

Supplementary Information for

Storing electrons from H₂ for transfer to CO₂, all at room temperature

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Experimental Section

Materials and Methods. All experiments were carried out under an N₂ atmosphere using standard Schlenk techniques and a glovebox. H₂ (99.9999%) and CO₂ gas (99.9999%) were purchased from Sumitomo Seika Chemical Co., Ltd, ¹³CO₂ gas (99%) were purchased from Shoko Co., Ltd, CD₃CN was purchased from Cambridge Isotope Laboratories, Inc, *n*-hexane was purchased from Kanto Chemical Co., inc, distilled water was purchased from Hayashi Pure Chemical Ind., Ltd, hydrochloric acid and CD₃OD were purchased from FUJIFILM Wako Pure Chemical Corporation and 2,2':6',2''-terpyridine (tpy) and [Ir^I(COD)(Cl)]₂ (COD = 1,5-cyclooctadiene) was purchased from Tokyo Chemical Industry Co. Ltd. These were used without further purification.

NMR spectra were recorded on a Bruker Avance III 600 FT-NMR spectrometer at 25 °C. ¹H and ¹³C NMR experiments in CD₃OD were measured using tetramethylsilane (TMS) as an internal standard. Electrospray ionisation mass spectrometry (ESI-MS) data were obtained by a JEOL JMS-T100LC AccuTOF. IR spectra were recorded on a PerkinElmer Spectrum Two as a solid state. Ultraviolet-visible-near-infrared (UV-vis-NIR) spectra were recorded on a JASCO V-670 UV-Visible-NIR Spectrophotometer (light pass length: 0.10 cm). Elemental analysis data were obtained by a Yanaco CHN-coder MT-5. X-ray photoelectron (XP) spectra were recorded on an ULVAC PHI 5000 VersaProbe II system with an Al anode X-ray source. Binding energies were calibrated by the C 1s peak of carbon at 284.5 eV.¹

[Ir^{II}₂(tpy)₂(CH₃CN)₂(Cl)₂]Cl₂ {[1]Cl₂**}**. An acetonitrile solution (18 mL) of tpy (0.14 g, 0.60 mmol) was added to an acetonitrile solution (30 mL) of [Ir^I(COD)(Cl)]₂ (0.20 g, 0.30 mmol) at room temperature. After stirring for 1 h at room temperature, the colour of the solution changed from yellow to blue. An HCl aqueous solution at pH 2 (100 mL) was added to the blue solution and stirred for 2 h at room temperature. After stirring for 4 h at 60 °C, the blue solution turns red. Then, the solvents were removed under reduced pressure. The residue was dissolved in water (3 mL) and acetonitrile (1 mL), and the solution was stirred under air for 12 h at 70 °C. Acetonitrile (50 mL) was added to the resulting solution to afford red solid. The red solid was collected by filtration and washed with acetonitrile (3 × 5 mL) and diethyl ether (3 × 5 mL) and dried in vacuo {yield: 87% based on [Ir^I(COD)(Cl)]₂}. ¹H NMR (600 MHz, in CD₃OD, referenced to TMS, 25 °C): δ 3.25 (s, 6H, -NCCCH₃), 7.67–7.70 (dd, 4H, 5 and 5''-H of tpy), 8.01–8.05 (dd, 2H, 4'-H of tpy), 8.06–8.09 (d, 4H, 3' and 5'-H of tpy), 8.10–8.15 (m, 8H, 3, 3', 5'

and 3''-*H* of tpy), 8.49–8.52 (d, 4H, 6 and 6''-*H* of tpy). ESI-MS (in methanol): m/z 461.0 {0.5[1–2CH₃CN]}⁺, relative intensity (*I*) = 100% in the range m/z 100–2000}. Anal. Calcd for [1]Cl₂·4H₂O: C₃₄H₃₆Cl₄Ir₂N₈O₄: C, 35.61; H, 3.16; N, 9.77%. Found: C, 35.55; H, 3.01; N, 9.62%.

[Ir^{II}(tpy)₂(CH₃CN)₂(Cl)₂](PF₆)₂ {[1](PF₆)₂}. An aqueous solution (10 mL) of NH₄PF₆ (45 mg, 0.28 mmol) and [1]Cl₂ (30 mg, 0.028 mmol) was stirred for 1 h at room temperature to afford red solid. The red solid was collected by filtration. The solid was washed with H₂O (3 × 3 mL) and dried in vacuo {yield: 83% based on [1]Cl₂}.

[Ir^I(tpy)(Cl)] (2). A methanol solution (5.0 mL) of [1]Cl₂ (50 mg, 0.047 mmol) and sodium acetate (7.6 mg, 0.093 mmol) was stirred under an H₂ atmosphere (0.1–0.8 MPa) for 6 h at room temperature to afford a blue solution. The solvent was removed under reduced pressure to afford dark blue solid. The solid was purified by a Sephadex LH-20 column eluted with methanol. The filtrate was evaporated under reduced pressure to yield black solid {yield: 94% based on [1]Cl₂}. ESI-MS (in methanol): m/z 454.1 {[2–Cl+N₂]}⁺, *I* = 100% in the range m/z 100–2000}. Anal. Calcd for [2]·H₂O: C₁₅H₁₃ClIrN₃O: C, 37.62; H, 2.74; N, 8.77%. Found: C, 37.31; H, 2.89; N, 9.00%.

