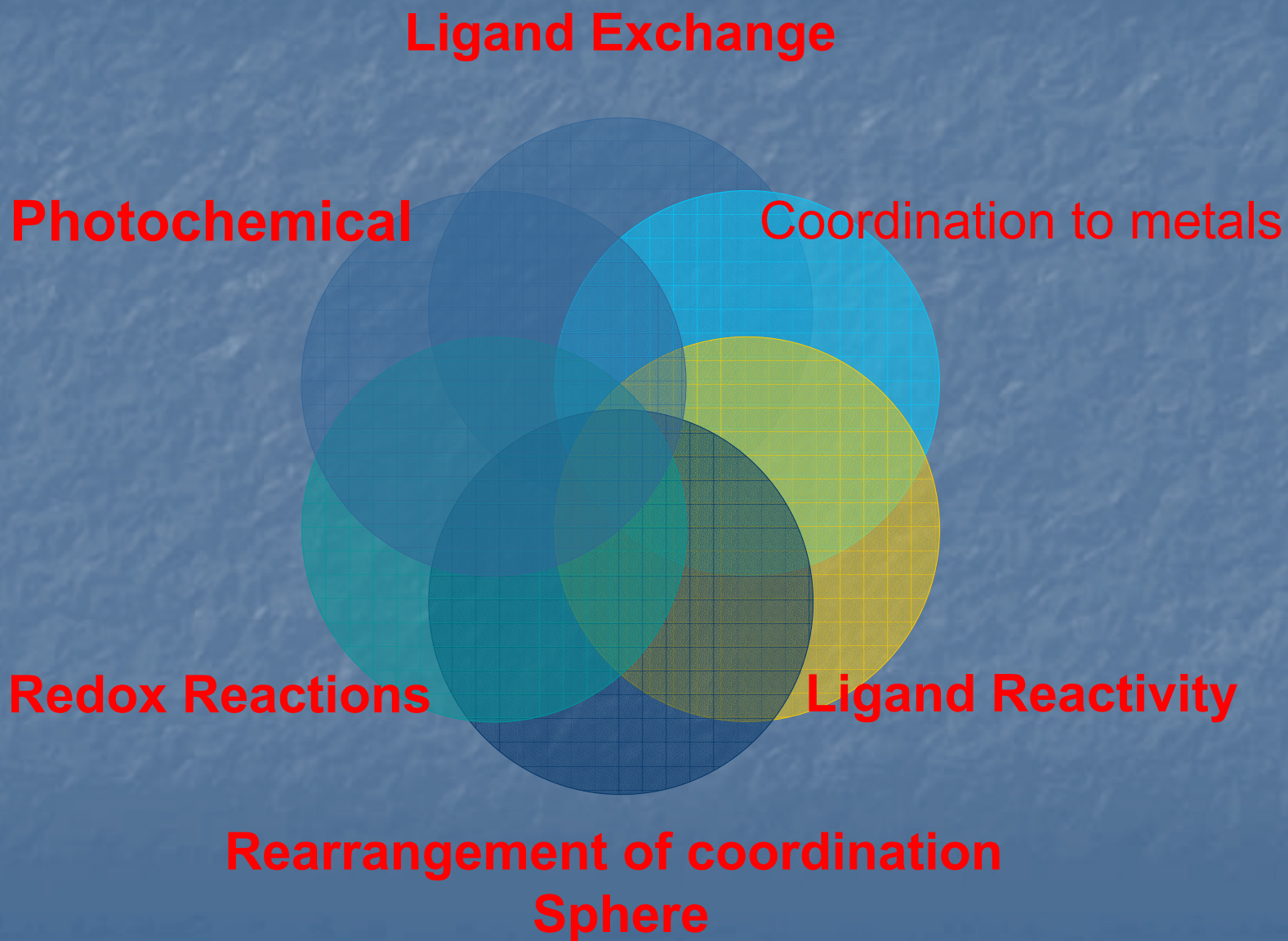


# Kinetic of Inorganic Reactions

Prof. Dr. Rehab Al Hassani

- **Introduction**
- **Ligand substitution reactions**
  - Octahedral Complexes
  - Square Planar
- **Textbook: B. Douglas, D. H. McDaniel, & J. J. Alexander, Concepts & Models of Inorganic Chemistry, 2<sup>nd</sup> edition, Wiley, New York**

# Some Chemistry of Transition Metals





# What are reaction mechanisms?

- Detail step-by-step analysis of reaction pathway.
- *i.e.* sequence of reactions involved in the conversion of reactants to products
- Rate Law
- 'Intimate' Mechanism refers to details of the mechanism at the molecular level.

# Reaction Profile

Consider the reaction:



$M + L \rightleftharpoons$   
Collisions  
of  $> \text{Energy}$

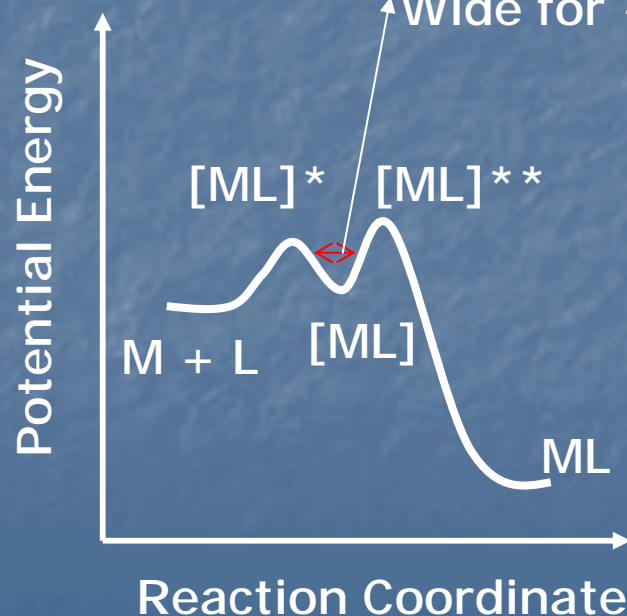
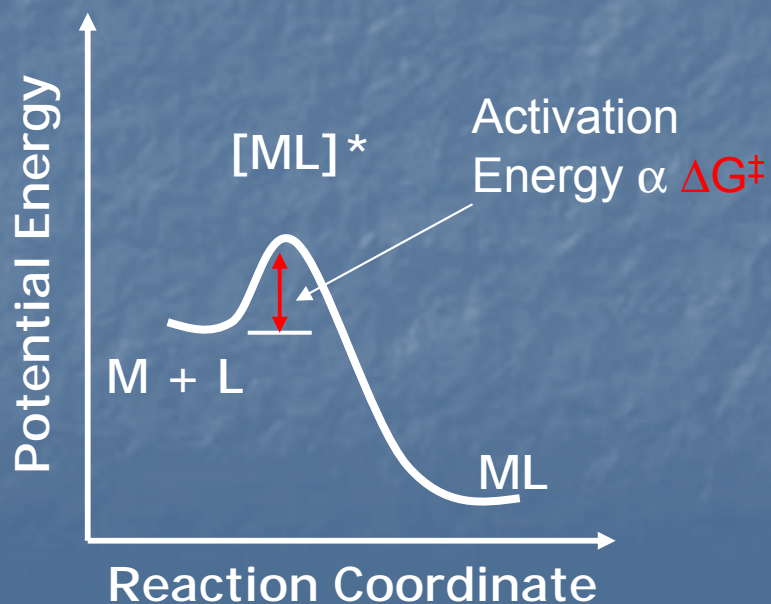
$[ML]^*$   
Activated Complex  
Transition State

$[ML] \rightleftharpoons$   
Intermediate

$[ML]**$   
Activated Complex

ML

Width related to entropy  
Narrow for  $-\Delta S$   
Wide for  $+\Delta S$



# Microscopic Reversibility

- Microscopic reversibility: at equilibrium both forward and reverse reactions proceed at equal rates backward and forward and along the reaction coordinate.



# Transition State Theory

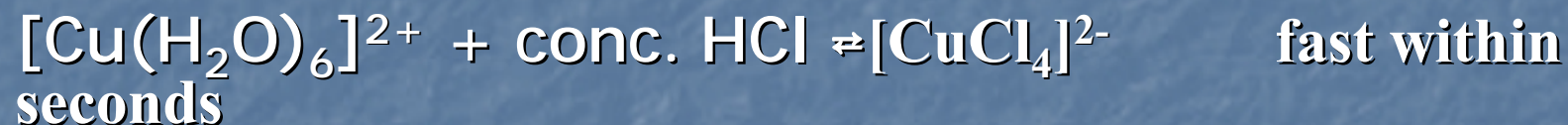
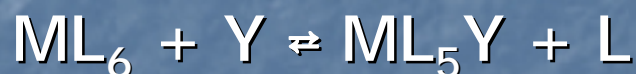
- Rate =  $k[L][M]$
- $k \propto K^\ddagger \propto \exp(-\Delta G^\ddagger/RT)$
- $k \propto \exp(\Delta S^\ddagger/R) \exp(-\Delta E_{\text{act}}/RT)$
- Fast reactions are favored by:
  - $\Delta S^\ddagger$  more positive.
  - $\Delta E_{\text{act}}$  less positive.
- Note since  $k$  is exponentially dependent on  $\Delta S^\ddagger$  and  $\Delta E_{\text{act}}$ , Small changes in  $k$  are not significant in the interpretation of the rate law.

# Type of Reactions

- Ligand Substitution reactions: are those in which the coordination sphere around the metal changes due exchange of one ligand (lewis base) with another ligand.

- e.g.

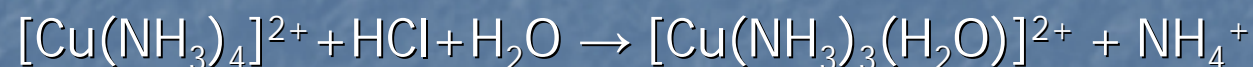
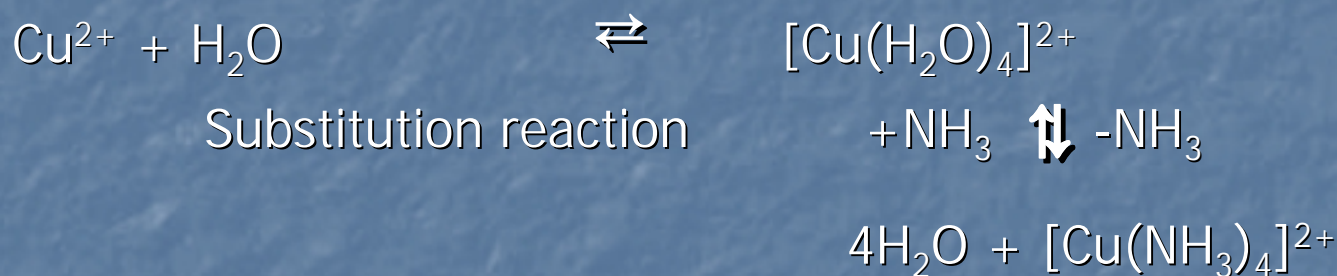
- Octahedral



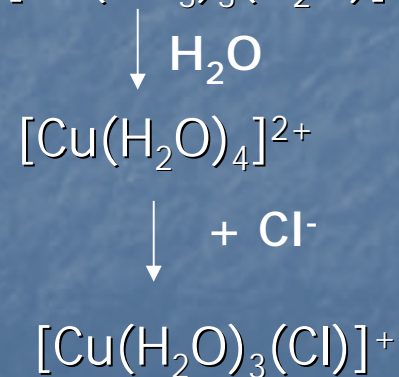
- Square Planar



# Examples of Substitution Reactions



Fast reactions

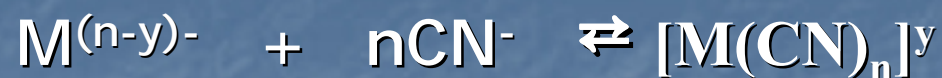




# Example

- $[\text{Co}(\text{NH}_3)_6]^{3+} + \text{H}_2\text{O} \rightarrow [\text{Co}(\text{NH}_3)_6(\text{H}_2\text{O})]^{3+}$   
Slow several days
- Lability and inertness: kinetic terms & unrelated to thermodynamic stability of compound and they refer to how quickly a reaction system reaches equilibrium.
- Inertness is kinetic stability

# Examples



$$K_f = [M(CN)_n]^y / [M^{n-y})][CN]^n$$

■ Compound	$K_f$	Exchange Rate
■ $[Ni(CN)_4]^{2-}$	$10^{30}$	very fast
■ <b><math>[Hg(CN)_4]^{2-}</math></b>	<b><math>10^{42}</math></b>	<b>very fast</b>
■ $[Fe(CN)_6]^{3-}$	$10^{44}$	very fast
■ $[Fe(CN)_6]^{4-}$	$10^{37}$	very fast
■ $[Pt(CN)_4]^{2-}$	$\sim 10^{40}$	$t_{1/2} = 1 \text{ min.}$

→  $[Hg(CN)_4]^{2-}$  Thermodynamically stable but kinetically labile, the same for  $[Ni(CN)_4]^{2-}$   
*i.e.* in solutions ligand exchange is fast but always with  $CN^-$ .

