

Synthesis, structure and catalytic activity of cycloruthenated carbonyl complexes containing arylazo phenolate ligands

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Abstract

A simple and convenient synthesis of a new class of air-stable mononuclear cyclometallated ruthenium(II) carbonyl 2-(aryloxy)phenolate complexes bearing triphenylarsine [Ru(ap-R)(AsPh₃)₂(CO)] has been described. The 2-(aryloxy)phenolate ligands behave as dianionic tridentate ligands and are coordinated to ruthenium through C, N and O by dissociation of the phenolic proton and the phenyl proton at the *ortho* position of the phenyl ring forming two five-membered chelate rings. These complexes have been characterized by elemental analysis, and FT-IR, ¹H NMR and UV–vis spectroscopies. In dichloromethane solution all the metal complexes exhibit characteristic metal-to-ligand charge transfer (MLCT) absorption and emission bands in the visible region. One of the complexes [Ru(ap-Cl)(AsPh₃)₂(CO)] was successfully characterized by X-ray crystallography. Cyclic voltammetric data of all the complexes show Ru^{III}/Ru^{II} oxidation and Ru^{II}/Ru^I reduction within the range of +0.75 to +0.86 V and –0.50 to –0.57 V respect to Ag/AgCl, respectively. The potentials are observed with respect to the electronic nature of substituents (R) in the 2-(aryloxy)phenolate ligands. Further, a complex (2) was tested as a new catalyst in the oxidation of primary and secondary alcohols in the presence of NMO as a more viable oxidant with moderate to high conversion. The formation of high valent Ru^{IV}=O species as a catalytic intermediate is proposed for the catalytic process.

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1. Introduction

The cyclometallation reaction, i.e., the intramolecular activation of aromatic C–H bonds of coordinated ligands by transition metals has been widely investigated in view of their growing chemistry [1–6]. Transition metal complexes that contain an azo ligand or its derivatives are well known and there are several coordination modes documented [7]. Formation of a metal carbon σ bond is important research targets in organometallic chemistry and the application of organometallic compounds to organic transformation has been of considerable interest [8]. The oxidation of primary and secondary alcohols to corresponding aldehydes and ketones is of tremendous importance in organic synthesis and many transition metal compounds have been used for this purpose [9]. It is to be noted that ruthenium compounds are intensively studied transition metal compounds and many

methodologies have been developed with them [10–13]. However, stoichiometric chemical oxidants were needed in most cases. From an environmental viewpoint, it is quite important to develop a mild and less toxic oxidation reaction systems. Numerous ruthenium complexes can selectively catalyze a large variety of oxidative transformations including the generation of dioxygen from water, the dihydroxylation of olefins, the oxidative dehydrogenation of alcohols to carbonyl compounds and the asymmetric epoxidation of alkenes, thus opening the way to the conversions of petroleum products to valuable oxygenate chemicals as well as, potentially, to the extraction of energy from renewable sources [14]. In early studies Oshima and co-workers reported that primary alcohols are selectively oxidized to aldehydes in the presence of secondary ones by using stoichiometric Ru(PPh₃)₃Cl₂ or a Ru(PPh₃)₃Cl₂ and TMSOOTMS system [15]. Ishii and co-workers successfully achieved aerobic oxidation using Ru(PPh₃)₃Cl₂ as the catalyst in the presence of hydroquinone without diminishing chemoselectivity [16]. Several ruthenium catalytic systems have been reported with a wide range of oxidants viz., *tert*-butyl hydroperoxide [17],

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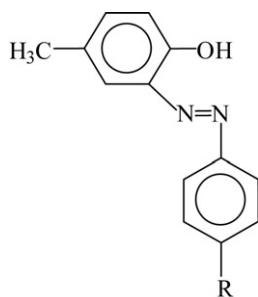


Fig. 1. Structure of 2-(aryloxy)phenol ligands, where R = H: H₂ap-H; Cl: H₂ap-Cl; Me: H₂ap-Me; OMe: H₂ap-OMe; OEt: H₂ap-OEt.

chloramine-T [18], benzoquinone [19], hydrogen peroxide [20], molecular oxygen [21], iodosylbenzene [22], NaIO₄ [23] and *N*-methylmorpholine-*N*-oxide (NMO) [18,24]. Further, the –N–N– and –O–N– donors of the ligands play an important role in the catalytic reactions. In addition, large number of transition metal phosphine/arsine complexes have been used in catalysis due to their characteristic steric and electronic properties [25]. In contrast to the considerable growth of literature on the chemistry of orthometallated complexes, to the best of our knowledge there are no reports available for catalytic oxidation of alcohols by cyclometallated ruthenium(II) 2-(aryloxy)phenolate complexes incorporating C–, N– and O– donors and triphenylarsine in the presence of NMO.

In view of the rich interest to understand these simple and inexpensive C, N, O donor ligands towards ruthenium, we have synthesized and characterized series of orthometallated ruthenium(II) carbonyl complexes containing 2-(aryloxy)phenol ligands and triphenylarsine. The molecular and electronic structure of the bivalent complexes are probed with the help of X-ray crystal structure in combination with FT-IR, ¹H NMR, electronic spectroscopy and emission properties. The relative stabilities of oxidation and reduction states are monitored electrochemically. Further, the synthesized complex effectively catalyze towards oxidation of primary and secondary alcohols in the presence of NMO as co-oxidant. The following 2-(aryloxy)phenol ligands (Fig. 1) were used to synthesis the mononuclear ruthenium(II) carbonyl complexes.

