E   Organometallic Rections 1: Reactions at the Metal

Three major classes of reactions:

1 Ligand Substitution
- associative (*cf.* S_N2)
- dissociative (*cf.* S_N1)
- interchange (not dealt with in this course)

2 Oxidative-addition
- concerted
- step-wise (nucleophilic)
- radical

3 Reductive-elimination
- concerted cis-elimination
- binuclear elimination

1 Ligand Substitution (especially in square planar complexes)

Ligand directing effects: some ligands preferentially direct
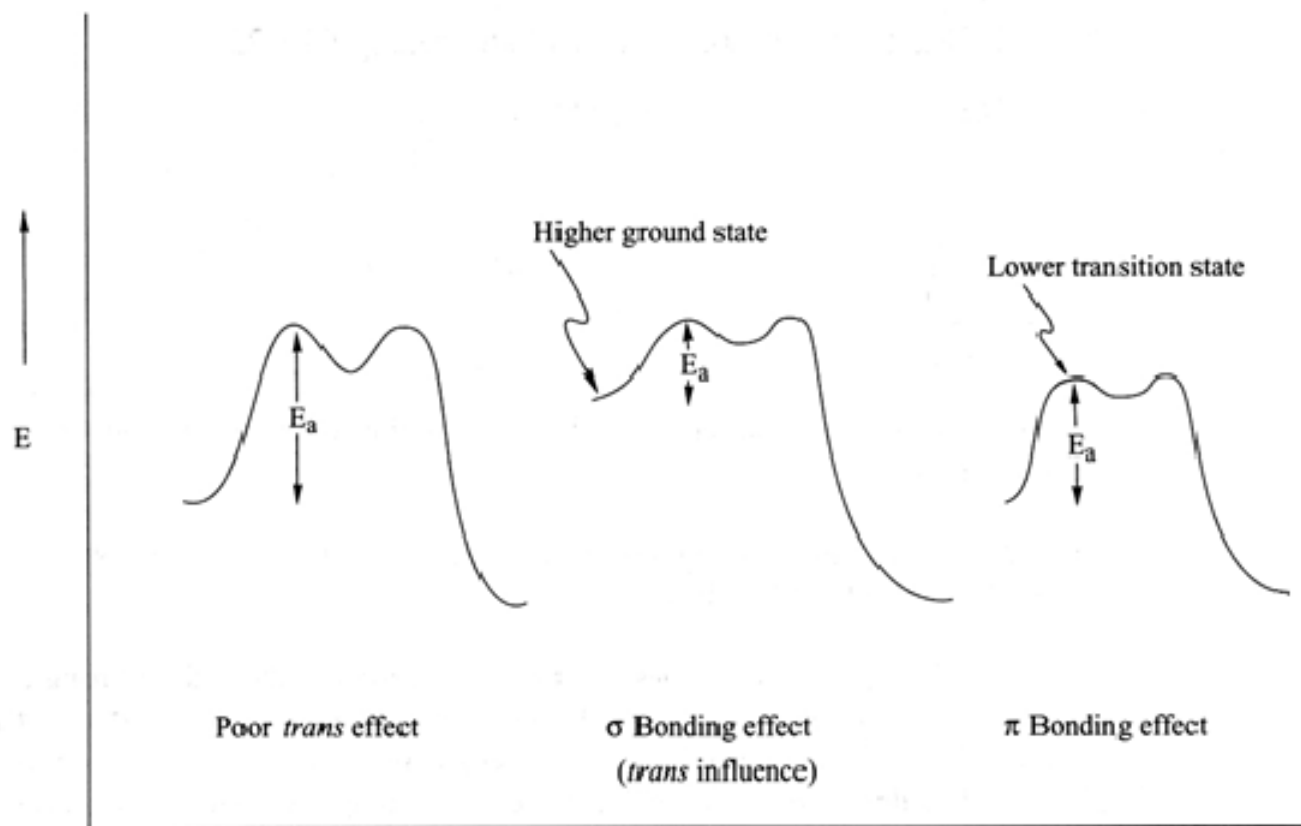substitution to the site trans to themselves (trans effect).

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*)
Fig. 7-2 text (middle, next page)

J_{PtP} = 3508 Hz

ν(Pt-Cl) = 303, 281 cm^{-1}

J_{PtP} = 2380 Hz

ν(Pt-Cl) = 339 cm^{-1}
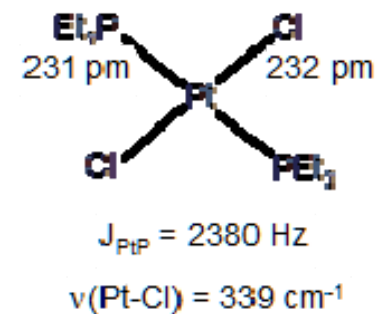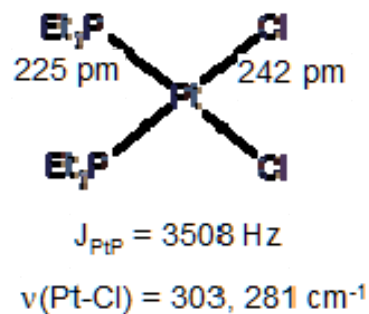
- strong σ-donors (H$^-$, PR$_3$, I$^-$, Me$^-$ etc.) weaken the M-L bond ***trans to***
themselves
- observable by IR (υ_{M-L}), X-ray (M-L bond length) and NMR (reduced
$^1J_{M-L}$ values)

Higher ground state

Lower transition state

E_a

E_a

E_a

E

Poor *trans* effect

σ Bonding effect
(*trans* influence)

