(1) <u>Solvent interactions</u>

Water is a ligand itself so it can become involved in the chemistry:

Overall reaction: $[L_5MX] + Y \rightarrow [L_5MY] + X$

1. (slow) $[L_5MX] + H_2O \rightarrow [L_5M(H_2O)] + X$
2. (fast) $[L_5M(H_2O)] + Y \rightarrow [L_5MY] + H_2O$

Two-steps, but one is very fast, so only the first one would contribute to the rate

In the end, you may not have realized that H_2O was involved in the chemistry.
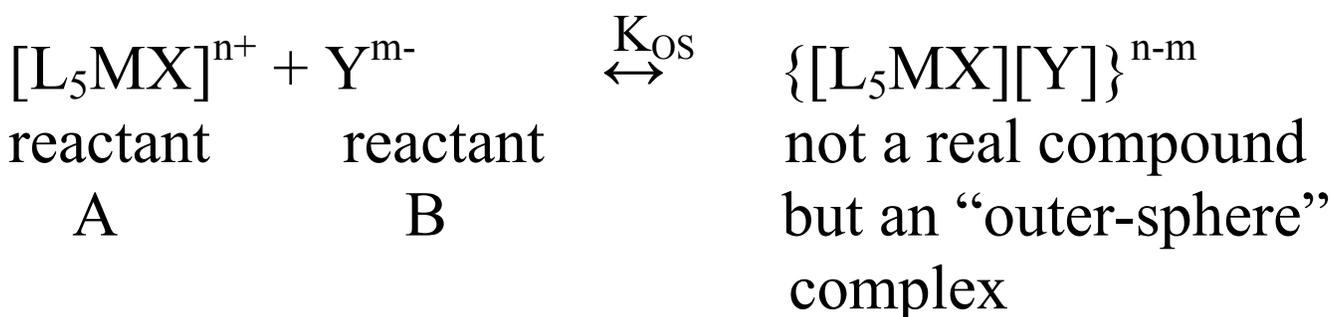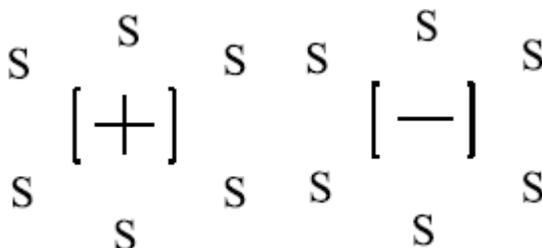(either step could be A or D)

Q. What would be a good way to probe whether H_2O was involved or not?

A. Change to a different solvent if possible

(2) **Ion – pair Formation**

this happens when

[+] [-] pairs form in solution rather than solvent – separated ions

$$\underset{S}{\overset{S}{}}\; S\; [+]\; \underset{S}{\overset{S}{}}\; S\; S\; [-]\; \underset{S}{\overset{S}{}}\; S$$

$$[L_5MX]^{n+} + Y^{m-} \overset{K_{OS}}{\longleftrightarrow} \{[L_5MX][Y]\}^{n-m}$$

reactant   reactant   not a real compound

   A   B   but an "outer-sphere" complex
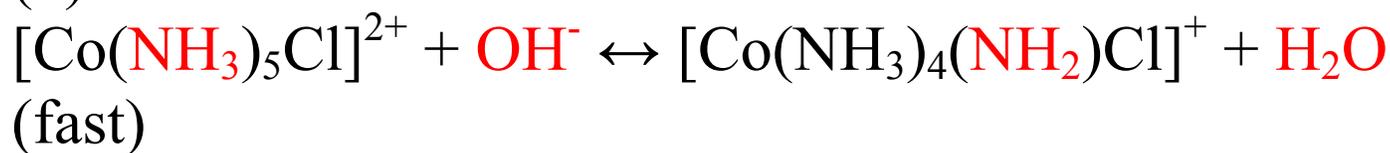
Equilibrium constant is K_{OS} or $K_{outer\ sphere}$

This ion-pair, formed by electrostatic interactions, affects the rate.

