Chapter 7

Catalytic activity studies

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7A. Hydrogenation of benzene catalysed by Ir(III) complexes

A wide variety of transition metal complexes are extensively studied as reagents or catalysts for organic synthesis. The catalytic activity of transition metal Schiff base complexes is highly dependent on the environment about the metal centre and their conformational flexibility (1). Small changes in the ligand framework enhance the steric and electronic effects of homogeneous metal complexes (2). The generally accepted order of catalyst activities for the elements of the transition series and their compounds is 2nd row > 1st row > 3rd row.

The catalytic activities of newly synthesised iridium(III) and ruthenium(III) Schiff base complexes are studied in this chapter. This chapter is broadly divided into two sections: Part A which provides the details of hydrogenation of benzene catalysed by Ir(III) complexes and Part B which gives oxidation of 2-ethyl-1-hexanol catalysed by ruthenium (III) complexes.

7A.1 Introduction

Iridium complexes have received much attention as efficient hydrogenation catalysts. Crabtree reported that iridium complex is a highly...
active catalyst for hydrogenation of highly hindered alkenes such as 2, 3-dimethyl-2-butene (3). Iridium complex-catalyzed hydrosilylations have also been reported (5-10). The activity of some common metals towards the hydrogenation of benzene and alkyl benzene decreases in the order of Rh > Ru > Ir > Pt > Ni > Pd > Co [11]. The complex Ru(II)(L)(Cl)(H$_2$O)$_2$·H$_2$O containing 3-hydroxyquinaxaline-2-carboxaldehyde-4-aminoantipyrine as the Schiff base were found to be effective catalysts for the hydrogenation of benzene (12).

Cleavage of the dihydrogen molecule is the important step in the hydrogenation reaction. 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 H$_2$ [13]. An increase in the N-basicity of the Schiff base ligand is found to increase the catalytic performance towards the metal catalyzed hydrogenation through such an interaction [14].

Therefore increased interactions are expected in the case of Schiff bases derived from 3-hydroxyquinaxaline-2-carboxaldehyde, which have more basic donor nitrogen atoms. The presence of quinoxaline ring provide electronic environment in the immediate coordination sphere of the metal thus allowing fine tuning of various catalytic properties of its complexes. These iridium(III) complexes derived from quinoxaline-2-carboxaldehyde exhibit excellent catalytic activity towards hydrogenation of benzene. In this chapter, the result of our studies on the catalytic activity of these complexes towards hydrogenation of benzene are presented.

7A.2 Experimental

7A.2.1 Materials

The details of the materials used for the synthesis and characterisation of Ir(III) Schiff base complexes are given in Chapter 2.
7A.2.2 Methods

The syntheses of the Schiff base ligands and their Iridium(III) complexes are given in Chapters 2 and 4.

7A.2.3 Catalytic activity measurements

The hydrogenation reactions were carried out in a 100 mL bench top mini-reactor made of stainless steel 316 (Autoclave Engineers, Division of Snap-tite, Inc. Pennsylvania). The reactor was charged with known quantities of the catalyst and benzene. Air was flushed out of the reactor with low-pressure of hydrogen, after which the inlet valve was closed and heating commenced with stirring at 600 rpm. When the designated temperature was reached, hydrogen was fed to the reactor at a predetermined pressure (time zero), which was maintained throughout the reaction with the help of a mass flow meter. During the run, samples (about 0.5 mL each) were withdrawn periodically and analyzed using a Chemito 8510 Gas Chromatograph using the column carbowax (15 %) and the products of the reaction were identified by using Varian 1200 L Single Quadrupole GC-MS.

