

Supplementary Information:**H₂ Production Mediated by CO₂ via Initial Reduction to Formate**

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I. General Information

Unless otherwise noted, all manipulations were carried out under a N₂ atmosphere using standard Schlenk technique. All solvents were purchased from Fisher Scientific. Benzimidazole (98%), sodium hydride (60% dispersion in mineral oil), phenylphosphine (10% wt. in hexanes), *n*-butyllithium solution (1.6 M in hexanes), 1,4-cyclohexadiene (97%), 2,2'-bipyridyl, trimethylamine ($\geq 99\%$), tetrabutylammonium hexafluorophosphate, and sodium formate-¹³C (99 atom %) were purchased from Sigma-Aldrich. 1,2-dichloroethane (certified ACS) was purchased from Fisher Scientific. Trifluoromethanesulfonic acid (98+%) and 1,1,3,3-tetramethyldisiloxane (97%) were purchased from Alfa Aesar. Ruthenium (III) chloride hydrate was purchased from Pressure Chemical. Sodium bicarbonate (¹³C, 99%) was purchased from Cambridge Isotope Labs. [Ru(Bz)Cl₂]₂¹ and [Ru(Bz)(bpy)(OTf)](OTf)₂² were synthesized according to previously published literature procedures. ¹H, ³¹P, and ¹³C NMR were taken on either a Bruker AV500, Bruker AV700, Bruker DRX500, or Bruker AV300 spectrometer. Anhydrous DMSO-d₆ was purchased from Sigma-Aldrich, all other NMR solvents were purchased from Cambridge Isotope Labs and were used as received. IR data were taken using a Bruker Vertex 70 FTIR with an ATR attachment. Headspace analysis for H₂ was performed on a SRI 8610C Gas Chromatograph using a 6' MS-13X column at 80 °C and Ar as the carrier gas. Microanalysis samples were weighed with a PerkinElmer Model AD-6 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Time-resolved luminescence decay experiments were measured on a Fluorotime 100 lifetime spectrometer in a time-correlated single-photon-counting arrangement. A 375 nm LED with a pulse repetition rate of 500 KHz was used as the light source with a 490 nm long-pass filter. The instrument response function (FWHM~1.4 ns) was collected using a scatterer (non-dairy creamer).

II. Synthesis

1-(N-chloroethyl)-1,3-benzimidazole (bimEtCl). In a typical reaction, benzimidazole (5.0 g, 42.5 mmol, 1eq) and sodium hydride (2.04 g, 51 mmol, 1.2 eq) were added to a flask with dichloroethane (100 mL) and placed under N₂. The reaction mixture was then heated at reflux overnight, whereupon the reaction mixture was cooled and quenched with H₂O (100 mL). The organic phase was then separated and the aqueous phase was extracted with dichloromethane (50 mL). The combined organics were then washed with aqueous NaOH (2 x 100 mL), H₂O

(100 mL), and brine (100 mL). The combined organics were then dried with MgSO_4 , filtered through celite, and the solvent was removed on a rotovap. Pentane (100 mL) was added to the resulting yellow oil and the product was sonicated for 30 minutes, which resulted in a white solid that was collected on a medium porosity frit and washed with pentane. Yield: 5.65 g (74%).

^1H NMR (300 MHz, CDCl_3) δ 7.99 (s, 1H), 7.84 (m, 2H), 7.50 – 7.24 (m, 2H), 4.54 (t, $J = 6.0$ Hz, 2H), 3.88 (t, $J = 6.0$ Hz, 2H)

PhP(Etbim)₂. In a N_2 glovebox, a Schlenk flask equipped with a stir bar was charged with phenylphosphine (0.61 g, 5.5 mmol, 1 eq) and anhydrous THF (30 mL). The reaction flask was sealed and removed from the glove box, was connected to a N_2 Schlenk line, and was cooled to -78 °C before *n*-butyllithium (0.78 g, 12.2 mmol, 2.2 eq) was slowly added via syringe. The reaction mixture turned a bright orange-red color and was allowed to warm to room temperature with vigorous stirring. After sitting at room temperature for 30 min, the reaction mixture was again cooled to -78 °C and a solution of bimEtCl (2.0 g, 11 mmol, 2 eq) in THF (20 mL) was added via cannula. The reaction mixture was warmed to room temperature and then heated at 55 °C overnight. After allowing the reaction mixture to cool, H_2O (100 mL) was added to the reaction vessel to quench the reaction and the organic phase was separated. The aqueous phase was washed with dichloromethane (2 x 80 mL). The organic layers were combined and washed with H_2O (2 x 100 mL) and brine (100 mL), then dried over MgSO_4 , filtered through celite, and the solvent removed on a rotovap to give a cloudy yellow oil. Diethylether (200 mL) was added and the flask was sonicated for 30 min. The resulting white powder was collected on a medium porosity frit and was washed with diethylether. Yield: 1.47 g (67%).

^1H NMR (500 MHz, CDCl_3) δ 7.76 (m, 4H), 7.53 – 7.43 (m, 5H), 7.31 – 7.18 (m, 6H), 4.15 (tdd, $J = 14.7, 12.1, 6.5$ Hz, 4H), 2.23 (d, $J = 29.3$ Hz, 4H)

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) δ -32.9

$[\text{Ru}(\text{Bz})(\text{bpy})(\text{PhP}(\text{EtbimH}^+)_2)](\text{PF}_6)_4$. A three-necked round bottom flask equipped with a stir bar was charged with $\text{PhP}(\text{Etbim})_2$ (818 mg, 2.1 mmol, 1 eq) and ethanol (50 mL). The mixture was degassed with N_2 . Trifluoromethanesulfonic acid (7.6 g, 5.0 mmol, 2.4 eq) was then carefully added to the reaction mixture via syringe and the mixture was stirred at room

temperature for 10 min with N₂ flowing over the reaction solution and venting through a needle. A solution of [Ru(Bz)(bpy)(OTf)](OTf) (1.30 g, 2.1 mmol, 1 eq) in ethanol (20 mL) was then added via syringe and the reaction was heated at reflux for 45 min. The reaction solution was then added to an aqueous solution of NH₄PF₆ (30 mL) and the ethanol was removed on the rotovap. A light yellow solid precipitated and was collected on a medium porosity frit. The solid was washed with water and diethylether. Yield: 1.80 g (65%).

