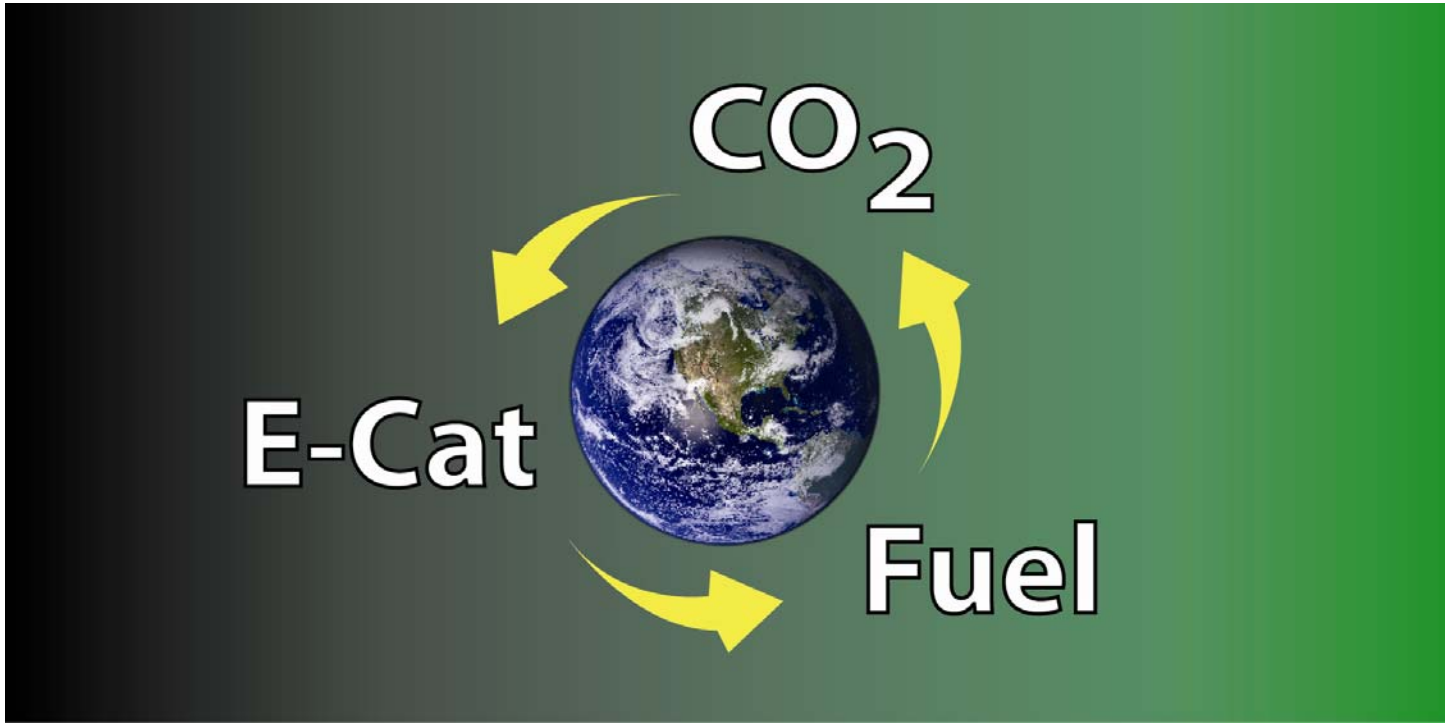
Overview of Chemical CCS, stripping, and utilization



Cliff Kubiak

UCSD

UCSanDiego

HELIOS SERC

The Splitting of CO_2 – Conversion to the simplest potential fuel

$$2\ CO_2 = 2\ CO + O_2$$

- Only scheme that produces a fuel (CO) and O_2, and recycles CO_2.
- $E^0 = -1.33$ V Only 0.1 V more energetic than H_2O splitting.
- Still have to deal with the hardest part of H_2O splitting: O_2 evolution.
- $CO_2 + 2\ H^+ + 2\ e^- = CO + H_2O$, $E^0 = -0.1$ V (NHE)
- $O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$, $E^0 = +1.23$ V (NHE)
- CO can be converted to H_2 and "synthesis gas" by "water gas shift": $CO + H_2O = CO_2 + H_2$; to gasoline by "Fischer-Tropsch" process; to ethanol by microbial process (Lanza Tech (NZ)).

The essential role of catalysis in conversion of solar energy to liquid fuels

The overall efficiency for the conversion of available sunlight to fuel:

$$\eta_{overall} =$$

$$\eta_{PV} \times \eta_i \times \Gamma_{cat} \times F \times TOF \times E^0/1000$$

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Conclusions about catalysis

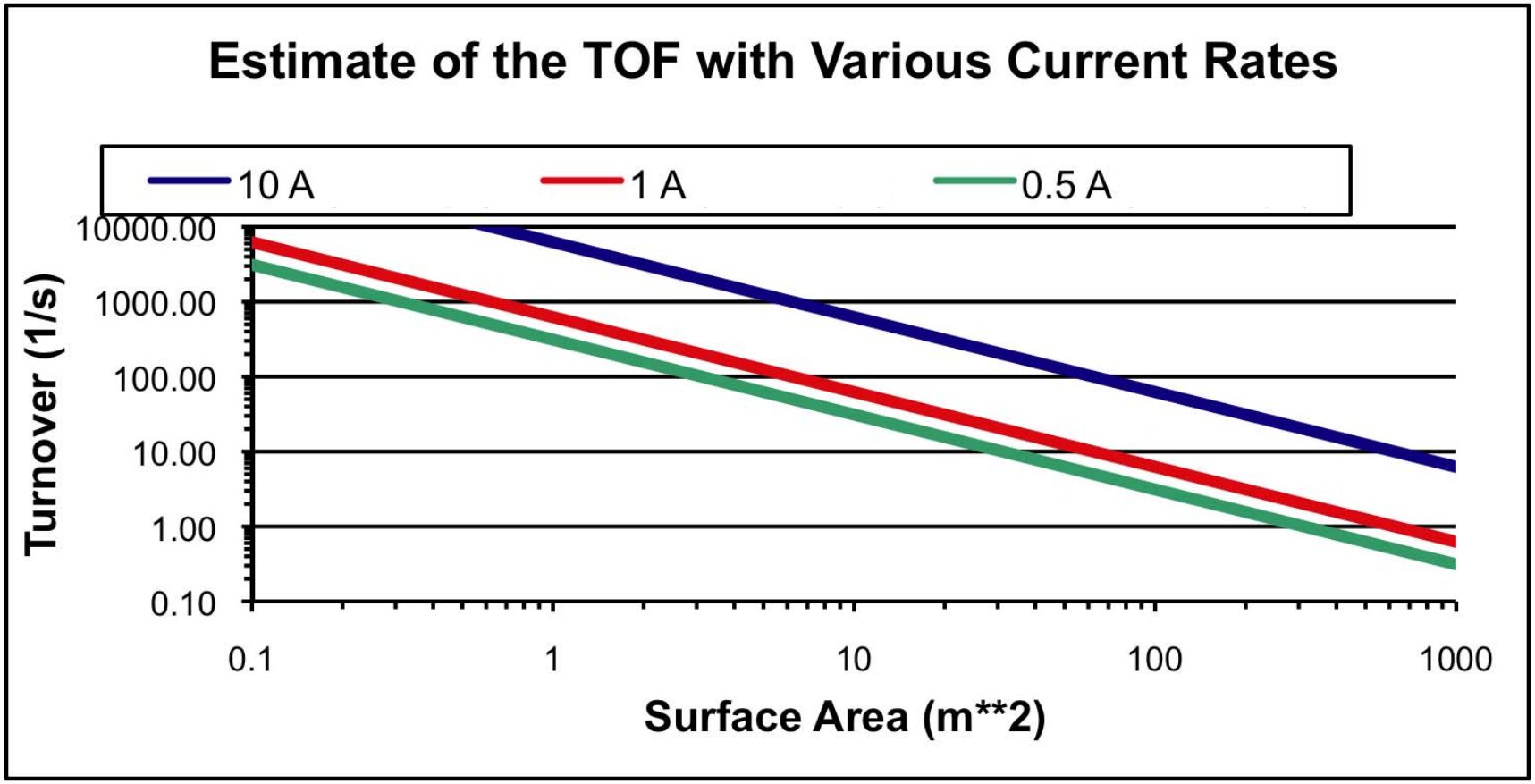
If you increase PV efficiency from *ca.* 20% to 30% (a gigantic step), you increase $\eta_{overall}$ by 50%

Current efficiencies are already pretty good.

If you increase TOF from $1s^{-1}$ to $1000s^{-1}$ (in the catalyst limited regime), you increase efficiency by a *thousand-fold*.

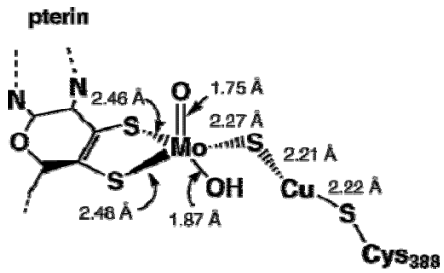
Catalyst TOF is the highest gain parameter in the overall efficiency of solar to chemical energy conversion.

Trade off between TOF and surface area at given current



Biology's CO_2 Catalysts
Lessons from nature

aerobic bacterium

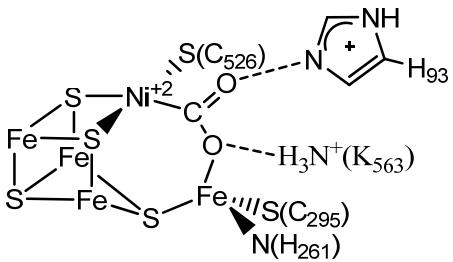


O. carboxidovorans

TOF 107s^{-1}

Dobbek, et al. *Proc. Natl. Acad. Sci*. 2002 Vol. **99** pp.15971

anaerobic bacterium

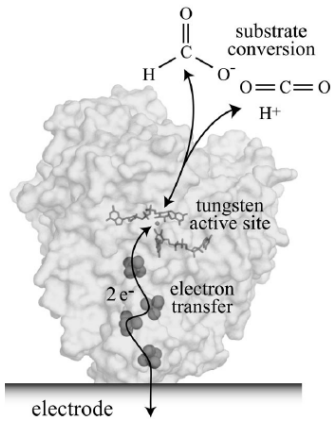


C. hydrogenoformans

TOF 31,000s^{-1}

Meyer, et al. *Science* 2001 Vol. **293** pp.1281

Reversible interconversion of carbon dioxide and formate by an electroactive enzyme



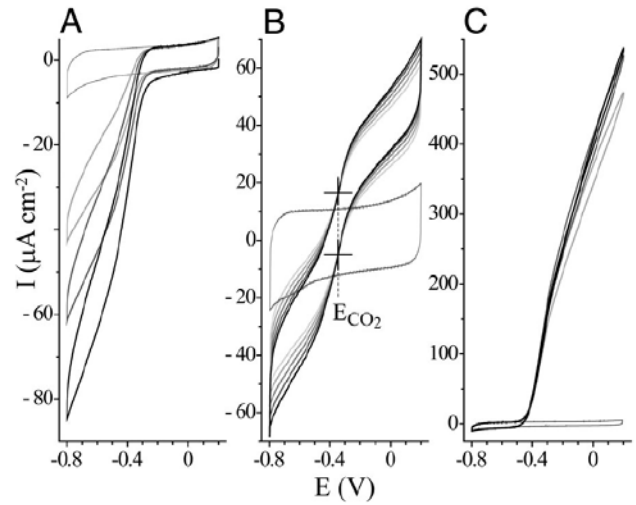
3,380s^{-1}

formate oxidation

282s^{-1}

CO_2 reduction

Anaerobic bacterium
Syntrophobacter fumaroxidans



A – 10mM CO_2

B – 10mM CO_2 & Formate

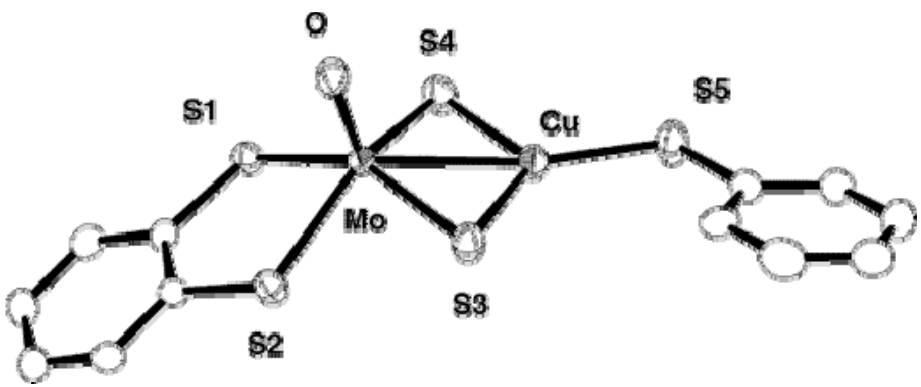
C – 10mM Formate

Applied potential, V	Faradaic efficiency, %	Thermodynamic efficiency, %
−0.41	102.1 ± 2.2	96.6
−0.51	98.6 ± 3.6	89.5
−0.61	98.0 ± 1.7	83.4
−0.81	97.3 ± 1.1	73.3

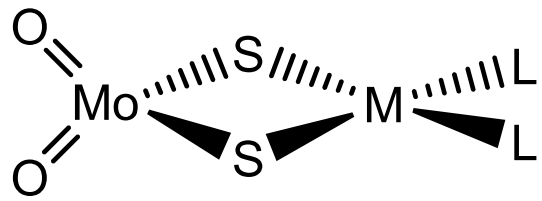
Hirst, et. al. *PNAS August 5, 2008 vol. 105 no. 31 10654-10658*

Bioinspired systems

- Thiomolybdates as multi-electron reservoirs
- Heterometallic CO_2 activation



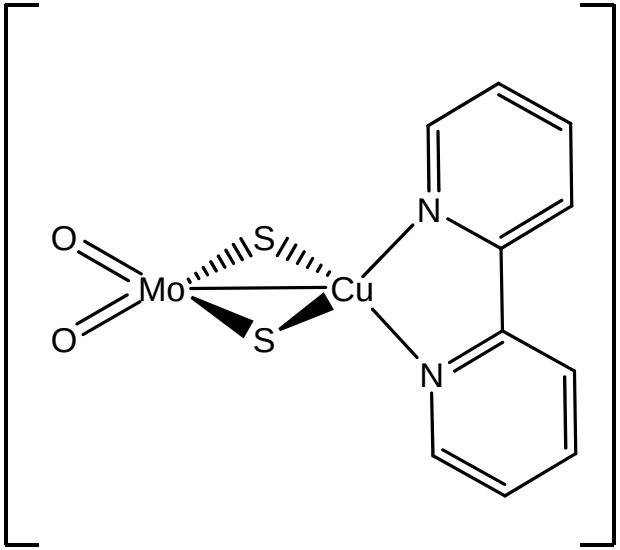
Tatsumi, et al. *Inorg. Chem.* 2005, **44**, 6034

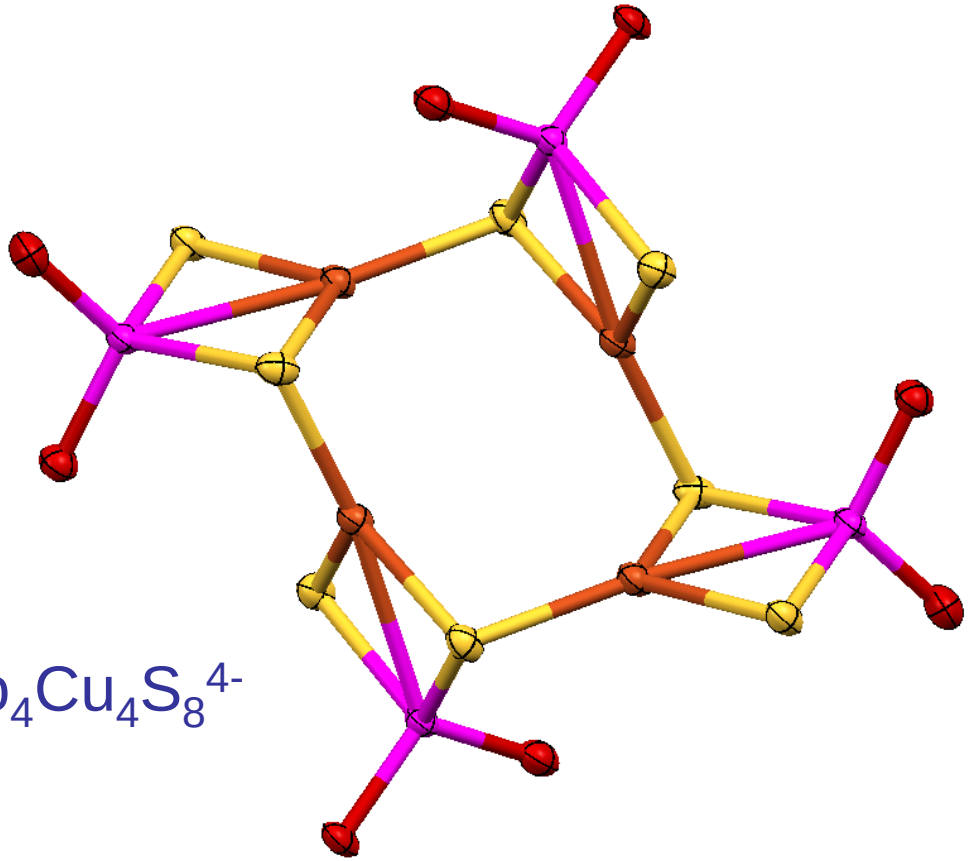


M = Cu, Ni
L = bpy, phen

A few promising results so far.

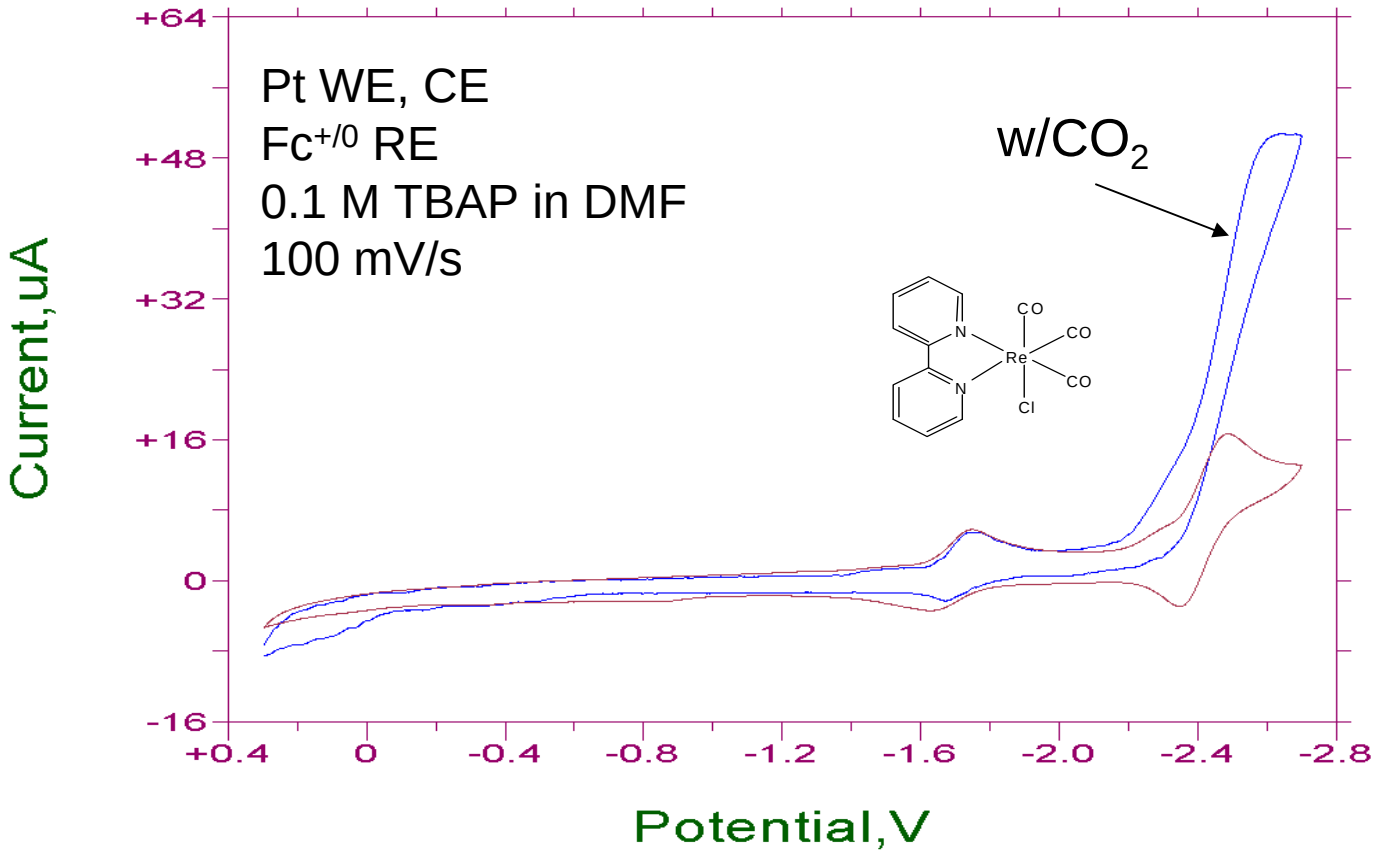
CODH Mimics





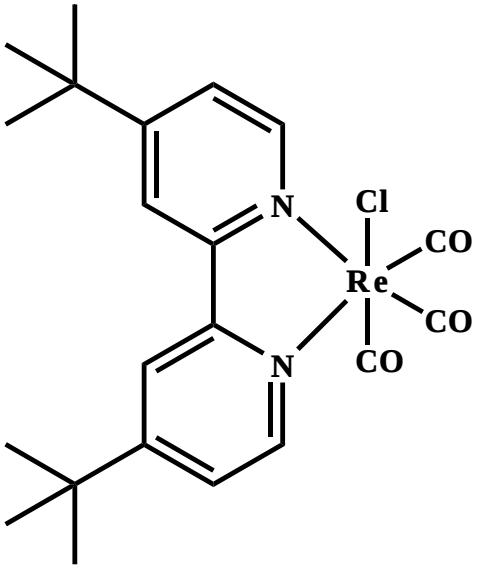
$Mo_4Cu_4S_8^{4-}$

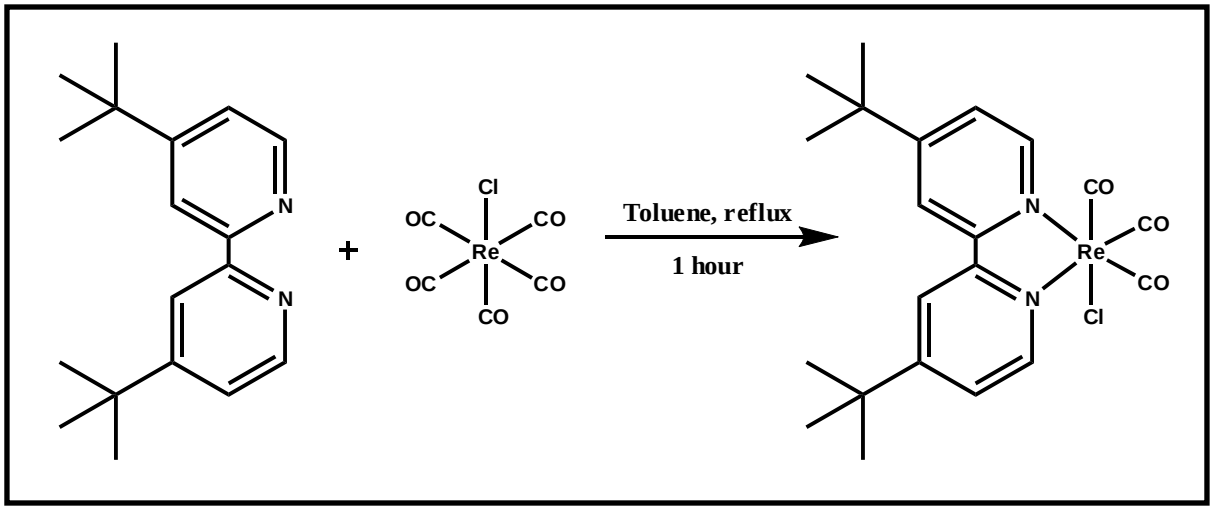
Catalyst tuning: $ReCl(CO)_3(bpy)$

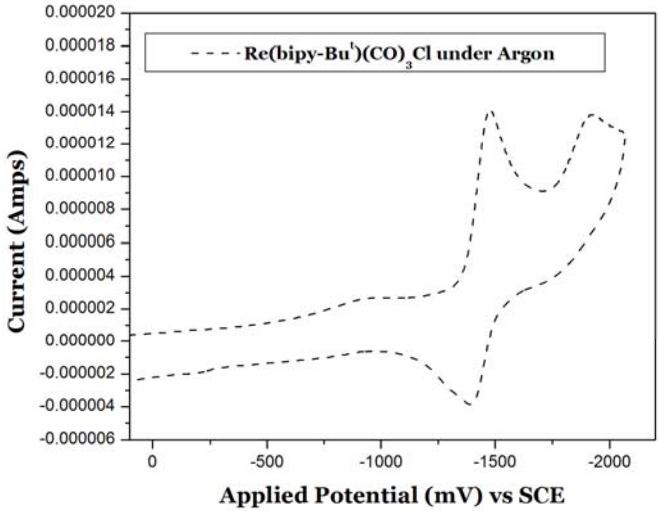


Lehn, J.M., *J. Chem. Soc., Chem. Commun.*, **1984**

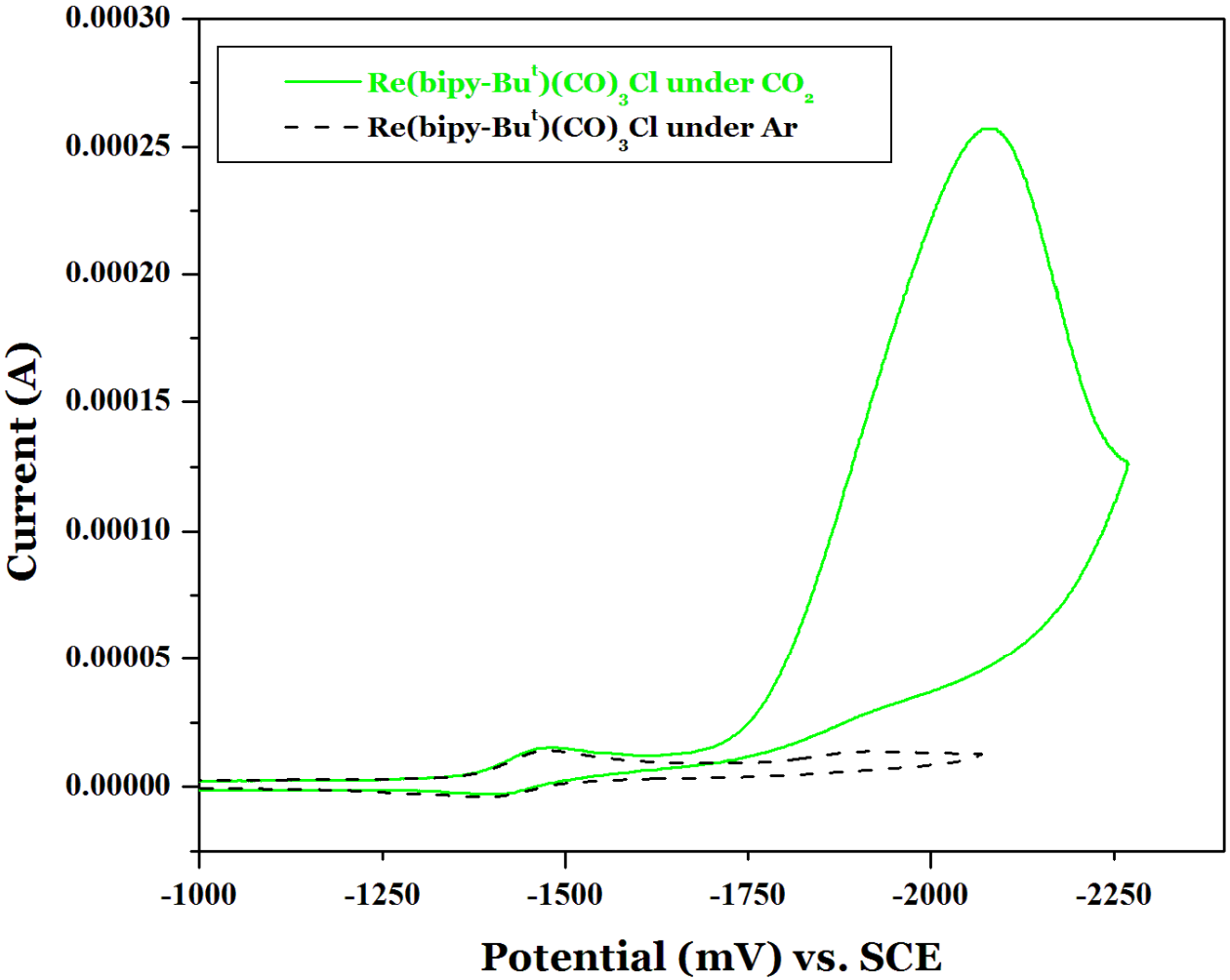
$Re(bipy\text{-}Bu^t)(CO)_3Cl$: An enhanced catalyst for the reduction of CO_2 and H^+



