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Ruthenium(III) complexes of amine-bis(phenolate) ligands as catalysts for transfer hydrogenation of ketones

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Abstract

Twelve ruthenium(III) complexes bearing amine-bis(phenolate) tripodal ligands of general formula $[Ru(L^1-L^3)(X)(EPh_3)_2]$ (where L^1-L^3 are dianionic tridentate chelator) have been synthesized by the reaction of ruthenium(III) precursors $[RuX_3(EPh_3)_3]$ (where E = P, X = Cl; E = As, X = Cl or Br) and $[RuBr_3(PPh_3)_2(CH_3OH)]$ with the tripodal tridentate ligands H_2L^1, H_2L^2 and H_2L^3 in benzene in 1:1 molar ratio. The newly synthesized complexes have been characterized by analytical (elemental and magnetic susceptibility) and spectral methods. The complexes are one electron paramagnetic (low-spin, d⁵) in nature. The EPR spectra of the powdered samples at RT and the liquid samples at LNT shows the presence of three different 'g' values ($g_x \neq g_y \neq g_z$) indicate a rhombic distortion around the ruthenium ion. The redox potentials indicate that all the complexes undergo one electron transfer process. The catalytic activity of one of the complexes [Ru(pcr-chx)Br(AsPh_3)_2] was examined in the transfer hydrogenation of ketones and was found to be efficient with conversion up to 99% in the presence of isopropanol/KOH.

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1. Introduction

Even though highly efficient catalytic systems for selective transformations are known [1-3], the design of efficient catalysts for large-scale applications is still a challenging problem. Noteworthy, a prerequisite for achieving high activity and selectivity is the fine tuning of the metal by introduction of ligands. With the high activity, ruthenium complexes play a central role in many organic transformations as versatile catalyst due to its reversible and accessible oxidation states [4]. Many research groups are developing the synthetic chemistry related to ruthenium complexes because of their multiple applications in many different scientific fields [5]. Ruthenium complexes have been used as catalysts or catalyst precursors for a variety of purposes including hydrogenation, oxidation, isomerisation, poly-

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merization, nucleophilic addition to multiple bonds and carbon-carbon bond formation [6]. The ability of transition metal catalysts to add or remove hydrogen from organic substrates by either direct or transfer hydrogenation process is a valuable synthetic tool [7]. Ruthenium complexes have a long pedigree as catalysts for transfer hydrogenation reactions in the presence of 2-propanol as hydrogen source [8,9]. Several recent examples of ruthenium N-heterocyclic carbene complexes [10-12], Ru(arene)-(diamine) [13] and Ru(BINAP)(diamine) [14] catalysts have become the most prominent members for the reduction of ketones in high yields. Pincer-type arylruthenium(II) complexes containing the monoanionic terdentate NCN and PCP ligands have been reported by van Koten as active catalysts for the transfer hydrogenation of ketones in the presence of *i*-PrOH and KOH [15]. A number of other groups have followed Noyori's work using XylBinap [16] and have demonstrated the use of other diphosphines that give rise to high activities and selectivities when used in this catalyst system [17]. Ruthenium(II) complex bearing the

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ligand 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine in isopropanol [18] has been proved to be an efficient catalyst for the transfer hydrogenation of ketones. The diversity of tertiary phosphines in terms of their Lewis basicity and bulkiness render them excellent candidates to tune the reactivity of octahedral complexes towards a variety of chemical processes, such as oxidative addition and substitution reactions [19]. Even though there are number of reports available on the transfer hydrogenation of ketones, to the best of our knowledge, there are no reports available for catalytic transfer hydrogenation of ketones by ruthenium tripodal complexes.

Tripodal ligands are in general facially coordinating tridentate chelate ligands which have received considerable attention in both coordination and organometallic chemistry. Over the past 20 years, there have been hundreds of published reports concerning various aspects of metal complexes which contain tripod ligands. Although the coordination properties of tripodal ligand have been extensively investigated using first row transition metals [20], few second and third row transition metals have been the target of studies with this kind of ligand. Tripodal complexes are of considerable interest as they find application in catalytic processes such as polymerization [21], epoxidation [22], enantioselective hydrogenation of olefins [23], Diels– Alder reaction [24], addition of TMS-CN to carbonyl compounds [25].

