Towards a Hydrogen Economy

New Chemistry for the Energy Transition

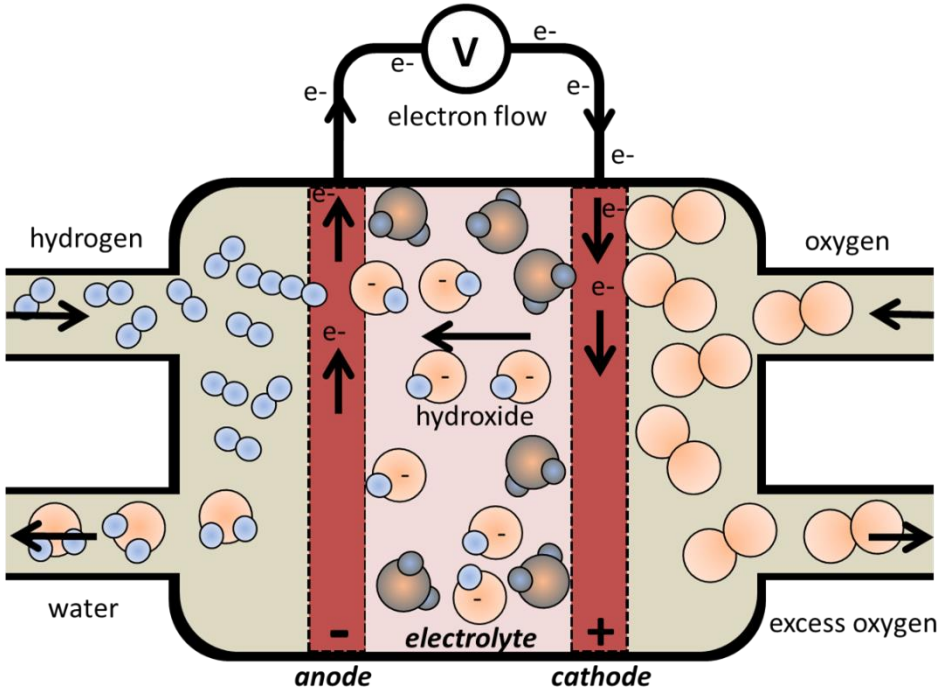
Prof. Bas de Bruin


WIND ENERGY
TRANSPORTATION
HYDROGEN
SOLAR ENERGY
H_2
HYDROGEN GAS STATION
HYDROGEN
1 H_2
HYDROGEN
HYDROGEN GENERATION
H_2
HYDROGEN ENGINE
+
-
HYDROGEN ATOM
HYDROGEN CAR

Hydrogen as a fuel

- Can be directly used in combustion engines (and for cooking)

- Fuel cells might be more efficient



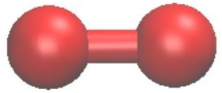
Sounds nice, but there are challenges:

- Fuel cells rely on expensive, non-abundant platinum
- Hydrogen production is not (yet) so energy efficient
- Hydrogen storage is particularly challenging
  - Very light, easily escapes
  - High pressure needed to make H_2 liquid (expensive)
  - Saftety issues

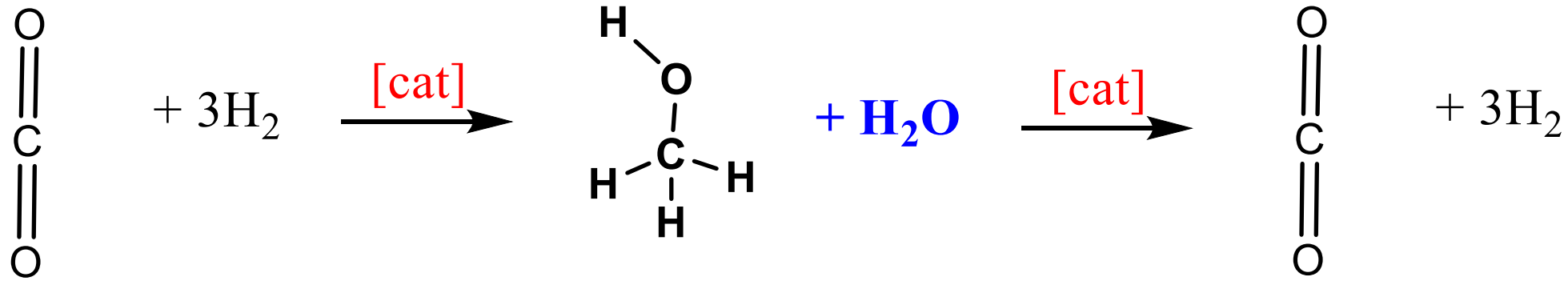
Not a solved problem! Ongoing research!

Hydrogen: Reversible Chemical Storage

- Potential future fuel for electricity production
- Difficult to produce, store and transport in a sustainable manner

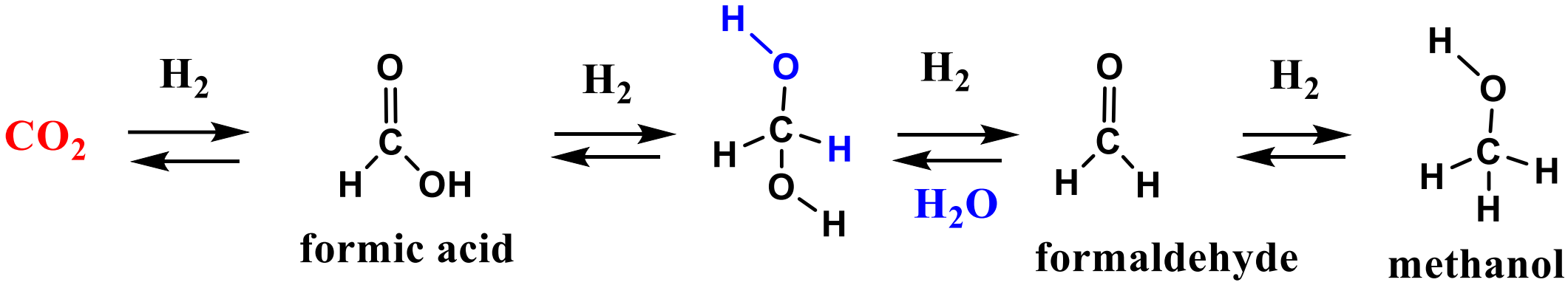


Reversible Chemical Storage of Hydrogen



In chemical steps:

Homogeneous catalysis is the solution?



