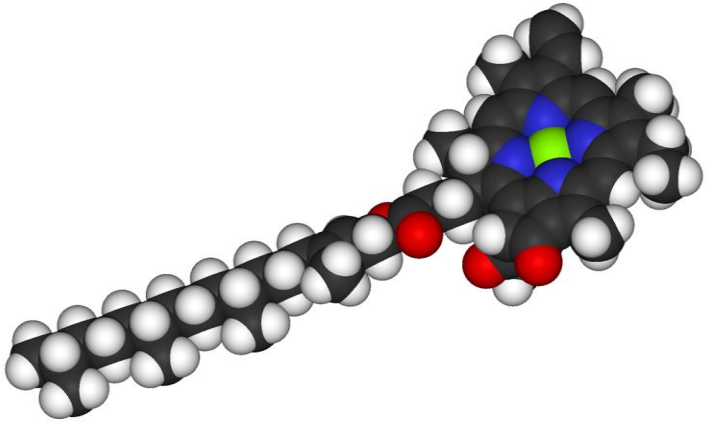
Chelates are Important in Biochemistry!



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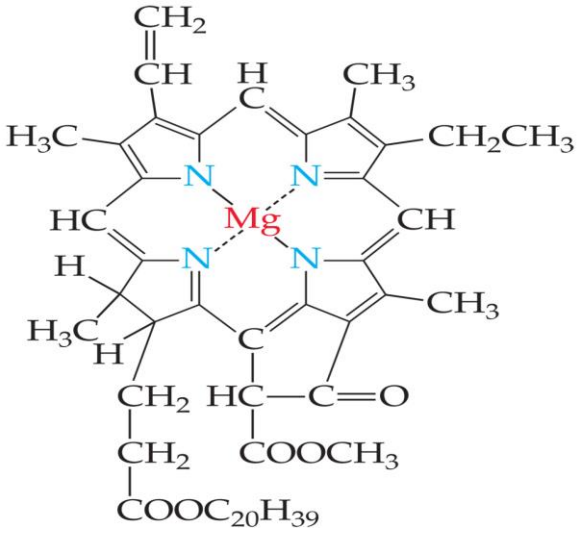
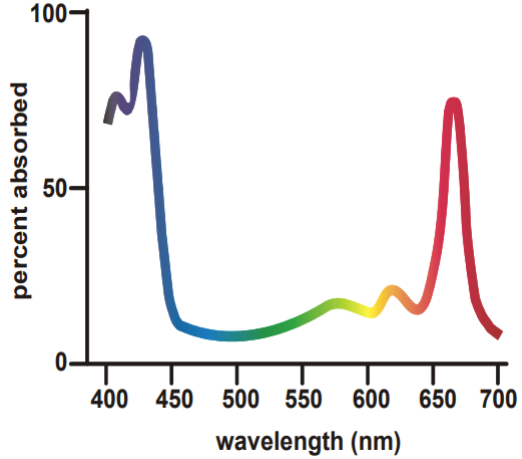
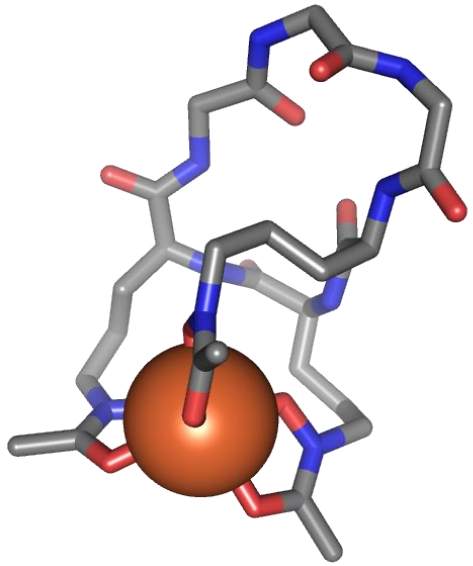
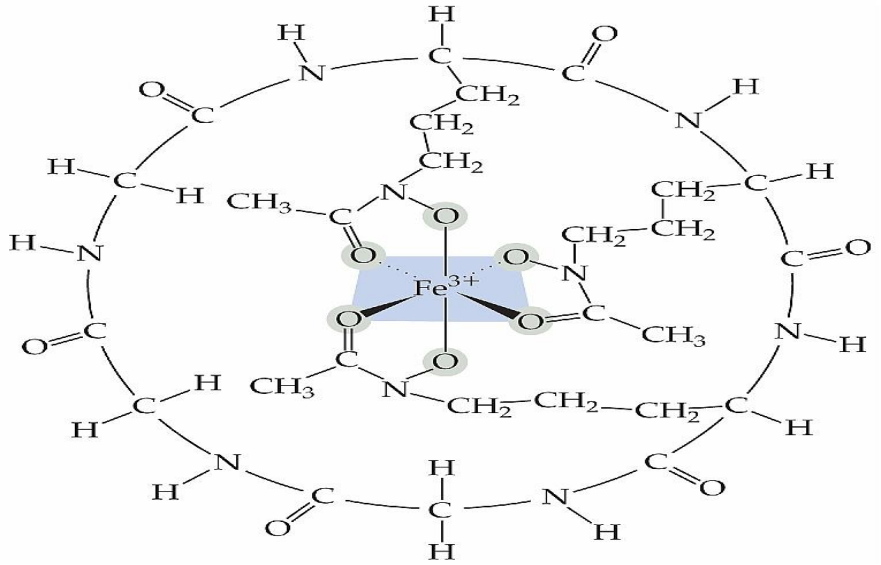


