

Supporting Information

A Carbon-Neutral CO₂ Capture, Conversion, and Utilization Cycle with Low-Temperature Regeneration of Sodium Hydroxide

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Table of Contents

1. Materials and methods	S2
2. Standard procedure for CO ₂ capture by aqueous hydroxide solutions	S2
2.1. Formation of bicarbonate salts in the solution after capture as seen by NMR	S4
3. Standard procedure for the hydrogenation reactions	S4
3.1. Representative NMR spectra of hydrogenation reaction	S6
4. Standard Procedure for CO ₂ capture from air	S8
5. Procedure for recycling studies	S8
6. Observing the catalytic resting state	S8
6.1. Correlation between TOF and catalyst molecular structure	S10
7. Fuel cell studies	S10
8. References	S14

1. Materials and methods

All hydrogenation experiments were carried out under an inert atmosphere (with N₂ or Ar) using standard Schlenk techniques. Complexes Ru-MACHO-BH (**C-1**, Strem Chemicals, 98%), Ru-MACHO (**C-2**, Strem Chemicals, 98%), RuHCIPNP^{*i*Pr}(CO) (**C-3**, Strem Chemicals, 97%), RuHCIPNP^{*Cy*}(CO) (**C-4**, Strem Chemicals, 97%), RuHCIPNP^{*t*Bu}(CO) (**C-5**, Strem Chemicals, 97%) were used as received without further purification. Complexes MnBrPNP^{*i*Pr}(CO)₂ (**C-6**), MnBrPNP^{*Cy*}(CO)₂ (**C-7**), FeHBrPNP^{*i*Pr}(CO) (**C-8**) and RuHCIPNP^{*Me*}P^{*Ph*}(CO) (**C-9**) were prepared by previously reported methods.^{1,2,3} All catalysts were weighed inside an argon filled glove box. Sodium hydroxide, potassium hydroxide, cesium hydroxide monohydrate, calcium hydroxide and lithium hydroxide monohydrate were purchased from commercial sources and used without further purification. 2-Methyltetrahydrofuran (2-MTHF, BTC), cyclopentyl methyl ether (CPME, Sigma-Aldrich), water (deionized) were sparged with N₂ for 1 h prior to use. 1,3,5-trimethoxybenzene (TMB) (Sigma-Aldrich, >99%), imizadole (Fischer Scientific, 99.7%), DMSO-d₆ (CIL, D-99.9%), and D₂O (CIL, D-99.5%) were used as received. ¹H and ¹³C NMR spectra were recorded on 400 MHz or 500 MHz, Varian NMR spectrometers. ¹H and ¹³C NMR chemical shifts were determined relative to the residual solvent signals (DMSO-d₆, D₂O) or internal standard (TMB/Im). CO₂ (Gilmore, instrument grade 4.0), and H₂ (Gilmore, ultra-high pure grade 5.0) were used without further purification.

Caution: Reactions are associated with H₂ gas. They should be carefully handled inside proper fume hoods without any flame, spark or static electricity sources nearby.

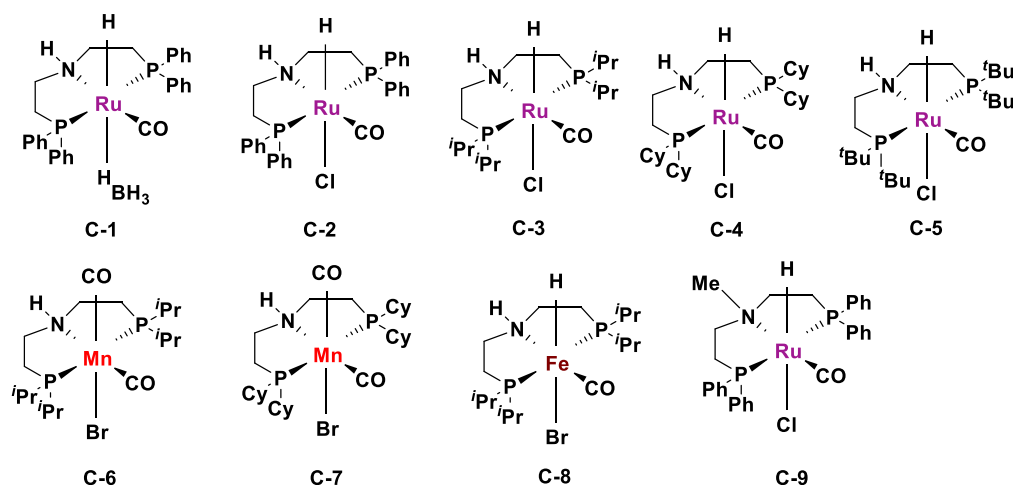


Figure S1. Catalytic complexes screened in this study

2. Standard procedure for CO₂ capture by aqueous hydroxide solutions

Metal hydroxide bases (13.8 mmol) were dissolved in water (10 mL) in a 30 mL vial equipped with a magnetic stir bar. The gases inside the vial was then removed under vacuum. CO₂ was then added into the vial while stirring the aqueous solution at 800 rpm and maintaining CO₂ pressure inside the vial at 1 psi above the atmospheric pressure (Figure S2 and S3). The amounts of CO₂ captured after 3 h were calculated through gravimetric analysis of the aqueous solutions before and after the capture. For CsOH and LiOH, their commercially available monohydrates (13.8 mmol) were used for capture.