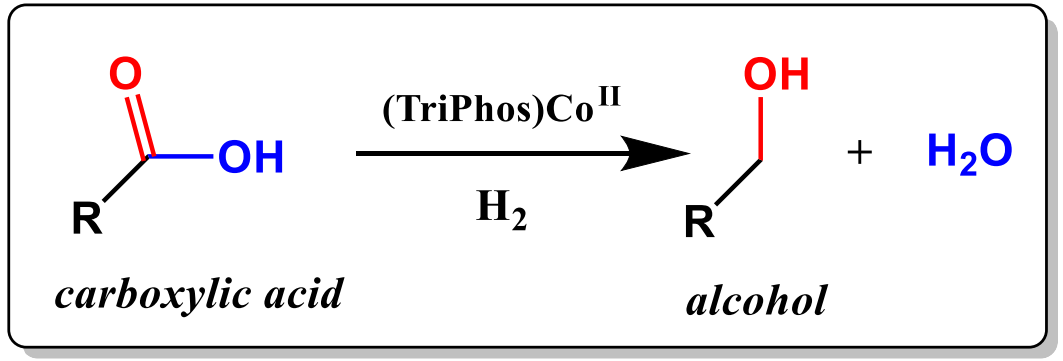
Challenges:

- Most known systems based on expensive, non-abundant metals (mostly ruthenium)
- Most known systems show low TONs (sensitive catalyts)
- Most known systems require high temperatures (thus driving the equilibria to the wrong side)
- Almost no examples of good catalysts with cheap, abundant, non-toxic metals

Not a solved problem! Ongoing research!

Carboxylic acid hydrogenation with Co^{II} catalysis



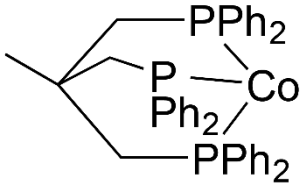




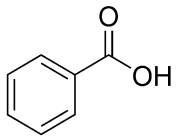
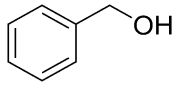
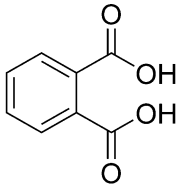
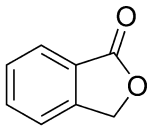
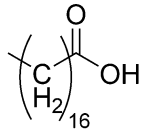
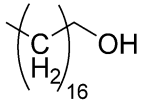
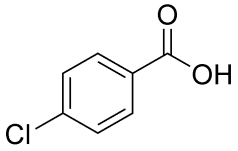
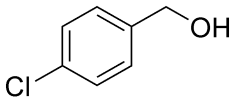
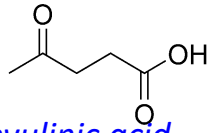
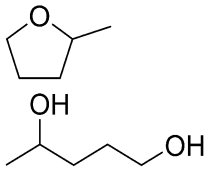
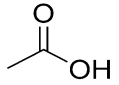
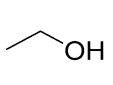
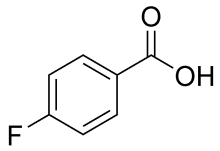
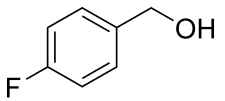
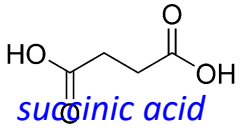
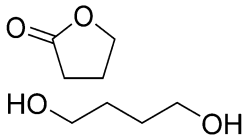
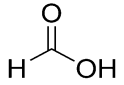
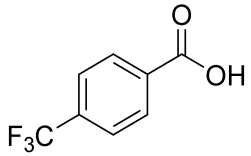
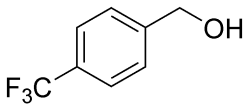
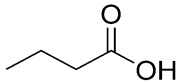
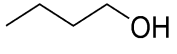
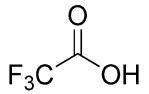
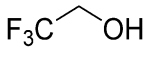
Broad substrate scope

Good yields

Relatively mild reaction conditions



Science, **2015**, *350 (6258), 298-302.*

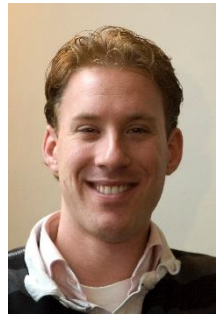
Substrate	Product	Substrate	Product(s)	Substrate	Product
					
5% (4h) 2.5%	>85 (65) >85 (62 / 39)	2.5%	>99 (71)	5%	95 (92)
		 *levulinic acid*			
5%	>99 (82 / 70)	10%	>99 (14 47)	0.25%*	94 (81)
				0.1%*	78 (48‡)
		 *succinic acid*			
5%	>99 (96 / 84)	2.5%	>85 (23 61)	0.5%	>99 (76)
				0.25%	56 (22§)
					
5%	98 (98 / 82)	5%	>99 (95)	125 ppm	97 (50‖)
		0.1%*	53 (17 / 5†)		