7A.3 Results and discussion

The iridium complexes [Ir(qc5in)Cl\(_3\)H\(_2\)O], [Ir(qc6in)Cl\(_3\)H\(_2\)O], [Ir(hqc5in) Cl\(_3\)(H\(_2\)O)], [Ir(hqc6in)Cl\(_3\)(H\(_2\)O)] and [Ir(hqaqn)Cl\(_3\)(H\(_2\)O)] were tested for its activity towards the hydrogenation of benzene. The reactions were carried out under solvent free conditions with 0.34 mol benzene, 30 bar dihydrogen pressure at a temperature of 80 °C, stirring speed of 600 rpm with 6.66 \times 10^{-6} mols of catalyst. The percentage conversion of benzene was noted after two hours of reaction (shown in Figure 7.1) and their turnover frequencies (TOF is the mol of benzene transformed per mole of the catalyst per hour) are given in Table 7.1. Generally reduction of benzene and alkyl benzenes results in the formation of fully hydrogenated cyclohexanes. In our study hydrogenation of benzene takes place to give cyclohexane and the partially hydrogenated product cyclohexene.
Table 7.1. TOF of Ir(III) complexes in the hydrogenation of benzene

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(qc5in)Cl₃H₂O]</td>
<td>1654</td>
</tr>
<tr>
<td>[Ir(qc6in)Cl₃H₂O]</td>
<td>1481</td>
</tr>
<tr>
<td>[Ir(hqc5in)Cl₃(H₂O)]</td>
<td>692</td>
</tr>
<tr>
<td>[Ir(hqc6in)Cl₃(H₂O)]</td>
<td>1803</td>
</tr>
<tr>
<td>[Ir(hqaqn)Cl₃(H₂O)]</td>
<td>2705</td>
</tr>
</tbody>
</table>

Figure 7.1. Percentage conversion of Ir(III) complexes in the hydrogenation reaction

Among these complexes, [Ir(hqaqn)Cl₃(H₂O)] was found to be most active. Hence a detailed study was carried out on the activity of this complex towards the hydrogenation of benzene. 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 80 °C, and 30 bar hydrogen pressure, turnover frequencies 2705 h⁻¹ have been found for the hydrogenation of benzene. This value is much higher than that reported for some of the mononuclear iridium-based catalysts in the homogeneous hydrogenation of arenes. 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...
Ir(III) cations more electron rich and thus promote the overlap of the filled metal d orbital and the empty sigma antibonding molecular orbital of the hydrogen.

### 7A.3.1 Effect of catalyst concentration

To study the influence of catalyst concentration on the reduction of benzene quantity of the catalyst was varied in the range \((5.01-10.00) \times 10^{-6}\) mol, while the substrate concentration (0.34 mol benzene, dihydrogen pressure (30 bars) and the temperature (80 °C) were kept constant (Table 7.2). In both cases an increase in catalyst concentration was found to raise the percentage conversion. However, with increase in catalyst concentration, change in the product distribution was observed. At lower concentrations of the catalyst, the fully hydrogenated product predominates but at increased catalyst concentrations partially hydrogenated product predominates. This would be due to the increase in catalytic active iridium sites with increase of catalyst concentration.

#### Table 7.2. Effect of the \([\text{Ir(hqaqn)}\text{Cl}_3(\text{H}_2\text{O})]\) in the hydrogenation of benzene

<table>
<thead>
<tr>
<th>[catalyst] ((10^{-6}\text{mol}))</th>
<th>[benzene] ((\text{mol}))</th>
<th>(\text{H}_2\text{pressure}) ((\text{bar}))</th>
<th>Temperature ((\text{ºC}))</th>
<th>Conversion ((%))</th>
<th>Selectivity ((%)^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.01</td>
<td>0.34</td>
<td>30</td>
<td>80</td>
<td>5.8</td>
<td>73</td>
</tr>
<tr>
<td>6.66</td>
<td>0.34</td>
<td>30</td>
<td>80</td>
<td>10.6</td>
<td>81</td>
</tr>
<tr>
<td>8.32</td>
<td>0.34</td>
<td>30</td>
<td>80</td>
<td>11.8</td>
<td>84</td>
</tr>
<tr>
<td>10.00</td>
<td>0.34</td>
<td>30</td>
<td>80</td>
<td>13.0</td>
<td>83</td>
</tr>
</tbody>
</table>

\(^b\) CA = cyclohexane, CE = cyclohexene and the product selectivity is CA (or CE) / (CA + CE)

