Studies on Transition-metal Nitrido and Oxo Complexes. Part 14.[1] Carboxylato Oxo-osmium(VI) and -ruthenium(VI) Complexes and their Reactions

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The new complexes $[OsO_2(OCOR)Cl_2]^-$ [R = Me, Et or CH(Me)Et] and $[RuO_2(OCOR)Cl_2]^-$ (R = Me, Et, Pr or CHF_2) have been prepared. In addition to functioning as catalytic oxidants for organic substrates in the presence of *N*-methylmorpholine *N*-oxide as co-oxidant, the acetato complexes $[MO_2(OCOMe)Cl_2]^-$ in particular can be used as precursors for a wide variety of complexes. New species prepared from these include $[OsO_2(NCO)_4]^{2-}$, $[OsO_2(SCN)_4]^{2-}$, $[OsO_2(acac)Cl_2]^-$ (acac = pentane-2,4-dionate), $[Os(terpy)Cl_3]^+$ (terpy = 2,2′:6′,2″-terpyridine), $[OsO_2(S_2CNEt_2)_2]$ and $[Ru(OH)(H_2O)(O_2COCR^1R^2)Cl_2]$ (R^1 = R^2 = Me or Et; R^1 = Me, R^2 = Et or Ph).

Carboxylato oxo complexes of osmium(VI) and ruthenium(VI) are of interest because they can be used as oxidants for organic substrates;[2] furthermore co-ordinated carboxylates might be expected to be good leaving groups so that such complexes should function as precursors for other complexes of the metals. We have reported[2] the crystal structure of $[PPh_4][RuO_2(OCOMe)Cl_2]$ and its use as a catalytic oxidant for organic substrates in the presence of *N*-methylmorpholine *N*-oxide (mmo) as co-oxidant. Here we report the isolation of other oxo-osmium(VI) and -ruthenium(VI) carboxylato complexes, and the reactions of the acetato species $[MO_2(OCOMe)Cl_2]^-$ (M = Ru or Os) with a variety of ligands to yield a number of known and new complexes.

A number of carboxylato oxo-osmium and -ruthenium complexes have been reported but most are soluble only in water, often with decomposition, and few in organic solvents. Salts of $[OsO_2(OCOMe)_3]^-$ (ref. 3) and *trans*-$[OsO_2L_2]^{2-}$ (L = salicylate,[4] oxalate,[5,6] or malonate[5]) have been reported, and we have recently made salts of $[OsO_2L_2]^{2-}$ (L = glycolate or quinate), $[(OsO_2)_2(tart)_3]^{4-}$ (tart = tartrate) and $[OsO_2(py)_2L]$ (py = pyridine; L = oxalate, lactate, α-hydroxy-α-phenylpropionate, citrate or 1,3,4,5-tetrahydroxycyclohexanecarboxylate).[6] The species $[OsO_2(py)_2L]$ (L = glycolate, 2-methyl-2-oxidopropionate isobutyrate, α-hydroxybenzeneacetate and salicylate)[7] are also known. There are fewer oxoruthenium carboxylates: $[RuO_2(ox)_2]^{2-}$ (ox = oxalate)[8] and $[RuO_2(py)_2(OCOMe)_2]$[9] have been reported, and we have recently made[10,11] oxoruthenium(V) complexes of α-hydroxycarboxylates $[RuO(O_2COCR^1R^2)_2]^-$ (R^1R^2 = Me_2, EtMe or PhMe), $[RuO\{O_2C(NH)CHEt\}_2]^-$ and $[OsO(O_2COCEt_2)_2]^-$.

Results and Discussion

(*a*) *Preparation of Complexes.*—The new complexes $[PPh_4][OsO_2(OCOMe)Cl_2]$, $[PPh_4][OsO_2(OCOEt)Cl_2]$ and $[PPh_4][OsO_2\{OCOCH(Me)Et\}Cl_2]$ were made from *trans*-$K_2[OsO_2(OMe)_4]$ and acetic, propionic or 2-methylbutyric acid in the presence of PPh_4Cl. The ruthenium complexes $[RuO_2(OCOMe)Cl_2]^-$, $[RuO_2(OCOEt)Cl_2]^-$ and $[RuO_2(OCOPr)Cl_2]^-$ were prepared by passing RuO_4 vapour into concentrated acetic, propionic or butyric acid containing PPh_4Cl; for the difluoroacetato complex, $[RuO_2(OCOCF_2H)Cl_2]^-$, a solution of RuO_4 in CCl_4 was added to the acid and PPh_4Cl in acetonitrile. The initial product of reaction of RuO_4 with acetic acid and PPh_4Cl is the dark green $[PPh_4][RuO_2(OCOMe)Cl_2]\cdot 2MeCO_2H$; the acetic acid of crystallisation is lost on recrystallisation from a dichloromethane–carbon tetrachloride mixture. The ^1H NMR spectrum of the first product showed two sharp resonances at δ 2.11 and 2.00 in a 2:1 ratio, assigned to the methyl resonances of free and co-ordinated acetate respectively. The spectrum of the recrystallised product however showed only the resonance at δ 2.00 due to co-ordinated acetate. It is interesting that $K[OsO_2(OCOMe)_3]\cdot 2MeCO_2H$ also contains two molecules of acetic acid of crystallisation.[3,12]

Attempts to prepare $[OsO_2(OCOR)Br_2]^-$ from $K_2[OsO_2(OMe)_4]$ with RCO_2H (R = Me, Et or Pr) and PPh_4Br gave *trans*-$[PPh_4][OsO_2Br_4]$.