In view of the growing interest in the catalytic activity of ruthenium complexes to act as an efficient catalyst in transfer hydrogenation of ketones, we herein report the synthesis of a series of hexacoordinated ruthenium(III) tripodal complexes containing PPh₃/AsPh₃. The characterization of the complexes were accomplished by analytical and spectral (FT-IR, UV–Vis and EPR) methods. The redox properties of the complexes have been studied by cyclic voltammetric technique. Further, one of the synthesized complexes has been effectively used as catalyst in transfer hydrogenation of ketones in the presence of isopropanol and KOH as base. The following symmetrical amine-bis(phenolate) tripodal ligands have been used to synthesis the ruthenium(III) complexes (Scheme 1).

2. Experimental

2.1. Reagents and materials

All the reagents used were chemically pure and AR grade. Solvents were purified and dried according to standard procedures [26]. $RuCl_3 \cdot 3H_2O$ was purchased from Loba Chemie Pvt. Ltd. and was used without further puri-



Scheme 1. Structure of tripodal ligands.

fication. The primary amines and *p*-cresol were purchased from Aldrich. The supporting electrolyte tetrabutyl ammonium perchlorate (TBAP) was dried in vacuum prior to use. The ketones and their corresponding alcohols, which were used in the catalytic studies, were purchased from Merck and Aldrich.

2.2. Physical measurements

The analysis of carbon, hydrogen and nitrogen were performed by analytic function testing VarioEL III CHNS elemental analyzer at STIC, Cochin University of Science and Technology, Cochin, India. FT-IR spectra were recorded in KBr pellets with a JASCO 460 plus spectrophotometer in the range 4000–400 cm⁻¹. A Cary 300 Bio UV–Vis Varian spectrophotometer was used to record the electronic spectra. Room temperature solid-state magnetic susceptibility measurements were carried out by EG and G model 155 vibrating sample magnetometer at IIT, Chennai. EPR spectra were recorded on JEOL JES-FA 200 EPR spectrometer at X-band frequencies for powder samples at 278 K and solution at 77 K (liquid nitrogen) with microwave power 1.00 mW, modulation amplitude 125 and the field being calibrated with diphenylpicryl hydrazyl (DPPH, g = 2.0037) at Pondicherry University, India. Electrochemical studies were performed using a Princeton EG and G-PARC model potentiostat with 0.05 M dichloromethane solutions of $[(n-C_4H_9)_4N]ClO_4$ (TBAP) as supporting electrolyte under a nitrogen atmosphere. A three-electrode cell was employed with glassy carbon working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. Melting points were recorded with a Boetius micro-heating table and are uncorrected. The conversion of products from the catalytic reactions was determined using HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25 μ m film thickness. The ruthenium(III) complexes [RuCl₃(PPh₃)₃], [RuCl₃-(AsPh₃)₃], [RuBr₃(AsPh₃)₃], [RuBr₃(PPh₃)₂(CH₃OH)] [27– 30] were prepared according to the literature reports.

2.3. Preparation of amine-bis(phenolate) tripodal ligands

A solution of *p*-cresol (20.0 mmol, 2.16 g), primary amines such as methylamine, cyclohexylamine and 2-aminopyridine (10.0 mmol, 0.31-0.99 g) and aqueous formaldehyde (1.15 g, 38.4 mmol) in methanol (5 mL) was stirred and refluxed for 18 h. The mixture was cooled in freezer overnight and the supernatant solution was decanted. The solid residue was washed with ice cold methanol, filtered, and washed thoroughly with cold methanol. The solid residue was then again washed with acetonitrile for recrystallization to give a colorless product [31].

Spectral and analytical data for ligands: H₂L1 (pcr-me) (white solid): M.p.: 58 °C. IR (KBr, cm⁻¹): 3442, 1260. ¹H NMR (400 MHz, CDCl₃): δ 10.6(s, 2H, OH), δ 6.9–8.0 (m, 6H, Ar–H), δ 3.3 (s, 4H, benzylic protons), δ 2.3 (s, 9H,

CH₃). *Anal.* Calc. for C₁₇H₂₁NO₂: C, 75.24; H, 7.80; N, 5.16. Found: C, 74.95; H, 7.68; N, 4.98%.

