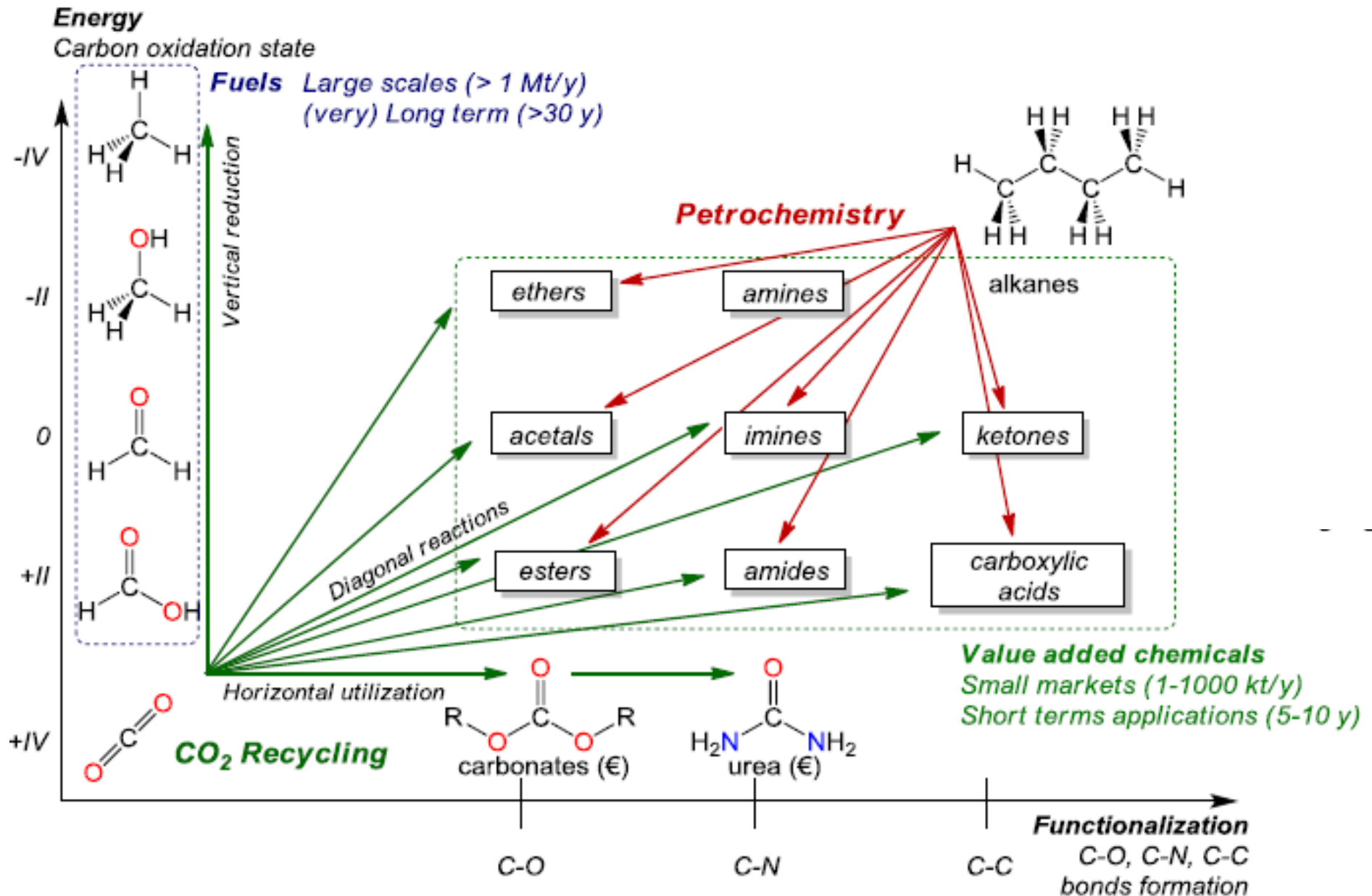
