

The Ultimate Carbon Source

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A Problem?

Or

A Solution?

	CO ₂	CO	NO _x	PM
2006	1900	10	0.6	0.7
2008	1900	7	0.3	0.07
2012	1650	1	0.03	0.03

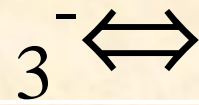
Lb/MWh

$$\Delta G = -394 \text{ kJmol}^{-1}$$

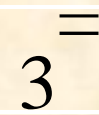
Stable



H₂O



+

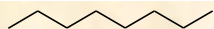


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- Fuel Consumption
- Scrubbing
- Sequestration
- Photosynthesis
- Chemicals
 - Urea and other
 - Carbon Monoxide
 - Methane
 - Ethylene

Advantages of Ethylene

Octane



5473 kJ/mol

Methane



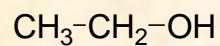
902 kJ/mol

Hydrogen



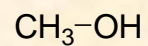
286 kJ/mol

Ethanol



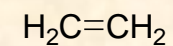
1366 kJ/mol

Methanol



726 kJ/mol

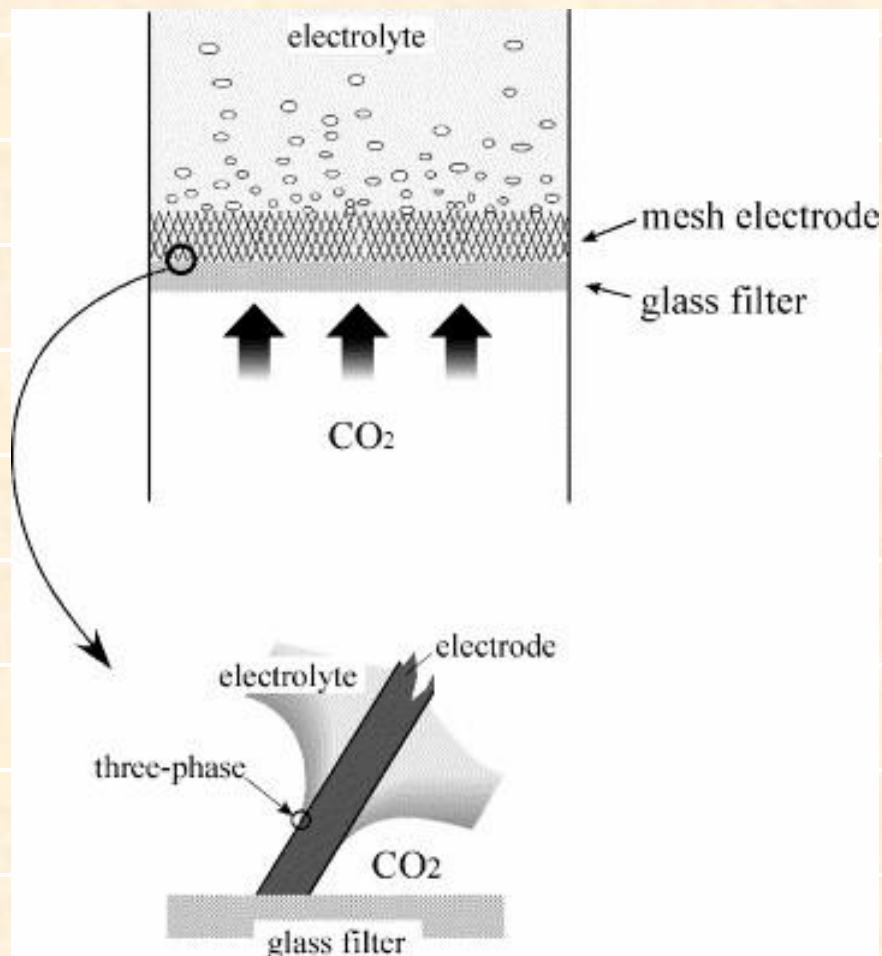
Ethylene



1411 kJ/mol

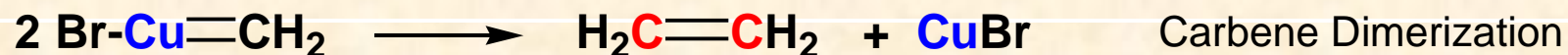
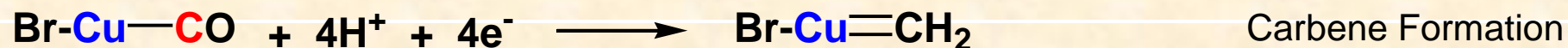
- Highest heat of combustion of common “alternative” fuels
- Can be easily transformed to liquid ethanol