π Bonding effect

Figure 7-2
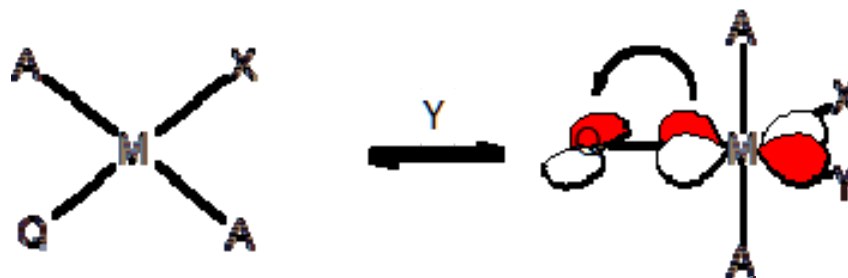Activation Energy and the *trans* Effect
The depth of the energy curve for the intermediate
and the relative heights of the two maxima will vary
with the specific reactants. (Adapted from G.L.
Miessler and D.A. Tarr, *Inorganic Chemistry*,
Prentice-Hall, Englewood Cliffs, NJ, 1991, 397.)
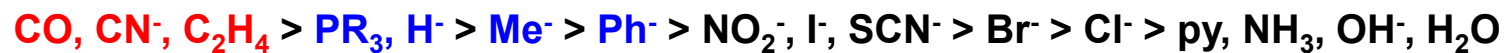
From Organometallic Chemistry by Spessard and Miessler

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

Fig 7-2 text (right)

- strong π-acceptors (*eg.* CO, C_2H_4, 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:

**CO, CN⁻, C₂H₄ > PR₃, H⁻ > Me⁻ > Ph⁻ > NO₂⁻, I⁻, SCN⁻ > Br⁻ > Cl⁻ > py, NH₃, OH⁻, H₂O**

Eg.   *trans*-Pt(PEt₃)₂**Cl**(L) + **py** → *trans*-Pt(PEt₃)₂(**py**)(L)⁺ + **Cl⁻**

L	k (M⁻¹s⁻¹)
H⁻, PEt₃	4
Ph⁻	10^{-2}
Cl⁻	10^{-4}

Associative (A) substitution

- most common for sq. planar 16 e$^-$ species

- usually proceeds with *retention* of configuration

- rate law is **1st order in complex** *and* **incoming ligand Y**
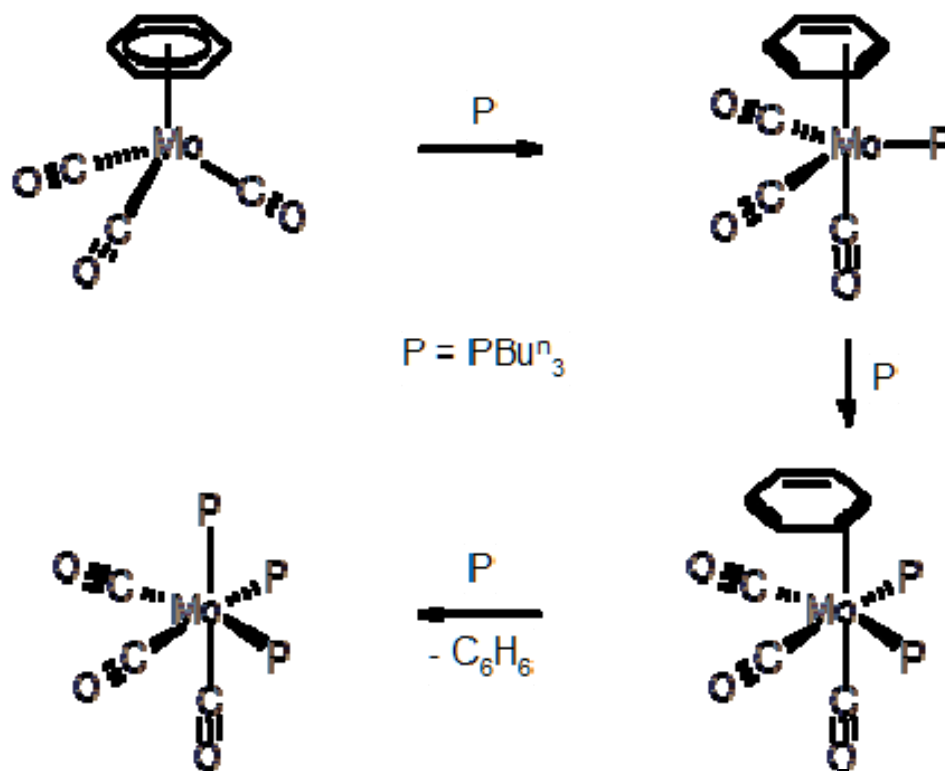
NB: **T** is a stronger trans labilizing