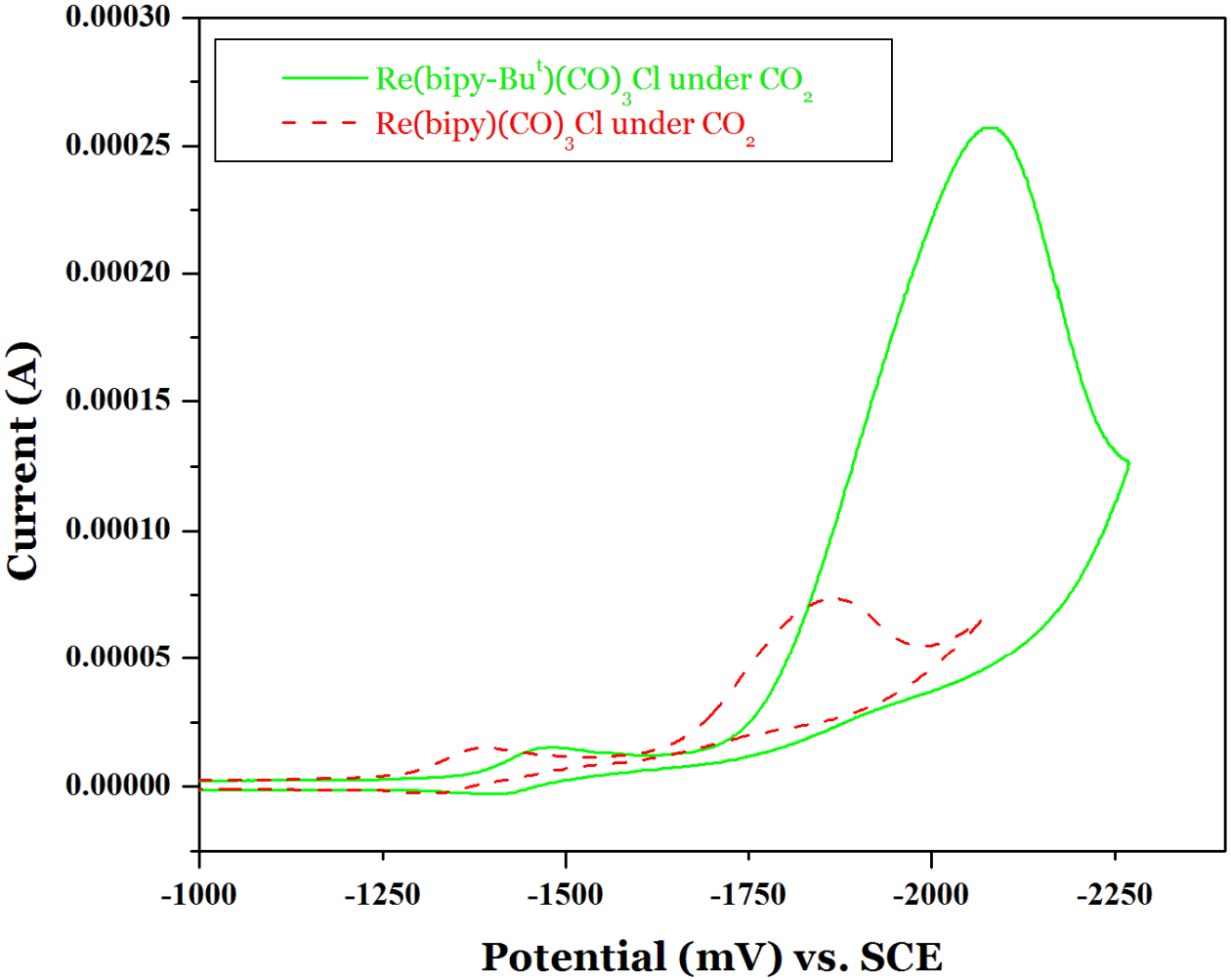




$Re(bipy\text{-}Bu^t)(CO)_3Cl$: An enhanced catalyst for the reduction of CO_2 and H^+



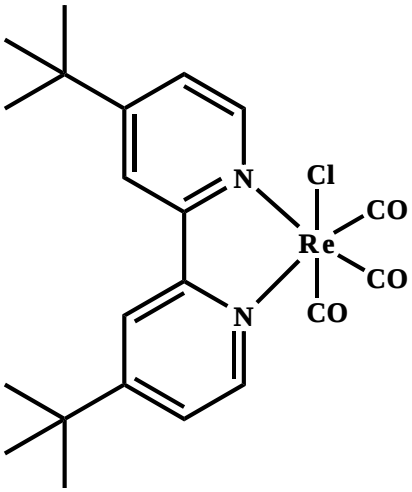
Re(bipy-Bu^t)(CO)$_3$Cl: An enhanced catalyst for the reduction of CO_2 and H^+



Turnover frequency comparison

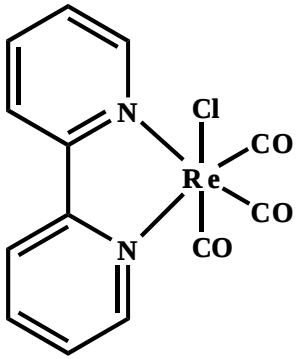
$$i_p = (2.69 \times 10^5)\, n^{3/2} \cdot A \cdot [C] \cdot v^{1/2} \cdot D^{1/2}$$

$$i_c = n \cdot F \cdot A \cdot [cat] \cdot (D \cdot k \cdot [Q]^y)^{1/2}$$



D_o = 4.6 x 10^{-6} cm^2/s

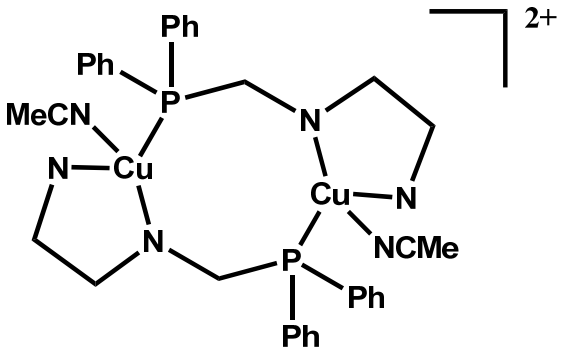
k = 1100 $M^{-1}s^{-1}$



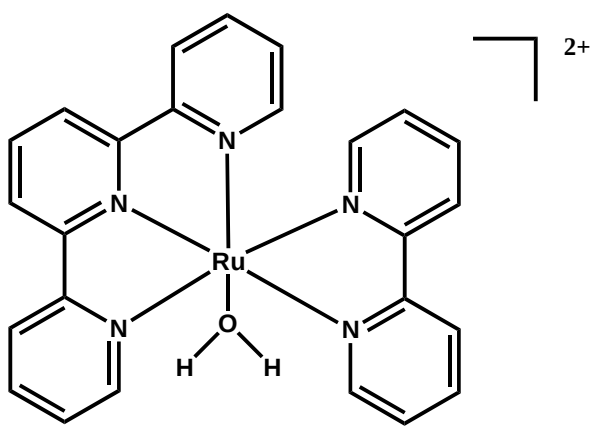
D_o = 5.3 x 10^{-6} cm^2/s

k = 60 $M^{-1}s^{-1}$

For D_0 comparison:



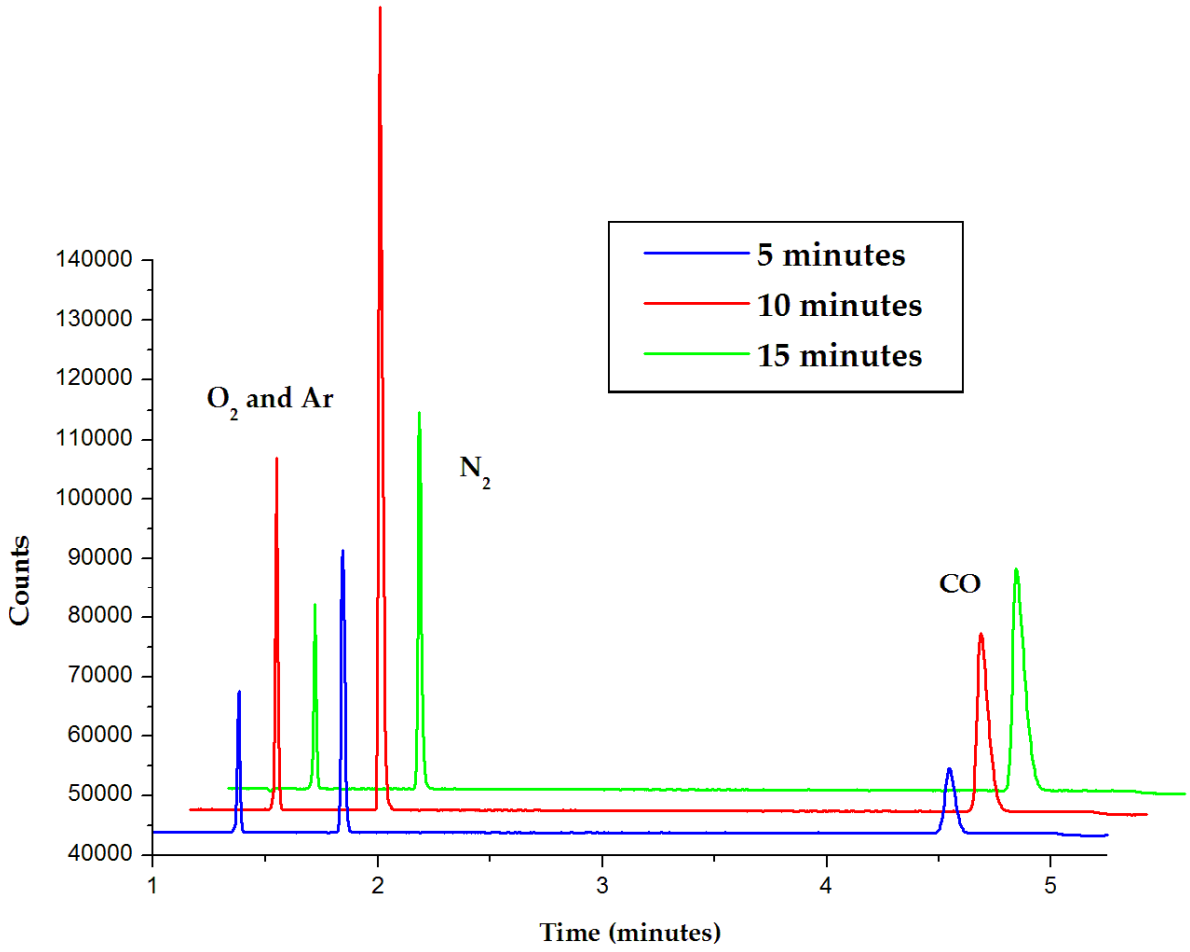
D_o = 2.2x10^{-6} cm^2/s



D_o = 4.0x10^{-6} cm^2/s

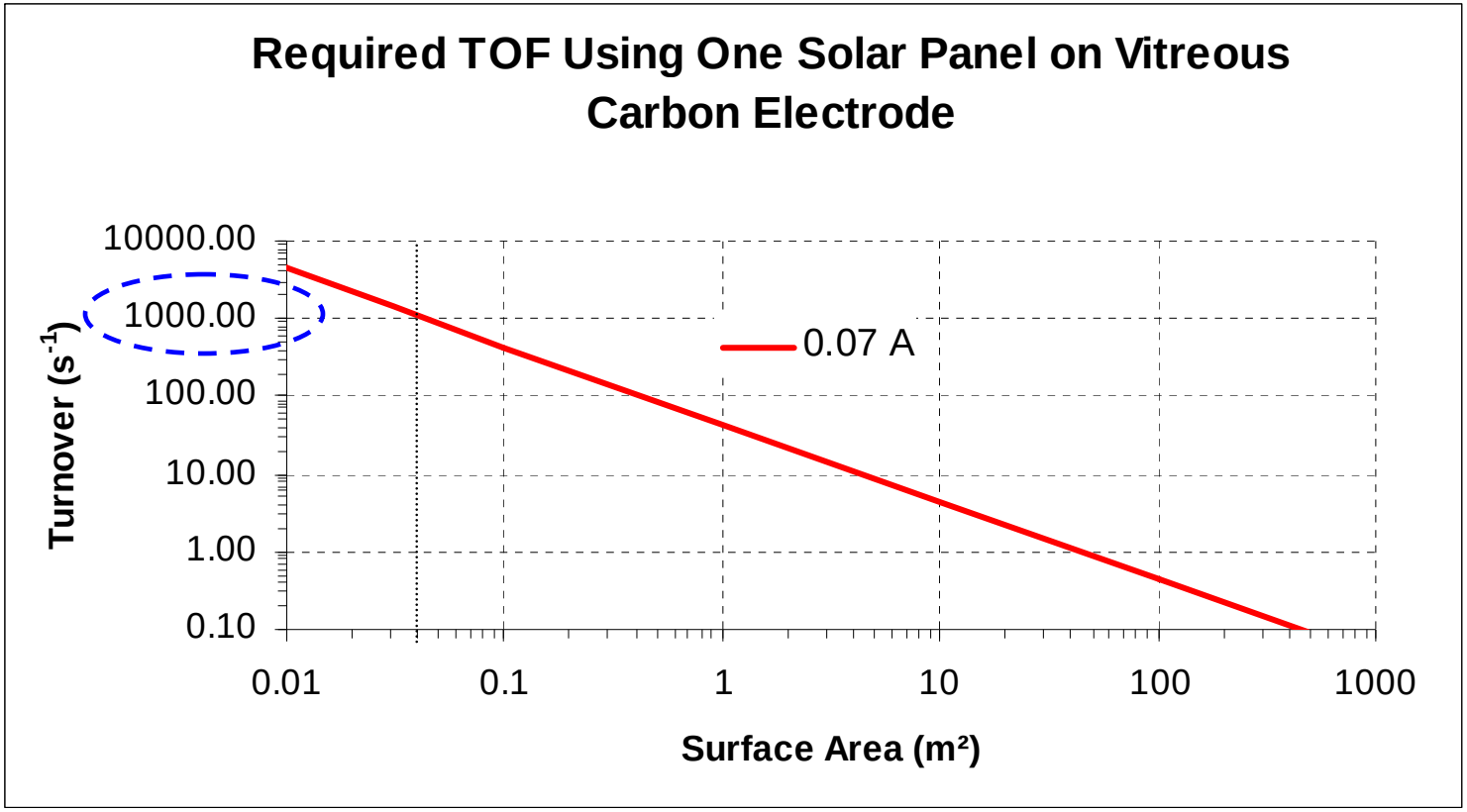
DuBois, et al. *J. Am. Chem. Soc.* **1991**, *113*, 8753-8764.
Kubiak, et al. *Inorg. Chem.* **1994**, *33*, 4723-4728.

