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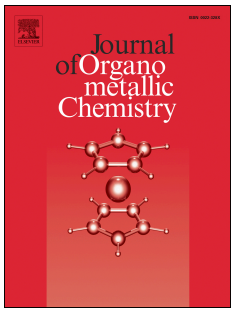

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Pushpanathan N. Sathishkumar, Neethi Raveendran, Nattamai S.P. Bhuvanesh, Ramasamy Karvembu

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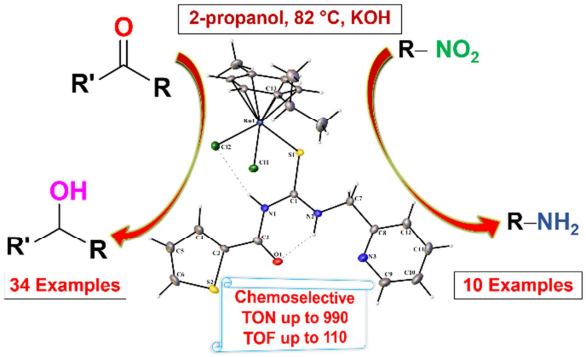


Chemoselective transfer hydrogenation of nitroarenes, ketones and aldehydes using acylthiourea based Ru(II)(*p*-cymene) complexes as precatalysts

Pushpanathan N Sathishkumar[a], Neethi Raveendran[a], Nattamai S. P. Bhuvanesh[b], Ramasamy Karvembu[a,*]

[a] *Department of Chemistry, National Institute of Technology, Tiruchirappalli-620015, India*

[b] *Department of Chemistry, Texas A & M University, College Station, TX 77842, USA*

Abstract

A new series of Ru(II)(η^6-*p*-cymene) complexes (**1-5**) was synthesized from pyridine based acylthiourea ligands (L_1-L_5) and [Ru(η^6-*p*-cymene)Cl_2]$_2$. All the ligands and complexes were well characterized by UV-Visible, FT-IR, mass and ^{1}H & ^{13}C NMR spectroscopic techniques. The molecular structures of the ligands (L_1, L_2, L_4, L_5) and complex **1** were confirmed using single crystal X-ray diffraction study. The Ru(II)(η^6-*p*-cymene) complexes (**1-5**) were proved to be efficient precatalysts for the transfer hydrogenation of carbonyl compounds and nitroarenes in the presence of 2-propanol as a hydrogen donor and KOH as a base. The catalytic transfer hydrogenation reactions were chemoselective towards the nitro group in presence of carbonyl group, which is a rare scenario in homogeneous catalysis. The catalyst was compatible with broad range of substrates which include conversion of furfural, quinone and many heterocycles. The catalytic reactions exhibited very high conversions (upto 100%) and excellent yields (upto 99%). Turn Over Number (TON) was found upto 990.

***Keywords*:** Ruthenium; arene; acylthiourea ligands; chemoselective; transfer hydrogenation

* Corresponding author.

E-mail address: kar@nitt.edu (R. Karvembu).

1. Introduction

Hydrogenation reactions play a vital role in modern organic synthesis. Transition metal catalyzed transfer hydrogenation (TH) is trending as it is an environment benign pathway. It doesn't need pressurized H_2 gas or expensive experimental setup. Recently, TH is directed towards the chemoselectivity and compatibility for a broad range of substrates with low catalyst loading, mild reaction conditions. Chemoselectivity and compatibility for a wide range of substrates are very important in pharmaceuticals since many drug molecules possess multi-functional moieties. The hydrogen source used should be readily available, cheaper and easy to handle. The hydrogenated products like alcohols, amines, etc have been used for the production of pharmaceuticals, dyes, fertilizers, fragrances, flavors, fuels, precursors for many fine chemicals etc [1,2].

Many phosphine based organoruthenium catalysts were reported for TH reactions. Since phosphine based ligands are expensive and less stable in air, an alternative ligand system is needed. The mechanism of catalytic TH reactions is influenced by both ligand and metal center. Noyori and coworkers discovered that the ligand containing N–H moiety enhances the activity of catalyst through bifunctional mechanism [3-5]. Acylthiourea ligands which are "phosphine free", contain N–H moiety, so the complexes of acylthiourea ligands are expected to follow bifunctional mechanistic pathway for the catalytic TH reactions. There is a possibility for introducing various substituents in acylthiourea derivatives, which can help in tuning the catalytic behaviour of their complexes [6]. Due to these significances, acylthiourea derivatives were used widely in both organocatalysis [7,8] and metal-based catalysis [9,10]. Ru(II)-arene based catalysts are well known for the transfer hydrogenation reactions [11]. Acylthiourea based Ru(II)-arene complexes have a wide range of applications in the field of bioinorganic chemistry [12,13] and catalysis. Sheeba *et. al*. reported the chiral acylthiourea based Ru(II)(*p*-cymene) complexes as pre-catalysts for asymmetric TH (ATH) of ketones with excellent conversions and enantiomeric excesses [14]. But the chemoselectivity of the reactions was not studied.

In general, nitro reduction was done by direct hydrogenation, catalytic TH, hydride transfer reductions, metal dissolving reductions or metal free reduction methodologies [15,16].

Mostly, the chemoselective TH of nitroarenes readily proceeded by catalytic TH through the heterogeneous pathway [17-23]. Many homogeneous TH reports are available for the chemoselective reduction of aldehydes, ketones, alkenes etc. But only a very few reports are available on the chemoselective TH of nitroarenes in homogeneous pathway [24-31]. As an interesting case, Jia *et. al*. reported the homogeneous reduction of nitroarenes using a series of Ru(II)(*p*-cymene) complexes containing Schiff base ligands as pre-catalysts and sodium tetrahydroborate as reducing agent in water. This system was not chemoselective since it reduced both ketone/aldehyde and nitro groups [32]. Recently, the same group reported half-sandwich Ru(II) phenolate−oxazoline complexes as catalysts for TH of nitroarenes. The catalysts have no chemoselectivity in the case of 4-nitrobenzaldehyde since it reduced both aldehyde and nitro groups [33]. Rohini *et. al*. reported the Ru(II)(benzene) complexes of dibenzosuberenyl appended acylthiourea as pre-catalysts for TH reactions in which nitro was chemoselectively reduced to amine. But the scope of the reaction was very limited as only one nitroarene was tested [34]. Herein we report the chemoselective TH of nitroarenes into amines and also TH of carbonyl compounds into their corresponding alcohols catalyzed by homogenous Ru(II)(η^6-*p*-cymene) pre-catalysts containing acylthiourea ligands under aerobic condition using 2-propanol as a hydrogen source and KOH as a base. We have extended the scope to broad range of substrates with excellent compatibility. Our catalytic system exhibited higher TON number than previously reported acylthiourea based Ru(II)-arene catalysts for TH/ATH reactions [14, 34-37]. Moreover, the ligands and catalysts were prepared from readily available precursors under mild conditions.

