

Reaction Mechanisms of Inorganic Compounds

C21J, 4 Lectures

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- Introduction
- Ligand substitution reactions
 - Octahedral Complexes
 - Square Planar
- Racemization Reactions
- Reference: Chapters 9
- Textbook: B. Douglas, D. H. McDaniel, & J. J. Alexander, Concepts & Models of Inorganic Chemistry, 2nd edition, Wiley, New York

Some Chemistry of Transition Metals

Ligand Exchange

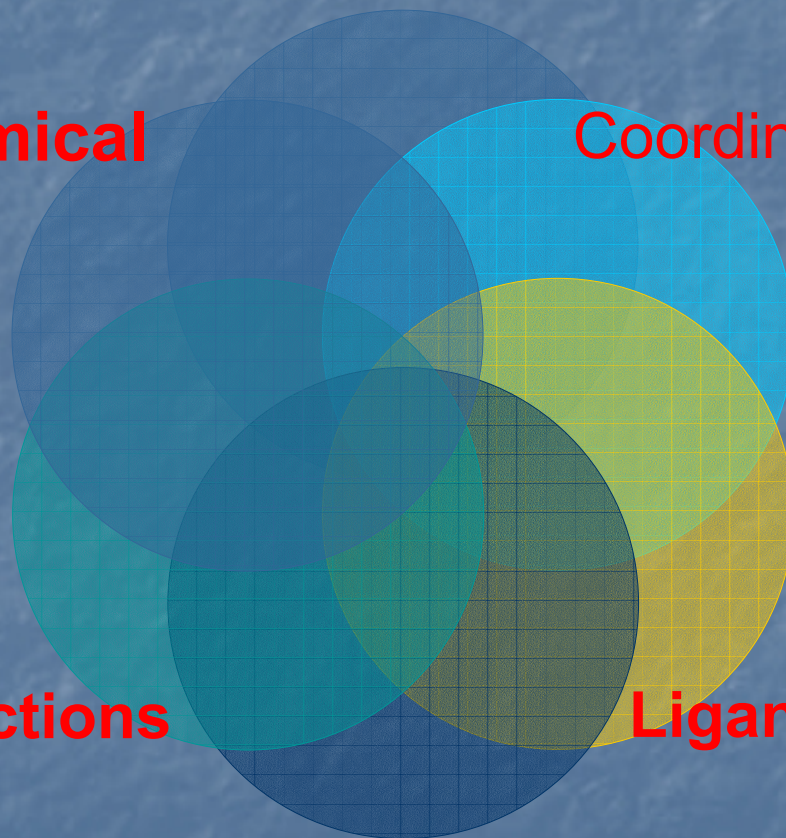
Photochemical

Coordination to metals

Redox Reactions

Ligand Reactivity

**Rearrangement of coordination
Sphere**



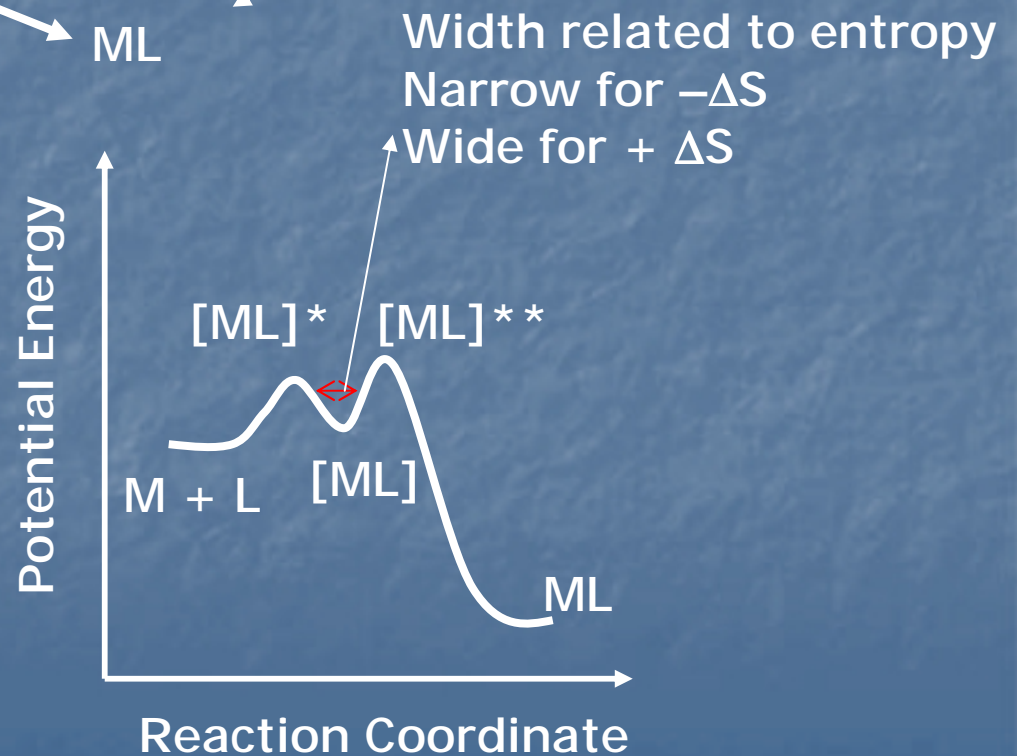
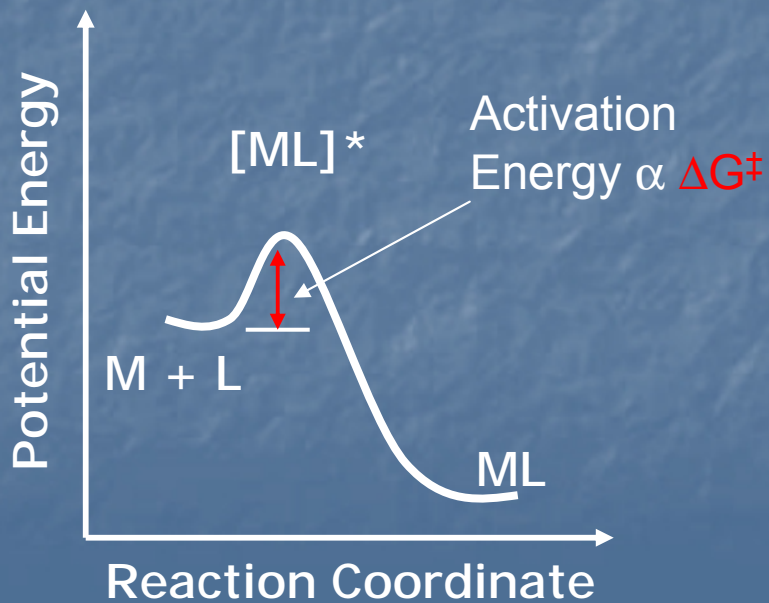
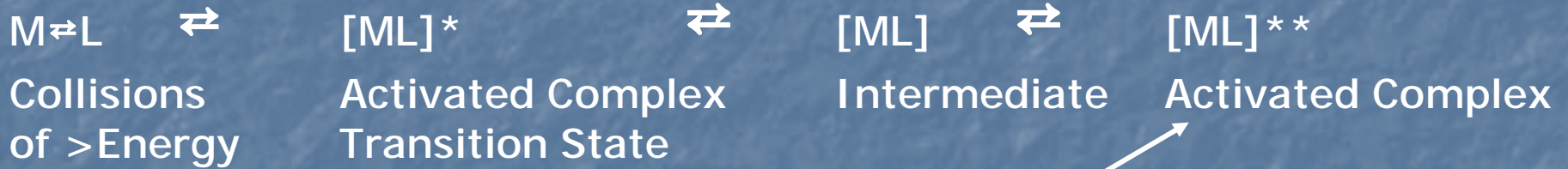
What are reaction mechanisms?

- 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:



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 = $k[L][M]$
- $k \propto K^\ddagger \propto \exp(-\Delta G^\ddagger/RT)$
- $k \propto \exp(\Delta S^\ddagger/R) \exp(-\Delta E_{\text{act}}/RT)$

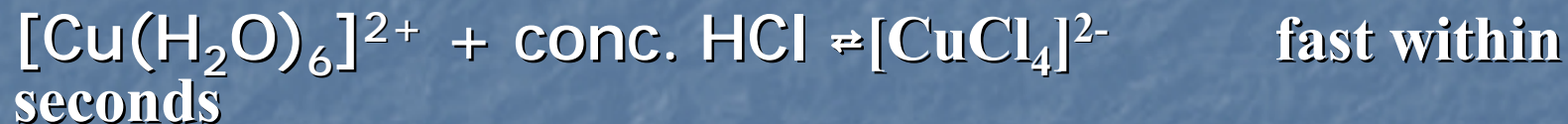
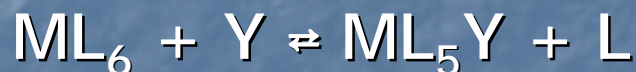
- Fast reactions are favored by:
 - ΔS^\ddagger more positive.
 - ΔE_{act} less positive.
- Note since k is exponentially dependent on ΔS^\ddagger and ΔE_{act} , Small changes in k are not significant in the interpretation of the rate law.

Type of Reactions

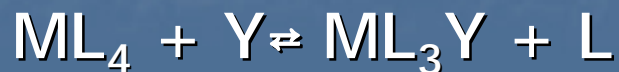
- Ligand Substitution reactions: are those in which the coordination sphere around the metal changes due exchange of one ligand (lewis base) with another ligand.

- e.g.

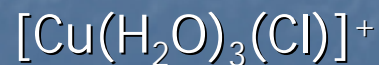
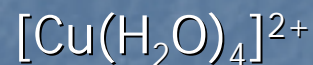
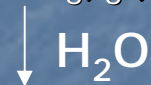
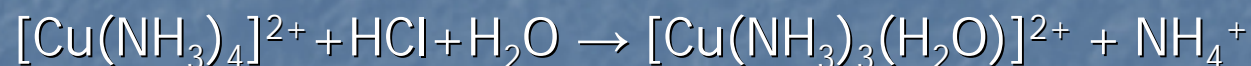
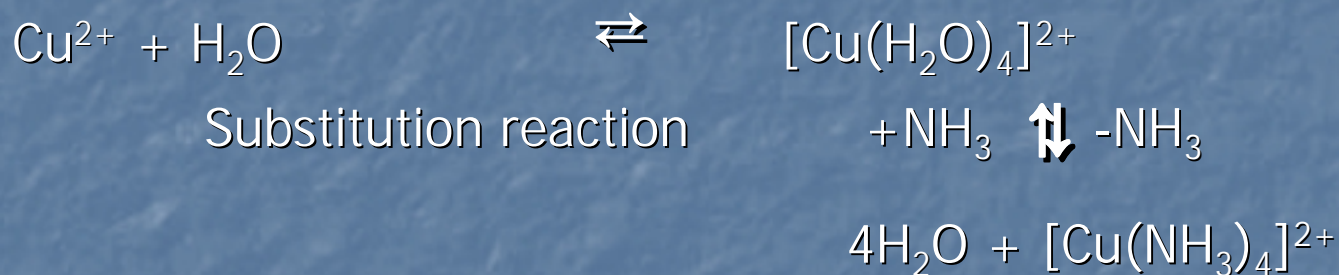
- Octahedral



- 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
■ $[Hg(CN)_4]^{2-}$	10^{42}	very fast
■ $[Fe(CN)_6]^{3-}$	10^{44}	very fast
■ $[Fe(CN)_6]^{4-}$	10^{37}	very fast
■ $[Pt(CN)_4]^{2-}$	$\sim 10^{40}$	$t_{1/2} = 1 \text{ min.}$

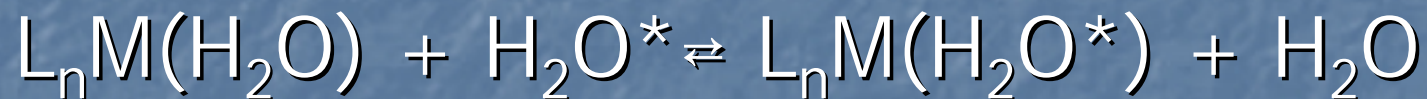
→ $[Hg(CN)_4]^{2-}$ Thermodynamically stable but kinetically labile, the same for $[Ni(CN)_4]^{2-}$
i.e. in solutions ligand exchange is fast but always with CN^- .