H₂L2 (pcr-chx) (white solid): M.p.: 157 °C. IR (KBr, cm⁻¹): 3440, 1274. ¹H NMR (400 MHz, CDCl₃): δ 10.5 (s, 2H, OH), δ 7.0–7.8 (m, 6H, Ar–H), δ 3.6 (s, 4H, benzylic protons), δ 2.2 (s, 6H, CH₃), δ 1.0–2.0 (br multiplets, 11 H). *Anal.* Calc. for C₂₂H₂₉NO₂: C, 77.83; H, 8.61; N, 4.12. Found: C, 77.61; H, 8.46; N, 3.88%.

H₂L3 (pcr-ampy) (white solid): M.p.: 150 °C. IR (KBr, cm⁻¹): 3445, 1251. ¹H NMR (400 MHz, CDCl₃): δ 9.8 (s, 2H, OH), δ 6.9–7.5 (m, 10H, Ar–H), δ 3.7 (s, 4H, benzylic protons), δ 2.2 (s, 6H, Ar–CH₃). *Anal.* Calc. for C₂₁H₂₂N₂O₂: C, 75.42; H, 6.53; N, 8.37. Found: C, 75.20; H, 6.34; N, 8.04%.

2.4. Synthesis of ruthenium(III) tripodal complexes

All the reactions were carried out under anhydrous conditions and were prepared by the following general procedure. To a benzene (20 cm^3) solution of the ruthenium(III) precursors $[RuX_3(EPh_3)_3]$ (0.120–0.157 g; 0.125 mmol) (E = P, X = Cl; E = As, X = Cl or Br) or [RuBr₃(PPh₃)₂(CH₃OH)] (0.112 g; 0.125 mmol) was added tripodal ligands (0.030-0.032 g; the appropriate 0.125 mmol) (H₂L1–H₂L3). The solution was allowed to heat under reflux for 7-8 h. The reactions were monitored by TLC. The reaction mixture gradually changed to deep color and the solvent was removed under reduced pressure. The residue was precipitated by addition of light petroleum ether (60–80 °C) and recrystallized from CH₂Cl₂/pet. ether (60-80 °C). The compounds were dried under vacuum (yield: 58-72%).

2.5. 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) 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 discussions

Ruthenium(III) precursors of the type $[RuX_3(EPh_3)_3]$ (E = P, X = Cl; E = As, X = Cl or Br) or $[RuBr_3(PPh_3)_2$ -(CH₃OH)] were allowed to react with the tripodal ligands (L1–L3) in 1:1 molar ratio in dry benzene resulting in the formation of low-spin ruthenium(III) complexes (Scheme 2). In all the reactions, the ligands replace two chlorides/ bromides, one triphenylphosphine or triphenylarsine and



Scheme 2. Structure of Ru(III) tripodal complexes.

a methanol molecule from the precursor complexes (see Table 1).

3.1. Spectroscopic characterization

Infrared spectra of the complexes show many sharp and strong vibrations within 400–1600 cm⁻¹ and the assignment of all these vibrations has not been attempted. However, the ligands exhibit bands in the region 1251–1274 cm⁻¹ corresponding to phenolic v_{C-O} stretching vibration. The coordination through phenolic oxygen is confirmed by the increase of v_{C-O} stretching at higher frequencies in the region 1258–1304 cm⁻¹ in all the complexes (Table 2). This was further supported by the disappearance of v_{OH} band in the range 3440–3445 cm⁻¹ in all the complexes. Further, the complexes show a strong band near 530, 690, 740 and 1556 cm⁻¹, which are due to PPh₃/AsPh₃ ligands. Besides, all the complexes show strong bands corresponding to v_{M-N} and v_{M-O} in the region 400–450 cm⁻¹ and 500–550 cm⁻¹, respectively [32,33].