2. Experimental section

2.1 Materials and methods

All the chemicals were obtained from commercial sources and used as received. The solvents were purified and dried by the standard procedures. $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ was synthesized by following a literature procedure [38]. Melting points were recorded with Sigma melting point apparatus. FT-IR spectra were recorded as KBr pellets with a Thermo Scientific Nicolet iS5 FT-IR spectrometer in the range of 4000-550 cm^{-1}. UV-Vis spectra were recorded in a Shimadzu UV-2600 instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz and 126 MHz spectrometer respectively. $CDCl_3$ / DMSO-d_6 were used as solvents and

tetramethylsilane (TMS) was used as an internal standard. HRMS was recorded on Thermo Exactive Orbitrap instrument. GC and GCMS analyses were performed using Shimadzu GC 2010 and Shimadzu GCMS-QP2010 Ultra respectively.

2.2 Synthesis of the ligands (L)

A solution of acyl chloride (5 mmol) in ethyl acetate (10 mL) was added to a solution of potassium thiocyanate (5 mmol) in ethyl acetate (10 mL). The mixture was refluxed for about 1 h. Then, the reaction mixture was cooled to room temperature and a solution of 2-(aminomethyl)pyridine (5 mmol) in ethyl acetate (10 mL) was added drop wise and then the reaction was continued for another 3 h at room temperature. The resulting solution was filtered. The filtrate was washed with water, dried in sodium sulphate and kept for crystallization.

[N-((pyridin-2-ylmethyl)carbamothioyl)thiophene-2-carboxamide] (L_1)

Yield: 73 %. Mp.: 169 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ, ppm 11.54 (s, 2H), 8.58 (d, J = 4.5 Hz, 1H), 8.41–8.32 (m, 1H), 8.07–7.98 (m, 1H), 7.81 (td, J = 7.7, 1.7 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.33 (dd, J = 7.1, 5.2 Hz, 1H), 7.24 (dd, J = 4.7, 4.1 Hz, 1H), 4.94 (d, J = 4.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 179.28, 160.81, 154.59, 149.48, 136.81, 136.31, 133.91, 130.56, 128.39, 122.65, 121.83, 50.88. FT-IR (KBr, cm^{-1}): 3143 (m; ν(amide N−H)), 3104 (m; ν(thiourea N−H)), 1657 (s; ν(C=O)), 1280 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 202, 231, 262, 288. ESI-MS (m/z): Found 278.04200 $[M + 1]^+$ (Calcd. 278.04218).

[N-((pyridin-2-ylmethyl)carbamothioyl)furan-2-carboxamide] (L_2)

Yield: 80 %. Mp.: 175°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ, ppm 11.44 (t, J = 4.6 Hz, 1H), 11.18 (s, 1H), 8.57 (d, J = 4.4 Hz, 1H), 8.05 (d, J = 1.0 Hz, 1H), 7.84–7.79 (m, 2H), 7.42 (d, J = 7.8 Hz, 1H), 7.33 (dd, J = 7.0, 5.2 Hz, 1H), 6.75 (dd, J = 3.6, 1.7 Hz, 1H), 4.94 (d, J = 4.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 179.19, 156.50, 154.61, 149.43, 146.15, 145.24, 136.80, 122.63, 121.83, 118.57, 113.28, 50.80. FT-IR (KBr, cm^{-1}): 3306 (m; ν(amide N−H)), 3222 (m; ν(thiourea N−H)), 1670 (s; ν(C=O)), 1271 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 203, 223, 270. ESI-MS (m/z): Found 262.06434 $[M+1]^+$ (Calcd. 262.06502).

[N-((pyridin-2-ylmethyl)carbamothioyl)benzamide] (L_3) [39,40]

Yield: 79 %. Mp.: 147°C. ^{1}H NMR (500 MHz, $CDCl_3$): *δ*, ppm 11.67 (s, 1H), 9.14 (s, 1H), 8.66 (d, *J* = 4.5 Hz, 1H), 7.94–7.85 (m, 2H), 7.70 (td, *J* = 7.7, 1.7 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.29–7.21 (m, 1H), 5.03 (d, *J* = 4.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ*, ppm 179.63, 166.62, 154.66, 149.50, 136.83, 133.50, 131.92, 129.13, 127.53, 122.66, 121.88, 50.86. FT-IR (KBr, cm^{-1}): 3187 (b; ν(amide N−H)) and ν(thiourea N−H)), 1667 (s; ν(C=O)), 1247 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 202, 225, 270. ESI-MS (m/z): Found 272.08561 $[M+1]^+$ (Calcd. 272.08576).

[2, 4-dichloro-N-((pyridin-2-ylmethyl)carbamothioyl)benzamide] (L_4)

Yield: 81 %. Mp.: 182°C. ^{1}H NMR (500 MHz, DMSO-d_6): *δ*, ppm 11.90 (s, 1H), 11.37 (t, *J* = 4.6 Hz, 1H), 8.58 (d, *J* = 4.4 Hz, 1H), 7.83 (td, *J* = 7.7, 1.6 Hz, 1H), 7.76 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.54 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.34 (dd, *J* = 7.0, 5.3 Hz, 1H), 4.94 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ*, ppm 178.83, 164.64, 154.38, 149.46, 138.91, 136.86, 132.04, 131.68, 130.77, 130.71, 127.98, 122.72, 121.92, 50.82. FT-IR (KBr, cm^{-1}): 3230 (b; ν(amide N−H)), 3149 ν(thiourea N−H)), 1684 (s; ν(C=O)), 1278 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 204, 229, 262, 281. ESI-MS (m/z): Found 340.00709 $[M+1]^+$ (Calcd. 340.00781).