### 7A.3.2 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 20 to 50 bar at 80 °C keeping both substrate concentration (0.34 mol benzene) and the catalyst loading \((6.66 \times 10^{-6}\) mol) constant. A favourable effect of conversion is observed with an increase of hydrogen pressure from 20 to 50 bars. The results of these studies are given in Table 7.3.
Table 7.3. Effect of dihydrogen pressure in the hydrogenation of benzene

<table>
<thead>
<tr>
<th>[catalyst] 10⁻⁶ mol</th>
<th>H₂ pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%) b</th>
<th>CA</th>
<th>CE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.66</td>
<td>20</td>
<td>80</td>
<td>6.6</td>
<td>70</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>6.66</td>
<td>30</td>
<td>80</td>
<td>10.6</td>
<td>81</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>6.66</td>
<td>40</td>
<td>80</td>
<td>11.8</td>
<td>85</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>6.66</td>
<td>50</td>
<td>80</td>
<td>13.6</td>
<td>86</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

b CA = cyclohexane, CE = cyclohexene and the product selectivity is CA (or CE) / (CA + CE)

7A.3.3 Effect of temperature

The effects of temperature on the hydrogenation of benzene investigated in the range 40-100 °C keeping all other parameters constant (Table 7.4). Percentage conversion and selectivity were seen to increase with increase of temperature.

Table 7.4. Effect of temperature in the hydrogenation of benzene

<table>
<thead>
<tr>
<th>[catalyst] 10⁻⁶ mol</th>
<th>H₂ pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%) b</th>
<th>CA</th>
<th>CE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.66</td>
<td>30</td>
<td>40</td>
<td>5.5</td>
<td>72</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>6.66</td>
<td>30</td>
<td>60</td>
<td>7.4</td>
<td>80</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>6.66</td>
<td>30</td>
<td>80</td>
<td>10.6</td>
<td>81</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>6.66</td>
<td>30</td>
<td>100</td>
<td>12.8</td>
<td>86</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

7B Oxidation of 2-ethyl-1-hexanol catalysed by ruthenium(III) complexes

7B.1 Introduction

Selective oxidation of primary alcohols to aldehydes is a long standing problem of organic chemistry. The oxidation of alcohols by many ruthenium Schiff base complexes has been reported (15-21).
Ruthenium complexes act as catalysts due to their reversible and accessible oxidation states. Ruthenium complexes are known to mediate alcohol oxidation using variety of oxidants such as PhIO (22), NMO (23), BrO$_3^-$ (24), S$_2$O$_8^{2-}$ (25), $t$-BuOOH (26) and O$_2$ or air (27). The results of our studies on the oxidation of 2-ethyl-1-hexanol using Ru(III) complexes are presented in this chapter.

7B.2 Experimental
7B.2.1 Materials

The details of the materials used for the synthesis and characterisation of Ru Schiff base complexes are given in Chapter 2.

7B.2.2 Methods

The details of the syntheses of Schiff bases and their Ru complexes are given in Chapters 2 and 5.

7B.2.3 Catalytic activity measurements

Catalytic oxidation was carried out in a two-necked RB flask. Hydrogen peroxide (30%) was added through the septum to the magnetically stirred solution containing 2-ethyl-1-hexanol and the Ru(III) complexes. The reaction mixture was stirred and heated in a magnetic stirrer. The course of the reaction was monitored by periodically withdrawing small samples (about 0.4 mL each) which were analyzed by gas chromatography fitted with carbowax (15 %)

7B.3 Results and discussion

Oxidation of 2-ethyl-1-hexanol, a lipophilic alcohol, generally yields 2-ethyl-1-hexanal and 2-ethylhexanoic acid. Hydrogen peroxide was chosen as oxidant because it is inexpensive and liberates water as by product. The reaction is as follows (Scheme 7.1).
Scheme 7.1. Conversion of 2-ethyl-1-hexanol to 2-ethyl-1-hexanal

All the Ru(III) complexes were screened for their activity towards this oxidation. The results of this studies are given in the Table. Among these complexes, [Ru(hqaqn)Cl₃(H₂O)].H₂O was found to be the most active catalysts with 48% conversion. We carried out a blank experiment without the catalyst under identical conditions and no oxidation products were observed. To study suitable reaction conditions for maximum transformation detailed study was carried out on the activity of the complex, [Ru(hqaqn)Cl₃(H₂O)].H₂O by varying the reaction conditions: effect of the amount the catalyst, effect of temperature, effect of H₂O₂ and effect of time.