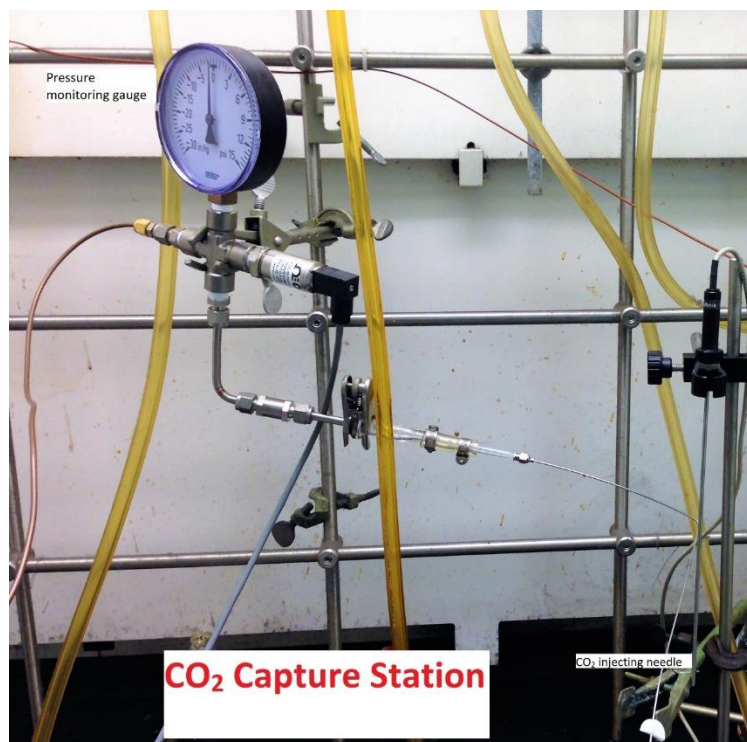


Figure S2. Image of CO₂ capture station

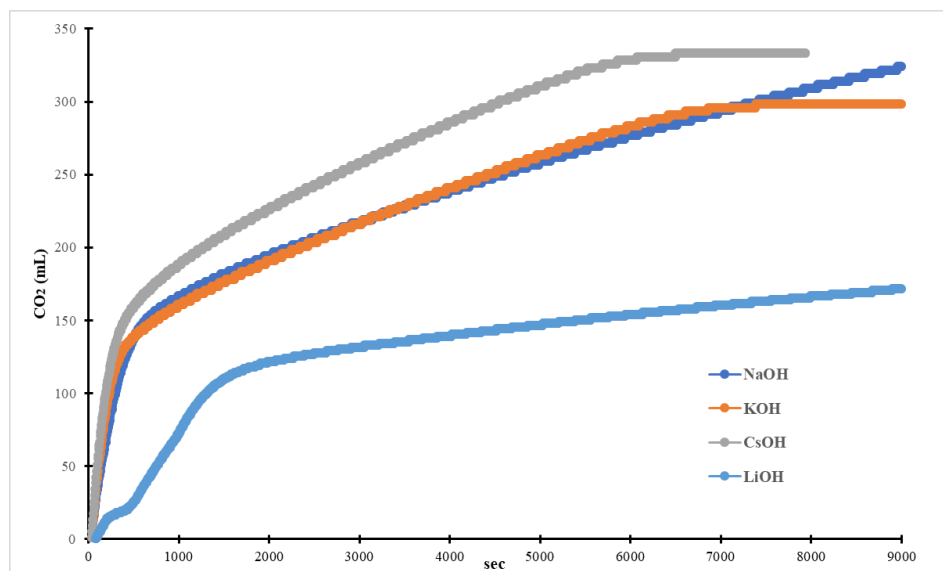


Figure S3. CO₂ capture with time for different hydroxide bases

2.1. Formation of bicarbonate salts in the solution after capture as seen by NMR

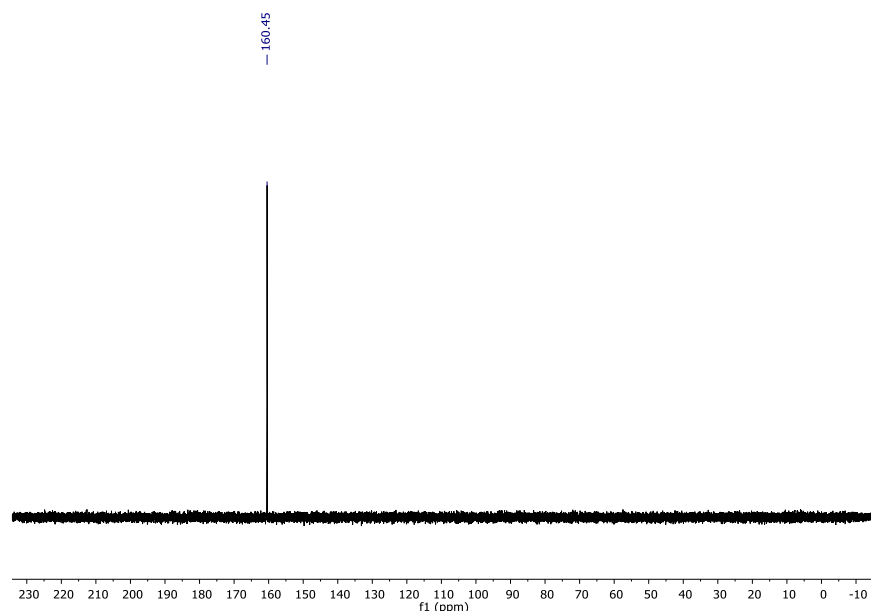


Figure S4. ^{13}C NMR spectra of aqueous NaOH solution after CO_2 capture. Reaction conditions: NaOH (550 mg), H_2O (10 mL).

