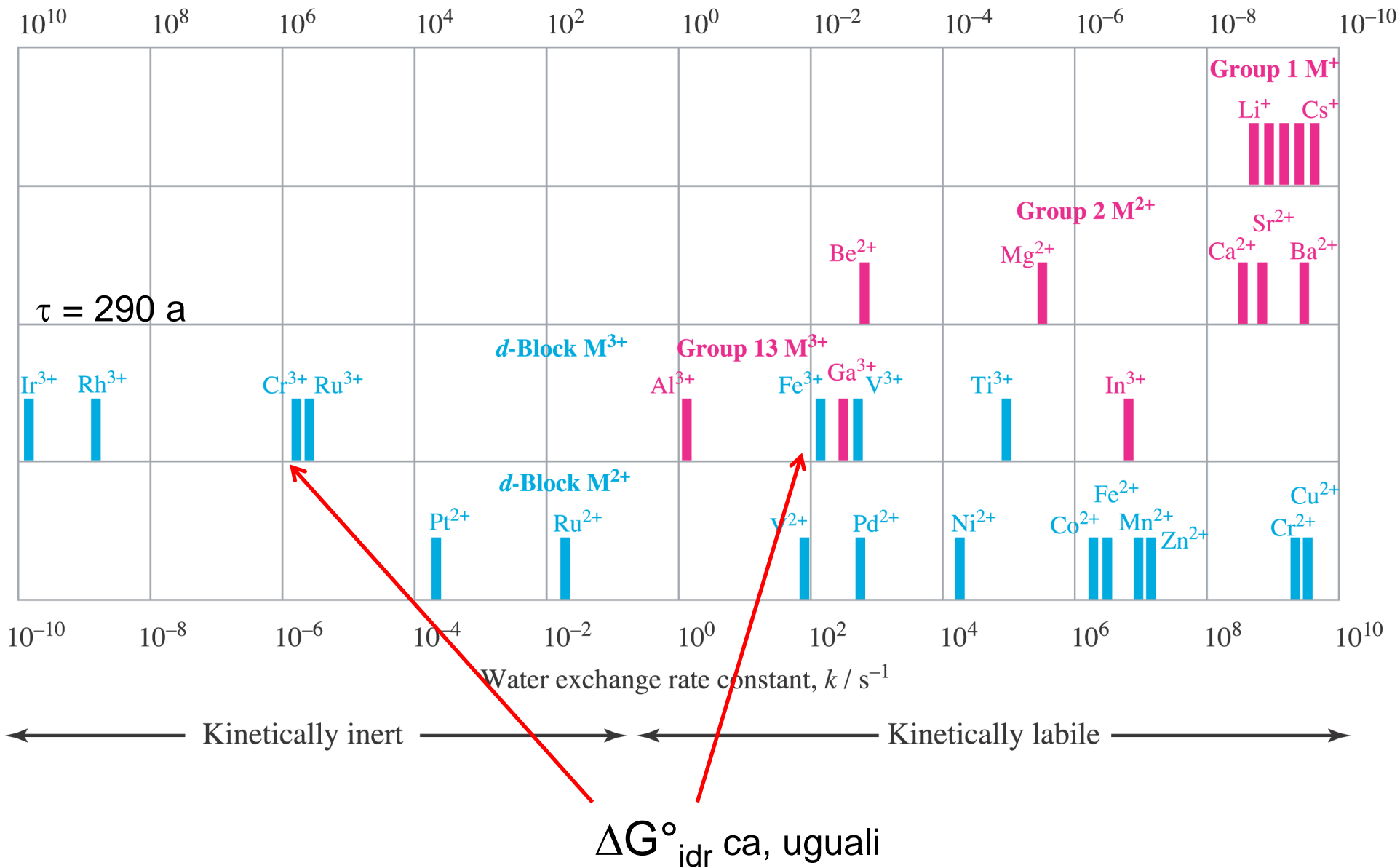
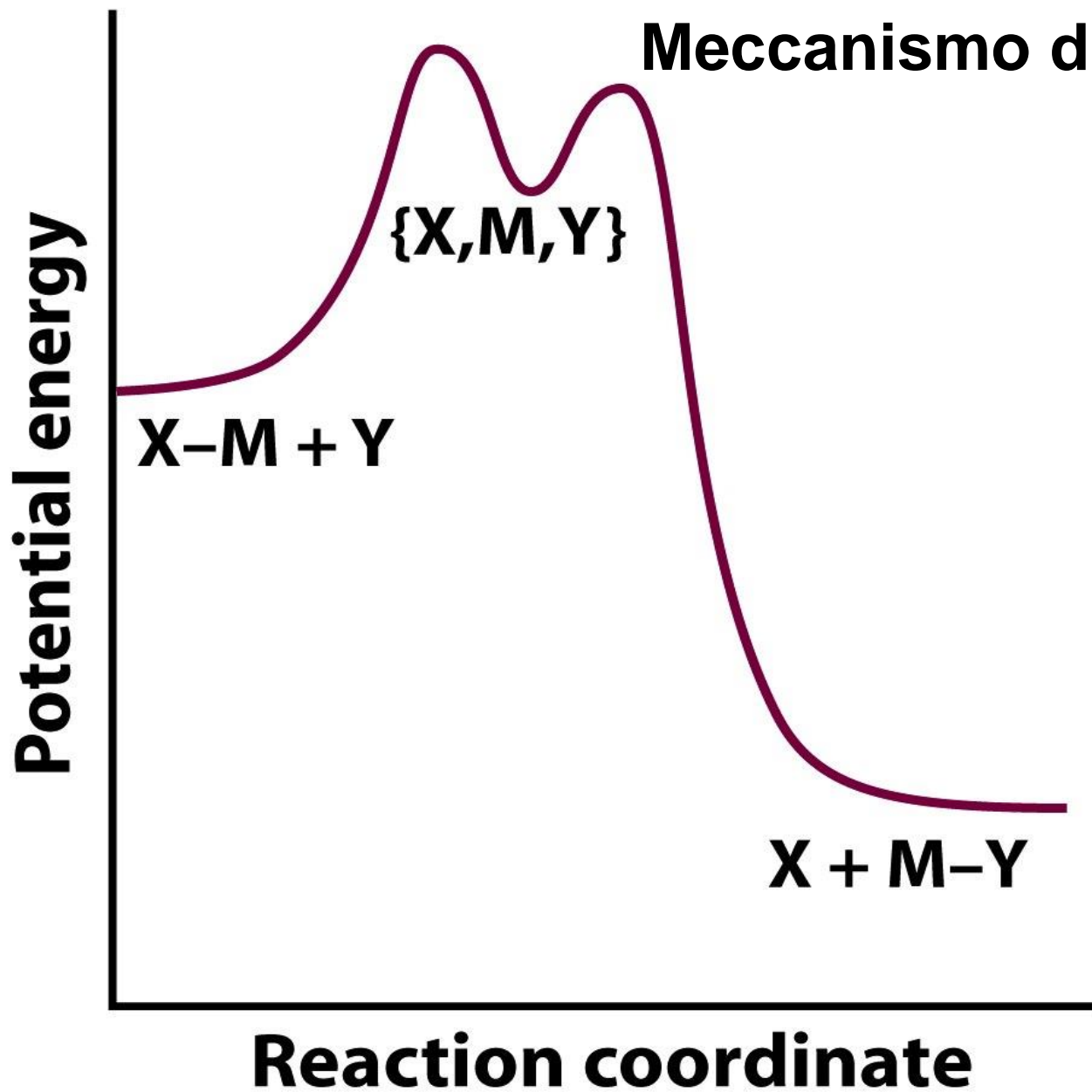
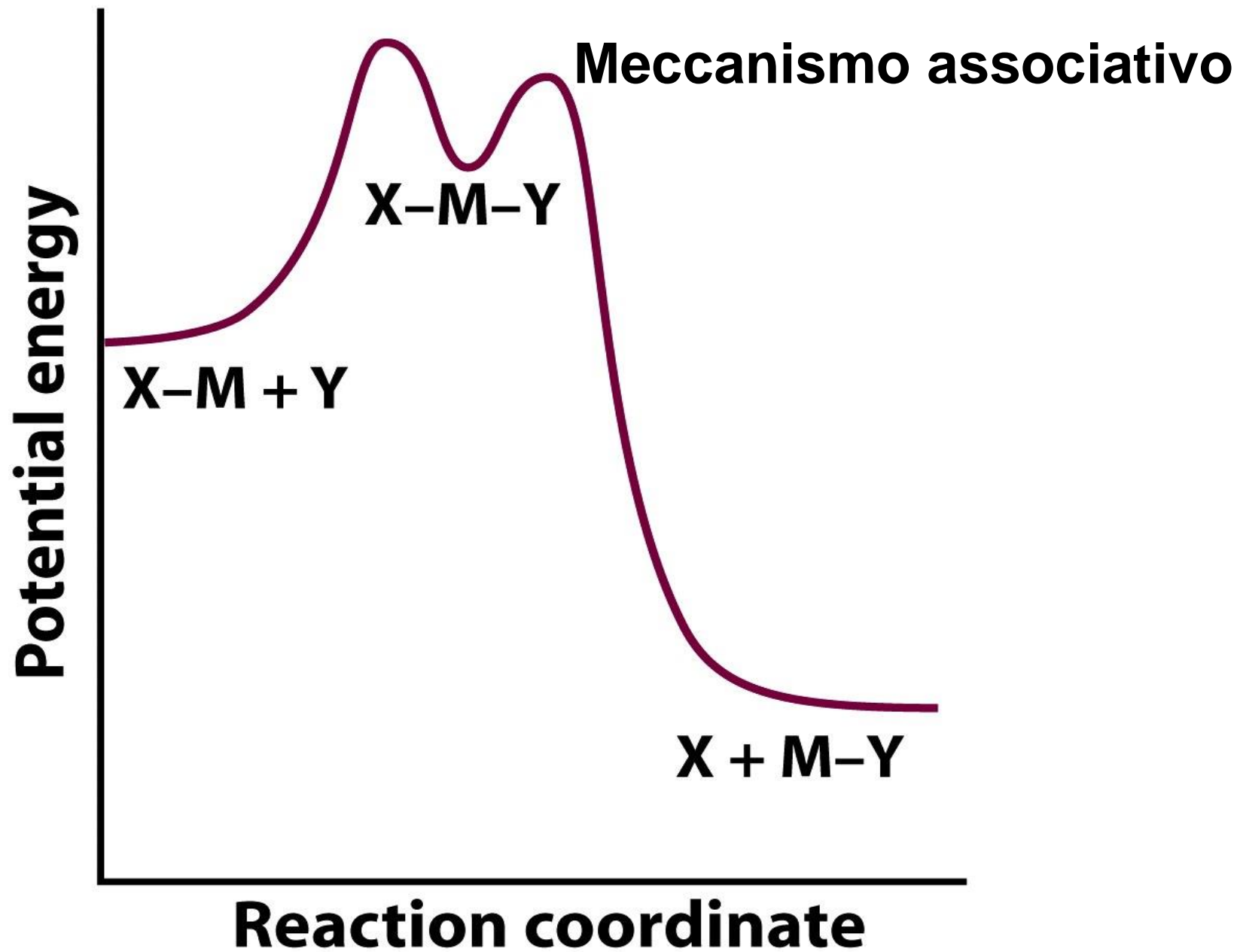


