Ruthenium(III) mediated C–H activation of azonaphthol: Synthesis, structural characterization and transfer hydrogenation of ketones

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Abstract

Treatment of [RuCl$_3$(PPh$_3$)$_3$] with 1-(arylazo)naphthol ligands in benzene under reflux afford air-stable new organoruthenium(III) complexes with general composition [Ru(an-R)Cl(PPh$_3$)$_2$] (where, R = H, Cl, CH$_3$, OCH$_3$, OC$_2$H$_5$) in fairly good yield. The 1-(arylazo)naphtholate ligands behave as dianionic tridentate C, N, O donors and coordinates to ruthenium through phenolic oxygen, azo nitrogen and ortho carbon generate two five-membered chelate rings. The composition of the complexes have been established by analytical (elemental analysis and magnetic susceptibility measurement) and spectral (FT-IR, UV–Vis, EPR) methods. The complexes are paramagnetic (low-spin, d^5) in nature and in dichloromethane solution show intense d–d transitions and ligand-to-metal charge transfer (LMCT) transitions in the visible region. The solution EPR spectrum of complex [Ru(an-CH$_3$)Cl(PPh$_3$)$_2$] (3) in dichloromethane at 77 K shows rhombic distortion around the ruthenium ion with three different 'g' values ($g_x \neq g_y \neq g_z$). The single crystal structure of the complex [Ru(an-OCH$_3$)Cl(PPh$_3$)$_2$] (4) has been characterised by X-ray crystallography, indicates the presence of a distorted octahedral geometry in these complexes. All the complexes exhibit one quasi-reversible oxidative response in the range 0.60–0.79 V (Ru^{IV}/Ru^{III}) and two quasi-reversible reductive responses (Ru^{III}/Ru^{II}; Ru^{II}/Ru^{I}) within the range −0.50 to −0.62 V and −0.93 to −0.98 V respectively. The formal potential of all the couples correlate linearly with the Hammett constant of the para substituent in arylazo fragment of the 1-(arylazo)naphtholate ligand. Further, the catalytic efficiency of one of the ruthenium complexes (4) was determined for the transfer hydrogenation of ketones with an excellent yield up to 99% in the presence of isopropanol/KOH.
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Keywords: Ru(III); C–H activation; Crystal structure; Electrochemistry; Catalytic transfer hydrogenation

1. Introduction

Coordination of ruthenium by ligand of different types is of significant importance [1–3] because of the fascinating reactivities exhibited by the resultant complexes and the nature of the ligand that dictates the property of those complexes. Among the various ligand systems, arylazo ligands **I** are potentially able to form M–C bonds or metallacycles due to π-acidic nature of the azo function [4]. Particularly the azo (–N=N–) group due to its strong π-acid character stabilizes ruthenium in lower oxidation states while phenolate oxygen being a hard base stabilizes the higher oxidation states of the metal ion [5]. It has been found in the literature that the arylazo phenol ligands are known to coordinate metal ions usually in a bidentate fashion with N, O donor forming a six-membered chelate ring. However, under forced conditions these ligands undergo C–H activation by transition metal ions and leads to the formation of cyclometalated compounds. Since, the first cyclometalated complex was synthesized [6], cyclometala-

tion has become an important part of organometallic chemistry and several reviews covering the subject have appeared [7,8].

I

II L = PPh$_3$ or AsPh$_3$

III

X = Cl or Br
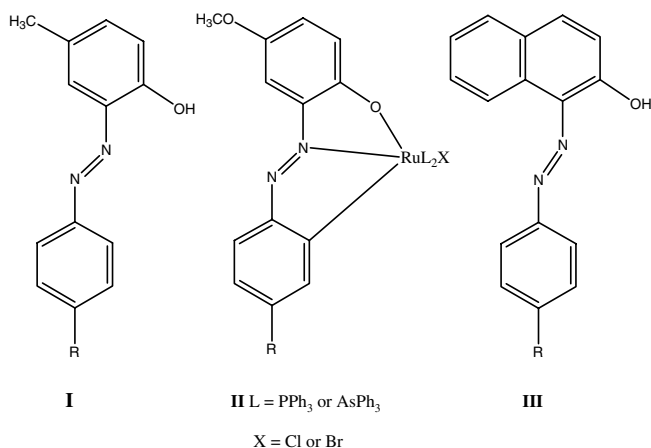
Cyclometalated compounds show important applications, such as their use in regiospecific organic and organometallic reactions [9], insertion reactions [10], the synthesis of new metal mesogenic compounds [11] and in biologically active compounds [12]. Even though a number of reports are known for cyclometalated ruthenium(II) complexes [13–15], only very little has been covered on cyclometalated ruthenium(III) complexes [16–19] **II** in the literature including our recent reports.

Further 1-(arylazo)naphthols **III** are also potential ligands that coordinate to metal ion normally through oxygen and nitrogen in a bidentate manner. The naphthyl group in this ligand is more reactive, a better electron donating agent and provides greater steric crowding compared to the phenyl ring. So far two reports are available on the reaction of these ligands with ruthenium(II) [15] and ruthenium(III) [5] precursors and in both the above said reactions the arylazo naphthols behaved as a monoanionic bidentate N, O donor ligands. In the present work we have used a set of 1-(arylazo)naphthol as targeted ligands **3** to synthesize new cyclometalated ruthenium(III) complexes via C–H activation. The interest behind the choice of this azonaphthol is that it can also act as dianionic tridentate C,N,O donor which generates a five-membered metallacycles.

Recent advances in hydrogenation catalysts are revolutionizing carbonyl reduction chemistry [20]. The hydrogenation of carbonyl compounds using *iso*-propanol as a hydrogen source to alcohols is one of the most applied processes in organic chemistry [21] as illustrated by several useful applications in recent years [22]. Among the different metal catalyzed hydrogenation reactions, ruthenium-based catalytic systems are found to be effective in the transfer hydrogenation of ketones [23] and imines [24,25]. The ability of ruthenium complexes to dehydrogenate alcohols and deliver the hydrides to a ketone [26] or an α,β-unsaturated ketone has made them useful as transfer hydrogenation

catalysts [27]. Pioneering work by Noyori, in the mid 1990s, showed that ruthenium complexes of the type [(diphosphine)-RuCl$_2$-(diamine)] used in 2-propanol in the presence of a base are very efficient and selective catalysts for the asymmetric reduction of unfunctionalised ketones [28]. Since Noyori's work using XylBinap [29] a number of other groups have demonstrated the use of other diphosphines that give rise to high activities and selectivities when used in this catalyst system [30]. Van Koten reported pincer-type arylruthenium(II) complexes containing the monoanionic terdentate NCN and PCP ligands and are used as active catalysts for the transfer hydrogenation of ketones in the presence of *i*-PrOH and KOH [31]. Further, transfer hydrogenation of ketones was efficiently carried out with a ruthenium(II) complex bearing the ligand 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine in isopropanol [32]. Hence, it is well known from the literature that most of the cyclometalated ruthenium(II) complexes [33] containing different types of ligand including chiral versions have been successfully used as effective catalysts for transfer hydrogenation of ketones and the ruthenium(III) complexes are completely neglected for this purpose.

Therefore we focused our interest on the synthesis, characterization and catalytic application of ruthenium(III) complexes and we have observed that the ruthenium(III) complexes show excellent performance in catalytic transfer hydrogenation of ketones than classical ruthenium(II) complexes. Herein, we describe the synthesis of a series of five cyclometalated ruthenium(III) complexes via C–H activation of 1-(arylazo)naphthol ligands. The molecular and electronic structure of the complexes are probed with the help of X-ray crystal structure, in combination with FT-IR, electronic and EPR spectra. The relative stabilities of oxidation and reduction states are monitored electrochemically. One of the complexes is employed as catalyst for ketone hydrogenation in the presence of 2-propanol and KOH.