3. Standard procedure for the hydrogenation reactions

The capture of CO_2 in aqueous hydroxide solutions were performed prior to hydrogenation reactions. Upon completion of capture, in a nitrogen-filled chamber, the CO_2 loaded hydroxide solution, catalyst **C-1/C-2/C-3/C-4/C-5/C-6/C-7/C-8/C-9**, and solvent (5 mL/1 mL) (2-MTHF, CPME) were added to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. The vessel was then filled with H_2 to the desired pressure (50 bar). The reaction mixture was then stirred with a magnetic stirrer for 5 minutes (800 rpm) and subsequently placed in a preheated oil bath with stirring at 800 rpm. The internal temperature of the reaction mixture (80 $^\circ\text{C}$), and pressure inside the reactor were monitored and recorded through the LabVIEW 8.6 software (Figure S6). After heating for a given period of time (12 h), the reactor was cooled down to room temperature. The gas inside the vessel was then slowly released. Upon opening the reaction vessel, a solution was obtained with two distinct layers (Figure S5). After transferring the whole solution into a 15 mL centrifuge tube, the two layers were separated. A known amount of TMB was added as an internal standard to the top 2-MTHF layer which was then analyzed by ^1H and ^{13}C NMR with DMSO-d_6 as the deuterated solvent. A known amount of imidazole was added to bottom aqueous layer as an internal standard, followed by ^1H and ^{13}C NMR analysis with D_2O as the deuterated solvent. Yields were determined through ^1H NMR from integration ratios (relaxation delay = 10 seconds). The reaction completion time was assigned based on the cessation in pressure decrease inside the reaction vessel during the reaction.

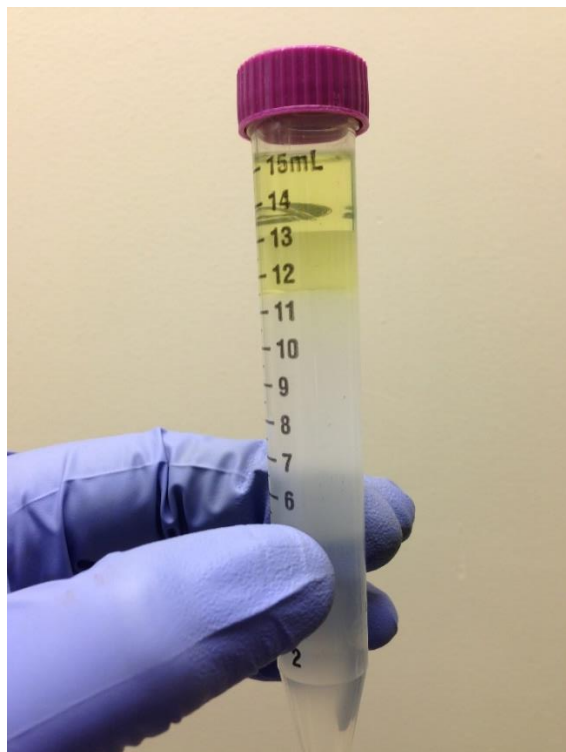


Figure S5. Biphasic solution obtained after hydrogenation

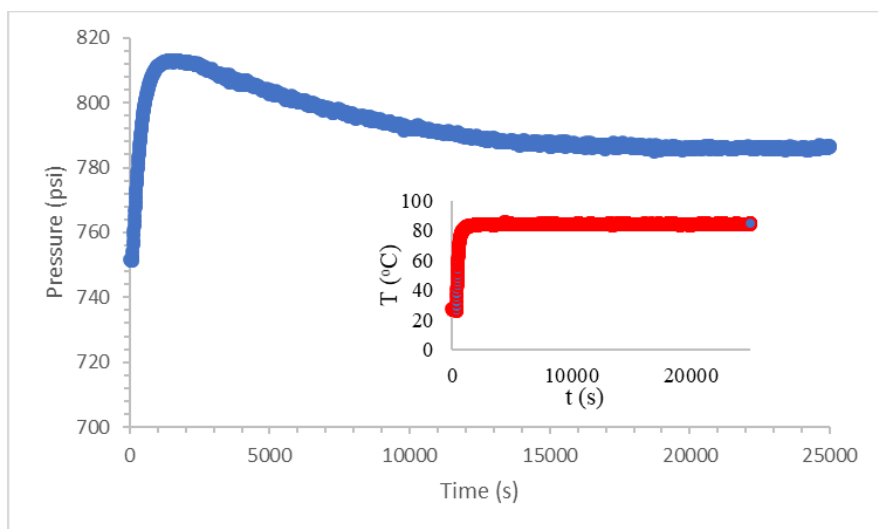


Figure S6. Pressure and temperature profile with time in a typical hydrogenation reaction with catalyst C-2

3.1. Representative spectra of hydrogenation reaction

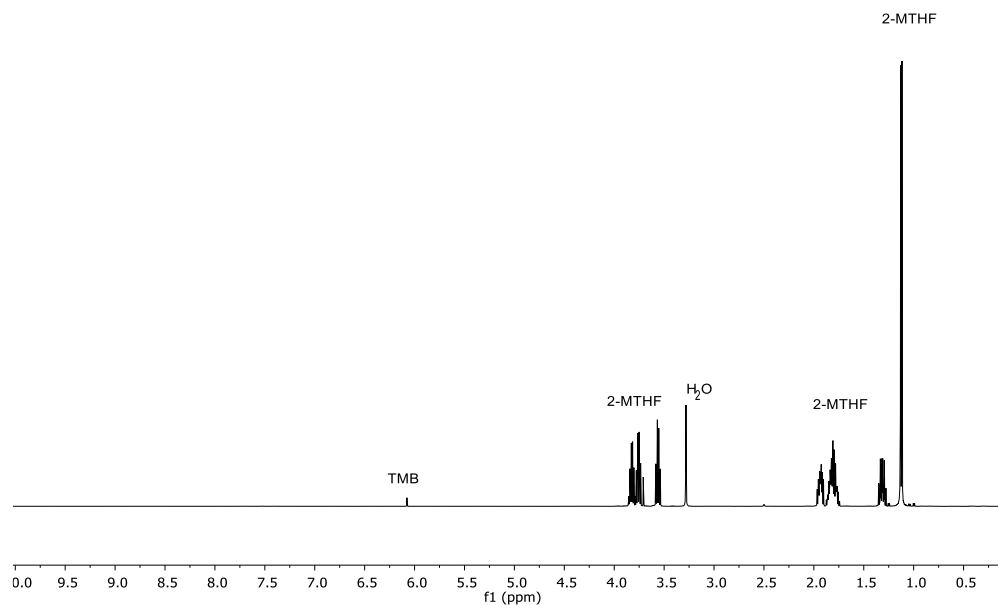


Figure S7: Typical ¹H spectra of the top organic layer after hydrogenation reaction of captured CO₂ (Table 2)

