



## Hydrogenation of various organic substrates using polystyrene anchored orthometallated ruthenium (II) complex as catalyst

S.M. Islam<sup>a,\*</sup>, K. Tuhina<sup>b</sup>, M. Mubarak<sup>a</sup>, P. Mondal<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Kalyani, Kalyani, Nadia 741235, W.B., India

<sup>b</sup> Department of Chemistry, B.S. College, S-24 P.G.S., 743329, West Bengal, India

### ARTICLE INFO

#### Article history:

Received 13 May 2008

Received in revised form 9 September 2008

Accepted 11 September 2008

Available online 18 September 2008

#### Keywords:

Hydrogenation

Polymer anchored

Orthometallated ruthenium (II) complex

Nitroorganics

Alkenes

Nitriles

Ketones

### ABSTRACT

The catalytic activity of orthometallated complex  $[\text{Ru}(\text{azb})(\text{CO})_2\text{Cl}]_2$  (Hazb = azobenzene) anchored to macroporous polystyrene beads was investigated towards the reduction of organic nitrocompounds, alkenes, alkynes, nitriles, Schiff bases, ketones and aldehydes under high pressure, high temperature conditions in mild coordinating media. Comparative studies have been done with the corresponding unsupported metal complexes. The polymer catalyst was found to be comparable to its homogeneous counterpart in activity and product selectivity but superior in stability and reusability. A tentative reduction mechanism was proposed on the basis of kinetic studies and the isolation of reactive intermediates.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Various metal ions and their complexes have been used widely in homogeneous catalyzed reactions but inherent disadvantages associated with homogeneous catalysis were minimized by using supported metal complexes, which sometime have shown high catalytic activities in comparison to unsupported analogues [1–3]. The high chemoselectivity of supported catalysts was due to stereospecific control of interactions of active sites with reactants in comparison to free and unsupported complexes. The supported catalysts are easily recovered without any substantial loss in their catalytic activity [3–9] but homogeneous catalysts are not recovered easily.

Among the numerous homogeneous catalysts used for the reduction of unsaturated organic compounds [10–15], only few are stable enough to reduce nitro-compounds, ketones and nitriles under high temperature, high pressure conditions [16–19].

The polymer anchored metal complex catalysts which may be separated easily from the product mixture and reused are expected to have higher chemical and thermal stabilities. These advantages make the polymer anchored catalysts more attractive than their homogeneous counterpart [20]. The sterically hindered metal atom may favour product selectivity.

Among the immobilized complex catalysts used for this purpose, the complexes of iron (III) [21], palladium (II) [22,23], platinum (II) [24,25], rhodium (I) [26,27], ruthenium (III) [28,29], manganese [30] and nickel (II) [31,32] and some others supported on various polymers are worth being mentioned.

The excellent catalytic activities of some orthometallated transition metal complexes towards the reduction of unsaturated organic compounds in mild coordinating media [15,33] prompted us to extend our catalytic investigations to similar complexes anchored to suitable polymers and to study the effect of anchoring on their catalytic activities.

The objective of the present work is to investigate the catalytic activity of orthometallated azobenzene complex of ruthenium (II) anchored to macroporous polystyrene beads towards the reduction of various unsaturated organic substrates. Comparative studies have been done with the corresponding unsupported metal complexes to investigate the effect of anchoring of the metal complexes on polymer supports toward their catalytic activities.

\* Corresponding author. Tel.: +91 33 2582 8750; fax: +91 33 2582 8282.  
E-mail address: [manir65@rediffmail.com](mailto:manir65@rediffmail.com) (S.M. Islam).

## 2. Experimental

### 2.1. Materials

Analytical grade reagents and freshly distilled solvents, pure and dry hydrogen gas and predistilled solvents were used throughout the investigation. The liquid substrates were predistilled and dried by appropriate molecular sieve and the solid substrates were recrystallized before use. The chemical analysis was done by the usual procedure [34].

Macroporous polystyrene beads, crosslinked with 2% divinylbenzene (Art No. 22094-9) were supplied as hard, insoluble 20–25 mesh spheres of average pore diameter 800 Å by Aldrich Chemical Company, USA. Ruthenium (III) chloride trihydrate ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ) was purchased from Arora Matthey and was used as such without further purification.

### 2.2. Hydrogenation procedure

In a typical experiment, DMF suspension of the required amount of catalyst was taken in the glass-lined autoclave which was first evacuated, flushed with dry and pure hydrogen and then allowed to attain the temperature of the oil-bath. The substrates in DMF solution were introduced in the autoclave which was quickly subjected to the desired hydrogen pressure. The reaction mixture was magnetically stirred during the reaction period and the experimental parameter were suitably adjusted and kept constant during the run. At the end, the reactor was quenched in ice-salt mixture and the components in the product mixtures were identified and estimated by GC using authentic samples as standard. The products were also identified by IR and NMR spectra whenever possible.

### 2.3. Preparation of catalyst

The outline for the preparation of polystyrene anchored orthometallated ruthenium (II) complex,  $\text{P}-[(\text{azb})(\text{CO})_2\text{Ru}\cdot\text{Cl}]_2$  (P = polystyrene backbone and H-azb = azobenzene) is shown in Scheme 1. The complex was prepared by reacting polymer anchored azobenzene ligand with (i)  $[\text{Ru}(\text{CO})_2\text{Cl}_2\text{S}_2]$  or (ii)  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  under high  $P_{\text{CO}}$ . Details procedures are given in the supporting information (Section 1).

The species p-nitro polystyrene (1), polystyrene amino hydrochloride (2), p-amino polystyrene (3), and polystyrene anchored azobenzene ligand (4) required for the synthesis of the present catalyst,  $\text{P}-[(\text{azb})(\text{CO})_2\text{Ru}\cdot\text{Cl}]_2$  (5) were prepared according to the literature methods [35–37].

### 2.4. Characterization of the complexes

The characterizations of insoluble functionalized polymers (1–4) and their ruthenium (II) complexes,  $\text{P}-[(\text{azb})(\text{CO})_2\text{Ru}\cdot\text{Cl}]_2$  (5) were done according to the literature methods [34–40]. Details procedures are given in the supporting information (Section 2).

