Organometallic Chemistry and Homogeneous Catalysis

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Lecture N7

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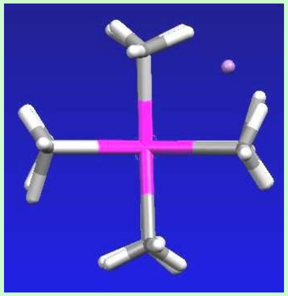
Types of reactions in the coordination sphere of TMC

6 main types of reactions with TMC:

1. Ligand substitutions
2. Oxidative addition
3. Reductive elimination
4. Insertion
5. Elimination
6. Nucleophilic attack on ligand



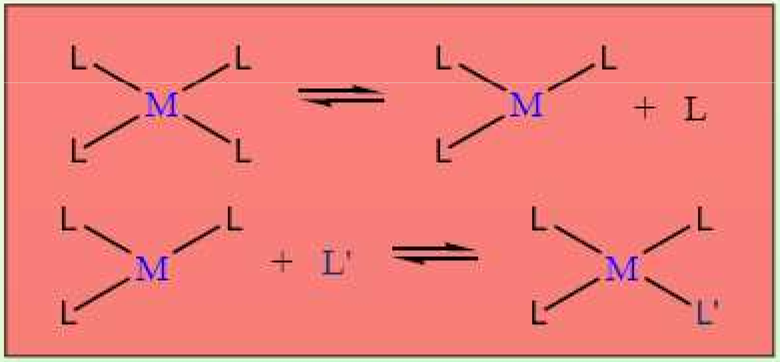
1. Ligand substitutions

A substitution reaction is one in which an existing ligand on a metal center is replaced by another ligand:

$$ML_n + L' \longrightarrow ML_{n-1}L' + L$$

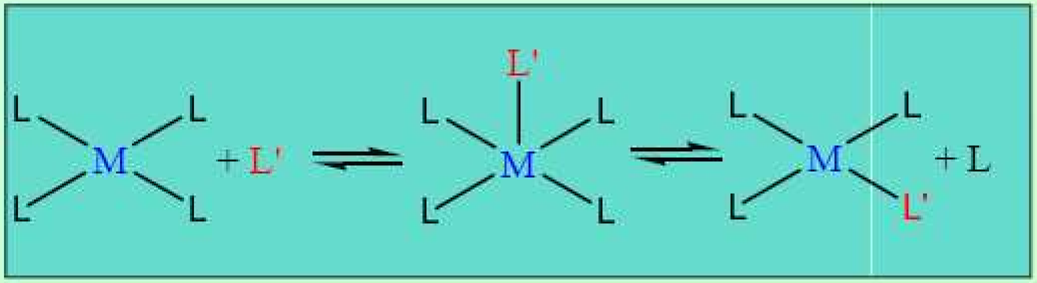
Organic chemistry looks at substitution reactions in terms of S_N1 and S_N2 mechanisms. In organometallic chemistry we have 3 possible mechanisms:

Dissociative (D)



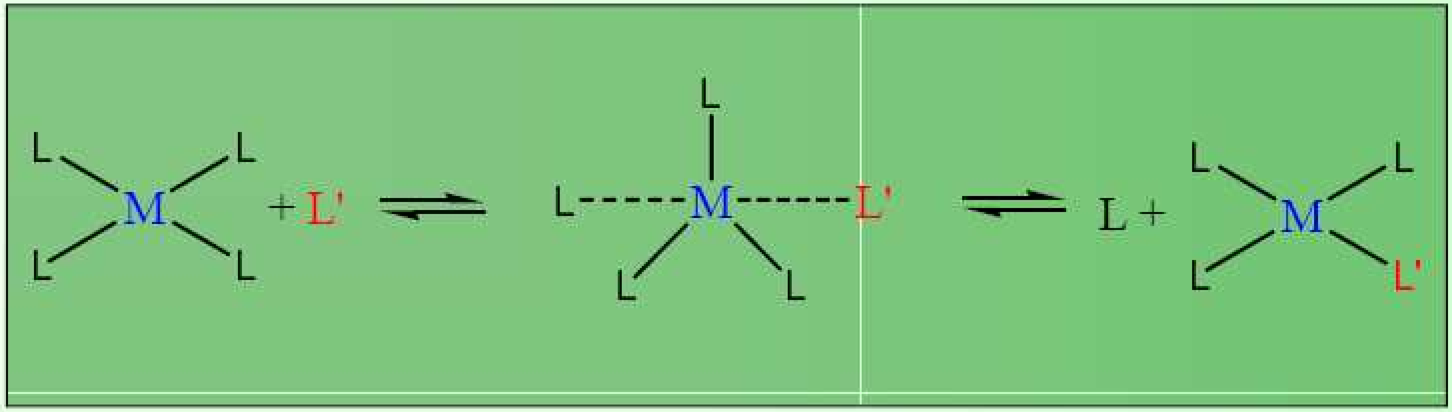
Dissociative – get intermediate of reduced coordination number, which lives long enough to equilibrate with its surroundings before entry of X. Analogous to S_N1.

Associative (A)

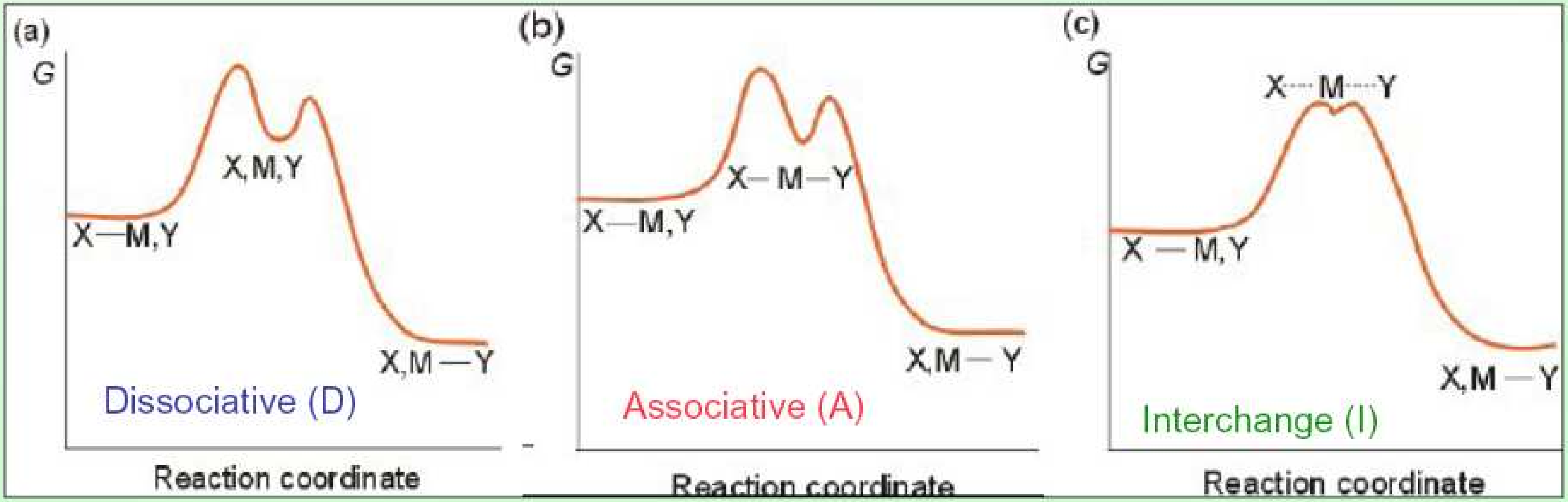


Associative – get intermediate of increased coordination number, which lives long enough to equilibrate with its surroundings before loss of L. No analogue in organic chemistry.

Interchange (I)



Interchange – both the entering and leaving groups are simultaneously bound to the metal ion. No discrete intermediate. Analogous to S_N2.