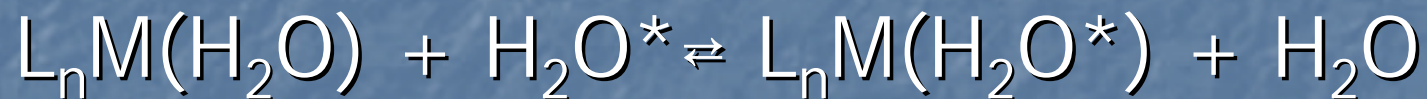
# Thermodynamics versus Kinetics

- Thermodynamics → Stability  
(stable/unstable) →  $K_f$  Formation  
Constant
- Kinetics → lability and inertness → rate  
of replacement of ligands (bases)



# Ligand Substitution Reactions in Octahedral Compounds

- Kinetics of H<sub>2</sub>O exchange



(see Figure 1)

# Kinetics of Water Exchange

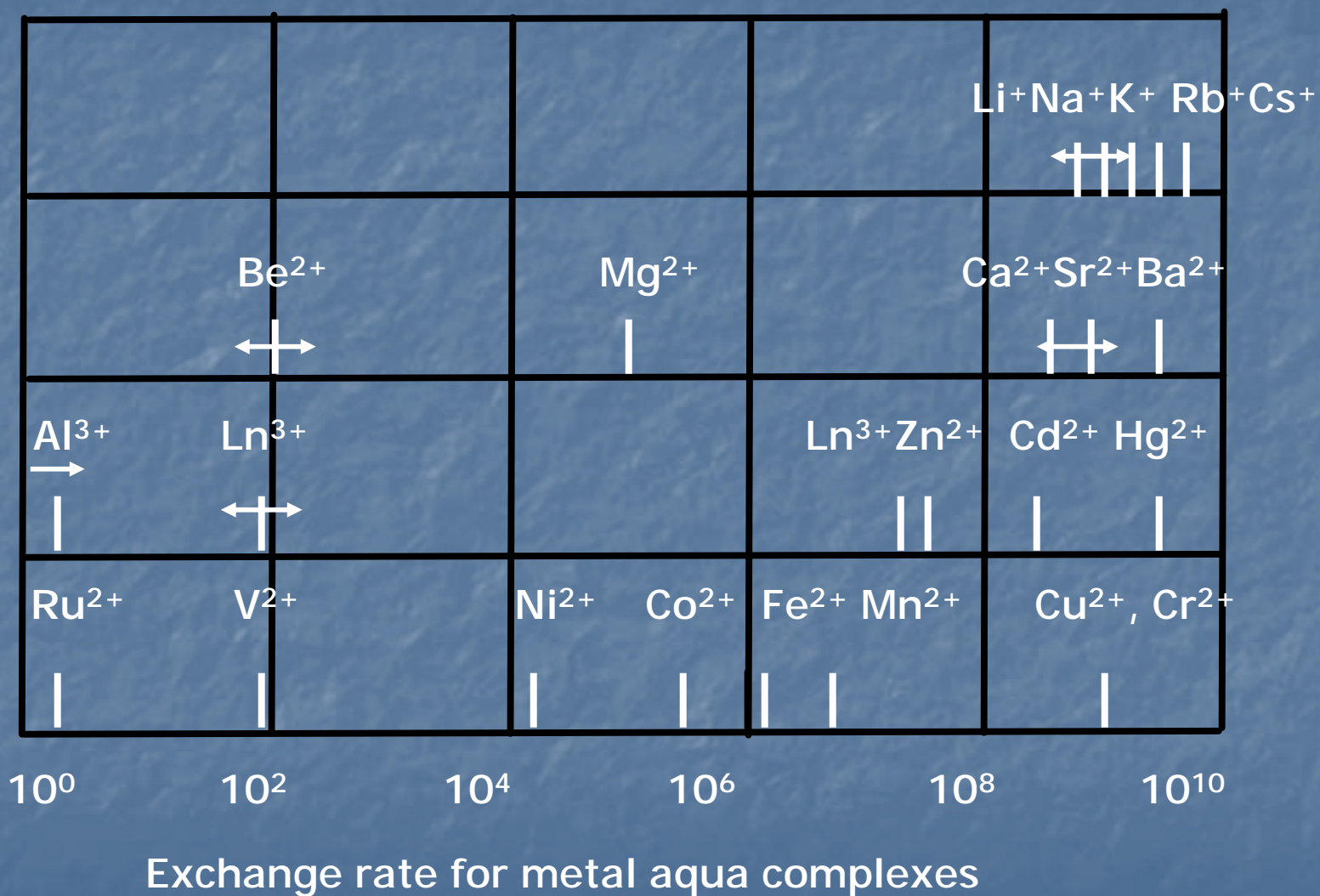


Figure 1

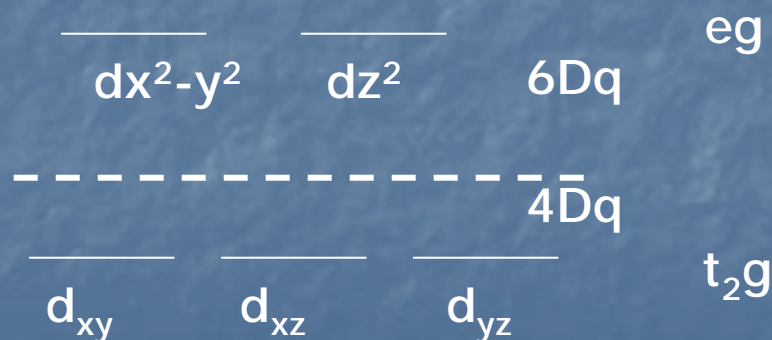
# Langford & Gray Classes for Water Exchange

- Class I Very fast (diffusion control),  $k > 10^8 \text{ sec}^{-1}$ . The ions in this class are those of alkali metals and alkaline earths (except for  $\text{Be}^{2+}$  &  $\text{Mg}^{2+}$ ), Group IIB (except for  $\text{Zn}^{2+}$ ),  $\text{Cr}^{2+}$  and  $\text{Cu}^{2+}$ .
- Class II Exchange-rate constants are between  $10^4$ - $10^8 \text{ sec}^{-1}$ . The divalent first row transition metal ions (except for  $\text{V}^{2+}$ ,  $\text{Cr}^{2+}$  &  $\text{Cu}^{2+}$ ) as well as  $\text{Mg}^{2+}$  and the trivalent lanthanide ions.
- Class III Exchange-rate constants are between 1 and  $10^4 \text{ sec}^{-1}$ . This class includes  $\text{Be}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$  and several trivalent first-row transition metal ions.
- Class IV Exchange rate constants between  $10^{-6}$  to  $10^{-1} \text{ sec}^{-1}$ . Member of the set are  $\text{Cr}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Rh}^{3+}$ ,  $\text{Ir}^{3+}$  and  $\text{Pt}^{2+}$ . Inert.



# Factors that affect water exchange substitution reactions

- Ionic potential =  $q/r$ ; charge & size of metal ions
- Ions with high ionic potential  $\rightarrow$  slow reactions suggesting that the main contribution to the activation energy is the **breaking of bond to the leaving group**.
- d-electronic configuration
- $\rightarrow$  metal ions in strong LFSE  $\rightarrow$  slow substitution
- $O_h$



# Spectroelectrochemical Series

$\text{CN}^- > \text{phen} \sim \text{NO}_2^- > \text{en} > \text{NH}_3 \sim \text{py} > \text{H}_2\text{O} > \text{C}_2\text{O}_4^{2-} > \text{OH}^- > \text{F}^- > \text{S}^{2-} > \text{Cl}^- > \text{Br}^- > \text{I}^-$

In strong field metal ions in  $d^3$ ,  $d^4$ ,  $d^5$ , &  $d^6$  are **inert**  
*i.e.* **HIGH LFSE**

$\text{O}_h \rightarrow$  high spin  $d^8$  such as  $\text{Ni}^{II}$

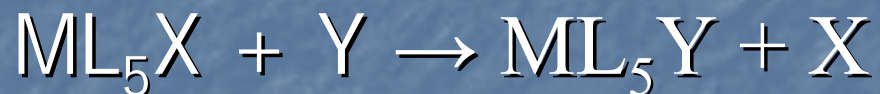
& low spin  $d^8$  such as  $\text{Rh(I)}$ ,  $\text{Ir(I)}$ ,  $\text{Ni(II)}$ ,  $\text{Pd(II)}$ ,  $\text{Pt(II)}$  &

Square planar  $\text{Au(III)}$  are **labile**.

React faster than  $d^6$  &  $d^3$

For  $\text{Cu}^{2+}$  &  $\text{Cr}^{2+}$  the fast exchange is due to Jahn-Teller distortion in the ground state which makes the axial bonds longer than the equatorial bonds.

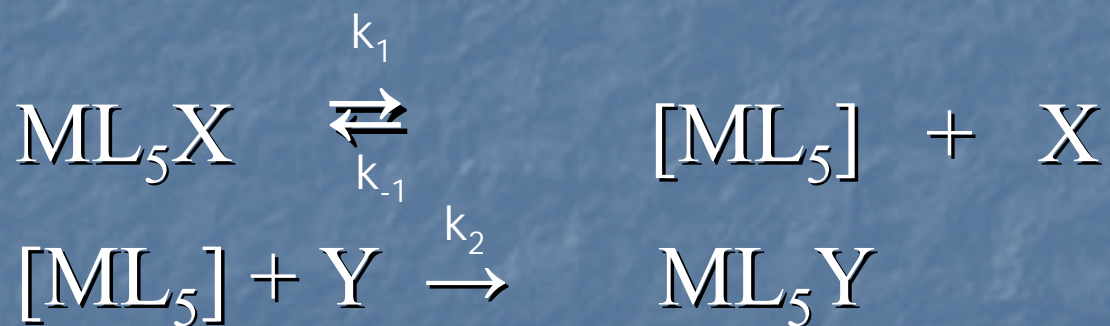
# Mechanism of Ligand Substitution in $O_h$ Compounds



Where  $X$  is leaving group

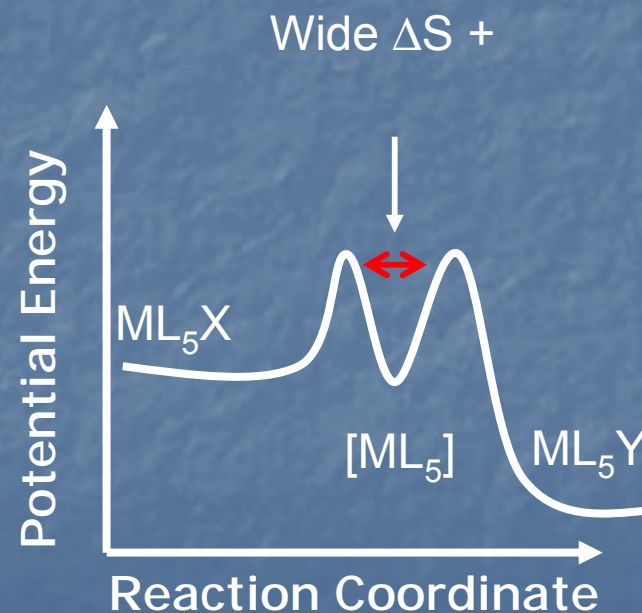
$Y$  is entering group

Consider the following mechanism



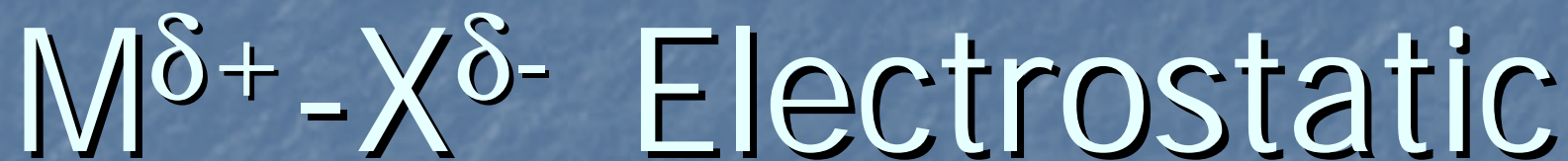
Dissociative pathway-D-type

**Key: M-X bond breakage,  $[ML_5]$  is intermediate**





# Factors that affect the Strength of M-X Bond



- **Charge on metal Center**-increase positive charge, M-X bond strengthen
- **Size of metal center**-increase size of metal center, M-X bond weaken
- **Charge of leaving group**, increase negative charge on X, M-X bond strengthen.
- **Size of leaving ligand**, increase size of leaving group, M-X bond weaken
- **Charge on other ligands** (**spectator**), increase negative on other ligands, M-X bond weaken
- **Size of spectator ligands**, increase size of other ligands, M-X bond weaken

## Rate Law for Dissociative Mechanism

- $\text{Rate} = d[\text{L}_5\text{MY}]/dt = k_2[\text{L}_5\text{M}][\text{Y}]$

Apply the **steady-state approximation** to  $\text{L}_5\text{M}$

- $$d[\text{L}_5\text{M}]/dt = 0 = k_1[\text{L}_5\text{MX}] - k_{-1}[\text{L}_5\text{M}][\text{X}] - k_2[\text{L}_5\text{M}][\text{Y}]$$

$$\therefore [\text{L}_5\text{M}] = k_1[\text{L}_5\text{MX}] / (k_{-1}[\text{X}] + k_2[\text{Y}])$$

$$\& \text{Rate} = (k_1 k_2 [\text{L}_5\text{MX}][\text{Y}]) / (k_{-1}[\text{X}] + k_2[\text{Y}])$$

**Bimolecular**

# Dissociative Mechanism, D-type

If  $k_2[y] \gg k_{-1}[X]$ ; i.e. pseudo 1<sup>st</sup> order

$\therefore \text{Rate} = k_1[\text{LnMX}]$  unimolecular

e.g. aquation and anation of inert  $d^6 \text{Co}^{\text{III}}$  compounds of the type  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ .

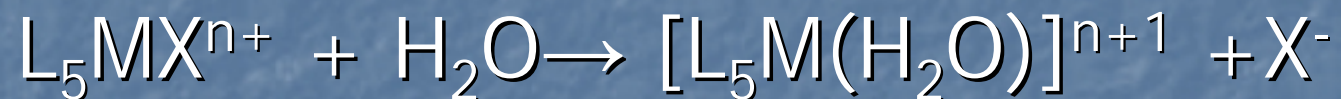
For this mechanism  $[\text{L}_5\text{M}]$  is an intermediate that has an appreciable lifetime and can be detected.

**Note true examples of D-type are not common.**

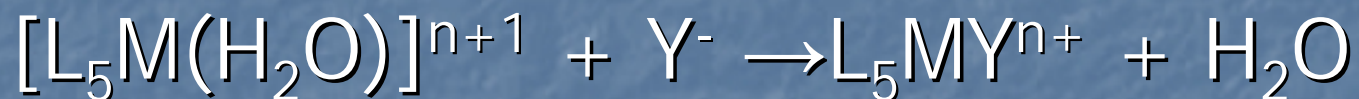


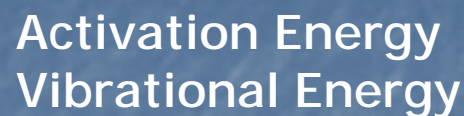
# Aquation or acid hydrolysis

- Aquation or acid hydrolysis



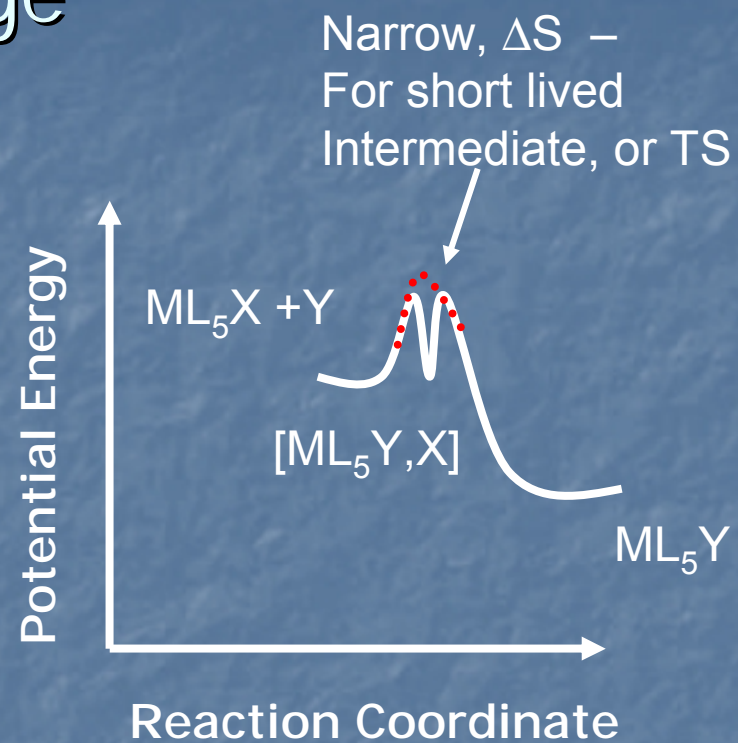
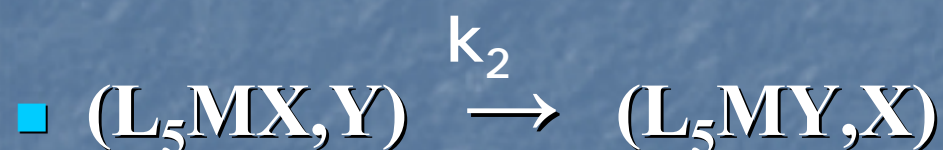
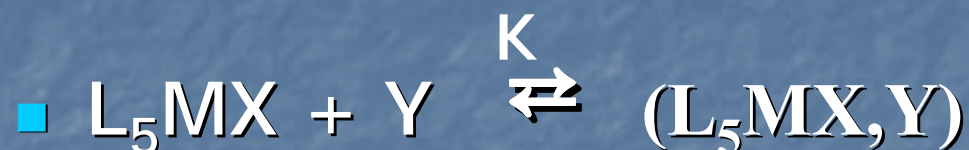
- Anation





- $(I_d)$

# Plausible Mechanism for $I_d$ Dissociative Interchange



- The magnitude of  $K$  depends on the ionic charge being larger when  $Y$  and the metal complex are of opposite charge.
- The likelihood of  $Y$  present in the outersphere depends on  $[Y]$ , as indicated in step 1.



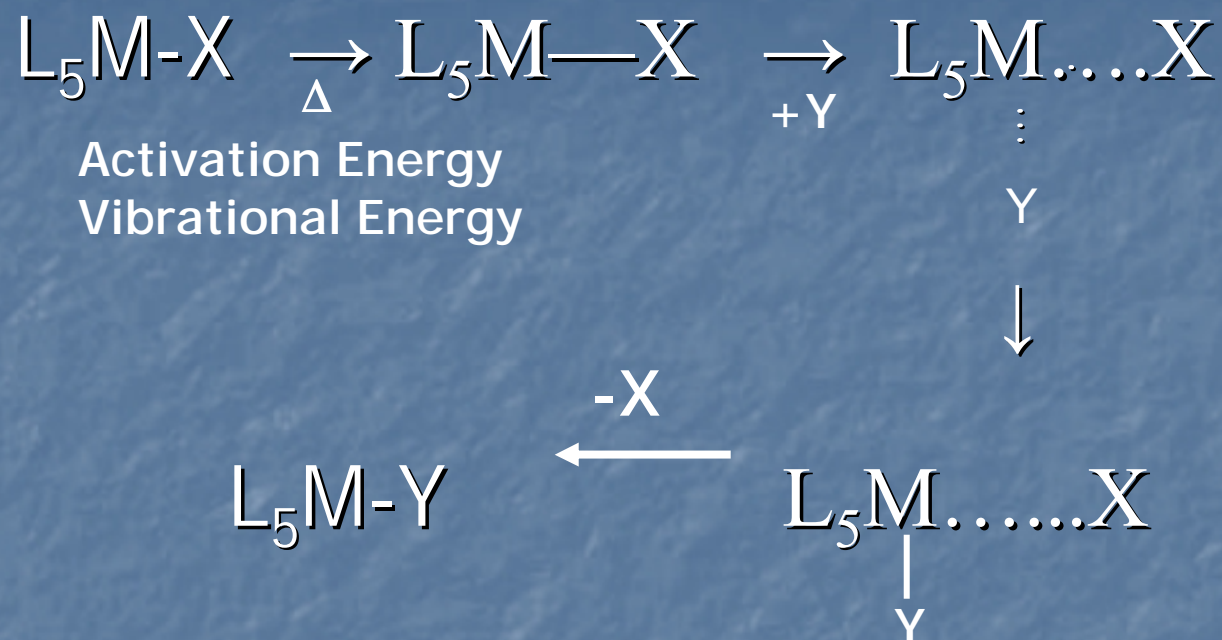
# Rate Law for Dissociative Interchange

- The experimental parameter accessible here is the initial concentration of the reactant complex  $[L_5MX]_0$  which in solution containing Y exists partly in the form of outersphere complex
- $[L_5MX]_0 = [L_5MX] + [L_5MX, Y]$
- $K = k_1/k_2 = [L_5MX, Y]/[Y][L_5MX]$
- $\therefore [L_5MX, Y] = K[Y][L_5MX]$
- &  $[L_5MX]_0 = [L_5MX] + K[Y][L_5MX]$
- Hence
- $[L_5MX] = [L_5MX]_0/(1 + K[Y])$
- $\text{Rate} = -dL_5MX/dt = k_2[L_5MX, Y]$
- $\text{Rate} = k_2K[L_5MX]_0[Y]/(1 + K[Y])$

# Associative (a) Mechanism

- $L_5MX + Y \xrightleftharpoons[k_{-1}]{k_1} L_5MXY$
- $L_5MXY \xrightarrow{k_2} L_5MY + X$
- $\text{Rate} = k_1[L_5MX][Y]/(k_{-1} + k_2)$
- No example for  $O_h$

## Associative Interchange ( $I_a$ ) Mechanism



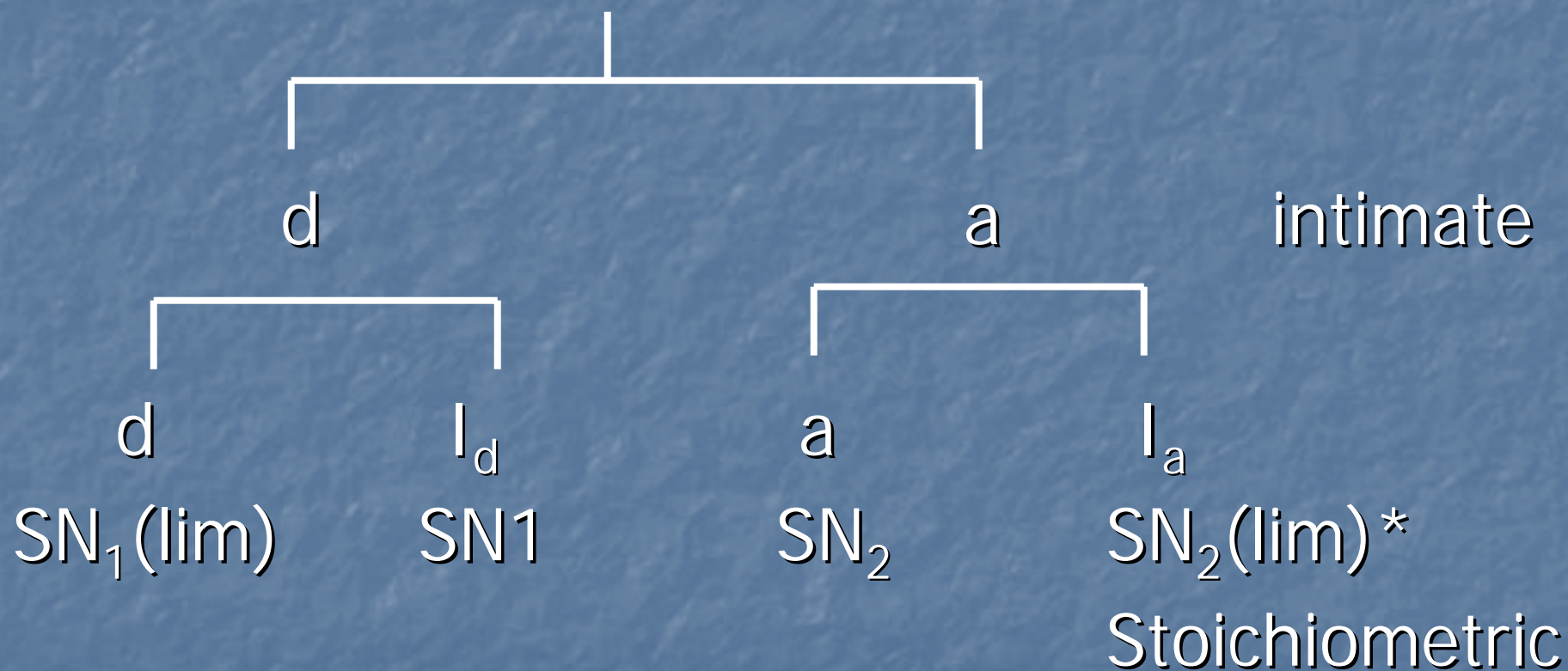
**Key:** M-Y bond starts to form before M-X bond starts to cleave.