2. Experimental

2.1. Materials and instrumentation

Commercial RuCl$_3$ · 3H$_2$O was purchased from Loba-Chemie Pvt. Ltd. All the reagents used were chemically pure and are of analytical reagent grade. The solvents were purified and dried according to standard procedures. The primary amines were purchased from Aldrich. The supporting electrolyte tetrabutyl ammonium perchlorate (*n*-Bu$_4$NClO$_4$) was dried in vacuum prior to use. The precursor complex [RuCl$_3$(PPh$_3$)$_3$] [34] was prepared by reported literature method. The azonaphthols were prepared by coupling diazotized aniline and *p*-substituted anilines with β-naphthol.

The microanalysis of carbon, hydrogen and nitrogen were recorded by analytic function testing Vario EL III CHNS elemental analyzer at STIC, Cochin University of Science and Technology, Cochin, India. Infrared spectra

were taken on a Jasco 400 Plus, FTIR Spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets. Electronic spectra of the complexes in dichloromethane were recorded on a Cary 300 Bio UV–Vis Varian spectrophotometer. The room temperature magnetic susceptibilities were measured on an EG and G model 155 vibrating sample magnetometer at SAIC, IIT, Chennai, India. EPR measurements were made with JEOL JES-FA200 X-band EPR spectrometer for powder samples at room temperature and solution at 77 K (liquid nitrogen) at Pondicherry University, Pondicherry, India. All spectra were calibrated with the help of DPPH ($g = 2.0037$). Cyclic voltammetric measurements were carried out using a Princeton EG and G-PARC model potentiostat. Results were obtained using dichloromethane solutions of [(n-C$_4$H$_9$)$_4$N](ClO$_4$) (TBAP) as supporting electrolyte under nitrogen atmosphere. A three electrode cell was employed with glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. The catalytic yields were determined using 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. Synthesis of ruthenium(III)1-(arylazo)naphtholate complexes

The complexes [Ru(L$^{1-5}$)(Cl)(PPh$_3$)$_2$] **1–5** were synthesized from the reactions of [RuCl$_3$(PPh$_3$)$_3$] with the ligands L^1–L^5 by following a general procedure strictly under anhydrous conditions.

[Ru(an-R)(Cl)(PPh$_3$)$_2$]. The ruthenium precursor [RuCl$_3$(PPh$_3$)$_3$] (0.15 mmol; 0.135 g) and 1-(arylazo)naphtholate ligands (H$_2$an–R) (where R = –H:H$_2$an–H; –Cl: H$_2$an–Cl; –Me:H$_2$an–Me; –OMe:H$_2$an–OMe; –OEt:H$_2$-an–OEt) (0.15 mmol; 0.037–0.044 g) were taken in 20 ml of benzene. The progress of the reaction was monitored periodically by TLC while the mixture was heated under reflux. After 12 h, the reaction mixtures were cooled to room temperature and solids, if any were filtered off. Filtrate was then evaporated under reduced pressure, which was then subjected to purification by using column chromatography using silica gel (100–200 mesh) and chloroform as eluent. A green solid complex was obtained on complete evaporation of the solvent. The elemental (CHN) analysis is consistent with the composition proposed for all the complexes.

[Ru(an-H)(Cl)(PPh$_3$)$_2$] (**1**). Yield: 45%; Anal. Calc. for C$_{52}$H$_{40}$ClN$_2$OP$_2$Ru: C, 68.78; H, 4.41; N, 3.08. Found: C, 68.62; H, 4.34; N, 2.96%; IR (KBr pellets): 1315 (ν_{C-O}), 1376 ($\nu_{N=N}$) cm^{-1}.

[Ru(an-Cl)(Cl)(PPh$_3$)$_2$] (**2**). Yield: 50%; Anal. Calc. for C$_{52}$H$_{39}$Cl$_2$N$_2$OP$_2$Ru: C, 66.26; H, 4.14; N, 2.97. Found: C, 66.10; H, 3.88; N, 2.84%; IR (KBr pellets): 1302 (ν_{C-O}), 1384 ($\nu_{N=N}$) cm^{-1}.

[Ru(an-Me)(Cl)(PPh$_3$)$_2$] (**3**). Yield: 54%; Anal. Calc. for C$_{53}$H$_{42}$ClN$_2$OP$_2$Ru: C, 69.04; H, 4.56; N, 3.04. Found: C, 68.88; H, 4.22; N, 2.89%; IR (KBr pellets): 1298 (ν_{C-O}), 1380 ($\nu_{N=N}$) cm^{-1}.

[Ru(an-OMe)(Cl)(PPh$_3$)$_2$] (**4**). Yield: 60%; Anal. Calc. for C$_{53}$H$_{42}$ClN$_2$O$_2$P$_2$Ru: C, 67.86; H, 4.48; N, 2.98. Found: C, 67.54; H, 4.19; N, 2.75%; IR (KBr pellets): 1312 (ν_{C-O}), 1378 ($\nu_{N=N}$) cm^{-1}.

[Ru(an-OEt)(Cl)(PPh$_3$)$_2$] (**5**). Yield: 62%; Anal. Calc. for C$_{54}$H$_{44}$ClN$_2$O$_2$P$_2$Ru: C, 68.12; H, 4.62; N, 2.94. Found: C, 67.98; H, 4.32; N%, 2.67; IR (KBr pellets): 1288 (ν_{C-O}), 1388 ($\nu_{N=N}$) cm^{-1}.

2.3. X-ray crystallography

Single crystals of [Ru(L^4)(Cl)(PPh$_3$)$_2$] (**4**) are grown by slow evaporation from a dichloromethane–methanol solution at room temperature. Significant crystal data collection and refinement parameters are listed in Table 3. A single crystal of suitable size was covered with Paratone oil, mounted on the top of a glass fiber, and transferred to a Stoe IPDS diffractometer using monochromated Mo Kα radiation ($kI = 0.71073$). Data were collected at 183 K. Corrections were made for Lorentz and polarization effects as well as for absorption (numerical). The structure was solved with direct method using SIR-97 [35] and was refined by full matrix least-squares method [36] on F^2 with SHELXL-97. Non-hydrogen atoms were refined with anisotropy thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

2.4. Typical procedure for catalytic transfer hydrogenation

Under an inert atmosphere a mixture containing ketones (3.75 mmol), the ruthenium catalyst (0.0125 mmol) and 0.0625 mmol of KOH was heated to reflux in 10 ml of *i*-PrOH for appropriate period of time as mentioned. The catalyst was removed as precipitate from the reaction mixture by the addition of diethyl ether followed by filtration and subsequent neutralization with 5 ml of 1 M HCl. Then the ether layer was passed through a short path of silica gel and the filtrate was subjected to GC analysis. The hydrogenated product was identified and was determined with authentic sample.

3. Results and discussion

A series of organoruthenium(III) derivatives was conveniently accessed from the direct cyclometalation of azonaphthols with [RuCl$_3$(PPh$_3$)$_3$]. The cyclometalated compounds of the general formula [Ru(L$^{1-5}$)Cl(PPh$_3$)$_2$] (where L = 1-(arylazo)naphtholate ligands) described in this paper were synthesized in good yield via C–H activation of five 1-(arylazo)naphthol ligands abbreviated as (H$_2$an–R) (where R = –H, –Cl, –Me, –OMe, –OEt) by [RuCl$_3$(PPh$_3$)$_3$] in dry benzene in equimolar ratio. It has been observed that the 1-(arylazo)naphthol ligands behave as dianionic tridentate and replace two chlorides and one triphenylphosphine from the ruthenium(III) precursor. Since the Ru(III) center is a strong Lewis acid, the

activation of C–H of the ligand proceeded effectively and the oxidation state of ruthenium remains unchanged during the formation of cyclometalated species. All the complexes are found to be air stable in both the solid and the liquid states at room temperature and are non-hygroscopic in nature. The synthesized ruthenium(III) complexes are soluble in common solvents such as chloroform, dichloromethane, toluene and benzene producing intense green solution.