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 H₂O exchange



(see Figure 1)

Kinetics of Water Exchange

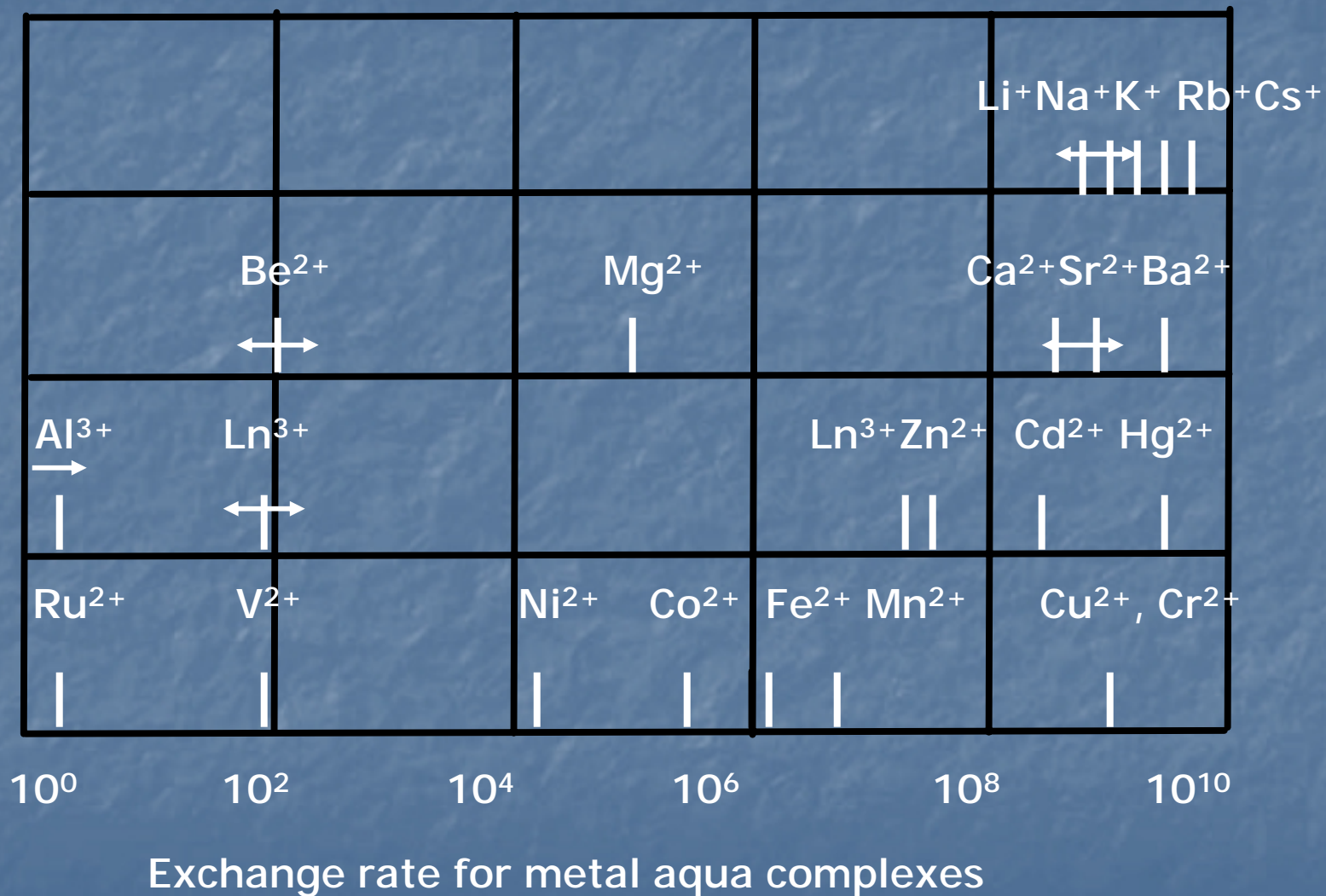


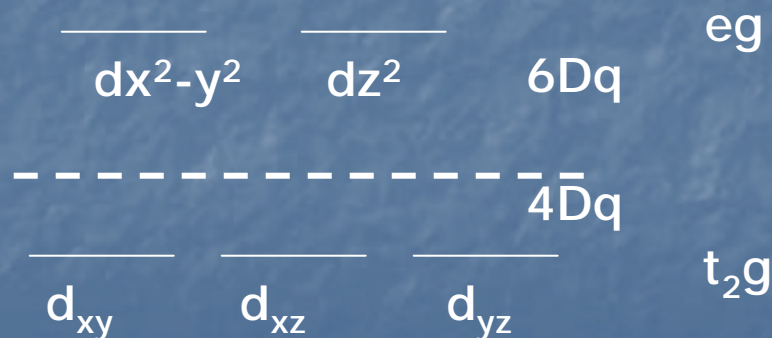
Figure 1

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 Be^{2+} & Mg^{2+}), Group IIB (except for Zn^{2+}), Cr^{2+} and Cu^{2+} .
- Class II Exchange-rate constants are between 10^4 - 10^8 sec^{-1} . The divalent first row transition metal ions (except for V^{2+} , Cr^{2+} & Cu^{2+}) as well as Mg^{2+} and the trivalent lanthanide ions.
- Class III Exchange-rate constants are between 1 and 10^4 sec^{-1} . This class includes Be^{2+} , V^{2+} , Al^{3+} , Ga^{3+} and several trivalent first-row transition metal ions.
- Class IV Exchange rate constants between 10^{-6} to 10^{-1} sec^{-1} . Member of the set are Cr^{3+} , Co^{3+} , Rh^{3+} , Ir^{3+} and 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**

$O_h \rightarrow$ high spin d^8 such as Ni^{II}

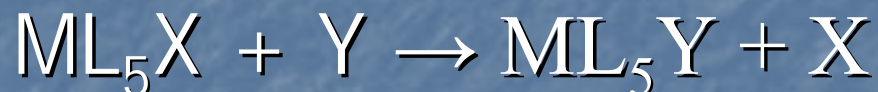
& low spin d^8 such as Rh(I) , Ir(I) , Ni(II) , Pd(II) , Pt(II) &

Square planar Au(III) are **labile**.

React faster than d^6 & d^3

For Cu^{2+} & 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.

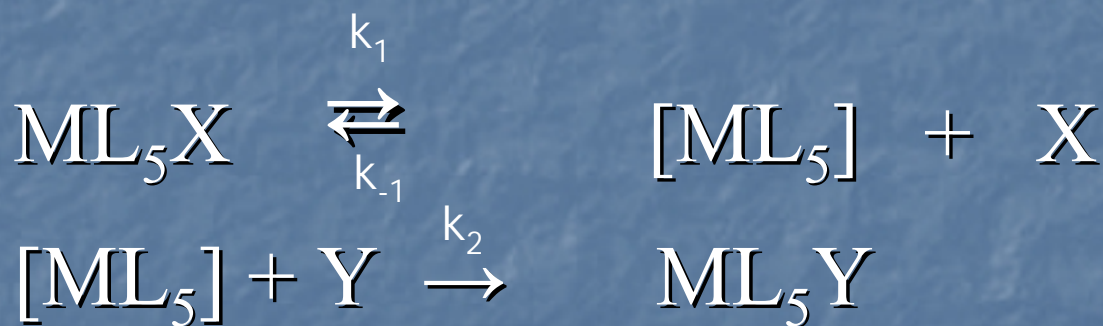
Mechanism of Ligand Substitution in O_h Compounds



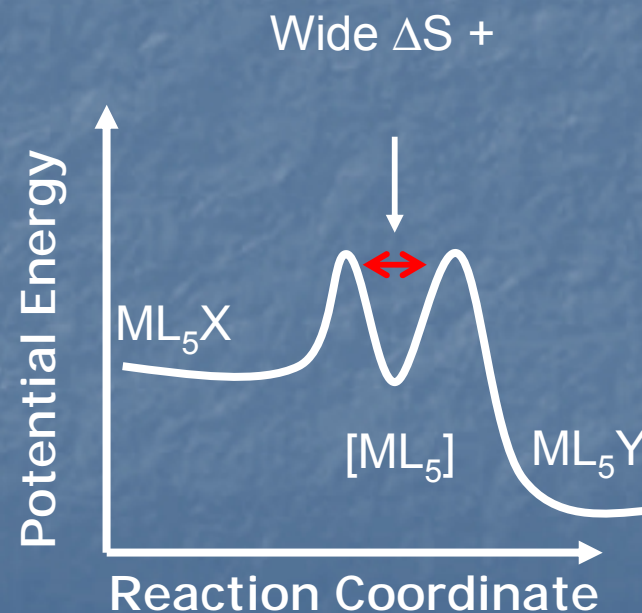
Where X is leaving group

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

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

Apply the **steady-state approximation to L_5M**

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

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

& Rate = $(k_1k_2[\text{L}_5\text{MX}][\text{Y}]) / (k_{-1}[\text{X}] + k_2[\text{Y}])$

Bimolecular

Dissociative Mechanism, D-type

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

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

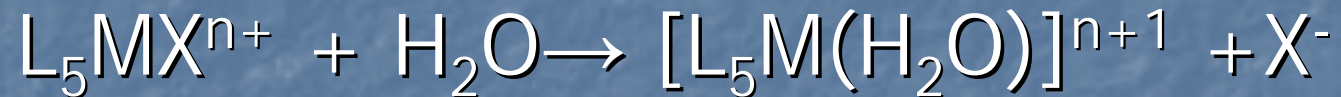
e.g. aquation and anation of inert $d^6 \text{Co}^{\text{III}}$ compounds of the type $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$.

