


Article

Iridium Complex Catalyzed Hydrogen Production from Glucose and Various Monosaccharides

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Abstract: A new catalytic system has been developed for hydrogen production from various monosaccharides, mainly glucose, as a starting material under reflux conditions in water in the presence of a water-soluble dicationic iridium complex bearing a functional bipyridine ligand. For example, the reaction of D-glucose in water under reflux for 20 h in the presence of [Cp*Ir(6,6'-dihydroxy-2,2'-bipyridine)(H₂O)]²⁺[OTf]⁻₂ (1.0 mol %) (Cp*: pentamethylcyclopentadienyl, OTf: trifluoromethanesulfonate) resulted in the production of hydrogen gas in 95% yield. In the present catalytic reaction, it was experimentally suggested that dehydrogenation of the alcoholic moiety at 1-position of glucose proceeded.

Keywords: iridium catalyst; water-soluble catalyst; hydrogen production; glucose; monosaccharides



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1. Introduction

Hydrogen is important as a raw material for the industrial production of ammonia and methanol [1–5]. In addition, it is an essential industrial reagent in the refining and desulfurization of petroleum [6–8]. Hydrogen is also used in large quantities in industrial processes such as turning unsaturated fats into saturated oils and fats, metal alloying and iron flashmaking, and electronics manufacturing (creating semiconductors, LEDs, displays, and photovoltaic segments) [9]. Furthermore, in addition to these industrial applications, hydrogen has been promoted as an energy carrier because it can easily be converted into other energy forms, namely, electrical energy or mechanical energy, with only harmless water as a by-product of the energy conversion [10,11]. Hydrogen has attracted attention as a next-generation energy carrier to replace fossil fuel resources because it has the advantage of exceedingly high energy density per weight.

Under this background, there is a need to develop new techniques to produce hydrogen using sustainable and available resources as feedstock [12,13]. In this context, biomass is expected to be a starting material for producing hydrogen, with the biomass mainly comprised of saccharides.

Research into developing a reaction to produce hydrogen using saccharides as starting material has been carried out for a relatively long time [14]. There are a number of reported reactions in which saccharides are dehydrogenated using heterogeneous catalysts [15–17] or enzyme catalysts [18,19] to obtain hydrogen. However, most of the reported examples using heterogeneous catalysts are reactions done under high temperature conditions above 300 °C using expensive noble metals. Furthermore, there are many catalytic systems that produce hydrogen gas mixed with carbon monoxide, carbon dioxide, or methane, instead of highly pure hydrogen, which is often difficult to produce. On the other hand, in the case of a reaction using an enzyme catalyst, it is often possible to obtain hydrogen from a saccharide under mild conditions. However, there are associated disadvantages such as long reaction times, reaction conditions requiring precise control, and time-consuming culturing of enzymes.

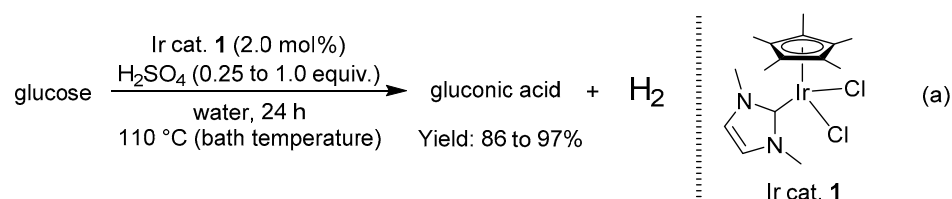
In view of these circumstances, there have been great expectations to realize hydrogen production from saccharides under mild conditions within a short reaction time using artificial homogeneous transition metal catalysts. It would be particularly significant if a water-soluble monosaccharide such as glucose was used as the starting material and hydrogen could be efficiently produced by catalytic dehydrogenation in an aqueous medium.