3.1. Characterization

Infrared spectra of the complexes $[Ru(L^{1-5})Cl(PPh_3)_2]$ are very similar and they exhibit many sharp and strong vibrations within 1600–400 cm^{-1}. However, the infrared spectra of all the ligands exhibit bands around 1425–1434 cm^{-1} and 1270–1278 cm^{-1} corresponding to azo $v_{(-N=N-)}$ and phenolic $v_{(C-O)}$ stretching frequencies respectively. On complexation $v_{(-N=N-)}$ appears at lower frequency in the range 1376–1388 cm^{-1} and this red shift supports the coordination of N(azo) to ruthenium ion [37]. The band corresponding to phenolic $v_{(C-O)}$ stretching is shifted to higher frequency in the range 1288–1315 cm^{-1} in all the complexes confirming that the other coordination site is the phenolic oxygen [38]. This was further supported by the disappearance of $v_{(OH)}$ band in the range 3439–3450 cm^{-1} in all the complexes. In addition, the bands near 535, 695, 740, 1556 cm^{-1} in the spectra of all the complexes are attributed to the presence of PPh$_3$ ligands [37,39]. The confirmation for the cyclometalation is shown by extra bands in the IR spectrum of the complexes in the 700–800 cm^{-1} and 1100 cm^{-1} regions characteristic of an ortho-disubstituted benzene nucleus [40].

Electronic spectra of all the complexes have been recorded in dichloromethane solution in the range 800–200 nm. Spectral data are displayed in Table 1 and a selected spectrum is shown in Fig. 1. The ground state of ruthenium(III) in an octahedral environment is $^2T_{2g}$ arising from the t_{2g}^5 configuration and the first excited doublet levels in the order of increasing energy are $^2A_{2g}$ and $^2T_{1g}$, arising from $t_{2g}^4 e_g^1$ configuration. Hence, two bands
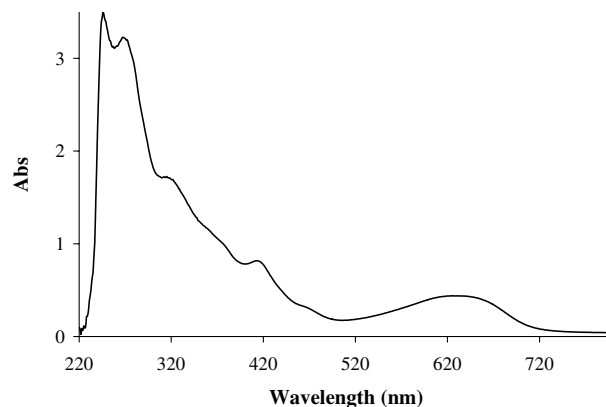

Fig. 1. Electronic spectrum of $[Ru(an-OCH_3)Cl(PPh_3)_2]$.

corresponding to $^2T_{2g} \rightarrow ^2A_{2g}$ and $^2T_{2g} \rightarrow ^2T_{1g}$ are possible. All the complexes show four to five intense absorptions in the region 633–242 nm. The intense absorptions in the region of 633–620 nm are attributed to d–d transitions and the absorptions observed in the region 430–413 nm are probably due to charge transfer transitions (LMCT) taking place from the filled ligand (HOMO) orbital to the singly-occupied ruthenium t$_2$ orbital (HOMO). The absorptions in the ultraviolet region below 380 nm are very similar and are attributable to the transitions within the ligand orbitals (n–π*, π–π*) taking place in the 1-(arylazo)naphtholate ligands. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around ruthenium(III) ion similar to that of other ruthenium(III) octahedral complexes [19].

The room temperature magnetic susceptibility measurement of the complexes in the range 1.81–1.92 BM, shows that these complexes are one electron paramagnetic, which is in accordance with the +3 state of ruthenium (low spin d^5; $S = 1/2$) in an octahedral environment in these complexes. The solid state EPR spectra of all the complexes were recorded in X-band frequencies at room temperature. The 'g' values are given in Table 2 and a representative spectrum is shown in Fig. 2a. The low spin d^5 configuration is a good probe of molecular structure and bonding since the observed 'g' values are very sensitive to small changes in the structure and to metal–ligand covalency. The EPR spectra of all the complexes exhibit an anisotropy spectrum with $g_\perp$ around 2.03–2.60 and $g_\parallel$ around 1.90–1.99. For an octahedral field with tetragonal distortion $g_x = g_y \neq g_z$ and hence, two 'g' values also indicate an axial symmetry for these complexes and hence, trans position are assigned

Table 1
Electronic spectral data of the ruthenium(III)1-(arylazo)naphtholate complexes

Complexes	λ_{max} (nm) ε (dm^3/mol/cm)
$[Ru(an-H)Cl(PPh_3)_2]$ (**1**)	620[a] (1098), 430[b] (2564), 344 (8674), 275 (15 685), 235 (18 945)
$[Ru(an-Cl)Cl(PPh_3)_2]$ (**2**)	633[a] (1480), 479[c] (2010), 420[b] (3470), 374 (4230), 269 (12 513), 245 (15 800)
$[Ru(an-Me)Cl(PPh_3)_2]$ (**3**)	626[a] (730), 422[b] (1905), 365 (8542), 242 (10 465)
$[Ru(an-OMe)Cl(PPh_3)_2]$ (**4**)	625[a] (2220), 413[b] (4135), 314 (8715), 269 (16 365), 250 (17 170)
$[Ru(an-OEt)Cl(PPh_3)_2]$ (**5**)	622[a] (2245), 472[c] (3975), 415[b] (6430), 366 (7665), 320 (9975), 260 (21 630)

[a] d–d transition.
[b] Charge transfer (LMCT) transition.
[c] Shoulder.

Table 2
EPR data of ruthenium(III)1-(aryalazo)naphtholate complexes

Complexes	g_x	g_y	g_z	$\langle g \rangle^*$
1	2.12	2.12	1.91	2.05
2	2.10	2.10	1.94	2.04
3	2.03	2.03	1.90	1.98
4	2.04	2.04	1.99	2.02
5	2.60	2.60	1.93	2.37

$\langle g \rangle^* = [1/3 g_x^2 + 1/3 g_y^2 + 1/3 g_z^2]^{1/2}$.
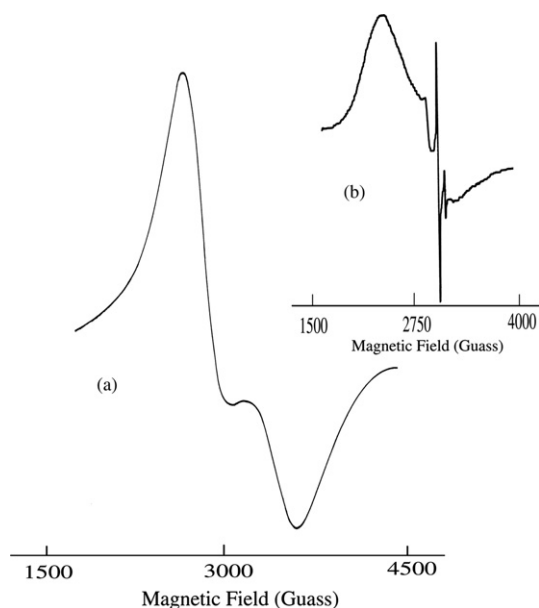
Fig. 2. EPR spectra of (a) [Ru(an-OC$_2$H$_5$)Cl(PPh$_3$)$_2$]; (b) [Ru(an-CH$_3$)Cl(PPh$_3$)$_2$] in dichloromethane in solution at 77 K.

