

RUTHENIUM(II), RUTHENIUM(III) AND OSMIUM(III) COMPLEXES WITH N,N-NEUTRAL DONOR LIGANDS, AND THEIR CATALYTIC OXIDATIVE PROPERTIES

By

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مترابكات الروثينيوم الثنائي والثلاثي والأوزميوم الثلاثي مع المرتبكات المعطية المتعادلة للنتروجين - نتروجين وخواصها في الأكسدة الحفزية

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تم تحضير عدد من المترابكات الجديدة للروثينيوم الثنائي والثلاثي وكذلك الأوزميوم الثلاثي مع مرتبكات ثنائية المخلب متعادلة الشحنة من نوع النتروجين - نتروجين . وقد تم التعرف على تلك المترابكات بالطرق الطيفية المختلفة ودرست بجهاز الفولتامتر الدائري . ووجد أن مترابكات الروثينيوم الثلاثي أكثر كفاءة كعوامل مؤكسدة حفازه للكحولات الأولية والثانوية التي تتأكسد إلى الدهيدات و كيتونات .

Key Words: Ruthenium complexes, Osmium complexes, Catalytic oxidation

ABSTRACT

A number of new complexes $[Ru^{II}Cl_2(PPh_3)_2L]$, $[Ru^{III}X_3(AsPh_3)L]$ and $[Os^{III}Cl_3(PPh_3)L']$ [$L = o$ -anthranilonitrile(anth), o -phenylenediamine(phdm), 1,10-phenanthroline(phen), 2,2'-bipyridine(bipy); $L' = Phen$, bipy; $X = Cl, Br$] have been prepared. They were characterized by spectroscopic techniques and investigated by cyclic voltammetry. The ruthenium(III) complexes were found to be more efficient catalytic oxidants than those of ruthenium(II), while osmium(III) complexes showed a weak catalytic activity. In the presence of N-methylmorpholine-N-oxide as a co-oxidant, the ruthenium catalysts oxidised primary alcohols to aldehydes and secondary alcohols to ketones.

INTRODUCTION

Reflux of the complex $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(PPh_3)_4]$ in CS_2 gives the dimeric species $[RuCl_2(Ph)_2(PPh_3)_2]_2$, which in turn tends to react with 2,2'-bipyridine (bipy) or 1,10-phenanthroline(phen) in methanol or benzene solution and forms dark brown complexes of the respective formulae $[RuCl_2(PPh_3)_2(phen)]$ and $[Ru_2Cl_2(PPh_3)_4(bipy)_2]Cl_2$ [1]. The former complex and those of $[Ru_2Cl_2(PPh_3)_4L_2]Cl_4$ ($L = phen, bipy$)[2] have also been prepared from $[RuCl_2(PPh_3)_3]$ and the phen (or bipy) ligand in MeOH[1] and CH_2Cl_2 [2] solutions, respectively. On refluxing aliphatic nitriles (RCN) with $[RuCl_2(PPh_3)_3]$ in acetone and toluene solutions, *cis*- and *trans*-isomers of dinitrile complexes $[RuCl_2(RCN)_2(PPh_3)_2]$ have been isolated[3]

Ruthenium(III) complexes $[RuX_3(AsPh_3)L]$ ($L = phen, bipy$; $X = Cl, Br$) have been obtained[2] but not fully characterized and no work has so far been reported on similar complexes of osmium (III).

This work reports the preparation and characterization of the complexes $[Ru^{II}Cl_2(PPh_3)_2L]$, $[Ru^{III}X_3(AsPh_3)L]$ and $[Os^{III}Cl_3(PPh_3)L']$ [$L = o$ -anthranilonitrile(anth), o -phenylenediamine(Phdm), phen and bipy; $L' = phen, bipy$; $X = Cl, Br$]. The electrochemical behaviour and catalytic oxidation of alcohols by such complexes in the presence of N-methylmorpholine-N-oxide(NMO) also are reported, with reference to $[Ru^{II}Cl_2(PPh_3)_2L]$ ($L = PPh_3, O, N$ -neutral donor ligand)[4,5] and $[M^{III}Cl_2(PPh_3)_2L]$ [$M = Ru, Os, L = O, O(N)$ -donor ligand (-1)[4, 6-8].

EXPERIMENTAL

Preparation of Complexes

1. $[\text{RuCl}_2(\text{PPh}_3)_2(\text{anth})]$

The complex $[\text{RuCl}_2(\text{PPh}_3)_3]$, **A** [9] (0.25 mmol) was added to a degassed, methanolic solution (20 ml) containing *o*-anthranilo nitrile (anth) (0.37 mmol). The mixture was refluxed on water bath for 1.5 h under N_2 during which the dark crystals of **A** were dissolved and the solution becomes yellow with the isolation of yellow precipitate. The product was filtered off, washed with degassed methanol, ether and dried in vacuo. The yellow compound changes into green on exposure to air for several hours.

Similar procedures were used to prepare the other ruthenium(II) complexes, **2-4**.

$\text{RuCl}_3(\text{AsPh}_3)(\text{anth})$, **5a**. Modification of the literature procedures [2] for $[\text{RuX}_3(\text{AsPh}_3)\text{L}]$ ($\text{X} = \text{Cl}, \text{Br}$, $\text{L} = \text{phen}, \text{bipy}$) synthesis was used. The complex $[\text{RuCl}_3(\text{AsPh}_3)_2\text{MeOH}]$, **B** (0.25 mmol) was dissolved in a degassed CH_2Cl_2 (20 ml) solution containing the ligand, anth. (0.32 mmol). The mixture was stirred for 0.5 hours under N_2 atmosphere where a green solution was obtained, concentrated to its half volume by N_2 bubbling through. Addition of *n*-hexane (20 ml) with continuous stirring gave a green precipitate which was filtered off, washed with degassed methanol, ether and dried in vacuo.

The analogous bromo complex **5b** was similarly prepared from $[\text{RuBr}_3(\text{AsPh}_3)_2\text{MeOH}]$ [9]. Similar methods were used for synthesis of the other ruthenium(III) complexes **6-8b**.

$[\text{OsCl}_3(\text{PPh}_3)\text{L}]$ ($\text{L} = \text{Phen}, \text{bipy}$), **9** and **10** was used for $[\text{OsCl}_2(\text{PPh}_3)_2\text{MeOH}]$, **C**, which was synthesised as previously reported [10]. To the complex **C**, (0.25 mmol) dissolved in hot methanol (100 ml) was added to the ligand phen or bipy (0.37 mmol). The mixture gave brownish solution on reflux, and after 1 h brown microcrystals were formed which were filtered off, washed with methanol and ether, and dried in vacuo.

Yields of ruthenium complexes were 40-60%, and around 50% for those of osmium.

Catalytic oxidations by complexes

The oxidation of *p*-methoxybenzyl alcohol by $[\text{RuCl}_3(\text{AsPh}_3)(\text{bipy})]$, **8a** is typical. To a solution of *p*-methoxybenzyl alcohol (1 mmol) was added NMO (2.7 mmol) in CH_2Cl_2 (20 ml) and 5×10^{-3} mmol of compound **8a**. The solution was stirred for 2 h in the presence of 4 Å molecular sieves (0.5 g). The mixture was

then evaporated to dryness and extracted with ether (2 x 25 ml). The combined ethereal extracts were filtered and evaporated to give *p*-methoxybenzaldehyde which was characterised and quantified as 2,4-dinitrophenylhydrazone derivative.

Physical techniques

IR spectra were measured on a Perkin-Elmer 883 spectrophotometer or Nicolet 510 P FT-IR model as paraffin mulls between CsI plates or as KBr discs. The electronic spectra were measured on a Varian 634 UV-VIS spectrometer or a Perkin Elmer 552. ^1H NMR spectrum was measured on a Bruker AT-FT 100. Cyclic voltammetric studies were carried out on a potentiostat/wave generator (Oxford Electrodes) using platinum working electrode in conjunction with a Philips PM 8043 X-Y recorder. Magnetic measurements were made on a Johnson Matthey magnetic susceptibility balance.

