# Supporting Information for Catalytic Hydrogenation of CO<sub>2</sub> at a Structurally Rigidified Cobalt Center

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### **Contents**

**Experimental Section** 

Figure S1. <sup>1</sup>H NMR spectrum of (<sup>acri</sup>PNP)Co(OCHO) 2a in C<sub>6</sub>D<sub>6</sub>.

Figure S2. <sup>1</sup>H NMR spectrum of (PNP)Co(OCHO) 2b in C<sub>6</sub>D<sub>6</sub>.

**Figure S3.** <sup>1</sup>H NMR spectrum of (acriPNP)H in C<sub>6</sub>D<sub>6</sub>.

Figure S4. <sup>13</sup>C NMR spectrum of ( $^{acri}PNP$ )H in C<sub>6</sub>D<sub>6</sub>.

Figure S5. <sup>31</sup>P NMR spectrum of (<sup>acri</sup>PNP)H in C<sub>6</sub>D<sub>6</sub>.

Figure S6. <sup>1</sup>H NMR spectrum for  $CO_2$  hydrogenation with 2a in  $D_2O$ .

**Figure S7.** <sup>31</sup>P NMR spectra of 2 equivalents of triphenylphosphine oxide and 1 equivalent of (a) a ( $^{acri}$ PNP)H ligand and (b) a (PNP)H ligand in C<sub>6</sub>D<sub>6</sub>.

Figure S8. <sup>31</sup>P NMR spectra of (a) 2a and (b) the reaction of 2a and [DBUH][Formate] in  $C_6D_6$ .

Figure S9. <sup>1</sup>H NMR spectrum of (PNP)H from the reaction of 2b and [DBUH][Formate] in C<sub>6</sub>D<sub>6</sub>.

Figure S10. <sup>31</sup>P NMR spectra of (a) 2b and (b) the reaction of 2b and [DBUH][Formate] in  $C_6D_6$ .

Figure S11. <sup>1</sup>H NMR spectra of resulting products of catalytic CO<sub>2</sub> hydrogenation with (a) 2a and (b) 2b in C<sub>6</sub>D<sub>6</sub>.

Figure S12. <sup>31</sup>P NMR spectra of resulting products of catalytic CO<sub>2</sub> hydrogenation using **2a** after (a) 0 hr, (b) 0.5

hr and (c) 2 hr in  $C_6D_6$ .

**Figure S13.** <sup>31</sup>P NMR spectra of resulting products of catalytic CO<sub>2</sub> hydrogenation using **2b** after (a) 0 hr, (b) 0.5 hr and (c) 2 hr in  $C_6D_6$ .

**Figure S14.** <sup>1</sup>H NMR spectra of (a) **2a** and the reaction of **2a** with (b) DBU, (c) LiOTf, (d) DBU and LiOTf and (e) DBU, LiOTf and  $H_2$  in 1:1 THF:C<sub>6</sub>D<sub>6</sub>.

Figure S15. Solid-state structure of 2a.

Table S1. Selected bond distances and angles for 2a.

Figure S16. Solid-state structure of 2b.

 Table S2. Selected bond distances and angles for 2b.

Table S3. Crystallographic data of complexes 2a and 2b.

Figure S17. UV-Vis spectrum of 2a.

Figure S18. UV-Vis spectrum of 2b.

Figure S19. UV-Vis spectra of 2a and the reaction mixture of 2a and [DBUH][Formate].

Figure S20. UV-Vis spectra of 2b and the reaction mixture of 2b and [DBUH][Formate].

Figure S21 IR spectra of 2a and 2a-<sup>13</sup>CO<sub>2</sub>.

Figure S22 IR spectra of 2b and 2b-<sup>13</sup>CO<sub>2</sub>.

Figure S23. X-Band EPR spectrum of 2a in toluene at 10K.

Figure S24. X-Band EPR spectrum of 2b in toluene at 10K.

Table S4. Summary of EPR spectroscopic parameters for 2a and 2b.

**Table S5.** Base screening for **a** and **b** catalyzed CO<sub>2</sub> hydrogenation.

Table S6. Solvent screening for 2a catalyzed hydrogenation of CO<sub>2</sub> at 100 °C.

Table S7. Reaction profiles for 2a and 2b catalyzed CO<sub>2</sub> hydrogenation at 80 °C.

Table S8. Reaction profiles for 2a and 2b catalyzed CO<sub>2</sub> hydrogenation at 100 °C.

#### **Computational Details**

Figure S25. Experimental and TD-DFT-predicted absorption spectra of 2a.

Figure S26. Experimental and TD-DFT-predicted absorption spectra of 2b.

Table S7. Selected bond indices for 2a and 2b from NBO analysis.

Reference

## **Experimental Section**

*General Considerations.* All manipulations were carried out using standard Schlenk or glovebox techniques under a N<sub>2</sub> or Ar atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thoroughly sparging with Ar gas followed by passage through an activated alumina column. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. {( $\mu$ -PNP)Co}, **1a**, (acriPNP)Li(THF) and [DBUH][Formate] were prepared according to literature method.<sup>1-3</sup> Elemental analyses were carried out at KAIST Central Research Instrument Facility on Thermo Scientific FLASH 2000 series instrument. Deuterated solvents were purchased from Euriso-top, degassed, and dried over activated 4 Å molecular sieves prior to use.

*X-ray Crystallography.* The diffraction data of **2a** and **2b** were collected on a Bruker D8 QUEST. A suitable size and quality of crystal was coated with Paratone-*N* oil and mounted on a MiTeGen MicroLoop. The data were collected with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 120 K. Cell parameters were determined and refined by SMART program.<sup>4</sup> Data reduction was performed using SAINT software.<sup>5</sup> An empirical absorption correction was applied using the SADABS program.<sup>6</sup> The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F<sup>2</sup> by using the SHELXTL/PC package.<sup>7</sup> Unless otherwise noted, hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Full crystallographic details can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data\_request/cif (CCDC 1958471-1958472 for **2a** and **2b**).

*Spectroscopic Measurements.* Bruker 400 spectrometers were used to measure <sup>1</sup>H NMR spectra. The chemical shifts for <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were quoted in part per million (ppm) referenced to residual solvent peaks. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet. Coupling constants, *J*, were reported in hertz unit (Hz). The chemical shifts for <sup>31</sup>P NMR spectra were quoted in part per million (ppm) referenced to external phosphoric acid as 0.0 ppm. Solution magnetic moments were determined by the Evans' method.<sup>8</sup> UV-Vis spectra were measured using an Agilent Cary 60 UV-Vis spectrophotometer with a 1 cm two-window quartz spectrophotometer cell sealed with a screw-cap purchased from Hellma Analytics (117.100-QS). Infrared spectra were recorded in KBr pellet by Agilent Cary 630. Frequencies are given in reciprocal centimeters (cm<sup>-1</sup>) and only selected absorbances are reported.

*CW and Pulsed-EPR Spectroscopy.* All EPR measurements were carried out at Korea Basic Science Institute (KBSI) in Seoul, Korea. CW X-band EPR spectra of **2a** and **2b** were collected on a Bruker EMX plus 6/1 spectrometer equipped with an Oxford Instrument ESR900 liquid He cryostat using an Oxford ITC 503 temperature controller. Spectra were collected with the following experimental parameters: microwave frequency, 9.6 GHz; microwave power, 0.96 mW; modulation amplitude, 10 G; modulation frequency, 100 kHz; temperature, 10 K. The CW-EPR simulations were performed using EasySpin.<sup>9</sup>

Synthesis of (acriPNP)Co(OCHO) (2a). In a 100 mL Schlenk tube, a solution of (acriPNP)CoH (168 mg, 318 µmol) in 10 mL of benzene was degassed by four freeze-pump-thaw cycles on the Schlenk line. CO<sub>2</sub>(g) was charged at ambient pressure and temperature. Volatiles were removed under vacuum. The resulting product (acriPNP)Co(OCHO) (2a, 171 mg, 147 µmol, 94%) was obtained as green powder after washing with pentane. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  32.6 (s), 30.0 (s), 12.5 (s), 7.84 (s), 6.78 (s), 3.27 (s), 1.13 (s), -6.37(s). IR (KBr, cm<sup>-1</sup>):  $v_{CH,formate} = 2811$ ,  $v_{CO} = 1623$ ,  $v_{Ar} = 1619$ .  $\mu_{eff}$ : 2.45  $\mu_B$  (C<sub>6</sub>D<sub>6</sub>, 25 °C, Evans' method). UV-Vis [THF, nm (L mol<sup>-1</sup> cm<sup>-1</sup>)]: 285 (18,000), 312 (16,000), 381 (4,500), 446 (1,300), 600 (1,100). Anal. Calcd. for C<sub>30</sub>H<sub>46</sub>CoNO<sub>2</sub>P<sub>2</sub>: C, 62.93; H, 7.92; N, 2.45. Found: C, 63.01; H, 7.96; N, 2.37. Crystals suitable for X-ray diffraction were obtained by recrystallization of saturated pentane solution of **2a** at -35 °C.

**Synthesis of (PNP)Co(OCHO) (2b).** In a 100 mL Schlenk tube, a solution of {( $\mu$ -PNP)Co}<sub>2</sub> (147 mg, 146 µmol) in 10 mL of benzene was degassed by four freeze-pump-thaw cycles on the Schlenk line. H<sub>2</sub>(g) was exposed at ambient pressure. The reaction mixture was stirred at 100 °C for 2 hrs. After the solution was frozen, the head-space gas was eliminated under vacuum and CO<sub>2</sub> was charged at ambient pressure. Volatiles were removed under vacuum. The resulting product (PNP)Co(OCHO) (**2b**, 143 mg, 269 µmol, 92.6%) was obtained as dark green powder after washing with pentane. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  29.3 (s), 24.3 (s), 8.41 (s), 3.38 (s), 2.10 (s), 1.25 (s), 1.04 (s), -23.2 (s). IR (KBr, cm<sup>-1</sup>):  $v_{CH,formate} = 2811$ ,  $v_{CO} = 1623$ ,  $v_{Ar} = 1606$ .  $\mu_{eff}$ : 2.18  $\mu_B$  (C<sub>6</sub>D<sub>6</sub>, 25 °C, Evans' method). UV-Vis [THF, nm (L mol<sup>-1</sup> cm<sup>-1</sup>)]: 277 (18,000), 322 (17,000), 387 (3,600), 434 (1,500), 579 (1,000). Anal. Calcd. for C<sub>27</sub>H<sub>42</sub>CoNO<sub>2</sub>P<sub>2</sub>: C, 60.78; H, 7.93; N, 2.63. Found: C, 60.90; H, 7.76; N, 2.63. C, 60.87; H, 7.33; N, 2.48. X-ray quality crystals were grown by cooling down of a saturated pentane solution of **2b** at -35 °C.

**Synthesis of** (acriPNP)**H.** To a (acriPNP)Li(THF) (226 mg, 428 µmol) in 10 mL of toluene, 100 mL of degassed water was added under N<sub>2</sub> atmosphere *via* cannula transfer. The reaction mixture was stirred at room temperature for 30 min. Volatiles are removed under vacuum. The resulting product (acriPNP)H (201 mg, 400 µmol, 93.4%) was obtained as pale yellow powder after washing with pentane. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  9.79 (t, *J*<sub>PH</sub> = 9.2 Hz, 1H), 7.22 (s, 2H), 7.09 (s, 2H), 2.29 (s, 6H), 2.09 (m, 4H), 1.54 (s, 6H), 1.16 (q, *J* = 16 Hz, 8 Hz, 12H), 0.98 (q, *J* = 12 Hz, 8 Hz, 12H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  143.29 (s), 143.06 (s), 131.16 (s), 129.51 (t, *J* = 3 Hz), 126.83 (s), 117.70 (d, *J* = 17 Hz), 37.06 (t, *J* = 2 Hz), 29.65 (s), 23.89 (s), 21.39 (s), 20.55 (s), 20.35 (s), 19.35 (s), 19.25 (s). <sup>31</sup>P NMR (141 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  – 16.90 (s). Anal. Calcd. for C<sub>29</sub>H<sub>45</sub>NP<sub>2</sub>: C, 74.17; H, 9.66; N, 2.98. Found: C, 74.50; H, 9.92; N, 2.63.

**Standard procedure for hydrogenation of carbon dioxide.** To a stainless Parr reactor, a 5 mL solution of catalyst and 1,8-diazabicycloundec-7-ene (DBU) in THF was added and pressurized by equimolecular  $CO_2$  and  $H_2$  mixture gas. The reaction mixture was stirred at appropriate temperature. *N*,*N*-Dimethylformamide (100 mg, 1.37 mmol) was added to the reaction mixture as an internal standard and the mixture was dissolved in D<sub>2</sub>O for an estimation of the yield by using <sup>1</sup>H NMR spectrum. A representative spectrum of the reaction mixture is shown in Figure S6.

**Quantification of free ligands after hydrogenation of carbon dioxide.** After the standard procedure for hydrogenation of carbon dioxide, the gas was released at ambient temperature and the reactor was taken into the drybox. 2 equivalent of OPPh<sub>3</sub> solution in THF is added to

the reaction mixture and dried over vacuum. The mixture was dissolved in  $C_6D_6$  for an estimation of the yield by using <sup>31</sup>P NMR spectrum.

Reaction of 2a and 2b with [DBUH][Formate] followed by NMR experiments. To a mixture of 2 (49 µmol) and triphenylphosphine oxide (28 mg, 98 µmol) as internal standard in 5 mL of THF, [DBUH][Formate] (49 mg, 250 µmol) was added at room temperature and the reaction mixture was stirred at room temperature for 30 min. 500 µL of the reaction mixture was added to the 100 µL of  $C_6D_6$ . The resulting product (PNP)H<sup>10</sup> was detected and quantified by <sup>31</sup>P NMR spectroscopy in the presence of triphenylphosphine oxide as an internal standard.

Reaction of 2a and 2b with [DBUH][Formate] followed by UV-Vis experiments. In a 20 mL of volumetric flask, 2a and 2b (17  $\mu$ mol) was dissolved by THF and 4 mL of the solution was added to the [DBUH][Formate] (4 mg, 20  $\mu$ mol) in a UV cell. The UV-Vis data (400 nm  $< \lambda < 800$  nm) were collected after 5 min. The time stacked UV-Vis spectra show the consumption of 2b.

**Reaction of 2a with DBU, LiOTf and H<sub>2</sub>.** In a NMR tube equipped with J-Young valve, DBU (15  $\mu$ L, 95  $\mu$ mol) and LiOTf (14mg, 95  $\mu$ mol) were added to a solution of **2a** (11 mg, 19  $\mu$ mol) was dissolved in 0.3 mL of 1:1 THF:C<sub>6</sub>D<sub>6</sub>. The reaction of **2a** and LiOTf reveals that the significant change of **2a** were observed from 32.3 (s), 29.6 (s), 12.3 (s), 7.69 (s), -6.54 (s) to 34.0 (s), 30.7 (s), 13.2 (s), 7.87 (s), -6.87 (s), in <sup>1</sup>H NMR spectra, respectively. After degassed by three freeze-pump-thaw cycles on the Schlenk line, H<sub>2</sub>(g) was charged at ambient pressure and room temperature. The reaction mixture was shaken at room temperature for 1 hr and the generation of **1a** was observed in <sup>1</sup>H NMR spectrum.

Figure S1. <sup>1</sup>H NMR spectrum of (<sup>acri</sup>PNP)Co(OCHO) (2a) in C<sub>6</sub>D<sub>6</sub> at room temperature.



Figure S2. <sup>1</sup>H NMR spectrum of (PNP)Co(OCHO) (2b) in C<sub>6</sub>D<sub>6</sub> at room temperature.







**Figure S6.** <sup>1</sup>H NMR spectrum for CO<sub>2</sub> hydrogenation with ( $^{acri}$ PNP)Co(OCHO) in D<sub>2</sub>O at room temperature (•: formate, •: *N*,*N*-dimethylformamide).



**Figure S7.** <sup>31</sup>P NMR spectra of 2 equivalent of triphenylphosphine oxide and 1 equivalent of (a) a (acriPNP)H ligand and (b) a (PNP)H ligand in  $C_6D_6$  (•: triphenylphosphine oxide, •: (acriPNP)H, •: (PNP)H).



**Figure S8.** <sup>31</sup>P NMR spectra of (a) ( $^{acri}$ PNP)Co(OCHO) (**2a**) in C<sub>6</sub>D<sub>6</sub> and (b) the reaction of **2a** and 5 equiv. of [DBUH][Formate] in C<sub>6</sub>D<sub>6</sub> at room temperature in the presence of triphenylphosphine oxide as an internal standard (•: triphenylphosphine oxide).





**Figure S10.** <sup>31</sup>P NMR spectra of (a) (PNP)Co(OCHO) (**2b**) in C<sub>6</sub>D<sub>6</sub> and (b) the reaction of **2b** and 5 equiv. of [DBUH][formate] in C<sub>6</sub>D<sub>6</sub> at room temperature in the presence of triphenylphosphine oxide as an internal standard (•: triphenylphosphine oxide, •: (PNP)H).







**Figure S12.** <sup>31</sup>P NMR spectra of resulting products of catalytic CO<sub>2</sub> hydrogenation using **2a** after (a) 0 hr, (b) 0.5 hr, (c) 1 hr and (d) 2 hr in  $C_6D_6$  (•: triphenylphosphine oxide, •: (acriPNP)H).



**Figure S13.** <sup>31</sup>P NMR spectra of resulting products of catalytic CO<sub>2</sub> hydrogenation using **2b** after (a) 0 hr, (b) 0.5 hr, (c) 1 hr and (d) 2 hr in C<sub>6</sub>D<sub>6</sub> (•: triphenylphosphine oxide, •: (PNP)H), •: unknown species).



**Figure S14.** <sup>1</sup>H NMR spectra of (a) **2a** and the reaction of **2a** with (b) DBU, (c) LiOTf, and (d) DBU and LiOTf and (e) DBU, LiOTf and  $H_2$  in 1:1 THF:C<sub>6</sub>D<sub>6</sub> at room temperature (•: **2a**, •: unknown species, •: **1a** and •: free formate.



Figure S15. Solid-state structure of (acriPNP)Co(OCHO) (2a). All hydrogen atoms of an acriPNP ligand are omitted for clarity.



Table S1. Selected bond distances and angles for 2a (Å and °).

Bond distance		Bond angle	
d <sub>Co1-P1</sub>	2.2063(4)	∠P1-Co1-P2	171.56(2)
d <sub>Co1-P2</sub>	2.2178(4)	∠N1-Co1-O1	162.02(6)
d <sub>Col-N1</sub>	1.897(1)	∠Co1-O1-C30	108.1(1)
d <sub>Co1-O1</sub>	1.961(1)	∠O1-C30-O2	123.6(2)
d <sub>C30-O1</sub>	1.257(2)		
d <sub>C30-O2</sub>	1.226(3)		

Figure S16. Solid-state structure of (PNP)Co(OCHO) (2b). All hydrogen atoms of a PNP ligand are omitted for clarity.



Table S2. Selected bond distances and angles for 2b (Å and °).

		Bond angle	
d <sub>Co1-P1</sub>	2.2258(9)	∠P1-Co1-P2	167.00(3)
d <sub>Co1-P2</sub>	2.2272(8)	∠N1-Co1-O1	177.0(1)
d <sub>Co1-N1</sub>	1.899(2)	∠Co1-O1-C27	114.2(3)
d <sub>Co1-O1</sub>	1.928(2)	∠01-C27-O2	126.8(4)
d <sub>C27-O1</sub>	1.237(5)		
d <sub>C27-O2</sub>	1.233(6)		

 Table S3. Crystallographic data of complexes 2a and 2b.

Complex	2a	2b
Temperature	120 K	120 K
CCDC Deposition #	1958471	1958472
Formula	C30H46CoNO2P2	C27H41CoNO2P2
Crystal description	Platy	Platy
Crystal size, [mm]	0.400x0.270x0.270	0.250x0.220x0.200
FW, [g/mol]	573.55	532.48
Space group	P 21/c	P n a 21
Crystal system	Monoclinic	Orthorhomibic
a, [Å]	13.9653(8)	16.8714(6)
b, [Å]	13.9491(8)	16.8263(7)
c, [Å]	16.1003(9)	9.7085(3)
α, [°]	90	90
β, [°]	105.571(2)	90
γ, [°]	90	90
Ζ	4	4
$\rho_{\text{cacld}}, [g/\text{cm}]$	1.261	1.283
Absorption coefficient	0.700	0.762
No. of reflections	97502	51231
No. of unique reflections	6928	7639
2θmax, [°]	54.998	64.038
R <sub>int</sub>	0.0281	0.0669
No. of parameters(restraints)	337(0)	308(1)
Final R	0.0350	0.0401
GoF	1.079	1.016

Figure S17. UV-Vis spectra of (acriPNP)Co(OCHO) (2a) in THF at room temperature.



Figure S18. UV-Vis spectrum of (PNP)Co(OCHO) (2b) in THF at room temperature.



**Figure S19.** UV-Vis spectra of (acriPNP)Co(OCHO) (**2a**, black) and the reaction mixture of **2a** and [DBUH][Formate] (red) in THF at room temperature.



**Figure S20.** UV-Vis spectra of (PNP)Co(OCHO) (**2b**, black) and the reaction mixture of **2b** and [DBUH][Formate] (red) in THF at room temperature.



**Figure S21.** IR spectra of (acriPNP)Co(OCHO) (**2a**) and (acriPNP)Co(O<sup>13</sup>CHO) (**2a-**<sup>13</sup>CO<sub>2</sub>, red) (KBr pellet).



**Figure S22.** IR spectra of (PNP)Co(OCHO) (**2b**, black) and (PNP)Co(O<sup>13</sup>CHO) (**2b-**<sup>13</sup>CO<sub>2</sub>, red) (KBr pellet).



**Figure S23.** X-Band EPR spectra of (<sup>acri</sup>PNP)Co(OCHO) (**2a**) in toluene (black) at 10 K with a simulated spectrum (red).



**Figure S24.** X-Band EPR spectra of (PNP)Co(OCHO) (**2b**) in toluene (black) at 10 K with a simulated spectrum (red).



	2a	2b
g	3.44, 2.09, 1.73	3.48, 2.12, 1.66
А	750, 0, 0	150, 0, 0
gstrain	0.24, 0.12, 0.09	0.24, 0.14, 0.13
Astrain	150, 150, 0	150, 0, 0

Table S4. Summary of EPR spectroscopic parameters for 2a and 2b.

Table S5. Base screening for a and b catalyzed CO<sub>2</sub> hydrogenation.

Entry	Catalyst	Base	Time	TON <sup>b</sup>
1	a	Verkade's	2	26
		Base		
2	a	NEt <sub>3</sub>	2	0
3	a	DBU	1	950
4	a	DBU	2	1,300
5	b	DBU	1	30
6	b	DBU	2	550

<sup>a</sup>Reaction condition: 40 bar of 1:1 CO<sub>2</sub> and H<sub>2</sub> mixture gas, 0.8 mM catalyst, 2.3 M of base in 5 mL of THF at 100 °C. <sup>b</sup>Average TON for three or more trials.

Table S6. Solvent screening for 2a catalyzed CO<sub>2</sub> hydrogenation.

Entry	Solvent	TON <sup>b</sup>
1	toluene	940
2	THF	1,600
3	MeCN	1,100

<sup>a</sup>Reaction condition: 40 bar of 1:1 CO<sub>2</sub> and H<sub>2</sub> mixture gas, 0.8 mM catalyst, 2.3 M DBU in 5 mL of solvent at 100 °C for 2 hr. <sup>b</sup>Average TON for three or more trials.

Table S7. Reaction profiles for 2a and 2b catalyzed CO<sub>2</sub> hydrogenation at 80 °C.

Entry	Catalyst	Time (hr)	TON <sup>b</sup>
1	2a	0.5	710
2	2a	1	810
3	2a	2	950
4	2a	3	1100
5	2a	4	1400
6	2a	6	1300
7	2a	8	1400
8	2b	0.5	240
9	2b	1	290
10	2b	2	290
11	2b	3	410

12	2b	4	380
13	<b>2b</b>	6	390
14	<b>2b</b>	8	445

<sup>a</sup>Reaction condition: 40 bar of 1:1 CO<sub>2</sub> and H<sub>2</sub> mixture gas, 0.16 mM catalyst, 790 mM of DBU in 5 mL of THF at 80 °C. <sup>b</sup>Average TON for three or more trials.

Table S8. Reaction profiles for 2a and 2b catalyzed CO<sub>2</sub> hydrogenation at 100 °C.

Entry	Catalyst	Time	TON <sup>b</sup>
1	2a	30 min	900
2	2a	1 hr	1,200
3	2a	2 hrs	1,600
4	2b	1 hr	144
5	2b	2 hrs	300

<sup>a</sup>Reaction condition:  $1:1 \text{ CO}_2$  and  $H_2$  mixture gas, 0.8 mM catalyst, 2.3 M of DBU in 5 mL of THF at 100 °C. <sup>b</sup>Average TON for three or more trials.

*Computational details.* Geometry optimizations were performed with the Gaussian 09<sup>11</sup> with the BP86 functional.<sup>12-14</sup> The def2-tzvp basis set<sup>15</sup> was used for describing all atoms. NBO analysis were performed with the Gaussian 09<sup>11</sup> with the B3LYP functional.<sup>16-18</sup> The initial geometry for (<sup>acri</sup>PNP)Co(OCHO) (**2a**) and (PNP)Co(OCHO) (**2b**) computational model was obtained from their corresponding X-ray crystal structure. Optimized structure of **2a** and **2b** were verified using frequency calculations to confirm the absence of any imaginary frequency.

Figure S25. Experimental (black) and TD-DFT-predicted (red) absorption spectra of (acriPNP)Co(OCHO) (2a).



**Figure S26.** Experimental (black) and TD-DFT-predicted (red) absorption spectra of (PNP)Co(OCHO) (**2b**).



**Table S7.** Selected bond indices for (acriPNP)Co(OCHO) (2a) and (PNP)Co(OCHO) (2b) from NBO analysis.

Wiberg Bond Index	(acriPNP)Co(OCHO)	(PNP)Co(OCHO)
Co–P	0.7044/0.7026	0.6806/0.6760
Co–N	0.6084	0.5579
Со-О	0.4743	0.4525

## Reference

- (1) J. Choi, Y. Lee, Angew. Chem. Int. Ed. 2019, 58, 8727.
- (2) A. R. Fout, F. Basuli, H. Fan, J. Tomaszewski, J. C. Huffman, M.-H. Baik, D. J. Mindiola, *Angew. Chem. Int. Ed.* 2006, **45**, 3291.
- (3) Y. Yang, H. Fan, Q. Meng, Z. Zhang, G. Yang, B. Han, Chem. Commun. 2017, 53, 8850.
- (4) SMART (version 5.0), data collection software; Bruker AXS, Inc., Madison, WI, 1998.
- (5) SAINT (version 5.0), data integration software; Bruker AXS, Inc., Madison, WI, 1998.

- (6) G. M. Sheldrick, SADABS: program for absorption correction with the Bruker SMART system; Universität Göttingen, Germany, 1996.
- (7) G. M. Sheldrick, SHELXTL (version 6.1), Bruker AXS, Inc., Madison, WI, 2000.
- (8) (a) D. F. Evans, J. Chem. Soc. 1959, 2003; (b) S. K. Sur, J. Magn. Reson. 1989, 82,169.
- (9) S. Stoll, A. Schweiger, J. Magn. Reso. 2006, 178, 42.
- (10) L. Fan, B. B. Foxman, O. V. Ozerov, Organometallics 2004, 23, 326.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, **2013**.
- (12) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
- (13) J. P. Perdew, Phys. Rev. B, 1986, 34, 7406.
- (14) J. P. Perdew, *Phys. Rev. B*, 1988, **38**, 3098.
- (15) F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297.
- (16) A. D. Becke, J. Chem. Phys., 1993, 98, 5648.
- (17) C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785.
- (18) S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys., 1980, 58, 1200.