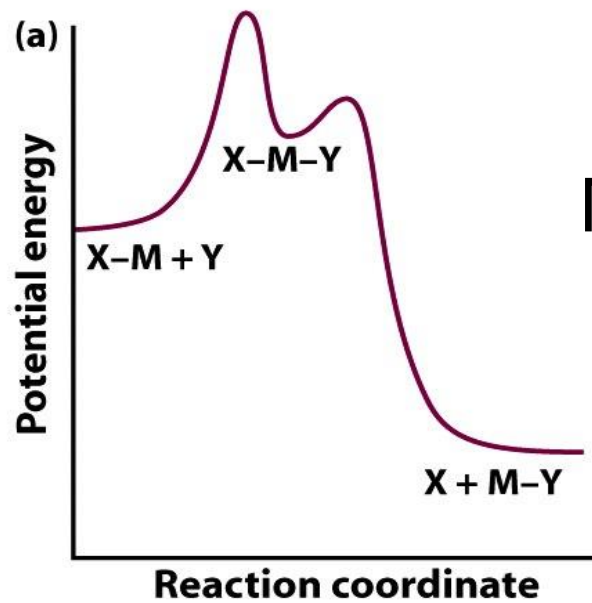
Average residence time for H<sub>2</sub>O molecule in first hydration shell / s



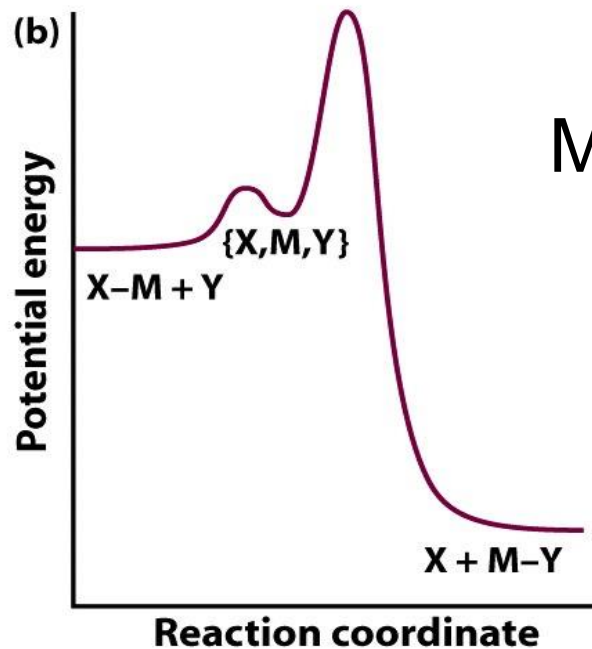
# Meccanismo dissociativo



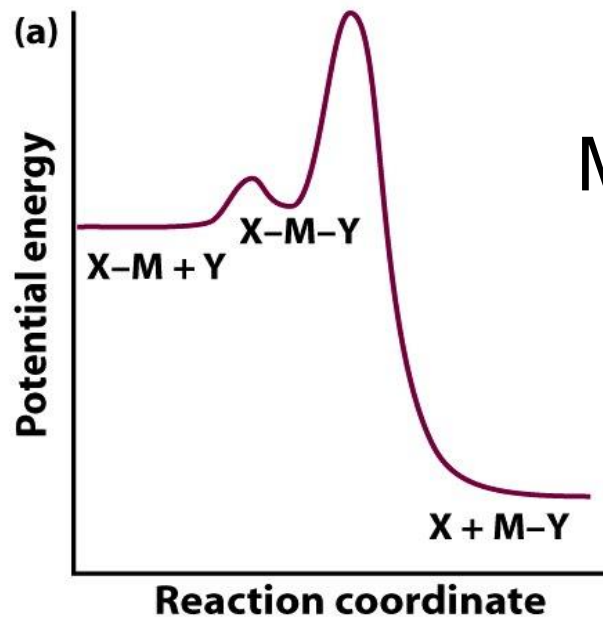




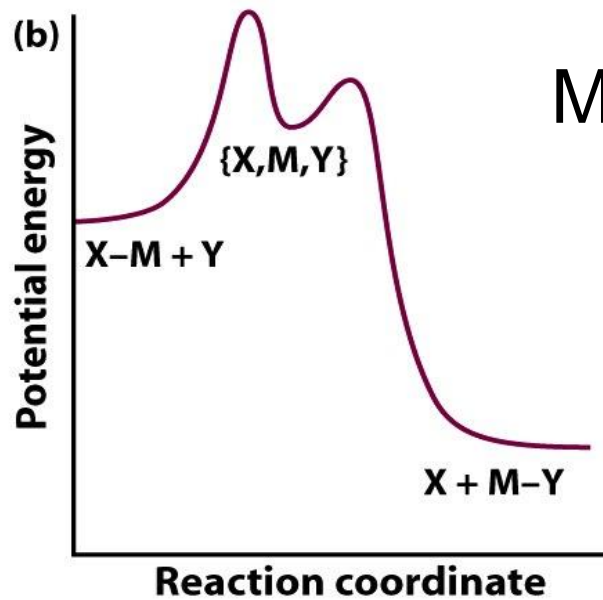
Meccanismo associativo  
stadio lento associativo



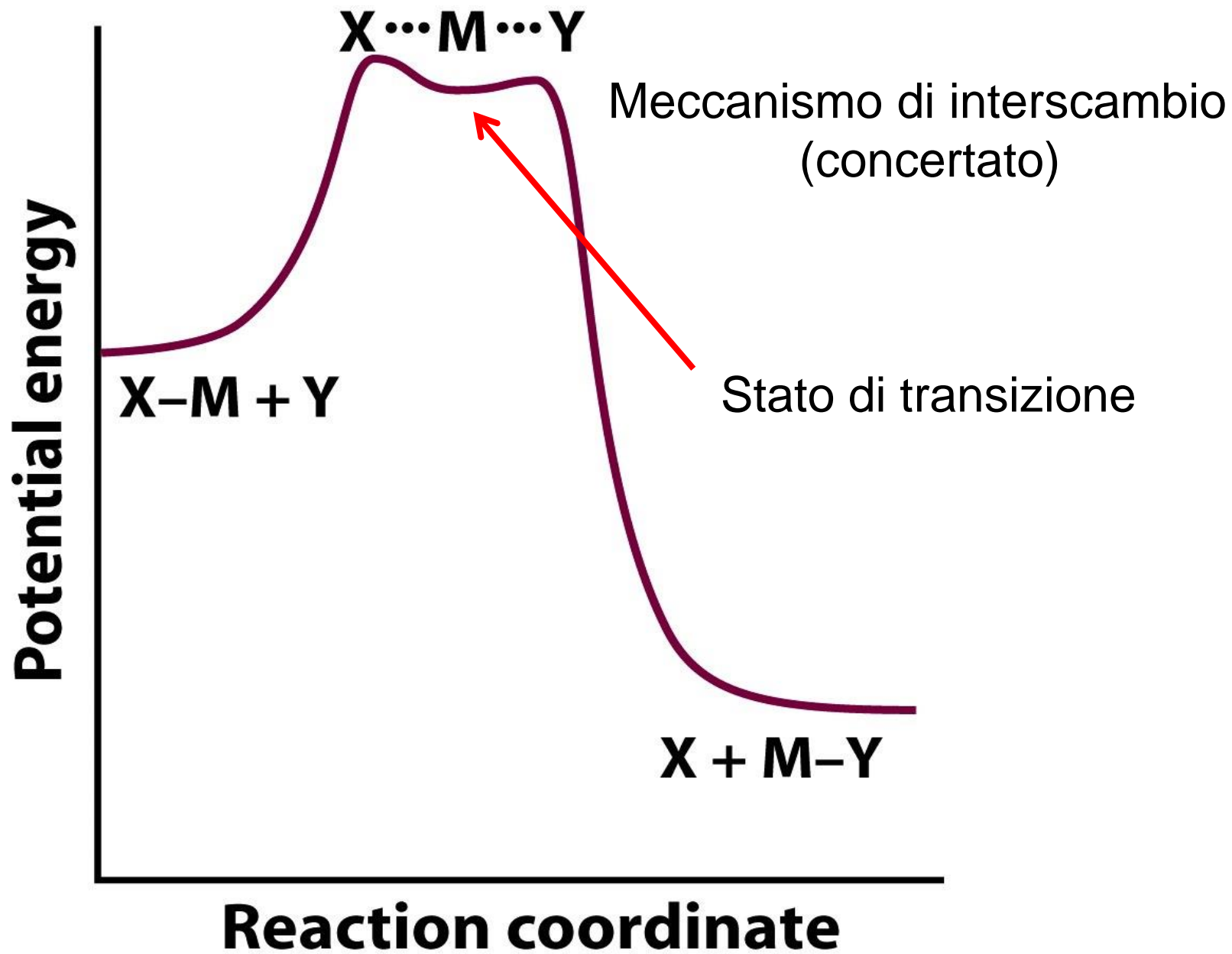
Meccanismo dissociativo  
stadio lento associativo



