

**NEWLY DEVELOPED ANCHORED Ru(II)-N-HETEROCYCLIC
CARBENE COMPLEX AND ITS APPLICATIONS****¹*Undrala Sushen and ²Awanija Chouhan**

¹Department of Organic Chemistry, Dr. Sushen Research Lab, Gokul Group of Institutes,
Hyderabad, India.

²Department of Pharmaceutical Chemistry, Bhojjam Narasimhulu Pharmacy College for
Women, Saidabad, Hyderabad.

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Corresponding Author*Dr. Undrala Sushen**

Department of Organic
Chemistry, Dr. Sushen
Research Lab, Gokul Group
of Institutes, Hyderabad,
India.

ABSTRACT

Using Augustine's method, a new heterogenized Ru(II)-N-heterocyclic carbene complex was prepared on Al₂O₃ support. The anchored catalyst was characterized by spectroscopic methods and was applied in the hydrogenation of different olefins, aldehydes and ketones. The hydrogenations were performed in aqueous medium on homogeneous and heterogenized complexes. The immobilized complex had a reasonable activity and selectivity at the same time it was possible to filter out from the reaction mixture and to recycle in several subsequent runs.

KEYWORDS: Anchored Ru complexes, hydrogenations, enantio
selective, catalyst.

INTRODUCTION

Selectivity is becoming more and more important issue in today's life in the fine chemical industry. This trend can be explained by both economic and environmental considerations. Consequently there is an increasing demand towards the study of selective syntheses, which usually require selective catalysts. Comparing the selectivity, homogeneous catalysts generally dominates their heterogeneous counterparts. However there are several advantages such as easy handling, recyclability etc. which make the heterogeneous systems more desirable in industrial applications. A new version of catalyst has been introduced by combination of the two systems provides features which cannot be realized neither by homogeneous nor by heterogeneous catalysis alone. The heterogenized complexes can

successfully combine the high selectivity and activity of homogeneous complexes with the easy separation and recyclability of the heterogeneous systems. That is why the study of heterogenized homogeneous complexes has a new renaissance nowadays.^[1,2,3] *N*-heterocyclic carbene complexes represent a very useful family of organo-metallic complexes, which can catalyze a great deal of important reactions, among others: hydrogenation, hydrogen-transfer, hydrosilylation, hydroformylation and C-C coupling reactions.^[3-6] A new water-soluble Ru-*N*-heterocyclic carbene (NHC) complex was recently prepared and applied in the hydrogenation of various starting materials, such as alkenes, aldehydes and ketones.^[7] The $[\text{RuCl}_2\text{L}(\text{C}_{10}\text{H}_{14})]$ ($\text{L} = 1\text{-butyl-3-methylimidazol-2-ylidene}$, $\text{C}_{10}\text{H}_{14} = p\text{-cymene}$) complex was stable toward decomposition in aqueous solvent in a wide range pH and up to a relatively high temperature (80°C). This catalyst was active and selective in the hydrogenation of alkenes, oxo compounds, and the redox isomerization of allyl alcohol. A new heterogenized Ru(II)-*N*-heterocyclic carbene complex was prepared on Al_2O_3 . In this paper we want to report the systematic study of the preparation, characterization and application of this new, heterogenized $[\text{RuCl}_2\text{L}(\text{C}_{10}\text{H}_{14})]$ complex in the hydrogenation of olefins, aldehydes and ketones in aqueous solution.

EXPERIMENTAL

Preparation and anchoring of the complex

$[\text{RuCl}_2\text{L}(\text{C}_{10}\text{H}_{14})]$ complex was synthesized by a published procedure.^[7] The anchoring of the complex was done by a method developed by Augustine.^[11-13] 1.5 g of Al_2O_3 (CAMAG, basic) was suspended in 30 mL of methanol. 386.7 mg (0.15 mmol) of phosphotungstic acid hydrate (PTA) was dissolved in 25 mL of methanol and this solution was added drop wise into the alumina suspension with efficient stirring. The stirring was continued for two days at room temperature, under an Ar atmosphere. The solid residue was filtered out and was suspended in 30 mL of methanol. 45 mg (0.1 mmol) of $[\text{RuCl}_2\text{L}(\text{C}_{10}\text{H}_{14})]$ complex was dissolved in 40 mL of deoxygenated methanol and this solution was dropped slowly with stirring to the suspension. The stirring was continued for another two days. The solution was removed and the solid residue was washed with methanol, until a colorless solution was obtained. The light brown solid material was dried at 30°C for two hours in vacuum and for one day under argon. 1.5 g light brown catalyst was obtained.

