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Ruthenium(II) and (III) bipyridine complexes and their catalytic oxidation properties for organic compounds

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Abstract—The new complexes $[Ru^{II}(bpy)_2L](PF_6)$ and $[Ru^{III}(bpy)_2Cl_2]X$ (bpy = 2,2′-bipyridine; HL = acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, dibenzolymethane or tropolone; X = IO_4 and PF_6) have been prepared and characterized by spectroscopic measurements and also investigated by cyclic voltammetry. They effectively catalyze the oxidation of alcohols, 3,5-di-*t*-butycatechol and alkane in the presence of *t*-butyl hydroperoxide or *N*-methylmorpholine-*N*-oxide as co-oxidants. © 1997 Elsevier Science Ltd

Keywords: ruthenium complexes; bipyridine complexes; catalytic oxidation.

Although ruthenium tetroxide is known as a vigorous and non-selective oxidant, it catalytically oxidizes aromatic rings in the presence of $NaIO_4$ with poor yield and after reaction for several days at 60°C [1]. A highly effective catalytic system generated *in situ* by reaction of *cis*-$\{Ru(bpy)_2Cl_2]$ with $NaIO_4$ in CH_2Cl_2—H_2O solution at room temperature mimics RuO_4 in chemoselective degradation of a variety of phenyl and fused hydroaromatic substrates to their corresponding monocarboxylic and dicarboxylic acids [2,3]. In the present study we report the preparation and characterization of the useful catalyst formed from $[Ru(bpy)_2Cl_2]$ and $NaIO_4$ and also the new complexes $[Ru^{II}(bpy)_2L](PF_6)$ [L = monoanions of acetylacetone (acac); trifluoroacetylacetone (tfacac); hexafluoroacetylacetone(hfacac); dibenzoylmethane(dbm) and tropolone(trop), 2-hydroxy-2,4,6-cycloheptatrienone]. Only analytical and spectral data have been mentioned for $[Ru^{II}(bpy)_2acac]Cl \cdot 3H_2O$ [4]. Redox properties of the present complexes are also reported in comparison with that very recently [5] published for $[Ru^{II}(bpy)_2L'](ClO_4)$ (L′ = salicylaldiminate or 2-(arylazo)phenolate anion). The use of these complexes as catalytic oxidants for alcohols, catechol and alkanes in the presence of *t*-butyl hydroperoxide (*t*-BuOOH) or *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidants is described in this paper.

RESULTS AND DISCUSSION

Reaction of *cis*-$[Ru(bpy)_2Cl_2]$ (**A**) with the O,O-donor ligands (HL) in aqueous solution and reflux for 0.5 h afforded good yields (60–90%) of the desired complexes isolated as hexafluorophosphate salts, $[Ru(bpy)_2L](PF_6)$ (**I–V**). There is no need for the use of Ag^+ to displace the chloride ligands of the complex **A** during preparation of $[Ru^{II}(bpy)_2L'](ClO_4)$ [HL′ = O,N-donor ligand(−1)] [5,6]. Attempts to oxidize the complexes **I–V** by Ce^{VI}, $NaIO_4$ or $Na_2S_2O_8$ in order to get similar related complexes to those reported [5] for $[Ru^{III}(bpy)_2L']^{2+}$ were unsuccessful. However, oxidations of the complex **A** by aqueous $NaIO_4$ or $Na_2S_2O_8$ in the presence of NH_4PF_6 gave the complexes $[Ru(bpy)_2Cl_2](IO_4)$ (**VI**) and $[Ru(bpy)_2Cl_2](PF_6)$ (**VII**), respectively. Analytical data of the complexes (Table 1) are in a good agreement with their compositions. The complexes are soluble in dichloromethane, DMSO and CH_3CN and their molar conductivities in the latter solvent show that they behave as 1 : 1 electrolytes as expected (Table 1). The complexes **I–V** were found to be diamagnetic at room temperature; the other complexes **VI** and **VII** are paramagnetic and have magnetic moments (μ_{eff})