In 2018, Garcia and Mata et al. reported that gluconic acid was formed by the reaction of glucose in aqueous solvents using iridium complex catalysis, accompanied by hydrogen evolution (Scheme 1a) [20–22]. This is particularly noteworthy because glucose is sustainably available as a natural resource. However, to efficiently proceed with the dehydrogenation reaction, the usage of strong acids such as sulfuric acid and hydrochloric acid was essential, and the amount of iridium catalyst used was relatively large at 2.0 mol %.

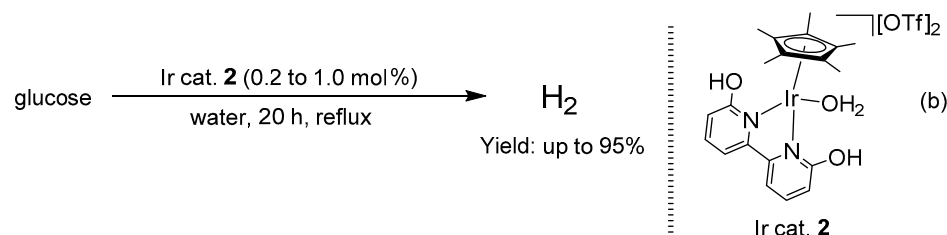
Our research group has developed water-soluble iridium catalysts that demonstrate high catalytic activity for the dehydrogenation reaction of alcohols and has reported the synthesis of aldehydes and ketones by the simple dehydrogenation of primary and secondary alcohols [23,24]. In addition, catalytic lactone synthesis involving the evolution of hydrogen using diol as a starting material has also been reported [25].

In this study, we developed a new catalytic system to produce hydrogen under reflux conditions in water in the presence of a water-soluble dicationic iridium catalyst using various monosaccharides, mainly glucose, as a starting material. As a result, we found that hydrogen could be efficiently obtained from these monosaccharides without the need for the addition of acids or bases and with less catalyst (from 0.2 to 1.0 mol %) than the previously reported examples (Scheme 1b).

Iridium-catalyzed dehydrogenation of glucose under acidic conditions by Garcia and Mata^[20]



This work: Iridium-catalyzed hydrogen production from glucose under neutral conditions



Scheme 1. Iridium-catalyzed dehydrogenation of glucose in water: (a) under acidic conditions report by Garcia and Mata et al. (b) under neutral conditions reported in this work.

2. Results and Discussion

The structures of the iridium catalysts used in this study are shown in Figure 1.

When D-glucose (5.0 mmol) was heated under reflux in water (15 mL) for 20 h in the presence of catalyst 1 (0.2 mol %), which was used under highly acidic conditions in the previous research by Garcia and Mata, only very low yield (7%) of hydrogen was generated (Table 1, entry 1) [26]. In contrast, when water-soluble dicationic catalyst 2, which was previously developed for the dehydrogenative oxidation of simple alcohols in water, was employed for the dehydrogenation of glucose; hydrogen was obtained in 76% yield (entry 2). In this dehydrogenation reaction, it is important that the complex

catalyst is dicationic and soluble in water, and that it has 6,6'-dihydroxy-2,2'-bipyridine as a ligand. In other words, no hydrogen was produced when $[\text{Cp}^*\text{IrCl}_2]_2$ (Cp^* : pentamethylcyclopentadienyl), which is not soluble in water (entry 3), or $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3][\text{OTf}]_2$ having no 6,6'-dihydroxy-2,2'-bipyridine ligand was used as the catalyst (entry 4). In addition, the presence of a hydroxy group at the 6,6'-position of the ligand is very important for catalytic performance. For example, hydrogen was not produced in the reaction using catalyst 3 with no hydroxy groups (entry 5) or catalyst 4 with a hydroxy group at the 4,4'-positions (entry 6). Subsequently, the reaction using catalyst 5 with tetrafluoroborate anion was carried out to investigate the influence of the counter anion (entry 7). In this case, although the yield of hydrogen was slightly reduced, there was no large difference from that when using catalyst 2. The yield was successfully improved to 95% by increasing the amount of the catalyst 2 to 1.0 mol %, (entry 8). The time course of hydrogen generation in the reaction of entry 8 was examined, and the results are shown in Figure 2.

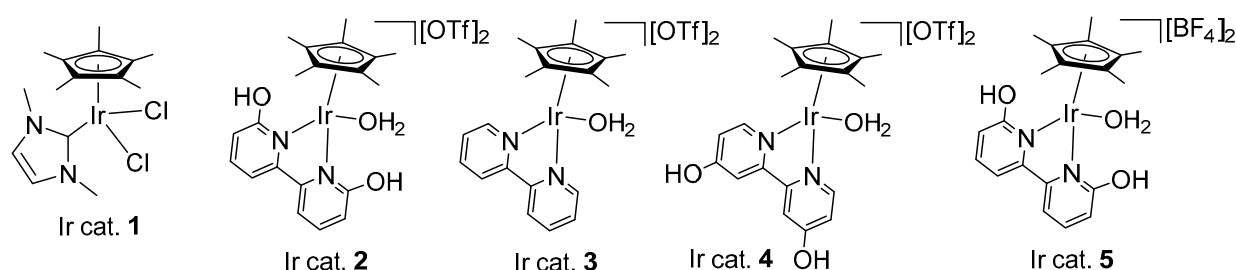


Figure 1. A series of iridium catalysts used for the dehydrogenation of glucose in this study.

Table 1. Hydrogen production from D-glucose catalyzed by various iridium complexes.

Entry	Catalyst (mol %)	Yield of Hydrogen (%) ^a
1	1 (0.20 mol %)	7
2	2 (0.20 mol %)	76
3	$[\text{Cp}^*\text{IrCl}_2]_2$ (0.20 mol % Ir)	0
4	$[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3][\text{OTf}]_2$ (0.20 mol %)	trace
5	3 (0.20 mol %)	trace
6	4 (0.20 mol %)	trace
7	5 (0.20 mol %)	71
8	2 (1.0 mol %)	95

^a Yield of hydrogen gas collected in a gas burette. The molar amount of hydrogen gas was calculated using the ideal gas law.

In the dehydrogenation reaction of glucose catalyzed by iridium complex catalyst 2, a simultaneous parallel experiment of alkene hydrogenation was performed to confirm that the obtained gas was highly-pure hydrogen. Simultaneous parallel experiments were carried out by connecting flask **A**, in which the dehydrogenation of glucose (5.0 mmol) in the presence of catalyst 2 was proceeding, and flask **B**, in which 1-decene (5.0 mmol) was heated to 50 °C in benzene solvent in the presence of $\text{RhCl}(\text{PPh}_3)_3$ (2.0 mol %), using a rubber tube (Scheme 2). As shown in entry 2 of Table 1, 76% of hydrogen is expected to be produced in flask **A**. By this simultaneous parallel experiment, decane was obtained in 74% yield in the reaction in flask **B**. This result indicates that the gas produced using glucose as a starting material in the presence of catalyst 2 is highly-pure hydrogen and does not contain a component that inhibits the catalytic hydrogenation of an alkene. In addition, gas chromatographic analysis of the gas obtained by dehydrogenation of glucose was carried

out to confirm that it was highly-pure hydrogen (the results are given in Figure S2 in the supporting information).

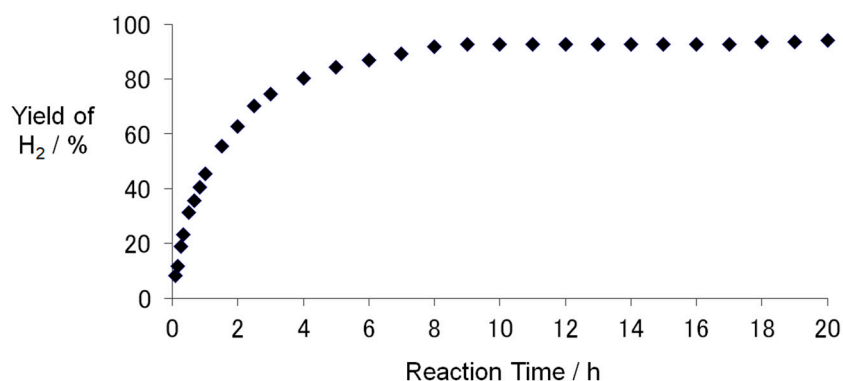
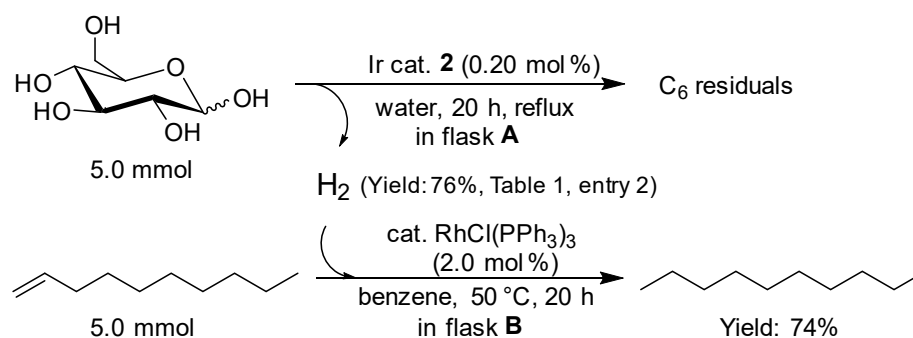


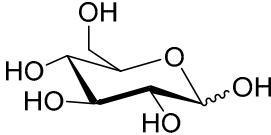
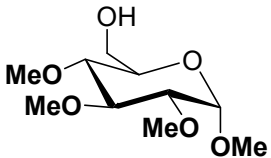
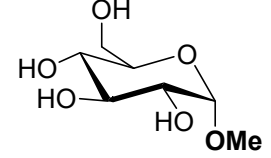
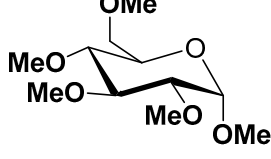
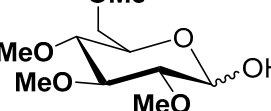
Figure 2. Time-resolved profile of the yield of hydrogen for the dehydrogenation of D-glucose (Table 1, entry 8).



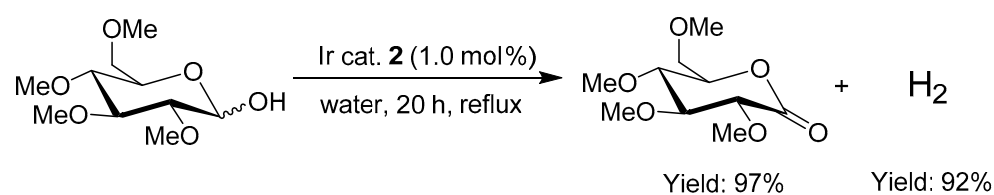
Scheme 2. A simultaneous parallel experiment: Hydrogenation of 1-decene with hydrogen produced by the dehydrogenation of glucose.

There are five alcoholic hydroxy groups in the D-glucose molecule. To ascertain the site at which the dehydrogenation reaction by the iridium complex catalyst **2** proceeds, experiments using glucose analogues with protected hydroxy groups were conducted (Table 2). First, the reaction of normal D-glucose is re-listed as entry 1 (the yield of hydrogen is 95%). Next, for the glucose analogue in which hydroxy groups other than the 6-position were methoxy protected, a very low yield (8%) of hydrogen was obtained (entry 2). For the glucose analogue in which only the hydroxy group at 1-position was methoxy protected, the hydrogen yield was greatly reduced to 14% (entry 3). No hydrogen was produced for the glucose analogue in which all hydroxy groups were methoxy protected (entry 4). Finally, for the glucose analogue in which all hydroxy groups but that at the 1-position were protected, the hydrogen yield was 92%, and it was found that the hydrogen yield not significantly different from that obtained when using unprotected glucose (entry 5). These results indicate that dehydrogenation from the hydroxy group at the 1-position proceeds during the hydrogen production reaction from glucose by catalyst **2**. Incidentally, the organic product obtained in 97% yield in the experiment of entry 5 was found to be a gluconolactone derivative with a lactone structure (Figure 3). Based on these results, it is likely that gluconolactone is formed after the dehydrogenation of glucose.

Table 2. Hydrogen production from various glucose analogues having protected hydroxy groups.

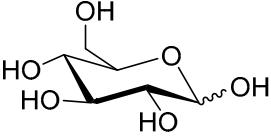
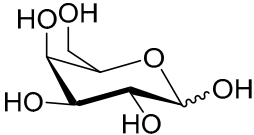
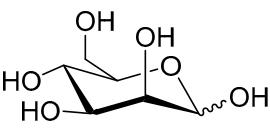
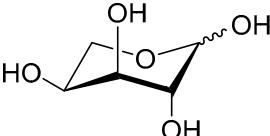
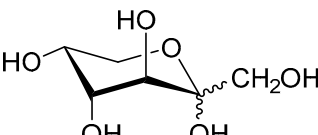
Entry	Substrate	Yield of Hydrogen (%) ^a
1		95
2		8
3		14
4		0
5		92

^a Yield of hydrogen gas collected in a gas burette. The molar amount of hydrogen gas was calculated using the ideal gas law.

**Figure 3.** Isolation of a gluconolactone derivative with a lactone structure formed by the reaction shown in entry 5 in Table 2.

We then investigated the dehydrogenation of various monosaccharides using iridium catalyst **2** (Table 3). Hydrogen was produced in good yields in the case of the feedstocks, D-galactose, D-mannose, and L-arabinose, that can form lactone structures by dehydrogenation (entries 2–4). In the case of D-fructose, a starting material in which dehydrogenation from a hydroxy group at the 1-position is difficult, the hydrogen yield was greatly reduced (entry 5).

Table 3. Hydrogen production from various monosaccharides using the iridium catalyst 2.

Entry	Substrate	Yield of Hydrogen (%) ^a
1		95
2		87
3		83
4		83
5		11

^a Yield of hydrogen gas collected in a gas burette. The molar amount of hydrogen gas was calculated using the ideal gas law.

3. Materials and Methods

3.1. General

All reactions and manipulations were performed under argon atmosphere using standard Schlenk techniques. ¹H and ¹³C{¹H} NMR spectra were recorded on JEOL ECS-400 or ECX-500 spectrometers. Gas chromatograph analyses of hydrogen were performed on a GL-Sciences GC390 gas chromatograph with packed columns (Molecular Sieve 5A and Gaskuropack 54). Gas chromatograph analysis of organic product was performed on a GL-Sciences GC353B gas chromatograph with a capillary column (GL-Sciences TC-17 and TC-WAX). Silica-gel column chromatography was performed using Wako-gel C-200 (Wako Pure Chemical Corporation). The iridium catalysts, [Cp*IrCl₂]₂ [27], [Cp*Ir(H₂O)₃][OTf]₂ [28], and 1 to 5 [10,29–31] were prepared according to the literature methods. Various glucose analogues having protected hydroxy groups used in Table 2 were prepared according to the literature methods [32–34]. Organic solvent was distilled under an argon atmosphere with an appropriate drying agent. Other reagents were commercially available and were used as received.