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

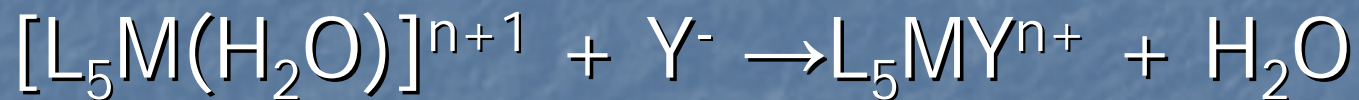
Note true examples of D-type are not common.

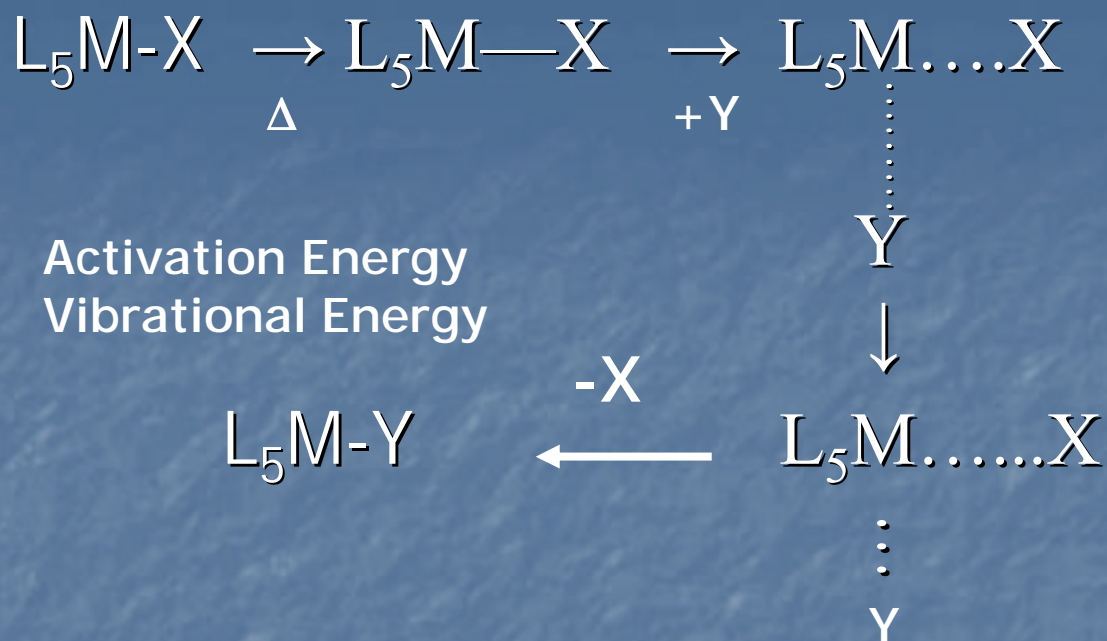
Aquation or acid hydrolysis

- Aquation or acid hydrolysis



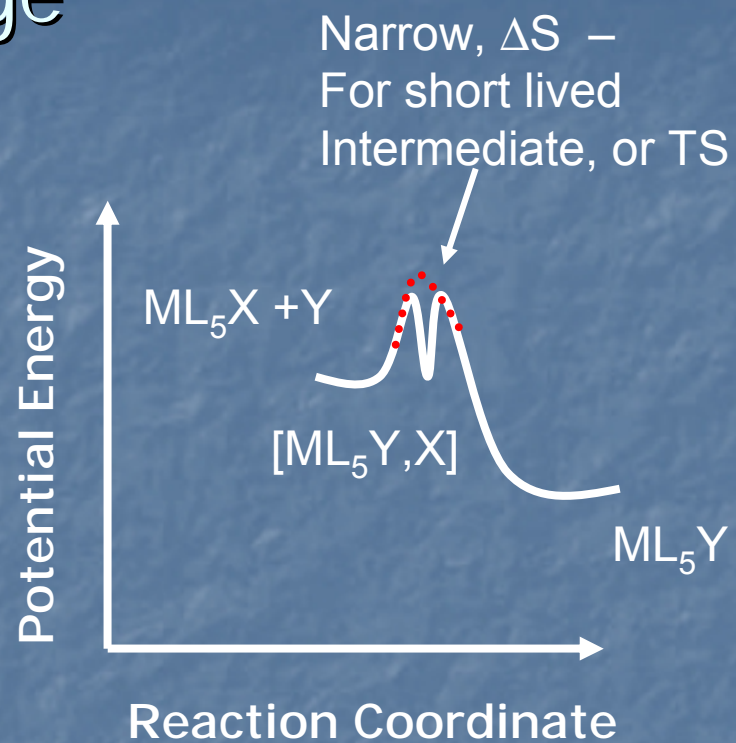
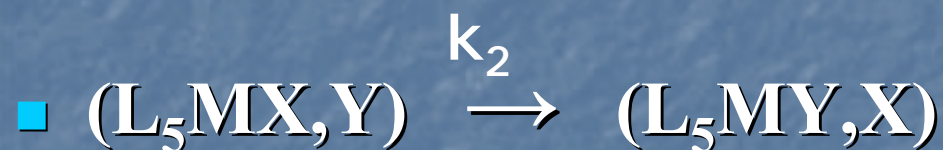
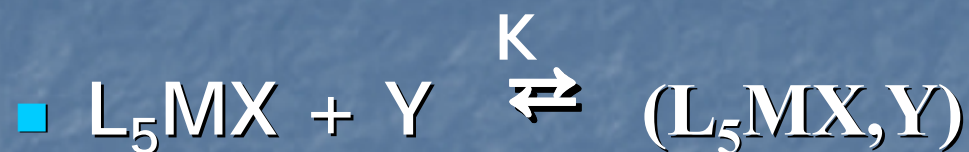
- Anation





- The rate is insensitive to the identity of Y, Implication is that both entering and leaving groups are weakly bound in the transition state. This is known as Dissociative interchange (I_d).
- **No stable intermediate is observed**

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

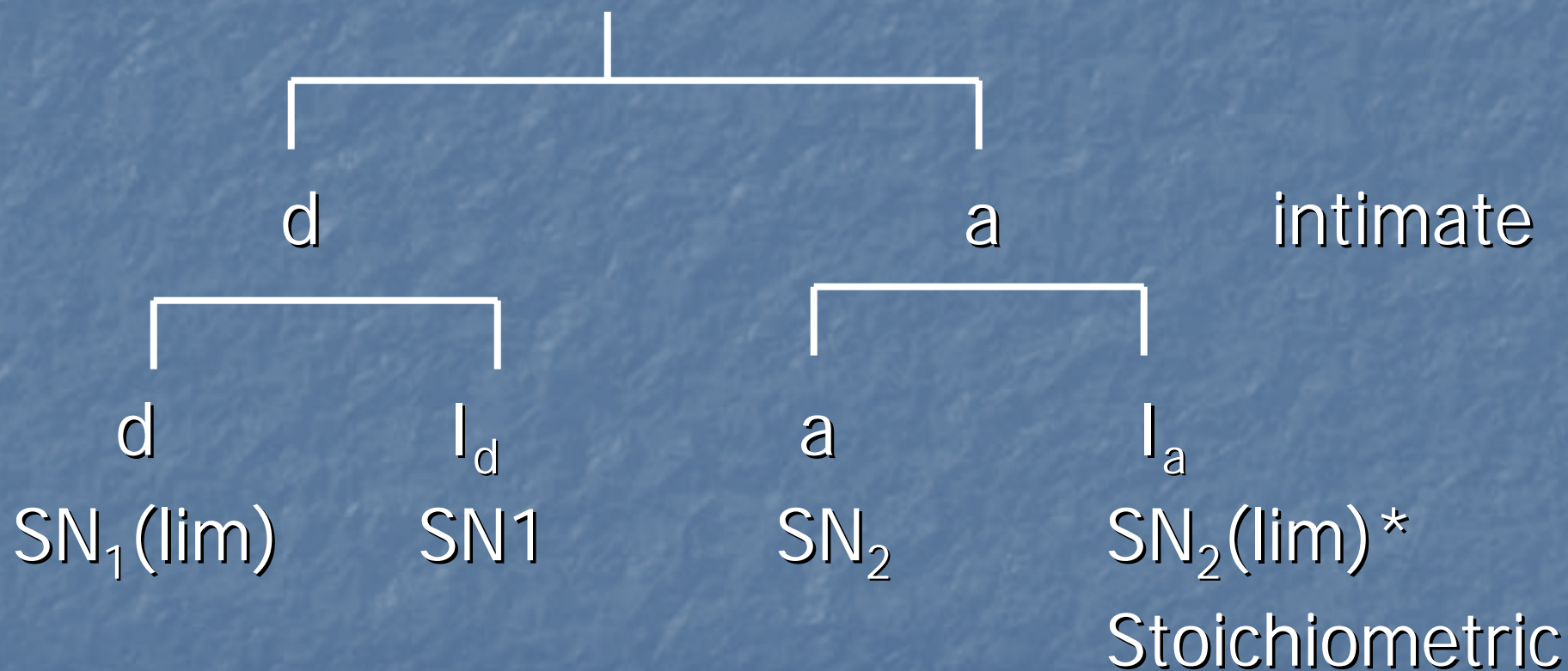
- The experimental parameter accessible here is the initial concentration of the reactant complex $[L_5MX]_0$ which in solution containing Y exists partly in the form of outersphere complex
- $[L_5MX]_0 = [L_5MX] + [L_5MX, Y]$
- $K = k_1/k_2 = [L_5MX, Y]/[Y][L_5MX]$
- $\therefore [L_5MX, Y] = K[Y][L_5MX]$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

Summary

Inorganic Reaction Mechanisms



SN_1 & SN_2 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.

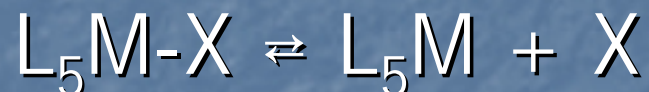
A always second order as long as the final step is not reversible.