[Ir^{III}(tpy)(COO)(CH₃CN)(Cl)] (3). Acetonitrile (6.0 mL), acetone (2.0 mL) and dichloromethane (1.0 mL) were added to **2** (4.0 mg, 8.7 μmol). The suspension was stirred under a CO₂ atmosphere (0.5 MPa) for 48 h at room temperature. The resulting solution was analysed by ESI-MS. ESI-MS (in CH₃CN/acetone/dichloromethane): m/z 547.0 {[3+H]}⁺, *I* = 70% in the range m/z 100–2000}.

[Ir^{III}(tpy)(COO)(CD₃CN)(Cl)] (D₃-labelled 3). [Ir^{III}(tpy)(COO)(CD₃CN)(Cl)] was prepared by the same method for the synthesis of **3** except the use of CD₃CN instead of CH₃CN. ESI-MS (in CD₃CN/acetone/dichloromethane): m/z 550.0 {[D₃-labelled 3+H]}⁺, *I* = 50% in the range m/z 100–2000}.

[Ir^{III}(tpy)(COOCH₃)(NHCOCH₃)(Cl)] (4). A methanol/acetonitrile (1/1) solution (40 mL) of **2** (40 mg, 87 μmol) was stirred under a CO₂ atmosphere (0.5 MPa) for 12 h at room temperature. Diethyl ether (300 mL) and hexane (160 mL) were added to the resulting solution to yield a brown solid (yield: 72% based on **2**). ¹H NMR (600 MHz, in CD₃OD, referenced to TMS, 25 °C): δ 2.40 {s, 3H, –HNC(O)CH₃}, 3.21 {s, 3H, –C(O)OCH₃}, 7.86–7.90 (dd, 2H, 5 and 5''-*H* of tpy), 8.32–8.36 (dd, 2H, 4 and 4''-*H* of tpy), 8.37–8.42 (dd, 1H, 4'-*H* of tpy), 8.58–8.62 (d, 2H, 3' and 5'-*H* of tpy),

8.63–8.65 (d, 2H, 3 and 3''-H of tpy), 8.78–8.81 (d, 2H, 6 and 6''-H of tpy). ¹³C NMR (150 MHz, in CD₃OD, referenced to TMS, 25 °C): δ 25.3, 48.1, 124.3, 125.9, 129.3, 141.5, 141.7, 147.0, 153.9, 157.8, 160.2, 182.6. FT-IR (cm⁻¹, solid state): 1602 (ν_{C=O}). ESI-MS (in acetonitrile): *m/z* 543.1 {[4-Cl]⁺, *I* = 100% in the range *m/z* 100–2000}. Anal. Calcd for [4]·H₂O: C₁₉H₂₀ClIr N₄O₄: C, 38.29; H, 3.38; N, 9.40%. Found: C, 38.61; H, 3.43; N, 9.35%.

[Ir^{III}(tpy)(COOCD₃)(NDCOCH₃)(Cl)] (D₄-labelled 4). A CD₃OD/CH₃CN (1/1) solution (2 mL) of **2** (2 mg, 4.35 μmol) was stirred under a CO₂ atmosphere (0.5 MPa) for 12 h at room temperature. The resulting solution was analysed by ESI-MS. ESI-MS (in CD₃OD/CH₃CN): *m/z* 547.1 {[D₄-labelled 4-Cl]⁺, *I* = 100% in the range *m/z* 100–2000}.

[Ir^{III}(tpy)(COOCH₃)(NHC OCD₃)(Cl)] (D₃-labelled 4). A CH₃OH/CD₃CN (1/1) solution (2 mL) of **2** (2 mg, 4.35 μmol) was stirred under a CO₂ atmosphere (0.5 MPa) for 12 h at room temperature. The resulting solution was analysed by ESI-MS. ESI-MS (in CH₃OH/CD₃CN): *m/z* 546.1 {[D₃-labelled 4-Cl]⁺, *I* = 100% in the range *m/z* 100–2000}.

Formation of 4 in the presence of H₂¹⁸O. A methanol/acetonitrile (1/1) solution (2 mL) of **2** (2 mg, 4.35 μmol) with H₂¹⁸O (10 μL) was stirred under a CO₂ atmosphere (0.5 MPa) for 12 h at room temperature. The resulting solution was analysed by ESI-MS. ESI-MS (in methanol): *m/z* 543.1 {[4-Cl]⁺, *I* = 100% in the range *m/z* 100–2000}.

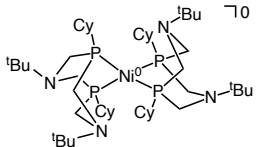
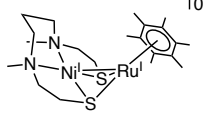
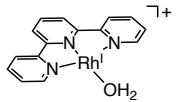
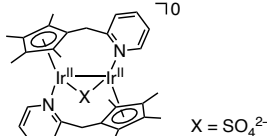
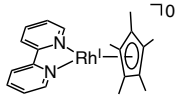
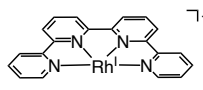
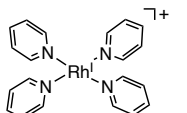
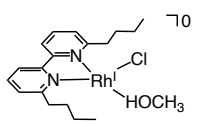
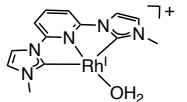
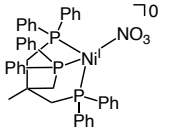
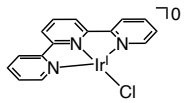
pH Adjustment. The pH values of the solutions were determined by a pH meter (IQ Scientific Instruments, Inc., IQ200) equipped with a stainless-steel micro pH probe (IQ Scientific Instruments, Inc., PH15-SS).