Catalyst characterization

FT-IR spectra of the support, the Ru complexes and the heterogenized samples were recorded on a PE Spectrum One spectrophotometer, in the range of 400 – 4000 cm^{-1} , in KBr pellets. The metal content of the anchored catalysts was determined using a JOBIN YVON 24 type ICP-AES instrument; samples were dissolved in cc. HNO_3 .

Hydrogenation experiments

Allyl alcohol, propanal, cinnamaldehyde, acetophenone and acetone were hydrogenated in a batch reactor of 30 mL capacity under 0.4 MPa hydrogen pressure. Approximately the same conditions were applied in alcoholic and in aqueous media. In ethanol: 4.7 mg (10.42 μmol) soluble or 150 mg (9.99 μmol Ru) heterogenized catalysts were dissolved or suspended in 3 mL of anhydrous ethanol. 3 μL $(\text{C}_2\text{H}_5)_3\text{N}$ and 0.4 mmol of the substrate were added and the reactor was pressurized with H_2 . The reactions were initiated by starting the stirring at 65°C. In water: 6.3 mg (14 μmol) homogeneous or 200 mg (14.72 μmol Ru) heterogenized catalysts were added into 3 mL of water. After adding 3 mL of phosphate buffer, 1.0 mmol of substrate was injected, the reactor was pressurized with H_2 and the reaction was initiated by starting the stirring at 80°C. Samples were taken every hour from the reaction mixture and the products were analyzed by capillary gas chromatography (Hewlett Packard 5890 Series II) using a HP-FFAP (nitroterephthalic acid modified PEG) column at 70°C.

Catalysts recycling

The heterogenized catalysts were used in several subsequent runs. At the end of the reactions the liquid was removed by a Pasteur pipette, the solid catalyst was washed with ethanol and dried in vacuum under Ar, for further reused.

RESULTS AND DISCUSSION

With the final goal of extending the application of heterogenized complexes we have prepared a new heterogenized *N*-heterocyclic carbene complex catalyst $[\text{RuCl}_2\text{L}(\text{C}_{10}\text{H}_{14})]$ on Al_2O_3 which was characterized by spectroscopic methods. The catalyst was applied in the hydrogenation of various substrates including aldehydes, ketones and allyl alcohol. The substrates were hydrogenated in aqueous media, checking the applicability of the heterogenized complex in water. To our knowledge this is the first example of applying a heterogenized *N*-heterocyclic carbene complex catalyst in aqueous medium.

Characterization of the catalyst

The heterogenized complex was characterized by FT-IR spectroscopy. The FT-IR spectra of the support, the $[\text{RuCl}_2\text{L}(\text{C}_{10}\text{H}_{14})]$ complex and the heterogenized sample were all taken. The spectrum of the heterogenized complex showed the bands at 1380 cm^{-1} and 1470 cm^{-1} , characteristic for the $[\text{RuCl}_2\text{L}(\text{C}_{10}\text{H}_{14})]$ complex, which suggests the complex was anchored to the support unchanged.