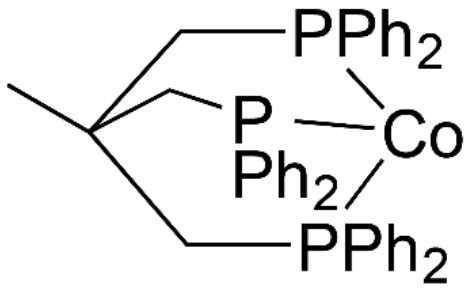
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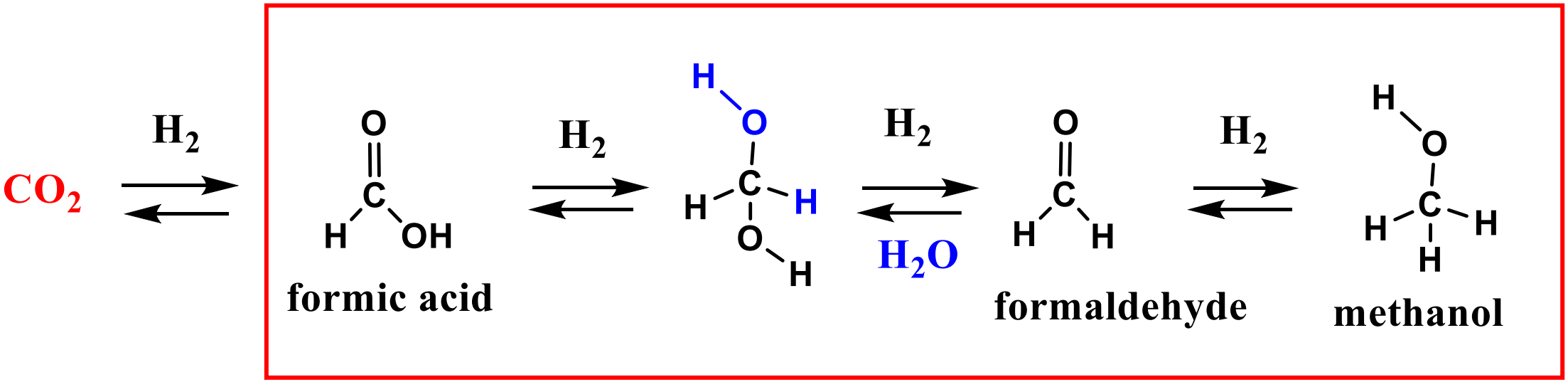
THF
(* in neat acid)

100 °C,
80 bar H_2

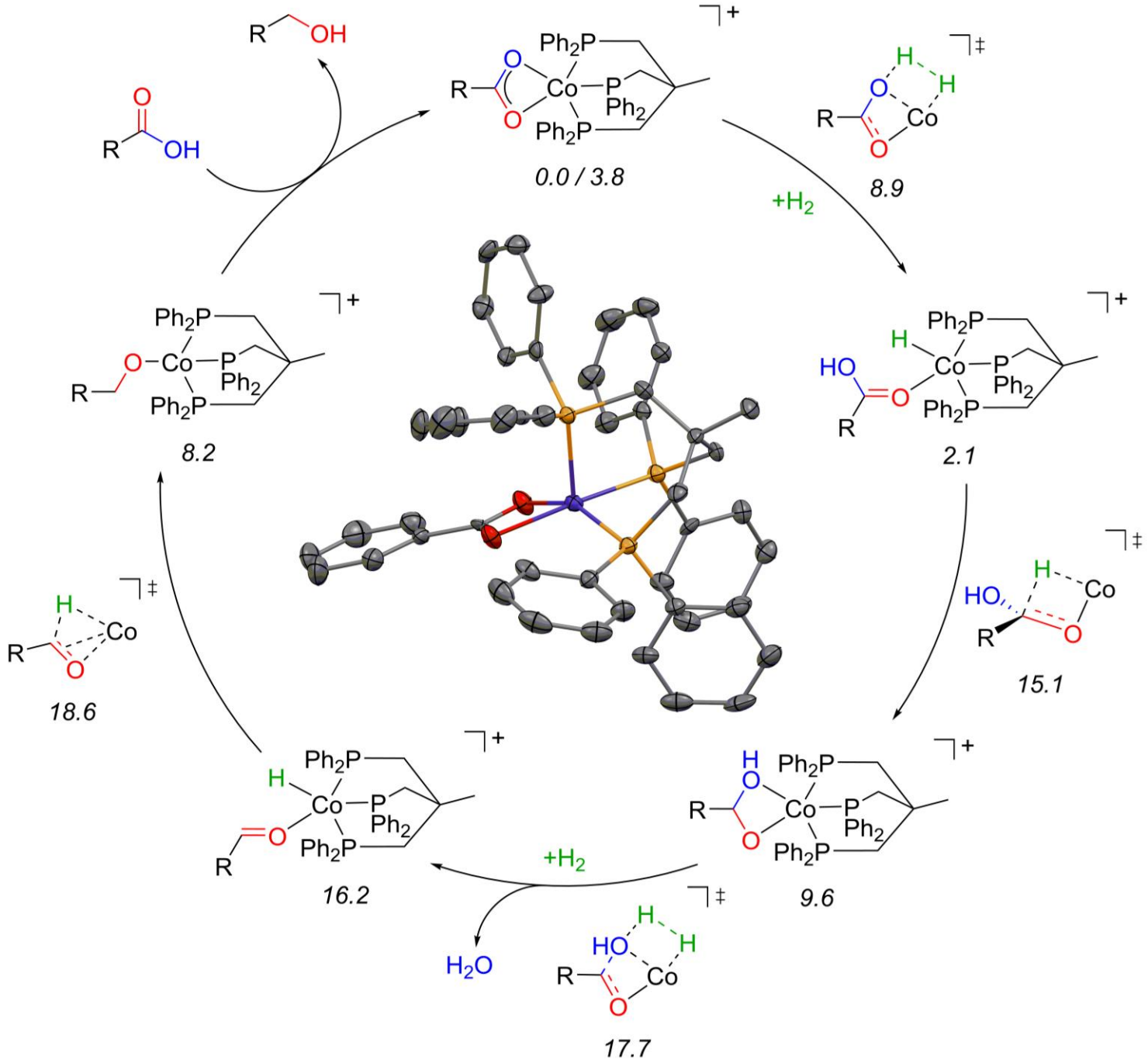
cat. loading in %
conversion (yield)







