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New application of an anchored Ru(II)-*N*-heterocyclic carbene complex

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A new, heterogenized Ru(II)-*N*-heterocyclic carbene complex was prepared via the method developed by Augustine. The anchored catalyst was characterized by spectros-copic methods and was applied in the hydrogenation of different olefins, aldehydes and ketones. The hydrogenations were performed both in alcohol and in aqueous media on homogeneous and heterogenized complexes. The immobilized complex had a reasonable activity in both conditions and at the same time it was possible to filter out from the reaction mixture and to recycle in several subsequent runs.

KEY WORDS: anchored Ru complex; hydrogenations; alcoholic solution; aqueous solution.

1. Introduction

Selectivity has become a more and more important issue nowadays 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 surpass their heterogeneous counterparts. However there are several advantages – easy handling, recyclability – which make the heterogeneous systems more desirable in industrial applications. The combination of the two systems provides features which can not 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 [1–3].

The *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 [4–7]. 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 [8]. The $[RuCl_2L(C_{10}H_{14})]$ (L = 1-butyl-3-methylimidazol-2-ylidene, $C_{10}H_{14}$ = *p*-cymene) complex was stable toward decomposition in aqueous solvent in a wide pH range and up to a relatively high temperature (80 °C). This catalyst was active and selective in the hydrogenation of alkenes and oxo compounds, and the redox isomerization of allyl alcohol.

Despite of the great interest in immobilized catalysts, only a few papers can be found on the field of heterogenized NHC complexes. Buchmeiser and co-workers have developed two different approaches to prepare heterogenized *N*-heterocyclic carbene complexes [9–11]. They used a ''grafting from'' approach, were polymerizable NHC-precursors have been grafted onto a norborn-2-ene (NBE) based monolithic support prepared via ring opening metathesis polymerization (ROMP), taking advantage of the living character of ROMP. The other synthetic route is based on a ''grafting to'' approach and entails the synthesis of oligomeric NHC-precursors and their selective chain-end functionalization with tri(etoxy)silane groups. These telechelic polymers were grafted on silica using standard silane chemistry. All heterogenized NHC complex precursors were successfully converted into the corresponding NHC-based second generation Grubbs catalysts and used for various metathesis reactions including ROMP, RCM, and cross-metathesis.

Considering the valuable family of the NHC complexes it seems to be worthwhile to study some other heterogenization methods of these compounds. In this paper we want to report the systematic study of the preparation, characterization and application of this new, heterogenized $[RuCl_2L(C_{10}H_{14})]$ complex.

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2. Experimental

2.1. Preparation and anchoring of the complex

$[RuCl_2L(C_{10}H_{14})]$ was synthesized by a published procedure [7].

The anchoring of the complex was done by a method developed by Augustine [12–14]. 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 dropwise 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 $[RuCl_2L(C_{10}H_{14})]$ 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 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.

2.2. Catalyst characterization

FT-IR spectra of the support, the Rh complexes and the heterogenized samples were recorded on a PE Spectrum One spectrophotometer, in the range of $400 - 4000cm^{-1}$, 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.

2.3. Hydrogenation experiments

Allyl alcohol, propanal, cinnamaldehyde, acetophenone or acetone were hydrogenated in a batch reactor of 20 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 $\mu L(C_2H_5)_3N$ 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 (nitroterephtalic acid modified PEG) column at 70 °C.

2.4. 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 under Ar and vacuum, then reused.

3. 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 $[RuCl_2L(C_{10}H_{14})]$ 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 two different solvents both in alcoholic and 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.

3.1. Characterization of the catalyst

The heterogenized complex was characterized by FT-IR spectroscopy. The FT-IR spectra of the support, the $[RuCl_2L(C_{10}H_{14})]$ complex and the heterogenized sample were all taken. (figure 1. Solid line represents the heterogenized sample, dotted line the metal complex) The spectrum of the heterogenized complex (but not that of the support) showed the bands at $1380cm^{-1}$, and $1470cm^{-1}$, characteristic for the $[RuCl_2L(C_{10}H_{14})]$ complex, which suggests the complex was anchored to the support unchanged.