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Table 1. Analytical, IR and thermal gravimetric data for the complexes

Compound	Colour	Analysis Found (Calc.), % C	H	N	Λ_M (Ω^{-1} cm^2 M^{-1})	IR data, wavenumbers (cm) ($C\cdots O$)	$\nu(C\cdots C)$	$\nu(PF_6)$	Other bands	Assignments	Thermal gravimetric data Decomposition temp.range, °C	Weight loss due to O,O-donor ligand (−1) Found (Calc.), %
I [Ru(bpy)$_2$acac](PF$_6$)	Dark brown	45.5	3.5	8.4	135	1565s	1266m	839vs	1400s		325–395	15.0 (15.1)
		(45.2)	(3.4)	(8.4)				558s				
II (Ru(bpy)$_2$tfacac](PF$_6$)	Reddish brown	42.0	2.7	7.8	118	1591s	1298vs	843vs	1365w		310–370	20.5 (21.5)
		(42.2)	(2.8)	(7.9)			1267m	558s				
III [Ru(bpy)$_2$hfacac](PF$_6$)	Reddish brown	39.1	2.2	7.2	132	1577m	1264vs	841vs	1464s		280–370	31.4 (27.1)
		(39.2)	(2.2)	(7.3)				558s	1336m			
IV [Ru(bpy)$_2$dbm](PF$_6$)	Reddish brown	53.5	3.4	7.1	142	1522vs	1264m	840vs	1404s		310–450	27.0 (28.6)
		(53.8)	(3.5)	(7.2)				558m				
V [Ru(bpy)$_2$trop](PF$_6$)	Reddish brown	47.6	3.0	8.1	120			835vs	1505s	$\nu(C{=}O)$	340–380	15.5 (17.8)
		(47.7)	(3.1)	(8.2)				558s	1352s	$\nu(C{-}O)$		
VI [Ru(bpy)$_2$Cl$_2$](IO$_4$)·H$_2$O	Reddish orange	34.4	2.4	8.0[a]	105				850s	$\nu^{as}(IO_4)$	200–210	
		(34.6)	(2.6)	(8.1)					340s 312s	$\nu(Ru{-}Cl)$		
VII [Ru(bpy)$_2$Cl$_2$](PF$_6$)	Reddish orange	38.0	2.4	8.8	110			836vs	342s			
		(38.2)	(2.5)	(8.9)					321m	$\nu(Ru{-}Cl)$		

[a] Cl%, 10.3 (10.2); I%, 18.0 (18.3).

of 1.92 and 1.89 BM, respectively, close the spin only value (1.73 BM) for one unpaired electron. This suggests the low-spin d^5 $(t_{2g})^5$ configuration for the ruthenium(III) ion in an octahedral environment, as is the case for other ruthenium(III) and osmium(III) complexes [7,8].

The thermal stabilities of the complexes have been investigated. The complexes **I**–**V** are stable till 280–340°C after which this range their weight loss seems corresponding to the coordinated O,O-donor ligand (L), (Table 1). The complex **VI** shows a weight loss (2.5%) at 70°C corresponding to that of a hydrated water molecule and becomes stable till 200°C after which a sharp decomposition occurs (200–210°C) equivalent to the sum of IO_4 and bpy molecules. A gradual unidentified decomposition for the compound **VII** was found in the range 220–370°C.

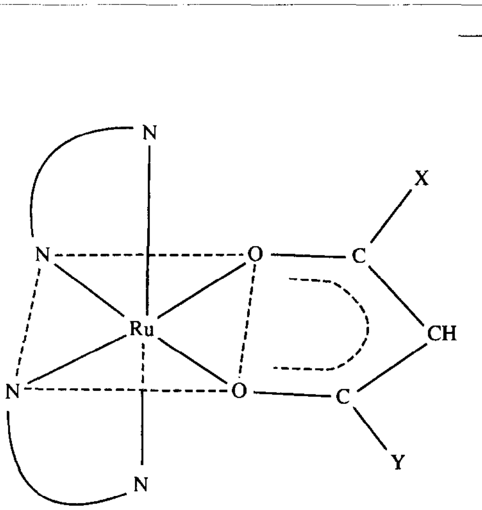
Spectroscopic properties

The IR spectral data (Table 1) are consistent with the structures of complexes and indicate that the ligand (HL) is coordinated in the normal manner through O,O-donor sites [9–12] and the *cis*-geometry of the dichloro ligands is shown [13].

The UV-Vis spectra (Table 2) of the complexes **I**–**V** showed metal-to-ligand charge transfer transitions as similarly observed for $[Ru^{II}(bpy)_2L']^+$ [HL′ = O,N-Schiff base ligand (−1)] [5]. The complexes **VI** and **VII** showed bands similar to those found for *cis*-$[Ru^{III}(bpy)_2Cl]^+$ [14,15].

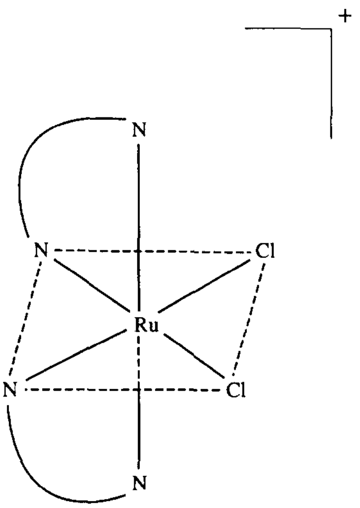
The ^1H NMR data for the complexes **I**, **II** and **V** (Table 2) are in accordance with the proposed structures illustrated below (e.g. **I** and **II**); the non-isomeric nature of these complexes is found in contrast to those observed for $[M^{II}(PPh_3)_2tfacac]$ (M = Ru or Os) [16].

The ESR spectra of the solid sample of $[Ru(bpy)_2Cl_2]IO_4$ (**VI**) at room temperature showed a spectrum similar to that reported for $[Ru^{III}Cl_2(PPh_3)_2L']$ [HL′ = O,O-donor ligand(−1)] [17,18] and $[RuCl_3(PPh_3)_2MeOH]$ [19] where only two g values were obtained ($g_\parallel = 2.36$; $g_\perp = 1.63$). The spectrum is typical for large axial distortion of an elongated octahedral ruthenium(III) ion environment; and consequently we suggest the structure of the cation of **VI** also below.



I : X = Y = CH_3
II : X = CH_3, Y = CF_3

(N—N = 2,2′-bipyridine)



VI

Redox properties

The electron-transfer properties of the complexes have been studied in dichloromethane solution by cyclic voltammetric techniques (Table 2 and Fig. 1(a) as a representative example). The voltammograms of the complexes **I**–**V** show one metal centred oxidation and two ligand (bpy)-based reductions at positive and negative potentials, respectively. At positive potentials the reversible oxidation wave is shown; $E_{1/2} = +0.12$–$+0.90$ V and $\Delta E = 60$–80 mV which is close to that anticipated for a Nerstian one-electron process ($\Delta E = 59$ mV) [20]. This wave corresponds to Ru^{II}/Ru^{III} oxidation similar to those found for $[Ru^{II}(bpy)_2L'](ClO_4)$ [5], $[Ru^{II}(PPh_3)_2L'_2]$ [21] and $[Ru^{II}Cl_2(PPh_3)_2L']$ [22] (L′ = O,N-neutral [22] or monoanion [5,21] donor ligand). There is a considerable negative shift for Ru^{II}/Ru^{III} oxidation potential compared to that for $[Ru^{II}(bpy)_3]^{2+}$ ($E_{1/2} = 1.30$ V) [23] which shows ability of O,O-donor ligands to stabilize the higher oxidation states of ruthenium. This

