Oxo Complexes of Ruthenium with N,N′-Donors as Oxidation Catalysts for Alkenes, Alkanes and Alcohols, and their Osmium Analogues†

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Catalysis of the epoxidation of alkenes and oxidation of alkanes and alcohols by a variety of *bis*-bipy (2,2′-bipyridyl) and *bis*-phen (1,10-phenanthroline) ruthenium complexes with $NaIO_4$ or $[NBu_4]IO_4$ as co-oxidants has been investigated together with similar oxidations with $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$. The new complexes $[RuO_2(bipy)\{TeO_2(OH)_4\}]$ and $[OsO_2(L\text{–}L)\{IO_3(OH)_3\}]$ (L–L = bipy, phen or 2,2′-dipyridylamine) have been prepared and characterised.

There is much current interest in the application of ruthenium complexes as catalysts for organic oxidations,[2,3] particularly for the oxidation of alkenes[4–6] alkanes[6,7] and alcohols.[2,8] This paper is concerned with an investigation of the use of ruthenium bipyridyl complexes and related species as catalysts for the oxidation of such substrates.

We have also studied oxidations of these substrates catalysed by $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ **1** (bipy = 2,2′-bipyridyl), a complex reported in a preliminary communication,[9] and report new complexes of ruthenium and osmium related to **1**.

Results and Discussion

(*a*) *Catalytic Epoxidations of Alkenes.*—(*i*) *Epoxidations by* $RuCl_3\cdot nH_2O$ *and bipyridyl with periodate.* Balavoine *et al.*[10] noted that a suspension of $RuCl_3\cdot nH_2O$ and bipy in a biphasic CH_2Cl_2–water mixture would catalyse stereospecifically the epoxidation of a number of cyclic and linear alkenes, aqueous periodate (IO_4^-) being used as co-oxidant; in subsequent work it was shown that normal and substituted phenanthrolines, particularly 3,4,7,8-tetramethylphenanthroline (tmphen), were also effective catalysts.[11] It was suggested[10] that an oxo-ruthenate intermediate was involved but such an intermediate was not identified. Meyer and co-workers have shown that $[Ru^{IV}O(bipy)_2(py)]^{2+}$ and $[Ru^{IV}O(terpy)(bipy)]^{2+}$ (py = pyridine, terpy = 2,2′:6′,2″-terpyridyl) will, with a phase-transfer catalyst, epoxidise *cis*- and *trans*-stilbenes and styrene in CH_2Cl_2–water with hypochlorite (ClO^-) as co-oxidant.[12] The complex *cis*-$[RuCl_2(bipy)_2]$ will epoxidise oleic acid followed by hydrolysis to give 9,10-epoxyoctadecanoic acid in *tert*-butanol with hydrogen peroxide (H_2O_2) as co-oxidant,[13] while *cis*-$[Ru^{VI}O_2(dmphen)_2]^{2+}$(dmphen = 2,9-dimethyl-1,10-phenanthroline) will epoxidise norborn-2-ene, cyclohexene and *trans*-β-methylstyrene at 55 °C under 3 atm pressure of dioxygen.[14] None of these systems is as effective as the simple Balavoine reaction, however, and we have attempted here to simulate and extend this reaction with well characterised ruthenium complexes.

In Table 1 we report a number of epoxidations of cyclic and linear alkenes, using Balavoine's original procedure[10] (treating $RuCl_3\cdot nH_2O$ with excess bipy in CH_2Cl_2–water at 0–5 °C over a 15 h period with $NaIO_4$ as co-oxidant). We confirm and extend the original results with new substrates, and for the first time report catalytic turnovers (ratio of moles of product to moles of catalyst, the latter being based on the amount of ruthenium used). Reactions at higher temperatures or over shorter reaction periods result in decreased yields and turnovers. The use of a number of different co-oxidants was also investigated: sodium bromate gave no epoxide at all, while cerium(IV) ammonium nitrate or *tert*-butyl hydroperoxide gave only small amounts of epoxide. It seems therefore that $NaIO_4$ is essential to the reaction, though $[NBu_4]IO_4$ was not as effective a co-oxidant.

It is not clear what the effective oxidant is in the Balavoine procedures: commercial ruthenium trichloride is well known to be a complex mixture of species, and the green/brown product formed by the reaction of it with excess bipy under the conditions reported[10] gave a suspension of an ill-defined material which we were unable to characterise.

(*ii*) *Epoxidations with established ruthenium* N,N′-*donor complexes.* In view of the uncertainty of the nature of the Balavoine catalyst, we carried out epoxidations using the same conditions as above with a variety of well-characterised ruthenium–bipy or –phen systems. In Table 2 our yields and catalytic turnovers for the epoxidation of cyclooctene by a number of such species are listed. Cyclooctene was used as the substrate since with the Balavoine procedure it is cleanly oxidised and the epoxide easily isolated.

It is clear that *cis*-$[RuCl_2(bipy)_2]$, despite its effectiveness as an epoxidant for oleic acid with hydrogen peroxide,[13] is not particularly effective as an epoxidation catalyst (with IO_4^- as co-oxidant) under these conditions, and is unlikely to be the source of the catalytic properties exhibited by Balavoine's $RuCl_3$–bipy reagent. The same is true of $[Hbipy][Ru^{III}Cl_4(bipy)]$ and $[Ru^{III}(OH)(H_2O)(bipy)_2]^{2+}$. However, both *cis*-$[Ru^{II}(CO_3)(bipy)_2]$ and *trans*-$[Ru^{II}(H_2O)_2(bipy)_2]^{2+}$ are very effective catalysts (in aqueous solution at pH 2–3 the former is converted to the latter) as is the blue-violet dimer $[(bipy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bipy)_2]^{4+}$; rather less effective, surprisingly, is *trans*-$[Ru^{VI}O_2(bipy)_2]^{2+}$. It is known that $[Ru^{IV}O(bipy)_2(py)]^{2+}$ and $[Ru^{IV}O(terpy)(bipy)]^{2+}$ will function as epoxidation catalysts in the presence of ClO^- as co-oxidant[12] so it would be expected that the known species *trans*-$[Ru^{IV}O(H_2O)(bipy)_2]^{2+}$ should be a good candidate for epoxidation catalysis. There are minimal preparative details for this complex in the literature[15,16] but we have prepared and