Chlorophyll a





http://en.wikipedia.org/wiki/File:Ferrichrome.png

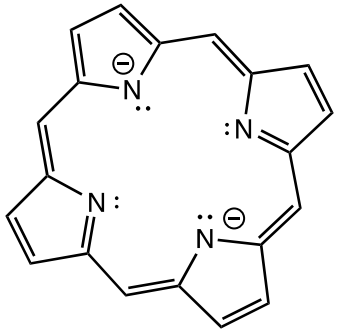


Ferrichrome

Poll Question

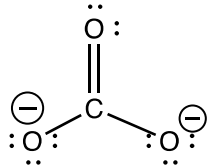
Which of the following molecules is NOT a chelating agent?

i. porphyrin



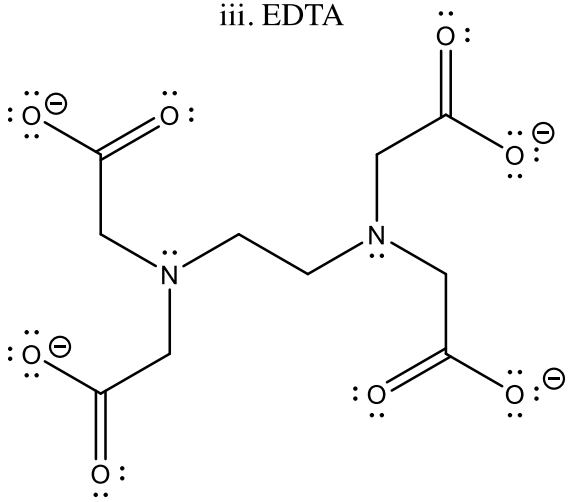
A

ii. carbonate



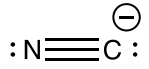
B

iii. EDTA



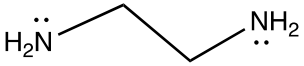
C

iv. cyanide



D

v. ethylenediamine



E

Next Week Glance

Due Today:

Optional HW 7.5

MON	TUE	WED	THU	FRI
3/27	3/28	3/29	3/30	3/31
HW 8 Metal Complex Rxns		**Discussion 8**	**HW 8.5 Optional**	

Read the wikibook chapter 5.4

Read Miessler 14.1 – 14.3

Bonus Reading if you are **really interested** in ligand substitution:

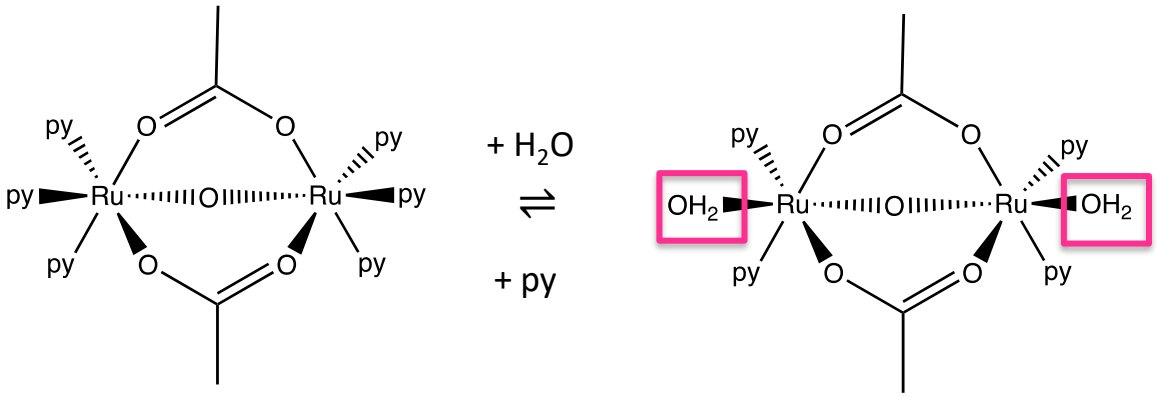
Pages: 104-112 in *The Organometallic Chemistry of the Transition Metals* by Robert Crabtree

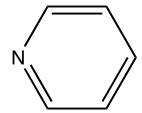
Inorganic Materials: Ligand Substitution Reactions
Wikibook Chapter 5.11
Miessler 12.2.1, 12.7, 14.1.1, 14.2
Shriver 4.11

Lesson Goals:

- Describe the difference between thermodynamic and kinetic effects on ligand exchange
- Explain how CFSE affects ligand substitution rates
- Give examples of metals that tend to form labile complexes
- Give examples of metals that tend to form substitutionally inert complexes
- Draw the mechanism and predict the intermediates, transition states, and products for associative, dissociative and interchange mechanisms
- Explain the trans effect and its implications for ligand substitution reactions
- Give examples of strongly and weakly trans-directing ligands