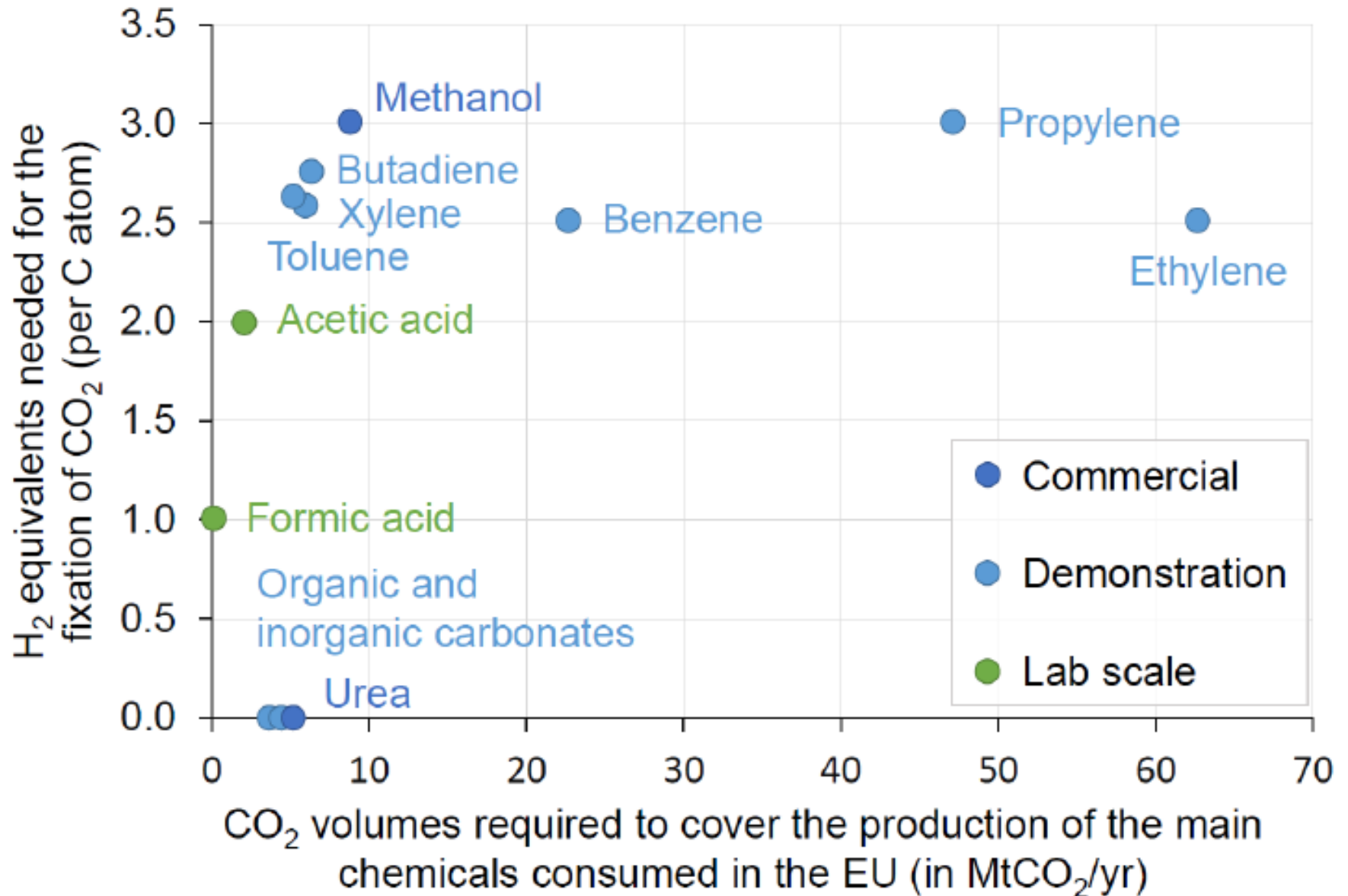