2. Experimental

2.1. Physical methods

The analysis of carbon, hydrogen and nitrogen were performed in a Carlo-Erba 1106-model 240 Perkin-Elmer analyzer at Sophisticated Test and Instrumentation Centre (STIC), Cochin University, Kochi, India. FT-IR spectra were recorded in KBr pellets with a JASCO 400 plus spectrophotometer. A CARY 300 Bio UV-visible Varian spectrophotometer was used to record the electronic spectra. ¹H NMR spectra were recorded on a Bruker 400 MHz instrument using tetramethylsilane (TMS) as an internal reference. Emission intensity measurements were carried out by using a Jasco FP-6500 spectrofluorimeter with 5 nm exit slit. Electrochemical measurements were made using a Prince-

ton EG and G-PARC model potentiostat using a glassy carbon working electrode, Pt wire as counter electrode and all the potentials were referenced to the Ag/AgCl electrode. Melting points were recorded with a Boetius micro-heating table and are uncorrected. The catalytic yields were determined using a HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness.

2.2. Materials

All the reagents used were chemically pure or analytical reagent grade. Solvents were purified and dried according to standard procedures. RuCl₃·3H₂O was purchased from Loba Chemie Pvt. Ltd., Bombay, India and was used without further purification. The alcohols and their corresponding ketones or aldehydes, which were used in the catalytic studies, were purchased from Merck and Aldrich.

2.3. Synthetic methods

The ruthenium(II) precursor complex [RuHCl(CO)(AsPh₃)₃], was prepared according to literature method [26]. The 2-(aryloxy)phenol ligands were prepared by coupling diazotized aniline and *p*-substituted anilines with *p*-cresol [27].

2.3.1. Synthesis of ruthenium(II) carbonyl 2-(aryloxy)phenolate complexes

Synthesis of ruthenium(II) carbonyl 2-(aryloxy)phenolate complexes was carried out under strictly anhydrous conditions. The ruthenium(II) complex [RuHCl(CO)(AsPh₃)₃] [0.16 mmol; 0.150 g] and 2-(aryloxy)phenol ligands (H₂ap-R) (where R = –H, –Cl, –Me, –OMe, –OEt) (0.16 mmol; 0.033–0.041 g) were taken in 20 ml benzene. The mixture was heated under reflux for 5 h until a deep green solution was obtained and the reactions were monitored by thin layer chromatography. The solvent was then evaporated under reduced pressure, which was subjected to purification by silica gel column chromatography. On elution with chloroform the separated green band was collected. The ruthenium complexes were obtained as crystalline solid of yield ~70% upon complete evaporation of the solvent.

2.3.1.1. [Ru(*ap*-H)(AsPh₃)₂(CO)] (1). Anal. Calcd. for C₅₀H₄₀N₂O₂As₂Ru: C, 63.09; H, 4.23; N, 2.94; found: C, 62.87; H, 4.06; N, 2.83. FT-IR (KBr disc, cm⁻¹): 1934, 1382, 1299. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 6.75–8.15 (m, Ar-H), 1.24 (s, 3H, CH₃). UV λ_{max} (nm) (ε (M⁻¹ cm⁻¹)): 545 (1328), 402 (5572), 323 (11,632), 269 (14,772). Emission λ_{max} (nm): 464.

2.3.1.2. [Ru(*ap*-Cl)(AsPh₃)₂(CO)] (2). Anal. Calcd. for C₅₀H₃₉N₂O₂ClAs₂Ru: C, 60.89; H, 3.98; N, 2.83; found: C, 60.73; H, 3.78; N, 2.62. FT-IR (KBr disc, cm⁻¹): 1940, 1380, 1310. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 6.90–8.61 (m, Ar-H), 1.18 (s, 3H, CH₃). UV λ_{max} (nm) (ε (M⁻¹ cm⁻¹)): 541 (1464), 404 (9180), 328 (14,836), 274 (17,682). Emission λ_{max} (nm): 502.

2.3.1.3. [Ru(ap-Me)(AsPh₃)₂(CO)] (3). Anal. Calcd. for C₅₁H₄₂N₂O₂As₂Ru: C, 63.42; H, 4.38; N, 2.89; found: C, 63.13; H, 4.17; N, 2.65. FT-IR (KBr disc, cm⁻¹): 1937, 1375, 1285. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 6.85–8.15 (m, Ar-H), 2.24 (s, 3H, CH₃), 1.30 (s, 3H, CH₃). UV λ_{max} (nm) (ε (M⁻¹ cm⁻¹)): 549 (1960), 400 (4920), 335 (11,965), 272 (14,944). Emission λ_{max} (nm): 440.

2.3.1.4. [Ru(ap-OMe)(AsPh₃)₂(CO)] (4). Anal. Calcd. for C₅₁H₄₂N₂O₃As₂Ru: C, 62.38; H, 4.31; N, 2.85; found: C, 62.17; H, 4.16; N, 2.73. FT-IR (KBr disc, cm⁻¹): 1937, 1389, 1315. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.2–8.1 (m, Ar-H), 1.34 (s, 3H, CH₃), 3.95 (s, 3H, OCH₃). UV λ_{max} (nm) (ε (M⁻¹ cm⁻¹)): 544 (1924), 399 (6040), 336 (12,980), 275 (15,392). Emission λ_{max} (nm): 482.

