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Efficient and recyclable Ru(II) arene thioamide catalysts for transfer hydrogenation of ketones: Influence of substituent on catalytic outcome

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ABSTRACT

Six cationic ruthenium(II) arene thioamide complexes with the general molecular formula [Ru(η^6-*p*-cymene)(PPh_3)(L)]$^+$ [where, L = pyridine-2-thioamide and its derivatives] have been successfully synthesized from the reaction of [Ru(η^6-*p*-cymene)Cl_2]$_2$ with chelating thioamide ligands and PPh_3 in methanol in 1:2 M ratio respectively. All the complexes were isolated as their BPh_4^- salts and were fully characterized by analytical and spectral (FT-IR, UV-Vis and ^{1}H-NMR) methods. The solid-state structure of one of the complexes, [Ru(η^6-*p*-cymene)(PPh_3)(L4)]BPh_4 (**4**) (L4 = *N*-(2, 4, 6-Trimethylphenyl)pyridine-2-thiocarboxamide) has been established by X-ray single crystal diffraction which indicates a pseudo-octahedral (piano-stool) coordination geometry is present in the complex. The ruthenium(II) complexes have been examined for the transfer hydrogenation of various aromatic, heterocycle and cyclic ketones. The formation of ruthenium(II) hydride is confirmed by ^{1}H- NMR and is proposed as the catalytic intermediate in this reaction. Under the optimized conditions, these ruthenium complexes served as excellent catalyst precursors which smoothly reduce the ketones with conversion up to 100%. The influence of other variables on the transfer hydrogenation reaction such as solvent, base, temperature, time, catalyst loading and substrate scope is also reported. Furthermore, the catalyst could be easily recovered and reused at least three times without obvious loss of conversions.

1. Introduction

Although the direct hydrogenation of ketones is more widely applied, transfer hydrogenation (TH) is an attractive alternative method. So far, the TH reaction has been extensively studied and continues to generate a high degree of interest, given the need to develop environmentally friendly and simple processes [1]. The development of new and effective catalytic systems for TH reaction by simple solvent as the proton source like 2-proponal and formaldehyde continues to be the focus of many efforts designed to develop new technologies for future industrial applications [2–4]. There has been rapid growth in the various transition metal complexes such as rhodium [5,6], iridium [7], iron [8], rhenium and osmium [9] employed for the TH of ketones. However, ruthenium complexes are found to be excellent catalysts TH of ketones and there by particular attention has been devoted to them [10]. The most outstanding results have been obtained by Noyori's group who discovered and developed the catalyst [$RuCl_2$(diphosphine)(-diamine)] with >99% yield [11]. In continuous, several works have been reported on TH reactions catalysed by ruthenium complexes containing various chelating ligands [12–16]. Cationic 1-(2-methylpyridine)phosphole cymene ruthenium chloride catalysed TH has been reported with moderate to excellent conversions [17]. In addition, Ru(II) benzene complexes containing tridendate chelating ligands have been reported as catalysts for the reduction of ketones to the corresponding alcohols with conversion is up to 98% within 5–7 h [18] Ruthenium complexes of the type [$RuCl_2$(*p*-cymene)(1,3-dialkyl-imidazolidin-2-ylidene)] complexes have been used as efficient catalysts for TH of ketones with excellent yields [19].

Arene ruthenium(II) complexes containing different ligands such as Schiff bases [20], aryl azo [21], pincer [22], carbene [23] and tripodal [24] are known in the literature. However, arene ruthenium complexes bearing thioamides containing–NHS unit are

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relatively less. Thioamides (tautomeric forms **Ia** and **Ib)** are versatile ligands which can coordinate to metal as neutral thione or in their deprotonated thiol form (Scheme 1). It has been found in the literature that the thiocarboxamide ligands are known to coordinate metal ions usually in a bidentate fashion with an N,S donor forming a five membered chelate ring. However, sulphur containing SCS pincers have gained recognition because of the added stability *via* tridentate coordination imparts to the formation of pincer complex. In terms of sulphur Lewis base donors, thioamides are a relatively unexplored compound class in the design of ligands. Palladium(II), gold(III), and platinum(II) complexes have been reported for the bidentate coordination [25]. Arene ruthenium metallacycles containing anionic chelating thioamides have been reported [26]. Recently, deprotonation-induced structural changes in ruthenium pincer complexes with secondary thioamide groups have been reported [27].

With the objective of promoting the catalysts for TH reactions, we focus our interest on synthesis of ruthenium(II) arene complexes and its catalytic application towards TH reaction [28]. Herein, we describe the report on synthesis of ruthenium(II) arene *p*-cymene complexes containing pyridine-2-thioamide ligands and triphenylphosphine. The composition of the complexes has been established by analytical and spectral (IR, UV-Vis, and NMR) methods. The molecular structure of complex **4** has been determined by diffraction analysis on single crystals. Further, the new cationic ruthenium complexes were demonstrated to be efficient catalysts for the TH of the various aromatic/heterocycle and aliphatic ketones to their corresponding secondary alcohols.

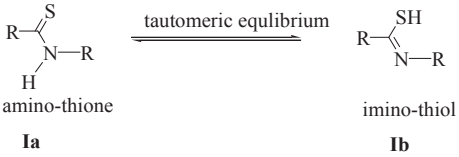
2. Experimental section

2.1. Materials

Commercially available $RuCl_3 \cdot 3H_2O$ was used as supplied from Loba Chemie. All the reagents used were chemically pure and analytical grade. The solvents were freshly distilled using the standard procedures. 2-methyl pyridine, sulphur, aniline derivatives and the ketones used for catalysis were purchased from Sigma-Aldrich and were used as received. The precursor complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ [29] and the substituted pyridine-2-thioamide ligands [30] were prepared by the literature reports.