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† Studies on Transition-metal Nitrido and Oxo Complexes. Part 15.[1]
Non-SI units employed: atm ≈ 101 325 Pa, $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

Table 1 Alkene epoxidation catalysed by ruthenium complexes

Substrate	Product	Yield (%) (turnover) Method A	Method B	Method C
Cyclopentene	Cyclopentene oxide	15 (38)	49 (123)	48 (120)
Cyclohexene	Cyclohexene oxide	11(28)	58 (145)	60 (150)
Cyclooctene	Cyclooctene oxide	72 (180)	75 (188)	83 (208)
Cyclododecene	Cyclododecene oxide	38 (95)	38 (95)	56 (140)
Styrene	Styrene oxide	36 (90)	30 (75)	25 (63)
trans-Stilbene	*trans*-Stilbene oxide	64 (160)	99 (248)	99 (249)
cis-Stilbene	*cis*-Stilbene oxide			75 (188)
Oct-1-ene	Oct-1-ene oxide	47 (118)	42 (105)	16 (40)
Dec-1-ene	Dec-1-ene oxide	49 (123)	51 (128)	45 (113)
Dodec-1-ene	Dodec-1-ene oxide	6 (15)	10 (25)	14 (55)
2,3-Dimethylbut-1-ene	2,3-Dimethylbut-1-ene oxide	35 (93)	46 (115)	59 (148)
2,3-Dimethylbut-2-ene	2,3-Dimethylbut-2-ene oxide	29 (73)	30 (75)	64 (161)
2,4,4-Trimethylpent-1-ene	2,4,4-Trimethylpent-1-ene oxide	5 (13)	11 (28)	5 (13)

Oxidations catalysed by $RuCl_3$–bipy (method A), *trans*-$[Ru(H_2O)_2(bipy)_2]^{2+}$ (method B) or $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ (method C), all with periodate as co-oxidant.

Table 2 Epoxidation of cyclooctene by various ruthenium N,N′-donor complexes

Complex	Yield (%) (turnover)
$RuCl_3$–bipy	72 (180)
$RuCl_3$–bipyridyl ketone	99 (248)
$RuCl_3$–dpa	50 (125)
$RuCl_3$–phen	41 (103)
$RuCl_3$–tmphen	99 (248)
cis-$[RuCl_2(bipy)_2]\cdot2H_2O$	52 (130)
cis-$[RuCl_2(phen)_2]\cdot2H_2O$	43 (108)
cis-$[Ru(CO_3)(bipy)_2]\cdot4H_2O$	68 (132)
$[Hbipy][RuCl_4(bipy)]$	28 (56)
trans-$[Ru(H_2O)_2(bipy)_2][PF_6]_2\cdot H_2O$	80 (200)
$[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2][PF_6]_4\cdot H_2O$	95 (238)
$[Ru(OH)(H_2O)(bipy)_2][ClO_4]_2\cdot H_2O$	68 (170)
$[RuO(H_2O)(bipy)_2][ClO_4]_2\cdot H_2O$	75 (188)
trans-$[RuO_2(bipy)_2][ClO_4]_2\cdot H_2O$	64 (128)
$[Ru(OH)(IO_3)(bipy)_2][PF_6]_2\cdot0.5H_2O$	75 (188)

characterised it as the perchlorate salt by two new routes: reaction of equimolar amounts of *trans*-$[Ru^{VI}O_2(bipy)_2]^{2+}$ and cyclooctene in aqueous solution, and also by reaction of *trans*-$[Ru^{II}(H_2O)_2(bipy)_2]^{2+}$ with cerium(IV). As expected it is indeed an efficient catalyst.

Since *trans*-$[Ru^{II}(H_2O)_2(bipy)_2]^{2+}$ is an effective and easily accessible epoxidant, superior to the Balavoine $RuCl_3$–bipy reagent, we carried out a number of oxidations with it (Table 1). The optimum conditions for the reaction are still those used for $RuCl_3$–bipy, *i.e.* use of a CH_2Cl_2–H_2O mixture at 0–5 °C with aqueous $NaIO_4$ over a 15 h period.

(*iii*) *Kinetics of epoxidation by trans*-$[Ru^{II}(H_2O)_2(bipy)_2]^{2+}$. We have carried out a preliminary study of the kinetics of the reaction of *trans*-$[Ru^{II}(H_2O)_2(bipy)_2]^{2+}$ with an excess of cyclooctene in a biphasic CH_2Cl_2–H_2O mixture at 2 °C using excess $NaIO_4$ as co-oxidant. The most significant observation under these conditions is that the reaction has a substantial induction period ($t_{\frac{1}{2}} \approx 3$ h); subsequently the reaction is pseudo-first order with respect to the substrate. Detailed kinetic studies are planned in order to determine the nature and source of this induction period which represents a significant fraction of the overall reaction time.