The electronic spectra of all the complexes were recorded in dichloromethane solution in the range 800-200 nm. All the complexes exhibit three to four absorption bands in the region 754-231 nm and are listed in Table 2. The ground state of ruthenium(III) is ${}^{2}T_{2g}$ and the first excited doublet levels in the order of increasing energy are ${}^{2}A_{2g}$ and ${}^{2}A_{1g}$, both arise from $t_{2g}{}^{4}e_{\sigma}{}^{1}$ configuration. The bands observed in the region of 754–600 nm are attributable to d-d transitions and the absorptions observed in the region of 575-403 nm are probably due to charge transfer transitions taking place from the filled ligand (HOMO) orbital to the singly-occupied ruthenium t₂ orbital (LUMO). In most of the ruthenium(III) complexes the charge transfer bands of the type $L_{\pi y} \to T_{2g}$ are prominent in the low energy region, which obscures the weaker bands due to d-d transitions [34]. It is therefore difficult to assign conclusively the bands of ruthenium(III) complexes that appear in the visible region. However, the extinction

Table 1	
Analytical data of rutheniur	m(III) tripodal complexes

S. no. Complexes	Complexes	Empirical formula	Color	Melting point (°C)	Elemental analysis Found (calculated) (%)		
					С	Н	Ν
1	[Ru(pcr-me)Cl(PPh ₃) ₂]	C53H49NO2ClP2Ru	brown	172	68.13 (68.41)	4.88 (5.27)	1.79 (1.50)
2	[Ru(pcr-me)Cl(AsPh ₃) ₂]	C53H49NO2ClAs2Ru	brown	164	62.16 (62.50)	4.68 (4.81)	1.25 (1.37)
3	$[Ru(pcr-me)Br(AsPh_3)_2]$	C53H49NO2BrAs2Ru	brown	186	59.58 (59.88)	4.46 (4.61)	1.19 (1.32)
4	$[Ru(pcr-me)Br(PPh_3)_2]$	C53H49NO2BrP2Ru	brown	178	65.65 (65.30)	4.88 (5.03)	1.20 (1.44)
5	[Ru(pcr-chx)Cl(PPh ₃) ₂]	C58H57NO2ClP2Ru	green	192	69.44 (69.77)	5.52 (5.71)	1.43 (1.40)
6	[Ru(pcr-chx)Cl(AsPh ₃) ₂]	C58H57NO2ClAs2Ru	brown	182	63.82 (64.11)	5.05 (5.25)	1.60 (1.29)
7	$[Ru(pcr-chx)Br(AsPh_3)_2]$	C58H57NO2BrAs2Ru	brown	165	61.22 (61.59)	4.98 (5.04)	1.04 (1.24)
8	$[Ru(pcr-chx)Br(PPh_3)_2]$	C58H57NO2BrP2Ru	brown	192	66.39 (66.79)	5.45 (5.47)	1.08 (1.34)
9	$[Ru(pcr-ampy)Cl(PPh_3)_2]$	C57H50NO2ClP2Ru	brown	188	68.64 (68.91)	4.89 (5.03)	2.69 (2.82)
10	[Ru(pcr-ampy)Cl(AsPh ₃) ₂]	C57H50NO2ClAs2Ru	brown	189	63.03 (63.30)	4.72 (4.62)	2.48 (2.59)
11	$[Ru(pcr-ampy)Br(AsPh_3)_2]$	C57H50NO2BrAs2Ru	brown	178	60.46 (60.79)	4.41 (4.44)	2.22 (2.48)
12	[Ru(pcr-ampy)Br(PPh ₃) ₂]	C ₅₇ H ₅₀ NO ₂ BrP ₂ Ru	brown	182	65.64 (65.95)	4.72 (4.82)	2.34 (2.69)

co-efficient for the bands in the 754–600 nm region are found to be very low as compared to that of charge transfer bands. Hence, the band around 754–600 nm have been assigned to ${}^{2}T_{2g} \rightarrow {}^{2}A_{2g}$ transition. The absorptions in the ultraviolet region below 400 nm are due to the intraligand transitions (n– π^{*} , π – π^{*}). The pattern of the electronic spectra of all the complexes indicate the presence of an octahedral environment around ruthenium(III) ion similar to that of other ruthenium(III) octahedral complexes [35–37].