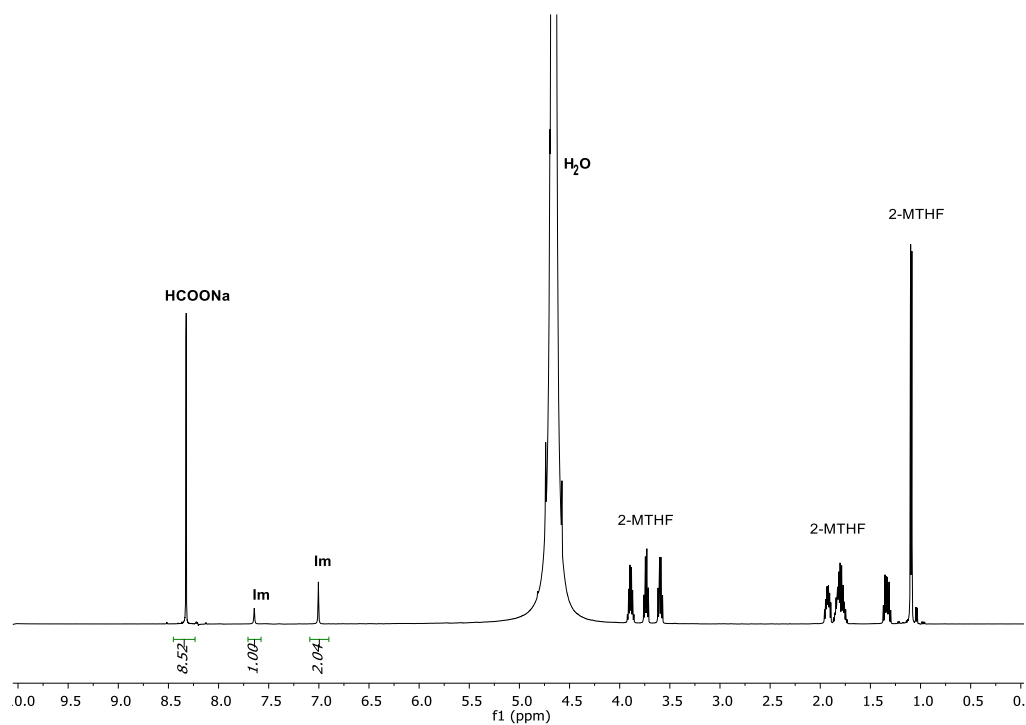


Figure S8: Typical ¹H spectra of the bottom aqueous layer after hydrogenation reaction of captured CO₂ (Table 2)

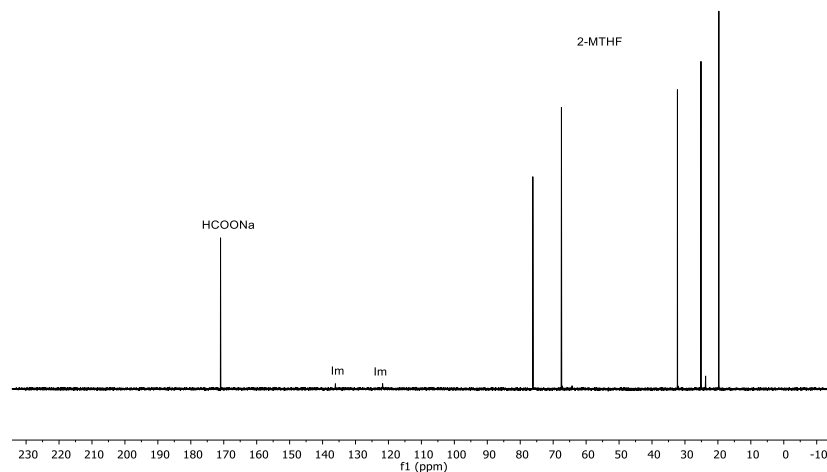


Figure S9: Typical ^{13}C spectra of the bottom aqueous layer after hydrogenation reaction of captured CO_2 (Table 2)

4. Standard Procedure of CO_2 capture from air

In a 30 mL vial, 0.6 g NaOH was dissolved in 15 mL water. Atmospheric air containing 408 ppm CO_2 was then bubbled through the solution at a flow-rate 200 mL/min for 64 h through a pump. 5 mL of additional water was added after 40 h. After the completion of CO_2 capture, the final solution had ~10 mL of water due to water evaporation while bubbling air. The resulting solution was then sparged with N_2 for 30 mins. Afterwards, 500 μL of THF was added to the solution as an internal standard and the amount of CO_2 captured was calculated through ^{13}C NMR analysis (relaxation delay = 25 seconds). The remaining solution was used for hydrogenation with 5 mL THF as the organic solvent.

