H_2O$ and others to *trans*-$[Ru_2O_6(py)_4]$. [c] 1,2,3,4-Tetrahydro-1-naphthenol. [d] α-Phenylbenzenemethanol.

this respect to other ruthenium(VI) complexes, *e.g.* $[RuO_2(bipy)Cl_2]$ (bipy = 2,2′-bipyridine), $[PPh_4][RuO_2Cl_3]$,[16] *trans*-$Ba[RuO_3(OH)_2]$,[16] *trans*-$[RuO_2(py)_2(O_2CMe)_2]$,[8] and *trans*-$[Ru^{II}O_2(tmtatd)][Y]_2$ (tmtatd = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, Y = ClO_4 or PF_6).[29] They differ, however, from these complexes in that their action can be rendered catalytic.

On the basis of their stoicheiometric reactions under N_2 with 4-methoxybenzyl alcohol, we find that they function as four-electron oxidants {eight electrons overall for $[Ru_2O_6(py)_4]$, *i.e.* four electrons per ruthenium atom}. Such oxidations are listed in Table 2; it will be noted that, as with $[RuO_2(bipy)Cl_2]$, $[PPh_4][RuO_2Cl_3]$,[16] and *trans*-$[RuO_2(py)_2(O_2CMe)_2]$,[8] but unlike *trans*-$[RuO_3(OH)_2]^{2-}$ [15,16] or *trans*-$[RuO_2(HIO_6)_2]^{6-}$,[1] double bonds are not attacked by the oxidant. These oxidations can be rendered catalytic by the use of *N*-methylmorpholine *N*-oxide (mmo) as a co-oxidant (turnovers of up to 135 have been achieved) or, somewhat less effectively, with $[NBu^n_4][IO_4]$ (turnovers of up to 85). Under the conditions used in these oxidations neither mmo nor $[NBu^n_4][IO_4]$ alone, in CH_2Cl_2, reacts with the alcohols used. It is also possible to carry out relatively large-scale oxidations with these species: thus, 13.8 g of 4-methoxybenzyl alcohol are converted into 13.0 g of the corresponding aldehyde (95% yield) in 3.5 h by 8.1×10^{-4} mol dm^{-3} $[Ru_2O_6(py)_4]$, and 0.3 mol dm^{-3} mmo (a turnover of 123 with a yield of 98% of 4-methoxybenzaldehyde) while a turnover of 65 was obtained with the same substrate using the catalyst *trans*-$[RuO_2(py)_4][BF_4]_2{\cdot}H_2O$ with mmo.

Although we find that *trans*-$[RuO_2(py)_2Cl_2]$ and *trans*-$[RuO_2(py)_2Br_2]$ function as oxidants, their utility for this purpose is limited by their low solubility in organic solvents. The osmium complexes *trans*-$[OsO_2(py)_3(H_2O)]^{2+}$, *trans*-$[OsO_2(py)_2Cl_2]$, and *trans*-$[OsO_2(py)_2Br_2]$ are very weak oxidants only; thus *trans*-$[OsO_2(py)_3(H_2O)]^{2+}$ oxidised 4-methoxybenzyl alcohol in MeCN to 58% of the corresponding aldehyde, on the assumption that the complex functioned as a four-electron oxidant, after 4 h.

We find that reaction of $[Ru_2O_6(py)_4]$ with 2 mol dm^{-3} HCl, followed by gentle heating gives $[Hpy]_3[Ru^{II}Cl_3]_3$ {the complex previously believed to be $[Ru(py)_2Cl_4]$[30] but later shown to be the trimer[31]}. The complexes *trans*-$[RuO_2(py)_2X_2]$ react with methanolic pyridine under reflux to give *trans*-$[Ru(py)_4X_2]$ (X = Cl or Br).

We confirm the observation[11] that '$[RuO_4(py)_2]$' (*i.e.*, $[Ru_2O_6(py)_4]$) reacts with 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) to give species which analyse as $[Ru(OH)_2(py)_2(bipy)]{\cdot}3H_2O$ and $[Ru(OH)_2(py)_2(phen)]{\cdot}1.5H_2O$.

It seems likely that the species claimed as '$[RuO_4{\cdot}bipy]$' and '$[RuO_3(phen)]_2O$'[32,33] could well be ruthenium(VI) species, especially as they were reported to oxidise hydroquinone and methanol.[34]

Pyridine N-*Oxide* (pyo) *Complexes*.—In the early stages of this work we believed that '$[RuO_4(py)_2]$' might be $[RuO_2(OH)_2(py)(pyo)]$ or $[Ru_2O_6(pyo)_2(py)_2]$, so we sought to prepare simple pyridine *N*-oxide complexes of ruthenium and osmium as models for such systems. Although many pyridine *N*-oxide complexes of transition metals are known,[27,35] none has been reported for ruthenium or osmium.

