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Complexes of some Platinum Group Metals with Hydrazone Ligands and their Catalytic Oxidative Properties

A. M. El-Hendawy*, **A. H. Al-Kubaisi**, and **A. F. Shoair**

Chemistry Department, Faculty of Science, University of Qatar, Doha, Qatar

Summary. New complexes of ruthenium(II), ruthenium(III), osmium(III) and palladium(II) have been prepared with a neutral bidendate hydrazone ligand derived from antipyrine-4-carboxaldehyde and benzoylhydrazine. Ruthenium(III) complexes have also been synthesized from monobasic bidendate ligands prepared from benzaldehyde and benzoyl or *p*-substituted (Me, Cl) benzoyl hydrazine. The complexes were characterized by spectroscopic techniques and investigated by cyclic voltammetry. The efficient catalytic oxidation of alcohols and 3,5-*di*-^{t}butyl catechol in the presence of N-methylmorpholine-N-oxide or *m*-chloroperbenzoic acid as co-oxidants is reported.

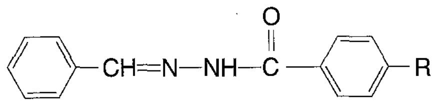
Keywords. Platinum metals; Hydrazone ligands; Catalytic oxidation.

Komplexe einiger Platinmetalle mit Hydrazonliganden und ihre katalytischen oxidativen Eigenschaften

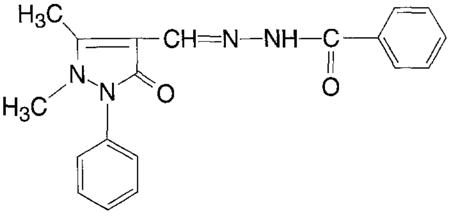
Zusammenfassung. Neue Komplexe von Ru(II), Ru(III), Os(III) und Pd(II) mit einem aus Antipyrin-4-carbaldehyd und Benzoylhydrazin hergestellten neutralen bidentaten Hydrazonliganden wurden synthetisiert. Im Fall von Ru(III) wurden auch aus Benzaldehyd und verschiedenen Benzoylhydrazinen gewonnene monobasische bidentate Liganden eingesetzt. Die Komplexe wurden mittels spektroskopischer Methoden charakterisiert und mit Hilfe der cyclischen Voltammetrie untersucht. Es wird über die effiziente katalytische Oxidation von Alkoholen und 3,5-*di*-^{t}Butyl-katechol in Gegenwart von N-Methyl-morpholin-N-oxid oder *m*-Chlorperbenzoesäure als Co-Oxidantien berichtet.

Introduction

Coordination compounds of arylhydrazones have been reported to act as enzyme inhibitors [1] and have useful pharmocological applications [2, 3]. In recent years, an increasing number of metal complexes of hydrazones has been studied [4–6], particularly those of palladium(II), platinum(II), and rhodium(III) which was reported to have potential antitumer activity [7]. Hitherto no reports have been made on complexes of Ru(II), Ru(III), Os(III), and Pd(II) with antipyrine-4-carboxaldehyde benzoylhydrazone (H*acbh*) and benzaldehyde benzoyl or *p*-substituted benzoyl (Me, Cl) hydrazones (H*bhz*, H*p*-Me*bhz*, and H*p*-Cl*bhz*). The possibility of keto-enol tautomerism of the $>$C=N–NH–$\underset{|}{\mathrm{C}}$O moiety can lead to varying bonding



(H*R*—*bhz*; *R* = H, Me, or Cl)



(H*acbh*)

Fig. 1. Structure of the ligands

and stereochemical behaviour in the complexes. The synthesis, spectroscopic characterization, and electron transfer properties of the present complexes are reported as well as their reactivities as catalytic oxidants for alcohols and 3,5-*di*-^{t}butyl catechol with respect to ruthenium(III) and osmium(III) complexes [8, 9]. The structures of the ligands are shown in Fig. 1.

