# Chapter IV: Molecular Catalysis for $CO_2$ Reduction


seppo.net
CO2
EAT IT!!
WE PROMISED THE WORLD
YOU CAN DO IT !!!!
CO2
Seppo Leinonen 2017/ seppo.net

# Table of contents

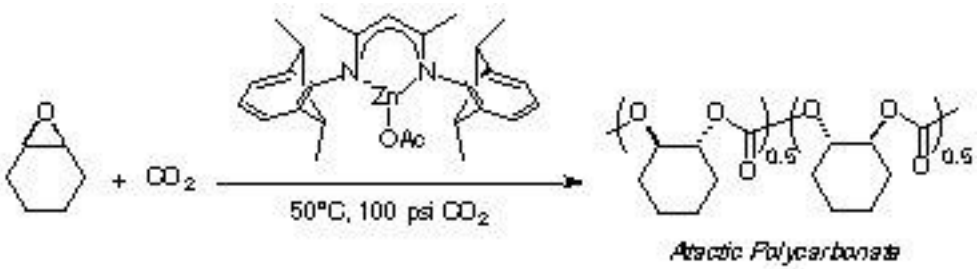
# I. Scale of $CO_2$ chemistry

# Chemical methods of removing (utilizing) $CO_2$

1. plant more trees (capacity, respiration balance)
2. make coca-cola etc.
3. make urea, carbonate, etc.

$$2\ NH_3 + CO_2 \rightarrow H_2N\text{-}COONH_4$$
$$H_2N\text{-}COONH_4 \rightarrow (NH_2)_2CO + H_2O$$

4. make bio-degradable polymer




Nice, useful, and sometimes profitable chemistry
All small scale compared to the 20 billions of tons of $CO_2$ released every year...

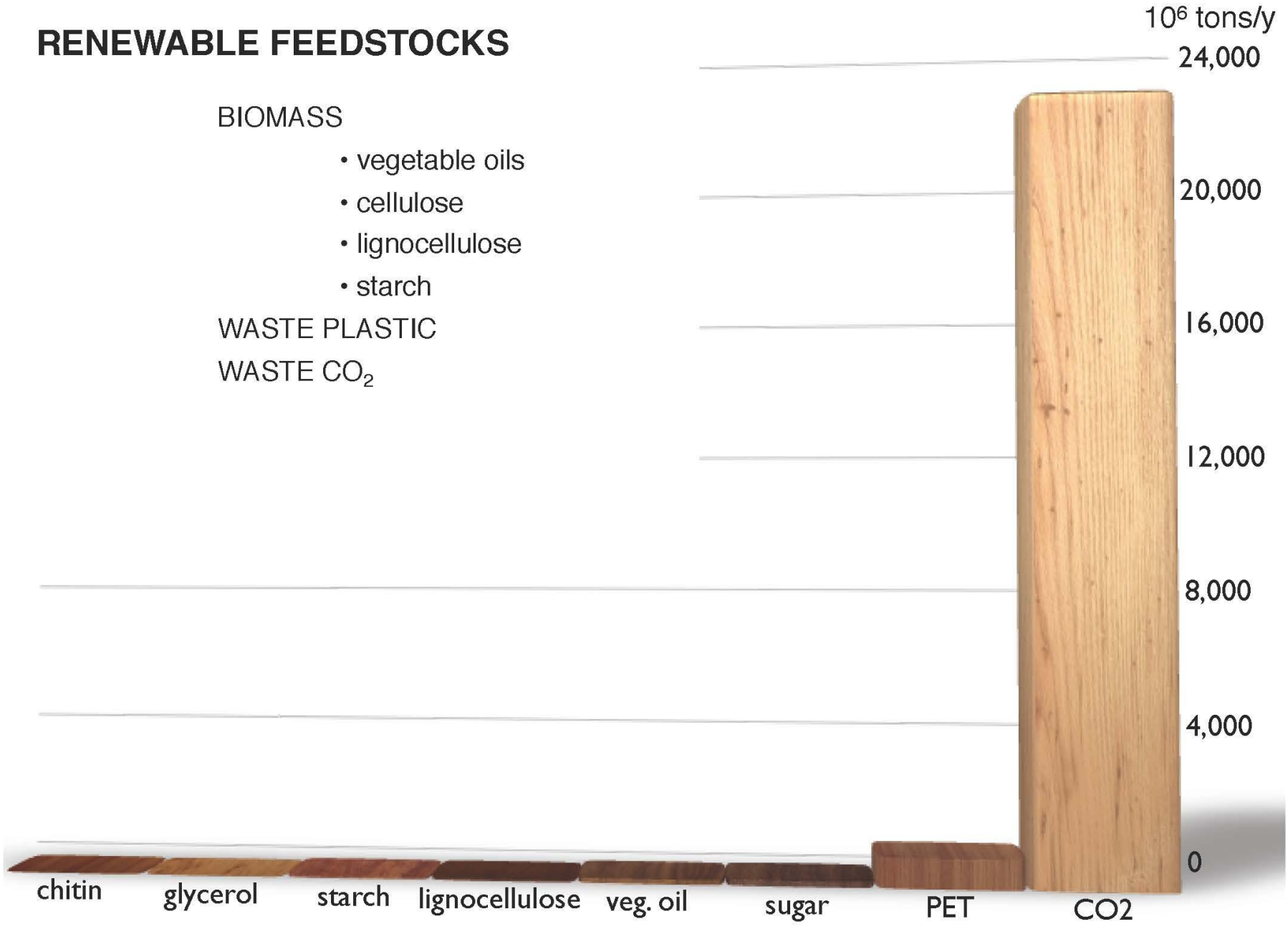
# RENEWABLE FEEDSTOCKS

BIOMASS

- vegetable oils
- cellulose
- lignocellulose
- starch

WASTE PLASTIC

WASTE $CO_2$



# Some $CO_2$ chemistry that are scalable

1. With hydrogen – consider $CO_2$ as a storage media for $H_2$
   Hydrogen need to be produced from renewable energies via water splitting

**Option A:**

$CO_2 + H_2 \rightarrow HCOOH$

Use:

(1) Formic acid can be used as energy source for formic acid fuel cell

(2) Formic acid is a liquid, and it is easy to carry. Formic acid can decompose to $CO_2$ and $H_2$ easily, with the help of a catalyst. So formic acid can be considered as a hydrogen storage materials. 4.3 wt%.