Science, **2015**, *350 (6258), 298-302.*

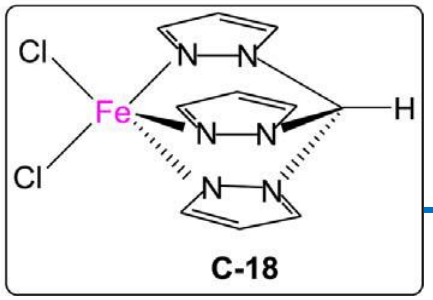


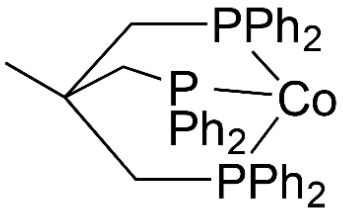
mechanism

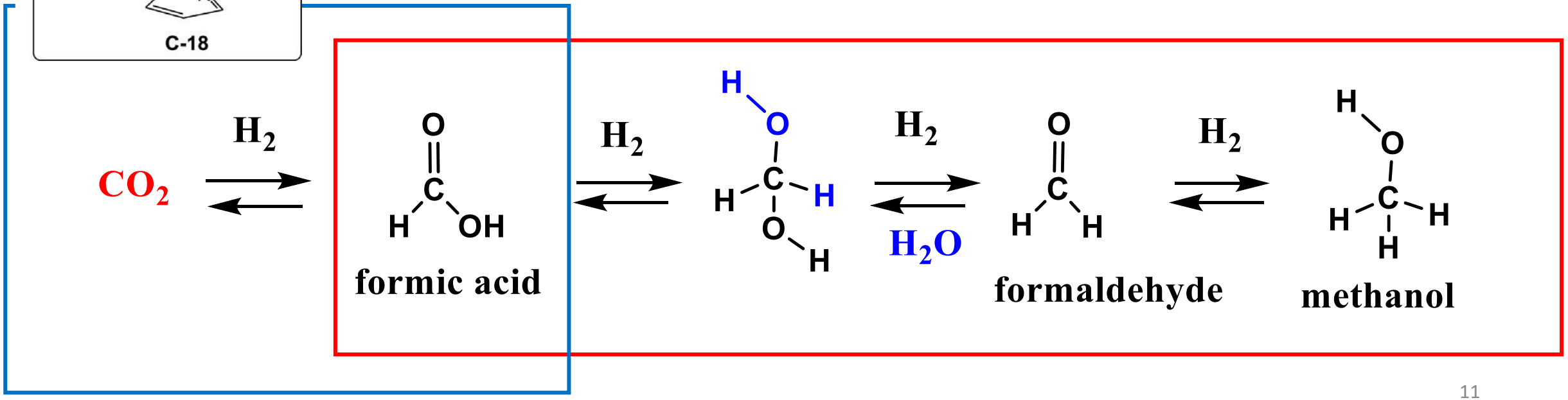
Science, **2015**, *350 (6258), 298.*

Next challenges:

Combine the cobalt catalyst with other catalysts:







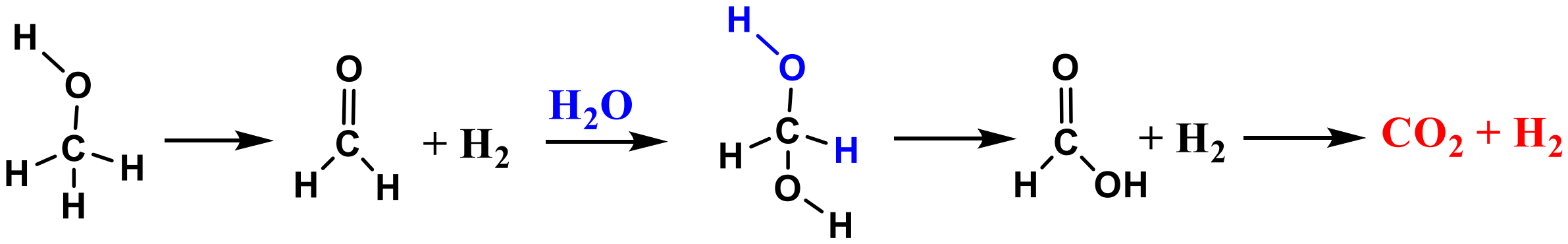
Remaining Challenges in CO_2 hydrogenation:

- Metals need to be cheap & abundant
- TOFs (speed) and TONs (durability) need to be high
- Catalysts should not interfere with each other

- Pressure and temperature should be as low as possible
  (optimum might be different for both catalysts)

Not a solved problem! Ongoing research!

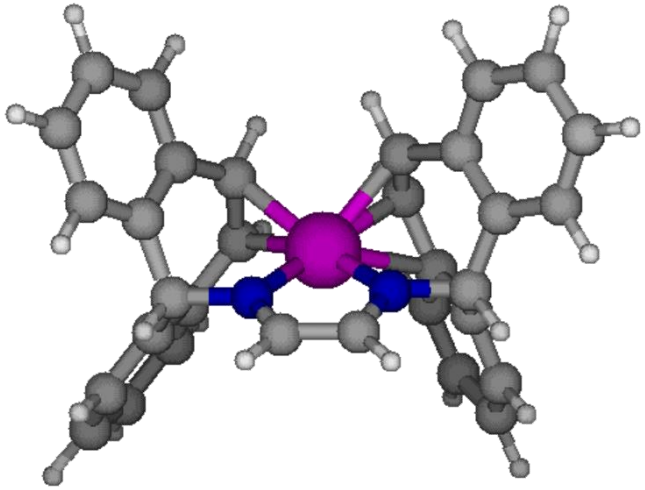
The reverse process:



Why?:

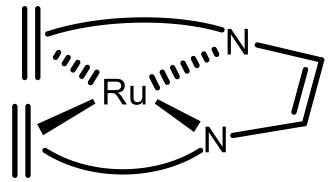
- Methanol, being a liquid, seems ideal for storage and transport of hydrogen
- Release of 3 molecules H_2 from 1 molecule of methanol
- Fuel cell applications