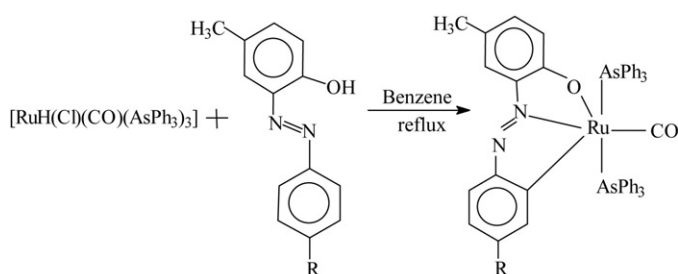
2.3.1.5. [Ru(ap-OEt)(AsPh₃)₂(CO)] (5). Anal. Calcd. for C₅₂H₄₄N₂O₃As₂Ru: C, 62.71; H, 4.45; N, 2.81; found: C, 62.59; H, 4.29; N, 2.73. FT-IR (KBr disc, cm⁻¹): 1945, 1373, 1311. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 6.75–7.85 (m, Ar-H), 1.20 (s, 3H, CH₃), 4.01 (q, 2H, OCH₂), 1.45 (t, 3H, CH₃). UV λ_{max} (nm) (ε (M⁻¹ cm⁻¹)): 537 (1328), 395 (10,668), 331 (11,704), 263 (14,832). Emission λ_{max} (nm): 496.

2.4. X-ray crystallography

Single crystal suitable for X-ray diffraction was grown from mixture of chloroform/acetonitrile solution at room temperature. The single crystals of suitable size were covered with Paratone oil, mounted on the top of a glass fiber, and transferred to a Stoe IPDS diffractometer using mono-chromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were collected at 183 K. Corrections were made for Lorentz and polarization effects as well as for absorption (numerical). Structures were solved by a direct method using SHELXS-97 for Sir 97 and were refined by the full-matrix least-squares method on F^2 with SHELXL-97 [28]. Non-hydrogen atoms were refined with anisotropy thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

2.5. Catalytic oxidation procedure

Catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones by ruthenium(II) carbonyl complex was studied in the presence of NMO as co-oxidant. A typical reaction using the complex [Ru(ap-Cl)(AsPh₃)₂(CO)] (2) as a catalyst and primary or secondary alcohol as substrates at a 1:100 molar ratio was conducted as follows. A solution of ruthenium complex (2) (0.01 mmol) in 20 cm³ CH₂Cl₂ was added to the solution of substrate (1 mmol) and NMO (3 mmol). The solution mixture was refluxed for 3 h and the solvent was then evaporated from the mother liquor under reduced pressure. The residue was then extracted with pet. ether (60–80 °C) (20 cm³) and was analyzed by GC. The oxidation products are commercially available, and were identified by GC co-injection with authentic samples.



Scheme 1. Structure of cyclometallated ruthenium(II) complexes, where R = H; ap-H (1), R = Cl; ap-Cl (2), R = Me; ap-Me (3), R = OMe; ap-OMe (4), R = OEt; ap-OEt (5).

3. Results and discussion

3.1. Synthesis

Organoruthenium complexes of the general formula [Ru(ap-R)(AsPh₃)₂(CO)] (where ap-R = CNO donors of 2-(aryloxy)phenolate ligands) were synthesized by the reaction of [RuHCl(CO)(AsPh₃)₃] precursor with equal molar of respective 2-(aryloxy)phenolate ligands under reflux in dry benzene. The 2-(aryloxy)phenolate ligands were observed to undergo C–H activation at one *ortho* position of the phenyl ring in the aryloxy fragment leading to the formation of five-membered cyclometallated complexes (Scheme 1). It has been observed that aryloxy phenolate ligands replace one hydride, one chloride and one AsPh₃ from ruthenium(II) precursor and the oxidation state of ruthenium remains unchanged during the formation of orthometallated species. All the complexes are green in colour and found to be air stable in both the solid and liquid states at room temperature, and non-hygroscopic in nature. The synthesized ruthenium(II) carbonyl complexes are highly soluble in common solvents such as chloroform, dichloromethane, toluene and benzene producing intense green solutions. Elemental analyses (C, H and N) were consistent with the composition proposed for all complexes.

3.2. FT-IR spectroscopy

The IR spectra of all the ligands exhibit significant bands around 1420–1435 and 1268–1278 cm⁻¹ which are tentatively assigned to $\nu_{\text{N=N}}$ and phenolic $\nu_{\text{C-O}}$ stretching, respectively. On complexation $\nu_{\text{N=N}}$ appears at 1373–1389 cm⁻¹ and the red shift corroborates the N (azo) coordination. In the spectra of all the complexes the coordination through phenolic oxygen is confirmed by the increase in C–O at higher frequencies in the region 1285–1315 cm⁻¹. The positive shift is further supported by the disappearance of the ν_{OH} band in the range 3430–3454 cm⁻¹ in all the complexes. The spectra of each complex shows a strong band in the region 1934–1945 cm⁻¹ due to the coordinated $\nu_{\text{C=O}}$ groups. Further, these complexes show a strong band near 530, 695, 740 and 1557 cm⁻¹ indicating the presence of coordinated AsPh₃ ligands. Besides, all the complexes show strong bands corresponding to $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ in the region 440–464 and 510–545 cm⁻¹, respectively [29–31].