- The entering group (Y) is strongly bound, and rate is sensitive to Y. Implication is that the entering group and leaving group are strongly bound in the transition state. This is known as Associative interchange. ( $I_a$ )



# Summary

## Inorganic Reaction Mechanisms



SN<sub>1</sub> & SN<sub>2</sub> are not good models for inorganic reaction mechanisms.\*

# Summary



$$\text{Rate} = a[L_5MX][Y]/(1 + b[Y])$$

Limiting conditions:

1.  $b[Y] \gg 1$ ;  $\therefore$  the reaction should be first order.
2.  $b[Y] \ll 1$ ;  $\therefore$  the reaction should be second order.
3.  $b[Y] = 1$   $\therefore$  the reaction should be of mixed order.

A always second order as long as the final step is not reversible.

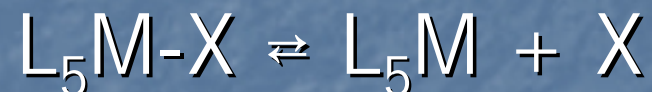
# Substitution inert ions

- $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Rh}^{3+}$ ,  $\text{Ir}^{3+}$ ,  $\text{Pt}^{4+}$  &  $\text{Ni}^{2+}$



# Intimate Mechanisms

- Nature of leaving & entering groups



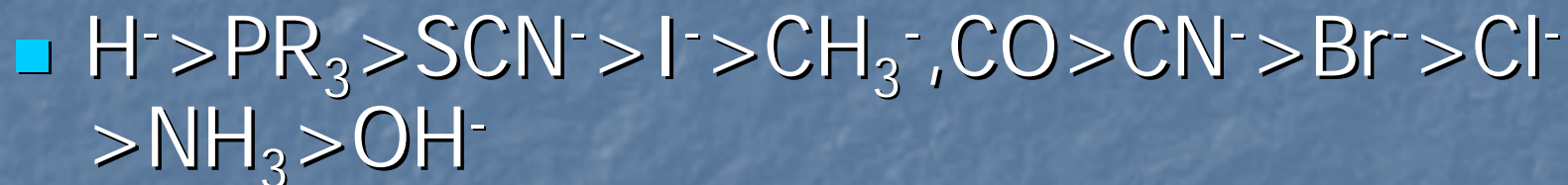
- For dissociative mechanism rate is dependent the leaving group

*i.e.* M-X bond strength

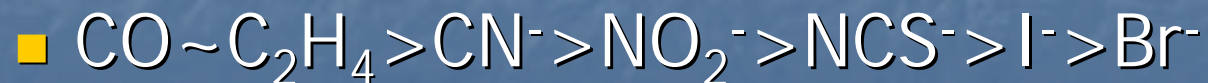
- $e^-$  - donor     $\sigma$ -donor like  $NH_3$ ,  $H^-$ ,  
                           $\pi$ -donor  $\rightarrow \sigma$  + filled  $\pi$ -orbital  
                          e.g.  $Br^-$ ,  $O^-$ ,  $C_p^-$ ,  $RO^-$ ,  $RN^{2-}$
- $e^-$ -acceptor  $\rightarrow \sigma$ -donor + empty  $\pi^*$   
orbitals e.g. CO

# Ligands

- $\sigma$ -donors



- $\pi$ -acceptors –



# Leaving group order for $O_h$ compounds

$HCO_3^- >> NO_3^- > I^- \sim H_2O \sim Br^- > Cl^- \sim$   
 $SO_4^{2-} > SCN^- > F^- > CH_3COO^- > NCS^-$   
 $> NO_2^- > NH_3 > OH^- > CN^-$



# Size of the Coordination Sphere & Metal ION

- Large Coordination sphere favors associative mechanism
- Small Coordination sphere favors dissociative d-type pathway.
- e.g.       $1^{\text{st}} \rightarrow \text{Oh}$  favors D-type  
               $2^{\text{nd}} \rightarrow \text{Oh}$  may be A-type  
               $3^{\text{rd}} \rightarrow \text{Oh}$  favors A-type

Compare water exchange in  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  &  
 $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$                       1:3

# Periodic Table of the Elements

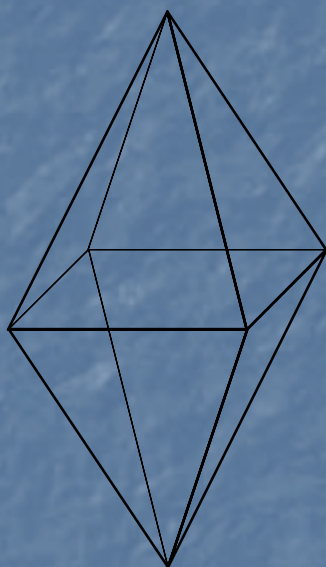
Periodic Table of the Elements																		18																	
1		2												3				4																	
H	2													Li	Be	B	C	N	O	F	Ne														
														Na	Mg	Al	Si	P	S	Cl	Ar														
3	4													5	6	7	8	9	10	11	12	13	14	15	16	17	18								
H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																		
Cs	Ba	* La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																		
Fr	Ra	+ Ac	Rf	Ha	106	107	108	109	110																										

\* Lanthanide  
Series

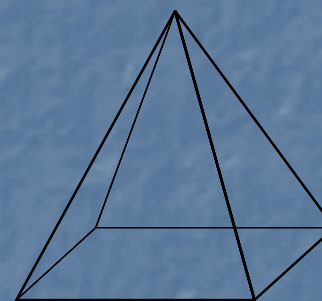
+ Actinide  
Series

<sup>58</sup> <b>Ce</b>	<sup>59</sup> <b>Pr</b>	<sup>60</sup> <b>Nd</b>	<sup>61</sup> <b>Pm</b>	<sup>62</sup> <b>Sm</b>	<sup>63</sup> <b>Eu</b>	<sup>64</sup> <b>Gd</b>	<sup>65</sup> <b>Tb</b>	<sup>66</sup> <b>Dy</b>	<sup>67</sup> <b>Ho</b>	<sup>68</sup> <b>Er</b>	<sup>69</sup> <b>Tm</b>	<sup>70</sup> <b>Yb</b>	<sup>71</sup> <b>Lu</b>
<sup>90</sup> <b>Th</b>	<sup>91</sup> <b>Pa</b>	<sup>92</sup> <b>U</b>	<sup>93</sup> <b>Np</b>	<sup>94</sup> <b>Pu</b>	<sup>95</sup> <b>Am</b>	<sup>96</sup> <b>Cm</b>	<sup>97</sup> <b>Bk</b>	<sup>98</sup> <b>Cf</b>	<sup>99</sup> <b>Es</b>	<sup>100</sup> <b>Fm</b>	<sup>101</sup> <b>Md</b>	<sup>102</sup> <b>No</b>	<sup>103</sup> <b>Lr</b>

# Coordination Sphere



Coordinatively saturated  
Favors D- type



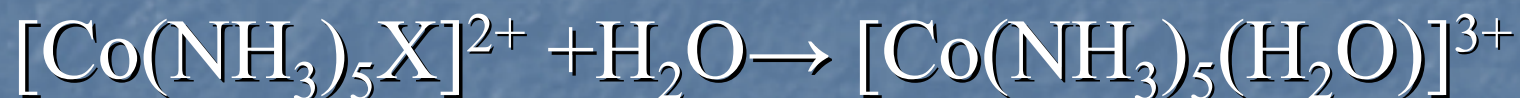
Coordinatively unsaturated  
Favors A-type



# Mechanism

- 1. Leaving group

e.g.



- Rate is dependent on leaving group and is independent on entering group.
- *i.e.* Co-X bond breaking is the rate determining step.
- Evidence?

# Aquation or acid hydrolysis

- Aquation or acid hydrolysis



- Anation



Rate constants for acid aquation of some  $O_h$  compounds of Co(III) of the type  $[\text{Co}(\text{NH}_3)_5(\text{X})]^{2+}$  at 25 C

Compound	k (sec <sup>-1</sup> )
$[\text{Co}(\text{NH}_3)_5(\text{OP}(\text{OCH}_3)_3)]^{3+}$	$2.5 \times 10^{-4}$
$[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]^{2+}$	$2.7 \times 10^{-5}$
$[\text{Co}(\text{NH}_3)_5(\text{I})]^{2+}$	$8.3 \times 10^{-6}$
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	$5.8 \times 10^{-6}$
$[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{2+}$	$1.7 \times 10^{-6}$
$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]^{+}$	$1.2 \times 10^{-6}$
$[\text{Co}(\text{NH}_3)_5(\text{F})]^{2+}$	$8.6 \times 10^{-8}$
$[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$	$2.1 \times 10^{-9}$
$[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$	$5.0 \times 10^{-10}$

**Note: k depends heavily On leaving group X**

**∴ Confirm Dissociative pathway**



## Limiting Rate constants for anation by $Y^{n-}$ and water exchange ( $k_e$ ) at 45 C $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$

$Y^{n-}$	$k \text{ (sec}^{-1}\text{)}$	$k/k_e$
$\text{H}_2\text{O}$	$100 \times 10^{-6}$	-
$\text{N}_3^-$	$100 \times 10^{-6}$	1.0
$\text{SO}_4^{2-}$	$24 \times 10^{-6}$	0.24
$\text{Cl}^-$	$21 \times 10^{-6}$	0.21
$\text{NCS}^-$	$16 \times 10^{-6}$	0.16
$\text{H}_2\text{O}$	$5.8 \times 10^{-6}$	-
$\text{H}_2\text{PO}_4^-$	$7.7 \times 10^{-7}$	0.13

Rate is insensitive to entering group

i.e. evidence support D-activation

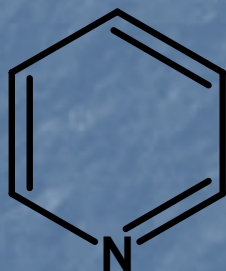
Further evidence come from the substitution studies of Y- by X-  
Where no direct substitution was Observed.

## Example

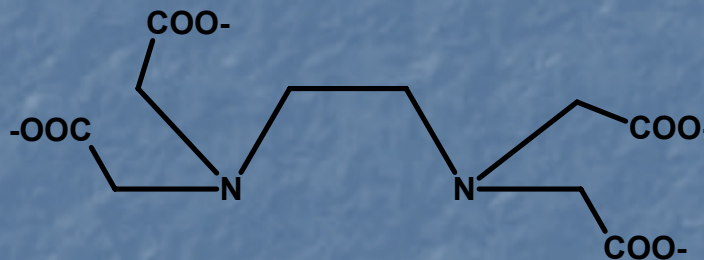
- $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^- + \text{L} \rightarrow [\text{Ru}(\text{edta})\text{L}]$
- $[\text{Ru}(\text{edta})\text{L}] + \text{H}_2\text{O} \rightarrow [\text{Ru}(\text{edta})(\text{H}_2\text{O})]^- + \text{L}$
- Rate constants for substitution by L ( $k_{\text{f}}$ ) of  $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$  and for aquation  $k_{\text{aq}}$  of  $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$  at 25°C

■ L	$k_{\text{f}} (\text{M}^{-1}\text{sec}^{-1})$	$k_{\text{aq}} (\text{sec}^{-1})$
■ Pyridine	$6.3 \times 10^3$	0.061
■ $\text{NCS}^-$	$2.7 \times 10^2$	0.5
■ $\text{CH}_3\text{CN}$	$3.0 \times 10$	3.2

# Ligands



pyridine



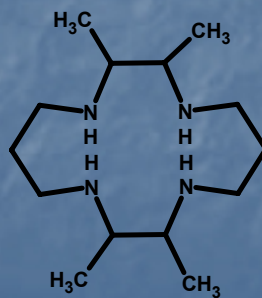
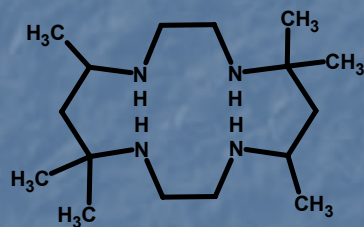
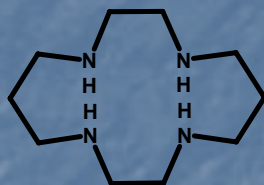
edta



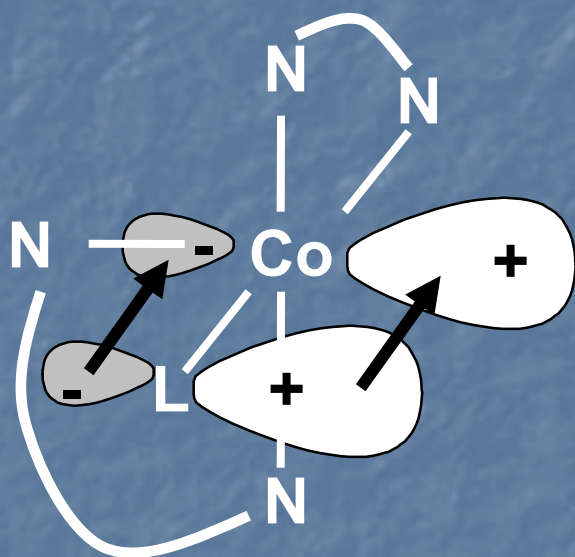
# Steric Effect of Inert Ligands

- Crowding around the metal ion will retard the rate of reactions that occur by an a-type mechanism and to speed up those occurring via a d-type mechanism.