Table 2. ^{1}H NMR, UV-visible and cyclic voltammetric data of complexes

			Voltammetric data (V) Oxidations			Reductions	
Compound	^{1}H NMR data, δ ppm[a]	UV-vis data, λ_{max}, nm[b] (ε, M^{-1} cm^{-1})	$E_{1/2}$	ΔE	E_{p_c}	E_{p_a}	ΔE
I	1.85 (s, 2Me), 5.45(s, γ—CH)	570sh(12,000), 522(10,400),	+0.47	0.060	−1.68	—	
	7.30(t, 2H), 7.90(m, 6H)	370(13,100), 297(63,200),			−1.76	−1.70	0.060
	8.25(t, 2H), 8.80(m, 6H)	249(35,900)					
II	2.05(s, Me), 5.95(s, γ—CH),	550sh(10,000), 494(10,500),	+0.65	0.060	−1.74	−1.62	0.120
	7.40(t, 2H), 7.90(m, 6H)	365(11,500), 294(58,200),			−1.80	−1.74	0.060
	8.35(t, 2H), 8.80(m, 6H)	246(38,900)					
III		774(235), 471(17,300), 344(9,900)	+0.90	0.060	−1.60	−1.48	0.120
		290(80,800), 245(30,700)			−1.76	−1.70	0.060
IV		508(18,700), 333(41,200),	+0.26	0.070	−1.94		
		296(112,600), 248(59,400)			−2.00	−1.94	0.060
V	7.15(d, 2H), 7.35(t, 3H)	529(19,700), 390(24,200)	+0.12	0.080	−1.98	–	
	6.85(t, 2H), 7.90(m, 6H)	298(94,100), 242(66,000)			−2.06	−1.98	0.080
	8.25(t, 2H), 8.85(m, 6H)						
VI		670sh(250), 550sh(420), 450sh			−0.07	−0.01	0.060
		(1,400), 380(4,870), 300(20,300)			−1.80		
VII		680sh(300), 553(850), 450sh			−0.24	−0.18	0.060
		(2,000), 380(6,490), 300(36,300),			−2.15		
		250(15,000)					

[a] In $(CD_3)_2SO$.

[b] In dichloromethane.

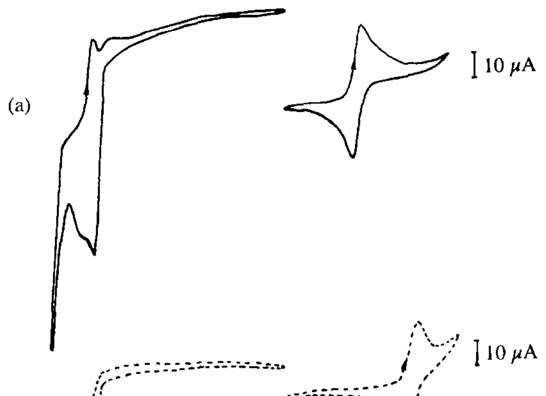


Fig. 1. Cyclic voltammogram with 0.1 M $(Bu^n_4)PF_6$ as supporting electrolyte; V *vs* Ag electrode; scan rate; 50 mV s^{-1}; (a) —, $[Ru(bpy)_2tfacac](PF_6)$, (10^{-3} M) in dichloroethane; (b) - - -, $[RuO(H_2O)(bpy)_2](PF_6)_2$, ($10^{-3}$ M) in CH_3CN.

oxidation potential, $E_{1/2}$ for Ru^{II}/Ru^{III} couple is found to be sensitive to the nature of the substituent in the O,O-donor ligand. It is shifted to lower or higher values (Table 2) relative to $[Ru(bpy)_2acac](PF_6)$, reflecting an increase of basicity with lower $E_{1/2}$ values at the O,O-donor ligand (L) change in the order;

hfacac < tfacac < acac < dbm < trop

The stabilities of Ru^{II} and Ru^{III} oxidation states in these complexes is reflected by the reversibility of these processes

$$[Ru^{II}(bpy)_2L]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} [Ru^{III}(bpy)_2L]^{2+}$$