Substitution inert ions

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

Intimate Mechanisms

- Nature of leaving & entering groups



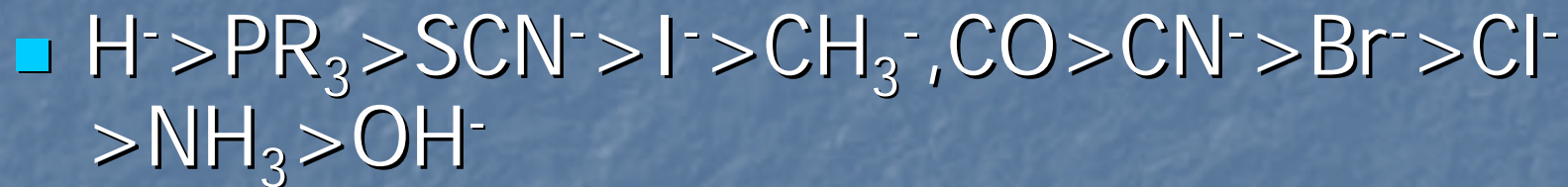
- For dissociative mechanism rate is dependent the leaving group

i.e. M-X bond strength

- e^- - donor σ -donor like NH_3 , H^- ,
 π -donor $\rightarrow \sigma$ + filled π -orbital
e.g. Br^- , O^- , C_p^- , RO^- , RN_2^-
- e^- -acceptor $\rightarrow \sigma$ -donor + empty π^*
orbitals e.g. CO

Ligands

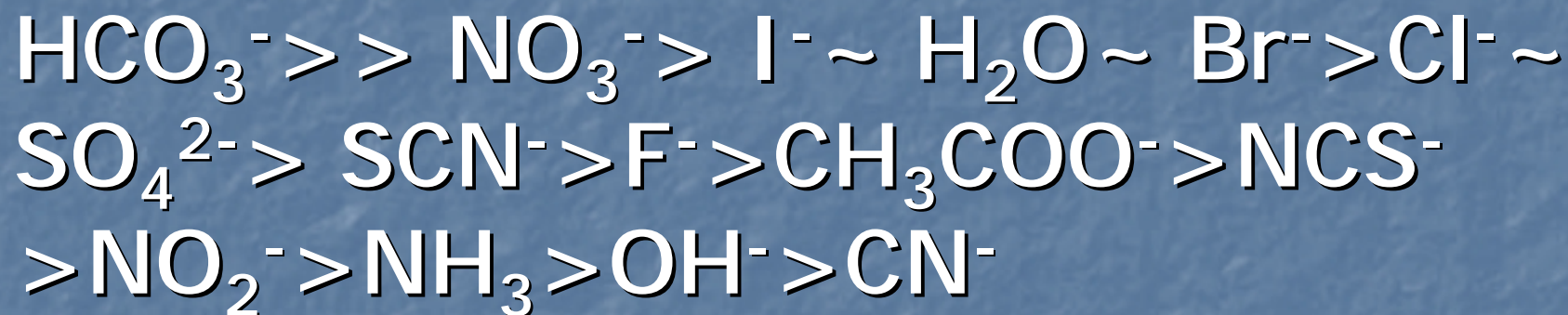
- σ -donors



- π -acceptors –



Leaving group order for O_h compounds



Size of the Coordination Sphere & Metal ION

- Large Coordination sphere favors associative mechanism
- Small Coordination sphere favors dissociative d-type pathway.
- e.g. 1st → Oh favors D-type
 2nd → Oh may be A-type
 3rd → 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

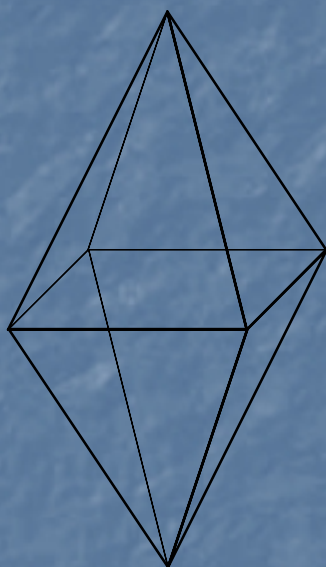
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 1	He 2	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	*La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	+Ac 89	Rf 104	Ha 105	106 106	107 107	108 108	109 109	110 110								

* Lanthanide Series

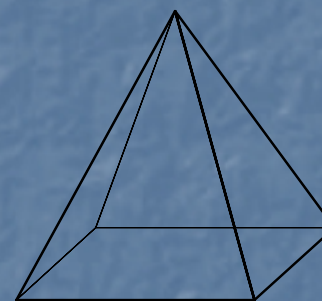
+ Actinide Series

88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Coordination Sphere



Coordinatively saturated
Favors D- type

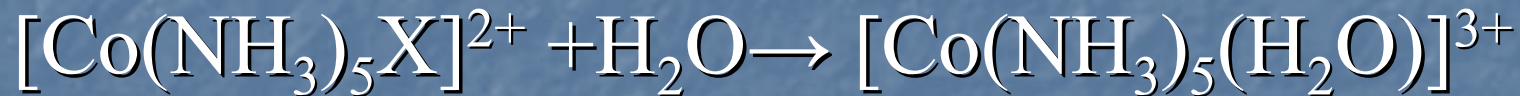


Coordinatively unsaturated
Favors A-type

Mechanism

- 1. Leaving group

e.g.



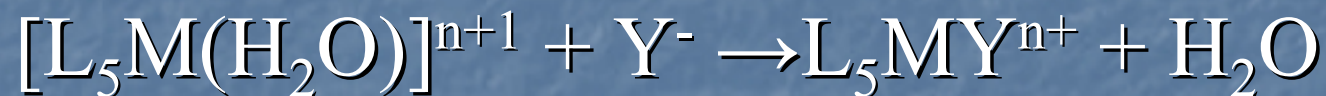
- Rate is dependent on leaving group and is independent on entering group.
- *i.e.* Co-X bond breaking is the rate determining step.
- Evidence?

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 ⁻¹)
$[\text{Co}(\text{NH}_3)_5(\text{OP}(\text{OCH}_3)_3)]^{3+}$	2.5×10^{-4}
$[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]^{2+}$	2.7×10^{-5}
$[\text{Co}(\text{NH}_3)_5(\text{I})]^{2+}$	8.3×10^{-6}
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	5.8×10^{-6}
$[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{2+}$	1.7×10^{-6}
$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]^+$	1.2×10^{-6}
$[\text{Co}(\text{NH}_3)_5(\text{F})]^{2+}$	8.6×10^{-8}
$[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$	2.1×10^{-9}
$[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$	5.0×10^{-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 (sec^{-1})	k/k_e
H_2O	100×10^{-6}	-
N_3^-	100×10^{-6}	1.0
SO_4^{2-}	24×10^{-6}	0.24
Cl^-	21×10^{-6}	0.21
NCS^-	16×10^{-6}	0.16
H_2O	5.8×10^{-6}	-
H_2PO_4^-	7.7×10^{-7}	0.13

Rate is insensitive to entering group

i.e. evidence support D-activation

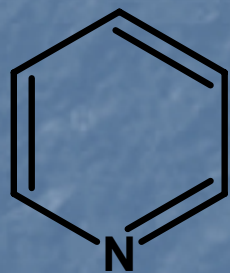
Further evidence come from the substitution studies of Y^- by X^- Where no direct substitution was Observed.

Example

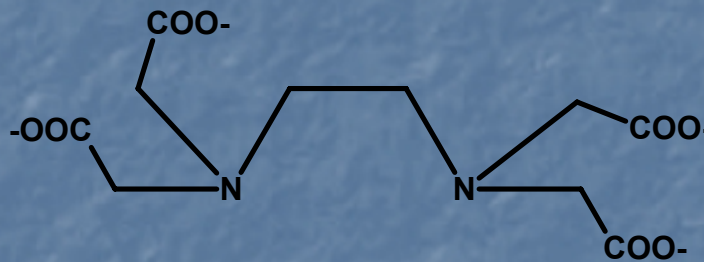
- $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^- + \text{L} \rightarrow [\text{Ru}(\text{edta})\text{L}]$
- $[\text{Ru}(\text{edta})\text{L}] + \text{H}_2\text{O} \rightarrow [\text{Ru}(\text{edta})(\text{H}_2\text{O})]^- + \text{L}$
- Rate constants for substitution by L (k_L) of $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$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

■ L	$k_L (\text{M}^{-1}\text{sec}^{-1})$	$k_{\text{aq}} (\text{sec}^{-1})$
■ Pyridine	6.3×10^3	0.061
■ NCS^-	2.7×10^2	0.5
■ CH_3CN	3.0×10	3.2

Ligands



pyridine

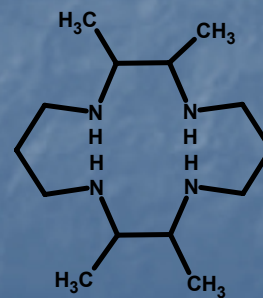
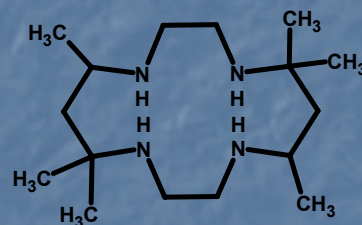
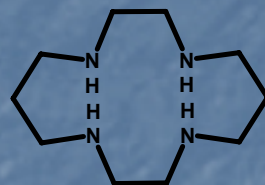


edta

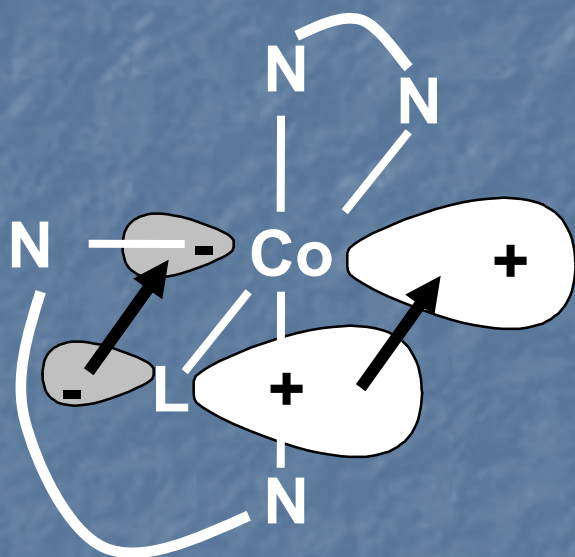
Steric Effect of Inert Ligands

- 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.

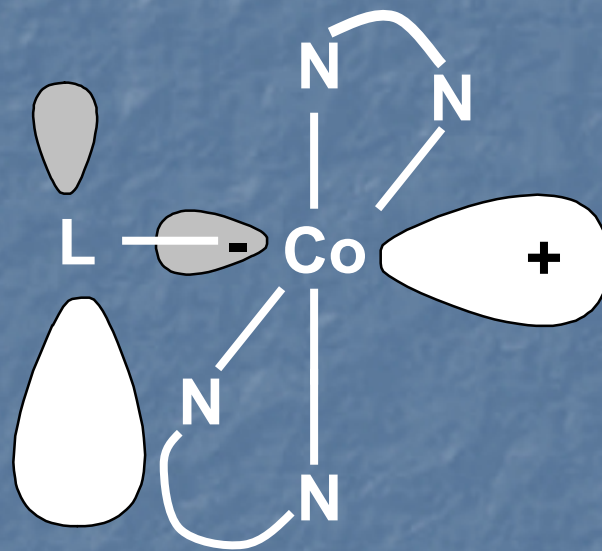
Steric Effect



Electronic Effect of Inert Ligands

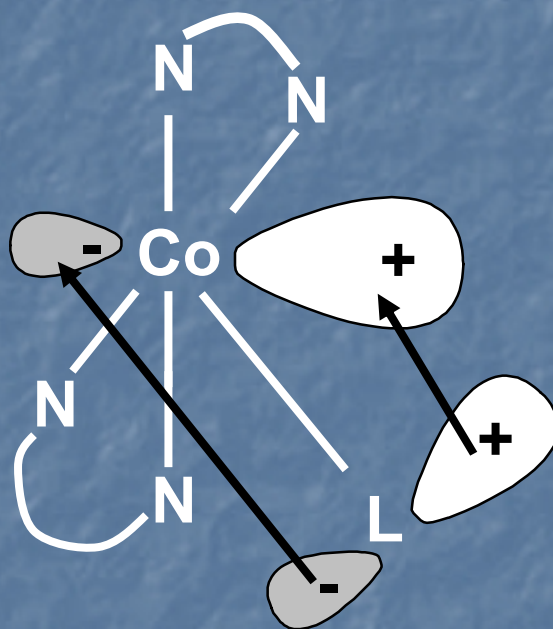


π -donation by a cis ligand into the p component of an empty d^2sp^3 hybrid.



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

Rearrangement



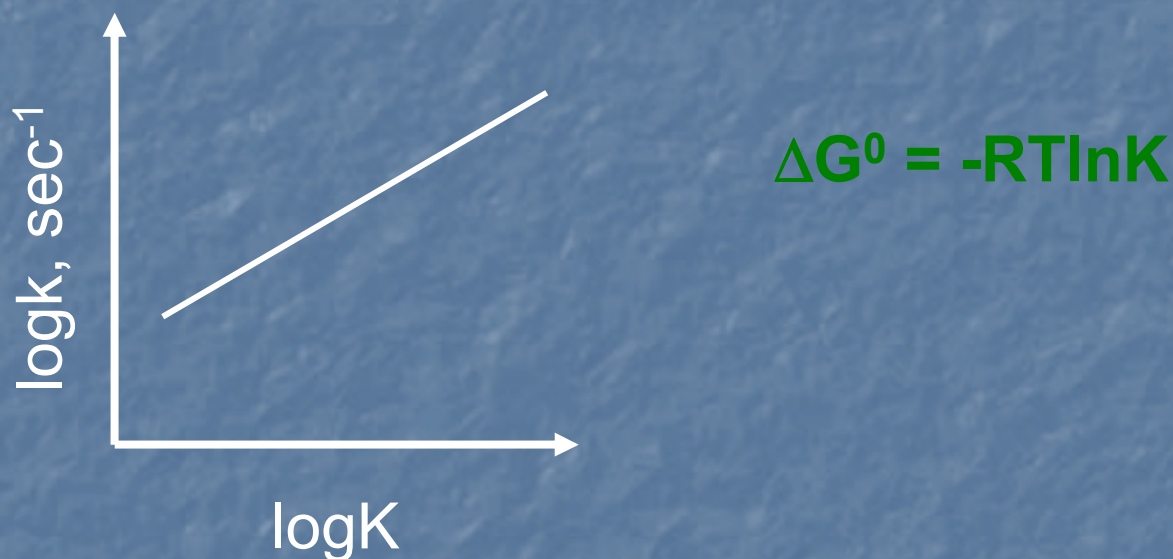
π -donation from trans Ligand can occur upon rearrangement to Trigonal bipyramidal

Activation Parameters

- ΔH^\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.
- ΔS^\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
- ΔS^\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.



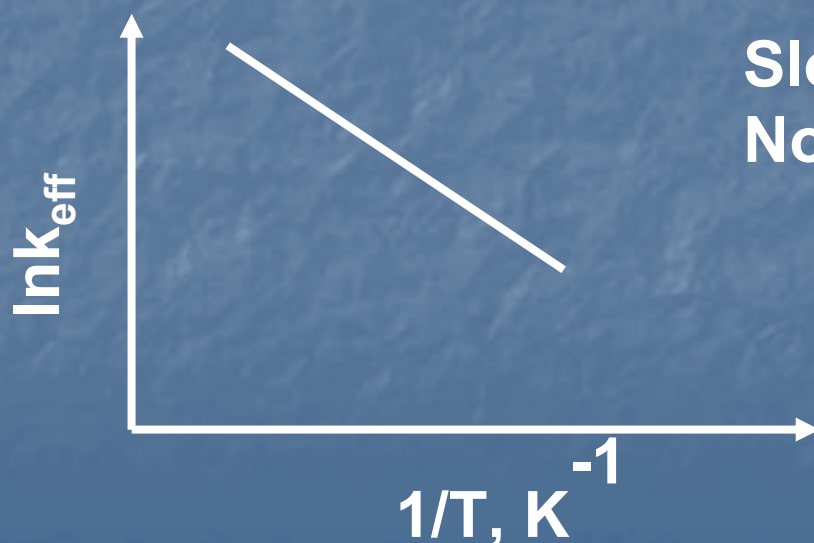
- Slope = 1 for dissociative; i.e. TS or intermediate falls late in the reaction coordinate; i.e. product-like
- Slope ~ 0.5 for associative, TS or [x] falls early in the reaction coordinate; i.e. reactants-like.
- Volume of activation + dissociative & - associative

Activation Parameters, The Eyring Equation

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

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

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

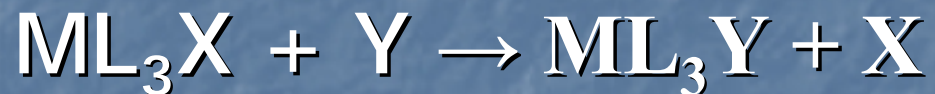
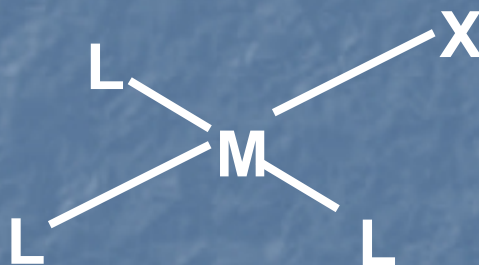


Slope = $-\Delta H^\ddagger/R$

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

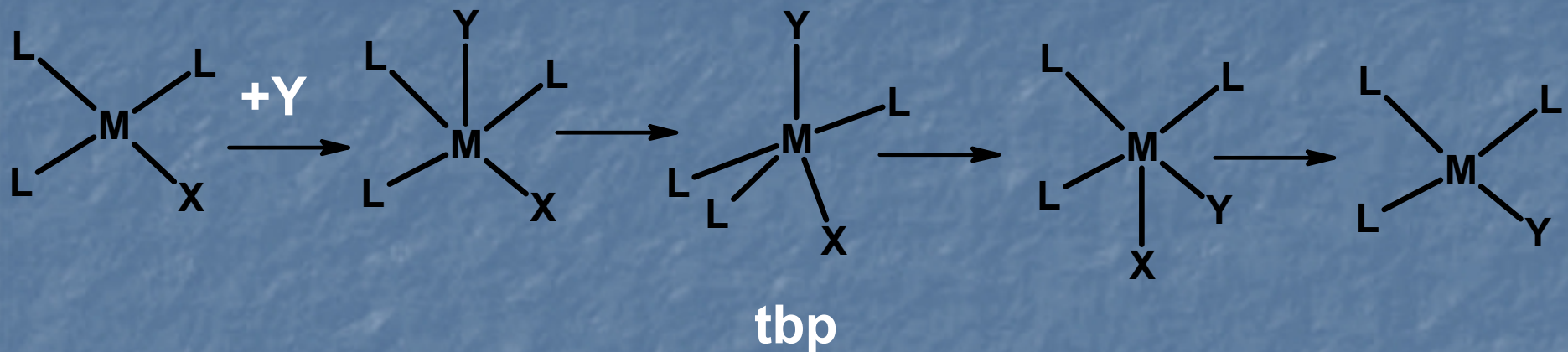
Ligand Substitution Reactions on Square Planar Complexes

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.



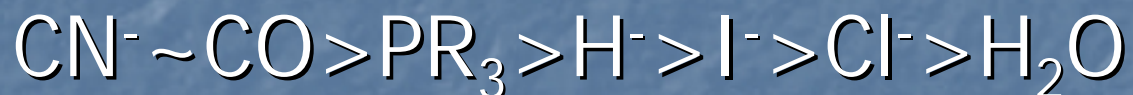
$$\text{Rate} = k_1[\text{ML}_3\text{X}] + k_2[\text{Y}][\text{ML}_3\text{X}]$$

Mechanism for Sq. Substitution

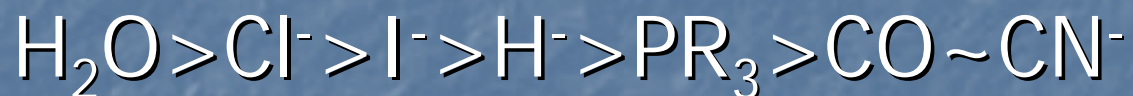


- Trigonal bipyramidal may be an intermediate for A type of TS for I_a
- 5-coordinate species may be isolated as in $[Ni(CN)_5]^{3-}$ and can be isolated as salt of $[Co(en)_3]^{3+}$
- Reactivity order $Ni^{II} > Pd^{II} > Pt^{II}$

- Nucleophilicity order for square planar compounds:



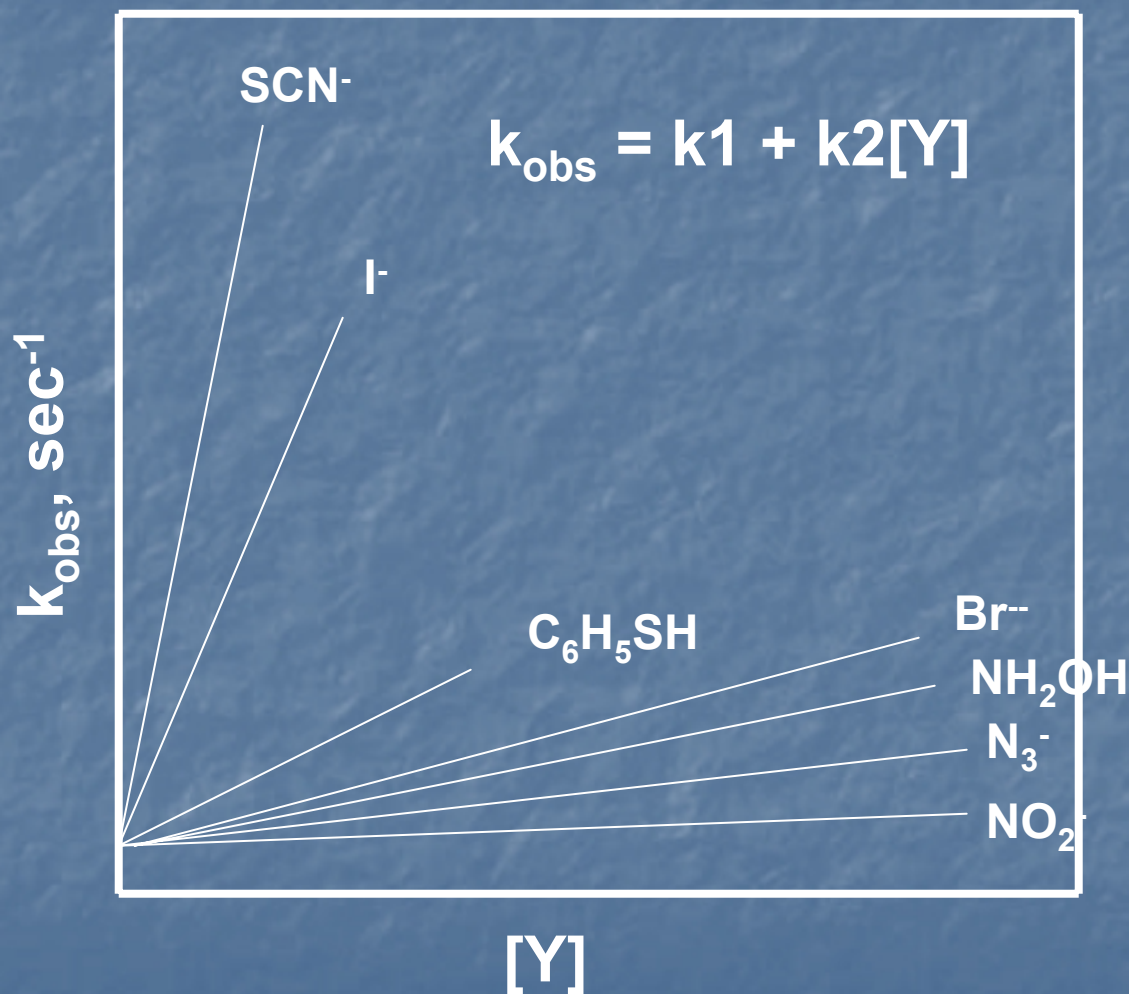
- Leaving group order



Rate Law

- Rate = $(k_1 + k_2[Y])[ML_3X]$
- Indicate two parallel reaction paths.
- In the presence of a large excess of the entering ligand $[Y]$ remains constant throughout the reaction
- Rate = $-d[ML_3X]/dt = k_{obs.}[ML_3X]$ where $k_{obs.} = k_1 + k_2[Y]$
- A plot of $k_{obs.}$ versus $[Y]$,
- Straight line with $k_1 =$ 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.

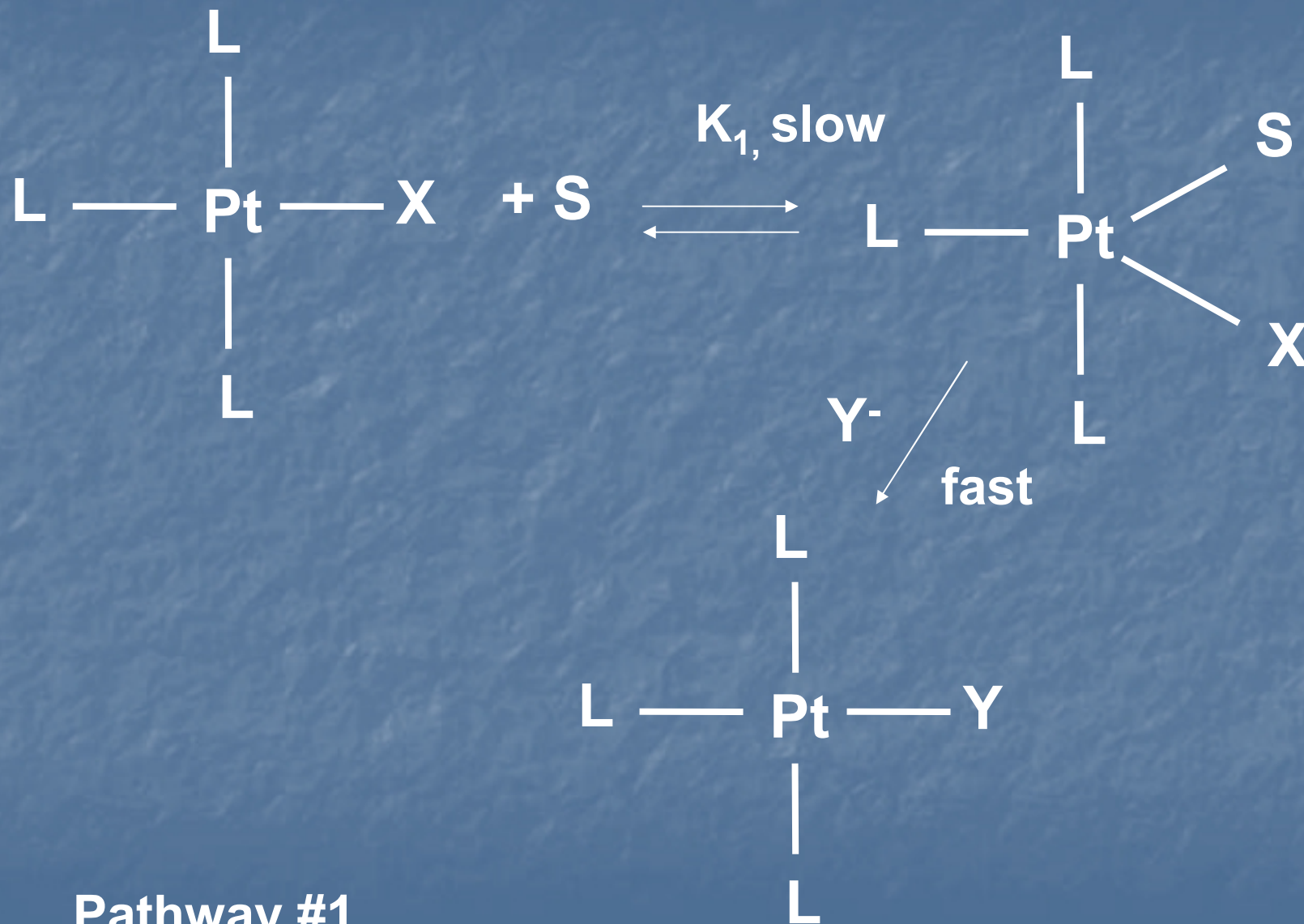
Rate Law

- 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

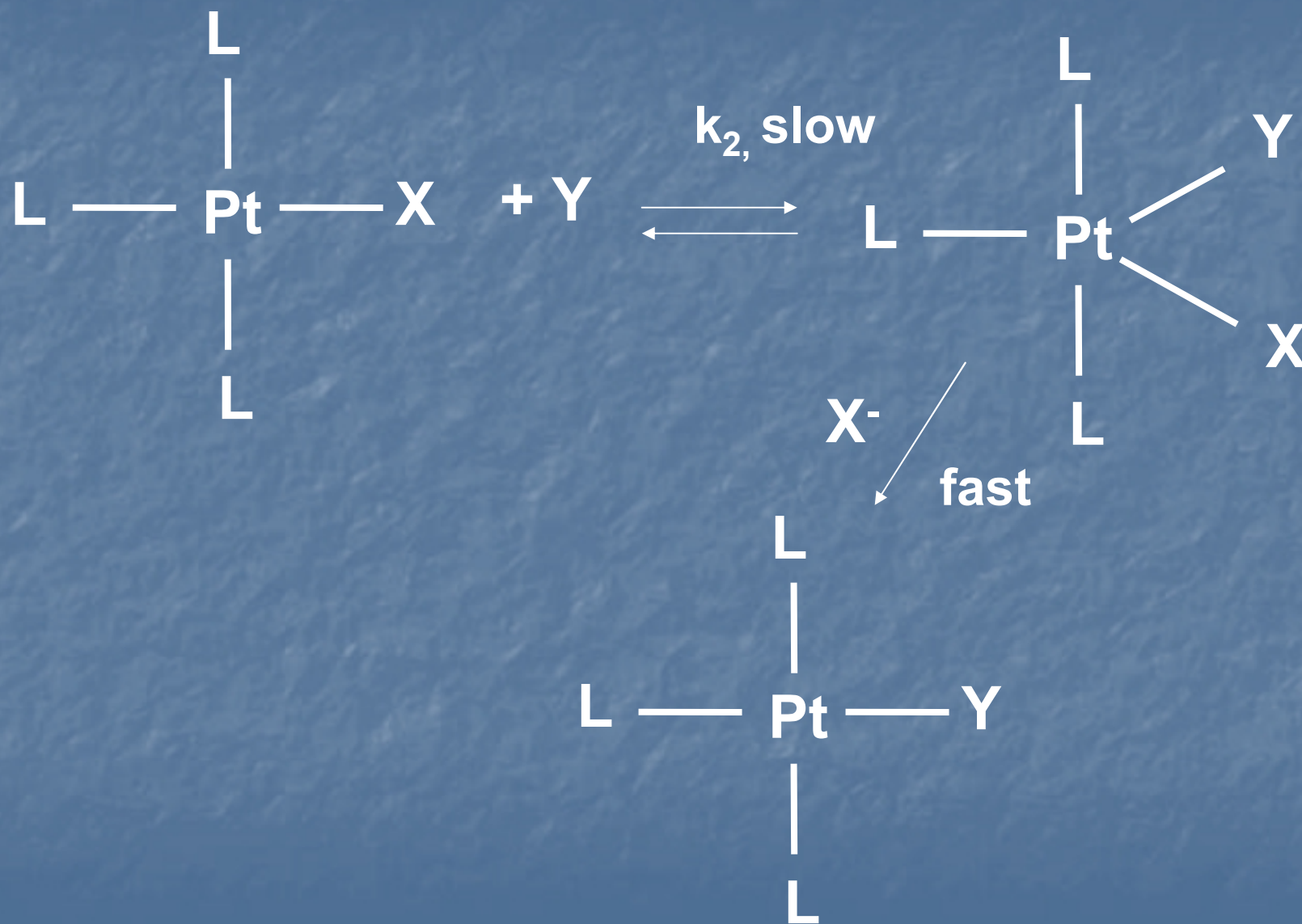
- Two pathways are involved:
- (1) first order in complex (k_1), does not involve Y in rate determining step. This mechanistic pathway is solvent mediated.
- (2) first order in complex and Y (k_2), Y involved in rate determining step

Mechanism



Pathway #1

Pathway 2



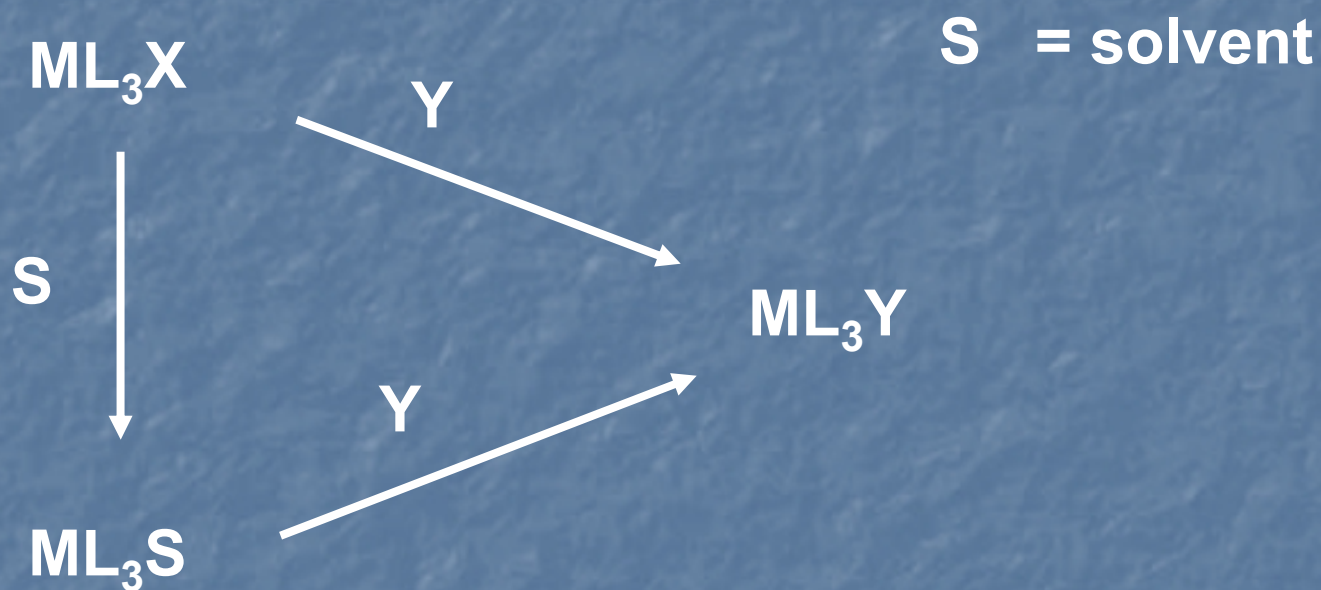
Summary

- 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) ML_3X 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
- $C_6H_5 > 2Me-C_6H_4 > 2,4,6-Me_3-C_6H_2^-$
- Note trans > cis
- For the substitution reaction
- $Pt(PEt_3)_2RCl + Y^- \rightarrow Pt(PEt_3)_2RY + Cl^-$

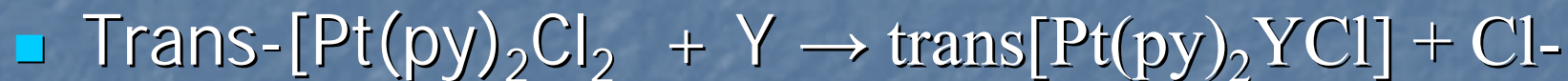
Rate law



- Schematic representation of parallel reactions

Effect of Entering & Leaving Ligands on Rate

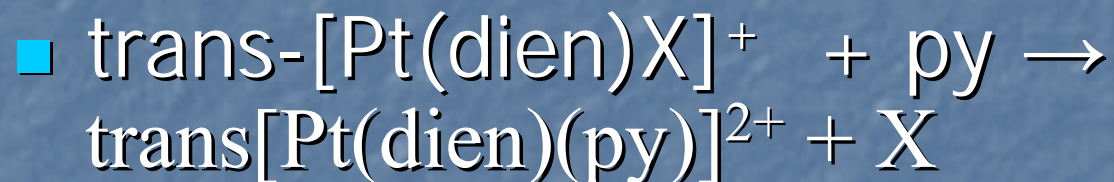
- Rate constants for ligand displacement in some square planar Pt(II) compounds



■ Y	T C	$k_2(\text{M}^{-1}\text{sec}^{-1})$	n_{Pt}
■ CH_3OH	25	2.7×10^{-7}	00
■ CH_3O^-	25	very slow	<2.4
■ Cl^-	30	4.5×10^{-4}	3.04
■ NH_3	30	4.7×10^{-4}	3.07
■ N_3^-	30	1.55×10^{-3}	3.58
■ I^-	30	1.07×10^{-1}	5.46
■ CN^-	25	4.00	7.14
■ 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	$k_{\text{obs}} (\text{M}^{-1}\text{sec}^{-1})$
■ CN ⁻	1.7x10 ⁻⁸
■ SCN ⁻	3.0x10 ⁻⁷
■ I ⁻	1.0x10 ⁻⁵
■ Cl ⁻	3.5x10 ⁻⁵
■ H ₂ O	1.9x10 ⁻³
■ 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 NH_3 , I^- , Cl^- , R^- , 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

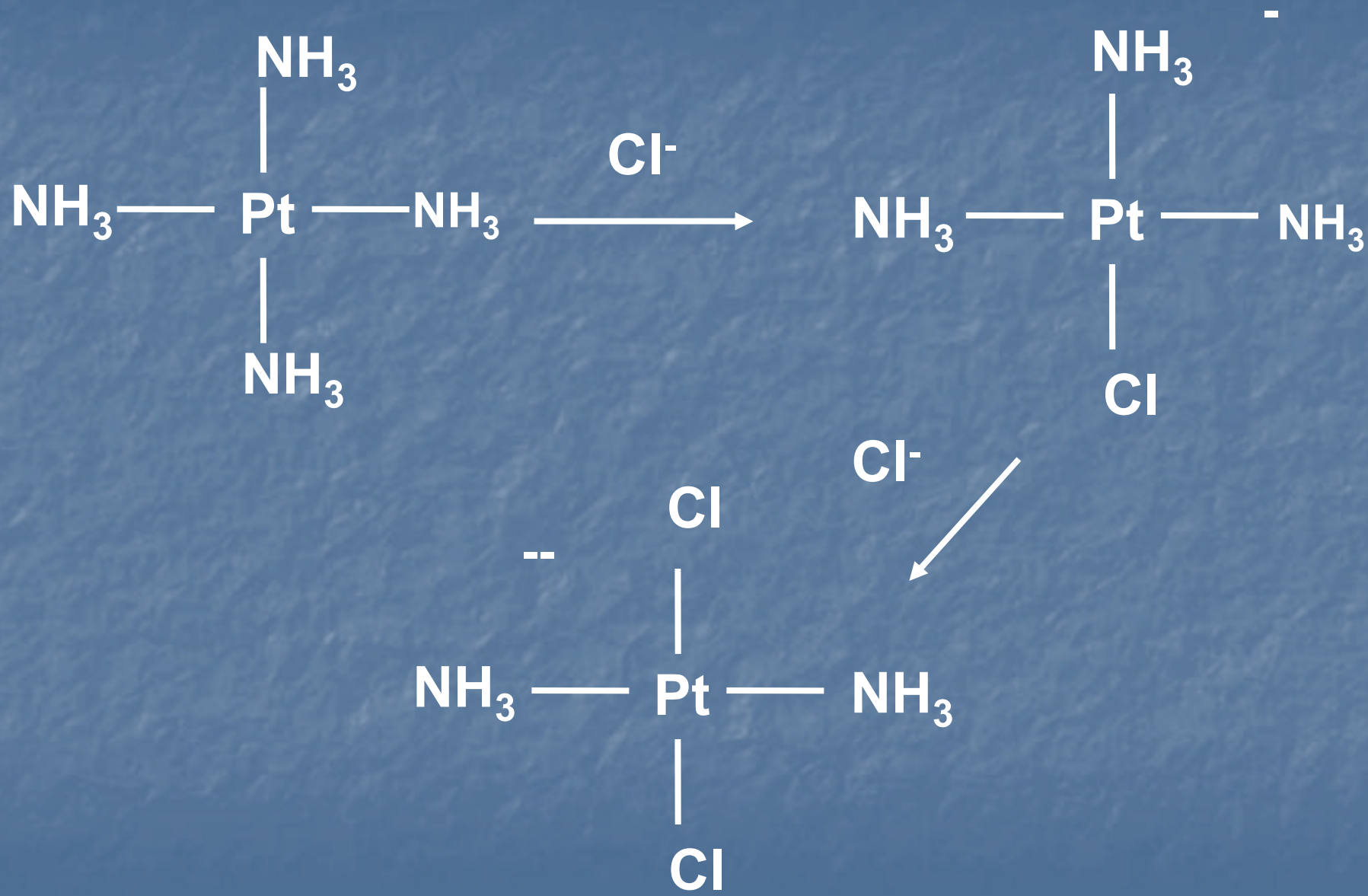
- $s_{n_{Pt}} = \log k_2(Y)/k_2(\text{solvent})$
- S = nucleophilicity discriminating factor
- $I^- > Br^- > Cl^- \gg F^-$
- $PR_3 > AsR_3 > SbR_3 \gg NR_3$
- Sulphur > Oxygen