¹H NMR (500 MHz, Acetonitrile-*d*₃) δ 9.13 (s, 2H), 8.91 (d, *J* = 5.7 Hz, 2H), 8.09 (td, *J* = 7.9, 1.3 Hz, 2H), 7.99 – 7.94 (m, 2H), 7.90 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.87 – 7.82 (m, 2H), 7.77 – 7.69 (m, 4H), 7.61 (ddd, *J* = 7.4, 5.6, 1.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.03 (td, *J* = 7.8, 2.8 Hz, 2H), 6.42 (s, 6H), 6.39 – 6.33 (m, 2H), 4.76 (dddd, *J* = 14.9, 12.0, 5.6, 3.5 Hz, 2H), 4.53 (tt, *J* = 14.3, 12.2, 6.2, 3.5 Hz, 2H), 3.64 (ddt, *J* = 15.4, 12.3, 6.1 Hz, 2H), 3.25 (dddd, *J* = 15.3, 12.5, 10.2, 3.5 Hz, 2H).

³¹P{¹H} NMR (202 MHz, CD₃CN) δ 23.9

Elemental Analysis – Predicted (Actual): C, 36.52(36.60); H, 2.99(2.98); N, 6.39(6.20)

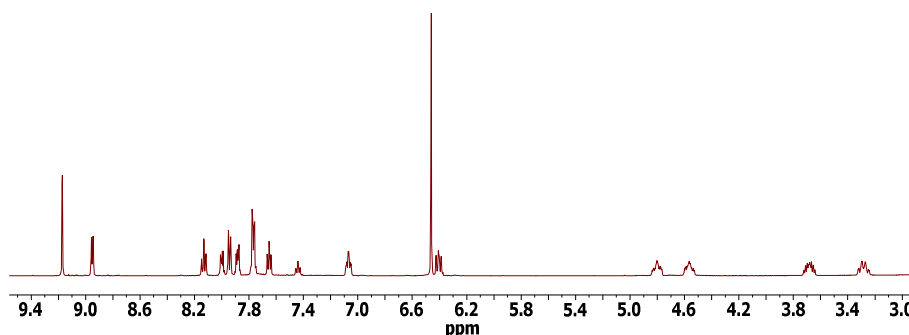


Figure S1. ¹H NMR spectrum (500 MHz, CD₃CN) of [Ru(Bz)(bpy)(PhP(EtbimH⁺)₂)](PF₆)₄.

[Ru(bpy)(PhP(Etbim)₂)(OH₂)](PF₆)₂, ([1-OH₂]²⁺). A three-necked flask was charged with [Ru(Bz)(bpy)(PhP(EtbimH⁺)₂)](PF₆)₄ (1.8 g, 1.4 mmol, 1 eq), trimethylamine (0.83 g, 8.2 mmol, 5.9 eq), and ethylene glycol (22 mL). The reaction solution was degassed with N₂ and then heated at 155 °C for 1h. After allowing the reaction mixture to cool, it was added to an aqueous NH₄PF₆ solution (100 mL). An orange solid precipitated, which was collected on medium porosity frit and was washed with water and diethylether. Yield 1.13 g (84%).

Elemental Analysis – Predicted (Actual): C, 42.38(41.76); H, 3.45(3.40); N, 8.72(8.27)

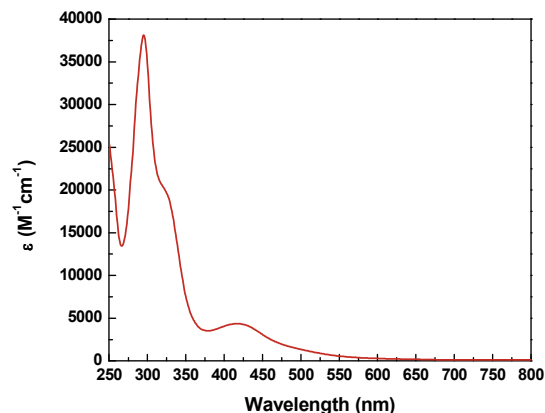


Figure S2. UV/vis spectrum of $[1\text{-OH}_2]^{2+}$ in DCM which displays an MLCT transition at 420 nm.

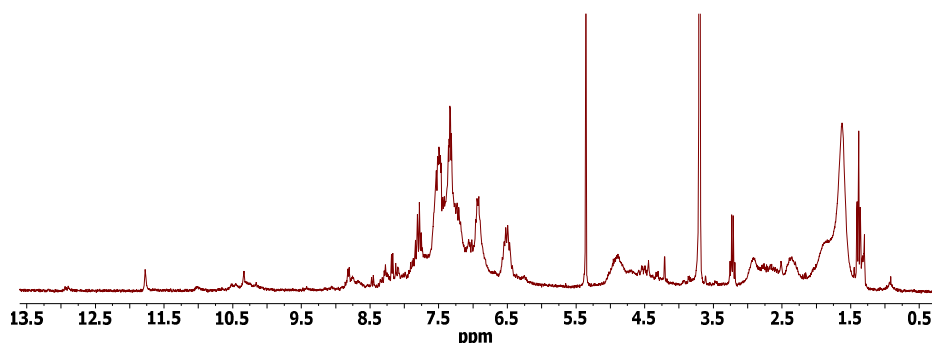


Figure S3. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of $[\text{Ru}(\text{bpy})(\text{PhP}(\text{Etbim})_2)(\text{OH}_2)](\text{PF}_6)_2$, $[1\text{-OH}_2]^{2+}$, from crude reaction in CD_2Cl_2 .

$[\text{Ru}(\text{bpy})(\text{PhP}(\text{Etbim})_2)(\text{Cl})](\text{PF}_6)$, $([1\text{-Cl}]^+)$. A vial equipped with a stir bar was charged with **1** (274 mg, 0.284 mmol, 1 eq) and NaCl (303 mg, 5.18, mmol, 18 eq) and methanol (20 ml) and was stirred for 1 hour at room temperature. The solution was transferred to a Schlenk bomb and all volatiles were removed under vacuum at 100 °C over the course of 1 hour. The evacuated Schlenk bomb and solids were brought into the glove box and the solids were dissolved in DCM and filtered through celite. The volatiles were removed via vacuum overnight giving 150 mg of a dark red powder (63.6% yield).