We found that reaction of RuO_4 with pyo, under the conditions used for making $[Ru_2O_6(py)_4]$, gave no identifiable products, but reaction with pyo·HCl under conditions analogous to those used for preparation of $[RuO_2(py)_2Cl_2]$ gave a dark red, explosive and pyrophoric material which was not investigated further. Reaction of $RuCl_3{\cdot}nH_2O$ with pyo in the presence of $[PF_6]^-$ gave ill defined materials. Thus we were unable to obtain well characterised ruthenium complexes of pyridine *N*-oxide.

However, although attempts to prepare $[Os_2O_6(pyo)_4]$ by using methods analogous to those used for $[Os_2O_6(py)_4]$ [2,6,36] failed, we found that reaction of OsO_4 in diethyl ether with pyo in acetone gave a yellow crystalline material OsO_4·pyo. The i.r. spectrum of this showed features in common with those of other pyo complexes.[27-35] The Raman and i.r. spectra were similar in profile, apart from the ν(N–O) bands near 1 200 cm^{-1}, to those of OsO_4·py [3,4] which is thought[4] to have a C_{3v} structure. In earlier work we showed that adducts OsO_4·L (L = pyridine, quinuclidine, isoquinoline, phthalazine, or pyridazine)[37] would react with alkenes, R, to give osmium(VI) ester complexes $[OsO_2(O_2R)L]_2$;[37-39] in the presence of an excess of ligand L, *trans*-$[OsO_2(O_2R)L_2]$ was formed.[39] With OsO_4·pyo we found that reaction with ethylene gave a low yield of $[OsO_2(O_2C_2H_4)(pyo)_2]$, but there is no reaction with cyclohexene. However, these alkenes do react with OsO_4 in the presence of an excess of pyo in acetone to give brown species of the form *trans*-$[OsO_2(pyo)_2(O_2R)]$. The Raman and i.r. spectra show the presence of the *trans* O=Os=O unit, the ^1H n.m.r. shifts of co-ordinated pyo[40] are clearly seen, and, in the case of the complex formed from ethylene, the methylene resonances are clearly discernible at δ 3.4 p.p.m. (Table 1). These complexes clearly contain five-membered diolato rings of the type established in a wide variety of osmium(VI) complexes.[37-39]

Cyclic voltammetry of OsO_4·pyo in MeCN using 0.1 mol dm^{-3} $[NBu^n{}_4]PF_6$ as supporting electrolyte and a Ag/AgCl reference electrode shows a reversible one-electron reduction, presumably to $[OsO_4]^-$, at $E = +0.14$ V ($\Delta E = 70$ mV); OsO_4 itself under the same conditions gives a similar wave at the same potential, as noted by Bilger *et al.*[41] For $[OsO_2(pyo)_2(O_2C_6H_{10})]$ under the same conditions, three reduction waves were observed; the first two ($E_{\frac{1}{2}} = +0.1$ V, $\Delta E = 40$ mV and $E_{\frac{1}{2}} = -0.31$ V, $\Delta E = 60$ mV) being reversible one-electron processes and the third ($E_{\frac{1}{2}} = -0.65$ V, $\Delta E = 100$ mV) a quasi-reversible one-electron process. These presumably involve Os^{VI}–Os^{V}, Os^{V}–Os^{IV}, and Os^{IV}–Os^{III} reductions.

Experimental

All new compounds prepared were found to be diamagnetic.

Potassium osmate, *trans*-$K_2[OsO_2(OH)_4]$, was prepared by the literature method.[42] Ruthenium tetroxide, RuO_4, was generated in vapour form by a method based on that of Nakata.[43] Dried ruthenium dioxide (0.3 g, 2.3 mmol) was added to sodium metaperiodate, $NaIO_4$ (5 g, 2.3 mmol), in water (20 cm^3) and N_2 gas bubbled in to sweep out the RuO_4 vapour.

