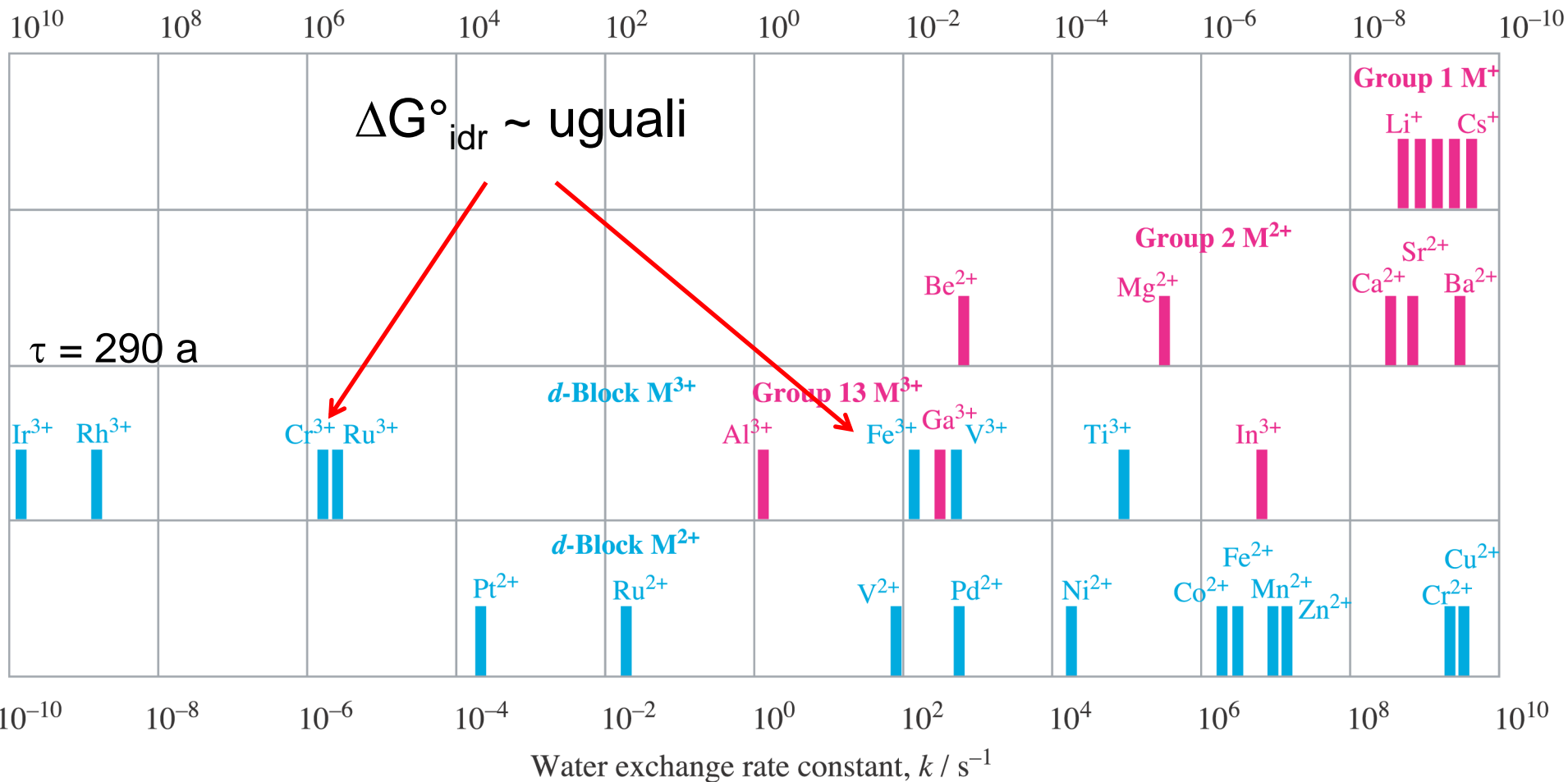


Average residence time for H₂O molecule in first hydration shell / s

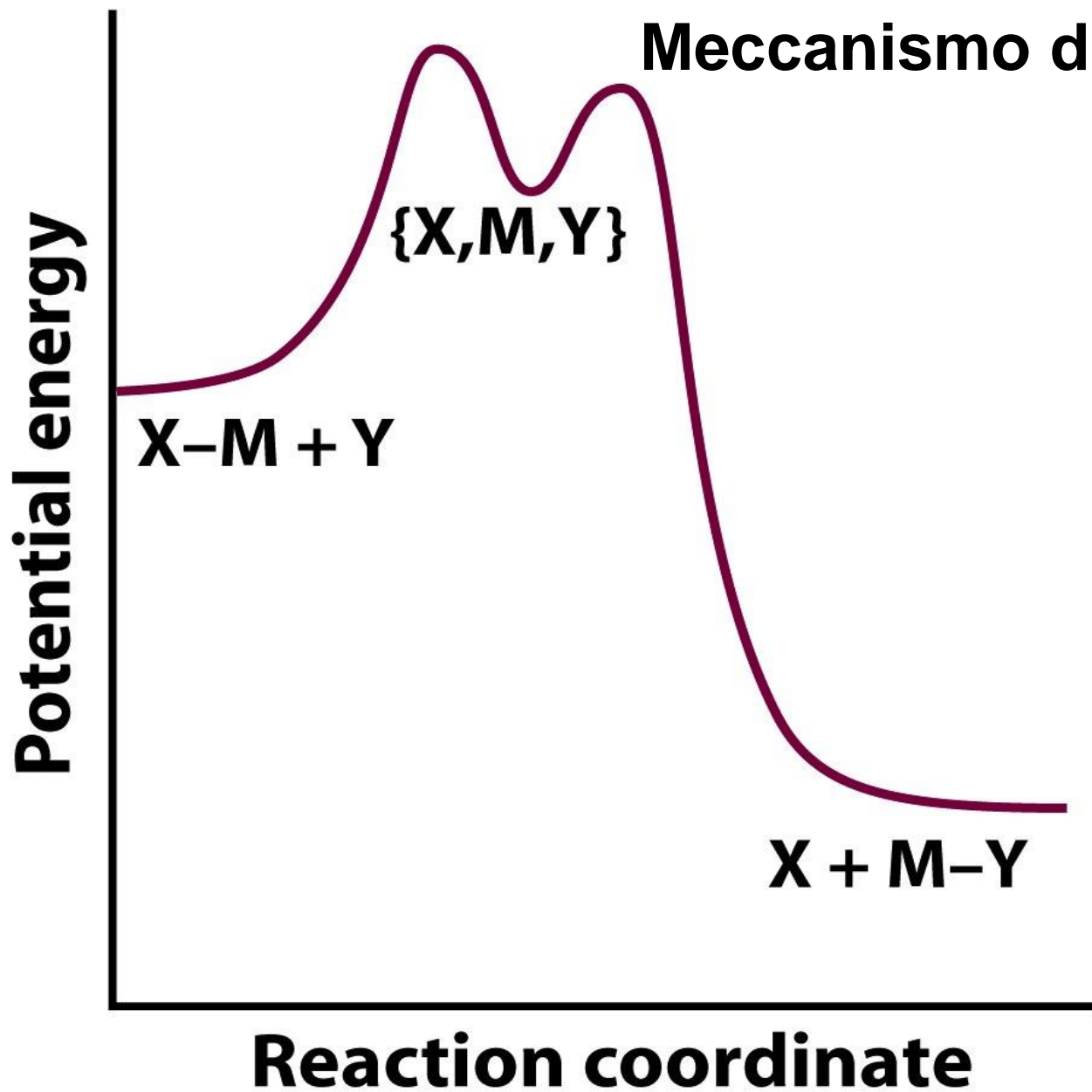