**Option B:**

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$

Use:

(1) Methanol can be used as energy source for methanol fuel cell

(2) Methanol can be used for direct combustion, to replace petro

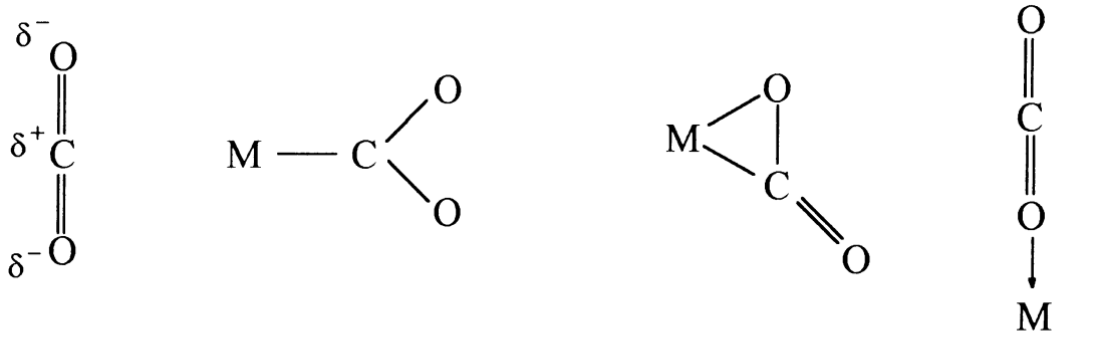
(3) Methanol is the starting materials to make nearly all chemical products that are produced from fossil resources

# II. Fundamental chemistry of $CO_2$

# Interactions of $CO_2$ and transition metals

A metal is often used to activate $CO_2$

Typical binding modes of $CO_2$



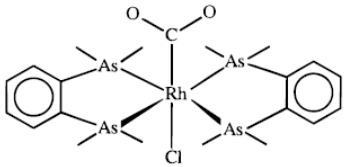

$\eta^1(C)$ $\eta^2(C, O)$ $\eta^1(O)$

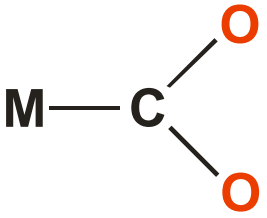
The first two coordination modes are commonly observed; the last one is rarely observed, but it might be invloved as unstable catalytic intermediates.

Yin et al. Coord. Chem. Rev. **1999**, 181, 27.