At the negative potentials two successive one-electron reductions are observed. The first reduction is a quasi-reversible (ΔE = 120 mV) or irreversible while the other at more negative potential is reversible. These are assigned to the reductions of the two bpy ligands [6] as shown in equations (1) and (2),

$$[Ru^{II}(bpy)_2L]^+ \quad + e \rightleftharpoons [Ru^{II}(bpy)(bpy)L] \qquad (1)$$

$$[Ru^{II}(bpy)(bpy)L] \quad + e \rightleftharpoons [Ru^{II}(bpy)_2L]^- \qquad (2)$$

The complexes $[Ru(bpy)_2Cl_2]X$ ($X = PF_6$, IO_4), **VI** and **VII** each show a reversible wave at negative potential which presumably arises from Ru^{III}/Ru^{II} reduction, similar to that found for $[MCl_2(EPh_3)_2L']$ [M = Ru, Os; E = P, As; L′ = O, O(N)-donor ligand(−1)] [11,17,22] and [Ru^{III}(salen)(PPh$_3$)(py)]ClO$_4$) [24]. An irreversible cathodic peak is only observed at −1.80 and −2.15 V for **VI** and **VII**, respectively indicating a reduction of one bpy molecule in these complexes.

For scan rates (SR) between 10–50 mV s^{-1}, the ratio $i_p/(SR)^{1/2}$ (i_p = peak current) was constant and the ratio of anodic to cathodic peak current is one, the peak separation being independent of the scan rate. This indicates that the electron transfer is reversible or approaches reversibility and the mass transfer is limited.

Catalytic oxidations

We have found that ruthenium(II) [21,22] and ruthenium(III) [7] complexes of triphenylphosphine (arsine) act as good catalysts in the presence of *N*-methylmorpholine-*N*-oxide (NMO) for selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. In our continuing work to find new efficient ruthenium catalysts, we have used the bipyridine complexes, **I** and **VII** for such catalytic oxidations in the presence of *t*-butyl hydroperoxide (*t*-BuOOH) as a cheaper and easy to handle co-oxidant, we have also studied oxidations for 3,5-di-*t*-butylcatechol (DTBCat) and alkane with reference to [Ru^{II}Cl$_2$(PPh$_3$)$_3$]/*t*-BuOOH system which has been reported for oxidation of these substrates [25,26]. In Table 3, we summarize the results for catalytic oxidations by [Ru^{II}(bpy)$_2$acac](PF$_6$) (**I**) and [Ru^{III}(bpy)$_2$Cl$_2$](PF$_6$) (**VII**) as typical examples. The oxidations were carried out at room temperature in dichloromethane when using *t*-BuOOH (3M) in dry benzene. Table 3 shows that both the complexes **I** and **VII** are good catalysts for oxidations of alcohols into the corresponding aldehydes or ketones and DTBCat into the corresponding *o*-benzoquinone (BQ). Similar yields and turnovers (near 100) are obtained corresponding to those reported by [RuCl$_2$(PPh$_3$)$_3$] [25]. Table 3 shows also that oxidations in dichloroethane are better than those in CH$_3$CN, as similarly observed for other catalysts [27,28]. Unsaturated alcohols, e.g. cinnamyl alcohol, is effectively oxidized without competing double bond attack. Alkylated arenes such as ethylbenzene and fluorene are effectively converted into acetophenone and fluorenone, respectively as similarly found with [RuCl$_2$(PPh$_3$)$_3$] [26]. In the presence of NMO as co-oxidant instead of *t*-BuOOH, low yields and turnovers are obtained for oxidations for alcohols (Table 3) while there is no oxidation product at all for alkane.

