Electronic Supplementary Information (ESI)

Efficient H₂ generation from formic acid using azole complexes in water

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General: All manipulations were carried out under an argon atmosphere. All aqueous solutions were degassed prior to use. ¹H NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer. ¹³C NMR spectra were recorded on a Bruker Avance 500 spectrometer. Mass spectra were recorded on a Waters ZQ2000 (ESI). Elemental analyses were carried out on an Eager 200 instrument. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. UV/Vis spectra were measured on a JASCO V-550. The pH values were measured on an Orion Model 3 STAR pH meter with a glass electrode after calibration to standard buffer solutions. The volume of evolved gas was determined by a gas meter (Shinagawa Corp., W-NK-05) and the generation rate was detected with a film flow meter (HORIBA STEC, SF-1U). The formate concentration was monitored by a HPLC on an anion-exclusion column (Tosoh TSK gel SCX(H^+)) with an aqueous phosphate solution (20 μ M) as an eluent and a UV detector ($\lambda = 210$ nm). The pressure in the reactor was measured by a pressure gauge (Swagelok S Model Transducer). [RhCp*Cl₂]₂ and [IrCp*Cl₂]₂ were purchased from Sterem Chemicals. Silver sulfate and ammonium chloride were purchased from JUNSEI Chemical. Glyoxal was purchased from Tokyo Chemical Industry. 2,2'-Bipyridine was purchased from Kanto Chemical. 2-(2-Pyridyl)benzimidazole was purchased from Wako. 2-(1H-Imidazole-2-yl)pyridine and 2,2'-bis(4,5-dimethylimidazole) were purchased from Alderich. 2,2'-Bis(4,5-dimethylimidazole) was purified by washing with methanol, isopropanol and dichloromethane before use. 2-(1H-Pyrazol-3-yl)pyridine was purchased from Alfa Aesar. $[IrCp^*(H_2O)_3][SO_4]$ and $[RhCp^*(H_2O)_3][SO_4]$ were prepared according to the literature procedure.¹ 2,2'-Biimidazole was prepared according to the literature procedure.²

Catalytic dehydrogenation of formic acid: Typically, a solution of complex (100 μ L, 10 mM) was added to a deaerated 10 mL sample of aqueous formic acid solution, and the mixture was stirred at the desired temperature. Bubbles were formed immediately after addition of the complex solution even at 40 °C. While the gas generation was easily detected by a film flow meter in the early stage (i.e., less than 10 minutes), the detection stability on a longer time scale is limited. Therefore, we used a gas meter (Shinagawa Corp., W-NK-05) for the determination of the total gas volume generated. The gas meter did not work in the early stage of gas generation because it requires an appropriate pressure change or a gas accumulation (approximately 5 mL). The induction period in Figure 2 is an artefact arising from the use of the gas meter.

Dehydrogenation of formic acid in closed system: The experiments were performed in a 20 mL glass autoclave. A solution of complex 7 (100 μ L, 1 μ M) was added to a deaerated aqueous 1 M formic acid solution (7 mL), and the mixture was stirred at 80 °C.

Procedure for catalytic hydrogenation of CO₂/bicarbonate: A degassed aqueous 2 M KHCO₃ solution (10 mL) of the complex was put in a 100 mL stainless steel reactor (ChemiStation, EYELA). The reactor was heated and then repressurized with 1 MPa of CO₂:H₂ (1:1). After 1 h, samples were removed and analyzed by HPLC.

UV studies of acid–base equilibrium: The pH of the solutions was adjusted by mixing the stock solutions of complex 7 (0.1 mM) in 0.02 N H_2SO_4 and 0.1 N NaOH. The UV/Vis spectra were measured after testing the pH value.

Synthesis of the complexes:

Complex 3: An aqueous solution (10 mL) of $[IrCp*(H_2O)_3][SO_4]$ (0.3 mmol, 144 mg) and 2-(1*H*-imidazole-2-yl)pyridine (0.3 mmol, 44 mg, 1 eq.) was stirred at 30 °C for 12 h. The solution was filtered. The filtrate was evaporated. Recrystallization from water gave yellow powder; yield (123 mg, 70 %). ¹H

NMR (400 MHz, D₂O): δ = 8.95 (dt, *J* = 5.6, 1.1 Hz, 1 H), 8.22-8.06 (*m*, 2H), 7.65 (ddd, *J* = 7.4, 5.6, 1.6 Hz, 1 H), 7.56 (dd, *J* = 19.2, 1.6 Hz, 2 H), 1.63 (s, 15 H); ¹³C NMR (100 MHz, D₂O): δ = 154.69, 152.37, 149.73, 144.41, 130.39, 129.91, 125.54, 124.45, 90.93, 10.75; IR (KBr): \bar{v} = 1622, 1474, 1203 1110, 791 cm⁻¹; UV/Vis: λ_{max} 272 nm; ESI-MS (*m/z*): [M–SO₄–H₂O–H]⁺; found, 472.1; Elemental analysis calcd. for C₁₈H₂₄IrN₃O₅S + H₂O: C, 34.83; H, 4.22; N, 6.77. Found: C, 34.74; H, 4.38; N, 6.52.