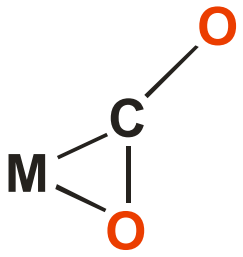
# Common coordination modes of $CO_2$

Herskowitz (1977)
$[(diars)_2M(CO_2)(Cl)]$
M = Ir, Rh



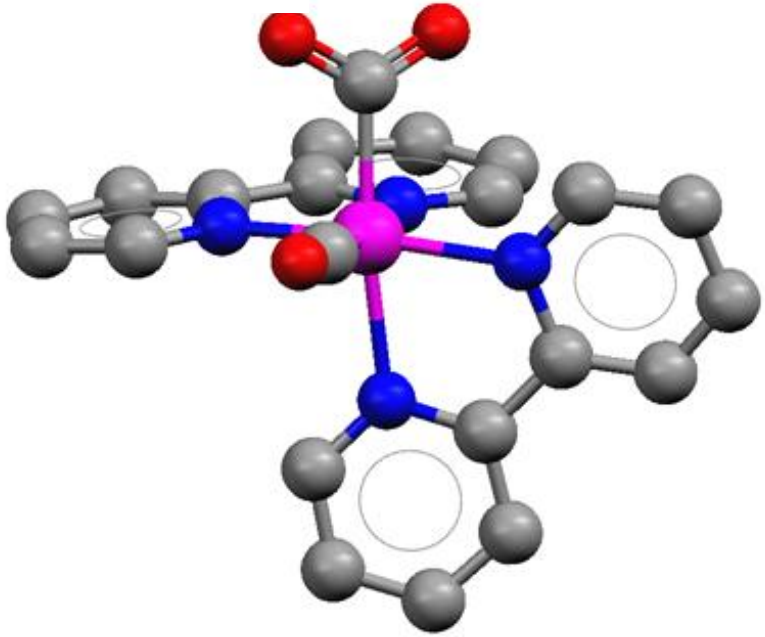



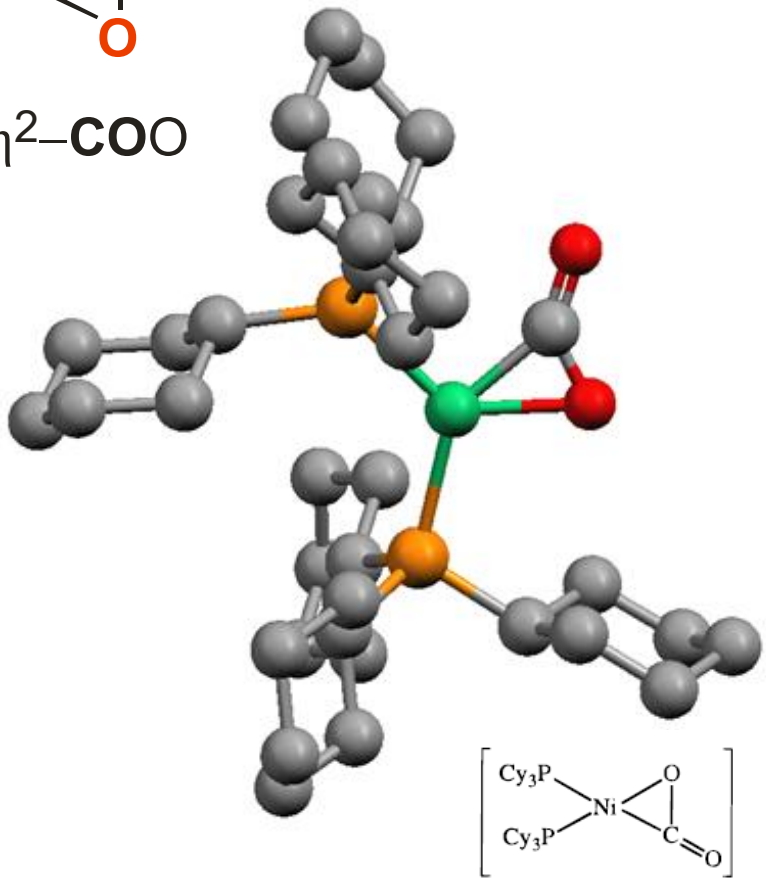

$\eta^1$–**C**$O_2$




$\eta^2$–**CO**O

Aresta (1975)
$[(Cy_3P)_2Ni(CO_2)]$





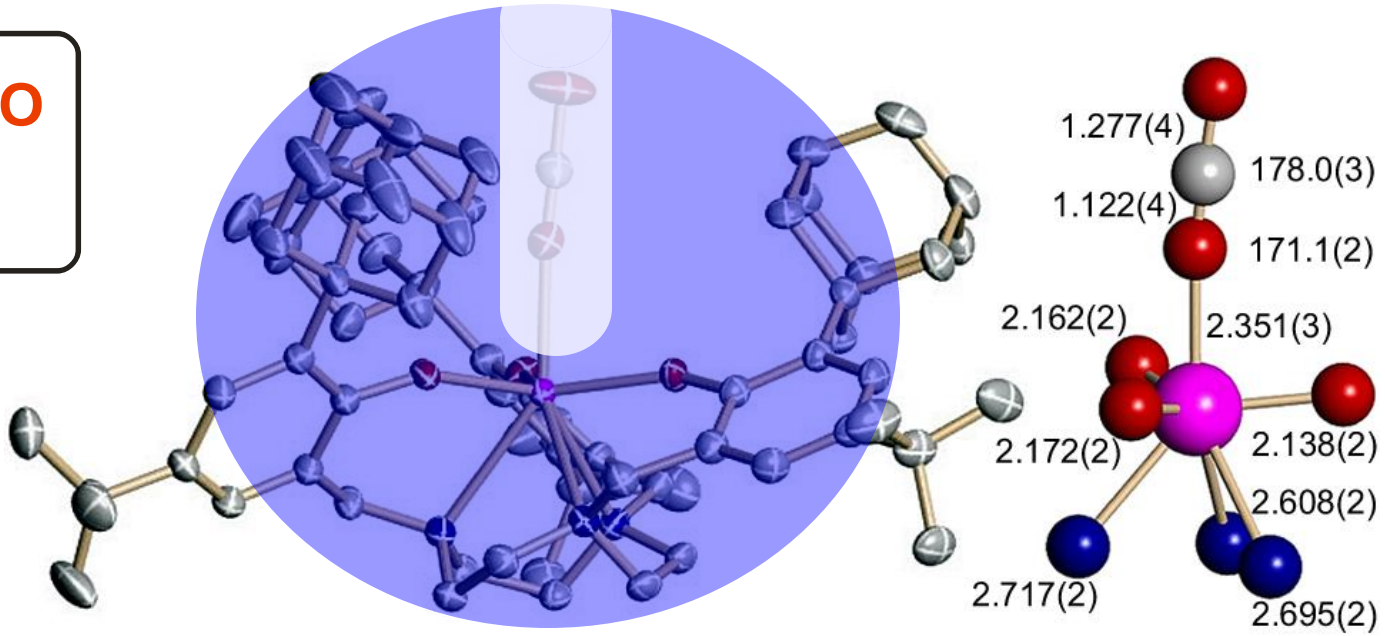

**H. Tanaka *et al.***
***Organometallics* (1992) *11*, 1450**

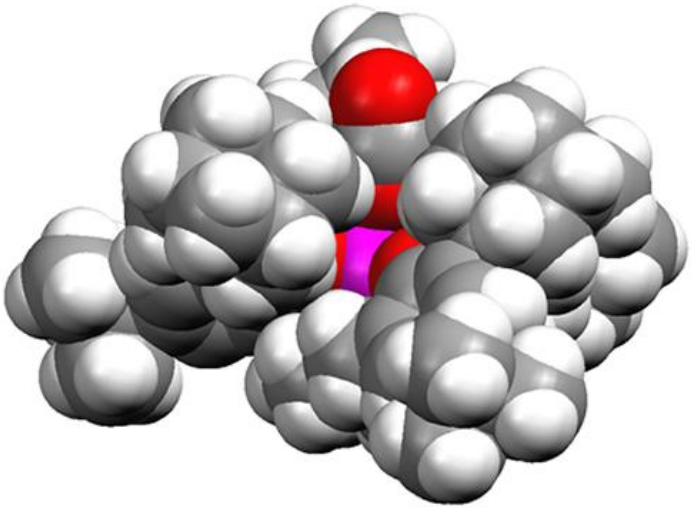
**A. Dohring *et al.***
***Z. Naturforsch.* (1985) *40*, 484**

# A rare coordination mode of $CO_2$

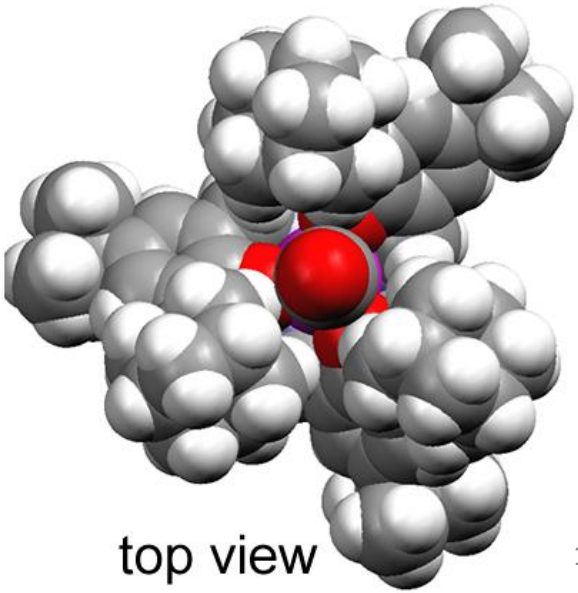
**M—O—C—O**

$\eta^1$–**O**CO



side view

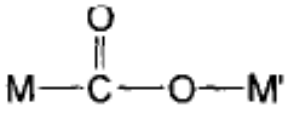


top view

I. Castro-Rodriguez & K. Meyer
in *Science* **2004**, *305*, 1757—17579.

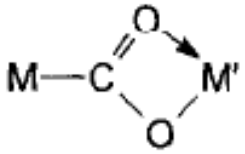
# $CO_2$ as a bridging ligand

The coordination of M to the central C atom results in a relatively high negative charge on the terminal O atoms and increase in their nucleophilicity, thus promoting its coordination to another metal (M' and M'').

