

Hydrogenation of benzene and toluene catalysed by ruthenium(II) complexes

<i>Contents</i>	8.1	Introduction
	8.2	Experimental
	8.3	Results and discussion
		Conclusions
		References

8.1 Introduction

The design and synthesis of transition metal complexes of Schiff base having oxygen and nitrogen donor atoms is an active area of research, as they offer opportunity for including substrate chirality, tuning metal centered electronic factor, and enhancing solubility and stability of either homogeneous or heterogeneous catalyst [1-3]. Schiff base complexes of transition metals including ruthenium are found to be effective catalysts for various chemical transformations [4-8]. A number of ruthenium complexes have been prepared earlier and extensively used as catalysts in hydrogenation reactions [9-17]. The hydrogenation of aromatic compounds to cyclic products is an important reaction in chemical industry [18-22]. Even though a lot of success has been achieved with regard to transition metal complex catalyzed hydrogenation of olefins [23-26], there are only a few reports on studies involving hydrogenation of arenes using homogeneous metal complex catalysts [27-34]. The catalytic activity of transition metal Schiff base complexes in a given process is highly dependent on the environment about the metal centre and their conformational flexibility [35]. By small changes in the ligand frame work it is possible to enhance the steric and electronic effects in homogeneous metal complexes [36]. In most of the transition metal catalyzed hydrogenation reactions, involvement of hydride complexes as the intermediate species or as starting materials was suggested [37]. A crucial step in the hydrogenation reaction is the cleavage of the dihydrogen molecule. Presence of an electron-rich atmosphere

around the metal centre facilitates breaking of the H–H bond by the interaction of the filled metal d orbital with the empty sigma antibonding molecular orbital of H₂ [37]. An increase in the N-basicity of the Schiff base ligand is found to increase the catalytic performance towards the metal catalyzed dehydrogenation/hydrogenation through such an interaction [38, 39]. Therefore increased interactions are expected in the case of Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde, which have more basic donor nitrogen atoms. The presence of quinoxaline ring may build a favourable steric topography and electronic environment in the immediate coordination sphere of the metal and thus allowing fine tuning of various catalytic and biological properties of its complexes. With this in view, we have synthesized new complexes derived from 3-hydroxyquinoxaline-2-carboxaldehyde, containing ruthenium in +2 oxidation state. These ruthenium(II) complexes exhibited excellent catalytic activity towards hydrogenation of benzene and toluene. Details of the synthesis and characterization of these metal complexes are presented in Chapter 5. In this chapter, the results of our studies on the catalytic activity of these complexes towards hydrogenation of benzene and toluene are presented.

8.2 Experimental

8.2.1 Materials

Details regarding the materials used for the preparation of ruthenium complexes and the catalytic hydrogenation of benzene and toluene are given in Chapter 2. Hydrogen gas with >99.8% purity supplied by Sterling Gases Ltd. (Cochin, India), was used as such for hydrogenation reactions.

8.2.2 Methods

The syntheses of the Schiff base ligands and their ruthenium(II) complexes are given in Chapters 2 and 5.

8.2.3 Catalytic activity measurements

Details regarding the hydrogenation experiments are given in [Chapter 2](#).

8.3 Results and discussion

The spectral characterisation of the Schiff base ligands and their metal(II) complexes of ruthenium are discussed in [Chapters 2 and 5](#).

8.3.1 Catalytic hydrogenation of benzene and toluene

Generally partial and complete reduction of benzene or alkyl benzene takes place with the major formation of fully reduced product. The activity of some common metals towards the hydrogenation of benzene and alkyl benzene decreases in the order: Rh > Ru > Pt > Ni > Pd > Co [40]. The five ruthenium complexes, [Ru₂(hqcdan)Cl₂].H₂O, [Ru₂(hqcdmn) Cl₂].H₂O, [Ru₂(hqcdac)Cl₂].H₂O, [Ru₂(hqcap)Cl₂(H₂O)].H₂O and [Ru(hqcaap)Cl(H₂O)₂].H₂O, were screened for its activity towards the hydrogenation of benzene and toluene. The reactions were carried out under solvent free conditions with 0.34 mol benzene/ 0.28 mol toluene, 80 °C temperature, 30 bar dihydrogen pressure, 600 rpm stirring speed and 2 mg catalyst. The percentage conversion of benzene/toluene was noted after two hours of reaction. The percentage conversion obtained with the complexes along with their turnover frequencies (TOF is the mol of benzene/toluene transformed per mole of the catalyst per hour) are given in [Table 1](#).

Table 1: Activity of ruthenium complexes in the hydrogenation of benzene and toluene ^a

[catalyst]	Conversion (%)		TOF (h ⁻¹)	
	Benzene	Toluene	Benzene	Toluene
[Ru ₂ (hqcdan)Cl ₂].H ₂ O	6.5	5.9	8,023	6,821
[Ru ₂ (hqcdmn)Cl ₂].H ₂ O	17.3	16.8	20,858	16,680
[Ru ₂ (hqcdac)Cl ₂].H ₂ O	12.4	11.8	15,111	11,842
[Ru ₂ (hqcap)Cl ₂ (H ₂ O)].H ₂ O	16.2	15.7	15,782	12,596
[Ru(hqcaap)Cl(H ₂ O) ₂].H ₂ O	8.8	7.4	8,219	5,800

^a General reaction conditions: 0.34 mol benzene/ 0.28 mol toluene, 80 °C temperature, 30 bar dihydrogen pressure, 2 mg catalyst, 600 rpm stirring speed, 2 h reaction time.