[N-((pyridin-2-ylmethyl)carbamothioyl)cyclohexanecarboxamide] (L_5)

Yield: 69 %. Mp.: 186°C. ^{1}H NMR (500 MHz, $CDCl_3$): *δ*, ppm 11.49 (s, 1H), 8.84 (s, 1H), 8.65–8.59 (m, 1H), 7.68 (td, *J* = 7.7, 1.7 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.22 (dd, *J* = 7.0, 5.4 Hz, 1H), 4.96 (d, *J* = 4.6 Hz, 2H), 2.23 (tt, *J* = 11.7, 3.5 Hz, 1H), 1.92 (dd, *J* = 13.7, 1.6 Hz, 2H), 1.86–1.80 (m, 2H), 1.72–1.67 (m, 1H), 1.49 (qd, *J* = 12.4, 2.9 Hz, 2H), 1.35–1.27 (m, 2H), 1.24–1.17 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ*, ppm 179.77, 176.59, 154.67, 149.48, 136.78, 122.60, 121.84, 77.30, 77.04, 76.79, 50.72, 45.94, 29.00, 25.44, 25.32. FT-IR (KBr, cm^{-1}): 3212 (b; ν(amide N−H)), 3181 ν(thiourea N−H)), 1689 (s; ν(C=O)), 1190 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 204, 221, 268. ESI-MS (m/z): Found 278.13254 $[M+1]^+$ (Calcd. 278.13271).

2.3 Synthesis of the complexes

A mixture of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (0.15 mmol) and L (0.3 mmol) was stirred in toluene (20 mL) at room temperature for about 4-5 h. Hexane was added to precipitate the product which was filtered, washed and dried *in vacuum*. The solid product was then crystallized in dichloromethane.

*$[RuCl_2(\eta^6\text{-}p\text{-cymene})L_1]$ (**1**)*

Yield: 83 %. Mp.: 220°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 11.94 (s, 1H), 11.00 (s, 1H), 8.65 (d, J = 4.6 Hz, 1H), 8.50–8.46 (m, 1H), 7.72 (td, J = 7.7, 1.6 Hz, 1H), 7.60 (dd, J = 4.9, 0.6 Hz, 1H), 7.32 (d, J = 7.8 Hz, 1H), 7.26 (dd, J = 9.6, 4.5 Hz, 1H), 7.12 (dd, J = 4.7, 4.2 Hz, 1H), 5.48 (d, J = 5.9 Hz, 2H), 5.31 (d, J = 5.9 Hz, 2H), 5.01 (d, J = 4.6 Hz, 2H), 3.09–2.98 (m, 1H), 2.30 (s, 3H), 1.34 (d, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 178.46, 162.81, 153.45, 149.47, 137.09, 136.30, 135.18, 134.19, 128.86, 122.90, 121.56, 103.44, 100.03, 84.30, 82.72, 77.31, 77.06, 76.80, 50.13, 30.48, 22.26, 18.39. FT-IR (KBr, cm^{-1}): 3228 (m; ν(amide N−H)), 3219 (m; ν(thiourea N−H)), 1688 (s; ν(C=O)), 1271 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 203, 260, 289, 445. ESI-MS (m/z): Found 512.04094 $[M\text{-}2H\text{-}2Cl+H]^+$ (Calcd. 512.04043).

*$[RuCl_2(\eta^6\text{-}p\text{-cymene})L_2]$ (**2**)*

Yield: 89 %. Mp.: 210°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 11.91 (s, 1H), 10.90 (s, 1H), 8.63 (d, J = 4.5 Hz, 1H), 7.93 (d, J = 3.6 Hz, 1H), 7.72 (td, J = 7.7, 1.1 Hz, 1H), 7.62 (s, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.28–7.25 (m, 2H), 6.51 (dd, J = 3.4, 1.3 Hz, 1H), 5.48 (d, J = 5.8 Hz, 2H), 5.30 (d, J = 5.8 Hz, 2H), 5.01 (d, J = 4.5 Hz, 2H), 3.08–2.98 (m, 1H), 2.30 (s, 3H), 1.34 (d, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 178.70, 158.35, 153.31, 149.18, 147.67, 144.81, 137.31, 122.98, 121.61, 121.22, 112.63, 103.49, 100.03, 84.27, 82.65, 49.93, 30.49, 22.26, 18.39. FT-IR (KBr, cm^{-1}): 3148 (m; ν(amide N−H)), 3128 (m; ν(thiourea N−H)), 1684 (s; ν(C=O)), 1253 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 206, 270, 451. ESI-MS (m/z): Found 496.06242 $[M\text{-}2H\text{-}2Cl+H]^+$ (Calcd. 496.06327).

*$[RuCl_2(\eta^6\text{-}p\text{-cymene})L_3]$ (**3**)*

Yield: 93 %. Mp.: 178°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 12.23 (s, 1H), 11.23 (s, 1H), 8.67 (d, J = 4.4 Hz, 1H), 8.27 (d, J = 7.6 Hz, 2H), 7.78–7.73 (m, 1H), 7.53 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.35 (d, J = 7.8 Hz, 1H), 7.32–7.27 (m, 1H), 5.47 (d, J = 5.9 Hz, 2H), 5.30 (d, J

= 5.9 Hz, 2H), 5.05 (d, *J* = 4.5 Hz, 2H), 3.08–2.98 (m, 1H), 2.28 (s, 3H), 1.33 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ*, ppm 179.19, 168.87, 153.48, 149.27, 137.34, 133.41, 131.24, 129.72, 128.48, 122.98, 121.73, 103.39, 99.99, 84.30, 82.76, 77.32, 77.06, 76.81, 50.04, 30.48, 22.26, 18.38. FT-IR (KBr, cm^{-1}): 3250 (m; ν(amide N−H)), 3231 (m; ν(thiourea N−H)), 1681 (s; ν(C=O)), 1192 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 202, 243,444. ESI-MS (m/z): Found 506.08401 $[M-2H-2Cl+H]^+$ (Calcd. 506.08401).

*[$RuCl_2(\eta^6$-p-cymene)L_4] (**4**)*

Yield: 84%. Mp.: 185°C. ^{1}H NMR (500 MHz, $CDCl_3$): *δ*, ppm 11.85 (s, 1H), 11.47 (s, 1H), 8.65 (d, *J* = 4.5 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 1.2 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 6.4 Hz, 1H), 5.43 (d, *J* = 5.8 Hz, 2H), 5.26 (d, *J* = 5.8 Hz, 2H), 5.03 (d, *J* = 4.4 Hz, 2H), 2.99 (m, 1H), 2.25 (s, 3H), 1.32 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ*, ppm 179.42, 166.80, 153.08, 149.32, 138.33, 137.34, 133.64, 132.31, 130.52, 130.00, 127.28, 123.07, 121.70, 103.45, 99.87, 84.05, 82.74, 50.06, 30.48, 22.22, 18.38. FT-IR (KBr, cm^{-1}): 3141 (m; ν(amide N−H)), 3049 (m; ν(thiourea N−H)), 1686 (s; ν(C=O)), 1246 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 203, 260, 290, 448. ESI-MS (m/z): Found 574.00343 $[M-2H-2Cl+H]^+$ (Calcd. 574.00606).