Table 7.5. Percentage conversion and turnover frequency of Ru(III) complexes

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% of conversion</th>
<th>TOF(h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(qc5in)Cl₃H₂O] H₂O</td>
<td>48</td>
<td>7905</td>
</tr>
<tr>
<td>[Ru(qc6in)Cl₃H₂O] H₂O</td>
<td>26</td>
<td>4285</td>
</tr>
<tr>
<td>[Ru(hqc5in)Cl₃(H₂O)] H₂O</td>
<td>4</td>
<td>660</td>
</tr>
<tr>
<td>[Ru(hqc6in)Cl₃(H₂O)]H₂O</td>
<td>12</td>
<td>1978</td>
</tr>
<tr>
<td>[Ru(hqaqn) Cl₃(H₂O)]H₂O</td>
<td>18</td>
<td>3017</td>
</tr>
</tbody>
</table>

Reaction conditions Reaction time-30 mts, Reaction temperature-313 K, 2-ethyl hexanol-- .20 mol, H₂O₂ - 9.7 mmol, Catalyst weight-6 mg

7B.3.1 Effect of amount of the catalyst

The reaction which carried out in the absence of catalyst did not yield any products. The influence of catalyst on the oxidation of 2-ethyl-1-hexanol was studied at 40°C by varying the amount of catalyst from 4.01 × 10⁻³ mol to 12.03 × 10⁻³ mol
keeping the amount of oxidant and substrate constant. The results of our studies are shown in the Figure 7.2.

![Graph showing catalytic activity](image)

**Figure 7.2. The influence of the amount of the catalyst**

From the graph it is clear that percentage conversion increases with increase in the amount of catalyst.

**7B.3.2 Influence of reaction temperature**

The reaction was studied over a wide range of temperature in 30 ml substrate from 273 K to 313 K keeping the amount of catalyst and oxidant constant. Selection of this particular temperature range is due to the reason that at higher temperatures the decomposition of H\textsubscript{2}O\textsubscript{2} takes place. The results of our studies are shown in Figure 7.3. At room temperature the percentage conversion was very poor. As the temperature increased, the conversion was found to increase but if the temperature is more than 313 K one more product was also formed it might be 2-ethylhexanoic acid. The optimum temperature for carrying out the reaction is 313 K. After this temperature there is a slight decrease in conversion which may be due to the accelerated decomposition of H\textsubscript{2}O\textsubscript{2}.
7B.3.3 Influence of reaction time

The influence of reaction time on the oxidation of 2-ethyl-1-hexanol was probed by carrying out the reaction with 6mg catalyst in 20 mol of ethyl- hexanol and 9.7 mmol of H₂O₂ at 30 minutes. The % of conversion increases with increase of time and acquires steady value after 30 minutes. The results of our studies are shown in the Figure 7.4.
7C Conclusions of catalytic activity studies

[Ir(hqaqn)Cl₃(H₂O)] exhibited maximum catalytic activity for the hydrogenation of benzene. Turnover frequencies of 2705 h⁻¹ have been found for the reduction of benzene (0.34 mol) at 80 ºC with 6.66 × 10⁻⁶ mol catalyst and at a hydrogen pressure of 30 bar in 600 rpm stirring speed. These values are much higher than that of some of the reported iridium complex catalysts for the homogeneous aromatic hydrogenation reactions.

Complete oxidation of 2-ethyl-1-hexanol occurs in 30 minutes at the temperature of 313 K in presence of H₂O₂ (9.7 mmol) as oxidant with high selectivity to the 2-ethylhexanal. [Ru(qc5in)Cl₃H₂O].H₂O shows high turnover frequency 7905 h⁻¹ in this oxidation reaction.

References


Catalytic activity studies