Results and Discussion

Hydrazone ligands are prepared by condensation of antipyrine-4-carboxaldehyde or benzaldehyde with the corresponding benozylhydrazine (or its *p*-substituted derivatives) in ethanol. The ligand H*acbh* was reacted with an equimolar amount of, $[Ru^{II}Cl_2(PPh_3)_3]$ (**A**) under nitrogen gas in refluxing degassed methanol. A diamagnetic yellow-orange, air stable precipitate was formed after 1 h of reflux. The reaction of $[Ru^{III}X_3(AsPh_3)_2MeOH]$ ($X = Cl, Br$) and $[OsCl_3(PPh_3)_2MeOH]$ with H*acbh* in refluxing MeOH for 0.5 h gave reddish brown (Ru) and olive green (Os) microcrystals. These complexes are paramagnetic and their magnetic moments are close to the spin only value for one unpaired electron (1.73 BM) (Table 1). This suggests a low spin d^5 $(t_{2g})^5$ configuration for the ruthenium(III) or osmium(III) ion in an octahedral environment as in the case of other ruthenium(III) and osmium(III) complexes [8–11]. The palladium complex was isolated from the aqueous solution obtained by stirring $Na_2[PdCl_4]$ and H*acbh* overnight.

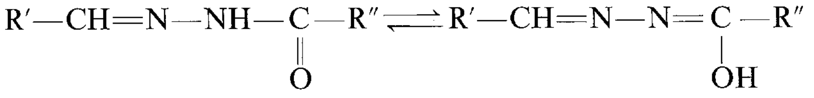
The ruthenium complexes of benzaldehyde benzoylhydrazone ligands (H*R*-*bhz*) were isolated from the reaction of the ruthenium(II) complex **A** and the corresponding ligands in refluxing benzene/methanol (1:1). Green microcrystals were obtained and found to be paramagnetic, corresponding to one unpaired electron in the case of ruthenium(III) products. These complexes were formed as expected in an oxidative substitution reaction [12] and *via* enolization of the hydrazone ligand H*R*-*bhz* (equations 1 and 2). The corresponding ruthenium(III) complex could be obtained from the reaction of the antipyrinehydrazone ligand and complex **A** as a reddish material after refluxing the reaction solution (methanol) for several hours and leaving it to stand for a few weeks. This means that the ligand H*acbh* does not exist to a significant extent in the enol form.

Table 1. Analytical, magnetic and IR spectroscopic data of complexes

	Compound	Colour	Found (Calcd.) (%)			μ_{eff} (B.M.)[a]	IR data (cm^{-1})[b]			other bands
			C	H	N		ν(C=O)	ν(C=N)	ν(M–Cl)	
1.1	[RuCl$_2$(PPh$_2$)$_2$(H*acbh*)]·2MeOH	yellow-orange	62.3	4.8	4.9	D	1618 s	1584 s	321 m	
			(62.5)	(5.1)	(5.1)		*1673* vs	*1630* s	300 w	
1.2	[RuCl$_3$(AsPh$_3$)(H*acbh*)]	brown	52.3	3.9	6.3	1.87	1618 s	1588 s	349 m	
			(52.4)	(3.9)	(6.6)				320 vs	
1.3	[RuBr$_3$(AsPh$_3$)(H*acbh*)]	reddish-brown	45.2	3.2	5.5	1.91	1617 s	1587 s		
			(45.3)	(3.4)	(5.7)					
1.4	[OsCl$_3$(PPh$_3$)(H*acbh*)]	olive-green	49.5	3.5	6.1	1.86	1615 s	1586 s	337 w	
			(49.7)	(3.7)	(6.3)				307 s	
1.5	[PdCl$_2$(H*acbh*)]	yellow	44.8	3.4	10.9	D	1617 s	1588 s	334 s	
			(44.6)	(3.5)	(11.0)				304 w	
2.1	[RuCl$_2$(PPh$_3$)$_2$(*bhz*)]	green	65.1	4.4	2.9	2.05		1580 m	344 w	1510 s
			(65.3)	(4.5)	(3.0)		*1645* s	*1600* s	330 s	
2.2	[RuCl$_2$(PPh$_3$)$_2$(*p*-Me-*bhz*)]	green	65.4	4.5	2.8	2.02		1610 m	343 w	1513 s
			(65.6)	(4.6)	(3.0)				325 m	
2.3	[RuCl$_2$(PPh$_3$)$_2$(*p*-Cl-*bhz*)]	green	62.6	4.1	2.7	1.97		1610 s	345 w	1510 s
			(62.9)	(4.2)	(2.9)				330 m	

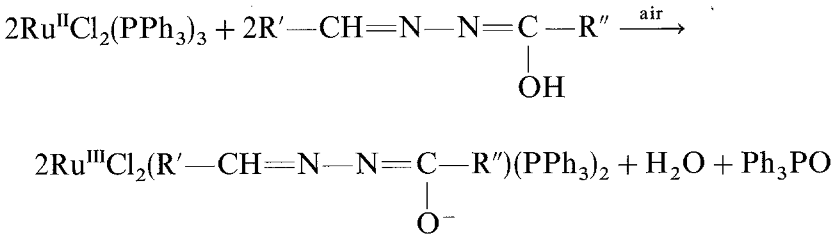
[a] D = diamagnetic; [b] data in italics refer to the corresponding ligands