of the complex [Ru(an-CH$_3$)Cl(PPh$_3$)$_2$] (**3**) (Fig. 2b) recorded in dichloromethane solution at 77 K shows rhombic spectrum with three different 'g' values ($g_x \neq g_y \neq g_z$; $g_x = 2.60$, $g_y = 2.03$, $g_z = 1.98$) in decreasing order of magnitude. Of these three major resonances, two are lower and one is higher than the field ($\sim$3200 G). From the spectra it is revealed that the t_g^5 configuration of the complexes is a positive hole in the t_{2g} subshell as $g_\perp > g_\parallel$. The observed rhombicity of the EPR spectrum is understandable in terms of the gross molecular symmetry of these complexes containing non-equivalent axes. The presence of rhombic distortion is apparent in the splitting of the perpendicular resonance into two spaced components (g_x and g_y). This is indicative of a gross change in the geometry of the complexes in solution. The rhombicity of the spectra reflects the asymmetry of electronic environments around ruthenium in these complexes [42]. Hence, the results from EPR spectral analysis indicate that these ruthenium(III)1-(arylazo)naphtholate complexes are significantly distorted from ideal octahedral geometry as observed in the crystal structure of [Ru(an-OCH$_3$)Cl(PPh$_3$)$_2$] (**4**).

3.2. X-ray structure

To find out the coordination mode of the 1-(arylazo)-naphtholate ligands in the complexes as well as the stereochemistry of the complexes, the molecular structure of one of the complexes [Ru(an-OCH$_3$)Cl(PPh$_3$)$_2$] (**4**) has been determined by single crystal X-ray diffraction. The ortep view is shown in Fig. 3. [Ru(an-OCH$_3$)Cl(PPh$_3$)$_2$] was

for triphenylphosphine groups. Over all the position of lines and nature of the EPR spectra of the complexes are characteristic of low spin ruthenium(III) octahedral complexes [41]. However, the EPR measurements in frozen solution, clearly demonstrates the presence of a rhombic ligand field component, as one might expect from the nature of the ligands around the metal ion. The EPR spectrum
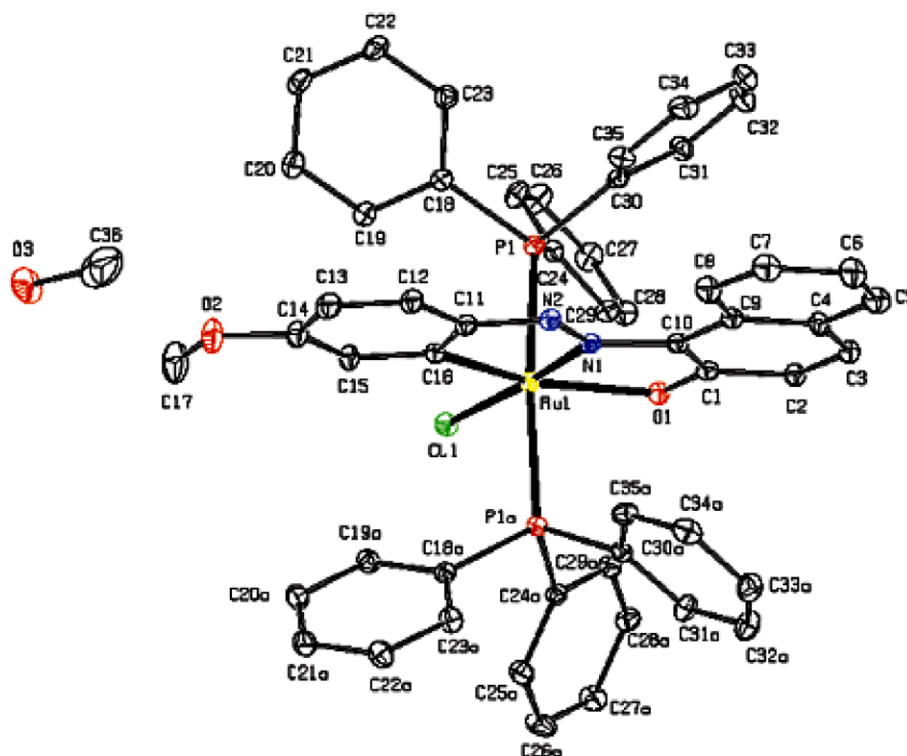

Fig. 3. The ORTEP diagram of the complex [Ru(an-OCH$_3$)Cl(PPh$_3$)$_2$] (**4**) showing 30% probability. For reasons of clarity, hydrogen atoms have been omitted.

crystallized with methanol as a solvent for crystallization. The summary of single crystal X-ray structures and refinement is shown in Table 3 and selected bond lengths and bond angles are given in Table 4. The molecular structure shows that the 1-(arylazo)naphtholate ligands are coordinated to ruthenium ion via dissociation of the phenolic proton as well as another proton from one ortho position of the phenyl ring in the arylazo fragment as a tridentate C, N, O-donor ligands at O, N, C with bite angles of 76.9(3)° O(1)–Ru(1)–N(1) and 76.3(3)° N(1)–Ru(1) C(16) and bond lengths of 2.149(6) Å Ru(1)–O(1), 2.033(8) Å Ru(1)–N(1) and 2.050(8) Å Ru(1)–C(16). The coordinated 1-(arylazo)naptholate ligand, chloride ion constitute one equatorial plane with the metal at the center where the chloride ion is trans to the coordinated azo (–N=N–) nitrogen. The N–N distance is 1.290(10) Å and is longer than the free azo bond length (1.25 Å) [43]. The increase in bond length is undoubtedly because of coordination of N(azo) that can lead to a decrease in the N–N bond order due to both σ- and π-acceptor character of the ligands – the latter character having a more pronounced effect and may be the reason for elongation [44]. This is an indication of metal–ligand π-interaction localised in the M-azo fragment. There are no H bonding interactions,

Table 3
Crystal data and structure refinement for complex **4**

Empirical formula	$C_{54}H_{46}ClN_2O_3P_2Ru$
Formula weight	969.39
Temperature (K)	183(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	Cm
Unit cell dimensions	
a (Å)	18.298(4)
b (Å)	15.361(3)
c (Å)	9.6987(19)
α (°)	90
β (°)	120.63(3)
γ (°)	90
Volume (Å^3)	2345.7(8)
Z	2
D_{calc} (Mg/m^3)	1.373
Absorption coefficient (mm^{-1})	0.505
F(000)	998
Crystal size (mm^3)	0.36 × 0.32 × 0.22
θ Range for data collection (°)	3.61–24.00
Index ranges	$-20 \leqslant h \leqslant 20$, $-17 \leqslant k \leqslant 17$, $-11 \leqslant l \leqslant 11$
Reflections collected	7581
Independent reflections [$R_{(int)}$]	3639 [0.0298]
Completeness to θ = 24.00° (%)	96.9
Absorption correction	Numerical
Maximum and minimum transmission	0.9165 and 0.8424
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3639/2/325
Goodness-of-fit on F^2	1.150
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0488$, $wR_2 = 0.1351$
R indices (all data)	$R_1 = 0.0495$, $wR_2 = 0.1357$
Largest difference in peak and hole (e Å^{-3})	1.471 and −0.486

