Hydrogen Generation from Glucose Catalyzed by Organoruthenium Catalysts under Mild Conditions

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**SI-1. Structures and synthesis of the 8 catalysts**

![Catalyst Structures](image)

**Figure S1. Corresponding structures of the 8 catalysts.**

Synthesis of \([\text{(p-cymene)Ru(NH}_3])\text{Cl}_2\): 200 mg \([\text{RuCl}_2(\text{p-cymene})]_2\) was stirred in 15 mL water at room temperature, forming a light brown suspension. Then 200 μL ammonia was dropped into the suspension slowly. Keep stirring at room temperature for 8 hours, the solid will dissolve and turn into pale yellow solution. Then dark brown product will be gained by evaporating solution under reduced pressure. Synthesis process refer to literature partially.\(^1,2\)

Synthesis of \([\text{Rh Cp}*(\text{NH}_3)]\text{Cl}_2\): 200 mg \([\text{Rh Cp}* \text{Cl}_2]_2\) was stirred in 15 mL water at room temperature, forming a pale yellow suspension. Then 200 L ammonia was dropped into the suspension slowly. Keep stirring at room temperature for 8 hours, the solid will dissolve and turn into reddish brown solution. Then reddish brown product will be gained by evaporating solution under reduced pressure. Synthesis process refer to literature partially.\(^3,4\)

Synthesis of \([\text{IrCp}(\text{phen})]\text{Cl}_2\): 1,10-phenanthroline and \([\text{Ir}^{\text{III}}(\text{Cp}*)(\text{Cl})_2]_2\) was mixed by the molar ratio of 2:1, \([\text{Ir}^{\text{III}}(\text{Cp}*)(\text{Cl})_2]_2\) (0.08 mmol) was added to dichloromethane (16 mL), two equivalents of the 1,10-phenanthroline was added to the above suspension. The mixture was stirred for 5 h at room temperature, until the color changed from orange to yellow-orange. The recrystallization was carried out on the reaction liquid using ice water, which gave the product a yellow powder in good yield.\(^5,6\)

Synthesis of \([\text{(p-cymene)Ir(H}_2\text{O}_3)]\text{SO}_4\): A round-bottom flask was charged with 300 mg \([\text{IrCp}*\text{Cl}_2]_2\) and 20 mL water, the suspension was stirred and heated to 50 °C. Then 306 mg \(\text{Ag}_2\text{SO}_4\) was added. During the reaction, the \([\text{IrCp}*\text{Cl}_2]_2\) dissolved...
gradually, and white precipitate formed. After 4 hours’ reaction, light yellow solution will be obtained after filtering. The product is obtained by evaporating filtrate under reduced pressure, dried in vacuo yielding 360 mg \([\text{IrCp}^*(\text{H}_2\text{O})_3]\text{SO}_4\). \(^7\)

Synthesis of \([\text{IrCp}^*(\text{bpym})]\text{Cl}_2\) and \([\text{RhCp}^*(\text{bpym})]\text{Cl}_2\): The pentamethylcyclopentadienyl complexes \([(\eta^5-\text{C}_5\text{Me}_5)\ M\ \text{Cl}_2]_2\) (\(M = \text{Rh}, \text{Ir}\)) react with 2 equiv. of 2, 2’-bipyrimidine (bpym) in methanol to form the cationic pentamethylcyclopentadienyl complexes \([(\eta^5-\text{C}_5\text{Me}_5)\ \text{RhCl}(\text{bpym})]^+\) and \([(\eta^5-\text{C}_5\text{Me}_5)\text{IrCl}(\text{bpym})]^+\). \(^6\)

Synthesis of \([(\text{p-cymene})\text{Ru}(\text{phen})]\text{Cl}_2\): 1,10-phenanthroline and \([\text{Ru}^{\text{III}}(\text{Cp}^*)(\text{Cl})_2]_2\) was mixed by the molar ratio of 2:1, \([\text{Ru}^{\text{III}}(\text{Cp}^*)(\text{Cl})_2]_2\) was added to dichloromethane, two equivalents of the 1,10-phenanthroline was added to the above suspension. The mixture was stirred for 5 h at room temperature. The recrystallization was carried out on the reaction liquid using ice water, which gave the product a yellowish powder in good yield. \(^6,8,9\)