^1H NMR (500 MHz, Methylene Chloride- d_2) δ 11.75 (s, 2H), 8.14 (d, $J = 5.4$ Hz, 2H), 7.80 (td, $J = 7.8, 1.5$ Hz, 2H), 7.73 (d, $J = 8.2$ Hz, 2H), 7.45 (t, $J = 7.3$ Hz, 4H), 7.35 – 7.25 (m, 6H), 7.17 (t, $J = 7.5$ Hz, 1H), 6.89 (td, $J = 7.8, 2.3$ Hz, 2H), 6.46 (t, $J = 8.8$ Hz, 2H), 4.92 (dddd, $J = 25.1, 14.4, 6.6, 4.2$ Hz, 2H), 4.49 (tdd, $J = 14.4, 10.7, 3.0$ Hz, 2H), 2.75 (dddd, $J = 14.9, 10.9, 7.0, 4.3$ Hz, 2H), 2.64 (dddd, $J = 14.7, 11.9, 6.4, 3.0$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ

195.89 (d, $J_{CP} = 15.1$ Hz), 155.84, 151.77, 137.30, 136.14, 133.82, 132.34, 131.99, 129.93, 129.10, 129.02, 127.98, 127.92, 126.72, 123.68, 123.23, 122.81, 111.00, 109.43, 43.51, 23.92

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2) δ 45.7

Elemental Analysis – Predicted (Actual): C, 48.84(48.51); H, 3.74(4.53); N, 10.05(9.84)

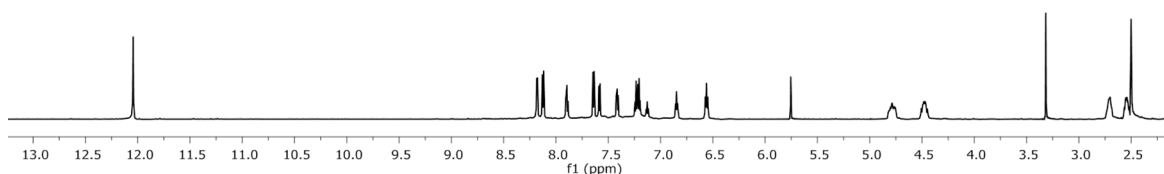


Figure S4. ^1H NMR spectrum (700 MHz, DMSO-d_6) of $[\mathbf{1-Cl}]^+$.

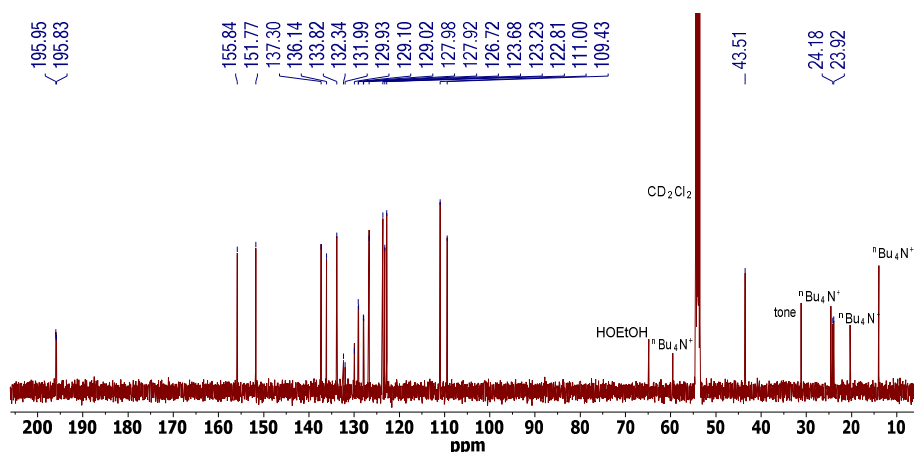


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CD_2Cl_2) of $[\text{Ru}(\text{bpy})(\text{PhP}(\text{Etbim})_2)(\text{Cl})](\text{PF}_6)$ ($[\mathbf{1-Cl}]^+$) from addition of $n\text{Bu}_4\text{NCl}$ to a sample of $[\mathbf{1-OH}_2]^{2+}$ in CD_2Cl_2 .

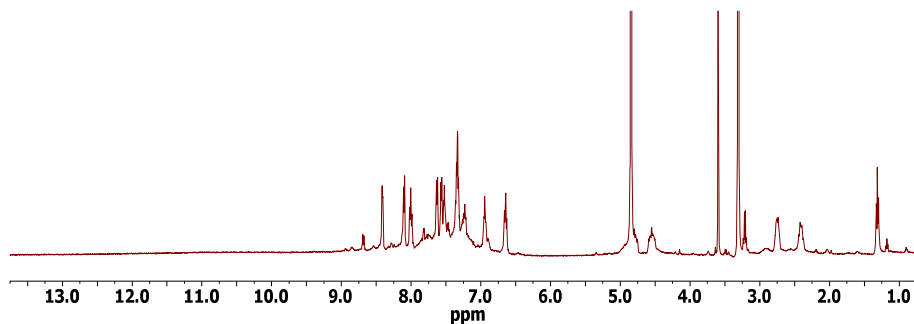


Figure S6. ^1H NMR spectrum (500 MHz, CD_3OD) of $[\mathbf{1-OH}_2]^{2+}$ showing distinct aromatic and CH_2 peaks as well as a lack of N-H peaks in the 10–13 ppm range presumably from H/D scrambling.

III. Mechanistic Studies

Formate-bridged bimetallic Ru complex (2). Open to air, a 20 ml glass vial equipped with a stir bar was charged with [**1-OH₂**]²⁺ (24.8 mg, 0.0257 mmol, 1 eq), sodium bicarbonate (2.8 mg, 0.0333 mg, 1.3 eq), and DCM (2 ml). The reaction mixture was allowed to stir for 12 hours before the solution was filtered through a syringe filter into an nmr tube. Crystals formed after several days on the inside edge of the NMR tube.

Complex **2** was also made from CO₂ by addition of a small piece of dry ice to an NMR tube containing [**1-OH₂**]²⁺ in DCM. Slow evaporation of the solution caused crystals of **2** to grow.

Monometallic Ru-formate (2m).

A mixture of [**1-OH₂**]²⁺ (21 mg, 0.022 mmol, 1 eq) and ¹³C-formate (1.5 mg, 0.022 mmol, 1 eq) were added to CD₂Cl₂ (1.5 mL) and sonicated for 30 min. After standing for 16 hours at room temperature, a yellow-orange solid precipitated and an IR was obtained of the solid. The mother liquor was decanted and the solid was dissolved in DMSO-*d*₆ for ¹H, ³¹P, and ¹³C NMR analysis.

¹H NMR (500 MHz, DMSO-*d*₆) δ 13.06 (s, 2H), 8.28 (d, *J* = 4.6 Hz, 2H), 8.15 (d, *J* = 8.3 Hz, 2H), 8.10 (dd, ¹*J*_{HC} = 193.8 Hz, ⁴*J*_{HP} = 6.2, 1H), 7.93 (t, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.50 (dd, *J* = 7.2, 1.7 Hz, 2H), 7.45 (t, *J* = 6.6 Hz, 2H), 7.25 (p, *J* = 7.0 Hz, 4H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 2H), 6.58 (t, *J* = 8.5 Hz, 2H), 4.96 – 4.80 (m, 2H), 4.41 (q, *J* = 13.2 Hz, 2H), 2.76 – 2.63 (m, 2H), 2.64 – 2.55 (m, 2H).

¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 170.30

³¹P{¹H} NMR (202 MHz, CD₂Cl₂) δ 51.9

Synthesis of Ruthenium carbamate in situ (3). ¹³C labeled sodium formate was dried in a Schlenk bomb under vacuum at 100 °C overnight before being transferred into a N₂ glove box. In a N₂ glovebox, a J-Young tube was charged with [**1-Cl**]⁺ (44.5 mg, 0.0532 mmol, 1 eq), ¹³C labeled sodium formate (5.7 mg, 0.0826 mmol, 1.6 eq), and anhydrous DMSO-*d*₆ (1.4 ml). The reaction

showed 100% conversion to **3** *in situ* after heating at 60 °C for 68 hours or after 2 hours at 100 °C.

^1H NMR (700 MHz, $\text{DMSO-}d_6$) δ 12.24 (s, 1H), 8.37 (tt, $J = 8.2, 1.0$ Hz, 2H), 8.22 (ddd, $J = 5.5, 1.7, 0.8$ Hz, 1H), 8.10 (ddd, $J = 5.4, 1.6, 0.8$ Hz, 1H), 8.03 (td, $J = 7.8, 1.6$ Hz, 1H), 8.01 (td, $J = 7.8, 1.6$ Hz, 1H), 7.99 (ddd, $J = 7.8, 1.3, 0.6$ Hz, 1H), 7.69 (dd, $J = 8.1, 4.8$ Hz, 2H), 7.56 – 7.50 (m, 2H), 7.46 (ddd, $J = 7.7, 5.4, 1.3$ Hz, 1H), 7.33 (td, $J = 7.8, 1.3$ Hz, 1H), 7.29 (td, $J = 7.7, 1.2$ Hz, 1H), 7.25 (td, $J = 7.7, 1.3$ Hz, 1H), 7.22 (td, $J = 7.6, 1.1$ Hz, 1H), 7.13 (tq, $J = 7.5, 1.1$ Hz, 1H), 6.89 (td, $J = 7.9, 1.9$ Hz, 2H), 6.64 (ddd, $J = 9.6, 8.1, 1.3$ Hz, 2H), 5.14 (ddt, $J = 30.0, 14.4, 4.6$ Hz, 1H), 4.83 (dddd, $J = 25.7, 14.7, 7.3, 4.1$ Hz, 1H), 4.63 (dddd, $J = 17.2, 13.9, 10.3, 2.7$ Hz, 1H), 4.50 (ddt, $J = 14.8, 9.8, 6.4$ Hz, 1H), 2.89 – 2.83 (m, 2H), 2.78 (dddd, $J = 14.7, 10.3, 7.1, 3.1$ Hz, 1H), 2.63 (dddd, $J = 14.7, 11.0, 7.7, 4.0$ Hz, 1H).

^{31}P NMR (283 MHz, $\text{DMSO-}d_6$) δ 45.53 (d, $^4J_{\text{PC}} = 7.0$ Hz).

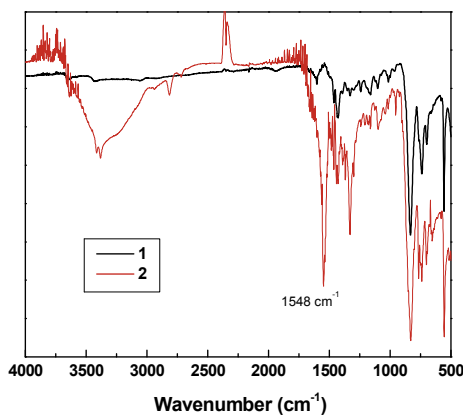


Figure S7. ATR-IR of powders of $[\mathbf{1-OH}_2]^{2+}$ and **2** showing a strong stretch at 1548 cm^{-1} for the bridging formate in **2**.

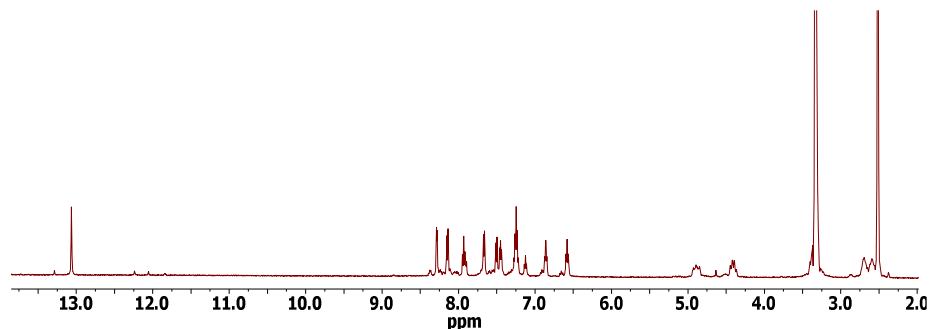


Figure S8. ^1H NMR spectrum (500 MHz, DMSO-d_6) of precipitate from reaction of ^{13}C -formate and $[\mathbf{1-OH}_2]^{2+}$ in DCM.