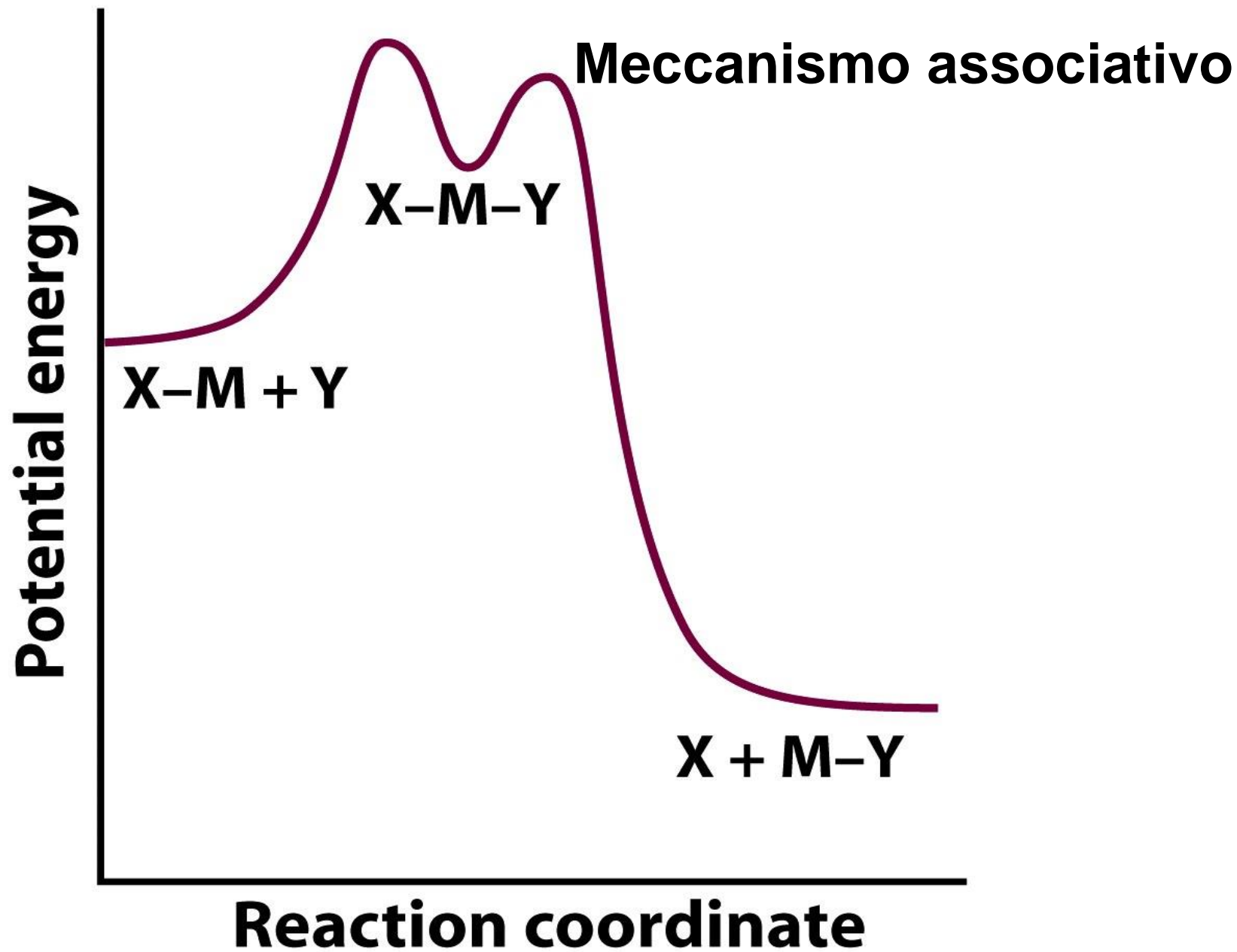
Kinetically inert

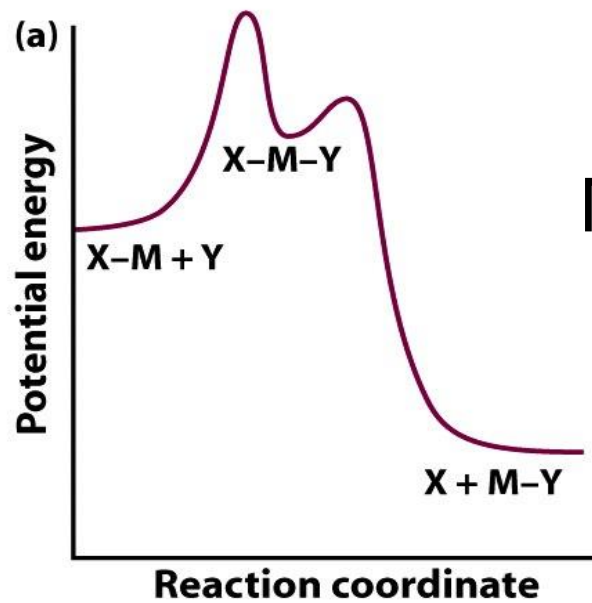
Kinetically labile

$t_{1/2} \approx 1 \text{ min}$

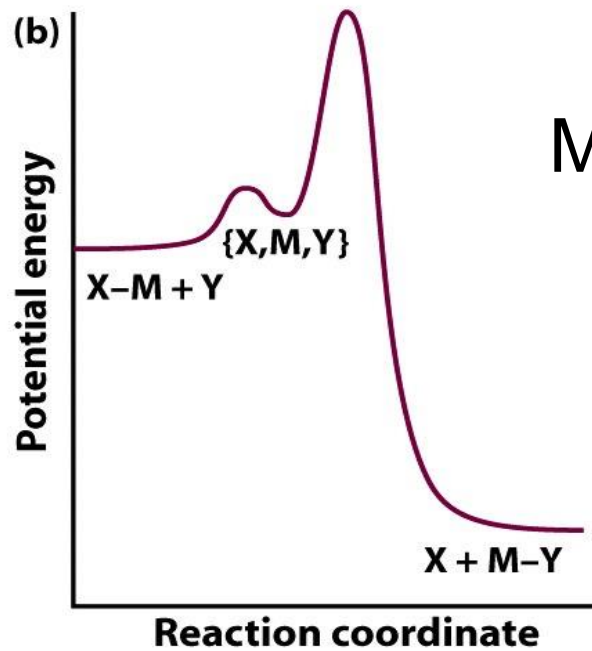
