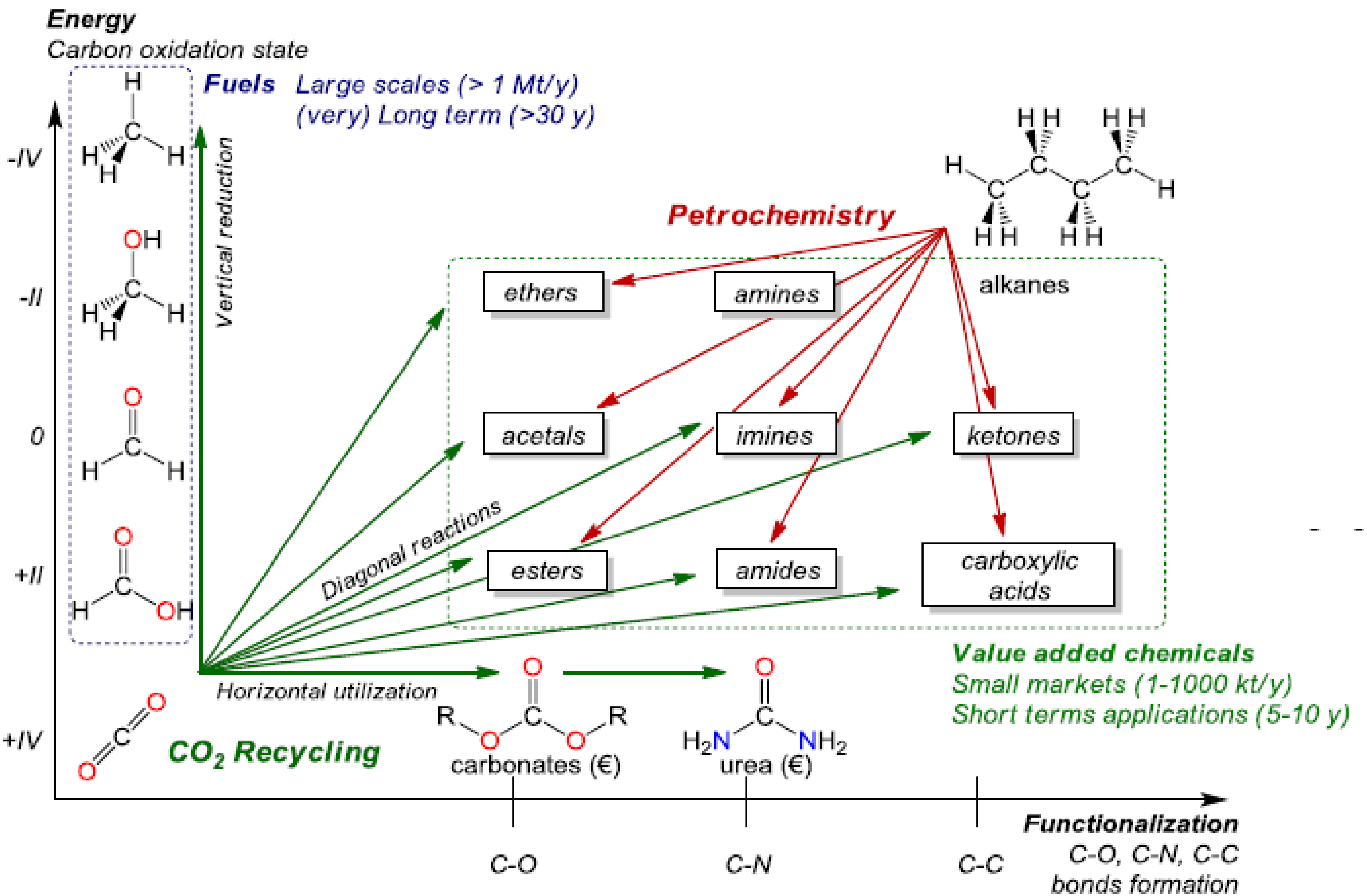
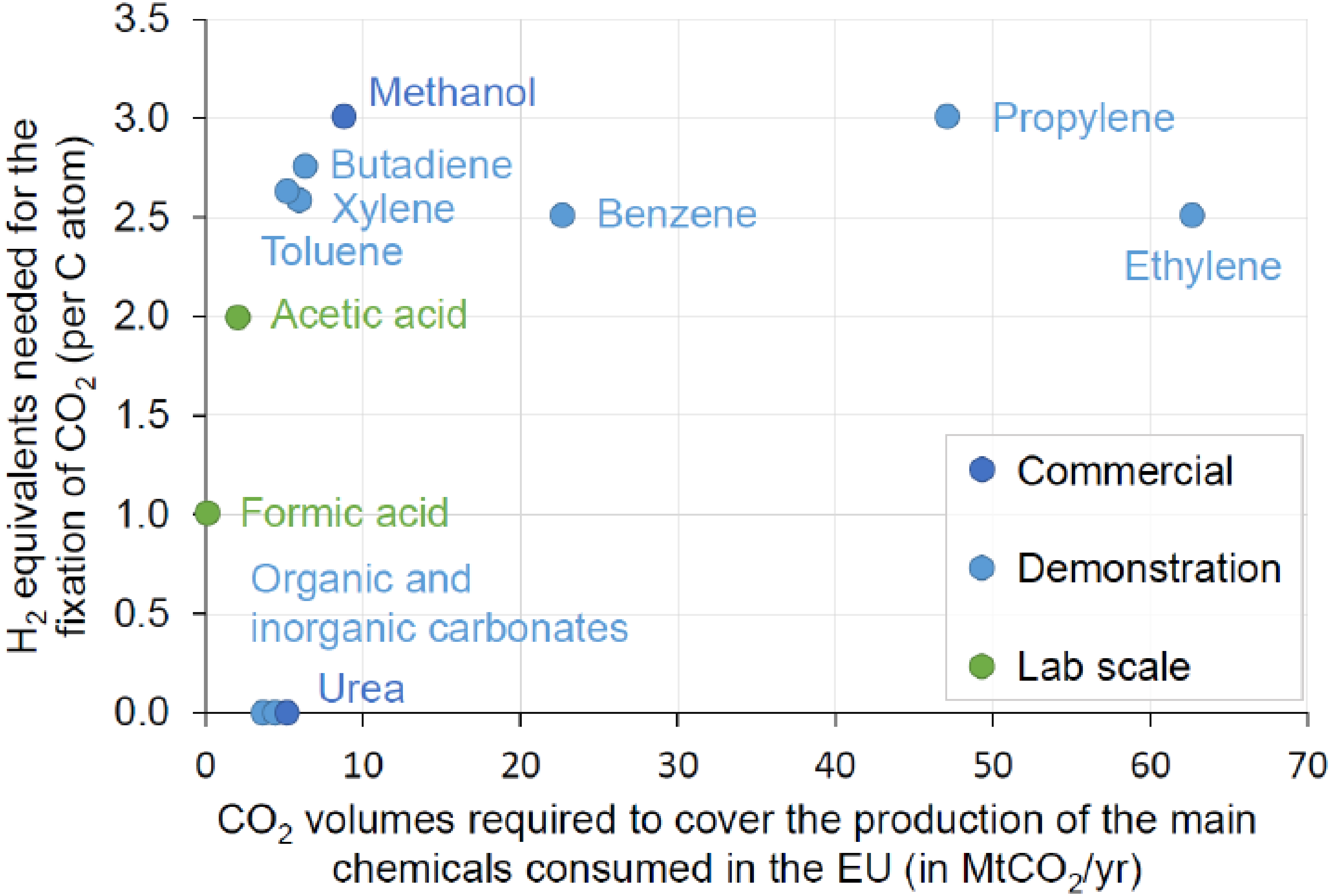
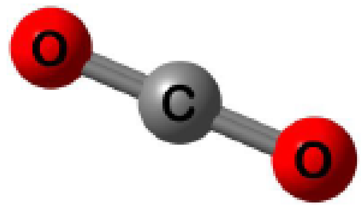
CO_2 as a C_1 building block



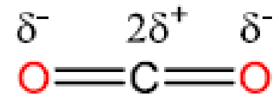
Carbon based products



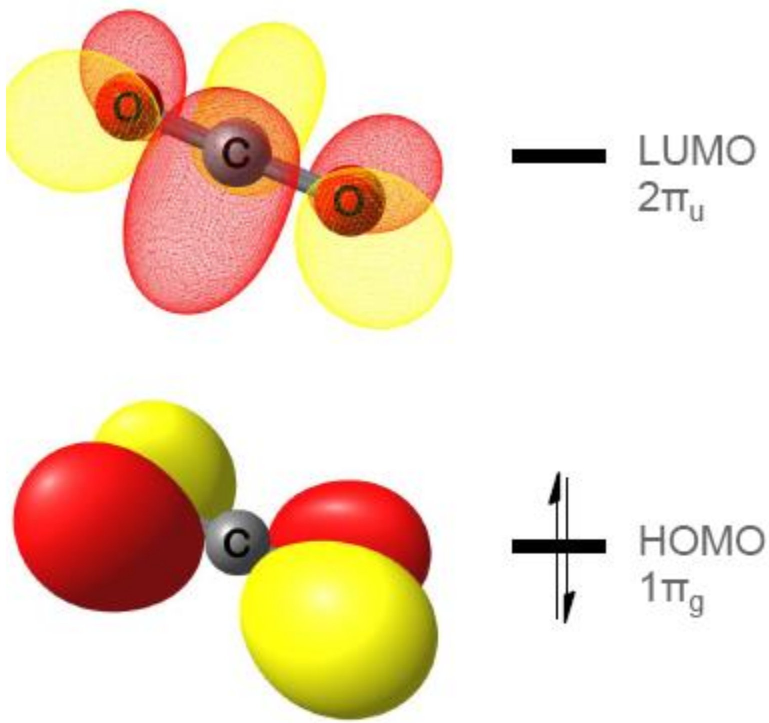
Carbon dioxide

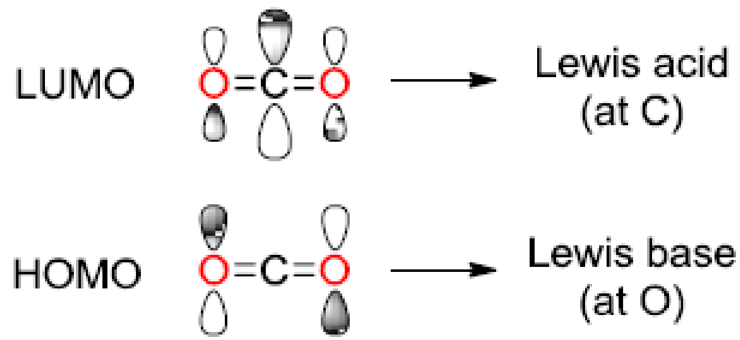


C-O: 1.16 Å



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





CO_2 Activation

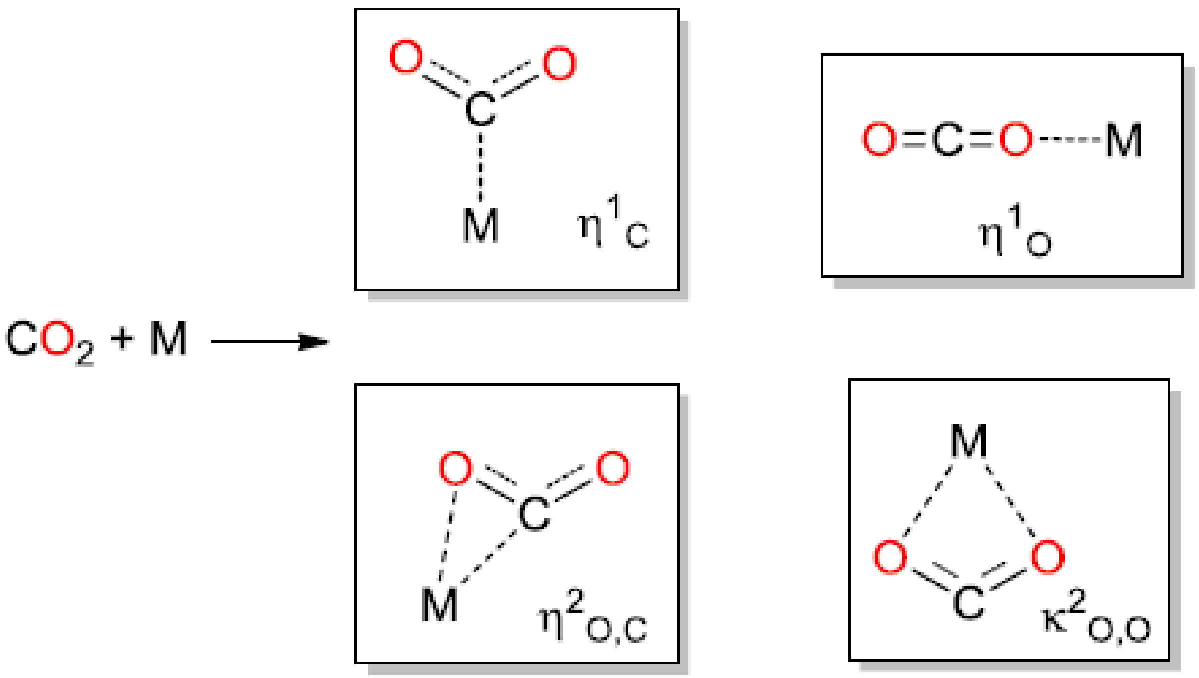
STRENGTHEN POINTS

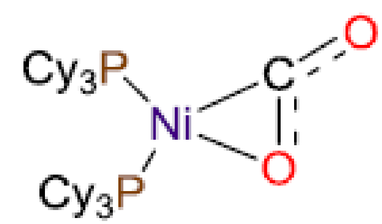
Cheap;
Nontoxic;
Widely available
(30 Gt/year (2014)).

WEAKNESS POINTS

High thermodynamic stability;
Low reactivity.

CO_2 coordination modes to transition metals

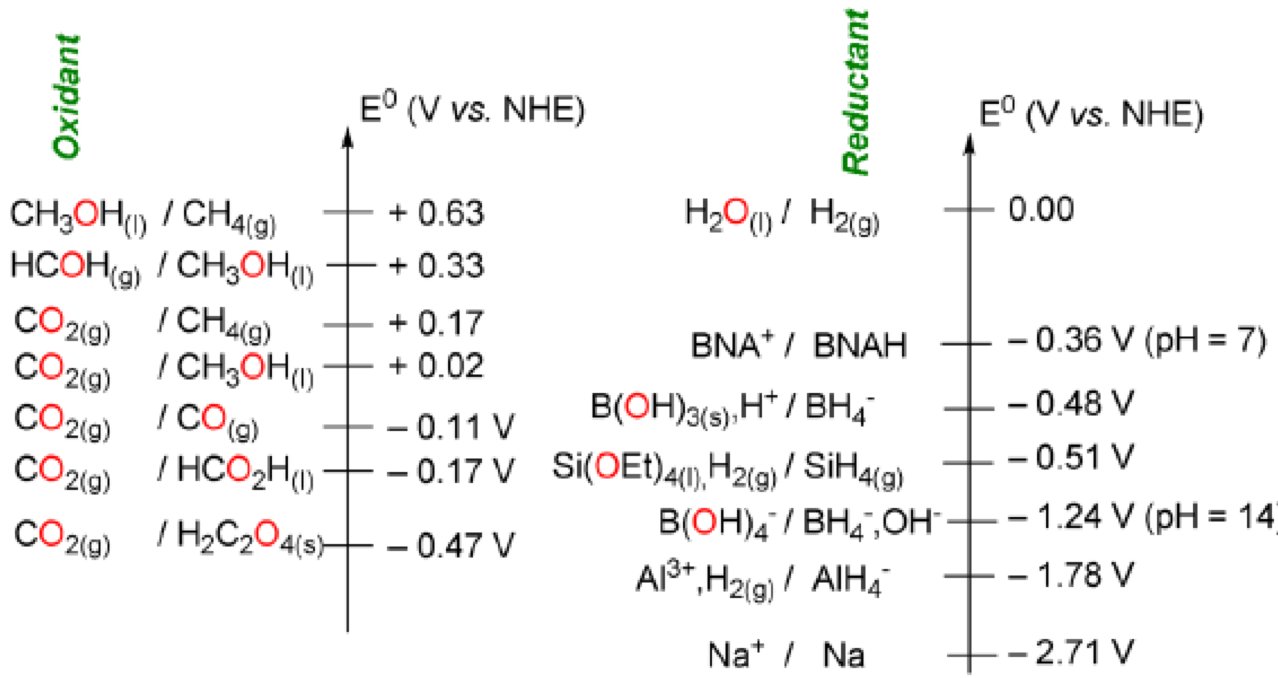




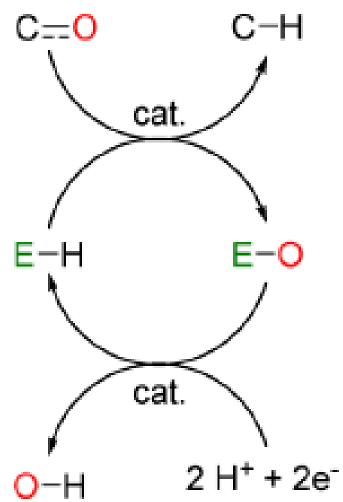
Aresta, 1975

Hydrogenation of CO_2

REDOX POTENTIALs



Involved reactions



Hydrogenation of CO_2 to

FORMIC ACID

It is endoergonic; it is entropically disfavored

ΔH^0 = -31.2 kJ/mol ΔG^0 = +32.9 kJ/mol T = 25 °C pH = 0

With the addition of a base, like NH_3

ΔH^0 = -84.3 kJ/mol ΔG^0 = -9.5 kJ/mol T = 25 °C

In polar solvents, like water

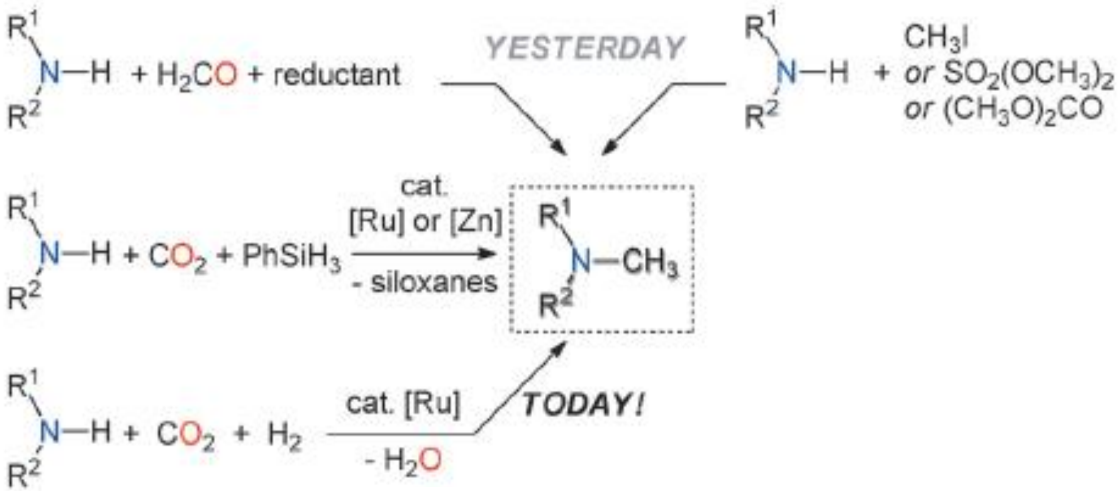
ΔG^0 = -4.0 kJ/mol T = 25 °C

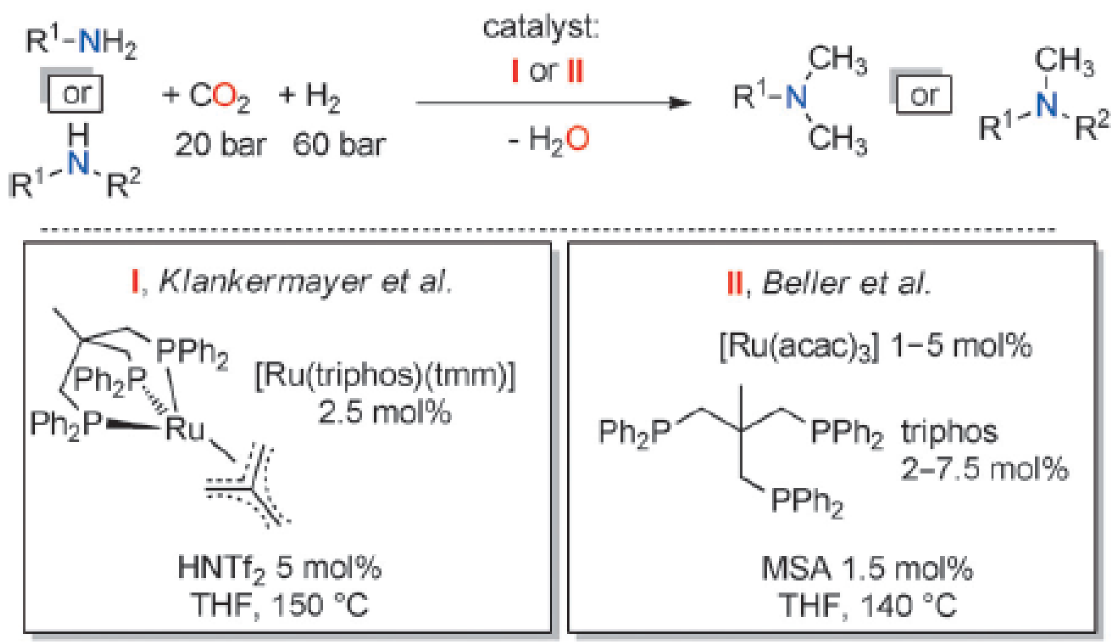
METHANOL

It is exoergonic; but kinetically difficult

ΔG^0 = -17.3 kJ/mol T = 25 °C pH = 0

Methylation of amines with CO_2 and H_2





20 examples up to 94% yield

33 examples up to 99% yield

Literature

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