Synthesis of \([(\text{p-cymene})\text{Ru}(\text{bpym})]\text{Cl}_2\): A mixture of \([(\eta^6-\text{p-PriC}_6\text{H}_4\text{Me})\text{Ru}(\mu-\text{Cl})\text{Cl}_2]\) and 2 equiv. of 2,2’-bipyrimidine is stirred in methanol at room temperature for 3 h, then filtered the solution. Removed the solvent under vacuo then the residue is taken up in dichloromethane and filtered. The filtrate is concentrated and diethylether is slowly added to precipitate an orange–brown solid. \(^6,10\)

SI-2. The set-up of the experimental procedures

As shown in Figure S2, an elongated reaction flask was selected as the reactor to overcome the interference of water vapor. The flask was sealed by a rubber plug with micro syringe. A semi liquid filled U-shaped tube was connected to the reactor with a 0.5 m stainless steel tube and a three-port valve. The volume content of the evolved gas could be calculated through changes of liquid levels in U-shaped tube.

![Diagram of the reaction process](image)

Figure S2. The schematic diagram of the reaction process.
SI-3. The interference of water vapor

In order to investigate the interference of water vapor, we did a blank test which operated with the same equipment and reactant (deionized water and glucose) but without Ru-catalyst addition. As can be seen from Figure S3, the effect of water vapor is negligible relative to the amount of gas produced.

We considered this possible problem in designing the research. An elongated reaction flask was selected as the reactor to overcome the interference of water vapor. Water vapor can condense rapidly on the bottleneck and drop back into the reaction solution during the measurement. Besides, the gas-flow rate was not very fast, water vapor would not be brought out in large amount.

Figure S3. Gas evolution vs. time for the glucose dehydrogenation by [(p-cymene)Ru(NH$_3$)$_2$]Cl$_2$ at 98 °C (blue curve). Volume change caused by water vapour at 98 °C (green curve).
SI-4. The characterization of the \([(p\text{-cymene})\text{Ru(NH}_3\text{)}\text{]}\text{Cl}_2\) catalyst after reaction

To investigate the aggregation problem, we take 1 mL of the reaction solution to centrifuge at different revolutions \((r)\) and at the same time, the UV-Vis spectra of the corresponding solutions are tested and compared.

The solutions remain transparent before and after centrifugation and no visible particles or stratification can be observed in Figure S4. As shown in Figure S4, peaks of the UV-Vis spectra of the solutions coincide with each other. So it is speculated that there is no formation of nanoparticles during the reaction process.

Figure S4. Photos of the reaction solution before and after centrifugation at different revolutions.
Figure S5. UV-Vis absorption spectra of solutions after centrifugation at different revolutions (r). r =6,000 (red line), r =9,000 (blue line), r =12,000 (black line).

### SI-5. Compassion table about the biomass dehydrogenation

**Table 1. Overview of the methods for the dehydrogenation of the biomass**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasification of biomass</td>
<td>Supercritical water</td>
<td>≥ 800 °C</td>
<td>High pressure</td>
</tr>
<tr>
<td>Reforming of biomass</td>
<td>Liquid water</td>
<td>≥ 500 °C</td>
<td>High pressure</td>
</tr>
<tr>
<td>This approach</td>
<td>Deionized water</td>
<td>98 °C</td>
<td>1 bar</td>
</tr>
</tbody>
</table>
SI-6. Experimental details about the glucose dehydrogenation reaction

All catalysts in Table 1 are homogeneous, they can dissolve and exist stably in water. We prepared the catalyst solution with a certain mass concentration, and then used the transferpette to transfer the solution accurately, so we could get a certain mass of catalyst.

SI-7. Gas chromatography of the glucose decomposition reaction

The gaseous product generated from glucose decomposition reaction was analyzed by GC-G5 (Beijing Persee General Instrument CO. Ltd), TCD, FID, molecular sieve 5A and methane conversion reactor assembled with the gas chromatography, N$_2$ was used as carrier gas. By means of a methane reformer, the detection limit of CO was below 10 ppm. TCD of the GC was used to detect H$_2$.

Figure S6 give the H$_2$ and CO$_2$ peaks of glucose decomposition catalysed by [(p-cymene)Ru(NH$_3$)$_3$]Cl$_2$. The Figure S6a and b both give the strong peak for H$_2$, no CO$_2$ was detected during the initial 10 minutes. Little CO$_2$ was detected after 10 h suggesting that decarboxylation and formic acid decomposition occurred subsequently.

