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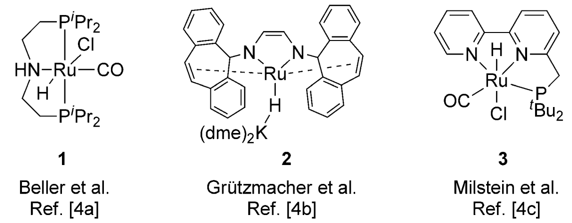
Hydrogen Production from a Methanol–Water Solution Catalyzed by an Anionic Iridium Complex Bearing a Functional Bipyridonate Ligand under Weakly Basic Conditions**

Ken-ichi Fujita, Ryoko Kawahara, Takuya Aikawa, and Ryohei Yamaguchi**

Abstract: *An efficient catalytic system for the production of hydrogen from a methanol–water solution has been developed using a new anionic iridium complex bearing a functional bipyridonate ligand as a catalyst. This system can be operated under mild conditions [weakly basic solution (0.046 mol L^{-1} NaOH) below 100 °C] without the use of an additional organic solvent. Long-term continuous hydrogen production from a methanol–water solution catalyzed by the anionic iridium complex was also achieved.*

Hydrogen is attracting considerable attention as an alternative energy source to fossil fuels.[1] The advantages of hydrogen as an energy source include 1) highest mass energy density of any fuel, 2) facile conversion to electrical energy as well as mechanical energy, and 3) generation of only water upon conversion to energy. To work toward a “hydrogen society” it is highly important to develop an efficient and practical method for the production of hydrogen from renewable and easy-to-handle resources. In this context, methanol is an ideal candidate substrate, because it is reproduced from carbon dioxide,[2] is liquid under ambient conditions, and possesses high hydrogen content.

Although heterogeneously catalyzed reforming of methanol producing hydrogen and carbon dioxide has been continuously studied and developed,[3] this process usually requires temperatures over 200 °C. On the other hand, a few reports on hydrogen production from methanol–water mixtures at temperatures below 100 °C have recently been reported. Most of these examples employ homogeneous ruthenium catalysts such as **1**–**3** (Scheme 1).[4–6] These catalytic reactions proceed through the following three elementary steps (Scheme 2): 1) dehydrogenation of methanol to formaldehyde, 2) hydration of formaldehyde followed by dehydrogenation generating formic acid, and 3) dehydrogenation of formic acid to carbon dioxide. Hydrogen production under relatively mild conditions below 100 °C has been achieved by these catalytic systems; however, strongly basic conditions (8.0 mol L^{-1} KOH)[7] and/or an additional organic solvent such as THF, toluene, and triglyme are required.[4,8,9] For practical applications, methanol–water mixtures without an organic solvent and lower concentrations of base are highly desirable.[5a]

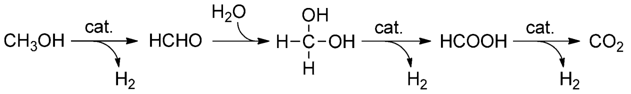


1
Beller et al.
Ref. [4a]

2
Grützmacher et al.
Ref. [4b]

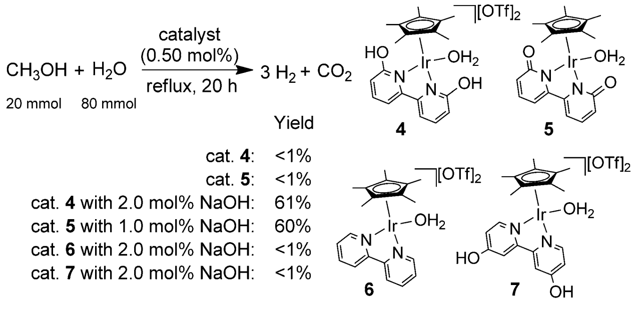
3
Milstein et al.
Ref. [4c]

Scheme 1. Homogeneous catalysts for hydrogen production from methanol–water mixtures. dme = dimethoxyethane.



Scheme 2. Pathway for homogeneously catalyzed hydrogen production from methanol–water mixtures.

We previously reported the dehydrogenative oxidation of alcohols[10] catalyzed by iridium complexes **4**[10c] and **5**[10d] (structures shown in Scheme 3) bearing functional bipyridine and bipyridonate ligands, respectively. Primary and secondary alcohols were efficiently converted to carbonyl products with accompanying evolution of hydrogen. Following the successful dehydrogenative oxidation of a variety of alcohols catalyzed by **4** and **5**, dehydrogenation of methanol must be an attractive target for hydrogen production. In this study, we report the synthesis of a new water-soluble anionic iridium



	Yield
cat. **4**:	<1%
cat. **5**:	<1%
cat. **4** with 2.0 mol% NaOH:	61%
cat. **5** with 1.0 mol% NaOH:	60%
cat. **6** with 2.0 mol% NaOH:	<1%
cat. **7** with 2.0 mol% NaOH:	<1%

Scheme 3. Hydrogen production from a methanol–water solution catalyzed by iridium complexes **4**–**7**.

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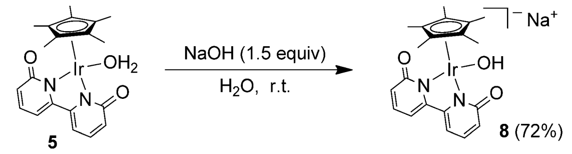
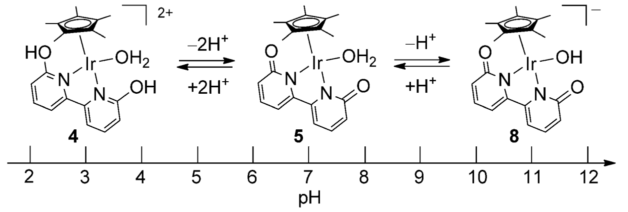
complex and its high catalytic activity for hydrogen production from a methanol–water solution.

Firstly, hydrogen production from a methanol–water solution was examined using **4** and **5** (Scheme 3). When the methanol–water solution (molar ratio of methanol/water = 1:4) was refluxed[11] for 20 h in the presence of **4** or **5** (0.50 mol %), the reaction did not proceed at all. However, addition of a catalytic amount of base (NaOH) greatly improved the activity, giving a mixed gas of hydrogen and carbon dioxide ($H_2/CO_2 = 3:1$) in 61 % (with **4**) and 60 % (with **5**) yields.[12] These results strongly suggest that a new catalytically active species must be generated from **4** and **5** under basic conditions. Conversely, complex **6**, with a bipyridine ligand without a hydroxy moiety, and complex **7**, with a 4,4′-dihydroxy-2,2′-bipyridine ligand, did not exhibit any catalytic activity, indicating that a 6,6′-difunctionalized ligand is critical to the effective catalyst for hydrogen production from a methanol–water solution.

Because basic conditions gave rise to effective hydrogen production, we attempted to isolate the new complex generated by the reaction of **5** with a base. When the reaction of **5** with NaOH (1.5 equiv) was conducted in water, anionic hydroxo complex **8** was obtained in 72 % yield [Eq. (1)]. The structure of **8** was elucidated by spectroscopic analysis and single-crystal X-ray analysis (see the Supporting Information, SI). Complex **8** was highly soluble in water and stable in air.



Interestingly, complexes **4**, **5**, and **8** were reversibly interconverted in water upon changing the pH value (Scheme 4).[13] When $NaOH_{aq}$ was added to the solution of **4** in water, precipitation of **5** was observed at pH 6.8.[14] Upon further addition of $NaOH_{aq}$, a clear solution of **8** was obtained at pH 12.0.[15] In the reverse process, addition of $HOTf_{aq}$ to the solution of **8** resulted in precipitation of **5** at pH 6.5 and a clear solution of **4** at pH 2.7.



Scheme 4. pH-Dependent interconversion of iridium complexes **4**, **5**, and **8**.

Table 1: Optimization of the reaction conditions for hydrogen production from a methanol–water solution catalyzed by **8**.[a]

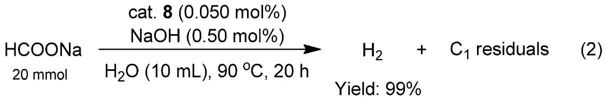
$$CH_3OH + H_2O \xrightarrow[\text{reflux, 20 h}]{\text{cat. }\mathbf{8}\text{ (0.50 mol\%)}\quad\text{NaOH (0–50 mol\%)}} 3\,H_2 + CO_2$$

Entry	CH_3OH/H_2O [mmol mmol^{-1}]	NaOH [mol %]	pH of solution start/end	Evolved H_2 [mmol]	Yield of H_2 [%]
1	20/20	0	9.5/7.4	4.9	8
2	20/80	0	9.0/7.0	6.2	10
3	20/140	0	8.4/6.9	2.8	5
4	20/80	0.30	10.2/7.6	34.9	58
5	20/80	0.50	11.1/8.2	50.2	84
6	20/80	1.0	11.6/8.4	48.0	80
7	20/80	5.0	> 13.0/10.3	37.2	62
8	20/80	50	> 13.0/ > 13.0	0.9	2

[a] Reaction was performed with methanol (20 mmol), water (20–140 mmol), **8** (0.50 mol %), and NaOH (0–50 mol %) under reflux conditions for 20 h.

Using anionic complex **8**, we investigated the optimum conditions for catalytic hydrogen production from a methanol–water solution (Table 1). When an equimolar mixture of methanol and water was refluxed in the presence of **8** (0.50 mol %) without the addition of base for 20 h, a mixed gas of hydrogen and carbon dioxide ($H_2/CO_2 = 3:1$) was evolved in 8 % yield (entry 1). The optimum ratio of methanol and water was determined to be 1:4, which afforded a 10 % yield of hydrogen (entries 1–3). In the reaction in entry 2, the pH value of the solution decreased from 9.0 to 7.0 during the reaction, which could be ascribed to the generation of carbon dioxide. Considering the pH-dependent reversible interconversion of the complexes (Scheme 4), catalytically active **8** must be converted to inactive **5** at the end of the reaction. Hence, addition of base (NaOH) was examined to keep the solution basic (entries 4–8). The highest yield of hydrogen (84 %) was obtained by addition of 0.50 mol % NaOH (entry 5).[16] In this case, the pH of the solution was kept at above 8.2 during the reaction, thus maintaining the catalytically active structure of **8**. However, addition of too much NaOH suppressed the reaction (entry 8).[17] Under the optimum conditions shown in entry 5, the concentration of base in the system was as low as ca. 0.046 mol L^{-1}. Thus, efficient catalytic hydrogen production from a methanol–water solution under desirable and mild conditions (weakly basic solution without an additional organic solvent below 100 °C) has been achieved using **8** as the catalyst.

Hydrogen production from a methanol–water solution catalyzed by **8** would proceed via formaldehyde and formic acid, as shown in Scheme 2. To obtain information about the reaction pathway, we conducted the dehydrogenation of a formaldehyde–water solution (Table 2).[18] Although **4** and **5** showed very low catalytic activities (entries 1 and 2), **8** exhibited higher activity, affording hydrogen in 57 % yield (entry 3). Furthermore, addition of NaOH (0.50 mol %) greatly improved the yield to 89 % (entry 4). Dehydrogenation of a sodium formate solution in water was also conducted [Eq. (2)].[19,20] The reaction of a sodium formate



$$\underset{\text{20 mmol}}{HCOONa} \xrightarrow[\text{H}_2\text{O (10 mL), 90 °C, 20 h}]{\text{cat. }\mathbf{8}\text{ (0.050 mol\%)}\quad\text{NaOH (0.50 mol\%)}} \underset{\text{Yield: 99\%}}{H_2 + C_1\text{ residuals}} \qquad (2)$$

