Square Planar Complexes + Associative Sub. Reactions

Square Planar Complexes often have the electron config d^8

Pd^{II}, Ni^{II}, Pt^{II}, Rh^{I}, Au^{III}, etc... → x^2-y^2

Usually low spin → xy

→ z^2

→ xz, yz

Strong π Acceptors

Substitution Rxns for ML_4

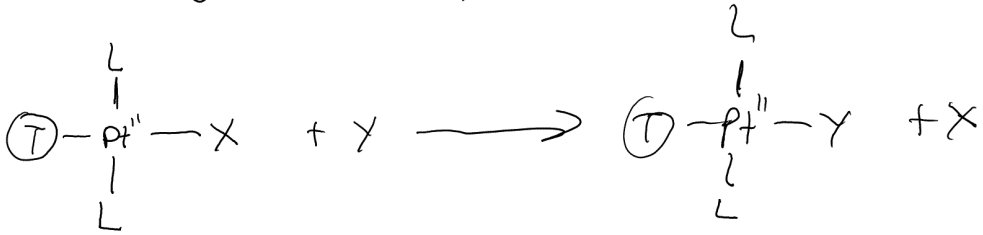
① Retention of Regiochemistry (trans → trans) (cis → cis)

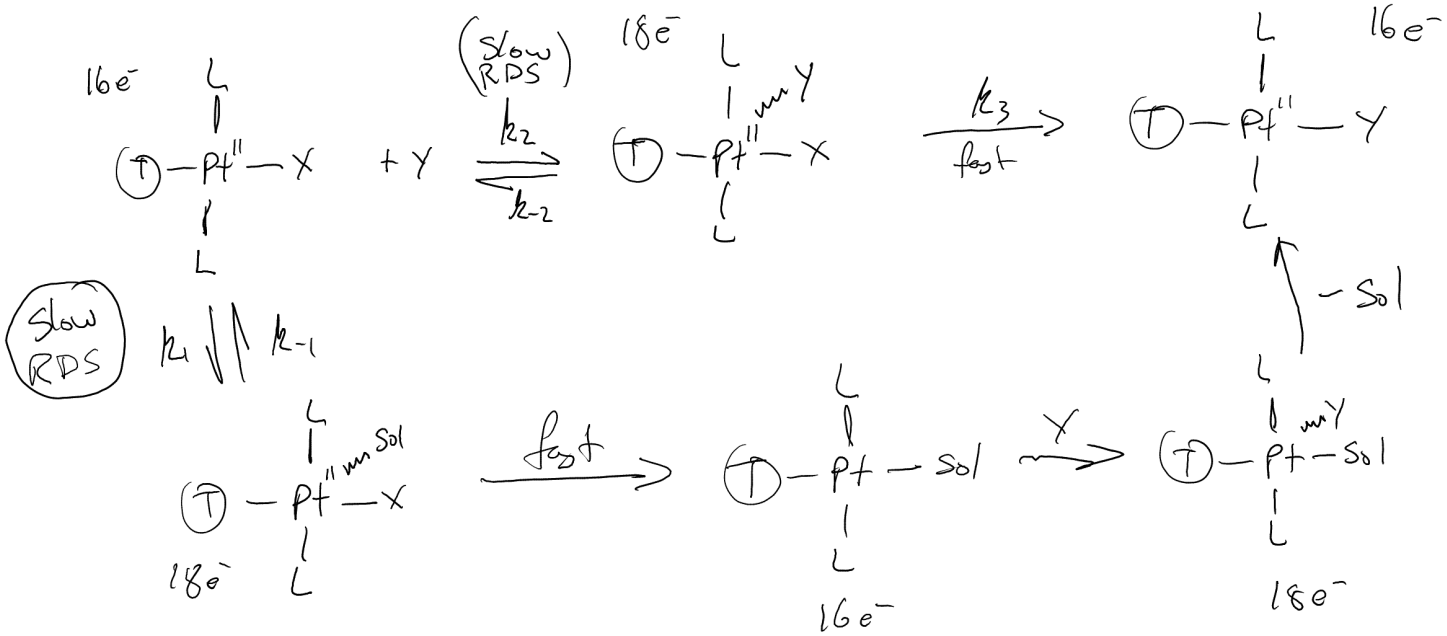
② Complicated Rate Law (biphasic)

$$\text{Rate} = k_1[ML_4] + k_2[ML_4][Y]$$

$\Delta H^{\ddagger}$ Large + Positive
$\Delta S^{\ddagger}$ Large + Negative
$\Delta V^{\ddagger}$ Large + Negative

③ Strong Solvent dependance





Mechanistic Details

[Y] appears in the rate term ∴ identity of Y should impact the kinetics

Y	$k\ (10^{-3}\ M^{-1}s^{-1})$
$P\phi_3$	49000
SCN^-	160
I^-	107
Br^-	3.7
N_3^-	1.5
NO_2^-	0.7
NH_3	0.5
Cl^-	0.4

Basolo + Pearson JACS 1965, 87, 241

10^7

Polarizable ligands result in fastest kinetics

↳ Pearson's Hard Soft Acid Base Theory (HSAB)

In general: $PR_3 > CN^- > SCN^- > I^- > Br^- > N_3^- > NO_2^- > PY > NH_3 \sim Cl$

Hard = Species that are small, highly charged, low polarizability + large electronegativity

Hard Bases - Low Energy HOMOs (OH^-, F^-, NH_3, CO_3^{2-}, etc....)

Hard Acids - High Energy LUMOs (H^+, Cr^{III}, Cr^{VI}, Ti^{IV}, BF_3, etc....)

Soft = Species that are large, low charge states, polarizable + low electronegativities

Soft Base - High Energy HOMOs (H^-, PR_3, SCN^-, I^-, RS^-, etc...)

Soft Acids - Low Energy LUMOs ($MeHg^+$, Pt^{2+}, Pd^{II}, Ag^I, Au^{III}, Rh^{III}, etc...)

Identity of leaving ligand X also influences kinetics

↳ Also controlled by HSAB

∴ Hard ligands (X) are substituted more rapidly than soft

good π acceptors

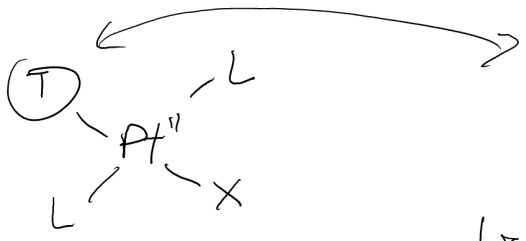
OH_2, NO_2^-, NH_3 CN^-, PR_3, CO

Basolo, Pearson + Gray
JACS 1960, 82, 4200

X	k ($M^{-1} s^{-1}$)
NO_3^-	Very fast
Cl^-	5.3×10^{-3}
Br^-	3.5×10^{-3}
I^-	1.5×10^{-3}
N_3^-	1.3×10^{-4}
SCN^-	4.6×10^{-5}
NO_2^-	3.6×10^{-6}
CN^-	2.8×10^{-6}

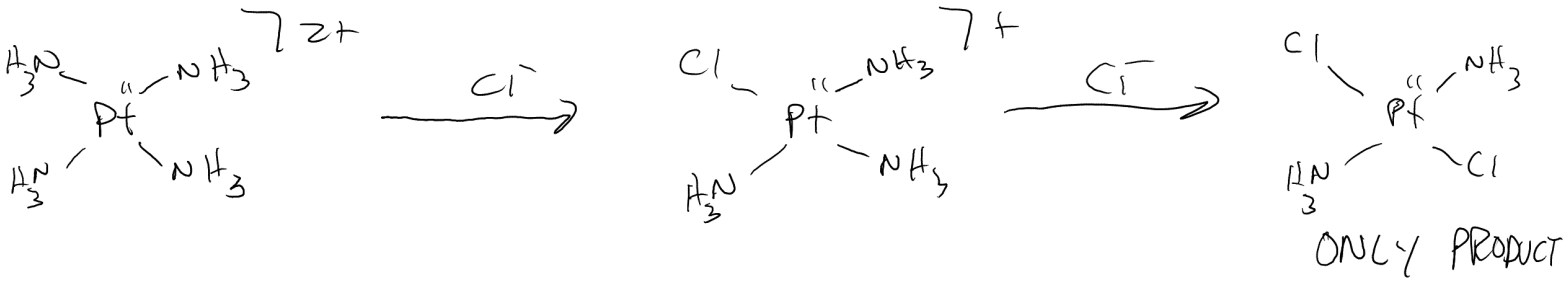
The placement of certain ligands on a TM complex can effect kinetics + Regioselectivity of substitution

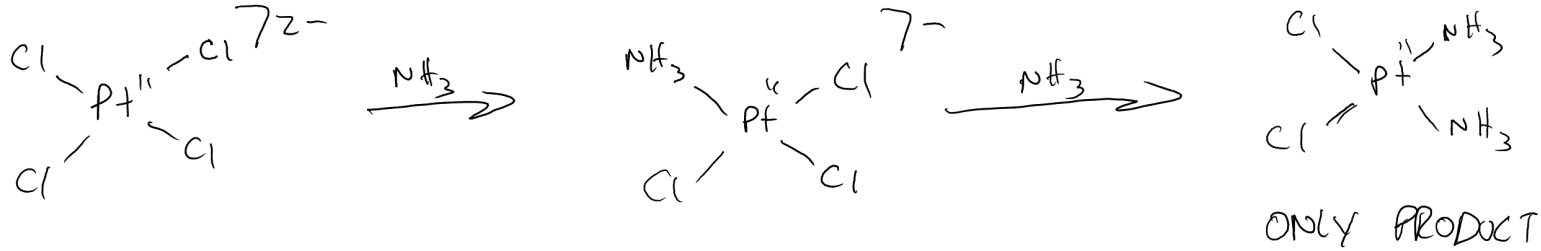
↳ Trans Effect (Charnyaev 1926)



Ligand trans to leaving group influences how easily the group can be replaced.

Ligands trans to Cl^- are displaced more readily than those trans to NH_3





The trans effect is controlled by 2 factors:

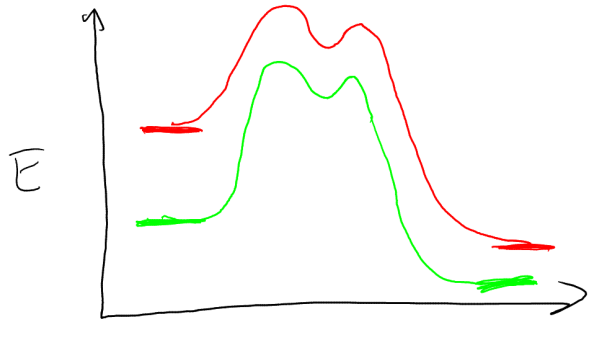
① Weakening of the Pt–X bond by T

② Stabilize the 5-coordinate TS

① Sigma Bonding Effects — the Pt–X bond is effected by the Pt–T bond because they involve the same orbitals

p_x $\quad$ $d_{x^2-y^2}$

Weaker Pt–X σ-bond increase the free energy of the reactant



Strong Trans effect (Strong Pt–T ∴ weak Pt–X)

Weak Trans effect (Weak Pt–T ∴ Strong Pt–X)

② Stabilization of 5-coordinate TS (π-bonding effects)

When T serves as a π-acceptor: move e^- deficient metal centers...

∴ Addition of 5th ligand (Y) which is the RDS ⇒ electrostatically favored

Strong T (good π-acceptor)

Weak T (poor π-acceptor)

The overall trans-effect ordering:

$\underbrace{CO, \sim CN^- \sim C_2H_4}_{\text{good } \pi\text{-acceptor}} > PR_3 \sim H^- > CH_3^- \sim SC(NH_2)_2 > C_6H_5 > NO_2^- > SCN^-$

$I^- > Br^- > Cl^- > py \sim NH_3 > OH^- > H_2O$