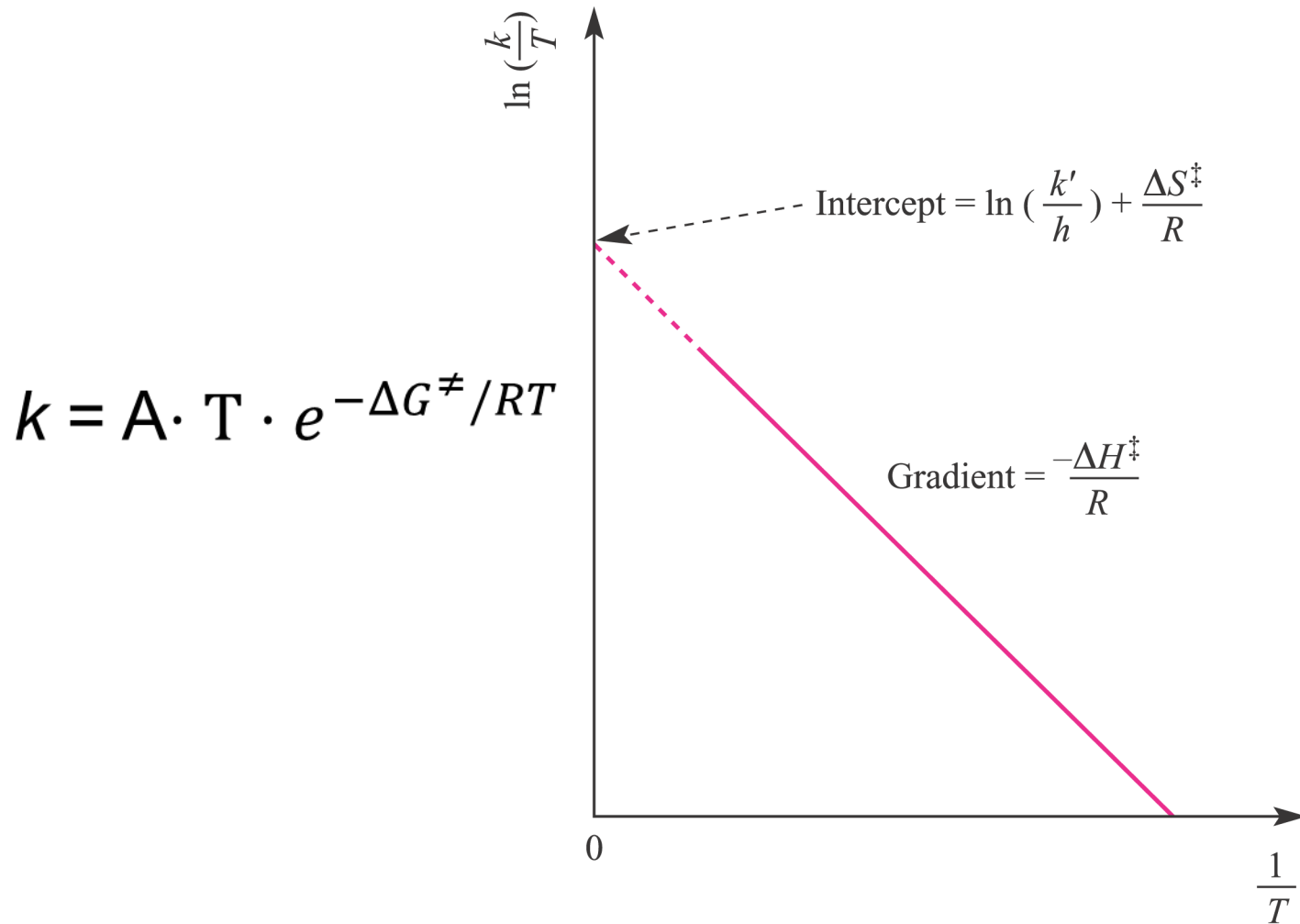
Meccanismo associativo  
stadio lento dissociativo



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  $\Delta S^\ddagger$  è ampiamente negativo  $\rightarrow$   
**meccanismo associativo**

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

$\Delta V^\ddagger$  = 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  $I_a$**

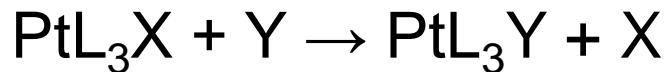
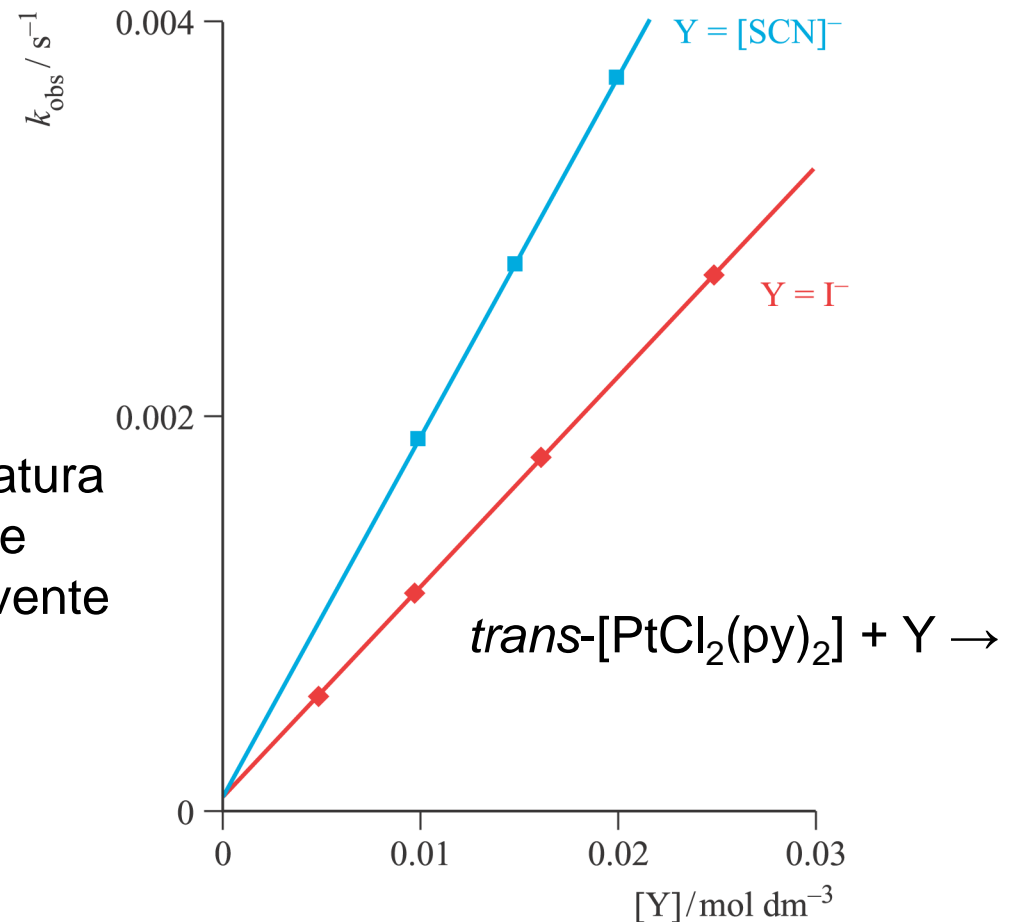
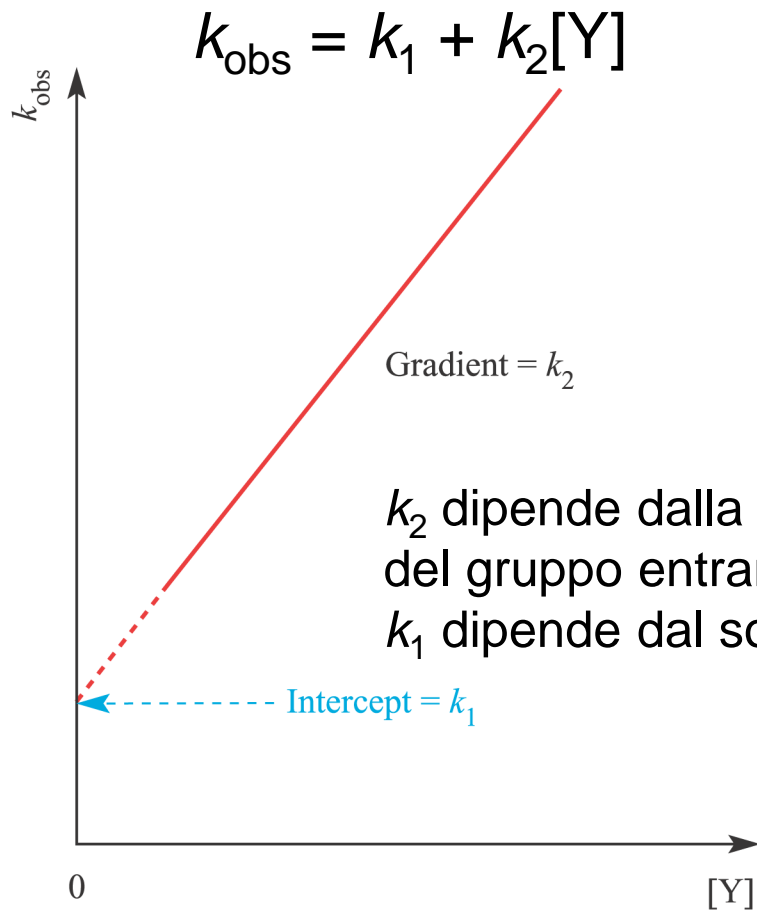
Le costanti cinetiche per la sostituzione di  $\text{Cl}^-$  con  $\text{H}_2\text{O}$  in



