The Steps of Activating a Prospective CO<sub>2</sub> Hydrogenation Catalyst with Combined CO<sub>2</sub> Capture and Reduction

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### Experimental

### **General Procedures**

All chemicals were purchased from commercial sources and used as received unless otherwise specified. Manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk and glovebox techniques under an atmosphere of argon or nitrogen. Solvents were sparged with nitrogen and dried over basic alumina in a custom dry solvent system. Tetrahydrofuran-d<sub>8</sub> was dried using NaK alloy and distilled. DBU was distilled over solid Na and stored under an atmosphere of nitrogen.

All kinetic data were collected on a 300 MHz Varian NMR instrument at 25°C.

#### **Synthetic Procedures**

#### cis-Ru(PNP)<sub>2</sub>Cl<sub>2</sub>.

A slurry of Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (514 mg, 1.1 mmol) in 20 mL of dichloromethane was treated with a solution of PNP (PNP = CH<sub>3</sub>N[CH<sub>2</sub>P(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>]) (500 mg, 2.1 mmol) dissolved in 2.0 mL dichloromethane. The reaction was allowed to stir for 5 hr after which the volume of the reaction was reduced to 5 mL. Pentane (25 ml) was added to the reaction flask that caused the precipitation of the product as a fine yellow solid. The product was collected by vacuum filtration and washed with diethylether (2 x 5 mL and ) followed by pentane (2 x 5 mL) to give the product as a fine yellow powder ( 600 mg, 88%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): Assignments made by 2-D TOCSY and HSQC.  $\delta$  1.06-1.26 (br m, 24H, -CH<sub>2</sub>-CH<sub>3</sub>), 1.39-1.46 (m, 2H, CH<sub>2</sub>-CH<sub>3</sub>), 1.65-1.68 (m, 4H, -CH<sub>2</sub>-CH<sub>3</sub>), 1.88-1.95 (m, 4H, -CH<sub>2</sub>-CH<sub>3</sub>), 2.24-2.27 (m, 2H, -N-CH<sub>2</sub>-P-), 2.37 (s, 6H, -N-CH<sub>3</sub>), 2.47-2.56 (br m, 12H, -N-CH<sub>2</sub>-P, CH<sub>3</sub>S(O)CH<sub>3</sub>), 2.75-2.82 (m, 2H, -CH<sub>2</sub>-CH<sub>3</sub>), 3.02-3.07 (m, 4H, -P-CH<sub>2</sub>-N-). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): AA'XX',  $\delta$  22.5 (pseudo t, splitting = 33.4 Hz), -0.12 (pseudo t, splitting = 33.4 Hz. Anal. Calcd. for C<sub>22</sub>H<sub>54</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>4</sub>Ru · C<sub>2</sub>H<sub>5</sub>SO: C, 40.00; H, 8.39; N, 3.89. Found: C, 39.90; H, 8.37; N, 3.81.

#### cis-Ru(PNP)<sub>2</sub>(H)<sub>2</sub>.

A J. Young tube containing a solution of cis-Ru(PNP)<sub>2</sub>Cl<sub>2</sub> in 0.55 mL of THF-d<sub>8</sub> was treated with 2.1 eq of 1.0M LiHBEt<sub>3</sub> in THF. The solution rapidly changed from bright yellow to a very pale yellow color. The tube was sealed and <sup>1</sup>H and <sup>31</sup>P data were collected. Complete conversion of the corresponding dichloride to the dihydride was observed as evidenced by the appearance of new <sup>1</sup>H and <sup>31</sup>P resonances to the spectra described above for cis-Ru(PNP)<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (THF-d<sub>8</sub>): -10.3 (m).  $\delta$  <sup>31</sup>P{<sup>1</sup>H} NMR (THF-d<sub>8</sub>):  $\delta$  31.6 (pseudo t, 30.3 Hz), 15.6 (pseudo t, splitting = 30.3Hz).

#### $[DBUH]^+[C_6H_{13}OCO_2]^-.$

An equimolar mixture of DBU and 1-hexanol was stirred in a stainless steel autoclave for 16 hours under ca. 15 atm of  $CO_2$ . The clear, viscous solution was stored under 2 atm of  $CO_2$ .

#### **General Procedure for NMR Kinetics Solution.**

A solution of cis-Ru(PNP)<sub>2</sub>Cl<sub>2</sub> (0.0156 mmol) in 0.550 mL of THF-d<sub>8</sub> was treated with 31.0  $\mu$ L (0.0310 mmol) of a 1.0 M LiHBEt<sub>3</sub> solution in THF. The solution immediately changed from bright yellow to a pale yellow color. 2  $\mu$ L of toluene was added to the solution as an NMR integration standard. The precipitated LiCl was allowed to settle and the clear solution was loaded into a J. Young NMR tube under inert atmosphere.

#### CO<sub>2</sub> Reduction with DBU.

2 equivalents of DBU (0.0156 mmol) were added to the solution of cis-Ru(PNP)<sub>2</sub>(H)<sub>2</sub>. For the addition of 2, 1, or 0.5 atm of CO<sub>2</sub>, the solution was freeze-pump-thaw degassed 3 times prior to addition of CO<sub>2</sub>. For reduction of 1 and 2 equivalents of CO<sub>2</sub>, well-sealed septa topped NMR tubes were used and CO<sub>2</sub> was injected into the tube with a gas-tight syringe. The tube was mixed by shaking and immediately inserted into the NMR instrument for analysis.