All complexes are soluble in CH_2Cl_2 or $ClCH_2CH_2Cl$. Their molar conductivities in these solvents are very low, and they are stable on exposure to air. Analytical data of the complexes indicate their formulae given in Table 1. The yield of H*acbh* complexes is 70–90%, whereas that of $[Ru^{III}Cl_2(PPh_3)_2(R\text{-}bhz)]$ is 50–60%.



$$R'{-}CH{=}N{-}NH{-}\underset{\underset{O}{\|}}{C}{-}R'' \rightleftharpoons R'{-}CH{=}N{-}N{=}\underset{\underset{OH}{|}}{C}{-}R'' \qquad (1)$$

H*R-bhz*
(R′ = Ph, R″ = R – Ph)



$$2Ru^{II}Cl_2(PPh_3)_3 + 2R'{-}CH{=}N{-}N{=}\underset{\underset{OH}{|}}{C}{-}R'' \xrightarrow{\text{air}}$$
$$2Ru^{III}Cl_2(R'{-}CH{=}N{-}N{=}\underset{\underset{O^-}{|}}{C}{-}R'')(PPh_3)_2 + H_2O + Ph_3PO \qquad (2)$$

The thermal stabilities of the ruthenium and osmium complexes (**1.1**, **1.2**, and **1.4**) have been investigated. The complexes are stable till 230 °C, although a gradual mass loss is observed with **1.1** corresponding to two molecules MeOH as indicated by the analytical data (Table 1); decomposition occurs above 230 °C. The ruthenium(III) complex **1.2** is more stable (up to 305 °C) a mass loss (36%) occurs in the range of 305–372 °C, corresponding to the coordinated Ph_3As group. Two consecutive decomposition temperatures were found at 334 and 438 °C.

Spectroscopic Properties

The IR spectra of the antipyrine hydrazone ligand H*acbh* shows a broad band near 3200 cm^{-1} and a strong one at 1673 cm^{-1}; they are tentatively assigned to ν(NH) and ν(C=O) vibrations of the hydrazone moiety. The former band still appears in its complexes, whereas the other one is shifted to lower wavenumbers by about 50 cm^{-1} as typically reported for ν(C=O) in $[PdCl_2L]$ (L = methyl-2-pyridyl ketone) [13]. The azomethine ν(C=N) mode is also shifted to lower wavenumbers by *ca.* 40 cm^{-1}. A medium band at 1600 cm^{-1} is observed in both the ligand and complexes, arising from the cyclic ν(C=O) frequency [14]. This suggests bonding of both the azomethine nitrogen and the carbonyl oxygen of the side chain without participation of the ring carbonyl oxygen in coordination. For the benzoylhydrazone ruthenium(III) complexes **2.1**–**2.3**, the ν(NH) vibration at 3200 cm^{-1} in the free ligand disappears in the complexes, but a new strong band appears near 1510 cm^{-1} which is attributed to $N{=}C{-}O^-$ vibrations (*via* enolization of C=O group, as found for complexes of related ligands [5]). This indicates the involvement of both the azomethine nitrogen C=N and the enolized oxygen C–OH (as shown in equation 1) in metal chelation. Two bands around 320 cm^{-1} were found in the chloro complexes which are due to $\nu(M\text{-Cl})$ vibrations and are indicative of a *cis*-geometry of dichloro ligands in complexes **1.1**, **1.5**, and **2.1**–**2.3** [13, 15]. The ν(Ru-Br) frequency in the bromo complex **1.3** is obscured by a medium band at 297 cm^{-1}. Bands due to the coordinated triphenylphosphine or arsine were found; the most important IR bands are listed in Table 1.

The ^1H NMR spectra of H*acbh* and $[RuCl_2(PPh_3)_2(\mathrm{H}\mathit{acbh})]\cdot 2MeOH$ were measured in $CDCl_3$. The azomethine proton displays a singlet at 6.9 ppm, whereas that of NH appears at 13.8 ppm. In the ruthenium complex, the resonance of the azomethine proton is probably obscured by the proton resonances of the phenyl rings (multiplet at 7.25 ppm), but the NH proton is highly shifted and seen at 15.5 ppm, suggesting an involvement of the neighbouring azomethine nitrogen and the carbonyl oxygen in the coordination of the ruthenium(II) ion. A singlet at 1.7 ppm corresponds to two methyl protons of solvated MeOH.