Reaction of a 1 : 10 mixture of [Ru(bpy)$_2$acac](PF$_6$) (**I**) and *t*-BuOOH (70% in aqueous solution) under the same oxidation conditions above gave greenish solution with a low yield of a yellow precipitate which could be isolated after evaporation under reduced pressure. This product is possibly the active species of the catalyst **I**, its analytical and IR data correspond to the formulae [RuO(H$_2$O)(bpy)$_2$](PF$_6$)$_2$ (**VIII**)

Table 3. Catalytic oxidations by ruthenium complexes

			t-BuOOH as co-oxidant[b]			NMO as co-oxidant		
Substrate	Catalyst	Product[a]	Time (h)	Yield (%)	Turnover[c]	Time (h)	Yield (%)	Turnover[c]
4-Methoxy α-hydroxy toluene	**I**	A	3	83	91	3	9	10
			3	27	30			
	VII	A	3	86	94	3	25	28
			3	60	66			
3,4-Methylenedioxyphenylmethanol	**I**	A	3	74	81	3	0	0
	VII	A	3	36	40	4	89	98
			3	3	4			
3-Phenyl-2-propen-2-ol	**I**	A	3	87	96	3	9	10
	VII	A	3	88	97	3	18	20
α-Hydroxy toluene	**I**	A	3	72	79			
	VII	A	3	63	69			
Diphenylmethanol	**I**	K	2.5	36	40			
	VII	K	2.5	68	74			
Cyclohexanol	**I**	K	2.5	27	30			
	VII	K	2.5	36	40			
3,5-Di-*t*-butyl catechol[d]	**I**	BQ	3.5	85	93			
	VII	BQ	3.5	63	69			
Ethylbenzene[d]	**I**	K	8	68	42			
	VII	K	8	58	35			
Fluorene[d]	**I**	K	4	64	70			
	VII	K	4	80	88			

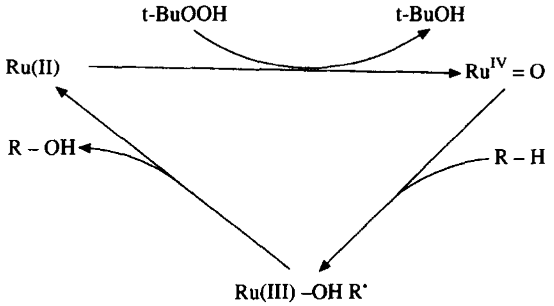
[a] A = corresponding aldehyde, K = corresponding ketone, BQ = corresponding *o*-benzoquinone.

[b] Underlined data for oxidations in CH$_3$CN.

[c] Turnover = moles of product/moles of catalyst.

[d] Product yield determined by GLC.

although $\nu(Ru{=}O)$ vibrations may be obscured by the strong broad band around 838 cm^{-1} arising from $\nu(PF_6)$ mode. The cyclic voltammetric measurements for **VIII** (Fig. 1(b)) showed a reversible wave, $E_{1/2} = 1.11$ V ($\Delta E = 60$ mV). This is presumably attributed to Ru^{IV}/Ru^{III} reduction since the complexes $[Ru^{III}(bpy)_2L']^{2+}$ [L′ = O,N-donor ligand(−1)] have an irreversible Ru^{III}/Ru^{IV} oxidation near 1.5 V [5]. Stepwise addition of H_2O_2 to $[Ru^{II}(dmp)_2(S)_2](PF_6)_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline; S = CH_3CN or H_2O) forms $[Ru^{IV}(O)(dpm)_2(S)](PF_6)_2$ and $[Ru^{VI}(O)_2(dmp)_2]$ $(PF_6)_2$ [29]. Thus the mechanism of alkane oxidation by the catalyst **I** in the presence of excess *t*-BuOOH is similar to that reported for $[RuCl_2(PPh_3)_3]$ [26,30] in which the oxoruthenium(IV) species formed is capable to abstract hydrogen atom alkane to give a radical pair, as shown below. We also assume that the catalytic oxidations of alcohols and catechol using *t*-BuOOH or NMO proceed *via* the formation of higher oxidation states of ruthenium species.