Two well-known catalysts for MeOH dehydrogenation

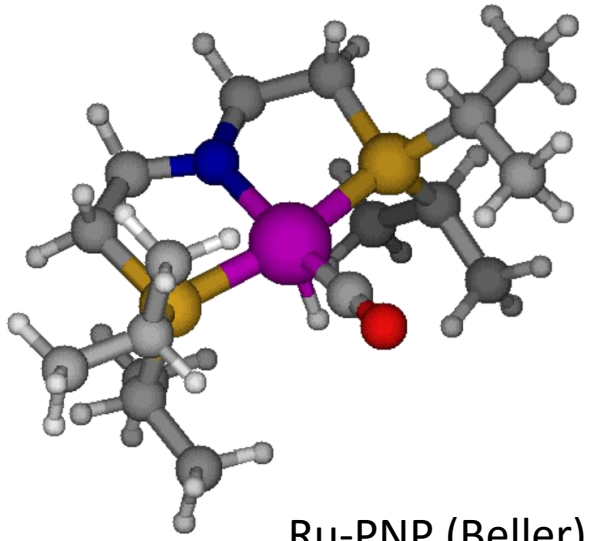


Ru(trop)$_2$dad (Grützmacher)

- **Additive free**
- Methanol:water ~ 1:1
- 90° C
- TOF ~ 50 h^{-1}

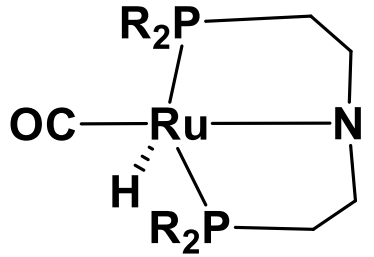


Nature Chemistry **5**, 342–347 (2013)



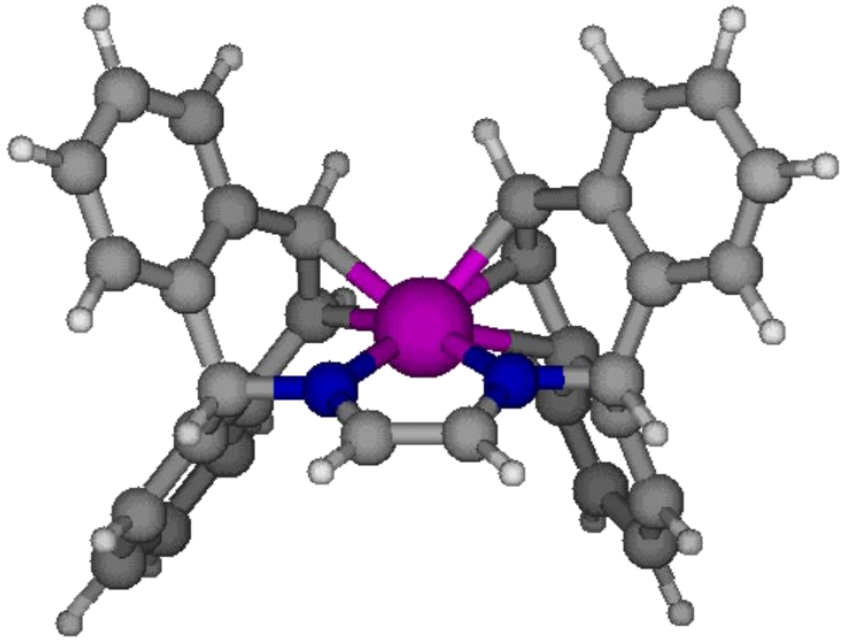
Ru-PNP (Beller)

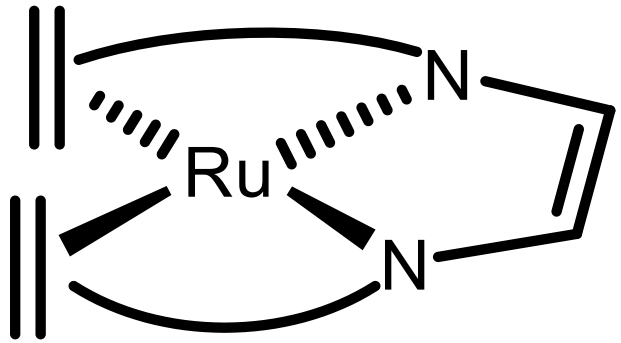
- **8 M KOH**
- Methanol:water = 9:1
- 90° C
- TOF ~ 4700 h^{-1}



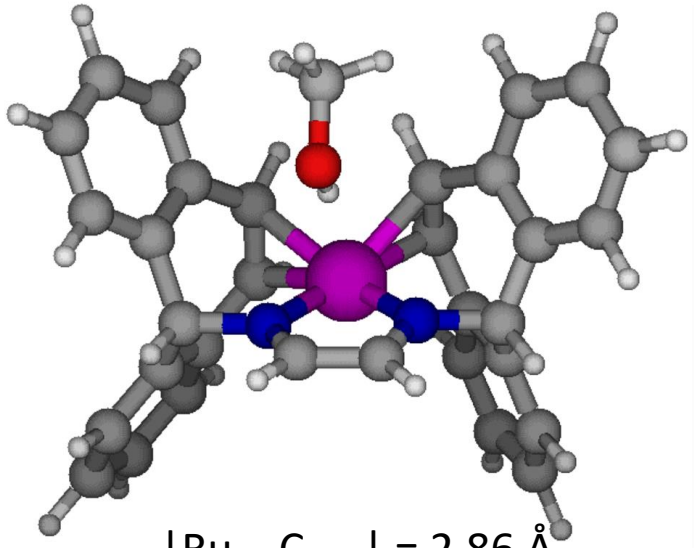
Nature **495**, 85– 89 (2013)