The species (5) is insoluble in all common solvents, thermally stable up to 200 °C and XRD pattern suggest its non-crystalline nature. The chemical analysis suggests that nearly 60% of the ligand moieties form complexes with the metal. Rigid structure of the polymer matrix allows only suitably positioned azobenzene moieties to form chloro or carbonyl bridged complexes.

## 3. Results and discussion

The catalytic activities of the species are as  $5 > 5' > 6 \approx 7$ . The species (5) is effective for the hydrogenation of functional groups

like  $-\text{NO}_2$ ,  $>\text{C}=\text{C}<$ ,  $>\text{C}=\text{O}$ ,  $>\text{C}=\text{N}-$ ,  $-\text{C}\equiv\text{C}-$ ,  $-\text{C}\equiv\text{N}$  only under relatively higher pressure and temperature.

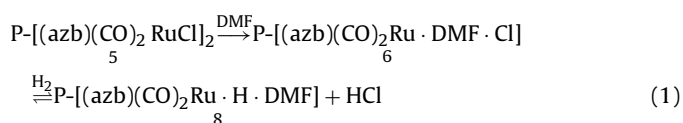
In order to study the effect of solvent, several solvents were employed in the hydrogenation of various organic substrates catalyzed by the above catalyst. The highest activity of the catalyst was observed in DMF, followed by DMSO and the reaction rate considerably slows down in stronger coordinated media like  $\text{CH}_3\text{CN}$ , and  $\text{PhCN}$ . In the presence of very strong ligands like py, pic, dipy,  $\text{PPh}_3$  reaction occurred at a very slow rate. In non-coordinating media like  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{CH}_3$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  the reaction rate is too slow to measure. Probably a moderately strong coordinating solvent capable of stabilizing the catalytic intermediate is necessary for the progress of the reaction. In completely non-coordinating media, the intermediates decompose so fast that the substrate do not get chance to coordinate with the metal atom centre. In presence of very strong coordinating media or strong ligand, the substrate is probably unable to replace these ligands from the metal atom centre and thereby no reaction occurred.

The substrates containing the  $>\text{C}=\text{C}<$  and  $-\text{C}\equiv\text{C}-$  groups were completely reduced with highest rate at  $\sim 70^\circ\text{C}$  under a hydrogen pressure of 30.0 bar (Table 1). Based on initial reduction rates, the substrates can be placed as

Styrene  $>$  isoprene  $>$  pent-1-ene  $>$  hex-1-ene  $>$  hept-1-ene  
 $>$  cyclohexene  $>$  maleicacid  $>$  fumaricacid

Reduction of alk-1-enes produced only the corresponding alkanes and no isomerized products. The steric crowding around the metal atom in the polymer matrix may restrict the 1-alkene coordination in a particular orientation leading to the formation of alkanes only. Table 1 indicates easy reduction of alkenes with delocalized  $\pi$ -electron system compared to those having substitution or non-delocalized system. Probably both steric crowding of the substituted groups and the electronic effects are responsible for this difference. Non-substituted alkenes with delocalized  $\pi$ -electron system are expected to form stronger [metal-alkene] complex. Hence the concentration of the latter is increased at the intermediate stage.

Both maleic and fumaric acids are reduced at lowest rates. The dissociation of these acids produces  $\text{H}^+$  and  $\text{RCOO}^-$ . The former decreases the concentration of the active species (8) as per Eq. (1) while the later blocks the active sites in (8) by coordination. Combination of these factors leads to the lowest reduction rates



Among the Schiff bases, only benzylideneaniline and N-methylbenzaldimine were reduced completely to the corresponding amines without any side products.  $>\text{C}=\text{N}-$  and  $>\text{C}=\text{C}<$  groups are reduced at comparable rates. The present catalyst system provides an easy approach to reduce the Schiff bases to pure secondary amines.

The catalyst system is efficient for the reduction of various nitroaromatics at 80 °C under a hydrogen pressure of 40.0 bar. The mono-nitroaromatics are reduced at higher rates than the dinitroaromatics. The final products in all cases were the corresponding anilines. The nitroaromatics may be placed in the following order as per their reduction rates:

$\text{C}_6\text{H}_5\text{NO}_2 >$  p- $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2 >$  p- $\text{ClC}_6\text{H}_4\text{NO}_2$   
 $>$  m- $\text{ClC}_6\text{H}_4\text{NO}_2 >$  o- $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2 >$  o- $\text{ClC}_6\text{H}_4\text{NO}_2$   
 $>$  p- $\text{HOC}_6\text{H}_4\text{NO}_2 >$  p- $\text{H}_2\text{NC}_6\text{H}_4\text{NO}_2$