sono tutte molto simili



**Meccanismo di tipo associativo**



equazione cinetica sperimentale

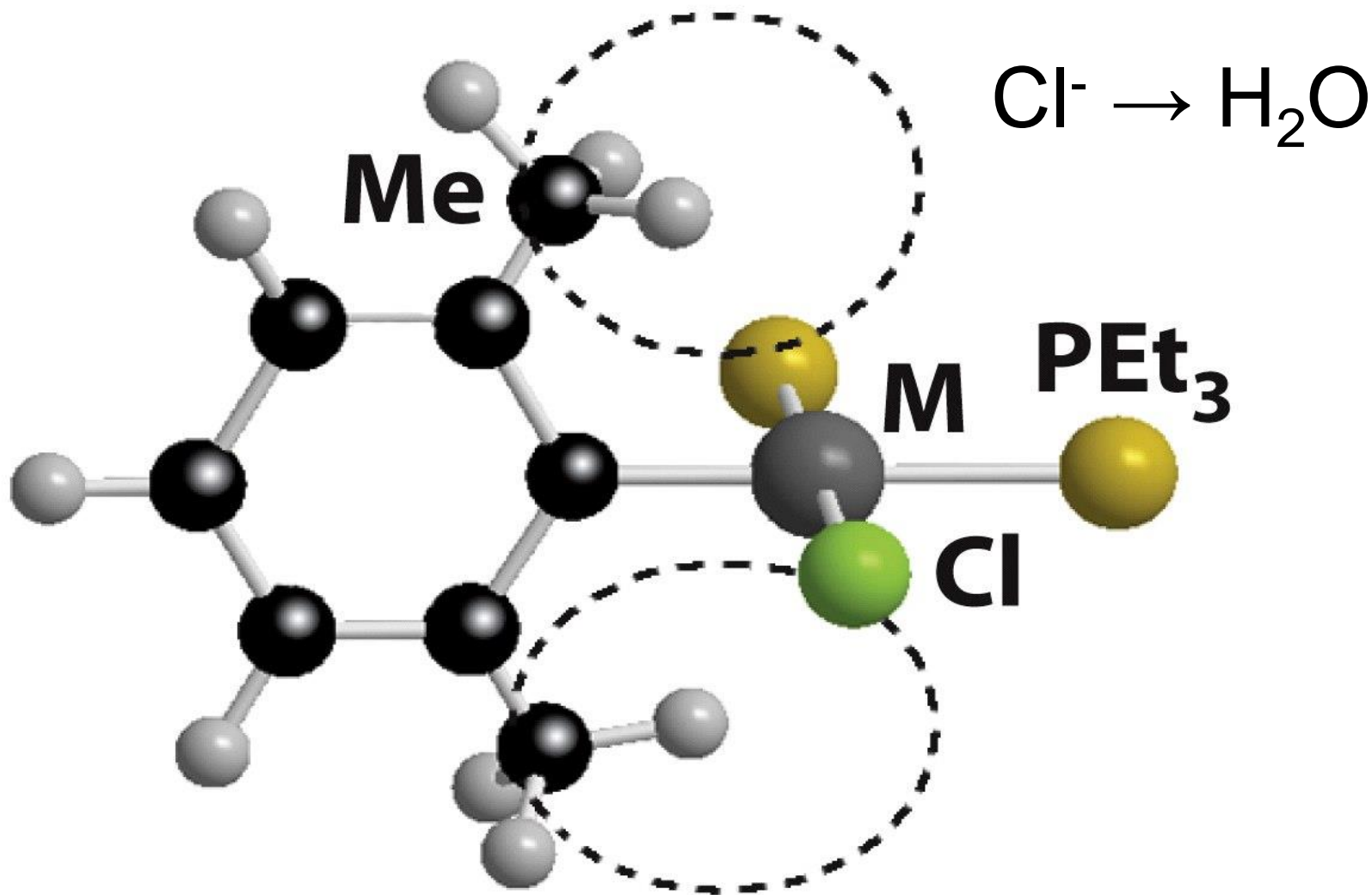
$$v = -\frac{d[\text{PtL}_3\text{X}]}{dt} = k_1[\text{PtL}_3\text{X}] + k_2[\text{PtL}_3\text{X}][\text{Y}] = k_{\text{obs}}[\text{PtL}_3\text{X}]$$

(in condizioni di pseudo primo ordine)

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

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

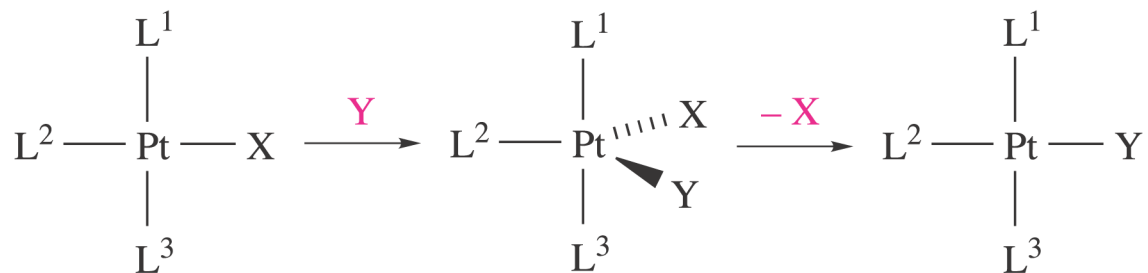
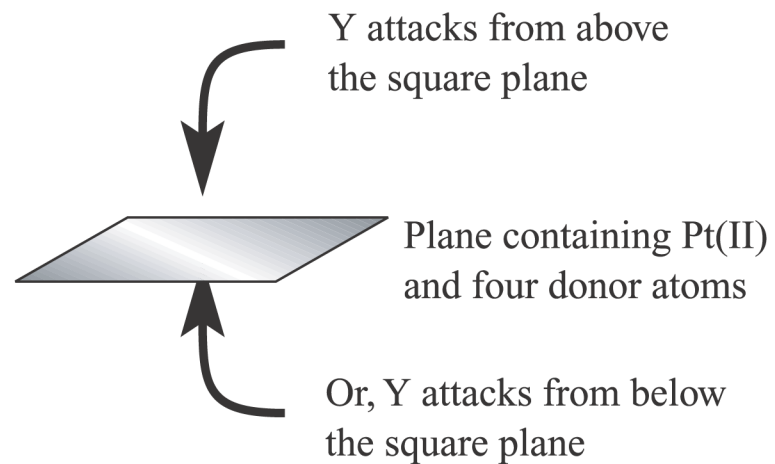
$k_1$  e  $k_2$  diminuiscono al crescere dell'ingombro sterico sia di Y che di L