Table 2: Dehydrogenation of a formaldehyde–water solution catalyzed by **4**, **5**, and **8**.[a]

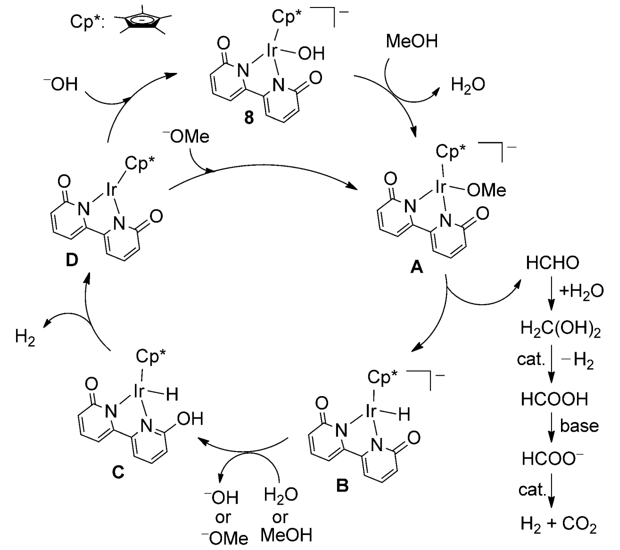
$$\underset{\text{20 mmol}}{\mathrm{HCHO}} + \underset{\text{80 mmol}}{\mathrm{H_2O}} \xrightarrow[\text{reflux, 20 h}]{\substack{\text{catalyst (0.50 mol\%)}\\ \text{NaOH (0 or 0.50 mol\%)}}} 2\,\mathrm{H_2} + \mathrm{CO_2}$$

Entry	Catalyst	NaOH [mol %]	Evolved H_2 [mmol]	Yield of H_2 [%]
1	**4**	0	4.9	12
2	**5**	0	5.1	13
3	**8**	0	22.7	57
4	**8**	0.50	35.5	89

[a] Reaction was performed with 37 % formaldehyde solution (20 mmol), water (80 mmol), iridium complex (0.50 mol %), and NaOH (0 or 0.50 mol %) under reflux conditions for 20 h.

solution in water in the presence of **8** (0.050 mol %) and NaOH (0.50 mol %) at 90 °C for 20 h resulted in the evolution of hydrogen in 99 % yield. These results, shown in Table 2 and Equation (2), clearly suggest that hydrogen production from a methanol–water solution catalyzed by **8** proceeds through the pathway shown in Scheme 2.

A possible catalytic cycle for the dehydrogenation of a methanol–water solution is presented in Scheme 5. Firstly, anionic methoxo species **A** would be formed by the reaction of **8** with methanol. β-Hydrogen elimination of **A** would occur to release formaldehyde and give anionic hydrido species **B**.[21] Protonation of the bipyridonate ligand by methanol or water would give neutral hydrido species **C**.[22] Protonolysis of the hydride on iridium with the hydroxy proton on the functional ligand would then occur to give neutral unsaturated species **D** accompanied by evolution of hydrogen. Finally, **8** or **A** would be regenerated by the reaction of **D** with a hydroxide or methoxide anion.[23] Successive dehydrogenation of formaldehyde through a formate ion to carbon dioxide would occur by a similar catalytic mechanism (see SI).



Scheme 5. Possible mechanism for the hydrogen production from a methanol–water solution catalyzed by **8**.

Based on these findings, we have designed a new system for long-term continuous hydrogen production from a methanol–water solution catalyzed by **8**. To construct the new system, the following two points were considered: 1) the substrates (methanol and water) should be continuously added to the system at the same rate as they are consumed, and 2) a small amount of base should be continuously added to keep the solution slightly basic and maintain the structure of **8**. Thus, we performed the reaction as follows (Figure 1).