(*b*) *Vibrational Spectra and Structure.*—Analytical and vibrational spectral data are in Table 1. The crystal structure of $[PPh_4][RuO_2(OCOMe)Cl_2]$ shows *trans* chloro ligands [Ru–Cl 2.37 Å, Cl–Ru–Cl 178.1(2)°];[2] the salt $K[OsO_2(OCOMe)_3]\cdot 2MeCO_2H$ has a closely related structure with *trans* monodentate acetato groups replacing the chloro ligands (Os–O 2.02 Å) and *cis* oxo ligands (Os=O 1.71 Å, O–Os–O 125.2°).[12] For $[PPh_4][RuO_2(OCOMe)Cl_2]$ the strong infrared band at 866 cm^{-1} and the weaker IR band at 891 cm^{-1} are assigned to the asymmetric and symmetric stretches $\nu_{asym}(RuO_2)$ and $\nu_{sym}(RuO_2)$ respectively of a *cis*-dioxo unit; they appear in the Raman spectrum with opposite order of intensities as expected. In solution in CH_2Cl_2 these IR bands are little shifted, suggesting retention of the solid-state structure; such bands are typical of *cis*-RuO_2 moieties,[2,13,14] and this is also the case for the complexes containing the *cis*-OsO_2 unit.[15] We have reported the Raman and IR spectra of $K[OsO_2(OCOMe)_3]\cdot 2MeCO_2H$,[16] known[12] to contain a *cis*-OsO_2 unit. Infrared bands of the complexes $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = Me, Et, Pr or CHF_2) are difficult to discern beneath those due to $[PPh_4]^+$, but for the acetate and propionate complexes the broad peaks near 1500 and 1450 cm^{-1} are assigned to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$, the asymmetric and symmetric stretches respectively of the carboxylate group, as found for other bidentate carboxylato complexes of osmium and ruthenium.[17] Bands near 300 cm^{-1} are assigned to metal–chloride stretches. On the basis of the similarity of appearance of the infrared spectrum of $[PPh_4][RuO_2(OCOMe)Cl_2]$ with those of the other new complexes we suggest that they all have similar structures (the structure of the acetato complex is illustrated) with *cis*-MO_2 units and bidentate carboxylate ligands. The similarity in profile of the infrared spectrum of solid $[PPh_4][RuO_2(OCOMe)Cl_2]$ with that of its solution in

Table 1 Analytical and vibrational data[a] for new ruthenium and osmium complexes

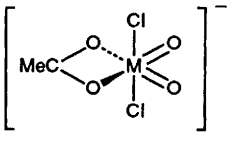
Complex	Analysis (%)				Selected vibrational data (cm^{-1})			
	C	H	N	X	ν_{asym}(M=O)	ν_{sym}(M=O)	ν(M–Cl)	ν_{asym}(O–C–O)
$[PPh_4][RuO_2(OCOMe)Cl_2]$	50.4 (50.1)	3.8 (4.0)	—	12.5 (11.8)	866s (866) *872w*	891m (886) *889s*	334s	1506m
$[PPh_4][RuO_2(OCOEt)Cl_2]$	52.2 (52.5)	4.2 (3.9)	—	12.2 (11.6)	864s	916w	329s	1501m
$[PPh_4][RuO_2(OCOPr)Cl_2]$	52.1 (51.0)	3.4 (3.4)	—	—	878s	891m	310s	—
$[PPh_4][RuO_2(OCOCHF_2)Cl_2]$	49.5 (49.0)	3.5 (3.3)	—	—	878s	891m	313s	—
$[Ru(py)_4Cl_2]Cl_2$	43.0 (43.0)	3.4 (3.6)	9.7 (10.0)	24.8 (25.4)	—	—	345s, 315s	—
$[Ru(phen)_2Cl_2]Cl_2$	47.2 (47.8)	2.8 (2.7)	8.9 (9.3)	23.8 (23.5)	—	—	320s, 315s	—
$[PPh_4][Ru(OH)(H_2O)(O_2COCEt_2)Cl_2]$	52.3 (53.3)	4.7 (4.9)	—	10.9 (10.3)	—	—	321m	1652vs
$[PPh_4][Ru(OH)(H_2O)(O_2COCMe_2)Cl_2]$	51.7 (51.4)	4.6 (4.6)	—	10.9 (11.0)	—		318m	1652vs
$[PPh_4][Ru(OH)(H_2O)(O_2COCEtMe)Cl_2]$	51.8 (52.4)	4.5 (4.7)	—	10.9 (10.6)	—	—	335m	1640vs
$[PPh_4][Ru(OH)(H_2O)(O_2COCPhMe)Cl_2]$	54.9 (55.6)	4.1 (4.4)	—	10.8 (10.0)	—	—	310m	1674vs
$[PPh_4][OsO_2(OCOMe)Cl_2]$	44.5 (45.1)	3.2 (3.5)	—	11.3 (10.4)	883s	851m	291s	—
$[PPh_4][OsO_2(OCOEt)Cl_2]$	46.2 (46.0)	3.3 (3.6)	—	11.0 (10.1)	914s	884m	297s	—
$[PPh_4]_2[OsO_2Br_4]$	47.3 (47.2)	3.2 (3.3)	—	26.0 (26.2)	849s	—	—	—
$[Os(bipy)Cl_4]$	24.9 (24.6)	1.5 (1.6)	5.7 (5.7)	28.5 (27.8)	—	—	321s, 302s	—
$[Os(terpy)Cl_3]Cl$	31.3 (31.9)	2.4 (2.0)	6.9 (7.4)	24.3 (25.1)	—	—	288s	—
$[PPh_4]_2[OsO_2(NCO)_4]$	58.5 (58.4)	3.6 (3.8)	5.0 (5.2)	—	833s	*876s*	365m[b]	2209vs[c]
$[PPh_4]_2[OsO_2(NCS)_4]$	55.6 (55.2)	3.4 (3.6)	4.9 (4.9)	—	841s	—	272m[b]	2087vs[c]
$[PPh_4][OsO_2(acac)Cl_2]$	47.1 (47.6)	3.5 (3.7)	—	10.1 (9.7)	858s	—	—	1562s, 1572s
$[Os(dbcat)_3]$	58.7 (59.2)	7.2 (7.1)	—	—	—	—	—	—
$[PPh_4]_2[OsO_2(S_2O_3)_2]$	51.4 (51.2)	3.5 (3.6)	—	—	830s	908m	—	—
$[OsO_2(S_2CNEt_2)_2]$	23.2 (23.7)	3.9 (3.7)	—	5.4 (5.3)	839s	*888s*	—	—
$[OsO_2(PPh_3)_2Cl_2]$	51.9 (52.9)	3.6 (3.7)	—	—	842s	—	—	—
$[Os(dppm)_2Cl_2]$	60.8 (62.0)	4.3 (4.6)	—	—	—	—	283m	—
$[Os(dppe)_2Cl_2]$	61.6 (62.6)	5.0 (5.1)	—	—	—	—	301m	—

