

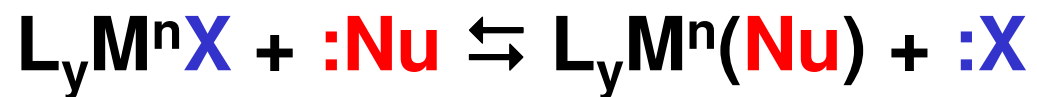
Corso di Chimica Generale ed Inorganica II
Laurea Triennale in Chimica

Prof. Vincenzo Busico

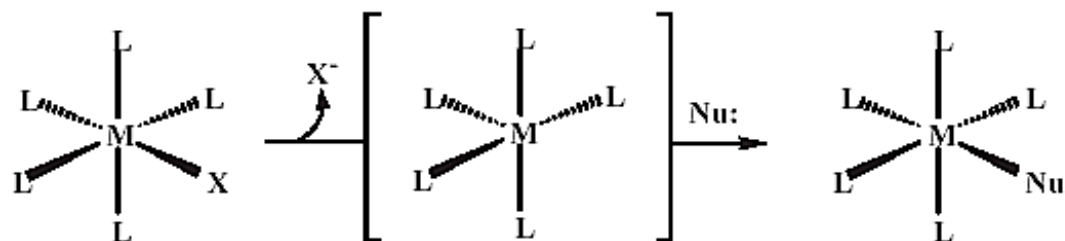
Lezione III.1

Reazioni Stechiometriche dei Composti di Coordinazione

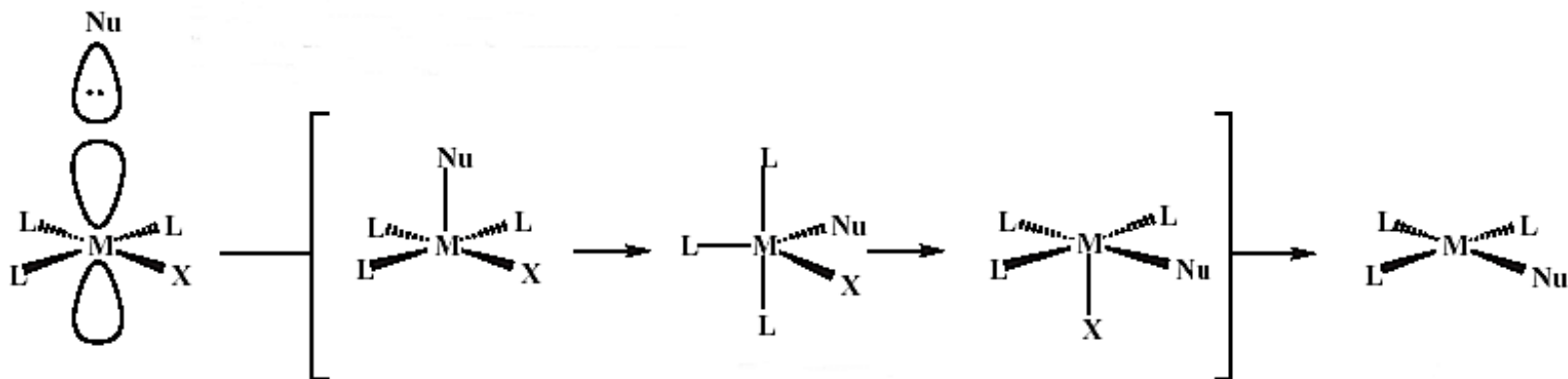
Ligand Substitution



Dissociative Mechanism ("Quasi-S_N1")

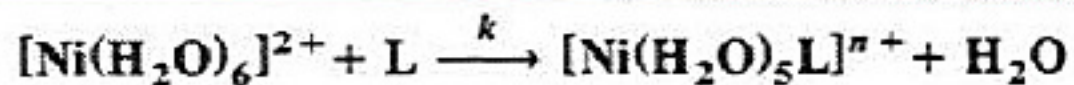


Associative Mechanism ("Quasi-S_N2")



An Example of Dissociative Substitution at Ni(II)

Rate Constants for Substitution Reactions of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

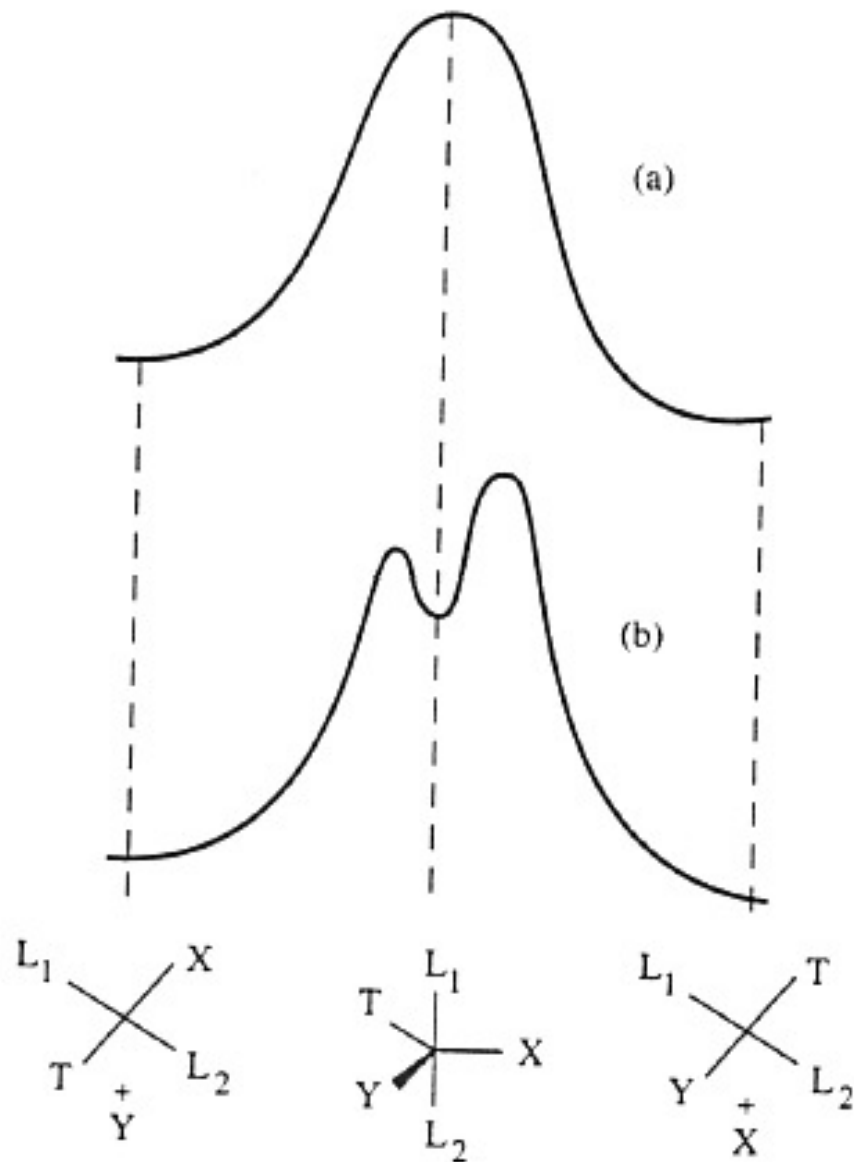


L	k, s^{-1}	$\log k$
F^-	8×10^3	3.9
SCN^-	6×10^3	3.8
CH_3COO^-	30×10^3	4.3
NH_3	3×10^3	3.5
H_2O	25×10^3	4.4

Source: Data from R. G. Wilkins, *Acc. Chem. Res.* 3 (1970): 408.

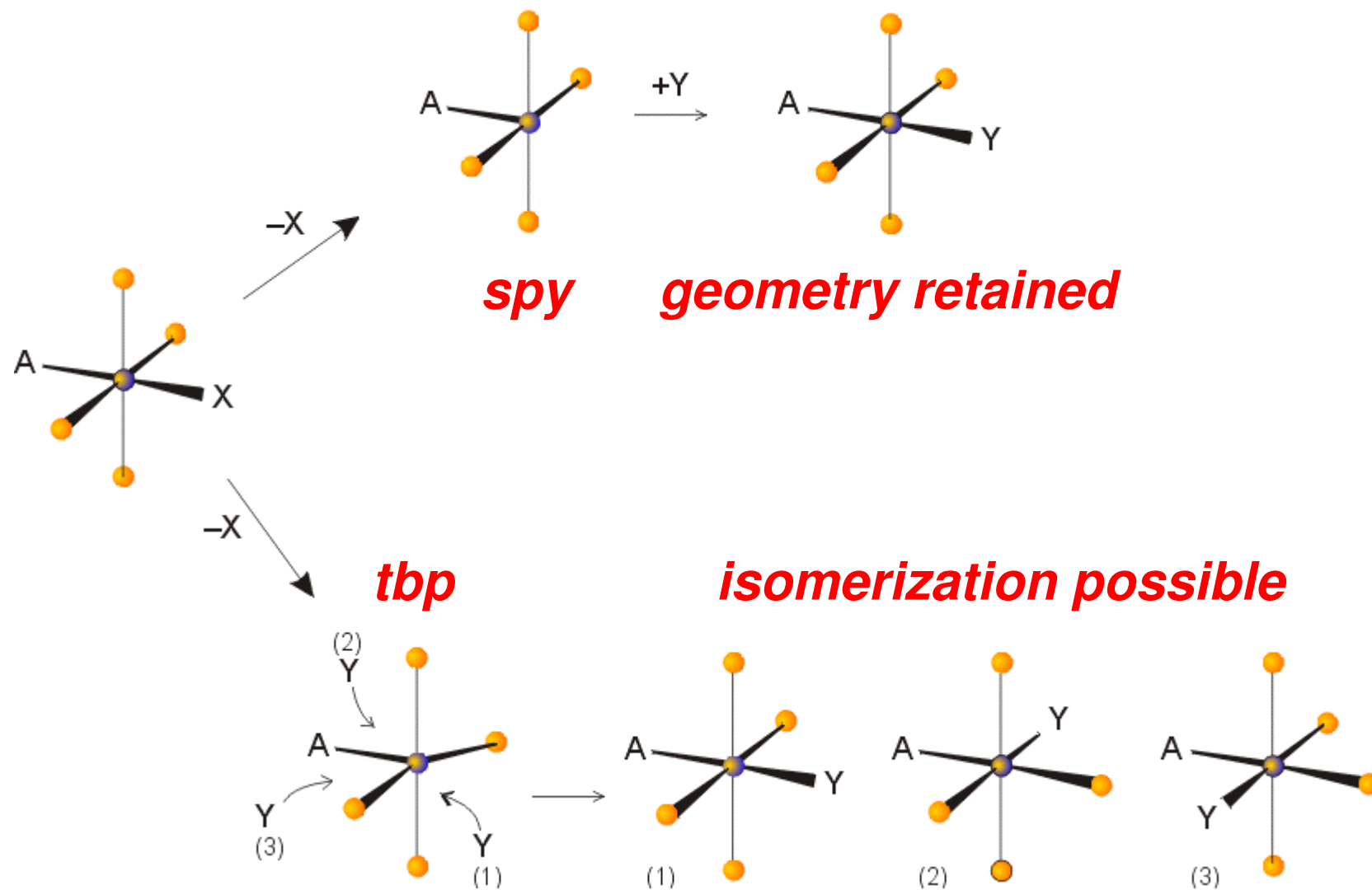
The rate is **independent** of the identity of L, the **entering ligand**

Mechanisms and Kinetics of Associative Substitutions

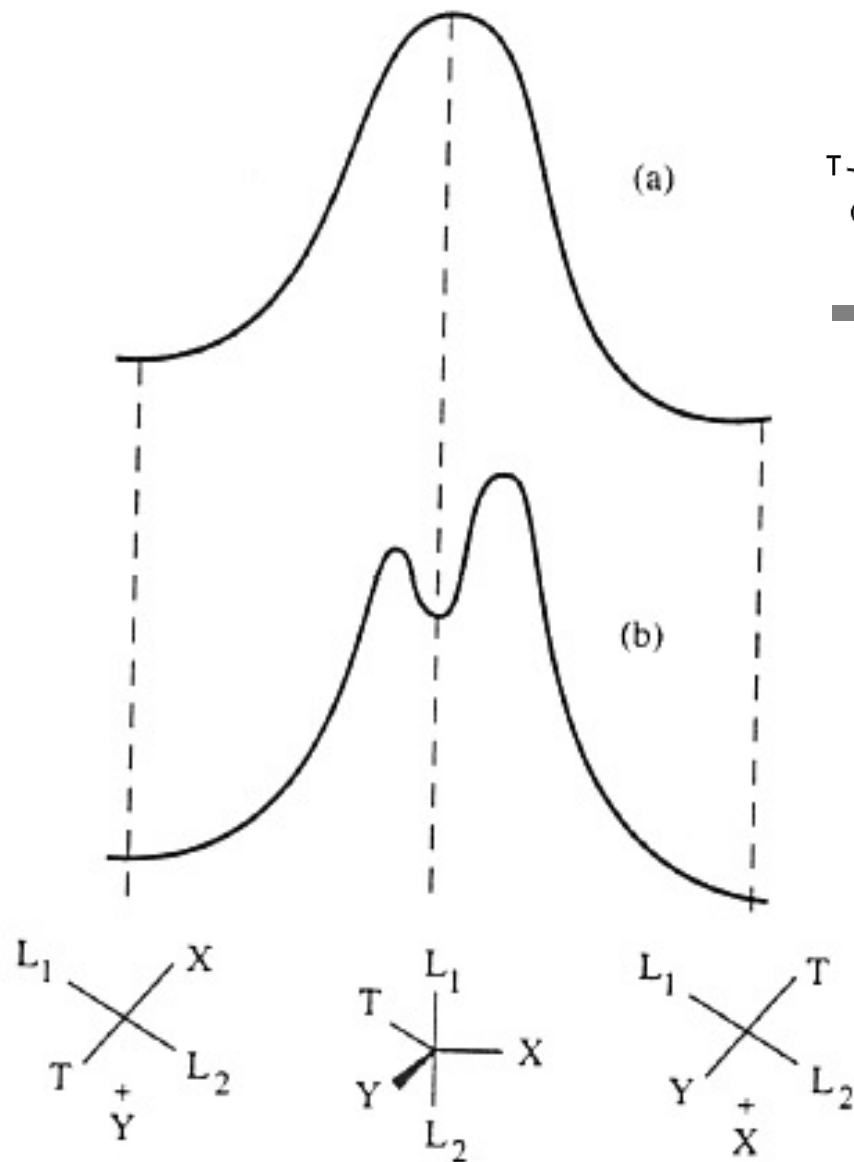


$$\underline{\underline{r = k[\text{ML}_2\text{TX}][\text{Y}]}}$$

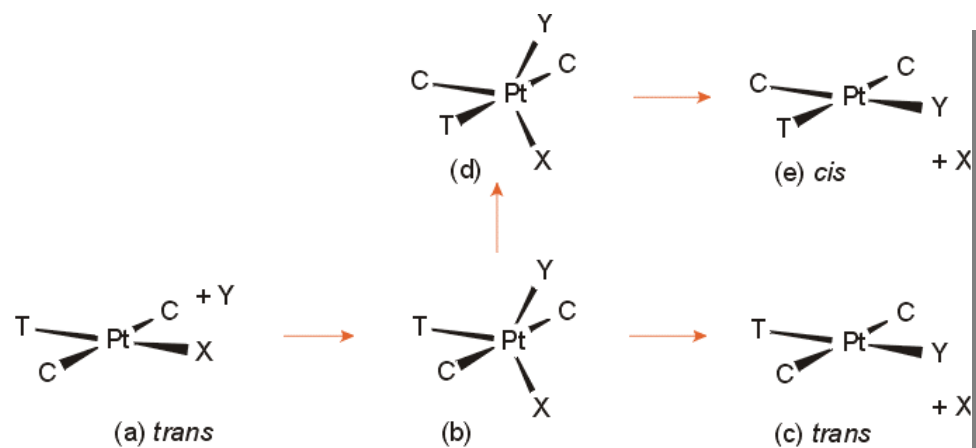
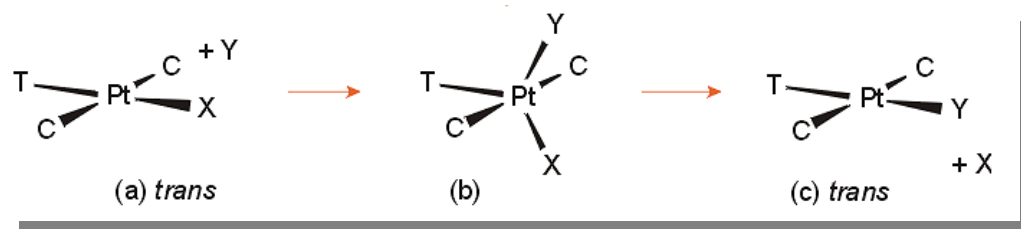
Stereochemistry of Dissociative Substitutions



Stereochemistry of Associative Substitutions



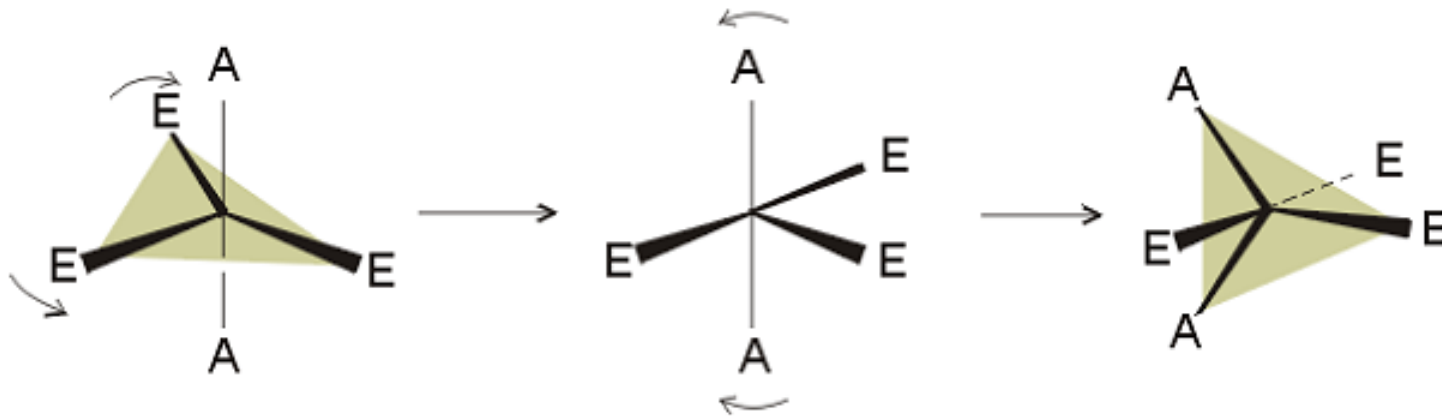
geometry retained



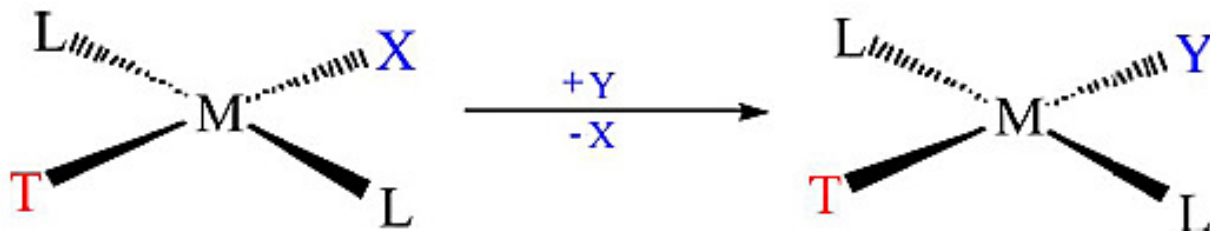
isomerization possible

Isomerization Reactions

- Similar to substitution reactions
- Berry Pseudorotation mixes axial and equatorial positions in a 5 coord TBP species
- Both square planar complexes which undergo A mechanisms or O_h complexes which undergo D or I_d mechanisms involve a 5 coordinate state so ... isomerization is possible

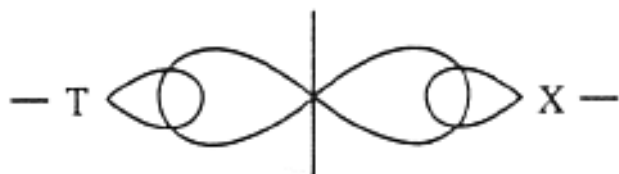
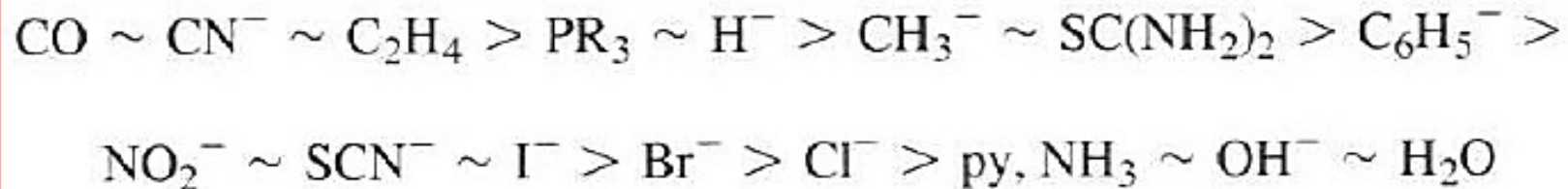


The 'Trans Effect'



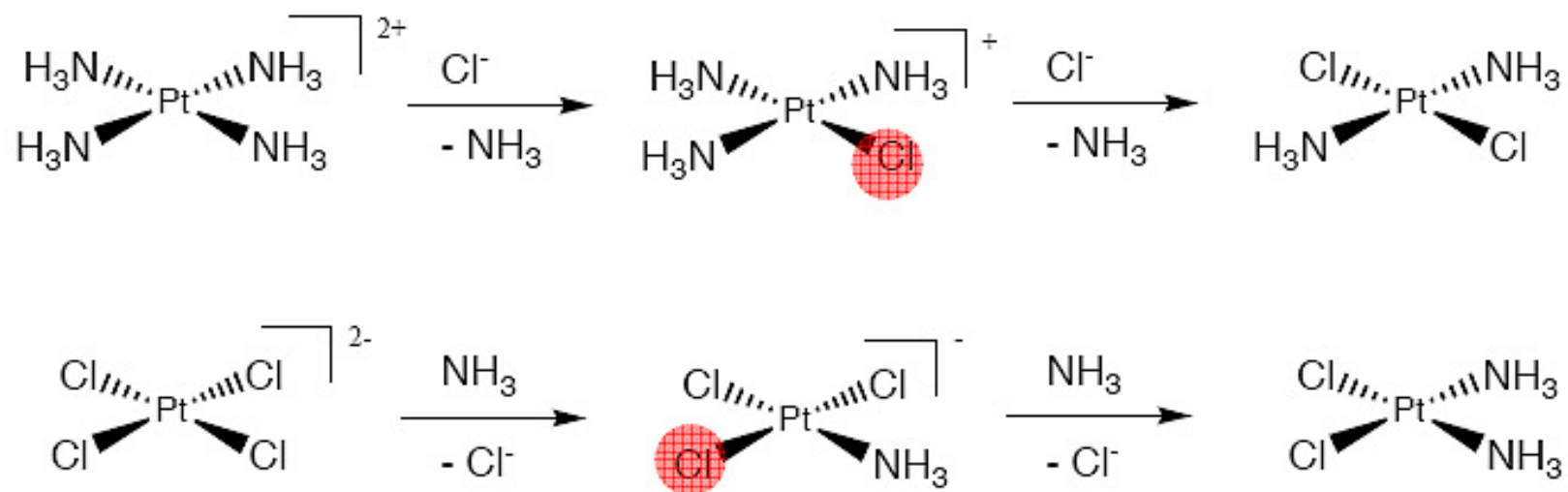
Trans effect: **The ability of a ligand (T) to labilize a ligand trans to it (X)**
T = a trans-directing ligand

The trans effect series

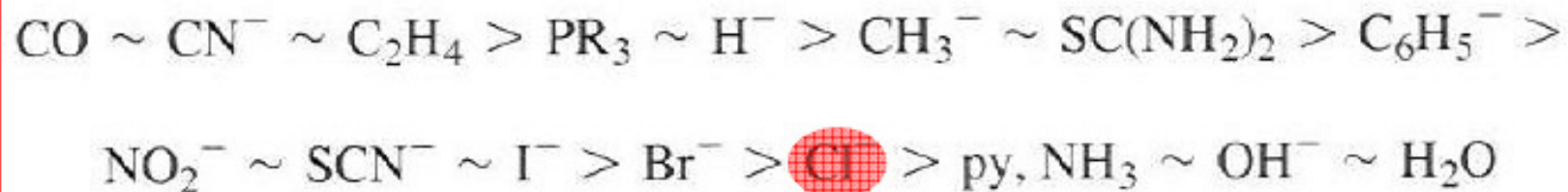


Partial explanation:
 σ donation by T weakens the M-X bond

The 'Trans Effect' in Inorganic Synthesis



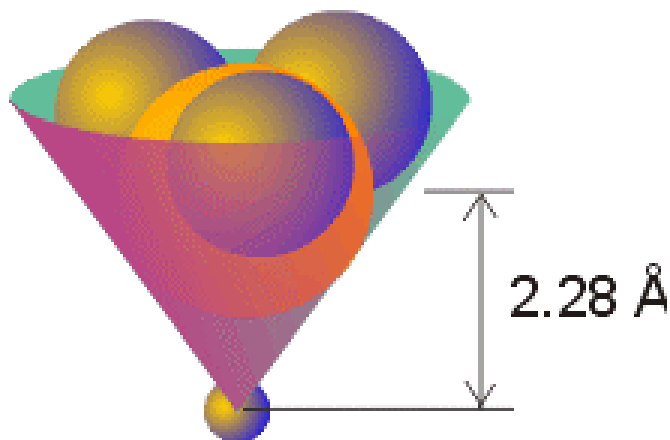
The trans effect series




A Few Thermodynamic & Kinetic Remarks

The rate and extent of the substitution of X with Y are critically related to the strength of the M-X and M-Y bond

The inherent components can be modulated by means of 'ancillary / spectator' ligands featuring proper steric and/or electronic effects

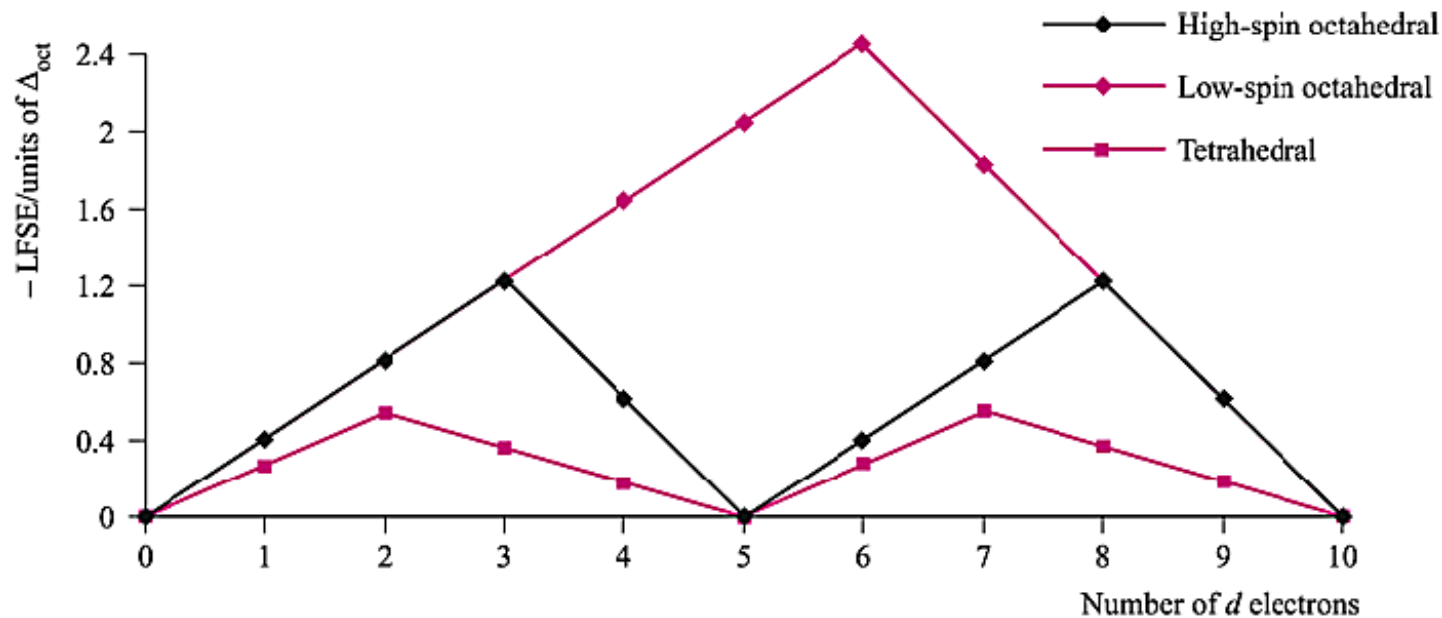


Tolman's Cone Angle Concept

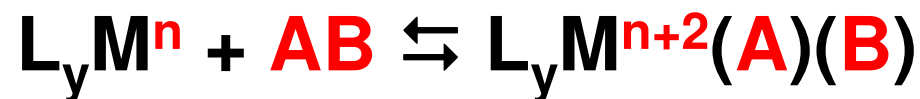
Ligands	Cone angle* θ (°)	Ligands	Cone angle* θ (°)
<i>phosphines</i>		<i>3^o amines</i>	
PH ₃	87	NH ₃	94
PF ₃	104	NMe ₃ ,	132
P(OMe) ₃	107	quinuclidine,	
PMe ₃	118	NMe ₂ Et	
PCl ₃	124	NMeEt ₂	145
	125	NEt ₃	150
PPhMe ₂	127	NPr ₃	160
PEt ₃	132	NPh ₃	166
PPh ₂ Me	136	NEt ₂ Ph	170
PPh ₂ Et	140	NBz ₃	210
PPh ₂ Pr	140	N(<i>i</i> -Pr) ₃	220
PPh ₃	145	<i>others</i>	
PPh ₂ Cy	153	H	75
PPhCy ₂	161	Me	90
PCy ₃	170	CO	95
P(<i>t</i> -Bu) ₃	182	Cp	136
P(<i>o</i> -tol) ₃	194		
P(mesityl) ₃	212		

'Inert' vs 'Labile'

- Inert: species that are unstable but survive for minutes or more
- Labile: species that react more rapidly than inert complexes
- Increasing Ligand Field Stabilization Energy improves inertness
- 2nd and 3rd row metals are generally more inert



Oxidative Addition / Reductive Elimination



Requisites for M:

- Availability of non-bonding electrons
- Accessibility of TWO coordination sites
- Similarly good stability of Oxidation Numbers n & (n+2)

Main examples of M^n/M^{n+2} pairs:

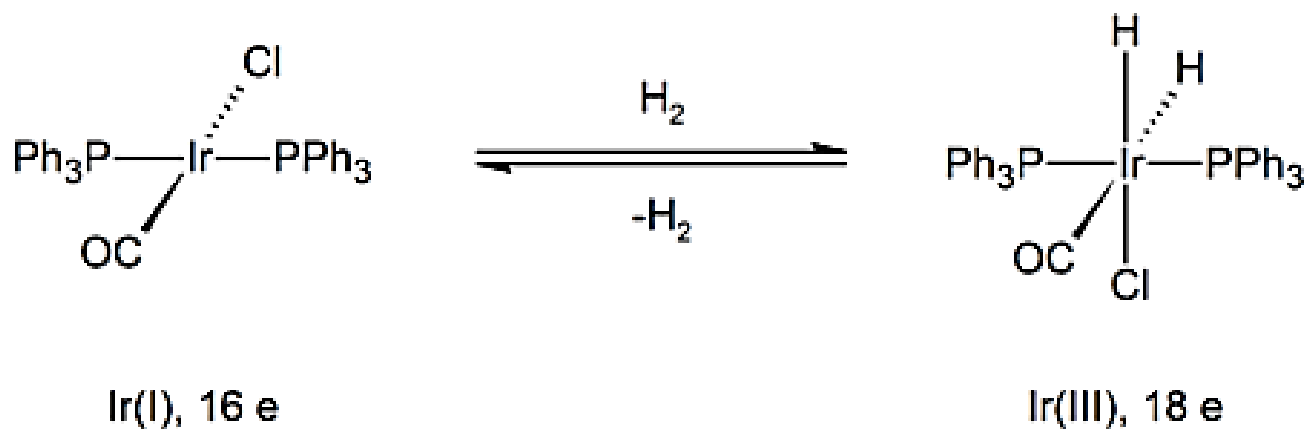
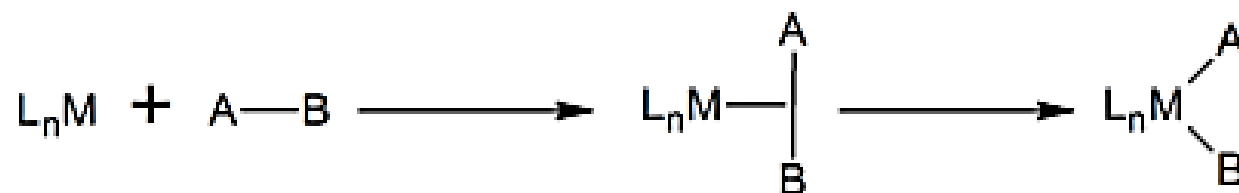
- Fe^0/Fe^{2+} ; Ru^0/Ru^{2+} ; Os^0/Os^{2+}
- Rh^+/Rh^{3+} ; Ir^+/Ir^{3+}
- Ni^0/Ni^{2+} ; Pd^0/Pd^{2+} ; Pt^0/Pt^{2+}
- Pd^{2+}/Pd^{4+} ; Pt^{2+}/Pt^{4+}

Main examples of **AB**:

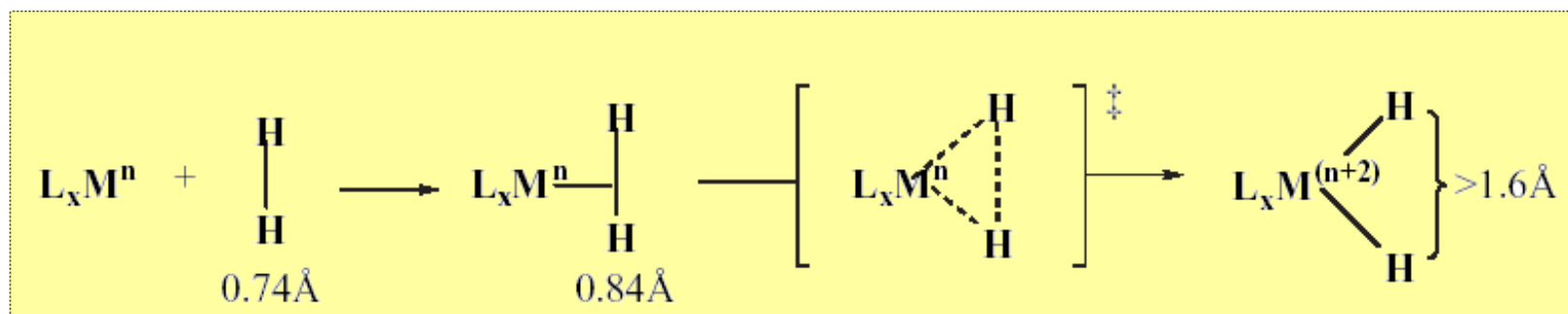
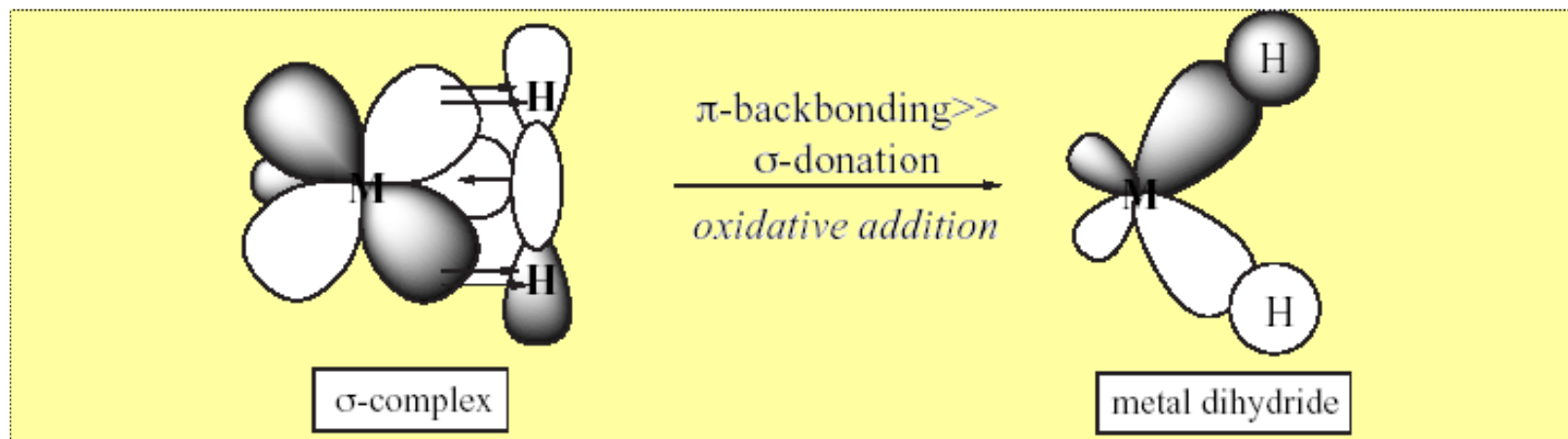
- (with separation of **A** & **B**) H_2 ; X_2 (X = halogen) ; HX ; RX ; ArX
- (without separation of **A** & **B**) O_2

Mechanisms of Oxidative Addition

i) Concerted

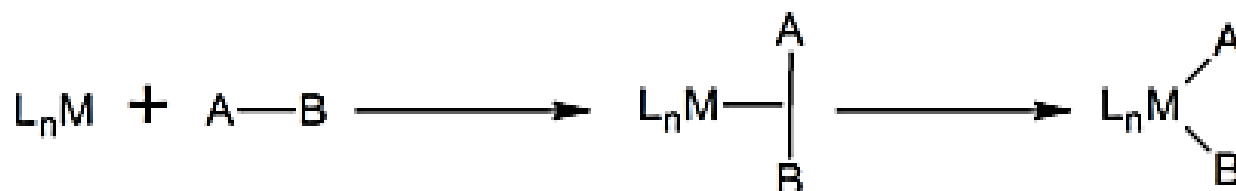


Oxidative Addition of H_2

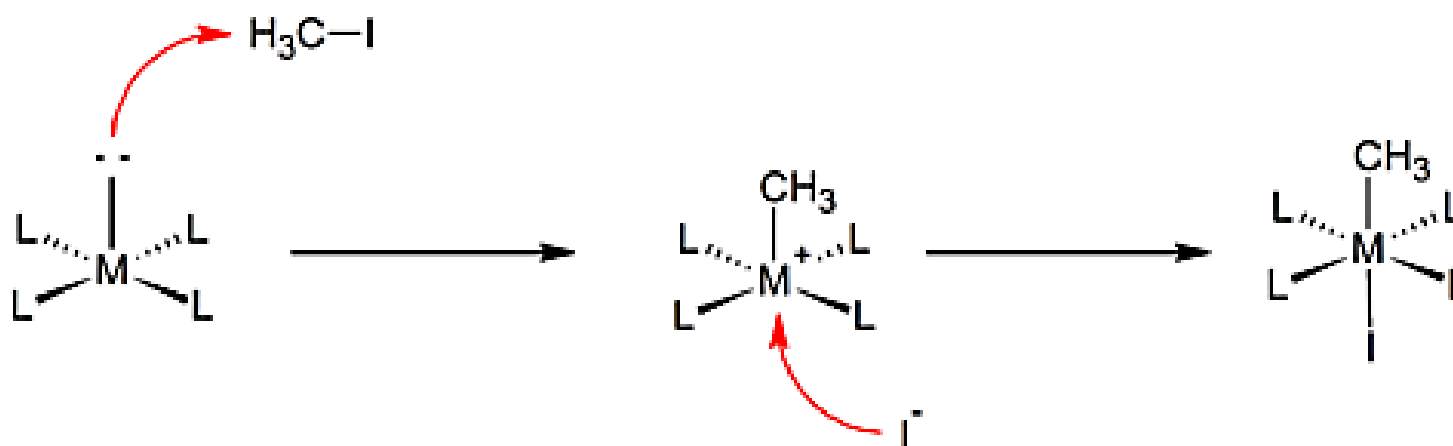


Mechanisms of Oxidative Addition (ctd)

i) Concerted



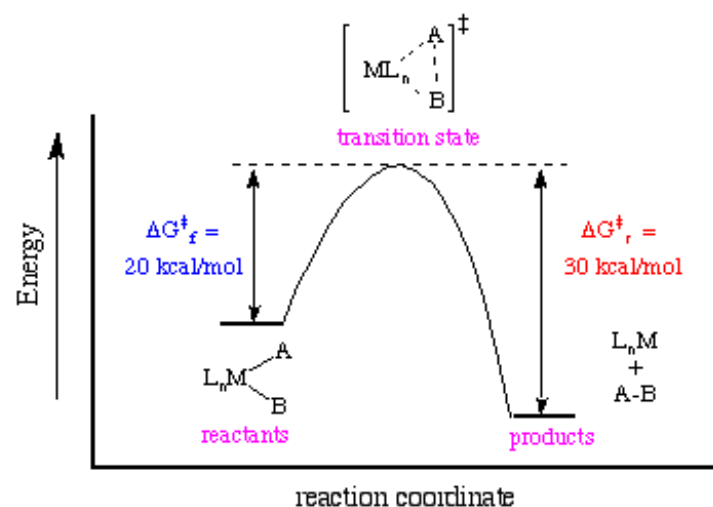
ii) Stepwise (S_N2 -Type) [typically for polar A-B]



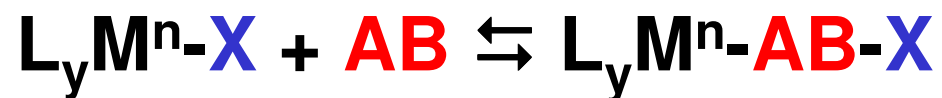
Principle of Microscopic Reversibility

- If a certain series of steps constitutes the mechanism of a forward reaction, the mechanism of the reverse reaction (under the same conditions) is given by the same steps traversed backwards – *or ...*
- The sequence of transition states and reactive intermediates in the mechanism of a reversible reaction must be the same, but in reverse order, for the backward reaction as for the forward reaction – *or ...*
- If the mechanism in one direction is known, then the mechanism in the opposite direction is known – *or ...*
- The lowest-energy pathway in the forward direction will be the lowest-energy pathway in the reverse direction

...as Applied to Oxidative Addition / Reductive Elimination



Insertion / Elimination

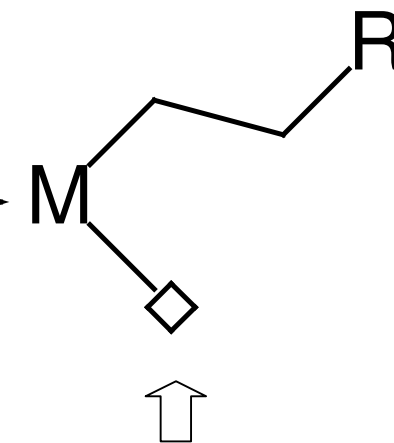
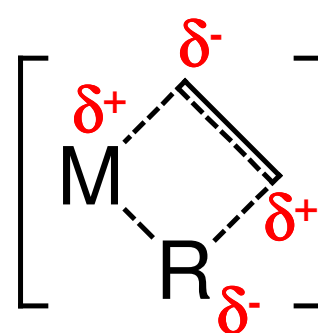
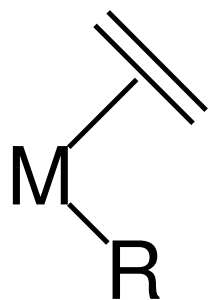
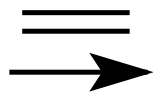
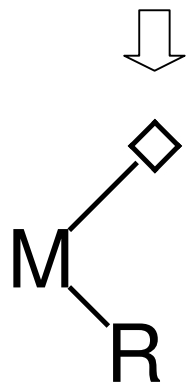


Important Examples:

AB	M-X	M-AB-X
$C \equiv O$	M-OH	M-(C=O)OH
	M-R	M-(C=O)R
	M-NR(R')	M-(C=O)NR(R')
$CH_2=CH_2$	M-H	M-CH ₂ -CH ₂ -H
	M-R	M-CH ₂ -CH ₂ -R
$CH_2=CHR$	M-H	M-CH ₂ -CHR-H
		M-CHR-CH ₂ -H
	M-R'	M-CH ₂ -CHR-R'
		M-CHR-CH ₂ -R'

Insertion of Ethene into M-R

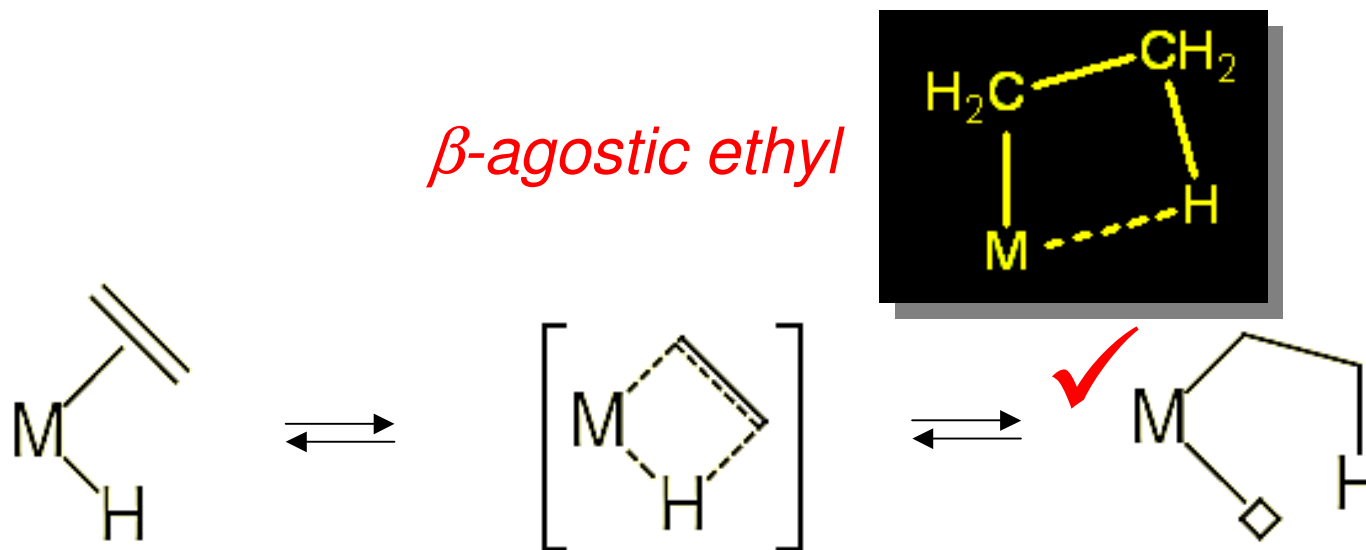
One vacant coordination site at M is needed



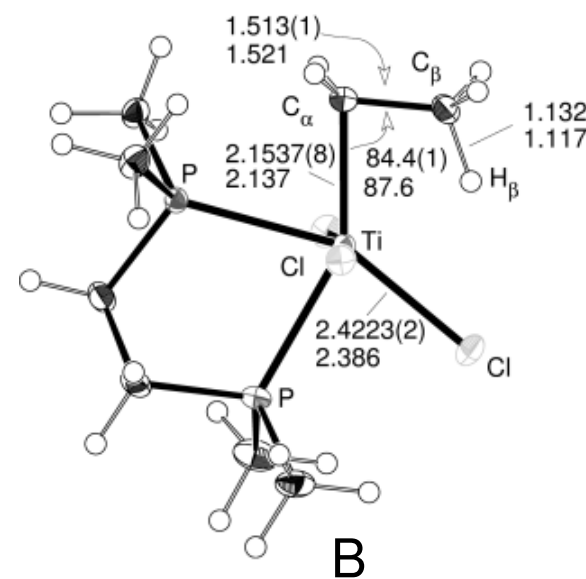
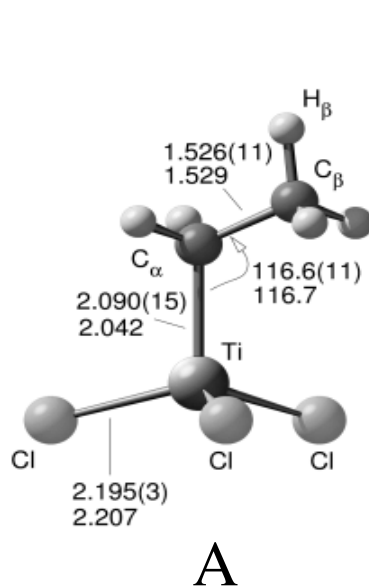
The C=C double bond is activated due to polarization and back-donation from M

The insertion is 'migratory' due to the principle of the least nuclear motion

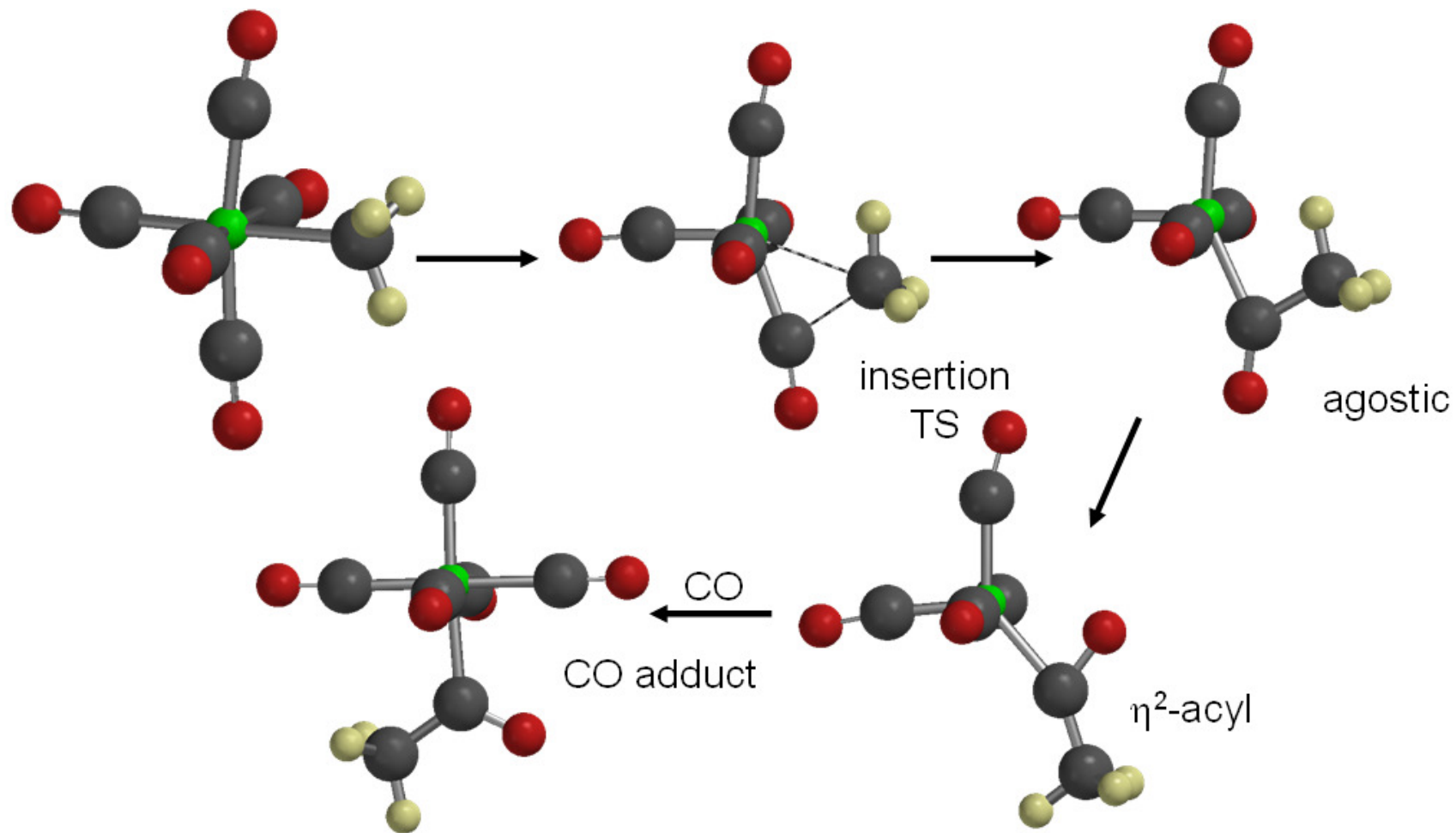
Insertion of Ethene into M-H



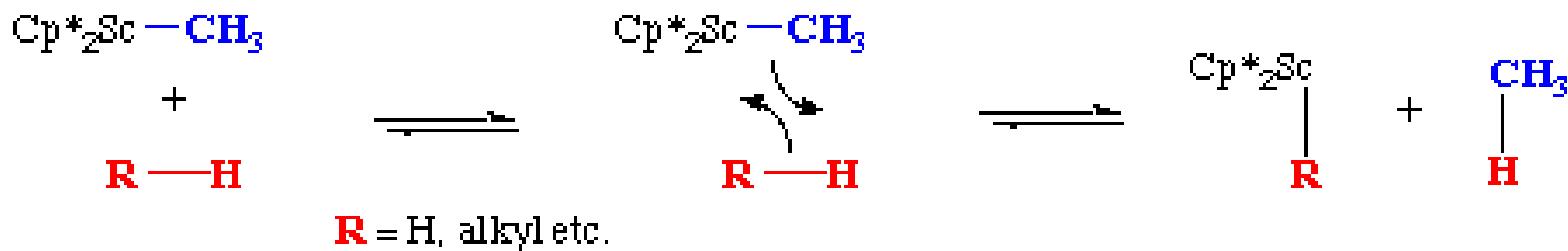
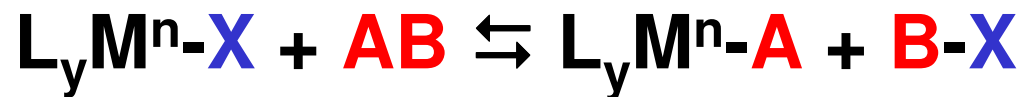
Crystallographic evidence of the β -agostic interaction



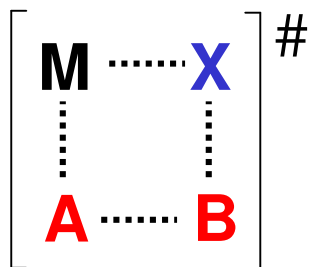
Insertion of CO into M-CH₃



Sigma-Bond Metathesis



Mechanism :



VS