Sodium Ruthenate Solution.—A solution of RuO_4 in CCl_4 (150 cm^3), containing 11.3 mmol of ruthenium, obtained by the method of Nakata,[43] was treated with 1 mol dm^{-3} NaOH (50 cm^3) with stirring overnight until a red-brown solution was obtained.

trans-*Dioxotetrakis(pyridine)ruthenium*(VI) *Tetrafluoroborate Hydrate*, *trans*-$[RuO_2(py)_4][BF_4]_2 \cdot H_2O$.—To a solution of $[RuO_4]^{2-}$ prepared as above (10 cm^3, 2.3 mmol Ru) was added sodium hydroxide (0.1 g, 2.5 mmol) with stirring. Pyridine (0.75 g, 9.5 mmol) was then added. After stirring for 10 min the mixture was cooled and diluted aqueous HBF_4 (1:2, *ca.* 2 cm^3) added dropwise until pH 9 was reached. A yellow crystalline precipitate was formed which was filtered off immediately, washed with a little cold water and diethyl ether, and then dried *in vacuo* (yield, 0.75 g, 1.17 mmol, 51%). Electronic spectrum in dmso: $\lambda_{max.}$ 400 (ε = 5 600) and 251 nm (15 680 dm^3 mol^{-1} cm^{-1}).

The hexafluorophosphate was prepared similarly, HPF_6 replacing HBF_4. The molar conductance of *trans*-$[RuO_2(py)_4][PF_6]_2 \cdot H_2O$ in MeCN is 263 Ω^{-1} cm^2. Electronic spectrum in MeCN: $\lambda_{max.}$ at 420 (ε = 3 840), 310 (7 020), and 250 nm (18 860 dm^3 mol^{-1} cm^{-1}).

trans-*Aquadioxotris(pyridine)osmium*(VI) *Tetrafluoroborate Hydrate*, *trans*-$[OsO_2(py)_3(H_2O)][BF_4]_2 \cdot H_2O$.—To potassium osmate (0.2 g, 0.54 mmol) dissolved in H_2O (5 cm^3) were added pyridine (0.5 g, 6.3 mmol) and $NaBF_4$ (0.12 g, 1.1 mmol) and the mixture stirred for 5 min, during which time the colour changed from violet to light brown and a white precipitate was formed. This was filtered off and the filtrate treated with dilute HBF_4 (1:2, 2 cm^3) with stirring. The solution was left to stand for 40 min during which time a yellow precipitate separated out and was filtered off, washed with a little water and then diethyl ether, and dried *in vacuo* over silica gel (yield, 0.28 g, 0.41 mmol, 77%). Molar conductance in water: 201.0 Ω^{-1} cm^2. Electronic spectrum in dmso: $\lambda_{max.}$ 367 (ε = 780), 310 (2 450), and 265 nm (14 400 dm^3 mol^{-1} cm^{-1}).

trans-*Dichlorodioxobis(pyridine)ruthenium*(VI), *trans*-$[RuO_2(py)_2Cl_2]$.—This was made by a modification of our earlier method.[9] To a solution of *trans*-$[RuO_3(OH)_2]^{2-}$ (10 cm^3, 2.3 mmol Ru) was added NaOH (0.1 g, 2.5 mmol) and pyridine (0.4 g, 5 mmol) and the mixture stirred. Dilute HCl (6 mol dm^{-3}) was added with stirring until a bulky yellow precipitate was formed which was filtered off, washed with a little cold water and diethyl ether, and finally dried over KOH (yield, 0.6 g, 1.6 mmol, 68%). Molar conductance in dmso: 6.3 Ω^{-1} cm^2. Electronic spectrum in dmso: $\lambda_{max.}$ 610 (ε = 1 920), 420 (3 830), 310 (4 700), and 262 nm (6 600 dm^3 mol^{-1} cm^{-1}).

The bromo complex was prepared similarly, HBr (1:2) replacing HCl. Molar conductance in dmso: 3.5 Ω^{-1} cm^2. Electronic spectrum in dmso: $\lambda_{max.}$ 580 (ε = 1 580), 420 (3 680), 312 (9 734), and 263 nm (24 445 dm^3 mol^{-1} cm^{-1}).

trans-*Dichlorodioxobis(pyridine)osmium*(VI), *trans*-$[OsO_2(py)_2Cl_2]$.—To a solution of potassium osmate (0.2 g, 0.54 mmol) in water (5 cm^3) was added pyridine (0.5 g, 6.3 mmol) and the mixture stirred for 10 min until a brown colour appeared. The mixture was cooled and dilute HCl (1:2, 2 cm^3) added with stirring and the solution left to stand for several hours at room temperature; a yellow precipitate started to appear after 1 h. This was filtered off, washed with cold water and diethyl ether, and dried *in vacuo* over KOH (yield, 0.2 g, 0.44 mmol, 82%). Electronic spectrum in dmso: $\lambda_{max.}$ 460 (sh) (ε = 704), 367 (704), 320 (2 000), and 266 nm (12 800 dm^3 mol^{-1} cm^{-1}).