[a] Solution data given in parentheses, Raman data in italics. [b] ν(Os–N). [c] ν(N≡C).

Table 2 Stoichiometric oxidations with $[PPh_4][RuO_2(OCOMe)Cl_2]$

Substrate	Product	Yield (%)	*t*/h
p-Methoxybenzyl alcohol	*p*-Methoxybenzaldehyde[a]	99	0.5
α-Tetralol	α-Tetralone[a]	98	1
Benzyl alcohol	Benzaldehyde[a]	99	1
Cinnamyl alcohol	Cinnamaldehyde[a]	100	0.5
Piperonyl alcohol	Piperonaldehyde[a,b]	78	1
Geraniol	Geranial[c,d]	92	0.5
Cyclooctanol	Cyclooctanone[a]	83	1
Citronellol	Citronellal[c,e]	81	0.5
Triphenylphosphine	Triphenylphosphine oxide[c]	98	1
Diphenylsulfide	Diphenyl sulfoxide[c]	70	6

[a] Product characterised and quantified by formation of the 2,4-dinitrophenylhydrazone derivative. [b] 3,4-(Methylenedioxy)benzaldehyde. [c] Product isolated (purified by column chromatography if necessary) and characterised by ^1H NMR and IR spectroscopy. [d] 3,7-Dimethylocta-2,5-dienal. [e] 3,7-Dimethyloct-6-enal.



CH_2Cl_2 suggests that the structure of the anion is retained in solution.

(*c*) $[MO_2(OCOMe)Cl_2]^-$ (M = Ru *or* Os) *as Oxidants.*—*Stoichiometric oxidations.* We have reported that, in the presence of an excess of *N*-methylmorpholine *N*-oxide (mmo) as co-oxidant in dichloromethane, $[RuO_2(OCOMe)Cl_2]^-$ is an excellent catalyst for the conversion of primary alcohols into aldehydes and of secondary alcohols into ketones without competing double-bond attack;[2] in this respect it resembles other oxoruthenium(VI) complexes which we have developed.[13,18–21] Unlike these and $[NPr_4][RuO_4]$[20,21] it is a more powerful oxidant in that it converts sulfides into sulfoxides and sulfones and triphenylphosphine into triphenylphosphine oxide (but not activated halides as originally reported;[2] mmo itself will oxidise these[22]). In Table 2 are given some stoichiometric oxidations effected by $[RuO_2(OCOMe)Cl_2]^-$, using 1 mol equivalent of oxidant to 1 mol of substrate. It is evident from these results that it functions stoichiometrically as a two-electron oxidant, as do other oxoruthenium(VI) complexes,[13,21] itself being reduced to a ruthenium(IV) species which we were unable to characterise.

Under stoichiometric conditions $[OsO_2(OCOMe)Cl_2]^-$ did not effect oxidations of the substrates in Table 2.