Table 4
Selected bond lengths (Å) and angles (°) for complex **4**

Bond lengths (Å)		Bond angles (°)	
Ru1–Cl	1 2.369 (3)	Cl1–Ru1–P1	87.69 (5)
Ru1–P1	2.4015 (13)	Cl1–Ru1–O1	108.88 (18)
Ru1–O1	2.149 (6)	Cl1–Ru1–N1	174.2 (2)
Ru1–N1	2.033 (8)	Cl1–Ru1–C16	97.9 (3)
Ru1–C16	2.050 (8)	Cl1–Ru1–P1	87.69 (5)
Ru1–P1a	2.4015 (13)	P1–Ru1–O1	86.62 (4)
P1–C18	1.834 (6)	P1–Ru1–N1	92.74 (5)
P1–C24	1.833 (6)	P1–Ru1–C16	94.64 (4)
P1–C30	1.823 (7)	P1–Ru1–P1i	170.12 (7)
O1–C1	1.304 (11)	O1–Ru1–N1	76.9 (3)
O2–C14	1.366 (14)	O1–Ru1–C16	153.2 (3)
O2–C17	1.36 (2)	P1–Ru1–O1	86.62 (4)
O3–C36	1.47 (5)	N1–Ru1–C16	76.3 (3)
N1–C10	1.405 (11)	P1–Ru1–N1	92.74 (5)
N1–N2	1.290 (10)	P1–Ru1–C16	94.64 (4)
N2–C11	1.379 (12)	Ru1–P1–C18	117.96 (19)
		Ru1–P1–C24	111.64 (19)
		Ru1–P1–C30	115.15 (19)
		C18–P1–C24	103.7 (3)
		C24–P1–C30	103.2 (3)
		Ru1–O1–C1	111.7 (5)
		Ru1–N1–C10	117.8 (6)
		Ru1–N1–N2	121.6 (6)
		Ru1–C16–C11	112.1 (6)
		Ru1–C16–C15	130.2 (8)

ESD in parenthesis.

however there is an aromatic π–π stacking interaction [45] between rings (C1–C4/C9–C10) and (C30–C35) with a centroid–centroid distance of 3.977(4) Å. The two PPh$_3$ ligands have taken up the remaining two axial positions, and hence, they are mutually trans, the Ru(1)–P(1) 2.4015(13) Å and Ru(1)–P(1a) 2.4015(13) Å bond distances are equal from the metal center. However, the Ru–N distance is found to be significantly longer than usual, and this elongation may be attributed to the strong trans effect of the coordinated chloride [46]. The Ru^{III}–O bond distance in these complexes are longer than reported for Ru(OH$_2$)$_6$$^{3+}$ and trans-Ru(bpy)$_2$–(OH)(OH$_2$)$^{2+}$ of bond distances 2.029(7) Å and 2.007(3) Å, respectively [47]. The lengthening of this Ru^{III}–O bond may be due to the trans effect of the C(16). Ruthenium is therefore sitting in a CNOP$_2$Cl coordination environment, which is distorted octahedral in nature as reflected in all the bond parameters around ruthenium. As all the complexes display similar spectral properties, the other four complexes are assumed to have similar structure to that of complex **4**.

3.3. Electrochemistry of the complexes

The electron transfer property of all the complexes were studied in dichloromethane solution by cyclic voltammetry under N$_2$ atmosphere using a glassy-carbon working electrode and the redox potentials are expressed with reference to SCE. All the complexes (1×10^{-3} M) are electroactive with respect to the metal centers and exhibited three redox
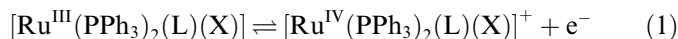
Table 5
Electrochemical data of the ruthenium(III)1-(arylazo)naphtholate complexes

Complexes	Ru^{IV}/Ru^{III}				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)	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV)
1	0.92	0.62	0.77	300	−0.42	−0.62	−0.52	200	−0.90	−1.03	−0.96	130
2	0.89	0.70	0.79	190	−0.41	−0.59	−0.50	180	−0.80	−1.07	−0.93	270
3	0.80	0.52	0.66	280	−0.47	−0.79	−0.63	320	−0.86	−1.02	−0.94	160
4	0.75	0.48	0.61	270	−0.49	−0.75	−0.62	260	−0.80	−1.17	−0.98	370
5	0.70	0.49	0.60	210	−0.50	−0.72	−0.61	220	−0.81	−1.09	−0.95	280

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}.

processes in the potential range +1.5 V to −1.5 V (0.05 M tetrabutyl ammonium perchlorate as supporting electrolyte at 298 K). The complexes display a quasi-reversible oxidative (Ru^{IV}/Ru^{III}) and two quasi-reversible reductive (Ru^{III}/Ru^{II}; Ru^{II}/Ru^{I}) responses on the positive and negative side of SCE, respectively at the scan rate of 100 mV s^{-1}. The potentials are summarized in Table 5 and a representative voltammogram is shown in Fig. 4. All the complexes showed well-defined waves $E_{1/2}$ lies in the range 0.61–0.79 V (Ru^{IV}/Ru^{III}) and −0.50 to −0.63 V (Ru^{III}/Ru^{II}) and −0.93 to −0.98 V (Ru^{II}/Ru^{I}). The redox processes are quasi-reversible in nature, characterized by a rather large peak-to-peak separation (ΔE_p) of 130–370 mV [48]. On comparison of its current height (i_{pa}) with that of the standard ferrocene/ferrocenium couple under identical experimental conditions reveals the one electron redox process [18,19]. The redox potentials E_{pc} and E_{pa} are virtually independent of the scan rates, supporting quasi-reversibility.

The first quasi-reversible response on the positive side is due to the one electron oxidation of Eq. (1)

$$[Ru^{III}(PPh_3)_2(L)(X)] \rightleftharpoons [Ru^{IV}(PPh_3)_2(L)(X)]^+ + e^- \qquad (1)$$

On further scan reversal on the negative side, two quasi-reversible reductive responses in Eqs. (2) and (3) were observed

$$[Ru^{III}(PPh_3)_2(L)(X)] + e^- \rightleftharpoons [Ru^{II}(PPh_3)_2(L)(X)]^- \qquad (2)$$

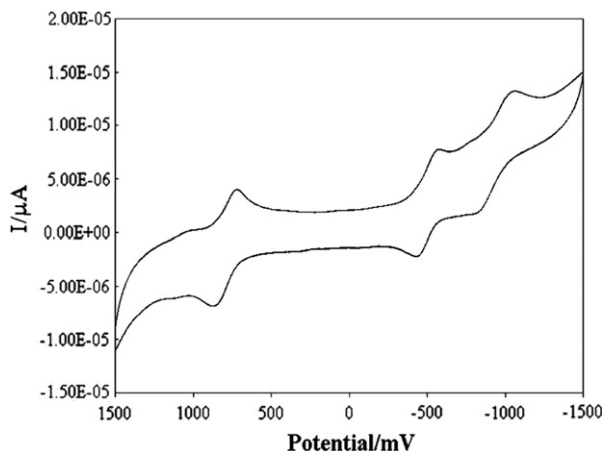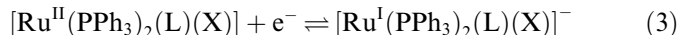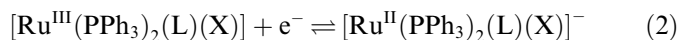$$[Ru^{II}(PPh_3)_2(L)(X)] + e^- \rightleftharpoons [Ru^{I}(PPh_3)_2(L)(X)]^- \qquad (3)$$

Fig. 4. Cyclic voltammogram of $[Ru(an-Cl)Cl(PPh_3)_2]$.