*[$RuCl_2(\eta^6$-p-cymene)L_5] (**5**)*

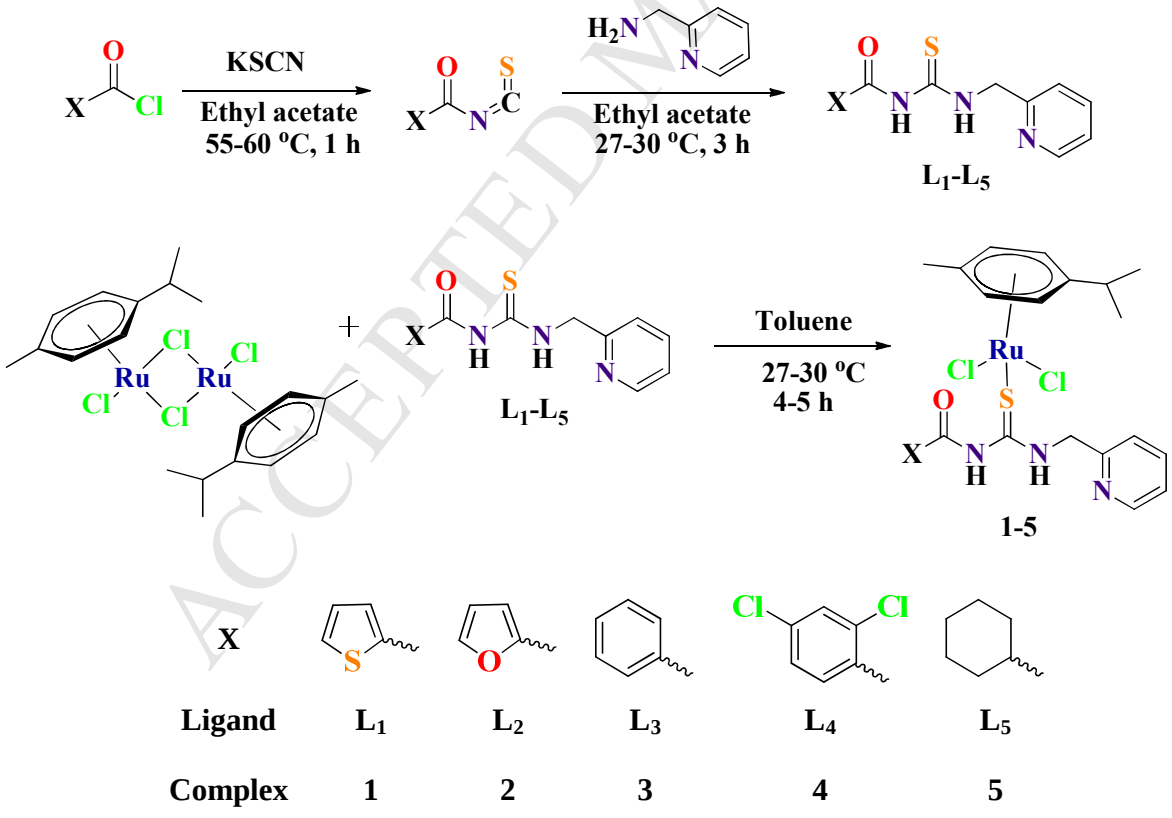
Yield: 81 %. Mp.: 190°C. ^{1}H NMR (500 MHz, $CDCl_3$): *δ*, ppm 11.70 (s, 1H), 10.80 (s, 1H), 8.62 (d, *J* = 4.4 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 7.1 Hz, 1H), 5.44 (d, *J* = 5.8 Hz, 2H), 5.28 (d, *J* = 5.8 Hz, 2H), 4.93 (d, *J* = 4.5 Hz, 2H), 3.02 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.39 (dt, *J* = 11.5, 3.3 Hz, 1H), 2.29 (s, 3H), 1.99–1.94 (m, 2H), 1.72 (dd, *J* = 9.9, 2.8 Hz, 4H), 1.62 (d, *J* = 12.8 Hz, 2H), 1.33 (d, *J* = 6.9 Hz, 6H), 1.28–1.23 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ*, ppm 178.81, 178.62, 153.49, 149.49, 137.05, 122.87, 121.58, 103.25, 99.90, 84.06, 82.67, 49.91, 45.59, 30.47, 28.22, 25.59, 25.11, 22.26, 18.46. FT-IR (KBr, cm^{-1}): 3197 (m; ν(amide N−H)), 3134 (m; ν(thiourea N−H)), 1700 (s; ν(C=O)), 1191 (s; ν(C=S)). UV-vis (Methanol): λ (nm) 204, 258, 437. ESI-MS (m/z): Found 512.13098 $[M-2H-2Cl+H]^+$ (Calcd. 512.13096).

2.4 Transfer hydrogenation of carbonyl/nitro compounds

Catalyst (0.1 mol %) and KOH (1 mmol) were dissolved in 2-propanol (4 mL). To this solution, substrate (1 mmol) was added and the mixture was refluxed (82 °C). The progress of the reaction was monitored by GC at regular intervals. After the completion of the reaction, the reaction mixture was cooled to room temperature and filtered through silica gel or alumina bed, and eluted using 50% ethyl acetate-hexane mixture. The eluted solution was reduced and analyzed by GC and/or GCMS.

3. Results and discussion

The acylthiourea ligands were synthesized from acyl chloride, potassium thiocyanate and 2-(aminomethyl)pyridine in ethyl acetate. The reaction between $[RuCl_2(\eta^6\text{-p-cymene})]_2$ and ligand (L) in toluene led to the formation of complexes of the type $[RuCl_2(\eta^6\text{-}p\text{-cymene})L]$ (Scheme 1).



Scheme 1 Synthesis of the ligands (L_1-L_5) and their Ru(II)(*p*-cymene) complexes (**1-5**)

3.1 Characterization

FT-IR spectra of the free ligands showed N–H, C=O and C=S stretching frequencies around 3104-3306, 1657-1689 and 1190-1280 cm^{-1} respectively. On complexation, C=S stretching frequency was decreased, which indicated the formation of the complexes through coordination of S in the acylthiourea ligands. Electronic spectra of the ligands and their complexes showed strong absorption bands in the range 202-231 and 243-290 nm which were attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. A less intense band at 437-451 nm in the spectra of the complexes indicated d→d transition.