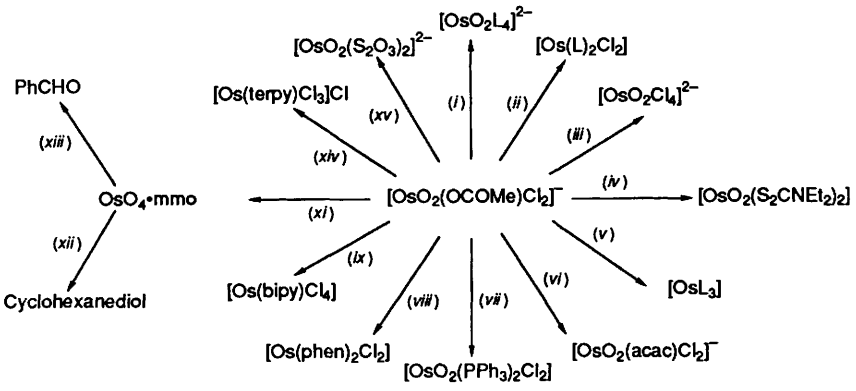
Catalytic oxidations. It was hoped that, by varying the nature of the co-ordinated carboxylate, the oxidising power of $[RuO_2(OCOMe)Cl_2]^-$ could be sufficiently changed to affect the pattern or selectivity of its oxidation reactions with alcohols, and to this end a comparison of oxidations of alcohols in dichloromethane with an excess of mmo with $[RuO_2(OCOMe)Cl_2]^-$ and $[RuO_2(OCOCF_2H)Cl_2]^-$ was made. However, the yields and turnovers given by these two complexes, under comparable conditions, were essentially the same for benzyl, *p*-methoxybenzyl, 3,4-methylenedioxylbenzyl (piperonyl), cinnamyl, 3,7-dimethyloct-6-en-1-ol (citronellol), geraniol and 2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropylmethyl (chrysanthemyl) alcohols, and for cyclooctanol and 1,2,3,4-tetrahydronaphthalen-1-ol (α-tetralol). This was also the case for the propionato and butyrato complexes with these substrates.

The bright blue solution of $[OsO_2(OCOMe)Cl_2]^-$ in dichloromethane instantly turns yellow if an excess of mmo is added, and the odour of OsO_4 is detectable; it is probable that a 1:1 adduct OsO_4·mmo is formed. Such a mixture will oxidise benzyl, *p*-methoxybenzyl and piperonyl alcohols to the aldehydes and α-tetralol to α-tetralone (3,4-dihydro-1*H*-naphthalen-2-one) in roughly the same times, yields and turnovers as does an equivalent solution of $[RuO_2(OCOMe)Cl_2]^-$ with mmo; unlike the latter however the reaction is not clean with unsaturated substrates, *e.g.* with cinnamyl or

Table 3 *cis*-Dihydroxylations of alkenes with different osmium catalysts*

Substrate	Product	Yield (%)	Catalyst
Styrene	1,2-Dihydroxy-2-phenylethane	82	OsO_4
Styrene	1,2-Dihydroxy-2-phenylethane	84	$[OsO_2(OCOMe)Cl_2]^-$
Styrene	1,2-Dihydroxy-2-phenylethane	86	$[OsO_2Br_4]^{2-}$
Cyclohexene	Cyclohexane-1,2-diol	95	$[OsO_2(OCOMe)Cl_2]^-$
Norborn-2-ene	Norbornane-2,3-diol	78	$[OsO_2(OCOMe)Cl_2]^-$
α-Methylstyrene	2-Methyl-2-phenylethane-1,2-diol	80	$[OsO_2(OCOMe)Cl_2]^-$
α-Methylstyrene	2-Methyl-2-phenylethane-1,2-diol	75	$[OsO_2Br_4]^{2-}$
4-Chlorostyrene	*p*-Chlorophenylethane-1,2-diol	62	$[OsO_2Br_4]^{2-}$

* All reactions were carried out using the published method for the OsO_4 catalyst.[23]



Scheme 1 (*i*) L = SCN^- or NCO^-; (*ii*) L_2 = dppm or dppe; (*iii*) NO, Cl^-; (*iv*) $S_2CNEt_2^-$; (*v*) L = dbcat; (*vi*) acac; (*vii*) PPh_3; (*viii*) phen, HCl, heat; (*ix*) bipy, HCl, heat; (*xi*) mmo; (*xii*) cyclohexene; (*xiii*) benzyl alcohol; (*xiv*) terpy, HCl; (*xv*) $S_2O_3^{2-}$

chrysanthamyl alcohols. This suggests that OsO_4 is reacting with the double bond, and indeed an OsO_4–mmo mixture is a well established organic reagent for the catalytic *cis* hydroxylation of alkenes.[23] We find that an $[OsO_2(OCOMe)Cl_2]^-$–mmo mixture in dichloromethane is an excellent reagent for the *cis* hydroxylation of styrene, α-methylstyrene, cyclohexene and nobornylene, using conventional work-up procedures.[23] For the reaction with styrene, using the same procedures, replacement of $[OsO_2(OCOMe)Cl_2]^-$ by an equivalent amount of OsO_4 gave the same yield, under comparable conditions, of 1,2-dihydroxy-2-phenylethane suggesting the acetato complex had been oxidised to OsO_4 by the mmo. It was found that another organic soluble oxoosmium salt, *trans*-$[PPh_4]_2[OsO_2Br_4]$, was equally as effective at promoting *cis* hydroxylations with excess of mmo (Table 3). Sharpless and co-workers[23] have shown too that $OsCl_3$ may be used as a substitute for OsO_4.