Ligand Substitution Reactions Govern the Synthesis, Stereochemistry, and Catalytic Chemistry of Complexes





py = pyridine

- Mechanisms are intimately related to reaction kinetics
- Mechanisms are inferred from experiments that:
  - ❖ examine the concentration dependence of the incoming and outgoing ligands on the reaction rate
  - ❖ detect intermediates
  - ❖ determine the stereochemistry of the reactants and products

Kinetics Describes Speed, while Thermodynamics Describes Stability

$Ni^{2+}(aq) + 4\ CN^{-}(aq) \rightleftharpoons [Ni(CN)_4]^{2-}(aq)$ $K_{eq} \approx 10^{30}\ M^{-4}$

Product is thermodynamically stable

$[Ni(CN)_4]^{2-}(aq) + {}^*CN^{-}(aq) \rightleftharpoons [Ni(CN)_3({}^*CN)]^{2-} + CN^{-}(aq)$ $k_{exchange} \approx 10^2\ M^{-1}s^{-1}$

It is also kinetically *labile*

Complexes are classified as **labile** when the activation energy (E_a) of ligand substitution is relatively low.

Complexes are classified as **labile** if the reaction $t_{1/2}$ is less than one minute

CFSE (LFSE) affects E_a, so it also affects rate

Reactant is thermodynamically unstable

$[Co(NH_3)_6]^{3+}(aq) + 6\ H_3O^{+}(aq) \rightleftharpoons [Co(H_2O)_6]^{3+}(aq) + 6\ NH_4^{+}(aq)$ $K_{eq} \approx 10^{30}$

Forward direction is spontaneous, but reactant is kinetically inert; high CFSE

Complexes are classified as **inert** when they react more slowly. However, they **DO NOT** resist LS, there is just a high E_a

Complexes are classified as **inert** if the reaction $t_{1/2}$ is greater than one minute

General Trends in Lability and Inertness

Complexes are classified as **inert** when the activation energy (E_a) of ligand substitution is relatively high. (Slow Reactions)

Complexes are classified as **labile** when the activation energy (E_a) of ligand substitution is relatively low. (Fast Reactions)

Hard Lewis acids;
strong metal-oxygen bonds

energetic cost of breaking symmetry is high

energetic cost of breaking O_h symmetry is low

Slow Reactions (Inert)	Moderate Rate	Fast Reactions (Labile)
d^3, low-spin d^4, d^5, and d^6		d^1, d^2, high-spin d^4, d^5, and d^6
Strong-field d^8 (square planar)	Weak-field d^8	d^7, d^9, d^{10}

TABLE 12.1 Rate Constants for Water Exchange in $[M(H_2O)_6]^{n+}$

Complex	$k(s^{-1})$ (298 K)	Electronic Configuration*
$[Ti(H_2O)_6]^{3+}$	1.8×10^5	t_{2g}^1
$[V(H_2O)_6]^{3+}$	5.0×10^2	t_{2g}^2
$[V(H_2O)_6]^{2+}$	8.7×10^1	t_{2g}^3
$[Cr(H_2O)_6]^{3+}$	2.4×10^{-6}	t_{2g}^3
$[Cr(H_2O)_6]^{2+}$	$> 10^8$	$t_{2g}^3 e_g^1$
$[Fe(H_2O)_6]^{3+}$	1.6×10^2	$t_{2g}^3 e_g^2$
$[Fe(H_2O)_6]^{2+}$	4.4×10^6	$t_{2g}^4 e_g^2$
$[Co(H_2O)_6]^{2+}$	3.2×10^6	$t_{2g}^5 e_g^2$
$[Ni(H_2O)_6]^{2+}$	3.2×10^4	$t_{2g}^6 e_g^2$
$[Cu(H_2O)_6]^{2+}$	4.4×10^9	$t_{2g}^6 e_g^3$
$[Zn(H_2O)_6]^{2+}$	$> 10^7$	$t_{2g}^6 e_g^4$

d^3; slower rate; **inert**

d^3; slower rate; **inert**

d^2; faster rate; **labile**

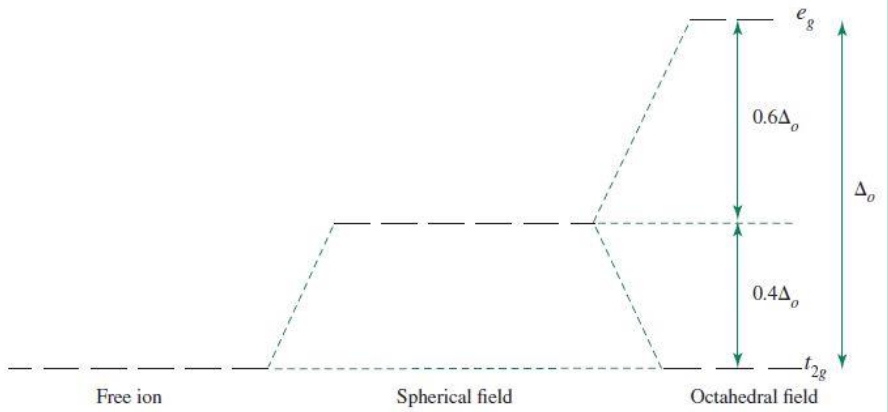
d^4 high spin; faster rate; **labile**

complexes **with NO electrons in the e_g orbitals** and **at least one electron in EACH t_{2g} orbital** tend to be inert, higher E_a

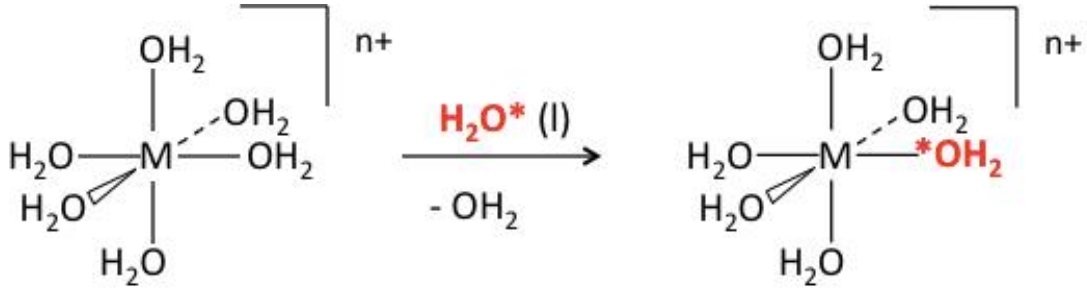
complexes **with electrons in the e_g orbitals** tend to be labile, lower E_a

The effects to exchange rate can be explained with CFSE

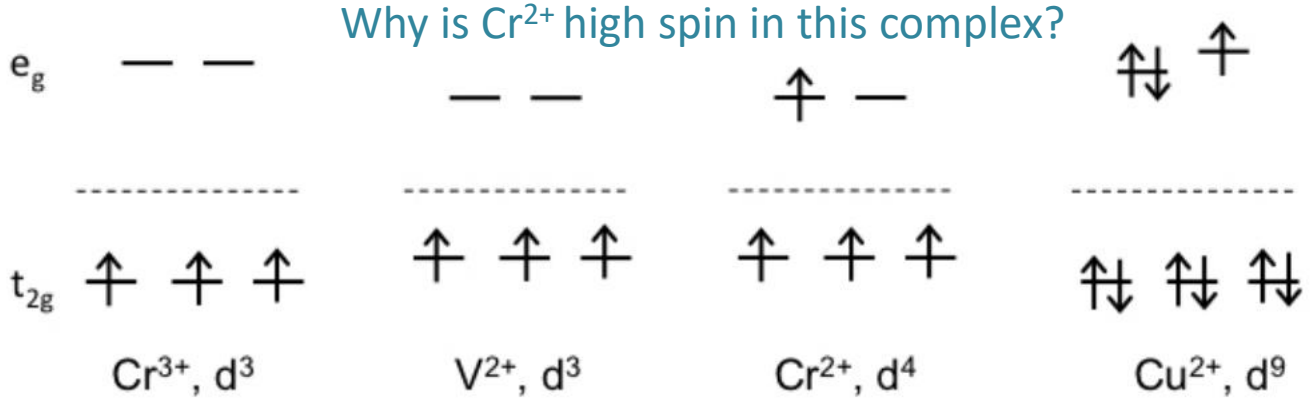
Quick Refresher!



CFSE = (t_{2g} e$^-$)(0.4Δ_o) – (e_g e$^-$)(0.6Δ_o)



Why is Cr^{2+} high spin in this complex?



Inert complexes tend to have a **high CFSE;** higher E_a; Slow

Labile complexes tend to have a **low CFSE;** lower E_a; Fast

Exchange Rate k (s^{-1})	1×10^{-6}	1×10^{-2}	1×10^{8}	1×10^{8}
CFSE	$1.2\ \Delta_o$	$1.2\ \Delta_o$	$0.6\ \Delta_o$	$0.6\ \Delta_o$
Classification	**inert**	**inert**	**labile**	**labile**