2.2. Physical measurements

Melting points were recorded in the Boetius micro-heating table and are uncorrected. The analysis of carbon, hydrogen, nitrogen and sulphur were performed at Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology, Kochi. Infrared spectra of complexes were recorded in KBr pellets with a Perkin-Elmer 597 spectrophotometer in the range 4000–400 cm^{-1}. Electronic spectra of the complexes were recorded in CH_2Cl_2 solution with a Cary 300 Bio UV–Vis Varian Spectrophotometer in the range 800–200 nm. The ^1H NMR spectra were recorded in $CDCl_3$ on Bruker (400 MHz) equipment with TMS (δ 0.00) as an internal standard. Organic compounds in catalysis were identified by gas chromatography (GC) using Bruker 436-GC using GC-FID detector equipped with a column (15 m - 0.25 mm - 0.25 mm) and high purity nitrogen as carrier gas.



Scheme 1. Thione and thiol forms of thioamide.

2.3. Synthesis of new ruthenium(II) arene thioamide complexes

A mixture containing $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ (50 mg, 0.082 mmol), thioamide (37.4–40.8 mg, 0.164 mmol) and PPh_3 (42.8 mg, 0.164 mmol) in MeOH (20 mL) and Et_3N (1 mL) was heated to reflux for 2 h. To the hot solution was added solid $NaBPh_4$ (58.6 mg, 0.164 mmol), which caused precipitation of an orange to brown solid on cooling. The product was isolated by filtration, washed with H_2O, a little cold MeOH, diethyl ether and was subsequently dried in vacuum. The resulting complexes were recrystallized from CH_2Cl_2/Pet.ether and dried under vacuum. The purity of the complexes was checked by TLC. Yield = 78–84%.

2.4. Analytical and spectral data for the complexes

2.4.1. $[(\eta^6\text{-}p\text{-cymene})Ru[\kappa^2\text{-}S,N\text{-}C_6H_4CS{=}N\text{-}(2\text{-}MePh)(PPh_3)]^+[BPh_4^-]$ (1)

Brown solid.Yield: 82%, M.p. 182 °C (with decomposition). Found: C, 74.80%; H, 5.78%; N, 2.63%; S, 3.09%. Calc. for $C_{65}H_{60}BN_2PRuS$: C, 74.77%; H, 5.79%; N, 2.68%; S, 3.07%. FT-IR (KBr cm^{-1}): 1586 ($\upsilon_{C=N}$); 1325 ($\upsilon_{C\text{-}S}$). UV–Vis (CH_2Cl_2; λ, nm): 425, 268, 229. NMR ($CDCl_3$): δ_H (400 MHz): 6.71–8.47 (m, 43H, Ar, PPh_3, BPh_4), 4.85–6.70 (d, 4H, cymene Ar–H), 2.3 (s, 3H, CH_3), 1.3 (s, 3H, cymene-CH_3), 0.88–0.92 (d, 6H, cymene-*i*-propyl methyl). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 171.5, 168.9, 167.5, 164.1, 162.3, 161.3, 152.4, 148.1, 137.9, 135.3, 131.9, 129.6, 129.3, 128.8, 128.0, 126.7, 123.2, 117.7, 105.5, 94.5, 81.2, 29.6, 21.7, 20.9, 20.2, 17.1.

2.4.2. $[(\eta^6\text{-}p\text{-cymene})Ru[\kappa^2\text{-}S,N\text{-}C_6H_4CS{=}N\text{-}(3\text{-}MePh)(PPh_3)]^+[BPh_4^-]$ (2)

Brown solid.Yield: 73%, M.p. 202 °C (with decomposition). Found: C, 74.81%; H, 5.81%; N, 2.61%; S, 3.07%. Calc. for $C_{65}H_{60}BN_2PRuS$: C, 74.77%; H, 5.79%; N, 2.68%; S, 3.07%. FT-IR (KBr cm^{-1}): 1591 ($\upsilon_{C=N}$); 1334 ($\upsilon_{C\text{-}S}$). UV–Vis (CH_2Cl_2; λ, nm): 430, 271, 228. NMR ($CDCl_3$): δ_H (400 MHz): 6.71–8.54 (m, 43H, Ar, PPh_3, BPh_4), 4.84–5.66 (d, 4H, cymene Ar–H), 2.34 (s, 3H, CH_3), 1.33 (s, 3H, cymene-CH_3), 1.29–2.1 (d, 6H, cymene-*i*-propyl methyl). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 168.5, 166.9, 163.7, 162.1, 161.7, 161.2, 158.9, 146.2, 138.9, 136.4, 132.1, 131.8, 130.9, 129.5, 127.8, 124.8, 121.9, 116.6, 111.2, 99.1, 86.1, 32.7, 23.7, 22.3, 21.7, 19.2.

2.4.3. $[(\eta^6\text{-}p\text{-cymene})Ru[\kappa^2\text{-}S,N\text{-}C_6H_4CS = N\text{-}(4\text{-}MePh)(PPh_3)]^+[BPh_4^-]$ (3)

Brown solid.Yield: 78%, M.p. 196 °C (with decomposition). Found: C, 74.71%; H, 5.78%; N, 2.65%; S, 3.06%. Calc. for $C_{65}H_{60}BN_2PRuS$: C, 74.77%; H, 5.79%; N, 2.68%; S, 3.07%. FT-IR (KBr cm^{-1}): 1599 ($\upsilon_{C=N}$); 1317 ($\upsilon_{C\text{-}S}$). UV–Vis (CH_2Cl_2; λ, nm): 421, 271, 231. NMR ($CDCl_3$): δ_H (400 MHz): 6.82–7.3 (m, 43H, Ar, PPh_3, BPh_4), 4.88–5.67 (d, 4H, cymene Ar–H), 2.36 (s, 3H, CH_3), 1.36 (s, 3H, cymene-CH_3), 0.91–0.96 (d, 6H, cymene-*i*-propyl methyl). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 169.5, 164.9, 164.4, 163.9, 163.4, 160.2, 156.7, 147.3, 138.1, 136.4, 134.1, 133.7, 131.3, 129.5, 128.7, 125.7, 122.0, 113.9, 106.9, 95.6, 82.8, 30.7, 24.7, 21.3, 21.2, 18.2.