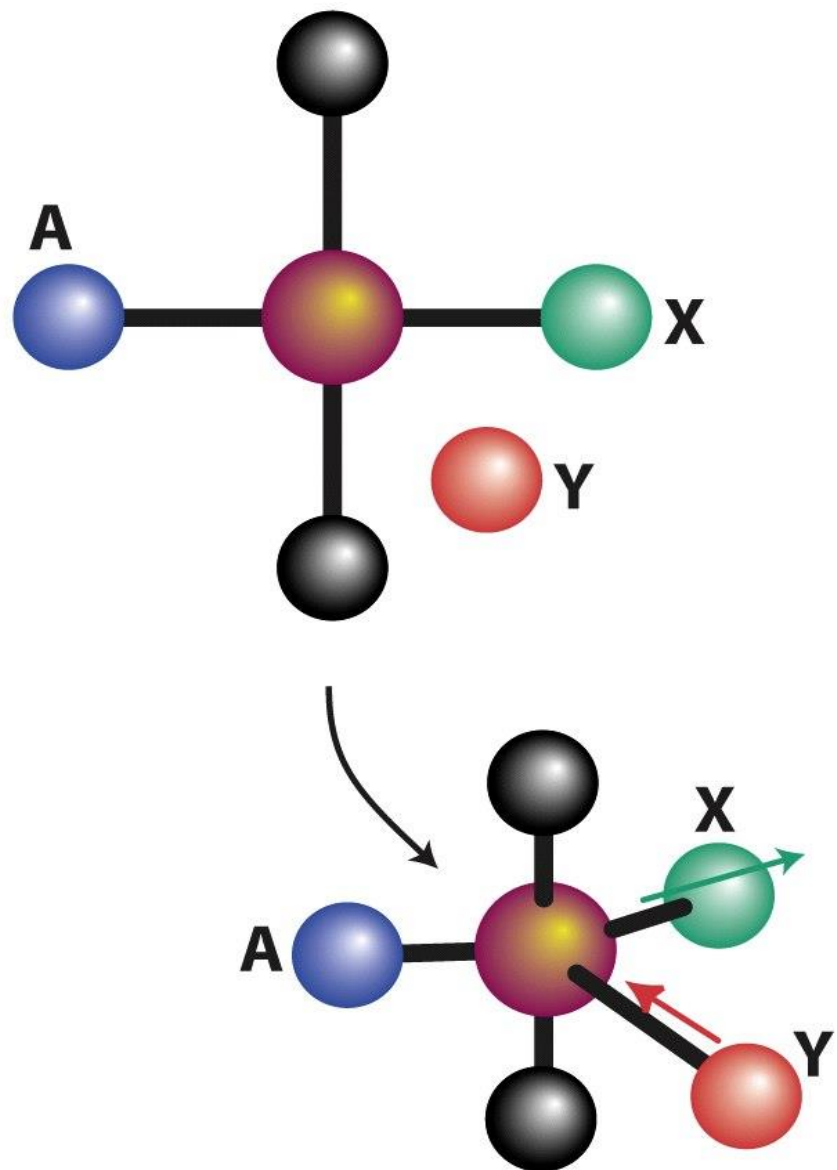


$k = 8 \times 10^{-2} \text{ s}^{-1}$  per L = py

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

# Ritenzione di configurazione



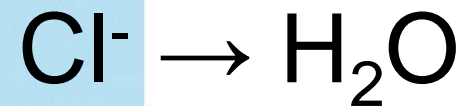


Effetto *trans*: è l'effetto che ha il legante in *trans* al gruppo uscente sulla sua velocità di sostituzione (i.e.: grande effetto *trans* = alta velocità di sostituzione).

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(PEt<sub>3</sub>)<sub>2</sub>L]

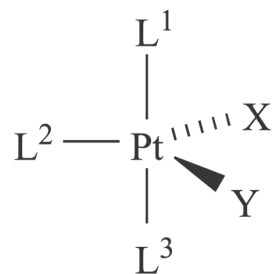


L	$k_1/\text{s}^{-1}$	$k_2/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
CH <sub>3</sub> <sup>-</sup>	$1.7 \times 10^{-4}$	$6.7 \times 10^{-2}$
C <sub>6</sub> H <sub>5</sub> <sup>-</sup>	$3.3 \times 10^{-5}$	$1.6 \times 10^{-2}$
Cl <sup>-</sup>	$1.0 \times 10^{-6}$	$4.0 \times 10^{-4}$
H <sup>-</sup>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

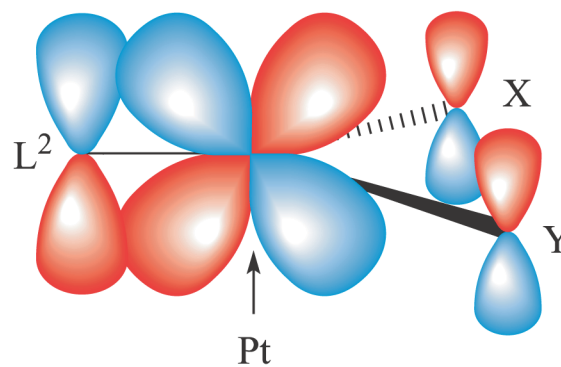
H<sub>2</sub>O ≈ OH<sup>-</sup> ≈ NH<sub>3</sub> ≈ py < Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup> ≈ NO<sub>2</sub><sup>-</sup> < Ph<sup>-</sup> < Me<sup>-</sup> < PR<sub>3</sub> ≈ H<sup>-</sup> « CO ≈ CN<sup>-</sup>

Sequenza sperimentale di effetto *trans*

# Effetto-*trans*: contributo cinetico



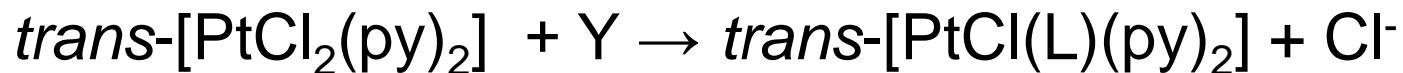
Trigonal bipyramidal  
transition state or  
intermediate



$\pi$ -Bonding in the trigonal plane

*nei complessi planari quadrati si ha 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*

Sequenza di nucleofilicità del gruppo entrante

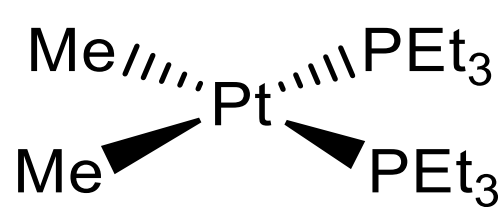


Nucleophile	Donor atom	$n_{\text{Pt}}$
$\text{Cl}^-$	Cl	3.04
$\text{I}^-$	I	5.42
$\text{CN}^-$	C	7.00
$\text{CH}_3\text{OH}$	O	0
$\text{C}_6\text{H}_5\text{SH}$	S	4.15
$\text{NH}_3$	N	3.06
$(\text{C}_6\text{H}_5)_3\text{P}$	P	8.79

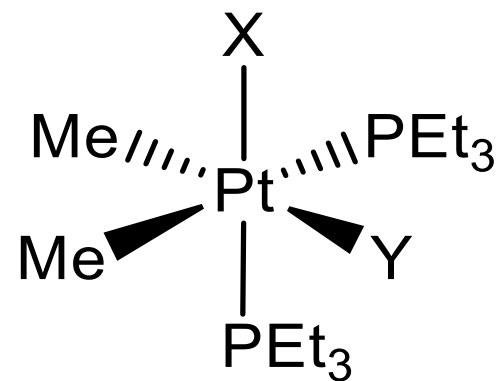
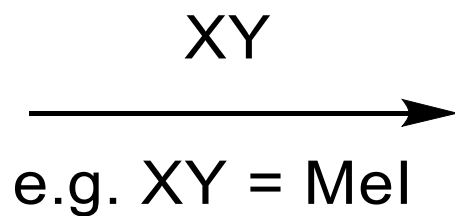
**parametro di nucleofilicità:**  $n_{\text{Pt}} = \log k_2/k'_2(\text{MeOH})$

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

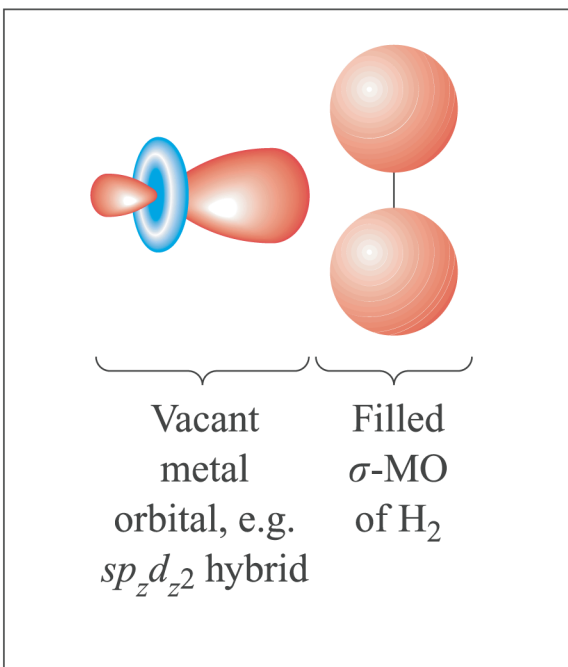
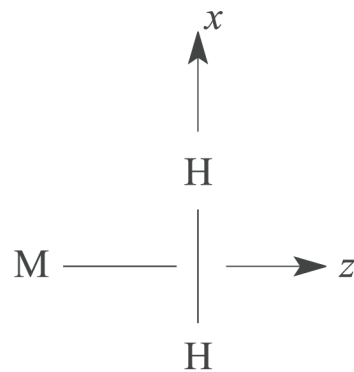
# Addizione ossidativa