- Soft bases are better nucleophiles for Pt^{II} as it is a soft acid

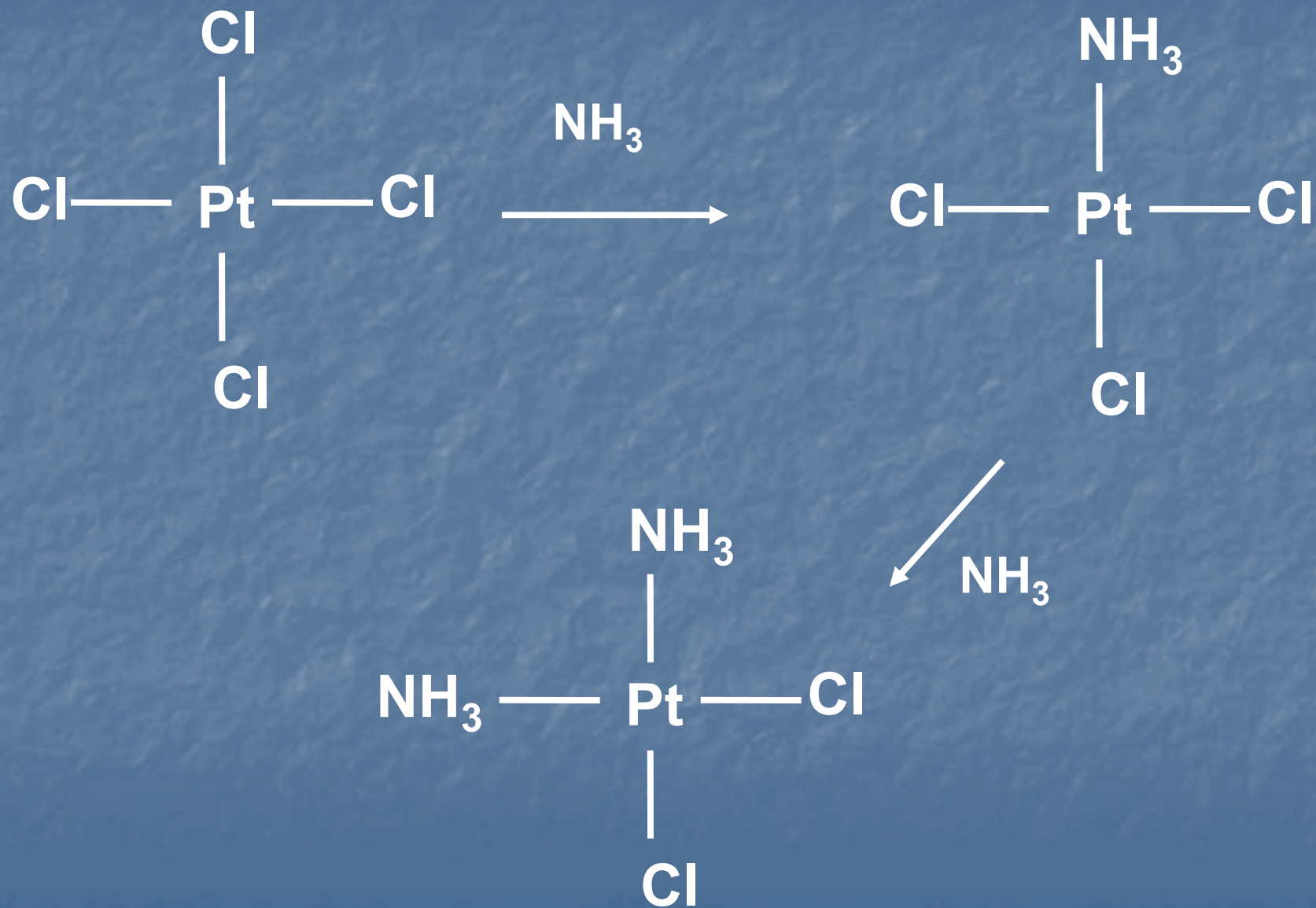
Trans –ligands & trans effect

- "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
- $H_2O \sim OH^- \sim NH_3 \sim NR_3 < Cl^- \sim Br^- < SCN^-$
 $\sim I^- \sim NO_2^- \sim C_6H_5^- < CH_3^- < PR_3 \sim AsR_3 \sim$
 $H^- < \text{olefins} \sim CO \sim CN^-$



Trans effect in synthesis



Try

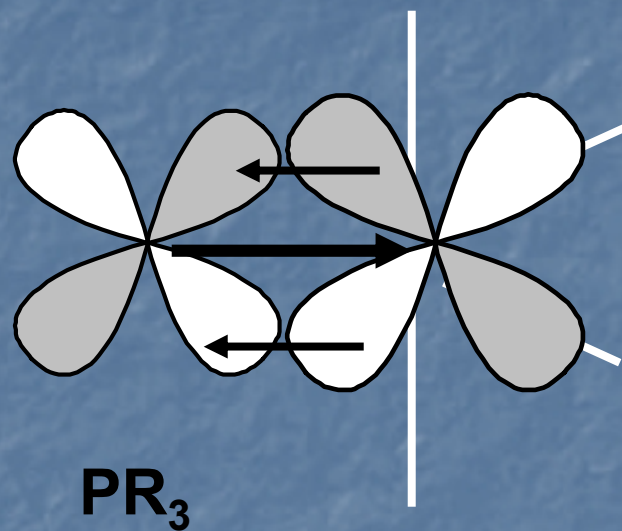
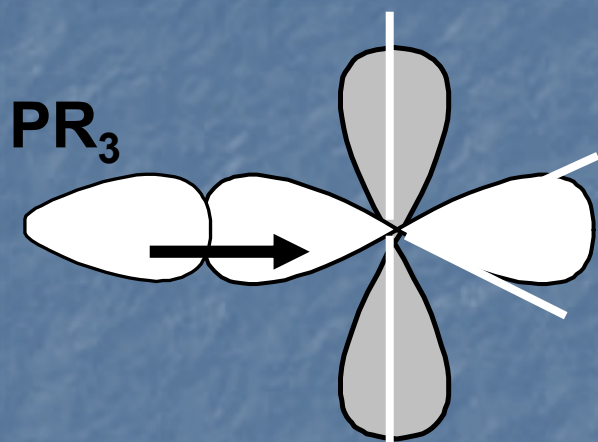
- Synthesis of *cis* and *trans*- isomers of $[\text{PtCl}_2(\text{NH}_3)(\text{PPh}_3)]$ given the reactants PPh_3 , NH_3 and $[\text{PtCl}_4]^{2-}$

Origin of the trans-effect-

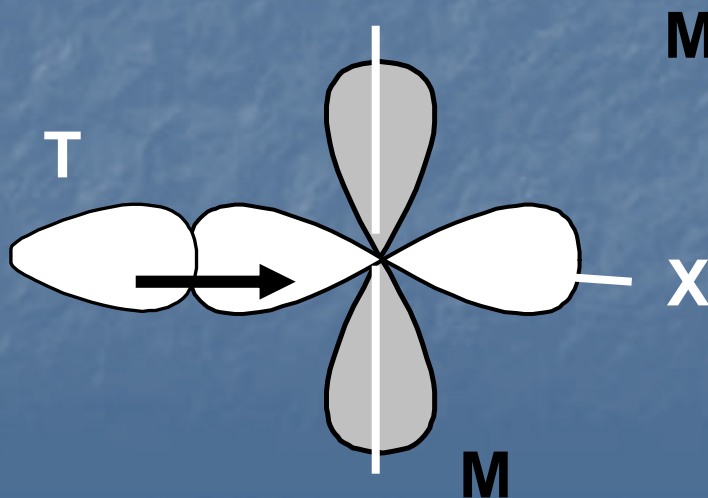
- Electronic (Molecular Orbitals)
 - σ -donor ligands such as H^- , R^- , increase electron density around the metal.
 - π -acceptor ligands such as CO , CN^- , PR_3 , p -back bonding weaken the bond trans to it.

Trans-effect

T.S. Tpy σ -donor π -acceptor



Ground state



Steric Effect of Inert Ligands

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

■ R	Solvent	Y=CN	Y =SC(NH2)2
■ C ₆ H ₅	methanol	3.61	3.30
■ C ₆ H ₅	DMSO	very fast	0.532
■ o-C ₆ H ₄ CH ₃	methanol	0.234	0.652
■ o-C ₆ H ₄ CH ₃	dmso	3.54	0.106
■ 2,6-C ₆ H ₃ (CH ₃) ₂	methanol	8.49x10 ⁻³	4.94x10 ⁻²
■ 2,6-C ₆ H ₃ (CH ₃) ₂	dmso	3.17x10 ⁻²	9.52x10 ⁻³

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

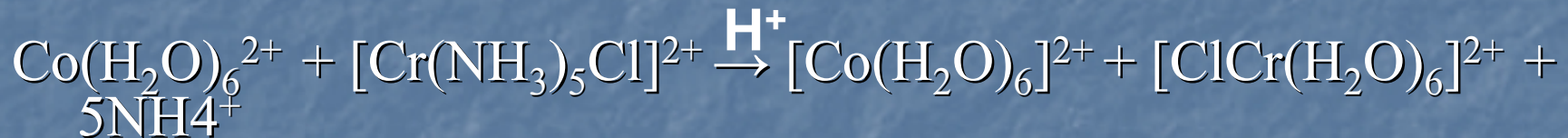
- (i) 1st order in substrate and nucleophile,
- (ii) k_1 (solvent) and k_2 (entering ligand)- solvent is important
- A number of factors determine reactivity
- (i) Nucleophilicity - different from basicity
- (ii) *cis* and *trans* effects - kinetic effects, not the same as *trans* influence - thermodynamic 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 Cr^{2+} & Cr^{3+}

$Co(H_2O)_6^{2+}$ (Labile) & $[Cr(NH_3)_5Cl]^{2+}$ (innert)



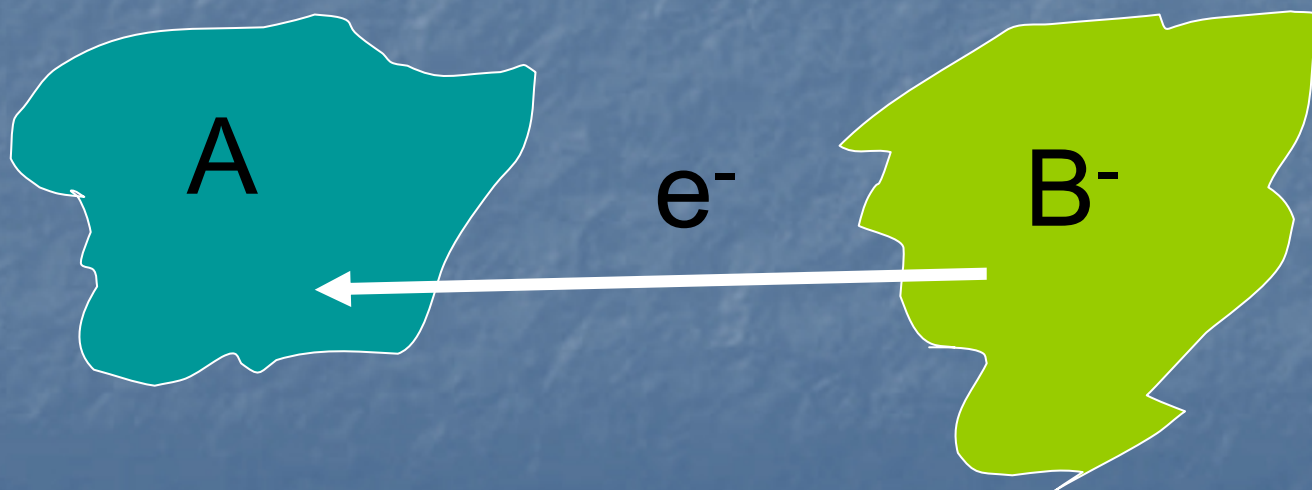
Inner sphere

- $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{Cr}^{2+} \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{ClCr}]^{4+}$
- $[\text{Co}(\text{NH}_3)_5\text{ClCr}]^{4+} \rightarrow \text{CrCl}^{2+} + [\text{Co}(\text{NH}_3)_5]^{2+}$
- $[\text{Co}(\text{NH}_3)_5]^{2+} + 5\text{H}^+ \rightleftharpoons \text{Co}^{2+} + 5\text{NH}_4^+$

- Cr^{3+} inert to substitution with
- $k = 2.9 \times 10^{-8} \text{ M}^{-1}\text{sec}^{-1}$ for Cl^- anation of 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 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

- $[\text{Fe}(\text{me}_2\text{bipy})_3]^{2+} + [\text{Fe}(\text{bipy})_3]^{3+} \rightleftharpoons [\text{Fe}(\text{me}_2\text{bipy})_3]^{3+} + [\text{Fe}(\text{bipy})_3]^{2+}$
- 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.