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 [RuCl(η^6-p-cymene)(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 Ru(p-cymene)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 NaOIPr [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 [(η^6-arene)Ru(A-B)X]+ 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 [η^6-p-cymene]RuCl(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 [Ru(η^6-p-cymene)(Cl)(L)] (I) (where L = mono anionic 2-naphthylazo-p-methylphenolate ligand) (Fig. 1) was reported earlier by our research group [27]. This
complex used as a catalyst for transfer hydrogenation of ketones.

![Chemical structure](image)

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

### 2.2. Procedure for Catalytic Transfer Hydrogenation

The complex, \([\text{Ru}(\eta^6-p\text{-cymene})(\text{Cl})(\text{L})]\) (1) (where \(L = \text{mono anionic 2-naphthylazo-p-methylphenolate ligand}\)) 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 isobutyryl 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

![Proposed mechanism](image)

**Scheme 1.** Proposed mechanism for transition metal catalyzed transfer hydrogenation, where \([\text{Ru}-\text{Cl} = [\text{Ru}(\eta^6-p\text{-cymene})(\text{Cl})(\text{L})]] (1).
The catalytic activity of the titled complex is better than similar ruthenium phenolate complexes [36].

4. CONCLUSION

In conclusion, the complex \([\text{Ru}(\eta^6-p\text{-cymene})(\text{Cl})(\text{L})](1)\) 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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