ligand than **A** or **X**

- **ΔS^* for this type of reaction is**
  large and negative
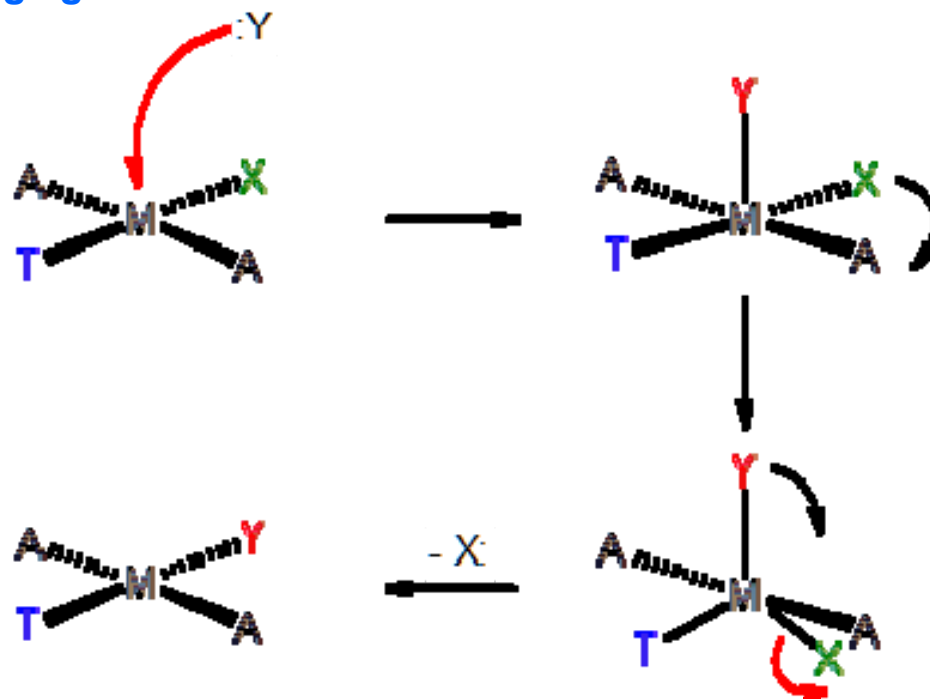
Associative mechanisms in formally 18e⁻ species

- only possible if a ligand can change hapticity and decrease the total e⁻ count

$P = PBu^n_3$

Dissociative (D) substitution

- common for octahedral 18 e$^-$ complexes

- rate: 1st order in complex and zero-order in incoming ligand

- rates depend on the metal and ligands present in ML$_6$ but 2nd row metals substitute faster than 1st or 3rd row metals (for unknown reasons)
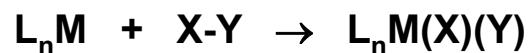
- **steric bulk** usually **increases the rate** of substitution:

$$\textit{cis}\text{-}Mo(CO)_4(PR_3)_2 + CO \rightarrow Mo(CO)_5(PR_3) + PR_3$$

PR_3	Cone angle (°)	$k\ (s^{-1})$
$PMePh_2$	122	1×10^{-5}
PPh_3	145	3×10^{-3}
$PPhCy_2$	162	6×10^{-2}

2 Oxidative addition

$$L_nM + X\text{-}Y \rightarrow L_nM(X)(Y)$$

- oxidation state increases by 2 units
- common for e- counts of 16e- or less

Vaska's complex (shown at right) is a classic example of 16 e⁻ d^8 compound that undergoes oxidative addition with a wide range of substrates and does so by a variety of mechanisms. Some of these mechanisms are dealt with in the following sections.
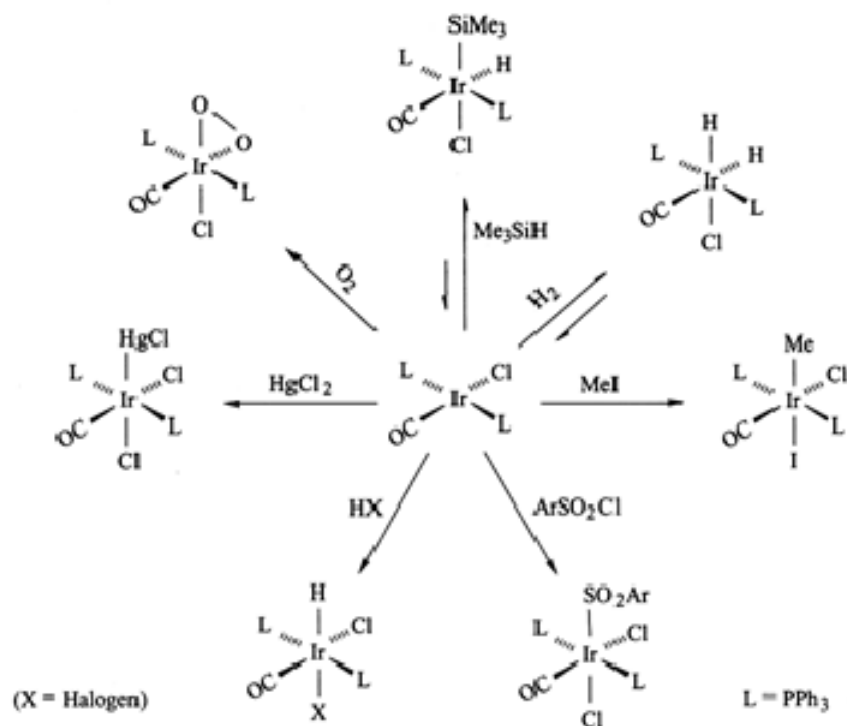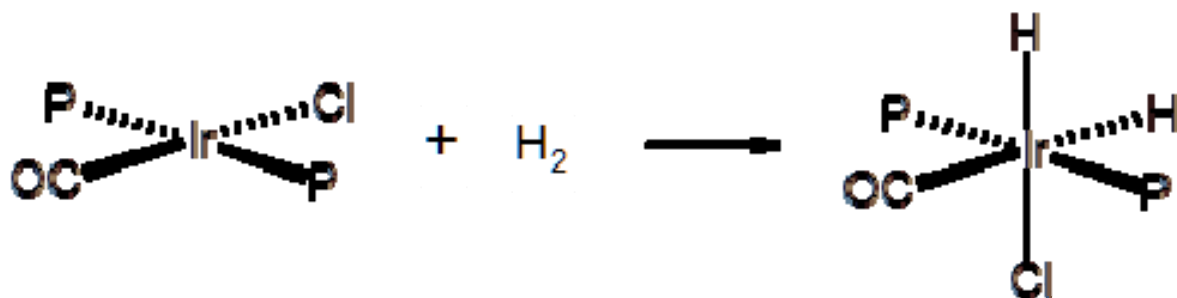