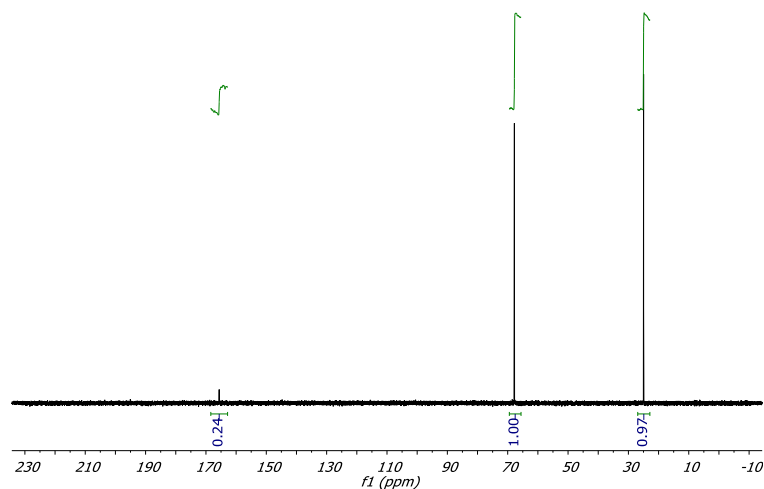


Figure S10. ^{13}C spectra of CO_2 captured from ambient air

5. Procedure for recycling studies

The capture of CO₂ in aqueous hydroxide solutions were performed prior to hydrogenation reactions. Upon completion of capture, in a nitrogen-filled chamber, the CO₂ loaded NaOH solution, catalyst **C-5** (5 μmol), and 2-MTHF (5 mL) were added to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. The vessel was then filled with H₂ to the desired pressure (50 bar). The reaction mixture was then stirred with a magnetic stirrer for 5 minutes (800 rpm) and subsequently placed in a preheated oil bath with stirring at 800 rpm. The internal temperature of the reaction mixture (80 °C), and pressure inside the reactor were monitored and recorded through the LabVIEW 8.6 software. After heating for a given period of time (12 h), the reactor was cooled to room temperature. The gases inside were then slowly released under a N₂ atmosphere. Upon opening the reaction vessel inside a N₂ chamber, a solution was obtained with two distinct layers. After transferring the whole solution in a 15 mL centrifuge tube, the two layers were separated in N₂ atmosphere. The bottom layer was washed with additional 2 mL of 2-MTHF, and the combined organic layer was transferred to a Schlenk flask and used directly for the next cycle. Meanwhile, a known amount of imidazole was added to bottom aqueous layer as internal standard, followed by its analysis by ¹H and ¹³C NMR with D₂O as the deuterated solvent. Yields were determined through ¹H NMR from the integration ratios of imidazole aromatic peaks with formate proton peak.

6. Observing the catalytic resting state

Procedure: In a nitrogen-filled chamber, sodium bicarbonate (0.1 mmol), catalyst **C-2** (25 μmol), THF-d₈ (1 mL) and water (0.2 mL) were added to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. The vessel was then filled with H₂ to the desired pressure (50 bar). The reaction mixture was then stirred with a magnetic stirrer for 5 minutes (800 rpm) and subsequently placed in a preheated oil bath with stirring at 800 rpm. The internal temperature of the reaction mixture (80 °C), and pressure inside the reactor were monitored and recorded through the LabVIEW 8.6 software. After heating for a given period of time (1 h), the reactor was cooled to room temperature. The gas inside were then slowly released in a N₂ atmosphere. Upon opening the reaction vessel inside a N₂ chamber, a pale-yellow solution was obtained. The solution was transferred inside a J. Young NMR tube and subsequently was analyzed through ¹H and ³¹P NMR spectroscopy. The chemical shifts of the ruthenium formate species matches the value previously reported in the literature.⁴