The UV/Vis spectra of the ruthenium and osmium complexes of H*acbh* were obtained in dichloroethane, whereas those of H*R-bhz* were recorded in CH_2Cl_2 at ambient temperature (Table 2). In **1.1**, a strong band at 486 nm is shown and assigned to metal-ligand charge transfer transitions $t_{2g}(Ru) \rightarrow \pi^*(L)$, similar to those found for $[Ru^{II}(\mathit{bipy})A'][ClO_4]$ (HA′ = arylazo-oxime) [16]. **1.2**–**1.4** show bands above 510 nm of either low ($\varepsilon = 500\,M^{-1}\cdot cm^{-1}$) or higher molar absorptivity, probably attributed to d–d transitions [17, 18] and ligand (π)-metal (d) transitions [9, 19, 20]. The weaker bands near 640 nm observed for **2.1**–**2.3** are characteristic of ruthenium(III) d–d transitions [17, 18, 21, 22]. The peaks below 300 nm are of the interligand π–π^* type [19, 20].

On the basis of both analytical and spectroscopic data together with the X-ray crystal structure determination of $[OsCl_3(NH_3)(PPh_3)_2]$ [23], we suggest structures of the complexes as shown in Fig. 2.

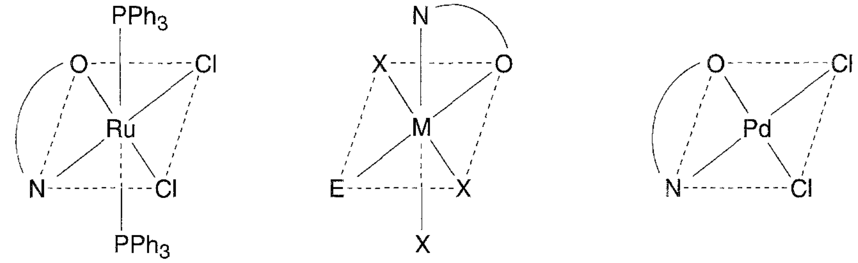
Electron-Transfer Properties

Cyclic voltammetry has been used to investigate the electron transfer properties of the complexes. Voltammetric data *vs.* a silver electrode for a 0.1 *M* ($^nBu_4N)PF_6$-dichloroethane solution (containing 10¯3 *M* of the complex) are presented in Table 2 and compared with $[Fe(C_5H_5)_2]^{0/+}$, $E_{1/2} = +0.44$ V and $\Delta E = 70$ mV for the cell used. The voltammogram of **1.1** reveals only an oxidation wave ($E_{1/2} = +0.49$ V, $\Delta E = 60$ mV, Fig. 3a) which corresponds to a Ru^{II}/Ru^{III} oxidation, similar to those found for ruthenium(II) complexes, *e.g.* $[Ru(\mathit{salen})(PPh_3)_2]$ [24] and $[RuCl_2(PPh_3)_2L]$ (L = Phen [25], L = benzoyl hydrazine [26]). The ruthenium(III) complexes **1.2** and **1.3** each show a reversible wave at a negative potential ($\Delta E = 60$–80 mV) and another wave at a positive potential ($\Delta E = 60$ mV) of similar current height (Fig. 3b). The former wave is assigned to a Ru^{III}/Ru^{II} reduction, whereas the wave at positive is due to Ru^{III}/Ru^{IV} oxidation similar to those observed for $[Ru^{II}(\mathit{salen})(PPh_3)(\mathit{py})][ClO_4]$ [27], $[Ru(\mathit{acac})_3]$ [28], and $[OsCl_2(PPh_3)(\mathit{acac})]$ [10]. A shift to a more negative potential (~ 0.7 V) is observed for the reduction wave of the chloro complex **1.2** compared with that of the analogous bromo complex **1.3** since we expect that the bromo complex is more readily reduced as reported for $[Os^{III}X_2(PPh_3)_2L]$ [29] (X = Cl, Br; HL = 2-hydroxypridine, 2-hydroxy-6-methylpyridine, and picolinic acid). One wave at negative potential and two successive waves at positive potentials are observed for $[OsCl_3(PPh_3)(\mathrm{H}\mathit{acbh})]$ similar to those of $[OsQ_2D]$ (Q = oxinate anion, D = β-diketonate anion) which is assigned to Os^{III}/Os^{II} reduction and Os^{III}/Os^{IV} and Os^{IV}/Os^{V} oxidations [30]. A cathodic peak at $E_{p,c} = -0.74$ V and an