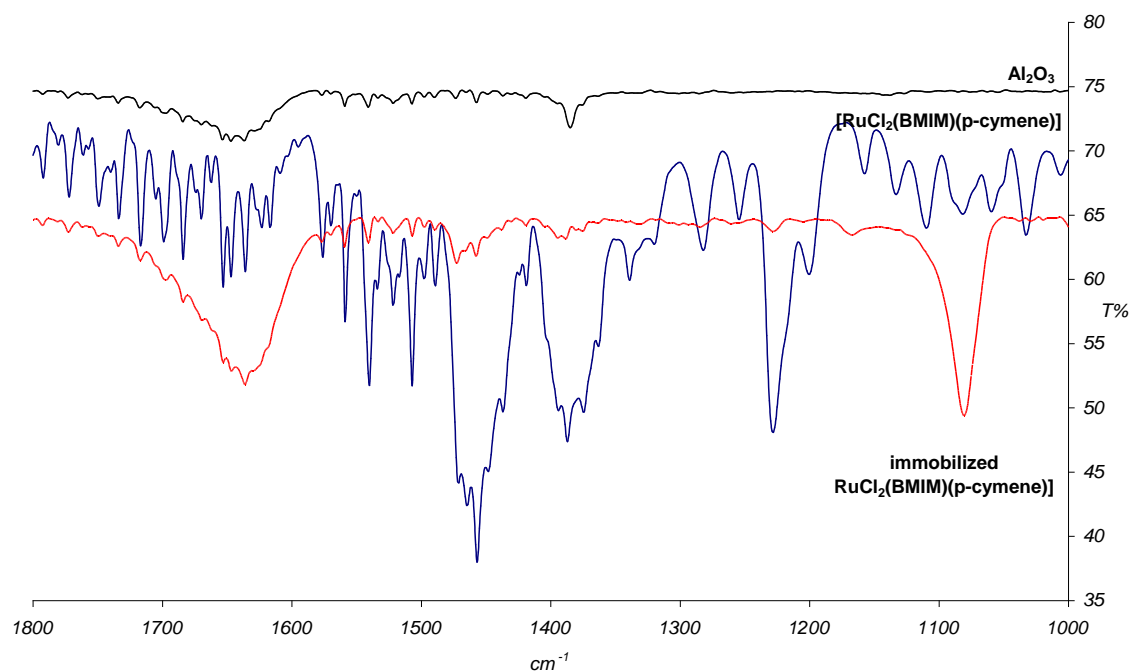


Figure 1. The FT-IR spectra of the $[\text{RuCl}_2\text{L}(\text{C}_{10}\text{H}_{14})]$ complex and the heterogenized samples.

The metal content of the heterogenized sample was determined by ICP-AES method and it was found $73.6\text{ }\mu\text{mol Ru/g}$ catalyst.

Hydrogenations in water

Water is an environmentally friendly solvent used more and more frequently in biphasic catalysis.^[19,20] Based on the results obtained in ethanol as solvent it seemed interesting to extend our studies into the use of aqueous media. To this end, the same substrates as before were hydrogenated in aqueous phosphate buffer (0.1 M, pH = 6.90). The results are shown in Table 3. To our knowledge, this is the first systematic examination of the performance of the same *N*-heterocyclic carbene complex catalyst, soluble and heterogenized, in the same reactions both in aqueous and organic solvents.

Table 1. Hydrogenation of various substrates on soluble and anchored [RuCl₂L(C₁₀H₁₄)] in water (L=1-butyl-3-methylimidazol-2-ylidene).

S.No	substrate	catalyst	Conversion (%)	TOF (h ⁻¹)
1	propanal	[RuCl ₂ L(C ₁₀ H ₁₄)]	100	74.3
		[RuCl ₂ L(C ₁₀ H ₁₄)]/Al ₂ O ₃	73.5	26.0
2	<i>trans</i> -cinnamaldehyde	[RuCl ₂ L(C ₁₀ H ₁₄)]	97.7	72.6
		[RuCl ₂ L(C ₁₀ H ₁₄)]/Al ₂ O ₃	70.7	25.0
3	allyl alcohol	[RuCl ₂ L(C ₁₀ H ₁₄)]	100	74.3
		[RuCl ₂ L(C ₁₀ H ₁₄)]/Al ₂ O ₃	35.0	12.4
4	acetophenone	[RuCl ₂ L(C ₁₀ H ₁₄)]	50.8	37.8
		[RuCl ₂ L(C ₁₀ H ₁₄)]/Al ₂ O ₃	41.7	14.7
5	acetone	[RuCl ₂ L(C ₁₀ H ₁₄)]	83.9	62.3
		[RuCl ₂ L(C ₁₀ H ₁₄)]/Al ₂ O ₃	22.3	7.9

