

Transfer Hydrogenation of Ketones Using Recyclable (η^6 -Arene) Ruthenium(II) Naphthylazo-*p*-Methyl Phenolate Complex

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Abstract: Recyclable (η^6 -*p*-cymene)-ruthenium(II) 2-naphthylazo-*p*-methylphenolate catalyst of formulation $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\text{L})]$ (where **L** = mono anionic 2-naphthylazo-*p*-methylphenolate ligand) is shown to be an efficient catalyst for transfer hydrogenation of a wide range of alkyl and aryl ketones in the presence of 2-propanol and KOH.

Keywords: Naphthylazo ligand, ruthenium-*p*-cymene complex, catalytic transfer hydrogenation.

1. INTRODUCTION

Current interest in the chemistry of half-sandwich (η^6 -arene)-ruthenium(II) complexes lies in the development of new catalytic systems for a variety of organic transfer hydrogenations and in the enantioselective asymmetric induction studies [1-3]. Ruthenium(II)-arene complexes display a three legged piano stool structure in which the metal center has a quasi-octahedral geometry. This structural feature opens the possibility to introduce in the molecule two types of stereogenic centers: the metal and the ligand. The O, N donor type of ligands has been prepared to optimize the catalytic potential of their metal complexes [4]. It has been found in the literature that the arylazophenol ligand is known to coordinate metal ions usually in a bidentate fashion with N, O donor forming a five-membered chelate ring. Particularly the azo (-N=N-) group due to its strong π -acid character stabilizes ruthenium in lower oxidation states while phenolate oxygen being a hard base stabilizes the higher oxidation state of the metal ion [5].

The reduction of ketones using catalytic hydrogenation transfer conditions with 2-propanol as hydrogen source has been largely investigated in the last years and several ruthenium complexes have proven to be efficient catalyst precursors in transfer hydrogenation [6-9]. Mathey and coworkers have reported the cationic $\text{Ru}(\text{-}p\text{-cymene})\text{Cl}$ chelate complex as catalyst for the hydrogen transfer process of ketones with very high TON and TOF [10]. Further, ruthenium CNN pincer complexes have been reported by Baratta and coworkers as highly active catalysts in the transfer hydrogenation of ketones in 2-propanol with $\text{NaO}i\text{Pr}$ [11].

The ability of ruthenium complexes to dehydrogenate alcohols and deliver the hydrides to a ketone [12,13] or an α,β -unsaturated ketone has made them useful as transfer hydrogenation catalysts [14]. The reaction conditions for transfer hydrogenations are economic, relatively mild and environmentally friendly. Metal complexes containing

bidentate ligands are normally used as catalysts in transfer hydrogenation reaction [15,16] and the nitrogen containing ligand lead to an increased catalytic activity [17].

In particular, half-sandwich ruthenium(II) complexes of the type $[(\eta^6\text{-arene})\text{Ru}(\text{A-B})\text{X}]^+ \text{X}^-$ (where A-B is an optically pure chiral bidentate ligand and X is a halide) have found to be efficient catalyst precursors for the transfer hydrogenation of ketones [18,19]. Recently, bifunctional transition metal-based molecular catalysts for transfer hydrogenation of ketones under different experimental conditions have been reviewed by Ikariya and coworkers [20]. Azophenol complexes of formula $[\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{L})]$ (**L** = mono anionic 2-naphthylazo-*p*-methylphenolate ligand) were used as effective catalyst for reduction of acetophenone [21]. Recently our group has reported ruthenium(III) complexes of amine-bis(phenolate) ligands as catalysts for transfer hydrogenation of a series of aliphatic and aromatic ketones [22]. Further, the influence of arene ring of η^6 -arene ruthenium(II) complexes containing the iminophosphorane-phosphine ligand in catalytic transfer hydrogenation of cyclohexanone have been described [23].