Types of LS

Dissociative Exchange

Intermediate with a **lower coordination number**

Mechanism labeled ***D***

Interchange Exchange

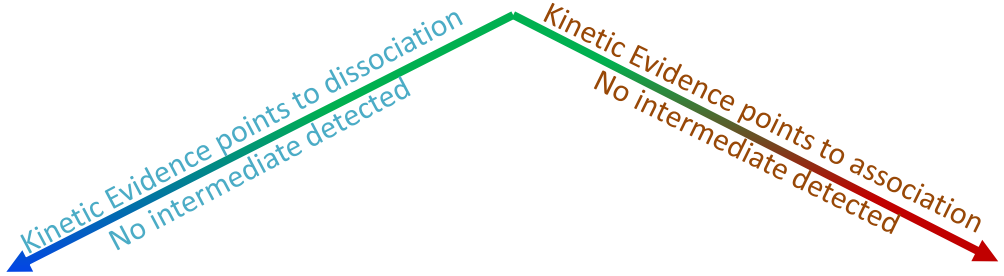
Detection of intermediates not possible

Mechanism labeled ***I***

Associative Exchange

Intermediate with a **higher coordination number**

Mechanism labeled ***A***



Dissociative Interchange

Ligand assistance is small; Reaction primarily dissociative

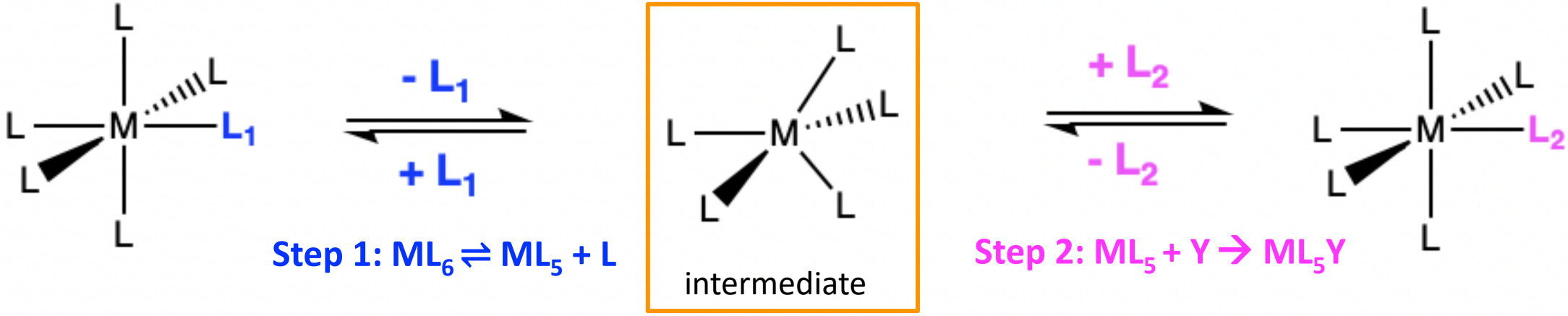
Mechanism labeled I_D

Associative Interchange

Incoming ligand forms bond to central atom before departure of other ligand via bond weakening

Mechanism labeled I_A

Dissociative Exchange Mechanism, *D*



Step 1: $ML_6 \rightleftharpoons ML_5 + L$

Step 2: $ML_5 + Y \rightarrow ML_5Y$

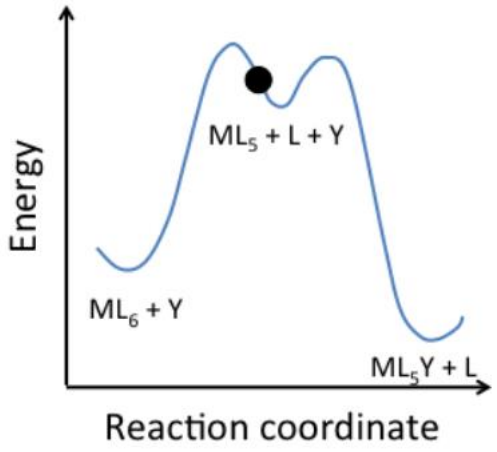
If the transition states are comparable E:

$$Rate = \frac{k_1 k_2 [Y][ML_n]}{k_{-1}[L] + k_2[Y]}$$

If the first step is rate determining and first transition state is highest E, the reaction is independent of [Y] ([Y] >> [L])and it is first order:

Saturation Kinetics

$$Rate = k_1[ML_n]$$



ΔS_{rxn} is always positive

Electronic and Steric Influence:

1. **Oxidation State**

   Higher OX State; Slower Exchange

   $[AlF_6]^{3-}$ > $[SiF_6]^{2-}$ > $[PF_6]^{1-}$ > $[SF_6]$

   +3 +4 +5 +6

2. **Ionic Radius**

   Smaller ion; Slower Exchange

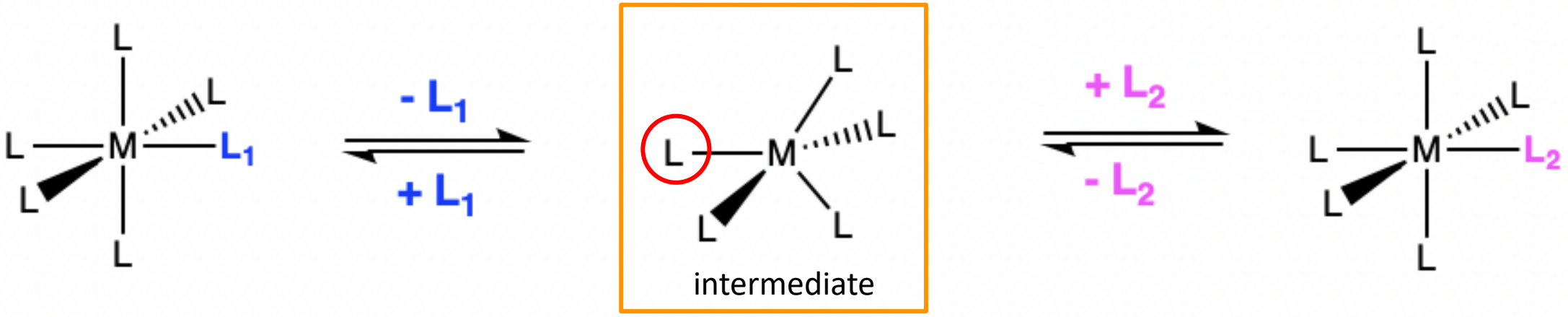
   $[Sr(H_2O)_6]^{2+}$ > $[Ca(H_2O)_6]^{2+}$ > $[Mg(H_2O)_6]^{2+}$