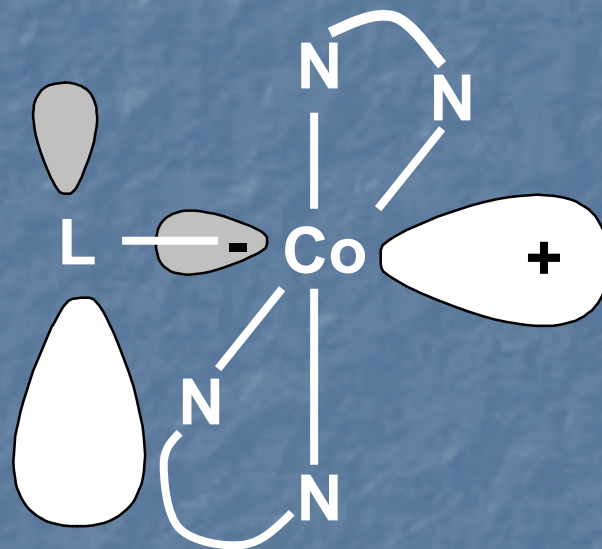
# Steric Effect



# Electronic Effect of Inert Ligands



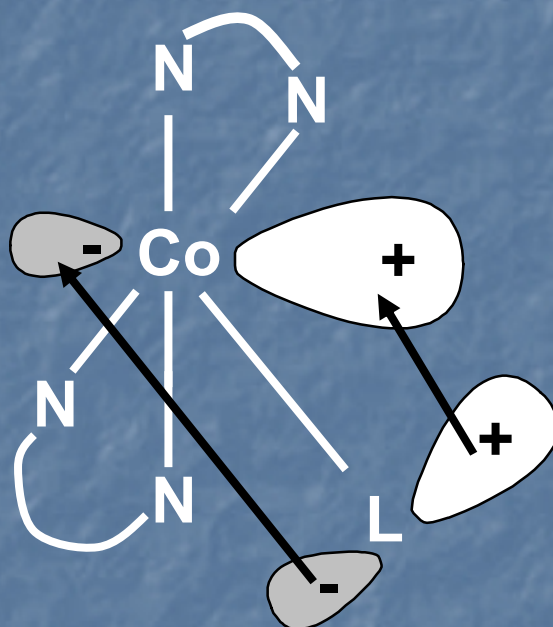
$\pi$ -donation by a cis ligand into the p component of an empty  $d^2sp^3$  hybrid.



$\pi$ -orbital of trans ligand is  $\perp$  to  $d^2sp^3$  hybrid.



# Rearrangement



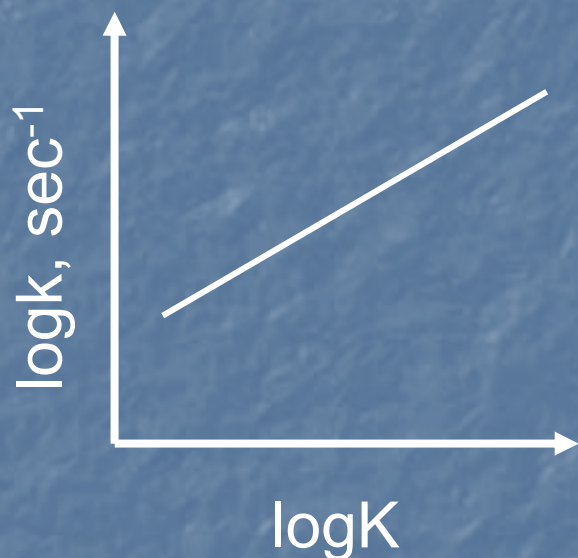
$\pi$ -donation from trans Ligand can occur upon rearrangement to Trigonal bipyramidal

# Activation Parameters

- $\Delta H^\ddagger$  Enthalpy of activation is a measure of the height of the energy barrier, particularly bond strengths within and between reactants, which must be overcome to attain the transition state;
- If  $\Delta H^\ddagger < D_{(M-X)}$ , then bond is broken during activation where  $D$  = dissociation energy.
- $\Delta S^\ddagger$  relates to probability of reaction-it includes contributions from steric bulk and orientation of reactants
- $\Delta S^\ddagger \sim 0$  for unimolecular reactions  
+ for dissociative
- The more negative the value of
- $\Delta S^\ddagger$  the lower the reaction rate.

# Activation Parameters

- $k \propto \Delta G^\ddagger$ ; more thermodynamically favored reactions proceed faster
- Hamond's postulate: Two consecutively occurring states that have similar energy along a reaction coordinate will involve only small structural reorganization.



$$\Delta G^\ddagger = -RT \ln K$$

- Slope = 1 for dissociative; i.e. TS or intermediate falls late in the reaction coordinate; i.e. product-like
- Slope  $\sim 0.5$  for associative, TS or [x] falls early in the reaction coordinate; i.e. reactants-like.
- Volume of activation + dissociative & - associative

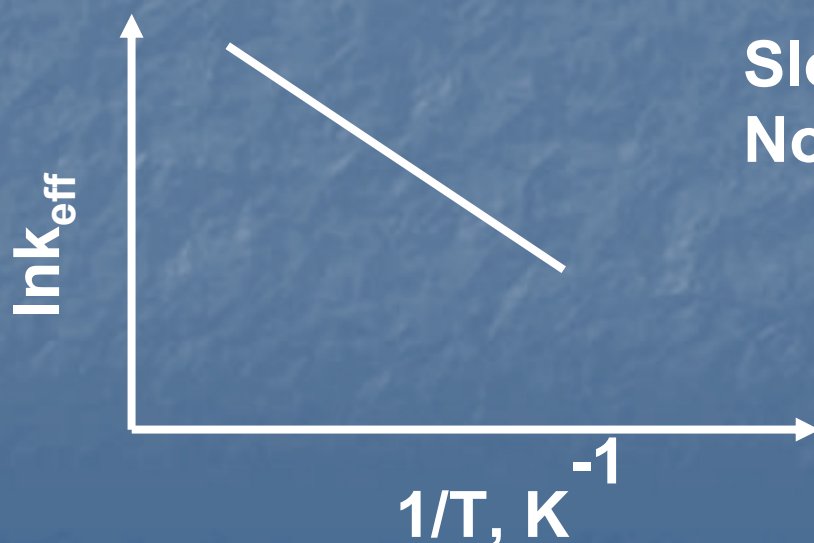


# Activation Parameters, The Eyring Equation

- $k = RT/Nh e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$
- $kNh/RT = e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$
- $k_{\text{eff}} = e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$

Where N is Avogadro's Number =  $6.02 \times 10^{23} \text{ mol}^{-1}$

H = Plank's constant =  $6.6 \times 10^{-34} \text{ J.S.}$

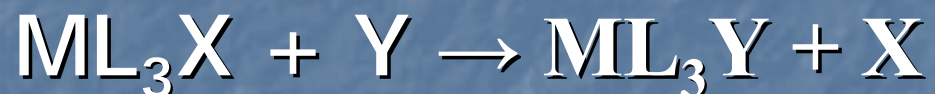
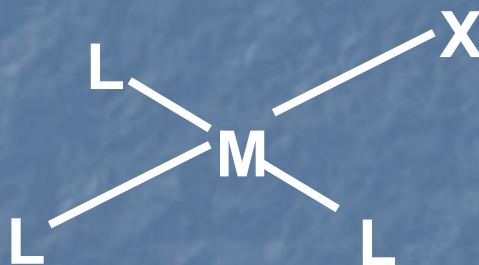


**Slope =  $-\Delta H^\ddagger/R$**

**Note :  $\Delta H^\ddagger = E_a - RT$**

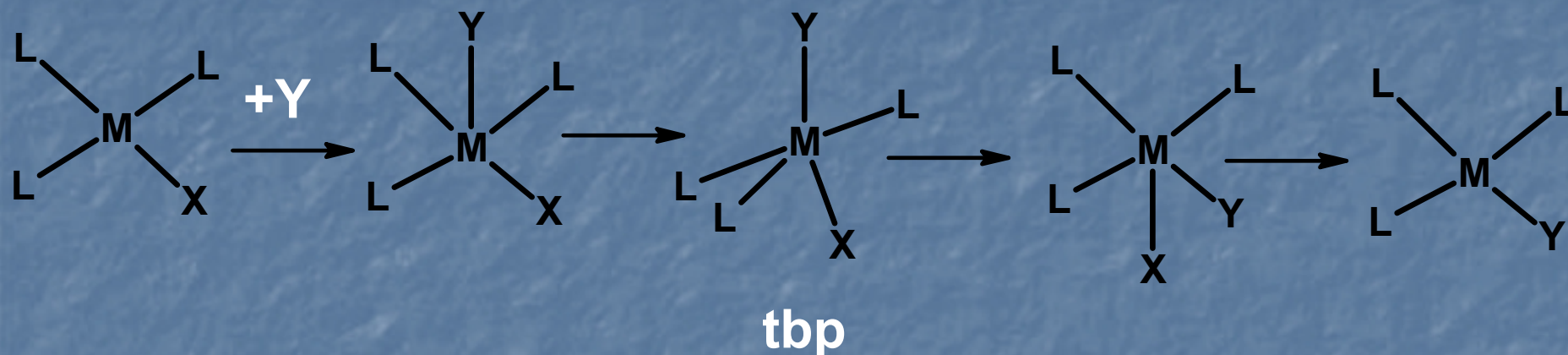
# Ligand Substitution Reactions on Square Planar Complexes

$d^8$  metal ions such as  $[\text{Au}^{\text{III}}, \text{Ni}^{\text{II}}, \text{Pd}^{\text{II}}, \text{Pt}^{\text{II}}, \text{Rh}^{\text{I}}$  and  $\text{Ir}^{\text{I}}]$  usually form four coordinate square planar compounds, especially with strong ligands.



$$\text{Rate} = k_1[\text{ML}_3\text{X}] + k_2[\text{Y}][\text{ML}_3\text{X}]$$

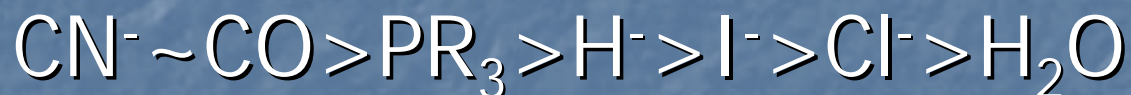
# Mechanism for Sq. Substitution



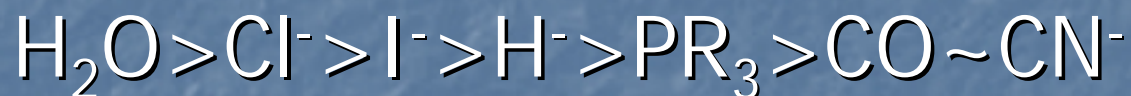
- Trigonal bipyramidal may be an intermediate for A type of TS for  $I_a$
- 5-coordinate species may be isolated as in  $[Ni(CN)_5]^{3-}$  and can be isolated as salt of  $[Co(en)_3]^{3+}$
- Reactivity order  $Ni^{II} > Pd^{II} > Pt^{II}$



- Nucleophilicity order for square planar compounds:



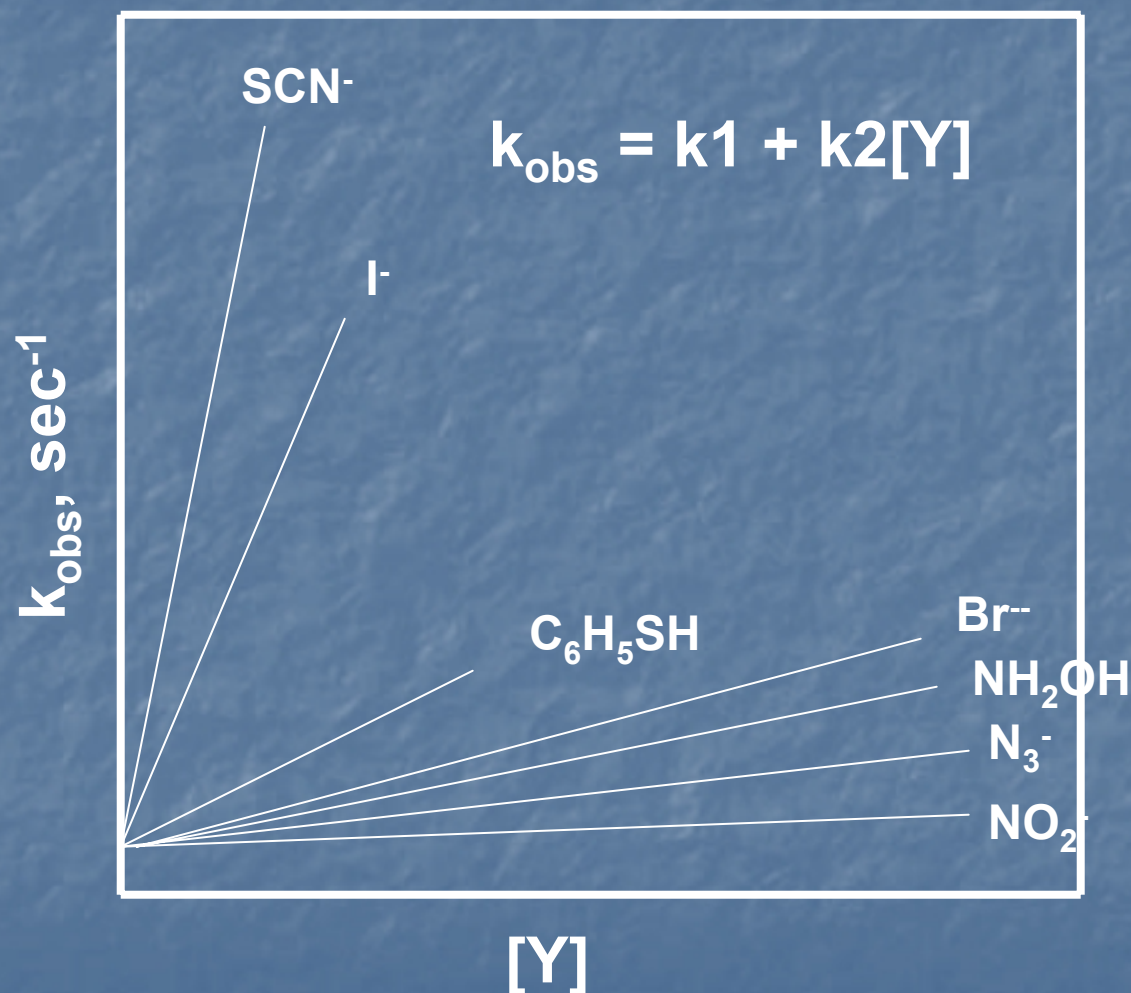
- Leaving group order



# Rate Law

- $\text{Rate} = (k_1 + k_2[Y])[\text{ML}_3\text{X}]$
- Indicate two parallel reaction paths.
- In the presence of a large excess of the entering ligand  $[Y]$  remains constant throughout the reaction
- $\text{Rate} = -d[\text{ML}_3\text{X}]/dt = k_{\text{obs.}}[\text{ML}_3\text{X}]$  where  $k_{\text{obs.}} = k_1 + k_2[Y]$
- A plot of  $k_{\text{obs.}}$  versus  $[Y]$ ,
- Straight line with  $k_1 = \text{intercept}$  and  $k_2$  is the nucleophilicity strength of  $Y$ .

# Rates of reaction of



- Rate of reaction of  $\text{trans-}[\text{Pt}(\text{py})_2\text{Cl}_2]$  in methanol @ 30 C as a function of the concentration of entering ligand.



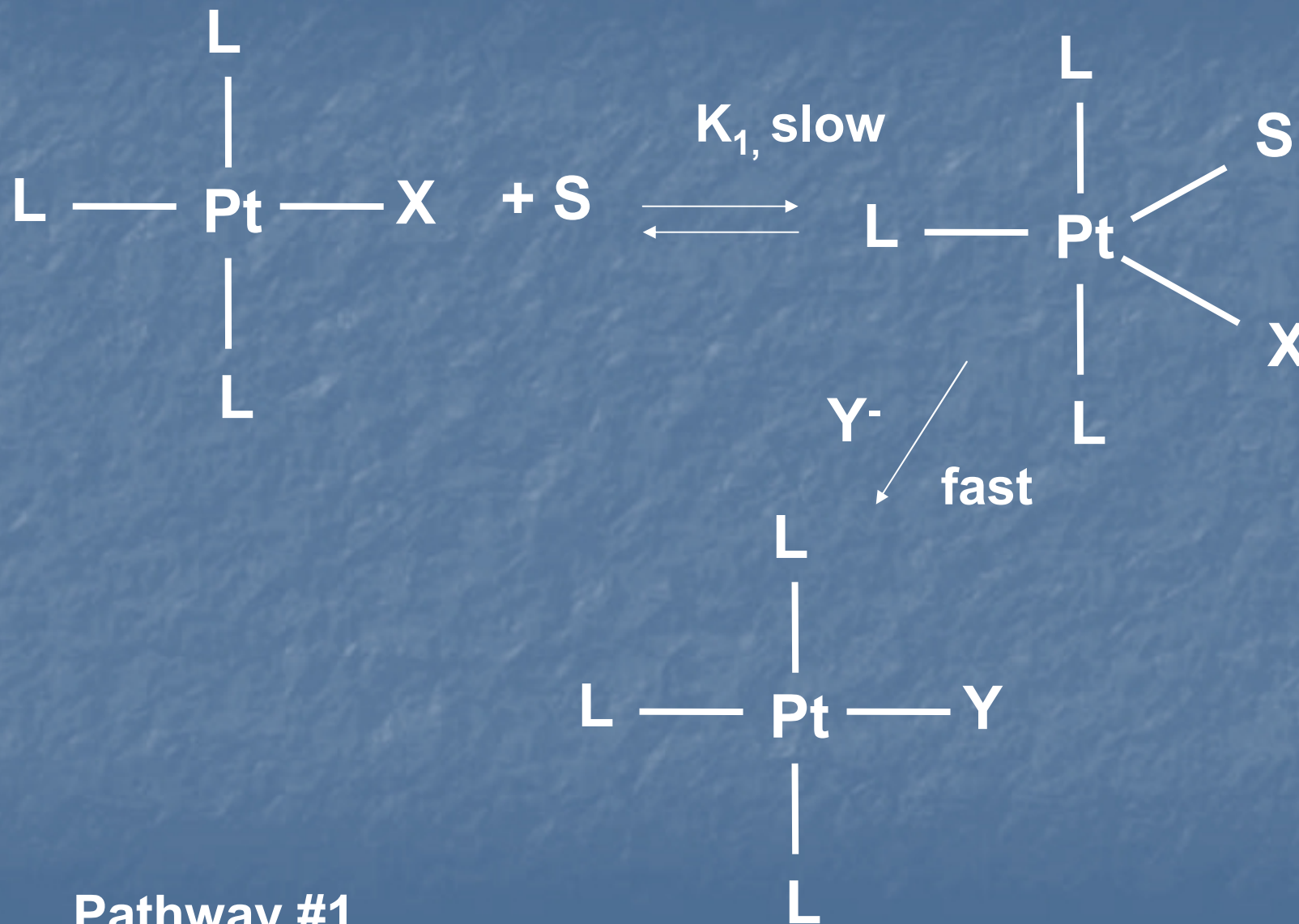
# Rate Law

- Note all ligands have the same intercept,  $k_1$ , implying that they go through the same species.
- $k_2$  is different from one ligand to another.
- Since the only species present in solution in addition to the ligands is the solvent molecules this implies that the solvent is involved in the first term and the second term in the ligand participation

# Summary

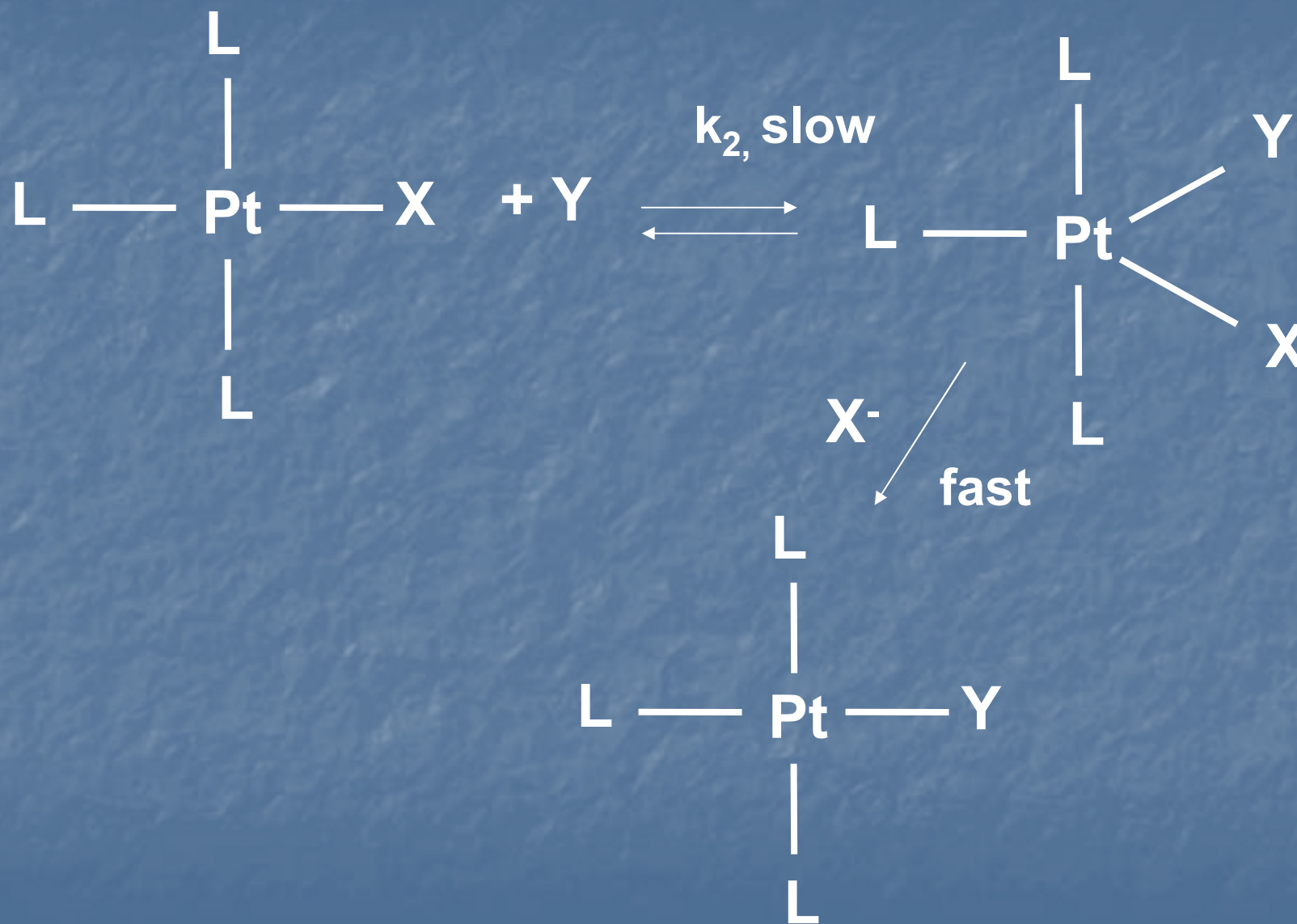
- Two pathways are involved:
- (1) first order in complex ( $k_1$ ), does not involve Y in rate determining step. This mechanistic pathway is solvent mediated.
- (2) first order in complex and Y ( $k_2$ ), Y involved in rate determining step

# Mechanism





# Pathway 2



# Summary

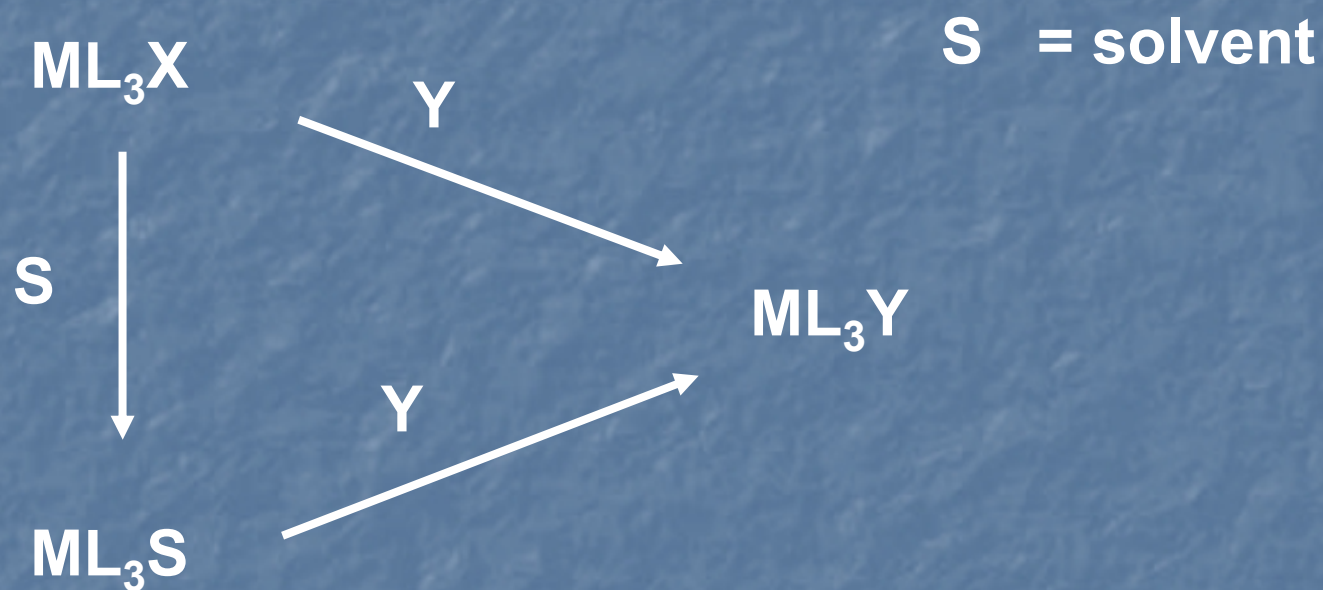
- Both reactions proceed via an associative process (A), involving a trigonal bipyramid transition state. Is there any chemical justification for this transition state?
- (i) Many five coordinate transition metal complexes are known, e.g.,  $\text{Fe}(\text{CO})_5$ ,  $[\text{CoL}_2(\text{CO})_3]^+$ ,  $[\text{Ni}(\text{CN})_5]^{3-}$
- (ii)  $\text{ML}_3\text{X}$  complexes are sterically and electronically unsaturated and have space for Y to coordinate.

# Evidence

- Rate law is consistent with associative mechanism
- Charge on the metal center-has no effect on the rate of reaction
- Steric effect-significant increase in rate was observed for less hindered ligands, trans- is faster than cis
- $\text{C}_6\text{H}_5 > 2\text{Me}-\text{C}_6\text{H}_4 > 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2^-$
- Note trans > cis
- For the substitution reaction
- $\text{Pt}(\text{PEt}_3)_2\text{RCl} + \text{Y}^- \rightarrow \text{Pt}(\text{PEt}_3)_2\text{RY} + \text{Cl}^-$



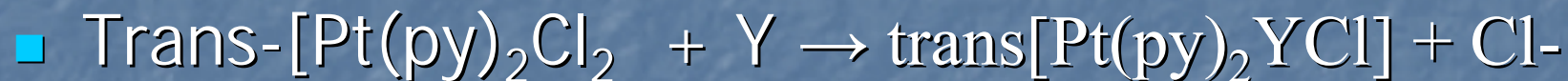
# Rate law



- Schematic representation of parallel reactions

# Effect of Entering & Leaving Ligands on Rate

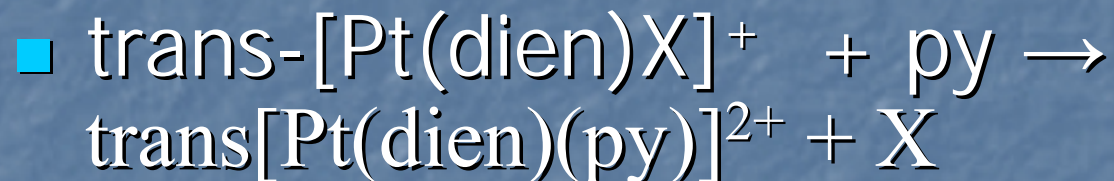
- Rate constants for ligand displacement in some square planar Pt(II) compounds



■ Y	T C	$k_2(\text{M}^{-1}\text{sec}^{-1})$	$n_{\text{Pt}}$
■ $\text{CH}_3\text{OH}$	25	$2.7 \times 10^{-7}$	00
■ $\text{CH}_3\text{O}^-$	25	very slow	<2.4
■ $\text{Cl}^-$	30	$4.5 \times 10^{-4}$	3.04
■ $\text{NH}_3$	30	$4.7 \times 10^{-4}$	3.07
■ $\text{N}_3^-$	30	$1.55 \times 10^{-3}$	3.58
■ $\text{I}^-$	30	$1.07 \times 10^{-1}$	5.46
■ $\text{CN}^-$	25	4.00	7.14
■ $\text{PPh}_3$	25	249	8.93

# Effect of Entering & Leaving Ligands on Rate

- Rate constants for ligand displacement in some square planar Pt(II) compounds



■ X	$k_{\text{obs}}(\text{M}^{-1}\text{sec}^{-1})$
■ $\text{CN}^-$	$1.7 \times 10^{-8}$
■ $\text{SCN}^-$	$3.0 \times 10^{-7}$
■ $\text{I}^-$	$1.0 \times 10^{-5}$
■ $\text{Cl}^-$	$3.5 \times 10^{-5}$
■ $\text{H}_2\text{O}$	$1.9 \times 10^{-3}$
■ $\text{NO}_3^-$	very fast



# Factors affecting rate of substitution

## 1. Nucleophilicity

- $\text{PtCl}_2\text{Py}_2 + \text{Y}^- \rightarrow \text{PtClYPy}_2 + \text{Cl}^-$
- Standard Reaction, and methanol as a standard nucleophile, a base with unshared pair of electrons such as  $\text{NH}_3$ ,  $\text{I}^-$ ,  $\text{Cl}^-$ ,  $\text{R}^-$ ,  $\text{PR}_3$
- $n_{\text{Pt}} = \log k_2(\text{Y}) / k_1(\text{CH}_3\text{OH}) = \log k_2(\text{Y}) - \log k_1(\text{CH}_3\text{OH})$
- Factors Affect Nucleophilicity
  - Basicity
  - Oxidation potential of Y

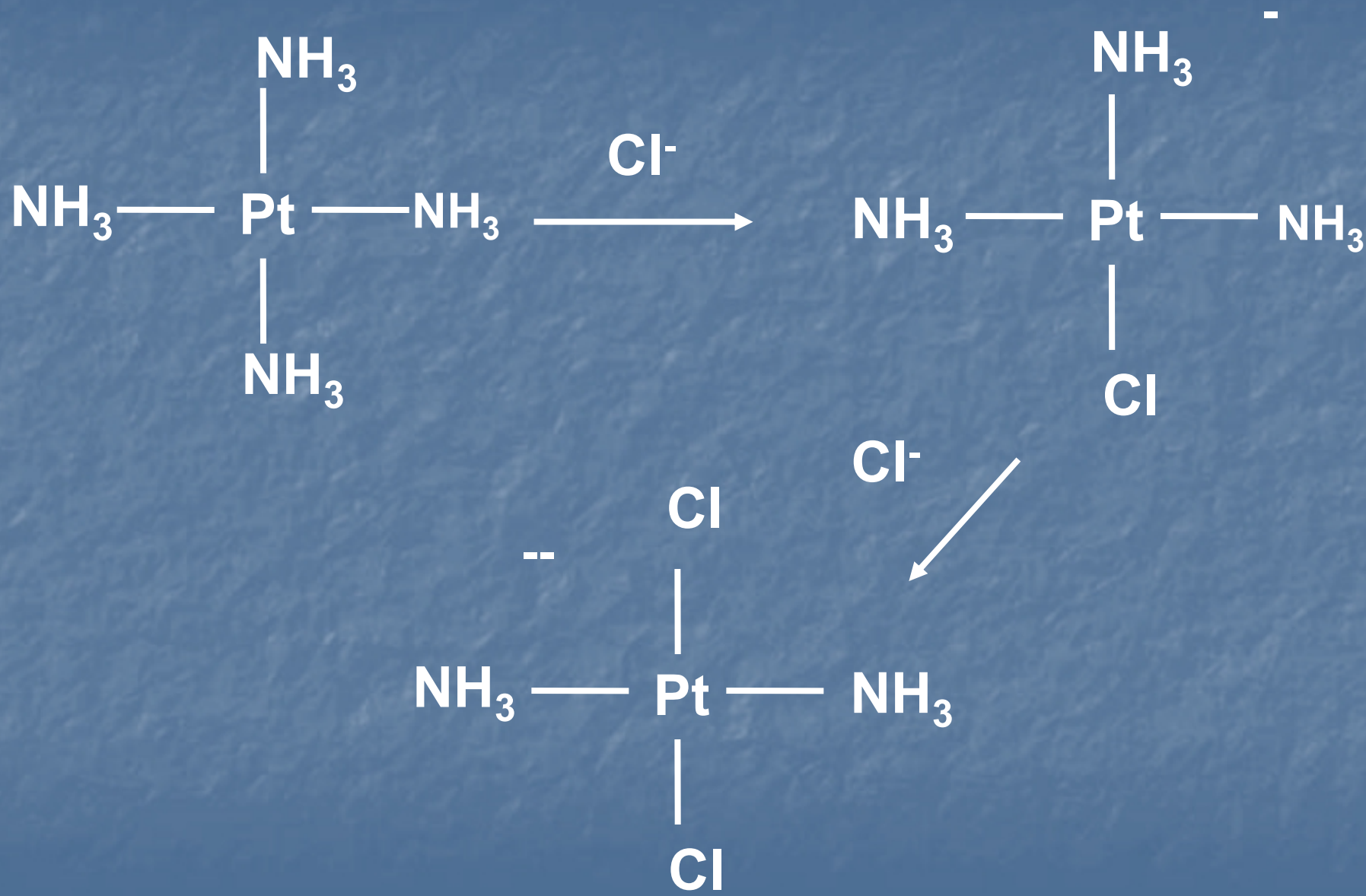
# Nucleophilicity order

- $sn_{Pt} = \log k_2(Y)/k_2(\text{solvent})$
- $S$  = nucleophilicity discriminating factor
- $I^- > Br^- > Cl^- >> F^-$
- $PR_3 > AsR_3 > SbR_3 >> NR_3$
- Sulphur > Oxygen
- Soft bases are better nucleophiles for  $Pt^{II}$  as it is a soft acid

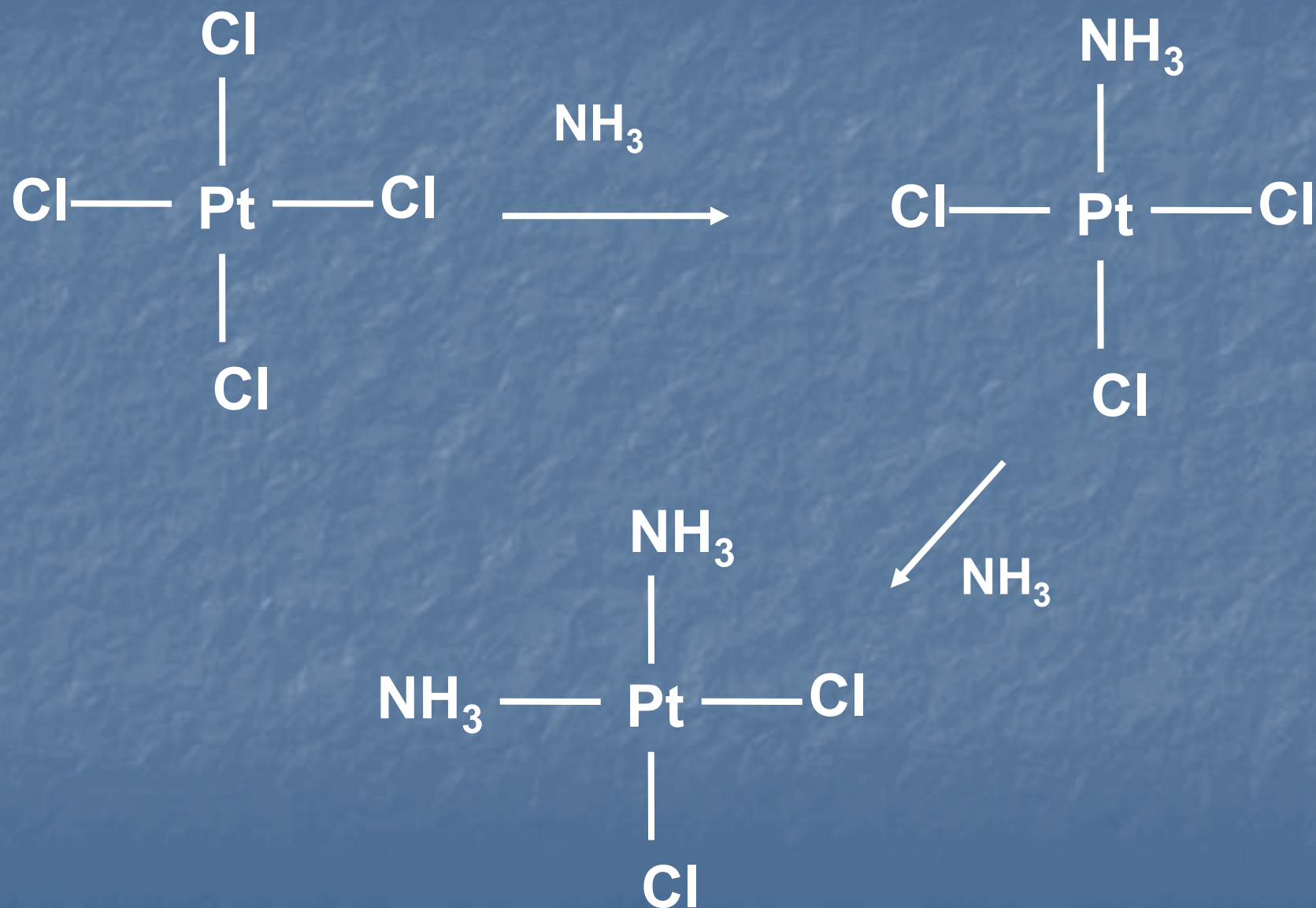
# Trans –ligands & trans effect

- "The *trans* effect is defined as the
- effect of a coordinated ligand upon the rate of substitution of ligands opposite to it."
- For Pt II compounds the order of trans effect
- $\text{H}_2\text{O} \sim \text{OH}^- \sim \text{NH}_3 \sim \text{NR}_3 < \text{Cl}^- \sim \text{Br}^- < \text{SCN}^-$   
 $\sim \text{I}^- \sim \text{NO}_2^- \sim \text{C}_6\text{H}_5^- < \text{CH}_3^- < \text{PR}_3 \sim \text{AsR}_3 \sim$   
 $\text{H}^- < \text{olefins} \sim \text{CO} \sim \text{CN}^-$





# Trans effect in synthesis



# Try

- Synthesis of *cis* and *trans*- isomers of  $[\text{PtCl}_2(\text{NH}_3)(\text{PPh}_3)]$  given the reactants  $\text{PPh}_3$ ,  $\text{NH}_3$  and  $[\text{PtCl}_4]^{2-}$

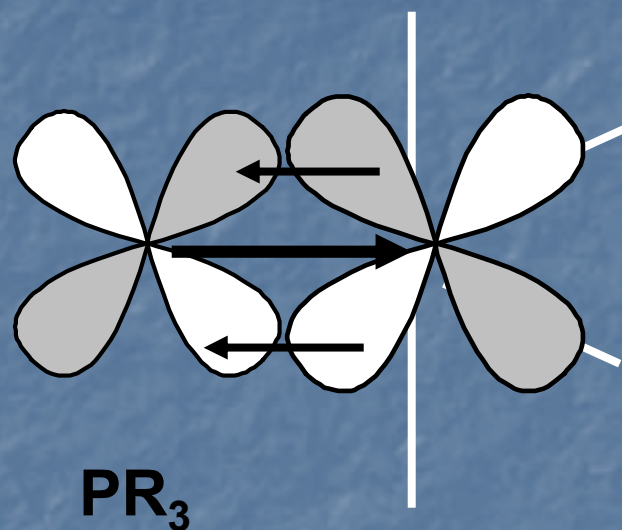
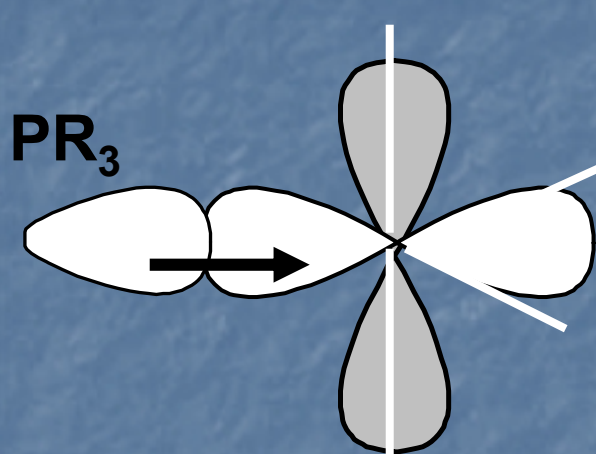


# Origin of the trans-effect-

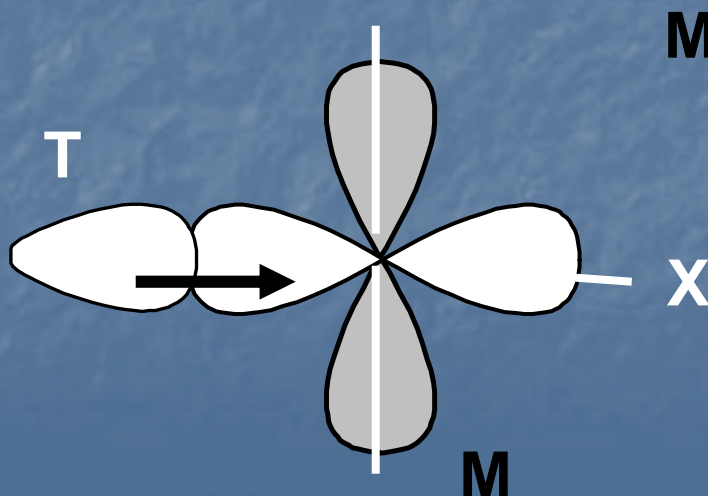
- Electronic (Molecular Orbitals)
  - $\sigma$ -donor ligands such as  $\text{H}^-$ ,  $\text{R}^-$ , increase electron density around the metal.
  - $\pi$ -acceptor ligands such as  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{PR}_3$ ,  $\pi$ -back bonding weaken the bond trans to it.

# Trans-effect

T.S. Tpy  $\sigma$ -donor  $\pi$ -acceptor



Ground state



# Steric Effect of Inert Ligands

- Steric effect is unclear
- $\text{Trans-Pt(PEt}_3)_2\text{RCl]} + \text{y} \rightarrow \text{trans-[Pt(PEt}_3)_2\text{RY]} + \text{Cl}^-$

■ R	Solvent	Y=CN	Y =SC(NH <sub>2</sub> ) <sub>2</sub>
■ C <sub>6</sub> H <sub>5</sub>	methanol	3.61	3.30
■ C <sub>6</sub> H <sub>5</sub>	DMSO	very fast	0.532
■ o-C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	methanol	0.234	0.652
■ o-C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	dmso	3.54	0.106
■ 2,6-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	methanol	8.49x10 <sup>-3</sup>	4.94x10 <sup>-2</sup>
■ 2,6-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	dmso	3.17x10 <sup>-2</sup>	9.52x10 <sup>-3</sup>



# Steric Effect

- Steric effect is significant, hints to dissociative pathway,
- i.e. although associative pathway is feasible but dissociative pathway may become operative in the presence of bulky Ligands.

# Conclusion

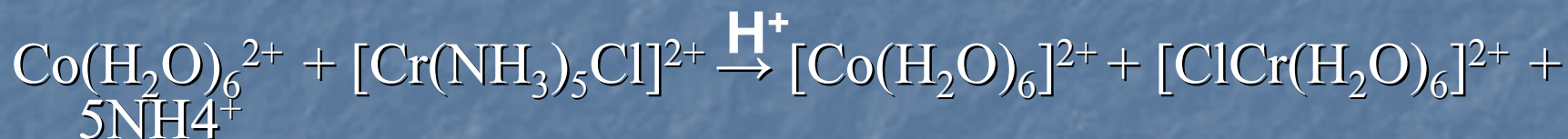
- (i) 1 st order in substrate and nucleophile,
- (ii)  $k_1$  (solvent) and  $k_2$  (entering ligand)- solvent is important
- A number of factors determine reactivity
- (i) Nucleophilicity - different from basicity
- (ii) *cis* and *trans* effects - kinetic effects, not the same as *trans* influence - thermodynamic effect
- (iii) Leaving group effect
- (iv) Rate depends on the metal M
- Predictive synthesis.

# Redox Reactions

- Electron-transfer
- $A + B^- \rightarrow A^- + B$
- 1. Inner sphere
- Transition state involve interpenetrating coordination sphere or bridging ligands or interaction between reactants which is common to both coordination sphere & serves as channel through which electron flows.

Taube & Meyer  $\text{Cr}^{2+}$  &  $\text{Cr}^{3+}$

$\text{Co}(\text{H}_2\text{O})_6^{2+}$  (Labile) &  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$  (inert)



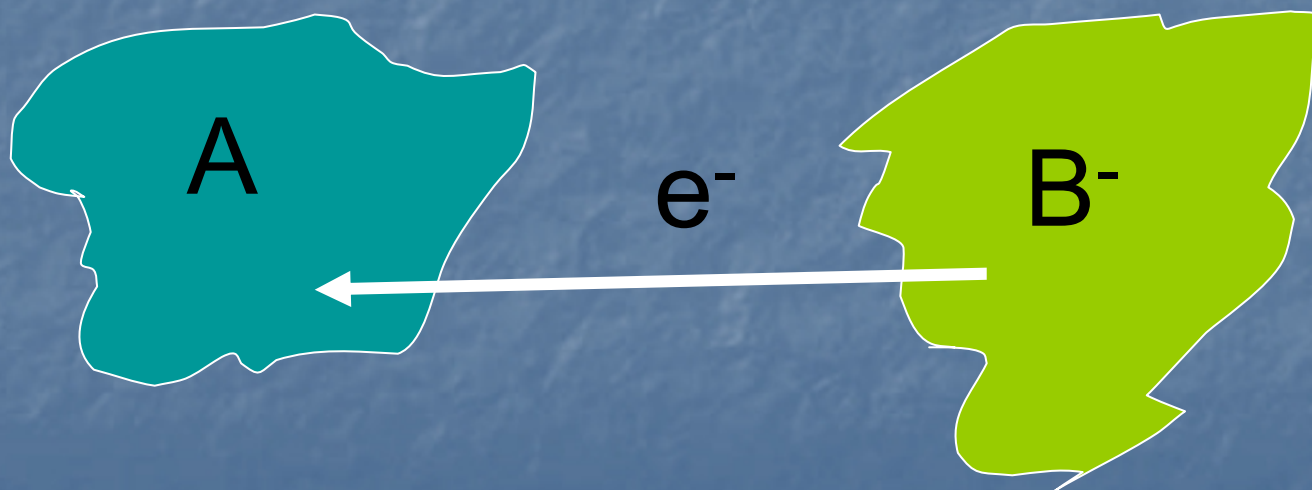


# Inner sphere

- $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{Cr}^{2+} \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{ClCr}]^{4+}$
- $[\text{Co}(\text{NH}_3)_5\text{ClCr}]^{4+} \rightarrow \text{CrCl}^{2+} + [\text{Co}(\text{NH}_3)_5]^{2+}$
- $[\text{Co}(\text{NH}_3)_5]^{2+} + 5\text{H}^+ \rightleftharpoons \text{Co}^{2+} + 5\text{NH}_4^+$
- $\text{Cr}^{3+}$  inert to substitution with
- $k = 2.9 \times 10^{-8} \text{ M}^{-1}\text{sec}^{-1}$  for  $\text{Cl}^-$  anation of  $\text{Cr}^{3+}$
- For the reduction  $k = 6 \times 10^5 \text{ M}^{-1}\text{sec}^{-1}$
- $\therefore$  Cr-Cl could not have been formed from substitution of free  $\text{Cl}^-$

# Outer-sphere Electron Transfer

- The interaction between the oxidant and reductant at the time of electron transfer is small, therefore the coordination shells are intact; i.e. through space , diffusion control



# Example Outer-sphere Electron Transfer

- $[\text{Fe}(\text{me}_2\text{bipy})_3]^{2+} + [\text{Fe}(\text{bipy})_3]^{3+} \rightleftharpoons [\text{Fe}(\text{me}_2\text{bipy})_3]^{3+} + [\text{Fe}(\text{bipy})_3]^{2+}$
- $\text{Rate} = k [\text{Fe}(\text{me}_2\text{bipy})_3]^{2+} [\text{Fe}(\text{bipy})_3]^{3+}$
- $= 10^8 \text{ M}^{-1}\text{sec}^{-1}$
- Rate of substitution is  $\sim 10^4 \text{ M}^{-1}\text{sec}^{-1}$
- For outer sphere the redox rate must be faster than the substitution rate.