![Figure S6. Gas chromatogram of generating gas from glucose dehydrogenation reaction using TCD at different reaction times. (a) The initial 10 minutes of gas chromatography from glucose reforming reaction. (b) The 10 h of gas chromatography from glucose reforming reaction.](image-url)
SI-8. Formaldehyde catalyzed by ruthenium catalyst

As shown in Figure S7a, we obtain the relationship between the gas volume and reaction time for AWS reaction by [(p-cymene)Ru(NH$_3$)$_2$]Cl$_2$. The AWS reaction can be understood as follows:

$$\text{HCHO} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{HCOOH} + \text{H}_2$$  \hspace{1cm} (1)

As you can see, the gas volume increases rapidly with time increase. Figure S7b gives the strong peak for hydrogen, no CO$_2$ was detected. These evidences state clearly that [(p-cymene) Ru (NH$_3$)$_2$] Cl$_2$ has a good catalytic activity for AWS reaction. Simultaneously, d-glucose acid was converted from the d-glucose.
SI-9. Formic acid catalyzed by ruthenium catalyst

As can be seen from Figure S8, the hydrogen production rate increases with the increase of formic acid concentration in the range of 0~3 M. It corresponds to the decarboxylation and formic acid decomposition in second and third steps.
SI-10. Stability of the [(p-cymene)Ru(NH₃)]Cl₂ catalyst

As shown in Figure S9, we repeated the experiment three times under the same conditions. For the first time, the catalyst worked for 300 minutes with a high reactivity and stability. For the latter three times, the reactivity of the catalyst decreased until a relatively stable reactivity was reached. On the whole, the catalyst could maintain stable for a long time.

In the first experiment (Figure S9a), the reaction was run using a d-C₆H₁₂O₆·H₂O (15 mmol) and deionized H₂O (2 mL) solution at 98 °C with sulphuric acid (pH=0.5, 5 μmol) and 2.8 μmol of catalyst, after 300 minutes, the system was cooled down to room temperature. In the second experiment (Figure S9b), 1 mL of d-C₆H₁₂O₆·H₂O solution was added to the reaction solution (a) and the latter was stirred for 15 minutes at room temperature. Afterwards the solution was heated up to 98 °C and gas evolution was restored, after 80 minutes, the system was cooled down to room temperature. Repeat the same process two times and the corresponding results are shown in Figure S9c and Figure S9d.

Figure S9. Dehydrogenation of glucose by [(p-cymene)Ru(NH₃)]Cl₂ at 98 °C. Reaction conditions: (a). d-C₆H₁₂O₆·H₂O 0.26 g (15 mmol), deionized H₂O (2 mL), sulphuric acid (pH=0.5, 5 μmol), [(p-cymene)Ru(NH₃)]Cl₂ (2.8 μmol). (b) Add 1 mL of d-C₆H₁₂O₆·H₂O solution into the reaction solution (a). (c) Add 1 mL of d-C₆H₁₂O₆·H₂O solution into the reaction solution (b). (d) Add 1 mL of d-C₆H₁₂O₆·H₂O solution into the reaction solution (c).
SI-11. $^1$H-NMR spectrums of the 8 catalysts

All commercial materials were used as received unless specified. The $^1$H-NMR spectrums were characterized by NMR (Varian Plus 400 MHz). Figure S12, Figure S13 and Figure S15 consist with the corresponding literatures respectively. $^1$H-NMR spectra of the rest catalysts consist well with conclusions in references, indicating that the complexes were synthesized and isolated rightly.

Figure S10. $^1$H-NMR spectrums of the [(p-cymene)Ru(NH$_3$)$_3$]Cl$_2$, CD$_4$O was used as the solvent. δH: 1.23 (6H, m), 2.15 (3H, d) 2.81 (1H, m), 3.54 (3H, m), 5.36 (1H, d), 5.45 (1H, d), 5.60 (1H, d), 5.70 (1H, d).

Figure S11. $^1$H-NMR spectrums of the [RhCp*(NH$_3$)$_3$]Cl$_2$, D$_2$O was used as the solvent. δH: 1.60 (15H, s), 1.19 (3H, t).
Figure S12. $^1$H-NMR spectrums of the $[\text{RhCp^*(bpym)Cl}_2$, D$_2$O was used as the solvent. $\delta$H: 1.72 (15H, s), 8.07 (2H, s), 8.75(2H, d), 9.33(2H, d).

Figure S13. $^1$H-NMR spectrums of the $[(\text{p-cymene})\text{Ru(phen)}]\text{Cl}_2$, D$_2$O was used as the solvent. $\delta$H: 0.87 (6H, s), 2.16 (3H, s), 2.52 (1H, s), 5.93 (2H, s), 6.17 (2H, s), 8.03 (4H, d), 8.66 (2H, s), 9.74(2H, S)
Figure S14. $^1$H-NMR spectrums of the [IrCp*(bpym)]Cl$_2$, D$_2$O was used as the solvent. $\delta$H: 1.71 (15H, s), 8.04 (2H, t), 9.29 (4H, m).

Figure S15. $^1$H-NMR spectrums of the [IrCp*(phen)]Cl$_2$, D$_2$O was used as the solvent. $\delta$H: 1.58 (15H, s), 8.00 (2H, m), 8.04 (2H, d), 8.64 (2H, d), 9.18 (2H, d).
Figure S16. $^1$H-NMR spectrums of the [(p-cymene)Ru(bpym)]Cl$_2$, D$_2$O was used as the solvent. δH: 1.17 (6H, m), 2.23(3H, s), 2.7(1H, t), 6.1(2H, m), 6.3(2H, d), 8.31(4H, m), 9.95(2H, m).

Figure S17. $^1$H-NMR spectrums of the [IrCp*(H$_2$O)$_3$]SO$_4$, D$_2$O was used as the solvent. δH: 1.63 (6H, s), 2.27(3H, s), 2.55(1H, s), 7.26(2H, d), 7.32(2H, d).
D-glucose, d-glucose acid and $\text{H}_2\text{SO}_4$ were tentatively identified in sample using Q Exactive, a high-resolution quadrupole Orbitrap mass spectrometer (Thermo Scientific, Germany), by detecting the accurate mass and matching the isotope abundance. The sample (5 μL) was directly injected into the inlet system. The mobile phase containing 50% water, 50% acetonitrile drove the sample into the mass spectrometry as flow rate of 0.25 mL min$^{-1}$. The mass spectrometer system was operated with a heated electrospray ionization (HESI) source in negative mode with a spray voltage of $-3.2$ kV. An S-lens RF level of 50%, a capillary temperature of 300 °C, and a mass resolution of 70,000. The runtime was 2 minutes for each sample. The mass tolerance of the precursor was below 5 ppm. Mass spectra were processed using the Xcalibur 2.1 software (Thermo Scientific).
Figure S18. Mass spectrum of the glucose decomposition reaction solution after 50 h.

The formation of d-glucose acid can be seen from Figure S18. In the presence of [(p-cymene)Ru(NH₃)₃]Cl₂, C-C bond of d-glucose acid cleave into formic acid, furan, furfural and other unknown residues.
SI-13. Calculation of TOF

TOF was calculated by Equation (2). \(^{12}\)

\[
\text{TOF} = \frac{V_{\text{total}}}{n_{\text{catalyst}}} \left( \frac{1}{t \cdot V_{m,20\,\degree C}} \right)
\]  

(2)

The calculation of \(V_{m,H_2,20\,\degree C}\) was carried out using van der Waals Equation (3), \(V_{\text{total}}\) is the total amount of gas produced, \(t\) is the reaction time required to produce these gases, \(n_{\text{catalyst}}\) is the molar quantities of catalyst.

\[
V_{m,H_2,20\,\degree C} = \frac{RT}{P} + b - \frac{a}{RT} = 24 \, \text{L/mol}
\]  

(3)

\[
\begin{align*}
R &= 8.3145 \, \text{m}^3 \, \text{Pa/ mol/ K} \\
T &= 298.15 \, \text{K} \\
p &= 101325 \, \text{Pa} \\
b &= 26.7 \times 10^{-6} \, \text{m}^3/\text{mol} \\
a &= 2.49 \times 10^{-10} \, \text{Pa} \cdot \text{m}^3/\text{mol}^2
\end{align*}
\]

SI-14. Notes and reference