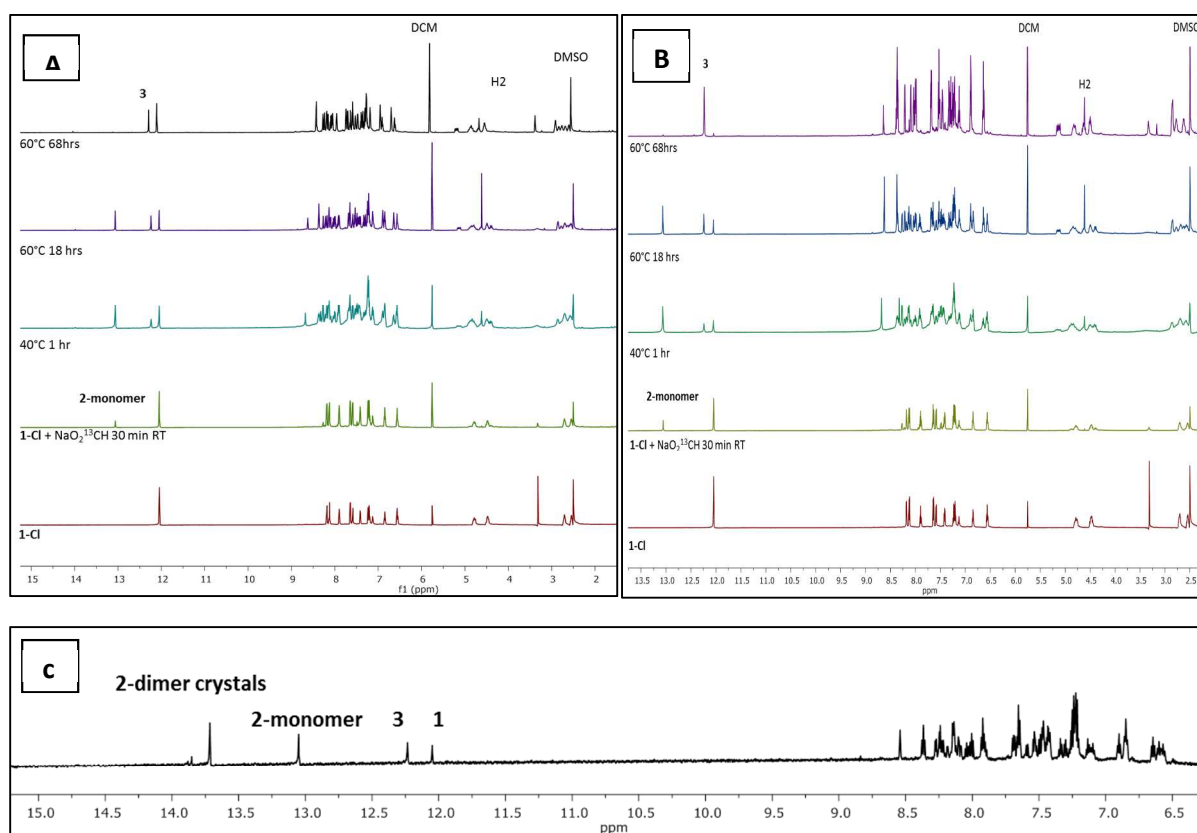


Figure S9. ^1H NMR spectrum of $[\mathbf{1-Cl}]^+$ plus 1 (A) and 0.5 (B) equivalents of NaHCO_2 showing formation of 1 equivalent of **3** and 0.5 equivalents of **3**, respectively, supporting the identity of the species in Figure S8 as the monometallic Ru-formate. (C) ^1H NMR of the N-H region of crystals of **2** dissolved in DMSO-d_6 after 10 minutes showing the spontaneous decomposition of **2** into $[\mathbf{1-OH}_2]^{2+}$ and the monometallic formate with partial conversion to **3**.

Reaction of HCO_3^- with $[\mathbf{1-OH}_2]^{2+}$ and added TMDS. A J-Young tube was charged with $[\mathbf{1-OH}_2]^{2+}$ (14 mg, 0.015 mmol, 1 eq), $\text{NaH}^{13}\text{CO}_3$ (12 mg, 0.15 mmol, 10 eq), and TMDS (26 μL , 0.15 mmol, 1 eq) in DMSO-d_6 and was heated at 50 °C for 16 hours. Complete conversion to **3** was observed by ^{13}C and ^{31}P NMR spectroscopy. Heating $[\mathbf{1-OH}_2]^{2+}$ under N_2 with $\text{NaH}^{13}\text{CO}_3$ and TMDS on the same scale in DMSO also led to formation of **3**. Complex **3** could be isolated from the reaction by precipitation with an aqueous solution of NH_4PF_6 followed by centrifugation. The solid was collected on a medium porosity frit and was washed with water and diethylether. Crystals of **3** were grown by slow evaporation of a DCM solution of **3**.

^1H NMR (500 MHz, DMSO-d_6) δ 12.24 (s, 1H), 8.38 (t, $J = 6.5$ Hz, 2H), 8.29 – 8.19 (m, 1H), 8.13 – 8.09 (m, 1H), 8.08 – 7.99 (m, 3H), 7.70 (d, $J = 7.8$ Hz, 2H), 7.57 – 7.45 (m, 3H), 7.39 – 7.20 (m, 4H), 7.18 – 7.10 (m, 1H), 6.97 – 6.87 (m, 2H), 6.65 (t, $J = 8.7$ Hz, 2H), 5.15 (dd, $J = 30.2, 13.7$ Hz, 1H), 4.85 (s, 1H), 4.64 (d, $J = 14.4$ Hz, 1H), 4.52 (d, $J = 12.7$ Hz, 1H), 2.93 – 2.73 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ 155.25

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2) δ 47.5

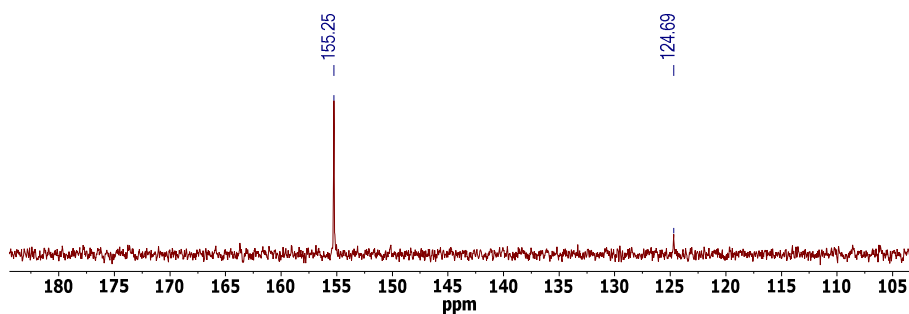


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, (126 MHz, DMSO-d_6) of reaction of $[\mathbf{1-OH}_2]^{2+}$, 10 equiv. $\text{NaH}^{13}\text{CO}_3$, and 10 equiv. TMDS at 50 °C for 16h showing only **3**.

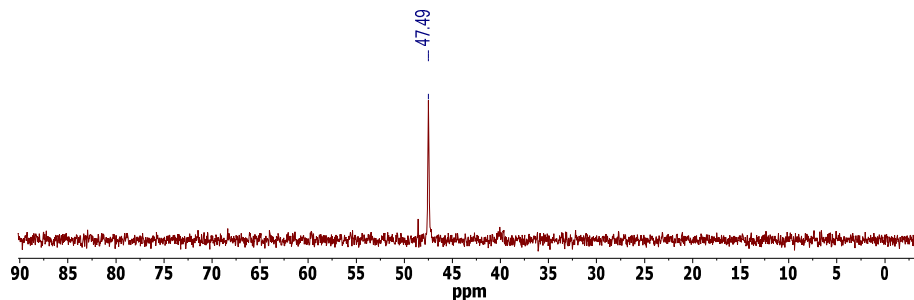


Figure S11. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, (202 MHz, DMSO-d_6) of reaction of $[\mathbf{1-OH}_2]^{2+}$, 10 equiv. $\text{NaH}^{13}\text{CO}_3$, and 10 equiv. TMDS at 50 °C for 16h showing only **3**.