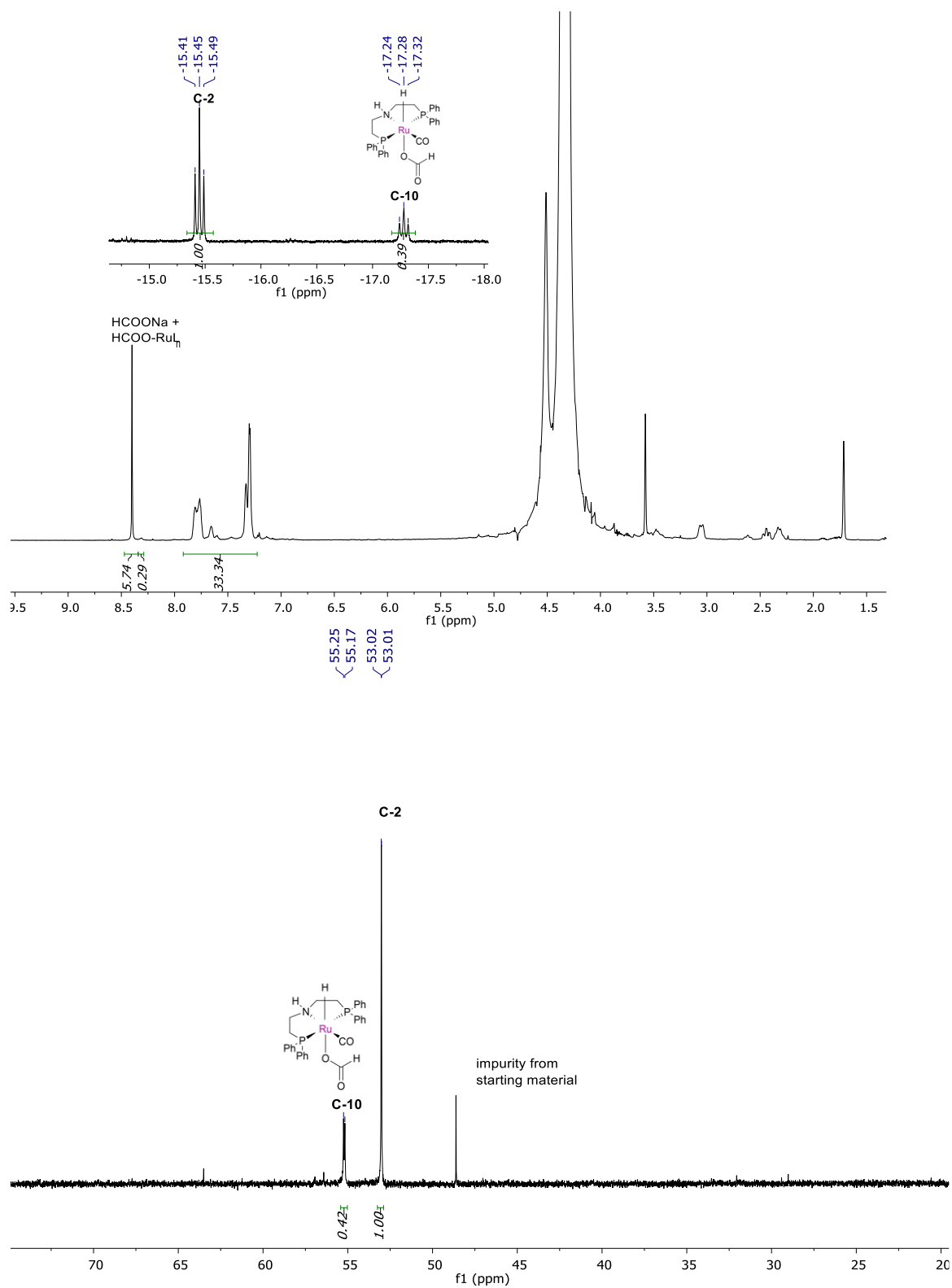
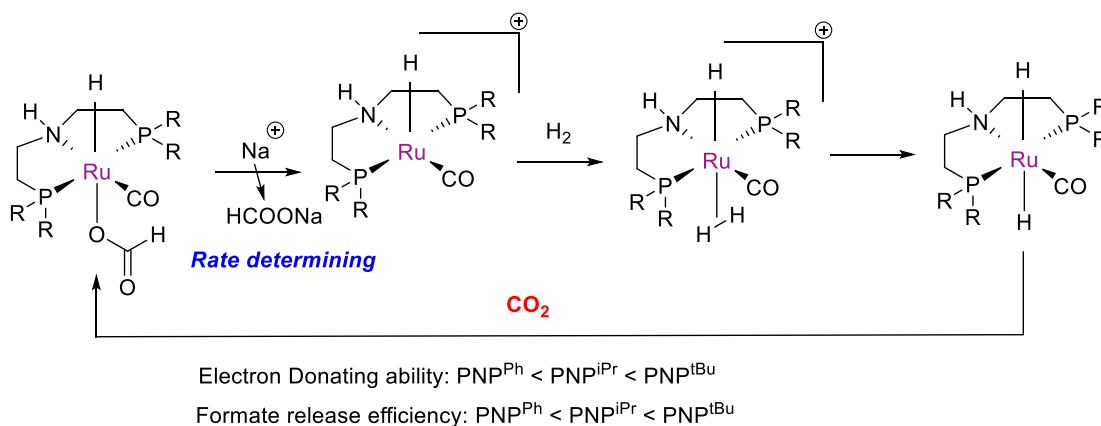


Figure S11. Observation of Ru formate species as catalytic resting state through ^1H (top) and ^{31}P (bottom) NMR

6.1. Correlation between TOF and catalyst molecular structure

As seen from the above NMR spectra, ruthenium formate species is observed under the reaction conditions as the catalytic resting state. Thus, one of the key rate determining step for the hydrogenation is the subsequent release of the formate from the catalyst metal center (Scheme S1). Hazari- Bernskoetter and others have previously reported extensively on the rate enhancement of this step in the presence of Lewis base such as LiBF_4 or LiOTf .⁶ Similarly, in this study we also observed the rate dependence on the metal ion present in the system. For example, when K^+ was used instead of Na^+ , as in KHCO_3 , an enhanced rate was observed due to higher heat of formation of HCOOK .

Scheme S1. Plausible mechanistic cycle of formate production



With regards to the correlation between the catalyst molecular structure and TOF observed, a certain trend can be expected. Given that the electron donating ability of PNP^{tBu} is higher than PNP^{iPr} , followed by PNP^{Ph} , the electron density at the metal center in case of $\text{R} = \text{tBu}$ would be higher than in the other cases. Our working hypothesis is that considering this increased electron density, the ejection of formate from the catalytic center becomes easier. As a result, the TOF increases along with the increasing donating ability of the PNP ligand. It would be interesting to study this proposed effect of ligands through DFT in future.

7. Fuel cell studies

Experimental procedure for the fabrication of the fuel cell

Carbon paper was sectioned into 4 cm^2 pieces and coated with catalysts. For the catalyst preparation, catalyst powders (20%-Pd/C and 40%-Pt/C) were mixed with appropriate amounts of ethanol and a neutral binder (Fluorinated Ethylene Propylene, 55% weight in water) and subject to sonication for 10 minutes. The resulting catalyst suspensions were then hand-brush painted onto teflonized carbon paper until 2.0 mg cm^{-2} of Pd was added for the anode and either 2.0 mg cm^{-2} of Pt or Pd were painted onto teflonized carbon paper for the cathode. The membrane (Nafion 211; the Na^+ membrane was prepared following previously reported procedure⁵) was then placed in between the catalyst coated carbon paper and pressed at 130 $^\circ\text{C}$ for 5 minutes applying 500 kilograms of force.

The membrane electrode assembly was placed between graphite separators; the Direct Formate Fuel Cell (DFFC) is depicted in Figure S12 and S13. The fuel cell measurements were performed using a Fuel Cell Test System 890B (Scribner Associates) at a temperature of 80 °C. Non heated ~1 M HCOONa solution obtained from the hydrogenation reaction was delivered through the anode compartment at a flow rate of 2.5 mL min⁻¹ while humidified O₂/air was passed through the cathode compartment at 100 mL min⁻¹ heated to 85 °C.