The potentials of both the oxidation (Ru^{IV}/Ru^{III}) and reduction (Ru^{III}/Ru^{II}; Ru^{II}/Ru^{I}) have been found to be sensitive to the nature of the substituent (R) in the 1-(arylazo)naphtholate ligands which perturbs both the metal oxidation and reduction. The potential increases linearly with increasing electron-withdrawing character of R. The half wave potentials ($E_{1/2}$) moves to negative value with electron donating substituent(s) in the aryl ring and reverse movement is observed for electron withdrawing group. The plot of formal potentials $E_{1/2}$ versus σ (σ – Hammett para substituent constant of R [49] R: $OCH_3 = -0.27$, $OC_2H_5 = -0.24$, $CH_3 = -0.17$, H = 0.00, Cl = 0.23) is found to be linear for all the three couples (Fig. 5). The slope of these lines, which is known as the reaction
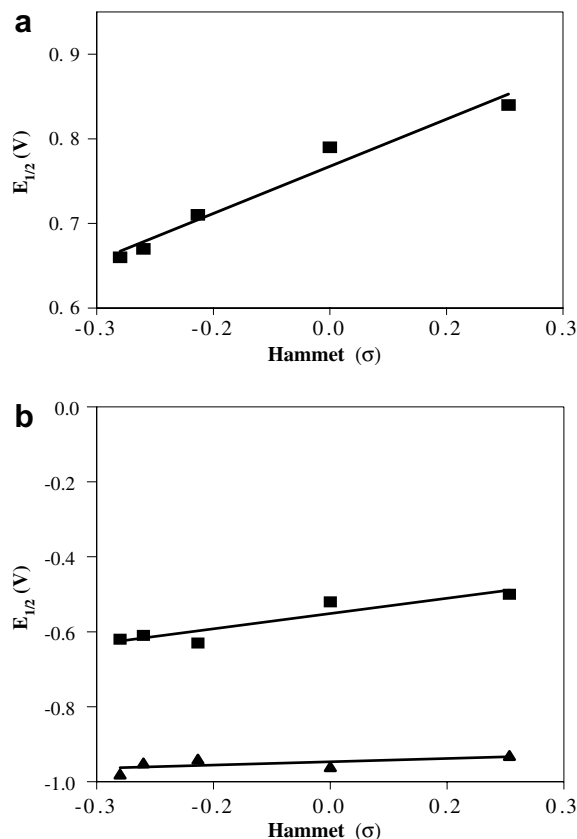

Fig. 5. Least-squares plot of (a) $E_{1/2}$ values oxidation (Ru^{IV}/Ru^{III}); (b) $E_{1/2}$ values reduction (Ru^{III}/Ru^{II}; Ru^{II}/Ru^{I}) potentials versus σ.

constant ρ [50] and is a measure of the sensitivity of $E_{1/2}$ with R is 0.36 for the Ru^{IV}/Ru^{III} couple, 0.17 for the Ru^{III}/Ru^{II} couple and 0.12 for the Ru^{II}/Ru^{I} couple. This shows that the nature of the para substituent R on the 1-(arylazo)naphtholate ligand, which is four bonds away from the electroactive metal center, can still influence the metal-centered potentials 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 state of ruthenium ion and the electron transfer reactions take place without gross changes in the stereochemistry of the complexes [5].

3.4. Catalytic activity in transfer hydrogenation of ketones

Catalytic transfer hydrogenation reaction in which hydrogen is transferred from one organic molecule to another by ruthenium complexes is well known and this prompted us to carry out this type of reactions. Representative types of aliphatic alkyl and aryl ketones were chosen to evaluate the performance of complex [Ru(an-OCH$_3$)-Cl(PPh$_3$)$_2$] (**4**) in transfer hydrogenation reaction in the presence of *iso*-propanol and KOH as promoter.

R, R' = alkyl (or) aryl
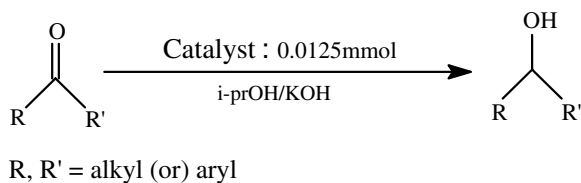
In order to optimize the reaction conditions, different catalyst:substrate ratios were tested and the results are summarized in Table 6. For this initial experiments cyclohexanone was selected as a test-substrate and allowed it to react in 2-propanol with catalytic quantities of organoruthenium(III) **4** complex in the presence of KOH. When increasing the C:S ratio to 1:400 or 1:500 in 2-propanol, the reaction still proceeds smoothly accompanied by a moderate drop in conversion. Thus, it was concluded that catalyst:substrate ratio of 1:300 is the best compromise between optimal reaction rate in 2-propanol.

Table 6
Catalytic transfer hydrogenation of cyclohexanone by [Ru(an-OCH$_3$) Cl(PPh$_3$)$_2$]/*i*-PrOH/KOH[a]

Entry	S/C	Time	Conversion[b] (%)
1	100:1	2	90.0
2	200:1	2	89.0
3	300:1	2	86.5
4	400:1	2	80.0
5	500:1	2	78.0

[a] Conditions: reactions were carried out at 80 °C using 1.25–6.255 mmol of cyclohexanone (5 ml isopropanol).
[b] 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 sample.

The catalytic reaction was carried out under a set of conditions (see experimental for reaction conditions) and a series of blank or control experiments suggest that none of RuCl$_3 \cdot$3H$_2$O, Ru(III) precursors or 1-(arylazo)napholate ligands alone or as a mixture causes these transformations under identical reaction conditions. This ascertained the necessity of ruthenium(III) complex to observe the ensuing catalytic transformations. Complex **4** efficiently catalyses the transfer hydrogenation of ketones with high yield and the results are summarized in Table 7. Under these conditions, the Ru–C σ is stable and the 1-(arylazo)naphtholate fragment is preserved.

The alcohols formed after the reflux for the time mentioned were determined by GC with authentic samples. In this method, the base facilitates the formation of a ruthenium alkoxide by abstracting the proton of the alcohol (Scheme 1), which then undergoes β-elimination to give a ruthenium-hydride which is the active catalyst. This classical mechanism is proposed by several workers on the studies of ruthenium complexes catalyzed transfer hydrogenation reaction by metal hydrides [22,23]. Though, no mechanistic studies have been performed, the catalytic transformation of ketones to alcohols follow the classical pathway in which the ketones coordinate to hydride-ruthenium metal intermediate (Scheme 2).

Both aliphatic and aromatic ketones are converted into their corresponding secondary alcohols with excellent conversions and turnover. The complex efficiently catalyzed the reduction of aliphatic ketones such as ethyl methyl ketone, methyl propyl ketone and isobutyl methyl ketone to their corresponding alcohols with 82.0%, 99.4% and 99.8% conversion, respectively. The conversion in case of acetophenone is 88.8%. The presence of electron withdrawing (Cl) and electron donating (OCH$_3$) substituents on the substrates (entries 2 and 3) plays a significant role in the conversion of ketones to alcohols. 4-chloro acetophenone is converted to corresponding alcohol in 93.7% and 4-methoxy acetophenone in 79.4% conversion. This may be expected as reduction involves the substrate gaining electrons and this would be more facile at an electron deficient center [51]. Assuming that these catalytic transformations follow the classical pathway in which the ketone coordinates to hydride-ruthenium intermediates [22,23], the observed effects seem to indicate that the hydride transfer from the metal to the coordinated ketone is the turnover-limiting step (rather than the ketone complexation) in the catalytic cycle [52]. Interestingly, the complex efficiently catalyses the reduction of five, six, seven and eight-membered cyclic ketones to the corresponding alcohols with 86.5% conversion in case of cyclohexanone and conversions >90% in case of cyclopentanone, cycloheptanone and cyclooctanone. The catalyst also efficiently catalyzed the reduction of diethyl ketone to 3-pentanol in 86% conversion.