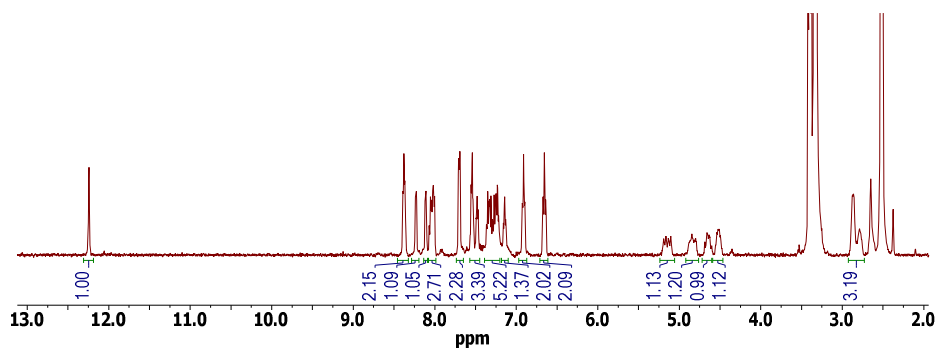


Figure S12. ^1H NMR spectrum, (500 MHz, DMSO-d_6) of reaction of $[\mathbf{1-OH}_2]^{2+}$, 10 equiv. $\text{NaH}^{13}\text{CO}_3$, and 10 equiv. TMDS at 50 °C for 16h showing only **3**. Spectrum obtained by precipitation of product from DMSO by addition of water and re-dissolution of precipitate.

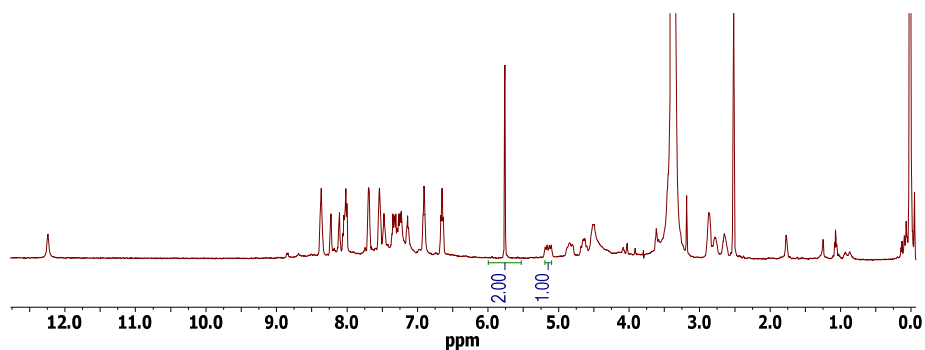


Figure S8. ^1H NMR spectrum, (500 MHz, DMSO-d_6) of reaction of $[\mathbf{1-OH}_2]^{2+}$, 10 equiv. $\text{NaH}^{13}\text{CO}_3$, and 10 equiv. TMDS at 50 °C for 16h showing only **3**. Reaction mixture was spiked with 1 equiv. CH_2Cl_2 as an internal standard immediately prior to NMR.

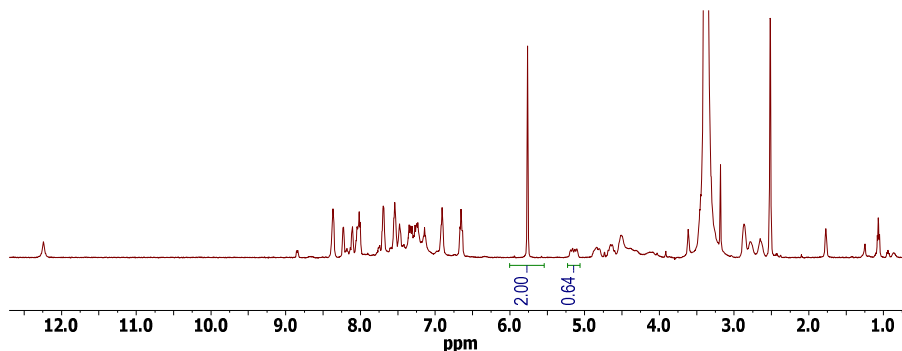


Figure S9. ¹H NMR spectrum, (500 MHz, DMSO-d₆) of reaction of [1-OH₂]²⁺ and 10 equiv. NaH¹³CO₃ at 50 °C for 16h showing only **3**. Reaction mixture was spiked with 1 equiv. CH₂Cl₂ as an internal standard immediately prior to NMR.

Synthesis of 3 by dehydrogenation of 2 or deprotonation of [1-OH₂]²⁺. Crystals of **2** formed from a DCM solution containing [1-OH₂]²⁺ (14 mg, 0.015 mmol, 1 eq) and NaH¹³CO₂ (1.0 mg, 0.015 mmol, 1 eq). The DCM was decanted and the crystals were dissolved into DMSO-d₆ for monitoring by NMR.

To test for H₂ evolution by GC analysis, [1-OH₂]²⁺ (70 mg, 0.07 mmol, 1 eq) and NaHCO₂ (5 mg, 0.07 mmol, 1 eq) were dissolved in acetone (5 mL) and sealed in a gas-tight vial. The reaction mixture was allowed to stir at room temperature for 1 h before a sample of the reaction vessel headspace (1 mL) was taken and analyzed by GC.

Formation of **3** by deprotonation and reaction with CO₂ was done by first mixing a solution of [1-OH₂]²⁺ (14 mg, 0.015 mmol) in CD₂Cl₂ with *n*BuLi (0.032 mmol) at -78 °C in a J-Young NMR tube in an N₂ glove box. The J-Young tube was evacuated with three freeze-pump-thaw cycles and then ¹³CO₂ was added to fill the headspace. Upon sitting at room temperature for 2 days a precipitate formed. The CD₂Cl₂ was decanted and the precipitate was dissolved in DMSO-d₆ for NMR analysis.

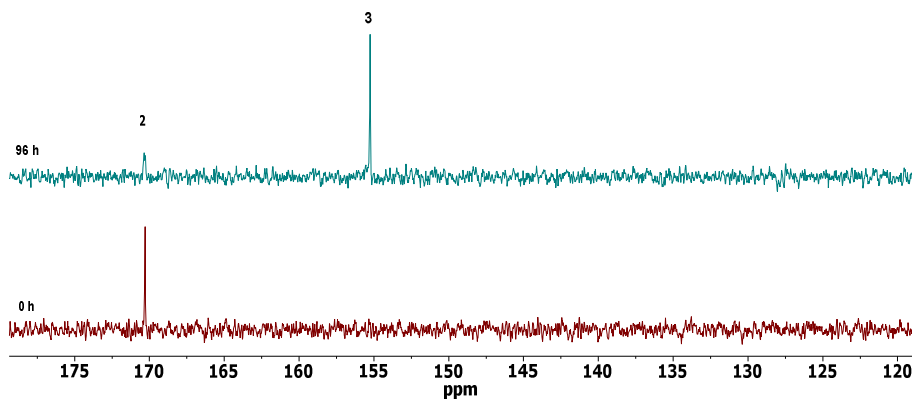


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (126 MHz, DMSO-d_6) of dehydrogenation reaction of **2** in DMSO at room temperature over the course of 4 days showing conversion from **2** to **3**.