**Table 1**  
Substrates and the corresponding products with catalyst P-[(azb)(CO)<sub>2</sub>RuCl]<sub>2</sub>.

Expt. no.	Substrate	Reaction time (h)	Initial turnover no. (min <sup>-1</sup> )	Product(s)	% Yield
1.	Styrene <sup>a</sup>	4.8	7.97	Ethylbenzene	97
2.	Isoprene <sup>a</sup>	5.2	7.16	2-Methylbutane	96
3.	1-Pentene <sup>a</sup>	5.6	6.91	Pentane	94
4.	1-Hexene <sup>a</sup>	5.9	6.61	Hexane	94
5.	1-Heptene <sup>a</sup>	6.0	6.12	Heptane	92
6.	Cyclohexene <sup>a</sup>	6.4	5.55	Cyclohexane	90
7.	Maleic acid <sup>a</sup>	7.2	4.38	Succinic acid	89
8.	Fumaric acid <sup>a</sup>	7.6	3.95	Succinic acid	88
9.	Diphenylacetylene <sup>a</sup>	4.8	7.31	1,2-Diphenylethane	92
10.	Phenylacetylene <sup>a</sup>	5.0	6.50	Ethylbenzene	92
11.	N-Methylbenzaldimine	5.2	7.52	N-Methylbenzylamine	96
12.	Benzylideneaniline <sup>a</sup>	4.8	7.96	N-Phenylbenzylamine	95
13.	Nitrobenzene <sup>b</sup>	5.6	7.38	Aniline	94
14.	p-Nitrotoluene <sup>b</sup>	5.9	5.98	p-Toluidine	90
15.	p-Chloronitrobenzene <sup>b</sup>	6.2	5.62	p-Chloroaniline	92
16.	o-Nitroaniline <sup>b</sup>	7.0	4.94	o-Phenelenediamine	88
17.	o-Nitrotoluene <sup>b</sup>	7.3	4.50	o-Toluidine	90
18.	1-Nitronaphthalene <sup>b</sup>	7.6	4.24	1-Aminonaphthalene	88
19.	o-Chloronitrobenzene <sup>b</sup>	7.8	4.01	o-Chloroaniline	87
20.	p-Nitroaniline <sup>b</sup>	7.9	3.56	p-Phenelenediamine	88
21.	p-Nitrophenol <sup>b</sup>	8.0	3.72	p-Aminophenol	86
22.	p-Dinitrobenzene <sup>c</sup>	6.8	4.06	p-Phenelenediamine	89
23.	m-Dinitrobenzene <sup>c</sup>	7.2	3.68	m-Phenelenediamine	86
24.	Nitromethane <sup>c</sup>	5.6	7.08	Methylamine	94
25.	Nitroethane <sup>c</sup>	5.8	6.15	Ethylamine	90
26.	1-Nitropropane <sup>c</sup>	6.0	5.76	1-Aminopropane	88
27.	2-Nitropropane <sup>c</sup>	6.4	5.30	2-Aminopropane	89
28.	Nitrocyclohexane <sup>c</sup>	7.2	4.46	Aminocyclohexane	86
29.	Benzaldehyde <sup>d</sup>	4.8	5.52	Benzylalcohol	88
30.	Benzophenone <sup>d</sup>	5.4	5.31	Diphenylmethanol	85
31.	Acetophenone <sup>d</sup>	6.4	3.80	Phenylmethylmethanol	86
32.	Benzoin <sup>d</sup>	6.2	4.56	Dihydrobenzoin	86
33.	Benzil <sup>d</sup>	6.1	4.48	Dihydrobenzoin	84
34.	Acetone <sup>d</sup>	6.6	3.65	2-Propanol	82
35.	Benzonitrile <sup>e</sup>	7.5	3.42	Dibenzylamine	92
				Benzyl amine	3
				Diethylamine	81
				Ethylamine	15

Reaction condition: [Sub] = 0.5 M; [Cat] =  $2.0 \times 10^{-4}$  mol l<sup>-1</sup>; medium = DMF; total volume = 10 ml; yield refers to G.C. analysis.

<sup>a</sup>  $P_{H_2}$  = 30.0 bar; T = 70 °C.

<sup>b</sup>  $P_{H_2}$  = 40.0 bar; T = 80 °C.

<sup>c</sup>  $P_{H_2}$  = 50.0 bar; T = 90 °C.

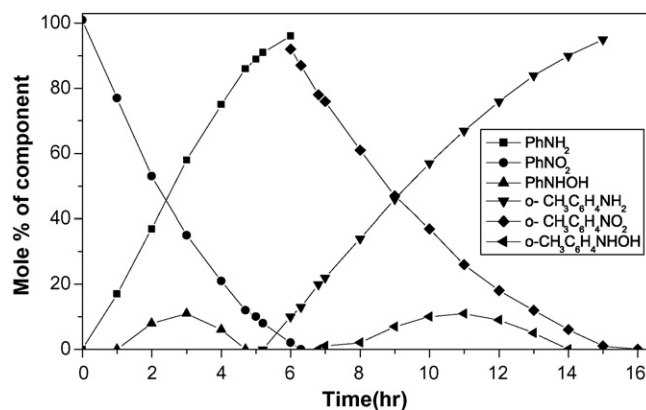
<sup>d</sup>  $P_{H_2}$  = 60.0 bar; T = 105 °C.

<sup>e</sup>  $P_{H_2}$  = 80.0 bar; T = 120 °C.

Preferential reductions are possible in case of mixture of nitrobenzene and o-nitrotoluene as substrates (Fig. 1). Both steric and electronic factors appear to be responsible for this preferential reduction [33]. During the reduction of mono-nitroaromatics, corresponding phenylhydroxylamines formed as intermediate (Fig. 1), are reduced at faster rates than the corresponding nitroaromatics. No other partially reduced nitroaromatics or coupled products could be detected at any stage. Attempts to selectively reduce nitrobenzene to corresponding phenylhydroxylamine by varying experimental parameters were unsuccessful.

Nitrobenzene and its p-substituted derivatives are reduced at the highest rate followed by ortho- and meta-substituted nitroaromatics in order. The steric factor probably dominates over the electronic factor to control the reduction rate. 4-nitro-o-xylene was reduced at a very slow rate while the more sterically hindered 2-nitro-m-xylidine could not be reduced at all. The reduction rates of p-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> and p-HOC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> are relatively low. Probably -NH<sub>2</sub> and -OH groups decreases the available sites for NO<sub>2</sub> coordination by partial blocking.

Reduction of dinitroaromatics to the corresponding diamines required higher temperature and pressure. Corresponding mono- or dihydroxylamines could not be detected at any intermediate stage. Sequential hydrogenation also occurred in this case (Fig. 2).



**Fig. 1.** Preferential hydrogenation of nitrobenzene in presence of o-nitrotoluene with the catalyst P-[(azb)Ru(CO)<sub>2</sub>Cl]<sub>2</sub>. [Cat] =  $2.0 \times 10^{-3}$  mol l<sup>-1</sup>;  $P_{H_2}$  = 40.0 bar; medium = DMF; total volume = 10 ml; T = 80 °C; [PhNO<sub>2</sub>] = 0.5 M; [o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>] = 0.5 M; ● = PhNO<sub>2</sub>; ■ = PhNH<sub>2</sub>; ▲ = PhNHOH; ◆ = o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>; ▼ = o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>; ◀ = o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NHOH.

**Table 2**  
Comparison of catalytic activities of [Ru(azb)(CO)<sub>2</sub>Cl]<sub>2</sub> (I) with P-[(azb)Ru(CO)<sub>2</sub>Cl]<sub>2</sub> (II).