2.4.4. $[(\eta^6\text{-}p\text{-cymene})Ru[\kappa^2\text{-}S,N\text{-}C_6H_4CS = N\text{-}(2,3,4\text{-}TriMePh)(PPh_3)]^+[BPh_4^-]$ ***(4)***

Brown solid.Yield: 75%, M.p. 206 °C (with decomposition). Found: C, 75.10%; H, 6.05%; N, 2.59%; S, 2.89%. Calc. for $C_{67}H_{64}BN_2PRuS$: C, 75.06%; H, 6.02%; N, 2.61%; S, 2.99%. FT-IR (KBr cm^{-1}): 1594 ($\upsilon_{C=N}$); 1338 ($\upsilon_{C\text{-}S}$). UV–Vis (CH_2Cl_2; λ, nm): 425, 268, 229. NMR ($CDCl_3$): δ_H (400 MHz): 6.63–8.38 (m, 41H, Ar, PPh_3,

BPh_4), 4.78–5.62 (d, 4H, cymene Ar–H), 2. 02, 2.17, 2.28 (s, 9H, CH_3), 1.35 (s, 3H, cymene-CH_3), 0.76–0.94 (d, 6H, cymene-*i*-propyl methyl).^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 171.2, 168.9, 166.9, 164.8, 164.3, 162.1, 155.2, 149.2, 139.4, 135.3, 132.8, 133.0, 130.7, 126.9, 124.5, 121.2, 112.8, 104.7, 98.1, 89.2, 31.9, 26.5, 24.0, 22.7, 22.5, 17.9.

2.4.5. [(η^6-p-cymene)Ru[κ^2-S,N-C_6H_4CS=N-(2-ClPh)(PPh_3)]$^+$[BPh_4^-] (5)

Brown solid. Yield: 84%, M.p. 214 °C (with decomposition). Found: C, 72.17%; H, 5.36%; N, 2.66%; S, 2.98%. Calc. for $C_{64}H_{57}BClN_2PRuS$: C, 72.21%; H, 5.40%; N, 2.63%; S, 3.01%. FT-IR (KBr cm^{-1}): 1578 ($\upsilon_{C=N}$); 1343 (υ_{C-S}). UV–Vis (CH_2Cl_2; λ, nm): 428, 261, 230. NMR ($CDCl_3$): δ_H (400 MHz): 6.75–8.46 (m, 43H, Ar, PPh_3, BPh_4), 4.91–5.71 (d, 4H, cymene Ar–H), 1.29 (s, 3H, cymene-CH_3), 0.91–0.94 (d, 6H, cymene-*i*-propyl methyl).^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 173.5, 165.5, 163.4, 162.9, 161.4, 160.8, 157.9, 145.2, 136.5, 137.9, 132.2, 127.7, 125.1, 124.9, 124.7, 124.1, 123.0, 116.7, 107.5, 94.6, 89.2, 31.5, 24.0, 21.2, 20.1.

2.4.6. [(η^6-p-cymene)Ru[κ^2-S,N-C_6H_4CS=N-(2-BrPh)(PPh_3)]$^+$[BPh_4^-] (6)

Brown solid.Yield: 80%, M.p. 188 °C (with decomposition). Found: C, 69.94%; H, 5.21%; N, 2.49%; S, 2.89%. Calc. for $C_{64}H_{57}BrBN_2PRuS$: C, 69.97%; H, 5.18%; N, 2.54%; S, 2.92%. FT-IR (KBr cm^{-1}): 1583 ($\upsilon_{C=N}$); 1324 (υ_{C-S}). UV–Vis (CH_2Cl_2; λ, nm): 440, 347, 238. NMR ($CDCl_3$): δ_H (400 MHz): 6.88–8.47 (m, 43H, Ar, PPh_3, BPh_4), 4.86–6.86 (d, 4H, cymene Ar–H), 1.27 (s, 3H, cymene-CH_3), 0.85–0.94 (d, 6H, cymene-*i*-propyl methyl).^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 169.5, 164.9, 164.4, 163.9, 163.4, 160.2, 156.7, 147.3, 138.1, 136.4, 134.1, 133.7, 131.3, 129.5, 128.7, 125.7, 122.0, 113.9, 106.9, 95.1, 2.82, 30.9, 20.7, 20.3, 19.2.

2.5. Single crystal X-ray diffraction study

Single crystal of [Ru(η^6-*p*-cymene)(PPh_3)(L4)]BPh_4 (**4**) was grown by slow evaporation of chloroform-methanol mixture at room temperature. 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 293 K and 173 K. Corrections were made for Lorentz and polarization effects as well as for absorption (None). The structure was solved with direct method using SIR-97 [31] and was refined by full matrix least-squares method [32] 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.

2.6. Typical procedure for transfer hydrogenation of ketones

The mixture of a ketone (0.2 mmol) and base (0.08 mmol)containing the catalyst (0.1 mol%) in 2-propanol (6 ml) was stirred at 82° C. After the reaction was complete, diethyl ether could be added to the mixture and extract the ruthenium complexes followed by filtration and neutralized with 1N HCl, washed with water and dried over anhydrous Na_2SO_4. Conversion obtained is related to the residual unreacted ketone. Percentage of conversion was calculated by using GC method of the crude mixture and compared with the authentic samples. Acetone was identified as only by-product 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.