The bromo complex was similarly prepared using dilute HBr (1:2); the precipitate formed at once. Molar conductance in dmso: 7.4 Ω^{-1} cm^2. Electronic spectrum in dmso: $\lambda_{max.}$ 367 (ε = 560), 310 (1 624), and 264 nm (11 200 dm^3 mol^{-1} cm^{-1}).

Di-μ-oxo-tetra(oxo)tetrakis(pyridine)diruthenium(VI), $[Ru_2O_6(py)_4]$.—*Method A*. A mixture of RuO_4–N_2 prepared as above was passed into an ice-cold aqueous solution (10 cm^3 water) containing pyridine (0.5 g, 6.3 mmol). The colour changed from yellow to orange and a reddish product precipitated after 20 min. The reaction was complete after 1 h; the dark red precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* over silica gel (yield, 0.3 g, 1.1 mmol, 50%).

Method B. To the *trans*-$[RuO_3(OH)_2]^{2-}$ solution (10 cm^3) prepared as above was added a solution of pyridinium hydrochloride (0.6 g, 5.2 mmol in 2 cm^3 of water) dropwise with stirring; a fine dark red precipitate was obtained. This was filtered off and treated as above (yield, 0.35 g, 1.1 mmol, 50%).

Method C. To a solution of *trans*-$[RuO_3(OH)_2]^{2-}$ (10 cm^3) was added pyridine (0.4 g, 5 mmol) with stirring, then dilute HBF_4 (1:3) was added carefully dropwise over *ca.* 20 min whereupon a fine dark red precipitate started to form. The addition was continued until the pH reached 8. The precipitate was treated as before (yield, 0.4 g, 1.3 mmol, 57%).

Electronic spectrum in CH_2Cl_2: $\lambda_{max.}$ 400 (ε = 5 600) and 251 nm (15 680 dm^3 mol^{-1} cm^{-1}).

Di-μ-oxo-tetra(oxo)tetrakis(pyridine)diosmium(VI), $[Os_2O_6(py)_4]\cdot6H_2O$ and $[Os_2O_6(py)_4]\cdot2H_2O$.—The hexahydrated complex was made by the literature method,[36] while the new dihydrate was prepared as follows.

To a solution of potassium osmate (0.2 g, 0.54 mmol) in water (4 cm^3) was added pyridinium hydrochloride (0.6 g, 5.2 mmol) and the mixture stirred for 10 min. A yellowish precipitate was formed, filtered off, washed with a little water and diethyl ether, and then dried *in vacuo* over silica gel (yield, *ca.* 55%).

trans-*Dichlorotetrakis(pyridine)ruthenium*(II) *Hydrate, trans*-$[Ru(py)_4Cl_2]\cdot H_2O$.—*Method A.* Hydrated ruthenium trichloride (0.5 g, 1.9 mmol) was dissolved in water (25 cm^3) and ethanol (40 cm^3) and the solution refluxed gently for 3—4 h. The resulting dark greenish solution was cooled to room temperature, an excess of pyridine (2 g, 25 mmol) added, and refluxing continued for another hour. The deep green solution was left to stand overnight, giving orange-red needles which were filtered off, washed with water and diethyl ether, and dried *in vacuo* (yield, 0.82, 1.7 mmol, 89%).

Method B. The complex *trans*-$[RuO_2(py)_2Cl_2]\cdot H_2O$ (0.38 g, 1 mol) was dissolved in MeOH (10 cm^3) and then pyridine (1.0 g, 12.6 mmol) added. The solution changed to green, was refluxed for 1 h, and then evaporated to low volume. The orange-red crystals were filtered off and treated as above (yield, 0.32 g, 0.66 mmol, 66%).

The bromo complex was similarly prepared starting from *trans*-$[RuO_2(py)_2Br_2]$.