In contrast to what is observed for most other catalysts, a significant advantage of these catalysts is their insensitivity toward air and moisture. In this way rigorous pretreatment

Table 7
Catalytic transfer hydrogenation of ketones by [Ru(an-OCH$_3$)Cl(PPh$_3$)$_2$]/i-PrOH/KOH[a]
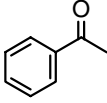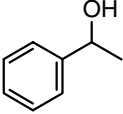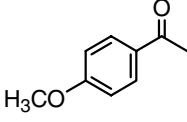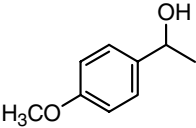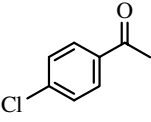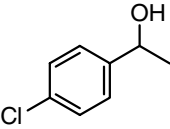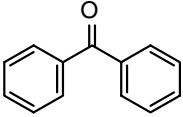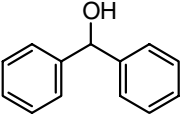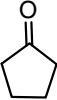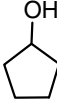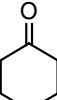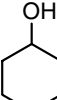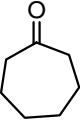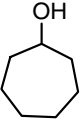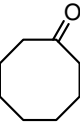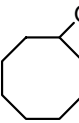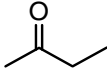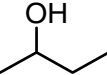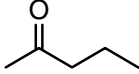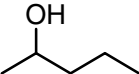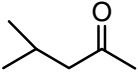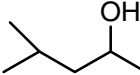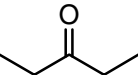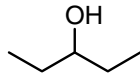
Entry	Substrates	Products	Time (h)	Conversion[b]	TON[c] (TOF)[d]
1			3	88.8	266(88)
2			2	79.4	238(119)
3			2	93.7	281(140)
4			2	96.9	290(145)
5			2	90.0	270(135)
6			2	86.5	259(129)
7			2	96.6	289(144)
8			2	92.0	276(138)
9			2	82.0	246(123)
10			2	99.4	298(149)

Table 7 (*continued*)

Entry	Substrates	Products	Time (h)	Conversion	TON[c] (TOF)[d]
11	O	OH	2	99.8	299(149)
12	O	OH	2	86.0	258(129)

[a] Conditions: reactions were carried out at 80 °C using 3.75 mmol of ketone (5 ml isopropanol); catalyst/ketone/KOH ratio 1:300:2.5.
[b] Yield of product was determined using a HP 6890 series GC-FID with DP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness and by comparison with authentic samples.
[c] TON = ratio of moles of product obtained to the moles of catalyst used.
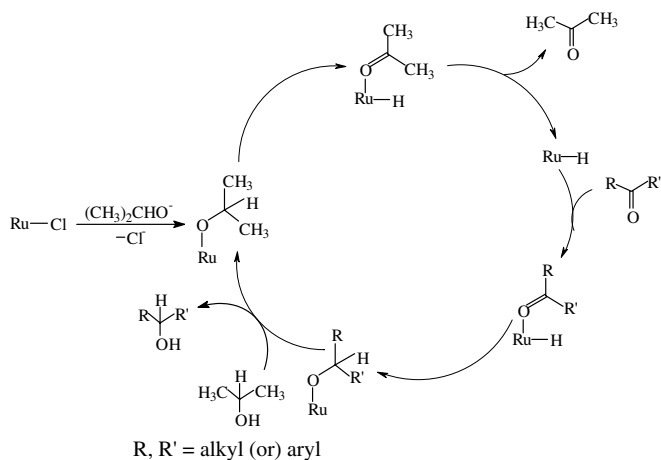[d] TOF (TON h^{-1}).
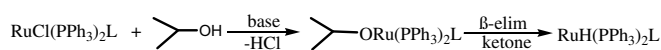
Scheme 1. The role of base (L = arylazo ligand).

Scheme 2. Proposed catalytic cycle for the transfer hydrogenation of ketones by cyclometalated Ru(III)1-(arylazo)naphtholate complex (**4**).

of solvents and substrates is avoided, thus reaction mixtures can be loaded into the reaction vessel in the open air and monitoring of the reaction progress becomes very convenient. Furthermore, the ease by which these catalysts are prepared offers another important advantage. The work up process is very simple for this catalytic system as the catalyst is stable in all organic solvents and it can be recovered. The only byproduct acetone was identified in all the cases. Although several catalytic systems have been reported to support transfer hydrogenation reactions of ketones, catalyst like cycloruthenated(III) complex is novel for its CNO donor, PPh$_3$ and Cl ligand environment.

4. Conclusions

It is demonstrated that [RuCl$_3$(PPh$_3$)$_3$] effectively mediate C–H activation of 1-(arylazo)naphthols and a series

of five new organoruthenium(III) complexes are obtained. The X-ray crystal structure of the complex (**4**) reveals a distorted octahedral environment around ruthenium. Further, the complex (**4**) has exhibited very high catalytic efficiency in transfer hydrogenation of both purely aliphatic as well as aromatic ketones in the presence of isopropanol/KOH. Results of present investigation suggests promising application of a new family of organoruthenium(III) complexes containing 1-(arylazo)naphthol in transition-metal promoted catalysis. We are currently perusing development of chiral organoruthenium(III) complexes for asymmetric catalysis.

Acknowledgements

Appendix A. Supplementary material

CCDC 606695 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Complete sets of refined positional coordinates as well as anisotropic thermal parameters and complete tabulations of bond lengths and bond angles are presented in the online version of this paper. Supplementary data associated with this article can be found, in the online version, at doi:-10.1016/j.jorganchem.2007. 04.042.

References

[1] W.Y. Wong, W.T. Wong, Coord. Chem. Rev. 146 (1995) 307.

[2] M.G. Richard, Coord. Chem. Rev. 141 (1995) 63.

[3] E.C. Constable, C.E. Housecroft, Coord. Chem. Rev. 134 (Part 2) (1994) 133.

[4] I. Omae, Chem. Rev. 79 (1979) 287.

[5] K. Siu, S.M. Peng, S. Bhattacharya, Polyhedron 18 (1999) 631.

[6] J.P. Kleiman, M. Dubeck, J. Am. Chem. Soc. 85 (1963) 1544.

[7] F. Mohr, S.H. Priver, S.K. Bhargava, M.A. Bennet, Coord. Chem. Rev. 250 (2006) 1851, and references therein.

[8] I. Omae, Coord. Chem. Rev. 248 (2004) 995.

[9] (a) J. Dupont, C.S. Consorti, Spencer, J. Chem. Rev. 105 (2005) 2527;
(b) M. Pfeffer, J.P. Sutter, M.A. Rotteveel, A. De Cian, J. Fisher, Tetrahedron 48 (1992) 2441.

[10] A.D. Ryabov, R. Van Eldik, G. Le Borgne, M. Pfeffer, Organometallics 12 (1993) 1386.

[11] P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 17 (1992) 215.

[12] K. Naresh Kumar, R. Ramesh, Y. Liu, J. Inorg. Biochem. 100 (2006) 18.

[13] S. Nag, P. Gupta, R.J. Butcher, S. Bhattacharya, Inorg. Chem. 43 (2004) 4814.

[14] P. Gupta, S. Dutta, F. Basuli, S.-M. Peng, G-H. Lee, S. Bhattacharya, Inorg. Chem. 45 (2006) 460.

[15] R.K. Rath, M. Nethaji, A.R. Chakravarty, J. Organomet. Chem. 633 (2001) 79.

[16] G. Venkatachalam, R. Ramesh, Tetrahedron Lett. 46 (2005) 5215.

[17] G. Venkatachalam, R. Ramesh, S.M. Mobin, J. Organomet. Chem. 690 (2005) 3937.

[18] G.K. Lahiri, S. Bhattacharya, M. Mukherjee, A.K. Mukherjee, A. Chakravorty, Inorg. Chem. 26 (1987) 3359.