3.2. Magnetic moments and EPR spectra

The complexes are uniformly paramagnetic with magnetic moments in the range of 1.81–1.93 BM, corresponds to one unpaired electron at 298 K (low-spin Ru^{III} , t_{2g}^{5}) in an octahedral environment. In a low-spin d⁵ system the ${}^{2}T_{2g}$ (octahedral) ground state is orbitally degenerate and will be affected by spin–orbit coupling and low-symmetry ligand-field effects, both of which will remove this degeneracy and influence the temperature dependence of the moment. The theory appropriate to such a situation has been described [38,39]. From powder susceptibility data

Table 2 IR and electronic spectral data of ruthenium(III) tripodal complexes^A

Complexes	$v_{(C-O)}$	$\lambda_{\max}(\varepsilon)$
1	1258	600 ^a (367), 350 (13444), 240 (17220)
2	1264	611 ^a (337), 427 ^b (1684), 263 (21492)
3	1270	740 ^a (207), 502 ^b (1505), 286 (12276), 237 (16412)
4	1274	540 ^b (2356), 270 (12160), 245 (16544)
5	1304	635 ^a (344), 426 ^b (2140), 353 (13476), 265 (18256)
6	1294	754 ^a (640), 562 ^b (2684), 394 (12342), 252 (18234)
7	1308	667 ^b (129), 403 ^b (2690), 248 (13248)
8	1292	575 ^b (1245), 274 (9160), 235 (14288)
9	1265	647 ^a (486), 439 ^b (4452), 356 (11652), 235 (17084)
10	1274	667 ^a (245), 445 ^b (3936), 307 (14756), 231 (14668)
11	1272	625 ^a (554), 446 ^b (3154), 275 (16436)
12	1286	604 (586) ^a , 564 (2562) ^b , 235 (20132)

^A Where v in cm⁻¹, λ_{max} in nm, ε in dm³ mol⁻¹ cm⁻¹.

 $^{a\ 2}T_{2g}\rightarrow {}^{2}A_{2g}.$

^b Charge transfer (LMCT).

alone it is not possible to accurately determine the symmetry or the magnitude of the low-symmetry ligand-field component.

However, epr measurements clearly demonstrate, at least in frozen solution, the presence of a rhombic ligandfield component, as one might expect from the nature of the ligands around the metal ion. The distortion of the pseudooctahedral complexes can be expressed as the sum of axial (Δ) and rhombic (V) components. The theory of EPR spectra of distorted octahedral low-spin d⁵ (idealized t_{2g}^{5} ground term from ${}^{2}T_{2g}$) complexes is documented in the literature [40]. The gyromagnetic tensor 'g' values are given in Table 3. The low-spin d⁵ 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 the powdered ruthenium(III) complexes have been recorded at room temperature which shows the presence of three different 'g' ($g_x = 2.29-2.43$, $g_y = 2.00-2.16$, $g_z =$ 1.84–1.92) values indicate a rhombic distortion [41,42] in the complexes and the trans position are assigned for triphenylphosphine/arsine. A similar pattern has been observed in the solution spectra of the complexes $[Ru(pcr-me)Br(AsPh_3)_2]$ (3) and $[Ru(pcr-ampy)Br(PPh_3)_2]$

Table 3				
EPR da	ita of ruthe	enium(III) tr	ripodal c	omplexes

Complexes	g_x	g_y	g_z	$\langle g \rangle^{\rm a}$
1	2.34	2.06	1.87	2.09
2	2.43	2.14	1.86	2.14
3	2.36	2.02	1.86	2.08
4	2.40	2.01	1.88	2.09
5	2.36	2.02	1.92	2.10
6	2.37	2.01	1.84	2.07
7	2.40	2.16	1.90	2.15
8	2.42	2.10	1.89	2.13
9	2.30	2.04	1.90	2.08
10	2.34	2.00	1.87	2.07
11	2.29	2.03	1.86	2.06
12	2.35	2.10	1.90	2.11

^a $[1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}$.

