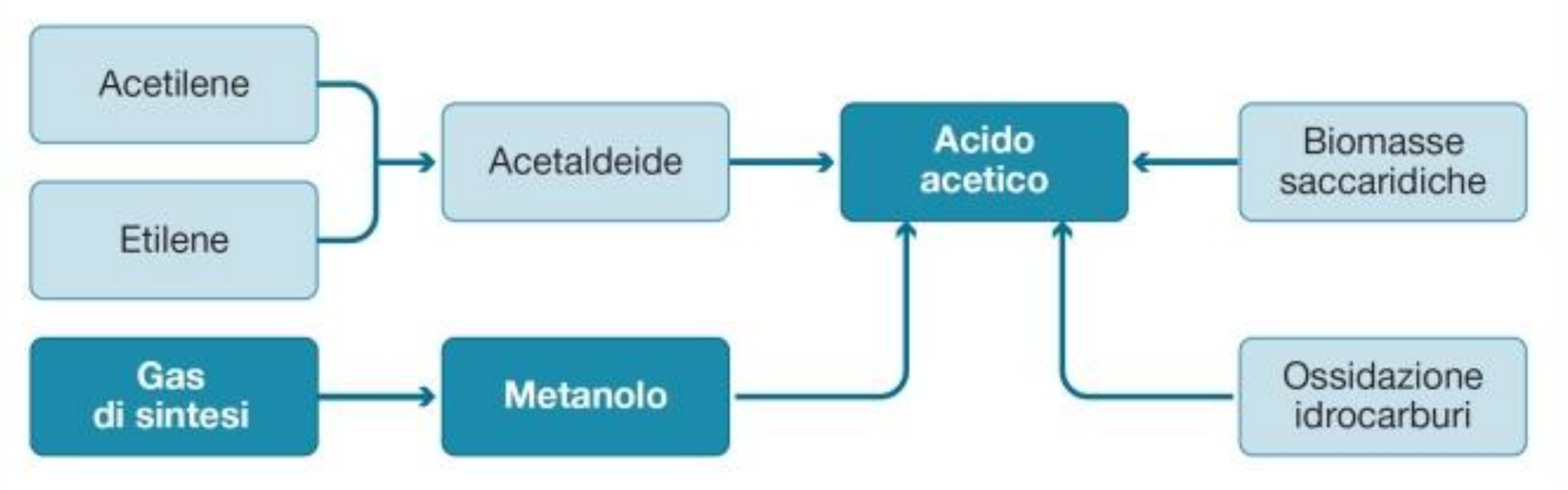
# *Synthesis of acetic acid*

## Industrial technologies for the synthesis

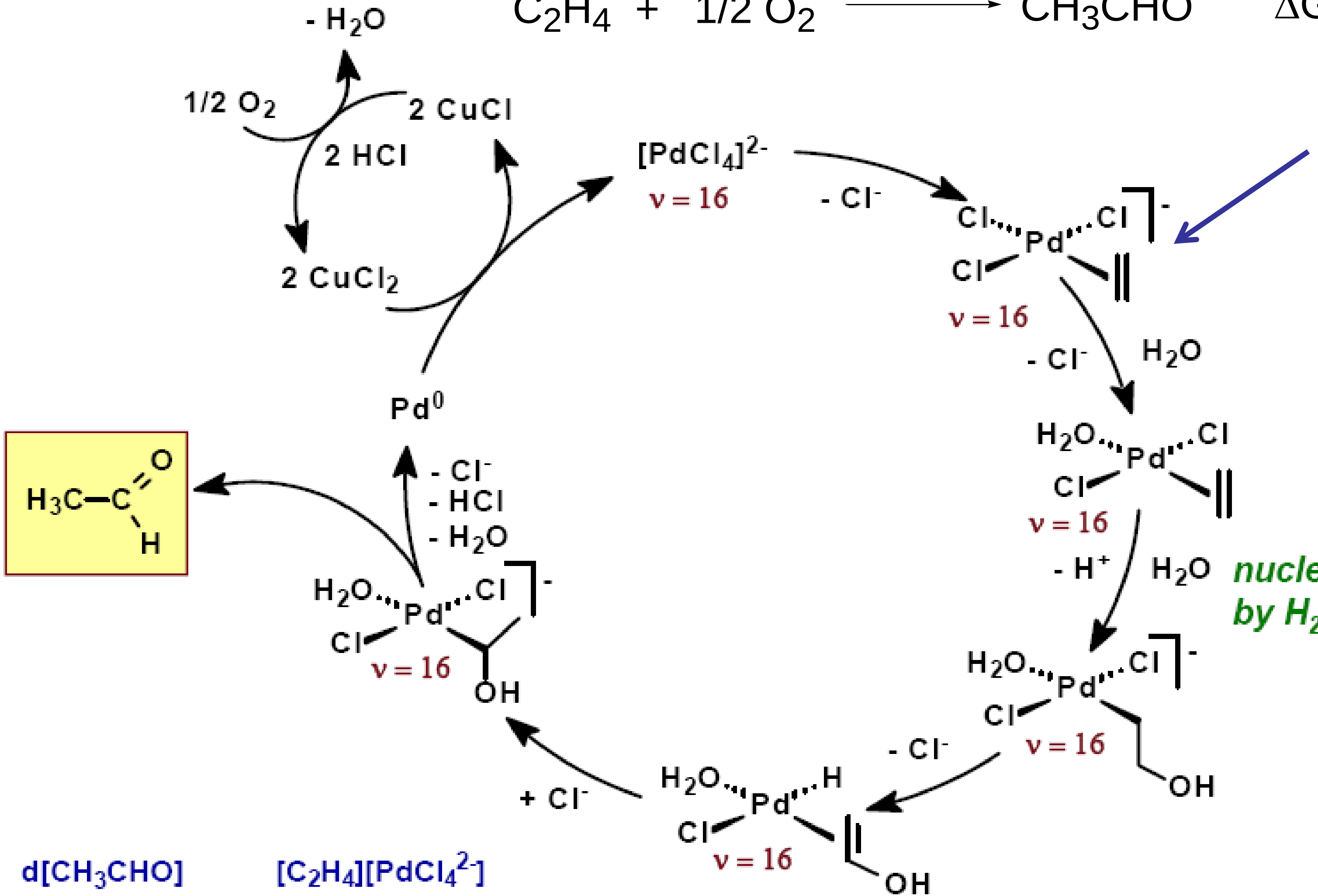


**In 2023 the production of acetic acid was of 18 million of metric tons.**

# Synthesis of acetic acid

## The Wacker process

$$C_2H_4 + 1/2\ O_2 \xrightarrow{cat} CH_3CHO \qquad \Delta G = -197\ \text{kJ mol}^{-1}$$