The metal content of the heterogenized sample was determined by ICP-AES method and it was found 73.6 μmol Ru/g catalyst.

3.2. Hydrogenations in ethanol

In our former studies we have prepared the heterogenized version of the $[\{RuCl_2(m\text{tppms})_2\}_2]$ complex and applied it in the hydrogenation of α,β-unsaturated aldehydes [15]. This catalyst was able to hydrogenate selectively the C=C or C=O double bond depending on the basicity of the solvent. In alcoholic media the basicity was varied by adding different amounts of $(C_2H_5)_3N$. Under such conditions, $[\{RuCl_2(m\text{tppms})_2\}_2]$ catalyzed the hydrogenation of *trans*-cinnamaldehyde exclusively at its C=O bond both in homogeneous and in heterogenized forms. Additionally, the heterogenized catalyst showed the advantages of the heterogeneous system: namely, easy separation and recyclability.

An excellent selectivity towards the C=O hydrogenation was also observed in the hydrogenation of *trans*-cynnamaldehyde on supported Pt catalysts [16, 17].

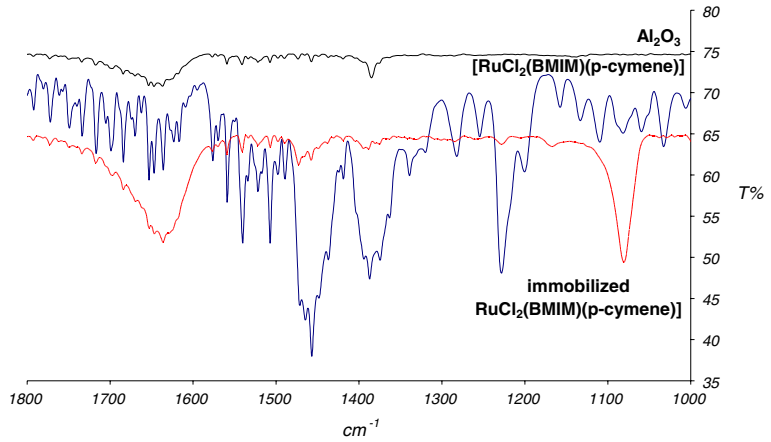

Figure 1. The FT-IR spectra of the $[RuCl_2L(C_{10}H_{14})]$ complex and the heterogenized samples.

In the present study, we applied the soluble and heterogenized *N*-heterocyclic carbene complex, $[RuCl_2L(C_{10}H_{14})]$, in alcoholic medium in the presence of $(C_2H_5)_3N$ for the hydrogenation of allyl alcohol, propanal, *trans*-cinnamaldehyde, acetone, and acetophenone, and the results are shown in table 1.

As table 1 clearly shows, both the homogeneous and the heterogenized complexes were active in the hydrogenation of the substrates possessing C=C or/and C=O functions. Hydrogenation of the C=O bond occurred with relatively good conversions, even in the case of acetone and acetophenone. This is a remarkable observation considering that both substrates have non activated C=O bonds, usually difficult to hydrogenate. During the hydrogenation of cinnamaldehyde both the C=C and C=O bonds were hydrogenated almost to equal extents. A small amount of the completely hydrogenated product, 3-phenylpropan-1-ol, was also formed. In the case of allyl alcohol a fast C=C hydrogenation occurred, and no redox isomerization observed, in contrast to the same reaction performed in homogeneous aqueous solution [8].

With all substrates, except propanal, the specific activities of the heterogenized complexes were lower than those of the homogeneous ones. This is an interesting observation, especially in the light of our former experience with heterogenized catalysts in other systems [18] when substantially higher specific activities were determined for the heterogenized catalysts than for their homogeneous counterparts. The possible explanation for this phenomenon may concern the availability of the metal complex catalyst on the surface of the support. It is likely that the *N*-heterocyclic carbene complex, $[RuCl_2L(C_{10}H_{14})]$, is strongly bound on the alumina surface by the basic nitrogens of the NHC ligand. This strong bonding could result in a worse availability and smaller activity of the complex.

We have also studied the hydrogenation of the same substrates with the $[RuCl_2L(C_{10}H_{14})]$ catalyst in the presence of triphenylphosphine. Interestingly, under such conditions neither acetone nor acetophenone could be hydrogenated, although both substrates reacted with reasonable conversions in the absence of PPh_3. Conversely, propanal, *trans*-cinnamaldehyde and allyl alcohol were hydrogenated with good conversions (table 2). Here again, selective C=O hydrogenation occurred in the case of *trans*-cinnamaldehyde, but some C=C hydrogenation was also detected (52.9 % and 4.4 %), as

Table 1
Hydrogenation of various substrates on soluble and heterogenized $[RuCl_2L(C_{10}H_{14})]$ in ethanol

Substrate	Catalyst	Conversion (%)	TOF (h^{-1})
propanal	$[RuCl_2L(C_{10}H_{14})]$	92.8	35.3
	$[RuCl_2L(C_{10}H_{14})]/Al_2O_3$	98.0	17.5
trans-cinnamaldehyde	$[RuCl_2L(C_{10}H_{14})]$	52.2	19.8
	$[RuCl_2L(C_{10}H_{14})]/Al_2O_3$	28.0	5.0
allyl alcohol	$[RuCl_2L(C_{10}H_{14})]$	100	38.0
	$[RuCl_2L(C_{10}H_{14})]/Al_2O_3$	25.4	4.5
acetophenone	$[RuCl_2L(C_{10}H_{14})]$	25.1	9.5
	$[RuCl_2L(C_{10}H_{14})]/Al_2O_3$	16.0	2.8
acetone	$[RuCl_2L(C_{10}H_{14})]$	24.2	9.2
	$[RuCl_2L(C_{10}H_{14})]/Al_2O_3$	16.9	3.0

Reaction conditions: 10.42 μmol $[RuCl_2L(C_{10}H_{14})]$ or 11.08 μmol Ru complex heterogenized catalyst, 42.7 μmol $(C_2H_5)_3N$, 396.0 μmol of substrate, 65 °C, 0.4 MPa H_2, t = 1h for homogeneous, 2 h for heterogenized catalyst, 3 mL ethanol.

Table 2
Hydrogenation of various substrates on soluble and heterogenized [$RuCl_2L(C_{10}H_{14})$] in the presence of PPh_3

Substrate	Catalyst	Conversion (%)	TOF (h^{-1})
propanal	[$RuCl_2L(C_{10}H_{14})$]	99.8	28.2
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	97.8	17.5
trans-cinnamaldehyde	[$RuCl_2L(C_{10}H_{14})$]	90.3	25.5
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	58.4	10.4
allyl alcohol	[$RuCl_2L(C_{10}H_{14})$]	98.2	27.7
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	24.0	4.3

Reaction conditions: 10.4 μmol homogeneous, 11.08 μmol Ru complex heterogenized sample, 85.4 μmol Et_3N, 51 μmol PPh_3, 396 μmol of substrate, 65 °C, 0.4 MPa H_2,t = 1h for homogeneous, 2 h for heterogenized complex.

was observed in the absence of PPh_3. A more detailed study is required for the clarification of the role of PPh_3 in these hydrogenations, but it seems likely that it replaces one of the Cl^- ligands in [$RuCl_2L(C_{10}H_{14})$], resulting in the formation of a new catalytic species.

3.3. 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 3 clearly shows, both the homogeneous and the heterogenized complexes were active in hydrogenation of C=C and C=O double bonds in aqueous media. As a matter of fact, the conversions in almost each case were higher than found in alcoholic solution. For both the soluble and the heterogenized catalysts the specific activities were found considerably higher in aqueous systems than in ethanol as solvent. Another remarkable observation is that the heterogenized complex produced similar conversions both in aqueous and in ethanolic solutions, that is no substantial drop was observed in the activity. 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.

3.4. 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.

It is clearly seen on figure 2 that the heterogenized Ru-NHC complex catalyzed the hydrogenations in three subsequent runs in alcohol without any significant change in activity. In other words our heterogenized complex is recyclable retaining its original catalytic properties.

Similar recycling experiments were done also in water, and the results can be seen on figure 3.

Similar to the case of the ethanolic systems, the results shown on figure 3, allow the conclusion, that the heterogenized Ru-NHC complexes retain their catalytic activity in several cycles in aqueous solvents, too.

Table 3
Hydrogenation of various substrates on soluble and heterogenized [$RuCl_2L(C_{10}H_{14})$] in water

substrate	catalyst	Conversion (%)	TOF (h^{-1})
propanal	[$RuCl_2L(C_{10}H_{14})$]	100	74.3
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	73.5	26.0
trans-cinnamaldehyde	[$RuCl_2L(C_{10}H_{14})$]	97.7	72.6
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	70.7	25.0
allyl alcohol	[$RuCl_2L(C_{10}H_{14})$]	100	74.3
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	35.0	12.4
acetophenone	[$RuCl_2L(C_{10}H_{14})$]	50.8	37.8
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	41.7	14.7
acetone	[$RuCl_2L(C_{10}H_{14})$]	83.9	62.3
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	22.3	7.9

Reaction conditions: 14 μmol $RuCl_2L(C_{10}H_{14})$, 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 H_2, t = 1h for homogeneous, 2 h for heterogenized complex.

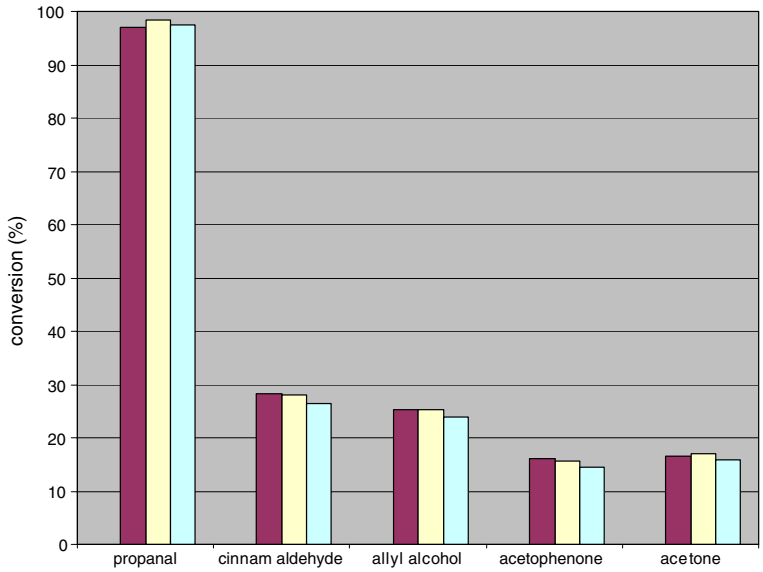

Figure 2. The activity of the heterogenized catalyst in the hydrogenation of various substrates in three subsequent runs in ethanol.

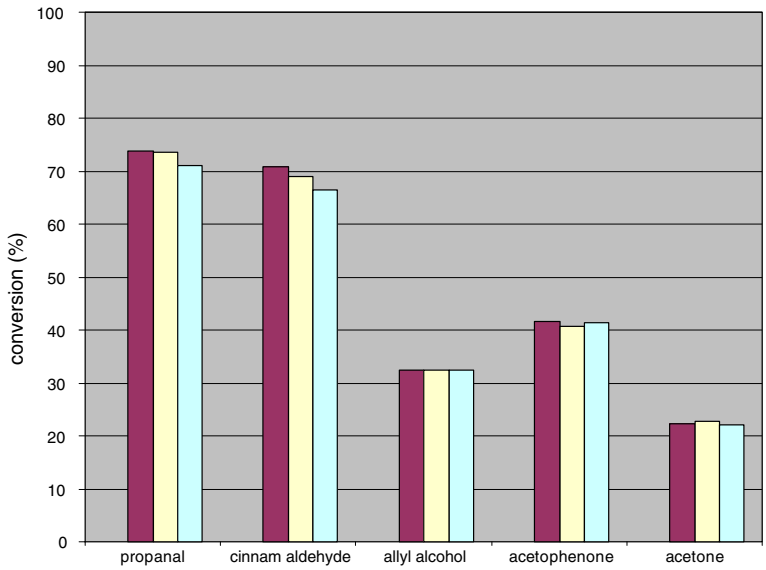

Figure 3. The activity of the heterogenized catalyst in the hydrogenation of various substrates in three subsequent runs in water.

4. Conclusions

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 – both in alcoholic and in aqueous media. Additionally, the prepared catalyst showed the advantages of the heterogeneous system, i.e. easy separation and efficient recycling.

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References

[1] J.M. Thomas, R. Raja and D.W. Lewis, Angew. Chem. Int. Ed. 44 (2005) 6456.
[2] C. Li, Catal. Rev. 46 (2004) 419.
[3] S. Kobayasi and R. Akiyama, Chem. Commun. (2003) 449.
[4] H.M. Lee, D.C. Smith, Z. He Jr., E.D. Stevens, C.S. Yi and S.P. Nolan, Organometallics 20 (2001) 794.

[5] A.C. Hillier, H.M. Lee, E.D. Stevens and S.P. Nolan, Organometallics 20 (2001) 4246.
[6] H. Kaur, F.K. Zinn, E.D. Stevens and S.P. Nolan, Organometallics 23 (2004) 1157.
[7] W.A. Herrmann, M. Elison, J. Fisher and C. Köcher, (Hoechst AG) U.S. Patent 5,663,451 (1997).
[8] P. Csabai and F. Joó, Organometallics 23 (2004) 5640.
[9] M. Mayr, B. Mayr and M.R. Buchmeiser, Stud. Surf. Sci. Catal. 143 (2002) 305.
[10] M. Mayr, K. Wurst, K-H. Ongania and M.R. Buchmeiser, Chem. Eur. J. 10 (2004) 5761.
[11] J.O. Krause, S.H. Lubbad, O. Nuyken and M.R. Buchmeiser, Macromol. Rapid Commun. 24 (2003) 875.
[12] R.L. Augustine, S.K. Tanielyan, S. Anderson and H. Yang, Chem. Commun. (1999) 1257.
[13] R.L. Augustine, S.K. Tanielyan, N. Mahata, Y. Gao, Á. Zsigmond and H. Yang, Appl. Catal. A-Gen. 256 (2003) 69.
[14] C. Reyes, Y. Gao, Á. Zsigmond, P. Goel, N. Mahata, S.K. Tanielyan, R.L. Augustine Catal. Org. React. (Dekker) 89 (2002) 627.
[15] Á. Zsigmond, I. Balatoni, K. Bogár, F. Notheisz and F. Joó, J. Catal. 227 (2004) 428.
[16] G. Szöllösi, B. Török, G. Szakonyi, I. Kun and M. Bartók, Appl. Catal. A: Gen. 172 (1998) 225.
[17] G. Szöllösi, B. Török, L. Baranyi and M. Bartók, J. Catal. 179 (1998) 619.
[18] Á. Zsigmond and F. Notheisz, Curr. Org. Chem., ed. Á. Molnár 10 (2006) 1655.
[19] F. Joó, *Aqueous Organometallic Catalysis*, (Kluwer, Dordrecht, The Netherlands, 2001).
[20] B. Cornils and W.A. Herrmann (eds.), *Aqueous-Phase Organometallic Catalysis*, 2nd ed. (Wiley-VCH, Weinheim, Germany, 2004).