X-ray Crystallographic Analysis. A single crystal of [1](PF₆)₂ was obtained by diffusion of diethyl ether into the acetonitrile solution. A single crystal of **4** was obtained by diffusion of diethyl ether into the reaction solution under an N₂ atmosphere. Measurements were made on a Rigaku XtalLAB/HyPix-6000HE with graphite monochromated Mo-Kα radiation (λ = 0.71070 Å). Data were collected and processed using the CrysAlis Pro program. All calculations were performed using the Olex2 except for refinement, which was performed using SHELXL-97. Crystallographic data for [1](PF₆)₂ and **4** have been deposited with the Cambridge Crystallographic Data Centre under reference numbers CCDC-2302205 and 2302206, respectively.

Table S1. Characterisation of Ir complexes 1–4

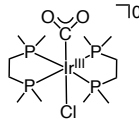
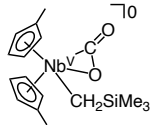
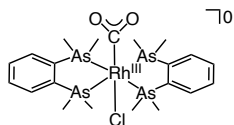
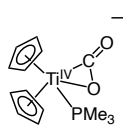
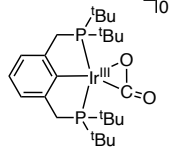
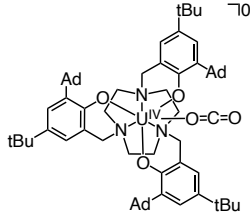
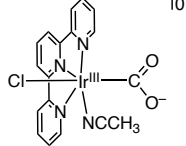
	Ir ^{II} dinuclear complex 1	Ir ^I low-valent complex 2	Ir ^{III} CO ₂ ²⁻ complex 3	Ir ^{III} methoxy- carbonyl complex 4
X-ray	Figure 1	–	–	Figure 4
ESI-MS	Figure S2	Figure 2	Figure 3	Figure S11
¹ H NMR	Figure S1	–	–	Figure S7
¹³ C NMR	–	–	–	Figure S8
UV-vis-NIR	Figure S4	Figure S4	–	Figure S6
XPS	Figure S3	Figure S3	–	–
FT-IR	–	–	–	Figure S10

Table S2. The hydrogenase model complexes that extract electrons from H₂ at room temperature and use it for the reduction of substrates at room temperature

Entry	Hydrogenase model complex	Substrates	Ref.
1 [†]		—	2
2		Cu ^{II}	3
3		O ₂	4
4		Cu ^{II}	5
5		aryl fluoride	6
6		methyl iodide	7
7		ferrocenium ion	8
8		aryl iodide	9
9		O ₂	10
10		ferrocenium ion	11
11		CO ₂	This work

[†]Electrochemical H₂ oxidation.

Table S3. Mononuclear CO₂-complex synthesised from the reaction of low-valent metal complex with CO₂ at room temperature or below

Entry	CO ₂	Detection method	Temp.	Electron source	Ref.
1		IR	r.t.	[Ir ^I (COE) ₂ (Cl)] ₂ COE = cyclooctene	12
2		X-ray, IR, NMR	r.t.	Na	13
3		X-ray	–	[Rh ^I (C ₂ H ₄) ₂ (Cl)] ₂	14
4		NMR, IR	r.t.	Mg	15
5		NMR, IR	r.t.	[Ir ^I (COD)(Cl)] ₂ COD = 1,5-cyclooctadiene	16
6		X-ray	r.t.	[U ^{III} (N(SiMe ₃) ₂) ₃]	17
7		ESI-MS	r.t.	H ₂	This work

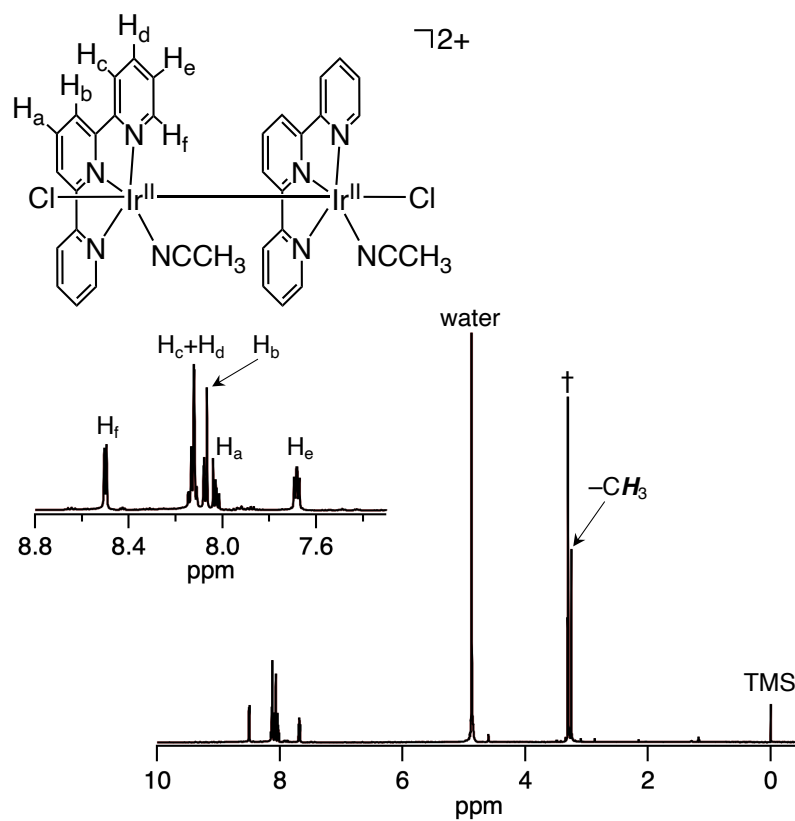


Fig. S1 A ^1H NMR spectrum of **1** in CD_3OD . †: Peak of methanol. Tetramethylsilane (TMS), reference with the methyl proton resonance set at 0.00 ppm. Inset: the enlarged ^1H NMR spectrum between 7.3 and 8.8 ppm.