Scheme 7.3
Oxidative Addition Reactions
of Vaska's Compound

a) Three-centre concerted additions

H-H, C-H and C-C additions are usually of this type

H_2 addition

Thermodynamics:

ΔH^o is roughly $2\ D_{(Ir-H)} - D_{(H-H)} =$

$2(-60) - (104) =$ **-16 kcal/mol (-67 kJ/mol)**

ΔS^o is negative and large: **-30 eu (-125 J mol^{-1} K^{-1})**

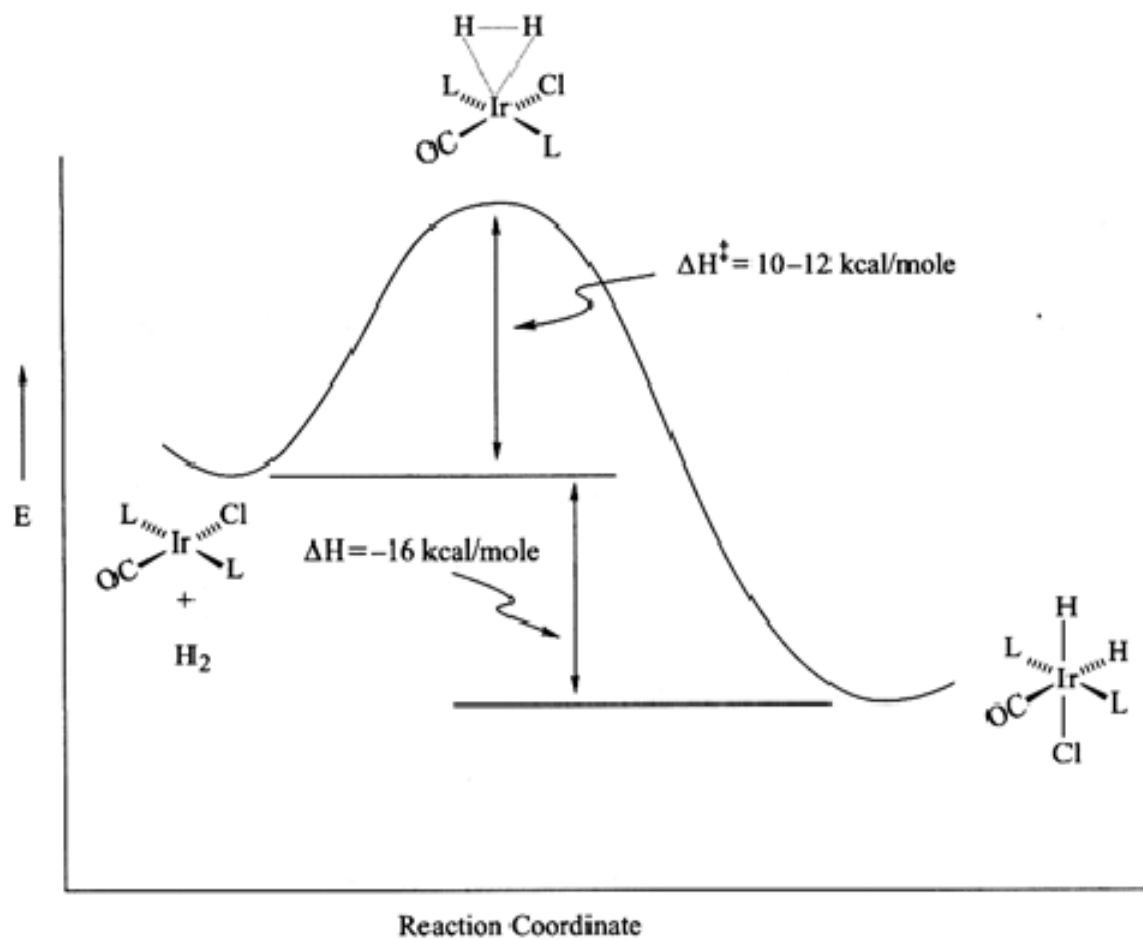therefore $\Delta G^o = -16 - (298)(30)/1000 =$ **-7 kcal/mol (-29 kJ/mol)**

This is a small enough value that the reaction may be reversible under appropriate conditions.

Kinetics

rate = k_{obs}[Complex][H_2]

consistent with a
concerted process

$\Delta H^{\ddagger} = 10-12$ kcal/mole

$\Delta H = -16$ kcal/mole

E

Reaction Coordinate

Figure 7·7
Reaction Coordinate-Energy
Diagram for the Addition of
H_2 to Vaska's Compound

M.O. picture for this reaction is straightforward:

(i) σ-donation from filled H_2 σ orbital

(i) π-back donation from metal orbital to H_2 σ*

It is interaction (ii) that
causes the H-H bond to break

Figure 7-8
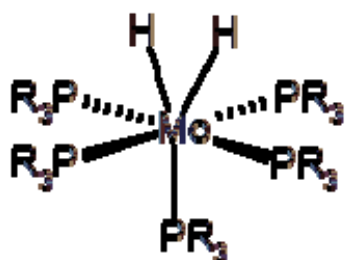Interactions of
Frontier Metal and H_2
Molecular Orbitals

d_{z^2} (LUMO)