Meccanismo dissociativo



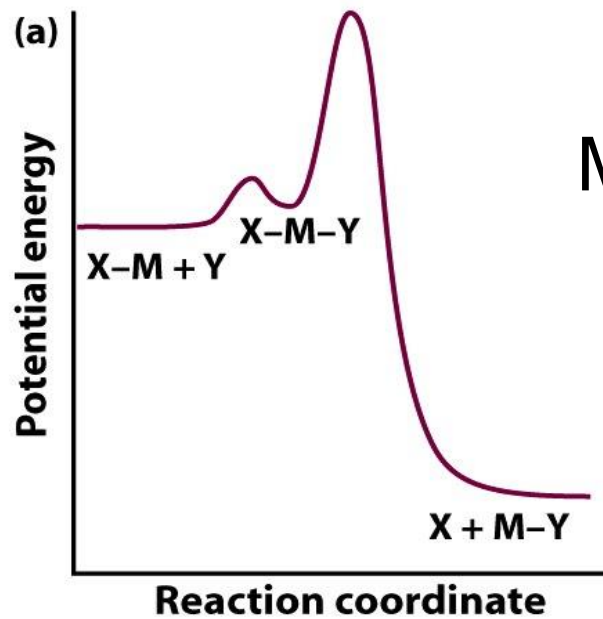




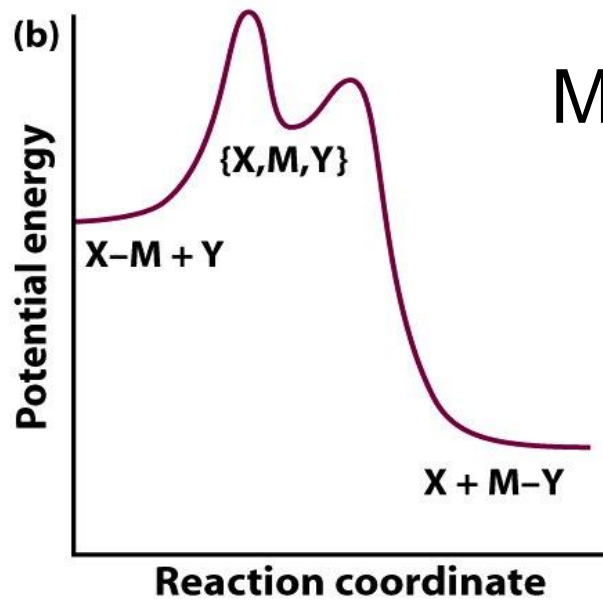
Meccanismo associativo
stadio lento associativo