In the ^{1}H NMR spectra of the ligands and their complexes, the amidic and thioamidic N–H protons were observed as singlet around 11.44-12.23 and 8.84-11.54 ppm respectively. The signals due to N–H were slightly deshielded in the spectra of the complexes. The aromatic protons of the ligands and their complexes were observed in the range 6.51-8.67 ppm. A doublet due to methylene protons was detected at 4.93-5.05 ppm. The new signals observed around 5.26-5.48 (d), 2.98-3.09 (m), 2.25-2.30 (s) and 1.32-1.34 (d) ppm in the spectra of the complexes indicated the presence of *p*-cymene. In the ^{13}C NMR spectra of the ligands and their complexes, signals were found around 178.5-179.8 and 156.5-178.6 ppm, which corresponded to the thiocarbonyl and carbonyl carbons respectively. The signal due to shielded methylene carbon appeared around 49.9-50.9 ppm. In the spectra of the complexes, new signals were observed in the range 82.6-103.5 and 18.3-30.5 ppm, which corresponded to the carbons of *p*-cymene. The cyclohexyl carbons of L_5 and **5** were observed around 22.2-45.6 ppm. The calculated $[M+H]^+$ mass of the ligands were exactly matching with the found mass. But in the case of the complexes, the two chloride ligands were labile; hence, the found mass of the complexes were matching with the calculated $[M-2H-2Cl+H]^+$ mass.[12] From the spectroscopic data, the formation of the ligands and their Ru(II)(*p*-cymene) complexes was confirmed.

3.2 Molecular structures

The molecular structure of ligands L_1, L_2, L_4 and L_5, and complex **1** was confirmed by single crystal X-ray crystallography. The ligands (L_1, L_2, L_4 and L_5) and complex **1** were crystallized by slow evaporation technique. L_1 crystallized in orthorhombic crystal system with space group $P2_12_12_1$ and seems to be a chiral molecule (Fig 1)**.** It was a twinned inversion crystal and its flack parameter was 0.4(11), close to 0.5. Hence, it was achiral which was further confirmed by polarimeter as no significant optical rotation value was observed. The ligands L_2, L_4 and L_5 crystallized in triclinic crystal system with *P-1* space group.

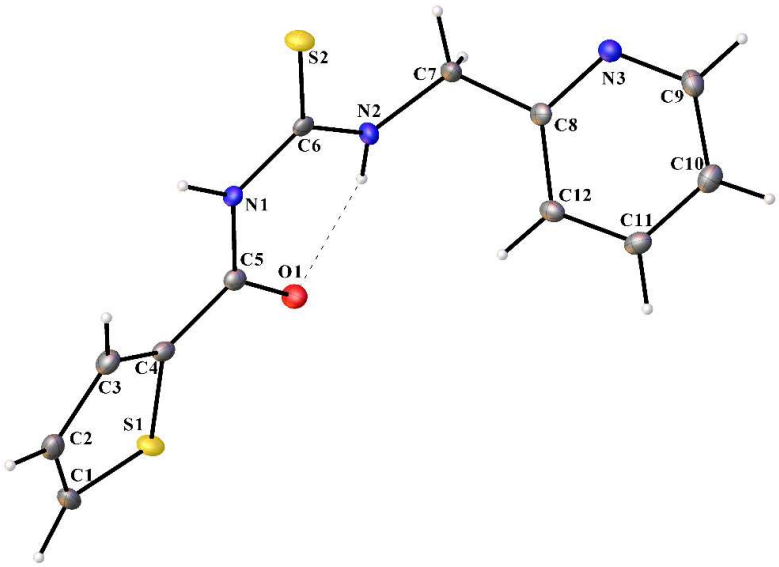


Fig. 1 Molecular structure of L_1 [Important bond lengths (Å) and angles (°): S(2)–C(6) 1.676(3), N(1)–C(6) 1.395(4), N(1)–H(1) 0.88, N(1)–C(5) 1.374(4), O(1)–C(5) 1.228(4), N(2)–C(6) 1.326(4), N(1)–H(2) 0.88, O(1)···H(2) 1.91, N(3)···H(1) 2.11, 1.98N(2)–C(6)–S(2) 125.3(2), N(1)–C(6)–S(2) 118.8(2), N(2)–C(6)–N(1) 115.9(3)].

Complex **1** crystallized in orthorhombic crystal system with *Pbca* space group. The inter- and intra-molecular hydrogen bonding interactions in the ligands and complex **1** were revealed. The intramolecular hydrogen bonding between H···O was strong since its bond length was less than 2 Å. The other hydrogen bonding interactions were weak since their bond lengths were

more than 2 Å. The centroid distance between *p*-cymene ring and Ru(II) was 1.664 Å. The monodentate neutral coordination mode of the ligand through S atom was confirmed from the crystal structure of **1**. Due to the coordination of S to Ru, the C=S bond length was increased from 1.676 to 1.708 Å. From the bond angles around Ru(II), the pseudo-octahedral geometry of **1** was confirmed (Fig 2).