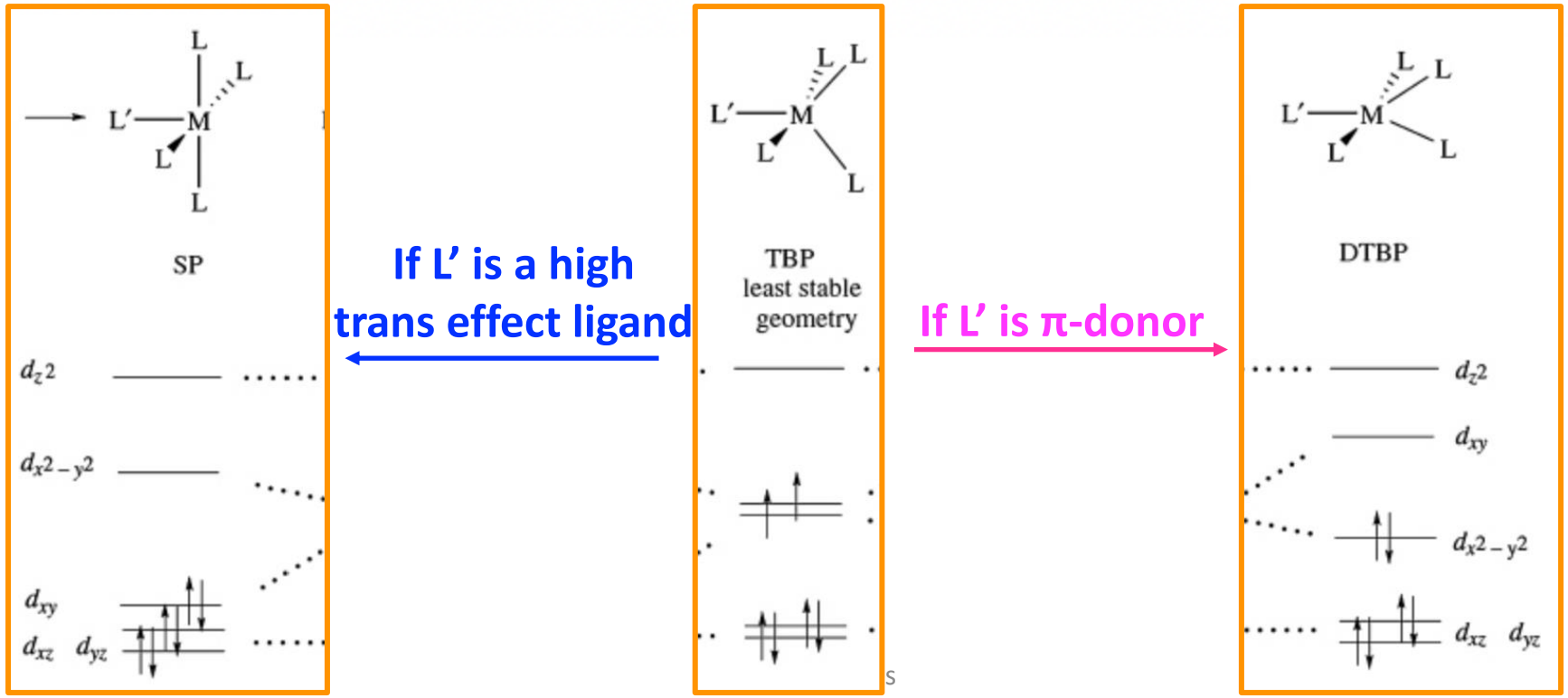
   112 pm 99 pm 66 pm

3. **Bulkiness**

   Bulky ligands experience accelerated dissociation

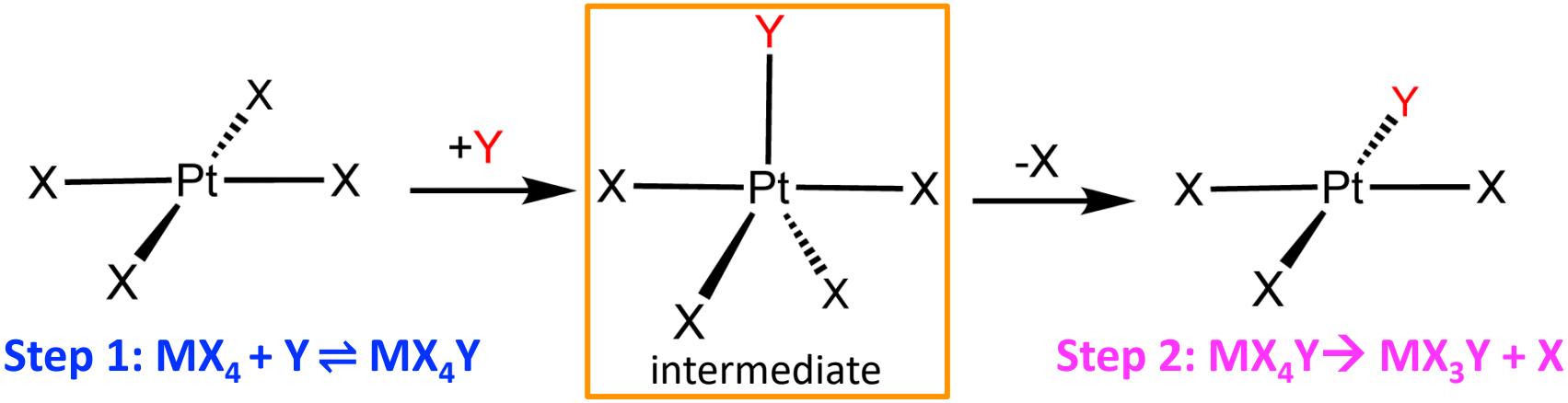
Dissociative Exchange Mechanism, *D*





Associative Exchange Mechanism, *A*

- Complexes that contain a ligand that can change its bonding to the metal (bending or hapticity)
- Square planar d^8 complexes

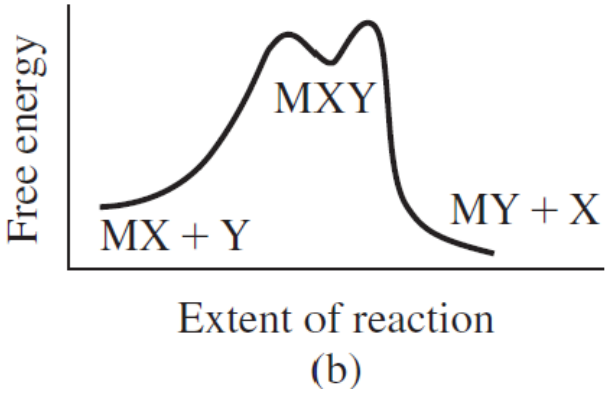


Step 1: $MX_4 + Y \rightleftharpoons MX_4Y$

Step 2: $MX_4Y \rightarrow MX_3Y + X$

Regardless of concentration; Second-order kinetics

$$Rate = k[ML_nX][Y]$$



ΔS_{rxn} is negative; increase in order in transition state

Saturation:

1. **Unsaturated (≤ 16 electron) complexes**
   Incoming ligand bind to metal center → Associative Substitution

2. **Saturated (18 electron) complexes**
   Ligand lost before incoming ligand is bound to metal center → Dissociative Substitution

The Trans Effect Controls the Stereochemistry of Reactions

Certain ligands are trans-directing ligands, and labilize the ligand on the opposite side of the metal

Chernyaev Trans-Effect Ligand Series

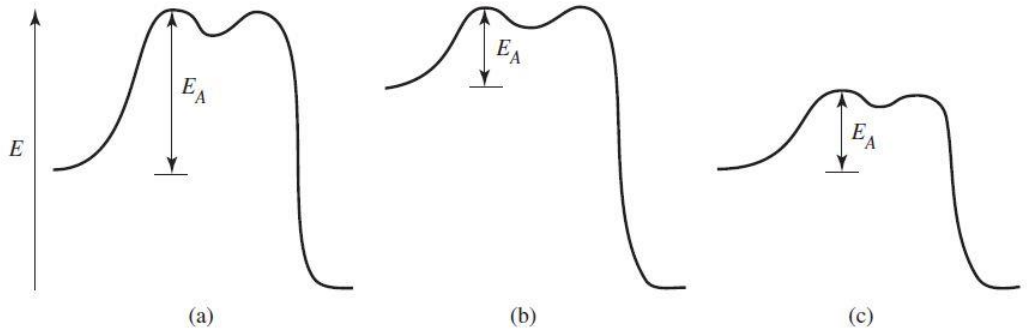
F^-, H_2O, OH^- < NH_3 < py < Cl^- < Br^- < I^-, SCN^-, NO_2^-, $SC(NH_2)_2$, Ph^- < SO_3^{2-} < PR_3, AsR_3, SR_2, CH_3^- < **H^-, NO, CO, CN^-, C_2H_4**

weak field ligands are
weak trans-directing ligands

strong field ligands are
strong trans-directing ligands

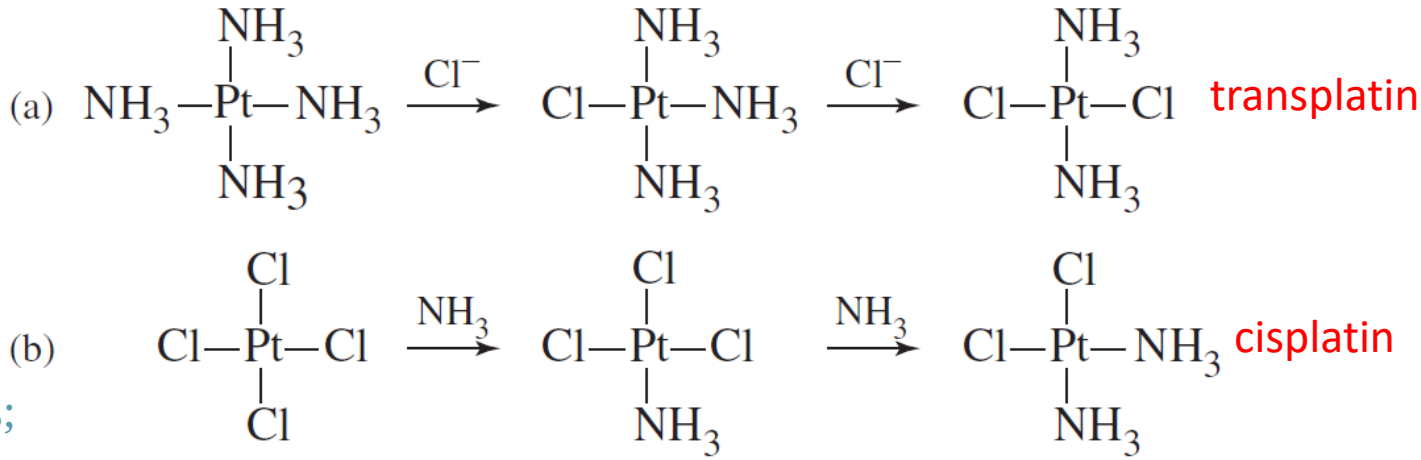
Cl^- has a stronger **TRANS EFFECT** than NH_3, thus the second Cl^- is placed trans to the first.