Meccanismo dissociativo
stadio lento associativo



Meccanismo associativo
stadio lento dissociativo



Meccanismo dissociativo
stadio lento dissociativo

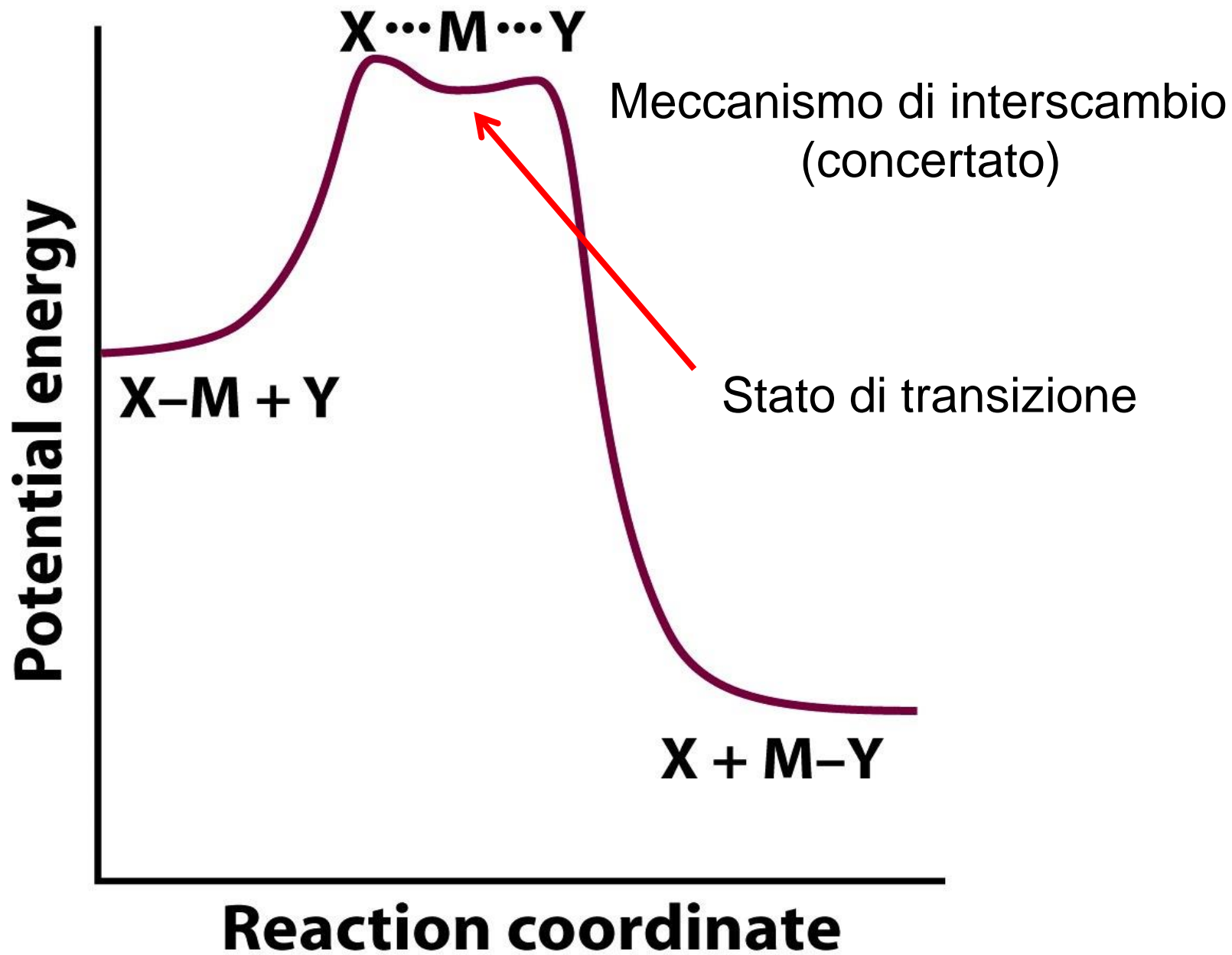
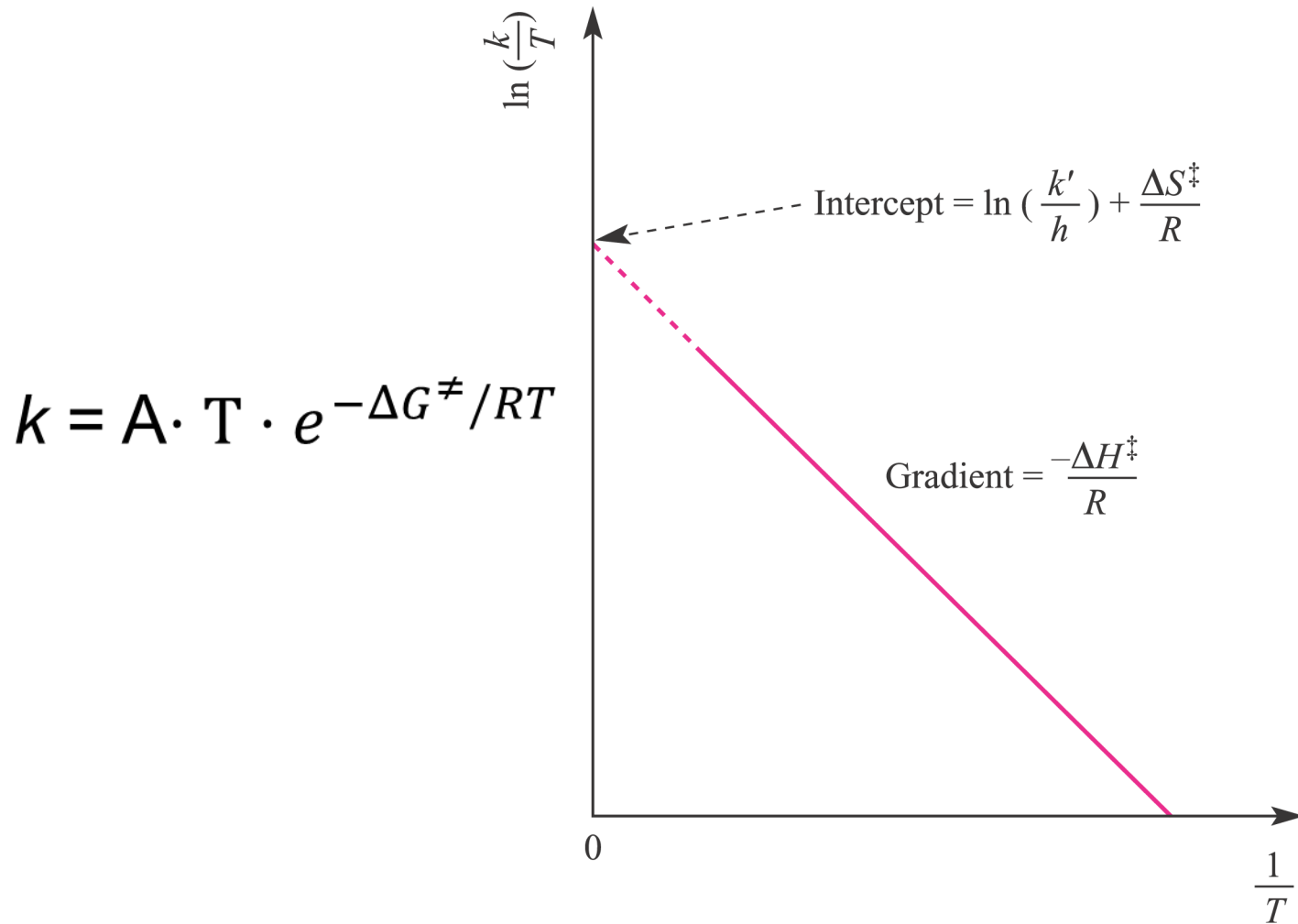


Diagramma di Eyring e parametri di attivazione



$$k = A \cdot T \cdot e^{-\Delta G^\ddagger / RT}$$

$$\ln(k/T) = \ln A - \Delta H^\ddagger / RT + \Delta S^\ddagger / R$$

Se ΔS^\ddagger è ampiamente negativo \rightarrow
meccanismo associativo

$$\frac{d(\ln k)}{dP} = - \frac{\Delta V^\ddagger}{RT}$$

ΔV^\ddagger = volume di attivazione

$\Delta V^\ddagger \ll 0 \rightarrow$ meccanismo associativo

$\Delta V^\ddagger \gg 0 \rightarrow$ meccanismo dissociativo

Sostituzioni su complessi planari quadrati

Reactants	$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$\Delta S^\ddagger / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta V^\ddagger / \text{cm}^3 \text{mol}^{-1}$
$[\text{Pt}(\text{dien})\text{Cl}]^+ + \text{H}_2\text{O}$	+84	-63	-10
$[\text{Pt}(\text{dien})\text{Cl}]^+ + [\text{N}_3]^-$	+65	-71	-8.5
<i>trans</i> - $[\text{PtCl}_2(\text{PEt}_3)_2] + \text{py}$	+14	-25	-14
<i>trans</i> - $[\text{PtCl}(\text{NO}_2)(\text{py})_2] + \text{py}$	+12	-24	-9

Meccanismo di tipo A o I_a

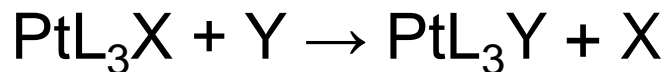
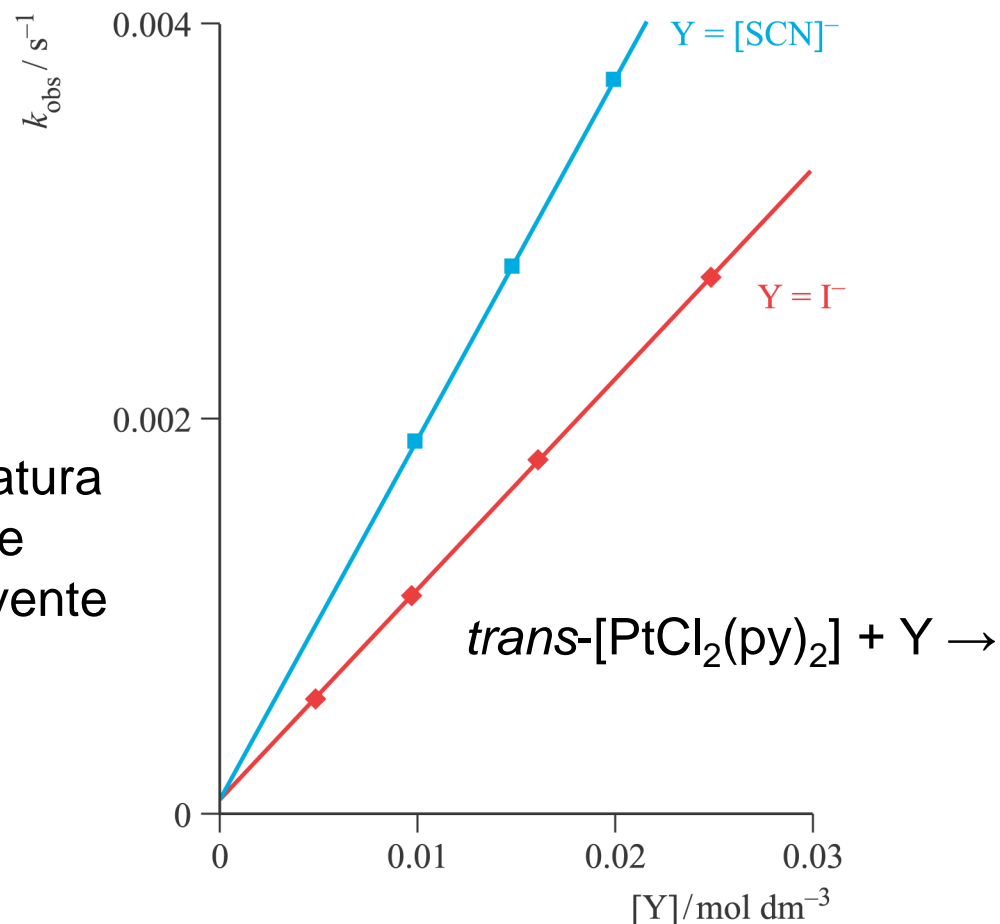
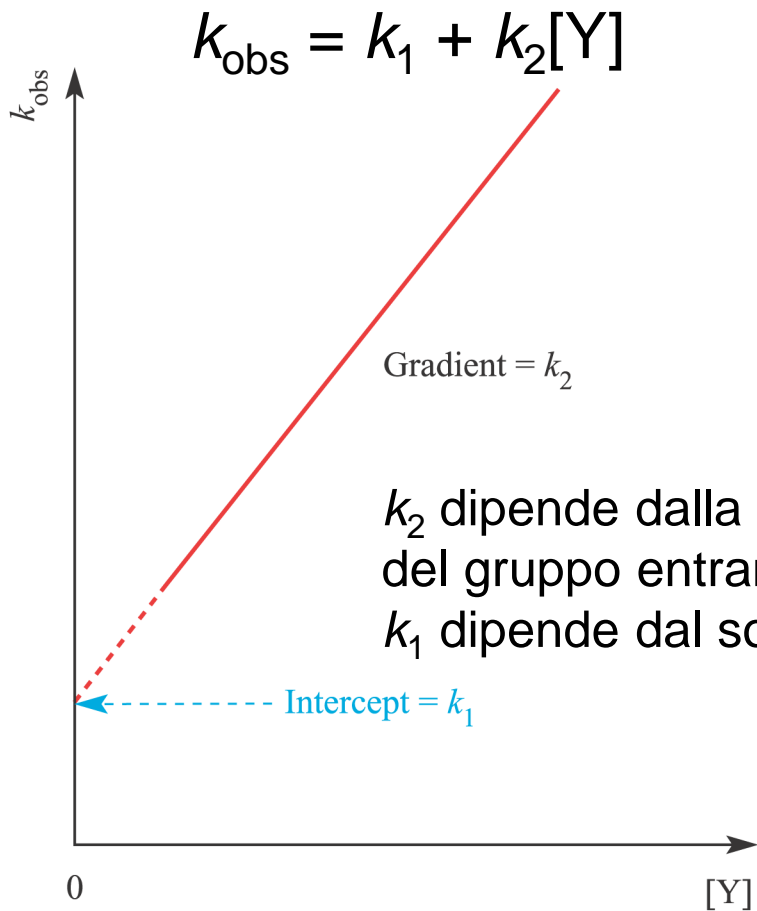
Le costanti cinetiche per la sostituzione di Cl^- con H_2O in



sono tutte molto simili



Meccanismo di tipo associativo



equazione cinetica sperimentale

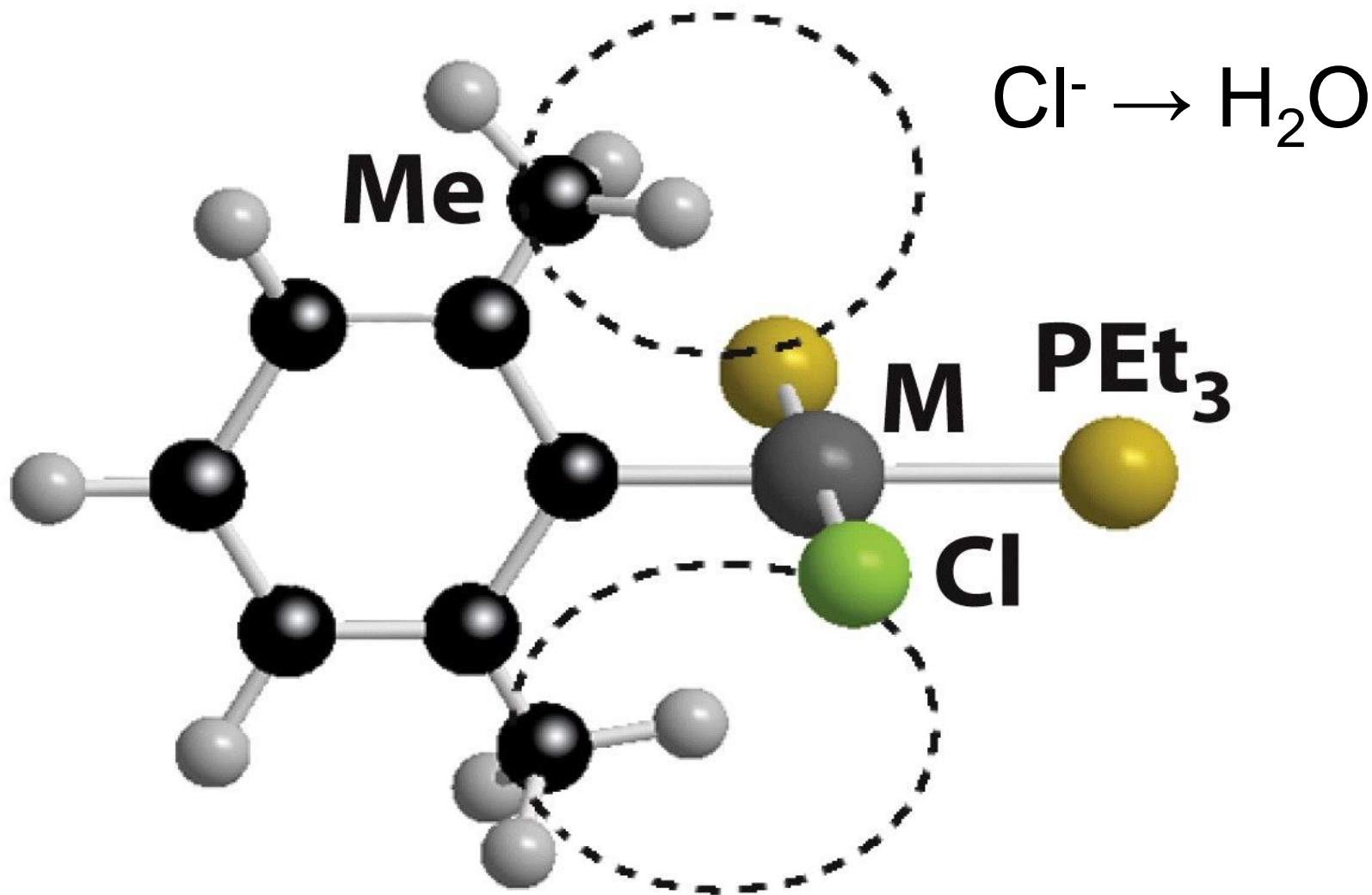
$$v = -\frac{d[\text{PtL}_3\text{X}]}{dt} = k_1[\text{PtL}_3\text{X}] + k_2[\text{PtL}_3\text{X}][\text{Y}] = k_{\text{obs}}[\text{PtL}_3\text{X}]$$

(in condizioni di pseudo primo ordine)

$$v = -d[\text{PtL}_3\text{X}]/dt = k_3[\text{PtL}_3\text{X}][\text{S}] + k_2[\text{PtL}_3\text{X}][\text{Y}]$$

$$k_1 = k_3[\text{S}]$$

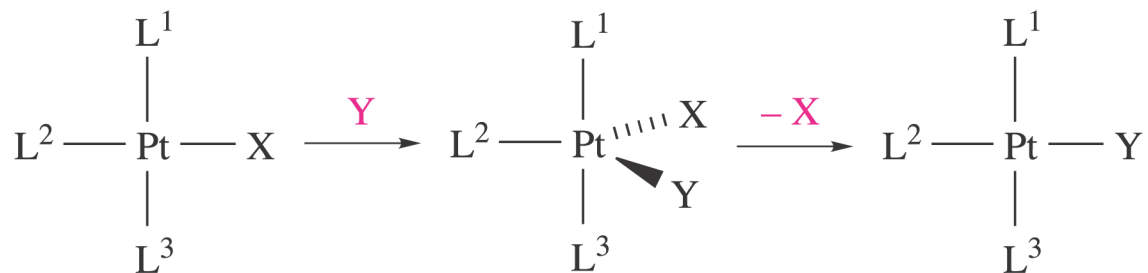
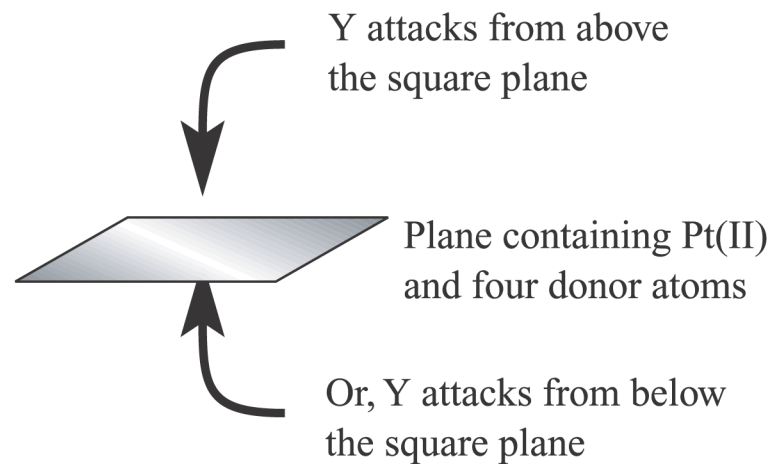
k_1 e k_2 diminuiscono al crescere dell'ingombro sterico sia di Y che di L