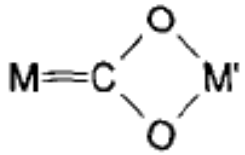



I

$\mu_2$–$\eta^2$




IIa



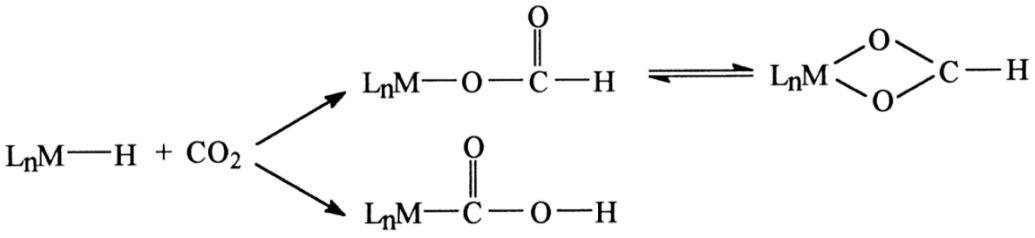

IIb

$\mu_2$–$\eta^3$

Leitner, W. Coord. Chem. Rev. **1996**, 153, 257-284

# A fundamental step in metal-catalyzed $CO_2$ reduction

$CO_2$ insert into M-H bond




formate, more common

carboxylic acid

In this reaction, $CO_2$ may or may not first coordinate to the metal

# Summary of fundamental chemistry of $CO_2$

- $CO_2$ is an inert molecule. The reactivity of $CO_2$ can be enhanced by interaction with a catalyst.
- Several basic coordination modes of $CO_2$ to metal(s) are known.
- Insertion of CO2 to a metal-H bond is an imporant step in chemical reduction of $CO_2$.

# III. Molecular catalysis for electrochemical reduction of $CO_2$

# Why electrochemical reduction $CO_2$?

Electrochemical $CO_2$ reduction is an alternative to water splitting

Energy stored:

Water splitting: $2\,H_2O \xrightarrow{\text{energy}} 2\,H_2 + O_2$ E = 1.23 V

$CO_2$ reduction:

$2CO_2 \xrightarrow{\text{energy}} 2\,CO + O_2$ E = 1.34 V

$2CO_2 + 2H_2O \xrightarrow{\text{energy}} 2\,HCOOH + O_2$ E = 1.43 V

$CO_2 + H_2O \xrightarrow{\text{energy}} HCOH + O_2$ E = 1.30 V

$2CO_2 + 4\,H_2O \xrightarrow{\text{energy}} 2\,H_3COH + 3\,O_2$ E = 1.20 V

$CO_2 + 2\,H_2O \xrightarrow{\text{energy}} H_4C + 2\,O_2$ E = 1.06 V

All these C-based fuels have higher density than $H_2$, so they are easier to store and transport.

An overall $CO_2$ reduction reaction consistes of two half reactions:
(1)Oxygen evolution reaction (OER)

$$2H_2O \rightarrow \ O_2 + 4\ H^+ + 4\ e^-$$

(2) Electrochemical $CO_2$ reduction

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$$
$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$
$$CO_2 + 4H^+ + 4e^- \longrightarrow HCOH + H_2O$$
$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$$
$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2\ H_2O$$

# Thermodynamic aspects of electrochemical $CO_2$ reduction

1 e reduction of $CO_2$ is difficult, because $CO_2^-$ radical is very unstable

$$CO_2 + e^- \longrightarrow \cdot CO_2 \qquad E^o < -1.5 \text{ V vs. RHE}$$

Multi-e reduction of $CO_2$ have lower thermodynamic potentials (vs. RHE)

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O \qquad E^o = -0.11 \text{ V}$$

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH \qquad E^o = -0.20 \text{ V}$$

$$CO_2 + 4H^+ + 4e^- \rightleftharpoons HCOH + H_2O \qquad E^o = -0.07 \text{ V}$$

$$CO_2 + 6H^+ + 6e^- \rightleftharpoons CH_3OH + H_2O \qquad E^o = 0.03 \text{ V}$$

$$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2\,H_2O \qquad E^o = 0.17 \text{ V}$$

Compare to hydrogen evolution:

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad E^o = 0 \text{ V}$$

# Challenge in electrochemical $CO_2$ reduction

Challenge for catalysis

1. The thermodynamic potentials of $CO_2$ reduction are close to hydrogen evolution. Proton is more reactive than $CO_2$. Therefore, hydrogen evolution is a common side reaction. To alleviate hydrogen evolution, CO2 reduction is commonly done in neutral to basic water, or in organic solvents.
2. Many carbon-based products are produced at similar potentials. The selectivity of $CO_2$ reduction is a problem.
3. Known catalysts have generally a low efficiency: small current density at high overpotentials.
4. The common problems for all electrocatalysts – cost and stability of catalysts

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$$
$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$
$$CO_2 + 4H^+ + 4e^- \longrightarrow HCOH + H_2O$$
$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$$
$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2\,H_2O$$

Among various $CO_2$ reduction reactions, we will only focus on the 2e reduction to form either CO or HCOOH as products. The 2e reduction is generally easier to control than 6e or 8e reduction, with simpler mechanisms.

$$2CO_2 \xrightarrow{\text{energy}} 2\,CO + O_2 \qquad E = 1.34\ V$$
$$2CO_2 + 2H_2O \xrightarrow{\text{energy}} 2\,HCOOH + O_2 \qquad E = 1.43\ V$$
$$CO_2 + H_2O \xrightarrow{\text{energy}} HCOH + O_2 \qquad E = 1.30\ V$$
$$2CO_2 + 4\,H_2O \xrightarrow{\text{energy}} 2\,H_3COH + 3\,O_2 \qquad E = 1.20\ V$$
$$CO_2 + 2\,H_2O \xrightarrow{\text{energy}} H_4C + 2\,O_2 \qquad E = 1.06\ V$$