Among these complexes, $[\text{Ru}_2(\text{hqcdmn})\text{Cl}_2]\cdot\text{H}_2\text{O}$ was found to be the most active. Hence a detailed study was carried out on the activity of this complex towards the hydrogenation of benzene and toluene. The reactions were performed under solvent free conditions by variation of catalyst and substrate concentrations, dihydrogen pressure, reaction time and temperature of reaction mixtures. At 60 °C, and 30 bar hydrogen pressure, turnover frequencies 7362 h^{-1} and 5873 h^{-1} have been found for the hydrogenation of benzene and toluene respectively. This value is much higher than that reported for some of the mononuclear ruthenium-based catalysts in the homogeneous hydrogenation of arenes [41,42]. This higher turnover frequency may be due to the presence of electron rich nitrogen atoms in the heterocyclic Schiff base which tends to make the central Ru(II) cations more electron rich and thus promote the overlap of the filled metal d orbital and the empty sigma antibonding molecular orbital of the H_2 . This effect in turn would favor the cleavage of the H–H bond, which is a crucial step in the hydrogenation reaction [43].

8.3.1.1 Effect of catalyst concentration

To study the influence of catalyst concentration on the reduction of benzene and toluene, quantity of the catalyst were varied in the range $(1.41\text{-}7.05) \times 10^{-6}$ mol, while the substrate concentration (0.34 mol benzene/0.28 mol toluene), dihydrogen pressure (30 bars) and the temperature (60 °C) were kept constant (Tables 2 and 3). In both cases an increase in catalyst concentration was found to raise the percentage conversion. However, with increase in catalyst concentration, there occurs a change in the product distribution. At lower concentrations of the catalyst the fully hydrogenated product predominant while at increased catalyst concentrations partially hydrogenated product, which dominates. This would be due to the increase in catalytic active ruthenium sites with increase in catalyst concentration.

Table 2: Effect of the [Ru₂(hqcdmn)Cl₂].H₂O in the hydrogenation of benzene ^a

[catalyst] (10 ⁻⁶ mol)	[benzene] (mol)	H ₂ pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (%) ^b	
					CA	CE
1.41	0.34	30	60	10.2	85	15
2.82	0.34	30	60	12.3	84	16
4.23	0.34	30	60	13.0	83	17
5.64	0.34	30	60	13.2	83	17
7.05	0.34	30	60	13.5	82	18

^a General reaction conditions: 0.34 mol benzene, 60 °C temperature, 30 bar dihydrogen pressure, 2.82 × 10⁻⁶ mol catalyst, 600 rpm stirring speed, 2 h reaction time. ^b CA = cyclohexane, CE = cyclohexene and the product selectivity is CA (or CE) / (CA + CE)

Table 3: Effect of the [Ru₂(hqcdmn)Cl₂].H₂O in the hydrogenation of toluene ^a

[catalyst] (10 ⁻⁶ mol)	[toluene] (mol)	H ₂ pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (%) ^b	
					MCA	MCE
1.41	0.28	30	60	11.7	86	14
2.82	0.28	30	60	11.8	85	15
4.23	0.28	30	60	12.6	84	16
5.64	0.28	30	60	12.9	84	16
7.05	0.28	30	60	13.2	83	17

^a General reaction conditions: 0.28 mol toluene, 60 °C temperature, 30 bar dihydrogen pressure, 2.82 × 10⁻⁶ mol catalyst, 600 rpm stirring speed, 2 h reaction time. ^b MCA = methyl cyclohexane, MCE = methyl cyclohexene and the product selectivity is MCA (or MCE) / (MCA + MCE)

8.3.1.2 Effect of dihydrogen pressure

To analyse the dependence of dihydrogen pressure on the reduction of benzene, a series of experiments were carried out by varying the pressure over the range of 10 to 50 bar at 60 °C keeping both substrate concentration (0.34 mol benzene/0.28 mol toluene) and the catalyst loading (2.82 × 10⁻⁶ mol) constant. A favourable effect of conversion is observed with an increase of hydrogen pressure from 10 up to 50 bars. The complex is more selective for fully hydrogenated product and this selectivity also increases as the hydrogen pressure increases (Tables 4 and 5).

Table 4: Effect of dihydrogen pressure in the hydrogenation of benzene ^a

[catalyst] (10 ⁻⁶ mol)	[benzene] (mol)	H ₂ pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (%) ^b	
					CA	CE
2.82	0.34	10	60	4.1	64	36
2.82	0.34	20	60	8.6	80	20
2.82	0.34	30	60	12.3	84	16
2.82	0.34	40	60	14.6	85	15
2.82	0.34	50	60	16.8	85	15

^a General reaction conditions: 0.34 mol benzene, 60 °C temperature, 30 bar dihydrogen pressure, 2.82 × 10⁻⁶ mol catalyst, 600 rpm stirring speed, 2 h reaction time. ^b CA = cyclohexane, CE = cyclohexene and the product selectivity is CA (or CE) / (CA + CE)

Table 5: Effect of dihydrogen pressure in the hydrogenation of toluene ^a.