Table 2. UV/Vis spectroscopic and cyclic voltammetric data of complexes

Compound	Solvent[a]	UV/Vis data λ_{max} (ε, $M^{-1} \cdot cm^{-1}$)	Voltammetric data (V) Reductions E_{pc}	E_{pa}	ΔE	Oxidations E_{pc}	E_{pa}	ΔE	Scan rate (mV/s)
1.1	*DCE*	486 (2900), 404 (9400), 325 (23000)				+0.46	+0.52	0.060	20, 50, 100
1.2	*DCE*	525 (580), 377 (13, 320), 331 (22, 640)	−1.30	−1.22	0.080	+0.73	+0.80	0.070	50, 100
1.3	*DCE*	512 (2250), 450 (2500), 400 (4150), 325 (5000)	−0.56	−0.50	0.060	+0.92	+0.98	0.060	50, 100
1.4	*DCE*	588 (1750), 486 sh (3500) 375 (12500), 316 (22,500)	−0.14	−0.07	0.070	+0.51 +1.00	+0.58 +1.12	0.070 0.120	20, 50
1.5	*DCE*		−0.74			+1.00	+1.12	0.120	50, 100
2.1	*DCM*	650 (180), 300 (37400) 274 (38, 200), 227 (70, 300)	−0.38	−0.30	0.080		+1.10		20, 50
2.2	*DCM*	635 (170), 367 (21, 800) 300 (42, 500), 269 (47, 600) 227 (82, 700)	−0.36	−0.28	0.080		+1.14		20, 50
2.3	*DCM*	640 (190), 330 (25, 400) 260 (50, 600), 225 (70, 500)	−0.36	−0.26	0.100		+1.10		20, 50

[a] *DCE* = dichloroethane; *DCM* = dichloromethane



1.1, 2.1–2.3 (N—O = H*acbh* or *R-bhz*)

1.2–1.4 (N—O = H*acbh*; *M* = Ru, *X* = Cl or Br, *E* = AsPh$_3$; *M* = Os, *X* = Cl, *E* = PPh$_3$)

1.5 (N—O = H*acbh*)

Fig. 2. Suggested structures of the complexes

oxidation wave of double current height at $E_{1/2} = +1.06$ V ($\Delta E = 120$ mV) were found for [PdCl$_2$(H*acbh*)], arising from Pd^{II}/Pd^{I} reduction [31] and Pd^{II}/Pd^{IV} oxidation, respectively.

The ruthenium(III) complexes [RuCl$_2$(PPh$_3$)$_2$(*R-bhz*)] (**2.1**–**2.3** show a negative potential wave (due to Ru^{III}/Ru^{II} reduction) and an anodic peak ($E_{p,a}$ near $+1.1$ V) of a current height twice that of the negative wave. This peak seems to be arising from an oxidation of Ru^{III} to higher oxidation states, *e.g.* Ru^{V} as is the case for [Ru^{III}Br$_2$(AsPh$_3$)$_2$*L*] (H*L* = O,O-donor ligand) [32]. The effect of different substituents (R = H, Me, Cl) on $E_{1/2}$ of reduction is negligible.

For scan rates between 20 and 100 mV·s^{-1}, the ratio $i_p/(SR)^{1/2}$ (i_p = peak current, SR = scan rate) is constant and the ratio of anodic to cathodic current i_{pc}/i_{pa} is approximately unity. The peak separation is independent of the scan rate and close to that anticipated for a *Nernstian* one-electron process ($\Delta E = 59$ mV) [33]. This indicates that the electron transfer is reversible or approaches reversibility and that mass transfer is limited.

Catalytic Oxidations

We have found that ruthenium(II) [25, 34] and ruthenium(III) [8, 9] complexes containing triphenylphosphine(arsine) act as good catalysts in the presence of N-methylmorpholine-N-oxide (*NMO*) for the 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 present complexes for such catalytic oxidations in the presence of *NMO* or *m*-chloroperbenzoic acid (*CPA*) as co-oxidants. In Table 3, we summarize the results for catalytic oxidations by [RuCl$_3$(AsPh$_3$)(H*acbh*)] as a typical example, compared with other ruthenium complexes in the presence of *NMO* or *CPA*. The oxidations were carried out at room temperature in CH$_2$Cl$_2$ when using *NMO* as co-oxidant. Table 3 shows that the catalyst [RuCl$_2$(PPh$_3$)$_2$(H*acbh*)] is better than **1.2** with respect to both yield and turnover of the corresponding aldehyde or ketone. Unsaturated alcohols, *e.g.* cinnamyl alcohol, are effectively oxidized without competing double bond attack, in contrast to the low yield of cinnamaldehyde obtained in the case of the catalysts [OsCl$_2$PPh$_3$)*L*$'_2$] (H*L*$'$ = O,O-donor ligand) [8, 35] and (4-^{t}Bu-*py*H)$_2$[RuO$_2$Cl$_4$]

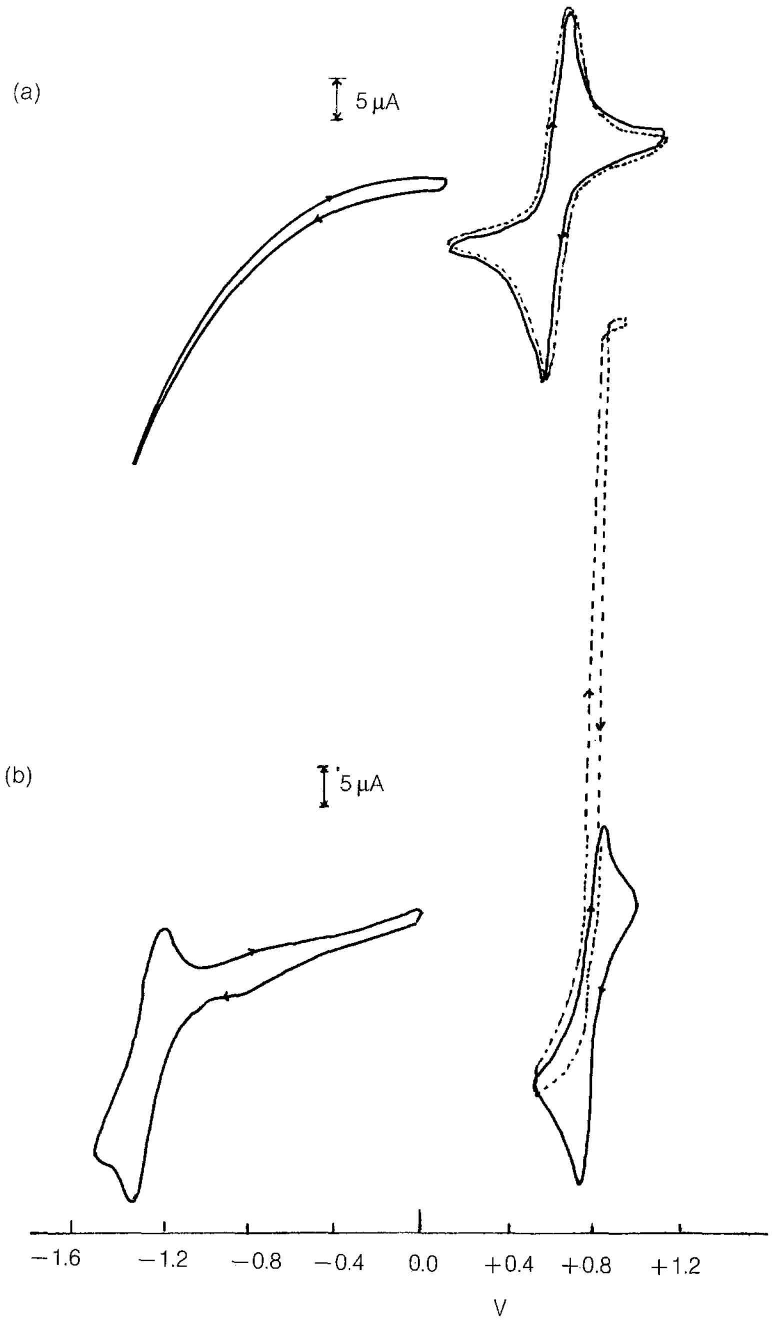


Fig. 3. Cyclic voltammogram in dichloroethane with 0.1 *M* (^{n}Bu$_4$N)PF$_6$ as the supporting electrolyte; V *vs.* Ag electrode; scan rate: 50 mVs^{-1}; in the absence of 2-propanol (———) and in the presence of 2% v/v 2-propanol (– – –); (a) [RuCl$_2$(PPh$_3$)$_2$(H*acbh*)]·2MeOH (10^{-3} *M*); (b) [RuCl$_3$(AsPh$_3$)(H*acbh*)] (10^{-3} *M*)