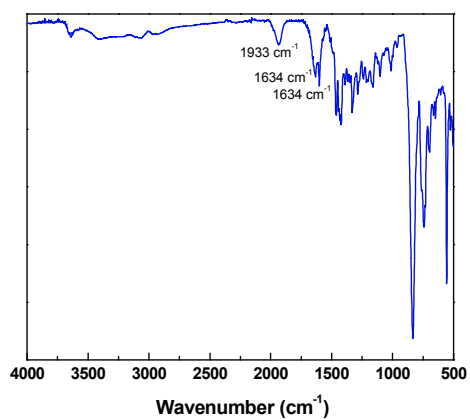


Figure S16. ATR-IR of powder of **3** showing two stretches at 1634 cm^{-1} and 1602 cm^{-1} consistent with a carbamate.

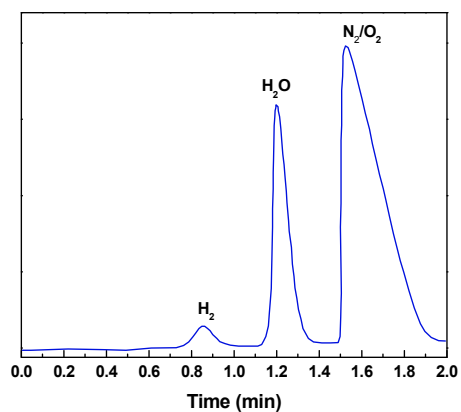


Figure S11. GC trace of 1 mL of headspace of reaction of $[\mathbf{1-OH}_2]^{2+}$ and NaHCO_2 in acetone at room temperature for 1 h.

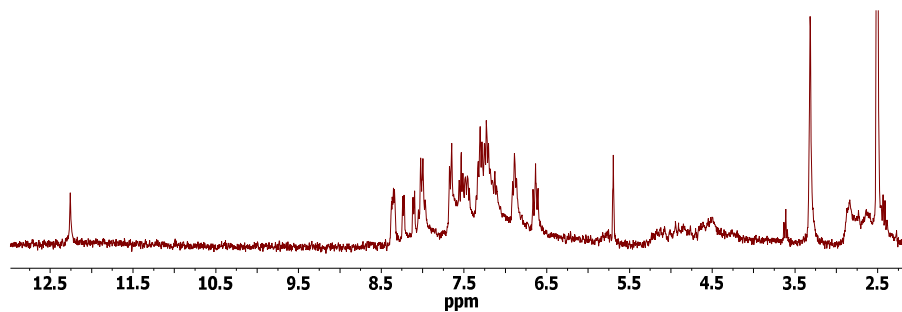


Figure S12. ¹H NMR spectrum (500 MHz, DMSO-*d*₆) of **3** formed by deprotonation of [**1-OH**₂]²⁺ in DCM followed by reaction with ¹³CO₂.

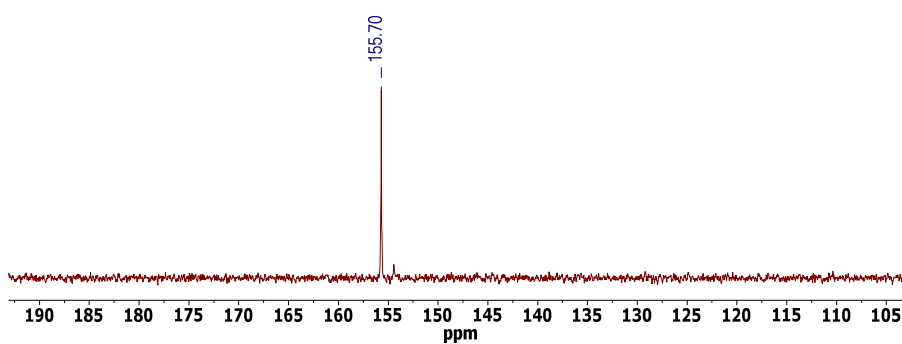


Figure S13. ¹³C{¹H} NMR spectrum (126 MHz, DMSO-*d*₆) of **3** formed by deprotonation of [**1-OH**₂]²⁺ in DCM followed by reaction with ¹³CO₂.

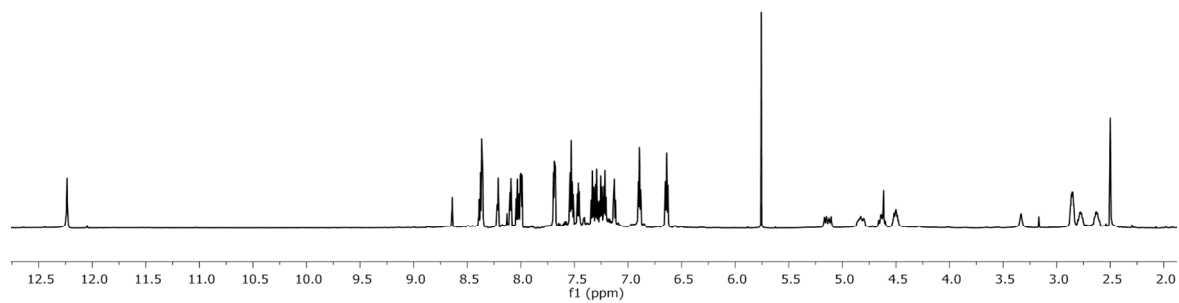


Figure S20. ¹H NMR (500 MHz, DMSO-*d*₆) spectrum of **3** (H₂ also present at 4.6 ppm).

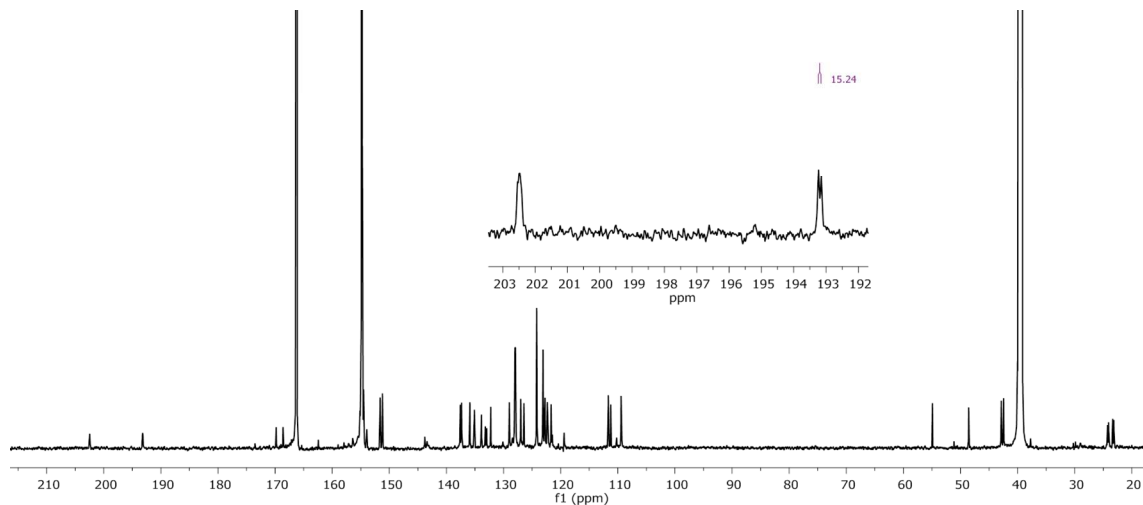


Figure S21. ^{13}C NMR (176 MHz, $\text{DMSO-}d_6$) spectrum of **3** with inset showing the two distinct carbene carbon atoms with distinct ^{13}C coupling to the one nearest the carbamate moiety.

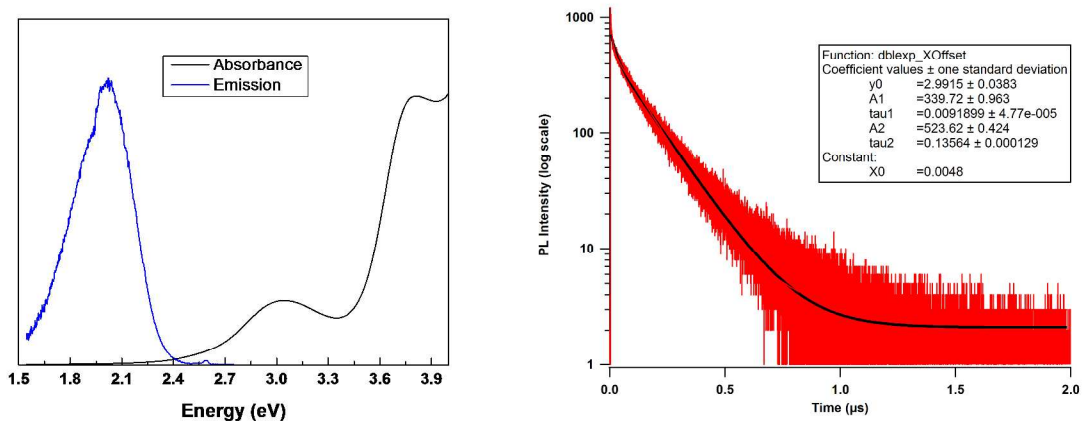


Figure S22. Overlaid UV/vis and emission spectra of **3** in MeOH (left) PL lifetime measurement (right) showing fit with a double exponential to give a lifetime of 140 ± 15 ns.

IV. Crystallographic Information

Table S1. Crystallographic information for Complex [1-Cl]⁺

Empirical formula	C ₄₈ H ₅₄ F ₁₈ N ₈ O ₄ P ₄ Ru	
Formula weight	1325.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 12.0184(12) Å	α = 90°.
	b = 44.108(5) Å	β = 117.748(5)°.
	c = 11.7885(12) Å	γ = 90°.
Volume	5530.6(10) Å ³	
Z	4	
Density (calculated)	1.592 Mg/m ³	
Absorption coefficient	0.505 mm ⁻¹	
F(000)	2688	
Crystal size	0.30 x 0.15 x 0.09 mm ³	
Theta range for data collection	1.85 to 26.45°.	
Index ranges	-15 ≤ h ≤ 15, -55 ≤ k ≤ 55, -14 ≤ l ≤ 14	
Reflections collected	163382	
Independent reflections	11297 [R(int) = 0.0807]	
Completeness to theta = 25.00°	99.2 %	
Max. and min. transmission	0.9560 and 0.8633	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11297 / 548 / 826	
Goodness-of-fit on F ²	1.158	
Final R indices [I > 2σ(I)]	R1 = 0.0794, wR2 = 0.1666	
R indices (all data)	R1 = 0.0867, wR2 = 0.1698	
Largest diff. peak and hole	1.760 and -1.566 e.Å ⁻³	

Table S2. Crystallographic information for Complex 2

Identification code	sef2_142_0ma	
Empirical formula	C ₇₁ H ₆₇ Cl ₄ F ₁₈ N ₁₂ O ₂ P ₅ Ru ₂	
Formula weight	1961.16	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 27.5062(15) Å	α = 90°.
	b = 12.3658(6) Å	β = 110.471(5)°.
	c = 24.5908(13) Å	γ = 90°.
Volume	7836.0(7) Å ³	
Z	4	
Density (calculated)	1.662 Mg/m ³	
Absorption coefficient	0.721 mm ⁻¹	
F(000)	3944	
Crystal size	0.15 x 0.10 x 0.08 mm ³	
Theta range for data collection	1.58 to 25.69°.	
Index ranges	-33 ≤ h ≤ 33, -14 ≤ k ≤ 14, -29 ≤ l ≤ 30	
Reflections collected	160385	

Independent reflections	7297 [R(int) = 0.0668]
Completeness to theta = 25.00°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9446 and 0.8995
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7297 / 3 / 531
Goodness-of-fit on F ²	1.085
Final R indices [I > 2sigma(I)]	R1 = 0.0544, wR2 = 0.1162
R indices (all data)	R1 = 0.0651, wR2 = 0.1209
Largest diff. peak and hole	1.251 and -1.141 e.Å ⁻³

Table S3. Crystallographic information for Complex 3

Identification code	mn_carbamate_0ma	
Empirical formula	C ₃₉ H ₄₂ F ₆ N ₆ O ₄ P ₂ Ru S ₂	
Formula weight	999.92	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 12.7105(10) Å	α = 90°.
	b = 25.453(2) Å	β = 94.334(4)°.
	c = 12.5290(9) Å	γ = 90°.
Volume	4041.8(5) Å ³	
Z	4	
Density (calculated)	1.643 Mg/m ³	
Absorption coefficient	0.649 mm ⁻¹	
F(000)	2040	
Crystal size	0.15 x 0.08 x 0.03 mm ³	
Theta range for data collection	1.60 to 26.76°.	
Index ranges	-15 ≤ h ≤ 16, -31 ≤ k ≤ 32, -15 ≤ l ≤ 15	
Reflections collected	117733	
Independent reflections	8457 [R(int) = 0.0817]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9808 and 0.9090	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8457 / 0 / 545	
Goodness-of-fit on F ²	1.048	
Final R indices [I > 2sigma(I)]	R1 = 0.0490, wR2 = 0.1255	
R indices (all data)	R1 = 0.0702, wR2 = 0.1387	
Largest diff. peak and hole	0.982 and -1.115 e.Å ⁻³	

(1) Bennett, M. A.; Smith, A. K. *J. Chem. Soc. Dalton Trans.* **1974**, 233-241.

(2) Norris, M. R.; Concepcion, J. J.; Glasson, C. R. K.; Fang, Z.; Lapides, A. M.; Ashford, D. L.; Templeton, J. L.; Meyer, T. J. *Inorg. Chem.* **2013**, *52*, 12492-12501.