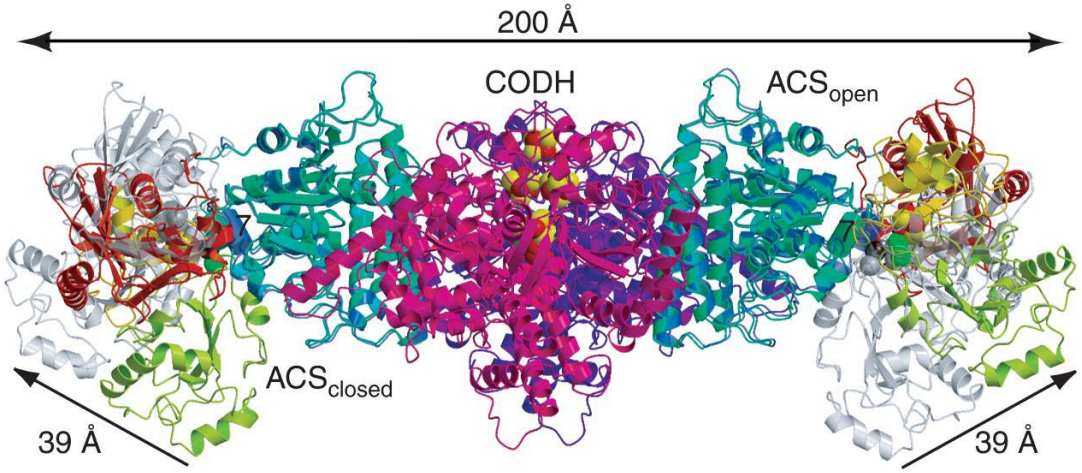
# III-1. A biological catalyst

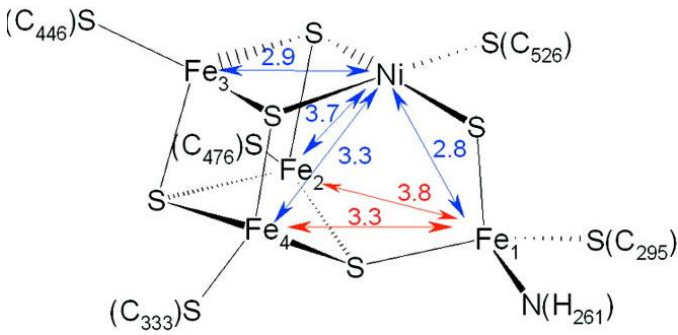
# Enzymatic $CO_2$ Reduction: FeNi-CODH

Carbon monoxide dehydrogenases (CODH) are enzymes that catalyze the electrochemical interconversion of $CO_2$ and CO.

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O$$

The anaerobic form of enzyme contains FeNi in the active site.

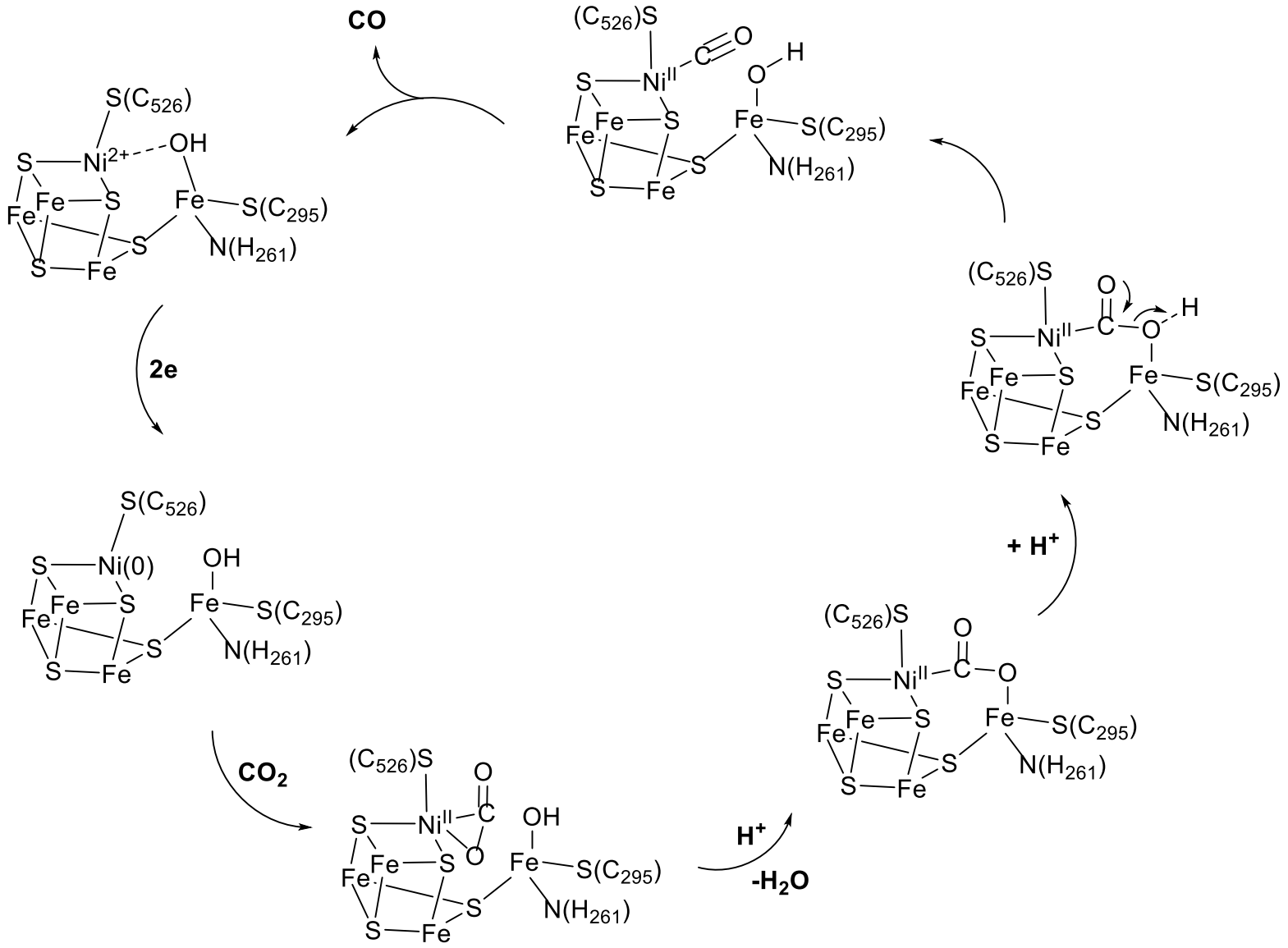



Active site

Crystal structure of FeNi-CODH (in a protein assembly).