[36]. The cyclic voltammogram (Fig. 3b) shows that the couple Ru^{III}/Ru^{IV} in the complex **1.2** disappears on adding 2% 2-propanol (v/v), similarly to that observed for the weaker catalytic oxidant [Ru^{II}(PPh$_3$)$_2$(*trop*)$_2$] [34] (*trop* = tropolonate anion(−1)), whereas the couple Ru^{II}/Ru^{III}, corresponding to catalyst **1.1**, is not effected by adding 2-propanol. Thus, it seems that the higher oxidation state formed in the

presence of excess co-oxidant and responsible for the catalytic cycle of oxidation is more stable with catalyst **1.1** than with **1.2**. The oxidation of *p*-methoxybenzyl alcohol by $[Ru^{III}Cl_2(PPh_3)_2(bhz)]$ (**2.1**) gave the highest turnover number (200), probably arising from easier formation of a higher ruthenium oxidation state (Ru^V) as shown by its voltammogram.

At room temperature and in presence of excess *CPA* instead of *NMO*, no oxidation products could be obtained in case of complex **1.2**, but catalyst **1.1** gave good yields of the oxidation products (Table 3). The complex **1.2** acts as a catalytic oxidant when activated at 55 °C except for piperonyl and cinnamyl alcohols. Blank experiments were conducted under similar conditions, but in the absence of complexes; in all cases no oxidation products were found.

Oxidation of 3,5-di-^{t}butyl catechol (*DTBCat*) by $[RuCl_2(PPh_3)_3]/O_2$ in tetrachloroethane gave an oxidation mixture product [37] of muconic acid anhydride and 2*H*-pyran-2-one. Catalytic oxidation of *DTBCat* by **1.1** and **1.2** in the presence of *NMO* under the conditions mentioned above for alcohols gave high yields of a pure *o*-benzoquinone derivative (*DTBBQ*) as red crystals (turnover number around 50). The co-oxidant *CPA* alone gave some non isolated product of *DTBBQ* under the same conditions.

The osmium complex **1.4** oxidizes *p*-methoxybenzyl alcohol to the aldehyde in the presence of *NMO* in 8 h (25% yield, turnover number 75). This corresponds to a weaker catalytic oxidant like $[OsCl_2(PPh_3)_2(acac)]$ [10]. The low reactivity of the osmium complex in comparison with its ruthenium analogue is not surprising: $[RuO_4]^-$ is a much better oxidant than $[OsO_4]^-$ [38]. The 5d electrons in the third row transition element osmium are less tightly held by the nucleus than the 4d electrons in its congener ruthenium. **1.5** gave no oxidation products under similar conditions in the presence of *NMO* or *CPA* for *p*-methoxybenzyl alcohol after 24 h reaction time.

Conclusion

Some of the prepared complexes, particularly those of ruthenium, can used as efficient catalysts for selective oxidation of primary alcohols to aldehydes, secondary alcohols to ketones, and the catechol derivative to *o*-benzoquinone. It is obvious from the cyclic voltammetric data that oxidations by ruthenium catalysts are likely to occur *via* ruthenium(III) or its higher oxidation states which should be accessible through chemical oxidation with common co-oxidants (*NMO* or *CPA*).

Experimental

Preparation of Complexes

$[RuCl_2(PPh_3)_2(\mathrm{H}acbh)]]2MeOH$ (**1.1**)

$[RuCl_2(PPh_3)_3]$ (**A**, [39], 0.5 mmol) was added under nitrogen to a degassed methanolic solution (10 cm^3) containing 0.75 mmol H*acbh*. The mixture was refluxed on a steam bath; the dark crystals of **A** dissolved rapidly, followed by the separation of a shiny yellow precipitate. Heating was continued for a 1 h under nitrogen. The precipitate and its solution were left to stand overnight under nitrogen and then filtered and washed carefully with a small amount of degassed methanol and ether and dried *in vacuo*.