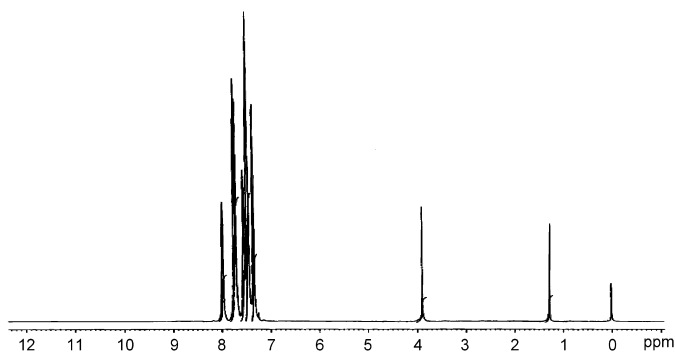


Fig. 2. ^1H NMR spectrum of complex (4).

3.3. NMR spectroscopy

The ^1H NMR spectra of the $[\text{Ru}(\text{ap-R})(\text{AsPh}_3)_2(\text{CO})]$ complexes have been recorded in CDCl_3 solution (Fig. 2). All the complexes show multiplets at δ 6.75–8.60 ppm due to the coordinated AsPh_3 ligands. Among the expected aromatic proton signals for the coordinated ap-R ligand, most have been clearly observed while a few could not be detected due to their overlap with their AsPh_3 signals. The distinct methyl resonance is displayed near δ 1.18–1.34 ppm for *p*-cresol fragment of 2-(arylo)phenolate ligands. Additional methyl signals are observed as singlet for complex 3 at δ 2.24 ppm and the methoxy signals are observed as singlet for complex 4 at δ 3.95 ppm. A triplet is observed for methyl protons for complex 5 at δ 1.45 ppm and OCH_2 protons appears as quartet in the region δ 4.01 ppm. A sharp singlet appeared for OH proton of all 2-(arylo)phenol ligands in the region δ 13.0 ppm is absent in all the complexes [32].

3.4. Electronic absorption spectroscopy

Electronic spectra of the complexes have been recorded in dichloromethane solution and a representative spectrum is shown in Fig. 3. All the ruthenium(II) 2-(arylo)phenolate complexes show three to four intense absorptions in the visible and ultraviolet region 549–263 nm. The intense absorption in the

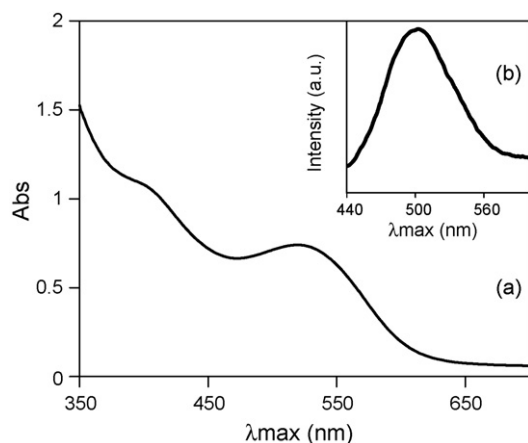


Fig. 3. (a) Electronic and (b) emission spectrum of complex 2.

visible region at 549–537 nm and the absorption at 395–404 nm are probably due to metal-to-ligand charge transfer transitions. The charge transfer transitions taking place from the highest filled ruthenium t_2 orbital (highest occupied molecular orbital) to the vacant π^* ($-\text{N}=\text{N}-$) orbital of the 2-(arylo)phenolate ligand (lowest unoccupied molecular orbital) or to the higher energy vacant orbitals of other fragment of ligands. It has been observed that multiple charge transfer transition in such mixed ligand complexes may result from the splitting of d orbitals of the metal and thus lower symmetry. Therefore, these may be a possibility of mixing of singlet and triplet configurations in the excited state through spin-orbit coupling [33]. In addition, the other high intensity bands in the 334–263 nm regions were characterized by ligand-centered (LC) transitions taking place in the three coordinated 2-(arylo)phenolate ligand. The absorption in the ultraviolet region may be attributed to usual $n-\pi^*$, $\pi-\pi^*$ transitions occurring within ligand orbitals. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around ruthenium(II) ion, similar to that of other ruthenium(II) octahedral complexes [34].

3.5. Emission study

Emission study of ruthenium(II) carbonyl complexes of ligands containing strong chromophoric groups often show in addition to intense MLCT transitions interesting luminescence properties [35,36], such properties have also been explored in the $[\text{Ru}(\text{ap-R})(\text{AsPh}_3)_2(\text{CO})]$ complexes. The luminescence studies were carried out in dichloromethane solutions at ambient temperature (298 K). When an excitation wavelength corresponding to the lowest energy absorption (\sim 500 nm) was used, no emission was observed. However, when an excitation wavelength of \sim 400 nm was used, all the $[\text{Ru}(\text{ap-R})(\text{AsPh}_3)_2(\text{CO})]$ complexes showed strong emission (Fig. 3) in the range of 440–502 nm. This indicates that transition of a metal electron to the metallated phenyl ring (or) *p*-cresol ring leads to photochemical excited state, which is much more stable compared to excitation of metal electron to π^* (azo $-\text{N}=\text{N}-$) [37].