Time progression of CO production in bulk electrolysis (Re catalyst)

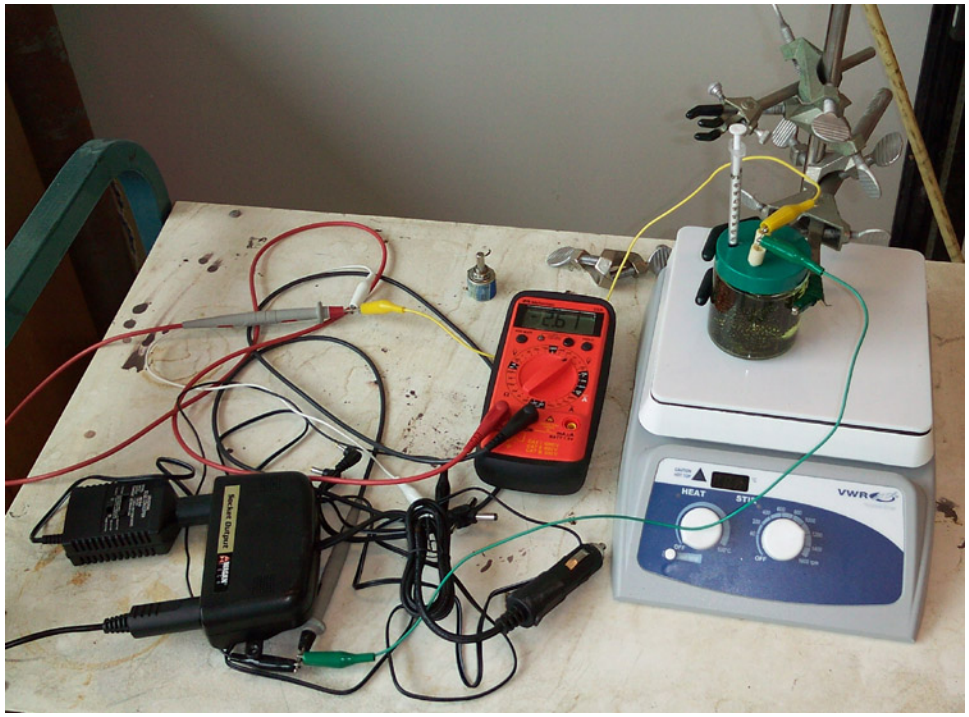


PV Operating Point

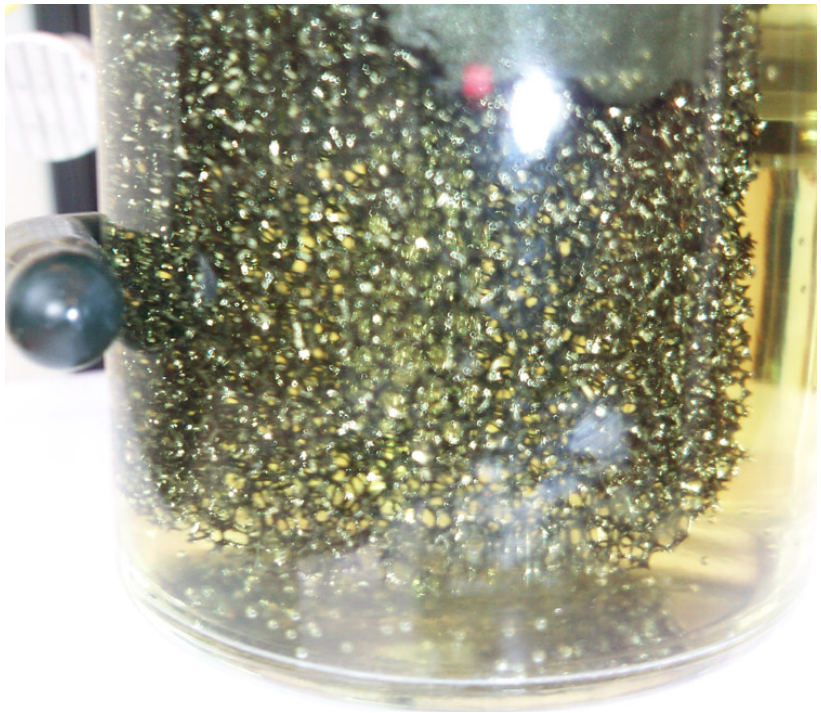
- 70 mA at .041 m^2 working electrode



Solar capture, conversion, and *electro*-catalysis (Re catalyst)



Solar panel, voltage control, bulk electrolysis cell



Photochemical CO_2 Splitting:
CO observed by GC (32 mL/h)
4% overall efficiency (sunlight)

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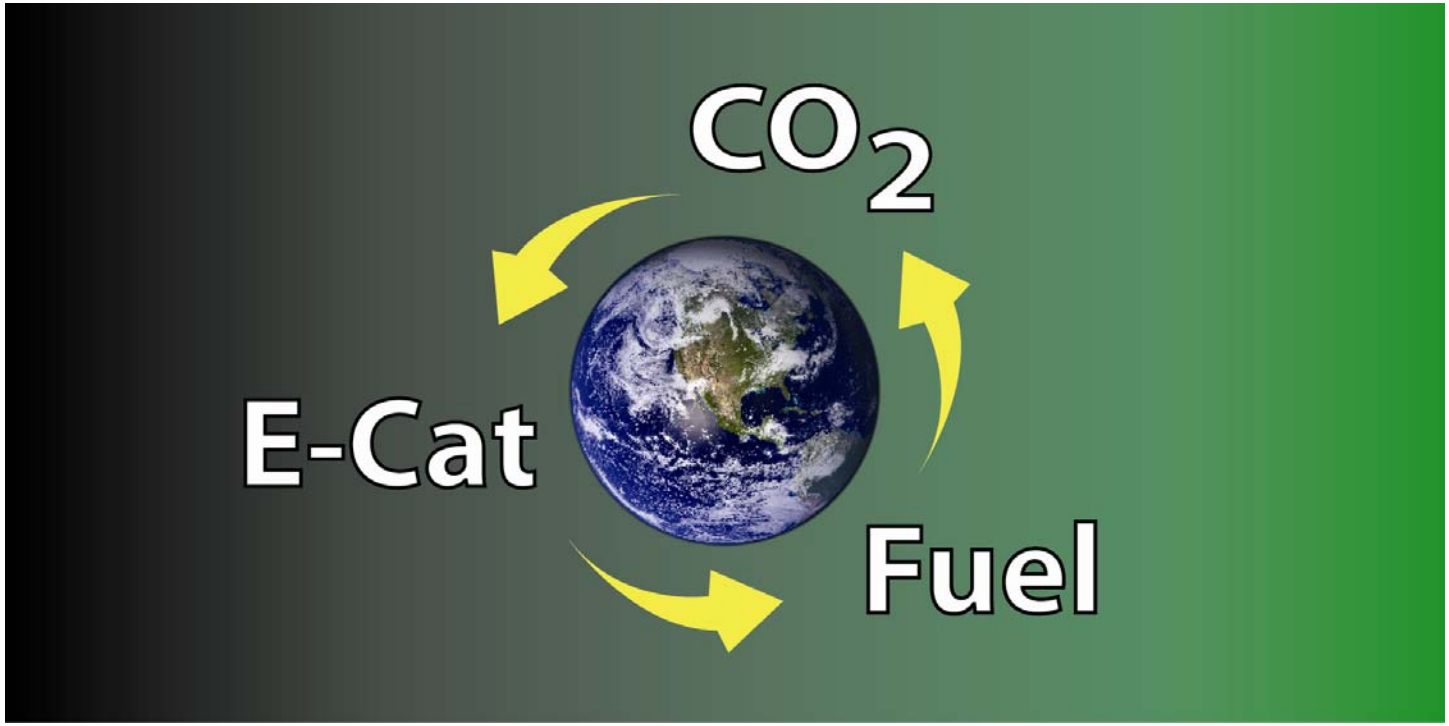
Next Big Challenge:



Direct Sequestration and Conversion of Atmospheric CO_2 (385 ppm)

Natural processes are continually removing carbon dioxide from the atmosphere

A field of switch grass removes CO_2 from the air at a net rate of ~15 ton per acre per yr

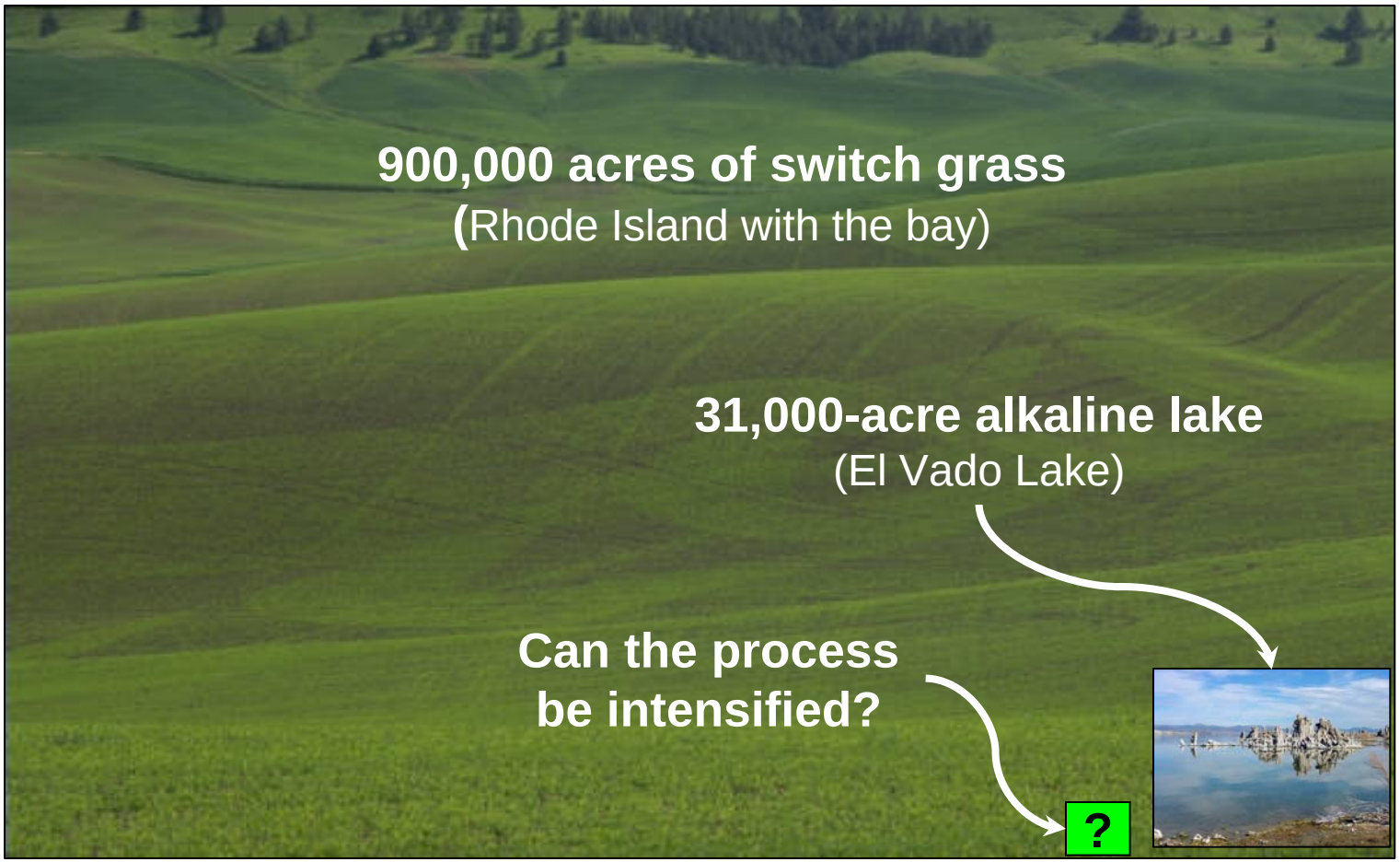
An alkaline lake absorbs CO_2 at an estimated rate of ~450 ton per acre per yr

From W. L. Kubic presentation

CO_2 to Fuels Preworkshop, Santa Fe, NM

May 1, 2009

Area needed to capture 14,000,000 tonne/yr of carbon dioxide



From W. L. Kubic presentation

CO_2 to Fuels Preworkshop, Santa Fe, NM

May 1, 2009

Does technology capable of removing carbon dioxide from the air exist?

- To be practical the process must
  - Reduce the carbon dioxide below current atmospheric levels of ~370 ppm
  - Produce a product stream containing carbon dioxide at much higher concentrations

- Processes exist for reducing carbon dioxide concentrations in gas to very low values
  - Adsorption can reduce CO_2 to <10 ppm (cryogenic air separation plants)
  - Membrane separation can reduce CO_2 to low levels (LNG plants)
  - Refrigerated methanol scrubbers reduce CO_2 to <10 ppm
  - Amine scrubbers reduce CO_2 to ~50 ppm (H_2, NH_3, and CH_3OH plants)
  - Carbonate scrubbers reduce CO_2 to ~100 ppm (H_2, NH_3, and CH_3OH plants)

- Some other possible processes
  - Methanation reduces CO_2 to <5 ppm (ammonia process)
  - Freezing carbon dioxide

From W. L. Kubic presentation
CO_2 to Fuels Preworkshop, Santa Fe, NM
May 1, 2009

Scrubbers

- Methanol scrubbers are too hazardous for large-scale removal of carbon dioxide from air
  - Toxic
  - Flammable
- Amine scrubbers are unsuitable for processing air
  - Ethanol amine solutions degrade in oxygen
  - The solutions have a foul odor
- Water scrubbers could work
  - No environmental or safety problems
  - Studied by Steinberg and Dong in the 1970s
  - Low capacity for absorbing carbon dioxide
- Carbonate and caustic scrubbers best suited for removing carbon dioxide from air
  - Pose no significant hazards and have no odors
  - Stable in oxygen environments
  - Studied by Stucki et al. in the 1990s