Entry no.	Substrate	Catalyst- I (homogeneous)		Catalyst-II (polymer anchored)		Product(s)
		Reaction time(h)	Yield	Reaction time(h)	Yield	
1.	1-Pentene <sup>a</sup>	5.0	96	5.2	94	Pentane
2.	Phenylacetylene <sup>a</sup>	4.5	94	5.0	92	Ethylbenzene
3.	o-Nitrotoluene <sup>a</sup>	6.5	92	7.3	90	p-Toluidine
4.	Nitromethane <sup>b</sup>	7.0	52 <sup>c</sup>	7.0	94	Methylamine
5.	Benzaldehyde <sup>b</sup>	7.0	59 <sup>c</sup>	7.0	88	Benzylalcohol
6.	Benzophenone <sup>b</sup>	7.0	50 <sup>c</sup>	7.0	85	Diphenylmethanol
7.	Acetone <sup>b</sup>	7.0	55 <sup>c</sup>	7.0	82	2-Propanol
8.	p-Dinitrobenzene <sup>b</sup>	7.5	46 <sup>c</sup>	7.5	89	p-Phenelenediamine
9.	Benzonitrile <sup>b</sup>	7.5	41 <sup>c</sup>	7.5	91	Dibenzylamine

Reaction condition: [Sub] = 0.5 M; [Cat] =  $2.0 \times 10^{-4}$  mol l<sup>-1</sup>; medium = DMF; total volume = 5 ml; yield refers to G.C. analysis.

<sup>a</sup> P<sub>H<sub>2</sub></sub> = 40.0 bar; T = 80 °C.

<sup>b</sup> P<sub>H<sub>2</sub></sub> = 150.0 bar; T = 200 °C.

<sup>c</sup> Catalyst decomposes.

**Table 3**  
Recycling of catalyst P-[(azb)(CO)<sub>2</sub> Ru.Cl]<sub>2</sub> for hydrogenation of various organic substrates.

Expt. no.	Substrate	Product(s)	1st recycle		3rd recycle		5th recycle	
			Initial turnover number (min <sup>-1</sup> )	% Yield	Initial turnover number (min <sup>-1</sup> )	% Yield	Initial turnover number (min <sup>-1</sup> )	% Yield
1.	1-Hexene <sup>a</sup>	Hexane	6.61	94	6.45	92	6.32	90
2.	Isoprene <sup>a</sup>	2-Methylbutane	7.16	96	7.04	94	6.85	93
3.	Phenylacetylene <sup>a</sup>	Ethylbenzene	6.50	92	6.32	90	6.12	88
4.	Maleic acid <sup>a</sup>	Succinic acid	4.38	89	4.22	87	4.05	85
5.	Nitrobenzene <sup>b</sup>	Aniline	7.38	94	7.16	92	7.01	90
6.	p-Nitrotoluene <sup>b</sup>	p-Toluidine	5.98	90	5.82	88	5.74	86
7.	Nitromethane <sup>c</sup>	Methylamine	7.08	94	6.88	91	6.75	89
8.	1-Nitropropane <sup>c</sup>	1-Aminopropane	5.76	88	5.62	87	5.49	86
9.	Benzophenone <sup>c</sup>	Diphenylmethanol	5.31	85	5.12	83	4.91	82
10.	Acetone <sup>d</sup>	2-Propanol	3.65	82	3.52	79	3.36	78
11.	Benzil <sup>d</sup>	Dihydrobenzoin	4.14	84	3.95	82	3.73	81
12.	m-Dinitrobenzene <sup>e</sup>	m-Phenelenediamine	3.68	86	3.51	84	3.40	83

Note: [sub] = 0.50 M; [Cat] ≈  $2.0 \times 10^{-4}$  mol l<sup>-1</sup> (fresh catalyst); medium = DMF; total volume = 10 ml; yields refer to G.C. analysis; [Cat] ≈  $(1.90-1.98) \times 10^{-4}$  mol l<sup>-1</sup> (after 5th recycle).

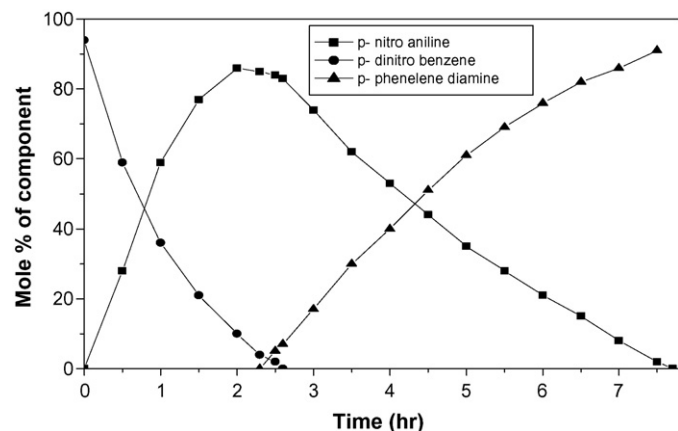
<sup>a</sup> P<sub>H<sub>2</sub></sub> = 30.0 bar; T = 70 °C.

<sup>b</sup> P<sub>H<sub>2</sub></sub> = 40.0 bar; T = 80 °C.

<sup>c</sup> P<sub>H<sub>2</sub></sub> = 50.0 bar; T = 90 °C.

<sup>d</sup> P<sub>H<sub>2</sub></sub> = 60.0 bar; T = 105 °C.

<sup>e</sup> P<sub>H<sub>2</sub></sub> = 80.0 bar; T = 120 °C.



**Fig. 2.** Sequential reduction of p-dinitrobenzene with the catalyst P-[(azb)Ru(CO)<sub>2</sub>Cl]<sub>2</sub>. [Cat] =  $2.0 \times 10^{-3}$  mol l<sup>-1</sup>; P<sub>H<sub>2</sub></sub> = 80 bar; medium = DMF; total volume = 10 ml; T = 120 °C; [p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>] = 0.5 M; -●- = p-dinitrobenzene; -■- = p-nitroaniline; -▲- = p-phenylenediamine.

The reductions of nitroalkanes required relatively more stringent conditions (T = ~90 °C, P<sub>H<sub>2</sub></sub> = 50.0 bar). They may be arranged in the following order on the basis of their reduction rates:

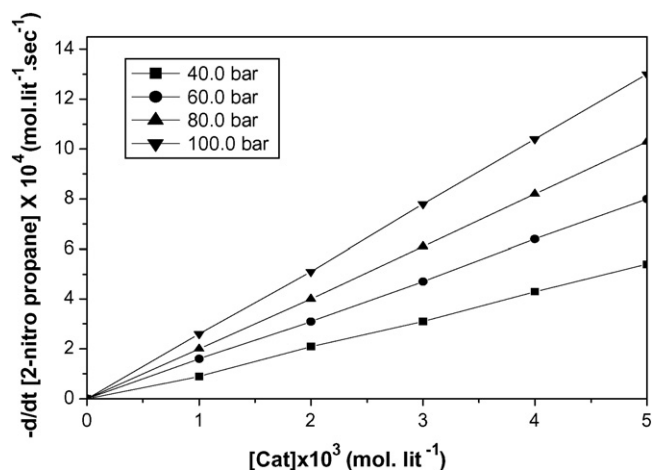
Nitromethane > nitroethane > 1-nitropropane  
> 2-nitropropane > nitrocyclohexane

Steric factors appear to control the reduction rate. Both the increase of chain length and branching lower the reduction rate. Here also, only alkylhydroxylamines which are very first reduced to the corresponding amines are formed as intermediate products.

The carbonyl compounds were reduced at ~105 °C under the hydrogen pressure of 60.0 bar to their corresponding alcohol. On the basis of initial rates of reduction, they may be arranged as

Benzaldehyde > benzophenone > benzoin ~ benzil  
> acetophenone > acetone

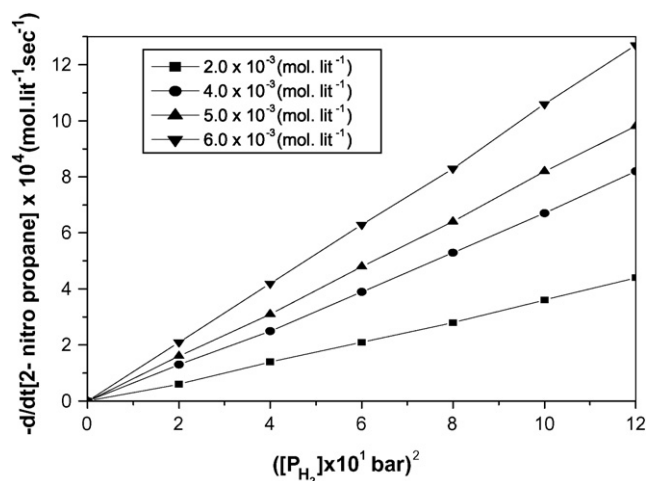
The higher reduction rates of benzaldehyde and benzophenone are due to their planarity while non-planar acetone is reduced at the slowest rate. The diketo compound, benzil undergoes stepwise reduction, first to benzoin and then to dihydrobenzoin.



**Fig. 3.** Rate dependence on catalyst concentration for the reduction of 2-nitropropane with P-[(azb)Ru(CO)<sub>2</sub>Cl]<sub>2</sub> as catalyst under various hydrogen pressure. [2-nitropropane] = 0.5 M; medium = DMF; total volume = 10 ml; T = 80 °C, P<sub>H<sub>2</sub></sub>: ■ = 40.0 bar; ● = 60.0 bar; ▲ = 80.0 bar; ▼ = 100.0 bar.

The nitriles were reduced under more severe conditions, i.e. T = 120 °C, P<sub>H<sub>2</sub></sub> = 80.0 bar. The major products were the corresponding secondary amines. In case of CH<sub>3</sub>CN, final products contain ethylamine (~15%) and diethylamine (~80%) while in case of C<sub>6</sub>H<sub>5</sub>CN the product was mainly (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>NH with very small amount of primary amine C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub> (<3%). The formation of R<sub>2</sub>NH (R = C<sub>2</sub>H<sub>5</sub>/C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) and liberation of NH<sub>3</sub> suggest the occurrence of some secondary reaction at intermediate stages. The nitriles, RCN (R = CH<sub>3</sub>, Ph) do not react with RCH<sub>2</sub>NH<sub>2</sub> in presence of catalyst at 120 °C. The initial addition of RCH<sub>2</sub>NH<sub>2</sub> (R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) during the reduction of RCN always increased the proportion of corresponding (RCH<sub>2</sub>)<sub>2</sub>NH in the final product mixture. When ethylamine or benzylamine (in absence of corresponding nitriles) are subjected to catalytic hydrogenation under identical experimental condition, the final reaction mixture contained only the unreacted substrates and no secondary amine. The secondary amines are, therefore, not formed by catalytic dimerization of primary amines with liberation of NH<sub>3</sub>. The products may be formed as per Scheme 2.

To understand the reaction mechanism, the reduction of C<sub>6</sub>H<sub>5</sub>CN was carried out in presence of acetic anhydride and sodium acetate.

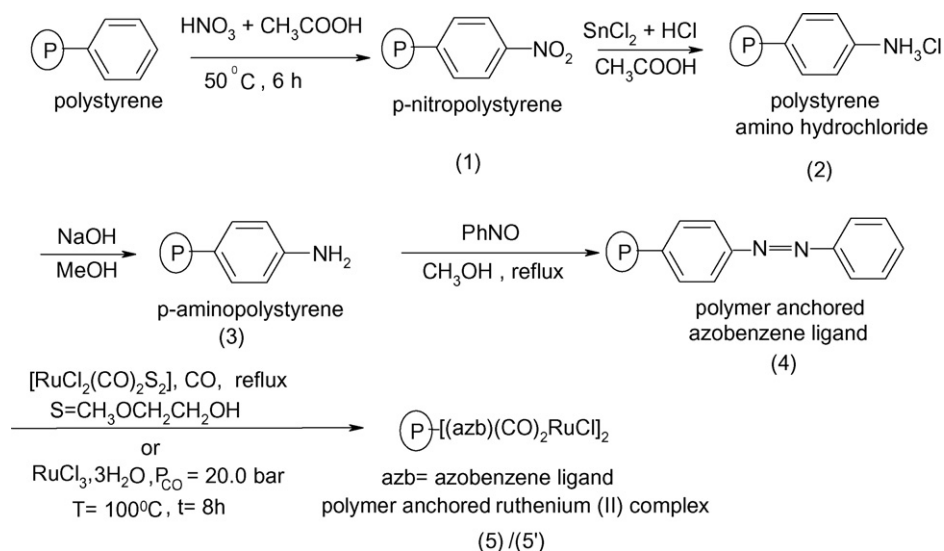


**Fig. 4.** Rate dependence on P<sub>H<sub>2</sub></sub> for the reduction of 2-nitropropane under various catalyst concentrations with P-[(azb)Ru(CO)<sub>2</sub>Cl]<sub>2</sub> as catalyst. [2-nitropropane] = 0.5 M; medium = DMF; T = 105 °C, [Cat]: ■ = 2.0 × 10<sup>-3</sup> mol l<sup>-1</sup>; ● = 4.0 × 10<sup>-3</sup> mol l<sup>-1</sup>; ▲ = 5.0 × 10<sup>-3</sup> mol l<sup>-1</sup>; ▼ = 6.0 × 10<sup>-3</sup> mol l<sup>-1</sup>.