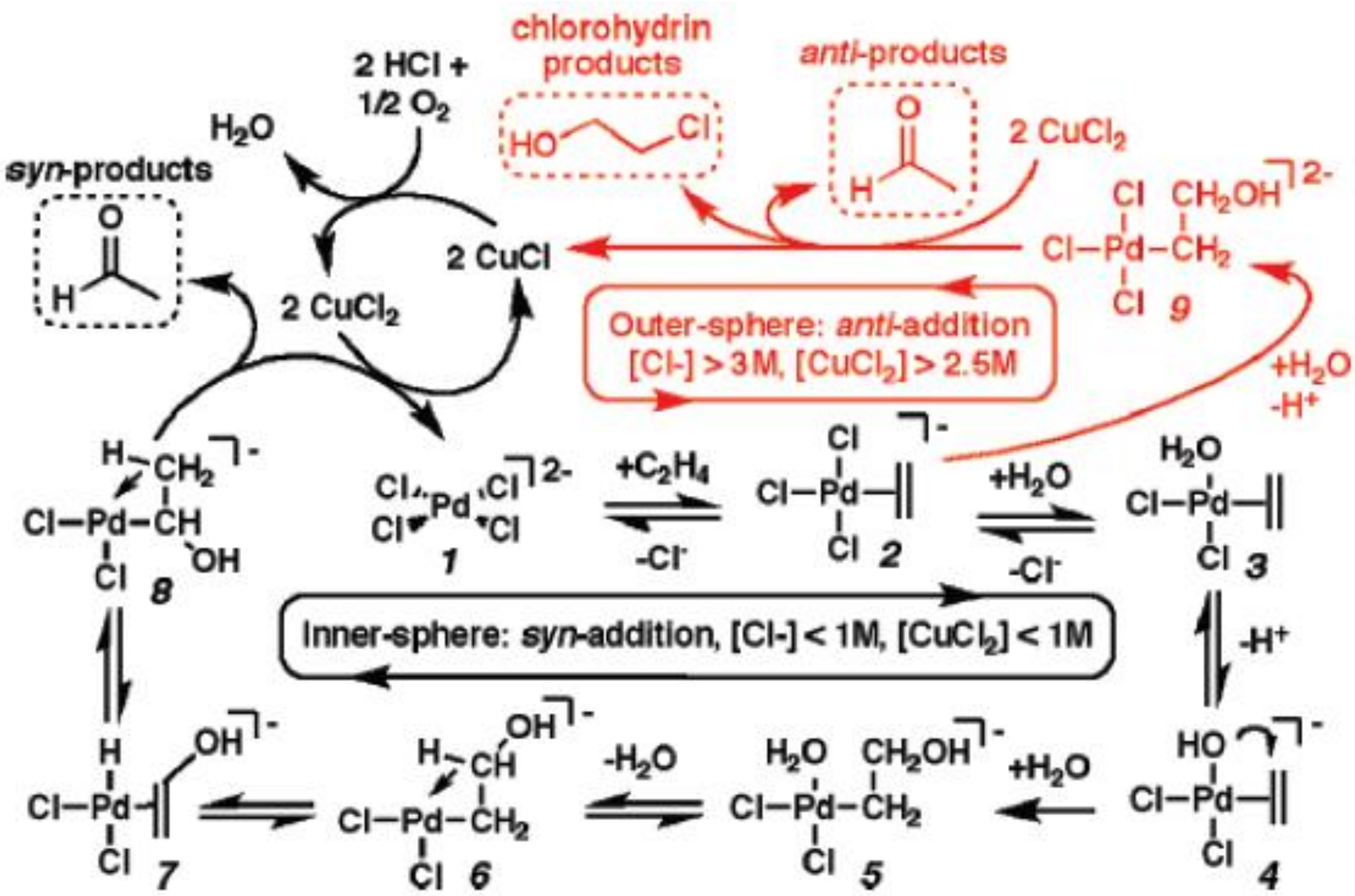
analogous of Zeise salt

*nucleophilic attack by $H_2O$*

◀

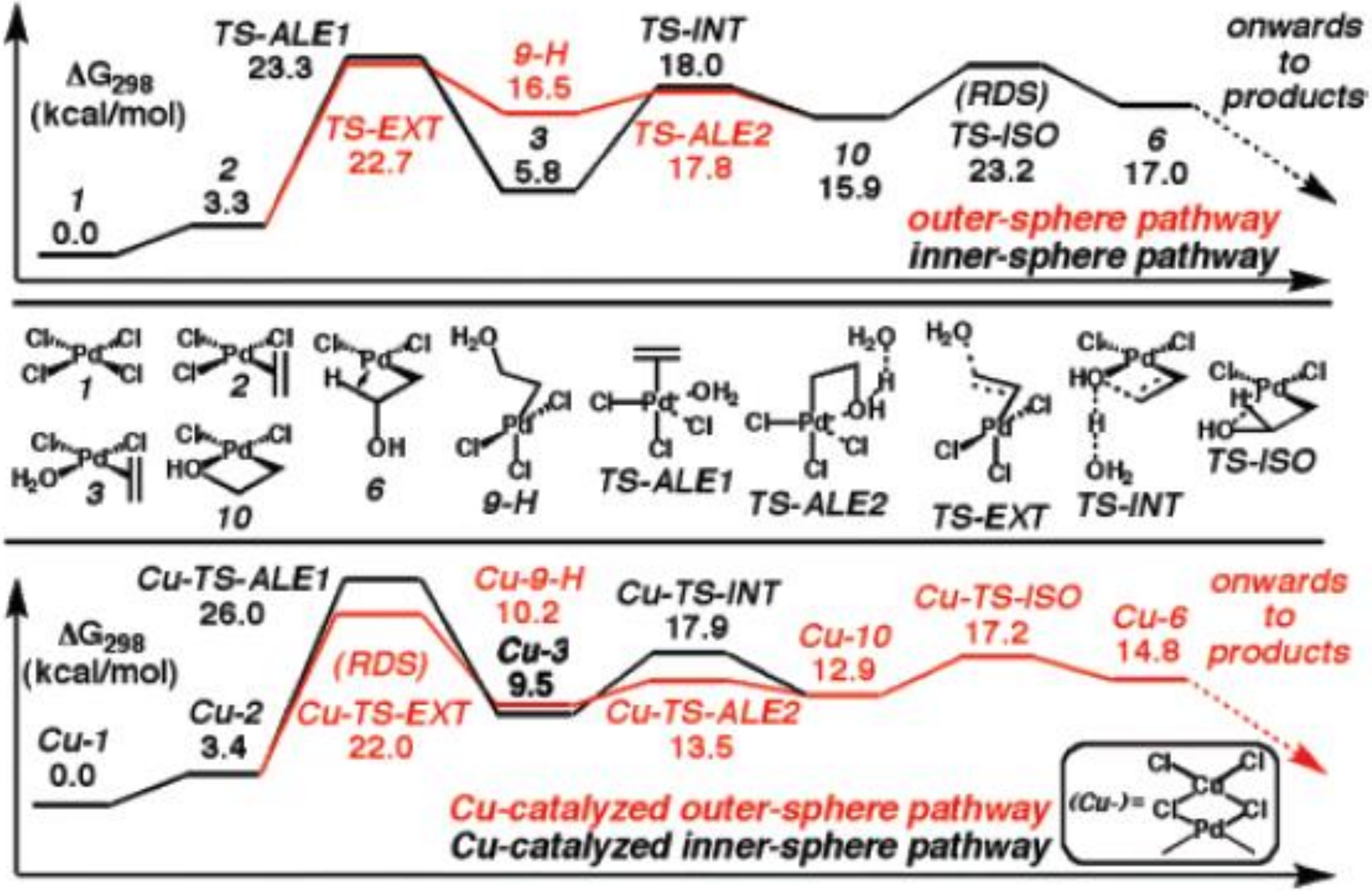
$$\frac{d[CH_3CHO]}{dt} = k\,\frac{[C_2H_4][PdCl_4^{2-}]}{[H^+][Cl^-]^2}$$

# *The recently reported mechanism*

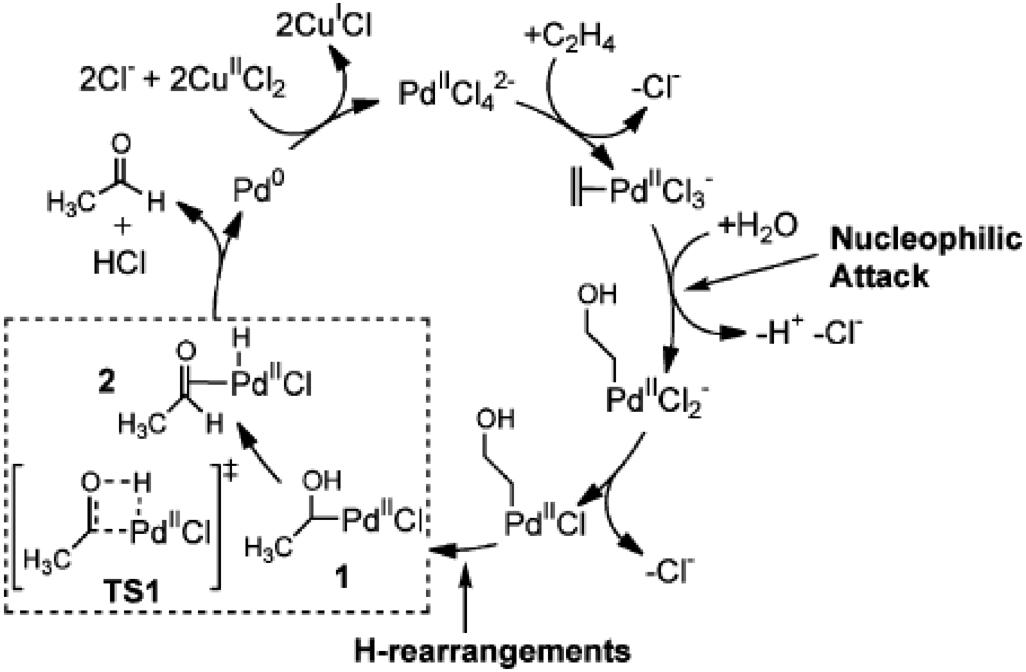


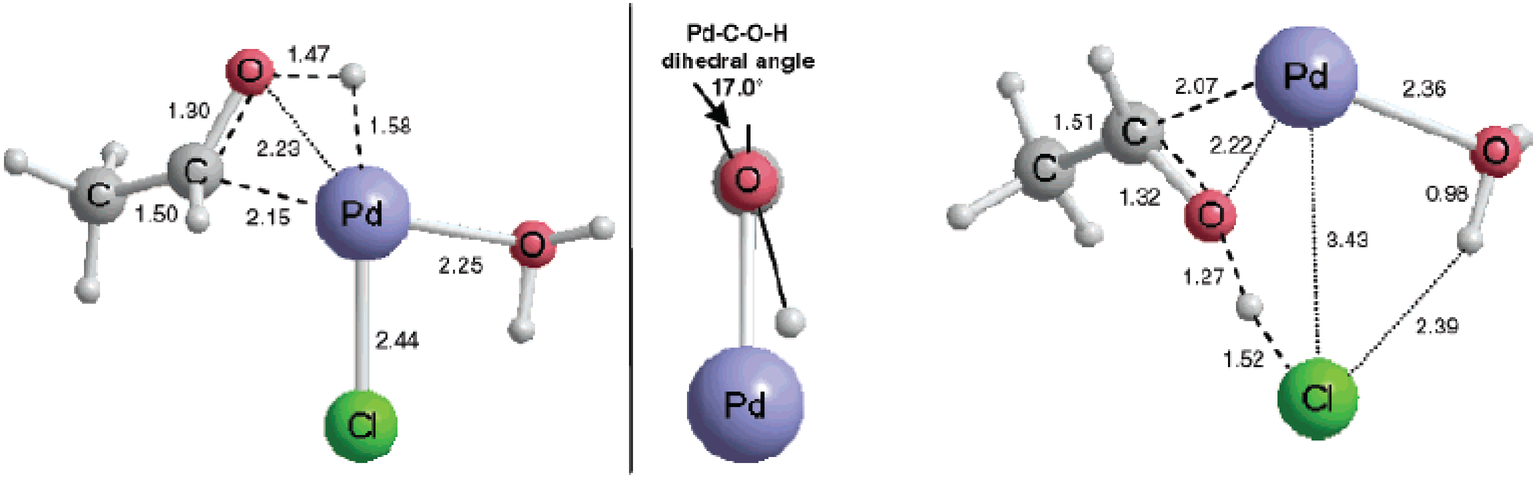
J. Oxgaard, W. A. Goddard, III et al *J. Am. Chem. Soc.* 2007, *1291*, 12342.

# The recently reported mechanism



# The recently reported mechanism





# Oxidation of Pd(0) to Pd(II) by the Cu(II) salt

$$\mathrm{Pd(0)} + 2\,[\mathrm{CuCl_4}]^{2-} \longrightarrow \mathrm{Pd}^{2+} + 2\,[\mathrm{CuCl_2}]^{-} + 4\,\mathrm{Cl}^{-}$$

$$2\,[\mathrm{CuCl_2}]^{-} + 1/2\,\mathrm{O_2} + 2\,\mathrm{H}^{+} + 4\,\mathrm{Cl}^{-} \longrightarrow 2\,[\mathrm{CuCl_4}]^{2-} + \mathrm{H_2O}$$

## One stage process

**Conversion limited to 40 % → Gas recycle necessary**

**High purity gases are needed: pure $O_2$; 99.9 % ethene**

**Ti-equipment needed (highly corrosive HCl in oxidative medium)**

**Low pressure**

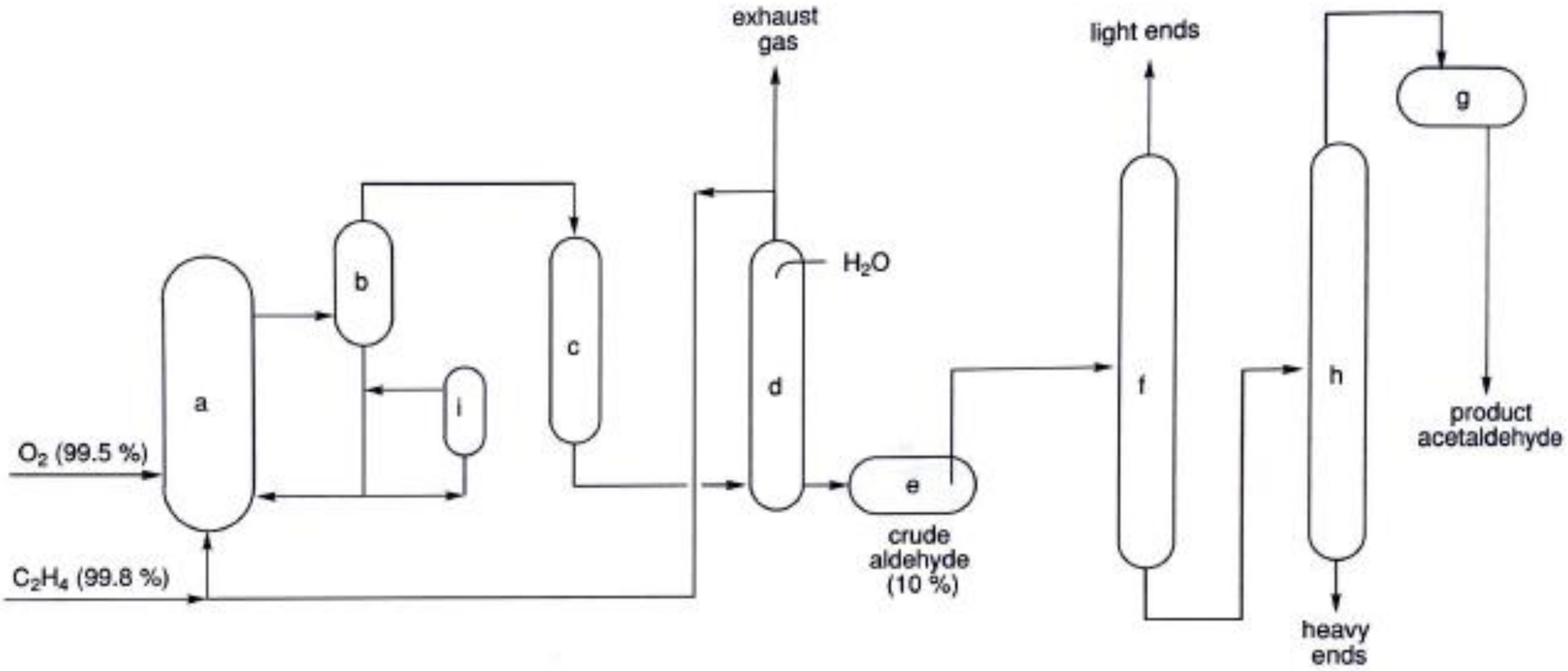
## Two stage process

**Total Conversion of ethene → No gas recycle**

**Raw Gas**

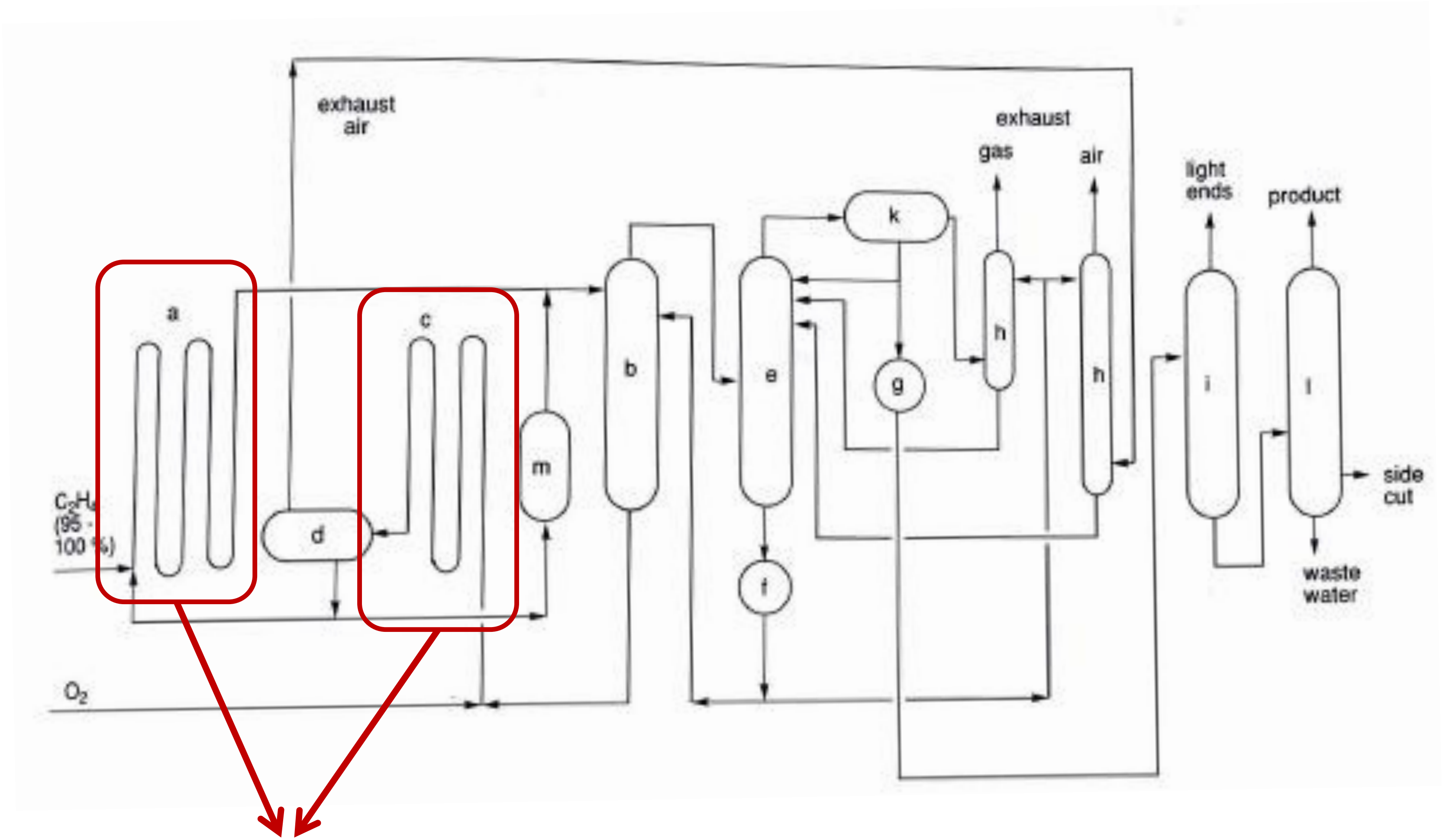
**Higher pressure + two reactors → Higher investiments**

# *Flow scheme of the Wacker process at one stage*



Reaction Conditions:
T = 100 - 130 °C; $P_{CO}$ = 4 - 10 bar.

# *Flow scheme of the Wacker process at two stages*



**reactors**

Reaction Conditions:
T = 100 - 130 °C; $P_{CO}$ = 10 bar.

# *The Monsanto process*

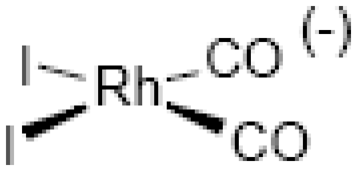
It is based on the carbonylation reaction of methanol

$$CH_3OH + CO \rightarrow CH_3COOH$$

*$\Delta G$, standard conditions, -75 kJ.mol$^{-1}$*

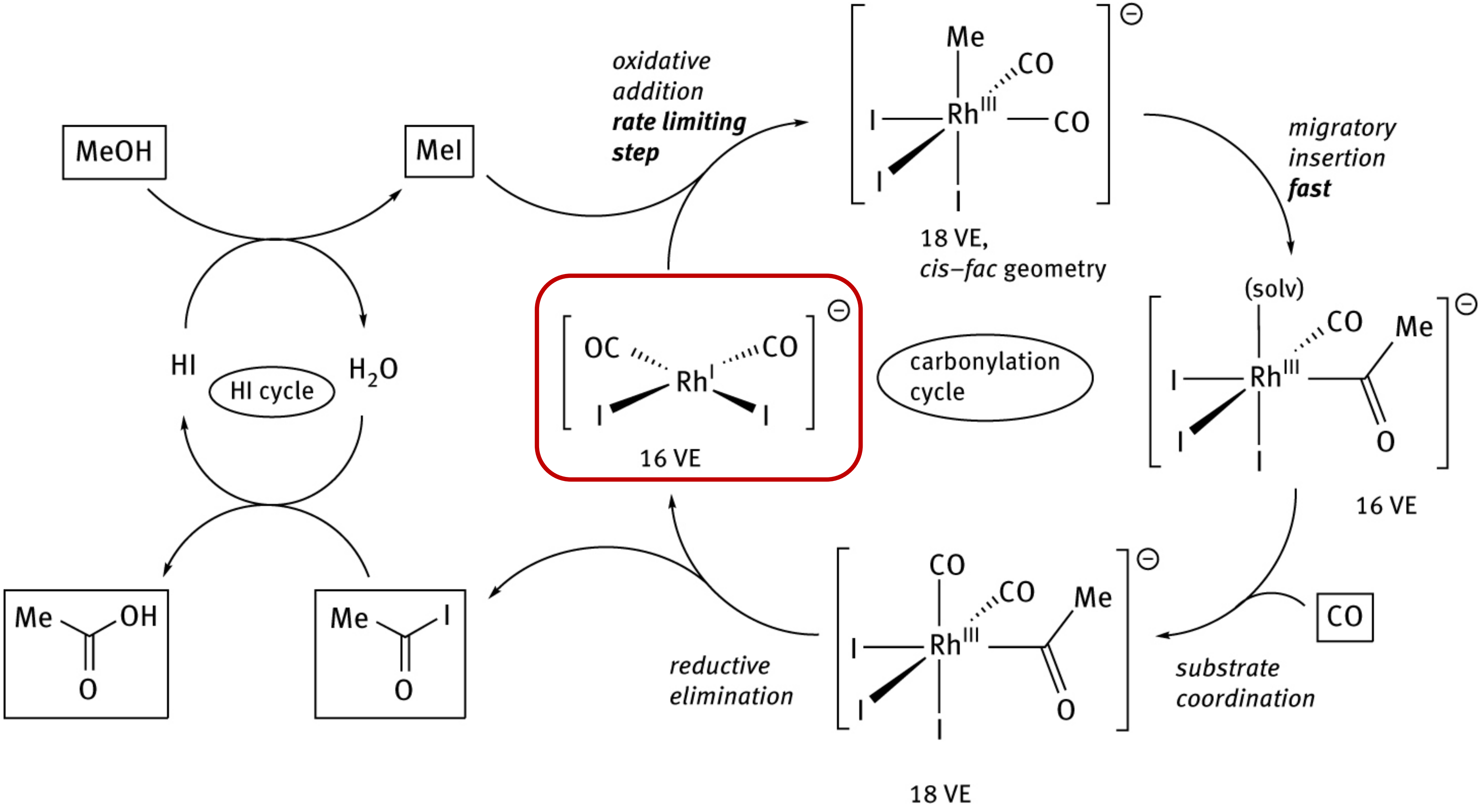
**ATOM EFFICIENCY = 100 %** **E FACTOR = 0**

in situ catalytic system:
$RhI_3$, CO e $H_2O$



$$CH_3OH + HI \rightleftarrows CH_3I + H_2O \qquad (1)$$

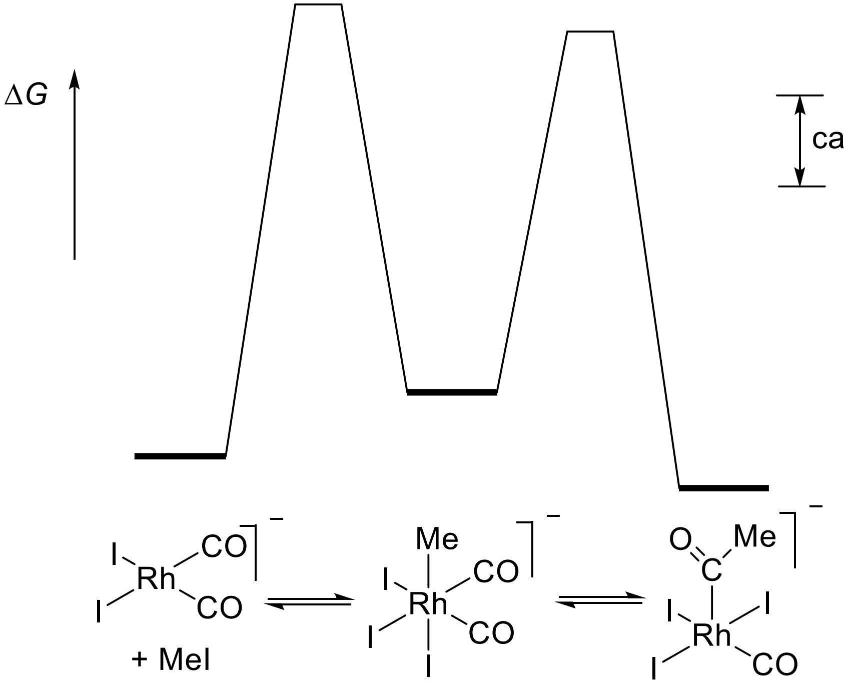
# The catalytic cycle



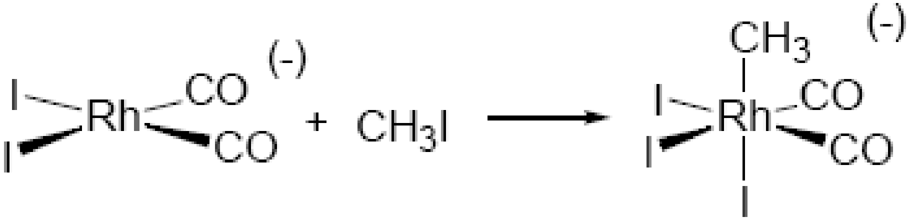
# The rate determining step of the catalytic cycle

Rate law: $v = k\,.[\mathrm{Rh\,I_2(CO)_2^-}].[\mathrm{CH_3I}]$

rate: $CH_3I > CH_3Br > CH_3Cl$



$K_1 = 4.5{\cdot}10^{-3}$ l/mol $K_2 = 3.2{\cdot}10^{3}$



$\nu_{CO}$: 2055 e 1984 $cm^{-1}$

$^{13}C$ NMR: two equivalent carbons with $J_{Rh}$ = 60 Hz

$^{13}C$ NMR: methyl group with $J_{Rh}$ = 14 Hz at $\delta$ = -0.6 ppm

# *Side reactions*

$$CO + H_2O \rightarrow H_2 + CO_2$$

$$RhI_2(CO)_2^- + OH^- \rightarrow RhI_2(CO)(CO_2H)^{2-}$$

$$RhI_2(CO)(CO_2H)^{2-} \rightarrow RhI_2(CO)(H)^{2-} + CO_2$$

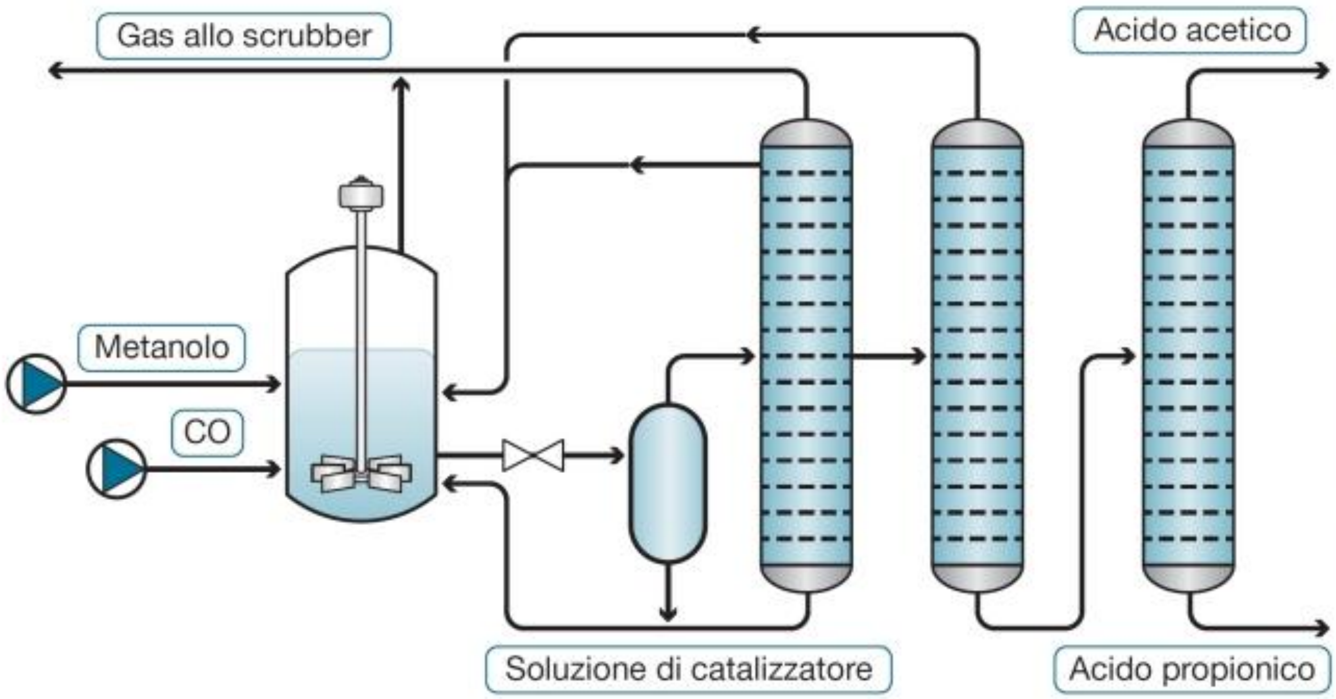
$$RhI_2(CO)(H)^{2-} + H^+ + CO \rightarrow RhI_2(CO)_2^- + H_2$$

---

$$CH_3RhI_3(CO)_2^- + HI \rightarrow CH_4 + RhI_4(CO)_2^-$$

$$RhI_2(CO)_2^- + 2\,HI \leftrightarrows H_2 + RhI_4(CO)_2^-$$

# *Flow scheme of Monsanto process*

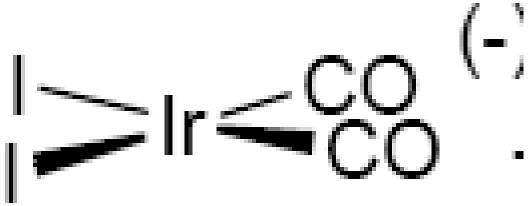


Reaction Conditions:
[Rh] = 10 mM; [$CH_3I$] = 1.5 M; T = 180 °C; $P_{CO}$ = 50 bar.

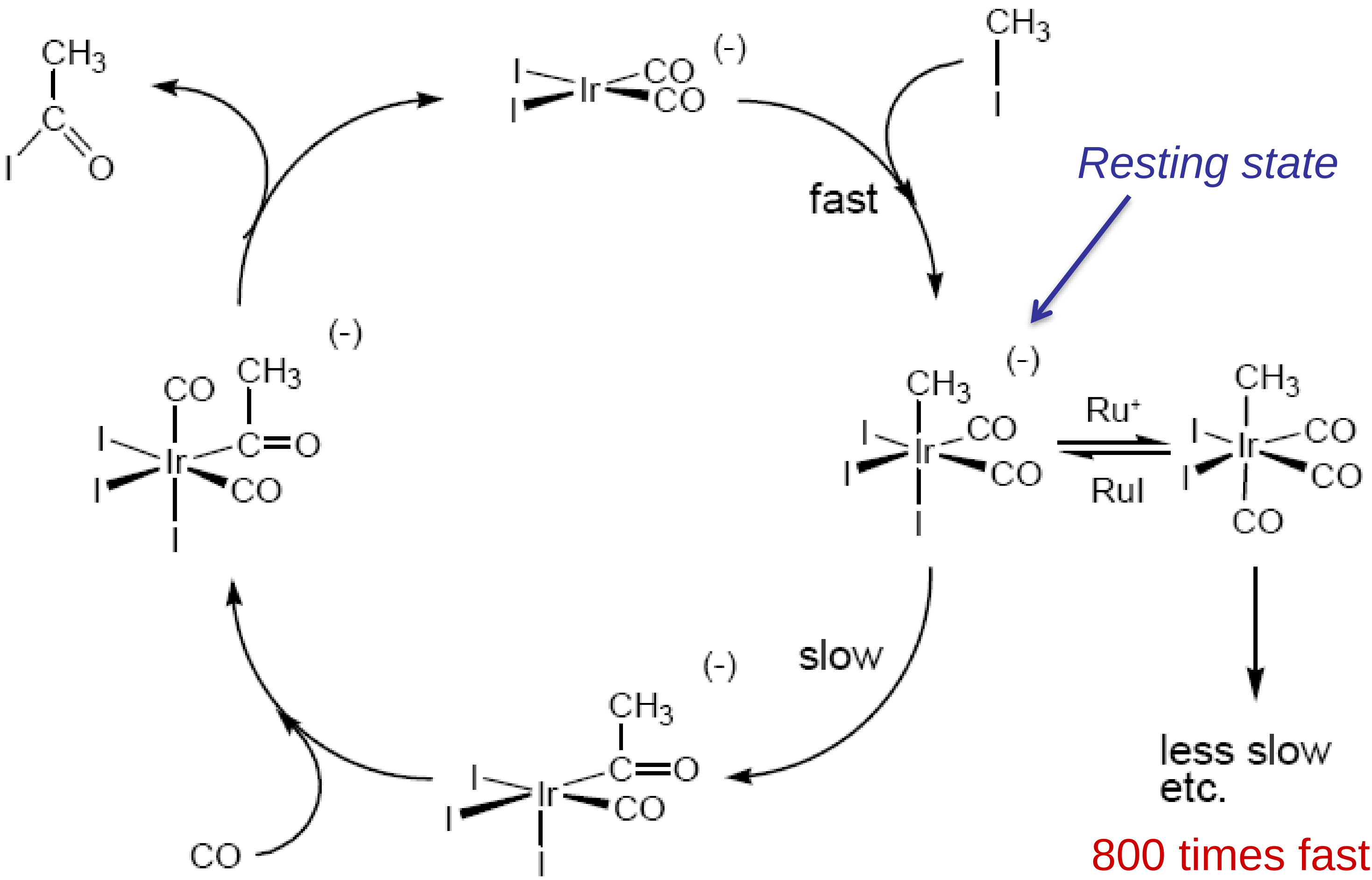
# *The CATIVA process*

It is based on the carbonylation reaction of methanol

It is based on an Iridium catalyst;
High rate at low water concentration;
High stability allowing a wide range of process condition;.
The catalyst is about 25 % faster than the Monsanto;
Thanks to lower content of sideproducts, the produced acetic acid is of better quality than that obtained by the Monsanto process.



# *The catalytic cycle*

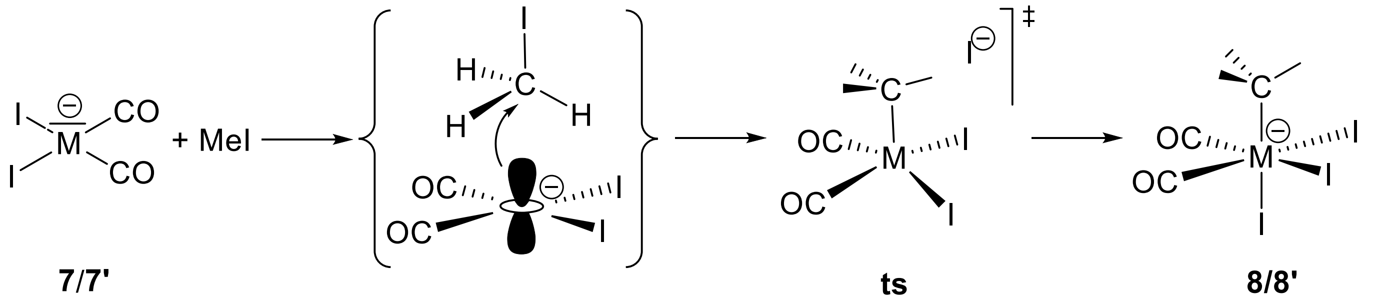


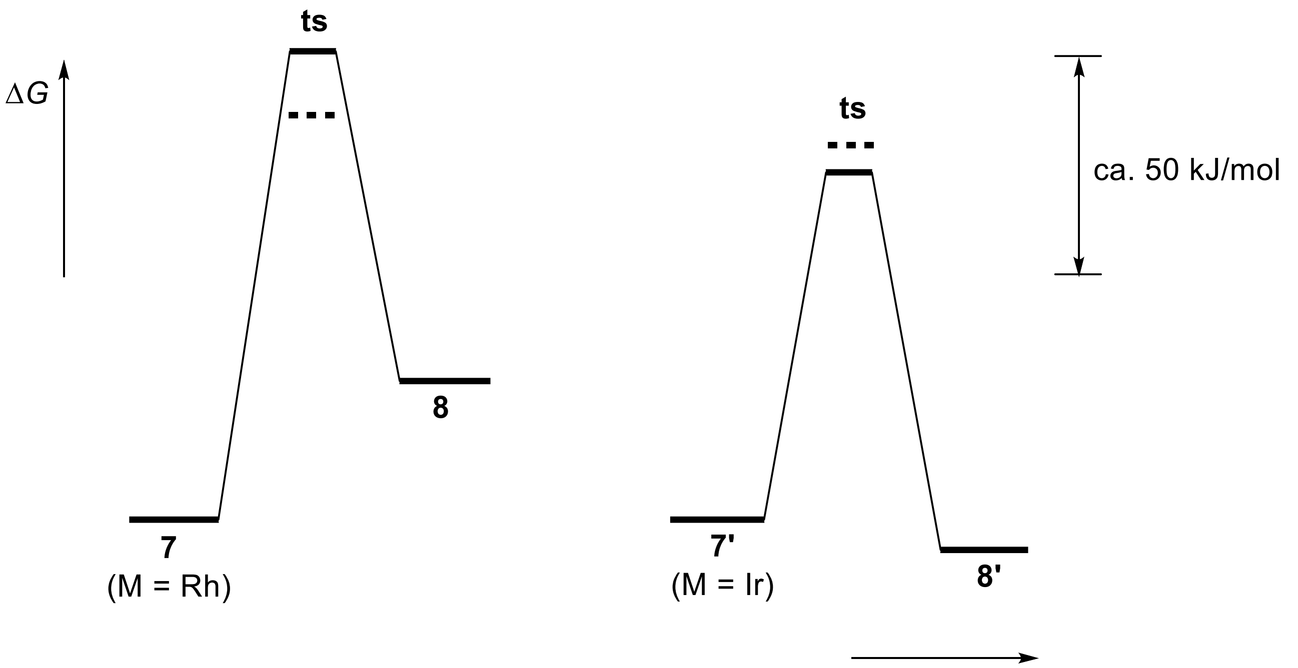
*Resting state*

800 times faster than the anionic catalyst

**The oxidative addition reaction is facile and it is no longer the rate determining step!**

# *The energy barriers of Monsanto and CATIVA processes*



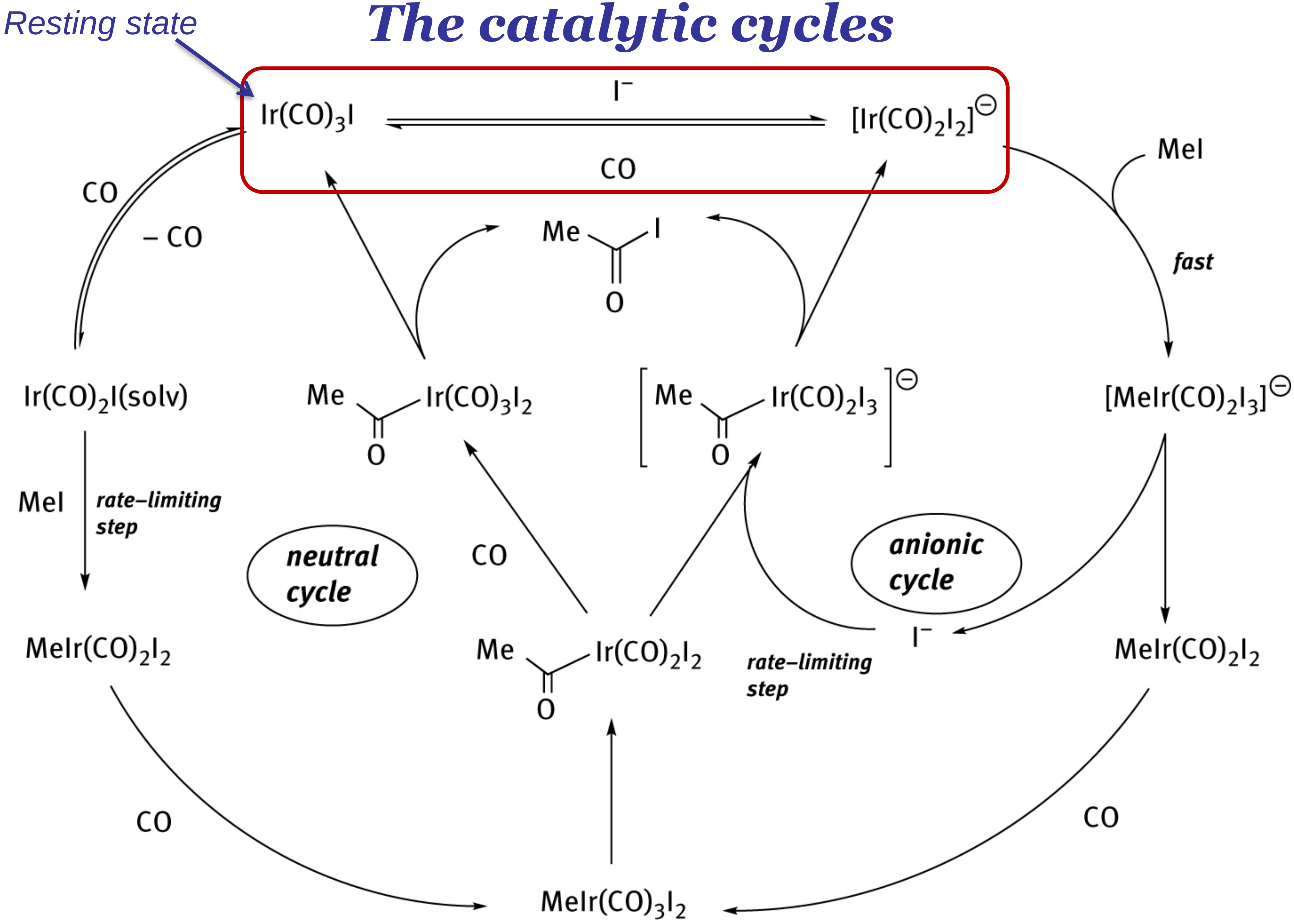


**Activation energy for the methyl migration reaction:**

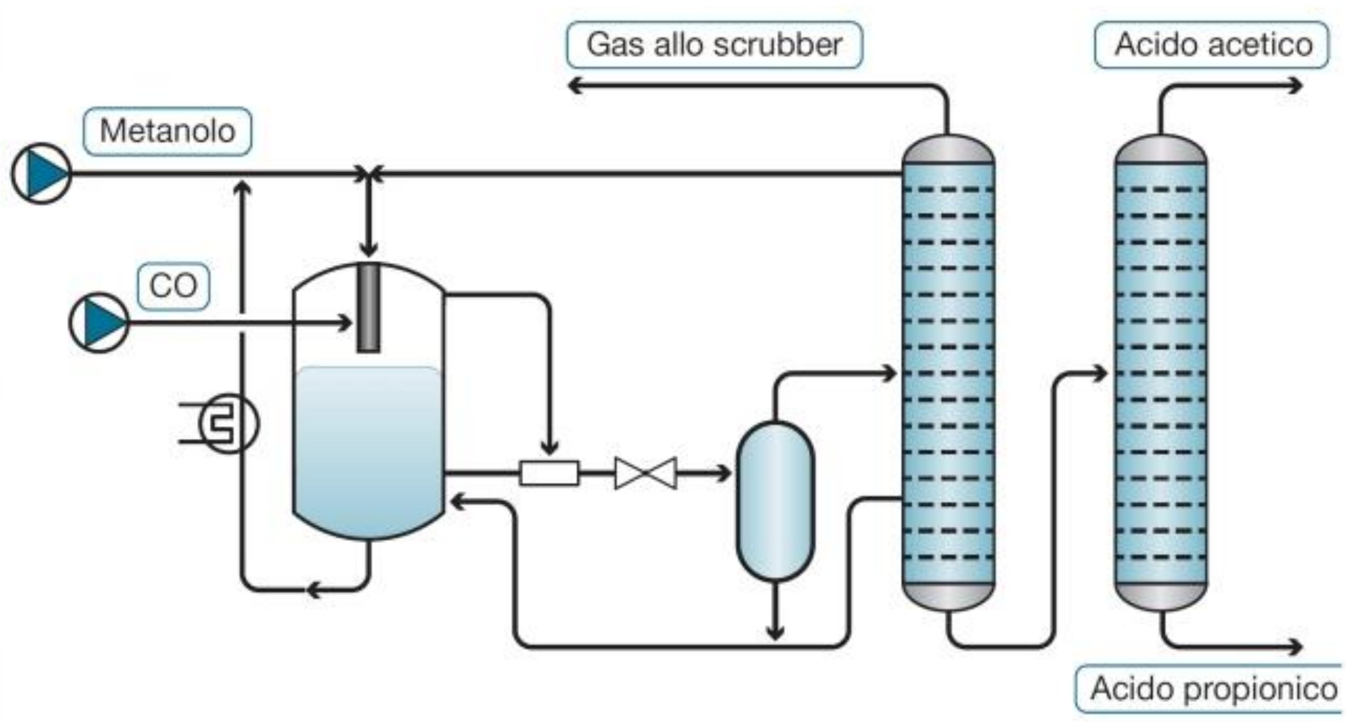
Experimental values: $\Delta G^{\#}$ = 128.5 kJ/mol (Ir); $\Delta G^{\#}$ = 81.1 kJ/mol (Rh)

Calculated values: $\Delta G^{\#}$ = 116.3 kJ/mol (Ir); $\Delta G^{\#}$ = 72.2 kJ/mol (Rh)

# The catalytic cycles

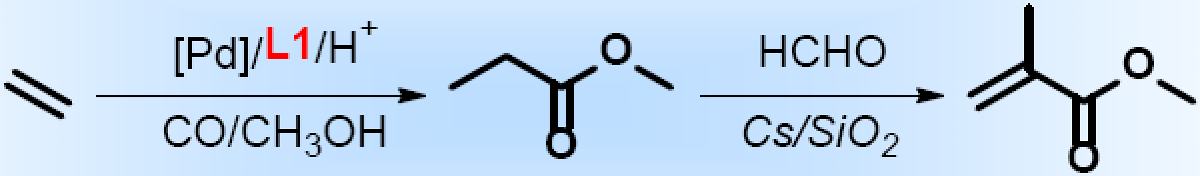


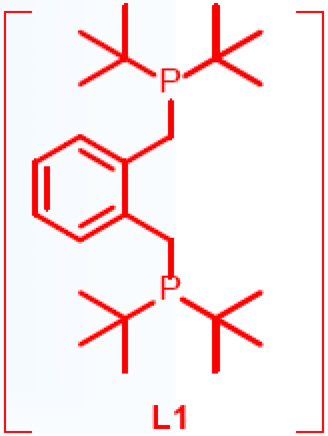
# *Flow scheme of CATIVA process*



Reaction Conditions:
[Rh] = 10 mM; $[CH_3I]$ = 1.5 M; T = 180 °C; $P_{CO}$ = 50 bar.

# *The Lucite process*
# *Methoxycarbonylation of ethene*



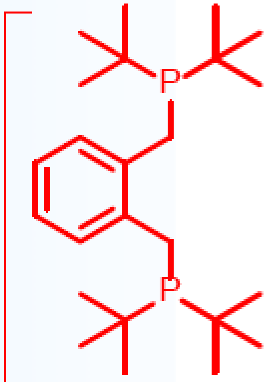


L1

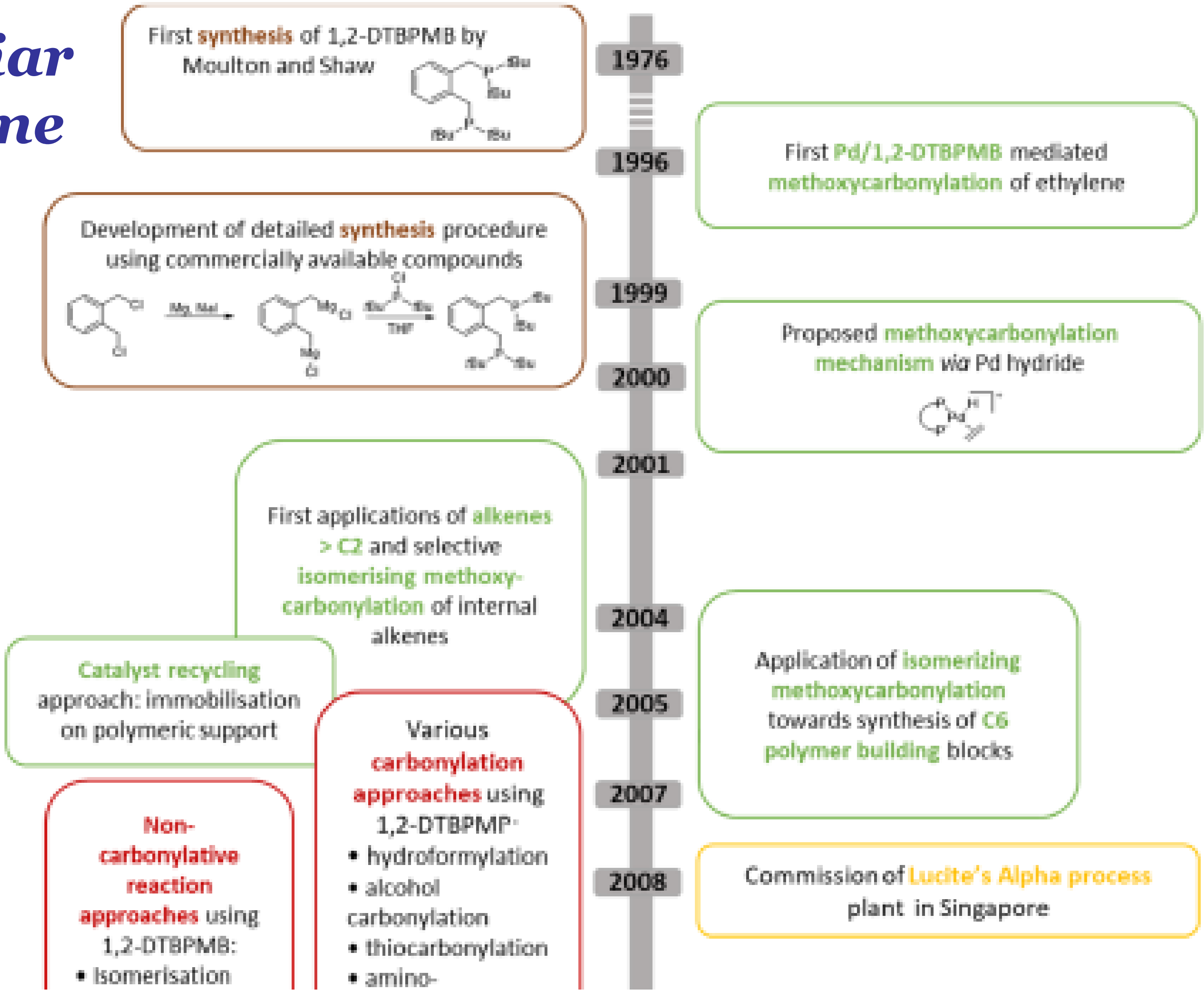
**Lucite alpha I: 120,000 t/y in Singapore**

**Lucite alpha II: 250,000 t/y in Saudi Arabia**

# *A peculiar diphosphine*



**L1**



First **synthesis** of 1,2-DTBPMB by Moulton and Shaw

First **Pd/1,2-DTBPMB** mediated **methoxycarbonylation** of ethylene

Development of detailed **synthesis** procedure using commercially available compounds

Proposed **methoxycarbonylation mechanism** *via* Pd hydride

First applications of **alkenes > C2** and selective **isomerising methoxy-carbonylation** of internal alkenes

Application of **isomerizing methoxycarbonylation** towards synthesis of **C6 polymer building** blocks

**Catalyst recycling** approach: immobilisation on polymeric support

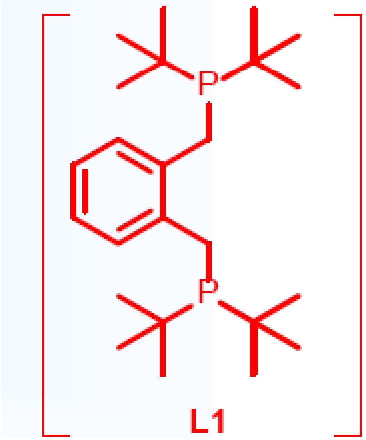
Various **carbonylation approaches** using 1,2-DTBPMP:
- hydroformylation
- alcohol carbonylation
- thiocarbonylation
- amino-

**Non-carbonylative reaction approaches** using 1,2-DTBPMB:
- Isomerisation

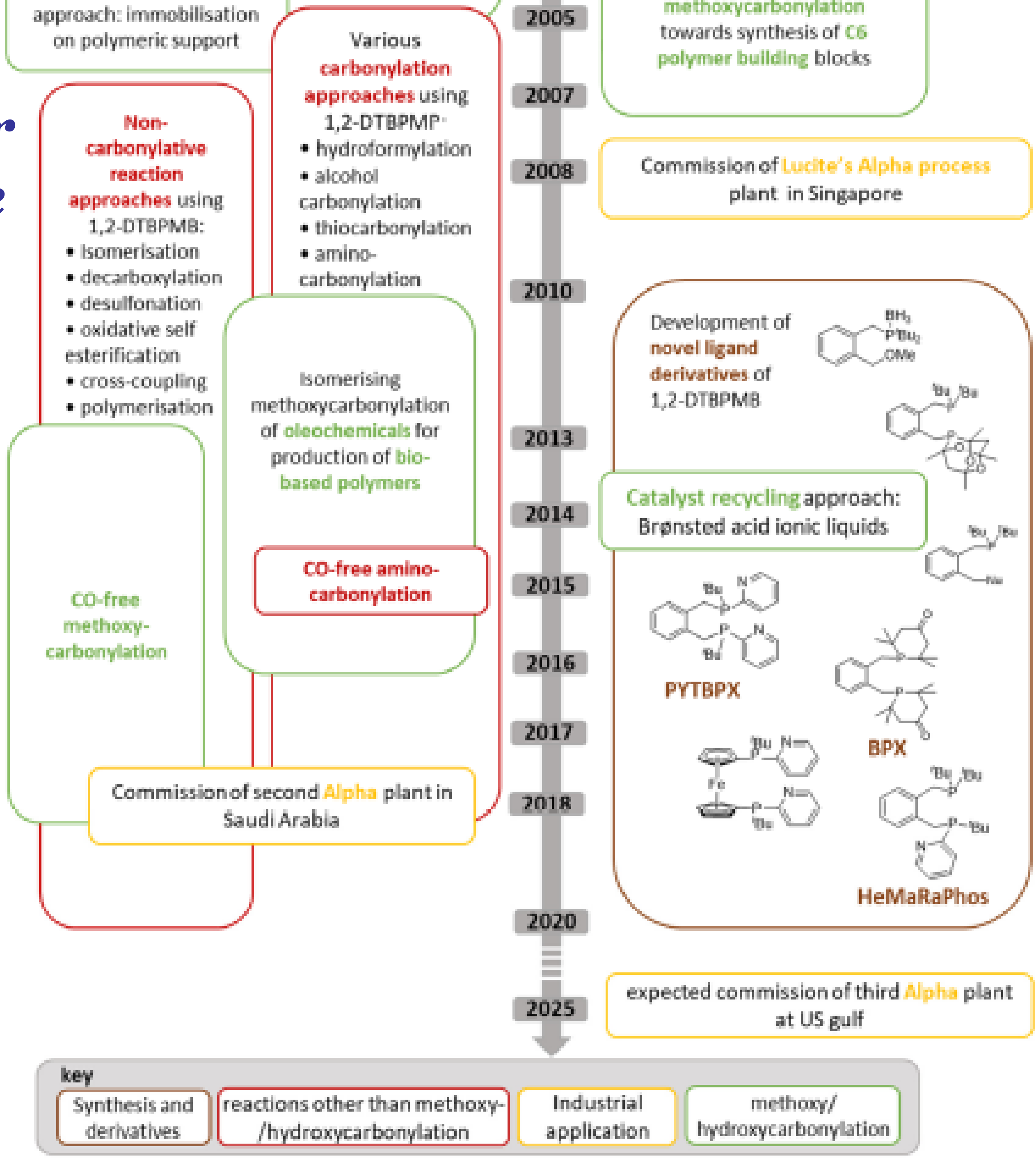
Commission of **Lucite's Alpha process** plant in Singapore

D. J. Cole-Hamilton et al *Chem. Rev.* 2021, *121*, 6610.

# *A peculiar diphosphine*



**L1**



2005

2007

2008

2010

2013

2014

2015

2016

2017

2018

2020

2025

approach: immobilisation on polymeric support

methoxycarbonylation towards synthesis of C6 polymer building blocks

Various carbonylation approaches using 1,2-DTBPMP:
- hydroformylation
- alcohol carbonylation
- thiocarbonylation
- amino-carbonylation

Non-carbonylative reaction approaches using 1,2-DTBPMB:
- Isomerisation
- decarboxylation
- desulfonation
- oxidative self esterification
- cross-coupling
- polymerisation

Commission of Lucite's Alpha process plant in Singapore

Development of novel ligand derivatives of 1,2-DTBPMB

Isomerising methoxycarbonylation of oleochemicals for production of bio-based polymers

Catalyst recycling approach: Brønsted acid ionic liquids

CO-free amino-carbonylation

CO-free methoxy-carbonylation

**PYTBPX**

**BPX**

**HeMaRaPhos**

Commission of second Alpha plant in Saudi Arabia

expected commission of third Alpha plant at US gulf

key

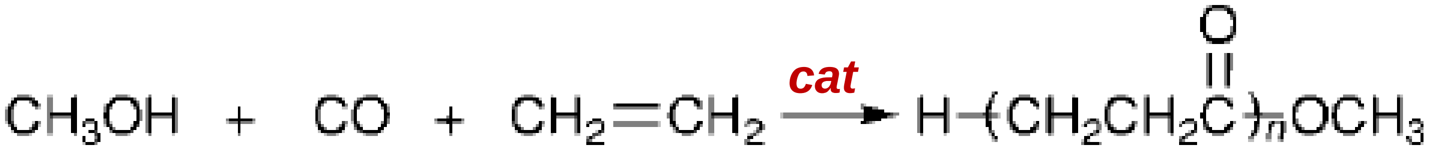
Synthesis and derivatives

reactions other than methoxy-/hydroxycarbonylation

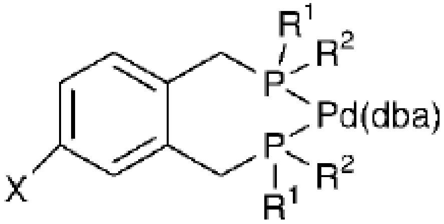
Industrial application

methoxy/ hydroxycarbonylation

# *Methoxycarbonylation of ethene*



$$CH_3OH + CO + CH_2{=}CH_2 \xrightarrow{cat} H{-}(CH_2CH_2\overset{O}{\overset{\|}{C}})_nOCH_3$$

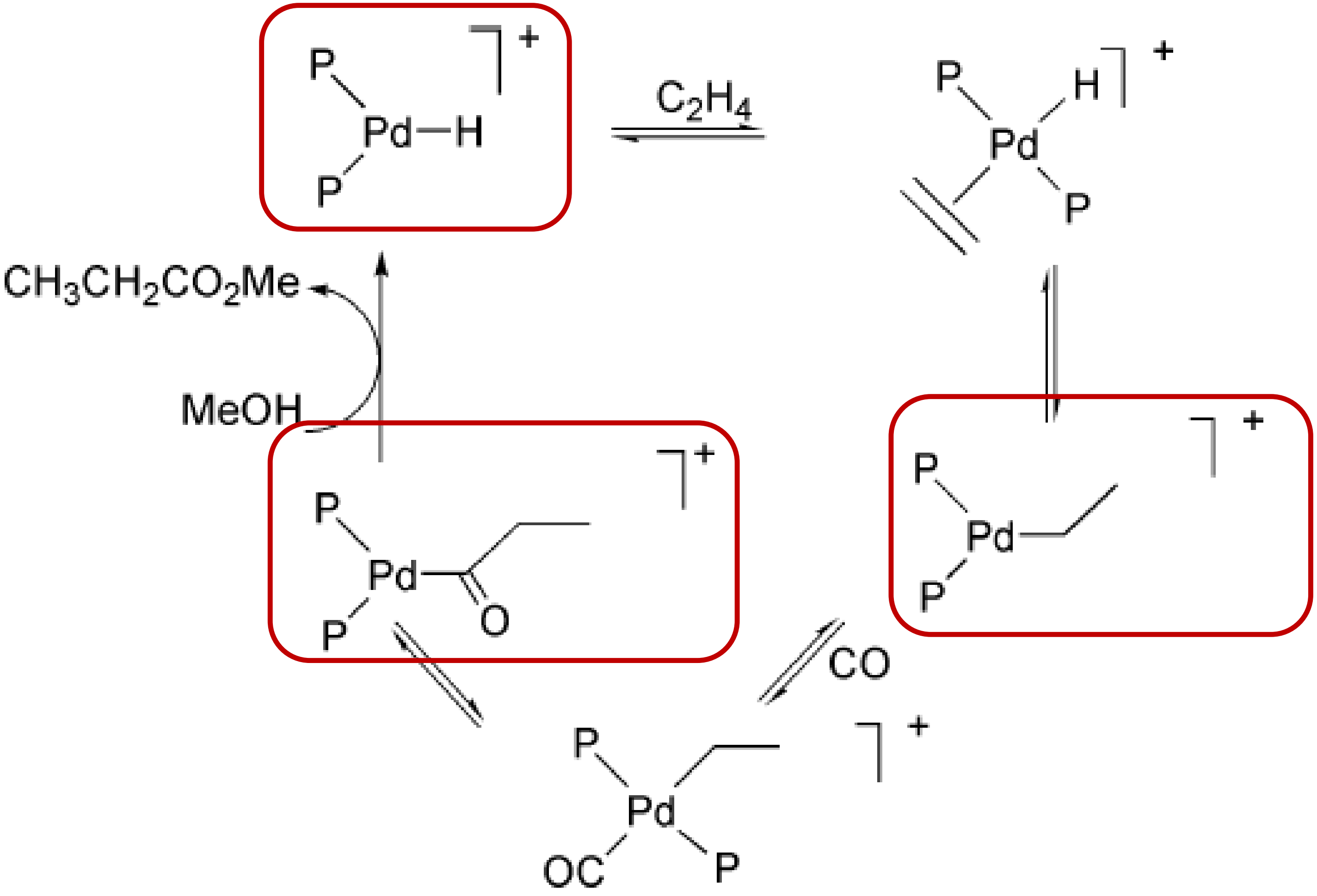


**1** $R^1 = R^2 = Bu^t$, X = H
**2** $R^1 = R^2 = Bu^t$, X = $NO_2$
**3** $R^1 = R^2 = Bu^t$, X = OMe
**4** $R^1 = R^2 = Pr^i$, X = H
**5** $R^1 = R^2 =$ Cy, X = H
**6** $R^1 = R^2 =$ Ph, X = H
**7** $R^1 = Bu^t$, $R^2 =$ Cy, X = H

| Complex | Activity$^b$ | Selectivity$^c$ (%) | P–Pd–P bite angle$^d$ (°) |
|---|---|---|---|
| **1** | 12 000 | 99.9 | 103.9 |
| **2** | 11 500 | 99.9 | |
| **3** | 11 800 | 99.9 | |
| **4** | 200 | 20 | 104.3 |
| **5** | 200 | 25 | 103.9 |
| **6** | 400 | 20 | 104.6 |
| **7** | 500 | 30 | |

Reaction Conditions:
$n_{Pd}$ = 0.01 mmol; $CH_3OH$ V = 300 mL; T = 80 °C;
$P_{tot}$ = 10 bar; $n_{CF3SO3H}$ = 0.2 mmol; t = 3 h.
$^b$ $mol_{Et}/mol_{Pd}\cdot h$.

# *The mechanism*



# *Flow scheme of Lucite process*