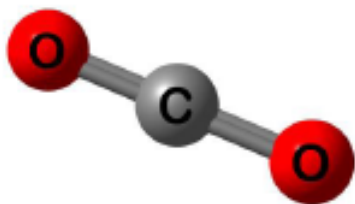
CO₂ as a C₁ building block



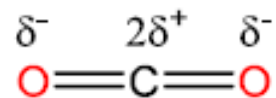
Carbon based products



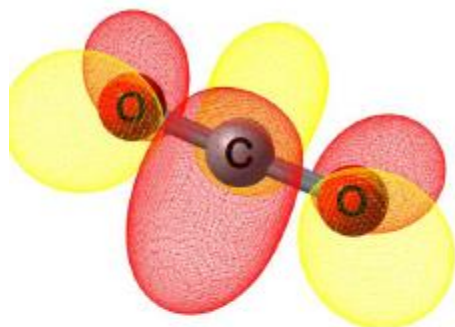
Carbon dioxide



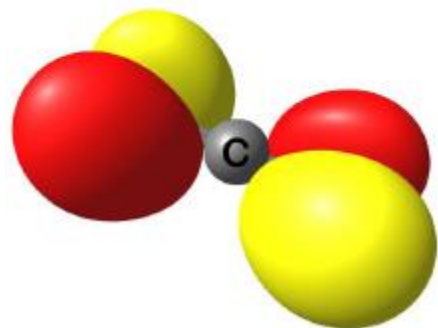
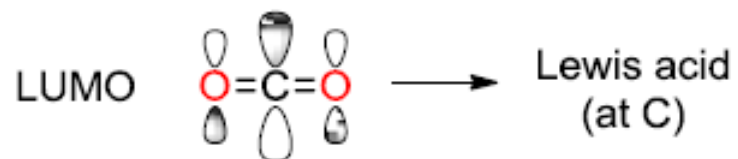
C-O: 1.16 Å



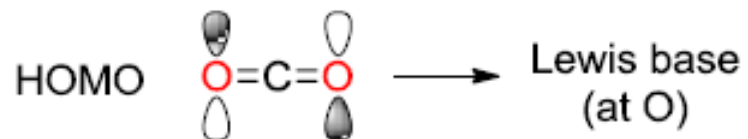
- Non-polar
- Electrophilic at C (Lewis acid)
- Nucleophilic at O (Lewis base)



— LUMO
 $2\pi_u$



↕ HOMO
 $1\pi_g$



CO₂ Activation

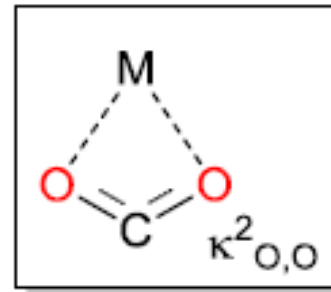
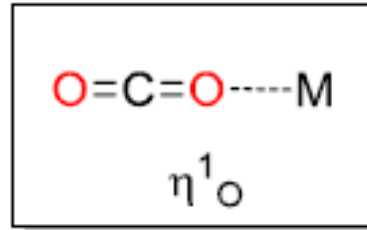
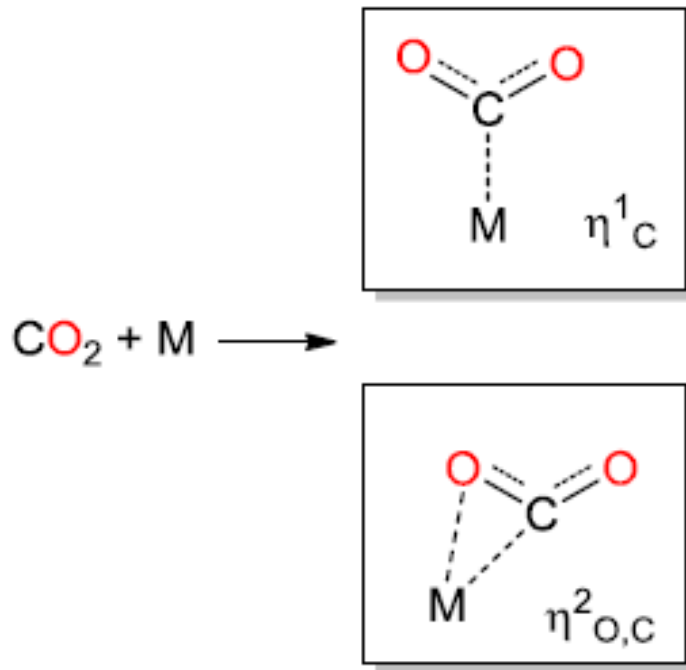
STRENGTHEN POINTS

Cheap;
Nontoxic;
Widely available
(30 Gt/year (2014)).

WEAKNESS POINTS

High thermodynamic stability;
Low reactivity.