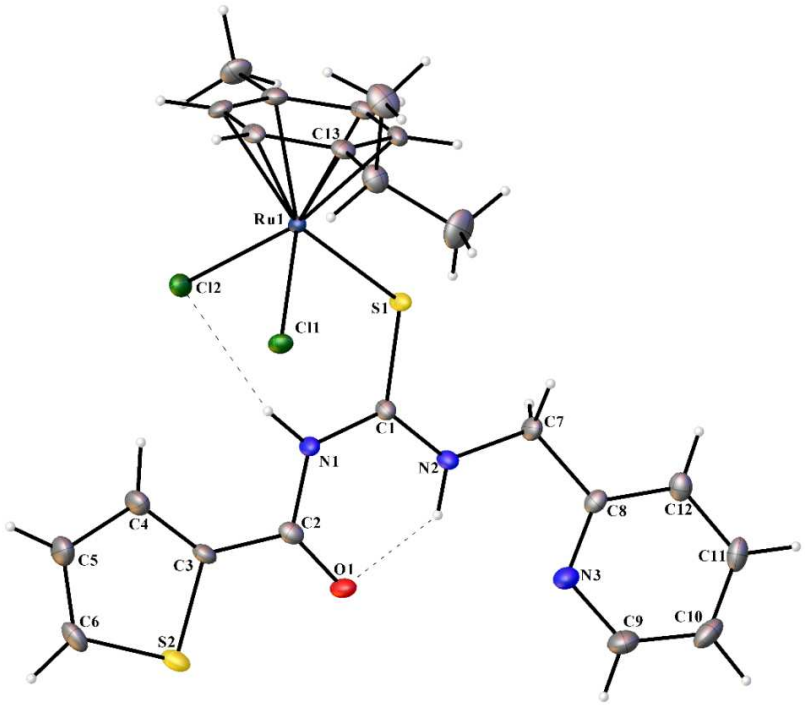


Fig. 2 Molecular structure of **1** [Important bond lengths (Å) and angles (°): Ru(1)–S(1) 2.4147(6), Ru(1)–Cl(1) 2.4278(6), Ru(1)–Cl(2) 2.4290(6), Ru(1)–C(13) 2.188(2), S(1)–C(1) 1.708(2), N(1)–C(1) 1.369(3), N(1)–H(1) 0.88, N(1)–C(2) 1.387(3), N(2)–H(2) 0.88, N(2)–C(1) 1.326(3), O(1)–C(2) 1.221(3), O(1)···H(2) 1.97, Cl(2)···H(1) 2.44, Cl(1)···H(1) 2.62, Cl(1)–Ru(1)–Cl(2) 87.66(2), S(1)–Ru(1)–Cl(1) 92.18(2), S(1)–Ru(1)–Cl(2) 90.68(2), C(13)–Ru(1)–Cl(1) 87.42(6), N(2)–C(1)–S(1) 120.28(18), N(1)–C(1)–S(1) 120.88(17), N(1)–C(1)–N(2) 118.8(2)].

3.3 Catalytic activity

The newly synthesized complexes were observed to be excellent precatalysts for the TH of carbonyl and nitro compounds using 2-propanol as a hydrogen source and KOH as a base. The reaction conditions were optimized using acetophenone as a model substrate (Table S3-S7). There was no significant conversion in the absence of a base. In the absence of the catalyst, the

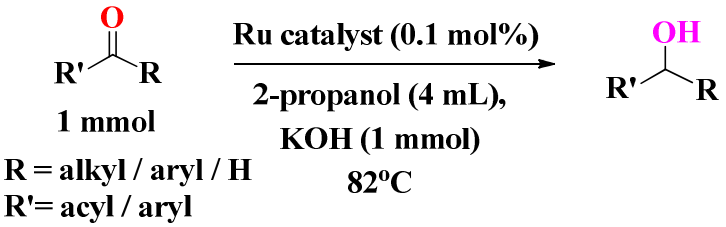
maximum conversion obtained was 34%. The effect of temperature was optimized and there was no significant conversion below 80 °C. The optimized molar ratio of the substrate : base : catalyst was 1:1:0.001. Though all the complexes showed good catalytic activity towards TH of acetophenone (99%), complex **1** was chosen for scope extension. The scope of the present system was extended to various substituted ketones, aldehydes and nitroarenes. All the substrates were reduced in good to excellent yields which were analyzed by GCMS. Some of the products were isolated and further confirmed by ^{1}H NMR study.

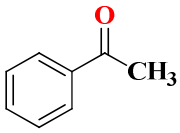
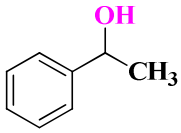
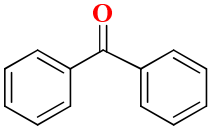
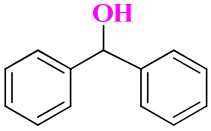
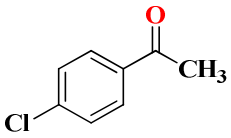
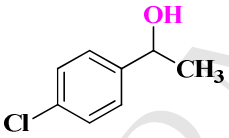
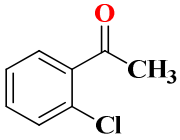
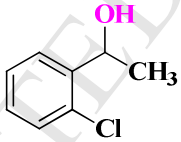
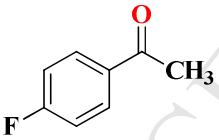
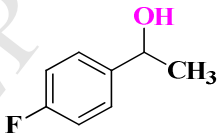
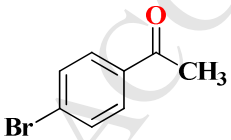
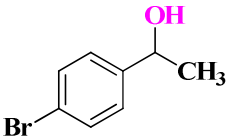
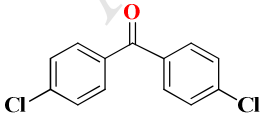
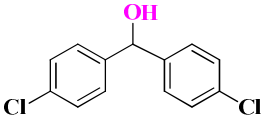
Analogous Ru(II) catalyst containing chiral acylthiourea ligand took 24 h for the conversion of acetophenone to 1-phenylethanol, but catalyst **1** containing pyridine based acylthiourea took only 14 h for the same conversion.[14] The electronic effect of the substituents present in the substrates played a predominant role. The substrates with electron withdrawing group were more reactive than those with electron donating group due to the increase of electron deficiency in the nitro/carbonyl group (Table 1 and 2). Thus, benzophenone took only 12 h for the complete conversion (Table 1, entry 2) whereas acetophenone took 14 h (Table 1, entry 1). Similarly, the substrates with electron releasing group required more than 14 h and even then, the conversion was incomplete (Table 1, entries 9-12; Table 2, entry 2). The alicyclic substrates were readily reduced with excellent TON and TOF values (Table 1, entries 13-14, 20-21, 34). Notably, the reduction of quinone was explored due to its biological and industrial significance. Only few reports were available for the metal based reduction of quinones [41]. Interestingly, entry 21 showed that the quinone was readily reduced to hydroquinone with high TON (990) and TOF (110). The bromo and fluoro substituted substrates showed moderate yield of corresponding alcohol due to the formation of hydrodehalogenated alcohol as side product (Table 1, entries 5, 6, 8, 27, 28). This was due to the labile nature of Br^{-} and F^{-}. But this was not the case with respect to chloro substituted substrates. The substrates with *para* substituent gave the corresponding alcohol readily than those with the *ortho* substituent due to the steric effect (Table 1, entries 3-4, 9-10, 24-26). In the case of entries 27 and 28, the conversion was 100 %, but the *ortho* substituted aldehyde yielded higher amount of product compared to the *para* substituted analogue. This was due to the easy formation of hydrodehalogenated alcohol as side product in the case of *para* substituted aldehyde. The TH of heterocyclic compounds is always a challenging one since there is a possibility of coordination of hetero atom to metal and poison the catalyst. It was observed in the present case that the catalyst readily reduced the heterocyclic