Production of Ethylene from CO₂



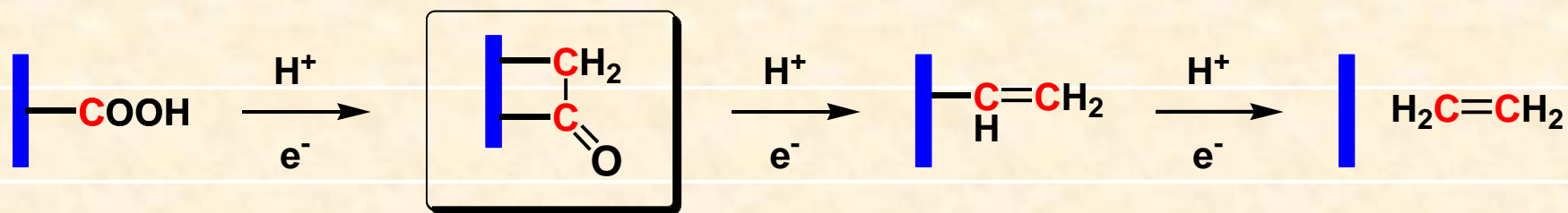
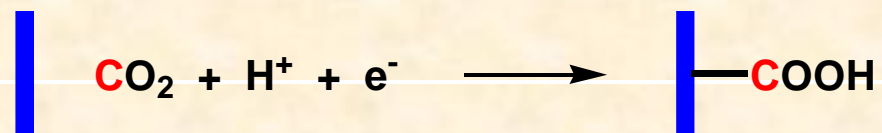
- Electrochemical reductions using copper electrodes generally produce CO and formate—not ethylene.
- So why does the 3-phase cell change the reaction's selectivity?
- Mechanistic Clue:
Plating of Cu(I) salts on the surface of the electrode enhances the rate of the reaction and the selectivity for ethylene formation.

Possible Mechanism #1: Carbene Dimerization



- Until recently, this was the generally accepted mechanism.
 - Copper(I)-Carbenes are common intermediates.

Possible Mechanism #2: via "Side-on" Intermediates



"Side-On" Intermediate

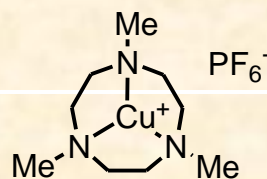
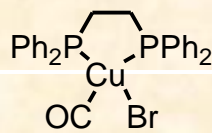
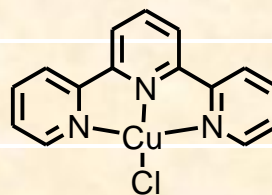
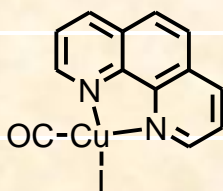
- The side-on intermediate was observed by I R.
- Ogura concluded that this mechanism must be correct.
 - Not necessarily a valid conclusion.

- Regardless of the mechanism, two Cu atoms must be involved in the formation of each molecule of ethylene.
- Can we construct discrete small-molecule catalysts that facilitate the bimolecular mechanism and reduce the required overpotential?
- Two possible solutions to this challenge:
 1. Homogeneous Monometallic Catalysts
 2. Bimetallic Catalysts (either homogeneous or heterogeneous)

Monometallic, Homogenous Catalysts

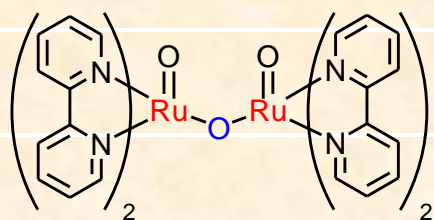
- The in situ formation of Cu(I) ions has been proposed, yet no experiments with soluble organometallic complexes have been attempted.
- Bimolecular catalytic reactions are common in solution phase chemistry.