RESULTS AND DISCUSSION

The ruthenium(II) complexes were formed by reflux of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with the different N, N-donor ligands in methanol under nitrogen, similar to the method mentioned for $[\text{RuCl}_2(\text{PPh}_3)_2(\text{phen})]$ [1] and $[\text{RuCl}_2(\text{PPh}_3)_2\text{L}]$ ($\text{L} = \text{O}$, N-neutral donor ligand [4]). Yellow or yellow-brown precipitates were isolated within 0.5-1.5 h. The ligand, *o*-anthranilonitrile (anth) reacts with $[\text{Ru}^{\text{III}}\text{X}_3(\text{AsPh}_3)_2\text{MeOH}]$ ($\text{X} = \text{Cl}, \text{Br}$) in CH_2Cl_2 solution under nitrogen with stirring for 0.5 h and gives green precipitates after solution concentration and *n*-hexane addition, while the other ligands afford reddish brown solids. Refluxing the methanolic solution of the complex $[\text{OsCl}_3(\text{PPh}_3)_2\text{MeOH}]$ with the ligands; phen and bipy for 1 h gives brown and brownish yellow microcrystals, respectively. The analytical data (Table I) indicate that these isolated complexes have the formulae $[\text{RuCl}_2(\text{PPh}_3)_2\text{L}]$, $\text{RuX}_3(\text{AsPh}_3)\text{L}$ and $[\text{OsCl}_3(\text{PPh}_3)\text{L}']$ ($\text{L} = \text{anth}, \text{phdm}, \text{phen}$ and bipy ; $\text{X} = \text{Cl}$ or Br). The complexes $[\text{RuCl}_2(\text{PPh}_3)_2\text{L}]$ ($\text{L} = \text{anth}, \text{phdm}$) are air-sensitive since their colour changes on exposure to air, while the other ruthenium and osmium complexes are air stable. Most of the complexes are fairly soluble in CH_2Cl_2 and their molar conductivities in CH_2Cl_2 or MeOH solvents are very low.

The complexes $[\text{RuCl}_2(\text{PPh}_3)_2\text{L}]$ were found to be diamagnetic at room temperature; the other complexes are paramagnetic and their magnetic moments lie in the range 1.40- 2.15 BM (Table 2) close to 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) and osmium(III) ions in an octahedral environment as in the case for other ruthenium(III) and osmium(III) complexes [4, 10-12].

Table 1
Analytical and IR spectroscopic data for complexes

Compound	Analysis			IR data, wavenumbers (cm ⁻¹) ^a			
	Found	(Calc.) (%)		$\nu(\text{NH}_2)$	$\nu(\text{C}\equiv\text{N})$	$\delta(\text{NH}_2)$	$\nu(\text{M-X})^b$
C	H	N					
1. [RuCl ₂ (PPh ₃) ₂ (anth)]	63.0 (63.4)	4.2 (4.4)	3.3 (3.4)	3430m, 3321m <u>3480m, 3380m</u>	2225m <u>2220s</u>	1630m <u>1640m</u>	321m, 302w
2. [RuCl ₂ (PPh ₃) ₂ (phdm)]	62.3 (62.7)	4.5 (4.7)	3.4 (3.5)	3440m, 3300m	--	1635s	322m, 307m
3. [RuCl ₂ (PPh ₃) ₂ (phen)]	65.2 (65.7)	4.1 (4.3)	3.1 (3.2)	-- --	--	--	325m, 285w
4. [RuCl ₂ (PPh ₃) ₂ (bipy)]	64.5 (64.8)	4.4 (4.5)	3.2 (3.3)	-- --	--	--	325m, 300w
5a. [RuCl ₃ (AsPh ₃)(anth)]	47.2 (47.5)	3.1 (3.3)	4.3 (4.4)	3420m, 3340m	2260m	1630m	330s
5b. [RuBr ₃ (AsPh ₃)(anth)]	39.0 (39.2)	2.7 (2.7)	3.7 (3.7)	3420m, 3340m	2240m	1625m	280w, 250w
6. [RuCl ₃ (AsPh ₃)(phdm)]	46.1 (46.3)	3.6 (3.7)	4.4 (4.5)	3400m, 3300m	--	1620m	325s
7. [RuCl ₃ (AsPh ₃)(phen)]	51.7 (51.9)	3.2 (3.3)	3.8 (4.0)	-- --	--	--	330s
8a. [RuCl ₃ (AsPh ₃)(bipy)]	50.1 (50.2)	3.4 (3.4)	4.1 (4.2)	-- --	--	--	330s
8b. [RuBr ₃ (AsPh ₃)(bipy)]	41.8 (41.9)	2.9 (2.9)	3.5 (3.5)	-- --	--	--	290w, 260m
9. [OsCl ₃ (PPh ₃)(phen)]	48.5 (48.7)	3.0 (3.1)	3.7 (3.8)	-- --	--	--	340w, 312m 280w
10. [OsCl ₃ (PPh ₃)(bipy)]	50.2 (50.4)	3.1 (3.2)	3.8 (3.9)	-- --	--	--	306s, 280w

^aUnderlined data refer to the corresponding free ligands. ^bM= Ru or Os; X=Cl or Br.