Pyridine N-*oxide–Tetraoxo-osmium*(VIII), $OsO_4\cdot ONC_5H_5$.—To osmium tetraoxide (0.25 g, 1 mmol) in CCl_4 (5 cm^3) was added pyridine *N*-oxide (0.22 g, 2.3 mmol) in acetone (2—3 cm^3). A bulky yellow precipitate was formed at once which was filtered off, washed with an excess of CCl_4 and diethyl ether, and finally dried *in vacuo* over silica gel (yield, 0.3 g, 0.86 mmol 86%).

trans-*Diolatodioxobis(pyridine* N-*oxide)osmium*(VI) *Complexes, trans*-$[OsO_2(ONC_5H_5)_2(O_2R)]$ (R = C_2H_4 *or* C_6H_{10}).—(*a*) *Reaction with ethylene.* Ethylene gas was passed into a solution of $OsO_4\cdot ONC_5H_5$) (0.17 g) in acetone (5 cm^3) for 20 min. The resulting brown precipitate was separated out and washed with acetone and then diethyl ether (yield, 30%). Alternatively, to a solution of OsO_4 (0.1 g, 0.4 mmol) in acetone (3 cm^3) was added an excess of pyridine *N*-oxide (0.5 g, 5.2 mmol) dissolved in acetone (3 cm^3) and then a slow stream of ethylene passed into the stirred solution for 15 min when a brown precipitate formed (yield, *ca.* 90%).

(*b*) *With cyclohexene.* No identified product was obtained starting with $OsO_4\cdot ONC_5H_5$ but the alternative method above was used with cyclohexene (0.1 g, 1.2 mmol) and the mixture shaken for a few minutes; some heat was evolved and a brown precipitate separated out, was filtered off, washed with a little acetone, and dried *in vacuo* over KOH (yield, 90%).

Oxidations.—(*a*) *Stoicheiometric.* The oxidation of cinnamyl alcohol is typical of the oxidation of a primary alcohol. Since there appears to be some aerobic catalysis, all stoicheiometric oxidations were carried out under a nitrogen atmosphere. To 1 mmol of the alcohol was added *trans*-$[Ru_2O_6(py)_4]$ (0.25 mmol) or *trans*-$[RuO_2(py)_4][BF_4]_2\cdot H_2O$ (0.5 mmol) in degassed CH_2Cl_2 (25 cm^3). The mixture was stirred and slowly became dark green and finally turned black. After 2 h the mixture was evaporated to dryness and extracted with diethyl ether (2 × 25 cm^3); the combined ethereal extracts were filtered and evaporated to yield cinnamaldehyde which was characterised and quantified as its 2,4-dinitrophenylhydrazone derivative.

(*b*) *Catalytic.* The oxidation of 4-methoxybenzyl alcohol is typical; the procedures for *trans*-$[Ru_2O_6(py)_4]$ and *trans*-$[RuO_2(py)_4][BF_4]_2\cdot H_2O$ were similar.

(*i*) *With* N-*methylmorpholine* N-*oxide* (*mmo*) *as co-oxidants.* To 4-methoxybenzyl alcohol (1 mmol) was added mmo (3 mmol) in CH_2Cl_2 (25 cm^3) and *trans*-$[Ru_2O_6(py)_4]$ (8.3 × 10^{-3} mmol). The solution was stirred for 2 h and treated as above for the stoicheiometric oxidation. A yield of 99% of 4-methoxybenzaldehyde was produced corresponding to a turnover of 120.

(*ii*) *With tetrabutylammonium periodate* $[NBu^n{}_4][IO_4]$ *as co-oxidant.* To 4-methoxybenzyl alcohol (1 mmol) was added $[NBu^n{}_4)][IO_4]$ (3 mmol) in CH_2Cl_2 (25 cm^3) and then 10^{-3} mmol of *trans*-$[Ru_2O_6(py)_4]$. The reaction was continued for 3 h and treated as above, 80% of 4-methoxybenzaldehyde was obtained corresponding to a turnover of 100.

In all cases the products were isolated as 2,4-dinitrophenylhydrazones, and these were compared with authentic samples.

Carbon, hydrogen, and nitrogen analyses were carried out by the Microanalytical Department of Imperial College. Ruthenium was analysed by atomic absorption measurements.

Raman spectra were run on pressed discs with KBr supports on a Spex Ramalog 5 instrument with 5 682 and 6 471 Å krypton-ion laser excitation, i.r. spectra on a Perkin-Elmer 683 instrument as liquid paraffin mulls between CsI plates or as KBr discs. Proton n.m.r. spectra were recorded on a Bruker WM 250-MHz instrument and δ values are quoted relative to tetramethylsilane for organic solvents, and relative to the sodium salt of (3-trimethylsilyl)propane-1-sulphonic acid for aqueous solutions. Cyclic voltammetry was performed on a potentiostat/wave generator made by Oxford Electrodes. Molar conductances were measured on a Digital Conductivity Meter PTI-18 for 10^{-3} mol dm^{-3} solutions of the complexes at 25 °C.

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