3.6. X-ray crystallography

To find out the coordination mode of the 2-(arylo)phenolate ligands in these complexes as well as the stereochemistry of the complexes, the structure of one of the complexes of this family $[\text{Ru}(\text{ap-Cl})(\text{AsPh}_3)_2(\text{CO})]$ (2) has been determined by X-ray crystallography and ORTEP view of the complex is shown in Fig. 4. The summary of single crystal X-ray structure refinement is shown in Table 1 and selected bond parameters are listed in Table 2. The structure shows that the 2-(arylo)phenolate ligand is coordinated to ruthenium in the expected tridentate fashion through C, N and O in addition two AsPh_3 and one carbonyl groups. Ruthenium is therefore sitting in a $\text{C}_2\text{N}_1\text{O}_1\text{As}_2$ coordination environment, which is distorted octahedral in nature as reflected in all the bond parameters around ruthenium. The 2-(arylo)phenolate ligand binds the metal center at O, N and C forming two five-membered

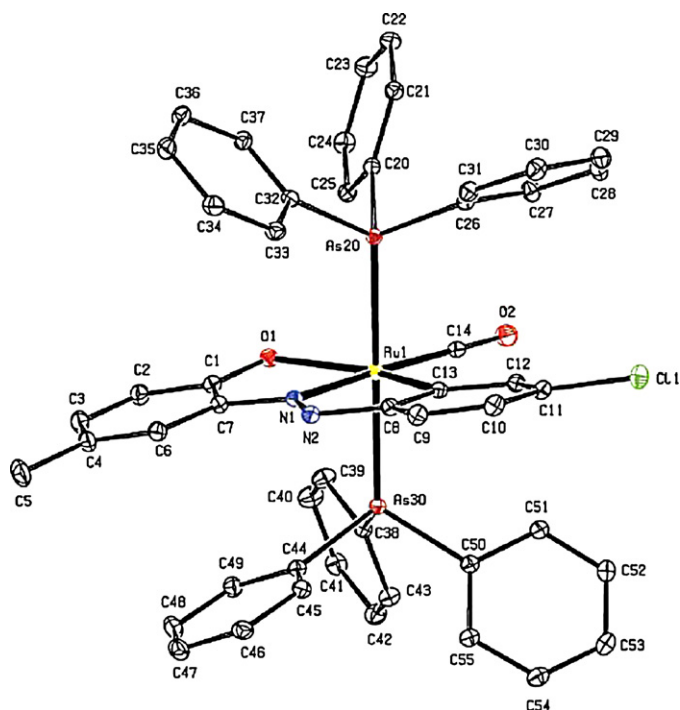


Fig. 4. ORTEP view of $[\text{Ru}(\text{ap-Cl})(\text{AsPh}_3)_2(\text{CO})]$ (**2**), the hydrogen atoms were omitted for clarity.

Table 1
Crystal data and structure refinement for complex $[\text{Ru}(\text{ap-Cl})(\text{AsPh}_3)_2(\text{CO})]$ (**2**)

Empirical formula	$\text{C}_{50}\text{H}_{39}\text{As}_2\text{ClN}_2\text{O}_2\text{Ru}$
Formula weight	986.19
Temperature	183(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 31.8258(13)$ Å, $\alpha = 90^\circ$ $b = 12.4205(4)$ Å, $\beta = 91.869(5)^\circ$ $c = 10.9318(4)$ Å, $\gamma = 90^\circ$
Volume	$4319.0(3)$ Å ³
Z	4
Density (calculated)	1.517 Mg/m ³
Absorption coefficient	1.988 mm ⁻¹
$F(000)$	1984
Crystal size	0.25 mm \times 0.22 mm \times 0.11 mm
Crystal description	Green block
Theta range for data collection	2.77 – 30.45°
Index ranges	$-45 \leq h \leq 45$, $-17 \leq k \leq 17$, $-13 \leq l \leq 15$
Reflections collected	41,435
Independent reflections	13,084 [$R(\text{int}) = 0.0561$]
Reflections observed	9433
Criterion for observation	$>2\sigma(I)$
Completeness to $\theta = 30.45^\circ$	99.6%
Absorption correction	Numerical
Maximum and minimum transmission	0.8292 and 0.6619
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13084/1/523
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0474$, $wR2 = 0.1289$
R indices (all data)	$R1 = 0.0629$, $wR2 = 0.1346$
Largest diff. peak and hole	1.075 and -0.534 Einstein Å ⁻³