(*iv*) *Nature of the epoxidation catalyst.* Although we are not clear about the nature of the active catalyst in the Balavoine $RuCl_3$–bipy system we have investigated the *trans*-$[Ru^{II}(H_2O)_2(bipy)_2]^{2+}$ reaction in some detail. We find that the electronic spectra of mixtures of *trans*-$[Ru^{II}(H_2O)_2(bipy)_2]^{2+}$ and IO_4^-, by the method of continuous variation, show that a 1 : 1 orange complex is formed with $\lambda_{max} = 484$ nm. {Such a spectrum is also obtained from $[Ru_2^{III}O\{(H_2O)(bipy)_2\}_2]^{4+}$ in the presence of excess aqueous $NaIO_4$.} A species having the same electronic spectrum is also obtained from a 1 : 1 mixture of $[Ru^{IV}O(H_2O)(bipy)_2]^{2+}$ and IO_3^- or a 1 : 1 mixture of $[Ru^{II}(CO_3)(bipy)_2]$ and periodic acid, $IO(OH)_5$. By conducting these reactions in the presence of excess of NH_4PF_6, an orange material $[Ru(OH)(IO_3)(bipy)_2][PF_6]_2\cdot0.5H_2O$ **2**, is obtained. It appears that *trans*-$[Ru^{II}(H_2O)_2(bipy)_2]^{2+}$ is oxidised by IO_4^- to $[Ru^{IV}(OH)(IO_3)(bipy)_2]^{2+}$ and that $[Ru^{IV}O(H_2O)(bipy)_2]^{2+}$ reacts with iodate (IO_3^-) to give the same species. No iodato complexes of ruthenium have been reported and we were unable, despite many attempts, to obtain suitable crystals of **2** for single-crystal X-ray analysis. However iodato complexes of other transition metals are known *e.g.* $Zr(IO_3)_4$[17] and $K_2[Mn(IO_3)_6]$;[18] these contain M–OIO_2 bonds. The infrared spectrum of **2** (see below) also suggests the presence of iodate groups, probably co-ordinated *via* an oxygen atom.

The magnetic moment of **2** (measured by the Gouy method) is 1.78 μ_B at room temperature. This value is low for ruthenium(IV) complexes (*ca.* 2.6–2.8 μ_B) but may arise from the low symmetry around the metal atom. The ^{31}P NMR spectrum of **2**, shows a septet at δ −145 with a coupling constant $^1J_{P-F}$ of 792 Hz, as expected for ionic PF_6^-.[19] Solutions of **2** are good epoxidation catalysts in CH_2Cl_2–H_2O mixtures at 2 °C with IO_4^- as co-oxidant; thus cyclooctene and *trans*-stilbene were epoxidised in yields of 72 and 94% respectively.

(*v*) *Isolation of* $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$, $[RuO_2(bipy)\{TeO_2(OH)_4\}]$ *and their osmium analogues.* We have briefly reported the X-ray crystal structure and the oxidation properties of $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ **1**;[9] the structure is shown diagrammatically in Fig. 1. The orange complex is made from RuO_4, $NaIO_4$ and bipy in water–acetone and functions as an excellent stereospecific epoxidation catalyst for cyclic and linear alkenes. The conditions are essentially the same as those first reported by Balavoine and co-workers[10,11] for the $RuCl_3$–bipy–IO_4^- reagent (*i.e.* over a 15 h period in a biphasic water–CH_2Cl_2 mixture at 2 °C). Data for its epoxidation properties are listed in Table 1 and it is clearly more effective as a catalyst than the Balavoine system and roughly comparable with *trans*-$[Ru^{II}(H_2O)_2(bipy)_2]^{2+}$–$IO_4^-$. Stoichiometrically **1** is a six-electron oxidant—thus 1 mole of **1** will oxidise 3 moles of cyclooctene, the Ru^{VI} being reduced to Ru^{II} {presumably as $[Ru(OH)_2(H_2O)_2(bipy)]$ or a related species} and I^{VII} to I^V (as IO_3^-). This behaviour is reminiscent of that of *trans*-$[Ru^{VI}O_2\{IO_5(OH)\}_2]^{6-}$, again a six-electron oxidant, giving RuO_2 and IO_3^- with alcohols.[20]

We have attempted to prepare ruthenium analogues of **1** with substituted bipyridyls and phenanthrolines, but so far have not been able to isolate pure products. However, $[OsO_2$(bipy-

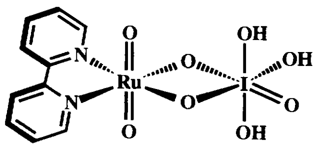

Fig. 1 Structure of the complex $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$

$\{IO_3(OH)_3\}]\cdot1.5H_2O$ can be made {from *trans*-$K_2[Os^{VI}O_2(OH)_4]$, bipy and $NaIO_4$} and a number of species of the type $[OsO_2(L\text{–}L')\{IO_3(OH)_3\}]$ have been isolated [L–L' = bipy, phen or 2,2'-dipyridylamine (dpa); see Experimental section]. It is often easier to isolate *trans*-dioxoosmium(VI) complexes than their *trans*-dioxoruthenium(VI) analogues with N-donor ligands.[21]

We have also isolated the tellurato complex $[RuO_2(bipy)\{TeO_2(OH)_4\}]$ **3** made from RuO_4, $Te(OH)_6$ and $NaIO_4$, but so far have not succeeded in obtaining the osmium analogue or crystals of **3** suitable for single-crystal X-ray studies (see below). Complex **3** functions as an overall four-electron oxidant only; it epoxidises alkenes (using the same conditions as those for **1** with periodate as co-oxidant). This is reminiscent of *trans*-$[Ru^{VI}O_2\{TeO_4(OH)_2\}_2]^{6-}$, which is a two-electron oxidant for alcohols, the tellurium(VI) ligand having no apparent oxidising effect on the organic substrate.[20] Attempts to use the osmium complexes, in particular $[OsO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ as epoxidation catalysts with IO_4^- as co-oxidant failed; OsO_4 is produced. This parallels our earlier observation that, whereas $[Ru^{VI}O_2(O_2CMe)Cl_2]^-$ with *N*-methylmorpholine-*N*-oxide (nmo) is an excellent oxidation catalyst for alcohols, $[Os^{VI}O_2(O_2CMe)Cl_2]^-$ is oxidised by nmo and this *cis*-hydroxylates the double bond in unsaturated alcohols.[1]

