(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

$$\text{ML}_3X + Y \xrightarrow{k_2} \text{ML}_3Y + X$$

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

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

Q. What does this series reflect?

A. Essentially the order of Pt$^{II}$ affinity for these ligands (their Lewis basicity or nucleophilicity)
Q. What do 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. \[ \text{PtLX}_3 + Y \rightarrow \text{PtLX}_2Y + X \]

Any of the three X ligands can be replaced by Y.

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

$$
\begin{align*}
\text{H}_2\text{O} & \sim \text{OH}^- \sim \text{NH}_3 \sim \text{py} < \text{Cl}^-, \text{Br}^- < \\
\text{SCN}^-, \text{I}^- & \sim \text{NO}_2^-, \text{Ph}^- < \\
\text{CH}_3^- & < \text{H}^- \sim \text{PR}_3 < < \text{C}_2\text{H}_4 \sim \text{CN}^- \sim \text{CO}
\end{align*}
$$

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 the ligand 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-orbitals in the transition state (intermediate) which is trigonal bipyramidal
Very useful for synthetic chemists to devise routes to new compounds!

Take for example the cis and trans isomers of $\text{Pt(NH}_3\text{)}_2\text{Cl}_2$

**How can we favor one product over the other?**

The product is cis-dichlorodiammineplatinum(II)

**Q.** What does this tell us?

**A.** that $\text{Cl}^-$ has a greater trans directing effect that $\text{NH}_3$

**Q.** How then to synthesize the trans derivative?

**A.** Use all $\text{NH}_3$ ligands in starting material
the product is trans-dichlorodiammineplatinum(II)

There is also another issue to consider which is called the “**Trans-Influence**” It follows the same trend as the Trans-Effect but it is a **ground state** phenomenon which means that it can be evaluated by studying the bonds observed in the X-ray crystal structure.
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:

\[
\text{Fe}^{2+}(aq) + \text{Ce}^{4+}(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{Ce}^{3+}(aq)
\]

Note, chemists don’t often write the actual formula for the water complex, but it is \(\text{Fe}(\text{H}_2\text{O})_6^{2+}\) ...
Two types:
(a) Outer – sphere
(b) Inner – sphere

**Outer – Sphere electron transfer**

The e\(^-\) transfer is faster than ligand substitution.

\[
[\text{Fe}^{II}(\text{CN})_6]^{4-} + [\text{Ir}^{IV}\text{Cl}_6]^{2-} \leftrightarrow [\text{Fe}^{III}(\text{CN})_6]^{3-} + [\text{Ir}^{III}\text{Cl}_6]^{3-}
\]

No ligands have changed place but the e\(^-\) has transferred.

**Two–Step process in Outer-Sphere**

(a) Outer-sphere ion-pair formation

\[
[\text{Fe}^{II}(\text{CN})_6]^{4-} + [\text{Ir}^{IV}\text{Cl}_6]^{2-} \leftrightarrow [\text{Fe}^{II}(\text{CN})_6]^{4-}/[\text{Ir}^{IV}\text{Cl}_6]^{2-}
\]

Ion-pair equilibrium

(b) Electron-Transfer

\[
[\text{Fe}^{II}(\text{CN})_6]^{4-}/[\text{Ir}^{IV}\text{Cl}_6]^{2-} \rightleftharpoons [\text{Fe}^{III}(\text{CN})_6]^{3-} + [\text{Ir}^{III}\text{Cl}_6]^{3-}
\]
Step (a) lowers the energy for e\textsuperscript{-} transfer by bringing reactants together (reduces internuclear separation)

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

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

Translation (what does the above mean?)
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)

\[
[\text{Co}^{\text{III}}(\text{NH}_3)_5X]^{2+} + \text{Cr}^{2+}_{\text{(aq)}} + 5\text{H}^+ \rightleftharpoons [\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5X]^{2+} + \text{Co}^{2+}_{\text{(aq)}} + 5\text{NH}_4^+
\]

This reaction goes through a ligand – bridged intermediate

**Example If X= Cl\(^-\)**

\[
[\text{Cr}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} + [\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+} \rightarrow \\
[(\text{H}_2\text{O})_5\text{Cr}^{\text{II}}\text{ClCo}^{\text{III}}(\text{NH}_3)_5]^{4+} \text{ (intermediate forms)} \\
\uparrow\downarrow \text{e}^{-}\text{transfer takes place} \\
[(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}\text{ClCo}^{\text{II}}(\text{NH}_3)_5]^{4+} \\
\downarrow\text{(intermediate falls apart)}
\]

\[
[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{Cl}]^{2+} + [\text{Co}^{\text{II}}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+} \downarrow \text{this reacts fast} \\
\text{in } \text{H}^+, \text{H}_2\text{O} \\
[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 5\text{NH}_4^+
\]
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\textsuperscript{-} 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
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 as portrayed in the Cotton book

1. Concerted motion of two axial (B\textsubscript{1} and B\textsubscript{2} here) ligands such that they are in a plane with B\textsubscript{4} and B\textsubscript{5} \rightarrow square pyramidal intermediate.
2. Conversion back to a tbp molecule this can occur with original two atoms going back (i.e. B\textsubscript{1} and B\textsubscript{2}) or the other two B\textsubscript{4} and B\textsubscript{5}

The original and final molecules are indistinguishable if all atoms are the same, as in the case of PF\textsubscript{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 \([M(en)_3]^{2+}\) \(\Delta\) and \(\Lambda\) can interconvert by a series of twists and a bond cleavage.