(12) at LNT and the 'g' values $g_x = 2.47$, $g_y = 2.30$, $g_z = 1.99$ and $g_x = 2.40$, $g_y = 2.06$, $g_z = 1.92$ for the complexes (3) and (12), respectively. These values fit very well with the values obtained for other similar ruthenium(III) complexes [42–44]. Further, we have simulated the EPR spectra of both powder (Fig. 1a) and liquid (Fig. 1b) samples. It has been observed that both the experimental and the simulated 'g' values are very close to each other.

3.3. Redox properties

The electrochemical properties of all the complexes have been examined cyclic voltametrically under N₂ atmosphere at glassy carbon working electrode in dichloromethane solution (0.05 M: NBu₄ClO₄) and the redox potentials are expressed with reference to Ag/AgCl. All the complexes $(1 \times 10^{-3} \text{ M})$ are electroactive with respect to the metal centers and exhibited two redox processes in the potential range +1.5 V to -1.5 V. The complexes display a reversible oxidative (Ru^{IV}/Ru^{III}) and an irreversible reductive responses (Ru^{III}/Ru^{III}) at the scan rate of 100 mV s⁻¹. The potentials are summarized in Table 4 and a represen-



Fig. 1. (a) EPR spectrum of [Ru(pcr-me)Br(AsPh₃)₂] (3) at RT (A, experimental and B, simulated). (b) EPR spectrum of [Ru(pcr-me)-Br(AsPh₃)₂] (3) at LNT (A, experimental and B, simulated).

Table 4			
Electrochemical dat	a of ruthenium(III)	tripodal	complexes

Complexes	Ru ^{IV} /F	Ru ^{III} /Ru ^{II}			
	$E_{\rm pa}$	$E_{\rm pa}$	$\Delta E_{\rm P} ({\rm mV})$	$E_{1/2}$ (V)	$E_{\rm pc}$
1	0.60	0.67	70	0.63	-0.77
2	0.64	0.72	80	0.68	-0.70
3	0.56	0.64	80	0.60	-0.72
4	0.75	0.83	80	0.79	-0.73
5	1.14	1.06	80	1.10	-0.76
6	0.98	0.90	80	0.94	-0.72
7	0.86	0.80	60	0.83	-0.75
8	0.90	0.98	80	0.94	-0.67
9	1.08	1.16	80	1.12	-0.72
10	0.63	0.71	80	0.67	-0.74
11	0.93	0.87	60	0.90	-0.75
12	0.91	0.84	70	0.87	-0.77

Supporting electrolyte: NBu₄ClO₄ (0.05 M); complex: 0.001 M; solvent: CH₂Cl₂ where E_{pa} and E_{pc} are anodic and cathodic potentials, respectively; scan rate: 100 mV s⁻¹.

tative voltamogram of a complex 6 is shown in Fig. 2. All the complexes showed well defined waves in the range $0.60-1.12 \text{ V} (\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}})$ and $-0.67 \text{ to } -0.77 \text{ V} (\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}})$ Ru^{II}). The oxidation potentials are reversible with peakto-peak separation (ΔE_p) values ranging from 60 to 80 mV corresponding to one electron process. The one electron process of the oxidation has been verified by comparing its current height (ipa) with that of ferrocene/ ferrocenium couple under identical experimental conditions [45]. The irreversibility observed for the reductive response may be due to the short live reduced state of the metal ion [46] or probably due to the fast dissociation of chloride or bromide ligand from the ruthenium(III) complexes [47]. There is not much variation in the potentials due to replacement of chlorides by bromides and triphenylphosphine by triphenylarsine.

3.4. Catalytic transfer hydrogenation of ketones

Ruthenium mediated transfer hydrogenation reactions are found to be effective catalytic systems in which hydrogen is transferred from one organic molecule to another and this made us to carry out this type of reactions. One



Fig. 2. Cyclic voltammogram of [Ru(pcr-chx)Cl(AsPh₃)₂].

of the complexes $[Ru(pcr-chx)Br(AsPh_3)_2]$ (7) is taken as model catalyst and the catalytic activity in the transfer hydrogenation of various aliphatic and aromatic ketones in the presence of isopropanol and KOH as promoter has been explored. The complex catalyzes the reduction of ketones to corresponding alcohols with >90% conversions in all cases and the results are listed in Table 5.



The necessity of the ruthenium complex to observe the ensuing transfer hydrogenation was ascertained by carrying out a series of blank or control experiments suggest that none of RuCl₃ · $3H_2O$, Ru(III) precursors or tripodal ligands alone or as a mixture causes these transformations under identical reaction conditions. The alcohols formed after the reflux was 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, which then undergoes β -elimination to give a ruthenium-hydride which is the active catalyst (Scheme 3). This classical mechanism is proposed by several workers on the studies of ruthenium complexes catalyzed transfer hydrogenation reaction by metal hydrides [48,49].

Excellent conversions are obtained for both aliphatic and aromatic ketones. Benzophenone was converted to benzhydrol in >98%. The complex efficiently catalyzed the reduction of aliphatic ketones such as methyl ethyl ketone, methyl propyl ketone, isobutyl methyl ketone and diethyl ketone to their corresponding alcohols with 99.6%, 98.8%, 97.8% and 90.5% conversions, respectively. The conversion in case of acetophenone is 90.8%. The presence of electron donating (OCH_3) and electron withdrawing (Cl) substituents on the substrates (entries 2 and 3) has marginal effect on the catalytic transfer hydrogenation of ketones. 4-Chloro acetophenone is converted to corresponding alcohol in 93.9% and in case of 4-methoxy acetophenone the conversion is 90.7%. Though the effect is minimal, the greater conversion in case of 3 compared to 2 may be due to the fact that reduction involves the substrate gaining electrons and this would be more facile at an electron deficient center [50]. Moreover, this catalyst efficiently catalyzes the reduction of cyclopentanone and cyclohexanone to corresponding alcohols cyclopentanol and cyclohexanol with 99.3% and 90.8% conversions, respectively. The complex showed also good catalytic activity for seven and eight membered cyclic ketones cycloheptanone and cyclooctanone with 99.3% and 97.9% conversions, respectively. The presence of a catalytic amount of base is necessary for the transfer hydrogenation of ketones. Though no mechanistic study has been carried out, the catalytic transformation is supposed to follow the classical pathway in which the ketone coordinates to hydride-ruthenium intermediates, the observed effects seem

Table 5

Catalytic transfer hydrogenation of ketones by [Ru(pcr-chx)Br(AsPh₃)₂]/ *i*-PrOH/KOH^a

Entry	Substrates	Products	Time (h)	Conversion ^b	TON
1		OH	1	90.8	272
2	H ₃ CO	OH H ₂ CO	1	90.7	272
3		OH CI	1	93.9	281
4		ОН	1	98.9	296
5		OH	1	99.3	297
6		OH OH	1	90.8	272
7		ОН	1	99.3	297
8	\bigcirc	OH	1	97.9	293
9	0	ОН	1	99.6	298
10	° , ,	OH	1	98.8	296
11	> L	OH 	1	97.8	293
12		он ∖ , , , , , , , , , , , , , , , , , , ,	1	90.5	271

^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 Ratio of moles of product obtained to the moles of catalyst used.

RuCl(PPh₃)₂L +
$$\longrightarrow$$
 OH $\xrightarrow{\text{base}}$ $\xrightarrow{}$ ORu(PPh₃)₂L $\xrightarrow{\beta\text{-elim}}$ RuH(PPh₃)₂L
Scheme 3. The role of base (L = arylazo ligand).

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 [51].

The only byproduct acetone was identified in all the cases. As the catalyst is stable in all organic solvents and it can be recovered and the work up process is also very simple for this catalytic system. Although several catalytic systems have been reported to support transfer hydrogenation reactions of ketones, ruthenium(III) tripodal complexes have been exploited for first time towards the catalytic transfer hydrogenation reactions.

4. Conclusions

In conclusion, we have synthesized and characterized a series of ruthenium(III) tripodal complexes. One of the complexes (7) has been found to be an efficient catalyst in transfer hydrogenation of both aliphatic as well as aromatic ketones in the presence of isopropanol/KOH. We are currently perusing development of some new chiral ruthenium complexes for asymmetric catalysis.

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