2.7. Recycling of the catalyst

After completion of the reaction, the solvent was removed under reduced pressure. The catalyst was removed by the addition of 15 ml of diethyl ether followed by filtration and subsequent neutralization with 1N HCl. The identity of the recovered catalyst is further confirmed by TLC and ^{1}H NMR spectrum before next cycle.

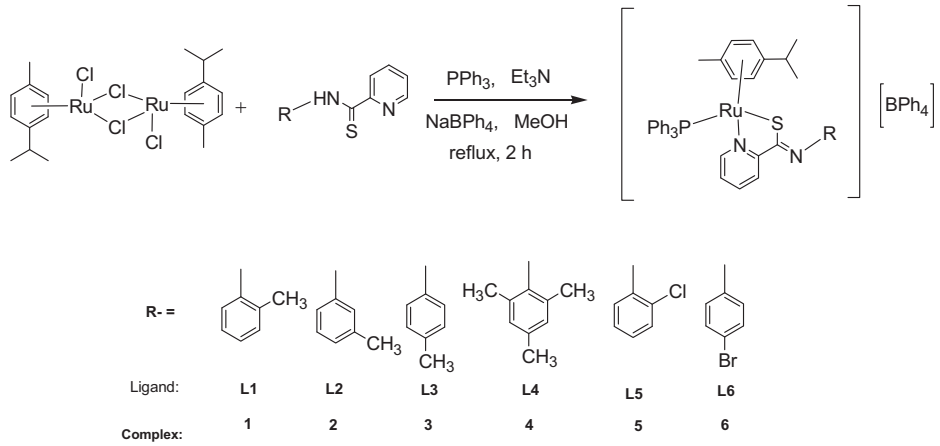
3. Results and discussion

3.1. Synthesis and spectroscopic study

The new cationic ruthenium(II) arene complexes bearing pyridine-2-thioamide of the type [Ru(η^6-*p*-cymene)(PPh_3)(L)]$^+$, (where L = pyridine-2-thioamide) (Scheme 2) have been obtained in good yields from the reaction of [Ru(η^6-*p*-cymene)Cl_2]$_2$ with pyridine-2-thioamide ligands and PPh_3 in methanol in 1:2 M ratio respectively. They are found to be diamagnetic, characteristic of the low spin d^6 ruthenium(II) complexes. In all the reaction, the ligand behaves as monoanionic bidentate N and S chelating ligands. All the complexes are brown in colour, air stable in both the solid and the liquid states at room temperature and soluble in common organic solvents, such as, chloroform, CH_2Cl_2, acetonitrile, DMF and DMSO producing intense brown coloured solution. The elemental data are in good agreement with the general molecular formula proposed for all the complexes.

The ligand thioamide exhibits thione-thiol tautomerism, since it contains a thioamide –NH–C=S functional group. The free ligand displays $\nu_{C=S}$ and ν_{N-H} absorptions at 792 cm^{-1} and 3180 cm^{-1} respectively and were disappeared upon complexation. These observations may be attributed to the enolization of –NH–C=S and subsequent coordination through the deprotonated sulphur [33]. The IR spectra of the complexes did not display ν_{S-H} at 2585-2570 cm^{-1} suggesting the deprotonation of the thiol proton prior to coordination [34]. Moreover, the new band appeared around 1270-1240 cm^{-1} which corresponds to ν_{C-S} for the thioamide complexes. In addition, other characteristic bands due to triphenylphosphine are also present around 1432-1436 cm^{-1} in the spectra for all the complexes [35]. A week intensity band is observed in the region of 1094 cm^{-1} for the characteristic coordinated pyridine moiety [36]. The electronic spectra of the complexes in CH_2Cl_2 solution showed three bands in the region 428-229 nm. The low intensity bands observed around 425–428 nm region has been assigned to metal to ligand charge transfer transition (MLCT). In addition, the other high intensity bands in the 229–230 nm regions may be attributed to usual n-π* and π-π* transition occurring within ligand orbitals and the pattern of electronic spectra (Fig. S1) is similar to that of other ruthenium(II) octahedral complexes [37].

The bonding arrangement is further confirmed by ^{1}H-NMR spectra. In the spectra of all the complexes, the multiplet observed at around 6.5–8.9 ppm is assigned to aromatic protons of the phenyl group of triphenylphosphine, thiocarboxamide ligands and the tetraphenylborate. The methyl protons appeared as singlets between 1.8 and 2.5 ppm region. The absence of –NH proton in the complexes indicates enolised form of the thiolate sulphur of the thioamide ligand on complexation and hence coordination to ruthenium is through thiolate sulphur. In addition, the two isopropyl methyl protons of the *p*-cymene appeared as two doublets between δ 0.7 and 0.9 ppm and the methine protons comes in between δ 1.9 and 2.2 ppm as septets. Further, the methyl group of the *p*-cymene appears as singlets between δ 1.2 and 1.4 ppm. The proton NMR data are gathered in the experimental section. The methyl group of the *p*-cymene is present as singlet around δ 1.3 ppm (Figs. S2–S7).



Scheme 2. Synthesis of cationic ruthenium(II) arene thioamide complexes.