[catalyst] (10 ⁻⁶ mol)	[toluene] (mol)	H ₂ pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (%) ^b	
					MCA	MCE
2.82	0.28	10	60	4.0	63	37
2.82	0.28	20	60	8.4	80	20
2.82	0.28	30	60	11.8	85	15
2.82	0.28	40	60	14.0	86	14
2.82	0.28	50	60	15.1	86	14

^a General reaction conditions: 0.28 mol toluene, 60 °C temperature, 30 bar dihydrogen pressure, 2.82 × 10⁻⁶ mol catalyst, 600 rpm stirring speed, 2 h reaction time. ^b MCA = methyl cyclohexane, MCE = methyl cyclohexene and the product selectivity is MCA (or MCE) / (MCA + MCE)

8.3.1.3 Effect of substrate concentration

The effect of substrate concentration on the hydrogenation was studied by varying its concentration in the range 0.34 mol-0.56 mol and 0.28 mol -0.47 mol for benzene and toluene respectively at a constant catalyst concentration of 2.82 × 10⁻⁶ mol at 60 °C and at 30 bar hydrogen pressure (Tables 6 and 7). The percentage conversion decreases whereas selectivity towards the fully reduced product increases.

Table 6: Effect of substrate in the hydrogenation of benzene ^a

[catalyst] (10 ⁻⁶ mol)	[benzene] (mol)	H ₂ pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (%) ^b	
					CA	CE
2.82	0.34	30	60	12.3	84	16
2.82	0.39	30	60	10.7	85	15
2.82	0.45	30	60	10.0	86	14
2.82	0.51	30	60	7.7	87	13
2.82	0.56	30	60	7.3	88	12

^a General reaction conditions: 0.34 mol benzene, 60 °C temperature, 30 bar dihydrogen pressure, 2.82 × 10⁻⁶ mol catalyst, 600 rpm stirring speed, 2 h reaction time. ^b CA = cyclohexane, CE = cyclohexene and the product selectivity is CA (or CE) / (CA + CE)

Table 7: Effect of substrate in the hydrogenation of toluene ^a

[catalyst] (10 ⁻⁶ mol)	[toluene] (mol)	H ₂ pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (%) ^b	
					MCA	MCE
2.82	0.28	30	60	11.8	85	15
2.82	0.33	30	60	10.9	87	13
2.82	0.38	30	60	9.5	88	12
2.82	0.42	30	60	8.4	88	12
2.82	0.47	30	60	7.3	88	12

^a General reaction conditions: 0.28 mol toluene, 60 °C temperature, 30 bar dihydrogen pressure, 2.82 × 10⁻⁶ mol catalyst, 600 rpm stirring speed, 2 h reaction time. ^b MCA = methyl cyclohexane, MCE = methyl cyclohexene and the product selectivity is MCA (or MCE) / (MCA + MCE)

8.3.1.4 Effect of temperature

The effects of temperature on the hydrogenation of benzene and toluene were investigated in the range 40-120 °C, all other parameters being kept constant (Tables 8 and 9). Percentage conversion and selectivity towards fully reduced product is seen to increase with elevation of temperature.

Table 8: Effect of temperature in the hydrogenation of benzene ^a

[catalyst] (10 ⁻⁶ mol)	[benzene] (mol)	H ₂ pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (%) ^b	
					CA	CE
2.82	0.34	30	60	12.3	84	16
2.82	0.34	30	40	4.7	74	26
2.82	0.34	30	80	17.3	85	15
2.82	0.34	30	100	20.9	85	15
2.82	0.34	30	120	23.2	86	14

^a General reaction conditions: 0.34 mol benzene, 60 °C temperature, 30 bar dihydrogen pressure, 2.82 × 10⁻⁶ mol catalyst, 600 rpm stirring speed, 2 h reaction time. ^b CA = cyclohexane, CE = cyclohexene and the product selectivity is CA (or CE) / (CA + CE)

Table 9: Effect of temperature in the hydrogenation of toluene ^a

[catalyst] (10 ⁻⁶ mol)	[toluene] (mol)	H ₂ pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (%) ^b	
					MCA	MCE
2.82	0.28	30	40	4.5	75	25
2.82	0.28	30	60	11.8	85	15
2.82	0.28	30	80	16.8	86	14
2.82	0.28	30	100	20.0	86	14
2.82	0.28	30	120	22.7	86	14

^a General reaction conditions: 0.28 mol toluene, 60 °C temperature, 30 bar dihydrogen pressure, 2.82 × 10⁻⁶ mol catalyst, 600 rpm stirring speed, 2 h reaction time. ^b MCA = methyl cyclohexane, MCE = methyl cyclohexene and the product selectivity is MCA (or MCE) / (MCA + MCE)

8.3.1.4 Effects of reaction time

In order to study the effect of time, reactions were carried out for 4 h with 2.82 × 10⁻⁶ mol of catalyst, substrate concentration of 0.34 mol benzene/0.28 mol toluene, 30 bar pressure at 60 °C with a stirring speed of 600 rpm. The products were analysed at 15 minute intervals and the results are shown in Figure 1. Conversion of benzene and toluene increases linearly with increase in time. In both the cases, the selectivity does not change significantly as the time elapses.