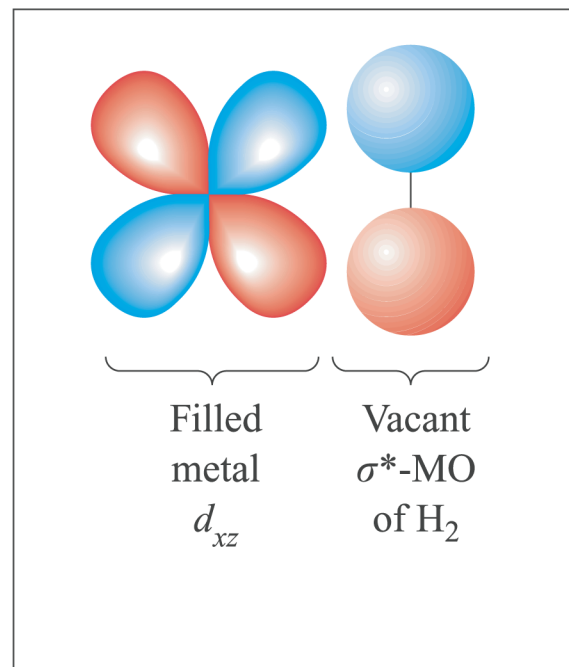
16e Pt(II)



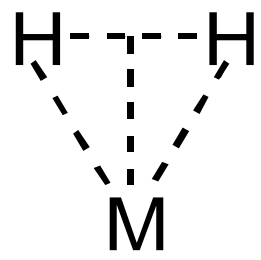
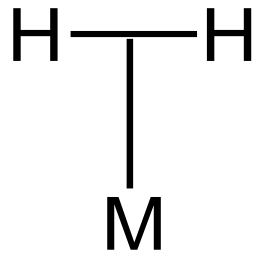
18e Pt(IV)



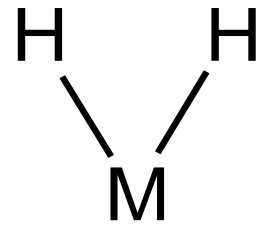
H<sub>2</sub>-to-M donation  
(a)



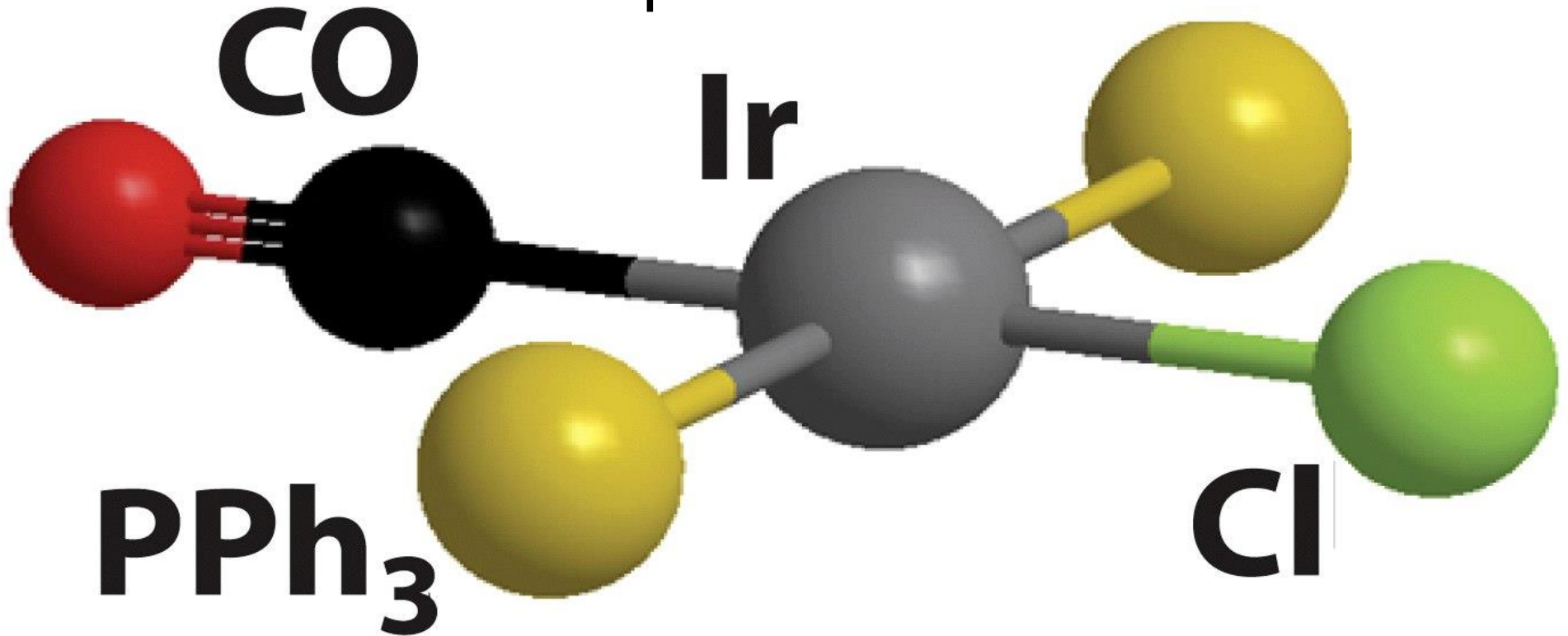
M-to-H<sub>2</sub> back-donation  
(b)