# Proposed mechanism of $CO_2$ reduction by FeNi-CODH






Kubiak et al. Chem. Soc. Rev. 2009, 38, 89.

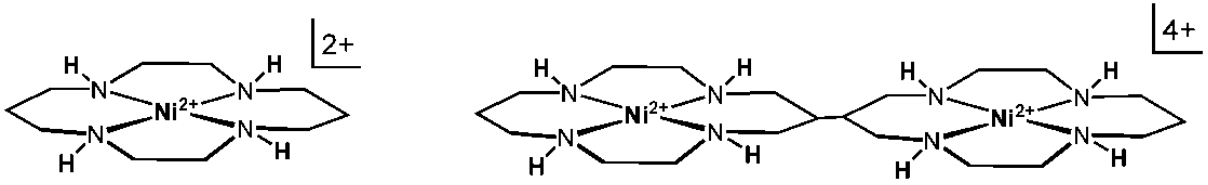
# III-2. Molecular catalysts

# Electrocatalytic 2 electron $CO_2$ reduction

$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O$ E = -0.11 V vs. RHE

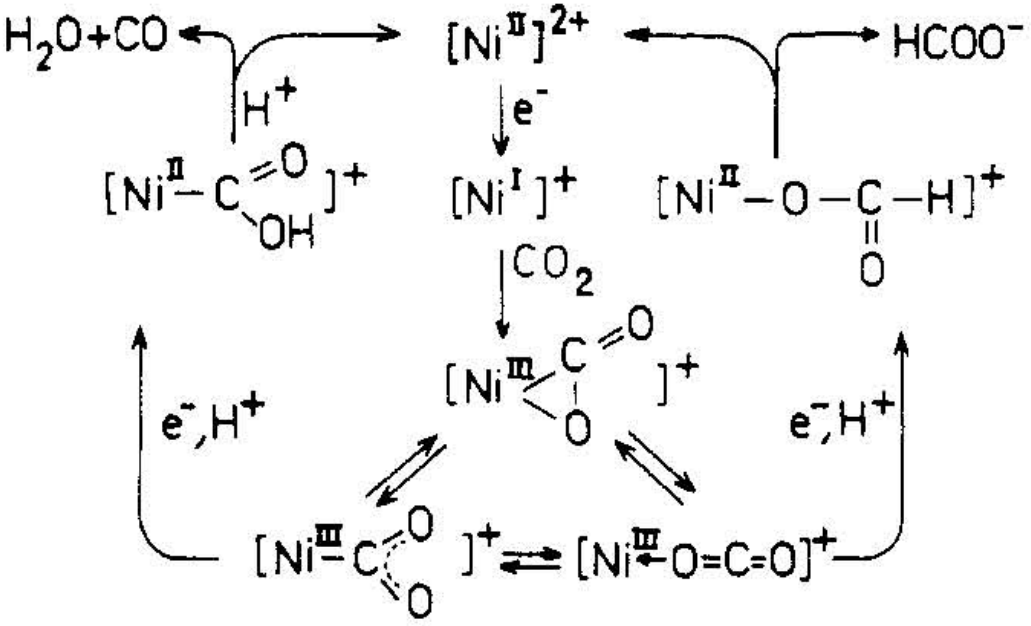
$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH$ E = -0.20 V vs. RHE

$2H^+ + 2e^- \rightleftharpoons H_2$ E = 0 V vs. RHE




These nickel complexes were found to catalyze $CO_2$ reuction in DMF
At -1.6 V vs. SCE; the product is a mixture of CO and HCOOH

# Origin of the different products

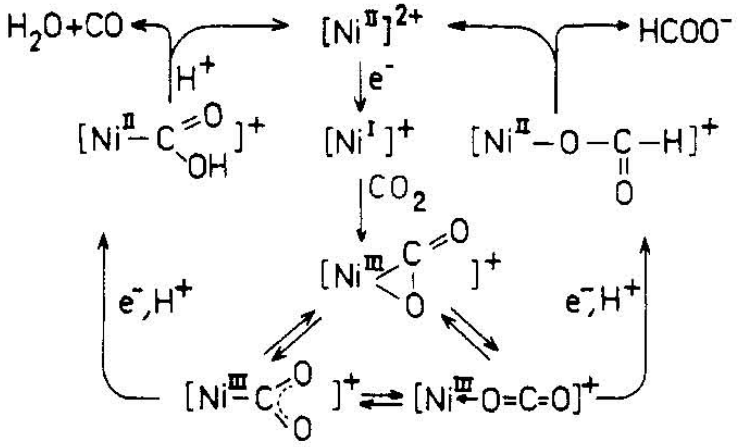


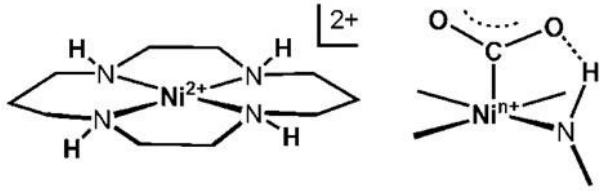

Whether CO or HCOOH is produced depending on the intermediates of Ni-$CO_2$ complex; A C-bound $CO_2$ leads to CO; a O-bound $CO_2$ leads to HCOOH

Collin, Sauvage et al. Inorg. Chem. 1988, 27, 1986.

# Selective 2 electron $CO_2$ Reduction: to CO

at pH>4 in water, however, only CO is produced with these complexes. At E = ~ -1 V vs. RHE. No HCOOH nor $H_2$ is produced. So the reaction is selective for CO formation.




