

Supporting Information

Mechanistic Insights into Ruthenium-Pincer-Catalyzed Amine-Assisted Homogeneous Hydrogenation of CO₂ to Methanol

Sayan Kar, Raktim Sen, Jotheeswari Kothandaraman, Alain Goeppert, Ryan Chowdhury, Socrates B. Munoz, Ralf Haiges, and G. K. Surya Prakash*

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661, United States.

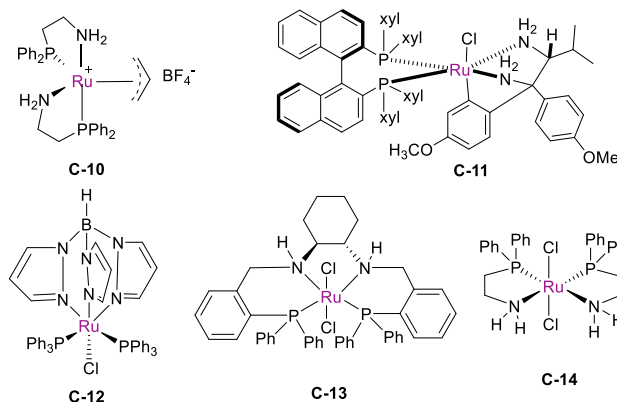
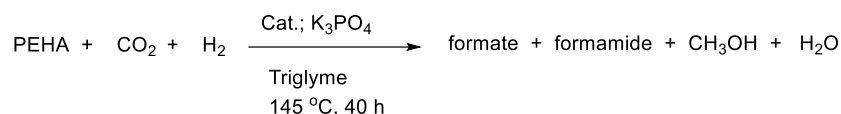
1. Materials and methods

All experiments were carried out under inert atmosphere using standard Schlenk techniques with the exclusion of moisture. Ru-Macho-BH (**C-1**, Strem, 98%), Ru-Macho (**C-2**, Strem, 98%), RuHCIPNP^{*ipr*}(CO) (**C-3**, Strem, 98%), RuHCIPNP^{*Cy*}(CO) (**C-4**, Strem, 98%), RuHCIPNP^{*Bu*}(CO) (**C-5**, Strem, 98%), Carbonylhydrido[6-(di-*t*-butylphosphinomethylene)-2-(*N,N*-diethylaminomethyl)-1,6-dihydropyridine]ruthenium(II) (**C-7**, Strem, 98%), Milstein acridine complex (**C-8**, Strem, 98%) were used without purification. RuCl₂PNP^{*Ph*}(NHC) (**C-6**) and RuHCIPN_{Me}P^{*Ph*} (**C-9**) were prepared following reported procedures.^{1,2} All solvents, triglyme (Alfa Aesar), toluene (Alfa Aesar) were degassed for 1 h prior to use. Ethylenediamine (**1**, Combi-Blocks, 98%), *N,N'*-dimethylethylenediamine (**2**, Combi-Blocks, 97%), *N*-methylethylenediamine (**3**, Combi-Blocks, 98%), *N,N*-dimethylethylenediamine (**4**, Combi-Blocks, 97%), *N,N,N'*-trimethylethylenediamine (**5**, Combi-Blocks, 98%), *N*-ethylhydroxyethylenediamine (**6**, Combi-Blocks, 95%), *N,N'*-diethylhydroxyethylenediamine (**7**, TCI America), piperidine (**8**, Sigma-Aldrich), diethylenetriamine (**9**, Sigma-Aldrich, 98%) were sparged with N₂ for 1 h prior to use. Pentaethylenhexamine, (PEHA, **10**, Sigma-Aldrich, 98%) was treated with vacuum for 1 h before use. *N,N'*-Bisformyl-*N,N'*-dimethylethylenediamine (**F-1**) was prepared following a reported procedure.³ All other chemicals were purchased from commercial vendors and used without further purification. ¹H and ¹³C NMR spectra were recorded on 400 MHz, 500 MHz, and 600 MHz Varian NMR spectrometers. ¹H and ¹³C NMR chemical shifts were determined relative to the residual solvent signals (dmso-d₆) or internal standard (TMB). The gas mixtures were analyzed using a Thermo gas chromatograph (column: Supelco, Carboxen 1010 plot, 30 m x 0.53 mm) equipped with a TCD detector (CO detection limit: 0.099 v/v%). 1:3 CO₂:H₂ (Airgas, certified standard-spec grade) was used without further purification. ATR-IR spectra was recorded on a Jasco FT/IR-4600 spectrometer.

2. Standard procedure for hydrogenation reactions

The procedure as reported previously by our group for this reaction was followed.⁴ Catalyst **C-1** to **C-14**, K₃PO₄, amine (**1-17**) and solvent (triglyme) were added in a nitrogen chamber to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. After pressurizing the reactor with a CO₂/3H₂ mixture, the LabVIEW 8.6 software was used to monitor and record the internal temperature and pressure of the reactor. The reaction mixture was stirred at room temperature (RT) for 30 min and then heated in a pre-heated oil bath to an internal temperature of 145 °C. After heating for a given amount of time, the reactor was cooled to RT and the gas mixture analyzed by GC. A biphasic reaction mixture containing a white oily material (lower layer) and a pale-yellow solution (upper layer) was obtained. Water was added to the above mixture until all the oily material was dissolved resulting in a homogeneous solution. 100 mg of 1,3,5-trimethoxybenzene was added as an internal standard to the reaction mixture. This mixture was then analyzed by ¹H and ¹³C NMR with a few drops of D₂O to lock the signals.