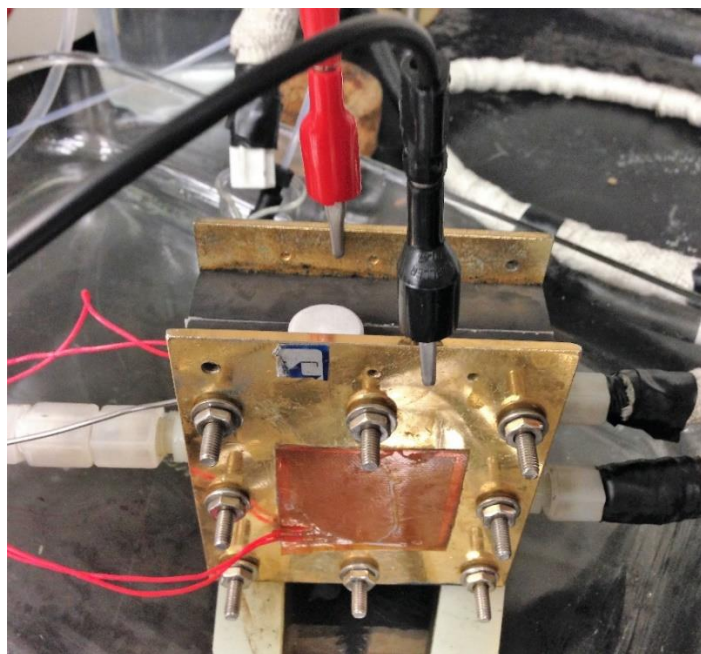
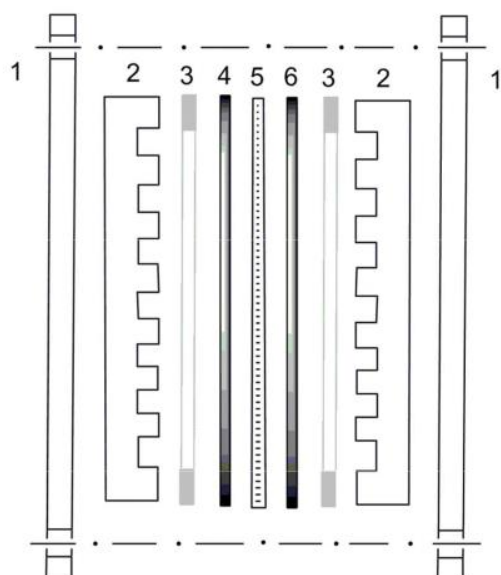


Figure S12. Image of the fuel cell used in this study



1. Brass current collector
2. Bipolar graphite plate
3. Teflon gasket
4. Formate electrode (anode)
5. Cation exchange membrane
6. O₂ electrode (cathode)

Figure S13. Schematic diagram of the fuel cell

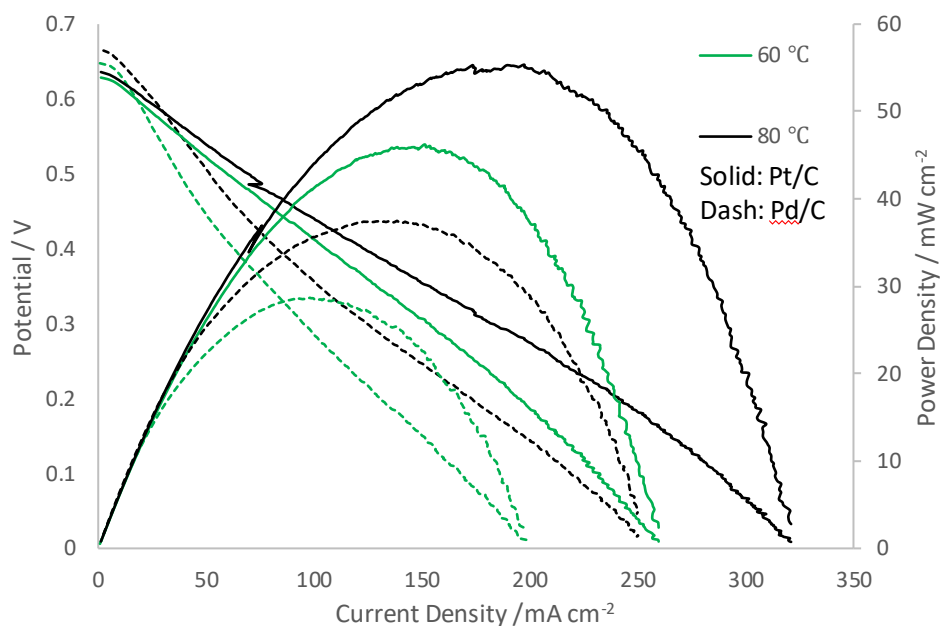


Figure S14. Change in power density and polarization curve with different cathode catalysts. Anode fuel: HCOONa , 1.0 M, 2.5 mL/min^{-1} ; Cathode oxidant: oxygen, 100 mL min^{-1} , ambient pressure; Anode electrode: Catalyst: Pd/C; Loading: $2.0 \text{ mg}_{\text{Pd}} \text{ cm}^{-2}$; Cathode electrode: Catalyst: Pd/C or Pt/C; Loading: 2.0 mg cm^{-2} ; CEM: Nafion 211.