(*d*) *Reactions of* $[MO_2(OCOMe)Cl_2]^-$.—These acetato complexes contain a good leaving group (acetate) and *cis*-oxo ligands. We have shown that the tetrahedral oxoosmium(VI) complex *cis*-$[OsO_2(S_2O_3)_2]^{2-}$ has a rich substitution chemistry partly because the two oxo ligands prefer to adopt the more usual *trans* position by forming octahedral complexes,[24] so it would be expected that $[MO_2(OCOMe)Cl_2]^-$ should be good precursors for other ruthenium and osmium complexes. In fact the osmium complex produces more easily characterisable materials than does the ruthenium species. In Scheme 1 we summarise some of the reactions of $[OsO_2(OCOMe)Cl_2]^-$ with a variety of ligands.

With N-*donors*. With pyridine (py) or 1,10-phenanthroline (phen), refluxing $[RuO_2(OCOMe)Cl_2]^-$ in ethanol and concentrated HCl gave orange-yellow $[Ru(py)_4Cl_2]Cl_2$ rather than the expected $[Ru(py)_4Cl_2]$[19] and the new orange-brown complex $[Ru(phen)_2Cl_2]Cl_2$; unexpectedly a similar reaction with 2,2′-bipyridyl (bipy) gave intractable products. Conversely $[OsO_2(OCOMe)Cl_2]^-$ gave intractable materials with pyridine and with 1,10-phenanthroline, but with 2,2′-bipyridyl in ethanol and HCl it gave the known red $[Os(bipy)Cl_4]$, this being an easier preparation of this complex than that in the literature.[25] Reaction of $[OsO_2(OCOMe)Cl_2]^-$ with 2,2′:6′,2″-terpyridine (terpy) in cold methanol and HCl gave the new complex $[Os(terpy)Cl_3]Cl$. With cyanate or thiocyanate in acetone, $[PPh_4][OsO_2(OCOMe)Cl_2]$ gave two new complexes, green $[PPh_4]_2[OsO_2(NCO)_4]$ and white $[PPh_4]_2[OsO_2(NCS)_4]$. In these the *trans* O=Os=O moiety is clearly evident in the infrared spectrum as bands at 833 and 841 cm^{-1} respectively, assigned to $\nu_{asym}(OsO_2)$; ν(CN) lies at 2209 and 2087 cm^{-1} respectively. It is likely that the cyanato complex is *N*-bonded since this is the case for virtually all such complexes; we believe the thiocyanato complex to be *N*- rather than *S*-bonded because of the appearance of a band at 272 cm^{-1} assigned provisionally to ν(Os–N); for $[Os(NCS)_6]^{3-}$ (*N*-bonded) such a band appears near 280 cm^{-1}.[26] The cyclic voltammogram of $[OsO_2(NCO)_4]^{2-}$ shows an irreversible couple (probably due to reduction of Os^{VI} to Os^{IV} at −1.87 V and an irreversible couple at +0.75 V, possibly oxidation of Os^{VI} to Os^{VIII} (measured in CH_2Cl_2 solution with 0.2 mol dm^{-3} NBu_4PF_6 as supporting electrolyte, potentials *versus* the ferrocene–ferrocenium couple at 0.00 V as internal reference).

With O-*donors*. Reaction of $[PPh_4][RuO_2(OCOMe)Cl_2]$ with the α-hydroxycarboxylic acids $HO_2CC(OH)R^1R^2$ (R^1-R^2 = Me_2, Et_2, EtMe or PhMe) gave red-brown species $[PPh_4][Ru(OH)(H_2O)(O_2COCR^1R^2)Cl_2]$. They are diamagnetic and show sharp ^1H NMR peaks; carboxylate vibrations were seen in the infrared near 1650 cm^{-1} and ν(RuCl) bands near 330 cm^{-1}. We have recently reported[10,11] salts of $[Ru^VO(O_2COCR^1R^2)_2]^-$ which have similar infrared spectra in the carboxylate region to those of these new complexes. The corresponding osmium complexes could not be isolated from $[OsO_2(OCOMe)Cl_2]^-$. With 3,5-di-*tert*-butylcatechol (H_2dbcat) or 3,5-di-*tert*-butyl-1,2-benzoquinone $[OsO_2(OCOMe)Cl_2]^-$ gave deep blue $[Os(dbcat)_3]$, a species which we have previously reported using a far less convenient preparation.[27] With pentane-2,4-dione (Hacac) in CH_2Cl_2 the new complex $[PPh_4][OsO_2(acac)Cl_2]$ was formed; the $\nu_{asym}(OsO_2)$ band at

858 cm^{-1} suggests the presence of a *trans* O=Os=O unit; no ruthenium analogue could be isolated. Reaction of $[RuO_2(OCOMe)Cl_2]^-$ with a variety of catechols, quinones and *o*-aminophenol gave intractable materials.

With S-*donors*. With aqueous thiosulfate ion and $[PPh_4][OsO_2(OCOMe)Cl_2]$ in acetone green microcrystalline $[PPh_4]_2[OsO_2(S_2O_3)_2]$ was formed; we have recently reported the preparation of this unusual complex from *trans*-$[OsO_2(OMe)_4]^{2-}$, thiosulfate and PPh_4Cl and have shown by single-crystal X-ray study that it has a distorted-tetrahedral structure with *S*-bonded monodentate thiosulfato ligands and *cis*-oxo ligands in the anion.[24] With $Na(S_2CNEt_2)$ in water an acetone solution of $[PPh_4][OsO_2(OCOMe)Cl_2]$ gave the new red complex $[OsO_2(S_2CNEt_2)_2]$. The infrared and Raman spectra show bands at 839 and 888 cm^{-1} respectively, assigned as $\nu_{asym}(OsO_2)$ and $\nu_{sym}(OsO_2)$ of a *trans* O=Os=O moiety. Cyclic voltammetry in dichloromethane solution with 0.2 mol dm^{-3} NBu_4PF_6 as supporting electrolyte showed two irreversible oxidations at +0.64 and +0.92 V (*vs.* ferrocene–ferrocenium at 0.00 V as internal reference), possibly due to oxidation to Os^{VII} and Os^{VIII} and an irreversible reduction at −1.66 V, probably due to Os^{IV}.

With halide donors. Reaction of $[MO_2(OCOMe)Cl_2]^-$ with PPh_4Cl gave the dark red known[13,14] $[PPh_4]_2[RuO_2Cl_4]$ or the golden-yellow $[PPh_4]_2[OsO_2Cl_4]$. The latter is also the final product of the anaerobic reaction of $[OsO_2(OCOMe)Cl_2]^-$ in CH_2Cl_2 with NO; the blue colour changes to bright purple-blue, due perhaps to formation of a nitrosyl complex, but on reduction in volume $[PPh_4]_2[OsO_2Cl_4]$ was isolated. Reaction of *trans*-$K_2[OsO_2(OMe)_4]$ with glacial acetic acid in the presence of PPh_4Br gave, not the hoped-for $[OsO_2(OCOMe)Br_2]^-$, but $[PPh_4]_2[OsO_2Br_4]$; the latter can also be prepared from *trans*-$K_2[OsO_2(OMe)_4]$ and HBr with PPh_4Br.

With P-*donors*. No tractable products could be isolated from reactions with $[RuO_2(OCOMe)Cl_2]^-$. However with PPh_3 in acetone $[PPh_4][OsO_2(OCOMe)Cl_2]^-$ gave the known[28] $[OsO_2(PPh_3)_2Cl_2]$ by a very simple preparative route. With bis(diphenylphosphino)methane (dppm) green[29] $[Os(dppm)_2Cl_2]$ was formed and with 1,2-bis(diphenylphosphino)ethane (dppe) the analogous[29] $[Os(dppe)_2Cl_2]$ was formed.

Experimental

Potassium trans-Tetramethoxodioxoosmate(VI), trans-$K_2[OsO_2(OMe)_4]$.—The preparation is a slight modification of that of Criegee *et al.*[3] Osmium tetraoxide (0.26 g, 1.02 mmol) was dissolved in methanol (3 cm^3). 1 mol dm^{-3} Potassium hydroxide in methanol (7 cm^3) was added, and the colour changed from red to brown and then to green. The green product was filtered off, washed with diethyl ether and air dried.

$[PPh_4][OsO_2(OCOMe)Cl_2]$.—Tetraphenylphosphonium chloride (0.1 g, 2.7×10^{-4} mol) was dissolved in the minimum quantity of glacial acetic acid and osmium tetraoxide (0.05 g, 1.2×10^{-4} mol) was added. The solution instantly became blue and a precipitate quickly formed. Stirring was continued for 20 min, then the blue microcrystalline powder was filtered off under suction. This crude product was dissolved in the minimum volume of dichloromethane and carbon tetrachloride (2 cm^3) added. The volume of the solution was reduced in *in vacuo* until a slight turbidity was seen, evaporation was stopped and the product crystallised as jade crystals.

$[PPh_4][OsO_2(OCOEt)Cl_2]$.—The reaction was carried out as for $[PPh_4][OsO_2(OCOMe)Cl_2]$, propionic acid being substituted for acetic acid.

$[PPh_4]_2[OsO_2Br_4]$.—To a solution of *trans*-$K_2[OsO_2(OMe)_4]$ in methanol (0.05 g, 1.2×10^{-4} mol) a solution of PPh_4Br (0.2 g, 4.8×10^{-4} mol) in HBr (3 cm^3) was added. A brown precipitate of the product rapidly formed. Alternatively, *trans*-$K_2[OsO_2(OMe)_4]$ (0.05 g, 1.2×10^{-4} mol) was added to a saturated solution of PPh_4Br (0.1 g, 2.4×10^{-4} mol) in glacial acetic or propionic acid. A brown precipitate formed and was recrystallised from a dichloromethane–carbon tetrachloride mixture.

$[Os(bipy)Cl_4]$.—The complex $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.15 g, 2×10^{-4} mol) was added to a solution of 2,2′-bipyridyl (0.8 g, 5.1×10^{-3} mol) and concentrated hydrochloric acid (1.6 cm^3, 0.015 mol) in ethanol (15 cm^3). The solution was refluxed with stirring for 3 h. The colour became deep orange-red. The mixture was filtered while hot to yield a red precipitate, which was dried *in vacuo* over silica gel.

$[Os(terpy)Cl_3]Cl$.—The complex $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.10 g, 1.4×10^{-4} mol) was added to a stirred solution of 2,2′:6′,2″-terpyridine (0.75 g, 3.2×10^{-4} mol) and concentrated HCl (1 cm^3, 0.01 mol) in methanol (15 cm^3) at room temperature. The yellow-green product rapidly formed as a flocculent precipitate which was filtered off and air dried.

$[PPh_4]_2[OsO_2(NCO)_4]$.—To a solution of $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.1 g, 1.4×10^{-4} mol) in acetone (10 cm^3) was added KNCO (0.05 g, 5×10^{-4} mol) in the minimum volume of water. The solution instantly turned a very pale pink. The reaction mixture was stirred for 20 min, the volume reduced *in vacuo* by *ca.* 50% and a small amount of water added. The white precipitate was filtered off and air dried.

$[PPh_4]_2[OsO_2(NCS)_4]$.—The complex $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.1 g, 1.4×10^{-4} mol) was dissolved in acetone (10 cm^3) and to it was added KSCN (0.05 g, 5.1×10^{-4} mol) in the minimum volume of water. A small amount of black precipitate immediately formed but the solution was stirred for 30 min, the precipitate filtered off and the filtrate left to stand. Brown-green crystals of product slowly formed over several hours, were filtered off and air dried.

$[PPh_4][OsO_2(acac)Cl_2]$.—The complex $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.1 g, 1.35×10^{-4} mol) was dissolved in dichloromethane (15 cm^3) and pentane-2,4-dione (0.1 g, 1×10^{-3} mol) added. The solution gradually became almost colourless after *ca.* 1 h. It was stirred at room temperature for 12 h after which time the solution was light brown. The volume was reduced *in vacuo* to *ca.* 1.5 cm^3 and an equal volume of carbon tetrachloride added. The brown, microcrystalline, solid product was filtered off.

$[Os(dbcat)_3]$.—The complex $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.1 g, 1.4×10^{-4} mol) and 3,5-di-*tert*-butylcatechol (0.1 g, 4.5×10^{-4} mol) were stirred together in chloroform (15 cm^3) for 1 h. The deep ink blue solution formed was reduced *in vacuo* and the product was run down a column of silica gel eluting with chloroform until the column was pale blue. The combined eluates were reduced *in vacuo* and the product recrystallised from dichloromethane–methanol (1:1) to give a low yield of the dark blue solid product. Alternatively $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.1 g, 1.4×10^{-4} mol) was added to a solution of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.1 g, 4.5×10^{-4} mol) in methanol. The solution colour slowly changed over 24 h through brown and green to a deep ink blue. The volume was reduced to *ca.* 2 cm^3 *in vacuo* and the dark blue solid precipitated filtered off.

$[PPh_4]_2[OsO_2(S_2O_3)_2]$.—The complex $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.1 g, 1.4×10^{-4} mol) was dissolved in acetone (10 cm^3) and $Na_2S_2O_3$ (0.15 g, 6×10^{-4} mol) dissolved in the minimum volume of water (*ca.* 2 cm^3) added. An immediate change in the colour of the solution from blue-green to brown-red resulted and then no further colour change was observed on stirring for 30 min. The volume was reduced *in vacuo* to *ca.* 3 cm^3 and the green microcrystalline precipitate was filtered off and air dried.

$[OsO_2(S_2CNEt_2)_2]$.—To $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.1 g, 1.4×10^{-4} mol) dissolved in acetone (10 cm^3) was added $Na(S_2CNEt_2)$ (0.12 g, 5.3×10^{-4} mol) dissolved in the minimum volume of water (*ca.* 2 cm^3). An orange-brown precipitate instantly formed: it was filtered off and air dried.

$[OsO_2(PPh_3)_2Cl_2]$.—To $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.1 g, 1.4×10^{-4} mol) in acetone was added triphenylphosphine (0.1 g, 3.8×10^{-4} mol). A dark precipitate quickly formed. The volume of the solution was reduced to approximately one half and the black-brown product filtered off and air dried.

$[Os(dppm)_2Cl_2]$.—To a solution of $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.08 g, 1.1×10^{-4} mol) in acetone (10 cm^3) was added dppm (0.1 g, 2.6×10^{-4} mol). The solution became green and slowly a yellow-green precipitate formed. The product was filtered off after 1 h.

$[Os(dppe)_2Cl_2]$.—To a solution of $[PPh_4][OsO_2(OCOMe)Cl_2]$ (0.08 g, 1.1×10^{-4} mol) in acetone (10 cm^3) was added dppe (0.1 g, 2.5×10^{-4} mol). The solution slowly changed from blue-green to brown over 2 h. The volume of the solution was then reduced by half *in vacuo* and an equal volume of hexane added to precipitate the product.

$[RuO_4]$.—Ruthenium tetraoxide was prepared in vapour form by a variant of the method of Nakata.[30] Hydrated ruthenium dioxide $RuO_2 \cdot 2H_2O$ (0.75 g, 4 mmol) was suspended in water (20 cm^3) and $NaIO_4$ (2.8 g, 13 mmol) added. The vapour was obtained by passing nitrogen through this mixture.

$[PPh_4][RuO_2(OCOMe)Cl_2]$.—Ruthenium tetraoxide generated as above was passed into a saturated solution of PPh_4Cl (0.94 g, 2.5 mmol) in glacial acetic acid. The solution became dark green. Passage of RuO_4 was continued until all the RuO_2 had been oxidised (*ca.* 6 h); the deep green solution was filtered to yield green crystals of $[PPh_4][RuO_2(OCOMe)Cl_2] \cdot 2MeCO_2H$. This complex (0.1 g, 0.14 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and CCl_4 (5 cm^3) added. The solution was reduced in volume by evaporation until slightly turbid, and was left to stand to produce green crystals of the product.

