

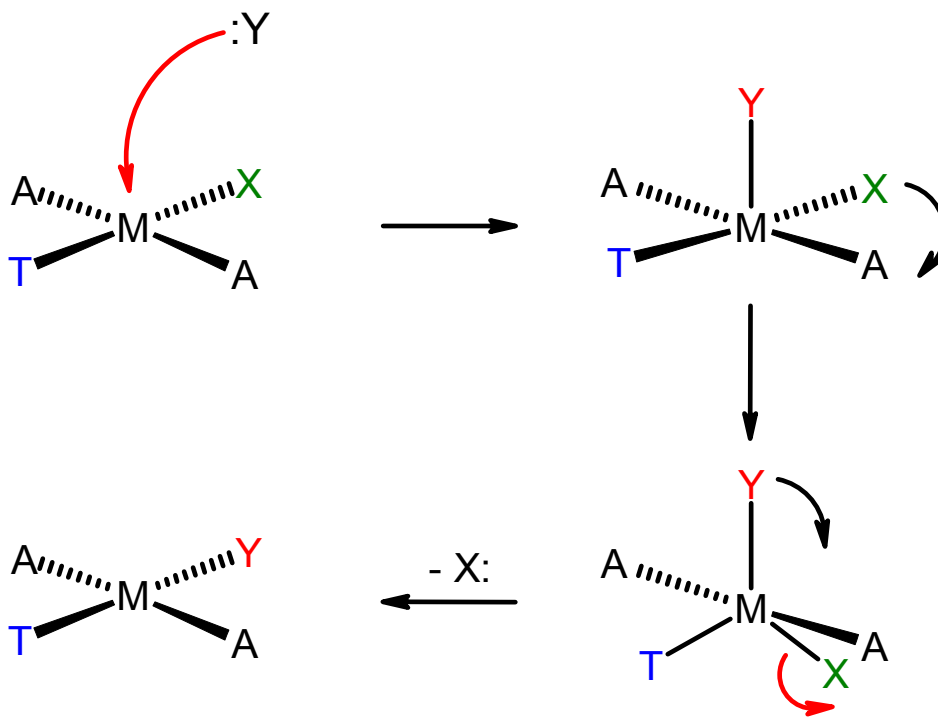
Substitution in Square Planar Metal Complexes

Extensively studied for square planar Ni^{2+} , Pd^{2+} and Pt^{2+} (d^8) substitutions in water and non-polar solvents:



- rates depend on $[\text{M}(\text{A})_2(\text{T})(\text{X})]$ and $[\text{Y}]$
- ΔS^\ddagger and ΔV^\ddagger are generally large and negative
- sensitive to nature of Y

What type of mechanism is it? A or I_A



Ligand directing effects: some ligands (denoted T in the previous reaction) preferentially direct substitution to the site trans to themselves (*kinetic trans effect*).

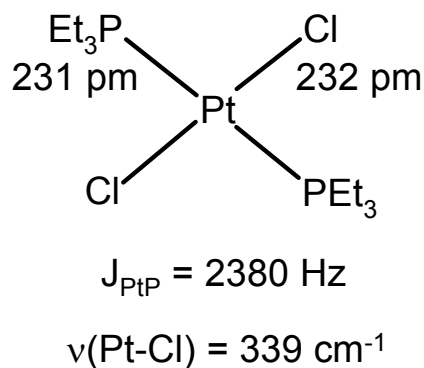
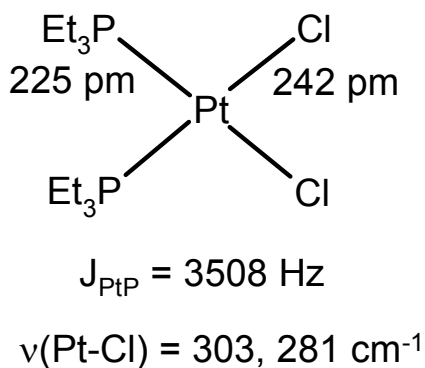
The *trans* effect of a ligand may be due to:

a) destabilization of the trans M-L bond in the ground state (also called the *trans influence*)

see: middle of Fig. 7-2, next page

(from Organometallic Chemistry by Spessard and Miessler)

- strong σ -donors (H^- , PR_3 , I^- , Me^- etc.) weaken the M-L bond *trans to themselves*
- observable by IR ($\nu_{\text{M-L}}$), X-ray (longer M-L bond length) and NMR (reduced $^1J_{\text{M-L}}$ values)



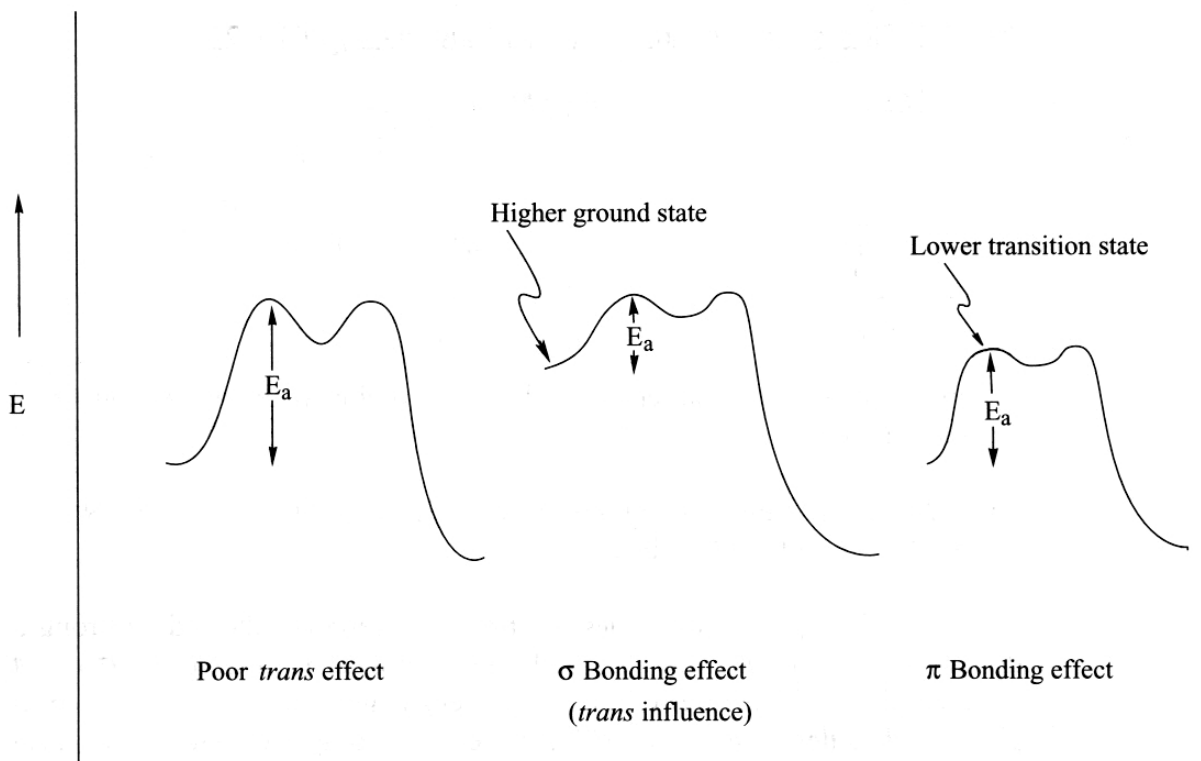


Figure 7-2

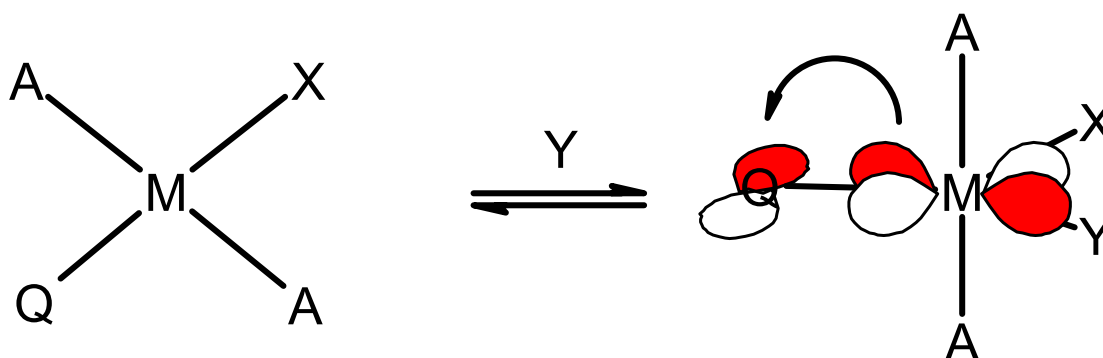
Activation Energy and the *trans* Effect

The depth of the energy curve for the intermediate and the relative heights of the two maxima will vary with the specific reactants. (Adapted from G.L. Miessler and D.A. Tarr, *Inorganic Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1991, 397.)

b) stabilization of the transition state (*true trans effect*)

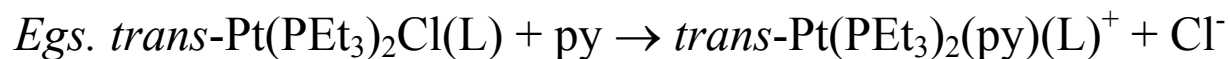
see: Fig 7-2, right on the page above

- strong π -acceptors (eg. CO, C₂H₄, NO⁺ etc.) remove electron density in the equatorial plane of 5-coordinate *tbp* transition states thus decreasing electrostatic repulsion



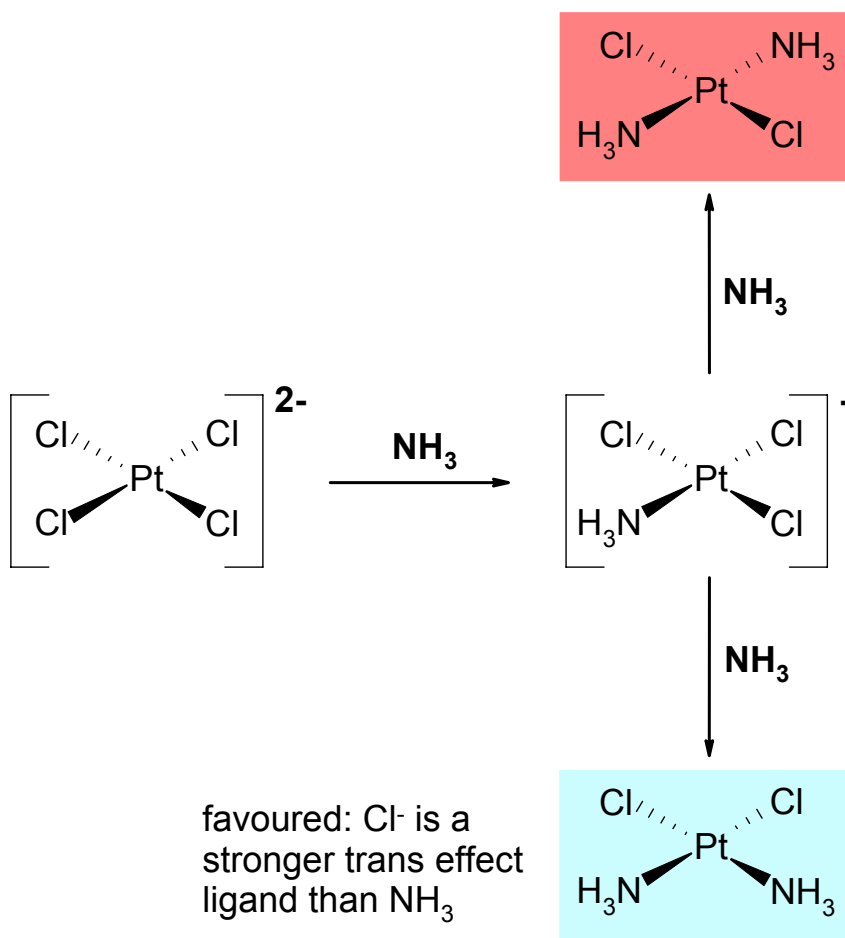
Combining σ - and π -effects gives the observed *trans effect* order:





L (trans)	k ($\text{M}^{-1}\text{s}^{-1}$)
H^- , PEt_3	4
Me^-	0.2
Ph^-	0.01
Cl^-	0.0001

Trans effect can *dictate the product obtained* as well:



Metal effects on square planar substitution:

- almost all examples of square planar geometry are d8 electron counts so electron counts are not a factor
- however, ΔCFSE going from SqP to TBP geometry is still unfavourable by $-0.242\Delta_{\text{oct}}$ so this adds to the barrier for square planar substitution and this is one of the main reasons why SqP substitution is slower for 2nd and 3rd row metals