3.2. Molecular structures

The solid-state molecular structure of one of the complexes [Ru(η^6-*p*- [Ru(η^6-*p*-cymene)(PPh_3)(L4)]BPh_4 (**4**) were resolved by single crystal X-ray crystallography. The summary of the refinement parameters are given in Table 1 and the selected bond lengths and bond angles are gathered in Tables 2 and 3. The corresponding ORTEP diagrams are reflected in Fig. 1. The complex (**4**) crystallizes in "P2 (1/c") space group. The *p*-cymene ligand is bonded to the ruthenium atom in η^6—fashion with ruthenium centroid. An ORTEP view of the complexes show clearly that the thiocarboxamide ligand coordinates in a bidentate manner to ruthenium ion *via* the pyridyl nitrogen and thiolate sulphur in addition to one PPh_3 and one *p*-cymene groups. The complex adopts the commonly observed piano-stool geometry as reported in many half-sandwich arene ruthenium(II) complexes [38]. In this case, the *p*-cymene ring forms the seat of the piano-stool, while the bidentate thioamide N, S and PPh_3 ligands form the three legs of the stool. Therefore, ruthenium(II) ion is sitting in a SNP (η^6-*p*-cymene) coordination environment. The thioamide ligand binds the metal center at N and S forming one five membered chelate ring with bite angles of 81.31(5)° N(1)-Ru(1)-S(1) and 89.46(5)° N(1)-Ru(1)-P(1). The bond lengths of Ru(1)-N(1) and Ru(1)-S(1) are 2.111(2) Å and 2.3481 (6) Å respectively. These bond distances are very similar to those observed in other ruthenium(II) complexes [39]. The Ru(1)-P(1) bond length 2.3513(6) Å is in agreement with other structurally characterized *p*-cymene ruthenium phosphine complexes [40]. The C—C bond distances in the *p*-cymene ligands of the complexes alternate in a long-short-long pattern, which is typically found for arene coordinated to ruthenium.

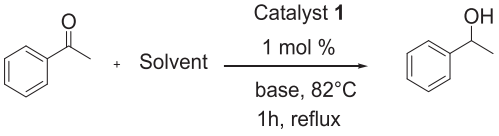
Table 1
Crystallographic data for complex 4.

	Complex (4)
Empirical formula	$C_{67}H_{64}BN_2PRuS$
Formula weight	1072.11
Temperature (K)	173
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	16.8096(5)
b (Å)	16.5312(5)
c (Å)	20.0667(6)
α (°)	90
β (°)	95.013(1)
γ (°)	90
Volume (Å^3)	5554.9(3)
Z	4
D_{calcd} (Mg/m^3)	1.282
Absorption coefficient	0.392
Data/restraints/parameters	17723/0/664
Goodness-of-fit on F2	1.083

Table 2
Selected bond lengths (Å) and bond angles for complex 4.

Bond lengths (Å)		Bond angles (°)	
Ru1 N1	2.111(2)	N1 Ru1 S1	81.31(5)
Ru1 S1	2.3481(6)	N1 Ru1 P1	89.46(5)
Ru1 P1	2.3513(6)	P1 Ru1 S1	87.35(2)
Ru1 C16	2.262(2)	N2 C6 S1	124.6(2)
Ru1 C17	2.209(2)	N2 C6 C5	118.9(2)
Ru1 C18	2.237(3)	C6 N2 C7	116.4(2)
Ru1 C19	2.272(2)	C17 Ru1 P1	120.97(6)
Ru1 C20	2.235(2)	C17 Ru1 N1	147.92(8)
Ru1 C21	2.251(2)	C17 Ru1 S1	89.63(6)

Table 3
Effect of solvent and base[a].



Entry	Solvent	Base	Conversion[b] (%)
1	Methanol	KOH	42
2	Ethanol	KOH	21
3	2-propanol	KOH	99
4	2-propanol	–	0
5	2-propanol	KOH	0[c]
6	2-propanol	NaOH	98
7	2-propanol	Na_2CO_3	69
8	2-propanol	K_2CO_3	65
9	2-propanol	Et_3N	31
10	2-propanol	Pyridine	12

[a] Reaction conditions: reactions were carried out at 82 °C using acetophenone (0.2 mmol), catalyst (1 mol%), base (0.08 mmol), solvent (6 mL).
[b] Conversion was monitored by GC analysis and are average of two runs.
[c] Reaction carried out in the absence of catalyst.

3.3. Catalytic transfer hydrogenation of ketones

Catalytic TH is being increasingly used in industry because of its

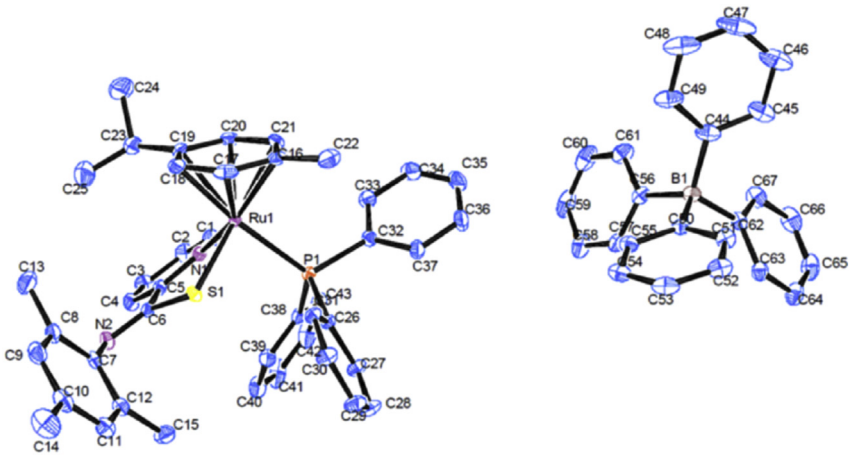


Fig. 1. The molecular structure of [Ru(η^6-*p*-cymene)(PPh_3)(L4)](BPh_4) (4).

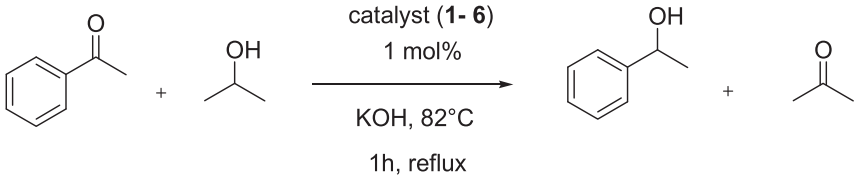
selectivity, efficiency, scope, simplicity, economic viability and also the growing awareness of the need for green chemistry. In general, recent aims have been to improve catalyst turnover and selectivity, either through more active catalysts or ones that can be recycled, to enable lower costs and higher purity products, as well as more productive, less wasteful processes. In order to optimize the reaction conditions, the effect of solvents, bases, time, temperature and catalyst: substrate ratios were studied.

