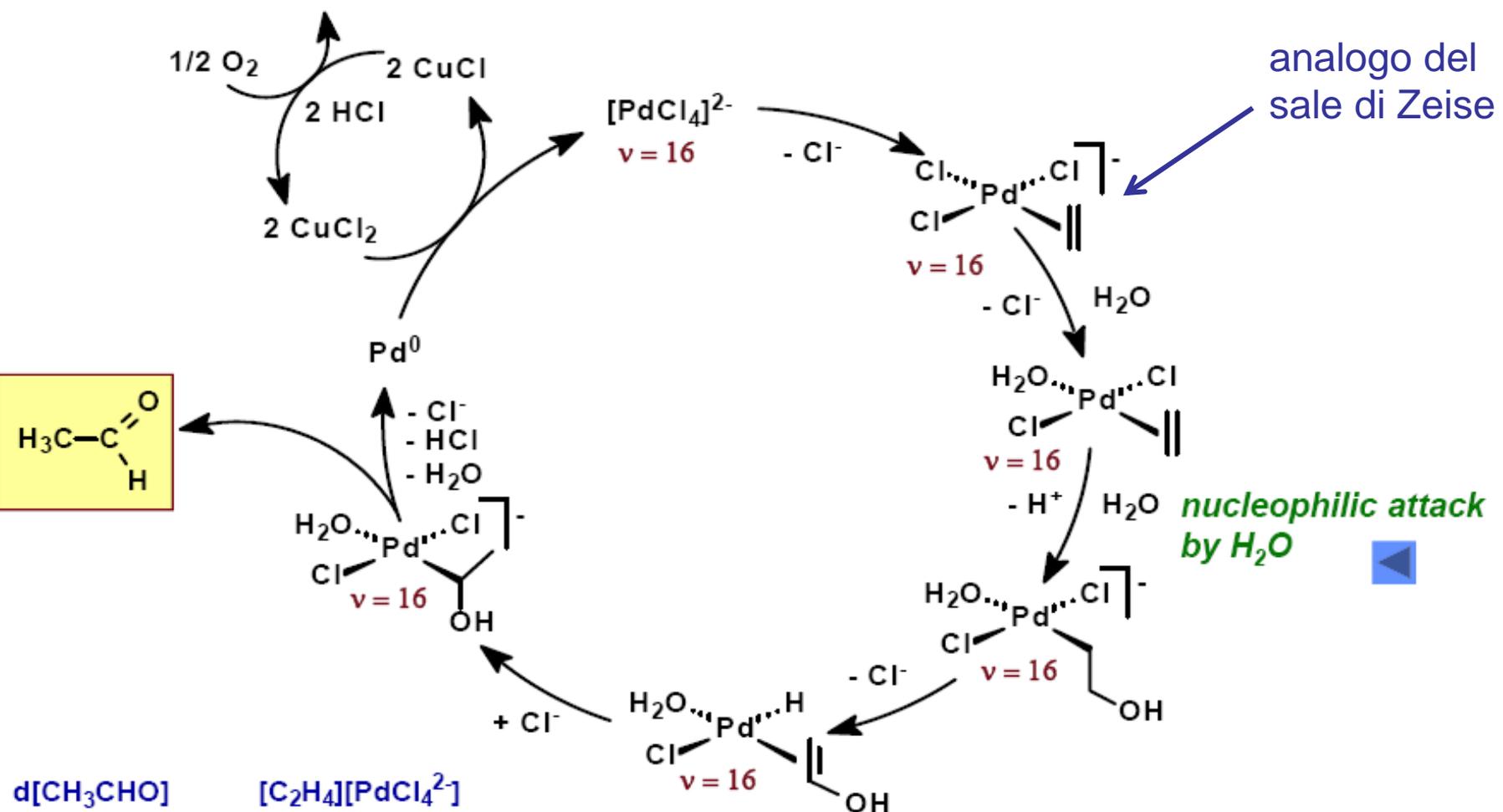
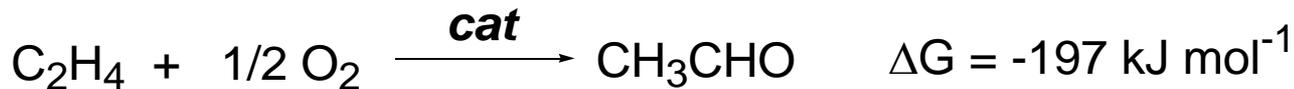