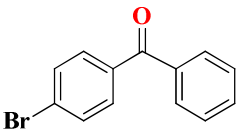
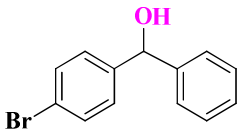
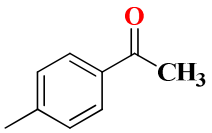
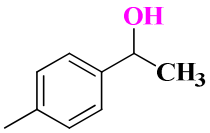
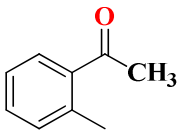
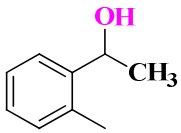
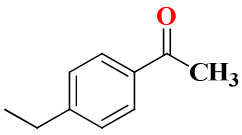
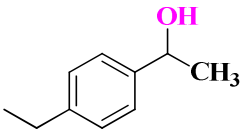
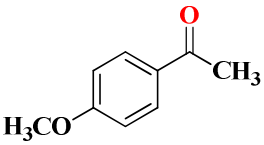
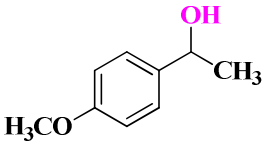
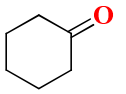
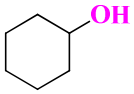
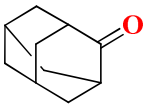
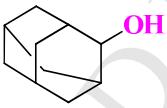
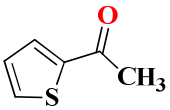
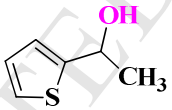
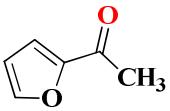
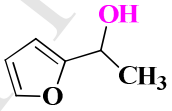
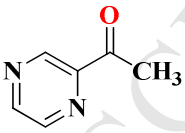
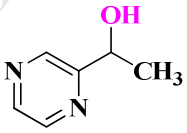
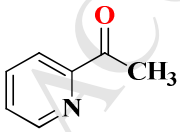
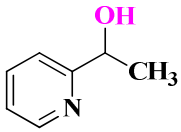
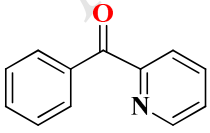
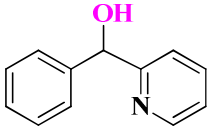
carbonyl compounds to their corresponding alcohols with excellent yields of up to 99% (Table 1, entries 15-20, 31-33). These heterocyclic alcohols have a wide range of applications in synthetic chemistry and pharmaceuticals. Interestingly, furfural was reduced to furfuryl alcohol which was a platform chemical in the biomass conversion. The conversion of furfural to furfuryl alcohol/furfuryl acetate/levulinic acid/γ-valerolactone has a significant value in biofuel research [42,43]. The TH of alkene was not successful, which led to the chemoselective reduction of unsaturated carbonyl compounds and nitroarenes. For instance, 3-cyclohexene-1-carboxaldehyde was selectively reduced to 3-cyclohexene-1-methanol with significant TON (890) (Table 1, entry 34).

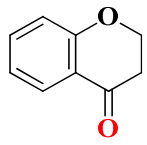
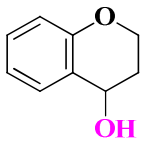
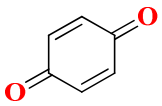
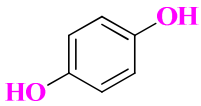
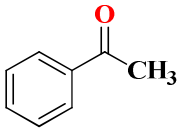
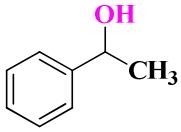
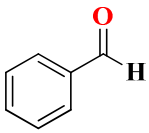
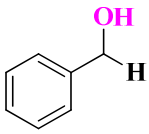
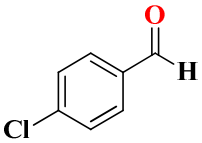
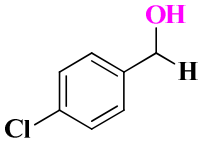
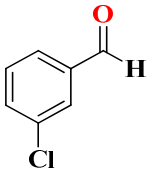
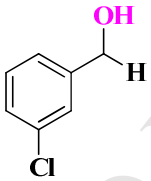
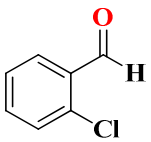
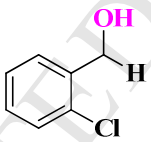
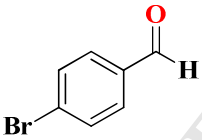
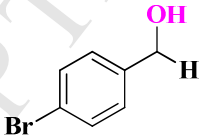
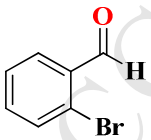
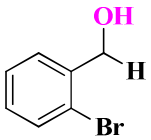
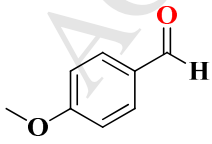
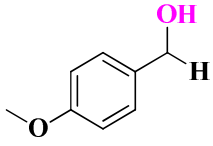
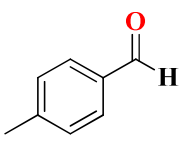
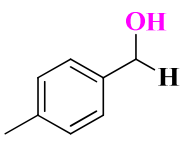
Interestingly, we have observed the chemoselective reduction of the nitro group in 3-nitroacetophenone with 99% yield. So, we have extended the scope to more nitroarenes and found that the nitroarenes with electron withdrawing substituent were readily reduced to their corresponding amines (Table 2, entries 5-10). But in the case of nitroarenes with electron donating substituent, the reaction was incomplete (Table 2, entry 2). The conversion was 100% during the reduction of nitrobenzene but the yield of aniline was only 46% (Table 2, entry 1). The lower yield was due to the formation of intermediate azobenzene. This clearly confirmed that the reduction of nitroarenes proceeded *via* azoxybenzene and azobenzene intermediates [44,45]. The importance of present catalytic system lies in chemoselectivity and wide substrate scope. Nitro group was selectively reduced to amine without the ketone/aldehyde was being reduced (Table 2, entries 8-10) with high TON. The chemoselective nitro reduction is of tremendous importance in organic synthesis particularly when multiple reducible functional groups are present. Thus, multistep reactions can be reduced to one step. In general, nitro reduction was done by classical Pd/C or other heterogeneous catalysts which require harsh experimental conditions [46-49]. The present catalytic system can replace the conventional catalysts.