Table 2
Selected bond lengths (Å) and bond angles ($^\circ$) of complex **2**

Bond lengths (Å)	
Ru(1)–C(14)	1.910(4)
Ru(1)–N(1)	2.048(3)
Ru(1)–C(13)	2.055(3)
Ru(1)–O(1)	2.218(2)
Ru(1)–As(20)	2.4527(4)
Ru(1)–As(30)	2.4616(4)
C(1)–O(1)	1.299(4)
C(4)–C(5)	1.518(5)
C(7)–N(1)	1.409(4)
C(8)–N(2)	1.416(4)
C(14)–O(2)	1.118(4)
Bond angles ($^\circ$)	
C(14)–Ru(1)–N(1)	175.82(13)
C(14)–Ru(1)–C(13)	98.70(14)
N(1)–Ru(1)–C(13)	77.26(12)
C(14)–Ru(1)–O(1)	105.92(12)
N(1)–Ru(1)–O(1)	78.17(10)
C(13)–Ru(1)–O(1)	155.25(10)
C(14)–Ru(1)–As(20)	88.11(9)
N(1)–Ru(1)–As(20)	92.71(7)
C(13)–Ru(1)–As(20)	87.16(8)
O(1)–Ru(1)–As(20)	91.04(6)
C(14)–Ru(1)–As(30)	90.64(9)
N(1)–Ru(1)–As(30)	88.60(7)
C(13)–Ru(1)–As(30)	94.00(8)
O(1)–Ru(1)–As(30)	88.36(6)
As(20)–Ru(1)–As(30)	178.419(15)

chelate rings with a bite angle of $\text{N}(1)\text{--Ru--O}(1) = 78.17(17)^\circ$ and $\text{N}(1)\text{--Ru--C}(13) = 77.26(12)^\circ$ and a bond length of $\text{Ru--C}(13) = 2.055(3)$ (Å), $\text{Ru--O}(1) = 2.218(2)$ (Å) and $\text{Ru--N}(1) = 2.048(3)$ (Å). The two AsPh_3 groups are mutually *trans* to each other and are almost equidistant from the metal center, the bond distance being $\text{Ru--As}(20) = 2.452(4)$ (Å) and $\text{Ru--As}(30) = 2.461(4)$ (Å). The $\text{Ru}^{\text{II}}\text{--CO}(\text{Ru--C}(14))$ bond length is found to be $1.910(4)$ (Å) which is much shorter than the $\text{Ru--C}(13)$ bond length.

3.7. Cyclic voltammetry

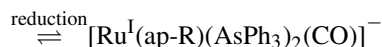
The electron transfer properties of the $[\text{Ru}(\text{ap-R})(\text{AsPh}_3)_2(\text{CO})]$ complexes have been studied in dichloromethane solution by cyclic voltammetrically at a glassy carbon working electrode and all the potentials are expressed with reference to Ag/AgCl . Voltammetric data are presented in Table 3 and a representative cyclic voltammogram is shown in Fig. 5. All these complexes (1×10^{-3}) show two voltammetric response, one quasi-reversible oxidation ($\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$) with $E_{1/2}$ values $+0.75$ to $+0.86$ V and one quasi-reversible reduction with $E_{1/2}$ values -0.50 to -0.57 V with respect to Ag/AgCl at a scan rate 100 mV s^{-1} . In general, the changes in oxidation and reduction potentials are probably due to the relative stabilization of ruthenium(II) over ruthenium(III) by a combination of σ and π effects exhibited by the ligand. The oxidation discerned is quasi-reversible in nature, characterized by a rather large peak-to-peak separation (ΔE_p) of 140 – 200 mV and the cathodic peak current (i_{pc}) is less than that of the anodic peak current (i_{pa}).

Table 3
Electrochemical data of ruthenium(II) carbonyl 2-(arylo)phenolate complexes

Complexes	Ru ^{III} /Ru ^{II}				Ru ^{II} /Ru ^I			
	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV)	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV)
1	0.75	0.89	0.82	140	−0.44	−0.60	−0.52	160
2	0.95	0.77	0.86	180	−0.40	−0.60	−0.50	200
3	0.90	0.72	0.81	180	−0.48	−0.66	−0.57	180
4	0.84	0.65	0.75	190	−0.45	−0.59	−0.52	140
5	0.84	0.70	0.77	140	−0.43	−0.59	−0.51	160

Supporting electrolyte: NBu_4ClO_4 (0.005 M); complex: 0.001 M; solvent: CH_2Cl_2 ; $\Delta E_p = E_{pa} - E_{pc}$ where E_{pa} and E_{pc} are anodic and cathodic potentials, respectively; $E_{1/2} = 0.5(E_{pa} + E_{pc})$; scan rate: 100 mV s^{-1} .

The one electron nature of this oxidation has been verified by comparing its current height (i_{pa}) with that of the standard ferrocene/ferrocenium couple under identical experimental conditions [38]. The redox potentials ($E_{1/2}$) are independent of the various scan rates, supporting quasi-reversibility. The couples at more positive and less negative potentials are believed to be corresponding to metal oxidation and metal reduction, respectively:



The oxidation and reduction potential is found to be sensitive to the nature of the substituents (R) present in the 2-(arylo)phenolate ligand increasing linearly (Fig. 6) with increasing electron withdrawing character of the substituents (expressed in terms of the Hammett substituent constant σ). The plot of $E_{1/2}$ versus σ (σ -Hammett constant of R: $\text{OCH}_3 = -0.27$, $\text{OC}_2\text{H}_5 = -0.24$, $\text{CH}_3 = -0.17$, $\text{H} = 0.00$, $\text{Cl} = 0.23$) [39] is linear for both couples with slopes (ρ) of 0.57 V ($\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$) and 0.21 V ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{I}}$) of all complexes. The linear correlation of $E_{1/2}$ versus σ with reasonable slopes (ρ) clearly shows that a single substituent on the 2-(arylo)phenolate ligands, which is four bonds away from the metal center, can influence the metal centered redox potential in a predictable manner. Hence, it is inferred from the electrochemical data that the present ligand system is ideally suitable for stabilizing the higher oxidation