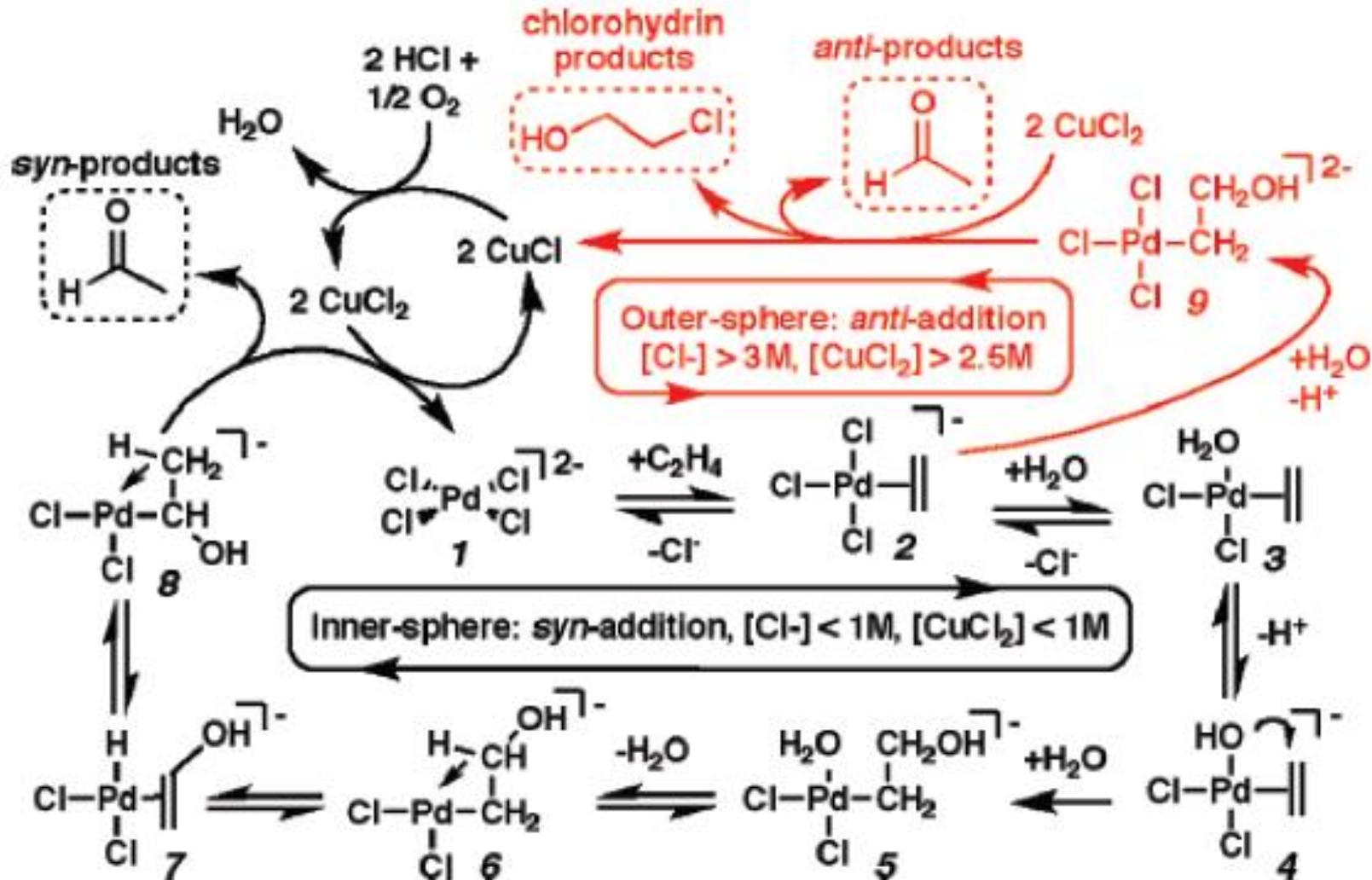
La sintesi dell'acido acetico

Il processo Wacker

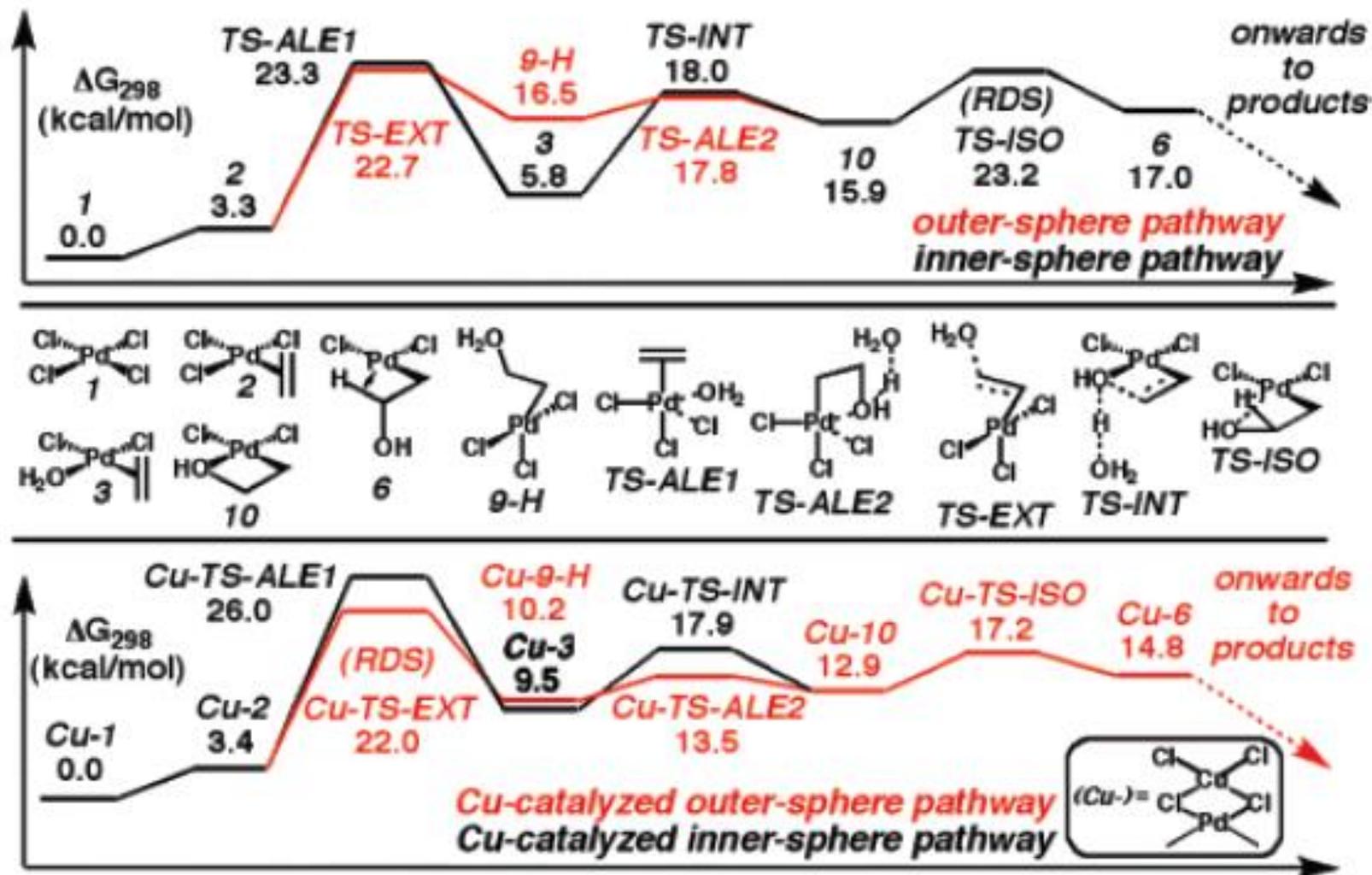


$$\frac{d[\text{CH}_3\text{CHO}]}{dt} = k \frac{[\text{C}_2\text{H}_4][\text{PdCl}_4^{2-}]}{[\text{H}^+][\text{Cl}^-]^2}$$

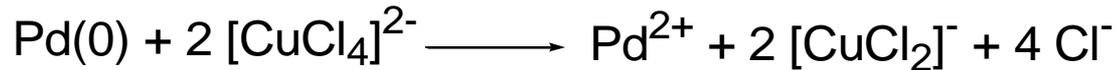
The recently reported mechanism



The recently reported mechanism



L'ossidazione di Pd(0) a Pd(II) ad opera del sale di Cu(II)



Processo a **stadio singolo**

Conversione massima 40 %  Necessario riciclo del gas

Necessari gas molto puri: O₂ puro;
etilene al 99.8 %.

Necessario valvole e tubature in Ti

Bassa pressione

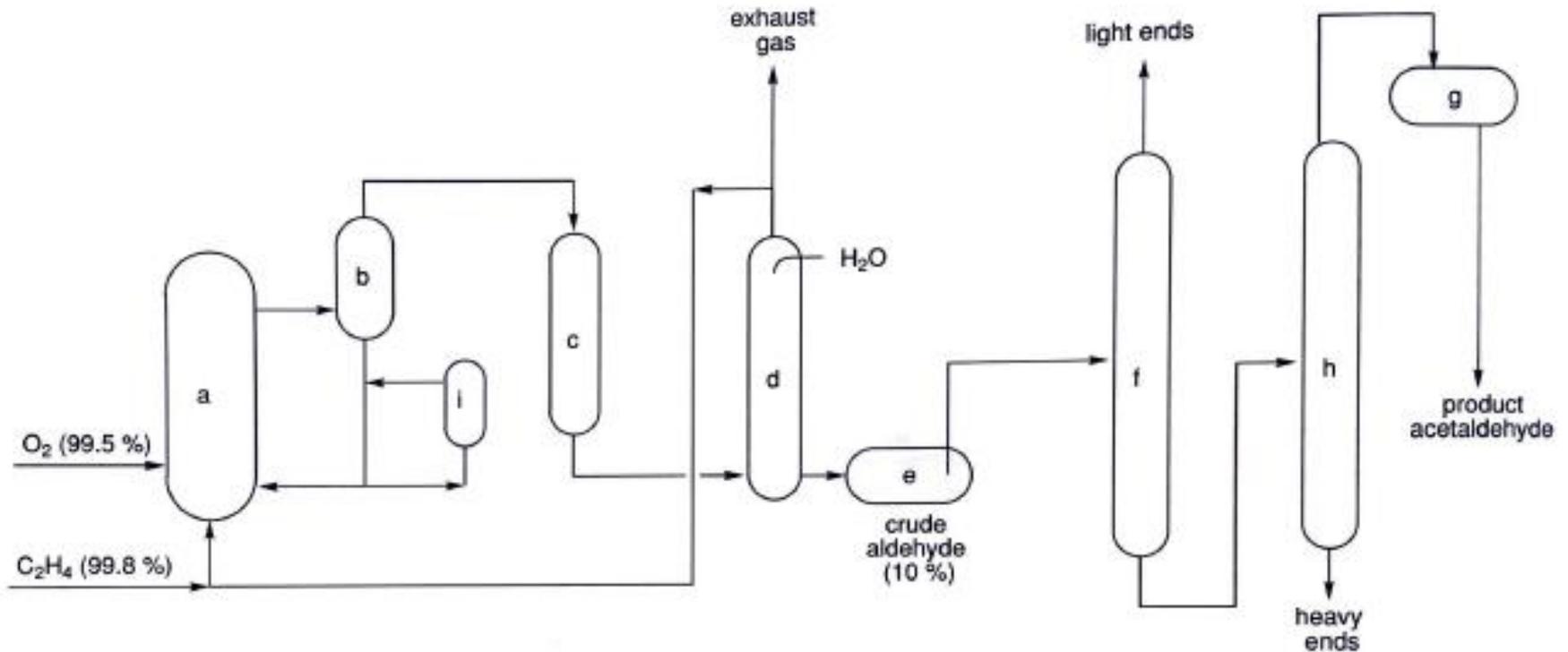
Processo a **due stadi**

Conversione completa  Nessun riciclo del gas

Gas grezzi

Alta pressione + due reattori  Investimenti elevati

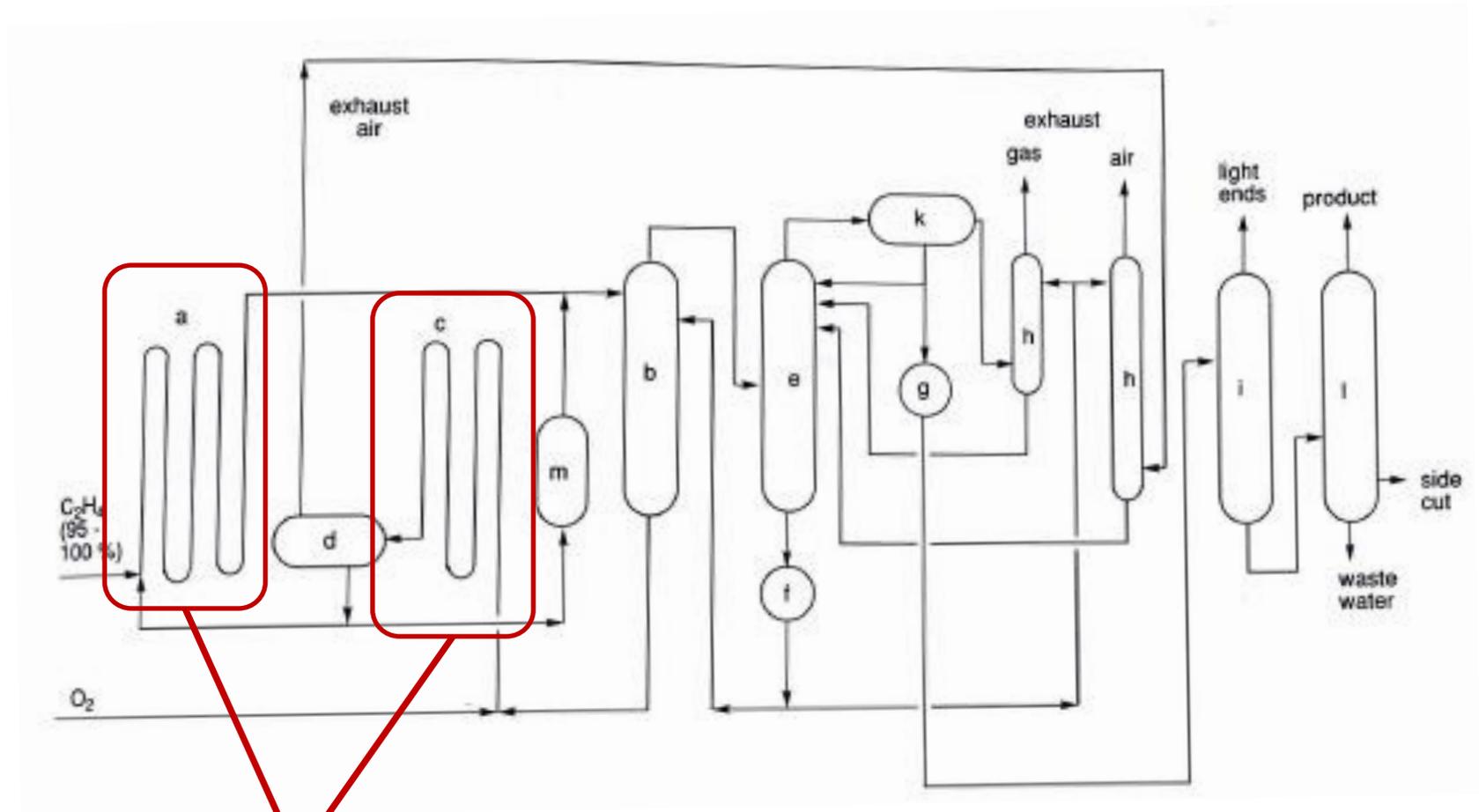
Lo schema del processo Wacker a stadio singolo



Condizioni di reazione:

$T = 100 - 130 \text{ } ^\circ\text{C}$; $P_{CO} = 4 - 10 \text{ bar}$.

Lo schema del processo Wacker a due stadi



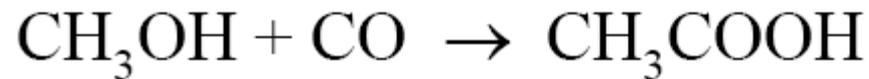
reattori

Condizioni di reazione:

$T = 100 - 130 \text{ }^\circ\text{C}$; $P_{CO} = 10 \text{ bar}$.

Il processo Monsanto

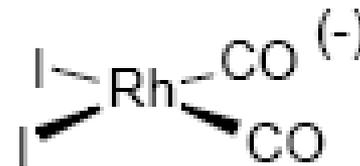
Si basa sulla reazione di **carbonilazione del metanolo**



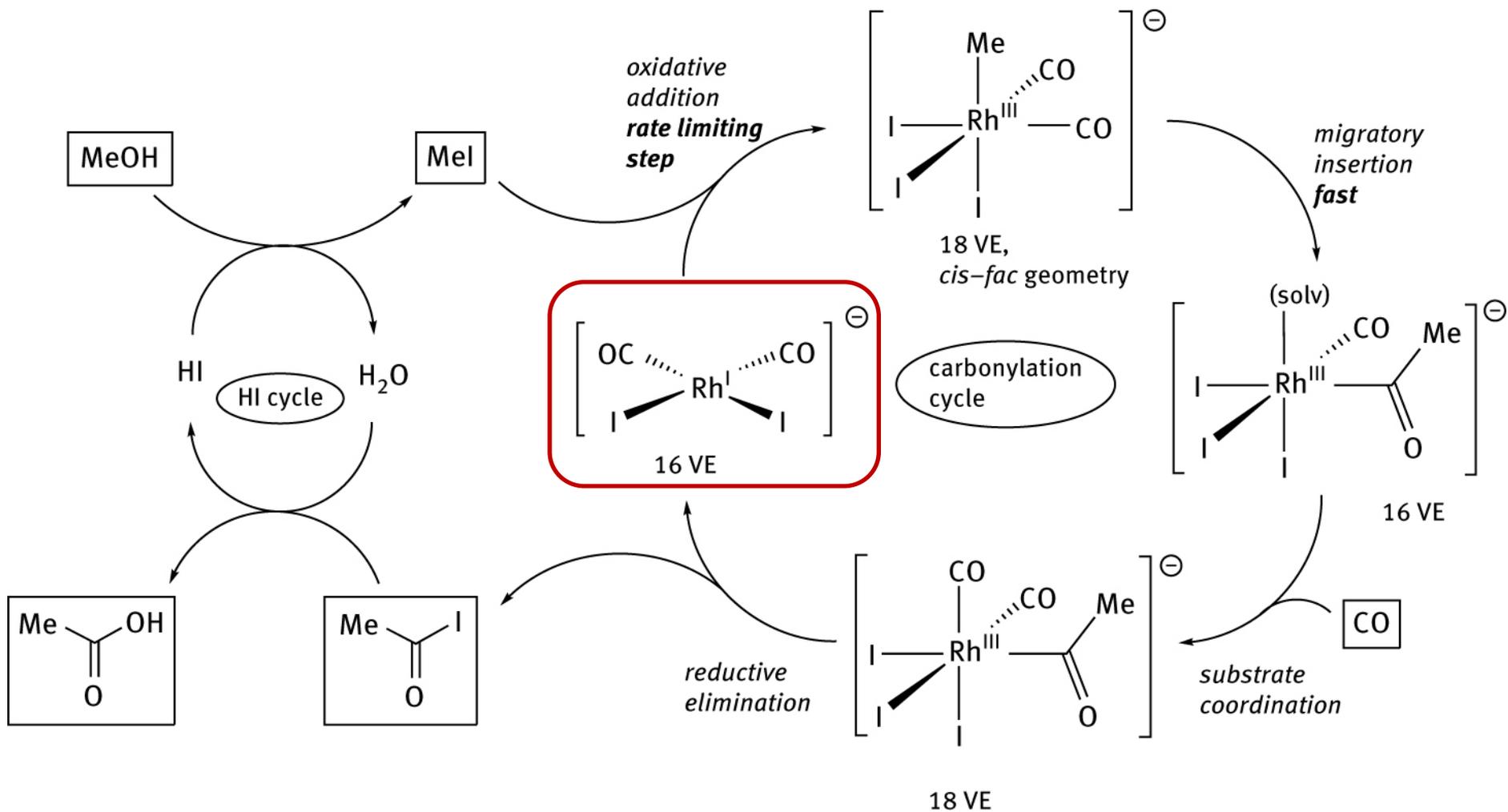
ΔG , standard conditions, -75 kJ.mol^{-1}

EFFICIENZA ATOMICA = 100 % FATTORE E = 0

Sistema catalitico **in situ**:
 RhI_3 , CO e H_2O



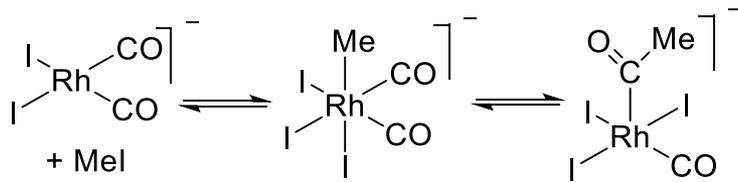
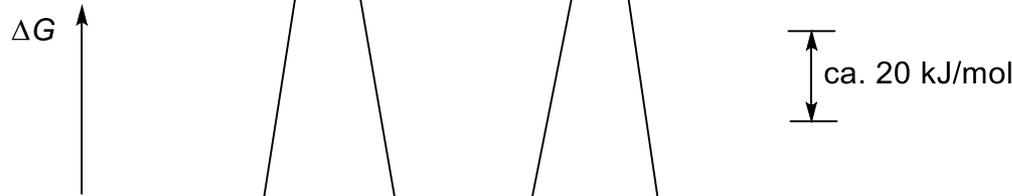
The catalytic cycle



The rate determining step of the catalytic cycle

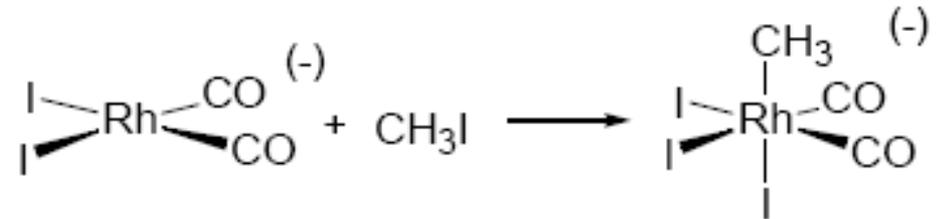
Rate law: $v = k \cdot [\text{Rh I}_2(\text{CO})_2^-] \cdot [\text{CH}_3\text{I}]$

v : $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl}$



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

$K_2 = 3.2 \cdot 10^3$

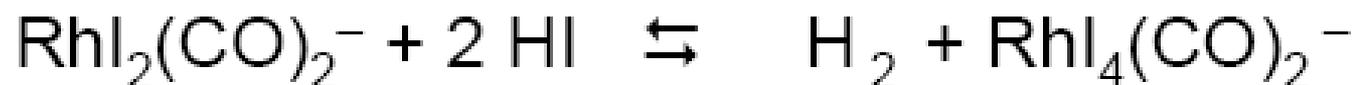


ν_{CO} : 2055 e 1984 cm^{-1}

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

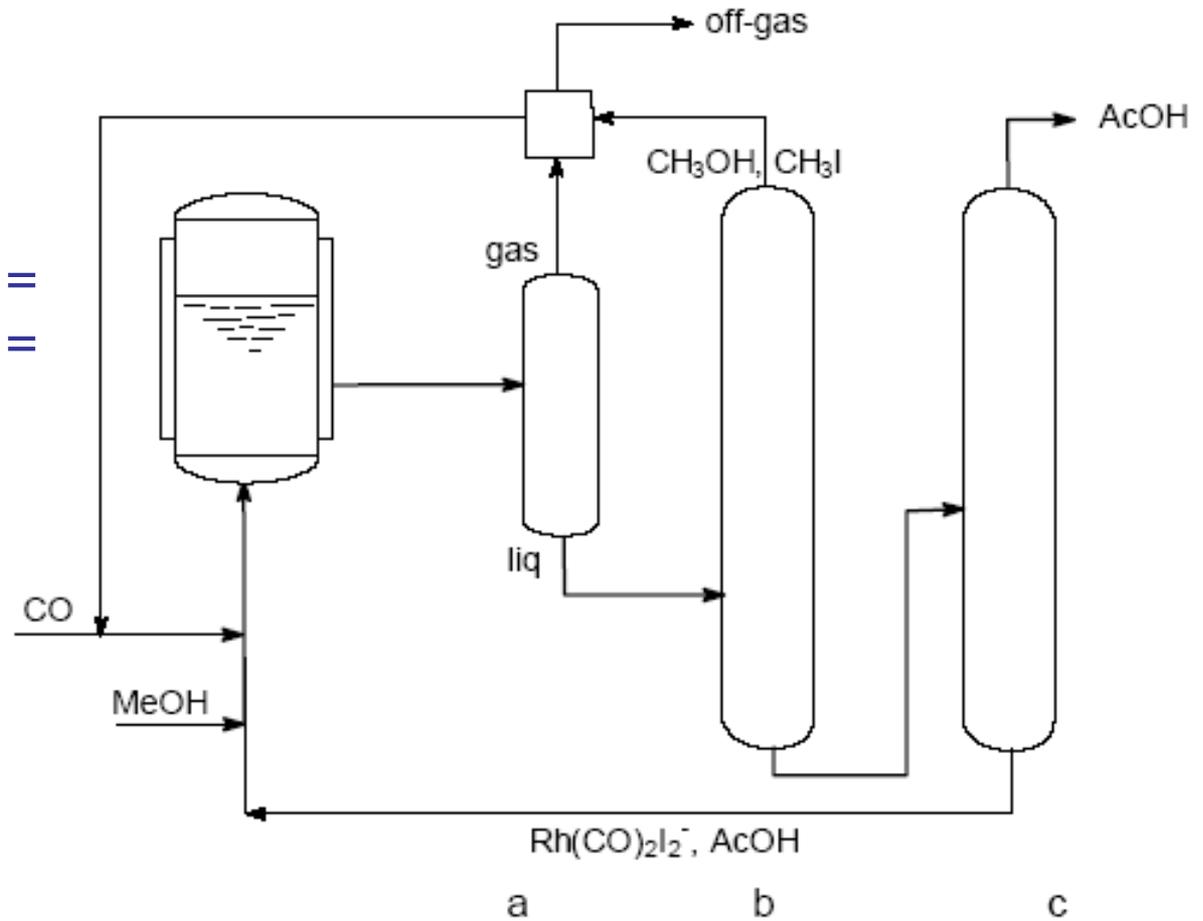
^{13}C NMR: methyl group with $J_{\text{Rh}} = 14 \text{ Hz}$ at $\delta = -0.6 \text{ ppm}$

Reazioni laterali



Lo schema del processo Monsanto

Condizioni di reazione:
[Rh] = 10 mM; [CH₃I] =
1.5 M; T = 180 °C; P_{CO} =
50 bar.



*Il processo **CATIVA***

Si basa sulla reazione di **carbonilazione del metanolo**

Ci sono 4 impianti dal 2003;

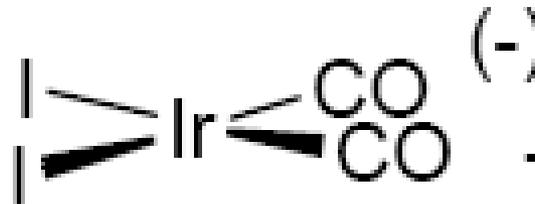
Si basa su un catalizzatore a base di **Iridio**;

Alta velocità a bassa concentrazione d'acqua;

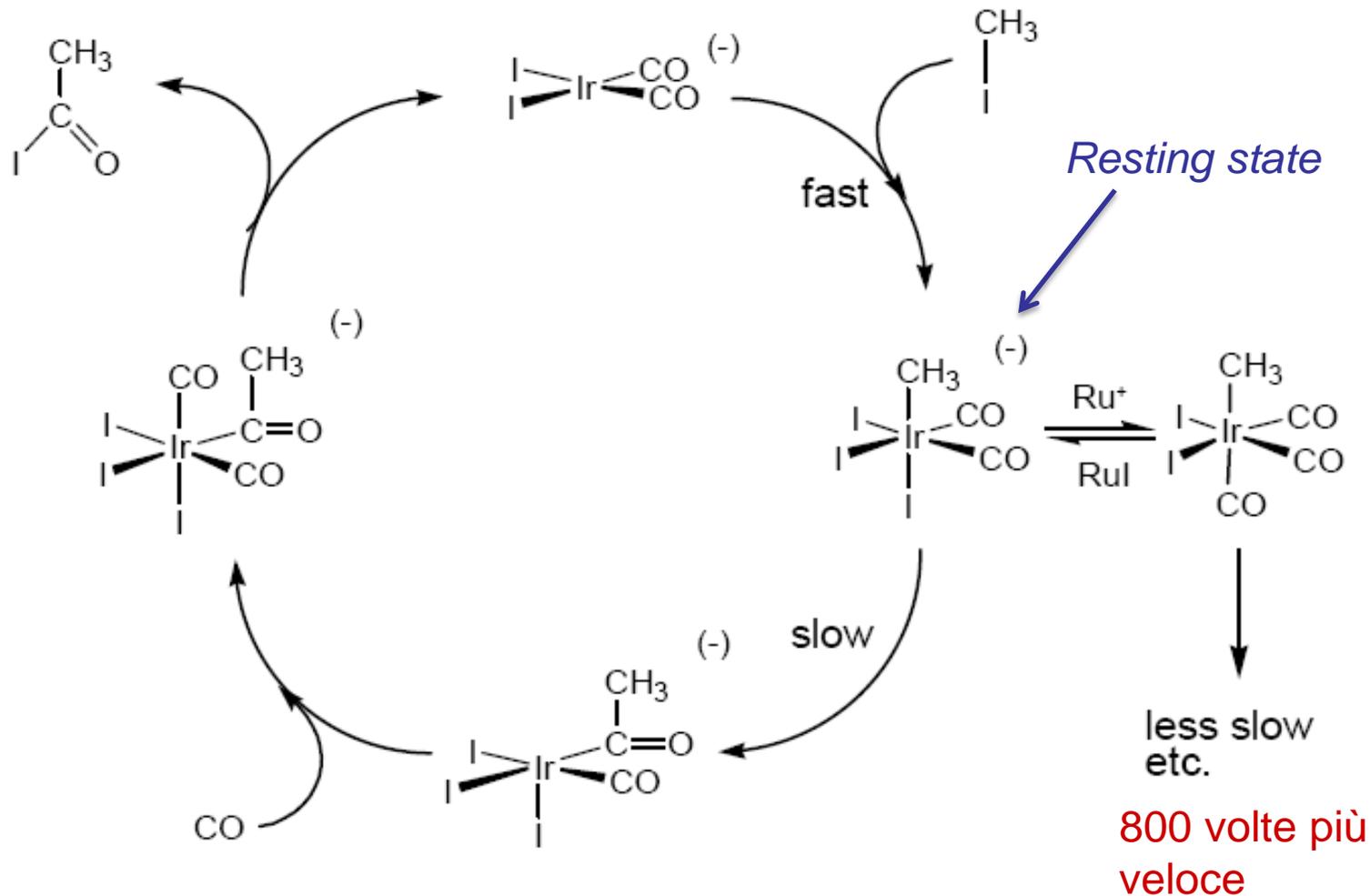
Maggiore stabilità su un intervallo più ampio di condizioni di reazione.

Il catalizzatore è il 25 % più veloce che nel Monsanto;

L'acido acetico prodotto è di qualità molto più alta, per un minore contenuto di sottoprodotti.

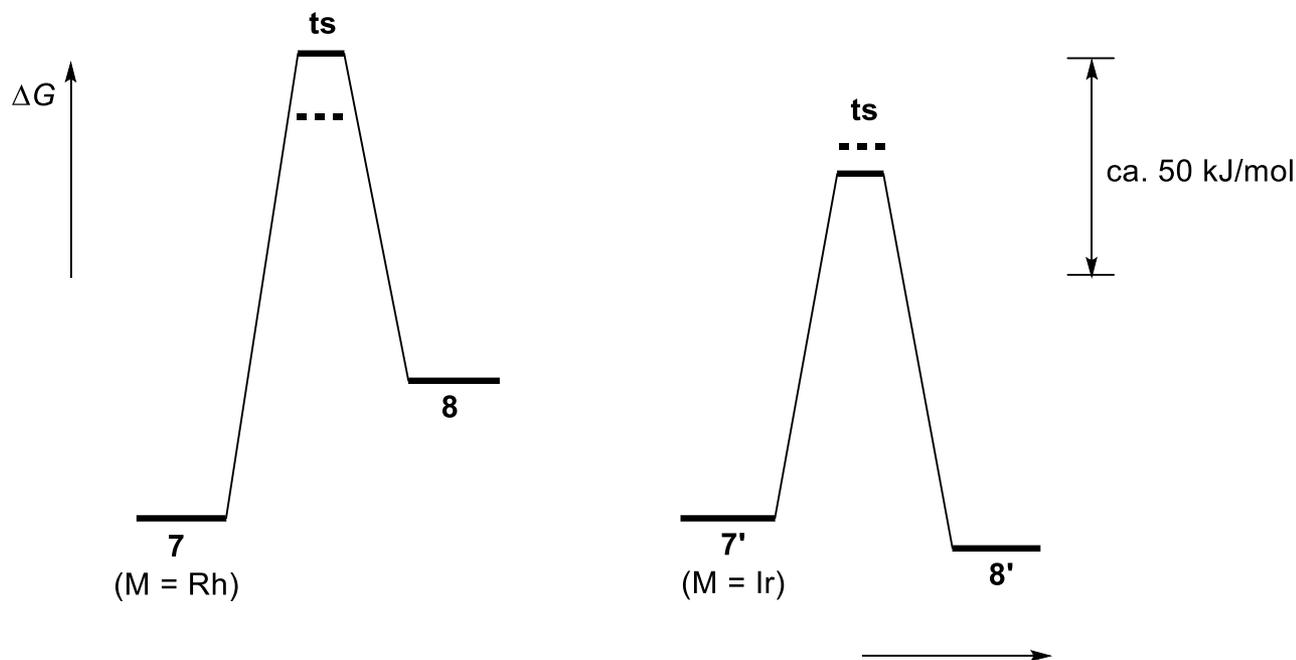
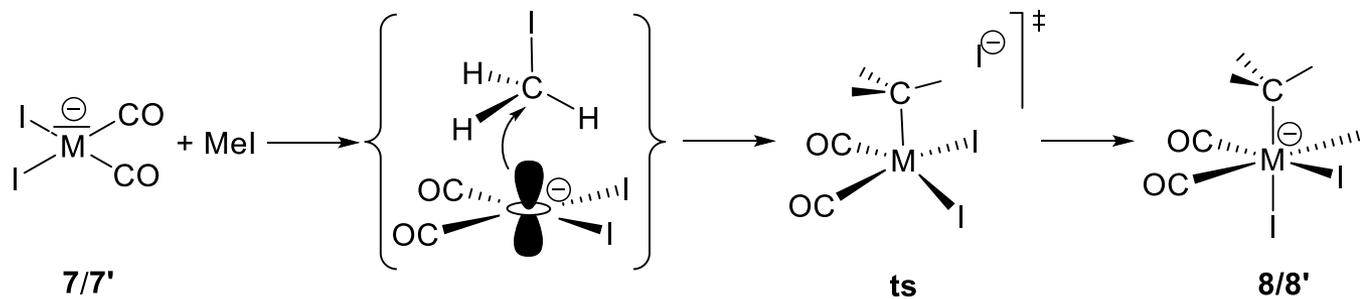


Il ciclo catalitico



La reazione di addizione ossidativa non è più il **rate determining step!**

L'energetica dei processi Monsanto e CATIVA



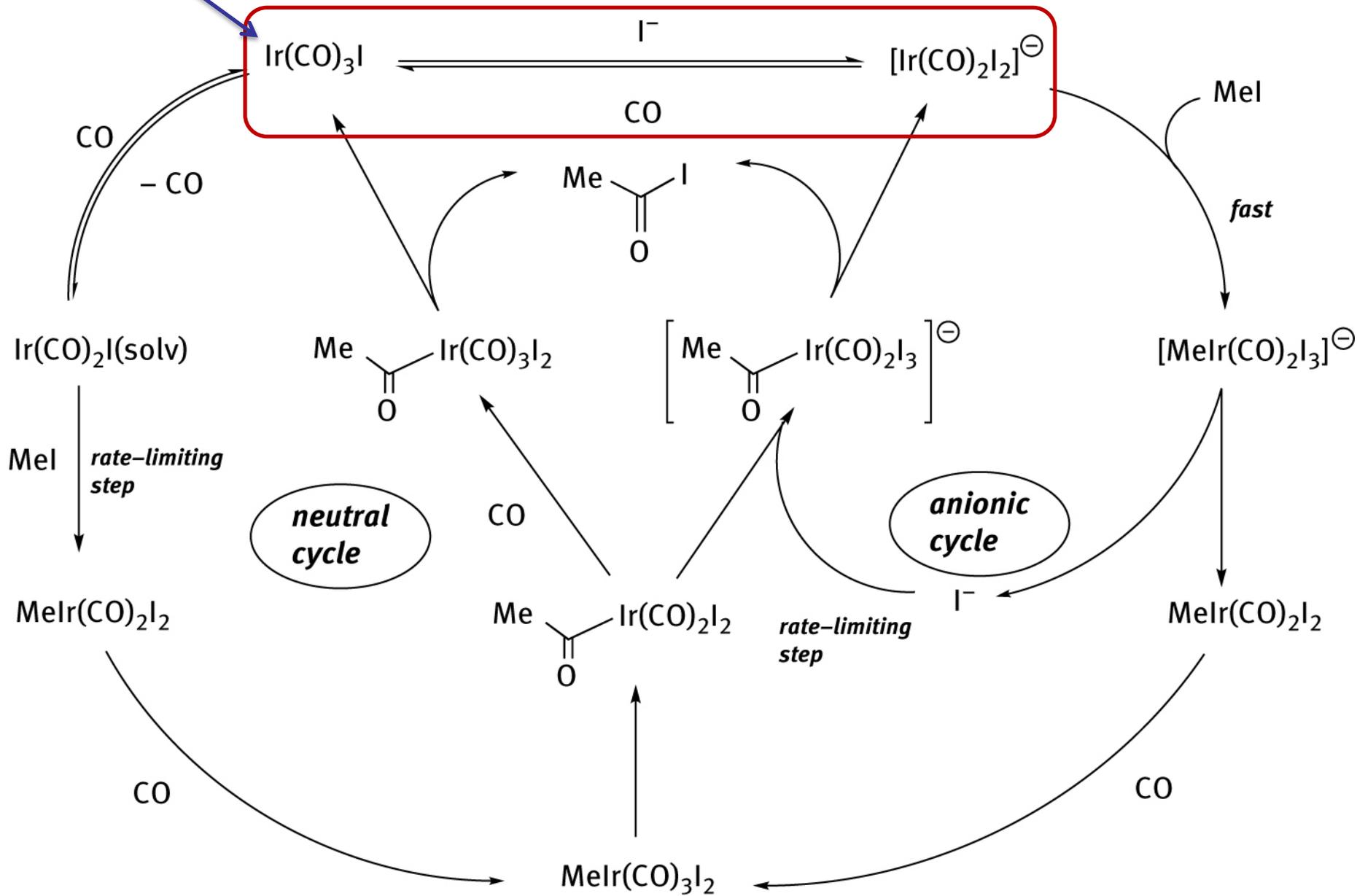
Energia libera di attivazione per la metil migrazione:

Sperimentali: $\Delta G^\ddagger = 128.5 \text{ kJ/mol}$ (Ir); $\Delta G^\ddagger = 81.1 \text{ kJ/mol}$ (Rh)

Teorici: $\Delta G^\ddagger = 116.3 \text{ kJ/mol}$ (Ir); $\Delta G^\ddagger = 72.2 \text{ kJ/mol}$ (Rh)

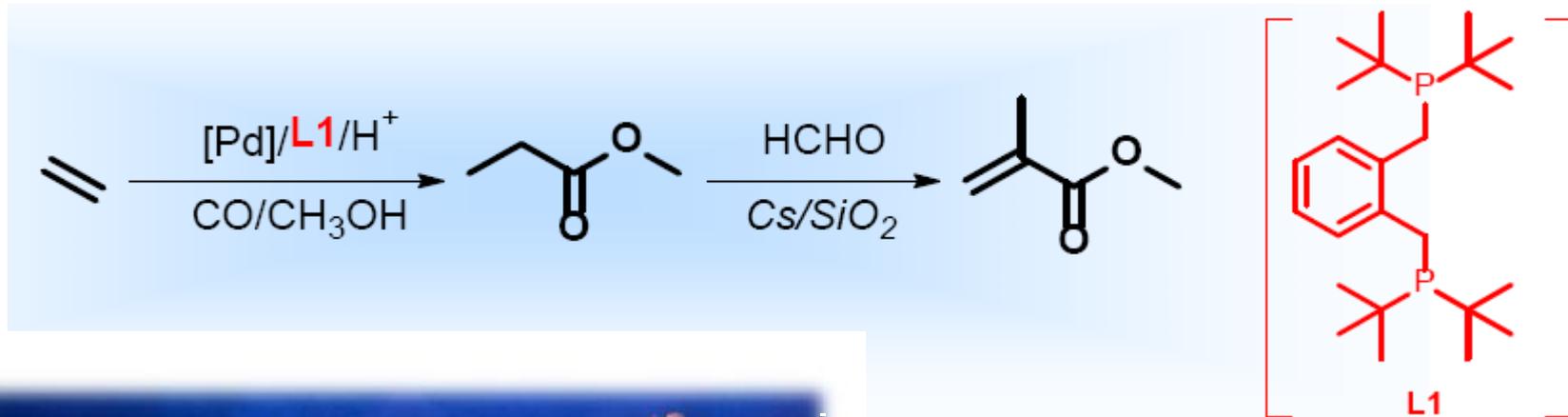
The catalytic cycles

Resting state



Il processo Lucite

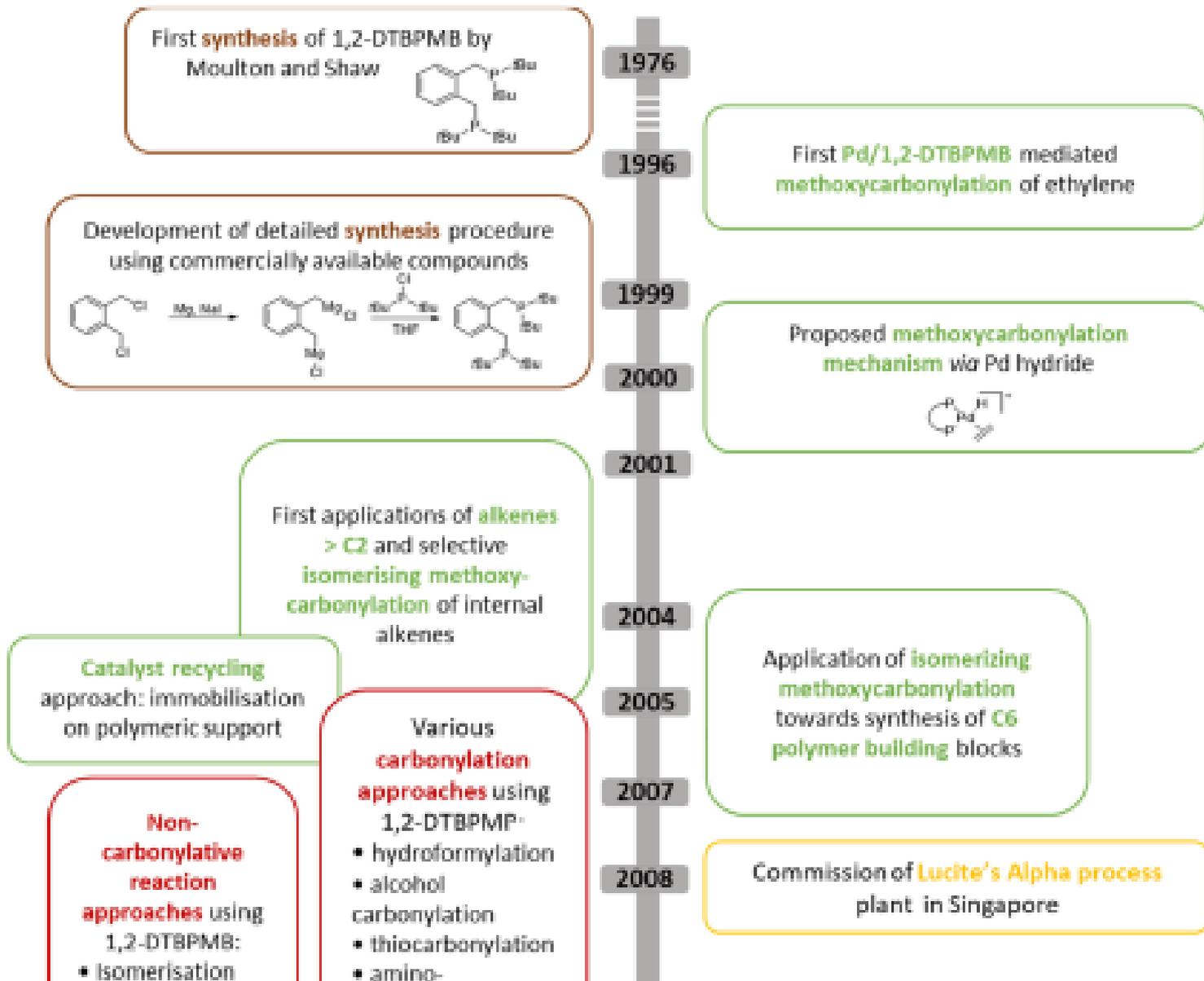
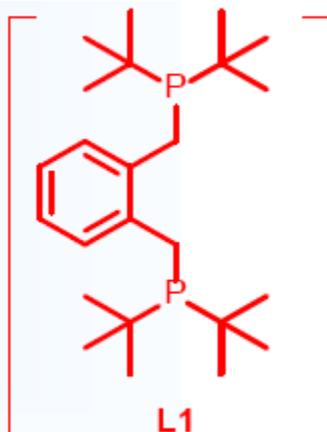
Metossi carbonilazione dell'etilene



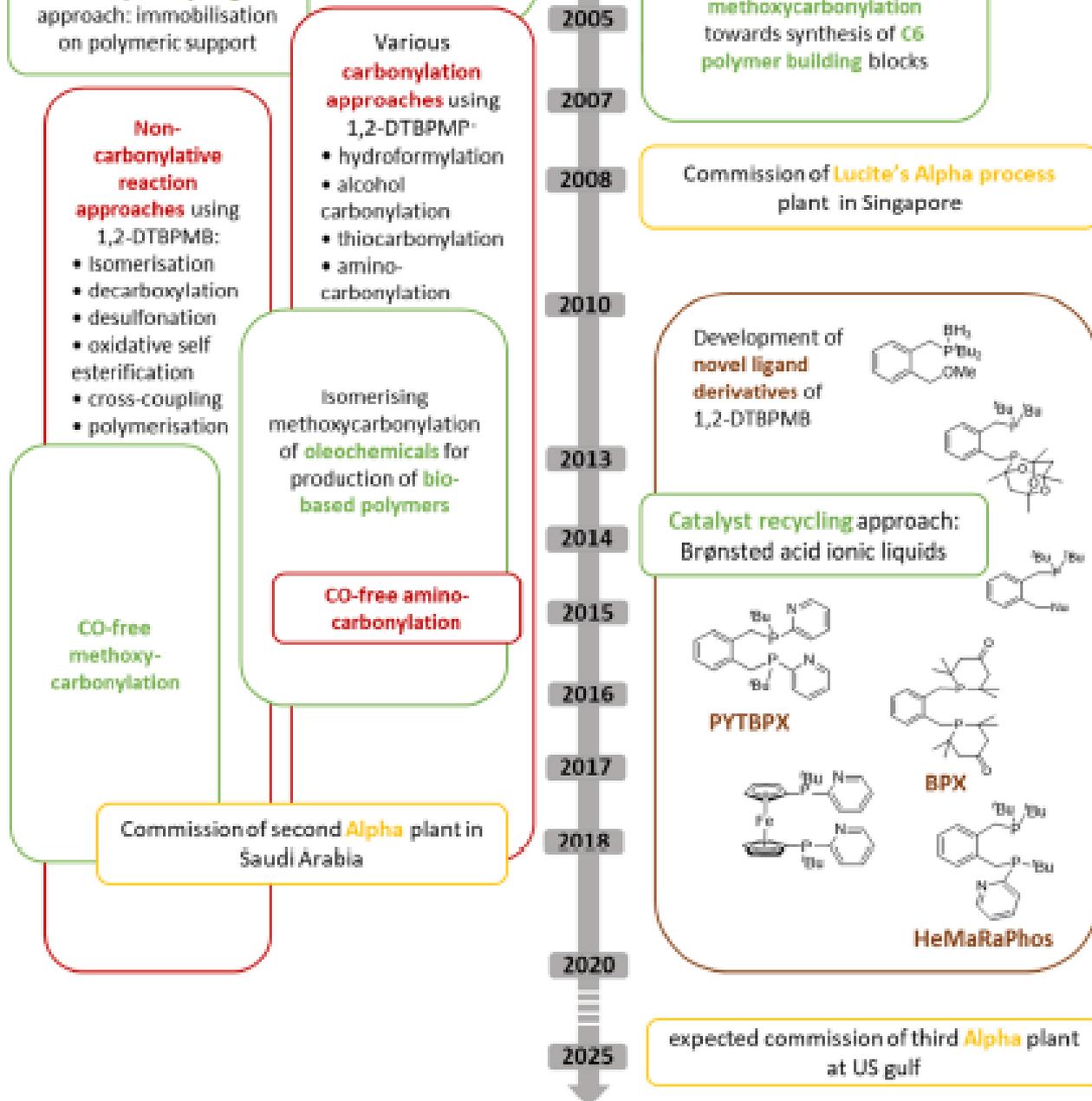
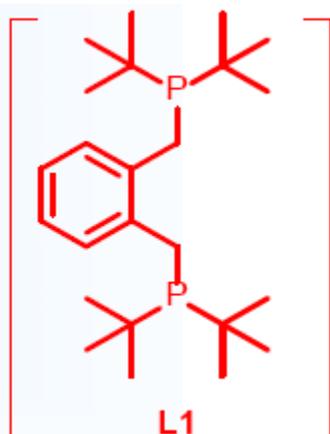
Lucite alpha I: 120,000 t/y in Singapore

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

L'unicità della difosfina



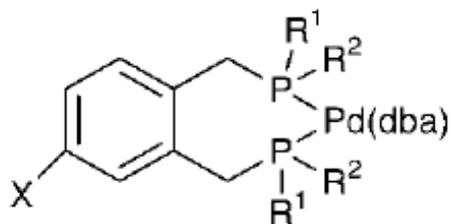
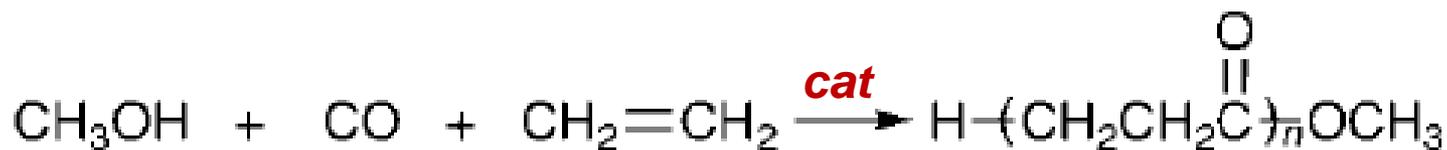
L'unicità della difosfina



key

- Synthesis and derivatives
- reactions other than methoxy-/hydroxycarbonylation
- Industrial application
- methoxy/hydroxycarbonylation

Metossi carbonilazione dell'etilene



	Complex	Activity ^b	Selectivity ^c (%)	P-Pd-P bite angle ^d (°)
1	R ¹ = R ² = Bu ^t , X = H	12 000	99.9	103.9
2	R ¹ = R ² = Bu ^t , X = NO ₂	11 500	99.9	
3	R ¹ = R ² = Bu ^t , X = OMe	11 800	99.9	
4	R ¹ = R ² = Pr ⁱ , X = H	200	20	104.3
5	R ¹ = R ² = Cy, X = H	200	25	103.9
6	R ¹ = R ² = Ph, X = H	400	20	104.6
7	R ¹ = Bu ^t , R ² = Cy, X = H	500	30	

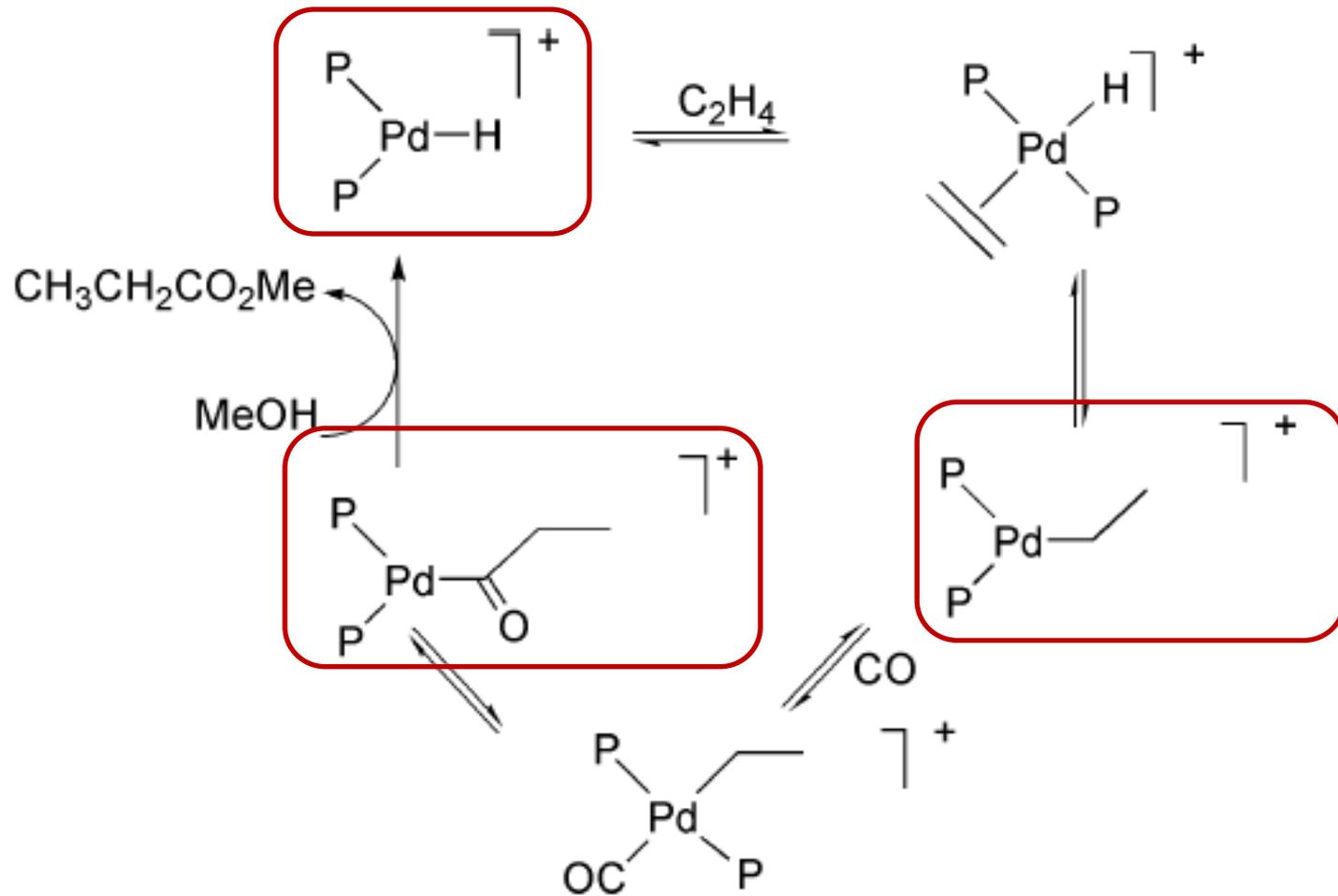
Condizioni di reazione:

$n_{\text{Pd}} = 0.01 \text{ mmol}$; $\text{CH}_3\text{OH } V = 300 \text{ mL}$; $T = 80 \text{ }^\circ\text{C}$;

$P_{\text{tot}} = 10 \text{ bar}$; $n_{\text{CF}_3\text{SO}_3\text{H}} = 0.2 \text{ mmol}$; $t = 3 \text{ h}$.

^b $\text{mol}_{\text{Et}}/\text{mol}_{\text{Pd}} \cdot \text{h}$.

Il meccanismo



Lo schema del processo Lucite