Addizione ossidativa

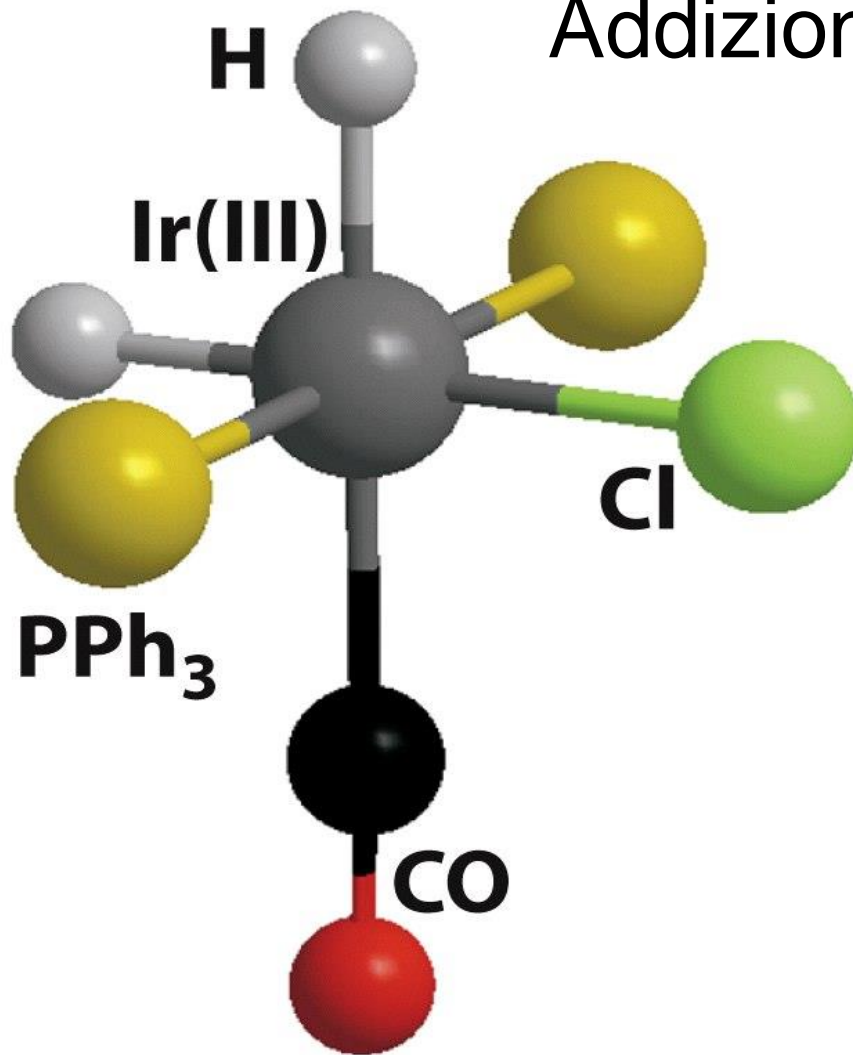


Complesso di Vaska

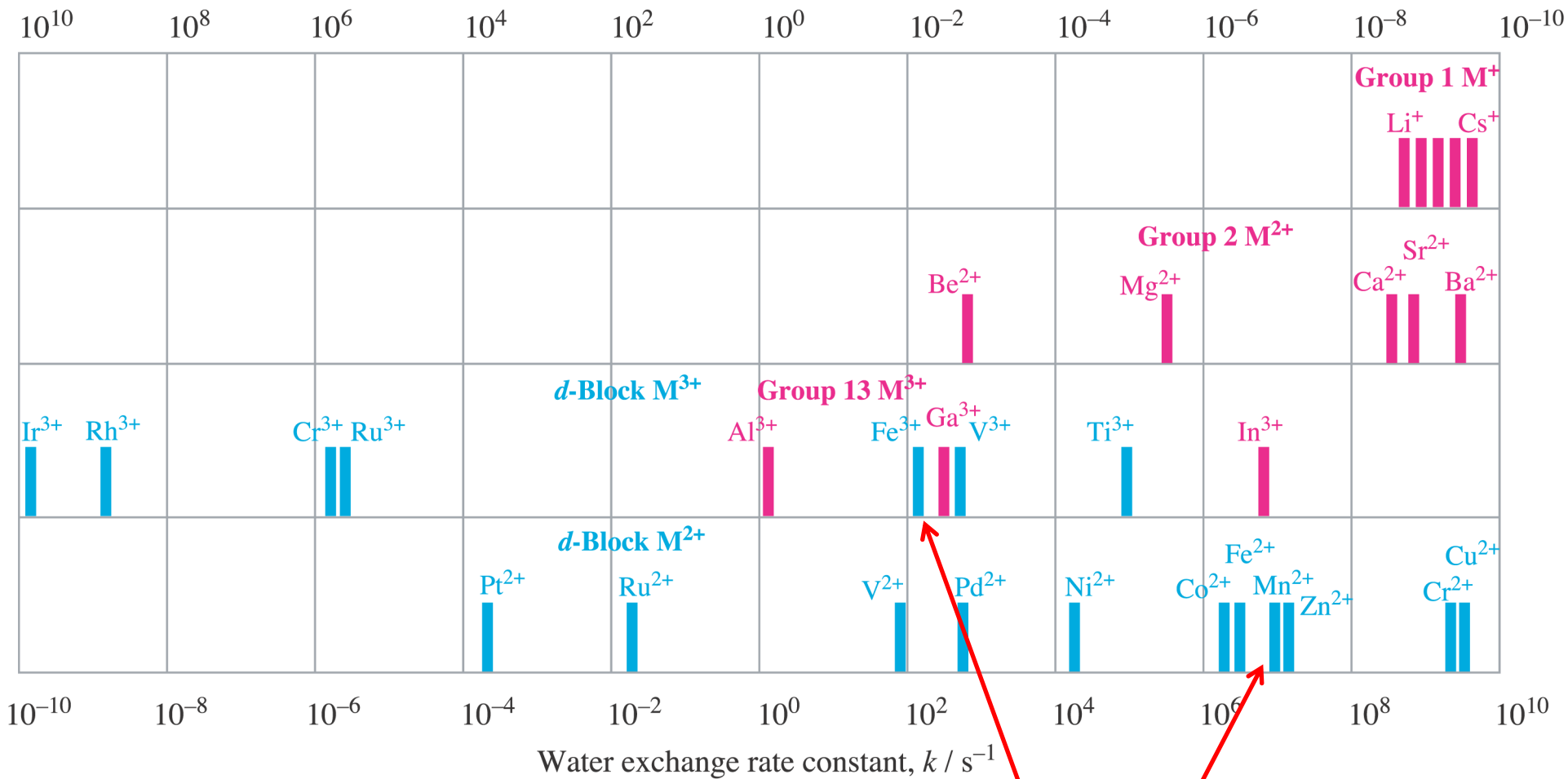




Addizione ossidativa

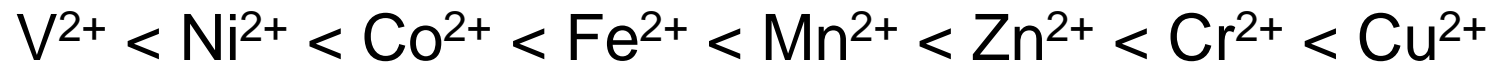


Average residence time for H<sub>2</sub>O molecule in first hydration shell / s



$d^5$  h.s.

Ordine di velocità osservato per lo scambio di H<sub>2</sub>O in



Nei complessi ottaedrici la velocità di sostituzione dipende dalla configurazione elettronica

# Legge cinetica sperimentale per sostituzioni in complessi ottaedrici



- ad alte concentrazioni di Y la velocità di sostituzione dipende solo da  $ML_6$  e non da Y, suggerendo un meccanismo dissociativo;
- a basse concentrazioni di Y la velocità della reazione dipende sia da Y che da  $ML_6$ , suggerendo un meccanismo associativo.

# Meccanismo di Eigen - Wilkins

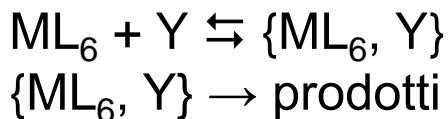
**Table 20.8** Complex formation by the  $[\text{Ni}(\text{OH}_2)_6]^{2+}$  ion  $\text{ML}_6 + \text{Y} \rightarrow$  prodotti

Ligand	$k_{\text{obs}}/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$K_E/(\text{dm}^3 \text{ mol}^{-1})$	$(k_{\text{obs}}/K_E)/\text{s}^{-1}$
$\text{CH}_3\text{CO}_2^-$	$1 \times 10^5$	3	$3 \times 10^4$
$\text{F}^-$	$8 \times 10^3$	1	$8 \times 10^3$
HF	$3 \times 10^3$	0.15	$2 \times 10^4$
$\text{H}_2\text{O}^*$			$3 \times 10^3$
$\text{NH}_3$	$5 \times 10^3$	0.15	$3 \times 10^4$
$[\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^+$	$4 \times 10^2$	0.02	$2 \times 10^4$
$\text{SCN}^-$	$6 \times 10^3$	1	$6 \times 10^3$

meccanismo associativo

meccanismo dissociativo

\* The solvent is always in encounter with the ion so that  $K_E$  is undefined and all rates are inherently first-order.



pre-equilibrio veloce, **complesso di incontro**  
*r.d.s.*

$$v = kK_E \frac{[\text{Y}][\text{M}]_{\text{tot}}}{1 + K_E[\text{Y}]}$$

$$k_{\text{obs}} = kK_E$$



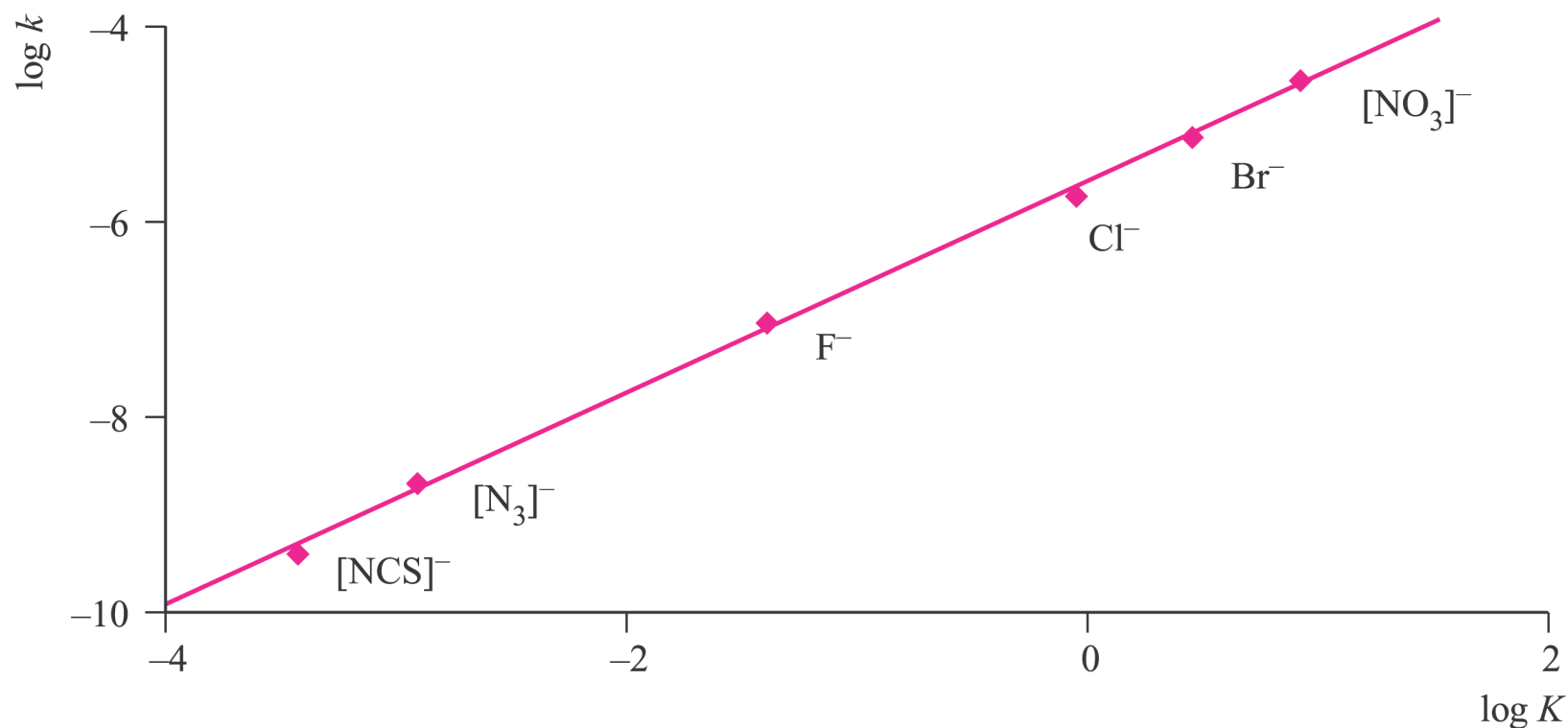
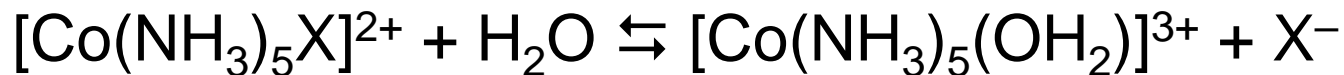
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Entering ligand, Y	$\text{NH}_3$	py	$[\text{MeCO}_2]^-$	$\text{F}^-$	$[\text{SCN}]^-$
$k \times 10^{-4} / \text{s}^{-1}$	3	3	3	0.8	0.6