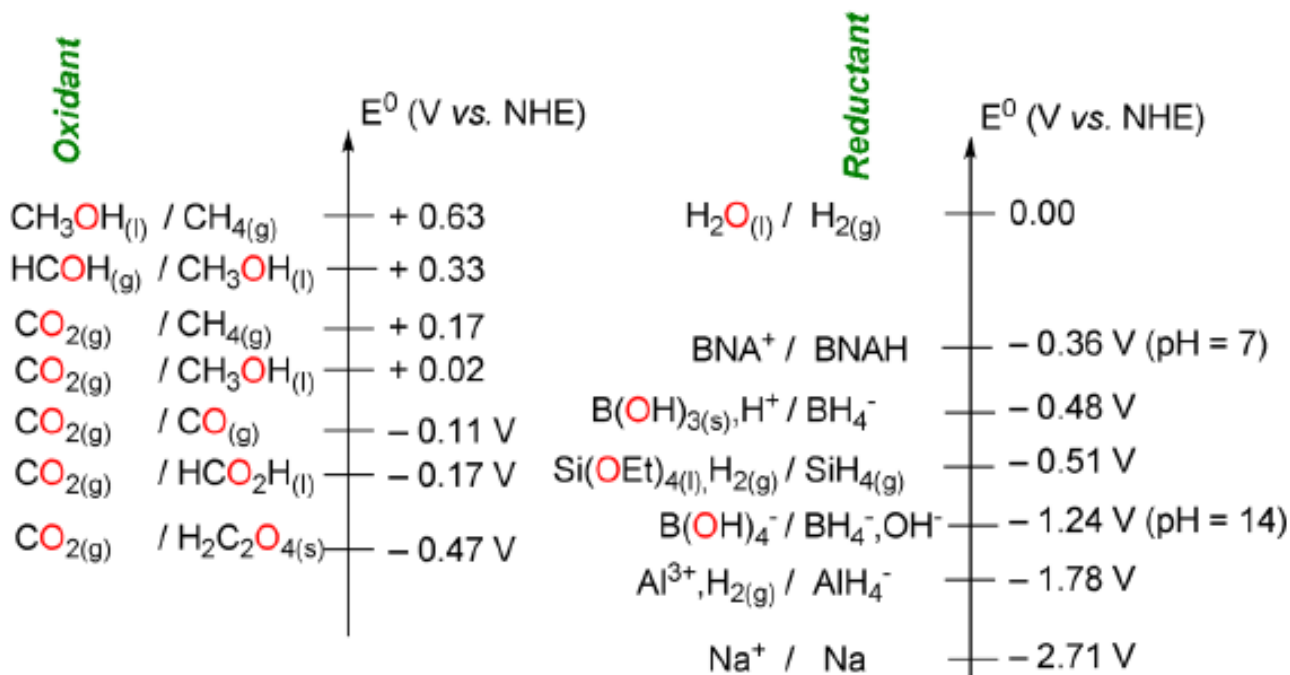
CO₂ coordination modes to transition metals



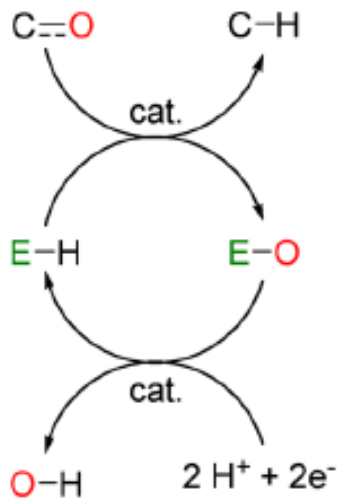
Aresta, 1975

Hydrogenation of CO₂

REDOX POTENTIALS



Involved reactions



Hydrogenation of CO₂ to

FORMIC ACID

It is endoergonic; it is entropically disfavored

$$\Delta H^0 = -31.2 \text{ kJ/mol} \quad \Delta G^0 = +32.9 \text{ kJ/mol} \quad T = 25 \text{ }^\circ\text{C} \quad \text{pH} = 0$$

With the addition of a base, like NH₃

$$\Delta H^0 = -84.3 \text{ kJ/mol} \quad \Delta G^0 = -9.5 \text{ kJ/mol} \quad T = 25 \text{ }^\circ\text{C}$$