Reaction Mechanisms

- Rate determining step
  - Associative depends strongly on incoming group
    - Variation of rate on different ligand groups
      - Formation of halides complexes with different rates for different halides
  - Dissociative is independent of ligand group
    - Replacement of water by ligand
      - Ammonia and pyridine found to have similar rates
      - Rate dependent on bond breaking of ligand on complex
  - Interchange mechanism
    - Associatively active if rate is dependent on new bond formation
    - Dissociatively active if rate dependent on bond breaking in complex

Rate Determining Step

- also denoted associative or dissociative
- associative (lowercase a)
  - the rate depends heavily on the entering group

$[PtCl(dien)]^+ + I^- \longrightarrow [PtI(dien)]^+ + Cl^-$

$[PtCl(dien)]^+ + Br^- \longrightarrow [PtBr(dien)]^+ + Cl^-$

- dissociative (lowercase d)
  - the rate is independent of the entering group

$[Ni(OH_2)_6]^{2+} + NH_3 \longrightarrow [Ni(OH_2)_5(NH_3)]^{2+} + H_2O$

What mechanism you can suppose for the reaction:

$$\mathrm{Ni(CO)_4} + {}^{13}\mathrm{CO} \rightleftharpoons \mathrm{Ni(CO)_3({}^{13}CO)} + \mathrm{CO}$$

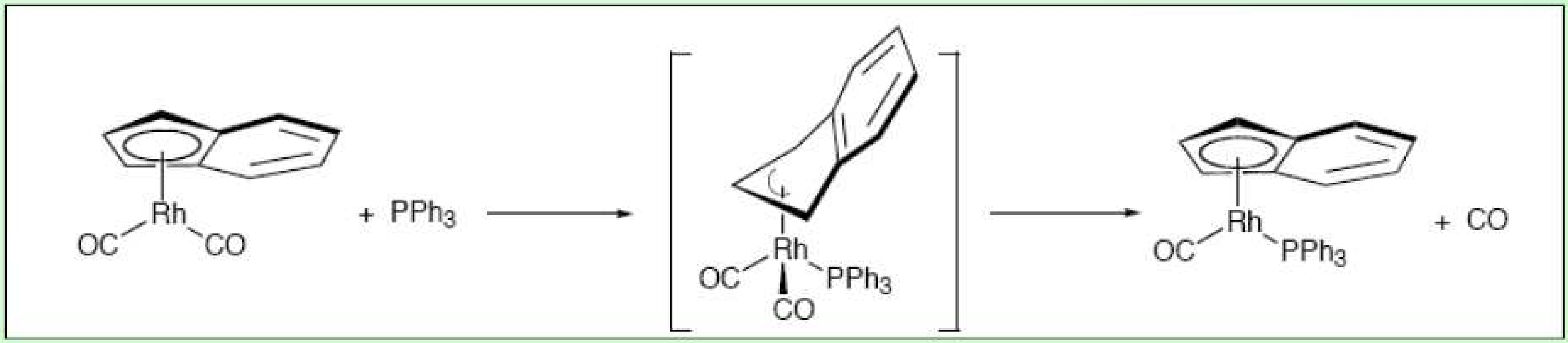
$\mathrm{Ni(CO)_4}$ – 18e$^-$ complex (saturated), no free d-orbitals for the coordination, so only dissociative mechanism is possible:

$$\mathrm{Ni(CO)_4} \rightleftharpoons \mathrm{Ni(CO)_3} + \mathrm{CO}$$

$$\mathrm{Ni(CO)_3} + {}^{13}\mathrm{CO} \rightleftharpoons \mathrm{Ni(CO)_3({}^{13}CO)}$$

Do 18 electron complexes undergo ligand substitution by an associative mechanism?

Yes, but usually only when a poly-hapto ligand can adopt a lower hapticity coordination. This is necessary to avoid a 20 e$^-$ intermediate.



Factors influencing ease of dissociation:

- 1^e row < 2^e row > 3^e row
- d^8-ML_5 > d^{10}-ML_4 > d^6-ML_6
- stable ligands (CO, olefins, Cl^-) dissociate easily (as opposed to e.g. CH_3, Cp).

The completeness of substitution depends on:

- formation bond strength
- excess of ligand (usually 2 - 10)

The rate of substitution depends on:

- breaking bond strength

For O-donor ligand the strength of M-L bond:

Increases in a <u>period</u> from the left to the right,
Decreases in a <u>group</u> from the top to the bottom

For P- and C-donor ligand the strength of M-L bond:

Increases in a <u>period</u> from the left to the right,
Increases in a <u>group</u> from the top to the bottom

Factors influence association and dissociation of ligands

Steric Factors

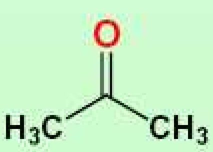
Bulky ligands occupy more space around a metal center and can block incoming ligands trying to access vacant coordination sites on a metal

$$Ni(PR_3)_4 \underset{25^{o}C}{\overset{K_D}{\rightleftharpoons}} Ni(PR_3)_3 + PR_3$$

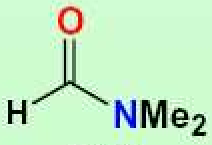
Ligand:	$P(OEt)_3$	P(O-*p*-tolyl)$_3$	P(O-*i*-Pr)$_3$	P(O-*o*-tolyl)$_3$	PPh_3
Cone angle:	109°	128°	130°	141°	145°
K_D :	$< 10^{-10}$	6×10^{-10}	2.7×10^{-5}	4×10^{-2}	> 1000

Solvent Effects

The coordinating ability of the solvent can often affect reactions. The presence of lone pairs and electron-rich donor atoms on the solvent usually makes it a better ligand:

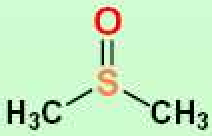


acetone



DMF

(dimethylformamide)



DMSO

(dimethylsulfoxide)

THF

(tetrahydrofuran)

$H_3C—OH$

methanol

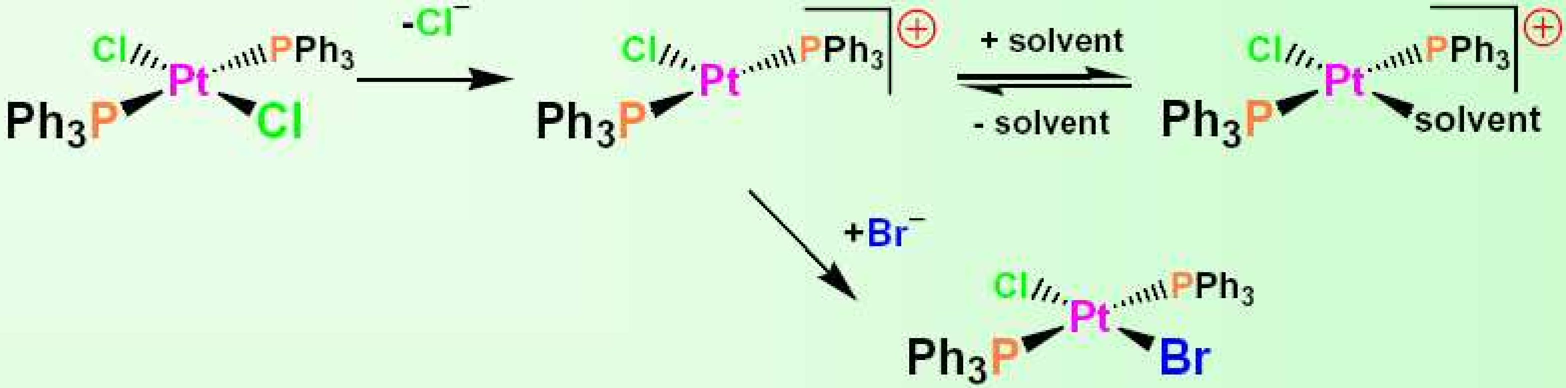
water

(rarely used)

$:N \equiv C—CH_3$

acetonitrile

The solvent is usually weakly coordinated and readily dissociates to constantly produce coordination vacancy:

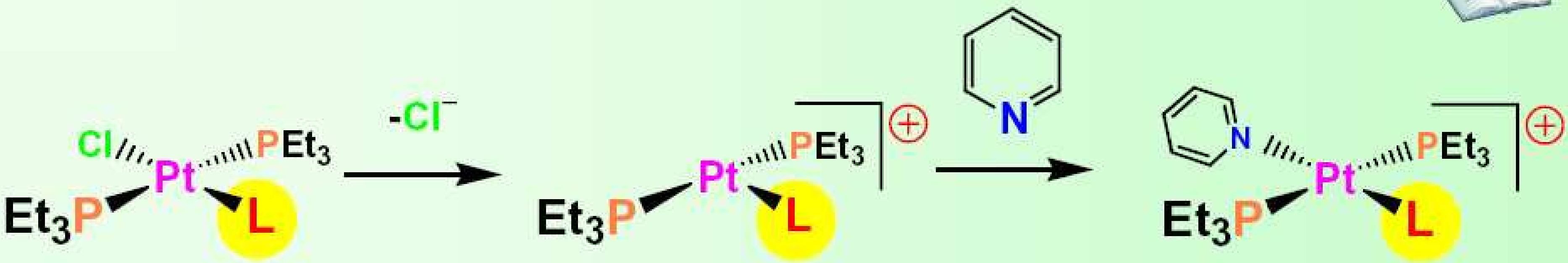


Sometimes it is important to proceed reaction in non-coordinative solvent. In such a case hexane or benzene is used; when more polar reaction media should be taken – CH_2Cl_2 or chlorobenzene could be used.