$\{[L_5MX][Y]\}^{n-m}$ forms first, so any other reactions that occur after, either (A) or (D), must include this step in their rate law
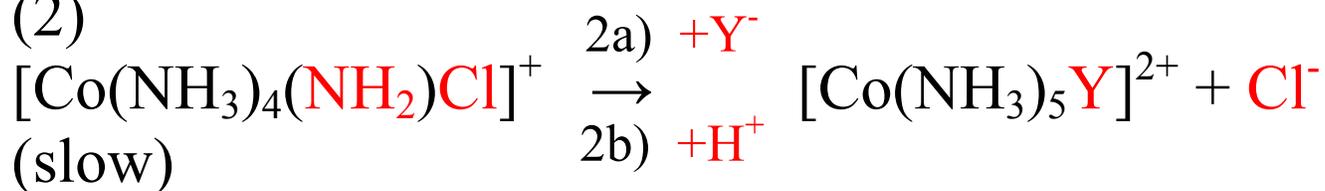
(3) Conjugate – base formation

OH⁻ is not always involved in a reaction, even if it appears in the rate expression, because it can attack a coordinated ligand first and create a base out of it.

(1)
$$[Co(NH_3)_5Cl]^{2+} + OH^- \leftrightarrow [Co(NH_3)_4(NH_2)Cl]^+ + H_2O$$
(fast)

(2)
$$[Co(NH_3)_4(NH_2)Cl]^+ \xrightarrow{\begin{array}{c} 2a) \ +Y^- \\ \longrightarrow \\ 2b) \ +H^+ \end{array}} [Co(NH_3)_5Y]^{2+} + Cl^-$$
(slow)

The $(NH_2)^-$ ligand is formed in the first step. This compound is reactive with Y^- and later protonation restores the NH_2^- ligand to NH_3. **Base catalyzed**.

(4) Anation reactions

Addition of an anion and substitution of a neutral ligand

classical case

$$[M(H_2O)_6]^{n+} + X^- \rightarrow [M(H_2O)_5X]^{(n-1)+} + H_2O$$
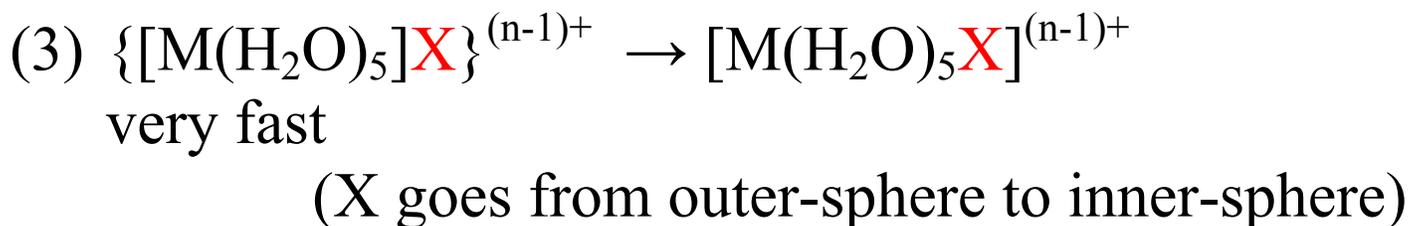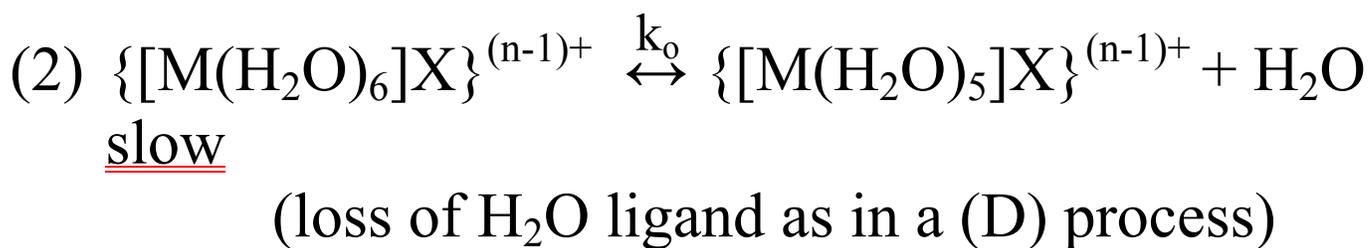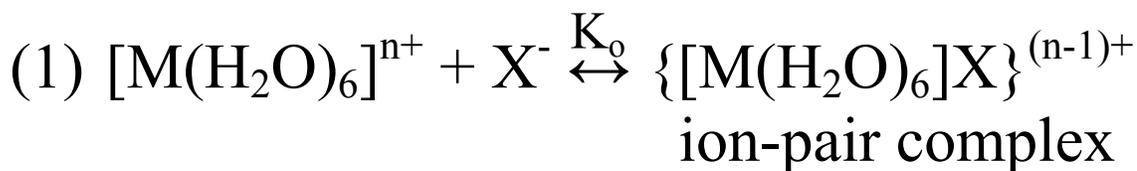
Very important reaction in terms of making new compounds from readily available metal aqua ion complexes:

Two empirical observations have been made about these reactions:

1.   For a particular aqua ion, the rates do not depend much on identity of X^-
     (< a factor of 10 difference)

2.   Rates for anation are practically the same as exchange of H_2O ligands with H_2O molecules in solution
     (only ~ 10 times slower)

Q. Why are anation reactions so insensitive to X^-?

A. Can be explained by invoking a three-step process:

(1) $[M(H_2O)_6]^{n+} + X^- \overset{K_o}{\leftrightarrow} \{[M(H_2O)_6]X\}^{(n-1)+}$
$\qquad\qquad\qquad\qquad$ ion-pair complex

(2) $\{[M(H_2O)_6]X\}^{(n-1)+} \overset{k_o}{\leftrightarrow} \{[M(H_2O)_5]X\}^{(n-1)+} + H_2O$
<u>slow</u>
$\qquad$ (loss of H_2O ligand as in a (D) process)

(3) $\{[M(H_2O)_5]X\}^{(n-1)+} \rightarrow [M(H_2O)_5X]^{(n-1)+}$
very fast
$\qquad$ (X goes from outer-sphere to inner-sphere)

$\qquad$ Step 3 is so fast that it does not contribute to the rate, so main contributors are step 1 and 2.

Overall second order rate law $= k_{obs}[M(H_2O)_6]^{n+}[X^-]$

k_{obs} = obsverved rate constant, which should be approx $K_{os} \cdot k_o$

↗   ↖

ion-pair   water
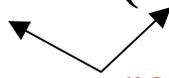outer-sphere   exchange
Equilibrium   step 2
step 1

$$k_{obs} = K_{os} \cdot k_o$$

k_{obs} and K_{os} can be experimentally determined and $k_{o.s.}$ can be estimated

<u>bottom line:</u> this allows for k_o to be determined. It has been observed that k_o values for these anation reaction are almost the same as simple water exchange k_o values for

$$[M(H_2O)_6]^{n+} + (H_2O)' \leftrightarrow [M(H_2O)_5(H_2O)'] + H_2O$$
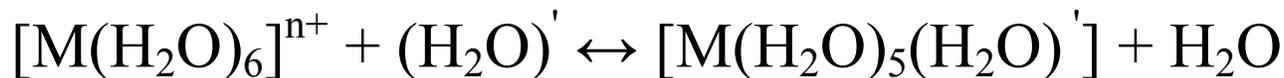
(5) Aquation Reactions (solvent intervention)

really the same

$$[CoA_5X]^{n+} + H_2O \rightarrow [CoA_5(H_2O)]^{(n-1)+} + X^-$$

First X^- is replaced by H_2O before any other reactions take place
(A is an amine ligand in this case)
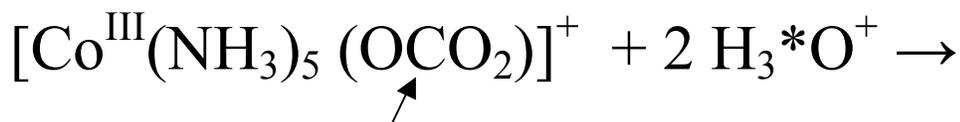
      (a) acid hydrolysis
      (b) base hydrolysis

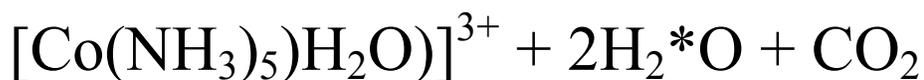The reaction can be performed at low and high pH values, and this determines the rate law.

(very complicated – we will just leave it at that)

(6) Ligand Assisted Reactions

Bonds within ligands can be broken

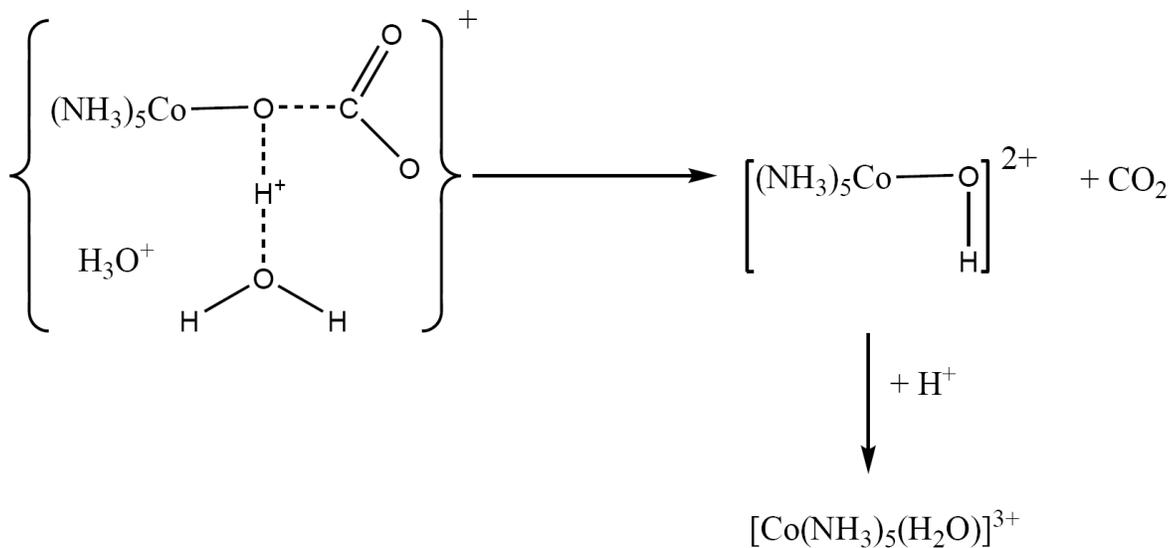$$[Co^{III}(NH_3)_5 (OCO_2)]^+ + 2\,H_3{*}O^+ \rightarrow$$

CO_3^{2-} ligand

$$[Co(NH_3)_5)H_2O)]^{3+} + 2H_2{*}O + CO_2$$

$H_2{*}O$, $H_3{*}O^+$ means isotopically labeled H_2O
(could be $H_2{}^{18}O$)

None of the labeled *O atoms wind up in the complex!

Q. What is the most likely mechanism that explains the facts?

A.

Note that the original O atom from a CO_3^{2-} ligand remains on the Co ion and becomes the basis for a new H_2O ligand

Main way that researchers find out mechanistic pathways is by isotopic labeling
(also D_2O is often used)

Besides **octahedral** <u>complexes</u> there are important reactions based on **square** **planar** **substitution** **chemistry**
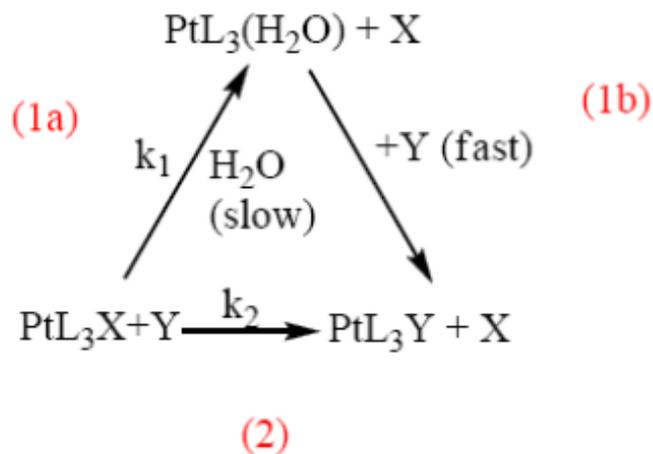
Since   is much

more open, it seems reasonable to expect most reactions to be (A) rather than (D) and this is the case in the general reaction:

$$PtL_3X + Y \rightarrow PtL_3Y + X$$

L-ligands   labile   incoming ligand
do not   ligand
substitute
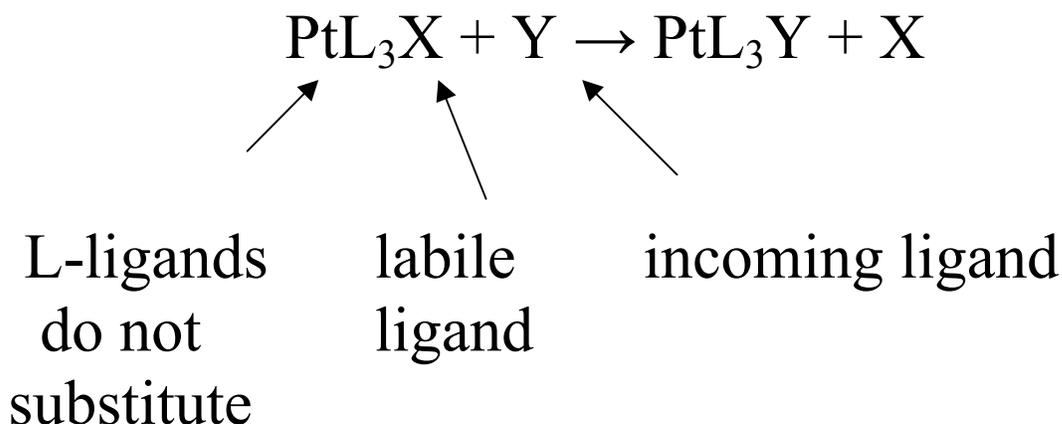
$$\text{overall rate} = k_1[\text{PtL}_3\text{X}] + k_2\,[\text{PtL}_3\text{X}][\text{Y}]$$