Examples of Possible Monometallic Cu(I) Catalysts



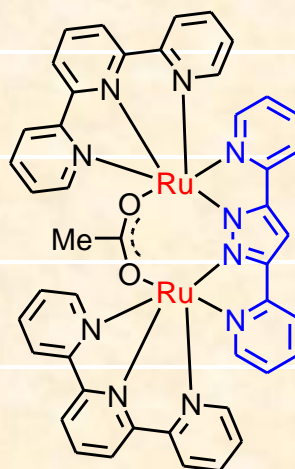
Other Energy-Related Bimetallic Catalysts

- The bimetallic electrochemical reaction of two substrate molecules to form a single molecule of product is very reminiscent of another energy-related reaction: **The electrochemical oxidation of water.**



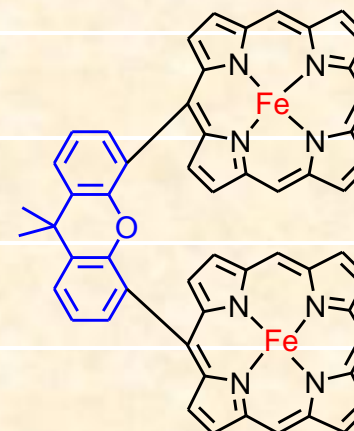
Meyer

JACS, **1985**, 107, 3855.



Llobet

JACS, **2004**, 126, 7798.

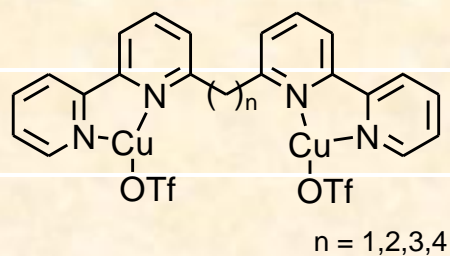


Nocera

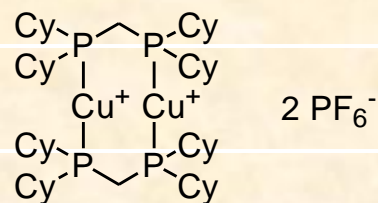
JACS, **2006**, 128, 6546.
(catalyzes the backwards reaction)

Proposed Bimetallic Catalysts

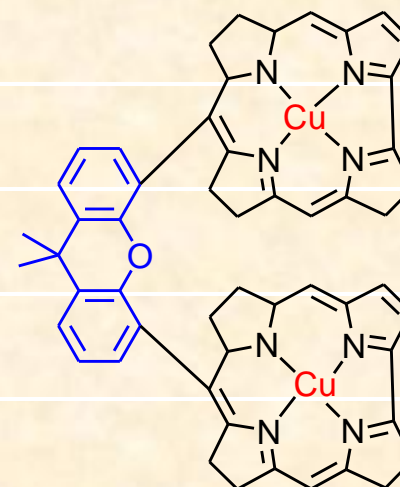
- Linking the two Cu(I) sites together should enhance the reaction—either by providing a stable structure for the “side-on” intermediate or placing the two copper-carbenes in close proximity.



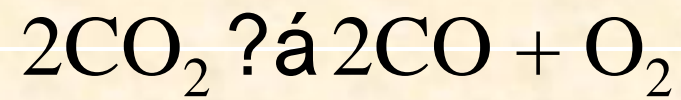
Bridged-bpy
Complexes



Bridging
Bis-Phosphines

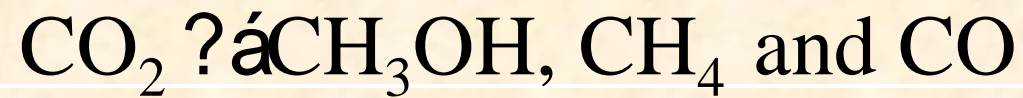


Corrin "Pack-man"
Complexes



Ni Cluster

P-GaP



Cu/TiO₂-NiO₂

- Incentives
- Catalyst: Cu
- Choice of Processes
- Literature Discrepancies
 - Mechanism
 - Non-aqueous electrolyte
 - Source of H
- Economics