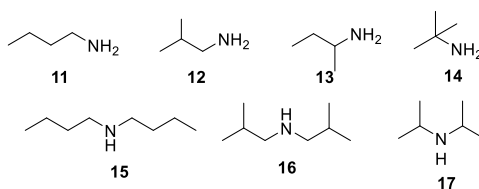
3. Table S1. Additional catalysts screened for CO₂ hydrogenation



Entry	Catalyst	formate (mmol)	formamide (mmol)	methanol (mmol)	CO (%) ^b	TON _{formate+formamide}	TON _{MeOH}
1	C-10	0.4	14.2	0	0	1460	0
2	C-11	0.2	7.5	0	0	770	0
3	C-12	0	4.4	trace	0	440	-
4	C-13	0.3	11.8	0	0	1210	0
5	C-14	0.5	8.7	0	0	920	0

Reaction conditions: PEHA (5.1 mmol), Cat. (10 μmol), K₃PO₄ (1 mmol); triglyme (10 mL); CO₂/3H₂ (75 bar), 145 °C, 40 h. Catalyst C-10 to C-14 were purchased from Strem Chemicals

4. Table S2. Monoamines screened for amine assisted CO₂ hydrogenation



Entry	Amine	formate (mmol)	formamide (mmol)	methanol (mmol)
1	11	4.7	7.8	0
2	12	1.6	5.5	0
3	13	4.4	1.8	0
4 ^a	14	4.3	0	0
5	15	3.8	2.3	0
6 ^b	16	0.6	0.1	0.2
7	17	3.6	0	0

Reaction conditions: Amine (20 mmol), C-1 (10 μmol), triglyme 10 mL, CO₂/3H₂ (75 bar) 145 °C, 20 h. yields were determined from ¹H NMR spectra with TMB as an internal standard. ^asolid white crystals of *t*-butylcarbamate were observed upon opening reaction vessel ^btoluene as solvent