What this rate law means is that there are two paths available for reaction

$$\text{PtL}_3(\text{H}_2\text{O}) + \text{X}$$

(1a) k_1 / H_2O (slow)   +Y (fast)   (1b)

$$\text{PtL}_3\text{X} + \text{Y} \xrightarrow{\;k_2\;} \text{PtL}_3\text{Y} + \text{X}$$

(2)

(a) a first order path with k_1 rate constant
     This path involves a two-step process (one slow and one fast) in which X is first replaced by water in the rate-determining step and then the water is replaced by Y in the second (fast step)

(b) a second order path with k_2 rate constant which involves direct replacement of X by Y

Both paths have been found to be involved Associative (A) processes with both (H_2O) and Y being bound to a five-coordinate intermediate in the two different pathways.

[PtL$_3$(H$_2$O)Y] in path 1

and

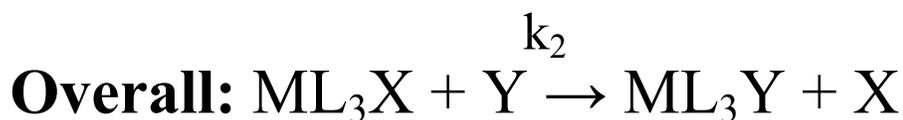[PtL$_3$XY] in path 2 where both X and Y bound to the five-coordinate intermediate

(these are not shown in the scheme)

If one wrote it out in full, you could represent each step as a truly associative process
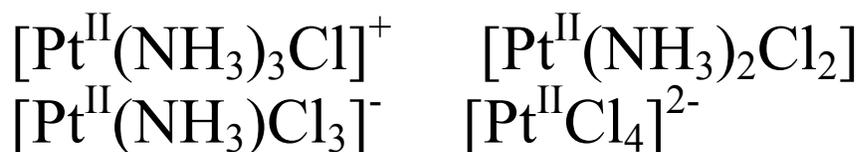
Path (1)
(a) ML$_3$X + H$_2$O → "[ML$_3$X(H$_2$O)]" → ML$_3$(H$_2$O) + X
(b) ML$_3$(H$_2$O) + Y → "[ML$_3$(H$_2$O)Y]" →ML$_3$Y + H$_2$O

Path (2)
And ML$_3$X + Y $\xrightarrow{k_2}$ "[ML$_3$XY]" → ML$_3$Y + X

Overall: ML$_3$X + Y $\xrightarrow{k_2}$ ML$_3$Y + X

Q. What effects square planar substitution rates?

A. Charge, sterics, ligand types, stereochemistry (geometric isomers)

(a) <u>Charge effects</u>

Pt^{II} complexes have been studied the most.

$[Pt^{II}(NH_3)_3Cl]^+$ $[Pt^{II}(NH_3)_2Cl_2]$
$[Pt^{II}(NH_3)Cl_3]^-$ $[Pt^{II}Cl_4]^{2-}$

Consider an aquation reaction where Cl^- is being replaced by H_2O

In the above compounds the rate constant k_1 varies only by a factor of 2.

Q. What does this tell you?

A. That the Pt – Cl bond does not break first.
<u>a Dissociative Process (D) is not happening</u> because high positive charges would make this harder to do. Obviously an Associate (A) process dominates. Associate Interchange (I_A)

    In other words… Pt – Cl bond breaking and Pt – OH_2 bond making are equally important

(b) <u>Steric effects</u>

<u>Q.</u> What happens to rates of (A) and (D) type when one has a bulky ligand?

<u>A.</u> (D) should be more favored – rates of loss of the bulky ligand would increase.

(A) should be less favored – rates of adding a new ligand to the "already crowded" coordination environment should be retarded

<u>In a Square Planar geometry</u>, if bulky ligands slow the rate, so (A) or (I_A) must be occurring.