Spectroscopic properties

The IR spectra of the complexes (Table I) showed bands due to triphenylphosphine, arsine and coordinated L. Characteristic bands of L are shifted to lower or higher wavenumbers. The medium bands around 3420 and 3300 cm⁻¹ observed for [RuCl₂(PPh₃)₂L] and RuX₃(AsPh₃)L (L= anth, phdm; X = Cl or Br) are tentatively assigned to $\nu_{\text{as}}(\text{NH}_2)$ and $\nu_{\text{s}}(\text{NH}_2)$ near 3470 and 3380 cm⁻¹ in the free ligands. The $\delta(\text{NH}_2)$ band has been shifted near 1625 cm⁻¹ as that found for similar ruthenium(II) and ruthenium(III) complexes[4]. The $\nu(\text{C}\equiv\text{N})$ vibration for the *o*-anthranilonitrile complex [Ru^{II}Cl₂(PPh₃)₂(anth)] is slightly shifted to 2225 cm⁻¹, due to $d\pi-p\pi^*$ back bonding known for ruthenium(II) complexes[13,14]; while its appearance at higher wavenumbers are found in corresponding ruthenium (III) complexes [RuX₃(PPh₃)(anth)] (X = Cl, Br). Two bands near 320 and

300 cm⁻¹ are observed in the ruthenium(II) complexes [RuCl₂(PPh₃)₂L] which are consistent with the $\nu(\text{Ru-Cl})$ vibrations of the dichloro ligands in *cis*-geometry as previously reported for *cis*-[RuCl₂(PPh₃)₂(RCN)₂][3]. No bridging chloride $\nu(\text{Ru-Cl})$ vibration observed below 250 cm⁻¹ as in the case for [Ru₂Cl₂(PPh₃)₄L₂]Cl₂ (L = bipy, phen)[2]. The strong band near 325 cm⁻¹ in the ruthenium(III) complexes which appears at lower wavenumbers in the osmium complexes (near 310 cm⁻¹) is likely to be due to $\nu(\text{M-Cl})$ modes (M= Ru, Os) as the case for [RuCl₃(AsPh₃)L] (L = phen, bipy)[2] and [Os^{III}Cl₂(PPh₃)L'] (L' = O,O-donor ligand[10]. The weak band around 270 cm⁻¹ in the bromo ruthenium(III) complexes is attributed to $\nu(\text{Ru-Br})$ vibration [7,15].

The UV-VIS spectra of the ruthenium(II) complexes in deaerated CH₂Cl₂ solution (Table 2) showed strong band

around 470 nm. This is assigned to metal-ligand charge transfer transition, $t_2(\text{Ru})-\pi^*(\text{L})$ similar to those found for $[\text{Ru}^{\text{II}}(\text{bipy})\text{A}][\text{ClO}_4]$ (HA = arylazo-oxime)[16]. The spectra of ruthenium(III) complexes in CH_2Cl_2 show bands above 545 nm of either low ($500 \text{ M}^{-1}\text{cm}^{-1}$) or higher molar absorptivity, probably attributed to d-d transition[17-19] and ligand(π)---metal(d) transitions[7,20-23]. The weaker ligand field bands in osmium(III) complexes may be obscured by the metal-ligand charge transfer bands at 480 and 440 nm[24]. The bands around 350 nm could arise from $\text{X}---t_2(\text{M})$ (X = Cl, Br; M = Ru, Os)[8,10,24,25]. The peak below 300 nm is of the interligand $\pi---\pi^*$ type[7,20,23]. The ^1H NMR spectrum of the complex

$[\text{RuCl}_2(\text{PPh}_3)_2(\text{phen})]$ in $(\text{CD}_3)_2\text{SO}$ shows signals characteristic of coordinated 1,10-phenanthroline. A multiplet composed of two doublets centred at δ 7.55 ppm is arising from H_3 , 8 protons and the doublets at 8.40 and 9.15 ppm are due to H_2 , 9 and H_4 , 7 protons, respectively. The signals at δ 8.10 ppm corresponds to H_5 , 6 remains unshifted while the other signals shifted to higher field in the complex compared to those of the free phen ligand. This is consistent with the electron withdrawal by the metal causing decreased electron density in aromatic ring; a similar effect is observed in other phenanthroline ruthenium(II) complexes[26,27].