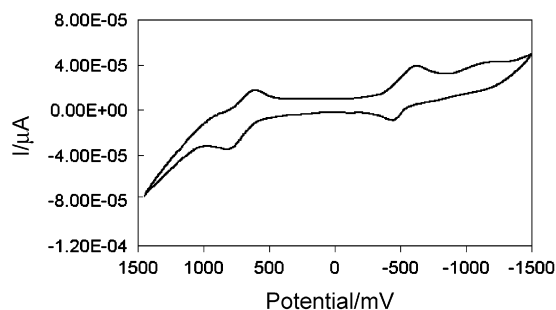


Fig. 5. Cyclic voltammogram of complex (4).

state of ruthenium ion and that the electron transfer reactions take place without gross changes in the stereochemistry of the complexes [40].

3.8. Catalytic oxidation

Ruthenium mediated oxidations are finding increasing application due to the unique properties of this extremely versatile transition metal, whose oxidation states can vary from $-II$ to $+VIII$ and this prompted us to carry out this type of reaction. The present work describes the catalytic oxidation of primary and secondary alcohols by the synthesized ruthenium(II) 2-(arylo)phenolate complex $[\text{Ru}(\text{ap-Cl})(\text{AsPh}_3)_2(\text{CO})]$ in CH_2Cl_2 in the presence of NMO and the by product water was removed by using about 0.25 g of molecular sieves. Complex $[\text{Ru}(\text{ap-Cl})(\text{AsPh}_3)_2(\text{CO})]$ (2) oxidizes primary alcohols to corresponding aldehydes and secondary alcohols to ketones with moderate to high conversion and the results are listed in Table 4 (entries 1–15). The aldehydes or ketones formed after 3 h of refluxing were determined by GC, and 2,4-

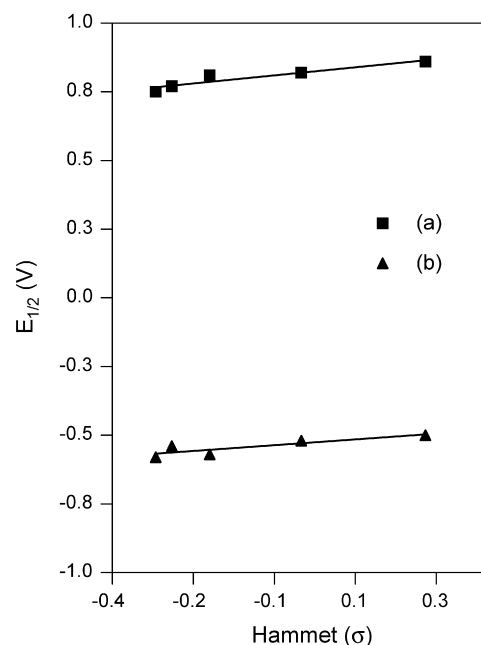
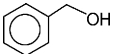
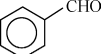
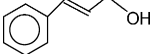
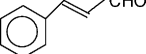
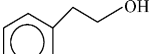
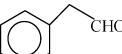
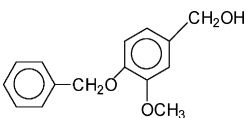
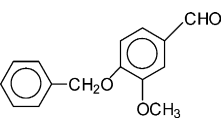
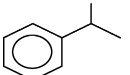
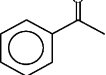
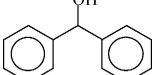
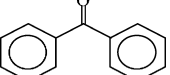
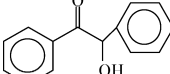
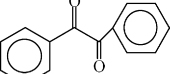










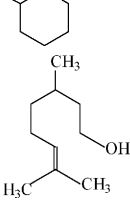
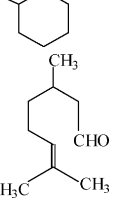
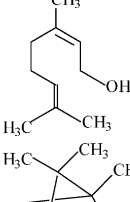
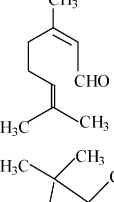
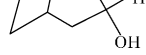
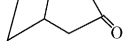


Fig. 6. Least-squares plot of $E_{1/2}$ values oxidation ($\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$) and reduction ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{I}}$) potentials of complexes 1–5 (where a = oxidation, b = reduction).

Table 4
Catalytic oxidation of alcohols to corresponding aldehydes and ketones with complex [Ru(ap-Cl)(AsPh₃)₂(CO)] (2) in the presence of NMO

Entry	Substrate	Product	Yield ^a (%)	Turnover ^b
1			60	60
2			>93	93
3			19 ^c (8) ^d	19
4			45 ^c	45
5			>99	99
6			>98	98
7			65 ^c	65
8			>94	94
9			>98	98
10			98	98
11			>99	99
12			>93	93
13			19 ^c (8) ^d , 38 ^c (14) ^d	19, 38
14			11 ^c (8) ^d , 38 ^c (14) ^d	11, 38
15			19 ^c (8) ^d	19

Substrate (1 mmol); NMO (3 mmol); complex (0.01 mmol); solvent dichloromethane.

^a Yield of product was determined using a HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness and by comparison with authentic samples.

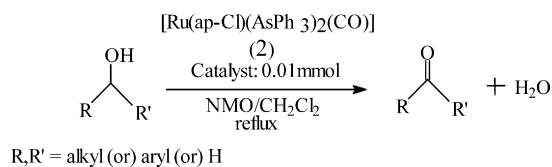
^b Moles of product per mole of catalyst.