In view of rich ability of η^6 -arene ruthenium(II) species to act as efficient catalyst in hydrogen transfer reaction between alcohols and ketones [24], the catalytic activity of the titled compound has been investigated and is employed as a catalyst for ketones hydrogenation in the presence of 2-propanol and KOH.

2. EXPERIMENTAL

2.1. Materials and Methods

The alcohols and their corresponding ketones or aldehydes, which were used in the catalytic studies, were purchased from Merck and Aldrich. The catalytic yields were determined using HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Solvents were purified and dried according to standard procedures [25]. Arene ruthenium(II) complex was prepared according to the reported literature [26]. Synthesis and characterization of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L})]$ (**1**) (where **L** = mono anionic 2-naphthylazo-*p*-methylphenolate ligand) (Fig. 1) was reported earlier by our research group [27]. This

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complex used as a catalyst for transfer hydrogenation of ketones.

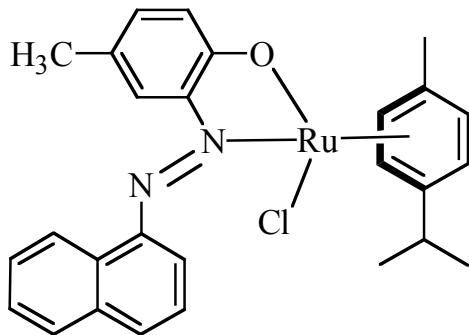
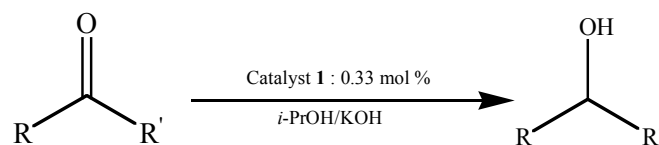


Fig. (1). Chemical structure of the catalyst, $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L})]$ (1).

2.2. Procedure for Catalytic Transfer Hydrogenation

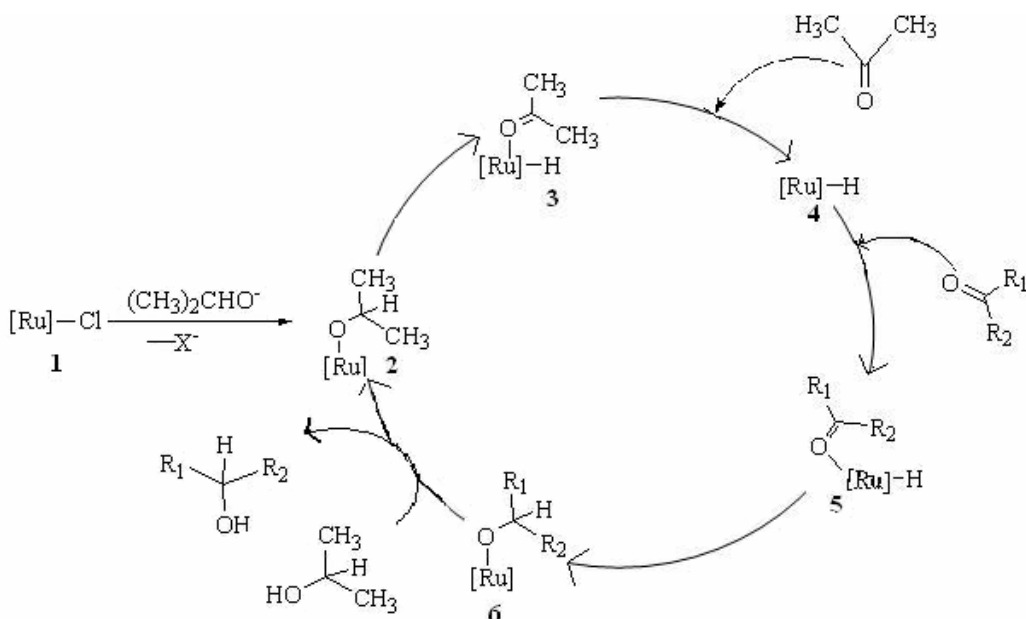
The complex, $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L})]$ (1) (where L = mono anionic 2-naphthylazo-*p*-methylphenolate ligand) is taken as model catalyst and the catalytic activity in transfer hydrogenation of aliphatic and aromatic ketones in the presence of 2-propanol and KOH has been explored. In a typical experiment, a mixture containing the ketone (3.75 mmol), ruthenium(II) complex (0.0125 mmol) and KOH (0.03 mmol) in 5 ml of 2-propanol (catalyst/substrate/base molar ratio = 1:300:2.5) were taken into round bottom flask and are heated to reflux for 1 h at 82 °C under nitrogen atmosphere. The catalyst was removed from the reaction mixture by the addition of hexane, followed by filtration and subsequent neutralization with 1 M HCl. The organic layer was filtered through the short path of silica gel by column chromatography and is subjected to GC analysis. The hydrogenated product was identified and compared with authentic samples.



3. RESULTS AND DISCUSSION

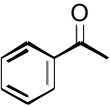
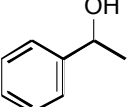
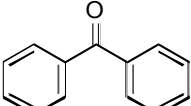
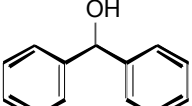
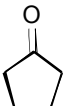
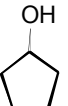
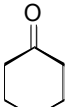
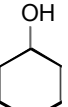
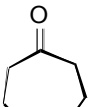
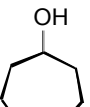
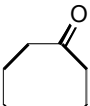
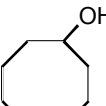
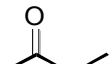
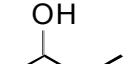
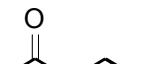
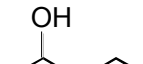
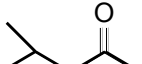
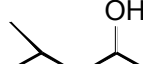
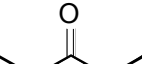
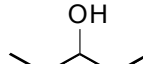
The catalyst performed efficiently in the conversion of ketones to alcohols and the results of this organic transformation are presented in Table 1. Both aliphatic and aromatic ketones are converted into their corresponding secondary alcohols with excellent conversions and turnover. The complex efficiently catalyzed the reduction of aliphatic ketones such as ethyl methyl ketone, methyl propyl ketone and isobutyl methyl ketone to their corresponding alcohols with 82.5%, 85% and 99.5% conversion respectively. The conversion in case of acetophenone is 89%. Benzophenone was converted into benzhydrol in 96% conversion. The catalyst also efficiently catalyzed the reduction of diethyl ketone to 3-pentanol in 84% conversion. Moreover, this catalyst shows good activity for the transfer hydrogenation of five, six, seven and eight membered cyclic ketones with excellent conversions. The conversions of 92% and 96% were obtained for cyclopentanol and cyclohexanol respectively and in case of cycloheptanol and cyclooctanol, 97.7% and 91% conversions were obtained. No transfer hydrogenation was observed in the absence of base.

The base facilitates the formation of ruthenium alkoxide by abstracting proton of the alcohol and subsequently alkoxide undergoes β -elimination to give ruthenium hydride, which is an active species in this reaction (Scheme 1). Assuming that these catalytic transformations follow the classical pathway in which the ketone coordinates to hydride-ruthenium intermediates as proposed by several research groups [28-32], the observed effects seem to indicate that the hydride transfer from the metal to the coordinated ketone is the turnover-limiting step (rather than the ketone complexation) in the catalytic cycle [33]. The



Scheme 1. Proposed mechanism for transition metal catalyzed transfer hydrogenation, where $[\text{Ru}]\text{-Cl} = [\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L})]$ (1).

Table 1. Catalytic Transfer Hydrogenation of Ketones by $[\text{Ru}(\eta^6\text{-}p\text{-Cymene})(\text{Cl})(\text{L})](1)$ / *i*-PrOH/KOH^a

Entry	Substrates	Products	Time(h)	Conversion (%)	TON ^b
1			1	89.0	267
2			1	96.0	288
3			1	92.0	276
4			1	96.0	288
5			1	97.7	292
6			1	91.0	273
7			1	82.5	247
8			1	85.0	255
9			1	99.5	278
10			1	84.0	252

^aConditions: reactions were carried out at 82 °C using 3.75 mmol of ketone (5 ml 2-propanol); catalyst/ketone/KOH ratio 1: 300: 2.5; Conversions were determined using a HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness and by comparison with authentic samples. ^bTON = ratio of moles of product obtained to the moles of catalyst used.

catalyst is recyclable and can be recovered after the catalytic cycle is completed and shows an efficient homogeneous hydrogen transfer reaction with no detectable loss of activity upon reuse [34,35]. The catalytic activity of the titled complex is better than similar ruthenium phenolate complexes [36].

4. CONCLUSION

In conclusion, the complex $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L})]$ (where **L** = mono anionic 2-naphthylazo-*p*-methylphenolate ligand) was developed as an efficient catalyst for the transfer of hydrogenation of a range of aliphatic/aromatic ketones with conversions up to 99.5%. Our ongoing research will

further explore the kinetics and the mechanism of the transfer hydrogenation process.

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REFERENCES

- [1] Brunner, H. Chiral Metal atoms in optically active organo-transition-metal compounds. *Adv. Organomet. Chem.*, **1980**, *18*, 151-206.

- [2] Ferstl, W.; Sakodinskaya, I.K.; Sutter, N.B.; Borgne, G.L.; Pfeffer, M.; Ryabov, A.D. Mechanism of alkyne insertion into the Ru-C bonds of orthoruthenated compounds featuring similarity of the Ru(II) and Pd(II) reactions. *Organometallics*, **1997**, *16*, 411-418.
- [3] Faller, J.W.; Parr, J. Synthesis, characterization, diastereoselectivity and catalytic activity of complexes of ruthenium with BINAP monoxide. *Organometallics*, **2000**, *19*, 1829-1832.
- [4] Thomas, C.M.; Mafia, R.; Thesrian, B.; Rusanov, E.; Evans, H.S.; Fink, G.S. New diphosphine ligands containing ethyleneglycol and amino alcohol spacers for the rhodium-catalyzed carbonylation of methanol. *Chem. Eur. J.*, **2002**, *8*, 3343-3352.
- [5] Sui, K.; Peng, S.M.; Bhattacharya, S. Chemistry of 2-(aryloxy)phenolate complexes of ruthenium: Synthesis, structure and reactivities. *Polyhedron*, **1999**, *18*, 631-640.
- [6] Matsumura, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. Asymmetric transfer hydrogenation of α , β -acetylenic ketones. *J. Am. Chem. Soc.*, **1997**, *119*, 8738-8739.
- [7] Gagliardo, M.; Chase, P. A.; Brouwer, S.; van Klínnk, G. P. M.; Van Koten, G. Electronic effects in PCP-pincer Ru(II)-Based hydrogen transfer catalysis. *Organometallics*, **2007**, *26*, 2219-2227.
- [8] Zotto, A.D.; Baratta, W.; Ballico, M.; Herdtweck, E.; Rigo, P. [RuCl₂(PPh₃)(PNN)] complexes as efficient catalysts in transfer hydrogenation of ketones. *Organometallics*, **2007**, *26*, 5636-5642.
- [9] Zhao, M.; Yu, Z.; Yan, S.; Li, Y. Room-temperature Ru(II)-catalyzed transfer hydrogenation of ketones and aldehydes in air. *Tetrahedron Lett.*, **2009**, *50*, 4624-4628.
- [10] Thoumazet, C.; Melaimi, M.; Ricard, L.; Mathey, F.; Floch, P.L. A cationic 1-(2-methylpyridine)phosphole cymene ruthenium chloride complex as an efficient catalyst in the transfer hydrogenation of ketones. *Organometallics*, **2003**, *22*, 1580-1581.
- [11] Baratta, W.; Ballico, M.; Del Zotto, A.; Herdtweck, E.; Magnolia, S.; Peloso, R.; Siega, K.; Toniutti, M.; Zangrando, E.; Rigo, P. Pincer CNN ruthenium(II) complexes with oxygen-containing ligands (O₂CR, OAr, OR, OSiR₃, O₃SCF₃): Synthesis, structure, and catalytic activity in fast transfer hydrogenation. *Organometallics*, **2009**, *28*, 4421-4430.
- [12] Noyori, R.; Akaya, H. BINAP: An efficient chiral element for asymmetric catalysis. *Acc. Chem. Res.*, **1990**, *23*, 345-350.
- [13] Dani, P.; Karlen, T.; Gossage, R.A.; Gladiali, S.; van Koten, G. Hydrogen-transfer catalysis with pincer-aryl ruthenium(II) complexes. *Angew. Chem., Int. Ed.* **2000**, *112*, 759-761.
- [14] Chowdhury, R.L.; Backvall, J.E. Efficient ruthenium-catalyzed transfer hydrogenation of ketones by propan-2-ol. *J. Chem. Soc., Chem. Commun.*, **1991**, 1063-1064.
- [15] Camacho, R.C.; Benítez, V.G.; Lagadec, R.L.; Morales, D.M.; Toscano, R.A. Ketone transfer hydrogenation reactions catalyzed by a phosphinite ruthenium PCP complex: The X-ray crystal structure of [C₆H₄-1,3-(OPPh₂)₂Ru(η^6 -p-cymene)Cl₂]₂. *J. Mol. Catal. A: Chem.*, **2006**, *247*, 124-129.
- [16] Venkatachalam, G.; Ramesh, R. Ruthenium(III) bis-bidentate Schiff base complexes mediated transfer hydrogenation of imines. *Inorg. Chem. Commun.*, **2006**, *9*, 703-707.
- [17] Fache, F.; Schulz, E.; Tommasino, M.L.; Lemaire, M. Nitrogen-containing ligands for asymmetric homogeneous and heterogeneous catalysis. *Chem. Rev.*, **2000**, *100*, 2159-2232.
- [18] Carrion, M.C.; Sepulveda, F.; Jalon, F.A.; Manzano, B.R. Base-free transfer hydrogenation of ketones using arene ruthenium(II) complexes. *Organometallics*, **2009**, *28*, 3822-3833.
- [19] Bacchi, A.; Pelagatti, P.; Pelizzi, C.; Rogolino, D. Diastereomeric half-sandwich Ru(II) cationic complexes containing amino amide ligands. Synthesis, solution properties, crystal structure and catalytic activity in transfer hydrogenation of acetophenone. *J. Organomet. Chem.*, **2009**, *694*, 3200-3211.
- [20] Ikariya, T.; Blacker, A.J. Asymmetric transfer hydrogenation of ketones with bifunctional transition metal-based molecular catalysts. *Acc. Chem. Res.*, **2007**, *40*, 1300-1308.
- [21] Rath, R.K.; Nethaji, M.; Chakravarty, A.R. Synthesis, crystal structure and catalytic properties of (*p*-cymene)ruthenium(II) azophenol complexes: Azophenyl to azophenol conversion by oxygen insertion to a ruthenium-carbon bond. *J. Organomet. Chem.*, **2001**, *633*, 79-84.
- [22] Kannan, S.; Naresh Kumar, K.; Ramesh, R. Ruthenium(III) complexes of amine-bis(phenolate) ligands as catalysts for transfer hydrogenation of ketones. *Polyhedron*, **2008**, *27*, 701-708.
- [23] Cadierno, V.; Crochet, P.; Alvarez, J.G.; Garrido, S.E.G.; Gimeno, J. Neutral and cationic (η^6 -arene)-ruthenium(II) complexes containing the iminophosphorane-phosphine ligand Ph₂PCH₂P(N-*p*-C₆F₄N)Ph₂: influence of the arene ring in catalytic transfer hydrogenation of cyclohexanone. *J. Organomet. Chem.*, **2002**, *663*, 32-39.
- [24] Pelagatti, P.; Carcelli, M.; Calbani, F.; Cassi, C.; Elviri, L.; Pelizzi, C.; Rizzotti, U.; Rogolino, D. Transfer hydrogenation of acetophenone catalyzed by half-sandwich ruthenium(II) complexes containing amino amide ligands. Detection of the catalytic intermediates by electrospray ionization mass spectrometry. *Organometallics*, **2005**, *24*, 5836-5844.
- [25] Vogel, A.I. Text Book of Practical Organic Chemistry, 5th ed., Longman, London, **1989**.
- [26] Bennett, M.A.; Smith, A.K. Arene ruthenium(II) complexes formed by dehydrogenation of cyclohexadienes with ruthenium(III) trichloride. *J. Chem. Soc., Dalton Trans.*, **1974**, 233-241.
- [27] Naresh Kumar, K.; Venkatachalam, G.; Ramesh, R.; Liu, Y. Half-sandwich para-cymene ruthenium(II) naphthylazophenolato complexes: Synthesis, molecular structure, light emission, redox behavior and catalytic oxidation properties. *Polyhedron*, **2008**, *27*, 157-166.
- [28] Noyori, R.; Hashiguchi, S.; Asymmetric transfer hydrogenation catalyzed by chiral ruthenium complexes. *Acc. Chem. Res.*, **1997**, *30*, 97-102.
- [29] Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, F.A.; Ikariya, T.; Noyori, R. Trans-[RuCl₂(phosphane)₂(1,2-diamine)] and chiral trans-[RuCl₂(diphosphane)(1,2-diamine)]: shelf-stable precatalysts for the rapid, productive, and stereoselective hydrogenation of ketones. *Angew. Chem. Int. Ed.*, **1998**, *37*, 1703-1707.
- [30] Kelson, E.P.; Phengsy, P.P. Synthesis and structure of a ruthenium(II) complex incorporating κ N bound 2-pyridonato ligands; a new catalytic system for transfer hydrogenation of ketones. *J. Chem. Soc., Dalton Trans.*, **2000**, 4023-4024.
- [31] Backvall, J.E. Transition metal hydrides as active intermediates in hydrogen transfer reactions. *J. Organomet. Chem.*, **2002**, *652*, 105-111.
- [32] Zhang, H.; Yang, C.B.; Li, Y.Y.; Donga, Z.R.; Gao, Z.X.; Nakamura, H.; Murata, K.; Ikariya, K. Highly efficient chiral metal cluster systems derived from Ru₃(CO)₁₂ and chiral diiminodiphosphines for the asymmetric transfer hydrogenation of ketones. *Chem. Commun.*, **2003**, 142-143.
- [33] Faller, J.W.; Lavoie, A.R. Catalysts for the asymmetric transfer hydrogenation of ketones derived from L-prolinamide and (*p*-cymene)RuCl₂ or (Cp* η -RuCl₂)₂. *Organometallics*, **2001**, *20*, 5245-5247.
- [34] Kingsbury, J.S.; Harrity, J.P.A.; Bonitatebus, P.J.; Hoveyda, A.H. A recyclable Ru-based metathesis catalyst. *J. Am. Chem. Soc.*, **1999**, *121*, 791-799.
- [35] Wu, X.; Mo, J.; Li, X.; Hyder, Z.; Xiao, J. Green chemistry: C-C coupling and asymmetric reduction by innovative catalysis. *Prog. Nat. Sci.*, **2008**, *18*, 639-652.
- [36] Kannan, S.; Ramesh, R.; Liu, Y. Ruthenium(III) mediated C-H activation of azonaphthol: Synthesis, structural characterization and transfer hydrogenation of ketones. *J. Organomet. Chem.*, **2007**, *692*, 3380-3391.

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