Table 2
Magnetic moments, UV-Vis and cyclic voltammetric data of the complexes

Compound	$\mu_{\text{eff}}(\text{BM})^{\text{a}}$	UV-VIS data, λ_{max} (nm) (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)	Voltammetric Data(V)							Scan rate mV. s^{-1}
			Reductions			Oxidations				
			E_{pc}	E_{pa}	ΔE	E_{pc}	E_{pa}	ΔE		
1	D	344(4590), 304(7870), 273(5500), 228(41400)	--	--	--	+0.74 +1.14	+0.80 +1.20	0.06 0.06	20, 50	
2	D	477(4080), 273(5800), 223(44000)	--	--	--	+0.60 +1.00	+0.72 +1.06	0.12 0.060	20, 50	
3	D	452(7300), 317(2400), 268(77500), 223(48900)				+0.32	+0.38	0.060	20, 50	
4	D	490(2660), 294(14600), 267(39700), 223(48900)	--	--	--	+0.34	+0.40	0.060	20, 50	
5a	1.95	592(520), 395(3385), 327(2975), 286(7725), 246(20150), 224(30000)	-0.32	-0.16	0.16	--	+1.44		20, 50, 100	
5b	2.05	710(470), 565(1450), 486(2215), 317(17700), 285(15500), 225(41900)	-0.18	-0.06	0.120	--	--		20, 50, 100	
6	2.15	512(1920), 470(3840), 360(2370), 298(2220), 280(7900), 225(35760)	-0.70	--	--	+0.68	+0.82	0.140	20, 50	
7	2.14	460(2440), 384(6650), 283(15150), 268(47050), 227(60800)	-0.30	-0.22	0.080	+1.20	+1.30	0.100	20, 50	
8a	1.85	476(2260), 400(5230), 286(21300) 250(41900), 227(26900)	-0.18	-0.10	0.080		+1.02		20, 50	
8b	2.00	550(2160), 450(3260), 390(2440) 290(17200), 246(48300)	-0.08	--	--	--	+1.06		20, 50	
9	1.84	780(210), 440(2700), 335(3800) 265(30800)	-0.54	-0.46	0.080	+0.86	+0.92	0.060	20, 50	
10	1.40	820, 480, 374, 340, 300	-0.56 -0.78	-0.50 -0.72	0.060 0.060	+0.86 +1.14	+0.92 +1.24	0.060 0.100	20, 50, 100	
10b			+0.09 ^b -0.16 ^b	+0.19 ^b -0.07 ^b	0.100 ^b 0.090 ^b					

^aD = Diamagnetic

^bCorresponding to the two isolated isomeric forms for the complex $[\text{Os}^{\text{III}}(\text{PPh}_3)_2\text{L}_2](\text{PF}_6)$ (HL = pyridine-2-thiol)[12].

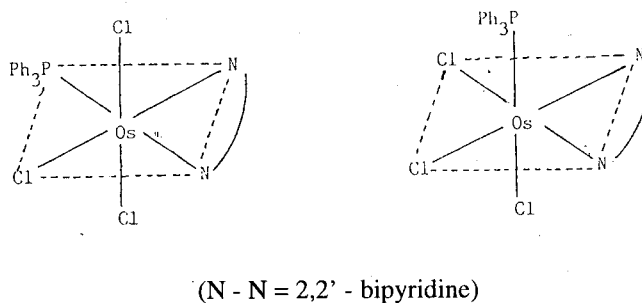
Redox properties

The electrochemical properties of the complexes were investigated by cyclic voltammetry. Voltammetric data versus a silver electrode for 0.1 M *n*-(Bu₄N)PF₆-CH₂Cl₂ solution are presented in Table 2. The voltammograms of the ruthenium(II) complexes do not show any reduction wave (or peak) at negative potentials[4,8] but do show two oxidation waves, each approaching reversibility similar to that found for [Ru^{II}(PPh₃)₂L₂] (L = tropolonate anion(-1))[8]. The peak separation ($\Delta E = 60$ mV) is close to that anticipated for a Nernstian one process (59 mV)[28]. These two oxidation waves correspond to Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} oxidations, respectively[8]. The complexes [Ru^{II}Cl₂(PPh₃)₂L'] (L' = phen, bipy) show only one oxidation wave ($\Delta E = 60$ mV), presumably due to Ru^{II}/Ru^{III} oxidation (Fig. 1a) which seems typical ruthenium(II) complexes, e.g., [Ru(PPh₃)₂(Salen)][29]. [Ru(bipy)₂A][ClO₄][16] and [RuCl₂(PPh₃)₂L'] [4] (H₂Salen = N, N-ethylenebis(salicylaldehyde); L' = O, N-neutral donor ligand).

The ruthenium(III) complexes show an irreversible wave (or peak) at negative potentials corresponding to Ru^{III}/Ru^{II} reduction[4,7,8,10]. At positive potentials the complexes [RuCl₃(AsPh₃)L] (L = phdm, phen) show a quasireversible oxidation wave of the same current height to that of the reduction (Fig. 1b), tentatively assigned to Ru^{III}/Ru^{IV} oxidation[8]. For [RuCl₃AsPh₃)L] (L = anth, bipy), there is an irreversible oxidation peak at $E_{p,a} = +1.02$ and $+1.44$ V of current height three times greater than that of the reduction wave, similar to those found for [RuCl₂(PPh₃)₂L'] [L' = O, O(N)-donor ligand (-1)][7], confirming formation of higher oxidation states of ruthenium other than Ru^{IV}[21]. A shift to more negative potential was observed (~ 0.10 V) for the reduction wave (or peak) for [RuCl₃(AsPh₃)L] (L = anth, bipy) compared with those of the analogous bromo complexes, since the bromo complexes as expected are more readily reduced[7,31].

The osmium(III) complex [Os^{III}Cl₃(PPh₃)(phen)] **9** shows a similar voltammogram to that of its ruthenium analogue complex **7**, but its oxidation wave at $E_{1/2} = +0.89$ V ($\Delta E = 60$ mV) which is presumably attributed to Os^{III}/Os^{IV}, is shifted to lower positive potential and the reduction wave (due to Os^{III}/Os^{II}) is also shifted to negative potential [10,31,32]. This shift in redox potentials to lower values in osmium complexes is expected as found for [MO₄]⁻ [33] and [MCl₂(EPh₃)₂NQ] (M = Ru, Os; E = P or As; HNQ = lawsone)[21]. So the ruthenium(III) complex **7** is expected to be more efficient oxidative catalyst than the corresponding osmium complex **9** (because it is more difficult to detach electrons from ruthenium). The complex [Os^{III}Cl₃(PPh₃)(bipy)], **10** showed two redox waves for oxidation and another two for reduction, each of similar peak height and the peak separation $E = 60$ mV. The current height is approximately half that of the osmium(III) phenanthroline complex **9** (Fig.2) under the same conditions and thus the bipyridine complex **10** is suggested to be a mixture of two isomers (shown below) difficult to separate. Its redox waves are similarly attributed to Os^{III}/Os^{IV} oxidation and Os^{III}/Os^{II} reduction as for the complex **9**. Two pseudo

reversible oxidation waves near $+0.77$ and $+1.02$ V (each due to Ru^{II}/Ru^{III}) were found for each of the complexes [Ru^{II}Br₂(SR₂)₂(Me₂SO)] (R = Me, Et) indicating that these complexes are mixtures of two geometric isomers[34]. Measurements of by-cyclic voltammetry were reported to be a convenient method for distinguishing *cis*- from *trans*-isomeric forms of [Ru^{II}Cl₂(PPh₃)(trpy)][35] and [Os^{III}(PPh₃)₂L₂](PF₆) (trpy = 2,2,2-terpyridine; HL = pyridine-2-thiol)[12].



For scan rates (SR) between 20 and 100 mV s⁻¹, the ratio $ip/(SR)^{1/2}$ (ip = 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 that the mass transfer is limited.