Reaction condition: 14 μmol RuCl₂L(C₁₀H₁₄), 14.7 μmol Ru complex heterogenized catalyst, 3 mL of phosphate buffer, (0.1 M, pH = 6.90), 1040 μmol of substrate, 80°C, 0.4 MPa H₂, t = 1 h for homogeneous, 2 h for heterogenized complex.

As Table 1 clearly shows, both the homogeneous and the heterogenized complexes were active in hydrogenation of C=C and C=O double bonds in aqueous media. For both the soluble and the heterogenized catalysts the specific activities were found considerably higher in aqueous systems than in other solvents. Another remarkable observation is that the heterogenized complex produced similar conversions as in homogeneous catalyst. However the specific activity of the heterogenized complex was about the half of those obtained in homogeneous systems. Nevertheless, it can be concluded, that the heterogenized catalysts, prepared by the method of Augustine, are suitable for use in aqueous reaction media, too.

Catalyst recycling

One of the major advantages of using heterogenized complexes is the possibility to recycle the catalyst. We have studied the recovery and reuse of the heterogenized Ru-NHC complex in the hydrogenation of several substrates, in three subsequent runs; the results can be seen on Figure 2.

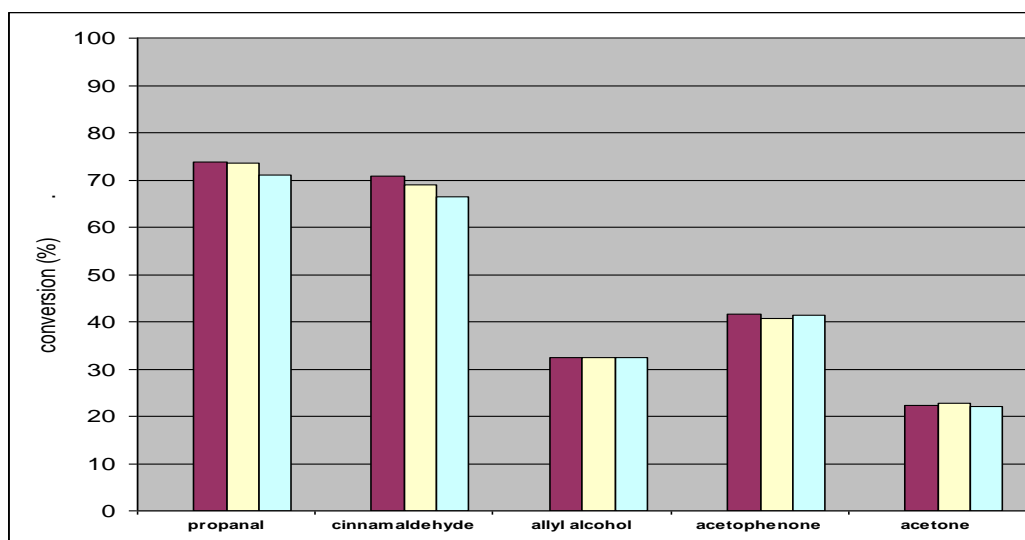


Figure 2. The activity of the heterogenized catalyst in the hydrogenation of various substrates in three subsequent runs in water.

CONCLUSION

A new heterogenized Ru(II)-*N*-heterocyclic carbene complex catalyst was synthesized, characterized by spectroscopic methods and applied in the hydrogenation of various C=C and C=O unsaturated substrates. The anchored catalyst hydrogenated both the C=C and the C=O double bonds with reasonable activity similar to the homogeneous catalyst in aqueous medium. Additionally, the prepared catalyst showed the advantages of the heterogeneous system, i.e. easy separation and efficient recycling.

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