d_{xz}-like (HOMO)
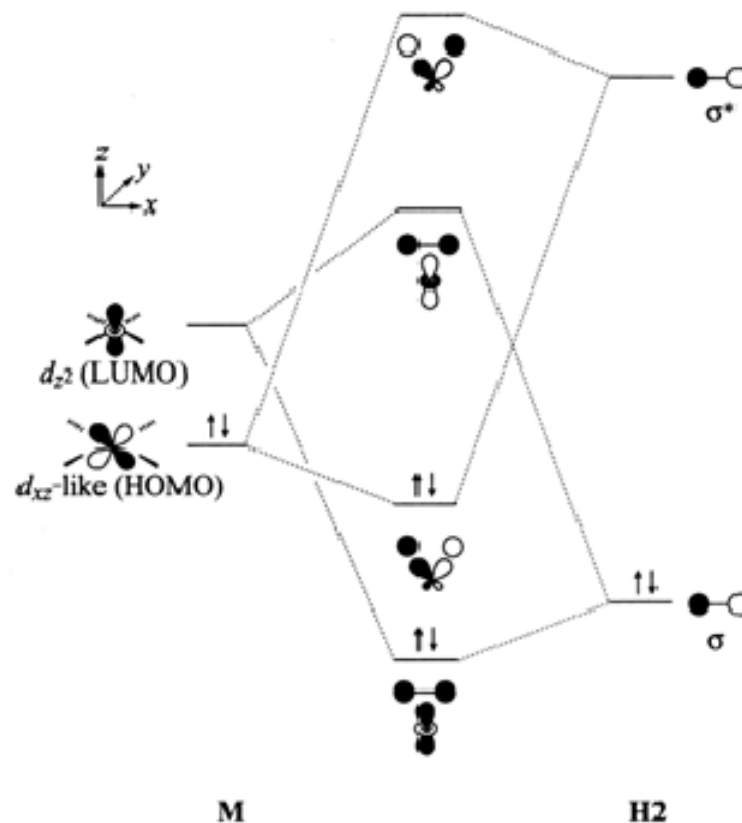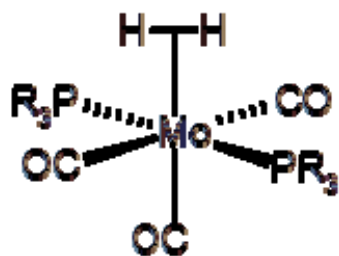
What is wrong with this diagram?
Spot two issues and correct them.

M   H2

σ*

σ

- metals with positive charges, higher oxidation states or competing π-acceptors cannot back donate well, so **stable η^2-H$_2$ complexes** are obtained:

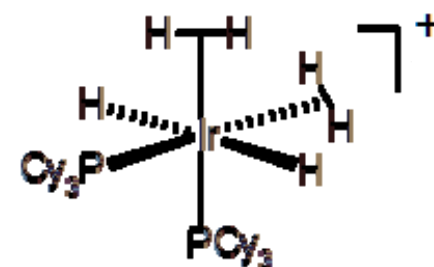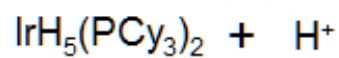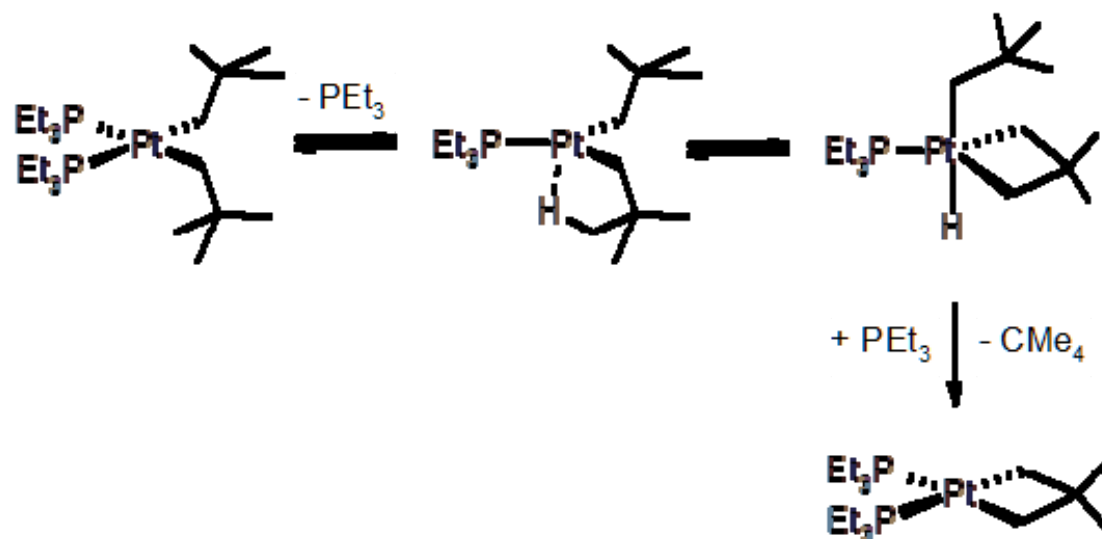**Compare:**

7-coordinate	6-coordinate		6-coordinate
18 electron	18 electron	$IrH_5(PCy_3)_2 + H^+ \longrightarrow$	18 electron
dihydride	dihydrogen		dihydrogen

C-H addition

intermolecular C-H activation is still rare but intramolecular cases (cyclometallation) are common (entropy effect)
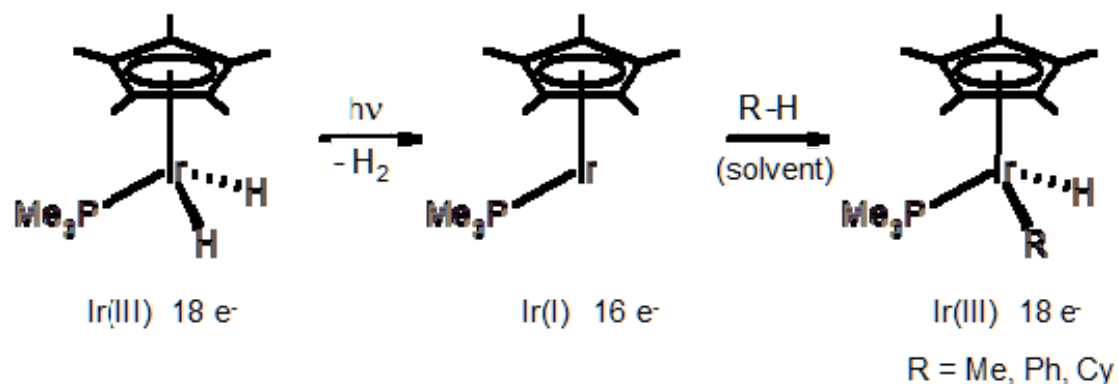
'C-H activation' is one of the most sought after reactions in organometallic chemistry: potential economic impact is huge.

Ir(III) 18 e⁻   Ir(I) 16 e⁻   Ir(III) 18 e⁻

R = Me, Ph, Cy

Some points about C-H addition:

- retention of configuration at C: C-H bond approaches metal side-on

- easier for Ar-H: higher M-aryl bond strengths

- more favourable for 2nd and 3rd row metals: higher M-C bond strength

- intermolecular usually only observed if intramolecular is difficult

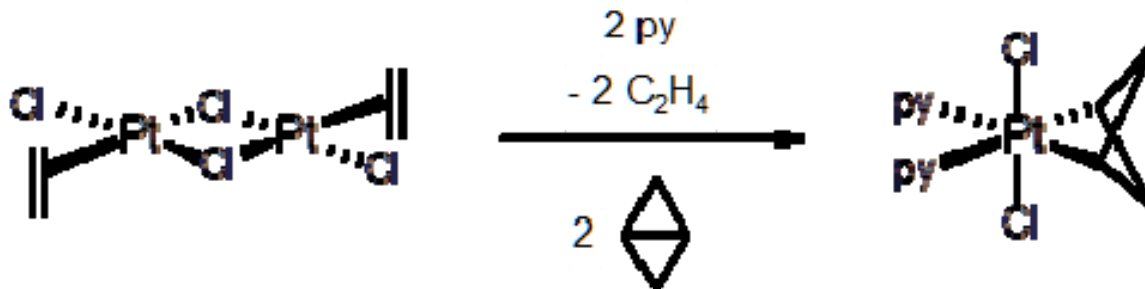- requires free site at the metal (< 18 e⁻) to occur

C-C additions

- **economic importance is high but so far 'cracking' of unstrained C-C bonds is limited to heterogeneous reactions**

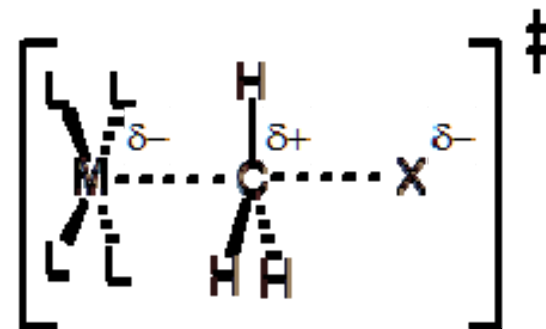$$[M] \quad + \quad \text{(alkane chain)} \quad \longrightarrow \quad M \text{(metallacycle)} \qquad \Delta H = 0$$
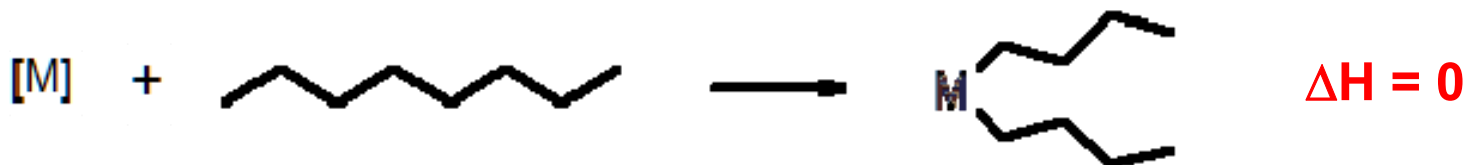
- **strained C-C bonds WILL do oxidative addition reactions due to relief of ring strain:**

b) Nucleophilic oxidative addition of RX

filled dz^2
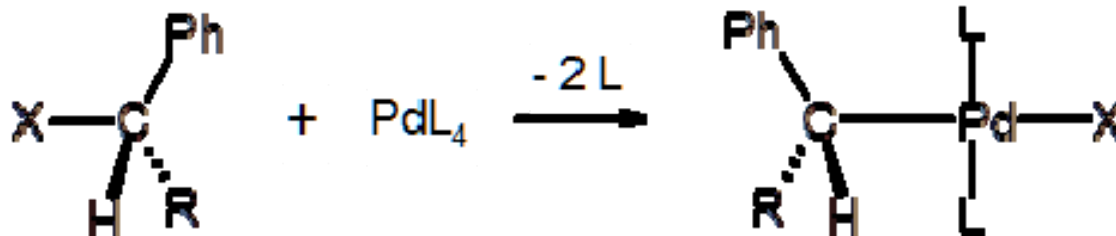
slow
r.d.s.

fast

rate = k_{obs}[M][RX]
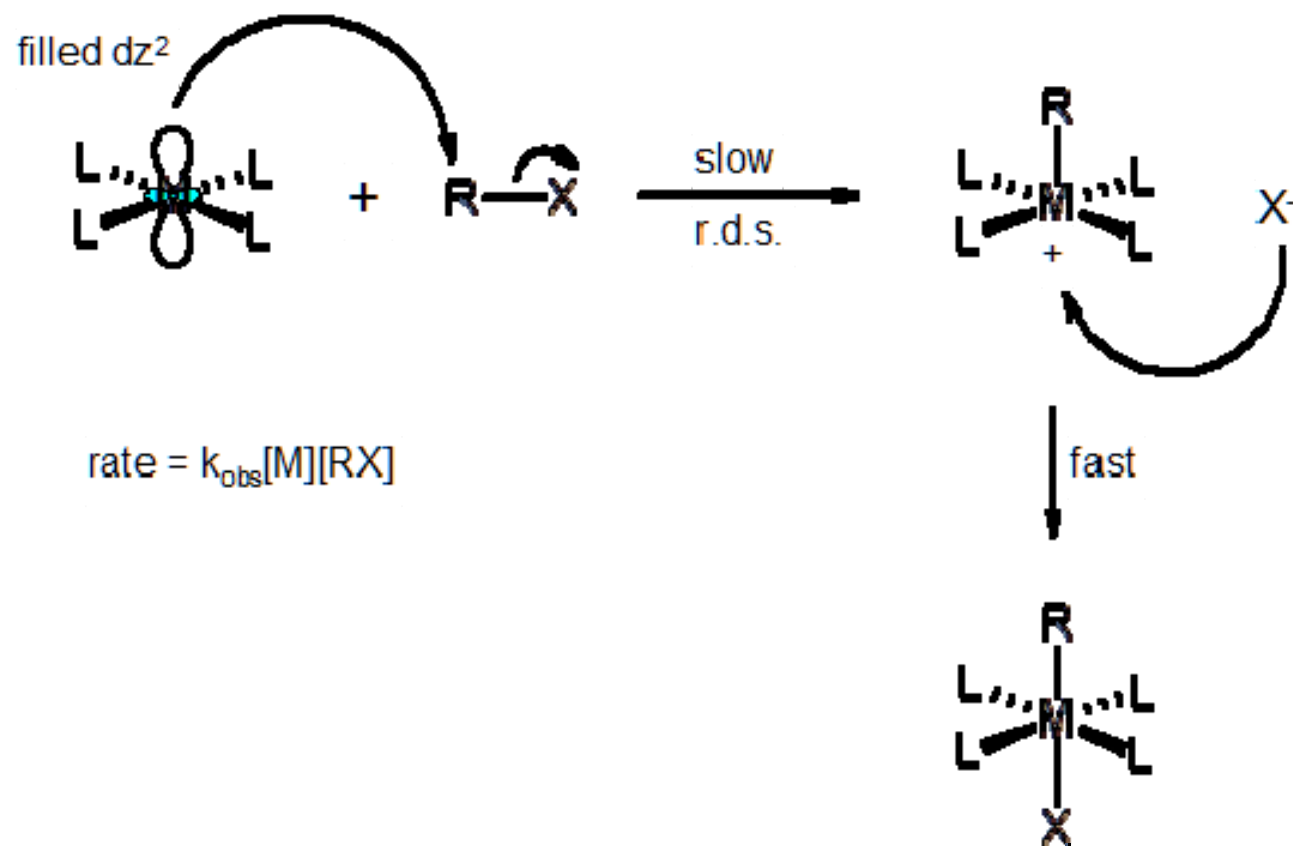
ΔS^* **is large and negative** suggesting an **S$_N$2-like transition state:**

$$\left[\begin{array}{c} L \\ M \cdots C \cdots X \\ L \quad L \end{array} \right]^{\ddagger}$$

- **rate depends on leaving group:**

  $CF_3SO_3^- > I^- > OTs^-, Br^- > Cl^-$

- **inversion** observed at C:

$$X-C + PdL_4 \xrightarrow{-2L} \text{product}$$

- **polar solvents increase rate** (polarized transition state)

- **electron-releasing ligands increase rate** (metal more nucleophilic)

c) Radical pathways

- often observed in odd electron systems such as Co(II) (d^7) or Mn(0) (d^7) but can even occur in even electron systems like Ir(I) (d^8):

$$\text{INIT} \bullet \; + \; \text{Ir(I)} \quad \rightarrow \quad \text{INIT-Ir(II)}$$

$$\text{INIT-Ir(II)} + \text{R-X} \quad \rightarrow \quad \text{INIT-Ir-X} \; + \; \text{R} \bullet$$

$$\text{R} \bullet \; + \; \text{Ir(I)} \quad \rightarrow \quad \text{R-Ir(II)}$$

$$\text{R-Ir(II)} \; + \; \text{R-X} \quad \rightarrow \quad \text{R-Ir-X} \; + \; \text{R} \bullet \qquad \textbf{when R is 3}° \textbf{ or 2}° \textbf{ but NOT for 1}° \textbf{ (R = Me, CH}_2\textbf{Ph)}$$

Evidence for a radical process:

- rate increases with initiators (peroxides, oxygen, light)
- rate decreases with radical scavengers
- racemization of stereochemistry at chiral C centres

3. Reductive elimination
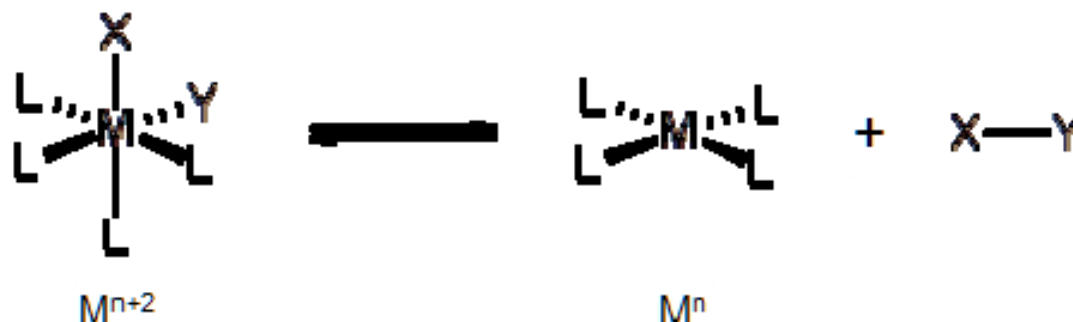
- very important as the C-C bond forming step in catalytic cycles (where X and Y are organic groups)
- *cis* orientation of X and Y is required for concerted elimination

- trans orientation must first isomerize to cis before reductive elimination can occur
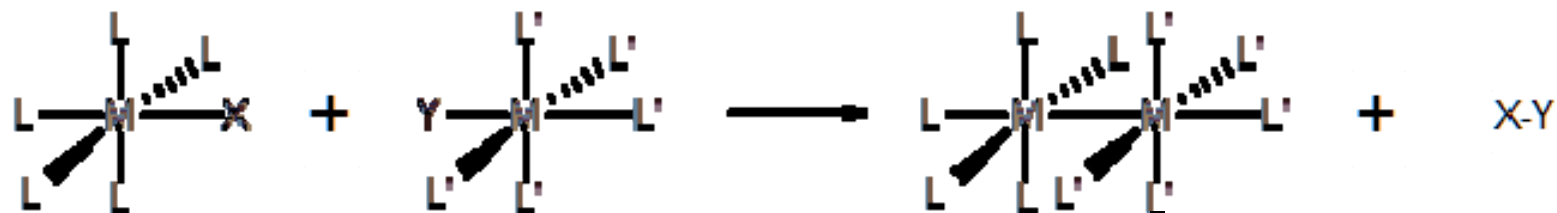- proceeds with *retention* of stereochemistry at C:
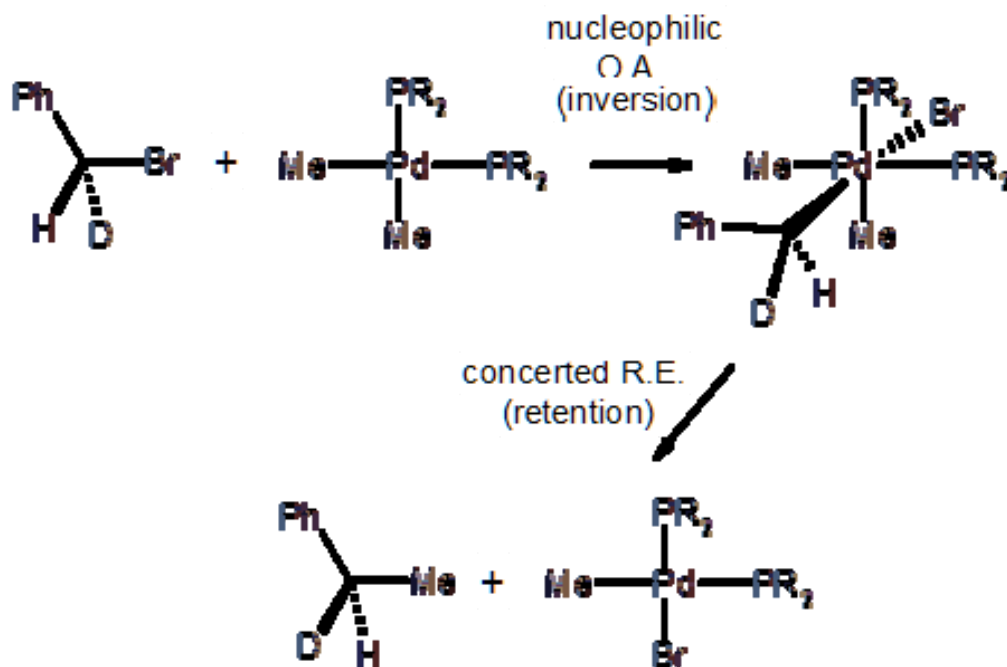
Favoured by:

- **bulky ligands** (relief of crowding)

- **high oxidation state**

- **ancillary ligands that can stabilize the lower oxidation state** (CO, alkenes, PR_3 etc.)

- **intermolecular** reductive elimination processes can be ruled out by conducting the *crossover experiment*:
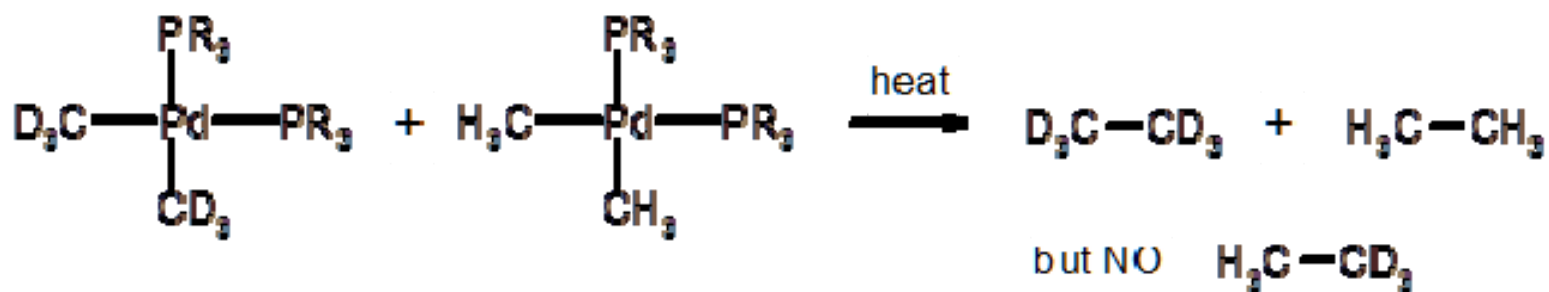
Binuclear reductive elimination

- results in **M-M bond formation** and $1e^-$ reduction per metal
- many examples go by a radical process
- can even occur in cases where simple R.E. might be expected: