Contents lists available at ScienceDirect



Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

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

S.M. Islam^{a,*}, K. Tuhina^b, M. Mubarak^a, P. Mondal^a

^a Department of Chemistry, University of Kalyani, Kalyani, Nadia 741235, W.B., India ^b 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 $[Ru(azb)(CO)_2Cl]_2$ (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 (S.M. Islam).

^{1381-1169/\$ -} see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.molcata.2008.09.010

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 (RuCl₃·3H₂O) 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, $P-[(azb)(CO)_2Ru\cdot CI]_2$ (P=polystyrene backbone and H-azb=azobenzene) is shown in Scheme 1. The complex was prepared by reacting polymer anchored azobenzene ligand with (i) [Ru(CO)_2Cl_2S_2] or (ii) RuCl_3·3H_2O under high P_{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, $P-[(azb)(CO)_2Ru\cdotCl]_2$ (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, P-[(azb)(CO)₂Ru·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 $200 \,^{\circ}$ 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 $-NO_2$, C=C<, C=O, C=N-, -C=C-, -C=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 CH₃CN, and PhCN. In the presence of very strong ligands like py, pic, dipy, PPh₃ reaction occurred at a very slow rate. In non-coordinating media like C₆H₆, C₆H₅CH₃, CHCl₃, and CCl₄ 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 >C=C< and -C=C- groups were completely reduced with highest rate at \sim 70 °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 π -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 π -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 H^+ and $RCOO^-$. 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

$$P-[(azb)(CO)_2 RuCl]_2 \xrightarrow{DMF} P-[(azb)(CO)_2 Ru \cdot DMF \cdot Cl]_6$$

$$\stackrel{H_2}{=} P-[(azb)(CO)_2 Ru \cdot H \cdot DMF] + HCl \qquad (1)$$

Among the Schiff bases, only benzylidineaniline and N-methylbenzaldimine were reduced completely to the corresponding amines without any side products. >C=N- and >C=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 $80 \,^{\circ}$ 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:

$$\begin{split} & \mathsf{C}_6\mathsf{H}_5\mathsf{NO}_2 > \mathsf{p}\text{-}\mathsf{CH}_3\mathsf{C}_6\mathsf{H}_4\mathsf{NO}_2 > \mathsf{p}\text{-}\mathsf{CIC}_6\mathsf{H}_4\mathsf{NO}_2 \\ & > \mathsf{m}\text{-}\mathsf{CIC}_6\mathsf{H}_4\mathsf{NO}_2 > \mathsf{o}\text{-}\mathsf{CH}_3\mathsf{C}_6\mathsf{H}_4\mathsf{NO}_2 > \mathsf{o}\text{-}\mathsf{CIC}_6\mathsf{H}_4\mathsf{NO}_2 \\ & > \mathsf{p}\text{-}\mathsf{HOC}_6\mathsf{H}_4\mathsf{NO}_2 > \mathsf{p}\text{-}\mathsf{H}_2\mathsf{NC}_6\mathsf{H}_4\mathsf{NO}_2 \end{split}$$

Table 1

Substrates and the corresponding products with catalyst P-[(azb)(CO)₂ RuCl]₂.

1. Styrene ³ 4.8 7.97 Ethylbenzene 97 2. Isoprene ⁴ 5.2 7.16 2-Methylbutane 96 3. 1-Pettene ⁴ 5.6 6.91 Pettane 94 4. 1-Hexne ⁴ 5.9 6.61 Hexane 94 5. 1-Heptene ⁴ 6.0 6.12 Heptane 92 6. Cyclobexene ⁴ 6.4 5.55 Cyclobexane 90 7. Maleic acid ⁴ 7.2 4.38 Succinic acid 89 9. Diphenylacetylene ⁴ 5.0 6.50 Ethylbenzylamine 92 10. Phenylacetylene ⁴ 5.0 6.50 N-Henylbenzylamine 95 12. Benzylinkenalimine 5.2 7.52 N-Methylbenzylamine 96 13. Nitrobenzene ⁶ 5.6 7.38 Aniline 94 14. p-Nitrotiluen ⁶ 7.6 4.24 o-Floneidmine 88 17. o-Nitrotoluene ⁶ 7.3 4.50 o-Toluidine 90 15. p-Chloronit	Expt. no.	Substrate	Reaction time (h)	Initial turnover no. (min ⁻¹)	Product(s)	% Yield 97	
2.Isoprene ^A 5.27.162-Methylbutane963.I-Pentnere ^A 5.66.10Pentane944.I-Hexne ^A 5.96.61Hexane945.I-Heptne ^A 6.06.12Heptane926.Cyclohexane ^A 6.45.5Cyclohexane907.Maleic acid ^A 7.24.38Succinic acid889.Diphenylacetylene ^A 4.87.311.2-Diphenylethane9210.Penylacetylene ^A 5.06.50Rhylbenzylamine9612.Benzylidinanilne ^A 4.87.96N-Phenylbenzylamine9613.Nitrobenzene ^b 5.67.38Aniline9414.p-Nitrotoluene ^b 5.95.82p-Chloronailine9215.p-Chloronailine ^A 7.64.241-Aminonaphthalene8817.o-Nitronainine ^b 7.64.241-Aminonaphthalene8618.1-Nitronaphthalene ^B 7.84.06p-Phenelenediamine8621.p-Nitrotoluene ^B 7.84.06p-Phenelenediamine8622.p-Nitrotoluene ^B 5.86.15Ethylamine9623.n-Dinitrobenzene ^B 5.86.15Ethylamine9624.p-Nitrotoluene ^B 7.86.15Ethylamine8625.p-Nitrotoluene ^B 5.86.15Ethylamine8624.n-Dinitrobenzene ^B 5.86.15	1.	Styrene ^a	4.8	7.97	Ethylbenzene		
3.1-Pentene ^A 5.66.91Pentane944.41-Hexene ^A 5.936.61Hexane945.1-Heptene ^A 6.06.12Heptane926.Cyclohexene ^A 6.45.55Cyclohexane907.Maleic acid ^A 7.24.38Succinic acid888.Fumaric acid ^A 7.24.38Succinic acid889.Diphenylacetylene ^A 5.06.50Ethylbenzylennylethane9210.N-Methylbenzylamine5.27.2N-Methylbenzylamine9612.Renzylidineaniline ^A 4.87.96N-Methylbenzylamine9113.Nitrobenzene ^b 5.95.98p-Toluidine9215.p-Chloronitrobenzene ^b 7.34.50o-Floneaniline8817.o -Nitrotoluene ^b 7.34.50o-Floneaniline8718.1-Nitrononitrobenzene ^b 7.84.61o-Chloroaniline8719.0-Chloronitrobenzene ^b 7.84.61o-Chloroaniline8819.0-Chloronitrobenzene ^b 7.84.61o-Phenelenediamine8821.p-Nitrophenol ^B 8.83.72p-Aminophenol8622.p-Nitrophenol ^B 5.86.15Hylamine9023.n-Nitrobenzene ^C 6.45.62p-Aminopropane8624.Nitroethane ^C 5.67.08Methylamine9125.p-Nitrophenol ^A <	2.	Isoprene ^a	5.2	7.16	2-Methylbutane	96	
4.1-Hexene ^A 5.96.61Hexane945.1-Heytene ^A 6.06.12Heytane926.Cyclohexane ^A 6.45.55Cyclohexane907.Maleic acid ^A 7.24.38Succinic acid889.Diphenylacctylene ^A 4.87.311.2-Diphenylethane9210.Penylacctylene ^A 5.06.50Ethylbenzene9211.N.Methylbenzialimine5.27.52N.Methylbenzialmine9612.Benzyldineanline ^A 5.67.38Aniline9113.Nitobenzene ^b 5.95.62p-Chioronaline8114.p-Nitrotoluene ^b 7.34.50o-Floudine8115.p-Chioronitrobenzene ^b 7.84.01o-Floudine8116.o-Nitronalline ^b 7.93.56p-Phenelendiamine8119.o-Chioronitrobenzene ^b 7.84.01o-Chioraniline8121.p-Nitrobenzene ^b 7.84.06p-Phenelendiamine8622.p-Nitrobenzene ^b 7.86.15Ethylamine9223.n-Dinitrobenzene ^c 5.86.15Ethylamine9424.Nitroethane ^c 5.27.023.689.049.0423.p-Nitrobenzene ^c 5.86.15Ethylamine9424.Nitroethane ^c 5.52Benzylacholo8625.Nitroethane ^c 5.52Benzylacholo <t< td=""><td>3.</td><td>1-Pentene^a</td><td>5.6</td><td>6.91</td><td>Pentane</td><td>94</td></t<>	3.	1-Pentene ^a	5.6	6.91	Pentane	94	
5.1-Heptene ^a 6.06.12Heptane926.Cycloheszne ^a 6.45.55Cycloheszne907.Maleic acid ^a 7.24.38Succinic acid818.Fumaric acid ^a 7.63.95Succinic acid829.Diphenylacetylene ^a 4.87.311.2-Diphenylethane9210.Phenylacetylene ^a 5.06.50Ethylbenzene9211.N-Methylbenzlalmine5.27.52N-Methylbenzylamine9512.Benzylidineaniline ^a 4.87.96N-Phenylbenzylamine9413.Nitrobenzene ^b 5.95.98p-Toluidine9414.p-Nitrotoluene ^b 7.04.50o-Phenelenelamine8817.o-Nitrotoluene ^b 7.84.01o-Choroaniline8720.p-Nitronalinle ^b 7.84.01o-Choroaniline8821.p-Nitrotoluene ^b 7.84.06p-Phenelenediamine8821.p-Nitrophenol ^a 8.67.708Methylamine9022.p-Nitrophenzene ^a 7.23.68m-Phenelenediamine8623.Nitroethane ^a 5.52Benzylicohol8624.Nitromethane ^a 7.24.66Aminocyclohexane8625.S.52Benzylicohol863.00Phenylimethanol8624.Nitropropane ^a 5.45.52Benzylicohol8625.Benzalichydref <t< td=""><td>4.</td><td>1-Hexene^a</td><td>5.9</td><td>6.61</td><td>Hexane</td><td>94</td></t<>	4.	1-Hexene ^a	5.9	6.61	Hexane	94	
6.Cyclohexane*6.45.5Cyclohexane907.Maleic acid*7.24.38Succinic acid888.Fumaric acid*7.63.95Succinic acid889.Diphenylacetylene*4.87.311.2-Diphenylethane9211.Prenylacetylene*5.06.50Ethylbenzene9211.N-Methylbenzaldimine5.27.52N-Methylbenzylamine9512.Benzyldineaniline*5.97.96N-Phenylbenzylamine9414.p-Nitrotoluene*5.95.62p-Chloroaniline9215.p-Chloronitrobenzene*6.25.62p-Chloroaniline8117.o-Nitrotoluene*7.34.50o-Thuidinine8819.o-Chloroaniline*7.84.01o-Chloroaniline8819.o-Chloroaniline*7.93.56p-Menelenediamine8821.p-Nitrobenzene*7.84.06p-Phenelenediamine8622.p-Nitrobenzene*7.86.15Ethylamine9423.m-Dinitrobenzene*5.67.08Methylamine9424.Nitroorethane*5.67.08Methylamine8623.p-Nitrobenzene*7.23.66p-Menelenediamine8624.Nitroorethane*5.67.08Methylamine9425.Nitroethane*7.23.66p-Mininopropane8624.Nitroorethane*5.2<	5.	1-Heptene ^a	6.0	6.12	Heptane	92	
7.Maleic acid ⁴ 7.24.38Succinic acid898.Fumaric acid ⁴ 7.63.95Succinic acid889.Diphenylacetylene ⁴ 4.87.311.2-Diphenylethane9210.N-Metylbenzylamine5.27.52N-Metylbenzylamine9512.Benzylidineaniline ⁴ 4.87.60N-Phenylbenzylamine9513.Nitrobenzene ^b 5.67.38Aniline9414.p-Klitorohitrobenzene ^b 6.25.98p-Chloroaniline9215.p-Chloronitrobenzene ^b 7.04.94o-Phenelenediamine8817.oo-Nitrotoluene ^b 7.64.24oo-Henelenediamine8118.1-Nitronaphthalene ^b 7.64.24oo-Henelenediamine8820.oNitrotoluene ^b 7.84.01o-Chloroaniline8821.p-Nitroaniline ^b 7.84.01o-Chloroaniline8822.p-Nitroaniline ^b 7.84.06p-Phenelenediamine8623.m-Dinitrobenzene ^b 7.86.16Minoporpane8924.Nitroothanene ^c 5.67.08Methylamine9025.Nitroothanene ^c 5.67.08Methylamine9124.Nitroothanene ^c 5.67.08Methylamine8125.Nitroothanene ^c 5.85.2Benzylacholo8826.1-Nitropopane ^c 5.85.2Benz	6.	Cyclohexene ^a	6.4	5.55	Cyclohexane	90	
8.Fumaric acid ⁴ 7.69.9Succinic acid889.Diphenylacetylene ⁴ 4.87.311.2-Diphenylethane9210.Phenylacetylene ³ 5.06.50Ethylbenzene9211.N-Methylbenzaldimine5.27.52N-Methylbenzylamine9513.Nitrobenzene ^b 5.67.38Aniline9414.p-Nitrotoluene ^b 5.95.82p-Chloroaniline9215.p-Chloronitrobenzene ^b 6.25.52p-Chloroaniline9216.o-Nitroaniline ^b 7.34.50o-Toluidine8817.o-Nitroaniline ^b 7.64.24o-Toluidine8818.1-Nitronaphthalene ^b 7.64.24o-Chloroaniline8720.p-Nitrobenzene ^b 7.84.01o-Chloroaniline8721.p-Nitrophenol ^b 7.84.02p-Phenelenediamine8622.p-Dinitrobenzene ^b 7.84.02p-Phenelenediamine8723.m-Dinitrobenzene ^b 7.84.02p-Phenelenediamine8824.ntoronamine ^b 7.23.68m-Dinitrobenzene8725.Nitroethane ^c 5.86.15Ethylamine9624.Nitropropane ^c 6.45.20Benzylachol8825.Nitroethane ^c 7.24.46Aminopropane8826.Nitroethane ^c 7.24.46Aminopropane8627.2-Nit	7.	Maleic acid ^a	7.2	4.38	Succinic acid	89	
9.Diphenylacetylene ^a 4.87.311.2-Diphenylethane9210.Phenylacetylene ^a 5.06.50Ethylbenzzene9211.N-Methylbenzaldimine5.27.52N-Methylbenzylamine9512.Benzylidineaniline ^a 4.87.96N.Phenylbenzylamine9213.Nitrobenzene ^b 5.97.38Aniline9215.p-Chloronitrobenzene ^b 6.25.28p-Chloroniline9216.o-Nitrotoluene ^b 7.34.50o-Toluidine8817.o-Nitrotoluene ^b 7.64.241-Aminoaphthalene8819.o-Chloronitrobenzene ^b 7.84.01o-Chloronailine8720.p-Nitronaline ^b 7.93.56p-Phenelenediamine8821.p-Nitrophend ^b 8.03.72p-Aminophenol8622.p-Dinitrobenzene ⁶ 5.67.08Methylamine9423.m-Dinitrobenzene ⁶ 5.67.08Methylamine9424.Nitromethane ⁶ 5.67.08Methylamine9623.m-Dinitrobenzene ⁶ 5.67.08Methylamine9624.Nitromethane ⁶ 5.86.15Ethylamine9625.Nitrotochane ⁶ 5.86.15Hubylanine9624.Nitrotochane ⁶ 5.2Benzylacholo8825.Benzdehyde ^d 4.85.2Benzylacholo8626.1-Nitropopane ⁶	8.	Fumaric acid ^a	7.6	3.95	Succinic acid	88	
10.Phenylacetylene ⁴ 5.06.50Ethylenzene9211.N-Methylbenzaldinine5.27.52N-Methylbenzylamine9512.Benzyldinenailine ⁴ 4.87.96N-Phenylbenzylamine9513.Nitrobenzene ^b 5.67.38Anlline9414.p-Nitrotoluene ^b 6.25.62p-Chloroaniline9215.p-Chloronitrobenzene ^b 6.25.62p-Chloroaniline8817.o-Nitrotoluene ^b 7.04.94o-Phenelenciamine8818.1-Nitronaline ^b 7.64.241-Aminonaphtalene8819.o-Chloronitrobenzene ^b 7.84.01o-Chloroaniline8720.p-Nitroaniline ^b 7.84.01o-Chloroaniline8821.p-Nitroaniline ^b 7.84.06p-Phenelenciamine8622.p-Dinitrobenzene ⁶ 7.23.68m-Phenelenciamine9623.m-Dinitrobenzene ⁶ 7.23.68m-Phenelenciamine8724.Nitromethane ^c 5.67.08Methylamine9425.Nitropropane ⁶ 6.45.761-Aminopropane8926.1-Nitropropane ⁶ 6.45.52Benzylatohol8627.2-Nitropropane ⁶ 6.45.52Benzylatohol8628.5.52Benzylatohol868629.Benzidehyde ^d 4.85.52Benzylatohol8631.Actophenon	9.	Diphenylacetylenea	4.8	7.31	1,2-Diphenylethane	92	
11.N-Methylbenzaldimine5.27.52N-Methylbenzylamine9612.Benzylidineaniline ⁴ 4.87.96N-Phenylbenzylamine9513.Nitrobenzene ⁶ 5.97.38Aniline9014.p-Nitrotolune ⁶ 5.95.98p-Toluidine9015.p-Chloronitrobenzene ⁶ 6.25.62p-Chloroniline9216.o-Nitrotolune ⁶ 7.04.94o-Phenelenediamine8817.o-Nitrotolune ⁶ 7.64.24i-Aminonaphthalene8719.o-Chloronitrobenzene ⁶ 7.84.01o-Chloroaniline8720.p-Nitroaniline ⁶ 7.93.56p-Phenelenediamine8821.p-Nitrophenol ¹⁶ 8.03.72p-Aminophenol8622.p-Dinitrobenzene ⁶ 6.84.06p-Phenelenediamine8623.m-Dinitrobenzene ⁶ 5.67.08Methylamine9024.Nitroethane ⁶ 5.67.781-Aminopropane8625.Nitroethane ⁶ 5.65.761-Aminopropane8826.1-Nitropropane ⁶ 6.45.302-Aminopropane8827.1-Nitropropane ⁶ 6.45.302-Aminopropane8828.Nitroethane ⁶ 5.45.31Biphenylmethanol8527.2-Nitropropane ⁶ 6.45.302-Aminopropane8828.Nitroethane ⁶ 5.45.31Diphenylmethanol86<	10.	Phenylacetylenea	5.0	6.50	Ethylbenzene	92	
12.Benzylidineaniline ^a 4.87.96N-Phenylbenzylamine9513.Nitrobenzene ^b 5.67.38Aniline9414.p-Nitrotolucne ^b 5.95.98p-Toluidine9015.p-Chloronitrobenzene ^b 6.25.62p-Chloroniline8216.o-Nitrotolucne ^b 7.04.94o-Phenelenediamine8817.o-Nitrotolucne ^b 7.64.241-Aminonaphthalene8819.o-Chloronitrobenzene ^b 7.84.01o-Chloroaniline8720.p-Nitroaniline ^b 7.93.56p-Phenelenediamine8821.p-Nitrophenol ^b 8.03.72p-Aminophenol8622.p-Dinitrobenzene ^c 6.84.06p-Phenelenediamine8923.m-Dinitrobenzene ^c 5.86.15Ethylamine9024.Nitroethane ^c 5.86.15Ethylamine9025.Nitroethane ^c 5.86.15Ethylamine9026.1-Nitropropane ^c 6.45.302-Aminopropane8627.2-Nitropropane ^c 6.45.31Diphenylmethanol8628.1-Nitropropane ^c 6.45.302-Aminopropane8629.Benzaldehyde ^d 5.45.31Diphenylmethanol8629.Benzaldehyde ^d 5.45.31Diphenylmethanol8631.Acetophenone ^d 5.45.31Diphenylmethanol8632.<	11.	N-Methylbenzaldimine	5.2	7.52	N-Methylbenzylamine	96	
13.Nitrobenzene ^b 5.67.38Aniline9414.p-Nitrobenzene ^b 5.95.98p-Toluidine9015.p-Chloronitrobenzene ^b 5.95.98p-Toluidine9015.p-Chloronitrobenzene ^b 7.04.94o-Phenelenediamine8817.o-Nitrotolutene ^b 7.34.50o-Toluidine9018.1-Nitronaphthalene ^b 7.64.241-Aminonaphthalene8819.o-Chloronitrobenzene ^b 7.84.01o-Chloroaniline8720.p-Nitroaniline ^b 7.93.56p-Phenelenediamine8621.p-Nitrophenol ^b 8.03.72p-Aminophenol8622.p-Dinitrobenzene ^e 7.23.68m-Phenelenediamine9423.m-Dinitrobenzene ^e 5.86.15Ethylamine9424.Nitroethane ^e 5.86.15Ethylamine9425.Nitroethane ^e 5.86.15Ethylamine8624.Nitropopane ^e 6.05.761-Aminopropane8625.Nitrogropane ^e 4.85.52Benzaldehyde ^d 8829.Benzaldehyde ^d 4.85.52Benzylalcohol8531.Acetophenone ^d 5.45.36Dihydrobenzoin8632.Benzaldehyde ^d 4.85.37Dihydrobenzoin8633.Benzil ^{id} 6.24.56Dihydrobenzoin8633.Benzil ^{id} <	12.	Benzylidineanilinea	4.8	7.96	N-Phenylbenzylamine	95	
14.p-Nitrotolueneb5.95.98p-Toluidine9015.p-Chloronitrobenzeneb6.25.62p-Chloronitine9216.o-Nitrotolueneb7.04.94o-Phenelenediamine8817.o-Nitrotolueneb7.34.50o-Toluidine8018.1-Nitronaphthaleneb7.64.241-Aminonaphthalene8819.o-Chloronitrobenzeneb7.84.01o-Chloronailine8720.p-Nitronalineb7.93.56p-Phenelenediamine8621.p-Nitrophenolb8.03.72p-Aminophenol8622.p-Dinitrobenzenece6.84.06p-Phenelenediamine8623.m-Dinitrobenzenece7.23.68m-Phenelenediamine9424.Nitromethanec5.67.08Methylamine9425.Nitrotonanec5.761-Aminopropane8826.Nitroptopanec6.45.302-Aminopropane8627.2-Nitropropanec6.45.52Benzylalcohol8630.Benzolhenoned5.45.31Diphenylmethanol8631.Acetophenoned6.43.80Phenylmethanol8632.Benzolind6.63.652-Propanol8633.Benzolind6.43.80Phenylmethanol8633.Benzolind6.63.652-Propanol8634.Acetophenoned6.23.652-Propanol </td <td>13.</td> <td>Nitrobenzene^b</td> <td>5.6</td> <td>7.38</td> <td>Aniline</td> <td>94</td>	13.	Nitrobenzene ^b	5.6	7.38	Aniline	94	
15.p-Chloronitrobenzeneb6.25.62p-Chloroniline9216.o-Nitronilineb7.04.94o-Phenelenediamine8817.o-Nitrotolueneb7.34.50o-Toluidine9018.1-Nitronaphthaleneb7.64.241-Aminonaphthalene8819.o-Chloronitrobenzeneb7.84.01o-Chloroniline8720.p-Nitronalilineb7.93.56p-Phenelenediamine8621.p-Nitrophenolb8.03.72p-Aminophenol8622.p-Dinitrobenzenec6.84.06p-Phenelenediamine8624.Nitromethanec5.67.08Methylamine9425.Nitroethanec5.86.15Ethylamine9026.1-Nitroppanec6.45.302-Aminopropane8927.2-Nitropropanec6.45.302-Aminopropane8628.Nitrocyclobexanec7.24.46Aminocyclobexane8629.Benzaldehyded4.85.52Benzylalcohol8530.Benzohenoned5.45.31Diphenylmethanol8631.Acetophenoned6.24.56Dihydrobenzoin8632.Benzoind6.14.48Dihydrobenzoin8633.Benzoind6.24.56Dihydrobenzoin8634.Acetophenoned6.23.652-Propanol8235.Benzointilee7.93.42Di	14.	p-Nitrotoluene ^b	5.9	5.98	p-Toluidine	90	
16.o-Nitroanilineb7.04.94o-Phenelenediamine8817.o-Nitrotolueneb7.34.50o-Toluidine9018.1-Nitronaphthaleneb7.64.241-Aminonaphthalene8819.o-Chloronitrobenzeneb7.84.01o-Chloroaniline8720.p-Nitroanilineb7.93.56p-Phenelenediamine8821.p-Nitrophenob8.03.72p-Aminophenol8622.p-Dinitrobenzenec6.84.06p-Phenelenediamine8923.m-Dinitrobenzenec5.67.08Methylamine9424.Nitromethanec5.67.08Methylamine9425.Nitromethanec5.67.08Methylamine8926.1-Nitropopanec6.05.761-Aminopropane8928.Nitrocyclohexanec7.24.46Aminoyclohexane8629.Benzaldehyded4.85.52Benzylachol8830.Benzoind6.43.80Phenylmethanol8631.Acetophenoned6.43.80Phenylmethanol8633.Benzoind6.14.48Dihydrobenzoin8434.Acetoned6.63.652-Propanol8235.Benzoind6.24.56Dihydrobenzoin8633.Benzoind6.63.652-Propanol8234.Acetoned6.63.652-Propanol82	15.	p-Chloronitrobenzene ^b	6.2	5.62	p-Chloroaniline	92	
17.o-Nitrodueneb7.34.50o-Toluidine9018.1-Nitroaphthaleneb7.64.241-Aminonaphthalene8819.o-Chloronitrobenzeneb7.84.01o-Chloroniline8720.p-Nitroanlineb7.93.56p-Phenelenediamine8621.p-Nitrophenolb8.03.72p-Aminophenol8622.p-Dinitrobenzenec6.84.06p-Phenelenediamine8923.m-Dinitrobenzenec7.23.68m-Phenelenediamine9024.Nitromethanec5.67.08Methylamine9025.Nitrotethanec6.05.761-Aminopropane8827.2-Nitropropanec6.05.302-Aminopropane8928.Nitrocyclohexanec7.24.46Aminocyclohexane8629.Benzaldehyded4.85.52Benzylalcohol8631.Acetophenoned5.45.31Diphenylmethanol8632.Benzoind6.24.56Dihydrobenzoin8633.Benzoind6.24.56Dihydrobenzoin8634.Acetoned6.14.48Dihydrobenzoin8635.Benzoinfilee7.53.42Dibneylamine9035.Benzoinfilee7.53.42Dihydrobenzoin8635.Benzoinfilee7.24.46Dihydrobenzoin8636.Benzoinfilee5.45.52Benzylanine </td <td>16.</td> <td>o-Nitroaniline^b</td> <td>7.0</td> <td>4.94</td> <td>o-Phenelenediamine</td> <td>88</td>	16.	o-Nitroaniline ^b	7.0	4.94	o-Phenelenediamine	88	
18.1-Nitronaphthaleneb7.64.241-Aminonaphthalene8819.o-Chloronitrobenzeneb7.84.01o-Chloroaniline8720.p-Nitroanilineb7.93.56p-Phenelenediamine8821.p-Nitrophenolb8.03.72p-Aminophenol8622.p-Dinitrobenzenee6.84.06p-Phenelenediamine8923.m-Dinitrobenzenee7.23.68m-Phenelenediamine8624.Nitromethanec5.67.08Methylamine9425.Nitrotethanec5.86.15Ethylamine9026.1-Nitropropanec6.05.761-Aminopropane8827.2-Nitropropanec6.45.302-Aminopropane8928.Nitrocyclohexanec7.24.46Aminocyclohexane8629.Benzolhenoned4.85.52Benzylachol8830.Benzolhenoned5.45.31Diphenylmethanol8531.Acetophenoned6.24.56Dihydrobenzoin8633.Benzild6.14.48Dihydrobenzoin8434.Acetoned6.63.652-Propanol8235.Benzonitrilee7.53.42Dibenzylamine9236.Acetonitilee7.93.22Diethylamine81	17.	o-Nitrotoluene ^b	7.3	4.50	o-Toluidine	90	
19.o-Chloronitrobenzene ^b 7.84.01o-Chloroniline8720.p-Nitroniline ^b 7.93.56p-Phenelenediamine8821.p-Nitrophenol ^b 8.03.72p-Aminophenol8622.p-Dinitrobenzene ^e 6.84.06p-Phenelenediamine8923.m-Dinitrobenzene ^e 7.23.68m-Phenelenediamine9424.Nitroethane ^c 5.67.08Methylamine9425.Nitroothane ^c 5.86.15Ethylamine9026.1-Nitropropane ^c 6.45.302-Aminopropane8827.2-Nitropropane ^c 6.45.302-Aminopropane8928.Nitrocyclohexane ^c 7.24.46Aminocyclohexane8629.Benzaldehyde ^d 4.85.52Benzylalcohol8830.Benzohenone ^d 6.43.80Phenylmethanol8631.Acetophenone ^d 6.43.80Phenylmethanol8632.Benzolif ^d 6.14.48Dihydrobenzoin8633.Benzil ^d 6.14.48Dihydrobenzoin8434.Acetone ^d 6.63.652-Propanol8235.Benzonitrile ^e 7.53.42Dibenzylamine9236.Acetonitrile ^e 7.93.22Diethylamine81	18.	1-Nitronaphthalene ^b	7.6	4.24	1-Aminonaphthalene	88	
20.p-Nitroanilineb7.93.56p-Phenelemediamine8821.p-Nitrophenolb8.03.72p-Aminophenol8622.p-Dinitrobenzenee6.84.06p-Phenelemediamine8923.m-Dinitrobenzenee7.23.68m-Phenelemediamine8624.Nitromethanee5.67.08Methylamine9025.Nitroethanee6.05.761-Aminopropane8827.2-Nitropropanee6.45.302-Aminopropane8928.Nitrocyclohexanee7.24.46Aminocyclohexane8629.Benzaldehyded4.85.52Benzylalcohol8530.Benzophenoned5.45.31Diphenylmethanol8632.Benzoind6.43.80Phenylmethylmethanol8631.Acetopenoned6.43.80Phenylmethylmethanol8633.Benzoind6.24.56Dihydrobenzoin8634.Acetoned6.63.652-Propanol8235.Benzointilee7.53.42Dibenzylamine9236.Acetonitilee7.93.22Diethylamine16	19.	o-Chloronitrobenzene ^b	7.8	4.01	o-Chloroaniline	87	
21.p-Nitrophenolh8.03.72p-Aminophenol8622.p-Dinitrobenzene ^e 6.84.06p-Phenelenediamine8923.m-Dinitrobenzene ^e 7.23.68m-Phenelenediamine8624.Nitromethane ^c 5.67.08Methylamine9025.Nitroethane ^c 5.86.15Ethylamine9026.1-Nitropropane ^c 6.05.761-Aminopropane8827.2-Nitroptopane ^c 6.45.302-Aminophenol8928.Nitrocyclohexane ^c 7.24.46Aminocyclohexane8629.Benzylalehone ^d 5.45.52Benzylalcohol8530.Benzophenone ^d 6.43.80Phenylmethanol8531.Acetophenone ^d 6.24.56Dihydrobenzoin8632.Benzoind6.24.56Dihydrobenzoin8633.Benzil ⁴ 6.14.48Dihydrobenzoin8434.Acetone ^d 6.63.652-Propanol8235.Benzointrile ^e 7.53.42Diberzylamine9236.Acetonitrile ^e 7.93.22Diethylamine81	20	p-Nitroaniline ^b	79	3 56	p-Phenelenediamine	88	
21.p Hatophend6.65.72p Hatophend6.622.p -Dinitrobenzene ^e 6.84.06p -Phenelenediamine8923.m -Dinitrobenzene ^e 7.23.68m -Phenelenediamine8624.Nitromethane ^c 5.67.08Methylamine9425.Nitroethane ^c 5.86.15Ethylamine9026.1-Nitropropane ^c 6.05.761-Aminopropane8827.2-Nitropropane ^c 6.45.302-Aminopropane8628.Nitrocyclohexane ^c 7.24.46Aminocyclohexane8629.Benzaldehyde ^d 4.85.52Benzylalcohol8830.Benzophenone ^d 5.45.31Diphenylmethanol8531.Acetophenone ^d 6.24.56Dihydrobenzoin8633.Benzil ^d 6.14.48Dihydrobenzoin8634.Acetone ^d 6.63.652-Propanol8235.Benzontrile ^e 7.53.42Dibenzylamine9236.Acetonitrile ^e 7.93.22Dictylamine81	21	p-Nitrophenol ^b	80	3 72	p-Aminophenol	86	
23.p bintrobenzence6.51.65p refine lendiamine8623.m-Dinitrobenzence7.23.68m-Phenelendiamine8624.Nitromethanec5.67.08Methylamine9425.Nitroethanec5.86.15Ethylamine9026.1-Nitropropanec6.05.761-Aminopropane8827.2-Nitropropanec6.45.302-Aminopropane8928.Nitrocyclohexanec7.24.46Aminocyclohexane8629.Benzaldehyded4.85.52Benzylalcohol8830.Benzophenoned5.45.31Diphenylmethanol8531.Acetophenoned6.43.80Phenylmethanol8632.Benzoind6.24.56Dihydrobenzoin8633.Benzild6.14.48Dihydrobenzoin8634.Acetoned6.63.652-Propanol8235.Benzoitrilee7.53.42Dibenzylamine9236.Acetonitrilee7.93.22Diethylamine81	21.	p-Dipitrobenzene ^e	6.8	4.06	n-Phenelenediamine	89	
24.Nitromethanec5.67.08Methylamine9425.Nitroethanec5.86.15Ethylamine9026.1-Nitropropanec6.05.761-Aminopropane8827.2-Nitropropanec6.45.302-Aminopropane8928.Nitrocyclohexanec7.24.46Aminocyclohexane8629.Benzaldehyded4.85.52Benzylalcohol8830.Benzophenoned5.45.31Diphenylmethanol8531.Acetophenoned6.43.80Phenylmethylmethanol8632.Benzolid6.24.56Dihydrobenzoin8633.Benzild6.14.48Dihydrobenzoin8434.Acetoned6.63.652-Propanol8235.Benzonitrile ^e 7.93.22Dienzylamine3136.Acetonitrile ^e 7.93.22Diethylamine81	22.	m-Dinitrobenzene ^e	7.2	3.68	m-Phenelenediamine	86	
25.Nitroethanec586.15Ethylamine9026.1-Nitropropanec6.05.761-Aminopropane8827.2-Nitropropanec6.45.302-Aminopropane8928.Nitrocyclohexanec7.24.46Aminocyclohexane8629.Benzaldehyded4.85.52Benzylalcohol8830.Benzophenoned5.45.31Diphenylmethanol8531.Acetophenoned6.43.80Phenylmethylomina8632.Benzoind6.24.56Dihydrobenzoin8434.Acetoned6.63.652-Propanol8235.Benzoitrilee7.53.42Dibenzylamine92Benzyl amine7.93.22Diethylamine81	23.	Nitromethane ^c	56	7.08	Methylamine	94	
26.1-Nitropropanec6.05.761-Aminopropane8827.2-Nitropropanec6.45.302-Aminopropane8928.Nitrocyclohexanec7.24.46Aminocyclohexane8629.Benzaldehyded4.85.52Benzylalcohol8830.Benzophenoned5.45.31Diphenylmethanol8531.Acetophenoned6.43.80Phenylmethylmethanol8632.Benzold6.24.56Dihydrobenzoin8633.Benzild6.14.48Dihydrobenzoin8634.Acetoned6.63.652-Propanol8235.Benzontrile ^e 7.53.42Dibenzylamine92Benzyl amine33.22Diethylamine81	25	Nitroethane ^c	5.8	6 15	Ethylamine	90	
27.2-Nitropropane ^c 645.302-Aminopropane8928.Nitrocyclohexane ^c 7.24.46Aminocyclohexane8629.Benzaldehyde ^d 4.85.52Benzylalcohol8830.Benzophenone ^d 5.45.31Diphenylmethanol8531.Acetophenone ^d 6.43.80Phenylmethylmethanol8632.Benzold6.24.56Dihydrobenzoin8633.Benzil ^d 6.14.48Dihydrobenzoin8434.Acetone ^d 6.63.652-Propanol8235.Benzoitrile ^e 7.53.42Dibenzylamine9236.Acetonitrile ^e 7.93.22Diethylamine81	26	1-Nitropropane ^c	60	5.76	1-Aminopropane	88	
28.Nitrocyclohexane ^c 7.24.46Aminocyclohexane8629.Benzaldehyde ^d 4.85.52Benzylalcohol8830.Benzophenone ^d 5.45.31Diphenylmethanol8531.Acetophenone ^d 6.43.80Phenylmethylmethanol8632.Benzoin ^d 6.24.56Dihydrobenzoin8633.Benzil ^d 6.14.48Dihydrobenzoin8634.Acetone ^d 6.63.652-Propanol8235.Benzoitrile ^e 7.53.42Dibenzylamine9236.Acetonitrile ^e 7.93.22Diethylamine81	27	2-Nitropropane ^c	64	5 30	2-Aminopropane	89	
29.Benzaldehyded4.85.52Benzylenold8830.Benzolhenoned5.45.31Diphenylmethanol8531.Acetophenoned6.43.80Phenylmethylmethanol8632.Benzoind6.24.56Dihydrobenzoin8633.Benzild6.14.48Dihydrobenzoin8434.Acetoned6.63.652-Propanol8235.Benzointile ^e 7.53.42Dibenzylamine92Benzyl amine33.22Diethylamine81	28	Nitrocyclohexane ^c	72	4 46	Aminocyclohexane	86	
30. Benzophenone ^d 5.4 5.31 Diphenylmethanol 85 31. Acetophenone ^d 6.4 3.80 Phenylmethylmethanol 86 32. Benzoin ^d 6.2 4.56 Dihydrobenzoin 86 33. Benzil ^d 6.1 4.48 Dihydrobenzoin 84 34. Acetone ^d 6.6 3.65 2-Propanol 82 35. Benzonitrile ^e 7.5 3.42 Dibenzylamine 92 Benzyl amine 3 36. Acetonitrile ^e 7.9 3.22 Diethylamine 81	29	Benzaldehyde ^d	48	5 52	Benzylalcohol	88	
31. Acetophenone ^d 6.4 3.80 Phenylmethalol 86 32. Benzoin ^d 6.2 4.56 Dihydrobenzoin 86 33. Benzil ^d 6.1 4.48 Dihydrobenzoin 84 34. Acetone ^d 6.6 3.65 2-Propanol 82 35. Benzointile ^e 7.5 3.42 Dibenzylamine 92 Benzyl amine 3 3 36. Acetonitrile ^e 7.9 3.22 Diethylamine 81	30	Benzonhenone ^d	54	5 31	Diphenylmethanol	85	
32. Benzoin ^d 6.2 4.56 Dihydrobenzoin 86 33. Benzil ^d 6.1 4.48 Dihydrobenzoin 84 34. Acetone ^d 6.6 3.65 2-Propanol 82 35. Benzoitrile ^e 7.5 3.42 Dibenzylamine 92 Benzyl amine 3 36. Acetonitrile ^e 7.9 3.22 Diethylamine 81	31	Acetophenone ^d	64	3.80	Phenylmethylmethanol	86	
33. Benzil ^d 6.1 4.48 Dihydrobenzoin 84 34. Acetone ^d 6.6 3.65 2-Propanol 82 35. Benzoitrile ^e 7.5 3.42 Dibenzylamine 92 Benzyl amine 3 3.22 Diethylamine 81	37	Benzoind	62	4.56	Dibydrobenzoin	86	
34. Acetone ^d 66 3.65 2-Propanol 82 35. Benzonitrile ^e 7.5 3.42 Dibenzylamine 92 36. Acetonitrile ^e 7.9 3.22 Diethylamine 81	32.	Benzild	6.1	4.50	Dihydrobenzoin	84	
34. Account 6.0 5.03 2-riopation 62 35. Benzonitrile ^e 7.5 3.42 Dibenzylamine 92 Benzyl amine 3 36. Acetonitrile ^e 7.9 3.22 Diethylamine 81	24	Acotopod	6.6	2.65	2 Propagal	0 1 07	
S. Benzolititile 7.5 5.42 Diotrizylamine 52 Benzyl amine 3 36. Acetonitrile ^e 7.9 3.22 Diethylamine 81	34. 25	Ronzonitrilo ^e	7.5	2.40	Dibonzulamino	02	
36. Acetonitrile ^e 7.9 3.22 Diethylamine 81	55.	Belizoniune	7.5	5.72	Popzyl amino	32	
50. Accounting 7.5 5.22 DictivityInfiline 01	36	Acetonitrile	7.9	3 3 3	Diethylamine	S 81	
etni/inmina 15	50.	Accontine	7.5	5.22	Ethylamine	15	

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

^a $P_{\text{H}_2} = 30.0 \text{ bar}; T = 70 \,^{\circ}\text{C}.$

^b $P_{\rm H_2} = 40.0 \, \rm bar; T = 80 \, ^{\circ} \rm C.$

^c $P_{\rm H_2} = 50.0 \, \rm bar; T = 90 \,^{\circ} \rm C.$

- ^d $P_{\rm H_2} = 60.0$ bar, $T = 105 \,^{\circ}$ C.
- ^e $P_{\text{H}_2} = 80.0 \text{ bar}; T = 120 \,^{\circ}\text{C}.$

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 $p-NH_2C_6H_4NO_2$ and $p-HOC_6H_4NO_2$ are relatively low. Probably $-NH_2$ and -OH groups decreases the available sites for NO_2 coordination by partial blocking.

Reduction of dinitroaromatics to the corresponding diamines required higher temperature and pressure. Corresponding monoor 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 onitrotoluene with the catalyst P-[(azb)Ru(CO)₂Cl]₂. [Cat]= $2.0 \times 10^{-3} \text{ mol} \text{l}^{-1}$; P_{H2} = 40.0 bar; medium=DMF; total volume=10 ml; T=80°C; [PhNO₂]=0.5 M; [0-CH₃C₆H₄NO₂]=0.5 M; -•-=PhNO₂; -•-=PhNH₂; -•-=PhNHOH; -•-=o-CH₃C₆H₄NO₂; -•-=o-CH₃C₆H₄NH₂; -•-=o-CH₃C₆H₄NHOH.

Table 2
Comparison of catalytic activities of $[Ru(azb)(CO)_2Cl]_2$ (I) with P- $[(azb)Ru(CO)_2Cl]_2$ (II).

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

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

^a $P_{\text{H}_2} = 40.0 \text{ bar}; T = 80 \,^{\circ}\text{C}.$

^b $P_{\text{H}_2} = 150.0 \text{ bar}; T = 200 \,^{\circ}\text{C}.$

^c Catalyst decomposes.

Table 3

Recycling of catalyst P-[(azb)(CO)₂ Ru.Cl)]₂ for hydrogenation of various organic substrates.

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

Note: [sub] = 0.50 M; [Cat] \approx 2.0 × 10⁻⁴ mol l⁻¹ (fresh catalyst); medium = DMF; total volume = 10 ml; yields refer to G.C. analysis; [Cat] \approx (1.90–1.98) × 10⁻⁴ mol l⁻¹ (after 5th recycle).

^a $P_{\rm H_2} = 30.0 \,\rm bar; T = 70\,^{\circ}C.$

^b $P_{\text{H}_2} = 40.0 \text{ bar}; T = 80 \,^{\circ}\text{C}.$

^c $P_{\text{H}_2} = 50.0 \text{ bar}; T = 90 \,^{\circ}\text{C}.$

^d $P_{\rm H_2} = 60.0 \,\rm bar; T = 105 \,^{\circ}C.$

^e $P_{\rm H_2} = 80.0 \,\rm bar; T = 120 \,^{\circ}C.$



Fig. 2. Sequential reduction of p-dinitrobenzene with the catalyst P-[(azb)Ru(CO)₂Cl]₂. [Cat] = 2.0×10^{-3} mol l⁻¹; $P_{H_2} = 80$ bar; medium = DMF; total volume = 10 ml; T = 120 °C; [p-NO₂C₆H₄NO₂] = 0.5 M; - Φ - = p-dinitrobenzene; - \blacksquare - = p-nitroaniline; -▲- = p-phenylenediamine.

The reductions of nitroalkanes required relatively more stringent conditions ($T = \sim 90 \circ C$, $P_{H_2} = 50.0 \text{ bar}$). 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 \sim 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)₂Cl]₂ as catalyst under various hydrogen pressure. [2-nitropropane] = 0.5 M; medium = DMF; total volume = 10 ml; $T = 80 \circ \text{C}$, P_{H_2} : - \blacksquare = 40.0 bar; - \blacksquare = 60.0 bar; - \blacksquare = 80.0 bar; - \blacksquare = 10.0 bar.

The nitriles were reduced under more severe conditions, i.e. $T = 120 \circ C$, $P_{H_2} = 80.0$ bar. The major products were the corresponding secondary amines. In case of CH₃CN, final products contain ethylamine (${\sim}15\%)$ and diethylamine (${\sim}80\%)$ while in case of C_6H_5CN the product was mainly $(C_6H_5CH_2)_2NH$ with very small amount of primary amine $C_6H_5CH_2NH_2$ (<3%). The formation of $R_2NH(R = C_2H_5/C_6H_5CH_2)$ and liberation of NH₃ suggest the occurrence of some secondary reaction at intermediate stages. The nitriles, RCN (R=CH₃, Ph) do not react with RCH₂NH₂ in presence of catalyst at $120 \circ C$. The initial addition of RCH₂NH₂ (R = CH₃, C_6H_5) during the reduction of RCN always increased the proportion of corresponding (RCH₂)₂NH 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 NH₃. The products may be formed as per Scheme 2.

To understand the reaction mechanism, the reduction of C_6H_5CN was carried out in presence of acetic anhydride and sodium acetate.



Fig. 4. Rate dependence on P_{H_2} for the reduction of 2-nitropropane under various catalyst concentrations with P-[(azb)Ru(CO)_2Cl]_2 as catalyst. [2-nitropropane]=0.5 M; medium=DMF; $T=105 \,^{\circ}\text{C}$, [Cat]: $-\blacksquare -= 2.0 \times 10^{-3} \,\text{mol}\,l^{-1}$; $-\bullet -= 4.0 \times 10^{-3} \,\text{mol}\,l^{-1}$; $-\bullet -= 5.0 \times 10^{-3} \,\text{mol}\,l^{-1}$; $-\bullet -= 6.0 \times 10^{-3} \,\text{mol}\,l^{-1}$.

The objective was to trap the $C_6H_5CH_2NH_2$ if formed by converting it to the corresponding acetylate. This will prevent $C_6H_5CH_2NH_2$ to react with the probable intermediate, $C_6H_5CH=NH$ and hence no secondary amine would be formed. The product mixture in this case contained only $C_6H_5CH_2NHCOCH_3$ and no secondary amine. The result suggests the formation of intermediate imine which reacts with the primary amine and H_2 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 $C_6H_5CH_2NH_2$ resulted in the formation of mainly $(C_6H_5CH_2)_2NH$ in case of PhCN reduction. In case of CH₃CN reductions, lower susceptibility of CH₃CH=NH to nucleophilic attack by $C_2H_5NH_2$ is responsible for the presence of small amount of CH₃CH₂NH₂ in the final product mixture.

The catalyst $P-[Ru(azb)(CO)_2Cl]_2$ is quite stable in dry atmosphere and can be repeatedly used for the reduction of the



Scheme 1.



Scheme 2.



k₁, RNO₂ k₂, DMF













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)₂Cl]₂ in DMF medium for the reduction of 2nitropropane 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 $(1.0-6.0) \times 10^{-3} \text{ mol} 1^{-1}$ (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

$$Rate = k[cat][P_{H_2}]^2$$
(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.

$$Slope = \frac{Rate}{[cat]}, \quad k = \frac{Slope}{[P_{H_2}]^2}$$

The *k* values lie between 1.40×10^{-6} and $1.56 \times 10^{-6} \text{ s}^{-1} \text{ bar}^{-2}$ 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

$$Slope = \frac{Rate}{[P_{H_2}]^2}, \quad k = \frac{Slope}{[cat]}$$

The *k* values lie between 1.50×10^{-6} and 1.60×10^{-6} s⁻¹ bar⁻² in the catalyst concentration range from 2.0×10^{-3} to 6.0×10^{-3} mol l⁻¹.

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

Rate = $k_6[10][H_2]^2$

$$[Cat]_T = [6] + [7] + [8] + [9] + [10] + [11]$$

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

$$\begin{aligned} [Cat]_T &= \frac{K_3[10][H_2]^2}{[RNO_2]} + \frac{K_2[10][H_2]^2}{[DMF]} + K_1[10][H_2]^2 + \frac{K_7[10][H_2]^2}{[DMF]} \\ &+ [10] + \frac{K_4[10][H_2]^2[RNHOH]}{[RNO_2][DMF]} \end{aligned}$$

$$[10] = \frac{[Cat]_{T}[RNO_{2}][DMF]}{[RNO_{2}][DMF] + [H_{2}]^{2} \{[DMF]K3 + K_{2}[RNO_{2}] + K_{1}[DMF][RNO_{2}] + K_{7}[RNO_{2}] + K_{4}[RNHOH] \}$$

$$Rate = k_6[10][H_2]^2 = \frac{k_6[Cat]_T[RNO_2][DMF][H_2]^2}{[RNO_2][DMF] + [H_2]^2 \{[DMF]K_3 + K_2[RNO_2] + K_{[DMF][RNO_2]} + K_7[RNO_2] + K_4[RNHOH]\}}$$

The concentration of $[H_2]$ is of the order of $10^{-2}\,M$ and hence $[H_2]^2\approx 10^{-4}\,M$ while $[RNO_2]\approx 1\,M$ and $DMF\approx 10.0\,M.$ Hence the equation reduces to

Rate =
$$\frac{k_6[Cat]_T[RNO_2][DMF][H_2]^2}{[RNO_2][DMF]} = k_6[Cat]_T[H_2]^2$$

Rate = $k[Cat]P_{H_2}^2$

4. Conclusions

The polymer-based orthometallated catalyst, P-[Ru(azb) (CO)₂Cl]₂, 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 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_{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. Likhar, 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] Z. 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.