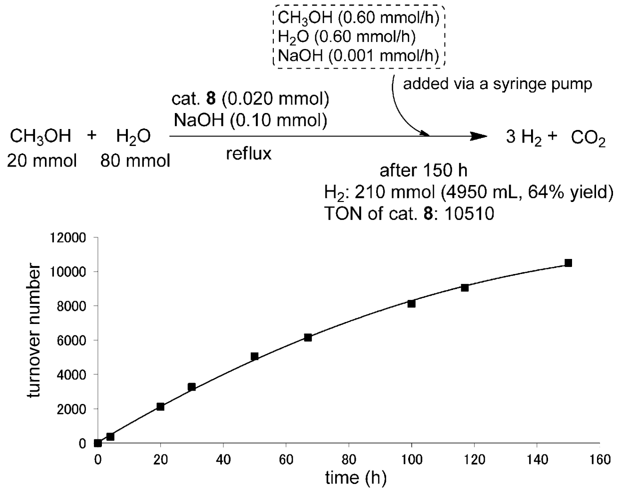


Figure 1. Long-term continuous hydrogen production from a methanol–water solution catalyzed by **8**.

Methanol (20 mmol), water (80 mmol), **8** (0.020 mmol), and NaOH (0.10 mmol) were placed in a flask and heated at reflux. During the reaction, a solution composed of methanol, water, and NaOH was continuously added through a syringe pump. The optimized rates of addition were 0.60 $\mathrm{mmol\,h^{-1}}$ for methanol and water, and 0.001 $\mathrm{mmol\,h^{-1}}$ for NaOH. According to this procedure, continuous hydrogen production was accomplished for 150 h giving 210 mmol (64 % based on methanol) of hydrogen, with the turnover number of **8** approaching 10510.

In summary, we have developed a new and efficient catalytic system for the production of hydrogen from a methanol–water solution using new anionic iridium complex **8** bearing a functional bipyridonate ligand as a catalyst. This system can be operated under mild conditions [weakly basic solution (0.046 $\mathrm{mol\,L^{-1}}$ NaOH) below 100 °C] without using an additional organic solvent. Long-term continuous hydrogen production from a methanol–water solution catalyzed by **8** was also achieved.

Keywords: dehydrogenation · homogeneous catalysis · hydrogen · iridium · methanol

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[13] The similar interconversion of **7** has been previously reported: Y. Himeda, N. Onozawa-Komatsuzaki, S. Miyazawa, H. Sugihara, T. Hirose, K. Kasuga, *Chem. Eur. J.* **2008**, *14*, 11076.

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[15] Quantitative formation of **8** at pH higher than 12.0 was ascertained by ^1H NMR analysis in D_2O.

[16] Organic bases were also effective. For example, the reaction of a methanol–water (1:4) solution in the presence of **8** (0.50 mol%) and 2,6-lutidine (0.50 mol%) resulted in 63% yield. We thank the referee for the valuable suggestion.

[17] Suppression of the reaction by too much NaOH is rationalized by considering the catalytic mechanism (Scheme 5). See Ref. [22].

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[20] When a formic acid–water solution was heated at 80 °C for 1 h in the presence of **8**, the reaction proceeded quantitatively. Because **8** must be immediately converted to **4** under acidic conditions, **4** would be highly active for dehydrogenation of a formic acid–water solution. Actually, the similar reaction catalyzed by **4** also proceeded almost quantitatively. See SI for details.

[21] We observed spectroscopic evidence of the formation of **B** from **8** by ^1H NMR analysis. We also performed the ESI-MS analysis of catalytically important iridium species in hydrogen production from a methanol–water solution catalyzed by **8**, and observed a peak probably corresponding to **B**. See SI for details.

[22] It is highly probable that protonation of **B** leading to **C** could be suppressed under too strongly basic conditions. Therefore, the reaction shown in entry 8 of Table 1 gave poor result.

[23] We spectroscopically observed the conversion of **B** to **8** that could be formed via **C** and **D**. See SI for details.

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