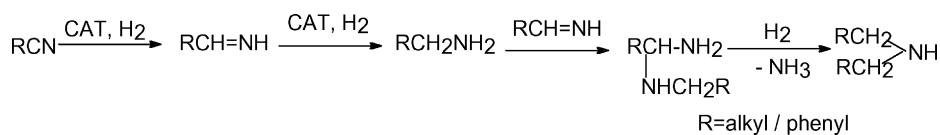
The objective was to trap the C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub> if formed by converting it to the corresponding acetylate. This will prevent C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub> to react with the probable intermediate, C<sub>6</sub>H<sub>5</sub>CH=NH and hence no secondary amine would be formed. The product mixture in this case contained only C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NHCOCH<sub>3</sub> and no secondary amine. The result suggests the formation of intermediate imine which reacts with the primary amine and H<sub>2</sub> to form the secondary amine and ammonia. Catalytic hydrogenation of benzonitrile under the same experimental condition was also conducted in presence of excess of ethylamine and the components detected in the product mixture were benzylamine (minor), N-ethylbenzylamine (major), dibenzylamine (trace) and ammonia.

Higher susceptibility of PhCH=NH to nucleophilic attack by C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub> resulted in the formation of mainly (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>NH in case of PhCN reduction. In case of CH<sub>3</sub>CN reductions, lower susceptibility of CH<sub>3</sub>CH=NH to nucleophilic attack by C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> is responsible for the presence of small amount of CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> in the final product mixture.

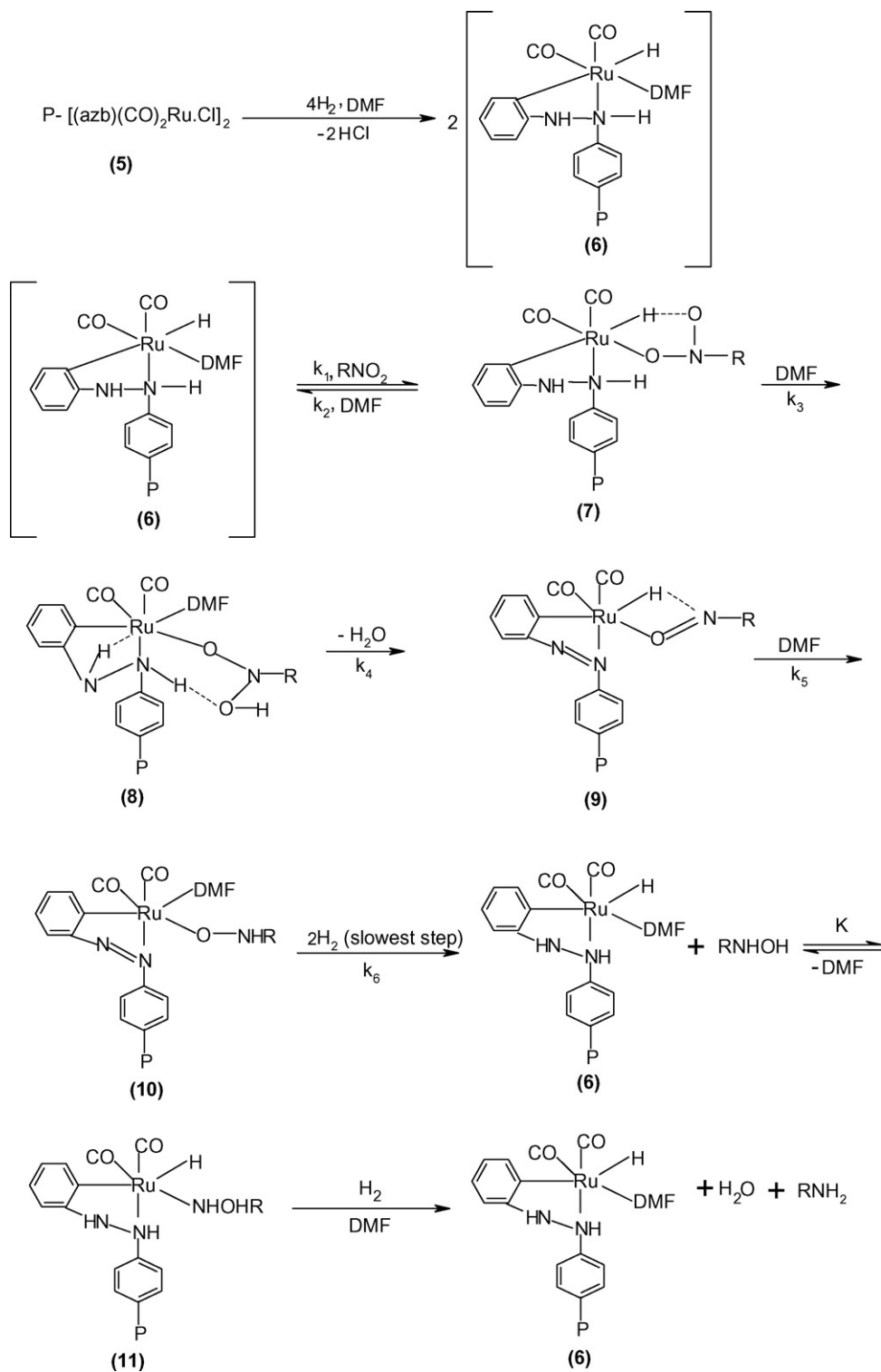
The catalyst P-[(Ru(azb)(CO)<sub>2</sub>Cl]<sub>2</sub> is quite stable in dry atmosphere and can be repeatedly used for the reduction of the



**Scheme 1.**



Scheme 2.