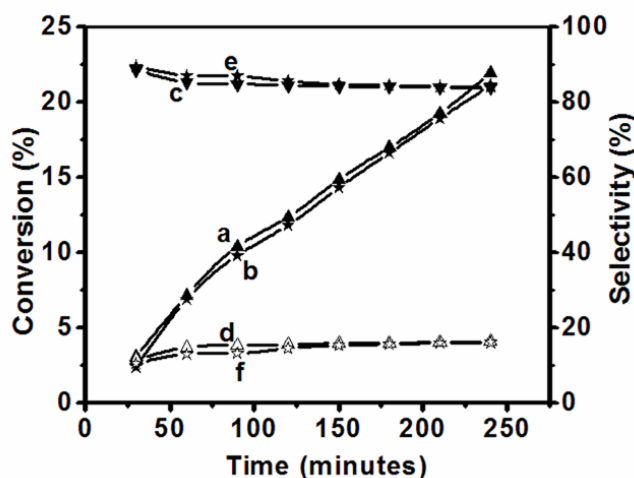


Figure 1: Effect of time; where a = conversion of benzene, b = conversion of toluene, c = CA selectivity for the hydrogenation of benzene, d = CE selectivity for the hydrogenation of benzene, e = MCA selectivity for the hydrogenation of toluene and f = MCE selectivity for the hydrogenation of toluene

8.3.2 Kinetics of hydrogenation of benzene using $[Ru_2(hqcdmn)Cl_2].H_2O$

The kinetics of hydrogenation of benzene was studied employing the initial rate method [44]. Initial rates were obtained by fitting the concentration–time data into the polynomial of the form $[C] = a_0 + a_1t + a_2t^2 + \dots$ where C and t represent concentration and time, respectively. a_0 , a_1 , a_2 , etc. are constants. The coefficient of ‘ t ’ gives the initial rate. This was done using Microsoft Excel. Catalytic runs were carried out at different catalyst and substrate concentrations and dihydrogen pressures. The data thus obtained is summarised in Table 10. Gas chromatographic estimation of the reaction mixture was done at intervals 15 min.

8.3.2.1 Order with respect to catalyst

The concentration of the catalyst was varied in the range of 1.41×10^{-6} to $7.05 \times 10^{-6} \text{ mol l}^{-1}$ range, (Table 10), while the benzene concentration (0.34 mol l^{-1}), dihydrogen pressure (30 bars or 1.02 mol l^{-1}) and the temperature ($60 \text{ }^\circ\text{C}$) were kept constant. A plot of initial rate versus concentration of the catalyst (Figure 2) yields a

straight line passing through the origin, suggesting first order with respect to the catalyst.

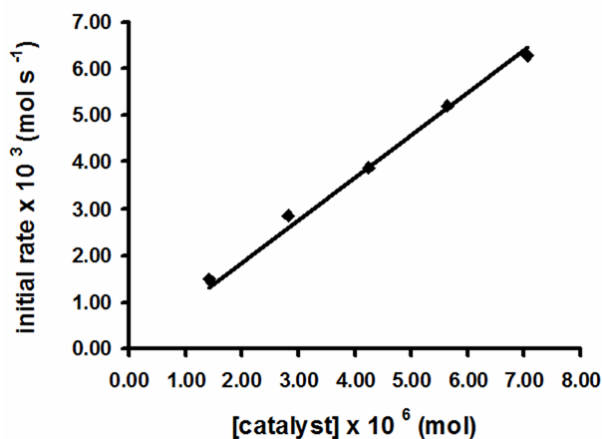


Figure 2: Plot of initial rate versus catalyst concentration

8.3.2.2 Order with respect to substrate

The effect of benzene concentration was studied in the range 0.34 to 0.56 mol l⁻¹ (Table 10) keeping constant catalyst concentration (2.82×10^{-5} mol l⁻¹) and dihydrogen pressure (30 bars or 1.02 mol l⁻¹) at 60 °C. A plot of initial rate versus [benzene] was a straight line (Figure 3) passing through origin indicating first order with respect to benzene.

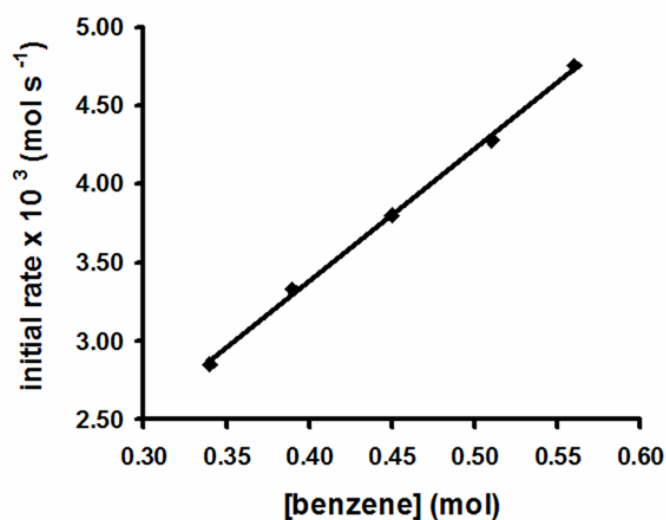


Figure 3: Plot of initial rate versus concentration of benzene

8.3.2.3 Order with respect to H_2

The effect of dihydrogen pressure at 60 °C was studied in the range, 10 to 50 bar (0.34 to 1.70 mol Γ^{-1}) (Table 10), with 0.34 mol Γ^{-1} of benzene and 2.82×10^{-5} mol Γ^{-1} catalyst. A plot of reciprocal of the initial rate versus the reciprocal dihydrogen pressure gives a straight line (Figure 4) with intercept, indicating Michaelis-Menten type of kinetics with respect to dihydrogen.