#### CO<sub>2</sub> Reduction with DBU and 1-hexanol.

2 equivalents of DBU (0.0312 mmol) and 2 equivalents of 1-hexanol (0.0312 mmol) were added to the solution of cis-Ru(PNP)<sub>2</sub>(H)<sub>2</sub>. The solution was freeze-pump-thaw degassed 3 times prior to addition of 2, 1, or 0.5 atm of CO<sub>2</sub>. The tube was mixed by shaking and immediately inserted into the NMR instrument for analysis.

#### [DBUH]<sup>+</sup>[C<sub>6</sub>H<sub>13</sub>OCO<sub>2</sub>]<sup>-</sup> Reduction.

2, 1, or 0.5 equivalents of  $[DBUH]^+[C_6H_{13}OCO_2]^-$  was added to the top of the J. Young NMR tube cap. The tube was sealed carefully to avoid mixing the solution until just prior to inserting the NMR instrument for analysis.

### **Thermodynamic Estimates**

Free energies of reactions in acetonitrile are presented. The free energy of the net reactions can be compared for given values of  $\mathbf{a}$  and  $\mathbf{c}$ . The two net reactions shown in Table S1 and S2 only differ by the term  $\mathbf{c}$ .

Table S 1. Free energy estimates for the reduction of CO<sub>2</sub>

$H^- + CO_{2(g)} \longrightarrow HCO_2^-$		-44	(1)
$H_{2(g)}$ $\longrightarrow$ $H^+$ + $H^-$		76.0	(2)
H <sup>+</sup> + Base	–1.364 p <i>K</i> a	а	(3)
$H_{2(g)}$ + Base + $CO_{2(g)}$ + HBase + $HCO_2^-$		b	(4)

Units in kcal/mol. **a** is the free energy for protonation of a base. **b** is the net free energy for the reduction of  $CO_2$  in the presence of a base.

Table S 2. Free energy estimates for the reduction of alkylcarbonate

$H^- + CO_{2(g)} \longrightarrow HCO_2^-$		-44	(1)
$H_{2(g)}$ $\longrightarrow$ $H^+$ + $H^-$		76.0	(2)
H⁺ + Base <del> →</del> ⁺HBase	–1.364 p <i>K</i> a	а	(3)
$ROCO_2^- + ^+HBase \longrightarrow ROH + CO_{2(g)} + Base$	-1.364 log(K <sub>eq</sub> )	С	(5)
$H_{2(q)} + ROCO_2^- \longrightarrow ROH + HCO_2^-$		d	(6)

Units in kcal/mol. **a** is the free energy for protonation of a base. **c** is the free energy of  $CO_2$  capture by a base and alcohol. **d** is the net free energy for the reduction of alkylcarbonate.

# [DBUH]<sup>+</sup> [C<sub>6</sub>H<sub>13</sub>OCO<sub>2</sub>]<sup>-</sup> Reduction



Figure S 1. Reduction of 1 equivalent of hexylcarbonate.



Figure S 2. Reduction of 2 equivalents of hexylcarbonate.





### CO<sub>2</sub> Reduction with 2 Equivalents DBU



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igure S 4. Reduction of 1 equivalent of CO<sub>2</sub>.



Figure S 5. Reduction of 2 equivalents of CO<sub>2</sub>.



Figure S 6. Reduction of 3.4 equivalents (0.5 atm) of CO<sub>2</sub>.









Figure S 8. Reduction of 13.6 equivalents (2 atm) of CO<sub>2</sub>.





**Concentration vs Time** 

Figure S 9. Reduction of 1 equivalent of CO<sub>2</sub>.



Figure S 10. Reduction of 2 equivalents of CO<sub>2</sub>.



Figure S 11. Reduction of 0.5 equivalents (3.4 atm) of CO<sub>2</sub>.



Figure S 12. Reduction of 6.8 equivalents (1 atm) of CO<sub>2</sub>.



Figure S 13. Reduction of 13.6 equivalents (2 atm) of CO<sub>2</sub>.



# CO<sub>2</sub> Reduction with 2 Equivalents of DBU and 2 Equivalents 1-Hexanol Concentration vs Time

Figure S 14. Reduction of 1 equivalent of CO<sub>2</sub>.



Figure S 15. Reduction of 2 equivalents of CO<sub>2</sub>.



Figure S 16. Reduction of 3.4 equivalents (0.5 atm) of CO<sub>2</sub>.



#### Figure S 17. Reduction of 6.8 equivalents (1 atm) of CO<sub>2</sub>.



Figure S 18. Reduction of 13.6 equivalents (2 atm) of CO<sub>2</sub>.



### **Comparison of Formate Formation Rates**

Figure S 19. Carbonate reduction.



Figure S 20. CO<sub>2</sub> reduction in the presence of 1 equivalent of DBU.



# CO2 Reduction (2 eq. DBU)

Figure S 21. CO<sub>2</sub> reduction in the presence of 2 equivalents of DBU.



Figure S 22. CO<sub>2</sub> reduction in the presence of 2 equivalents of DBU and 2 equivalents 1-hexanol.