In polar solvents, like water

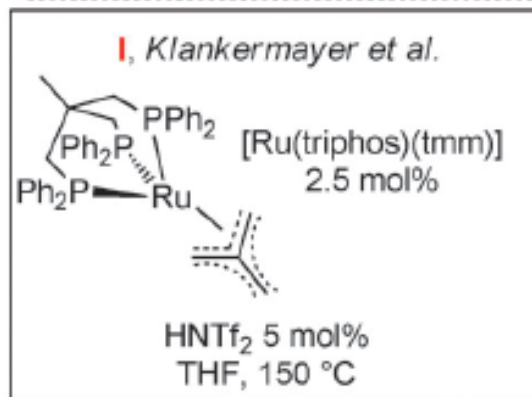
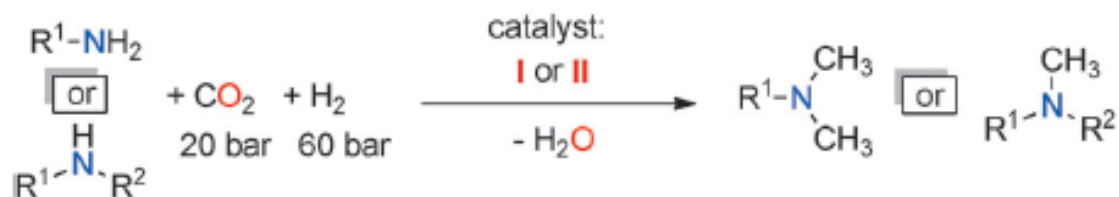
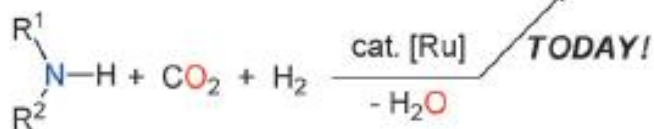
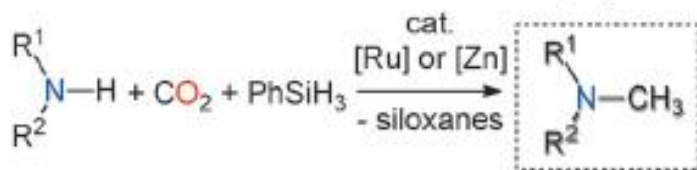
$$\Delta G^0 = -4.0 \text{ kJ/mol} \quad T = 25 \text{ }^\circ\text{C}$$

METHANOL

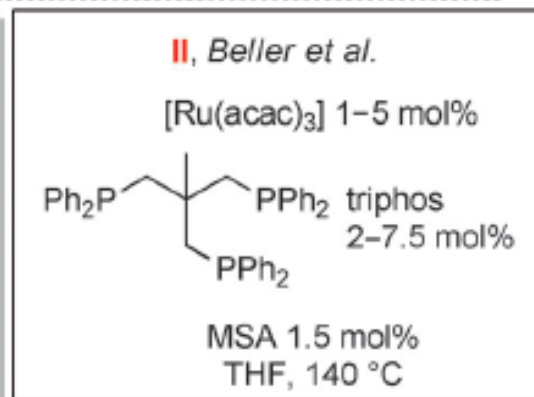
It is exoergonic; but kinetically difficult

$$\Delta G^0 = -17.3 \text{ kJ/mol} \quad T = 25 \text{ }^\circ\text{C} \quad \text{pH} = 0$$

Methylation of amines with CO_2 and H_2



20 examples up to 94% yield



33 examples up to 99% yield

Literature

- T. Cantat et al. *Angew. Chem. Int. Ed.* 2012, 51, 187.
T. Cantat et al. *Angew. Chem. Int. Ed.* 2014, 53, 2543.
T. Cantat et al. *ACS Catal.* 2017, 7, 2107.
-

Tutorial

- A. Azapagic et al. *J. of CO₂ Util.* 2015, 9, 82.
CCS vs CCU review 3 studenti

- M. Beller et al. *JACS* 2012, 134, 20701.
From CO₂ to HCOO⁻ articolo 2 studenti

- W. Leitner et al. *Chem. Sci.* 2015, 6, 693.
From CO₂ to CH₃OH articolo con DFT e meccanismo 3 studenti

- M. Beller et al. *Angew. Chem. Int. Ed.* 2013, 53, 12156.
From CO₂ to N-CH₃ articolo 2 studenti

o

- D. Vogt et al. *Chem. Eur. J.* 2014, 20, 12037.
From CO₂ to acrylate articolo 2 studenti