5. Representative NMR spectra for Table 2

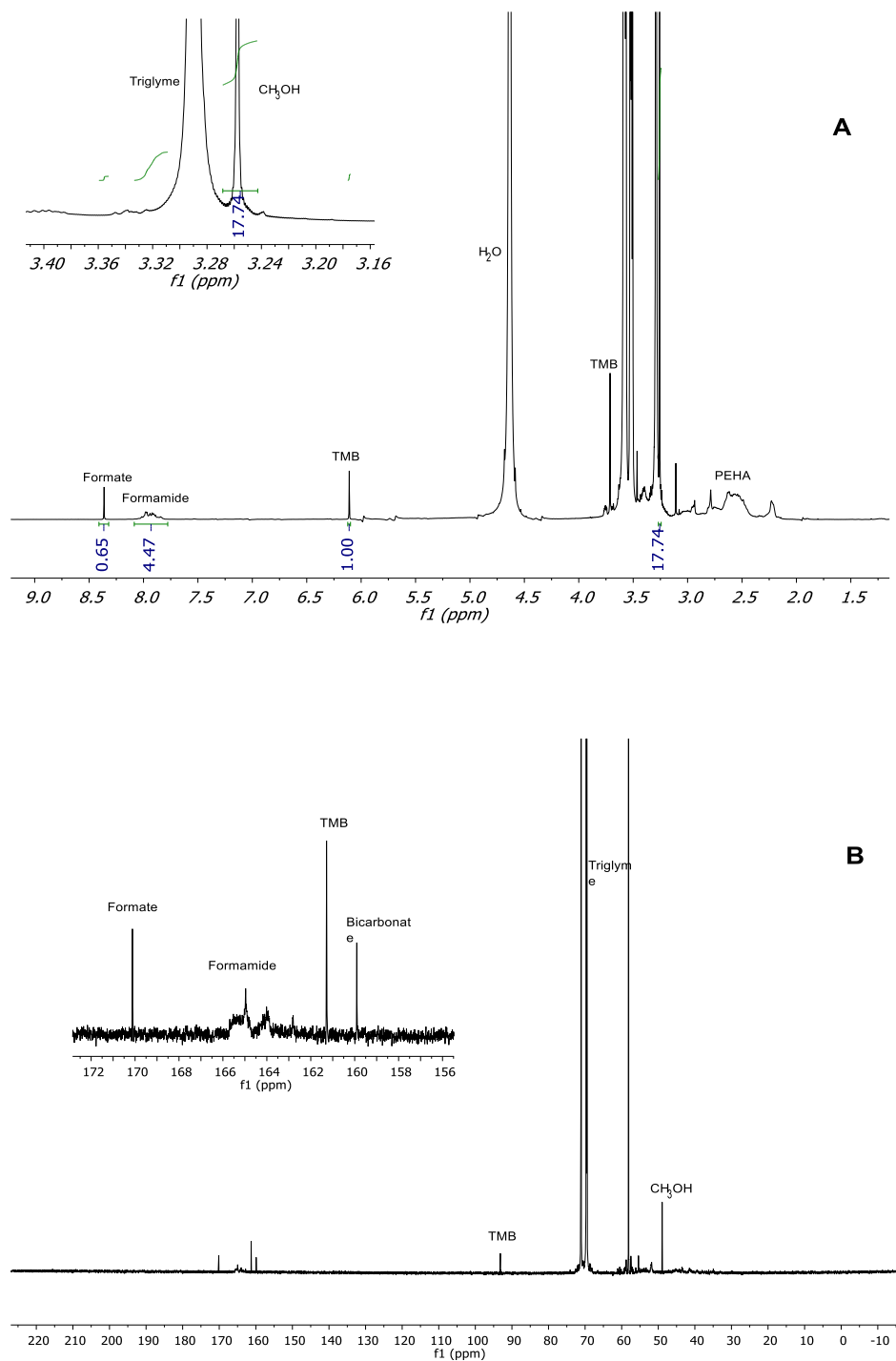


Figure S1. ^1H (A) and ^{13}C (B) NMR of the reaction mixture after hydrogenation (Table 2, entry 1)

6. Gas Chromatogram of the collected reaction gas mixture (Table 2, entry 1)

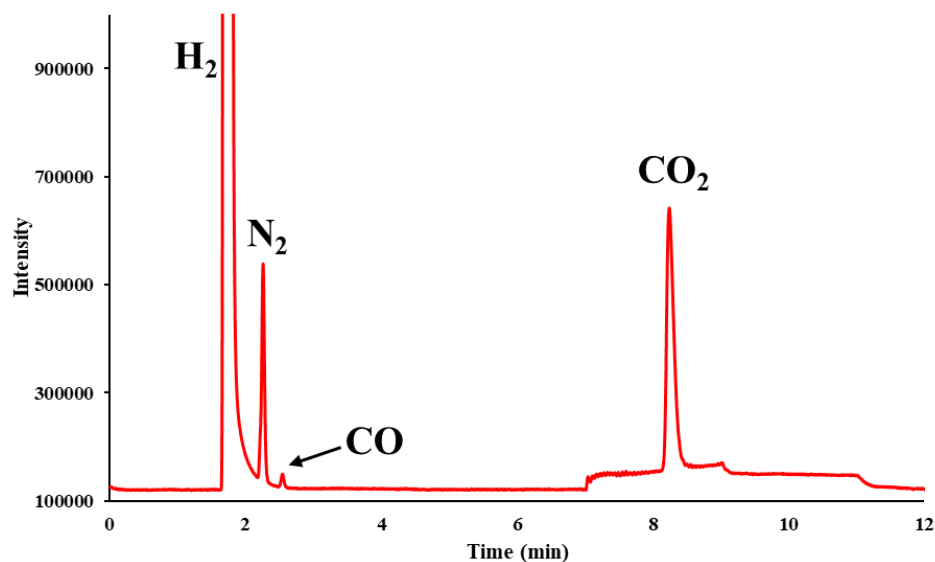


Figure S2. Typical GC spectra of the gas mixture after hydrogenation reaction

7. Representative proton NMR spectra for Table 3

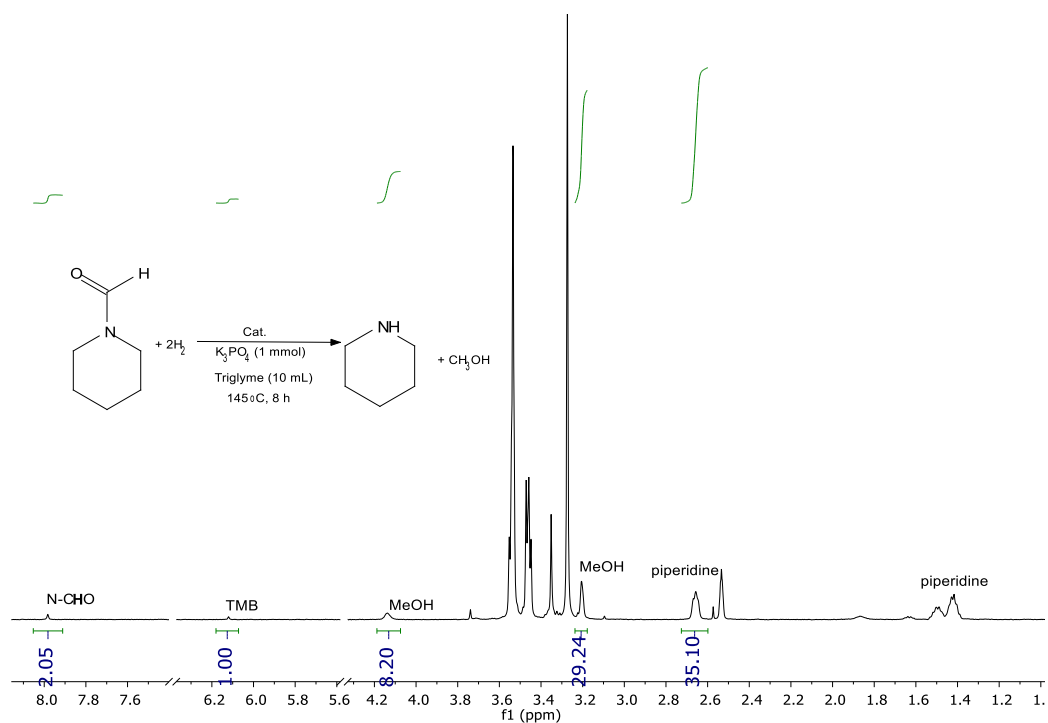
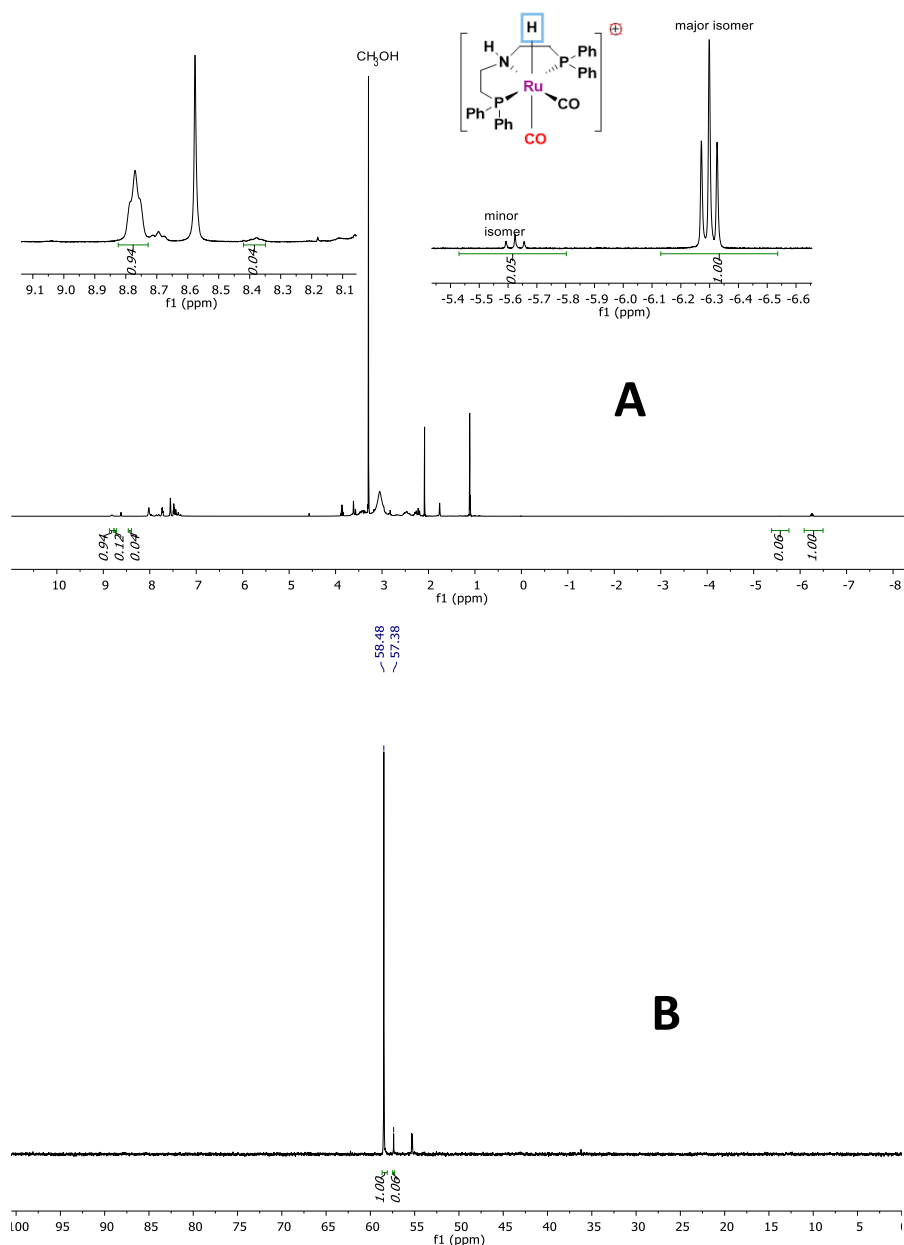


Figure S3. ^1H spectra of the solution after formamide hydrogenation Reaction conditions: Table 3, entry 3.

8. Mechanistic studies

8.1. Reaction procedure

Catalyst **C-1/ C-2/ C-3/ C-4/ C-5** (12 mg) was added to PEHA (10 mg), *t*-BuOK (22 mg) and THF- d_8 (1 ml) in a nitrogen chamber to a 125 mL Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. After pressurizing the reactor with 75 bar of a 1:3 CO₂/H₂ mixture, the LabVIEW 8.6 software was used to monitor and record the internal temperature and pressure of the reactor. The reaction mixture was stirred at RT for 30 min and then heated in an oil bath directly to 145 °C. After heating the reactor for 40 h, the reactor was cooled to room temperature and the gas mixture was analyzed by ATR-IR. A pale-yellow solution was obtained upon opening the reaction vessel. The pale-yellow solution was transferred into a J. Young NMR tube under N₂ atmosphere and analyzed by ¹H, ¹³C and ³¹P NMR.



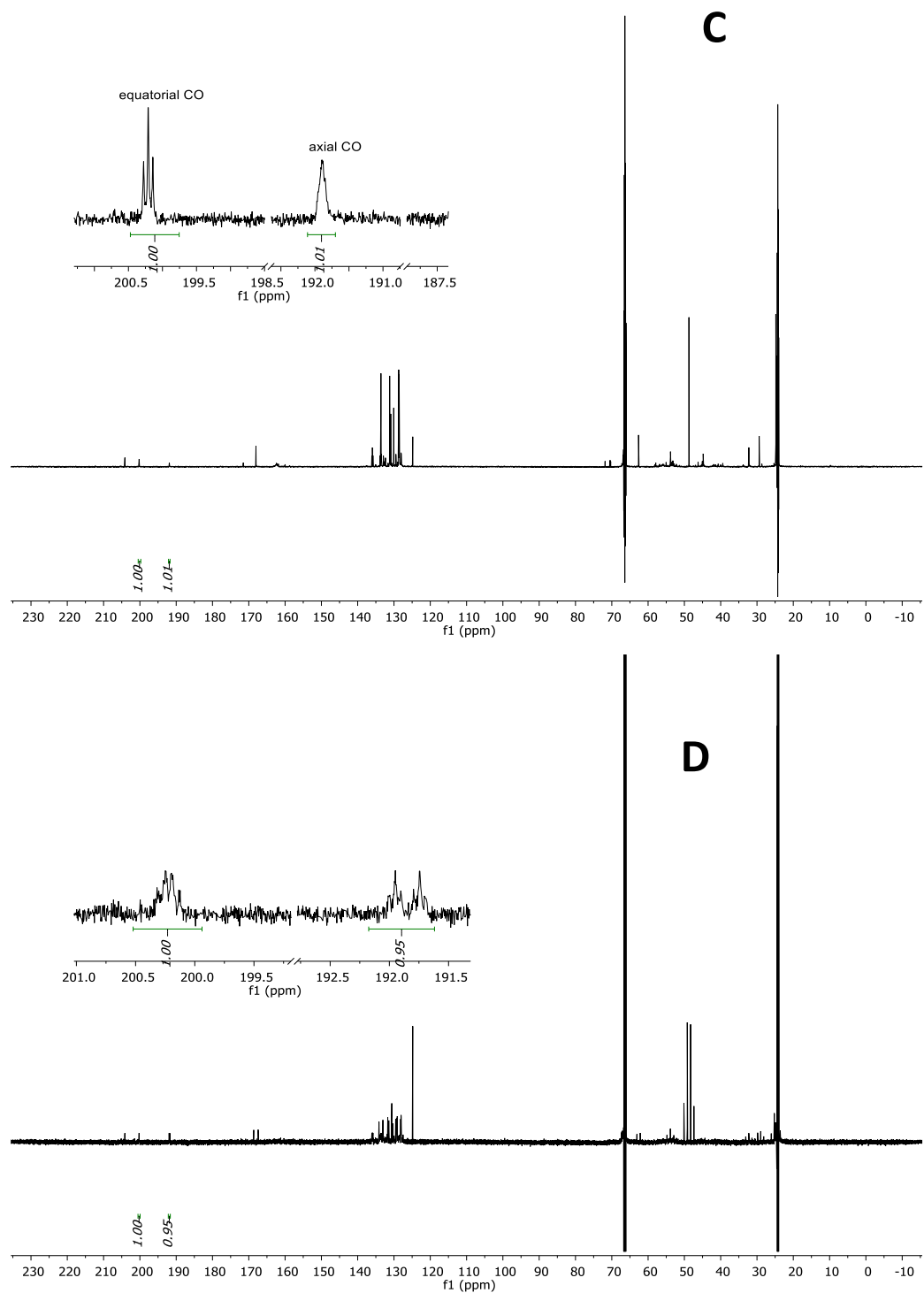


Figure S4. ^1H (A), ^{31}P (B), ^1H decoupled ^{13}C (C) and ^1H coupled ^{13}C (D) NMR of **C-1** biscarbonyl catalytic species (**C-1D**) containing reaction mixture.

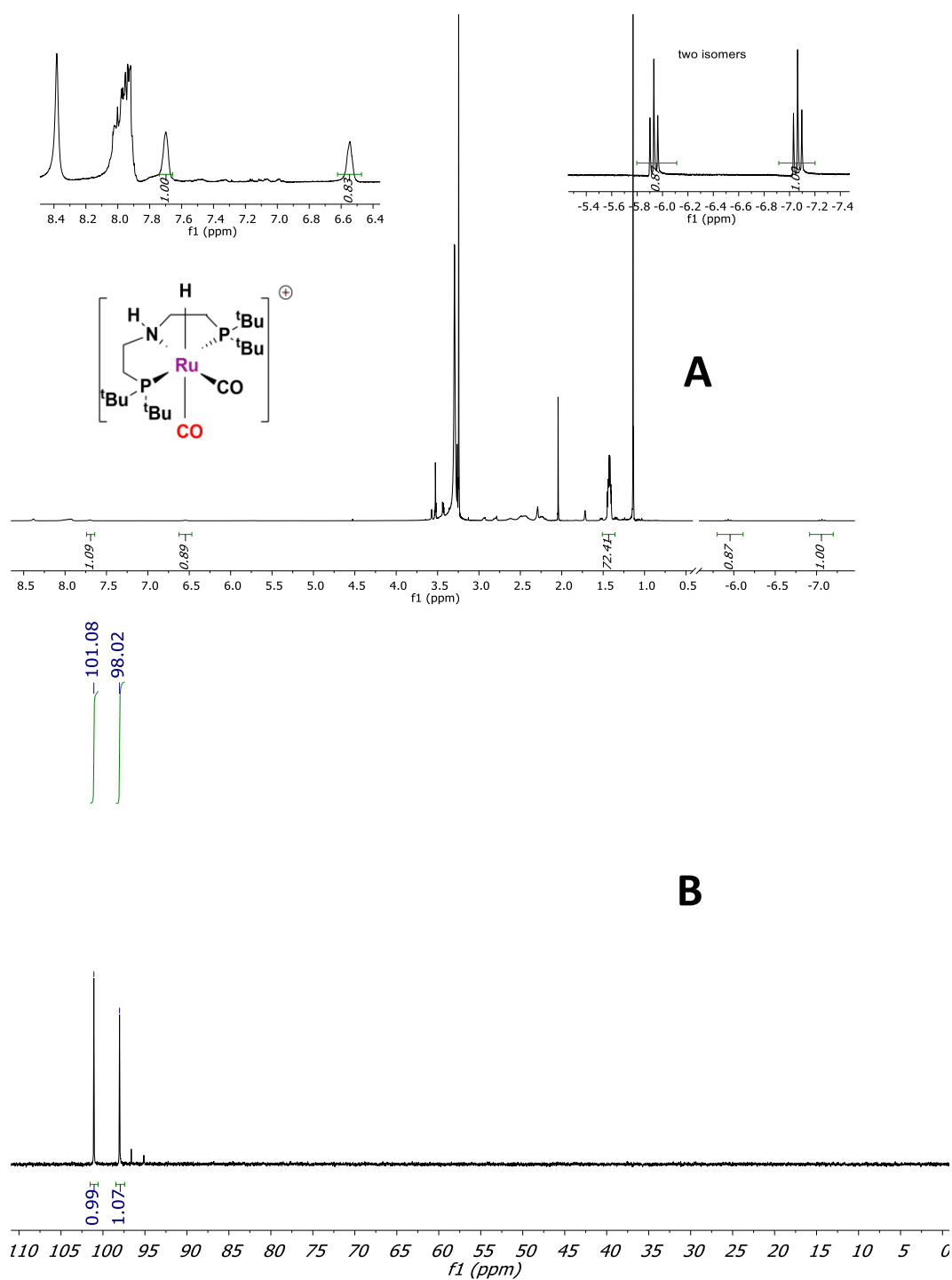


Figure S5. ¹H (A) and ³¹P NMR (B) of the C-5 biscarbonyl species (C-5D) containing reaction mixture. Two different isomers were observed based on relative orientation of N-H and Ru-H.

8.2. ATR-IR spectra of the obtained reaction gas mixture (for CO gas detection)

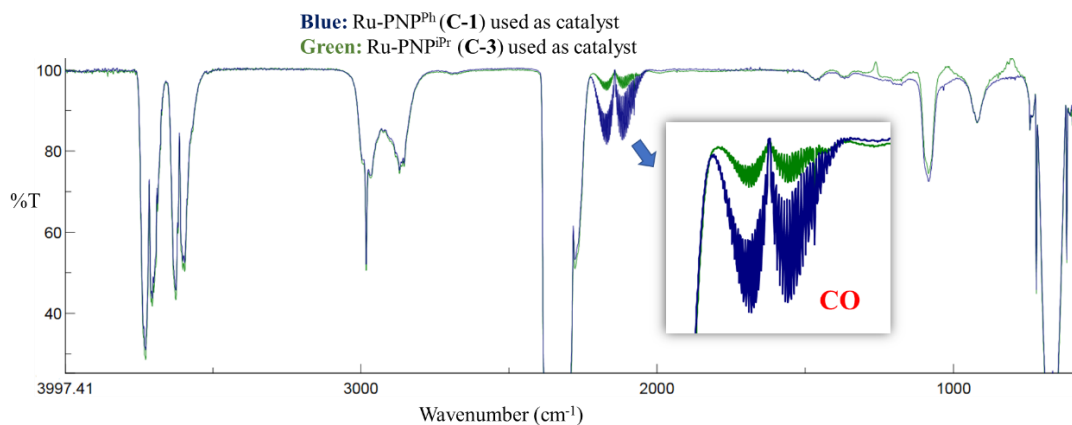


Figure S6. Observed free CO gas in ATR-IR after mechanistic investigation reactions.

8.3. Table S3. CO stretches of monocarbonyl and biscarbonyl complexes as observed in ATR-IR spectroscopy

Catalyst	CO stretch wavenumber (cm ⁻¹)
RuHCIPNP ^{Ph} (CO) [C-2]	1902
RuHCIPNP ^{iPr} (CO) [C-3]	1906
RuHCIPNP ^{Cy} (CO) [C-4]	1908
RuHCIPNP ^{Bu} (CO) [C-5]	1894
[RuHPNP ^{Ph} (CO) ₂] ⁺ [C-1D]	2052, 1964
[RuHPNP ^{iPr} (CO) ₂] ⁺ [C-3D]	2033, 1965
[RuHPNP ^{Cy} (CO) ₂] ⁺ [C-4D]	2033, 1966
[RuHPNP ^{Bu} (CO) ₂] ⁺ [C-5D]	1996, 1942

8.4. Table S4. Metal carbonyl bond lengths in various pincer biscarbonyl complexes

Complex	M-CO _{eq} (Å)	M-CO _{ax} (Å)	Reference
MnBrPNP ^{iPr} (CO) ₂	1.7810(17)	1.7507(16)	5
MnBrPNP ^{Cy} (CO) ₂	1.787(2)	1.754(3)	5
[FeHPNP ^{iPr} (CO) ₂] ⁺	1.7457(3)	1.8141(3)	6
[RuHPNP ^{Ph} (CO) ₂] ⁺	1.870(3)	1.980(3)	This work
[RuHPNP ^{Bu} (CO) ₂] ⁺	1.875(5)	1.971(5)	This work

8.5. Hydrogenation of biscarbonyl complex C-4D to monocarbonyl complex as observed in ATR-IR

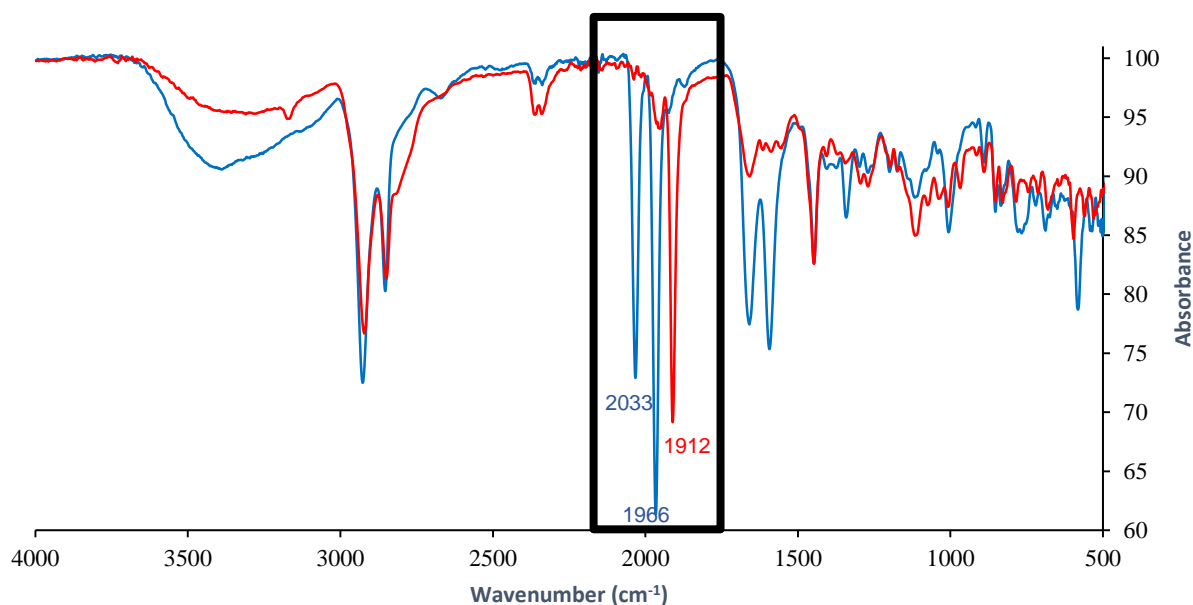


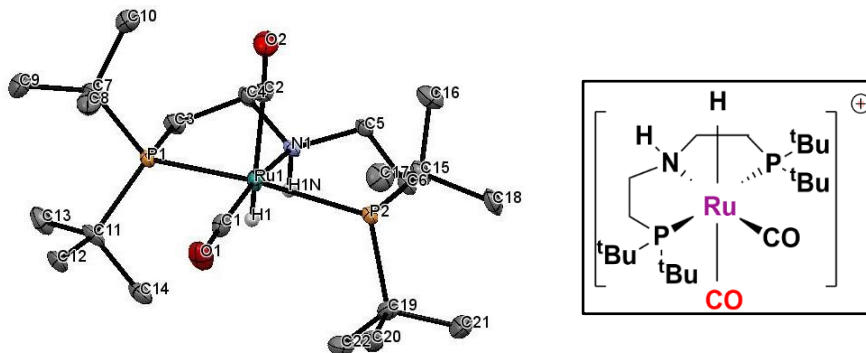
Figure S7. In blue, solution containing **C-4D** biscarbonyl complex obtained from the reaction in the mechanistic study; in red, after hydrogenation of the solution with 60 bar H₂ for 40 h at 145 °C. The loss of one carbonyl stretch signifies the formation of ruthenium dihydride monocarbonyl species.

9. Hydrogenation of formamides with biscarbonyl complexes (Table 4)

The reaction solutions obtained from the previously mentioned mechanistic studies (procedure detailed under section 8.1), containing the biscarbonyl complexes were used directly for the subsequent formamide hydrogenation reactions of Table 4. K₃PO₄, formamide (**F-1/F-2**), solvent (triglyme), and reaction solution containing the biscarbonyl complex were added into a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer a nitrogen chamber. After pressurizing the reactor with H₂, the LabVIEW 8.6 software was used to monitor and record the internal temperature and pressure of the reactor. The reaction mixture was stirred at room temperature (RT) for 30 min and then heated in a pre-heated oil bath to an internal temperature of 145 °C. After heating for a given amount of time, the reactor was cooled to RT and the gas mixture analyzed by GC. Upon opening the reaction vessel, a clear solution was obtained (colorless or pale yellow). 100 mg of 1,3,5-trimethoxybenzene was added as an internal standard to the reaction mixture. This mixture was then analyzed by ¹H and ¹³C NMR with a few drops of D₂O to lock the signals.

10. X-ray crystallography

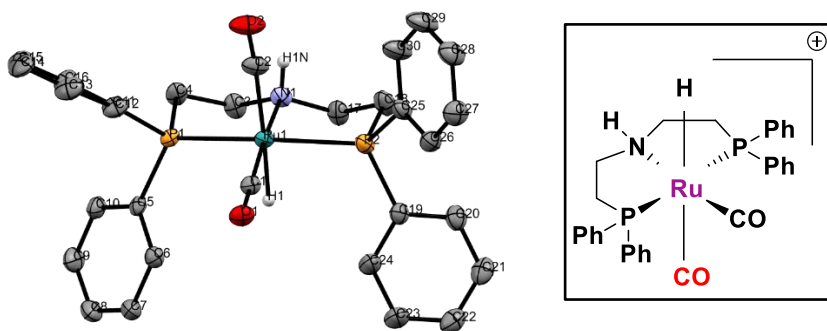
The X-ray intensity data were measured on a Bruker APEX DUO 3-circle platform diffractometer equipped with a APEX II CCD detector, using MoK α radiation from a fine-focus tube ($\lambda = 0.71073 \text{ \AA}$) monochromatized by a TRIUMPH curved-crystals monochromator. The frames were integrated using a Bruker SAINT V8.18C algorithm. Data were corrected for absorption effects using multi-scan method (SADABS). The structures were solved by intrinsic phasing and refined using Bruker SHELXTL Software Package.



Selected bond lengths (\AA) and angles ($^\circ$): Ru(1)-P(1) 2.3952(15), Ru(1)-P(2) 2.3851(16), Ru(1)-N(1) 2.180(4), Ru(1)-C(1) 1.870(5), Ru(1)-C(2) 1.971(5), P(1)-Ru(1)-P(2) 159.51(5), C(1)-Ru(1)-C(2) 94.0(2), C(2)-Ru(1)-N(1) 97.42(19)

C-5D.HCO₃.3H₂O

Chemical formula	C ₂₃ H ₅₃ NO ₈ P ₂ Ru	
Formula weight	634.67 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 \AA	
Crystal size	0.036 x 0.209 x 0.311 mm	
Crystal habit	clear colourless plate	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 12.463(7) \AA	$\alpha = 90^\circ$
	b = 15.073(8) \AA	$\beta = 90^\circ$
	c = 32.221(17) \AA	$\gamma = 90^\circ$
Volume	6053.(5) \AA^3	
Z	8	
Density (calculated)	1.393 g/cm ³	
Absorption coefficient	0.666 mm ⁻¹	
F(000)	2688	



Selected bond lengths (Å) and angles (°): Ru(1)-P(1) 2.3351(9), Ru(1)-P(2) 2.3474(9), Ru(1)-N(1) 2.187(3), Ru(1)-C(1) 1.870(3), Ru(1)-C(2) 1.980(3), P(1)-Ru(1)-P(2) 161.70(3), C(1)-Ru(1)-C(2) 94.58(13), C(2)-Ru(1)-N(1) 93.67(12)

C-2D.HCO₃

Chemical formula	C ₃₁ H ₃₁ NO ₅ P ₂ Ru	
Formula weight	660.58 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.116 x 0.177 x 0.377 mm	
Crystal habit	clear colourless prism	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.6522(17) Å	α = 76.100(3)°
	b = 12.368(2) Å	β = 83.249(3)°
	c = 16.043(3) Å	γ = 79.846(3)°
Volume	1635.3(6) Å ³	
Z	2	
Density (calculated)	1.342 g/cm ³	
Absorption coefficient	0.614 mm ⁻¹	
F(000)	676	

11. References

1. Han, Z.; Rong, L.; Wu, J.; Zhang, L.; Wang, Z.; Ding, K., Catalytic Hydrogenation of Cyclic Carbonates: A Practical Approach from CO₂ and Epoxides to Methanol and Diols. *Angew. Chem., Int. Ed.* **2012**, *51*, 13041-13045.
2. Ogata, O.; Nakayama, Y.; Nara, H.; Fujiwara, M.; Kayaki, Y., Atmospheric Hydrogenation of Esters Catalyzed by PNP-Ruthenium Complexes with an N-Heterocyclic Carbene Ligand. *Org. Lett.* **2016**, *18*, 3894-3897.
3. Barham, J. P.; Coulthard, G.; Emery, K. J.; Doni, E.; Cumine, F.; Nocera, G.; John, M. P.; Berlouis, L. E. A.; McGuire, T.; Tuttle, T.; Murphy, J. A., KOtBu: A Privileged Reagent for Electron Transfer Reactions? *J. Am. Chem. Soc.* **2016**, *138*, 7402-7410.
4. Kothandaraman, J.; Goeppert, A.; Czaun, M.; Olah, G. A.; Prakash, G. K. S., Conversion of CO₂ from Air into Methanol Using a Polyamine and a Homogeneous Ruthenium Catalyst. *J. Am. Chem. Soc.* **2016**, *138*, 778-781.
5. Elangovan, S.; Topf, C.; Fischer, S.; Jiao, H.; Spannenberg, A.; Baumann, W.; Ludwig, R.; Junge, K.; Beller, M., Selective Catalytic Hydrogenations of Nitriles, Ketones, and Aldehydes by Well-Defined Manganese Pincer Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 8809-8814.
6. Jayarathne, U.; Hazari, N.; Bernskoetter, W. H., Selective Iron-Catalyzed N-Formylation of Amines using Dihydrogen and Carbon Dioxide. *ACS Catal.* **2018**, *8*, 1338-1345.