Hydrogen Bonding

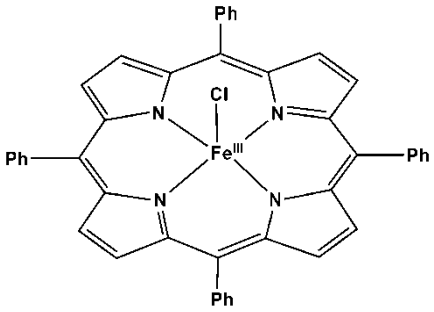
It is proposed that hydrogen bonding interaction between the NH ligand and the terminal O of coordinated $CO_2$ stablized the C-bound Ni-$CO_2$ intermedaite, so CO formation is selective.

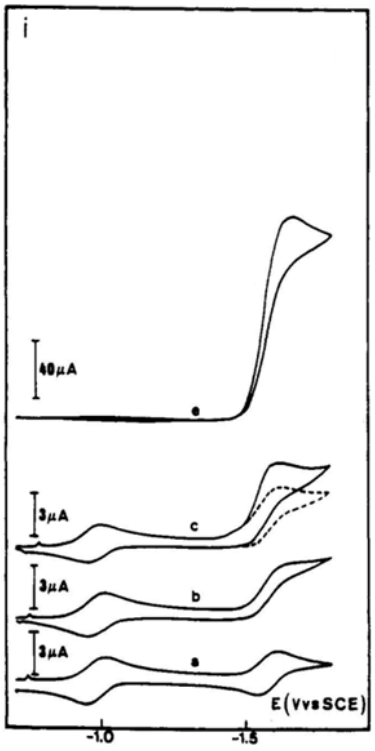
Sauvage et al. JACS **1986**, *108*, 7461.

Another example:  Iron-prophyrin complex again

# My face when I heard it is iron porphyrin again!

# Selective 2 electron $CO_2$ Reduction: to CO




**Cat + $CF_3CH_2OH$ +$CO_2$**
Big catalytic current for $CO_2$ reduction
**Only CO is produced**

**Cat + $CF_3CH_2OH$** Small catalytic current for HER

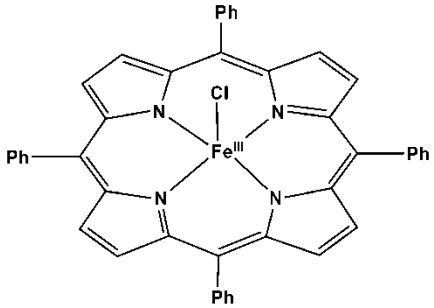
**Cat + $CO_2$** Small catalytic current for $CO_2$ reduction

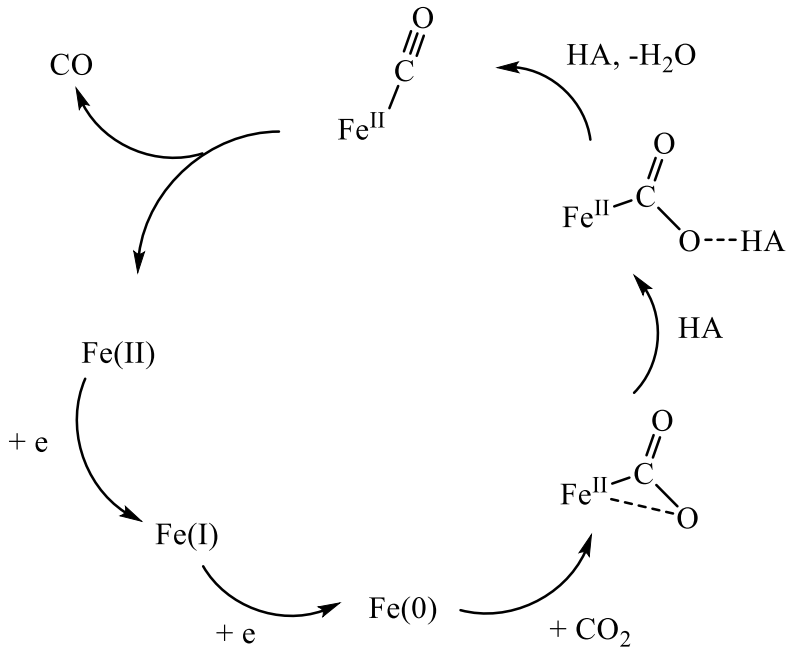
**Cat** (Fe(I) to Fe(0) at -1.6 V)

Saveant et al. JACS **1994**, *116*, 5015; JACS **1996**, *118*, 1769.

# Selective 2 electron $CO_2$ Reduction: to CO

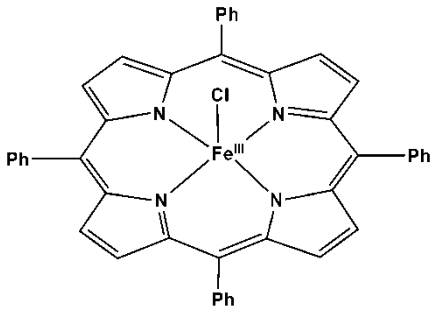
Proposed mechanism:



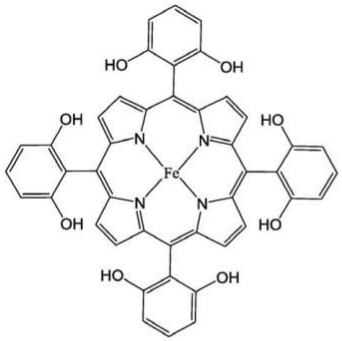
# How about putting hydrogen bonding units on the Fe-porphyrin complex?

from



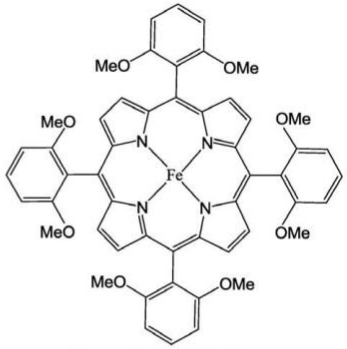

to

**FeTDHPP**




Iron 5,10,15,20-tetrakis(2',6'-dihydroxylphenyl)-porphyrin

**FeTDMPP**



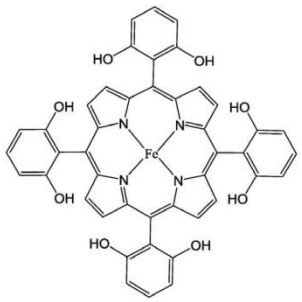

Iron 5,10,15,20-tetrakis(2',6'-dimethoxyphenyl)-porphyrin

FeTDHPP has a similar electronic property to FeTDMPP
FeTDHPP can engage in hydrogen bonding, while FeTDMPP cannot.