EXPERIMENTAL

Preparation of complexes

Preparation of $[Ru(bpy)_2acac](PF_6)$ (**I**). A modified method to that reported for preparation of $[Ru(bpy)_2acac]Cl \cdot 3H_2O$ [4] was used as follows. The complex *cis*-$[Ru(bpy)_2Cl_2] \cdot 2H_2O$ [31] (**A**) (0.5 mmol) was dissolved in water (30 cm^3) after stirring and heating at 75°C on a water bath for 0.5 h. Acetylacetone (0.5 cm^3) was added and heating continued for 1 h to give a reddish brown solution. The product was precipitated by addition of $(NH_4)PF_6$ (2.5 mmol), filtered and washed with water, diethyl ether and then dried *in vacuo*. A similar procedure was used to prepare the other ruthenium(II) complexes $[Ru(bpy)_2L](PF_6)$ **II**–**V** in which 1 : 2 molar ratio of the complex **A** to the ligand, HL was considered.

Preparation of $[Ru(bpy)_2Cl_2](IO_4) \cdot H_2O$ (**VI**). The complex **A** (0.52 g, 1 mmol) in CH_2Cl_2 (10 cm^3) was added to an aqueous solution (10 cm^3) of $NaIO_4$ (1.1 g, 5 mmol). The mixture was stirred vigorously for 1 h, after which time the purple colour was changed into a reddish brown precipitate. The product was filtered off, washed with water and then ether and dried *in vacuo*.

It should be noted that dissolution of the complex **A** in DMF (4 cm^3) followed by addition of the aqueous $NaIO_4$ and stirring for only 15 min, also gave the same complex **VI**.

Preparation of $[Ru(bpy)_2Cl_2](PF_6)$ (**VII**). To the complex **A** (0.26 g, 0.5 mmol) in DMF (3 cm^3) was added $Na_2S_2O_8$ (0.96 g, 4 mmol) in H_2O (10 cm^3) and NH_4PF_6 (0.32 g, 2 mmol). The mixture was stirred for 1 h during which a reddish orange precipitate formed. This was filtered off, washed with H_2O (3 × 5 cm^3) and then diethyl ether.

However, when the ruthenium(III) complex **VII** has been reacted with the O,O-donor ligands, e.g. acetylacetone after reflux of the aqueous solution, good microcrystals of the ruthenium(II) complex **I** were formed.

Catalytic oxidation by complexes

The oxidation of alkane by $[Ru(bpy)_2acac](PF_6)$ (**I**)/*t*-BuOOH is typical. The complex **I** (10^{-2} mmol) was dissolved in CH_2Cl_2 (20 cm^3) and fluorene or ethylbenzene (1 mmol) added. To the mixture was added *t*-BuOOH in dry benzene (4.8 mmol) and the solution stirred for 4–8 h, after which the purple colour changed into a yellowish solution. This was evaporated to dryness and extracted with Et_2O (3 × 20 cm^3) and the extracts combined. The solvent was then removed *in vacuo* and the residue analysed by GC. The same experiments were carried out for oxidation of other substrates using *t*-BuOOH with 2.4 and 1.2-equivalents of the alcohol and catechol, respectively, instead of 4.8 equivalents of alkane.

Similar experiments are used with NMO as co-oxidant in which 3 equivalents of it is added to the reaction mixture. The oxidation products are characterized and quantified as its dinitrophenylhydrazone derivative or by GC techniques.

IR spectra were measured on a Perkin-Elmer 883 spectrometer as paraffin mulls between CsI plates and KBr discs. ^1H NMR spectra were measured on a Brucker AT-FT 100 instrument (100 MHz). The electronic spectra were measured on a Lambda 2S UV/Vis spectrometer. Cyclic voltammetric studies were carried out on a potentiostat/wave generator (Oxford Electrodes) using a platinum working electrode in conjunction with a Philips PM 8043 X-Y recorder. Magnetic measurements were made on a Johnson Matthey magnetic susceptibility balance. The GC data were obtained on a HP 5890 Series II gas chromatograph equipped with FID using a 30 m SE-30 capillary column (0.25 mm i.d.). The thermal stability of the complexes was investigated using Perkin-Elmer TGA 7 unit (heating rate: 10°C min^{-1}).

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