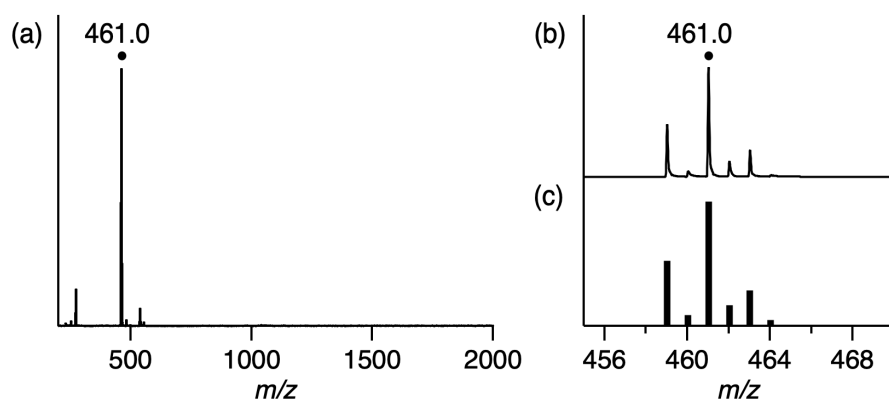


Fig. S2 (a) Positive-ion ESI mass spectrum of **1** in methanol. The signal at m/z 461.0 corresponds to half of $[\mathbf{1}-2\text{CH}_3\text{CN}]^+$. (b) The signal at m/z 461.0 for half of $[\mathbf{1}-2\text{CH}_3\text{CN}]^+$. (c) The calculated isotopic distribution for half of $[\mathbf{1}-2\text{CH}_3\text{CN}]^+$.

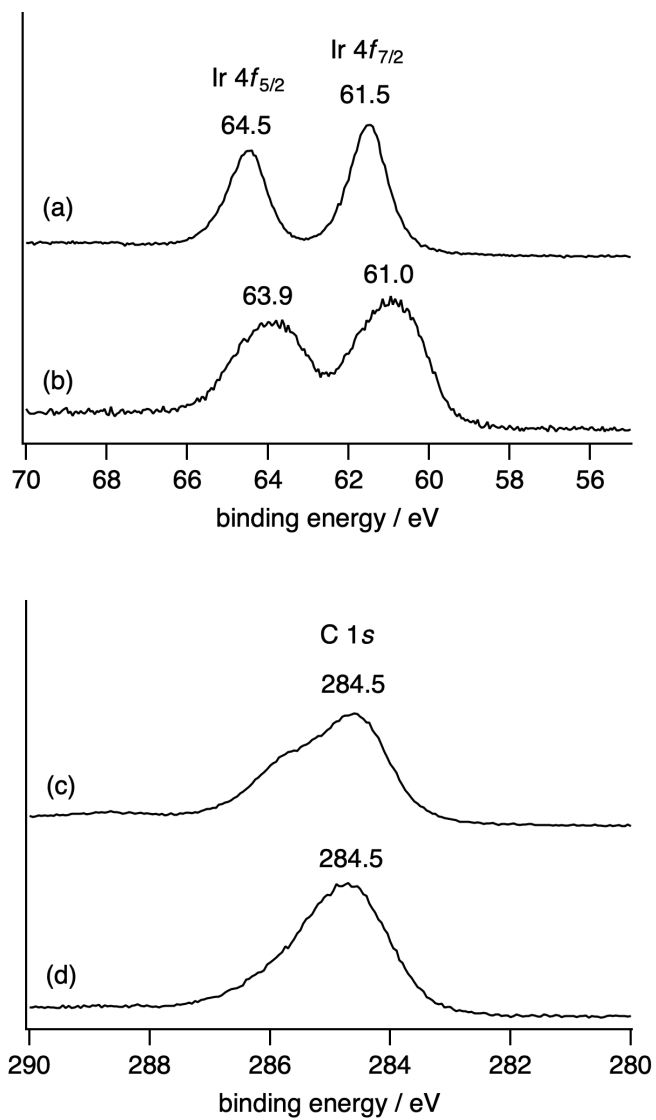


Fig. S3 XPS spectra of the Ir 4f region for (a) **1** and (b) **2** and the C 1s region for (c) **1** and (d) **2**.