Complex 4: This compound was prepared from $[IrCp^*(H_2O)_3][SO_4]$ (1 mmol, 478 mg) and 2-(1*H*-pyrazol-3-yl)pyridine (1 mmol, 145 mg, 1 eq.) according to the procedure described for the preparation of complex **3** yield (469.7 mg, 80 %); ¹H NMR (400 MHz, D₂O): $\delta = 8.91$ (d, J = 5.7 Hz, 1 H), 8.19-8.07 (m, 2 H), 8.04 (d, J = 2.9 Hz, 1 H), 7.63 (ddd, J = 7.3, 5.7, 1.9 Hz, 1 H), 7.09 (d, J = 2.9 Hz, 1 H), 1.63 (s, 15 H); ¹³C NMR (100 MHz, D₂O): $\delta = 155.91$, 154.21, 153.75, 144.44, 139.22, 130.19, 125.62, 107.73, 91.54, 10.85; IR (KBr): $\bar{v} = 1615$, 1458, 1192, 1113, 782 cm⁻¹; UV/Vis: λ_{max} 300 nm (shoulder peak); ESI-MS (*m/z*): [M–SO₄–H₂O–H]⁺; found, 472.1; Elemental analysis calcd. for C₁₈H₂₄IrN₃O₅S + H₂O: C, 34.83; H, 4.22; N, 6.77. Found: C, 35.22; H, 4.39; N, 6.85.

Complex 5: This compound was prepared from [IrCp*(H₂O)₃][SO₄] (0.3 mmol, 143 mg) and 2-(2-pyridyl)benzimidazole (0.3 mmol, 59 mg, 1 eq.) according to the procedure described for the preparation of complex **3**. yield (123.4 mg, 74 %); ¹H NMR (400 MHz, D₂O): δ = 9.11 (d, *J* = 5.4 Hz, 1 H), 8.37 (d, *J* = 7.8 Hz, 1 H), 8.30 (t, *J* = 7.9 Hz, 1 H), 7.91-7.75 (m, 3 H), 7.59-7.52 (m, 2 H), 1.67 (s, 15 H); ¹³C NMR (100 MHz, D₂O): δ = 156.70, 154.97, 149.74, 144.70, 141.09, 137.20, 132.07, 129.41, 128.44, 126.61, 119.22, 117.13, 91.52, 11.38; IR (KBr) : \bar{v} = 1625, 1459, 1118, 1027, 764 cm⁻¹; UV/Vis: λ_{max} 330 nm; ESI-MS (*m/z*): [M–SO₄–H₂O–H]⁺; found, 522.1; Elemental analysis calcd. for C₂₂H₂₆IrN₃O₅S + H₂O: C, 39.39; H, 4.21; N, 6.26. Found: C, 39.52; H, 4.19; N, 6.00.

Complex 6: This compound was prepared from $[IrCp^*(H_2O)_3][SO_4]$ (0.5 mmol, 240 mg) and 2,2'biimidazole (0.5 mmol, 67 mg, 1 eq.) according to the procedure described for the preparation of complex **3**. yield (267 mg, 93 %); ¹H NMR (400 MHz, D₂O): $\delta = 7.52$ (t, J = 1.6 Hz, 2 H), 7.41 (t, J = 1.6 Hz, 2 H), 1.67 (s, 15 H); ¹³C NMR (100 MHz, D₂O): $\delta = 143.52$, 129.77, 124.21, 90.04, 11.02; IR (KBr): $\bar{v} = 1633$, 1190, 1112, 621 cm⁻¹; UV/Vis: λ_{max} 289 nm; ESI-MS (m/z): $[M-SO_4-H_2O-H]^+$; found, 461.6. The analogous complex [IrCp*(bis-IM)Cl]⁺ was reported.³

Complex 7: This compound was prepared from [IrCp*(H₂O)₃][SO₄] (0.23 mmol, 109 mg) and 2,2'bis(4,5-dimethylimidazole) (0.23 mmol, 43.3 mg, 1 eq.) according to the procedure described for the preparation of complex **3**. yield (93.3 mg, 65 %); ¹H NMR (400 MHz, D₂O): $\delta = 2.28$ (s, 6 H), 2.18 (s, 6 H), 1.57 (s, 15 H); ¹³C NMR (100 MHz, D₂O): $\delta = 140.86$, 136.00, 129.61, 90.07, 14.57, 11.91; IR (KBr): $\bar{\upsilon} = 1593$, 1193, 1114, 799 cm⁻¹; UV/Vis: λ_{max} 314 nm; ESI-MS (*m/z*): [M–SO₄–H₂O–H]⁺; found, 517.1; Elemental analysis calcd. for C₂₀H₃₁IrN₄O₅S: C, 38.02; H, 4.95; N, 8.87. Found: C, 38.07; H, 4.78; N, 8.63.

Complex 8: A aqueous solution (10 mL) of [RhCp*(H₂O)₃][SO₄] (0.3 mmol, 117 mg) and 2,2'-bis(4,5-dimethylimidazole) (0.3 m mol, 57 mg, 1 eq.) was stirred at 30 °C for 12 h. The solution was filtered. The filtrate was evaporated. Recrystallization from water gave orange powder; yield (141 mg, 87 %); ¹H NMR (400 MHz, D₂O): δ = 2.31 (s, 6 H), 2.18 (s, 6 H), 1.59 (s, 15 H); ¹³C NMR (100 MHz, D₂O): δ = 139.23, 136.22, 129.62, 98.96, 14.62, 11.80; IR (KBr): \bar{v} = 1622, 1413, 1140 cm⁻¹; UV/Vis: λ_{max} 317 nm; ESI-MS (*m/z*): [M–SO₄–H₂O–H]⁺; found, 427.1; Elemental analysis calcd. for C₂₀H₃₁RhN₄O₆S: C, 43.00; H, 5.60; N, 10.00. Found: C, 42.8; H, 5.68; N, 9.65.

References:

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- 2. J. R. Cho, S. G. Cho, E. M. Goh, J. K. Kim, United States Patent, Mar. 30, 2004, US 6,713,631 B2
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Fig. S1. (a) The UV/Vis spectrum of **7** measured with pH varied from 2.5 to 12.5. (b) Absorbance changes at 300 nm, 315 nm, 330 nm and 375 nm as a function of pH change.

Catalyst	Conc. of catalyst (mM)	TOF ^a (h ⁻¹)	Time (h)	Minimum TON	Conversion (%)
1	2	0	-	-	-
3	0.5	110	6	430	21
4	0.5	15	6	240	12
5	0.5	60	6	410	20
6	0.1	2,640	5	4,550	45
7	0.1	5,580	4	5,000	50
8 ^b	0.5	920	8	850	43

Table S1. Dehydrogenation of formic acid/formate at pH 3.5.

Reaction conditions: 60 °C, 10 mL of 1 M aqueous sodium formate/formic acid (1/1). ^a The average value of the first 10 min. ^b Used 2 M aqueous formic acid.

Table S2. Dehydrogenation of formic acid using **7** under various catalyst concentrations and formic acid concentrations.

Conc. of catalyst	Conc. of formic acid	TOF ^a	Time	Minimum	Conversion
(mM)	(M)	(h ⁻)	(h)	ION	(%)
0.1	1	7,020	2	10,000	100
0.2	1	6,200	1.3	5,000	100
0.5	1	6,400	0.5	2,000	100
0.1	2	7,400	7	20,000	100
0.1	4	7,900	12	40,000	>99
0.1	8	6,900	-	-	-
0.2	2	7,500	3	10,000	100

Reaction conditions: 60 °C, 10 mL of aqueous formic acid. ^a The average value of the first 10 min.

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Catalvat	Conc. of catalyst	Temperature	TOF for 1 h
Catalyst	(mM)	(°C)	(h^{-1})
1	1	50	0.3
3	0.4	50	8.6
4	0.5	50	26
5	0.5	50	9.7
6	0.5	50	20
6	0.5	80	87
6	0.5	120	200
7	0.5	50	36
7	0.5	80	134
7	0.5	120	274
7	0.5	150	161
8	0.5	50	29

Table S3. Hydrogenation of CO₂/bicarbonate.

Reaction conditions: 10 mL of degassed 2 M KHCO₃ solution (pH 8.6), 1 MPa H₂/CO₂ (1/1).



UV/Vis spectrum of solution of complex 3-8 at room temperature in water: