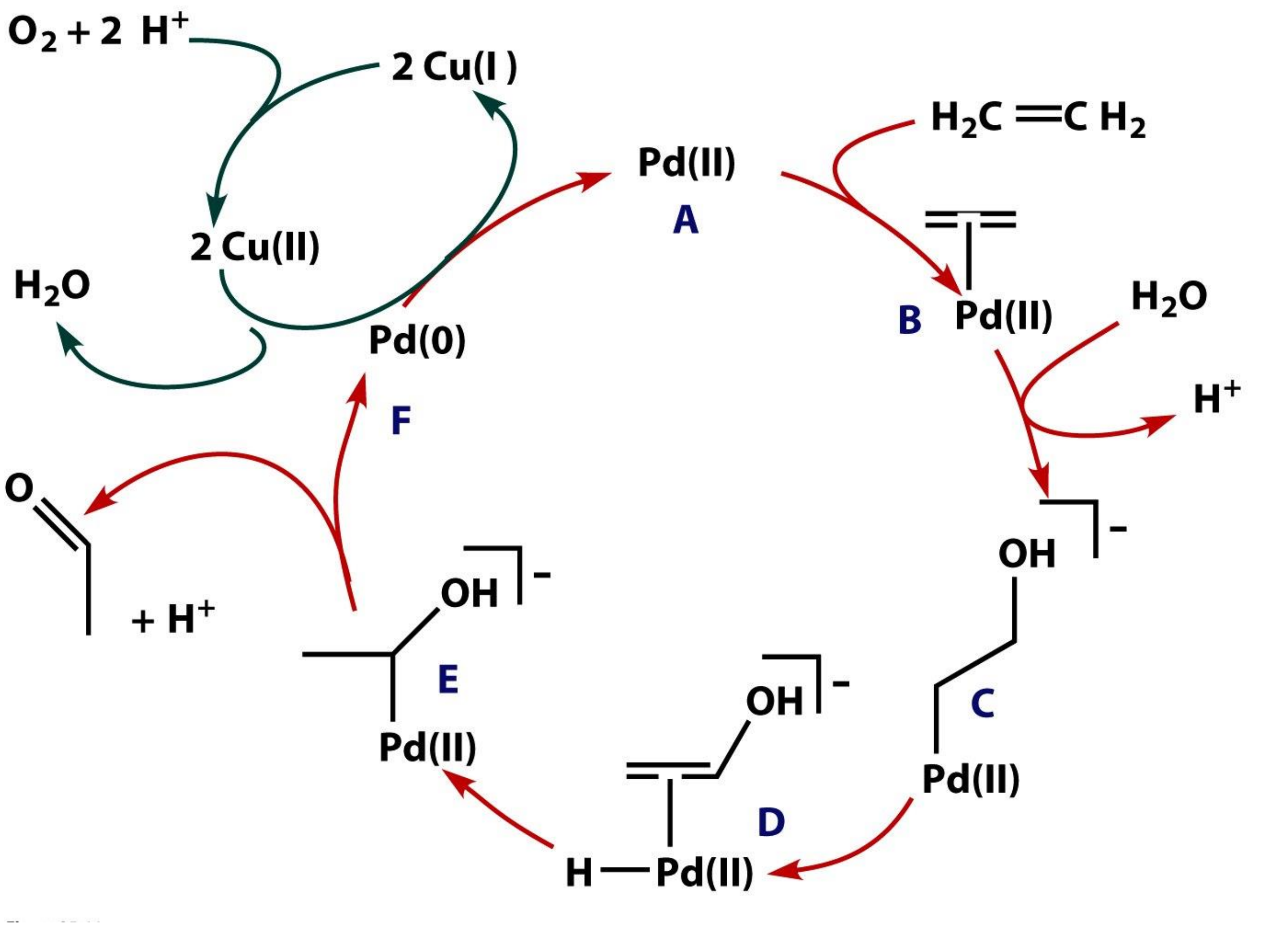
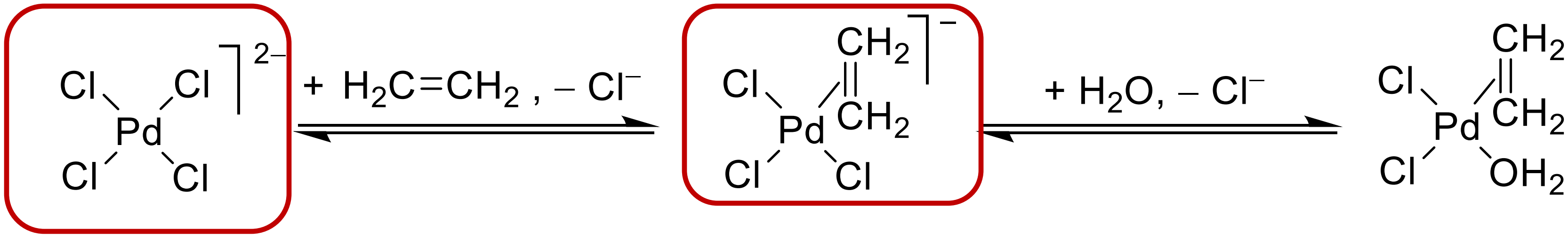
Synthesis of acetic acid

The Wacker process

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



The Pd(II) precursor



analogous of
Zeise's salt

From Pd(0) to Pd(II) oxidation by the Cu(II) salt

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

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

The Monsanto process

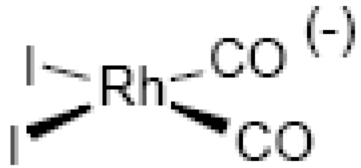
It is based on the carbonylation reaction of methanol

$$CH_3OH + CO \rightarrow CH_3COOH$$

ΔG, *standard conditions, -75 kJ.mol*$^{-1}$

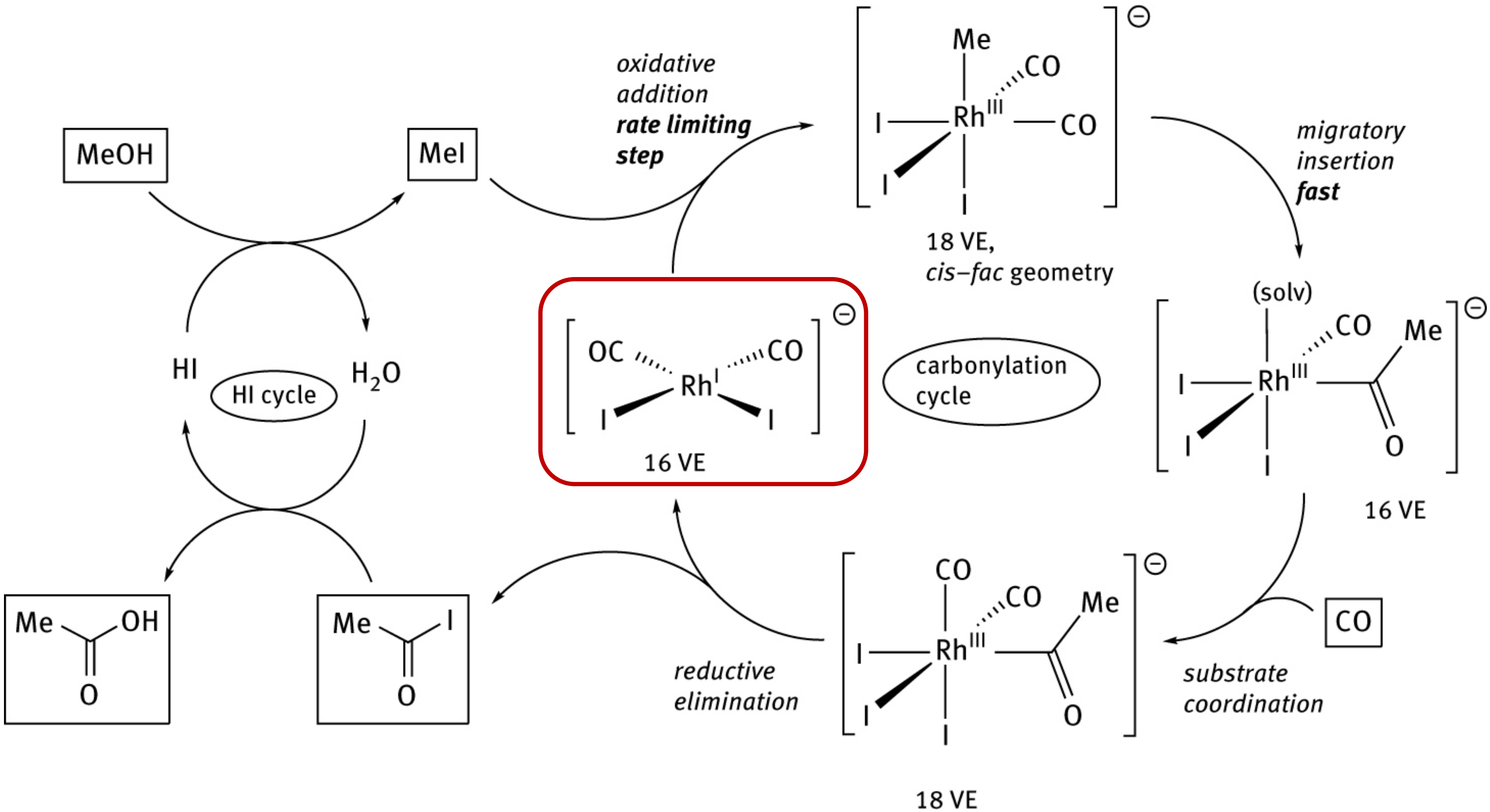
ATOM EFFICIENCY = 100 % **E FACTOR = 0**

in situ catalytic system:
RhI_3, CO e H_2O



$$CH_3OH + HI \leftrightarrows CH_3I + H_2O \quad (1)$$

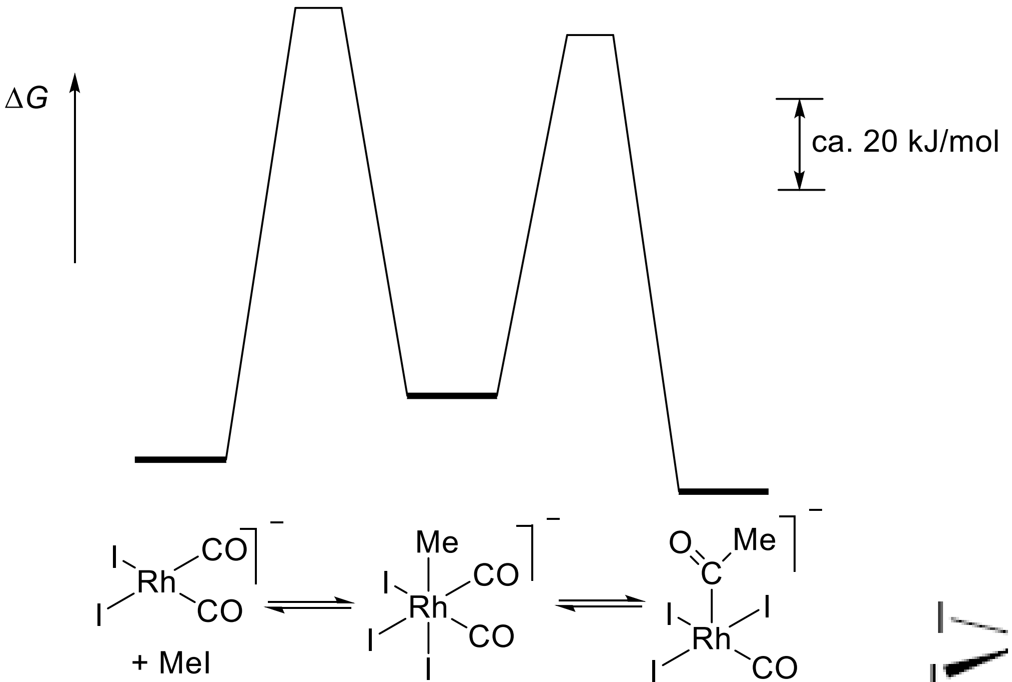
The catalytic cycle



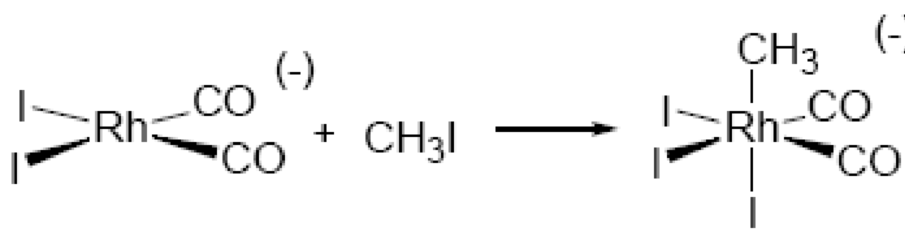
The rate determining step of the catalytic cycle

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

v: $CH_3I > CH_3Br > CH_3Cl$



$K_1 = 4.5\cdot10^{-3}$ l/mol $\quad K_2 = 3.2\cdot10^{3}$



ν_{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 δ = -0.6 ppm

Side reactions

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

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

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

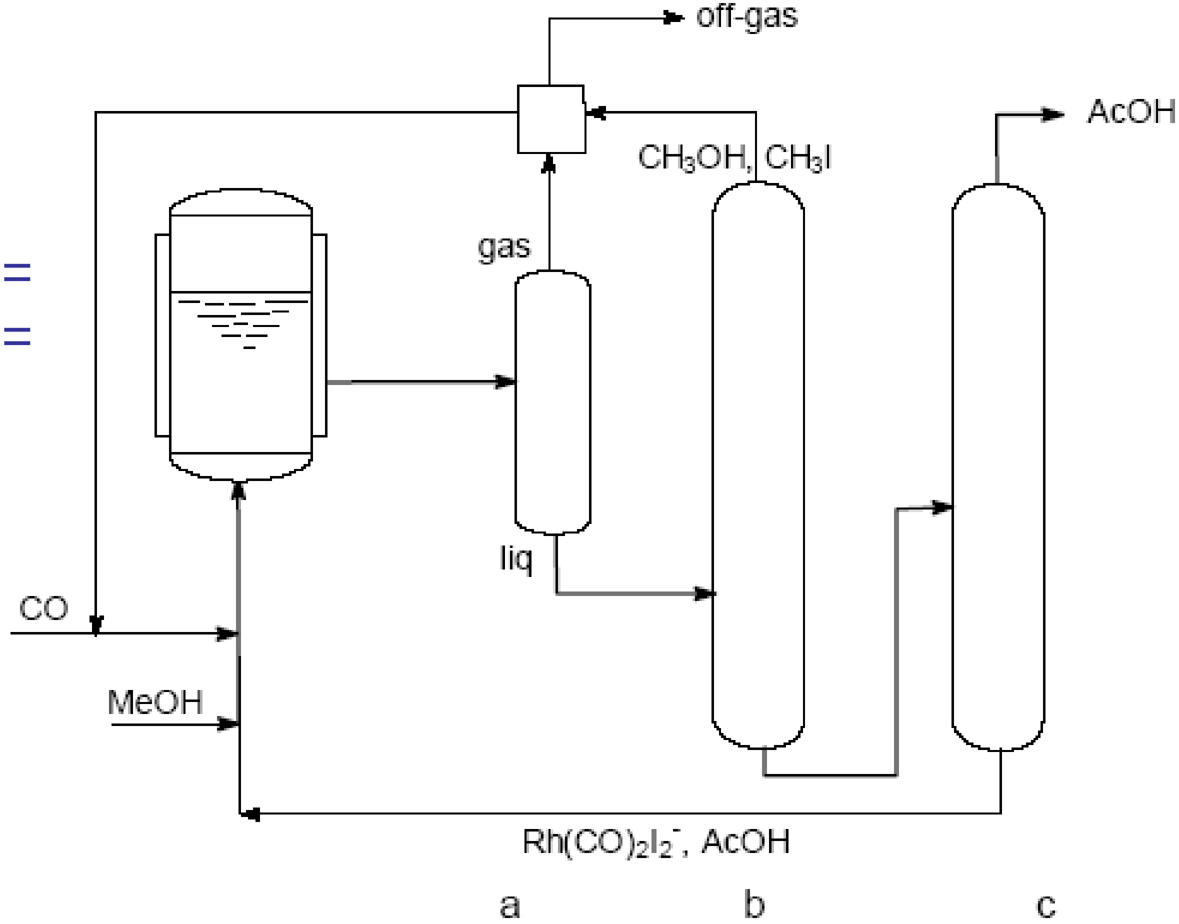
$$RhI_2(CO)(H)^{2-} + H^{+} + CO \rightarrow RhI_2(CO)_2^{-} + H_2$$

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

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

Process scheme Monsanto process

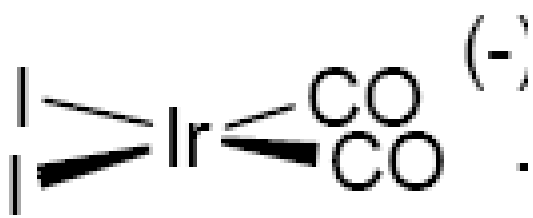
Reaction conditions:
[Rh] = 10 mM; [CH_3I] = 1.5 M; T = 180 °C; P_{CO} = 50 bar.



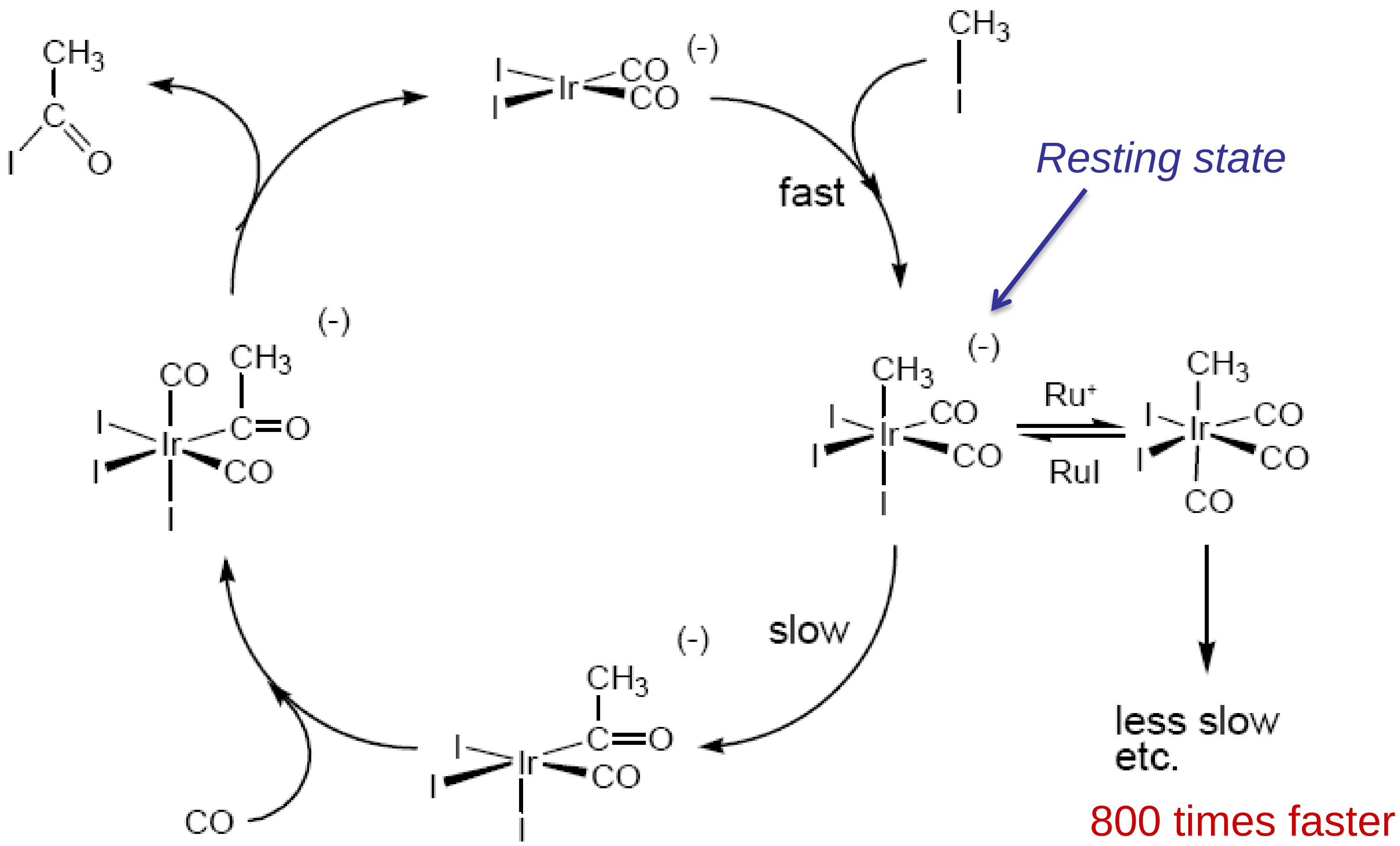
The CATIVA process

It is based on the carbonylation reaction of methanol

4 plants are in operation since 2003;
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.

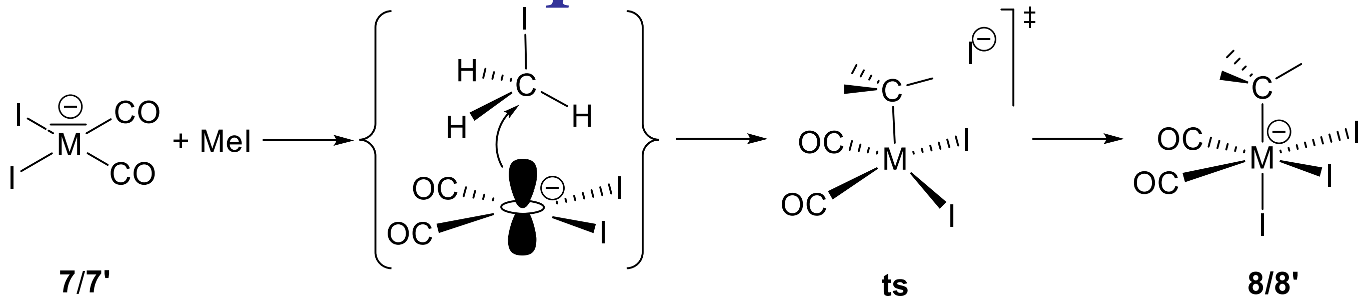


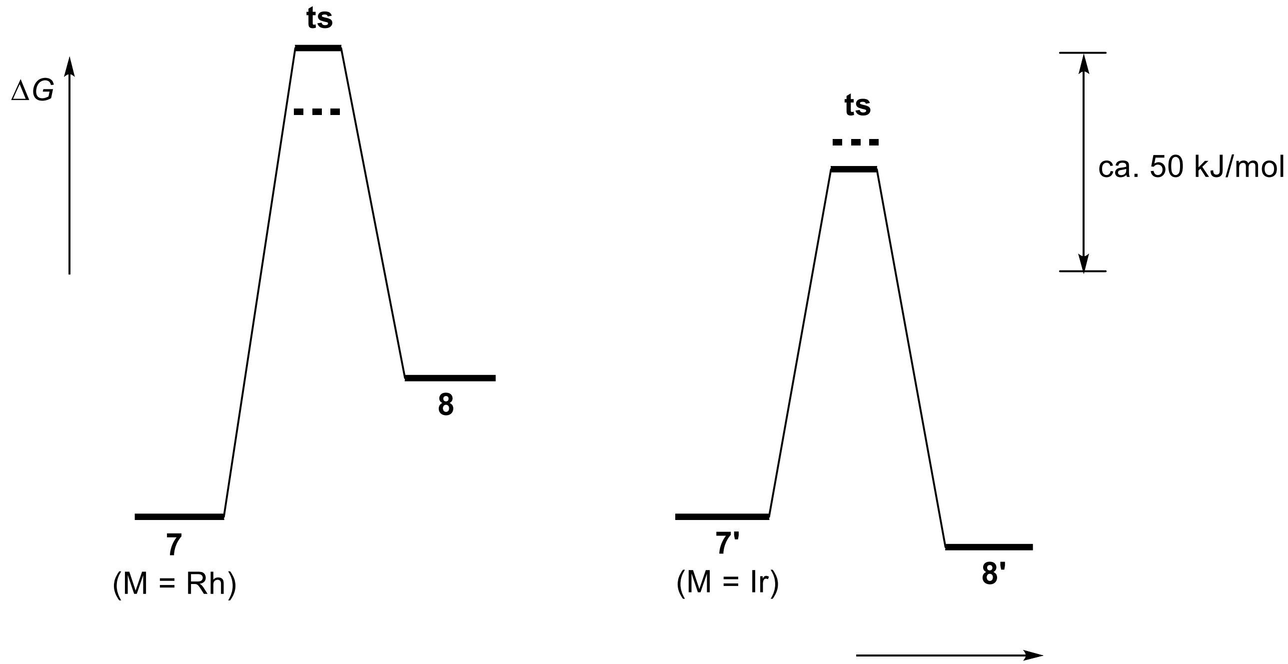
The catalytic cycle



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

The energetic in Monsanto and CATIVA processes





The Gibbs free energy for activation of the methyl migration:

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