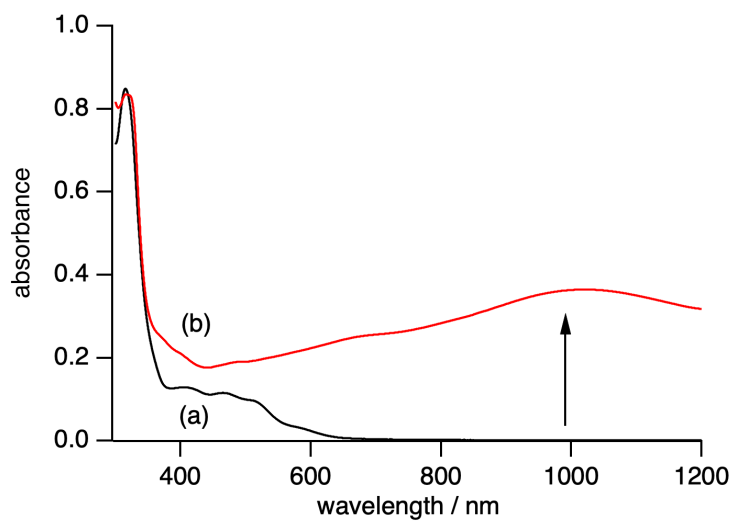


Fig. S4 UV-vis-NIR absorption spectra of (a) **1** (0.4 mM) in methanol and (b) **2** (0.8 mM) in methanol. The light path length is 0.1 cm.

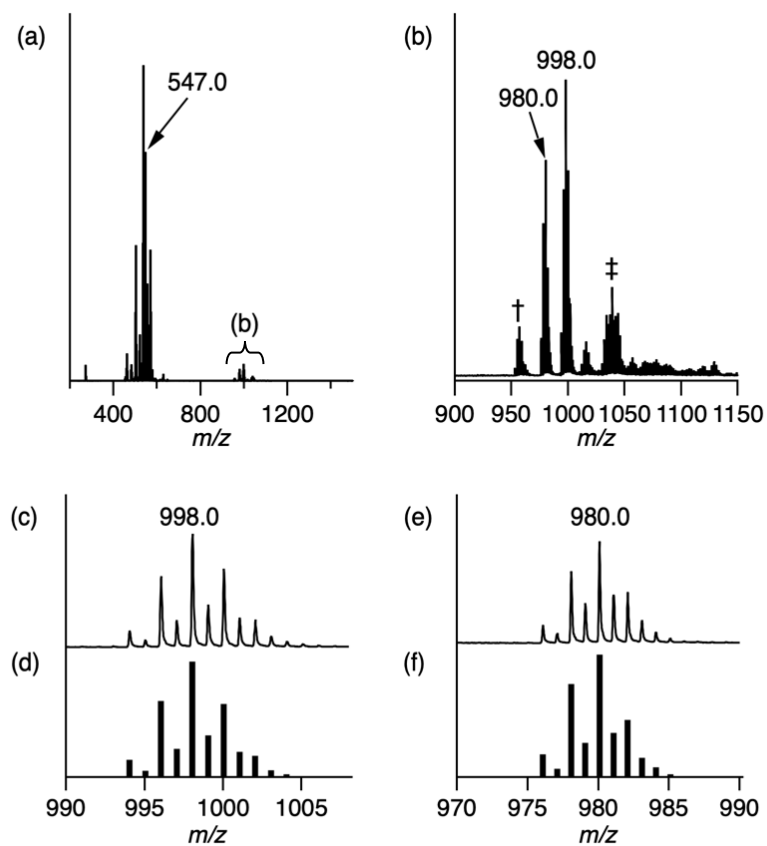


Fig. S5 (a) Positive-ion ESI mass spectrum of a thermodynamically transient **3** in CH₃CN/acetone/CH₂Cl₂. The signal at m/z 547.0 corresponds to $[\mathbf{3}+\text{H}]^+$. (b) The enlarged positive-ion ESI mass spectrum of **3** in CH₃CN/acetone/CH₂Cl₂ between m/z 900–1150. The signal at m/z 998.0 corresponds to $[\mathbf{1}-\text{CH}_3\text{CN}+\text{Cl}]^+$. The signal at m/z 980.0 corresponds to $[\mathbf{1}-2\text{CH}_3\text{CN}+\text{CH}_3\text{CONH}]^+$. †: m/z 957.0 for $[\mathbf{1}-2\text{CH}_3\text{CN}+\text{Cl}]^+$. ‡: Not assigned signal. (c) The signal at m/z 998.0 corresponds to $[\mathbf{1}-\text{CH}_3\text{CN}+\text{Cl}]^+$. (d) The calculated isotopic distribution for $[\mathbf{1}-\text{CH}_3\text{CN}+\text{Cl}]^+$. (e) The signal at m/z 980.0 corresponds to $[\mathbf{1}-2\text{CH}_3\text{CN}+\text{CH}_3\text{CONH}]^+$. (f) The calculated isotopic distribution for $[\mathbf{1}-2\text{CH}_3\text{CN}+\text{CH}_3\text{CONH}]^+$.

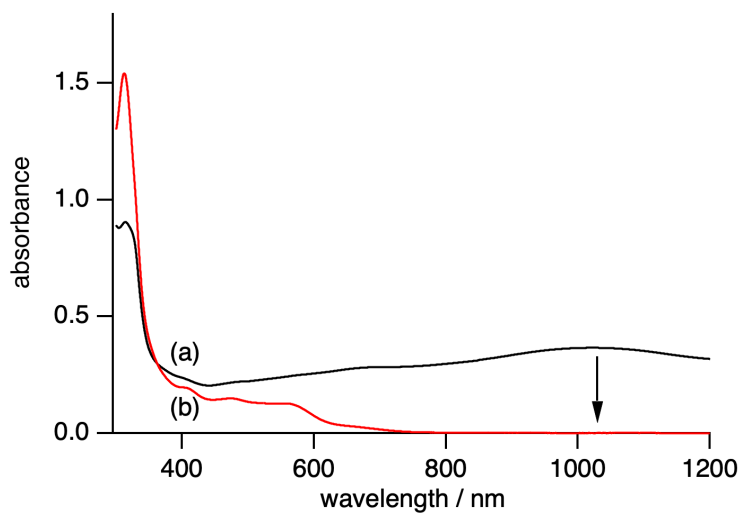


Fig. S6 UV-vis-NIR absorption spectra of (a) **2** (0.8 mM) in methanol/CH₃CN and (b) the reaction solution of **2** (0.8 mM) with CO₂ in methanol/CH₃CN. The light path length is 0.1 cm.