Trans Effect

The *trans effect* concerns the electronic effect of one ligand on another ligand when they are *trans* to one another. The classical *trans* effect involves two s-donating ligands *trans* to one another. The stronger s-donor ligand preferentially weakens the bond of the weaker s-donor ligand *trans* to it, making it easier to dissociate and do a ligand substitution reaction.

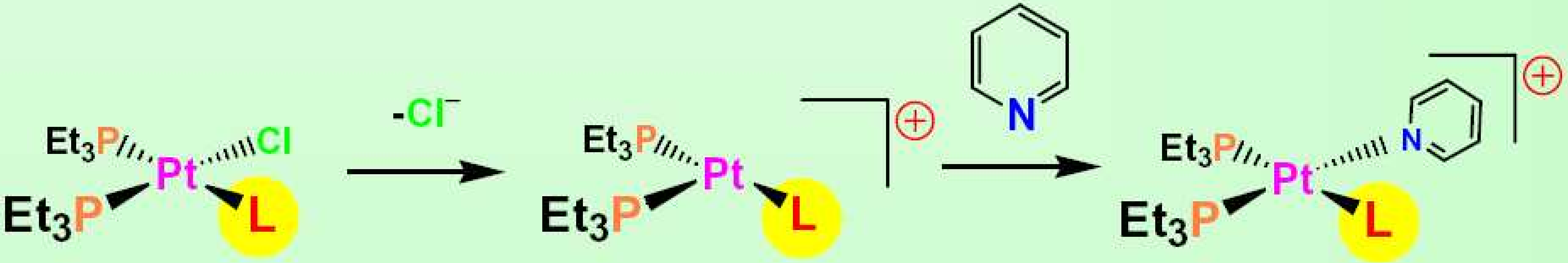
Trans-effect:



Relative rate of substitution based on *trans* ligand L :

$Cl^{-} = 1$, $Ph^{-} = 100$, $CH_3^{-} = 10^3$, $H^{-} = 10^4$

Cis-effect:



Relative rate of substitution based on *cis* ligand L :

$Cl^{-} = 1$, $Ph^{-} = 2$, $CH_3^{-} = 4$, $H^{-} = 4$

2. Oxidative addition

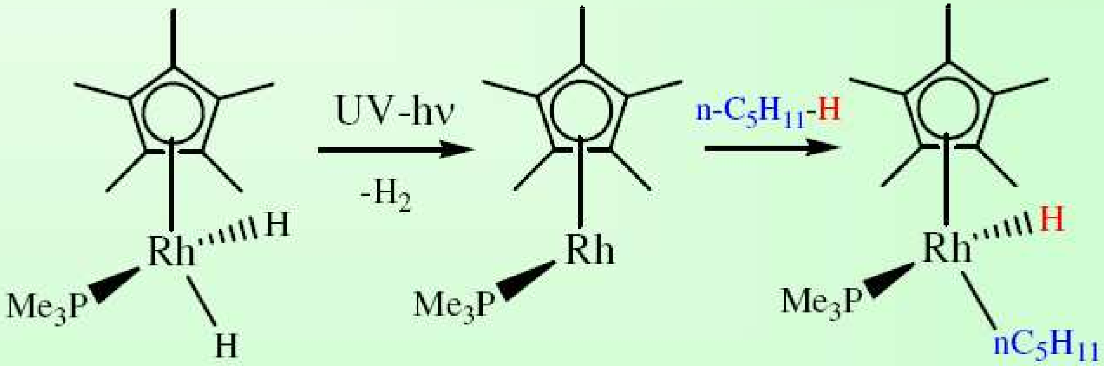
Main features of the oxidative addition:

1) Increasing of the oxidative state of TM
2) Increasing of the coordination number of TM (increasing of the number of ligands in the coordination sphere of TM)

$M^{n} \rightarrow M^{n+2}$:

$$\boxed{ML_n + X\text{-}Y \rightarrow X\text{-}ML_n\text{-}Y}$$

$$Mg + C_2H_5Cl \longrightarrow C_2H_5\text{-}Mg\text{-}Cl$$

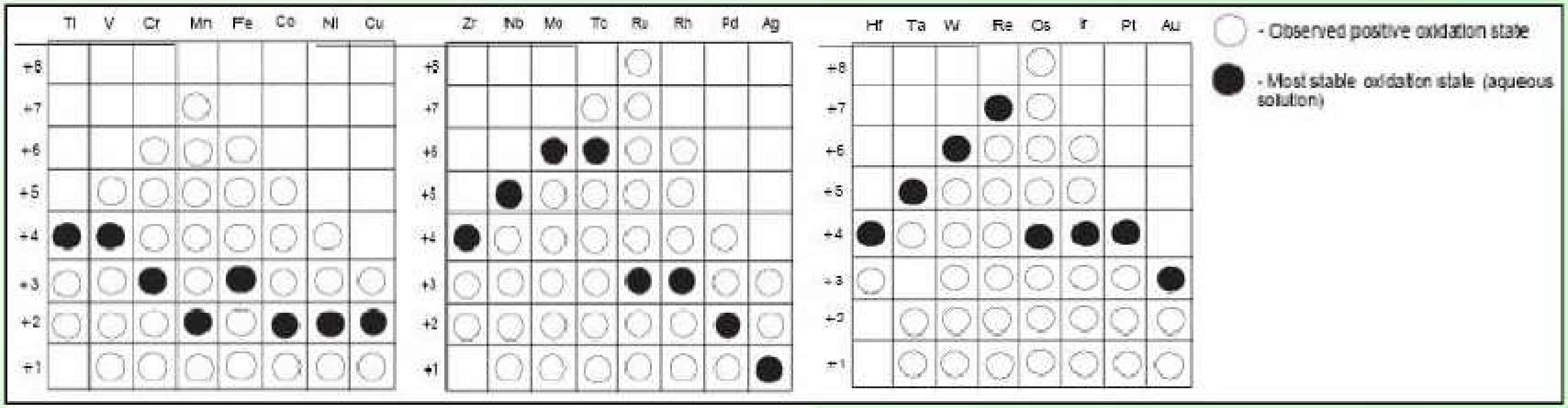


$M^{n} \rightarrow M^{n+1}$:

$$\boxed{2ML_n + X\text{-}Y \rightarrow ML_n\text{-}X + ML_n\text{-}Y}$$

$$(CO)_5Mn\text{-}Mn(CO)_5 + Br\text{-}Br \longrightarrow 2\ Br\text{-}Mn(CO)_5$$

Metal Complex: electron rich metals in low oxidation states, with strong donor ligands and a site of coordinative unsaturation.



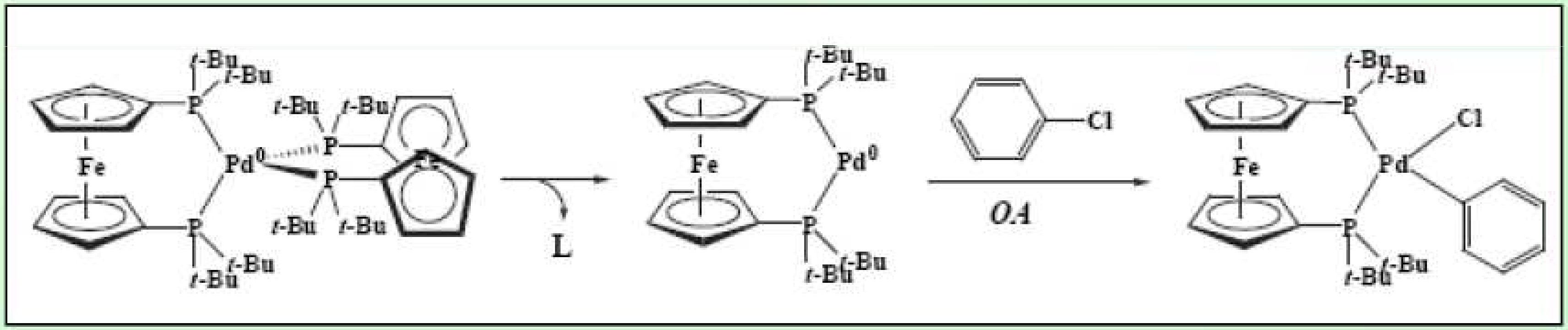
	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
+8								
+7				○				
+6			○	○	○			
+5		○	○	○	○	○		
+4	●	●	○	○	○	○	○	
+3	○	○	●	○	●	○	○	○
+2	○	○	○	●	○	●	●	●
+1		○	○	○	○	○	○	○

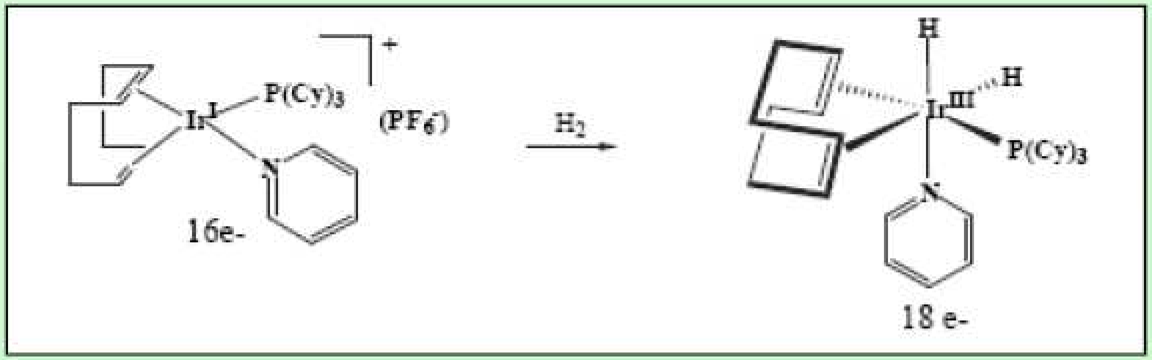
	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
+8					○			
+7				○	○			
+6			●	●	○	○		
+5		●	○	○	○	○		
+4	●	○	○	○	○	○	○	
+3	○	○	○	○	●	●	○	○
+2	○	○	○	○	○	○	●	○
+1		○	○	○	○	○	○	●

	Hf	Ta	W	Re	Os	Ir	Pt	Au
+8					○			
+7				●	○			
+6			●	○	○	○		
+5		●	○	○	○	○		
+4	●	○	○	○	●	●	●	
+3	○		○	○	○	○	○	●
+2		○	○	○	○	○	○	○
+1		○	○	○	○	○	○	○

○ - Observed positive oxidation state

● - Most stable oxidation state (aqueous solution)





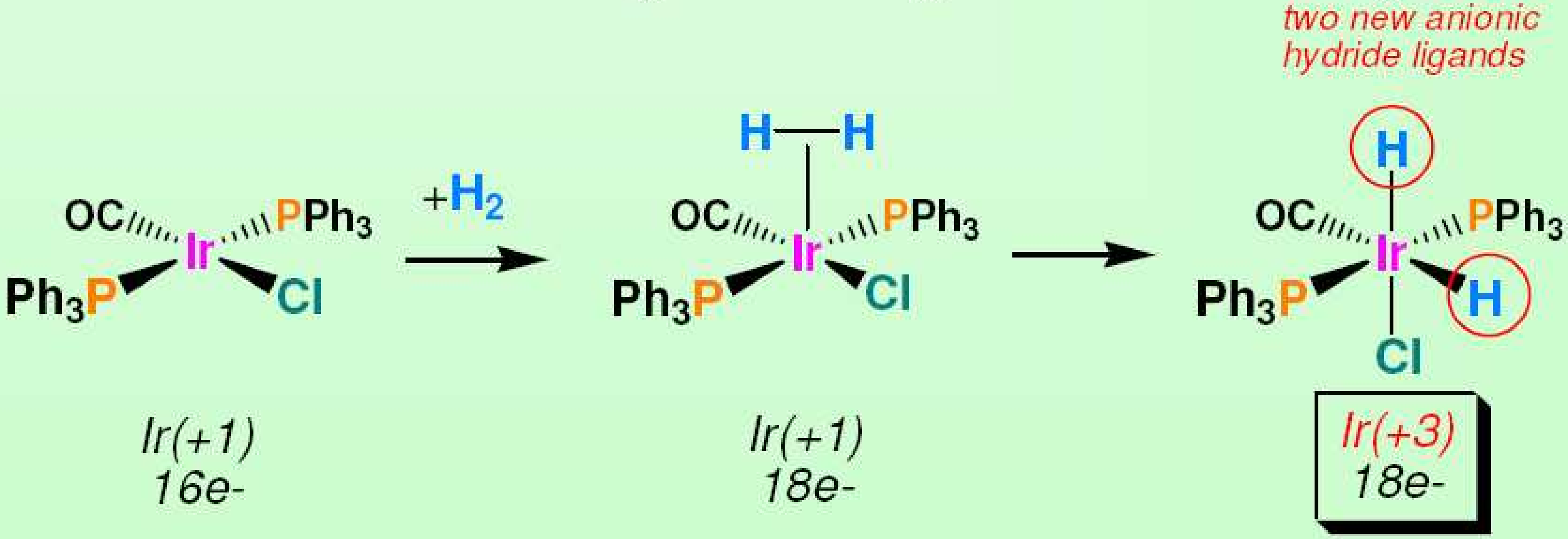
Requirements for TMC to participate in the oxidative addition:

1) Metal complex should be unsaturated (should have unoccupied orbital)

2) Atom of TM should have at least 1 pair of electrons. Disposition of both unoccupied orbital and pair of electrons should be favorable for the formation of new bonds

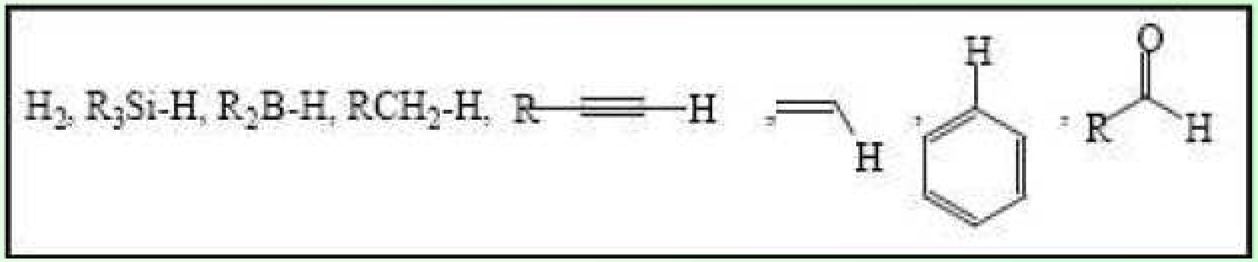
3) Low oxidation state (0, +1, +2) of TM favors oxidative addition

The transferring of the two electrons from the metal to the incoming ligand breaks a bond in that ligand forming two new anionic ligands:



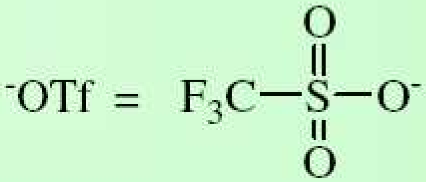
Substrates: two groups segregated into non-polar and polar. Currently, the most facile way to form C-M σ-bonds is with polar substrates (*e.g.* alkyl, aryl, and vinyl halides).

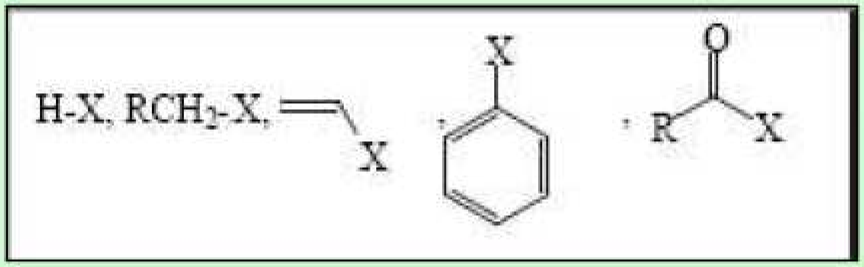
Non-polar substrates: R-H



Other non-polar substrates: S-S bonds, C-C bonds

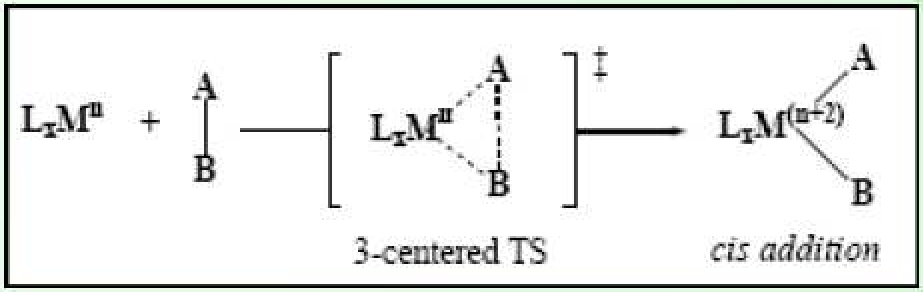
Polar substrates: R-X where X = I, Br, Cl, OTf


$^{-}OTf = F_3C{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O^{-}$

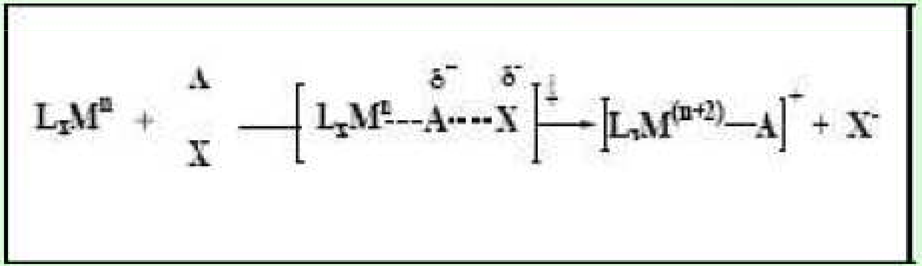


General OA Mechanisms:

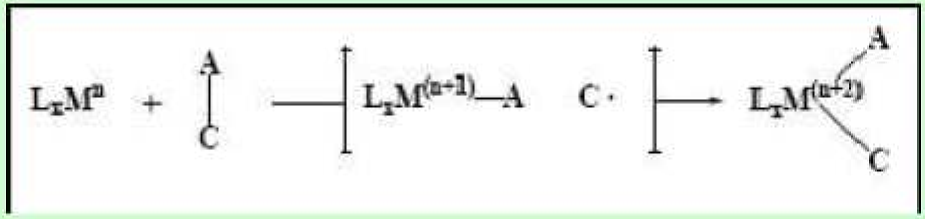
1. Concerted (generally for non-polar substrates)



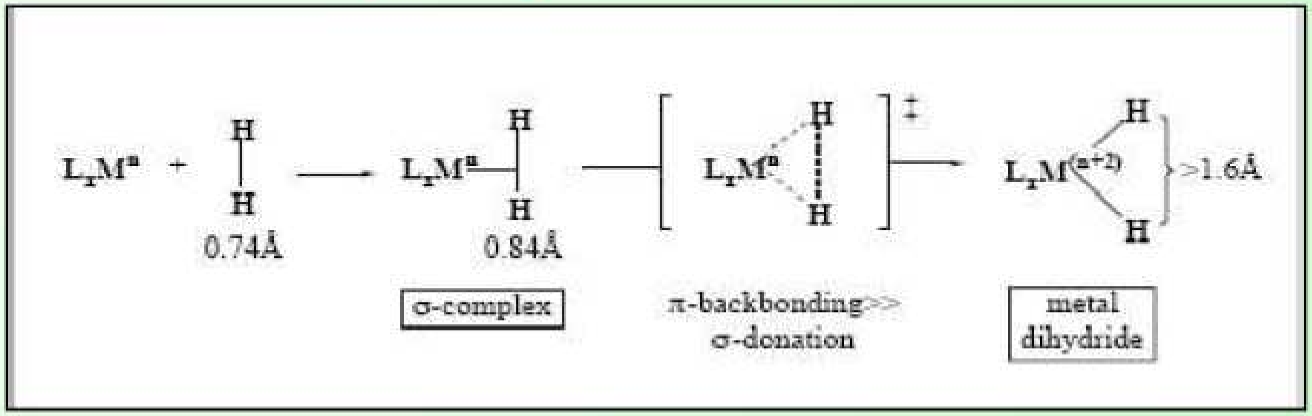
2. Nucleophilic displacement (generally for polar substrates)



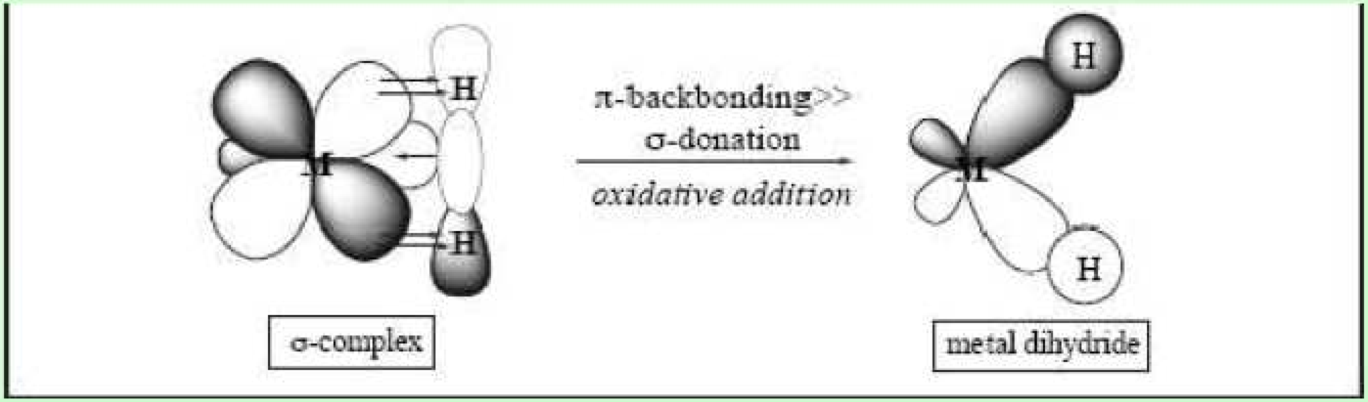
3. Radical (both non-polar and polar)



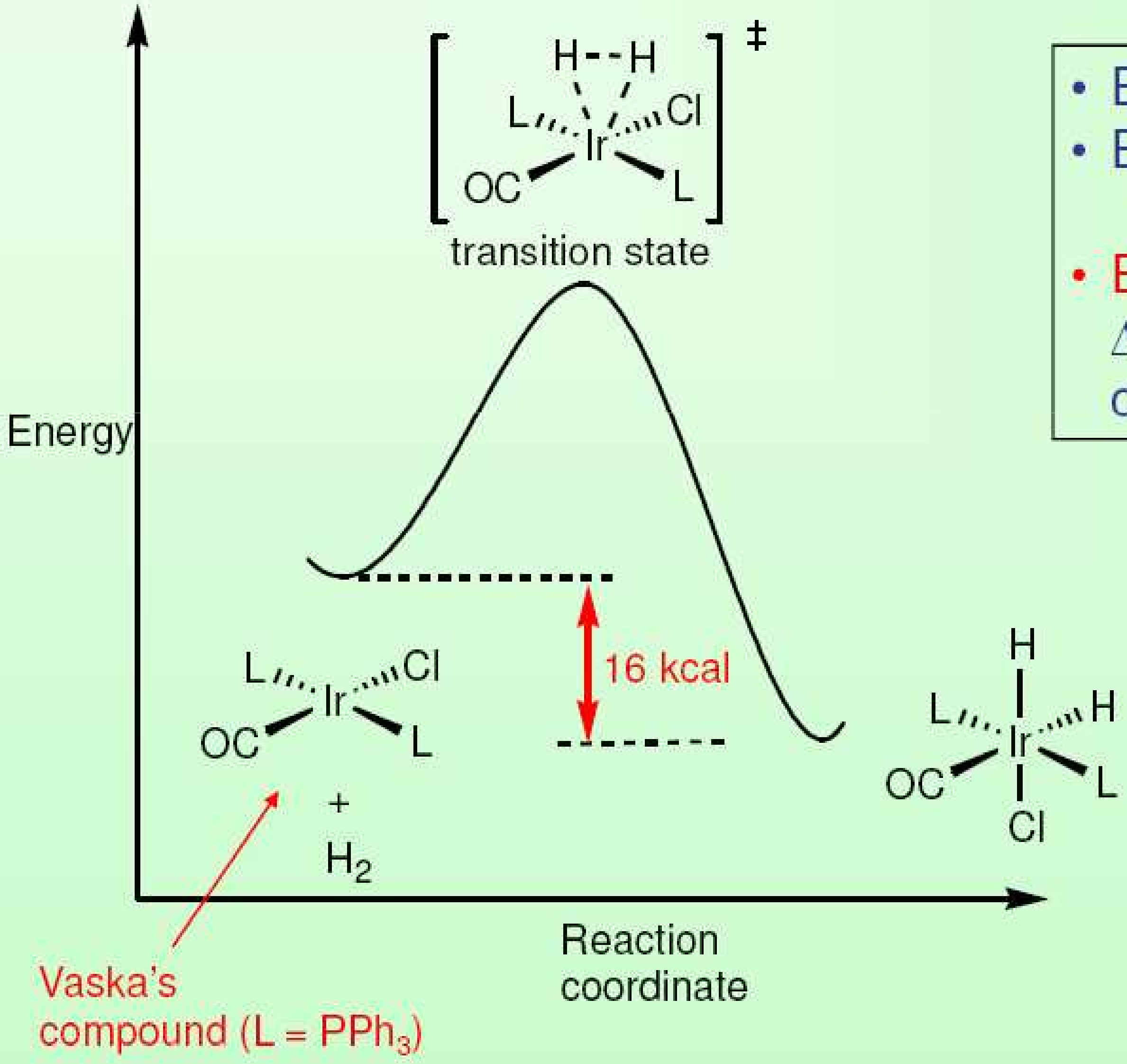
Concerted mechanism - usually through the σ-complex formation



σ-complex formation precedes an early (little σ-bond breaking), 3-centered transition state where strong π-backbonding results in oxidative addition of the bound substrate to the metal. The concerted mechanism is thought to operate primarily for non-polar substrates (*i.e.* H-H,C-H, Si-H, B-H) with electron rich, low valent metals. The spectroscopic identification of metal dihydrogen σ-complexes with H-H bond distances stretched between the non-bonding (0.74Å) and dihydride extremes (>1.6Å) provides strong support for this mechanism with H_2.

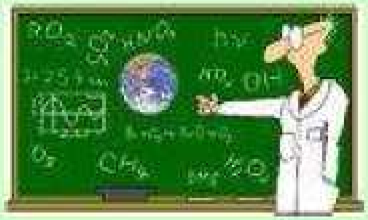


Three-centre OA; Vaska's compound

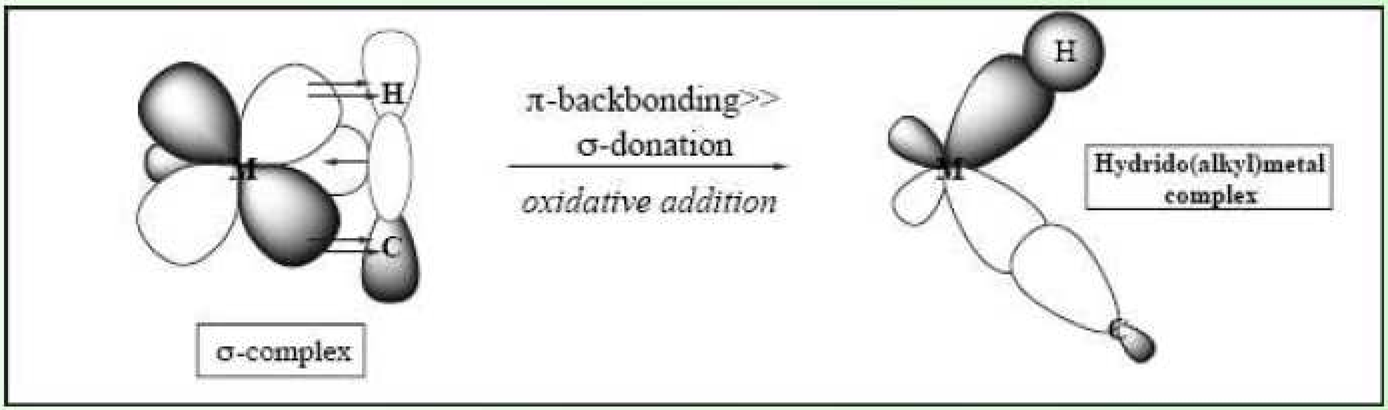


- E_{diss} of H_2 = 104 kcal
- E_{bde} of Ir-H = 60 kcal

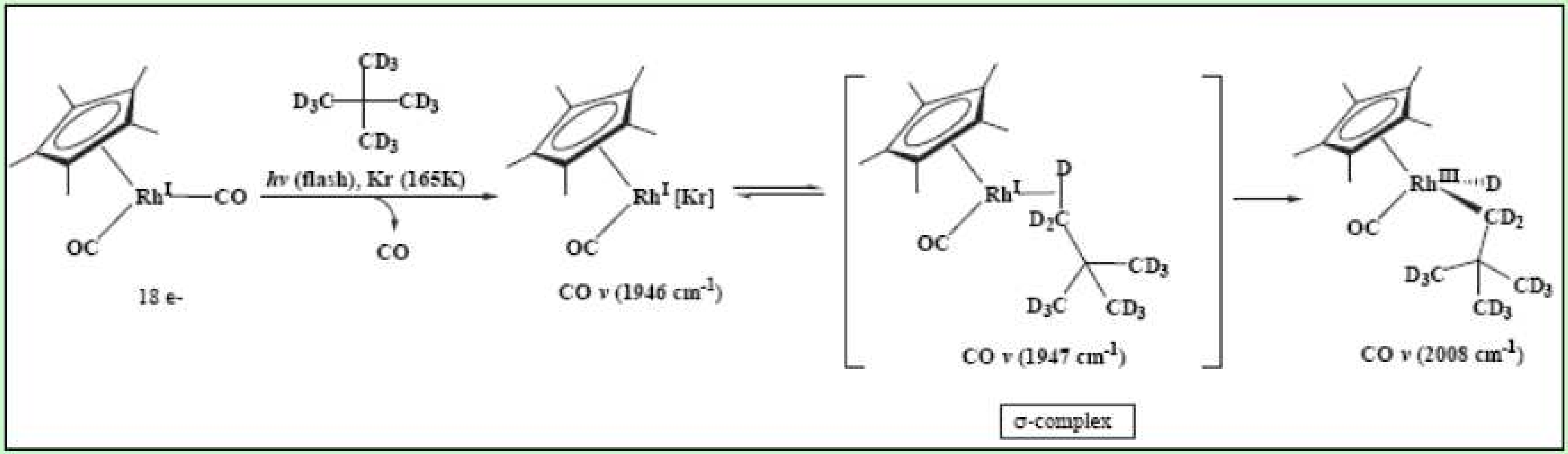
- Exothermic by 16 kcal, but ΔS is unfavorable, so ΔG often close to zero



sp^3 C-H OA via σ complex intermediates

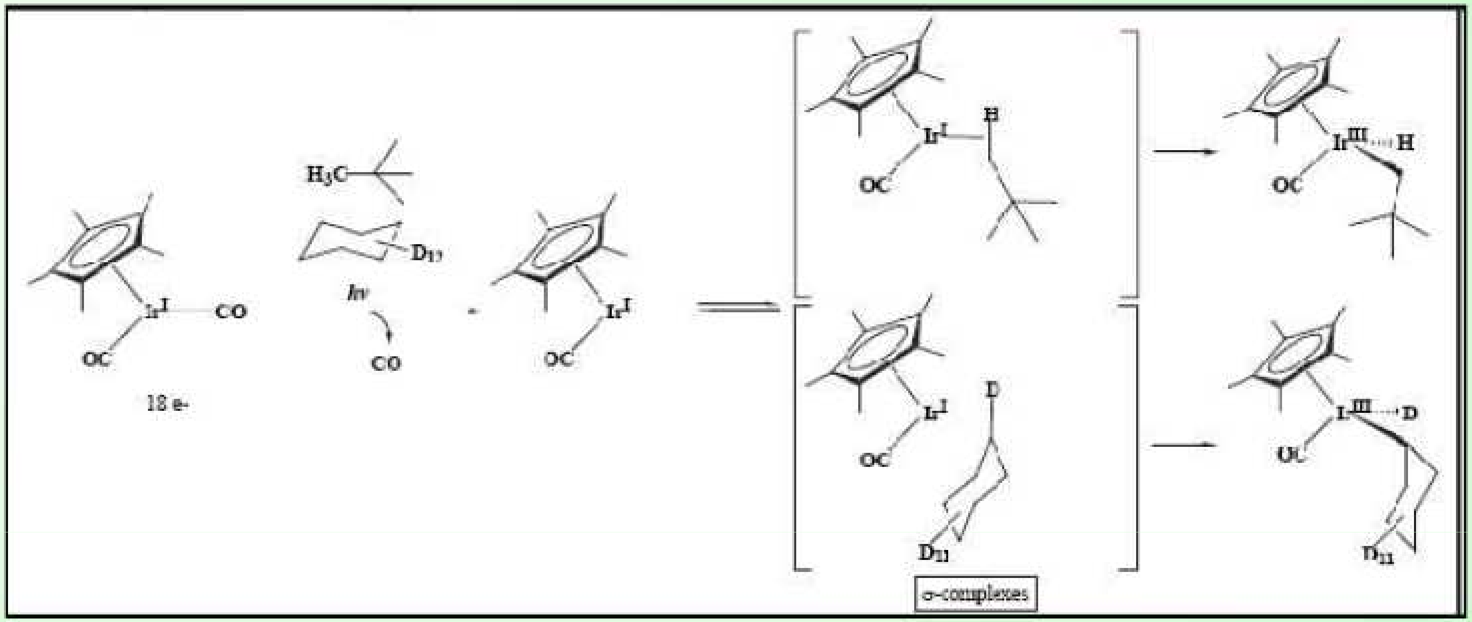


regioselectivity: sp^2 C-H > 1° sp^3 C-H > 2° sp^3 C-H >>> 3° sp^3 C-H. There is both a kinetic and thermodynamic preference to form the least sterically hindered C-M σ-bond. Kinetic preference: activation barrier to σ-complex formation is lower for less sterically hindered C-H bonds and bonds with more s character. Thermodynamic preference: stronger C-M bonds are formed

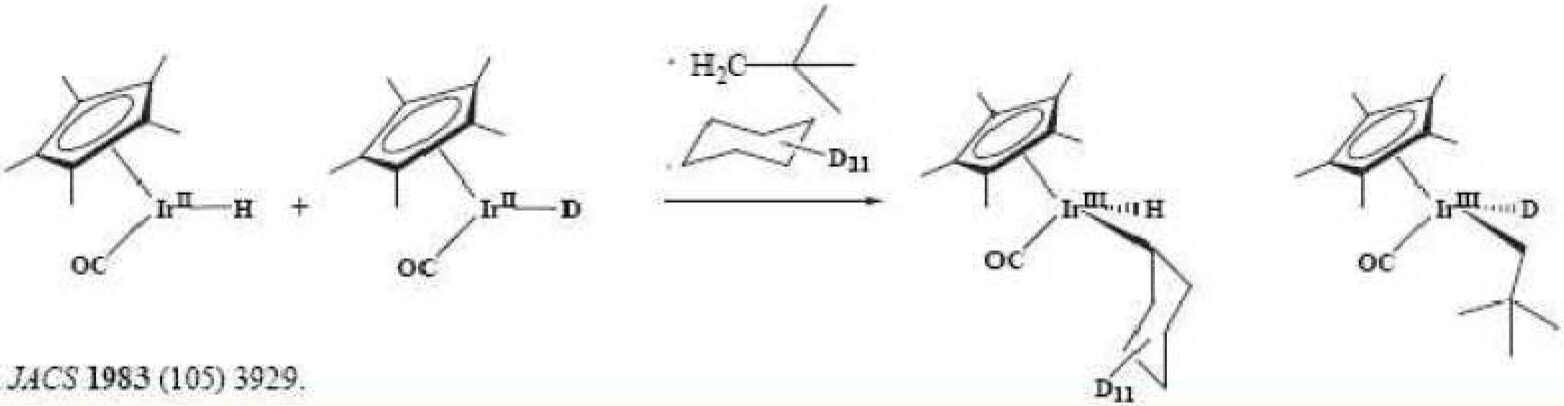


sp^3 C-H: concerted vs. radical

crossover experiment: evidence in support of a concerted mechanism:

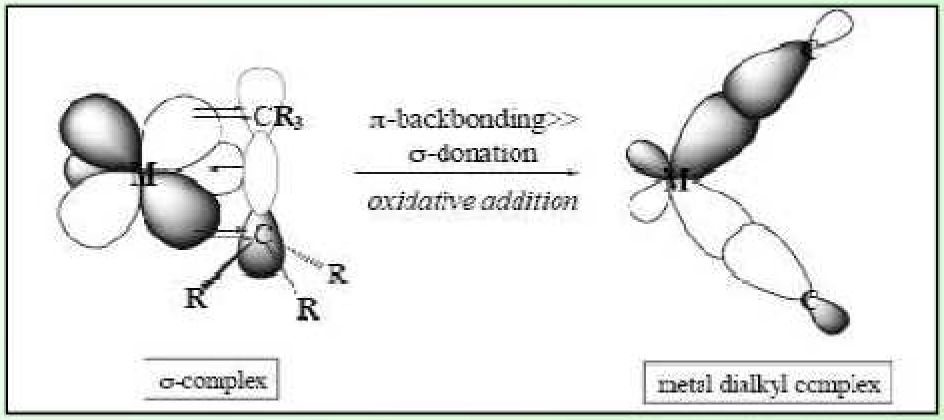


Less than 7% of the crossover products were observed by ^{1}H NMR. This may be indicative of a minor radical pathway.

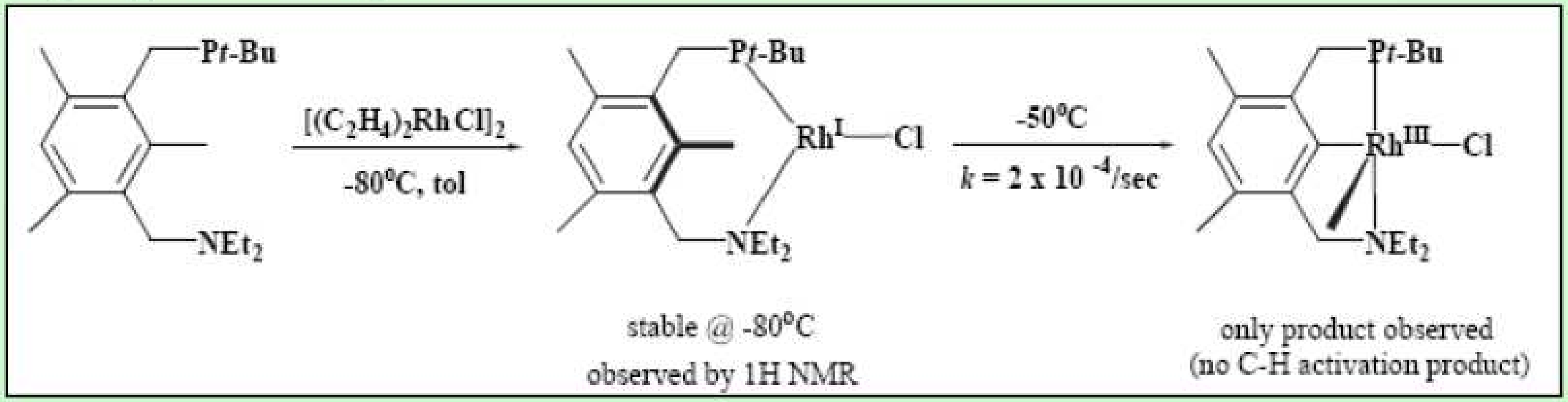


Bergman *JACS* **1983** (105) 3929.

OA: sp^3 C-sp^3 C



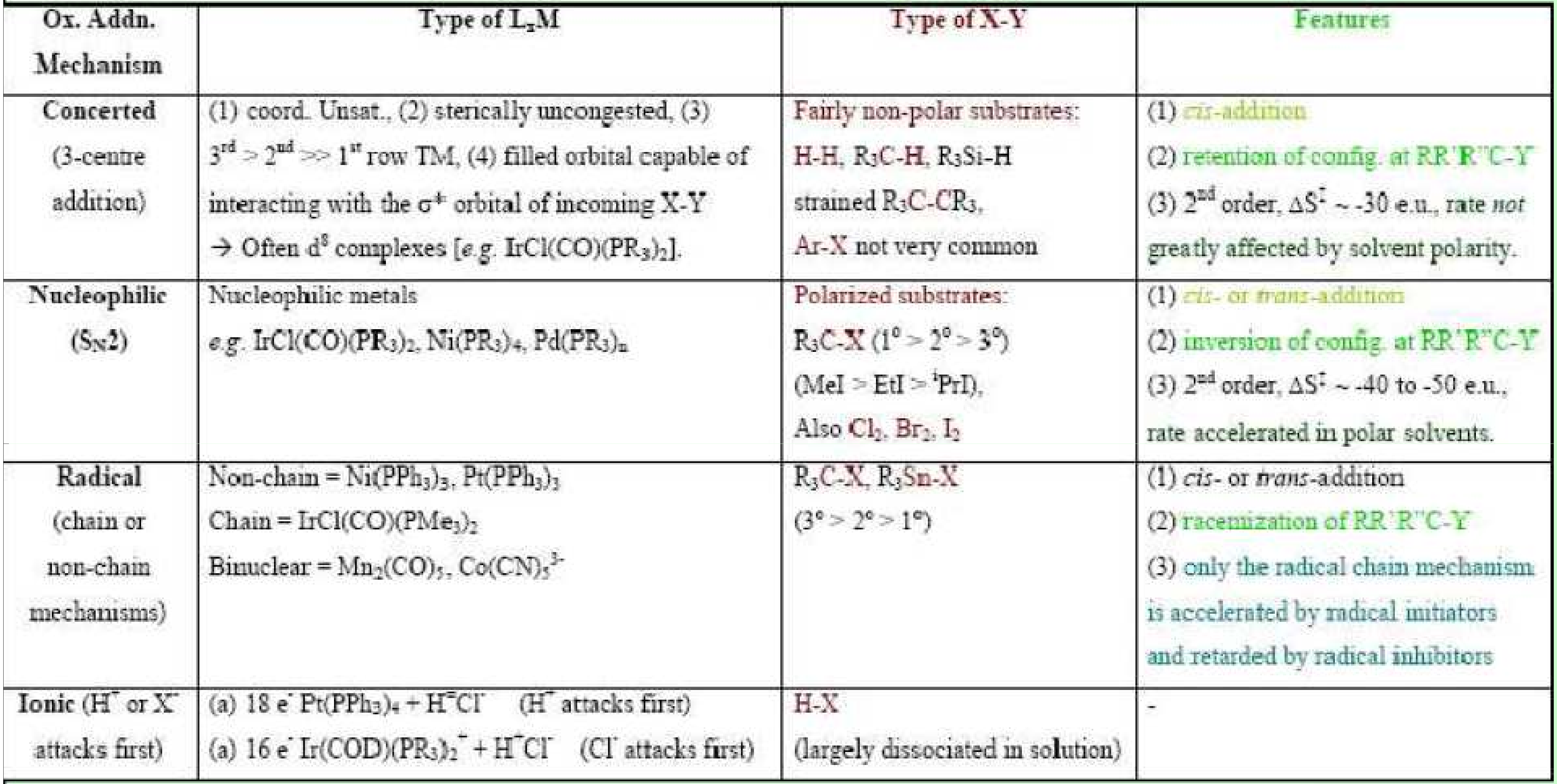
Even though bond dissociation energies of C-C bonds are lower than those of analogous C-H bonds (*e.g.* C_6H_5-CH_3:100 kcal/mol *vs.* C_6H_5-H: 110 kcal/mol), transition metal mediated OA's into C-C bonds are much more rare than those for analogous C-H bonds. Formation of the σ-complex is kinetically disfavored by steric repulsion between the metal complex and the carbon substituents and by the high directionality of the sp^3 C-sp^3 C bond that localizes the σ-bonding orbital deep between the carbon nuclei. Milstein and coworkers are able to overcome the kinetic barrier by approximating the C-C bond at the metal center.



stable @ -80°C
observed by 1H NMR

only product observed
(no C-H activation product)

MECHANISMS FOR OXIDATIVE ADDITION – AN OVERVIEW



Ox. Addn. Mechanism	Type of L_nM	Type of X-Y	Features
Concerted (3-centre addition)	(1) coord. Unsat., (2) sterically uncongested, (3) $3^{rd} > 2^{nd} >> 1^{st}$ row TM, (4) filled orbital capable of interacting with the σ^* orbital of incoming X-Y → Often d^8 complexes [*e.g.* $IrCl(CO)(PR_3)_2$].	Fairly non-polar substrates: H-H, R_3C-H, R_3Si-H strained R_3C-CR_3, Ar-X not very common	(1) *cis*-addition (2) retention of config. at RR'R''C-Y (3) 2^{nd} order, $\Delta S^{\ddagger}$ ~ -30 e.u., rate *not* greatly affected by solvent polarity.
Nucleophilic (S_N2)	Nucleophilic metals *e.g.* $IrCl(CO)(PR_3)_2$, $Ni(PR_3)_4$, $Pd(PR_3)_n$	Polarized substrates: R_3C-X ($1° > 2° > 3°$) (MeI > EtI > ^iPrI), Also Cl_2, Br_2, I_2	(1) *cis*- or *trans*-addition (2) inversion of config. at RR'R''C-Y (3) 2^{nd} order, $\Delta S^{\ddagger}$ ~ -40 to -50 e.u., rate accelerated in polar solvents.
Radical (chain or non-chain mechanisms)	Non-chain = $Ni(PPh_3)_3$, $Pt(PPh_3)_3$ Chain = $IrCl(CO)(PMe_3)_2$ Binuclear = $Mn_2(CO)_5$, $Co(CN)_5^{3-}$	R_3C-X, R_3Sn-X ($3° > 2° > 1°$)	(1) *cis*- or *trans*-addition (2) racemization of RR'R''C-Y (3) only the radical chain mechanism is accelerated by radical initiators and retarded by radical inhibitors
Ionic (H^+ or X^- attacks first)	(a) 18 e^- $Pt(PPh_3)_4$ + H^+Cl^- (H^+ attacks first) (a) 16 e^- $Ir(COD)(PR_3)_2^+$ + H^+Cl^- (Cl^- attacks first)	H-X (largely dissociated in solution)	-

In general : Non polar substrates (e.g. H-H, C-H, Si-H) → Concerted
Halogens (Cl_2, Br_2, I_2) → Nucleophilic
Alkyl halides → Nucleophilic (S_N2) or Radical
Acids (HCl, HBr, HI) → Ionic