$[PPh_4][RuO_2(OCOEt)Cl_2]$.—This complex was prepared as above, propionic acid replacing acetic acid, as dark green crystals.

$[PPh_4][RuO_2(OCOPr)Cl_2] \cdot H_2O$.—This complex, as green crystals, was similarly prepared using *n*-butyric in place of acetic acid.

$[PPh_4][RuO_2(OCOCF_2H)Cl_2]$.—The difluoroacetate was made as dark green crystals by addition of a solution of RuO_4 in CCl_4 (15 cm^3 of *ca.* 2×10^{-2} mol dm^{-3} solution) to a solution of PPh_4Cl (0.09 g, 2.5×10^{-4} mol) dissolved in MeCN (5 cm^3) and the acid (two drops). The solution was stirred for 1 h and the volume reduced to a minimum *in vacuo* to crystallise the product. The product was washed with a little CCl_4 and filtered off.

$[Ru(py)_4Cl_2]Cl_2$.—Pyridine (0.87 g, 1.1×10^{-2} mol) was dissolved in concentrated HCl (1.6 cm^3, 1.5×10^{-2} mol) and added to ethanol (20 cm^3) to form an ethanolic solution of [Hpy]Cl. To this solution $[PPh_4][RuO_2(OCOMe)Cl_2]$ (0.1 g, 1.66×10^{-4} mol) was added and the mixture refluxed for 2 h. The solid product was filtered off whilst the solution was still hot and the yellow solid was dried in a vacuum desiccator over silica gel.

$[Ru(phen)_2Cl_2]Cl_2$.—1,10-Phenanthroline (1.0 g, 5.55×10^{-3} mol) was dissolved in ethanol (20 cm^3) and concentrated hydrochloric acid (1.6 cm^3, 1.5×10^{-2} mol) added followed by $[PPh_4][RuO_2(OCOMe)Cl_2]$ (0.1 g, 1.66×10^{-4} mol). The solution was heated at reflux for 2 h and the hot solution filtered to yield the product as a brown-orange precipitate, which was dried in a vacuum desiccator over silica gel.

$[PPh_4][Ru(OH)(H_2O)(O_2COCEt_2)Cl_2]$.—2-Ethyl-2-hydroxybutyric acid (0.05 g, 3.8×10^{-4} mol) was dissolved in CH_2Cl_2 (15 cm^3) and $[PPh_4][RuO_2(OCOMe)Cl_2]$ (0.1 g, 1.66×10^{-4} mol) added. The solution was stirred for 1 h, slowly changing from green to deep red. It was reduced *in vacuo* and triturated with diethyl ether to yield the product as a deep red-purple solid, which was filtered off from the remaining solution and air dried.

$[PPh_4][Ru(OH)(H_2O)(O_2COCMe_2)Cl_2]$.—The reaction was carried out in the same way as for $[PPh_4][Ru(OH)(H_2O)(O_2COEt_2)Cl_2]$, 2-hydroxyisobutyric acid (0.04 g, 4.0×10^{-4} mol) replacing 2-ethyl-2-hydroxybutyric acid. The complexes $[PPh_4][Ru(OH)(H_2O)(O_2COCEtMe)Cl_2]$ and $[PPh_4][Ru(OH)(H_2O)(O_2COCPhMe)Cl_2]$ were similarly prepared using 2-hydroxy-2-methylbutyric acid (0.04 g, 4.1×10^{-4} mol) and α-hydroxy-2-phenylpropionic acid hemihydrate (0.07 g, 4×10^{-4} mol) as the ligands.

General Procedure for Stoichiometric Oxidations using $[MO_2(OCOMe)Cl_2]^-$ (M = Ru *or* Os).—To a solution of the alcohol (*ca.* 0.05 g) in CH_2Cl_2 (10 cm^3) were added 4 Å powdered molecular sieves and the complex (*ca.* 0.1 g, ≈1/3 equivalent). The solution was stirred at room temperature until the reaction had stopped as determined by TLC. The volume was reduced *in vacuo* and the residues taken up in diethyl ether (4×10 cm^3) and filtered through a pad of silica gel. The product was isolated or the 2,4-dinitrophenylhydrazine derivative prepared.

Typical cis-*Hydroxylation of Alkenes with* $[PPh_4][OsO_2(OCOMe)Cl_2]$, OsO_4 *or* $[PPh_4]_2[OsO_2Cl_4]$.—The method of Sharpless and co-workers[23] was used. The osmium complex (3.9×10^{-5} mol) was added to a stirred solution of styrene (0.1 g, 0.96×10^{-3} mol) and mmo (0.15 g, 1.3×10^{-3} mol) in acetone–water (1:1, 10 cm^3) protected from the light at room temperature. The reaction was followed by TLC and showed no further change after 5 h. Solid $Na_2S_2O_5$ (1.0 g) was added and the mixture stirred for 5 min. The reaction mixture was then diluted with CH_2Cl_2 (15 cm^3) and dried over magnesium sulfate; solids were filtered off and washed three times with dichloromethane. The combined filtrates were concentrated and the residual oil separated into its pure components by flash column chromatography eluting with diethyl ether–dichloromethane (1:1). The reaction gave *cis*-1,2-dihydroxy-2-phenylethane 0.109 g (83%) and a very small amount of by-product.

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