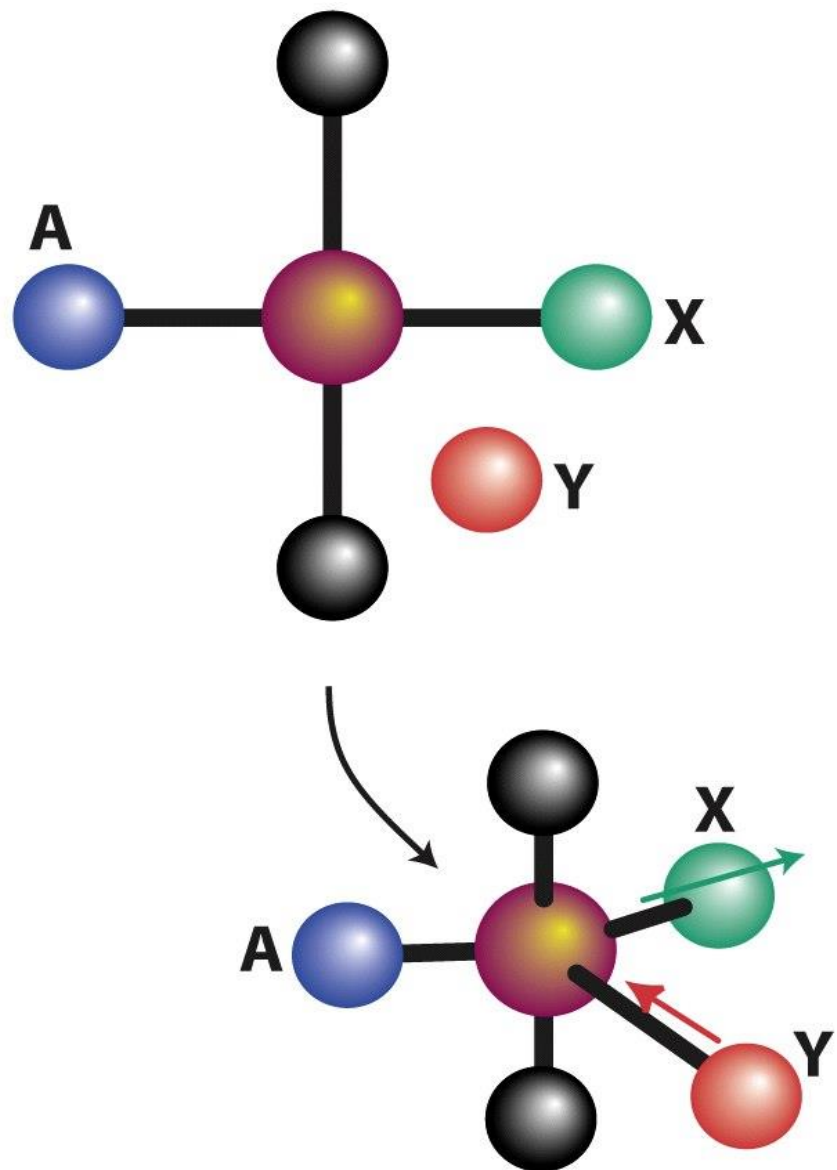


$k = 8 \times 10^{-2} \text{ s}^{-1}$ per L = py

$k = 1.0 \times 10^{-6} \text{ s}^{-1}$ per L = 2,6-dimetilpiridina

Ritenzione di configurazione

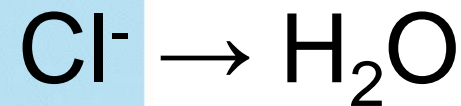




Effetto *trans*: è l'effetto che ha il legante in *trans* al gruppo uscente sulla sua velocità di sostituzione (i.e.: grande effetto *trans* = alta velocità di sostituzione).

Di conseguenza, in un complesso planare-quadrato la scelta del gruppo uscente – e quindi la natura del prodotto – è determinata in buona parte anche dalla natura del legante che gli sta in *trans* (se la sostituzione avviene sotto controllo cinetico).

Table 20.6 The effect of the *trans* ligand in reactions of *trans*-[PtCl(PEt₃)₂L]

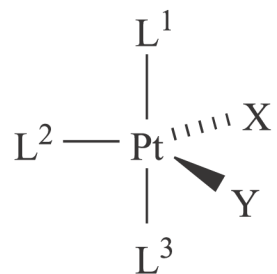


L	k_1/s^{-1}	$k_2/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
CH ₃ ⁻	1.7×10^{-4}	6.7×10^{-2}
C ₆ H ₅ ⁻	3.3×10^{-5}	1.6×10^{-2}
Cl ⁻	1.0×10^{-6}	4.0×10^{-4}
H ⁻	1.8×10^{-2}	4.2
PEt ₃	1.7×10^{-2}	3.8

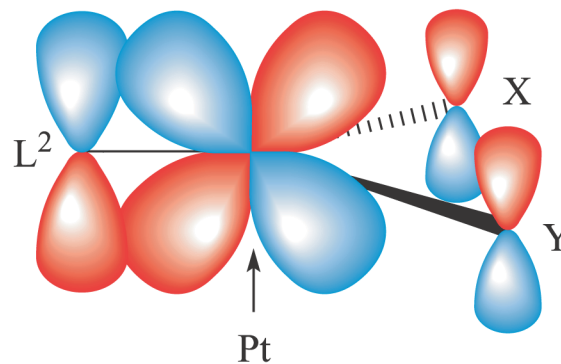
H₂O ≈ OH⁻ ≈ NH₃ ≈ py < Cl⁻ < Br⁻ < I⁻ ≈ NO₂⁻ < Ph⁻ < Me⁻ < PR₃ ≈ H⁻ « CO ≈ CN⁻

Sequenza sperimentale di effetto *trans*

Effetto-*trans*: contributo cinetico



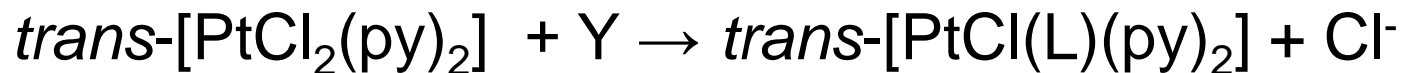
Trigonal bipyramidal
transition state or
intermediate



π -Bonding in the trigonal plane

nei complessi planari quadrati si ha (spesso) ritenzione di configurazione perché le sostituzioni avvengono (di solito) sotto controllo cinetico e l'intermedio che porta a ritenzione di configurazione è quello con l'energia di attivazione minore e non ha un tempo di vita sufficientemente lungo per riarrangiare

Sequenza di nucleofilicità del gruppo entrante

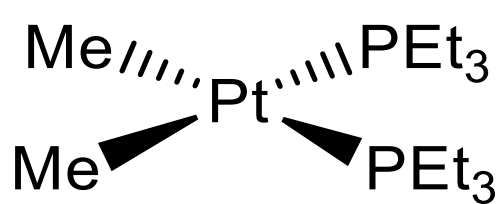


Nucleophile	Donor atom	n_{Pt}
Cl^-	Cl	3.04
I^-	I	5.42
CN^-	C	7.00
CH_3OH	O	0
$\text{C}_6\text{H}_5\text{SH}$	S	4.15
NH_3	N	3.06
$(\text{C}_6\text{H}_5)_3\text{P}$	P	8.79

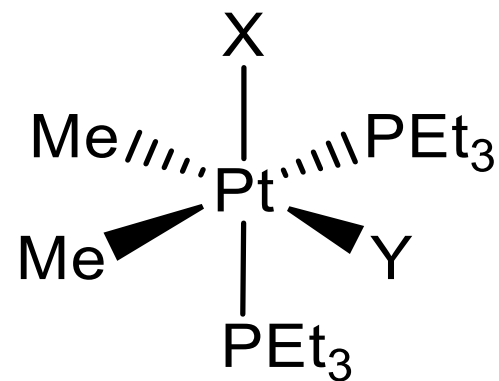
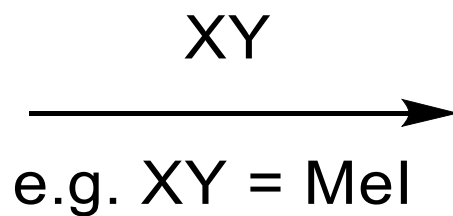
parametro di nucleofilicità: $n_{\text{Pt}} = \log k_2/k'_2(\text{MeOH})$

n_{Pt} non correla con la basicità di Brønsted di Y

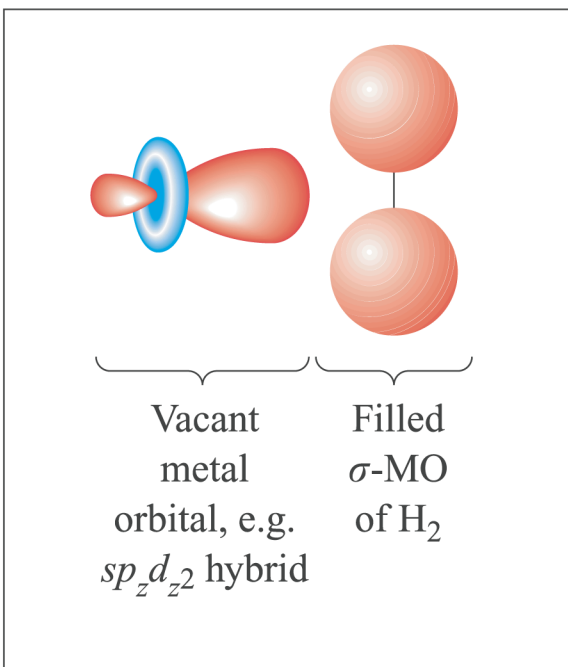
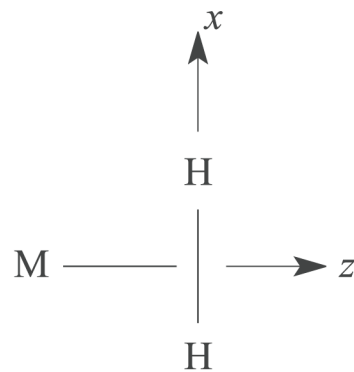
Addizione ossidativa



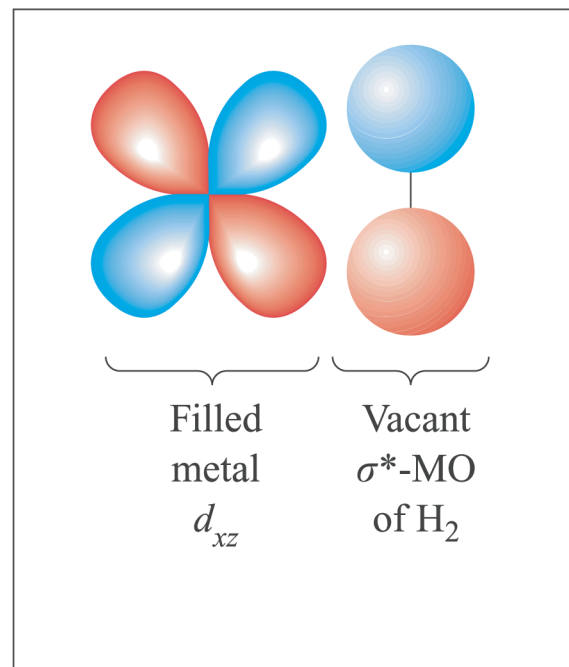
16e Pt(II)



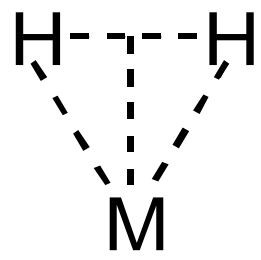
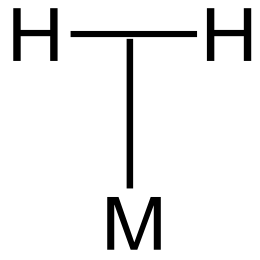
18e Pt(IV)



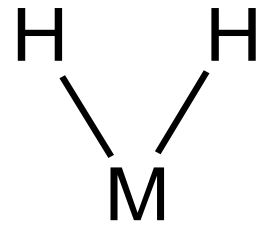
H_2 -to-M donation
 (a)



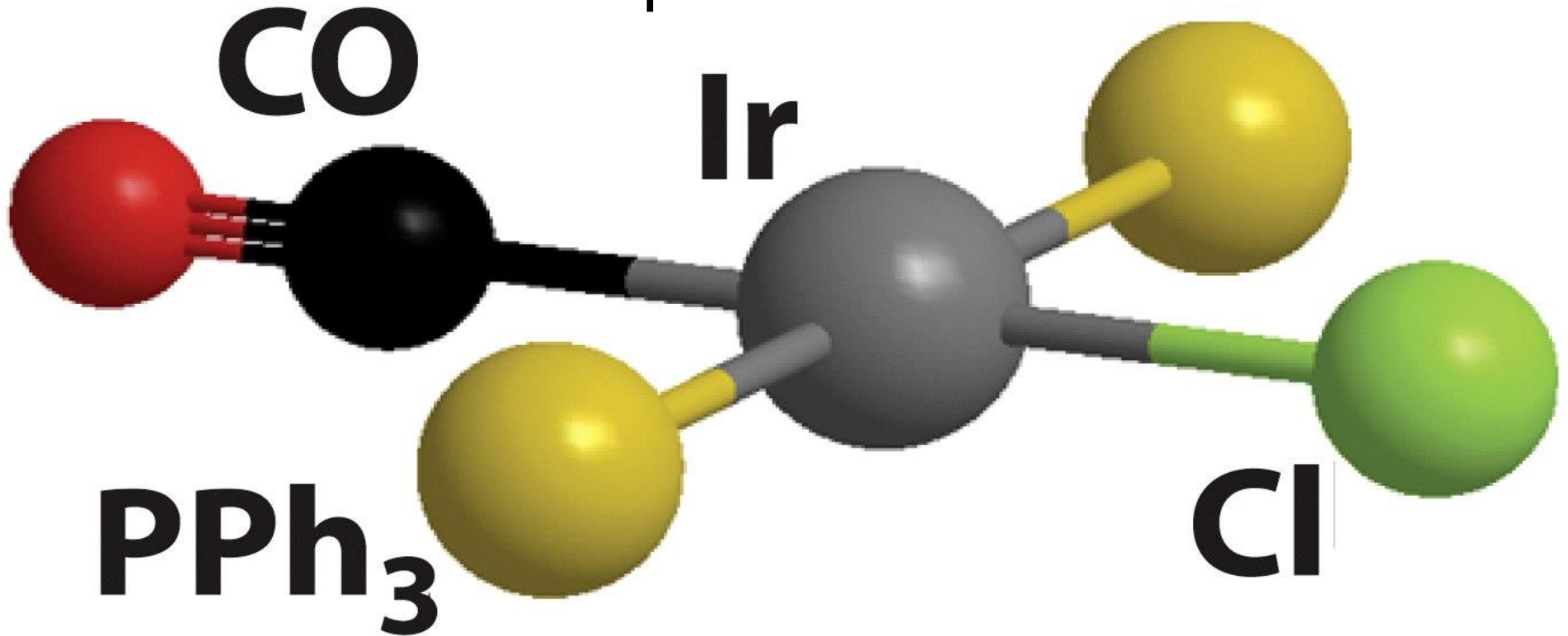
M-to- H_2 back-donation
 (b)



Addizione ossidativa



Complesso di Vaska



Addizione ossidativa