^c Isolated yield and confirmed by derivative.

^d Reaction hours.

^e Isolated yield, characterized by melting point, ¹H NMR and IR.

dinitrophenylhydrazone derivatives and there was no detectable oxidation in the absence of ruthenium complex.



Results of the present investigation suggest that the complexes are able to react efficiently with NMO to yield high valent ruthenium-oxo species responsible for dehydrogenation of alcohols. This was further supported by spectral changes that occur by addition of NMO to a dichloromethane solution of the ruthenium(II) complexes. The appearance of peak at 390 nm is attributed to the formation of $\text{Ru}^{\text{IV}}=\text{O}$ species (Fig. 7), which is in conformity with other oxo ruthenium(II) complexes [41–43]. Further support in favor of the formation of such species is identified by the IR spectrum of the solid mass (obtained by evaporation of the resultant solution to dryness), which shows a band at 860 cm^{-1} , characteristic of $\text{Ru}^{\text{IV}}=\text{O}$ species [41,42].

The oxidation of benzylalcohol to benzaldehyde results in 60% conversion and 4-benzyloxy-3-methoxy benzyl alcohol is converted to 4-benzyloxy-3-methoxy benzaldehyde yielded in 45%. Unsaturated cinnamyl alcohol is oxidized to cinnamaldehyde with >93% conversion without cleavage of carbon–carbon double bonds. This is an important characteristic of the ruthenium/NMO system. In addition to phenyl ethylalcohol, citronellol and geraniol takes longer reaction time for the conversion to corresponding aldehydes, which are confirmed by NMR and their yields are determined by 2,4-dinitrophenylhydrazone derivatives. The complex catalyzes the oxidation of aromatic secondary alcohols such as benzhydrol and 1-phenyl ethanol effectively into corresponding ketones in >97% yield. In the case of benzoin the oxidation product benzil is isolated and characterized by melting points, IR and ^1H NMR. In view of comparative evaluation, oxidation of benzoin is carried out in the presence of PPh_3 analogue $[\text{Ru}(\text{ap-Cl})(\text{PPh}_3)_2(\text{CO})]$ and the yield of 63% is attained, which is almost equal to catalytic efficiency of $[\text{Ru}(\text{ap-Cl})(\text{AsPh}_3)_2(\text{CO})]$. Further, the complexes effectively catalyze the aliphatic alcohols like butan-2-ol and 4-methylpentan-2-ol to the corresponding ketones with high conversions higher than 93% and the conversion of borneol is found to be lower. Moreover, the five, six and substituted six-membered cyclic alcohols are efficiently converted into corresponding ketones with high conversions higher than 92%. The *N*-methylmorpholine and water are the only by products during the course of the reaction. It has been observed that the complex **2** has high catalytic efficiency in the case of oxidation of primary and secondary alcohols when compared to similar ruthenium complexes as catalysts in the presence of NMO/*t*-BuOOH reported earlier [24(b),44–47].

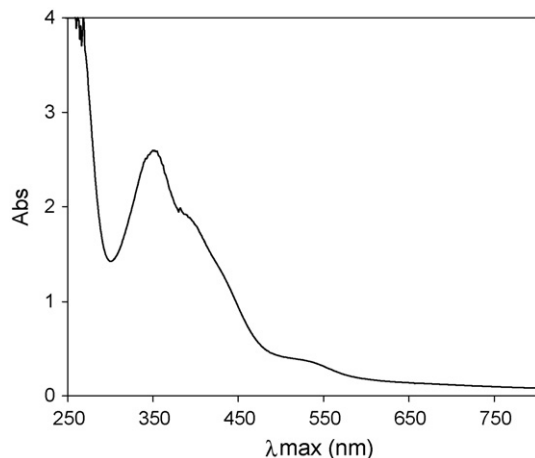


Fig. 7. Spectra of complex (2) + NMO (spectra taken after 30 min of mixing) in dichloromethane.

$[\text{Ru}(\text{ap-Cl})(\text{AsPh}_3)_2(\text{CO})]$. Further, the complexes effectively catalyze the aliphatic alcohols like butan-2-ol and 4-methylpentan-2-ol to the corresponding ketones with high conversions higher than 93% and the conversion of borneol is found to be lower. Moreover, the five, six and substituted six-membered cyclic alcohols are efficiently converted into corresponding ketones with high conversions higher than 92%. The *N*-methylmorpholine and water are the only by products during the course of the reaction. It has been observed that the complex **2** has high catalytic efficiency in the case of oxidation of primary and secondary alcohols when compared to similar ruthenium complexes as catalysts in the presence of NMO/*t*-BuOOH reported earlier [24(b),44–47].

4. Conclusion

A new class of cyclometallated ruthenium(II) carbonyl 2-(arylazo)phenolate complexes has been synthesized. The X-ray crystal structure of one of the complexes reveals a distorted octahedral environment around ruthenium. All the complexes exhibit characteristic metal-to-ligand charge transfer (MLCT) absorption and emission bands in the visible region. The complex (2) has proved to be a new and efficient catalyst in the oxidation of primary and secondary alcohols in the presence of NMO.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with Cambridge crystallographic center, CCDC no. 261331. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).

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