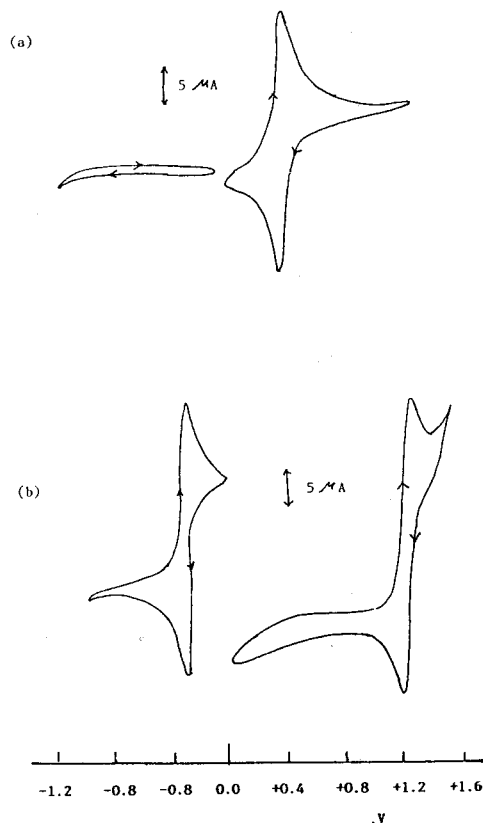


Fig. 1. Cyclic voltammogram in CH₂Cl₂ with 0.1 M *n*-(Bu₄N)PF₆ as supporting electrolyte; V vs Ag electrode, scan rate 20 mV s⁻¹ for
(a) [RuCl₂(PPh₃)₂(phen)] ($\approx 8 \times 10^{-4}$ M)
(b) [RuCl₃(AsPh₃)(phen)] ($\approx 10^{-3}$ M)

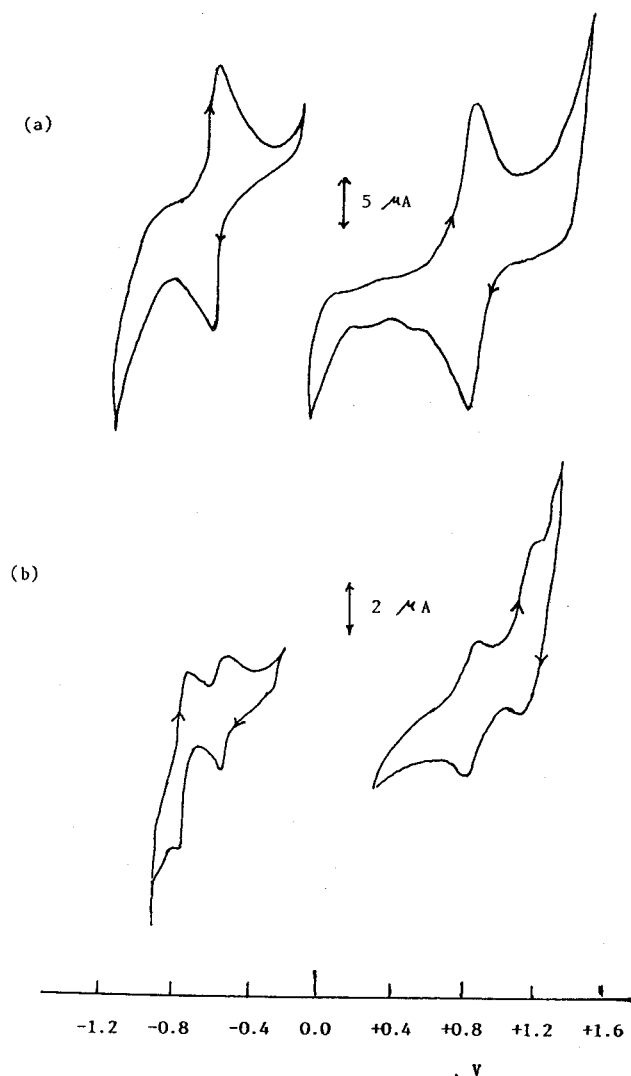


Fig. 2 Cyclic voltammogram in CH_2Cl_2 with 0.1 M $n\text{-(Bu}_4\text{N)PF}_6$ as supporting electrolyte; V vs Ag electrode, scan rate 50 mV s^{-1} for
(a) $[\text{OsCl}_3(\text{PPh}_3)(\text{phen})]$ ($\approx 10^{-3} \text{ M}$)
(b) $[\text{OsCl}_3(\text{PPh}_3)(\text{bipy})]$ ($\approx 10^{-3} \text{ M}$)

Catalytic oxidation

In our continuing work to find new ruthenium(II) and ruthenium(III) complexes that act as efficient catalysts in the presence of N-methylmorpholine-N-oxide (NMO) for selective oxidation of primary alcohols to aldehydes and secondary alcohols to ketones[4,7,21], we find that these complexes are better oxidative catalysts than those of dioxo-ruthenium[15,36-38] as they are easy to prepare with high yield. They are also less expensive, selective towards oxidation of alcohols and more efficient catalysts with high turnovers. The present ruthenium and osmium complexes have been used for such catalytic activity in the presence of