From W. L. Kubic presentation

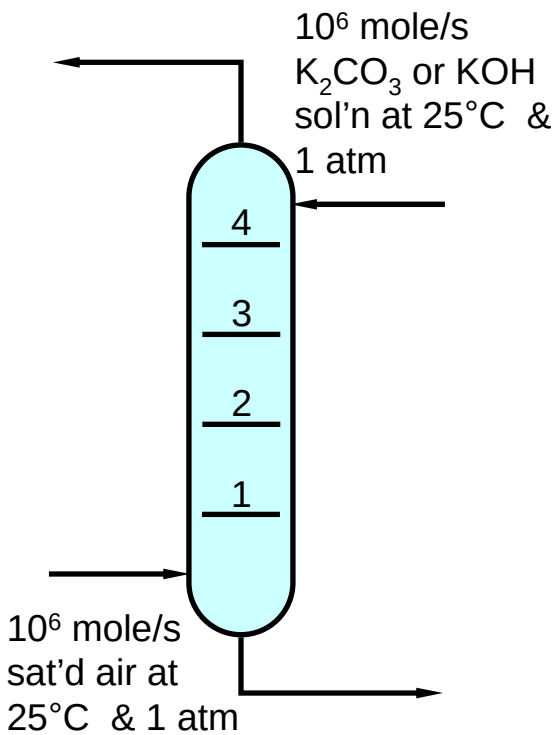
CO_2 to Fuels Preworkshop, Santa Fe, NM

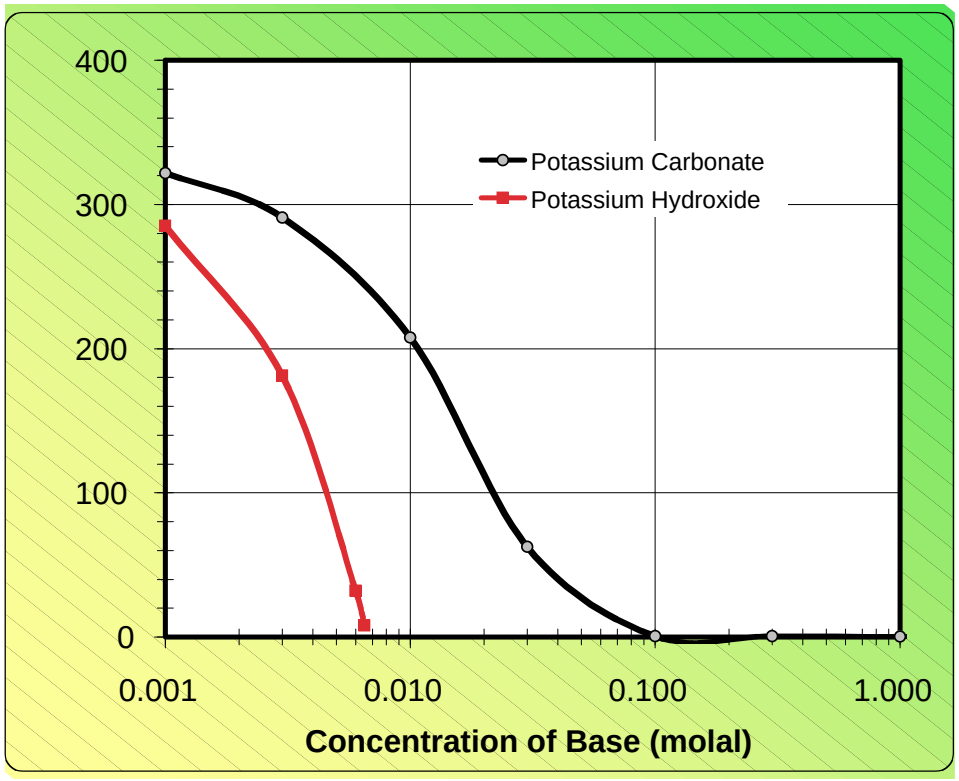
May 1, 2009

Carbon Dioxide is Readily Absorbed into Carbonate and Caustic Solutions

$$CO_2 + CO_3^{(2-)} + H_2O = 2\ HCO_3^{(-)}$$

$$CO_2 + 2\ OH^{(-)} = CO_3^{(2-)} + H_2O$$

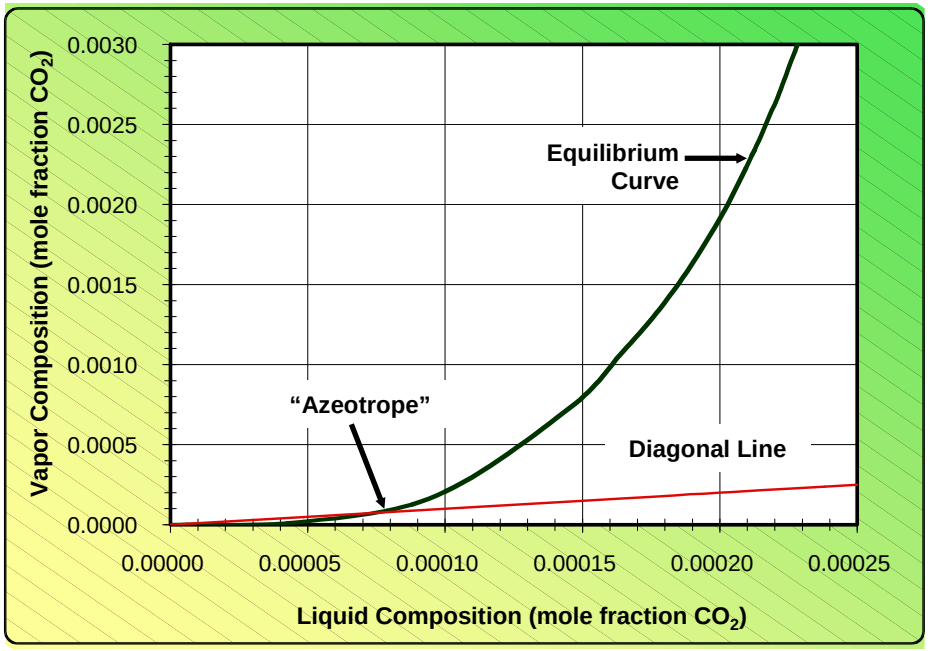




Vapor-Liquid Equilibrium Limits the Performance of the Stripping Column

- A carbonate solution forms an "azeotrope" with carbon dioxide
- The carbon dioxide mole fraction cannot be reduced below the azeotropic composition using a thermal stripping process
- The azeotrope prevents a conventional carbonate process from reducing carbon dioxide concentration below 100 ppm

Vapor-Liquid Equilibrium of Carbon Dioxide in a 0.02 M Potassium Carbonate Solution at 1 atm



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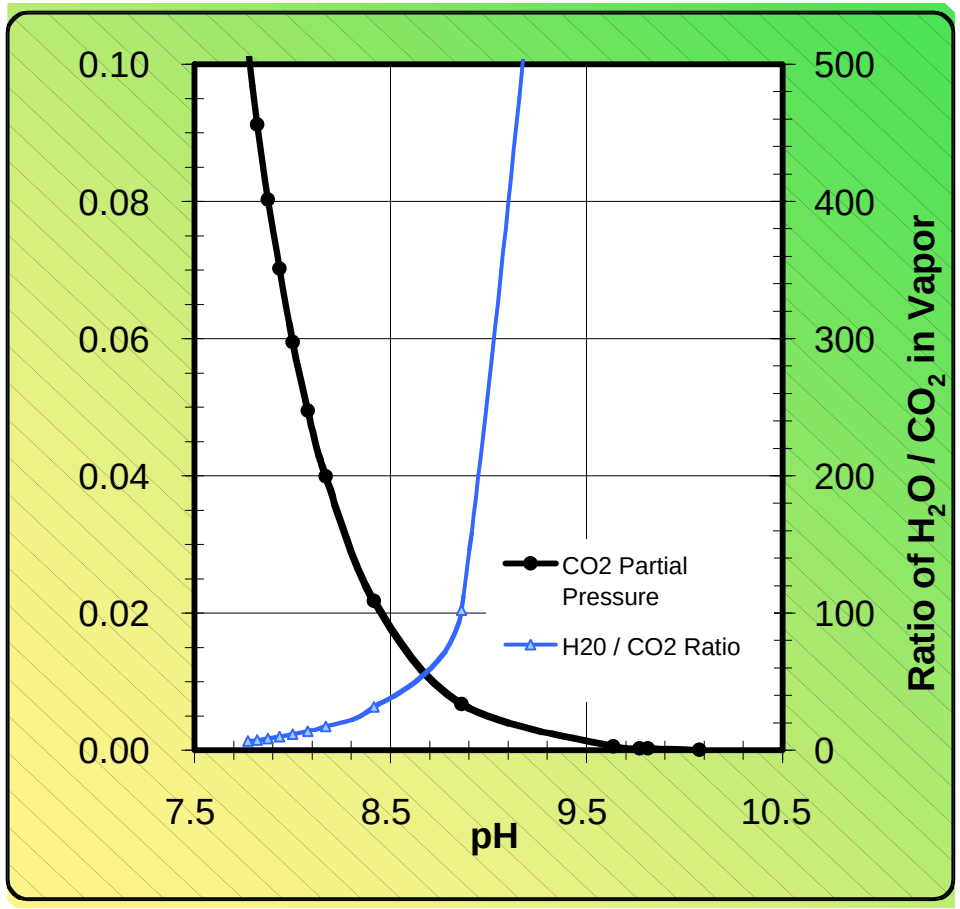
Carbon Dioxide Can Be Removed from a Carbonate Solution by Decreasing pH



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Lowering the pH of Carbonate Solutions

- Acidification equilibrium chemistry is well known
  - $CO_3^{(2-)} + H^{(+)} = HCO_3^{(-)}$
  - $HCO_3^{(-)} + H^{(+)} = CO_2 + H_2O$

- Adding acid to the carbonate solution introduces new processing problems
  - Additional anions are added to the solution that must be removed
  - The acid needs to be regenerated

- Removing hydroxide ions by electrolysis is equivalent to adding acid
  - Electrolytic acidification has been used for pH control in fermentation

Chemistry of Electrolytic Acidification

- Hydroxide ions are oxizized to oxygen at the anode
  - $2\ OH^{(-)} \rightarrow H_2O + 1/2\ O_2 + 2\ e^{(-)}$
- Removal of hydroxide ions shifts the carbonate/bicarbonate equilibrium in favor of bicarbonate
  - $CO_3^{(2-)} + H_2O = HCO_3^{(-)} + OH^{(-)}$
- Removal of hydroxide ions shifts the bicarbonate/carbon dioxide equilibrium in favor of carbon dioxide
  - $HCO_3^{(-)} + H_2O = CO_2 + OH^{(-)}$
- Electrolytic acidification produces a mixture of 66% carbon dioxide and 34% oxygen
  - This mixture can be separated easily with a conventional carbonate adsorption system

Electrolytic Acidification Prior Art

- Meyer Steinberg, US Patent 4,197,421, issued 1980
  - Part of a patent for synthetic fuels and feedstock production
  - Uses electrolytic carbon dioxide stripping for capture and recovery of atmospheric carbon dioxide
  - Also produces oxygen and hydrogen

- Pletcher et al., US Patent 5,245,551, issued 1993
  - Uses electrolytic cell to produce hydroxides without coproduction of chlorine
  - Carbonate solution fed to the anode
  - Produces carbon dioxide as a byproduct

- Stucki et al. *International Journal of Hydrogen Energy*, 1995
  - Describe a process for capture and recovery of atmospheric carbon dioxide that uses electrolytic carbon dioxide stripping
  - Report experimental data for stripping cell
  - Produces carbon dioxide and hydrogen

From W. L. Kubic presentation

CO_2 to Fuels Preworkshop, Santa Fe, NM

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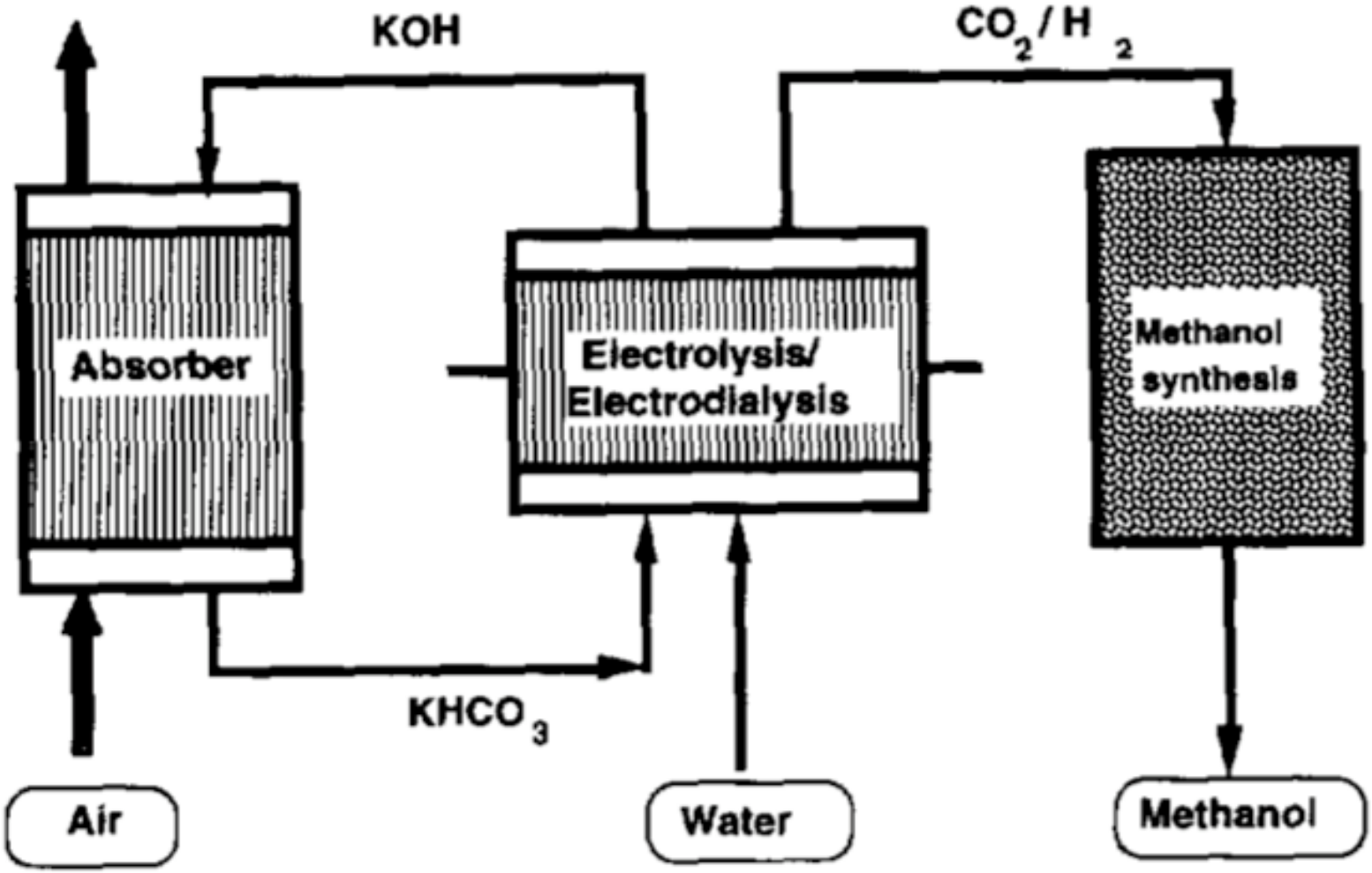
Combined water electrolysis/CO_2 stripping



Stucki, Schuler, and Constantinescu, *Int. J. Hydrogen Energy*, Vol. 20, No. 8, pp. 653-663, **1995**

Combined water electrolysis/CO_2 stripping

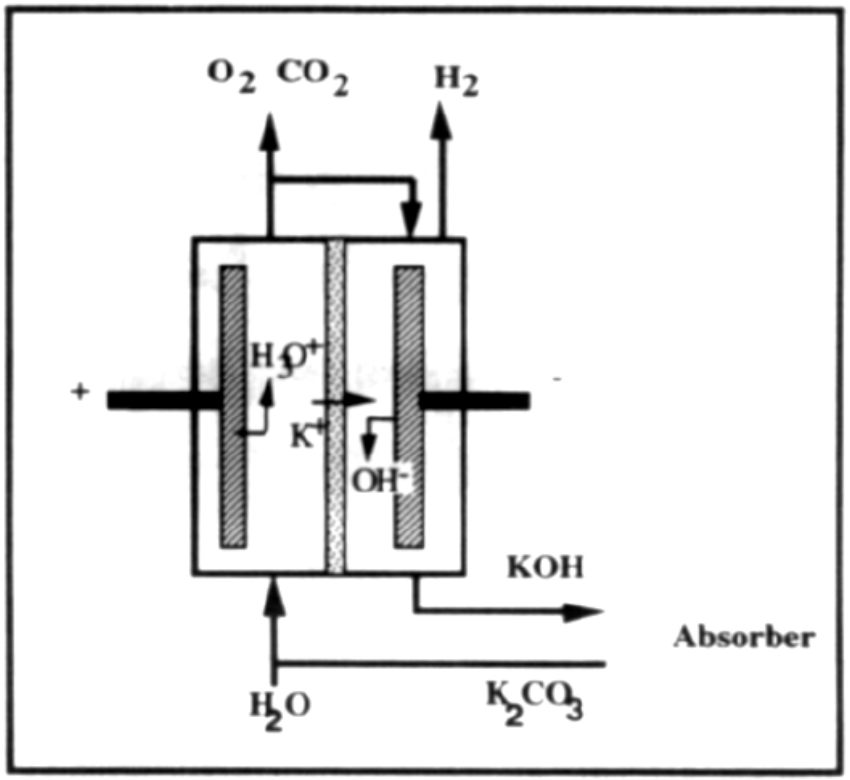


Fig. 2. Cation exchange membrane cell for electrolytic regeneration of absorption solution (KOH), CO_2 stripping and hydrogen generation. Current flow through the cell leads to KOH accumulation in the cathode compartment and CO_2 stripping in the anode compartment.

$$2\ H_2O + K_2CO_3 = \tfrac{1}{2}\ O_2 + H_2 + 2\ KOH + CO_2$$

Stucki, Schuler, and Constantinescu, *Int. J. Hydrogen Energy*, Vol. 20, No. 8, pp. 653-663, **1995**

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Bigger Challenges:

Chemically Reversible Electrolytic CO_2 Sequestration/Stripping

$$[Mn^{VII}O_4]^- + 5\,e^- + 8\,H^+ + 2\,H_2O = [Mn^{II}(H_2O)_6]^{2+},\ E^0(Mn^{VII/II})$$

Reduction of Mn(VII), CO_2 Sequestration:

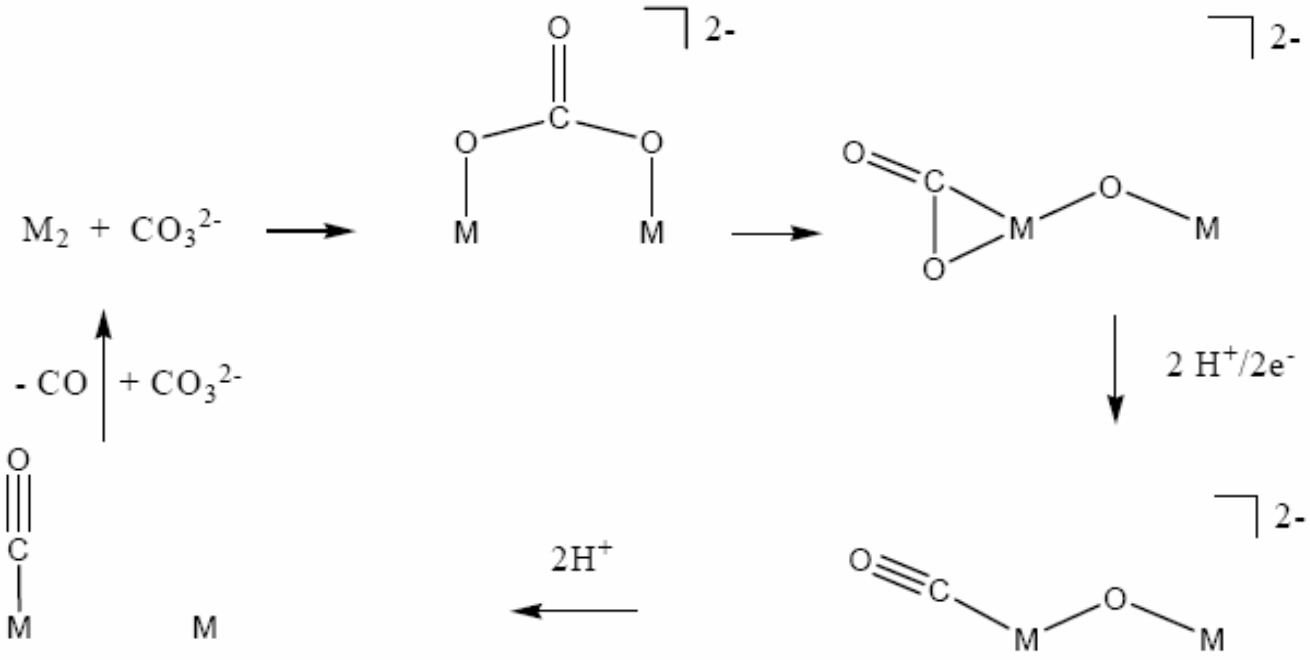
$$[Mn^{VII}O_4]^- + 5\,e^- + 8\,CO_2 + 10\,H_2O \rightarrow [Mn^{II}(H_2O)_6]^{2+} + 8\,HCO_3^-$$

Oxidation of Mn(II), CO_2 Stripping:

$$[Mn^{II}(H_2O)_6]^{2+} + 8\,HCO_3^- \rightarrow [Mn^{VII}O_4]^- + 5\,e^- + 8\,CO_2 + 10\,H_2O$$

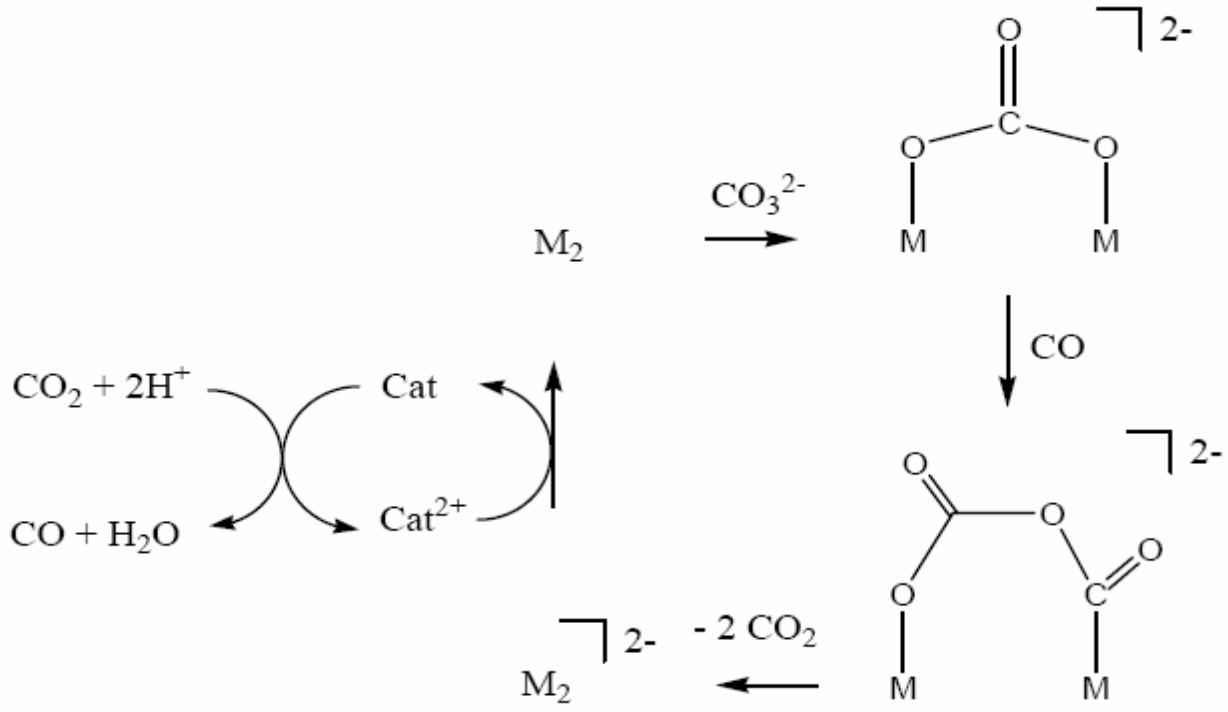
Bigger Challenges:

Direct Chemical Conversion of Carbonate to Liquid Fuel Precursors



Bigger Challenges:

Carbonate/CO Comproportionation Coupled to CO_2 Reduction



KUBIAK RESEARCH GROUP @ UCSD

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- *Starla Glover*
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- *Jerry Lin*
- *Ricky Ramsaran*
- *Sayak Roy*
- *Aaron Sathrum*
- *Julia Schöffel*
- *Candace Seu*
- *Jon Smieja*

X--Ray

– **Prof. Arnie Rheingold (X-ray Diffraction Facility at UCSD)**

Photo by Catherine Johnson, November 2005

UC San Diego

Electrochemical Potentials

$$CO_2 + 2\,H^+ + 2\,e^- = CO + H_2O, \quad E^0 = -0.1\ V$$

$$2\,H^+ + 2\,e^- = H_2, \quad E^0 = 0.0\ V$$

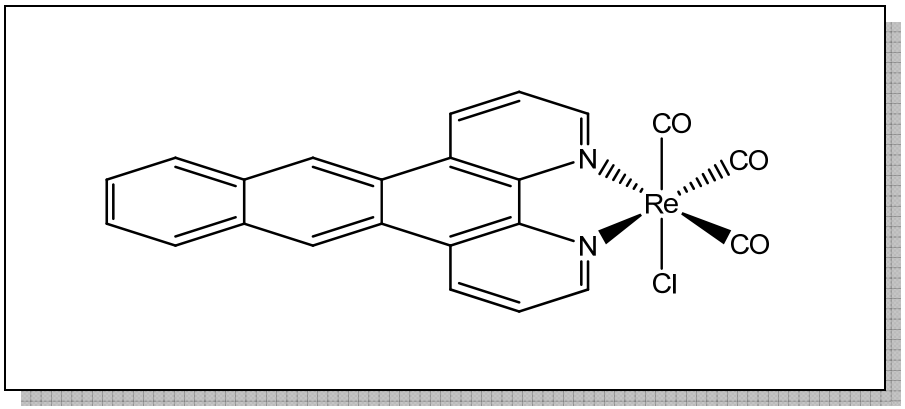
CO_2 and H_2O reduction have similar energy requirements .

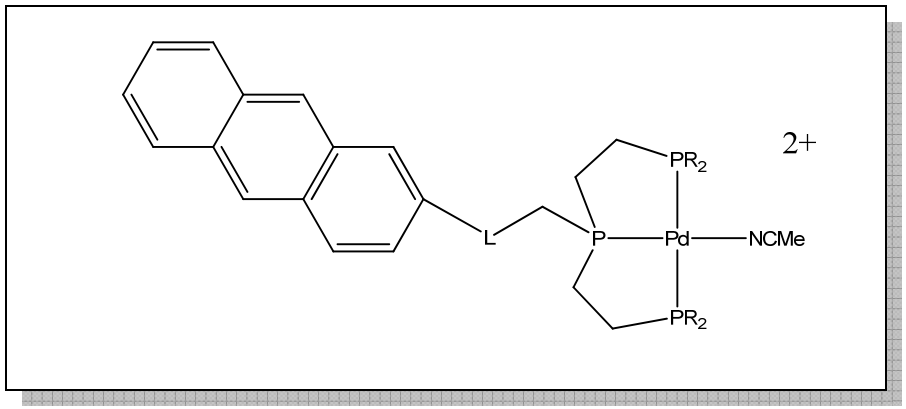
Postscript

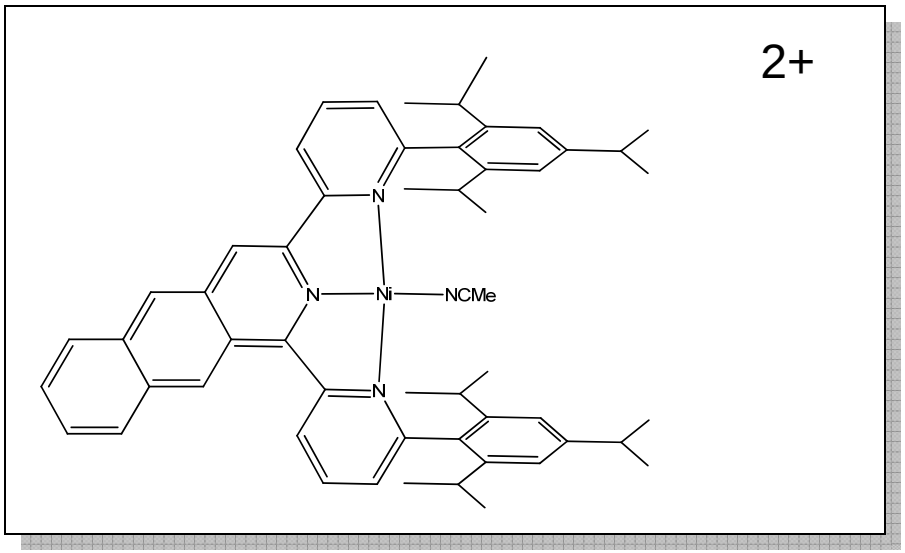
- The following slides contain data on other ligands and catalysts being synthesized for this project to attempt to develop a new generation of catalysts which use less expensive/more earth abundant metals.

Modification of catalysts

for adsorption onto carbon electrodes

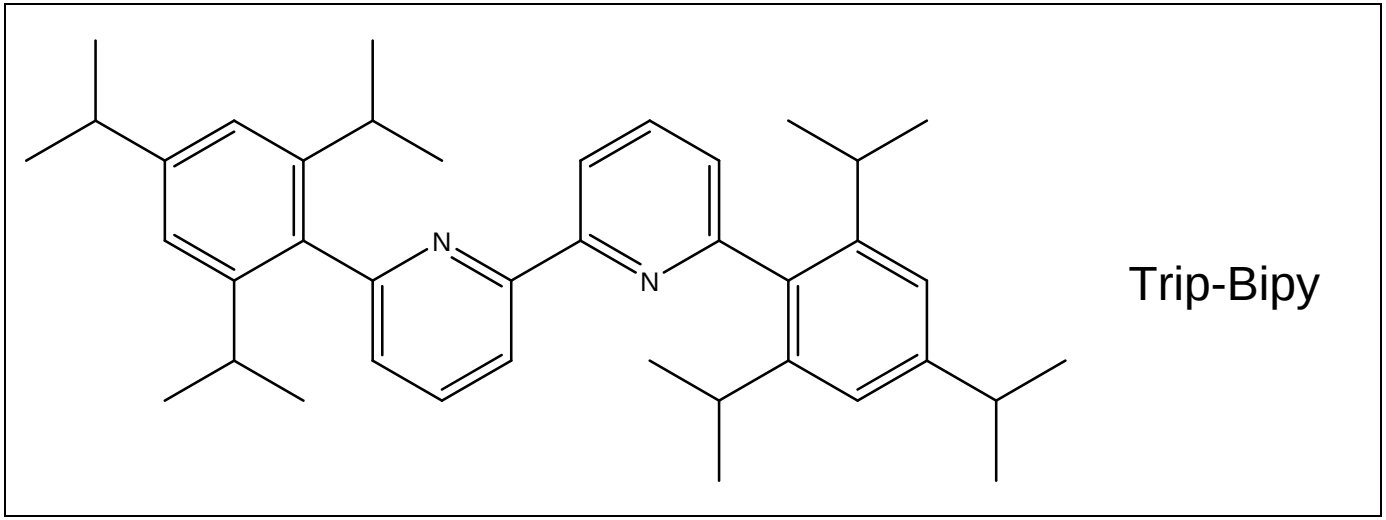


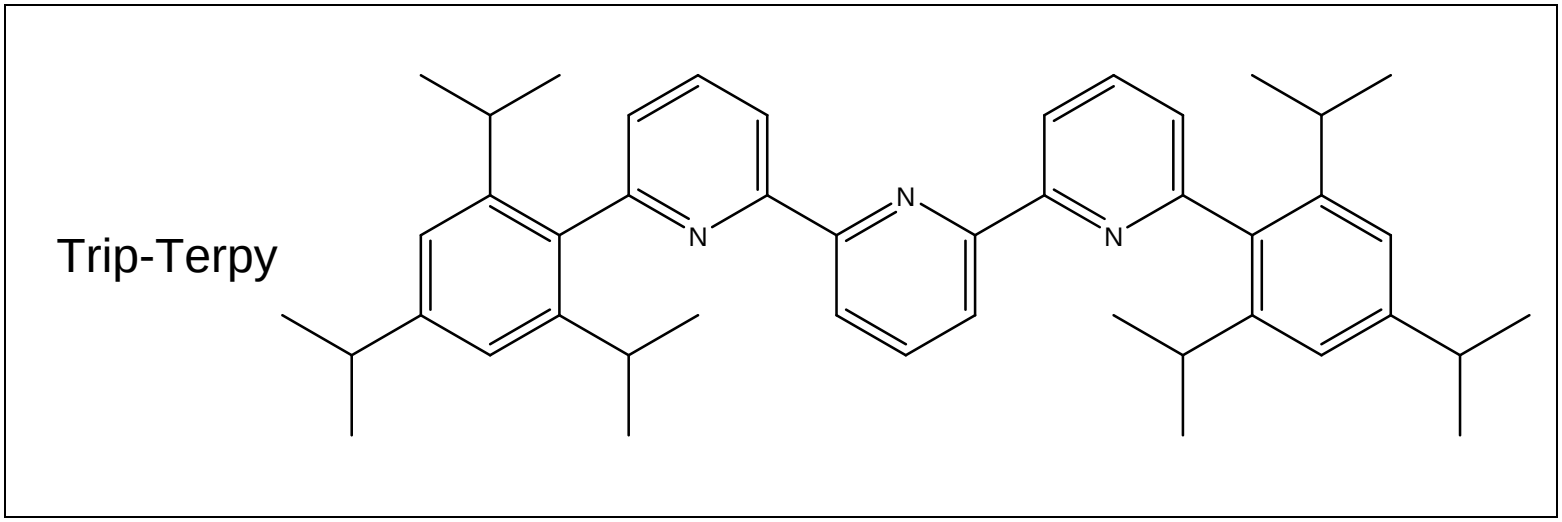




Bulky Bipyridines

for unsaturated metal centers/enhanced CO_2 binding



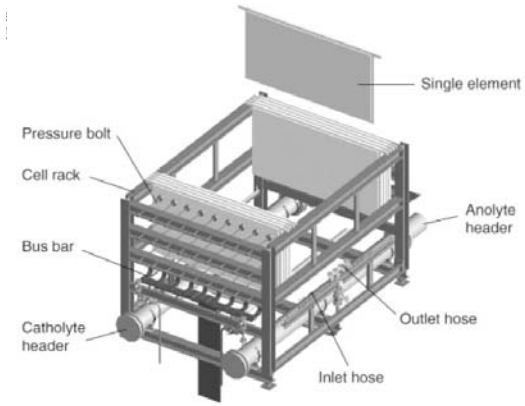


Equipment Availability

- An electrolytic stripping cell will resemble a chloralkali cell
  - Commercial chloralkali cell produces 29 - 82 ton NaOH/day
  - Corresponds to a carbon dioixde recovery of 30 - 86 ton CO_2/day

- A process with 36 large stripping cells is a realistic scale
  - Would be capable of producing 2800 tonne/day of carbon dioxide

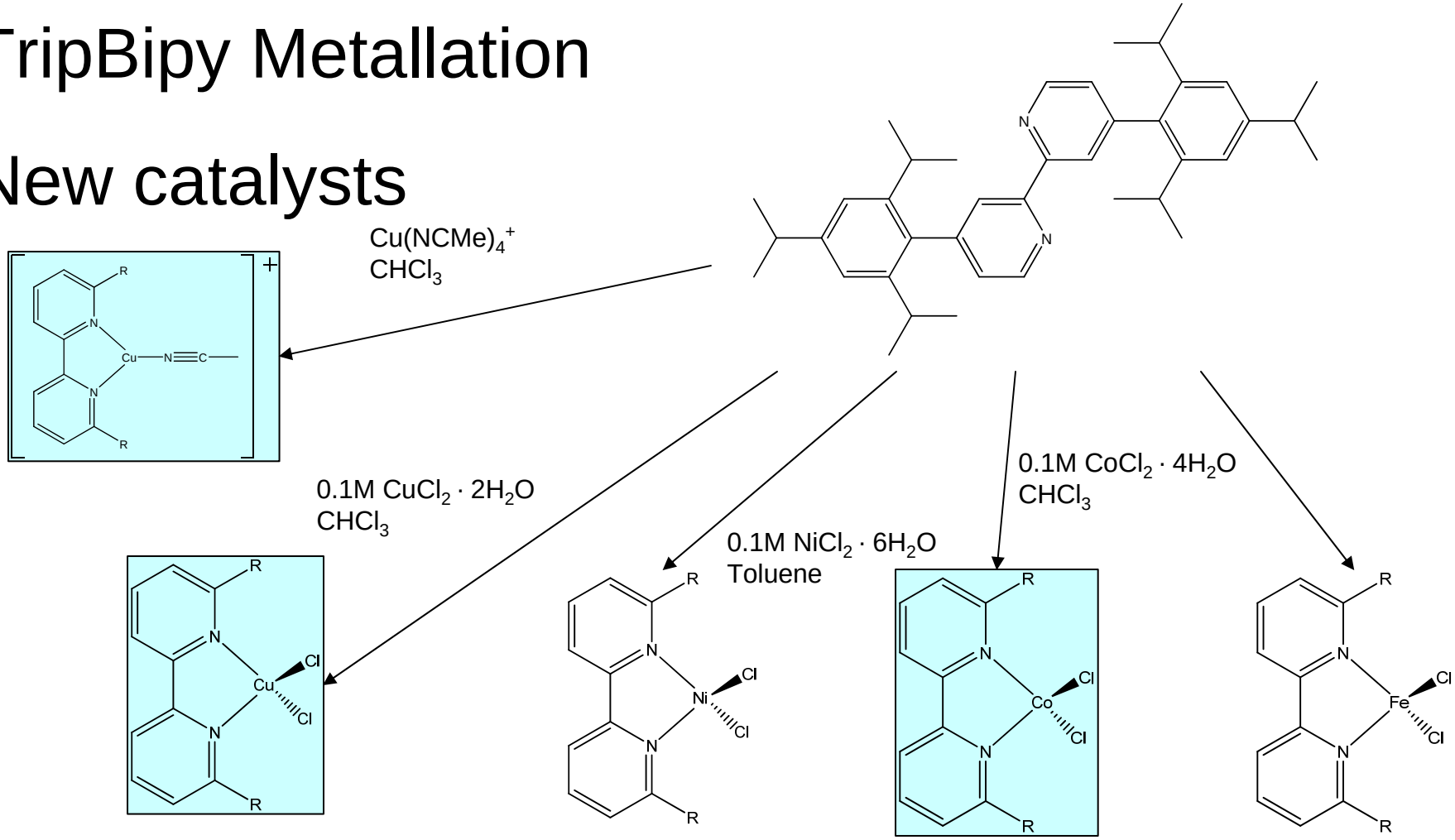
Kruppe-Uhde BM-2.7 Electrolyzer

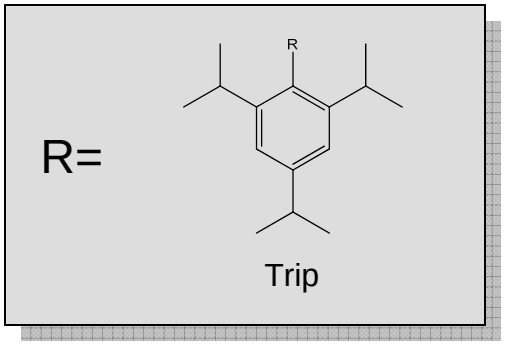


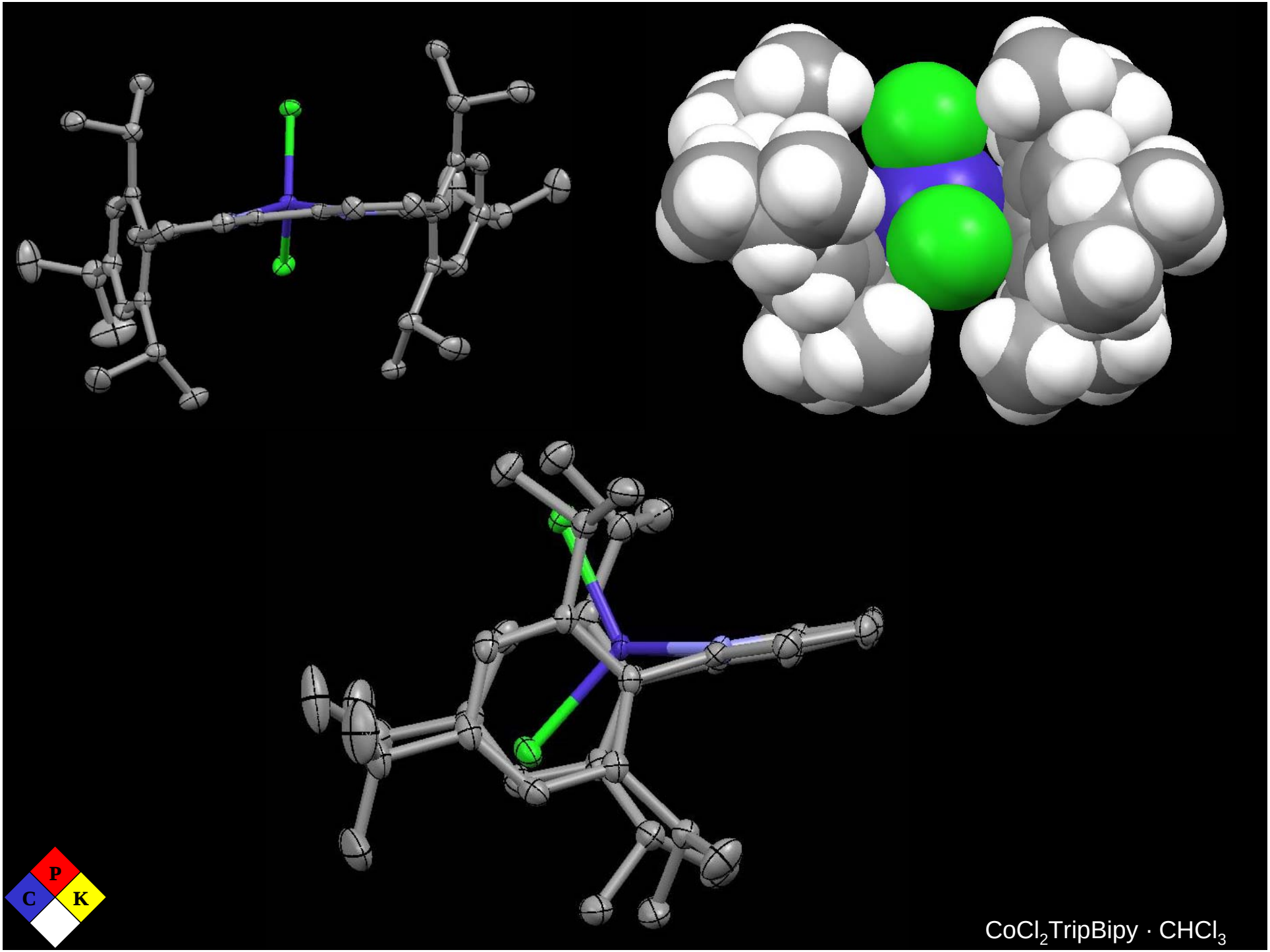
Plant with 36 Kruppe-Uhde BM-2.7 Electrolyzes