(*b*) *Catalytic Epoxidations of Alkanes.*—Few ruthenium-containing catalysts will oxidise alkanes; for the most part the products of such reactions are alcohols and ketones. Drago and co-workers[6] have shown that *cis*-$[Ru(dmphen)_2(solv)_2]^{2+}$ (solv = H_2O or MeCN) will catalyse the oxidation of cyclohexane and adamantane with H_2O_2 as co-oxidant at 75° C. Che and co-workers[22] investigated the abilities of various ruthenium complexes to oxidise alkanes in the presence of Bu^tOOH as co-oxidant under mild conditions (stirring at room temperature in benzene for 5 h); overall the yields were poor giving a mixture of products including alcohols, ketones and aldehydes. Murahashi *et al.*[23] have developed two efficient systems: a number of ruthenium catalysts were used for aerobic oxidation of alkanes in the presence of an aldehyde and a catalytic amount of acid, and, recently, $RuCl_3\cdot nH_2O$ was used to oxidise alkanes with peracetic acid as co-oxidant.[24] Very recently, Lau and Mak[25] have reported that an uncharacterised ruthenium oxo complex will, in the presence of bipy, oxidise cyclohexane with a variety of co-oxidants to a mixture of products.

We used *trans*-$[Ru(H_2O)_2(bipy)_2]^{2+}$ to catalyse the oxidation of various alkanes with *tert*-butyl hydroperoxide as co-oxidant at room temperatures. The yields were rather disappointing, giving a mixture of alcohols, aldehydes and ketones, but better yields were obtained for products with aromatic rings such as acetophenone, benzaldehyde and benzophenone (Table 3). However, $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ **1** is an effective catalyst for the oxidation of alkanes to alcohols or ketones when refluxed for 15 h in a biphasic water–CH_2Cl_2 system, with periodate as co-oxidant (see Table 3). The yields decrease as the ring size increases presumably due to the more stable nature of the starting alkanes. The linear alkanes are oxidised to the ketones but a number of oxidation products are formed. As in the previous system, substrates with an aromatic ring give higher yields of oxidation product.

Table 3 Alkane oxidations catalysed by ruthenium complexes

		Yield (%) (turnover)[a]	
Substrate	Product	Method A[b]	Method B[c]
Cyclopentane	Cyclopentanol	5 (10)	91 (114)
	Cyclopentanone	36	1
Cyclohexane	Cyclohexanol	13 (26)	87 (110)
	Cyclohexanone	24	8
Cycloheptane	Cycloheptanol	13 (26)	60 (75)
	Cycloheptanone	15	11
Cyclooctane	Cyclooctanol	10 (20)	31 (39)
	Cyclooctanone	12	12
Pentane	Pentan-2-ol	8 (16)	0
	Pentan-2-one	7	67 (84)
Hexane	Hexan-2-one	6 (12)	52 (65)
	Hexan-3-one	1	44
	Hexanal	8	0
Heptane	Heptan-2-one	2 (4)	15 (19)
	Heptan-3-one	5	18
	Heptan-4-one	4	7
	Heptanal	2	0
Octane	Octan-2-one	1 (2)	15 (19)
	Octan-3-one	2	14
Adamantane	Adamantan-2-ol	1 (2)	45 (56)
	Adamantanone	12	0
Diphenylmethane	Benzophenone	34 (68)	32 (40)
Ethylbenzene	Acetophenone	96 (192)	98 (123)
Tetrahydrofuran	Tetrahydrofuran-2-one	33 (66)	5 (7)
Toluene	Benzaldehyde	90 (180)	10 (13)

[a] Yields were determined by GC analysis and catalytic turnovers are based on the amount of catalyst used and calculated for the primary oxidation product only. [b] Method A: $[Ru(H_2O)_2(bipy)_2]^{2+}$–$Bu^tOOH$ with stirring at room temperature for 5 h in benzene. [c] Method B: $[RuO_2(bipy)\{IO_3(OH)_3\}]$–$IO_4^-$ with stirring at 80 °C in a biphasic CH_2Cl_2–water mixture.

(*c*) *Catalytic Oxidation of Alcohols.*—Oxo complexes of ruthenium have been found to be most effective catalysts for the selective oxidation of various organic substrates, particularly alcohols,[2,8] so the effectiveness of these bipyridyl reagents as alcohol oxidants was investigated.

(*i*) *Oxidations of alcohols catalysed by trans*-$[Ru(H_2O)_2(bipy)_2]^{2+}$, $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ *or* $[RuO_2(bipy)\{TeO_2(OH)_4\}]$. The system *trans*-$[Ru(H_2O)_2(bipy)_2]^{2+}$–$IO_4^-$ will oxidise both primary and secondary alcohols in organic media to give aldehydes and ketones respectively with $[NBu_4]IO_4$ and nmo as co-oxidants at room temperature (see Table 4). The oxidations using $[NBu_4]IO_4$ as co-oxidant gave, in nearly all cases, higher yields than the respective oxidations with nmo indicating that periodate is important in the catalytic reaction. We have already reported[9] that **1** oxidises alcohols.

As with alkenes, $[RuO_2(bipy)\{TeO_2(OH)_4\}]$ **3** functions stoichiometrically as a four-electron oxidant for alcohols, Ru^{VI} being reduced to Ru^{II}, without any apparent involvement of the tellurium(VI) ligand. With $[NBu_4]IO_4$ as co-oxidant (see Table 4) it is not a particularly good catalyst for alcohol oxidations. We have noted earlier that *trans*-$[RuO_2\{TeO_4(OH)_2\}]^{6-}$ is a relatively ineffectual oxidant for alcohols with IO_4^- as co-oxidant, and that the tellurium(VI) ligand is not involved in such oxidations, whereas in *trans*-$[Ru^{VI}O_2\{IO_5(OH)\}_2]^{6-}$ both the ruthenium(VI) and iodine(VII) centres function as oxidants.[20]

(*d*) *Vibrational Spectra and Structures of Ruthenium and Osmium Periodato and Tellurato Complexes.*—Since complexes of periodate(VII), iodate(V) and tellurate(VI) are relatively rare the experimental section reports the infrared spectra of the new complexes; only those bands not due to the N,N'-donor ligands, or the counter ion, are reported. Raman data could be obtained in a few cases only owing to the dark colour of the

Table 4 Alcohol oxidations catalysed by ruthenium complexes

		Yield (%) (turnover)		
Substrate	Product	Method A[a]	Method B[b]	Method C[c]
		53 (133)	23 (58)	38 (95)
		49 (123)	28 (70)	36 (90)
Cinnamyl alcohol	Cinnamaldehyde	75 (188)	36 (96)	28 (70)
Cycloheptanol	Cycloheptanone	20 (50)	17 (43)	18 (45)
Cyclohexanol	Cyclohexanone	21 (53)	14 (35)	16 (40)
Geraniol	Citral	30 (75)	17 (43)	15 (38)
(±)-Menthol	Menthone	5 (13)	3 (8)	15 (38)
4-Methylbenzyl alcohol	4-Methylbenzaldehyde	53 (133)	23 (58)	16 (40)
m-Nitrobenzyl alcohol	*m*-Nitrobenzaldehyde	54 (135)	36 (96)	45 (113)
α-Tetralol	α-Tetralone	80 (200)	32 (80)	14 (35)

[a] Method A: $[Ru(H_2O)_2(bipy)_2]^{2+}$–$IO_4^-$. [b] Method B: $[Ru(H_2O)_2(bipy)_2]^{2+}$–nmo. [c] Method C: $[RuO_2(bipy)\{TeO_2(OH)_4\}]$–$IO_4^-$

complexes, and low solubilities prevented the recording of solution spectra. The asymmetric and symmetric stretches $\nu_{asym}(MO_2)$ and $\nu_{sym}(MO_2)$ are based on our earlier observations of such modes.[20,21,26,27] Bands in the region 500–800 cm^{-1} probably arise from ν(IO) or ν(TeO) modes.[20,27,28] The infrared spectrum of $[Ru(OH)(IO_3)(bipy)_2][PF_6]_2\cdot 0.5H_2O$ **2** shows bands at 770, 765 and 663 cm^{-1} in addition to those of the hexafluorophosphate anion, similar to those bands reported in the literature for the co-ordinated iodate (IO_3^-) ligands.[18,29]

We believe that $[RuO_2(bipy)\{TeO_2(OH)_4\}]$ is likely to have the structure shown in Fig. 2; a recent single-crystal X-ray study of *trans*-$Rb_2Cs_4[OsO_2\{TeO_4(OH)_2\}_2]\cdot 16H_2O$ suggests that in the latter the hydroxo groups are in axial positions of the co-ordinated $[TeO_4(OH)_2]^{4-}$ anion, with two of the oxo ligands co-ordinating to the osmium atom.[30] In **3** it is probable that there is a related structure but with the four hydroxo groups as terminal ligands. Our tentative assignments of its vibrational spectrum are based on our earlier assignments for $K_6[RuO_2\{TeO_4(OH)_2\}]\cdot 4H_2O$.[20]

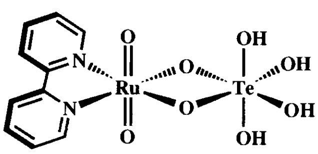

Fig. 2 Proposed structure of complex $[RuO_2(bipy)\{TeO_2(OH)_4\}]$

Experimental

The compounds $RuCl_3\cdot nH_2O$ and OsO_4 were obtained from Johnson Matthey Ltd. Other materials were obtained from Aldrich and used without further purification. The complex *cis*-$[RuCl_2(bipy)_2]$ was obtained by the method of Meyer and co-workers[31] and *trans*-$K_2[OsO_2(OH)_4]$ by Malin's procedure.[32] Other preparations of known complexes use the cited literature methods with minor adaptations.

(*a*) *Preparation of Ruthenium and Osmium Complexes.*—*cis*-$[Ru(CO_3)(bipy)_2]\cdot 4H_2O$.[33] The complex *cis*-$[RuCl_2(bipy)_2]$ (0.5 g, 0.97 mmol) was suspended in degassed water (40 cm^3) and refluxed under argon for 15 min. Anhydrous Na_2CO_3 (1.65 g, 15 mmol) was added and the mixture heated at reflux for a further 2 h. The burgundy red solution was filtered to yield a purple crystalline solid and washed with (3 × 15 cm^3) water. Yield 0.35 g, 0.7 mmol (72%) (Found: C, 46.3; H, 4.2; N, 10.2. Calc. for $C_{21}H_{24}N_4O_7Ru$: C, 46.2; H 4.4; N, 10.3%).

trans-$[Ru(H_2O)_2(bipy)_2][PF_6]_2\cdot H_2O$. This was prepared *via* a procedure modified from ref. 34. The complex *cis*-$[RuCl_2(bipy)_2]$ (0.6 g, 0.90 mmol) was heated to 60 °C in degassed water (10 cm^3) under nitrogen for 5 min. A saturated solution of NH_4PF_6 (4 cm^3) in 0.1 mol dm^{-3} perchloric acid was added dropwise. The reaction mixture was then cooled to 0 °C for 2 h and the resulting precipitate filtered off, washed with water and dried under vacuum. Yield, 0.27 g, 0.36 mmol (41%) (Found: C, 31.9; H, 3.1; N, 7.7. Calc. for $C_{20}H_{22}F_{12}N_4O_3P_2Ru$: C, 31.7, H, 2.9, N, 7.4%).

trans-$[Ru(OH)(H_2O)(bipy)_2][ClO_4]_2\cdot H_2O$.[35] The complex *cis*-$[Ru(CO_3)(bipy)_2]\cdot 4H_2O$ (0.05 g, 0.1 mmol) was dissolved in 0.1 mol dm^{-3} $HClO_4$ and exposed to light for 24 h. The solution was then filtered and the burgundy solid was collected by filtration. Yield 0.04 g, 0.05 mmol (50%) (Found: C, 36.6; H, 2.8; N, 7.7. Calc. for $C_{20}H_{21}Cl_2N_4O_{11}Ru$: C, 36.1; H 3.2; N 8.4%).

$[RuO(H_2O)(bipy)_2][ClO_4]_2\cdot H_2O$. This complex was prepared by two methods: (*a*) *trans*-$[RuO_2(bipy)_2][ClO_4]_2$ (0.065 g, 0.1 mmol) and cyclooctene (0.01 g, 0.1 mmol) were shaken in water for 15 h at 2 °C, after which time the UV/VIS spectrum was taken indicating the presence of the desired complex.

(*b*) The complex $[Ru(OH)(H_2O)(bipy)_2][ClO_4]_2$ (0.08 g, 0.14 mmol) was dissolved in water (10 cm^3) and 3 equivalents of cerium(IV) ammonium nitrate were added. The solution was stirred for 20 min at room temperature after which time the desired product had precipitated as a pale yellow solid. Yield 0.04 g, 0.05 mmol (36%) (Found: C, 36.2; H, 2.6; N, 8.8. Calc. for $C_{20}H_{20}Cl_2N_4O_{11}Ru$: C, 36.2; H, 3.0; N, 8.4%).

trans-$[RuO_2(bipy)_2][ClO_4]_2\cdot H_2O$.[36] To $[Ru(OH)(H_2O)(bipy)_2][ClO_4]_2$ (0.025 g, 0.03 mmol) was added cerium(IV) ammonium nitrate (0.1 g) in water (5 cm^3). The red solution immediately turned yellow whereupon a yellow precipitate was deposited and isolated by filtration. Yield 0.02 g, 0.02 mmol (66%) (Found C, 36.5; H, 2.1; N, 8.3. Calc. for $C_{20}H_{18}Cl_2N_4O_{11}Ru$: C, 36.3; H 2.7; N 8.5%).

$[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2][PF_6]_4\cdot H_2O$.[37] The complex *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ (1.1 g, 2.1 mmol) was dissolved in water (30 cm^3) and stirred at reflux for 5 min. Silver nitrate (0.92 g, 5.4 mmol) was added and the solution heated at reflux for a further 30 min. Silver chloride was deposited and was filtered off and the filtrate heated at reflux for an additional 30 min. A saturated solution of NH_4PF_6 (20 cm^3) was then added and the volume reduced to 30 cm^3. After refrigeration for 15 h, the deep blue-black microcrystalline solid was collected on a sintered funnel. Yield 0.8 g, 0.67 mmol (32%) (Found: C, 32.8; H, 2.2; N, 7.3. Calc. for $C_{40}H_{38}F_{24}N_8O_4P_4Ru_2$: C, 32.5; H, 2.6; N, 7.6%). λ_{max}/nm (CH_2Cl_2): 639 (ε 1968 dm^3 mol^{-1} cm^{-1}).

$[Ru(OH)(IO_3)(bipy)_2][PF_6]_2\cdot 0.5H_2O$. This complex can be prepared by two methods: (*a*) *trans*-$[Ru(H_2O)_2(bipy)_2][PF_6]_2\cdot H_2O$ (0.4 g, 0.4 mmol) was dissolved in water (20 cm^3) and 1 equivalent of $NaIO_4$ (0.084 g, 0.4 mmol) was added. After stirring for 10 min an excess of NH_4PF_6 (0.62 g, 4 mmol) was added and the mixture stirred for a further 20 min. The orange solution was allowed to stand for an hour after which time an orange-brown solid was deposited.

(*b*) The complex *cis*-$[Ru(CO_3)(bipy)_2]\cdot 4H_2O$ (0.3 g, 0.6 mmol) was dissolved in water (20 cm^3) and 1 equivalent of $IO(OH)_5$ (0.14 g, 0.6 mmol) was added. After stirring for 10 min an excess of NH_4PF_6 (0.62 g, 4 mmol) was added and stirred for a further 20 min. The orange solution was allowed to stand for an hour after which time an orange-brown solid was deposited (Found: C, 26.1; H, 1.4; I, 14.4; N, 5.9. Calc. for $C_{20}H_{18}F_{12}IN_4O_{4.5}P_2Ru$: C, 26.6; H, 2.0; I, 14.1; N, 6.2%). IR: 770s, 765s [$\nu_{asym}(IO)$] and 663vs cm^{-1} [$\nu_{sym}(IO)$].

$[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$.[9] Ruthenium tetraoxide was prepared in an aqueous periodate solution by the addition of $NaIO_4$ (1.89 g, 9 mmol) (in the minimum amount of water) to a suspension of RuO_2 (0.5 g, 4 mmol) in water (5 cm^3). This solution was then transferred to a solution of bipy (0.31 g, 2 mmol) in acetone–water (20 cm^3, 1:1). After stirring at room temperature for 5 min, an orange precipitate was deposited. Yield 1.26 g, 2.4 mmol (48%) (Found: C, 22.2; H, 2.0; N, 5.1. Calc. for $C_{10}H_{14}IN_2O_{9.5}Ru$: C, 22.1; H, 2.6; N, 5.2%). IR: 815vs [$\nu_{asym}(RuO_2)$], 729s, 686s [$\nu_{asym}(IO)$], 657vs, 571vs [$\nu_{sym}(IO)$] and 1072m cm^{-1} [$\delta(IOH)$]. Raman: 809 cm^{-1} [$\nu_{sym}(RuO_2)$].

$[RuO_2(bipy)\{TeO_2(OH)_4\}]$. Ruthenium tetraoxide was prepared in an aqueous periodate solution by the addition of $NaIO_4$ (1.89 g, 9 mmol) (in the minimum amount of water) to a suspension of RuO_2 (0.5 g, 4 mmol) in water (5 cm^3). This solution was then transferred to a solution of bipy (0.31 g, 2 mmol) in acetone–water (20 cm^3, 1:1) with $Te(OH)_6$ (1.7 g, 9 mmol). After stirring at room temperature for 5 min, a green precipitate was deposited. Yield 0.76 g, 1.4 mmol (29%) (Found: C, 22.8; H, 1.8; N, 5.3. Calc. for $C_{10}H_{12}N_2O_8RuTe$: C, 23.2; H, 2.3; N, 5.4%). IR: 821vs [$\nu_{asym}(RuO_2)$], 735s, 685s [$\nu_{asym}(TeO)$] and 1023m cm^{-1} [$\delta(TeOH)$]. Raman: 815 cm^{-1} [$\nu_{sym}(RuO_2)$].

$[OsO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$. The complex *trans*-$K_2[OsO_2(OH)_4]$ (0.16 g, 0.5 mmol) was dissolved in acetone–water (20 cm^3, 1:1) to which bipy (0.16 g, 1 mmol) was added. After stirring, $NaIO_4$ (0.24 g, 1.1 mmol) in the minimum amount of water was added and a pale brown solid was precipitated. The tellurato complex could not be isolated. Yield 0.12 g, 0.2 mmol (40%) (Found: C, 19.2, H, 1.8, N, 4.5. Calc. for $C_{10}H_{14}IN_2O_{9.5}Os$: C, 19.0; H, 2.2; N, 4.4%). IR: 833vs [$\nu_{asym}(OsO_2)$], 731s, 679s [$\nu_{asym}(IO)$], 654vs, 562vs [$\nu_{sym}(IO)$] and 1074m cm^{-1} [$\delta(IOH)$].

$[OsO_2(dpa)\{IO_3(OH)_3\}]$. The complex *trans*-$K_2[OsO_2(OH)_4]$ (0.16 g, 0.5 mmol) was dissolved in acetone–water (20 cm^3, 1:1) to which 2,2′-dipyridylamine (0.17 g, 1 mmol) was added. After stirring, $NaIO_4$ (0.24 g, 1.1 mmol) in the minimum amount of water was added and a green-brown solid was precipitated. Yield, 0.09 g, 0.14 mmol (28%) (Found: C, 19.9; H, 2.0; N, 6.6. Calc. for $C_{10}H_{12}IN_3O_8Os$: C, 19.4; H, 2.0; N, 6.8%). IR: 829vs [$\nu_{asym}(OsO_2)$], 724s, 671s [$\nu_{asym}(IO)$], 649vs, 549vs [$\nu_{sym}(IO)$] and 1068m cm^{-1} [$\delta(IOH)$].

$[OsO_2(phen)\{IO_3(OH)_3\}]$. The complex *trans*-$K_2[OsO_2(OH)_4]$ (0.16 g, 0.5 mmol) was dissolved in acetone–water (20 cm^3, 1:1) to which 1,10-phenanthroline (0.18 g, 1 mmol) was added. After stirring, $NaIO_4$ (0.24 g, 1.1 mmol) in the minimum amount of water was added and a green-brown solid was precipitated. Yield 0.18 g, 0.29 mmol (57%) (Found: C, 23.2; H, 2.2; N, 4.7. Calc. for $C_{12}H_{11}IN_2O_8Os$: C, 23.0; H 1.8; N, 4.5%). IR: 832vs [$\nu_{asym}(OsO_2)$], 730s, 679s [$\nu_{asym}(IO)$], 652vs, 559vs [$\nu_{sym}(IO)$] and 1068m cm^{-1} [$\delta(IOH)$].

(*b*) *General Procedures for Oxidations*.—(*i*) *Alkene epoxidations. Catalysed by* $RuCl_3$–bipy *with periodate*. The method of Balavoine *et al.*[10] was adapted for these. Ruthenium trichloride (0.004 g, 0.02 mmol) and 2,2-bipyridyl (0.125 g, 0.80 mmol) were stirred vigorously in water (20 cm^3) at 1.5 °C for 5 min. The alkene (2 mmol) was then added in dichloromethane (30 cm^3) with $NaIO_4$ (3.0 g, 14 mmol) and the colour changed from dark green to brown, the whole mixture then being stirred for 15 h at 1.5 °C. A solution of 1 mol dm^{-3} sodium hydroxide was then used to adjust the pH of the aqueous layer to 12 and the organic layer was separated. The aqueous layer was then extracted with dichloromethane (4 × 20 cm^3); the extracts combined and dried over anhydrous $MgSO_4$. The solvent was removed and the residues analysed by GC to identify the products and to calculate yields. The catalytic turnovers were determined from the moles of product formed compared to moles of $RuCl_3$ used.

Catalysed by other complexes. The ruthenium complex (0.02 mmol) was stirred vigorously in water (20 cm^3) at 1.5 °C for 5 min. The alkene (2 mmol) was then added in dichloromethane (30 cm^3) with $NaIO_4$ (3.0 g, 14 mmol) the whole mixture then being stirred for 15 h at 1.5 °C. A solution of 1 mol dm^{-3} sodium hydroxide was then used to adjust the pH of the aqueous layer to 12 and the organic layer was separated. The aqueous layer was then extracted with dichloromethane (4 × 20 cm^3); the extracts combined and dried over anhydrous $MgSO_4$. The solvent was removed and the residues analysed by GC to identify the products and to calculate yields. The catalytic turnovers were determined from the moles of product formed compared to moles of catalyst used.

Catalysed by $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$.[9] The complex $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$ (0.01 g, 0.02 mmol) was stirred vigorously in water (20 cm^3) at 1.5 °C for 5 min. The alkene (5 mmol) was then added in dichloromethane (30 cm^3) with $NaIO_4$ (3.0 g, 14 mmol) the whole mixture then being stirred for 15 h at 1.5 °C. A solution of 1 mol dm^{-3} sodium hydroxide was then used to adjust the pH of the aqueous layer to 12 and the organic layer was separated. The aqueous layer was then extracted with dichloromethane (4 × 20 cm^3); the extracts combined and dried over anhydrous $MgSO_4$. The solvent was removed and the residues analysed by GC to identify the products and to calculate yields. The catalytic turnovers were determined from the moles of product formed compared to moles of $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$ used.

(*ii*) *Oxidation of alkanes. Catalysed by trans*-$[Ru(H_2O)_2(bipy)_2][PF_6]_2\cdot H_2O$. The complex *trans*-$[Ru(H_2O)_2(bipy)_2][PF_6]_2\cdot H_2O$ (0.03 g, 0.05 mmol) was dissolved in Bu^tOOH (10 cm^3 of a 20% aqueous solution) and benzene (10 cm^3) with substrate (10 mmol). The mixture was stirred at room temperature for 5 h after which time the solutions were filtered through a pad of silica to remove the ruthenium catalyst. The yields were determined by GC and the catalytic turnovers for the primary oxidation products were determined from the moles of product formed compared to moles of *trans*-$[Ru(H_2O)_2(bipy)_2][PF_6]_2$ used.

Catalysed by $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$. The complex $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$ (0.02 g, 0.04 mmol) was dissolved in a biphasic CH_2Cl_2–water system with sodium periodate (1.6 g, 7.5 mmol) as co-oxidant and substrate (5 mmol). The mixture was stirred for 15 h at reflux after which time the solutions were cooled and the CH_2Cl_2 layer separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 25 cm^3) and the extracts combined. The solvent was then removed *in vacuo* and the residue analysed by GC. The catalytic turnovers for the primary oxidation products were determined from the moles of product formed compared to moles of $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$ used.

(*iii*) *Oxidation of alcohols. Catalysed by trans*-$[Ru(H_2O)_2(bipy)_2][PF_6]_2\cdot H_2O$. The complex *trans*-$[Ru(H_2O)_2(bipy)_2][PF_6]_2\cdot H_2O$ (0.015 g, 0.02 mmol) was added in one portion to a stirred mixture of the alcohol (5 mmol), *N*-methylmorpholine-*N*-oxide (0.9 g, 7.5 mmol) or $[NBu_4]IO_4$ (3.25 g, 7.5 mmol) and powdered molecular sieves (2.5 g) in dichloromethane (20 cm^3). After 3 h stirring at room temperature the mixture was filtered through a pad of silica eluting with dichloromethane. The filtrate was removed *in vacuo* and the residue analysed by preparation of the dinitrophenylhydrazine derivatives when nmo was co-oxidant and by GC when $[NBu_4]IO_4$ was used as co-oxidant. The catalytic turnovers were determined from the moles of product formed compared to moles of *trans*-$[Ru(H_2O)_2(bipy)_2][PF_6]_2$ used.

Catalysed by $[RuO_2(bipy)\{TeO_2(OH)_4\}]$. The complex $[RuO_2(bipy)\{TeO_2(OH)_4\}]$ (0.01 g, 0.02 mmol) was added in one portion to a stirred mixture of the alcohol (5 mmol), $[NBu_4]IO_4$ (3.25 g, 7.5 mmol) and powdered molecular sieves (2.5 g) in dichloromethane (20 cm^3). After 3 h stirring at room temperature the mixture was filtered through a pad of silica and eluted with dichloromethane. The filtrate was removed *in vacuo* by GC. The catalytic turnovers were determined from the moles of product formed compared to moles of $[RuO_2(bipy)\{TeO_2(OH)_4\}]$ used.

Instrumentation.—Infrared spectra were measured as KBr discs on a Perkin-Elmer 1720 FT instrument. Raman spectra were recorded on as spinning discs on a KBr matrix on a Spex Ramalog 5 instrument, with a Datamate data acquisition unit using excitation at 647.1 nm from a Coherent Radiation Innova 90 Krypton-ion laser, and as powders on a Perkin-Elmer 1760 X FT-IR instrument fitted with a 1700 X NIR FT-Raman accessory (Spectron Nd:YAG laser, 1064 nm excitation). Proton NMR spectra were measured on a JEOL EX-270 spectrometer (^1H, 270.05 MHz). The GC data were obtained on a Perkin-Elmer Autosystem instrument using a Perkin-Elmer stainless-steel column (2 m) packed with 5% Carbowax 20M on Chromasorb WHP AW (DCMS treated). Microanalyses were carried out by the Microanalytical Laboratories at Imperial College.

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