Supporting Information

Light-Driven Catalytic Hydrogenation of Carbon Dioxide at Low -Pressure by a Trinuclear Iridium Polyhydride Complex

Shoji Shitaya, Kotohiro Nomura, Akiko Inagaki*

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Experimental Procedures

General. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were treated with appropriate drying agents, distilled, and stored under a nitrogen atmosphere. All the chemicals were purchased from common commercial suppliers. ¹H, ³¹P, and ¹³C NMR spectra were acquired on a JEOL JNM-AL400 FT-NMR spectrometers. Solvents for NMR measurements (CD₃OD, (CD₃)₂CO CD₂Cl₂) were dried over molecular sieves, degassed, and stored under N₂. UV–vis absorption spectra were obtained on a JASCO V-670 spectrometer.

Standard procedure for catalytic hydrogenation of carbon dioxide. Catalyst and base (2.3 mmol) are dissolved in MeOH (3 mL) set to an appropriate concentration. 3-(trimethylsilyl)-1-propanesulfonate is added to the reaction mixture as an internal standard. To the 10 mL glass autoclave, the solution was charged under CO₂ atmosphere and pressurized by CO₂ (5 atm) and then by H₂ (5 atm) to make the condition pressurized to 10 atm in 1:1 gas ratio of CO₂ and H₂. (Caution! The total pressure of the glass autoclave should be kept under the suitable and specified pressure level of each container.) The reaction mixture was stirred under irradiation by 3 W LED lamp (λ = 395 nm) for 24 h. After the reaction, the solution was dried under reduced pressure and the obtained solid was analyzed by ¹H NMR in D₂O to calculate the yield.



Figure S1. ¹H NMR spectrum of formate salt with the internal standard to calculate TON (entry 5).



Figure S2. ¹H NMR spectrum of formate salt with the internal standard to calculate TON (entry 9).

1 + KOH (entry 14)



Figure S3. ¹H NMR spectrum of formate salt with the internal standard to calculate TON (entry 14).



Figure S4. Plausible reaction mechanism of CO_2 hydrogenation catalyzed by **2**, and the corresponding formate intermediate. Diphosphine ligands are omitted for clarity.

(a)

	(iv) after additional irradiation (30 min) after (iii)
	(iii) after additional irradiation (10 min) after (ii)
	(ii) after 24 h under dark
	(i) 0 h (start)
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	^1H NMR spectra (400 MHz, CD_2Cl_2, δ /ppm)
(b)	
	(iv) after additional irradiation (30 min) after (iii)
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	(i) 0 h (start)
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	$^{31}P{^{1}H}$ NMR spectra (162 MHz, CD ₂ Cl ₂ , δ /ppm)

Figure S5. D₂ exchange reaction monitored for 1. (a) ¹H NMR spectra, (b) $^{31}P{^{1}H}$ NMR spectra.

(iv) after additional irradiation (20 min) after (iii)



 ^{31}P NMR spectra (162 MHz, CD_3OD, δ /ppm)

(a)

Figure S6. D₂ exchange reaction monitored for **2**. (a) ¹H NMR spectra, (b) ³¹P{¹H} NMR spectra.





Figure S7. Time conversion of spectra of **2** under atmospheric CO₂ condition. (a) ¹H NMR (400 Hz, CD₃OD, r.t.) and (b) ³¹P{¹H} NMR (162 Hz, CD₃OD, r.t.). I stands for the intermediate species from **2** to **II**. II stands for the product formed through the reaction of **2** with CO₂, most probably the formate complex.