3.2. General Procedures for the Hydrogen Production from D-Glucose Catalyzed by Various Iridium Complexes

Under argon atmosphere, iridium catalyst (0.20 or 1.0 mol % Ir), D-glucose (5.0 mmol), and distilled water (15 mL) were placed in a flask equipped with a reflux condenser and a gas burette. The mixture was magnetically stirred under reflux for 20 h in an oil bath. The volume of the evolved hydrogen gas was measured by using a gas burette, and the yield of evolved hydrogen gas was calculated using the ideal gas law. The illustration of reaction apparatus is shown in Figure S1 in the supporting information. The purity of the

evolved hydrogen gas was confirmed by GC analysis. Details are shown in Figure S2 in the supporting information.

3.3. Procedure for the Simultaneous Parallel Experiment (Hydrogenation of 1-Decene with Hydrogen Produced by the Dehydrogenation of Glucose)

Under an atmosphere of argon, iridium catalyst **2** (0.20 mol %), D-glucose (5.0 mmol), and distilled water (15 mL) were placed in a flask **A**. In another flask **B**, under an atmosphere of argon, RhCl(PPh₃)₃ (2.0 mol %), 1-decene (5.0 mmol), and benzene (7.5 mL) were placed. The two flasks **A** and **B** were connected through a rubber tube. The mixture in the flask **A** was stirred under reflux for 20 h, while the mixture in the flask **B** was stirred at 50 °C. The yield of decane was determined by GC analysis using undecane as an internal standard.

3.4. General Procedures for the Hydrogen Production from Various Substrates

Under argon atmosphere, iridium catalyst **2** (1.0 mol %), substrate (5.0 mmol), and distilled water (15 mL) were placed in a flask equipped with a reflux condenser and a gas burette. The mixture was magnetically stirred under reflux for 20 h in an oil bath. The volume of the evolved hydrogen gas was measured by using a gas burette, and the yield of evolved hydrogen gas was calculated using the ideal gas law. The illustration of reaction apparatus is shown in Figure S1 in the supporting information. For the reaction shown in entry 5 of Table 2, the organic product was isolated by silica-gel chromatography (eluent: dichloromethane:methanol = 30:1) as illustrated in Figure 3. ¹H NMR (500 MHz, CDCl₃) [35]: δ 4.40 (ddd, *J* = 9, 4, 3 Hz, 1H), 3.84 (d, *J* = 6 Hz, 1H), 3.70–3.52 (m, 2H), 3.65 (m, 2H), 3.57 (s, 3H), 3.54 (s, 3H), 3.51 (s, 3H), 3.41 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 168.4, 82.1, 79.2, 77.4, 77.3, 70.6, 58.93, 58.86, 58.6, 58.3. These NMR spectra are shown in the supporting information.

4. Conclusions

In conclusion, we succeeded in developing a new catalytic system for hydrogen production from glucose and various monosaccharides using a dicationic water-soluble dicationic iridium catalyst **2** under reflux conditions in water. The addition of a strong acid or base is not required during the reaction. Hydrogen can be efficiently obtained from various kinds of monosaccharides with a relatively small amount of catalyst (0.2 to 1.0 mol %). It was experimentally suggested that the dehydrogenation of the alcoholic moiety at 1-position of monosaccharides proceeded. This method to obtain high-purity hydrogen conveniently under mild conditions using saccharides sustainably available from natural resources as raw materials can potentially form the basis for crucial technologies aimed at the transition to a hydrogen society in the future.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11080891/s1>, Figure S1: the reaction setup for hydrogen production from glucose and various monosaccharides, Figure S2: GC analysis of the evolved gas by the reaction of glucose under optimal conditions catalyzed by catalyst **2**.

Author Contributions: K.-i.F. guided the research, designed the experiments, and wrote the manuscript. T.I., T.T., and J.J. performed the experiments. S.F. supported the analysis of the experimental results and the writing of the manuscript. R.Y. also guided the research and helped to write the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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