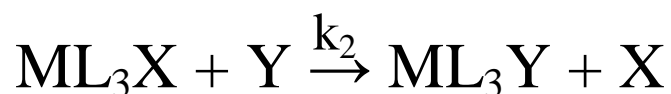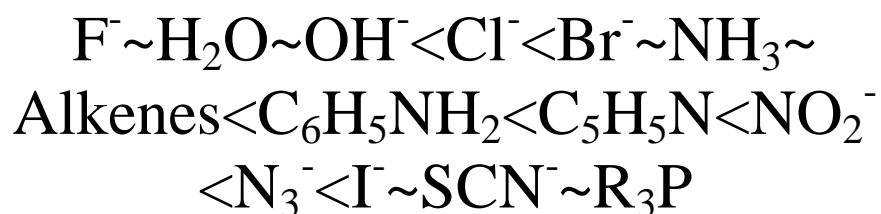## (c) Entering Ligand Effects

The second order rate constant k_2 in square planar complexes in the rate law below that we just discussed is strongly dependent on the nature of Y, the entering ligand
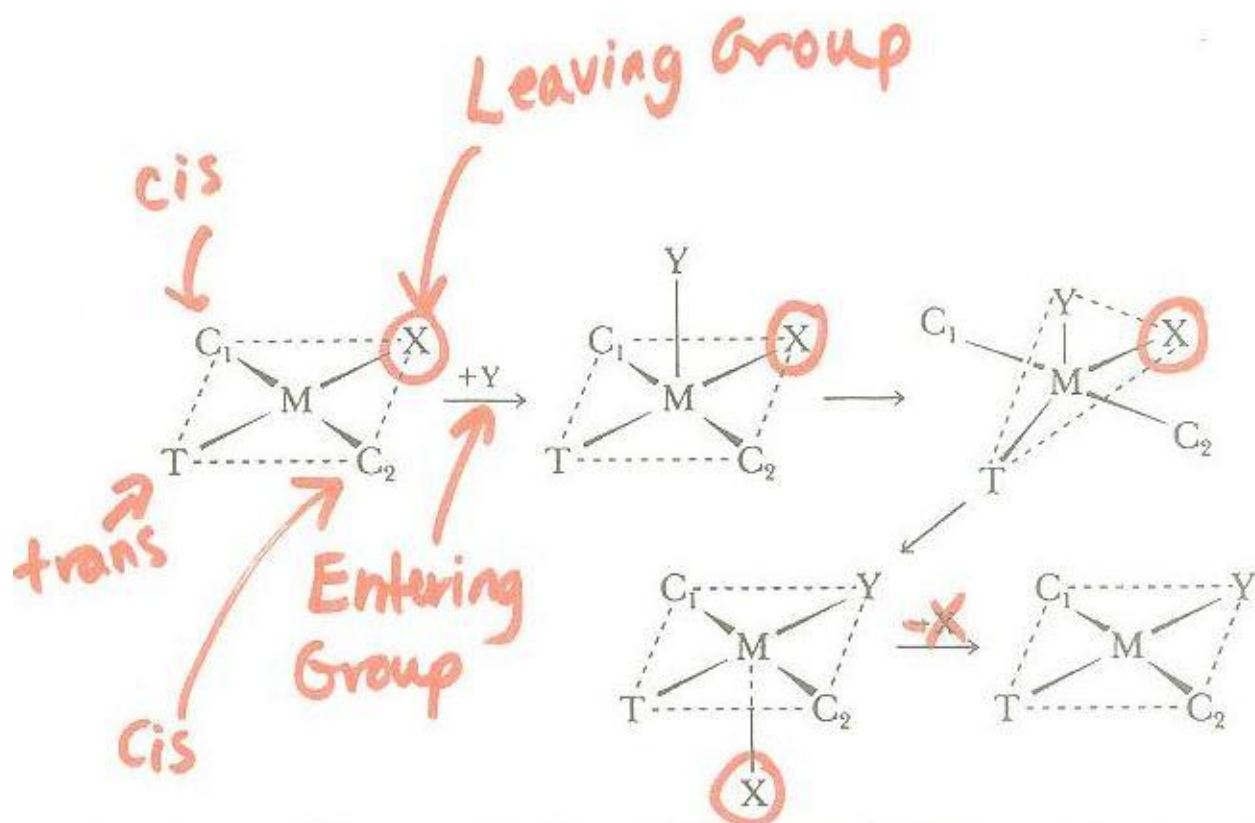
$$ML_3X + Y \xrightarrow{k_2} ML_3Y + X$$

<u>empirically derived series for Pt^{II} from k_2 values on left being (slow) to right (fast):</u>

$$F^-\sim H_2O\sim OH^-<Cl^-<Br^-\sim NH_3\sim$$
$$Alkenes<C_6H_5NH_2<C_5H_5N<NO_2^-$$
$$<N_3^-<I^-\sim SCN^-\sim R_3P$$

Q. What does this series reflect?

A. Essentially the order of Pt^{II} affinity for these ligands (their Lewis basicity or nucleophilicity)

(d) Sterochemistry

Leaving Group

cis

trans

cis

Entering Group

Y

C_1 ---- X

M

T ---- C_2

+Y

C_1 ---- X

M

T ---- C_2

C_1 --- X

Y

M

T

C_2

C_1 ---- Y

M

T ---- C_2

X

-X

C_1 ---- Y

M

T ---- C_2

Q. What does these drawings show about the typical associative mechanism for Square Planar Compounds?

A.

(1) Goes through Square pyramidal and trigonal bipyramidal intermediates that serve to exchange positions of X and Y

(2) cis and trans reactants react to form cis and trans products respectively

Non-Labile Ligands
The "Trans-effect"

The ligand trans to X, the leaving group, can have a profound influence on the rate of X substitution.

Ex. $PtLX_3 + Y \rightarrow PtLX_2Y + X$
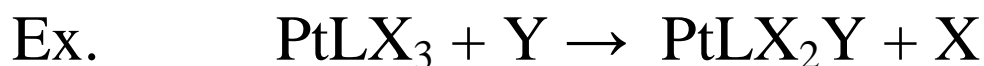
Any of the three X ligands can be replaced by Y.

Depending on L, the relative amounts of cis and trans products vary.

L and Y are trans

L and Y are cis
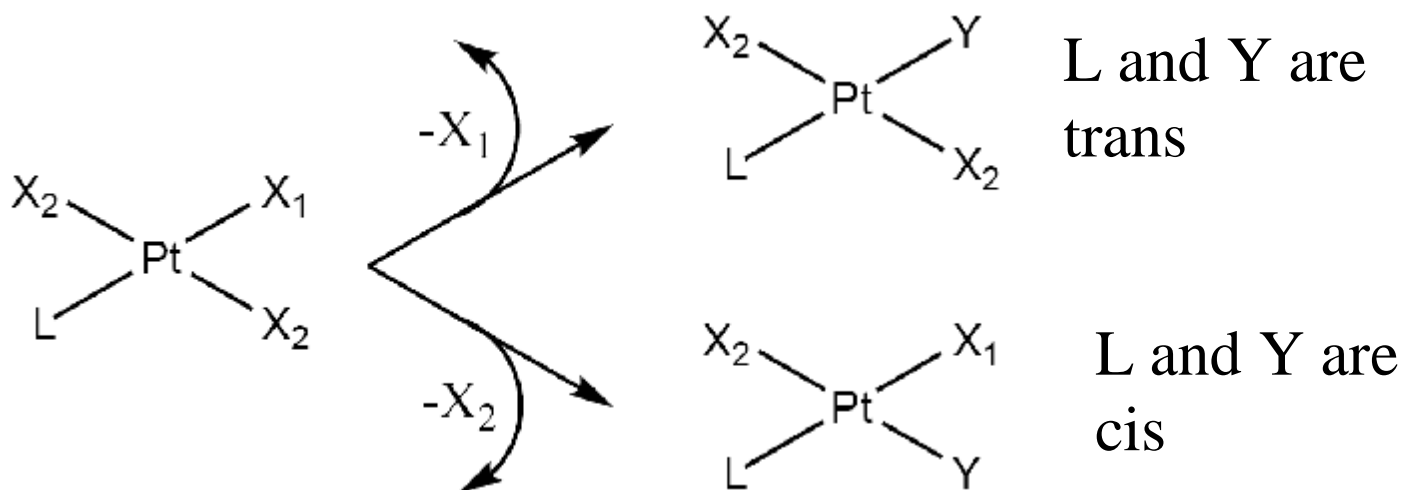
Strong "trans directing" L ligands will make the reaction favor the trans substitution product but if X_2 is more strongly "trans directing" then one would obtain cis isomer in the previous example.

Experimental work with $PtLX_3 + Y$ reactions has led to an ordering of ligands with respect to their tendency to be "strong trans directors"
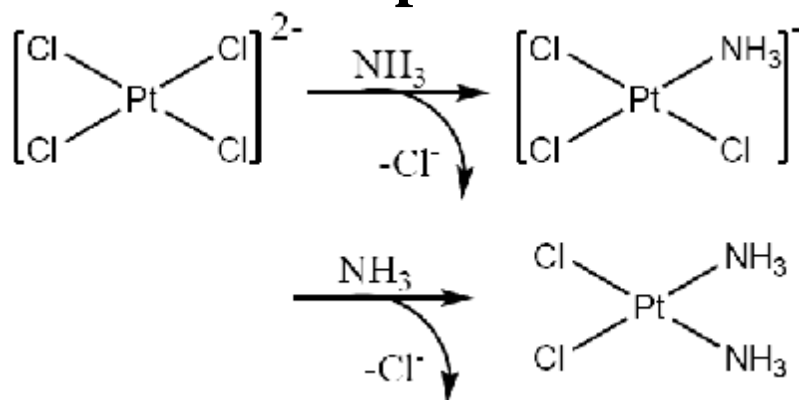
$$H_2O \sim OH^- \sim NH_3 \sim py < Cl^-, Br^- <$$
$$SCN^-, I^- \sim NO_2^-, Ph^- <$$
$$CH_3^- < H^- \sim PR_3 << C_2H_4 \sim CN^- \sim CO$$
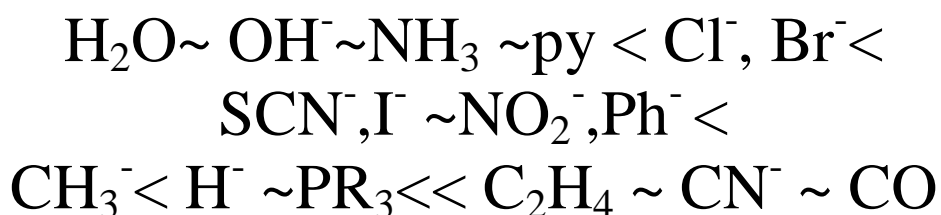
This series is also known as the *trans effect series – The ability to direct trans-substitution) and it spans a factor of about 10^6

Trans effect is solely a kinetic phenomenon which means that it promotes faster substitution rates for ligands trans to itself than ligands cis to itself. If you notice, among the strongest are CN^- and CO. these ligands can overlap strongly with the pi-oribitals in the transition state (intermediate) which is trigonal bipyramidal

Very useful for synthetic chemists to devise routes into new compounds!

Take for example the cis and trans isomers of $Pt(NH_3)_2Cl_2$

How can we favor one product over the other?

$$\left[\begin{array}{c} Cl \\ Cl \end{array}\!\!\!>Pt<\!\!\!\begin{array}{c} Cl \\ Cl \end{array}\right]^{2-} \xrightarrow[\text{-Cl}^-]{NH_3} \left[\begin{array}{c} Cl \\ Cl \end{array}\!\!\!>Pt<\!\!\!\begin{array}{c} NH_3 \\ Cl \end{array}\right]^{-}$$

$$\xrightarrow[\text{-Cl}^-]{NH_3} \begin{array}{c} Cl \\ Cl \end{array}\!\!\!>Pt<\!\!\!\begin{array}{c} NH_3 \\ NH_3 \end{array}$$
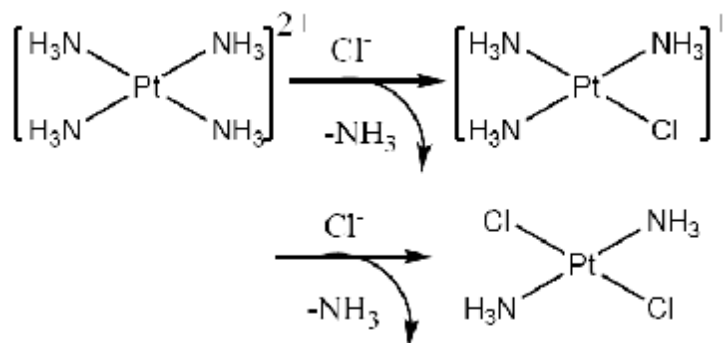
The product is cis-dichlorodiammineplatinum(II)

Q. What does this tell us?

A. that Cl⁻ has a greater trans directing effect that NH_3

Q. How then to synthesize the trans derivative?

A. Use all NH_3 ligands in starting material

product is trans-dichlorodiammineplatinum(II)

There is also another that is called the "Trans-Influence" It follows the same trend as the Trans-Effect but it is a ground state phenomenon. The ligands that are trans to strong ligands have longer (therefore weaker) bonds so they are substituted more easily.

As a "ground state" effect one ligand is weakening the bond trans to it by a competition for metal-ligand overlap. A strong ligand, L, polarizes the opposite ligand, X, by induced dipoles. Known as the:

Grinberg Polarization Theory
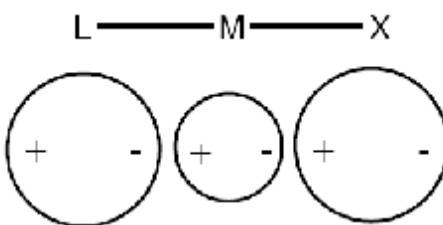
Arrangement of dipoles along the L-M-X axis

The orientation of the Metal dipole is such that it is repelling the negative charge (or electrons) on the X ligand. This weakens the M-X bond.

Electron-Transfer Reactions

Besides substitution reactions, redox or e⁻ transfer reactions are very important in transition metal chemistry

Simplest way to depict:

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$$
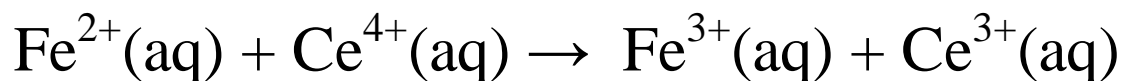
Note, chemists don't often write the actual formula for the water complex, but it is $Fe(H_2O)_6^{2+}$ ...

Two types:
(a) Outer – sphere
(b) Inner – sphere

Outer – Sphere electron transfer

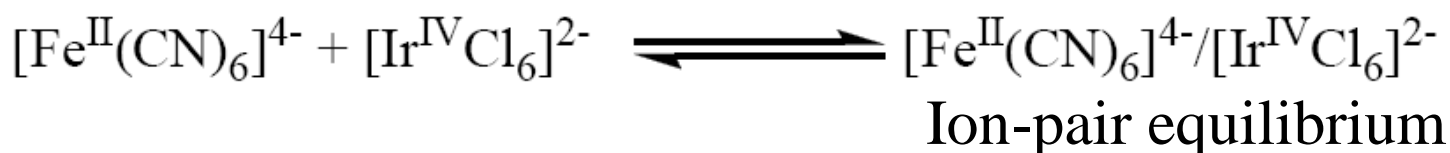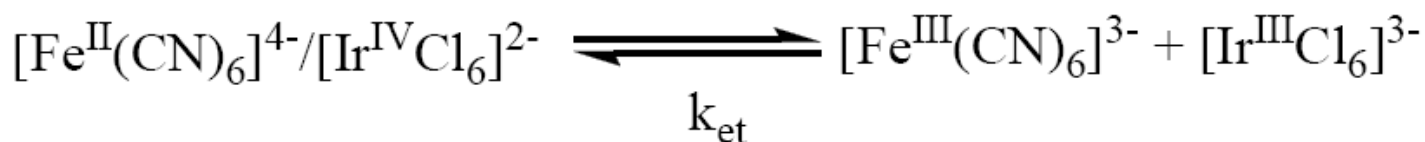The e⁻ transfer is faster than ligand substitution.

$$[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}Cl_6]^{2-} \rightleftharpoons [Fe^{III}(CN)_6]^{3-} + [Ir^{III}Cl_6]^{3-}$$

No ligands have changed place but the e⁻ has transferred.

Two–Step process in Outer-Sphere

(a) Outer-sphere ion-pair formation

$$[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}Cl_6]^{2-} \rightleftharpoons [Fe^{II}(CN)_6]^{4-}/[Ir^{IV}Cl_6]^{2-}$$

Ion-pair equilibrium

(b) Electron-Transfer

$$[Fe^{II}(CN)_6]^{4-}/[Ir^{IV}Cl_6]^{2-} \underset{k_{et}}{\rightleftharpoons} [Fe^{III}(CN)_6]^{3-} + [Ir^{III}Cl_6]^{3-}$$

Step (a) lowers the energy for e⁻ transfer by bringing reactants together (reduces internuclear separation)

The M-L distances are altered to allow the e^- transfer to take place adiabatically (without further change in E)

At Caltech, Rudy Marcus (Nobel Prize), recognized that e^- transfer should be adiabatic because electron motion is faster than nuclear motion

<u>Translation (what does the above mean?)</u>
The electron transfers quickly, once the M-L (internuclear) distances have become appropriately modified. This means that in the complex that is being oxidized, the M-L distances will become shorter because of higher OX. state of metal; conversely the M-L distances in the reduced complex (lower OX. state) will become longer.

Rate constants for outer-sphere electron transfer k_{et} vary from 10^{-4} to 10^9 (diffusion limit)

Q. Why such big differences?

A. Depends on the different amounts of energy required to change the M-L distances in the transition state (called reorganizational energy)
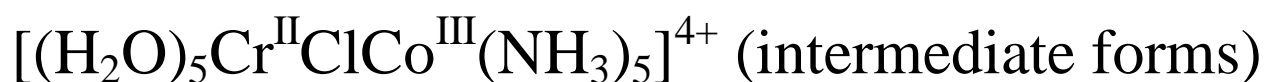
Inner-Sphere or Ligand – Bridged Electron Transfer Mechanism

Taube and co-workers are famous for this work. (Nobel Prize in Chem., 1984)

$$[Co^{III}(NH_3)_5X]^{2+} + Cr^{2+}{}_{(aq)} + 5H^+ \rightleftharpoons [Cr^{III}(H_2O)_5X]^{2+} + Co^{2+}{}_{(aq)} + 5NH_4^+$$
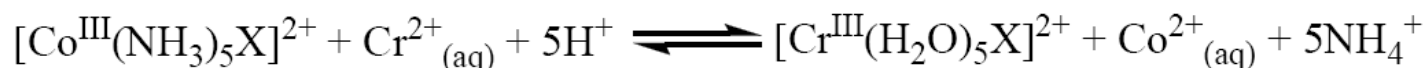
This reaction goes through a ligand – bridged intermediate

Ex. If X = Cl⁻

$$[Cr^{II}(H_2O)_6]^{2+} + [Co^{III}(NH_3)_5Cl]^{2+} \rightarrow$$

$$[(H_2O)_5Cr^{II}ClCo^{III}(NH_3)_5]^{4+} \text{ (intermediate forms)}$$
$$\uparrow\downarrow \text{ e}^-\text{transfer takes place}$$
$$[(H_2O)_5Cr^{III}ClCo^{II}(NH_3)_5]^{4+}$$

$$\downarrow(\text{intermediate falls apart})$$

$$[Cr^{III}(H_2O)_5Cl]^{2+} + [Co^{II}(NH_3)_5(H_2O)]^{2+}$$

$$\downarrow \text{ this reacts fast}$$

$$\text{in } H^+, H_2O$$

$$[Co(H_2O)_6]^{2+} + 5NH_4^+$$
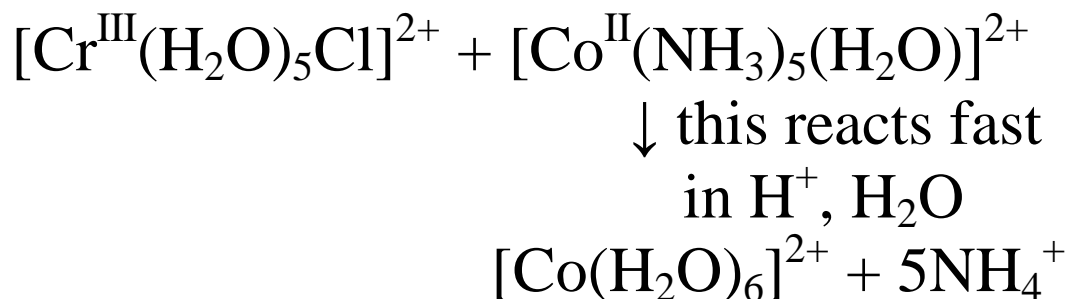
Q. What affects the rates of inner-sphere electron-transfer?

A. Nature of X bridge and its ability to "conduct" the electron from one metal to another. Better overlap with metals means higher rates of e⁻transfer
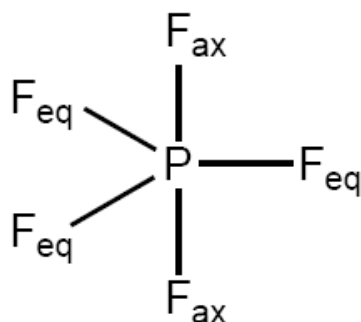
Final Topic in Chapter 6

Stereochemical Nonrigidity

Molecules are constantly fluctuating, i.e., their bonds stretch and bend but, not only that, some molecules change shape in solution such that they actually are fluxional

Five – Coordinate Complexes

PF$_5$

There are two types of ^{19}F nuclei in the molecule, so wouldn't you expect to see two sets of ^{19}F NMR spectrum?

Yes, but not if the molecular structure was changing rapidly in solution (i.e. if it was "fluxional")

R.S. Berry suggested a mechanism for rapid axial and equatorial exchange in TBP's. Called Berry Pseudo-rotation
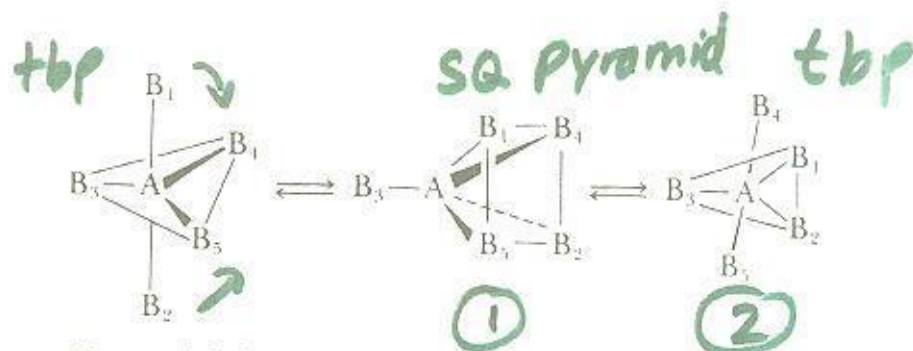
Two main steps

Figure 6-14 A simple mechanism that interchanges axial and equatorial ligands of a tbp by passage through an sp intermediate.

1. Concerted motion of two axial (B_1 and B_2 here) ligands such that they are in a plane with B_4 and B_5 →square pyramidal intermediate.
2. conversion back to a tbp molecule this can occur with original two atoms going back (i.e. B_1 and B_2) or the other two B_4 and B_5

The original and final molecules are indistinguishable if all atoms are the same, as in the case of PF_5

Because of this low-energy pathway, most five-coordinate complexes are fluxional.

Q. What about six-coordinate complexes?

A. Octahedral complexes are not usually fluxional. When they isomerize, it is because of ligand dissociation and not intramolecular rearrangement. One exception is racemization of (tris) chelate complexes. Non-superimposable $[M(en)_3]^{2+}$ Δ and Λ can interconvert by a series of twists and a bond cleavage.

Λ left　　　Δ right