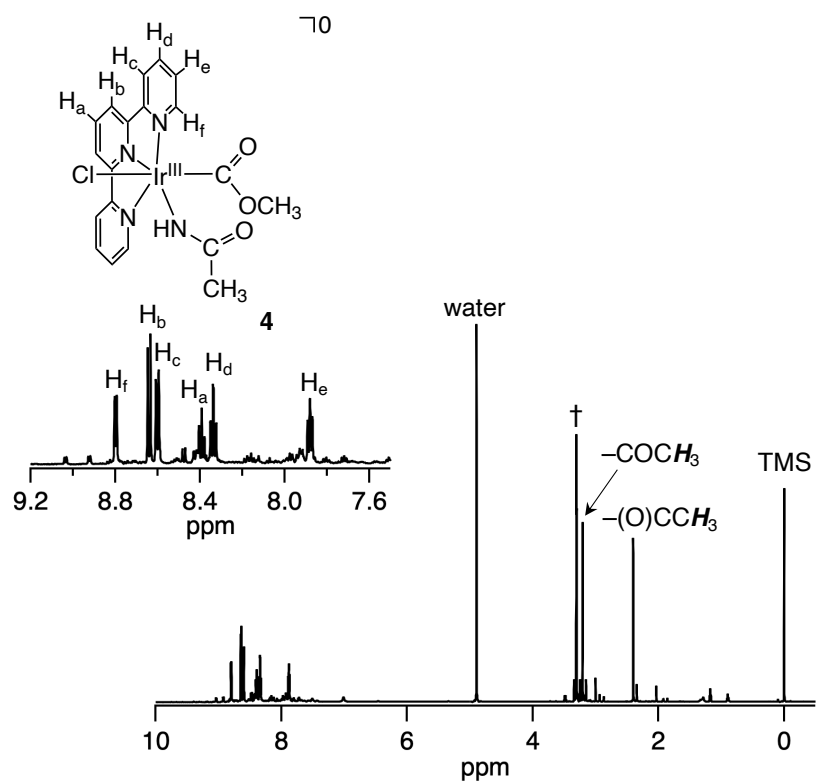


Fig. S7 A ¹H NMR spectrum of **4** in CD₃OD. †: peak of methanol. TMS, reference with the methyl proton resonance set at 0.00 ppm. Inset: the enlarged ¹H NMR spectrum between 7.5 and 9.2 ppm.

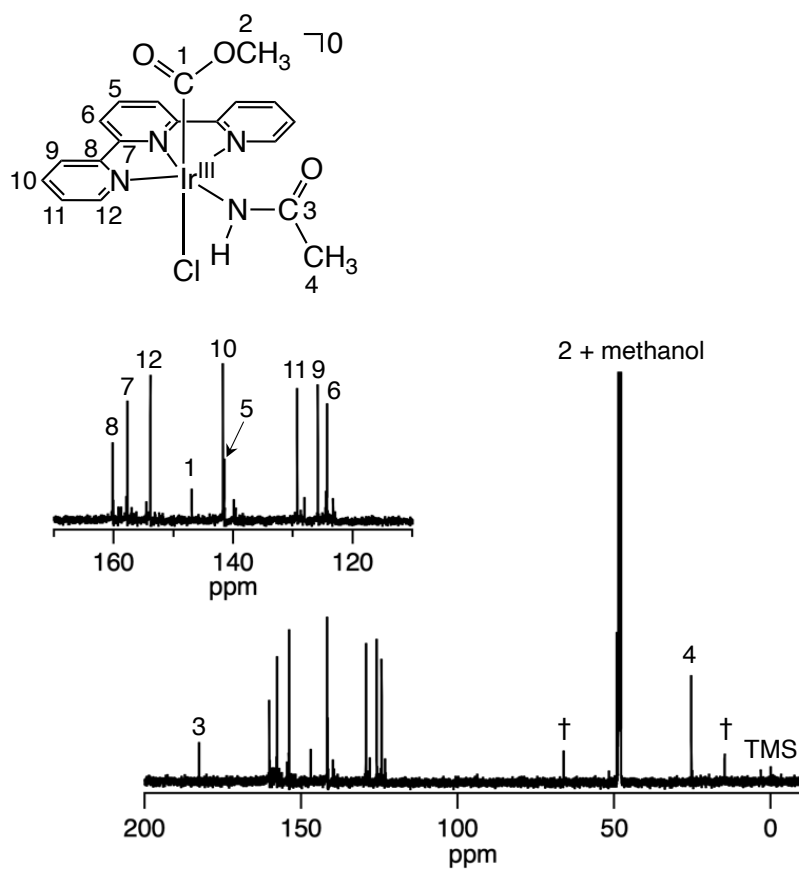


Fig. S8 A ^{13}C NMR spectrum of **4** in CD_3OD . †: Peaks of diethyl ether. TMS, reference with the methyl proton resonance set at 0.00 ppm. Inset: the enlarged ^{13}C NMR spectrum between 110 and 170 ppm.

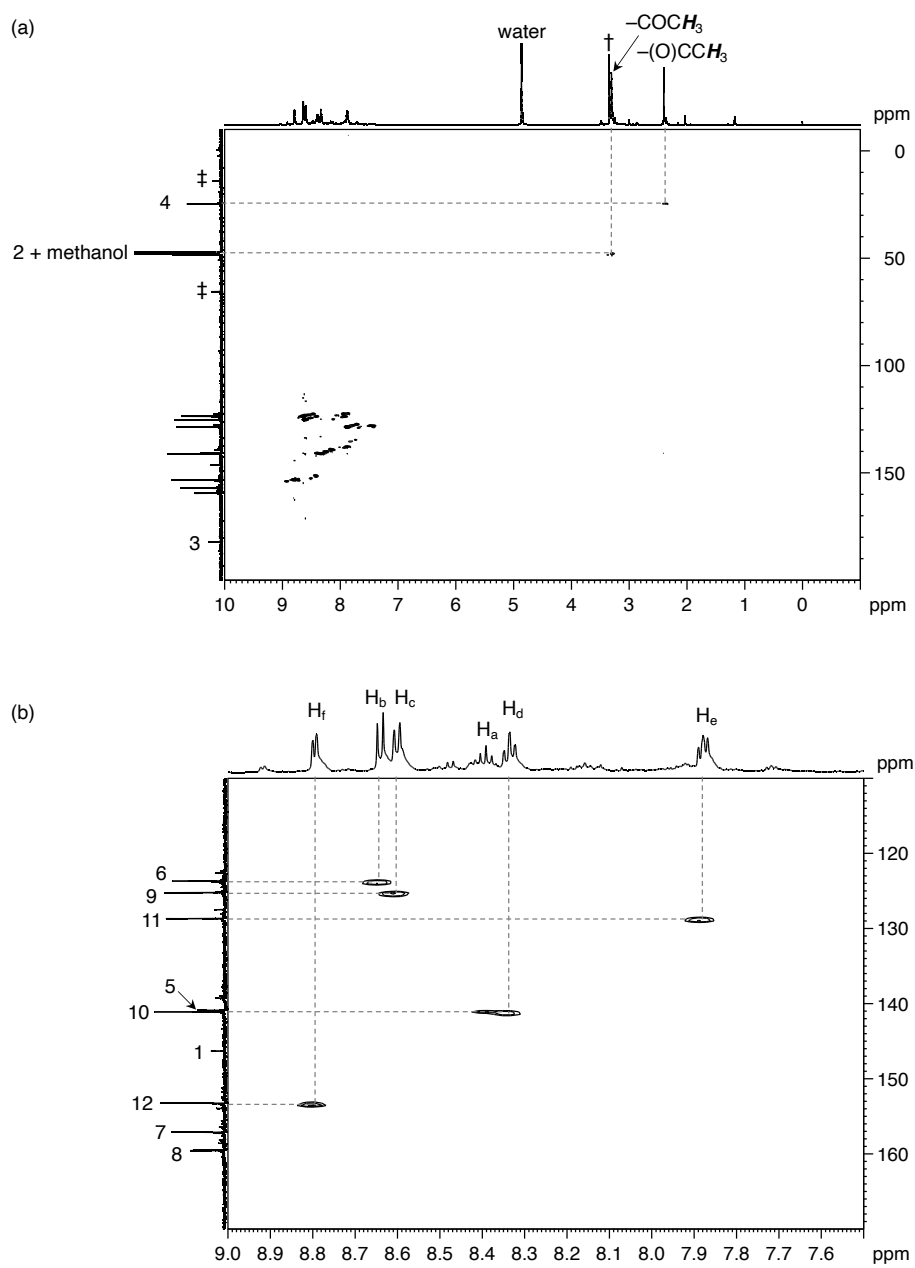


Fig. S9 (a) A heteronuclear single quantum correlation (HSQC) spectrum of **4** in CD₃OD. (b) The enlarged HSQC spectrum of **4** in the aromatic region. †: Peak of methanol. ‡: Peaks of diethyl ether.

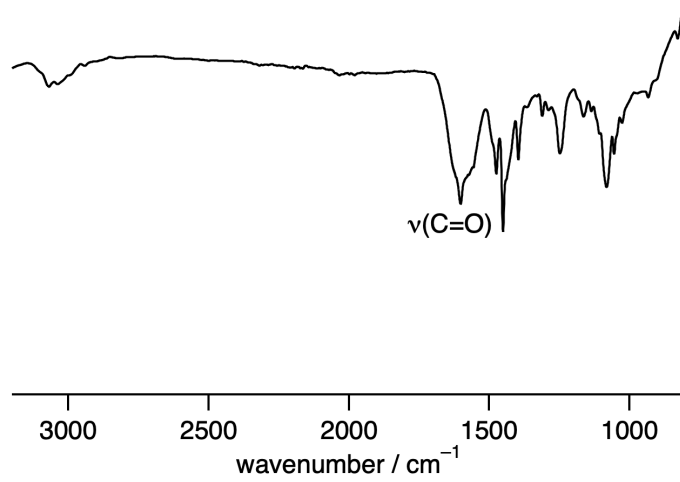


Fig. S10 An IR spectrum of **4**.

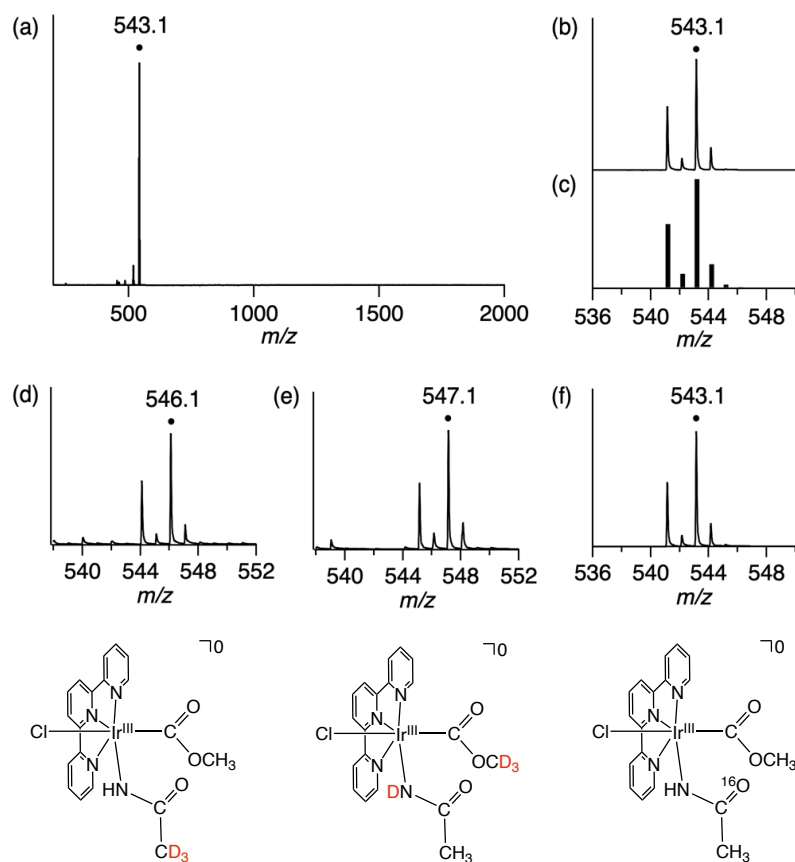


Fig. S11 (a) Positive-ion ESI mass spectrum of **4** in CH₃CN/methanol. The signal at m/z 543.1 corresponds to [**4**-Cl]⁺. (b) The signal at m/z 543.1 for [**4**-Cl]⁺. (c) The calculated isotopic distribution for [**4**-Cl]⁺. (d) Positive-ion ESI mass spectrum of the reaction solution of **2** with CO₂ in CD₃CN/methanol. The signal at m/z 546.1 corresponds to [D₃-labelled **4**-Cl]⁺. (e) Positive-ion ESI mass spectrum of the reaction solution of **2** with CO₂ in CH₃CN and CD₃OD. The signal at m/z 547.1 corresponds to [D₄-labelled **4**-Cl]⁺. (f) Positive-ion ESI mass spectrum of the reaction solution of **2** with CO₂ in CH₃CN and CH₃OH in the presence of H₂¹⁸O. The signal at m/z 543.1 corresponds to [**4**-Cl]⁺.

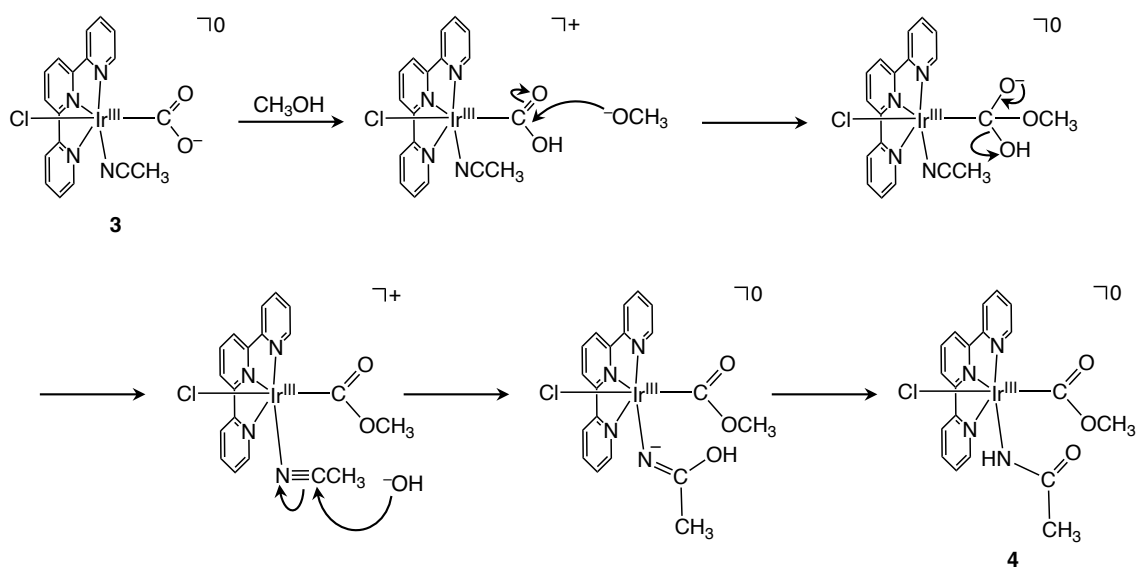


Fig. S12. Proposed reaction mechanism of the formation of **4** from **3** in the presence of methanol and CH₃CN.

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