$Ru(trop)_2dad$

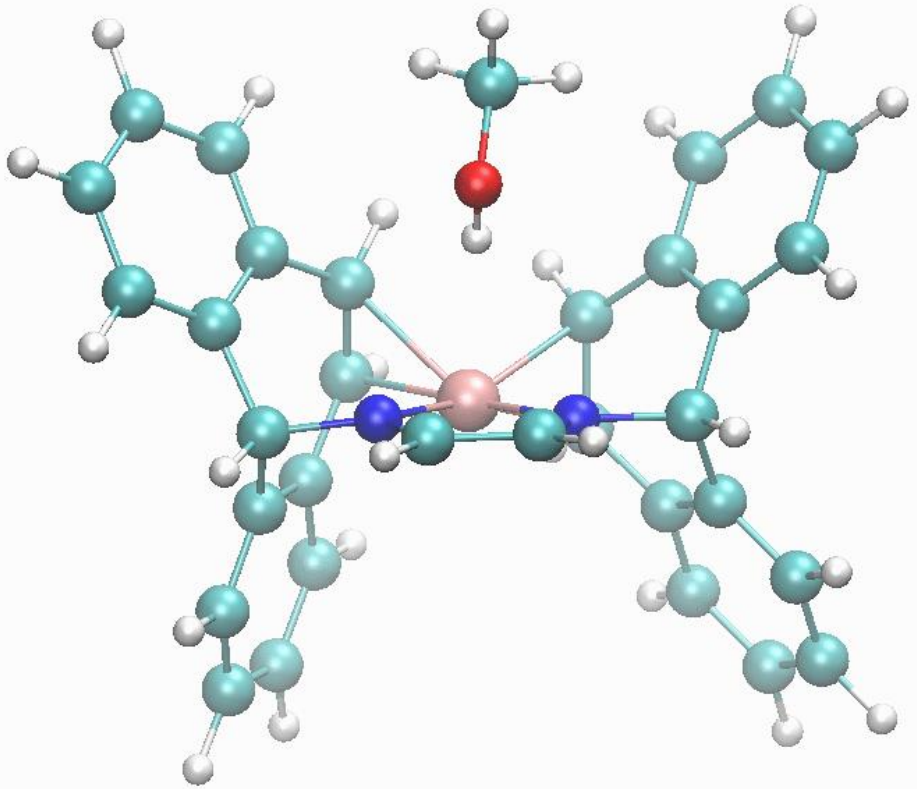


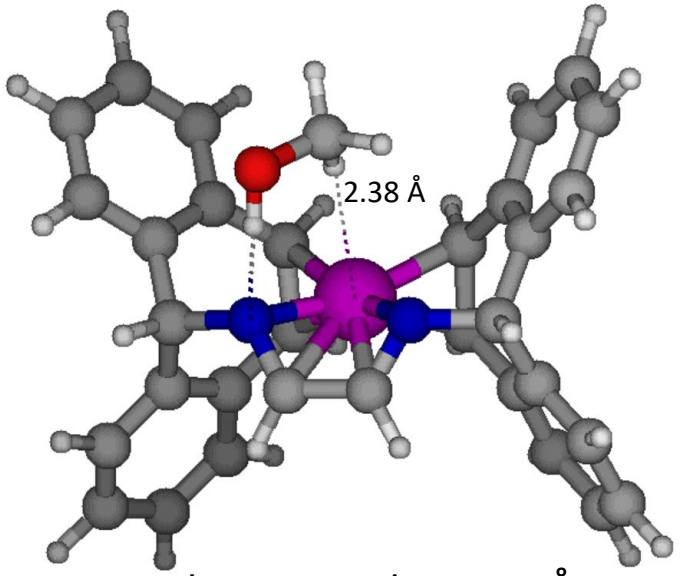


π – Coordination

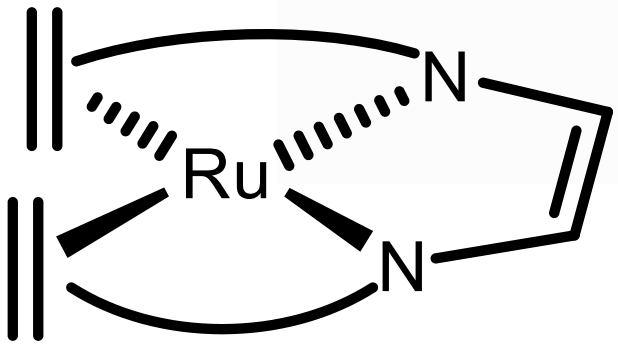


$|Ru - C_{DAD}| = 2.86$ Å



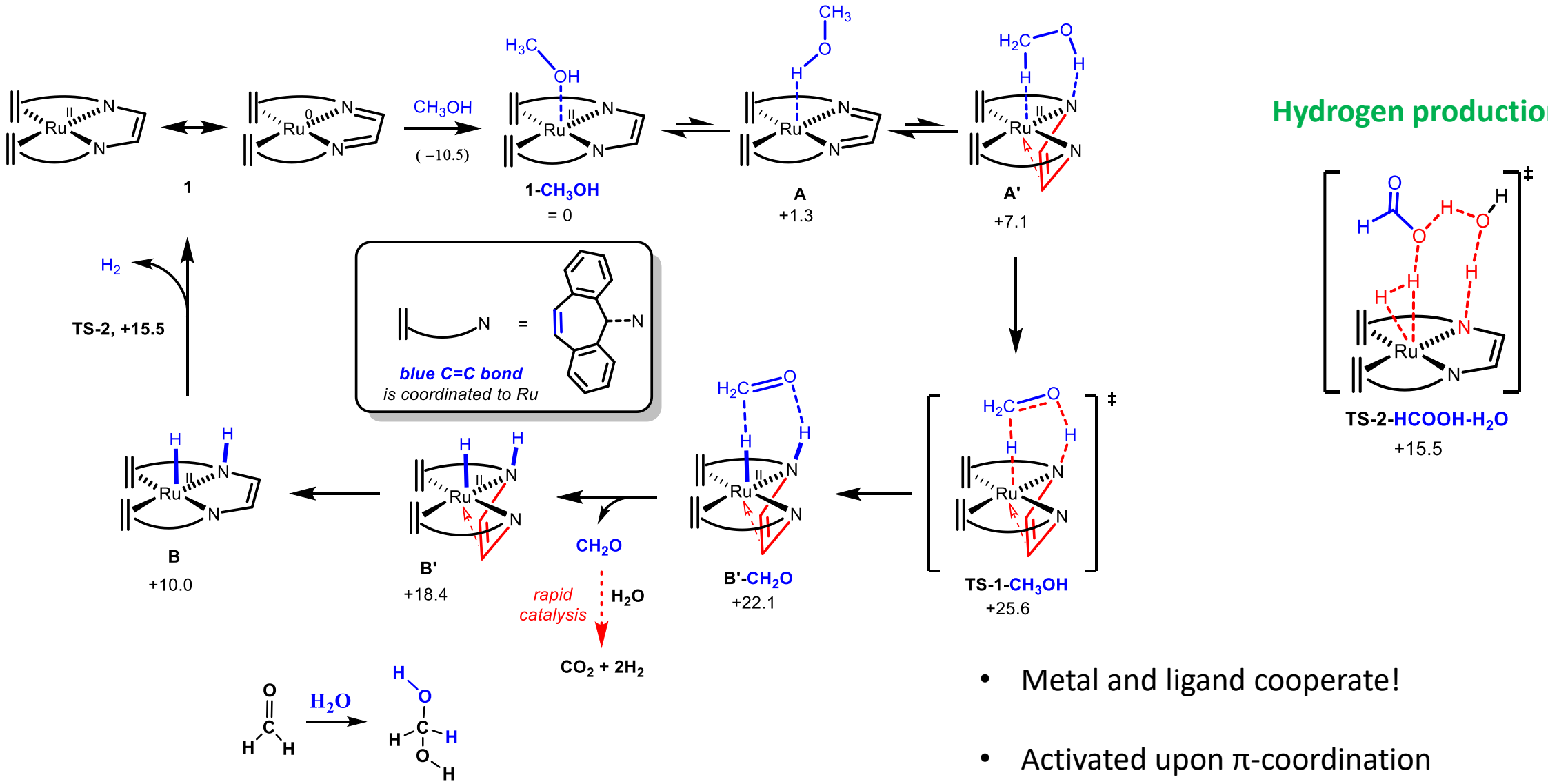


$|Ru - C_{DAD}| = 2.31$ Å



- **π** coordination
  - increases the basicity of N_{DAD}.
  - Substrate pre-organization.

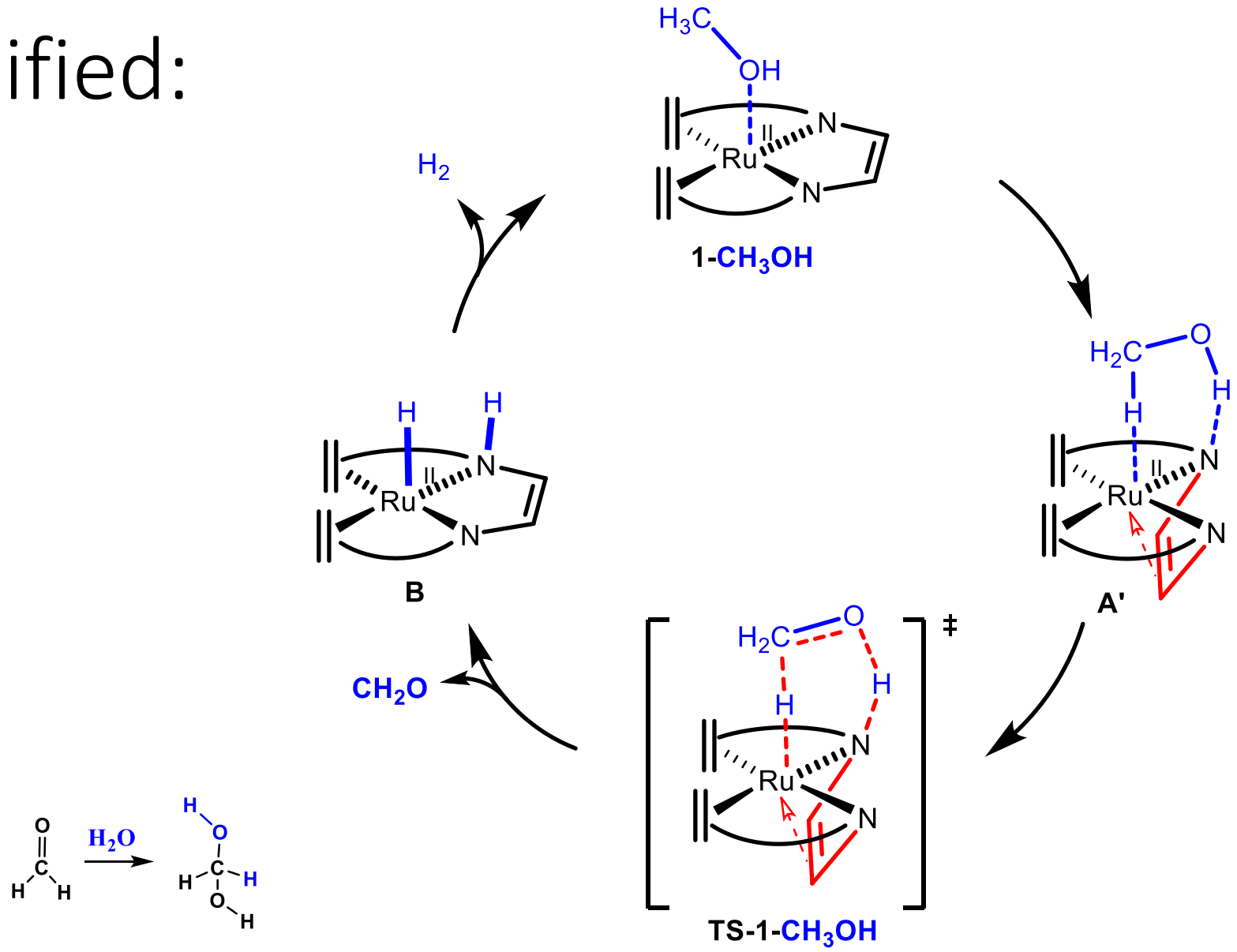
Catalytic Cycle (MeOH to formaldehyde)