[19] P.K. Sinha, J. Chakravarty, S. Bhattacharya, Polyhedron 16 (1997) 81.

[20] (a) C.P. Casey, N.A. Strotman, S.E. Beetner, J.B. Johnson, D.C. Priebe, T.E. Vos, B. Khodavandi, I.A. Guzei, Organometallics 25 (2006) 1230;
(b) G.A. Grasa, A.Z. Gerosa, W.P. Hems, J. Organomet. Chem. 691 (2006) 2332.

[21] E. Lindner, H.A. Mayer, I. Warad, K. Eichele, J. Organomet. Chem. 665 (2003) 176.

[22] (a) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994;
(b) I. Ojima, Catalytic Asymmetric Synthesis, second ed., Wiley, New York, 2000;
(c) R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97;
(d) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, F.A. England, T. Ikariya, R. Noyori, Angew. Chem., Int. Ed. 37 (1998) 1703;
(e) M.J. Palmer, M. Will, Tetrahedron: Asymmetry 10 (1999) 2045;
(f) J.-E. Backvall, J. Organomet. Chem. 652 (2002) 105.

[23] (a) E.P. Kelson, P.P. Phengsy, J. Chem. Soc., Dalton Trans. (2000) 4023;
(b) H. Zhang, B.C. Yang, Y.Y. Li, Z.R. Donga, J.X. Gao, H. Nakamura, K. Murata, T. Ikariya, Chem. Commun. (2003) 142;
(c) J. Hannedouche, G.J. Clarkson, M. Wills, J. Am. Chem. Soc. 126 (2004) 986.

[24] J.S. Chen, Y. Li, Z. Dong, B. Li, J. Gao, Tetrahedron Lett. 45 (2004) 8415.

[25] (a) G.Z. Wang, J.-E. Backvall, J. Chem. Soc., Chem. Comm. (1992) 980;
(b) N. Uematsi, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 4916;
(c) S.M.J. Samec, A.H. Ell, J.-E. Backvall, Chem. Commun. (2004) 2748.

[26] (a) R. Noyori, H. Takaya, Acc. Chem. Res. 23 (1990) 345;
(b) D.E. Linn, J. Halpern, J. Am. Chem. Soc. 109 (1987) 2969.

[27] R.L. Chowdhury, J.-E. Backvall, J. Chem. Soc., Chem. Commun. (1991) 1063.

[28] (a) R. Noyori, Angew. Chem., Int. Ed. 41 (2002) 2008;
(b) R. Noyori, T. Ohkuma, Angew. Chem., Int. Ed. 40 (2001) 40.

[29] (a) T. Ohkuma, M. Koizumi, H. Doucet, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 120 (1998) 13529;
(b) T. Ohkuma, D. Ishii, H. Takeno, R. Noyori, J. Am. Chem. Soc. 122 (2000) 6510;
(c) T. Ohkuma, M. Koizumi, H. Ikehira, T. Yokozawa, R. Noyori, Org. Lett. 2 (2000) 659.

[30] (a) A. Dominguez, A. Zanotti-Gerosa, W. Hems, Org. Lett. 6 (2004) 1927;
(b) J.W.H. Chen, W. Kwok, R. Guo, Z. Zhou, C.-H. Yeung, A.S.C. Chan, J. Org. Chem. 67 (2002) 7908;
(c) J. Xie, L. Wang, Y. Fu, S. Zhu, B. Fan, H. Duan, Q. Zhou, J. Am. Chem. Soc. 125 (2003) 4404.

[31] (a) M. Albrecht, B.M. Kocks, A.L. Spek, G. van Koten, J. Organomet. Chem. 624 (2001) 271;
(b) P. Dani, T. Karlen, R.A. Gossage, S. Gladiali, G. van Koten, Angew. Chem. 112 (2000) 759.

[32] H. Deng, Z. Yu, J. Dong, S. Wu, Organometallics 24 (2005) 4110.

[33] (a) J.B. Sortais, V. Ritleng, A. Voelklin, A. Holuigue, H. Smail, L. Barloy, C. Sirlin, G.K.M. Verzijl, J.A.F. Boogers, A.H.M. De Vries, J.G. De Vries, M. Pfeffer, Org. Lett. 7 (2005) 1247;
(b) D. Amoroso, A. Jabri, G.P.A. Yap, D.G. Gusev, E.N. Dos Sanntos, D.E. Fogg, Organometallics 23 (2004) 4047.

[34] J. Chatt, G.J. Leigh, D.M.P. Mingos, R.J. Paske, J. Chem. Soc. A (1968) 2636.

[35] (a) CELL, 2.92, 1999 ed.; STOE & Cie, GmbH: Darmstadt, Germany, 1999;
(b) A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.

[36] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Göttingen, 1997.

[37] (a) S. Goswami, R. Mukherjee, A. Chakravorty, Inorg. Chem. 22 (1983) 2825;
(b) B. Mondal, M.G. Walwalker, G.K. Lahiri, J. Chem. Soc., Dalton Trans. (2000) 4209.

[38] S. Kannan, R. Ramesh, Polyhedron 25 (2006) 3095.

[39] (a) A.K. Das, S.M. Peng, S. Bhattacharya, J. Chem. Soc., Dalton Trans. (2000) 181;
(b) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York, 1971.

[40] M.I. Bruce, Angew. Chem., Int. Ed. Engl. 16 (1977) 73, and references therein.

[41] (a) R. Ramesh, S. Maheswaran, J. Inorg. Biochem. 96 (2003) 457;
(b) M.M. Taqui Khan, D. Srinivas, R.I. Khureshy, N.H. Khan, Inorg. Chem. 29 (1990) 2320;
(c) O.K. Medhi, U. Agarwala, Inorg. Chem. 19 (1980) 1381.

[42] (a) N.C. Pramanik, S. Bhattacharya, Polyhedron 16 (1997) 3047;
(b) L.R. Dinelli, A.A. Batista, K. Wohnrath, M.P. de Araujo, S.L. Queiroz, M.R. Bonfadini, G. Oliva, O.R. Nascimento, P.W. Cyr, K.S. MacFarlane, B.R. James, Inorg. Chem. 38 (1999) 5341.

[43] S. Pal, T.K. Misra, C. Sinha, A.M.Z. Slawin, J. Derek Woollins, Polyhedron 19 (2000) 1925.

[44] T.K. Misra, D. Das, C. Sinha, P. Ghosh, C.K. Pal, Inorg. Chem. 37 (1998) 1672.

[45] C.A. Hunter, Chem. Soc. Rev. 23 (1994) 101.

[46] P.G. Douglas, B.L. Shaw, J. Chem. Soc. A (1970) 1556.

[47] (a) P. Bernhard, H.B. Burgi, J. Hauser, H. Lehmann, A. Ludi, Inorg. Chem. (1982) 3936;

(b) B. Durham, S.R. Wilson, D.J. Hodgson, T.J. Meyer, J. Am. Chem. Soc. 102 (1980) 600.

[48] P. Byabartta, J. Dinda, P.K. Santra, C. Sinha, K. Pannerselvam, F.L. Liao, T.H. Lu, J. Chem. Soc., Dalton Trans. (2001) 2825.

[49] L.P. Hammett, Physical Organic Chemistry, second ed., Mc Graw Hill, New York, 1970.

[50] R.N. Mukherjee, O.A. Rajan, A. Chakravorty, Inorg. Chem. 21 (1982) 785.

[51] J. Soleimannejad, A. Sisson, C. White, Inorg. Chim. Acta 352 (2003) 121.

[52] (a) J.W. Faller, A.R. Lavoie, Organometallics 20 (2001) 5245;
(b) J.W. Faller, A.R. Lavoie, Organometallics 21 (2003) 3493.