For the entire optimization, acetophenone was taken as test substrate for different conditions. To study the influence of solvents in our catalytic system, we have chosen the reaction between acetophenone (0.2 mmol), complex **1** (1 mol%)as the catalyst precursor in the presence of various solvents and KOH (0.08 mmol) as the base (Table 4) and the resulting mixture was monitored by gas chromatography. Methanol, ethanol and 2-propanol solvents were taken for investigation and 2-propanol is found to be a suitable system for the maximum conversion (98.7%) of acetophenone to 1-phenyl ethanol. On the other hand methanol, ethanol solvents gave less conversion (47%, 21%) than 2-propanol. Based on this conclusion 2-propanol was taken as a proton source for our investigation.

The choice of base was chosen, as a next step for the optimization. In the absence of base (Table 3, entry 4) no product was observed. The necessity of the ruthenium complex to observe the ensuing TH was ascertained by carrying out a series of blank or control experiments which suggest that none of Ru(II) arene precursors or thioamide ligand alone or as a mixture causes these transformations under identical reaction conditions (Table 3, entry 5). We initially carried out the reaction of acetophenone (0.2 mmol), using complex **1** (1 mol %) as a test catalyst in the presence of 2-propanol with different bases. Strong inorganic bases like NaOH or KOH gave higher conversions of 98% and 99% respectively. Weak inorganic bases such as Na_2CO_3 and K_2CO_3 show good conversions of 69% and 65% respectively. In organic bases such as triethylamine, pyridine we observed only traces amount of alcohols. The conversions are summarized in Table 3. Reduction of acetophenone into 1-phenyl ethanol could be achieved in high yield by increasing the temperature up to 82 °C.

We further examined the effect on performance of changing the R substituents on the thioamide coordinated to ruthenium. To this purpose, all the complexes (**1**–**6**) were tested as catalysts for TH of acetophenone as a model substrate using 2-propanol and KOH as a base at 82 °C. The catalytic reactions were performed using 0.2 mmol of acetophenone, 1 mol% of **1**–**6** and KOH (0.08 mmol) in 2-propanol reflux for 1 h at 82 °C. All the complexes were found to be effective catalysts affording conversions between 82% and 100% within 1 h and the results are summarized in Table 4. Complexes **5** and **6** containing chloro and bromo substituents show increased conversions 100% and 99% of reduced products respectively. The

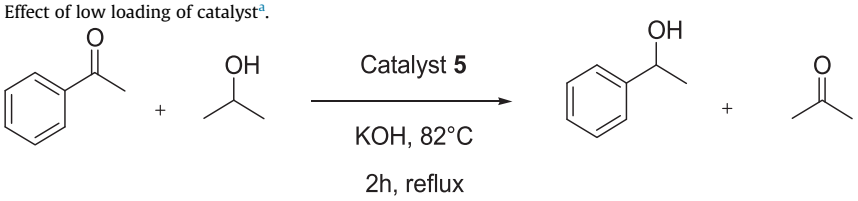
Table 4
Catalytic activity of the complexes[a].



Entry	Complex	Conversion[b] (%)
1	**1**	86
2	**2**	82
3	**3**	84
4	**4**	92
5	**5**	100
6	**6**	99

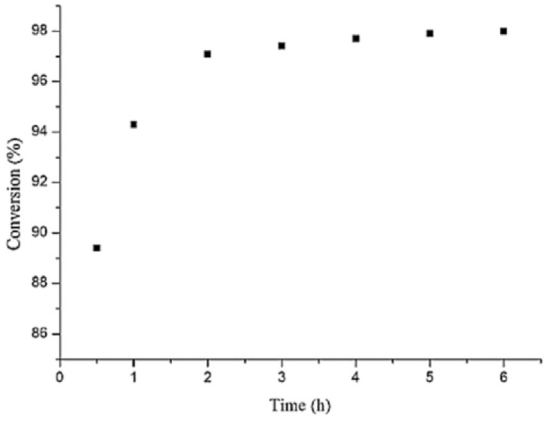
[a] Reaction conditions: reactions were carried out at 82 °C using acetophenone (0.2 mmol), catalyst (1 mol%), base (0.08 mmol) and *iso*-proponal (6 mL).
[b] Conversion was monitored by GC analysis and are average of two runs.

Table 5
Effect of low loading of catalyst[a].



Entry	Mol% Ru	Conversion[b](%)	TON[c]
1	1	100	100
2	0.3	99.8	333
3	0.2	99	495
4	0.1	97	970
5	0.06	81	1350
6	0.05	72	1440
7	0.04	51	1275
8	0.02	42	2100

[a] Reaction conditions: reactions were carried out at 82 °C using acetophenone (0.2 mmol), catalyst (1–0.02 mol%), base (0.08 mmol), 2-propanol (6 mL).
[b] The conversions reported in Table 5 are average of two runs for all catalytic reactions.
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

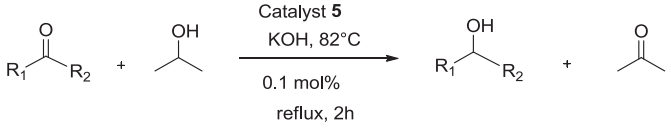


[a]Reaction conditions: reactions were carried out at 82 °C using acetophenone (0.2 mmol), catalyst (1-0.02 mol%), base (0.08 mmol), 2-propanol (6 mL).

Fig. 2. Influence of reaction time on the formation of 1-phenylethanol.

presence of electron withdrawing Cl and Br in the terminal nitrogen of the coordinated ligand may be responsible for the observed excellent catalytic activity over the other four complexes. The lowest conversion observed is 82% for complex **2**. From the observed results it was found that the catalytic efficiency of the complexes follows the order 2 < 3<1 < 4<6 < 5.

In order to optimize the effect of catalyst loading, different catalyst: substrate (C:S) ratios were tested in the TH reaction of acetophenone using complex **5** as catalyst in 2-propanol/KOH. The reaction proceeds with high conversion of acetophenone to 1-phenylethanol when a C: S ratio of 1:1000 (0.1 mol %) is used. When increasing the C:S ratio to 1:1500, 1:2000 and 1:2500 the reaction proceeds with good conversions. Further, the catalyst works well with low catalyst loading of C:S ratio 1:5000 (0.02 mol %) and shows conversion of 42%. The results are listed in Table 5. Thus it was concluded that catalyst: substrate ratio of 1:1000 is the best compromise between optimum reaction rate and C:S ratio. The conversions reported are averages of two runs in the case of all catalytic reactions.



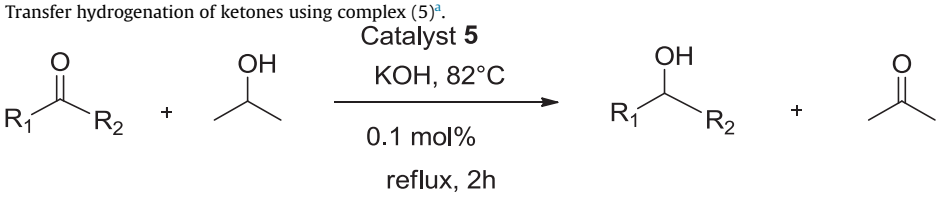
Scheme 3. Transfer hydrogenation of ketones.

The progress of formation of 1-phenylethanol as a function of time using the above optimized conditions is shown in Fig. 2. The results indicate the formation of 1-phenylethanol initially increased with the progress of the reaction, reached a maximum and then remain unchanged. A high conversion (100%) for the formation of 1-phenylethanol was observed at the optimum reaction time of 2 h. No noticeable improvement was observed even after extending the reaction time to 6 h. The results obtained from the optimization studies indicate clearly that excellent yields were achieved in the reduction of acetophenone to 1-phenylethanol when complex **5** was used as the catalytic precursor with a substrate-catalyst molar ratio 0.1 mol% in 2-propanol in the presence of KOH at 82 °C within 2 h.

To explore the scope of the new catalyst, a range of other ketones were reduced using catalyst **5** (Scheme 3). All the reactions were carried out under identical reaction conditions and the conversions were calculated using GC method. The results collected from the catalytic reactions are listed in Table 6 (Figs. S8–S39) and NMR data of the reduced products are given as supplementary material (Fig. S40).

The catalyst **5** reduces the acetophenone and its derivative with good to excellent conversions over a period of 2h. The conversion of acetophenone to 1-phenyl ethanol is obtained in 97%. Further, the selected catalyst was screened in the catalytic reduction of various derivatives of acetophenone to the corresponding secondary alcohols. It has been observed that the catalytic activity varies in the respect to substituent present in the acetophenone fragment. The electron withdrawing substituent present in the substrates found to be played a significant role in the conversion of ketone to alcohols. Substrate with electron withdrawing substituents such as Cl, Br and NO_2 (entries 2, 3 and 4) gave excellent to full conversions of 98%, 99% and 100%. The electron donating substituent present in the substrates observed to have slightly less activity in the reduction of ketones. In case of 4′-methyl acetophenone, 4′-methoxy acetophenone and 4′-hydroxy acetophenone, conversions to their corresponding alcohols are 89%, 92% and 91%respectively (entries 5,

Table 6
Transfer hydrogenation of ketones using complex (5)[a].



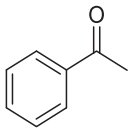
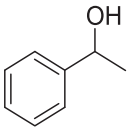
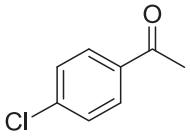
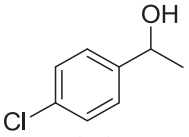
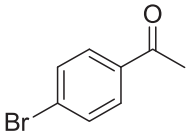
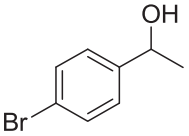
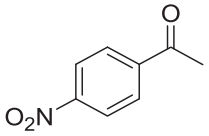
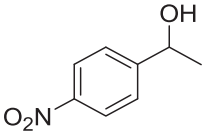
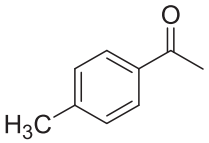
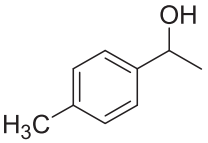
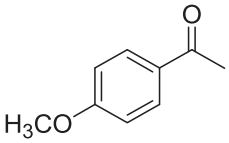
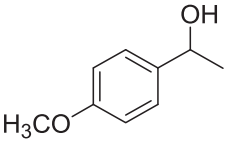
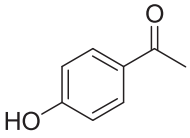
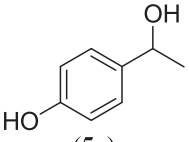
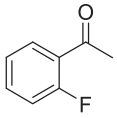
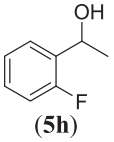
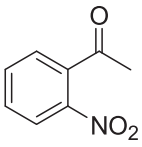
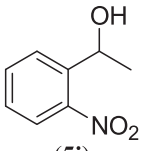
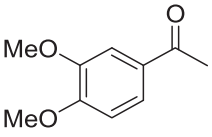
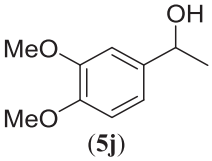
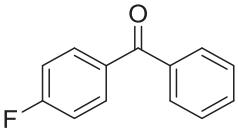
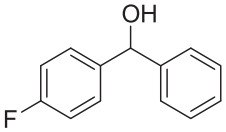
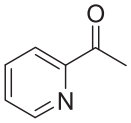
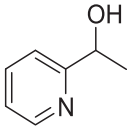
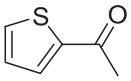
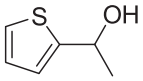
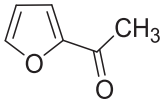
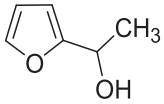
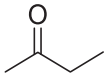
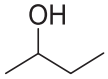
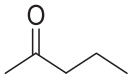
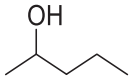
No	Substrate (3)	Product (5)	Conversion[b] (%)	TON[c]	TOF[d]	Isolated yield (%)
1		 (5a)	97	970	485	96.2
2		 (5b)	98	980	490	93.3
3		 (5c)	99	990	495	98.7
4		 (5d)	100	1000	500	100
5		 (5e)	89	890	445	87.9
6		 (5f)	92	920	460	91.5
7		 (5g)	91	910	455	89
8		 (5h)	100	1000	500	100