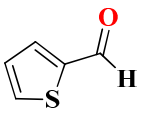
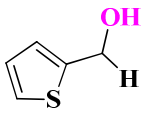
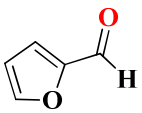
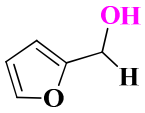
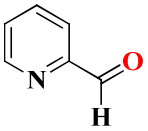
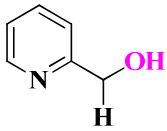
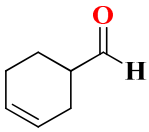
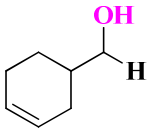
Table 1 Transfer hydrogenation of carbonyl compounds



Entry	Substrate	Product	Time (h)	Yield[b] (%)	TON[c]	TOF[d]
1			14	99	990	70.7
2			12	98	980	81.7
3			14	95	950	67.9
4			14	87	870	62.14
5			14	60	600	42.9
6			14	68	680	48.6
7			14	93	930	66.4

8			14	55	550	39.3
9			18	94	940	52.2
10[e]			18	65	650	36.1
11[e]			14	55	550	39.3
12[e]			18	70	700	38.9
13			12	98	980	81.6
14			12	99	990	82.5
15[e]			16	86	860	53.8
16			14	97	970	69.3
17			14	96	960	68.6
18			14	96	960	68.6
19			14	98	980	70.0

20[e]			12	89	890	74.2
21			9	99	990	110.0
22[f]			14	99	990	70.7
23			12	95	956	79.2
24			12	99	990	82.5
25			12	99	990	82.5
26			12	88	880	73.3
27			12	79	790	65.8
28			12	87	870	72.5
29			14	91	910	65.0
30			14	97	970	69.3

31			14	85	850	60.7
32			14	80	800	57.1
33			12	99	990	82.5
34			14	89	890	63.6

[b] Yield (%) was analyzed by GCMS

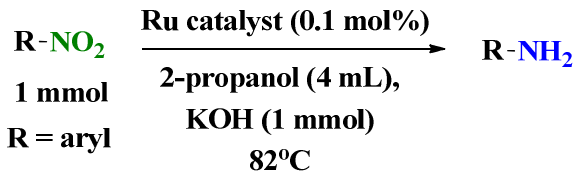
[c] Turn over number (TON) = No. of moles of product / No. of moles of catalyst

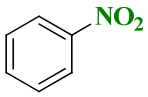
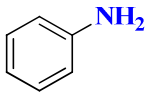
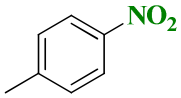
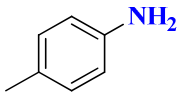
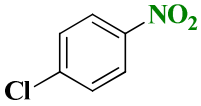
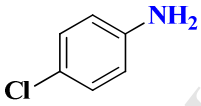
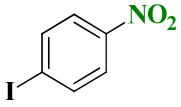
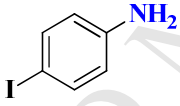
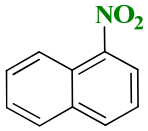
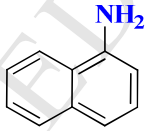
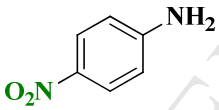
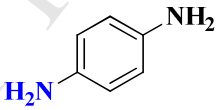
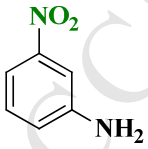
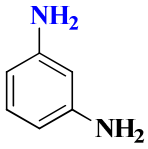
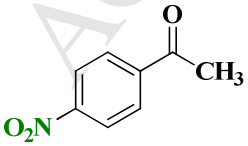
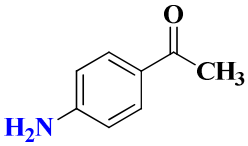
[d] Turn over frequency (TOF) = TON / Time in hours

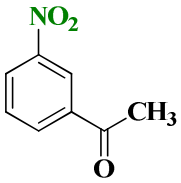
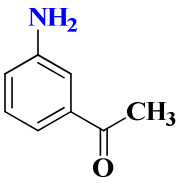
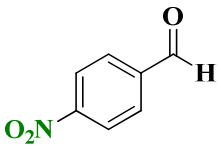
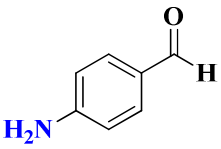
[e] Conversion was not 100%

[f] Mercury drop test

Table 2 Transfer hydrogenation of nitroarenes



Entry	Substrate	Product	Time (h)	Yield (%)	TON	TOF
1			16	46	460	28.9
2[e]			24	70	700	29.2
3			16	72	720	45.0
4			14	96	960	68.6
5			14	99	990	70.7
6			14	99	990	70.7
7			14	99	990	70.7
8			12	99	990	82.5

9			12	99	990	82.5
10			12	99	990	82.5

[b] Yield (%) was analyzed by GCMS

The reaction mechanism was similar to Noyori's outer sphere mechanism. The labile Cl^- was easily replaced by 2-propanol in the presence of KOH and led to the formation of active RuH species through intramolecular hydrogen transfer. Six-membered transition state was formed with the substrate through the bifunctional mechanism and desired product was eliminated. The common side product observed was corresponding acetates which was formed by the esterification of alcohol product with acetic acid formed from 2-propanol. The true catalyst (Ru–H species) was isolated and characterized by FT-IR spectrum in which peak at 2189 cm^{-1} corresponding to Ru–H stretching was observed. The homogeneity of the reaction was tested using mercury drop test which showed no formation of Ru amalgam as the conversion of acetophenone to 1-phenylethanol was 100% in presence of mercury under identical reaction conditions (Table 1, entry 22). This confirmed the absence of Ru particles in the reaction mixture and homogeneous pathway [50].

4. Conclusion

Ru(II)(η^6-*p*-cymene) complexes (**1**-**5**) containing pyridyl based acylthiourea ligands (L_1-L_5) was synthesized and characterized. The molecular structure of ligands L_1, L_2, L_4 and L_5, and complex **1** was confirmed by single crystal XRD study. All the complexes were found to be good pre-catalysts for the TH of ketones, aldehydes and nitroarenes. But alkene was unreactive with these catalysts and paved the way for the selective TH of unsaturated carbonyl compounds and nitroarenes. Remarkably, the nitro group was selectively reduced in the presence of carbonyl with these catalysts, which is unusual in homogeneous catalysis. The catalyst was compatible towards wide range of substrates including heterocycles.

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Highlights

- ✓ Ru(II)(η^6-*p*-cymene) complexes containing 2-(aminomethyl)pyridine based acylthiourea ligands were synthesized and characterized
- ✓ The molecular structure of ligands and one of the complexes was confirmed by single crystal XRD study
- ✓ All the complexes were found to be good pre-catalysts for the TH of ketones, aldehydes and nitroarenes
- ✓ Alkene was unreactive with these catalysts and paved the way for the selective TH of unsaturated carbonyl compounds and nitroarenes
- ✓ The catalysts were compatible with broad range of substrates which include furfural, quinone and heterocycles