NMO as co-oxidant and results are summarized in Table 3. The oxidations were carried out at room temperature in CH_2Cl_2 from which water was removed by using powdered molecular sieves. There was no detectable oxidation of alcohol in the absence of any ruthenium complex. The ruthenium complexes oxidize primary alcohols to the corresponding aldehydes and secondary alcohols to ketones with high yield and turnovers (up to 200). Also, the ruthenium catalysts are effective towards oxidation of unsaturated alcohol e.g., cinnamyl alcohol without competing double-bond attack, contrary to the low yield of cinnamaldehyde obtained in the case of the catalysts $[\text{Os}^{\text{III}}\text{Cl}_2(\text{PPh}_3)_2\text{L}']$ ($\text{HL}' = \text{O}$, O-donor ligand(-1))[6,21] and $(4\text{-t-But-pyH})_2[\text{RuO}_2\text{Cl}_4]$ [37]. It is clear from the oxidation of *p*-methoxybenzyl alcohol (Table 3) that ruthenium(III) complexes are more efficient catalytic oxidants than those of ruthenium(II) which is consistent with their difference in electrochemical behaviour (Table 2). The ruthenium complex $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_2(\text{phdm})]$, shows two reversible oxidation waves (due to $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$) while ruthenium(III) complexes **5a** and **8a** both have an irreversible oxidation peak of current height three times greater than that of its corresponding reduction wave. This corresponds to oxidation of ruthenium(III) to higher oxidation states more than Ru^{IV} [7,10]. The osmium(III) complexes **9** and **10** have not such oxidation peaks. It seems that this lack of reversibility for the oxidation waves reflects the reason for more efficient catalytic cycle of oxidation[8]. We have reported that the complexes $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{PPh}_3)_2(\text{acac})]$ [17] and $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{AsPh}_3)_2\text{NQ}]$ [21] are good catalytic oxidants for alcohols but with turnovers 50-100, lower than those obtained by the present ruthenium(III) complexes $[\text{RuCl}_3(\text{AsPh}_3)\text{L}]$. We believe that the greater number of labile chloro ligands enhance the formation of ruthenium higher oxidation states during the catalytic cycle of oxidation. A similar effect was also observed for $[\text{OsCl}_3(\text{PPh}_3)\text{L}]$ ($\text{L} = \text{phen, bipy}$) **9** and **10** which gave similar oxidation yields of *p*-methoxybenzaldehyde but after a short reaction time (only 3 h) compared to that given by $[\text{Os}^{\text{III}}\text{Cl}_2(\text{PPh}_3)_2(\text{acac})]$ (36 h)[10] under the same conditions. Reaction of ruthenium(III) Schiff base complexes with iodosobenzene (PhIO) was suggested to form oxo-ruthenium(V) complexes[39]. The formation of oxo-ruthenium(V) species was also reported for RuCl_3/NMO [40,41] or PhIO [42] systems and the mechanism was mentioned for oxidation of alcohols where ruthenium(III) is regenerated[40]. It is relevant from the cyclic voltammetric data that oxidation effected by catalysts are likely to occur *via* ruthenium and osmium in their higher oxidation states which should be accessible through chemical oxidation with the common co-oxidants[6,17,21,43].

Table 3
Catalytic Oxidation of Alcohols by Ruthenium and Osmium Complexes

Complex	Alcohol	Product ^a	Time(h)	Yield(%)	Turnover ^b
2	<i>p</i> -Methoxy benzyl	A	2.5	80	150
5a		A	2.0	90	200
7		A	2.0	80	150

Table 3 Contd.

Complex	Alcohol	Product ^a	Time(h)	Yield(%)	Turnover ^b
8a		A	2.0	70	200
9		A	3.0	12	40
10		A	3.0	15	40
2	Piperonyl	A	2.0	90	150
2	Benzyl	A	2.0	40	80
2	Cinnamyl	A	1.5	65	100
5a		A	2.0	65	100
2	Benzohydrol	K	2.5	95	100
5a		K	2.5	65	100
7		K	3.0	75	100
2	α -Tetralol	K	2.0	80	100

^aA = Corresponding aldehyde, K = Corresponding ketone^bTurnover = Moles of product/moles of catalyst.

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