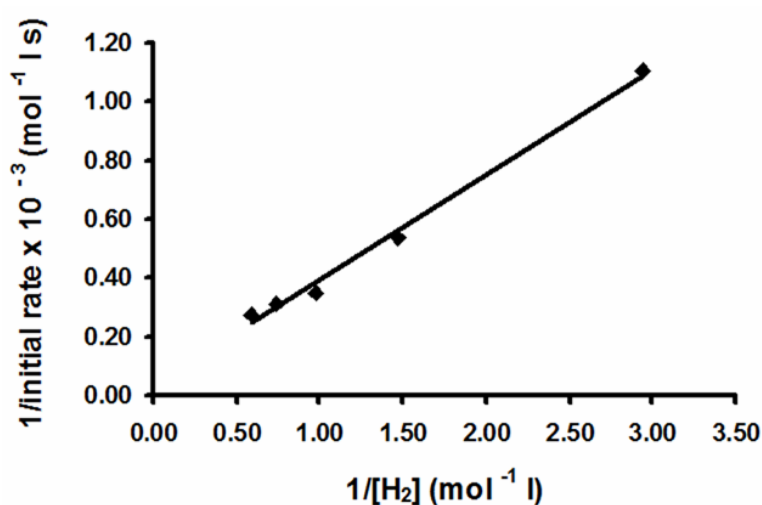


Figure 4: Plot of 1/initial rate versus 1/dihydrogen pressure

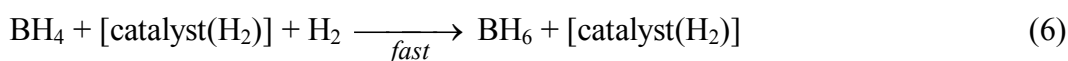
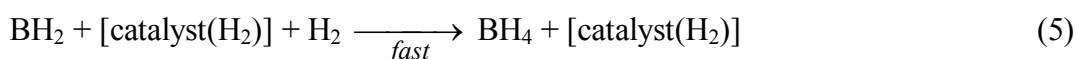
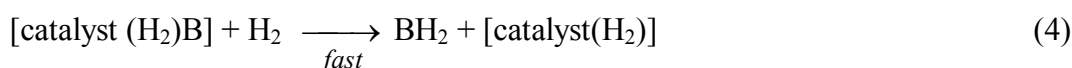
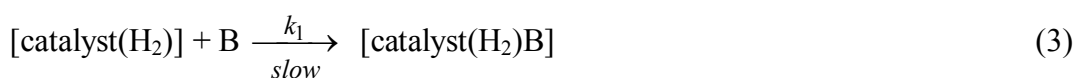
8.3.2.4 Derivation of experimental rate law

The results discussed above suggest that ruthenium(II) complex catalyses the hydrogenation of benzene according to the empirical rate equation,

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

$$\text{Rate} = \frac{-d[B]}{dt} = \frac{\{ a [\text{benzene}][H_2][\text{catalyst}] \}}{\{ b + c [H_2] \}} \quad (1)$$

As mentioned above, the reaction follows Michaelis-Menten kinetics with respect to $[H_2]$. In order to verify whether H_2 is coordinated to the catalyst, the intermediate complex was separated from the reaction mixtures. The IR spectrum (Figure 5) of the intermediate complex exhibits bands at 938 and 1560 cm^{-1} due to the symmetric and asymmetric M- H_2 stretches, respectively [45]. Presence of the H-H stretch at 2963 cm^{-1} and δ M-H bands at 697 and 468 cm^{-1} in the spectrum confirm the formation of a η^2 -dihydrogen complex [45,46]. Furthermore, the peak corresponding to coordinated water (at 3442 cm^{-1}) was not observed in the intermediate, suggesting that the coordination of the dihydrogen is through replacement of the coordinated water. Thus the kinetic analysis presented above allows proposing the following mechanism for the hydrogenation of benzene catalyzed by $[Ru_2(hqcdmn)Cl_2].H_2O$.



where 'B' represents benzene and 'catalyst' represents $[[Ru_2(hqcdmn)Cl_2].H_2O]$.

This mechanism leads to the rate equation,

$$\text{Rate} = \frac{-d[B]}{dt} = k_1[\text{catalyst}(H_2)]_e[B] \quad (7)$$

where $[\text{catalyst}(H_2)]_e = K [\text{catalyst}]_e [H_2]_e$ (from equation 2) and $[\text{catalyst}]_e =$

$$[\text{catalyst}]_o - [\text{catalyst}(H_2)]_e = \frac{[\text{catalyst}]_o}{1 + K[H_2]_e}. \text{ Since } [H_2] \gg [\text{catalyst}(H_2)], \text{ the}$$

equilibrium concentration of dihydrogen, $[H_2]_e$ can be assumed to be equal to its initial concentration, $[H_2]_o$.