Table 6 (*continued*)

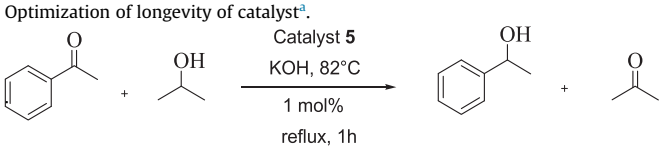
No	Substrate (3)	Product (5)	Conversion[b] (%)	TON[c]	TOF[d]	Isolated yield (%)
9		 (5i)	100	1000	500	100
10		 (5j)	99	990	495	98.4
11		 (5k)	100	1000	500	100
12		 (5l)	94	940	470	92.9
13		 (5m)	95	950	475	94.3
14		 (5n)	95	950	475	93.8
15		 (5o)	79	790	395	77.8
16		 (5p)	98	980	490	97.7

[a] Experimental conditions: reactions were carried out at 82 °C using ketone (0.2 mmol), catalyst (0. 1 mol %), base (0.08 mmol), 2-propanol (6 mL).
[b] Conversion was monitored by GC analysis.
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.
[d] Turnover frequency: moles of product per mole of catalyst per hour, in h^{-1}.

6 and 7). The introduction of electron withdrawing substituents to the para position of the aryl ring of the acetophenone decreased the electron density on the C–O bond and there by the activity was improved giving rise to easier hydrogenation. Substrates with *ortho*-substituted electron withdrawing groups such as fluoro and nitro play significant performance and catalyze with 100% conversions (entries 8 and 9). The dimethoxyacetophenone was underwent hydrogenation to 99% conversion. The scope the present catalyst is further explored to sterically hindered ketone (entry 11) and gave 100% conversion and this catalytic activity is better than the previously reported catalytic system [41] in terms of the reaction time, catalyst load and the conversion. Certain heterocycle ketones have been found to be either unreactive or reactive unless Lewis acid additives are added to the hydrogenations. This is presumably due to the deactivation of the catalyst by the heterocycle, through hydrogen bonding, deprotonation or coordination to ruthenium and the hence the hydrogenation of heterocycle ketones are less common. However, in our present protocol, interestingly heterocycle ketones are underwent the TH reaction to give the alcohols in high conversions of 94%–95% (entries 12, 13 and 14). The catalyst also displays good efficiency in the conversions of the aliphatic ketones (entries 15 and 16) to their corresponding alcohols (79%, 98%; entries 15 and 16).

The recovery and recycling of homogeneous Ru catalyst in TH

Table 7
Optimization of longevity of catalyst[a].



No. of cycles	Conversion[b] (%)
1	100
2	98.3
3	97.5
4	86.3
5	73.8

[a] Experimental conditions: reactions were carried out at 82 °C using acetophenone (0.2 mmol), catalyst 5 (0.002 mmol), base (0.08 mmol), 2-proponal (6 ml).
[b] Conversion was monitored by GC analysis.

are important from an economic point view due to high cost of ruthenium compounds as well as for preventing the contamination of the final products by toxic metals. Thus, recycling experiments were conducted by using catalyst **5** in the TH of acetophenone. The results presented in Table 7 show that catalyst could be used three times without much activity loss. As a result of its high polarity, good thermal stability and insensitivity to moisture and oxygen, catalyst **5** proved to be an efficient and recyclable catalyst for the TH of a wide range of ketones when using 2-propanol as hydrogen source. 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. Several workers proposed a mechanism [42] which involves formation of Ru-*iso*-propoxide species which undergoes β-hydride elimination leads to form ruthenium metal hydride species with the release of acetone. Insertion of ketone to Ru–H species, resulting in the secondary alkoxide which involves alcohol metathesis to give the alcoholic product and regenerate the original catalyst.

4. Conclusions

We have described the synthesis of novel class of cationic ruthenium(II) arene complexes containing thioamide and triphenylphosphine ligands of general formula $[Ru\text{-}\eta^6\text{-}(p\text{-cymene})(PPh_3)(L)]^+$. The composition of the complexes was accomplished by analytical and spectral (IR, UV-Vis and ^1H NMR) methods. Single crystal X-ray diffraction study of complex **4** confirm the coordination of thioamide to ruthenium center *via* pyridyl nitrogen and thiolate sulphur reveals the presence of piano-stool geometry around ruthenium ion. Further, the ruthenium(II) arene thioamide complexes were generated as efficient catalysts for TH of aryl/alkyl ketones to the corresponding secondary alcohols. The influence of different substituents of the ligand and substrates on the catalytic activity was also investigated. The catalyst works well with 0.1 mol% with the maximum conversion of 100%.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.02.016.

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