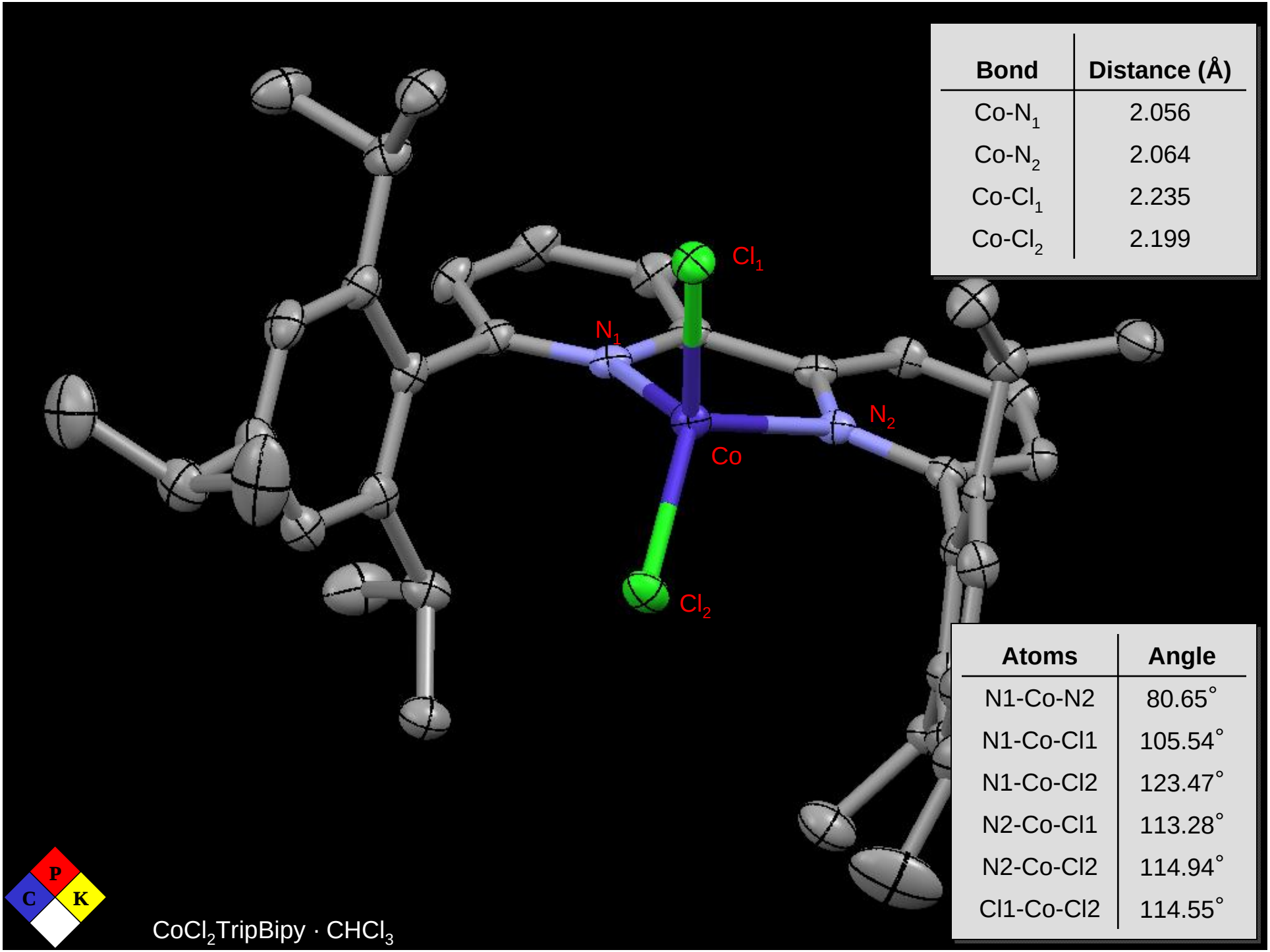
TripBipy Metallation

New catalysts






P
C
K
$CoCl_2TripBipy \cdot CHCl_3$



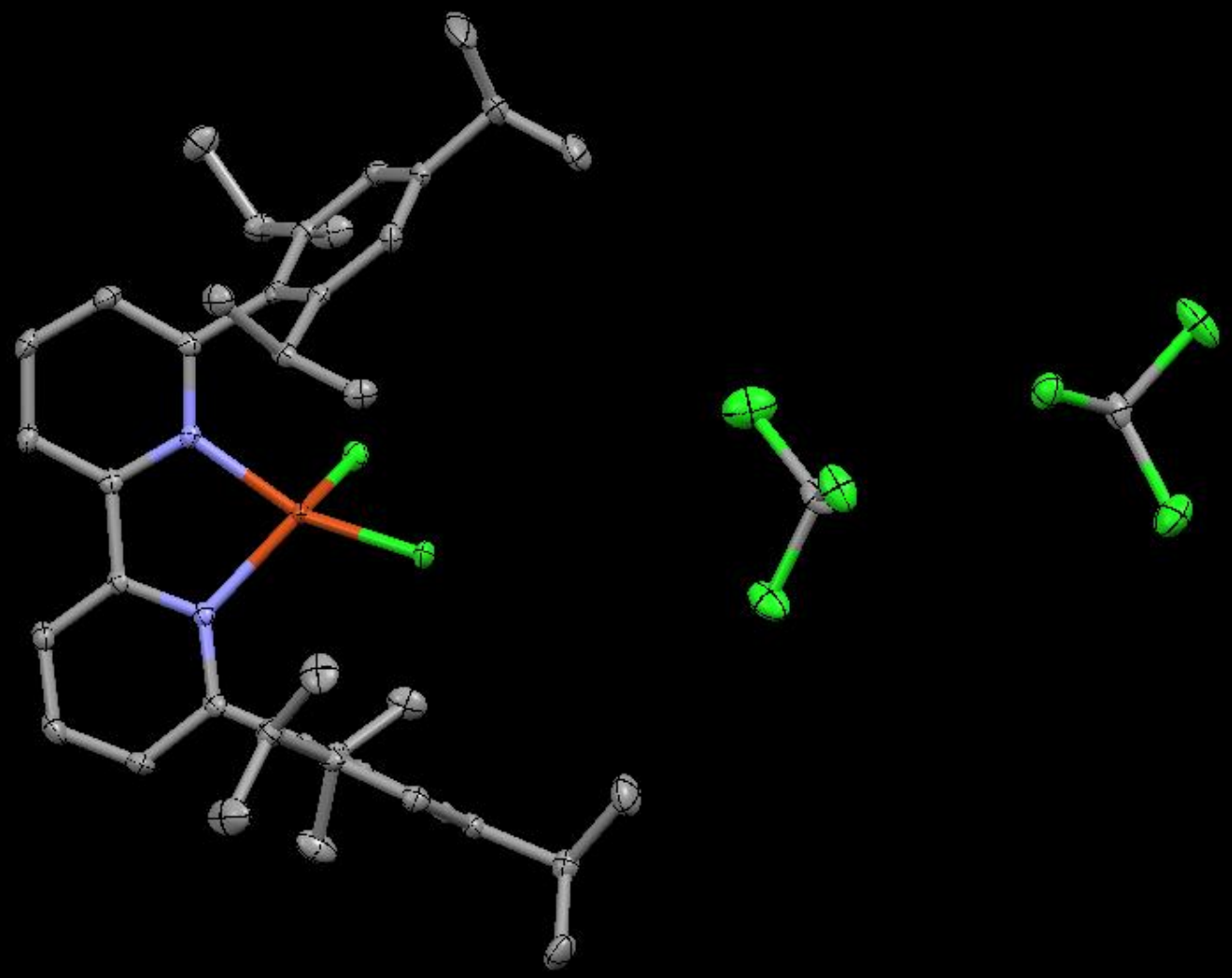
Bond	Distance (Å)
Co-N_1	2.056
Co-N_2	2.064
Co-Cl_1	2.235
Co-Cl_2	2.199

Atoms	Angle
N1-Co-N2	80.65°
N1-Co-Cl1	105.54°
N1-Co-Cl2	123.47°
N2-Co-Cl1	113.28°
N2-Co-Cl2	114.94°
Cl1-Co-Cl2	114.55°

$CoCl_2TripBipy \cdot CHCl_3$

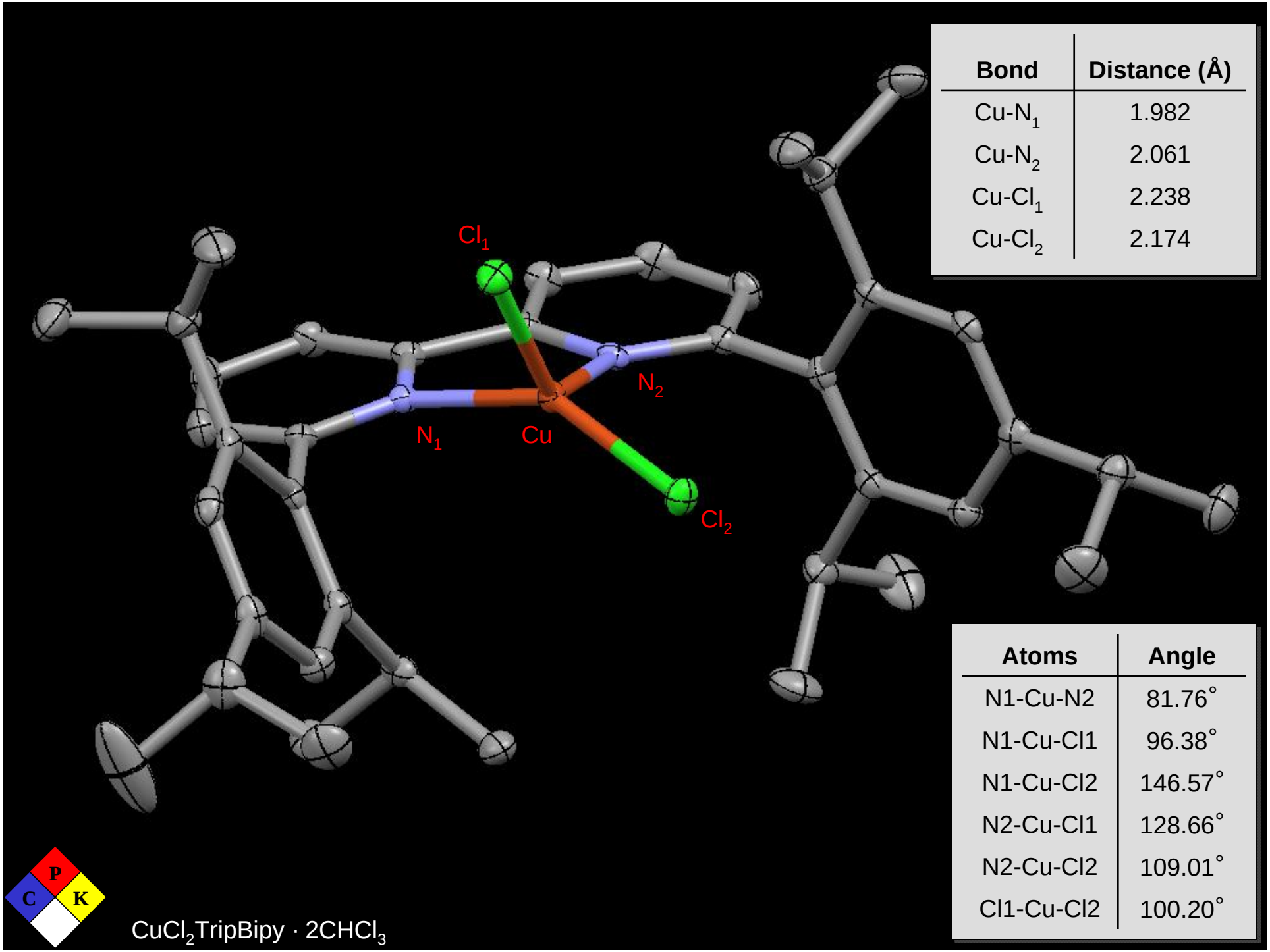
$CuCl_2TripBipy \cdot 2CHCl_3$

P 21 21 21



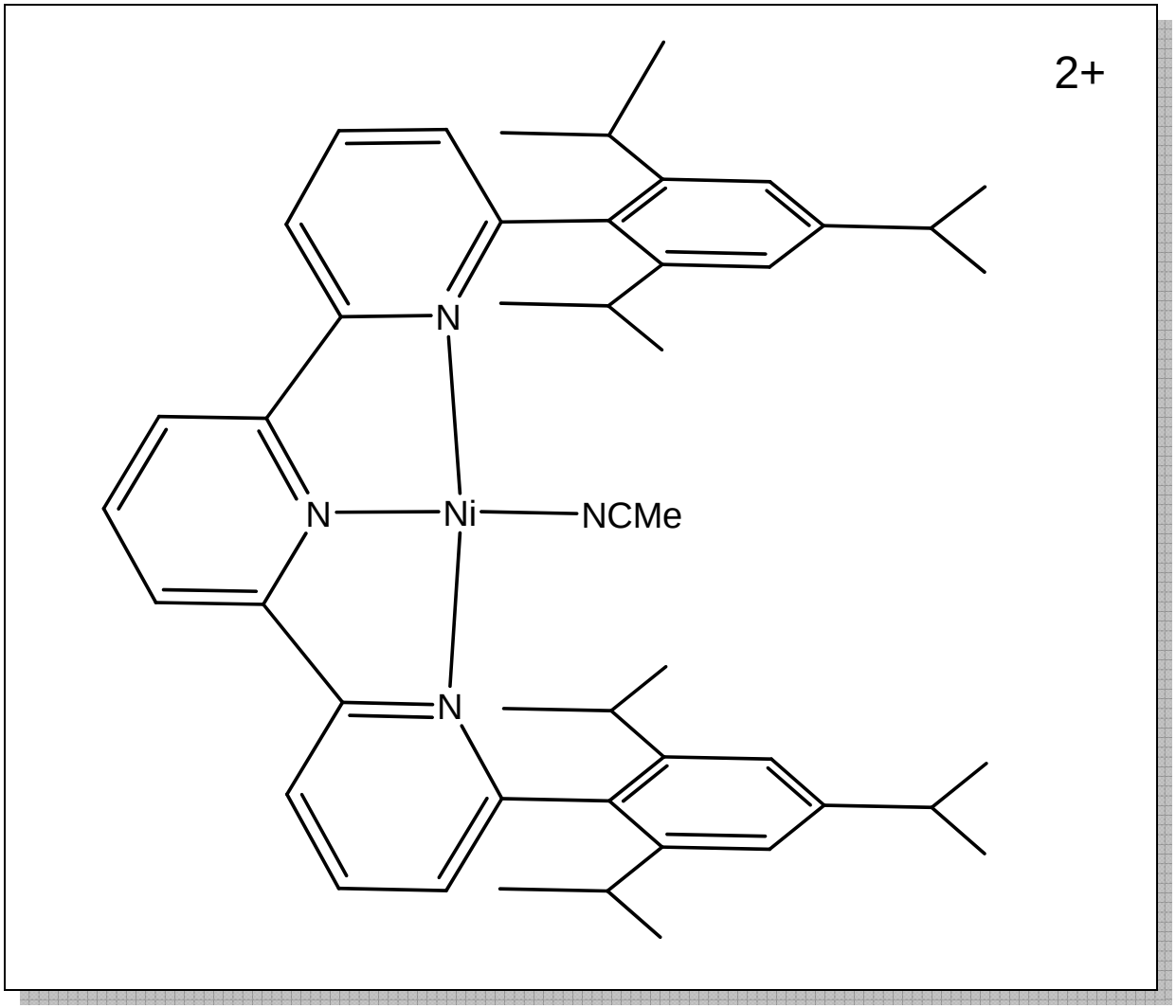
R^2=0.025

For data > 4σ



Bond	Distance (Å)
Cu-N_1	1.982
Cu-N_2	2.061
Cu-Cl_1	2.238
Cu-Cl_2	2.174

Atoms	Angle
N1-Cu-N2	81.76°
N1-Cu-Cl1	96.38°
N1-Cu-Cl2	146.57°
N2-Cu-Cl1	128.66°
N2-Cu-Cl2	109.01°
Cl1-Cu-Cl2	100.20°

$CuCl_2$TripBipy · $2CHCl_3$

Nickel Trip-Terpy for reduction of CO_2