Scheme 3. Reduction of 2-nitropropane.

same or different substrates without loss of catalytic activity. The polystyrene anchored catalyst is comparable to its homogeneous counterpart in activity and product selectivity (Table 2). The advantages are that it can withstand more stringent reaction conditions (Table 2) and can be easily separated and recycled (Table 3).

### 3.1. Reaction kinetics and mechanism

The kinetic studies were made with the present catalyst (5) P-[Ru(azb)(CO)<sub>2</sub>Cl]<sub>2</sub> in DMF medium for the reduction of 2-nitropropane under high pressure, high temperature conditions. The rate was determined by GC estimation of reaction mixture at 15 min intervals and the initial rate was calculated by graphical extrapolation of the rate curve to zero time. For the reduction of 2-nitropropane, the initial rate was found to follow first order dependence on Ru content of the catalyst in the range of (1.0–6.0) × 10<sup>-3</sup> mol l<sup>-1</sup> (Fig. 3), second order dependence on hydrogen pressure in the range of 40–100 bar (Fig. 4) and independent of substrate concentration in the range of 0.5–3.0 M.

From the kinetic data, the rate equation can be expressed as

$$\text{Rate} = k[\text{cat}][P_{\text{H}_2}]^2 \quad (2)$$

Details derivation of rate equation (Eq. (2)) is given in supporting information (Section 3). The rate constant was calculated from the slopes of the curves in Fig. 3.

$$\text{Slope} = \frac{\text{Rate}}{[\text{cat}]}, \quad k = \frac{\text{Slope}}{[P_{\text{H}_2}]^2}$$

The  $k$  values lie between 1.40 × 10<sup>-6</sup> and 1.56 × 10<sup>-6</sup> s<sup>-1</sup> bar<sup>-2</sup> in the range of hydrogen pressure of 40–100 bar.

The rate constant was also calculated from the slopes of the curves in Fig. 4.

From Fig. 4

$$\text{Slope} = \frac{\text{Rate}}{[P_{\text{H}_2}]^2}, \quad k = \frac{\text{Slope}}{[\text{cat}]}$$

The  $k$  values lie between 1.50 × 10<sup>-6</sup> and 1.60 × 10<sup>-6</sup> s<sup>-1</sup> bar<sup>-2</sup> in the catalyst concentration range from 2.0 × 10<sup>-3</sup> to 6.0 × 10<sup>-3</sup> mol l<sup>-1</sup>.

The almost constant values of  $k$  in both the cases indicates the correctness of Eq. (2).

The following tentative mechanism was suggested on the basis of experimental findings.

According to Scheme 3

$$\text{Rate} = k_6[10][\text{H}_2]^2$$

$$[\text{Cat}]_T = [6] + [7] + [8] + [9] + [10] + [11]$$

Putting the value of [6], [7], [8], [9], and [11] in terms of 10, we have

$$[\text{Cat}]_T = \frac{K_3[10][\text{H}_2]^2}{[\text{RNO}_2]} + \frac{K_2[10][\text{H}_2]^2}{[\text{DMF}]} + K_1[10][\text{H}_2]^2 + \frac{K_7[10][\text{H}_2]^2}{[\text{DMF}]} + [10] + \frac{K_4[10][\text{H}_2]^2[\text{RNHOH}]}{[\text{RNO}_2][\text{DMF}]}$$

$$[10] = \frac{[\text{Cat}]_T[\text{RNO}_2][\text{DMF}]}{[\text{RNO}_2][\text{DMF}] + [\text{H}_2]^2\{[\text{DMF}]K_3 + K_2[\text{RNO}_2] + K_1[\text{DMF}][\text{RNO}_2] + K_7[\text{RNO}_2] + K_4[\text{RNHOH}]\}}$$

$$\text{Rate} = k_6[10][\text{H}_2]^2 = \frac{k_6[\text{Cat}]_T[\text{RNO}_2][\text{DMF}][\text{H}_2]^2}{[\text{RNO}_2][\text{DMF}] + [\text{H}_2]^2\{[\text{DMF}]K_3 + K_2[\text{RNO}_2] + K_1[\text{DMF}][\text{RNO}_2] + K_7[\text{RNO}_2] + K_4[\text{RNHOH}]\}}$$

The concentration of [H<sub>2</sub>] is of the order of 10<sup>-2</sup> M and hence [H<sub>2</sub>]<sup>2</sup> ≈ 10<sup>-4</sup> M while [RNO<sub>2</sub>] ≈ 1 M and DMF ≈ 10.0 M. Hence the equation reduces to

$$\text{Rate} = \frac{k_6[\text{Cat}]_T[\text{RNO}_2][\text{DMF}][\text{H}_2]^2}{[\text{RNO}_2][\text{DMF}]} = k_6[\text{Cat}]_T[\text{H}_2]^2$$

$$\text{Rate} = k[\text{Cat}]P_{\text{H}_2}^2$$

## 4. Conclusions

The polymer-based orthometallated catalyst, P-[Ru(azb)(CO)<sub>2</sub>Cl]<sub>2</sub>, used in the present investigation is comparable to its homogeneous counterpart in activity and product selectivity but superior to the latter as (i) same specimen of the catalyst can be used repeatedly for the reduction of substrates of different nature without suffering any appreciable loss of activity, (ii) isolation of the used catalyst from the product mixture encounters no difficulty, (iii) catalyst can withstand more stringent reaction conditions and (iv) catalyst can be recycled several times and the fresh or used catalysts can be stored under a dry condition for a long time without any appreciable loss of its catalytic activities. Hence the present system may find wide applications in the synthesis of fine organic chemicals either in the laboratory or on an industrial scale.

The magnitude of the value of rate constant  $k$  indicates high activity of the catalyst and its constancy over a range of  $P_{\text{H}_2}$  and catalyst concentration confirms the rate equation.

## Acknowledgements

We thank the Department of Chemistry, Indian Institute of Technology, Kharagpur, for providing the instrumental support. One of the authors, K.T., is thankful to University Grants Commission (Eastern Region), India, for financial support. We acknowledge the following agencies for funding: DST, CSIR and UGC, New Delhi, India.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.09.010.

## References

- [1] B. Stefan, S. Agnisszker, S. Beata, Appl. Catal. A: Gen. 309 (2006) 85.
- [2] A. Akelah, A. Rehab, E.R. Kenawy, M.S. Zeid Abou, J. Appl. Polym. Sci. 101 (2) (2006) 1121.
- [3] S. Samanta, N.K. Mal, A. Bhaumik, J. Mol. Catal. A: Chem. 236 (2005) 7.
- [4] S. Mukherjee, S. Samanta, B.C. Roy, A. Bhaumik, Appl. Catal. A: Gen. 301 (2006) 79.
- [5] D.W. Yoo, J.H. Han, S.H. Nam, C. Kim, J.K. Lee, Inorg. Chem. Commun. 9 (2006) 654.
- [6] C. Yue, Z. Fei, S. Bitao, W. Yupu, J. Macromol. Sci. Part A: Pure Appl. Chem. 43 (6) (2006) 923.
- [7] P.R. Likhari, S. Roy, M. Roy, M. Lakshmi Kantam, R. De, J. Mol. Catal. A: Chem. 271 (2007) 57.
- [8] M. Lakshmi Kantam, M. Roy, S. Roy, B. Sreedhar, S.S. Madhavendra, B.M. Choudary, R.L. De, Tetrahedron 63 (2007) 8002.
- [9] M. Lakshmi Kantam, S. Roy, M. Roy, B. Sreedhar, B.M. Choudary, R.L. De, J. Mol. Catal. A: Chem. 273 (2007) 26.
- [10] K. Nomura, H. Ogura, Y. Imanishi, J. Mol. Catal. A: Chem. 178 (2002) 105.
- [11] A.M. Tafesh, M. Beller, Tetrahedron Lett. 36 (1995) 9305.
- [12] T.G. Ross, M.K. Vander Lee, A.J. Van Dillen, D.C. Koningsberger, J. Mol. Catal. A: Chem. 186 (2002) 13.

- [13] D.J. Darensbourg, F. Joo, M. Schalf, H. Werner, *Inorg. Chem.* 33 (1994) 200.
- [14] U. Mohring, M. Schafer, F. Kukla, M. Schlaf, H. Werner, *J. Mol. Catal.* 99 (1995) 55.
- [15] D.K. Mukherjee, B.K. Palit, C.R. Saha, *J. Mol. Catal.* 88 (1994) 57.
- [16] F. Hochard, H. Jobic, J. Massardier, A.J. Renouprez, *J. Mol. Catal.* 95 (1995) 165.
- [17] C. Viceute, G.B. Shulpen, B. Moreno, S. SaboEienne, B. Chaudret, *J. Mol. Catal.* 98 (1995) 25.
- [18] S. Ram, R.E. Ehremkanfer, *Tetrahedron Lett.* 25 (1984) 3415.
- [19] A. Bose, C.R. Saha, *J. Mol. Catal.* 49 (1989) 271.
- [20] K.C. Gupta, A.K. Sutar, *J. Mol. Catal.* 280 (2007) 173.
- [21] P. Morys, J. Schlieper, *J. Mol. Catal.* 95 (1995) 27.
- [22] N.M. Astorga, G. Pecchi, T.J. Pinnavaia, G.A. Manoli, P. Reyes, *J. Mol. Catal. A: Chem.* 247 (2006) 145.
- [23] A. Knapik, A. Drelinkiewicz, M. Szalenice, W. Makowski, A.W. Gora, A. Bukowska, W. Bukowski, J. Noworol, *J. Mol. Catal. A: Chem.* 279 (2008) 47.
- [24] Z.M. Michalska, Ł. Rogalski, K. Rózga-Wijas, J. Chojnowski, W. Fortuniak, M. Scibiorek, *J. Mol. Catal. A: Chem.* 208 (2004) 187.
- [25] B. Log, A. Tijani, R. Daste, F. Figueras, *J. Mol. Catal.* 79 (1993) 253.
- [26] J. Jaworska, S. Gobas, W. Mistra, J. Wrzyzy, *J. Mol. Catal.* 88 (1994) 13.
- [27] A. Riisager, K.M. Eriksen, J. Hjortkjaer, R. Fehrmann, *J. Mol. Catal. A: Chem.* 193 (2003) 259.
- [28] J.N. Shah, R.N. Ram, *J. Mol. Catal.* 83 (1993) 67.
- [29] L. Zhang, Y. Zhang, X.G. Zhou, R.X. Li, X.J. Li, K.C. Tin, N.B. Wong, *J. Mol. Catal. A: Chem.* 256 (2006) 171.
- [30] M.A. Wolfovich, R. Jothiramalingam, M.V. Landau, M. Herskowitz, B. Viswanathan, T.K. Varadarajan, *Appl. Catal. B: Environ.* 59 (2005) 91.
- [31] J.M. Compelo, R. Gurdeno, W. Luna, J.M. Marino, J. Morales, J.L. Tirado, *J. Mol. Catal.* 85 (1993) 305.
- [32] A. Saadi, R. Merabti, Z. Rassoul, M.M. Bettahar, *J. Mol. Catal. A: Chem.* 253 (2006) 79.
- [33] S.M. Islam, A. Bose, B.K. Palit, C.R. Saha, *J. Catal.* 173 (1998) 268.
- [34] A.I. Vogel, *Text Book of Practical Organic Chemistry (Quantitative Analysis)*, fifth ed., Longman, London, 1989.
- [35] R.B. King, E.M. Sweet, *J. Org. Chem.* 44 (1979) 385.
- [36] K. Hiraki, Y. Obayashi, Y. Oki, *Bull. Chem. Soc. Jpn.* 52 (1979) 1372.
- [37] K. Hiraki, Y. Obayashi, Y. Oki, *Bull. Chem. Soc. Jpn.* 52 (1979) 1372.
- [38] A.K. Singh, M. Katyal, R.P. Singh, *J. Indian Chem. Soc.* LIII (1976) 691.
- [39] H. Onoue, I. Moritani, *J. Organomet. Chem.* 43 (1972) 431.
- [40] S.M. Islam, D. Mal, B.K. Palit, C.R. Saha, *J. Mol. Catal. A: Chem.* 142 (1999) 169.