Strong σ-donor;
***trans* influence**



Not strong σ-donor
or π-acceptors;
Poor *trans* effect

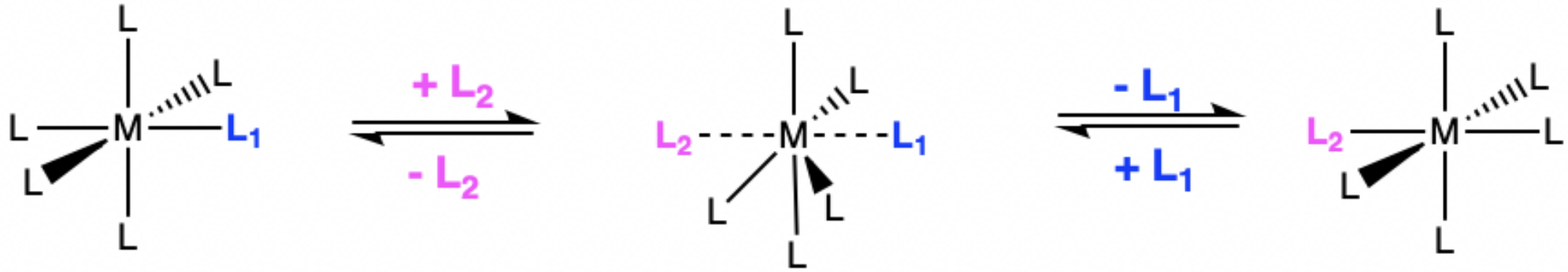
Strong π-acceptors;
***trans* effect**



Interchange Exchange Mechanism (I, I_a, I_d)

Only a transition state is formed, no intermediate

I_a is associative, I_d is dissociative, depends on strength of bonds in transition state



If substitution is irreversible;
Second-order kinetics

$$Rate = k_1[ML_6][X]$$

Step 1: $ML_6 + X \rightarrow ML_5X + L$

If substitution is reversible;
Much more complicated;
Approximated as pseudo first order

$$Rate = k_1[ML_6] - k_{-1}[ML_5X]$$

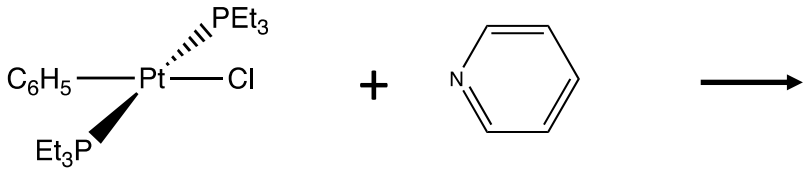
Assumes large ligand concentrations

How can you tell the mechanism of the reaction?

Measure the **kinetics**; concentration dependence on incoming ligand? First or second order?
Determine the **stereochemistry** of products; is it different for different starting materials? (transplatin)

Lecture 29 Activity – Ligand Substitution

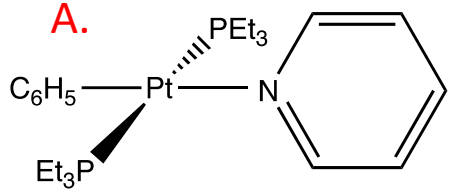
Draw a mechanism with arrows for the following reaction, and draw the predicted product:



$PEt_3 = P(C_2H_5)_3$ pyridine

What product do you predict will be formed?

A.



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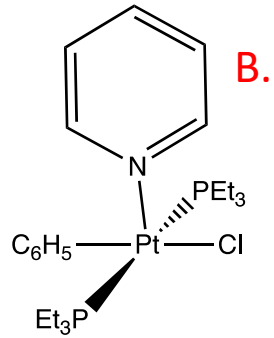

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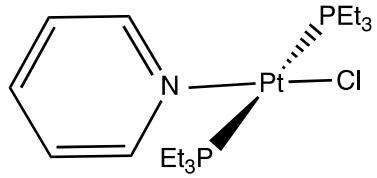

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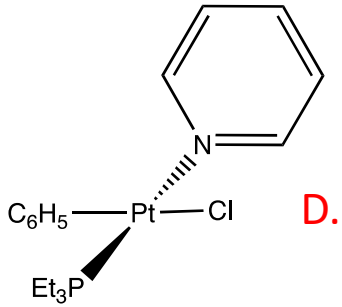

E. No reaction.