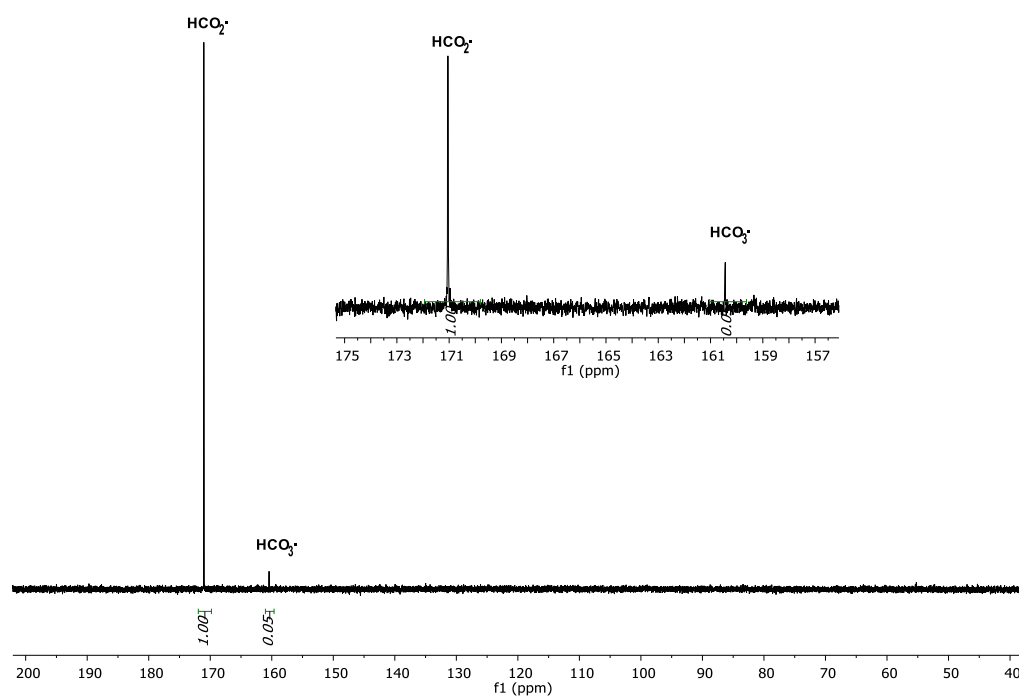


Figure S15. ^{13}C NMR of the anode solution showing the formation of NaHCO_3

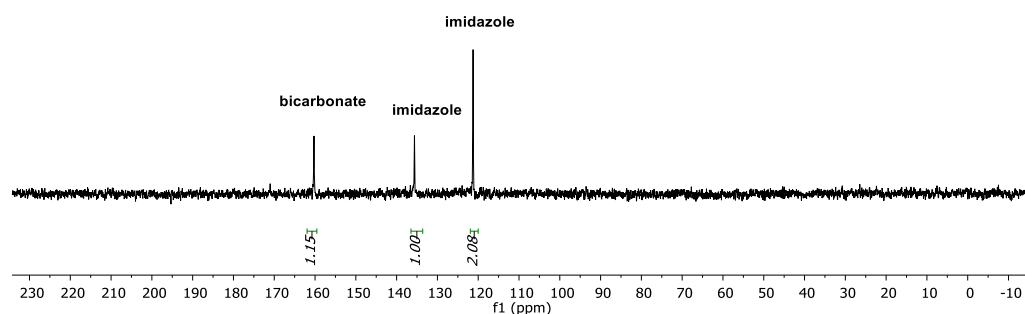


Figure S16. Observation of sodium bicarbonate after CO_2 capture with regenerated NaOH

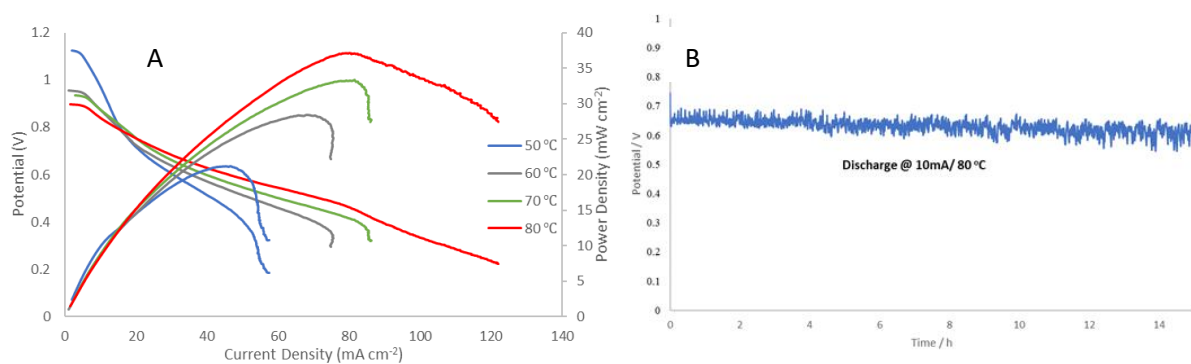


Figure S17. Polarization (A) and voltage vs time (B) curve with F-1850 membrane. Anode fuel: HCOONa , 1.0 M, 2.5 mL/min^{-1} ; Cathode oxidant: oxygen, 100 mL min^{-1} , ambient pressure; Anode electrode: Catalyst: Pd/C; Loading: $2.0 \text{ mg}_{\text{Pd}} \text{ cm}^{-2}$; Cathode electrode: Catalyst: Pd/C or Pt/C; Loading: 2.0 mg cm^{-2} ; CEM: F-1850. F-1850 membrane (Fumatech) was prepared by similar method as Nafion 211.

Table S1. Amounts of formate and carbonate crossover to cathode side with Nafion-211 and F-1850 membranes

CEM	Formate (mmol)	Carbonate (mmol)
Nafion-211	0.6	0.5
F-1850	0.05	0.3

Conditions: Anode fuel: HCOONa, 1.0 M, 2.5 mL/min⁻¹; Cathode oxidant: oxygen, 100 mL min⁻¹, ambient pressure; Anode electrode: Catalyst: Pd/C; Loading: 2.0 mgPd cm⁻²; Cathode electrode: Catalyst: Pt/C; Loading: 2.0 mg cm⁻²; discharge@ 10 mA, 80 °C time = 13h; the amount of formate and carbonate was calculated from ¹H and ¹³C NMR spectra, respectively, with imidazole as internal standard.

8. REFERENCES

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