Thus rate equation (7) can be written as,

$$\text{Rate} = \frac{-d[B]}{dt} = \frac{k_1 K [\text{catalyst}]_o [H_2]_o [B]_o}{\{1 + K [H_2]_o\}} \quad (8)$$

where the subscript 'o' stands for initial concentration.

Equation (8) is similar to the experimentally observed rate equation. Hence, the proposed mechanism explains all the observed kinetic results. The kinetic data for benzene suggests that an intermediate hydride/dihydrogen complex is the catalytically active species that controls the overall hydrogenation rate. Ruthenium hydride and dihydrogen complexes of ruthenium are recognized as active precatalysts or intermediates in the catalytic cycles of many hydrogenation reactions [47-57]. Thus it is to be inferred that the present complex acts as a catalyst precursor for the hydrogenation of benzene and toluene.

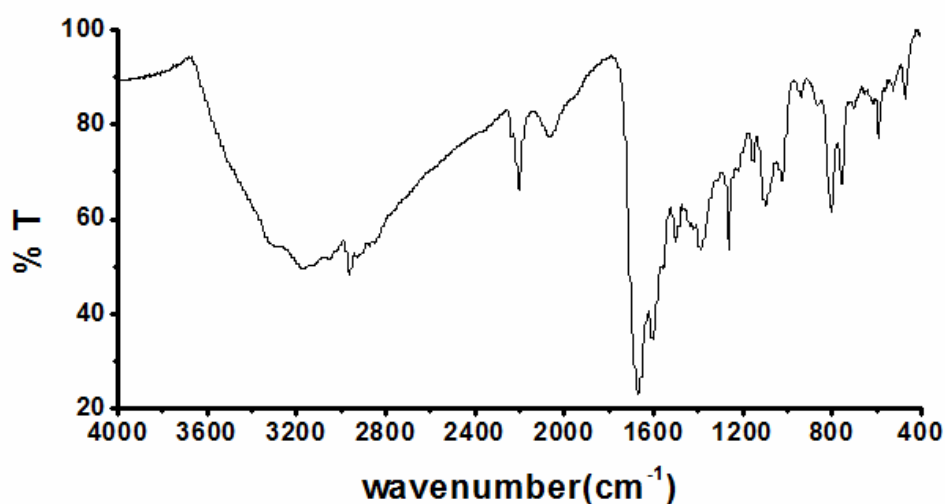


Figure 5: FT-IR spectrum of the intermediate ruthenium hydride complex

Table 10: The kinetic data for the $[\text{Ru}_2(\text{hqcdmn})\text{Cl}_2]\cdot\text{H}_2\text{O}$ catalyzed hydrogenation of benzene ^a.

[catalyst] (10^{-6} mol l ⁻¹)	[benzene] (mol l ⁻¹)	H ₂		Initial rate
		Pressure (bar)	Concentration (mol l ⁻¹)	
1.41	0.34	30	1.02	1.48×10^{-3} mol s ⁻¹
2.82	0.34	30	1.02	2.85×10^{-3} mol s ⁻¹
4.23	0.34	30	1.02	3.88×10^{-3} mol s ⁻¹
5.64	0.34	30	1.02	5.20×10^{-3} mol s ⁻¹
7.05	0.34	30	1.02	6.28×10^{-3} mol s ⁻¹
2.82	0.39	30	1.02	3.33×10^{-3} mol s ⁻¹
2.82	0.45	30	1.02	3.80×10^{-3} mol s ⁻¹
2.82	0.51	30	1.02	4.28×10^{-3} mol s ⁻¹
2.82	0.56	30	1.02	4.75×10^{-3} mol s ⁻¹
2.82	0.34	10	0.34	0.91×10^{-3} mol l ⁻¹ s ⁻¹
2.82	0.34	20	0.68	1.86×10^{-3} mol l ⁻¹ s ⁻¹
2.82	0.34	30	1.02	2.85×10^{-3} mol l ⁻¹ s ⁻¹
2.82	0.34	40	1.36	3.21×10^{-3} mol l ⁻¹ s ⁻¹
2.82	0.34	50	1.70	3.65×10^{-3} mol l ⁻¹ s ⁻¹

^a Other reaction conditions: 60 °C temperature, 600 rpm stirring speed and 2 h reaction time.

We carried out the same reaction under identical conditions with out the catalyst, with the organic ligand, with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$. In all these three cases no hydrogenation product was detected at the end of the reaction. These results proved that the hydrogenation was catalyzed by the added complex catalysts. Finke and co-workers [58-60] have reported that the hydrogenation of benzene under vigorous conditions (50-100 °C) using metal complexes proceeds through the formation of M(0) nanoclusters, which are not seen by naked eye. Here at the end of the reaction there were no black particles of ruthenium metal in the reaction mixture and the addition of mercury, as a selective poison for colloidal/nanoparticle catalysts, to the reaction system did not significantly affect the percentage conversion of benzene [61]. From these evidences we conclude that the hydrogenation in our system might have proceeded through a homogeneous mechanism and not through the formation of M(0) nanoparticles.

Conclusions

This chapter deals with the application of the ruthenium(II) complexes in the hydrogenation of benzene and toluene. All the complexes were screened for their catalytic activity and were found to be effective catalysts in the reduction of benzene and toluene. Catalytic experiments were carried out in a 100 mL bench top mini-reactor made of stainless steel 316 (Autoclave Engineers, Division of Snap-tite, Inc. PA). Partial as well as fully hydrogenated products were obtained during the reaction. A detailed kinetic study was carried out with $[\text{Ru}_2(\text{hqcdmn})\text{Cl}_2]\cdot\text{H}_2\text{O}$ as the catalyst as it gave maximum conversion in the screening study. Influence of various parameters on the rate of reaction was investigated. Turn over frequencies 7362 h^{-1} and 5873 h^{-1} have been found for the reduction of benzene (0.34 mol) and toluene (0.28 mol) respectively at $60\text{ }^\circ\text{C}$ with 2.82×10^{-6} mol catalyst and at a hydrogen pressure of 30 bar. An intermediate hydride complex, believed to be the catalytically active species, has been isolated and identified by FT-IR spectroscopy. This active species is presumed to control the overall hydrogenation rate.

References

- [1] L. Canali, D.C. Sherrington. *Chemical Society Reviews*, 28 (1999) 85–93.
- [2] T. Katsuki. *Chemical Reviews*, 140 (1995) 189–214.
- [3] K.C. Gupta, A.K. Sutar, *Coordination Chemistry Reviews*, 252 (2008) 1420–1450.
- [4] R. Karvembu, R. Prabhakaran, K. Natarajan. *Coordination Chemistry Reviews*, 249 (2005) 911–918.
- [5] K.O. Xavier, J. Chacko, K.K.M. Yusuff. *Applied Catalysis A: General*, 258 (2) (2004) 251–259.
- [6] N.R. Suja, K.K.M. Yusuff. *Journal of Applied Polymer Science*, 91 (6) (2004) 3710–3719.
- [7] S.C. Pearly, N. Sridevi, K.K.M. Yusuff. *Journal of Applied Polymer Science*, 105 (3) (2007) 997–1002.
- [8] P.S. Chittilappilly, N. Sridevi, K.K.M. Yusuff. *Journal of Molecular Catalysis A: Chemical*, 286 (2008) 92–97.
- [9] R. Drozdak, B. Allaert, N. Ledoux, I. Dragutan, V. Dragutan, F. Verpoort. *Coordination Chemistry Reviews*, 249 (2005) 3055–3074.
- [10] K. Abdur-Rashid, S.E. Clapham, A. Hadzovic, J.N. Harvey, A.J. Lough, R.H. Morris. *Journal of the American Chemical Society*, 124 (2002) 15104–15118.
- [11] P.J. Baricelli, L. Izaguirre, J. Lopez, E. Lujano, F. Lopez-Linares. *Journal of Molecular Catalysis A: Chemical*, 208 (2004) 67–72.
- [12] B. Chen, U. Dingerdissen, J.G.E. Krauter, H.G.J. Lansink Rotgerink, K. Mobus, D.J. Ostgard, P. Panster, T.H. Riermeier, S. Seebald, T. Tacke, H. Trauthwein. *Applied Catalysis A: General*, 280 (2005) 17–46.
- [13] E.G. Fidalgo, L. Plasseraud, G. Suss-Fink. *Journal of Molecular Catalysis A: Chemical*, 132 (1998) 5–12.
- [14] R. Noyori, S. Hashiguchi. *Accounts of Chemical Research*, 30 (1997) 97–102.
- [15] K. Nomura, H. Ogura, Y. Imanishi. *Journal of Molecular Catalysis A: Chemical*, 178 (2002) 105–114.
- [16] D.U. Parmar, S.D. Bhatt, H.C. Bajaj, R.V. Jasra. *Journal of Molecular Catalysis A: Chemical*, 202 (2003) 9–15.

- [17] C.A. Sandoval, T. Ohkuma, K. Muniz, R. Noyori. *Journal of the American Chemical Society*, 125 (2003) 13490–13503.
- [18] G.C. Bond, F. Garin, G. Maire. *Applied Catalysis*, 41 (1988) 313–335.
- [19] C. Morin, D. Simon, P. Sautet. *Surface Science*, 600 (2006) 1339–1350.
- [20] P.A. Rautanen, J.R. Aittamaa, A.O.I. Krause. *Industrial and Engineering Chemistry Research*, 39 (11) (2000) 4032–4039.
- [21] M.C. Rakowski, F.J. Hirsekorn, L.S. Stuhl, E.L. Muetterties. *Inorganic Chemistry*, 15 (1976) 2379–2382.
- [22] A. Stanislaus, B.H. Cooper. *Catalysis Reviews - Science and Engineering*, 36 (1) (1994) 75–123.
- [23] A. Andriollo, A. Bolivar, F.A. Lopez, D.E. Pdez. *Inorganica Chimica Acta*, 238 (1995) 187–192.
- [24] P.J. Baricelli, G. Rodriguez, M. Rodriguez, E. Lujano, F. Lopez-Linares. *Applied Catalysis A: General*, 239 (2003) 25–34.
- [25] C. Daguene, R. Scopelliti, P.J. Dyson. *Organometallics*, 23 (2004) 4849–4857.
- [26] D.G. Holah, A.N. Hughes, B.C. Hui, C.T. Kan. *Journal of Catalysis*, 48 (1977) 340–344.
- [27] I.M. Angulo, E. Bouwman. *Journal of Molecular Catalysis A: Chemical*, 175 (2001) 65–72.
- [28] I.M. Angulo, S.M. Lok, V.F. Quiroga Norambuena, M. Lutz, A. L. Spek, E. Bouwman. *Journal of Molecular Catalysis A: Chemical*, 187 (2002) 55–67.
- [29] C. Daguene, P. J. Dyson. *Catalysis Communications*, 4 (2003) 153–157.
- [30] J. Lin, C.U. Pittman Jr. *Journal of Organometallic Chemistry*, 512 (1996) 69–78.
- [31] Z. Yang, M. Ebihara, T. Kawamura. *Journal of Molecular Catalysis A: Chemical*, 158 (2000) 509–514.
- [32] A.F. Borowski, S. Sabo-Etienne, B. Chaudret. *Journal of Molecular Catalysis A: Chemical*, 174 (2001) 69–79.
- [33] J.A. Widegren, M.A. Bennett, R.G. Fink. *Journal of the American Chemical Society*, 125 (34) (2003) 10301–10310.
- [34] E. L. Muetterties, J. R. Bleeke. *Accounts of Chemical Research*, 12 (9) (1979) 324–331.
- [35] N.S. Venkataramanan, G. Kuppuraj, S. Rajagopal. *Coordination Chemistry Reviews*, 249 (2005) 1249–1268.

- [36] V. Dragutan, I. Dragutan, L. Delaude, A. Demonceau. *Coordination Chemistry Reviews*, 251 (2007) 765–794.
- [37] E.A. Cagnola, M.E. Quiroga, D.A. Liprandi, P.C. L'Argentiere. *Applied Catalysis A: General*, 2004, 274, 205–212.
- [38] A. Boettcher, H. Elias, E.G. Jaeger, H. Langfelderova, M. Mazur, L. Muller, H. Paulus, P. Pelikan, M. Rudolph, M. Valko. *Inorganic Chemistry*, 32 (1993) 4131–4138.
- [39] P. Chen, B. Fan, M. Song, C. Jin, J. Ma, R. Li. *Catalysis Communications*, 7 (2006) 969–973.
- [40] R.L. Augustine. *Heterogeneous Catalysis for the Synthetic Chemist*. Marcel Dekker, New York, 1996 (Chapter 17).
- [41] L. Zhang, Y. Zhang, X-G Zhou, R-X Li, X-J Li, K.C. Tin, N-B Wong. *Journal of Molecular Catalysis A: Chemical*, 256 (2006) 171–177.
- [42] A. F. Borowski, S. Sabo-Etienne, B. Chaudret. *Journal of Molecular Catalysis A: Chemical*, 174 (2001) 69–79.
- [43] P. Chen, B. Fan, M. Song, C. Jin, J. Ma, R. Li. *Catalysis Communications*, 7 (2006) 969–973.
- [44] S. Mayadevi, N. Sridevi, K.K.M. Yusuff. *Indian Journal of Chemistry Section A: Inorganic, Bio-inorganic, Physical, Theoretical and Analytical Chemistry*, 37 (1998) 413–417.
- [45] G. Y. Kubas. *Accounts of Chemical Research*, 21 (1988) 120–128.
- [46] P. J. Jessop, R. H. Morris. *Coordination Chemistry Reviews*, 121 (1992) 155–284.
- [47] B.R. James. *Catalysis Today*, 37 (1997) 209–221.
- [48] R. Noyori, T. Ohkuma. *Angewandte Chemie International Edition*, 40 (2001) 40–74.
- [49] G. Zassinovich, G. Mestroni, S. Gladiali. *Chemical Reviews*, 92 (5) (1992) 1051–1069.
- [50] T. Naota, H. Takaya, S.-I. Murahashi. *Chemical Reviews*, 98 (7) (1998) 2599–2660.
- [51] R.A. Sanchez-Delgado, M. Rosales. *Coordination Chemistry Reviews*, 196 (2000) 249–280.
- [52] J.E. Backvall. *Journal of Organometallic Chemistry*, 652 (2002) 105–111.
- [53] F. Joo. *Accounts of Chemical Research*, 35 (2002) 738–745.
- [54] G.J. Kubas, *Metal Dihydrogen and Sigma-Bond Complexes*, Kluwer Academic Publishers/Plenum Press, New York, 2001.

- [55] M.A. Esteruelas, L.A. Oro. *Chemical Reviews*, 98 (1998) 577-588.
- [56] S. Sabo-Etienne, B. Chaudret. *Coordination Chemistry Reviews*, 178-180 (1998) 381-407.
- [57] S.E. Clapham, A. Hadzovic, R.H. Morris. *Coordination Chemistry Reviews*, 248 (2004) 2201–2237.
- [58] J.A. Widegren, R.G. Finke. *Journal of Molecular Catalysis A: Chemical*, 191 (2003) 187–207.
- [59] C.M. Hagen, J.A. Widegren, P.M. Maitlis, R.G. Finke. *Journal of the American Chemical Society*, 127 (2005) 4423–4432.
- [60] Y. Lin, R.G. Finke. *Inorganic Chemistry*, 33 (1994) 4891–4910.
- [61] T. Suarez, A. Guzman, B. Fontal, M. Reyes, F. Bellandi, R.R. Contreras, P. Cancines, G. Leon, L. Rojas. *Transition Metal Chemistry*, 31 (2006) 176–180.