Hydrogen production

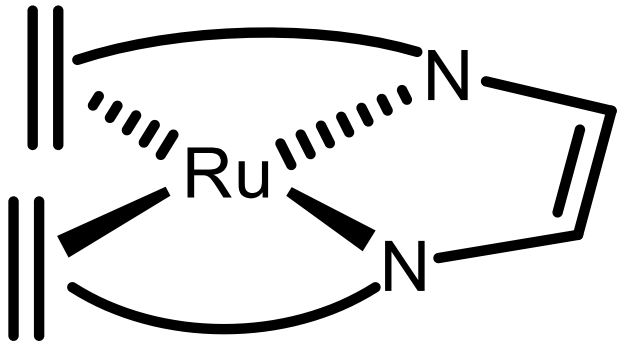
- Metal and ligand cooperate!
- Activated upon π-coordination

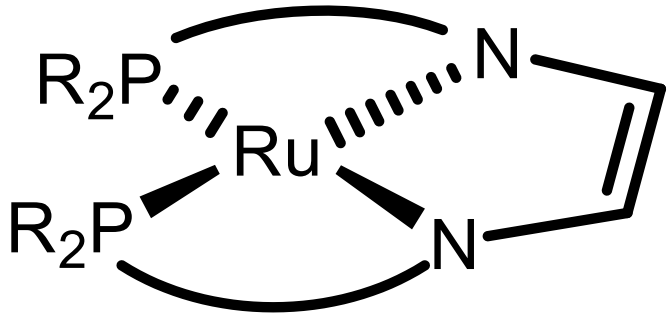
Simplified:



Remaining Challenges in MeOH dehydrogenation:

- TOF (speed) needs to be increased!



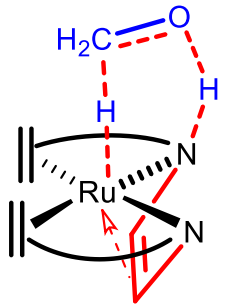


- Ruthenium is too expensive and not abundant

Not a solved problem! Ongoing research!

Conclusions

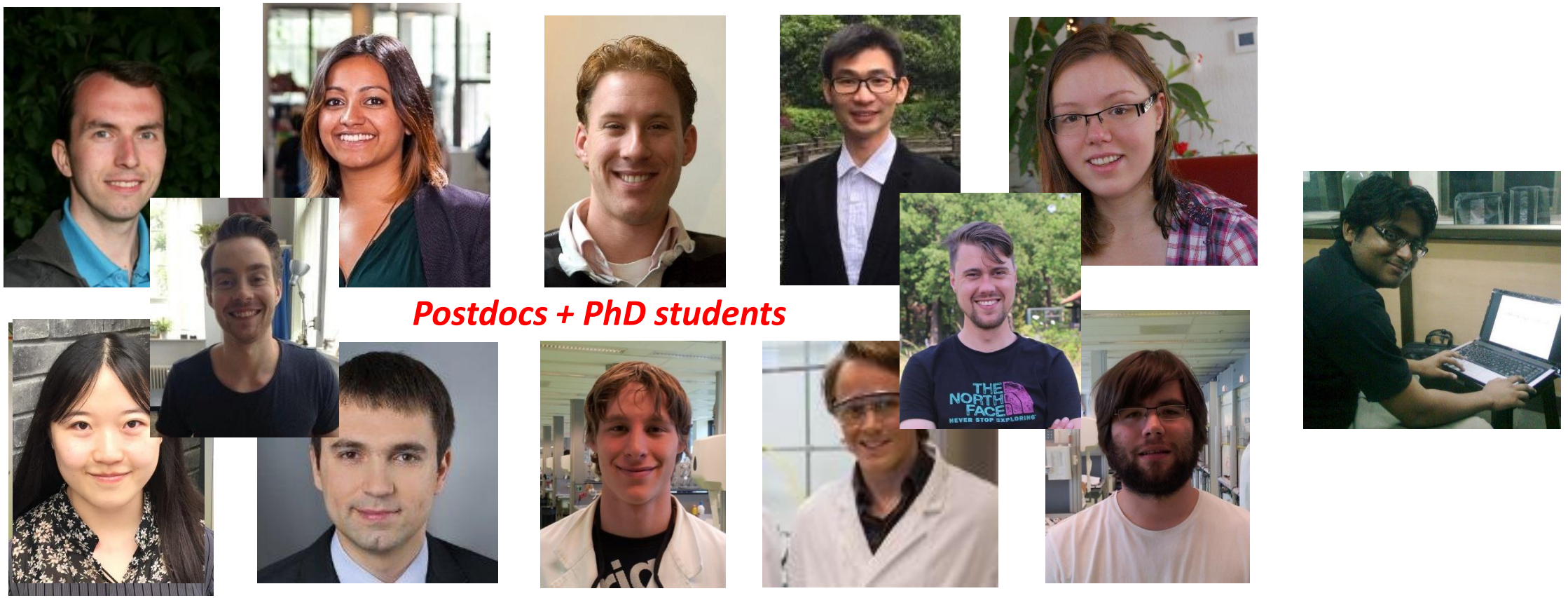
- Good prospects to develop truly efficient CO_2 hydrogenation and methanol dehydrogenation using homogeneneous catalysis



- Metal-ligand coorperativity is important
- Metal price and abundancy is of key importance; we need to replace systems based on of platinum, ruthenium etc. by Fe, Co, etc.
- Operation temperatures and pressures of known systems currently too high; efficiencies and catalyst stabilities too low

Not a solved problem! Ongoing research!

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