---

La velocità non dipende dalla natura del gruppo entrante → *meccanismo dissociativo*

Dipendenza della velocità di sostituzione dalla natura del **gruppo uscente**

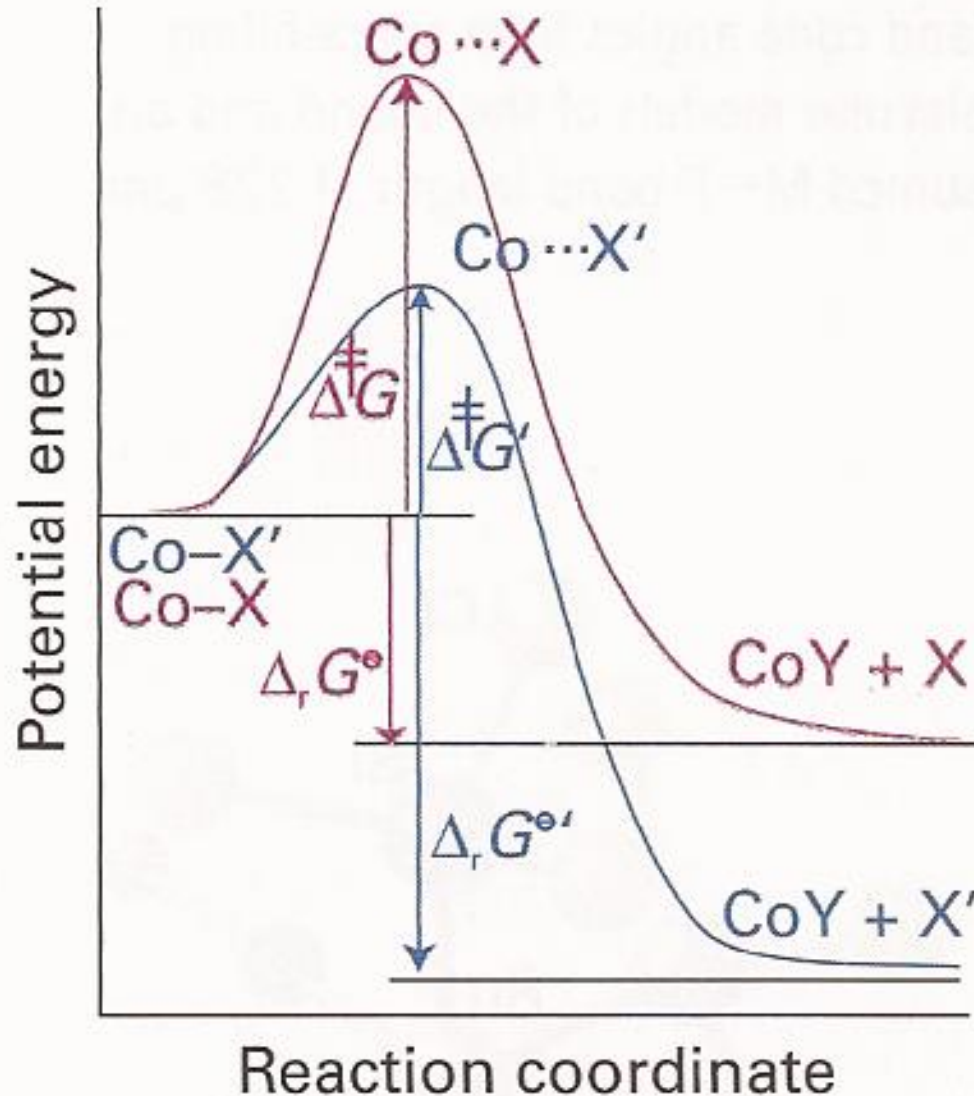


**LFER: *Linear Free Energy Relation* (fra  $\Delta G^\ddagger$  e  $\Delta G^\circ$ )**

*più il legame M-X è debole (cioè la K è grande) e più la sostituzione è veloce*

# LFER: *Linear Free Energy Relation*

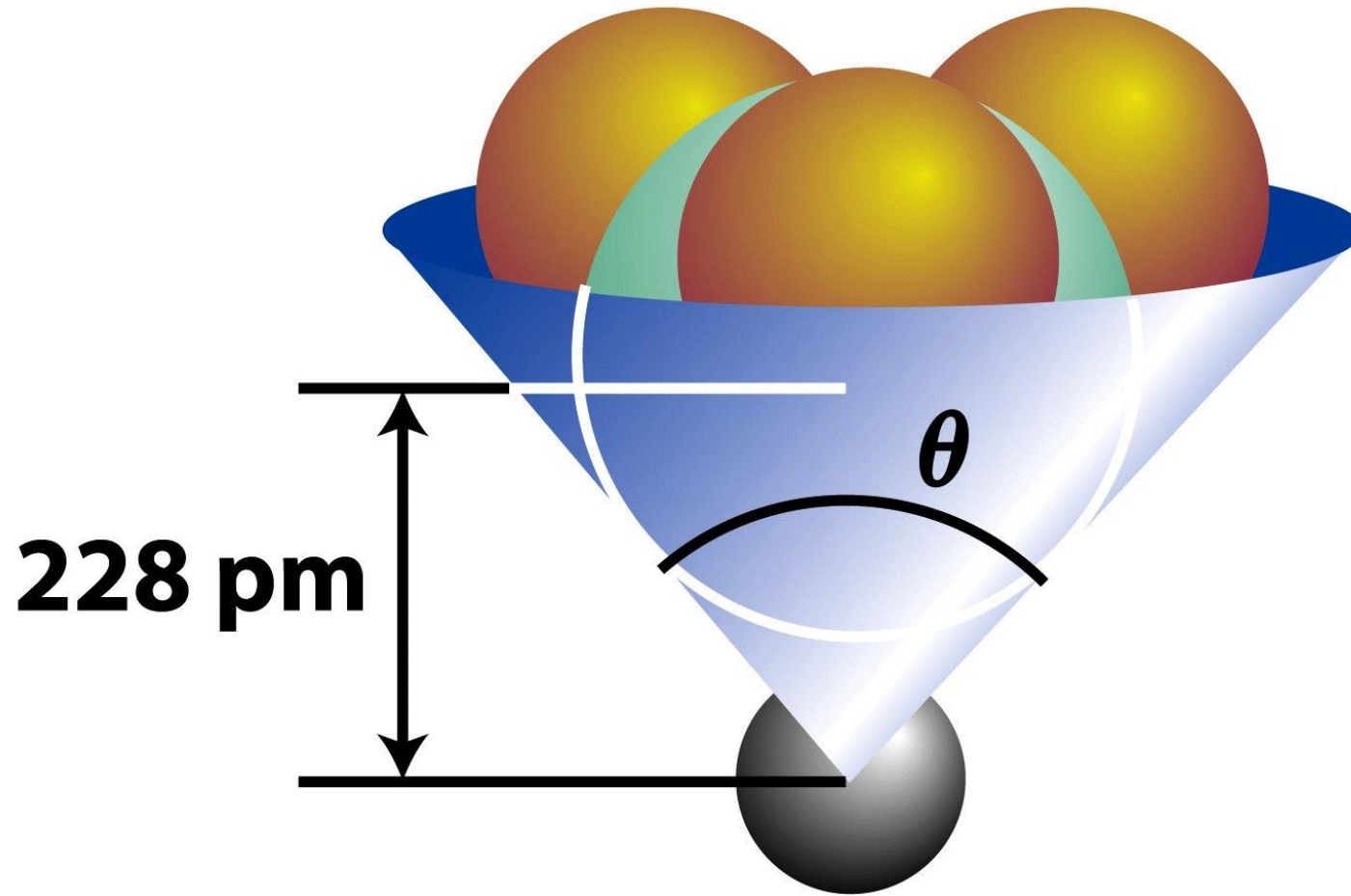
relazione lineare fra  $\Delta G^\ddagger$  e  $\Delta G^\circ$  con pendenza praticamente unitaria



*lo stato di transizione è molto simile al prodotto*

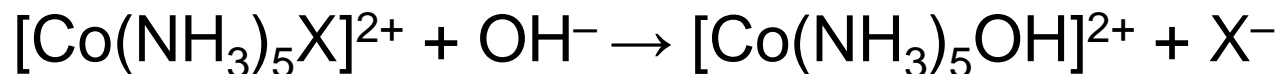


# Angolo di cono di Tolman



Per il dmsO l'angolo di cono di Tolman vale  $\theta = 112^\circ$  per dmsO- $\kappa$ S, e  $\theta = 100^\circ$  per dmsO- $\kappa$ O

# Idrolisi catalizzata da base ( $S_N1cb$ )



$$v = k_{\text{obs}}[\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]$$

Legge cinetica apparentemente di tipo associativo