Table 3. Catalytic oxidations by $[RuCl_3(AsPh_3)(Hacbh)]$ (**1.2**)

Substrate	Product[a]	*NMO*[b,c] as co-oxidant			*m*-Chloroperbenzoic acid as co-oxidant[b,d]		
		time (h)	yield (%)	turnover number[e]	time (h)	yield (%)	turnover number[e]
p-Methoxybenzyl alcohol	A	3	90	150	3	70	100
		3	*97*	*150*	*2*	*80*	*100*
		(3)	(90)	(200)			
Piperonyl alcohol	A	3	85	150	[d]	[d]	[d]
		3	*98*	*150*	[d]	[d]	[d]
Cinnamyl alcohol	A	2.5	72	100	[d]	[d]	[d]
		2	*92*	*150*	*3*	*50*	*100*
Furfuryl alcohol	A	3	75	100	3	55	100
α-Tetralol	K	3.5	75	100	3	55	100
		2	*85*	*100*	*3*	*70*	*100*
Benzohydrol	K	3	60	100	3	60	100
3,5-*di*-^{t}butyl catechol	BQ	24	50	40			
		24	*60*	*60*			

[a] A: corresponding aldehyde, K = corresponding ketone, BQ = corresponding *o*-benzoquinone; [b] data in italics correspond to $[RuCl_2(PPh_3)_2(Hacbh)]\cdot 2MeOH$ (**1.1**); [c] data in parantheses: $[RuCl_2(PPh_3)_2(bhz)]$; [d] no oxidation products obtained; [e] moles of product/moles of catalyst

$[RuCl_3(AsPh_3)(H$*acbh*$)]$ (**1.2**)

$[RuCl_3(AsPh_3)_2MeOH]$ (**B** [39], 0.25 mmol) in methanol (100 cm^4) was refluxed and the H*acbh* (0.35 mmol) was added. The mixture was refluxed for 0.5 h; after that time, brown microcrystals were obtained, filtered off, washed with methanol and then ether, and dried *in vacuo*. The analogous bromo complex (**1.3**) was similarly prepared from $[RuBr_3(AsPh_3)_2MeOH]$ [39]. The same procedure was used to synthesize the osmium complex **1.4** starting with $[OsCl_3(PPh_3)_2MeOH]$ [10] instead of **B**.

$[PdCl_2(H$*acbh*$)]$ (**1.5**)

The complex $K_2[PdCl_4]$ (1.2 mmol) in 15 cm^3 water was stirred overnight with finely powdered H*acbh* (1 mmol). The yellow precipitate was isolated, filtered, washed with a small amount of $CHCl_3$ and then ether and dried *in vacuo* over P_2O_5.

$[RuCl_2(PPh_3)($*R-bhz*$)]$ (**2.1**–**2.3**)

H*R-bhz* (*R* = Me, Cl; 0.6 mmol) was reacted with $[RuCl_2(PPh_3)_3]$ (**A**, 0.5 mmol) in refluxing mixed solvents (benzene/methanol = 1:1, 20 cm^3) for 2 h. A green solution replaced the dark crystals of **A**. After standing overnight, the microcrystals formed were filtered off, washed with MeOH and ether, and dried *in vacuo*.

Catalytic Oxidations

The oxidation of *p*-methoxybenzyl alcohol is typical. To a solution of alcohol (1 mmol), the co-oxidant *NMO* (3 mmol) in CH_2Cl_2 (20 cm^3) or *CPA* (3 mmol) in dichloroethane (20 cm^3) was added at 55 °C. The solution was stirred for 2–3 h after adding the catalyst **1.2** (10^{-2} mmol). The mixture was evaporated to dryness and extracted with Et_2O ($2 \times 25\,cm^3$). The combined ethereal extracts were filtered and evaporated to give *p*-methoxybenzaldehyde which was characterized and quantified as its dinitrophenylhydrazone derivative. The same experiment was carried out using 3,5-*di*-^{t}butyl catechol instead of *p*-methoxybenzyl alcohol.

Physical Techniques

IR spectra were measured on a Nicolet 510 P FT-IR spectrophotometer as paraffin mulls between CsI plates and as KBr discs. The elecronic spectra were measured on a Lamda 2S UV/Vis spectrometer. ^1H NMR spectra was measured on a Bruker AT-FT 100 instrument (100 MHz). Cyclic voltammetric studies were carried out on a potentiostat/wave generator (Oxford Electrodes) using a platinum working electrode in conjuction with a Philips PM 8043 X-Y recorder. Magnetic measurements were made on a Johnson-Matthey magnetic susceptibility balance. The thermal stability of the complexes was investigated using Perkin-Elmer TGA 7 unit (heating rate: 10 °C·min^{-1}).

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