Saveant et al. Science 2012, 338, 90.

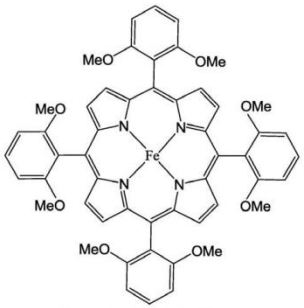
# How about putting hydrogen bonding units on the Fe-porphyrin complex?

**FeTDHPP**

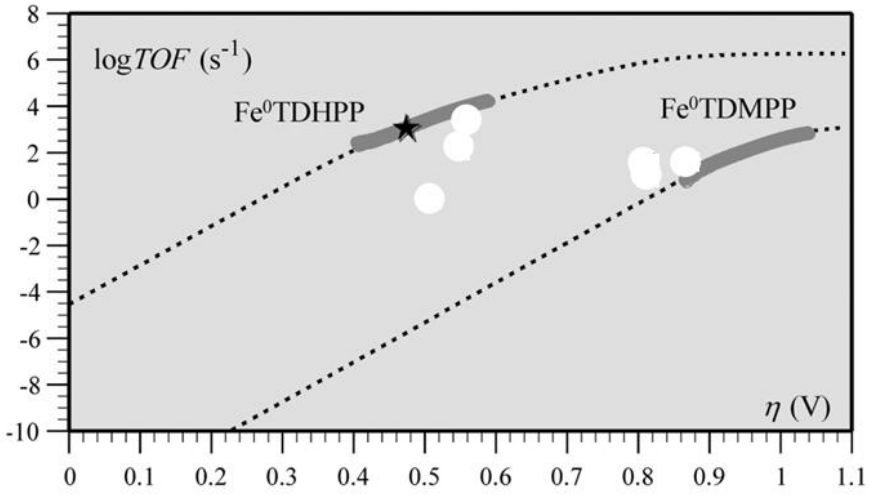



Iron 5,10,15,20-tetrakis(2',6'-dihydroxylphenyl)-porphyrin

**FeTDMPP**




Iron 5,10,15,20-tetrakis(2',6'-dimethoxyphenyl)-porphyrin

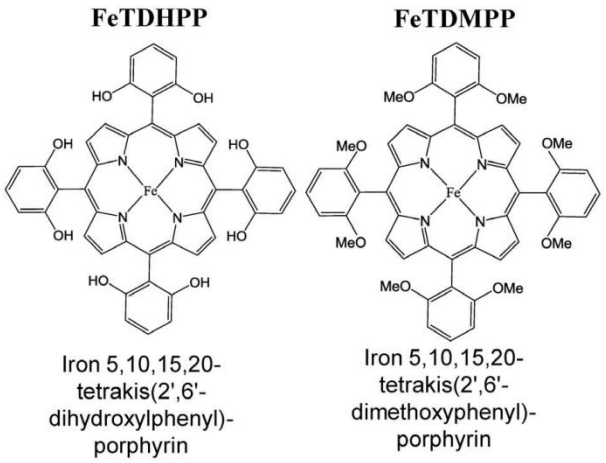


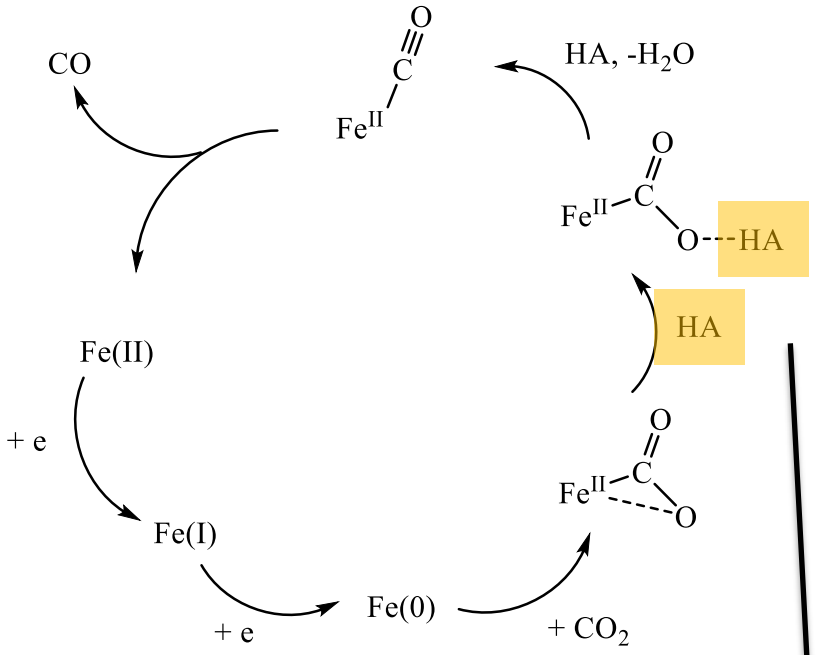

Having a hydrogen bonding unit in the molecule shifts the overpotential towards smaller values while maintaining similar turnover frequencies.

Saveant et al. Science 2012, 338, 90.

# Selective 2 electron $CO_2$ Reduction: to CO

Proposed mechanism:




Intra-molecular proton donor speeds up the reaction

# Conclusion

- The $CO_2$ emission is at a massive scale; only chemistry that uses a huge amount of $CO_2$ might have an impact in decreasing the global $CO_2$ emission.

- $CO_2$ is a relatively inert molecule that can be activated by a metal catalyst.

- Molecular complexes can serve as catalysts for electrocatalytic $CO_2$ reduction. The most abundant examples concern 2-electron reduction of $CO_2$ to form formate or CO. The selectivity might be controlled by tuning the ligand environment of the metal catalysts.