

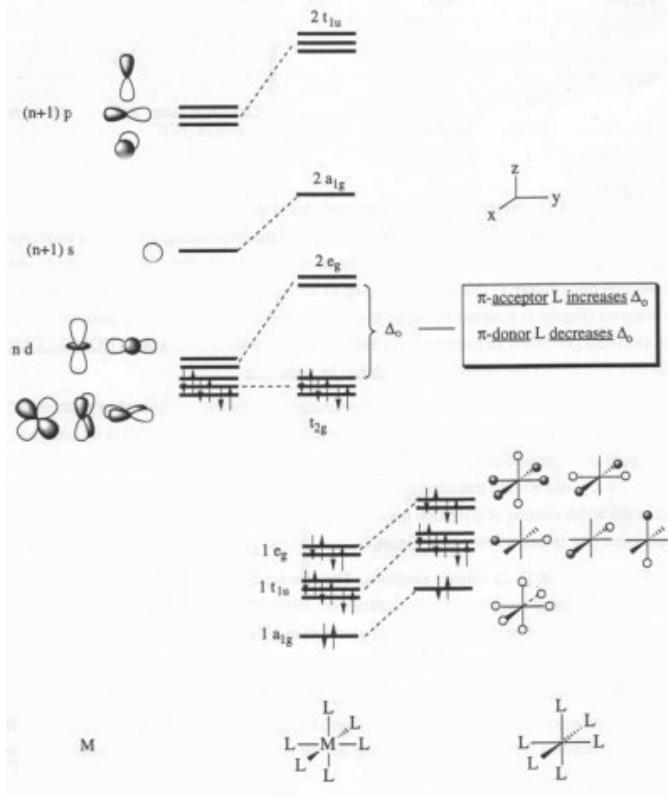
GENERAL ORGANOMETALLICS NOTES

The 18 Electron Rule

The 18 electron rule comes about in a similar way to the octet rule encountered for p block compounds, where a model of filling all bonding orbitals gives a stable compound.

It states that "Stable organometallic complexes are formed when the sum of the neutral metal valence electrons plus the sum of the electrons considered to be donated by the ligand (and taking into account any net charge) equals eighteen".

Thus, for octahedral and tetrahedral complexes, this would mean filling of the following MO:



Exceptions –

Only applies to TMs. It is typically obeyed by complexes with $d^{n>2}$ and strong π -acceptor ligands.

A class system was introduced to highlight deviations:

Class I:

12 – 22 valence electrons. Comes about when e_g are only weakly antibonding and t_{2g} are not receiving / donating electrons. Thus it applies for 1st row Transition Metals (e_g low in Energy) and weak field ligands (t_{2g} not used).

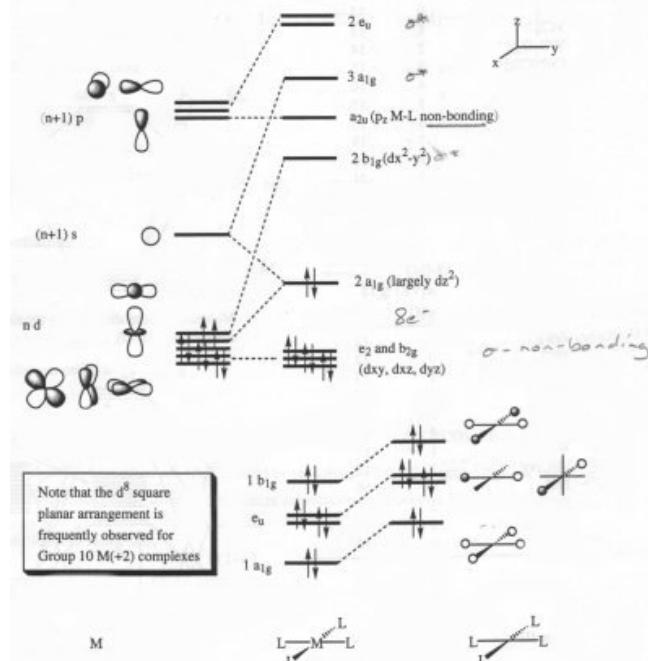
Class II:

Up to 18 valence electrons. e_g now too high in energy to be used, so common for 2nd/3rd row TM's and strong field ligands (good σ -donors).

Class III:

Obey 18 electron rule. t_{2g} are π -bonding (occupied) with e_g strongly antibonding. This is the vast majority for Organometallic TM's.

Another major exception is Square Planar Complexes, where a 16 electron rule applies instead. This is because now the splitting appears as:



Other exceptions are usually due to steric factors, particularly in the early TM's (low valence electron counts). For example, $(Cp)_2TiCl_2$ will not add another ligand and remains as 16 electrons, due to too much crowding with the bulky Cp Ligands.

Coordinative Unsaturation:

Complexes with less than an 18e count are said to be this, and there may be a tendency to add further ligands. This is because there must be one or more vacant orbitals able to accept electrons.

Counting Electrons

Formal Oxidation State:

OS = Charge on complex – Sum of charges formally assigned to the ligands on removal from metal centre.

d^n electron count:

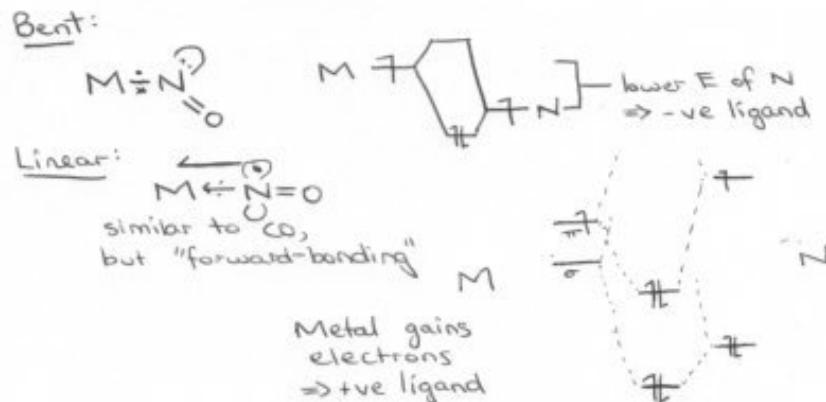
d^n give you the number of electrons associated with the metal.

d^n = metal group number – formal OS.

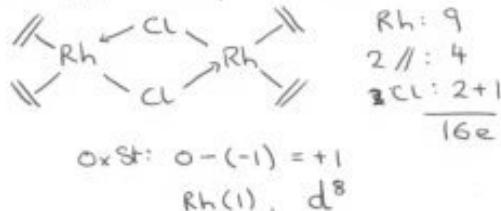
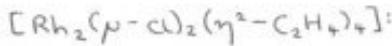
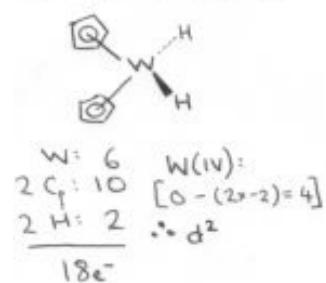
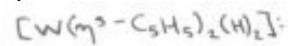
Formal charges and electron counts are assigned to typical ligands as follows:

LIGAND	ELECTRONS	CHARGE
Alkyl	1	-1
Aryl	1	-1
Hydride	1	-1
Alkene	2	0
Alkyne	2 or 4	0 or -2
Allyl	1 or 3	-1
Cyclo C_nH_n	Depends on η	$n = 5 \Rightarrow -1$ $n = 6 \Rightarrow 0$ $n = 7 \Rightarrow +1 \text{ or } -3$ $n = 8 \Rightarrow -2$
Carbene	2	0 (Fischer) or -2 (Schrock)
Carbyne	3	0 or -3
Carbonyl	2	0
Nitrosyl*	1 (bent) or 3 (linear)	-1 (bent) or +1 (linear)

* Nitrosyl – NO, may be linear or bent.



Some examples of counts:



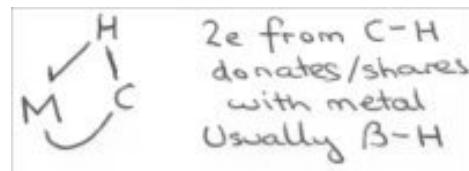
Bonding Modes

There are 3 different types:

- 1) Terminal. 1 electron donors, 1-ligands, 2c-2e. Standard type, e.g. L_nM-Cp .
- 2) Bridging (less common). 3c2e often.



- 3) Agostic alkyls.

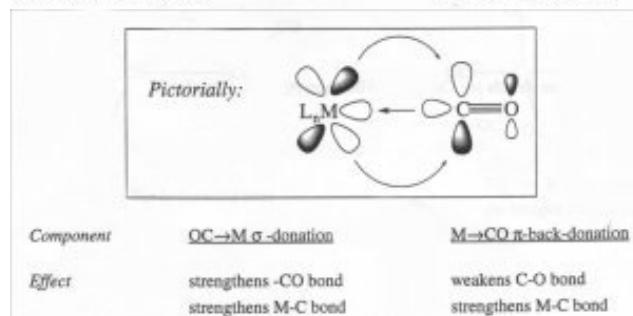
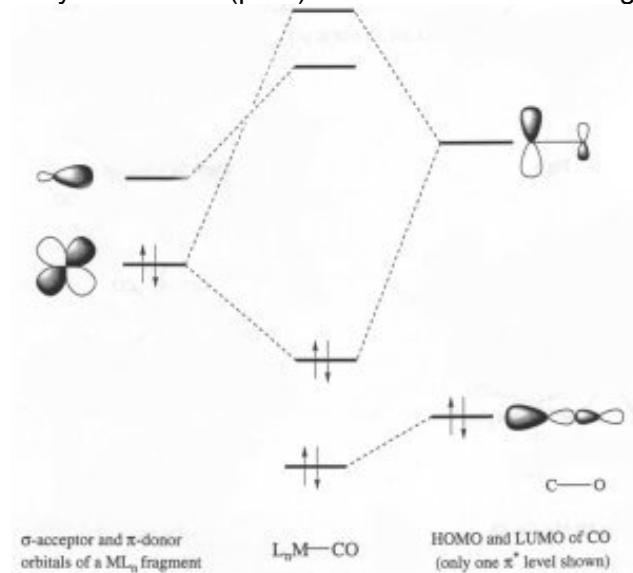


Alkyls

- M-C bond strength increases with increasing p hybridisation:
 $M-CR_3 < M=CR_2 < M-C\equiv CR$
- M-C bond strength increases down a TM Group (see Transition Metals in general).
- M-C bond strength increases across a Series.
- M-C bond strength typically similar to main group metals. However, TM alkyls kinetically much less stable. TM alkyls have low energy d orbitals, which leads to low energy decomposition routes. Compounds such as $TiMe_4$ dimerise (the dimer decomposes easily), while $PbMe_4$ requires bond homolysis to decompose.
- Kinetic stabilisation can be affected by block vacant coordination sites, or using bulky alkyl groups without β -hydrogens. Also, 18 electron complexes prevent β -H elimination as well.

Carbonyls

Carbonyl ligands bind by σ -donation (poor) and also π -back-bonding (significant).



Factors that affect back-bonding:

How much the metal can donate its electrons (i.e. its d count). If it has more d electrons to donate, then the backbonding will be stronger.

- Charge on the metal. A more positive metal is less likely to donate its electrons. Thus backbonding has a greater stabilising influence on low oxidation state metals, as they are able to back-bond more effectively (will relinquish their electrons more easily).
- Other Ligand present. An electron-withdrawing ligand such as Cp will reduce the degree of back-bonding. Conversely ligands such as alkyls reduce the degree of electron withdrawal.
- Coordination Modes. The CO ligand can be terminal, doubly bridging or even triply bridging. This bridging tends to reduce CO bond strength due to greater population of π^* CO.

The consequence of more back-bonding is a stronger M-C and a weaker C=O bond. Thus, the strength can be indirectly measured by infra-red spectroscopy, where a lower stretching frequency indicates more back-bonding occurring (weaker C=O).

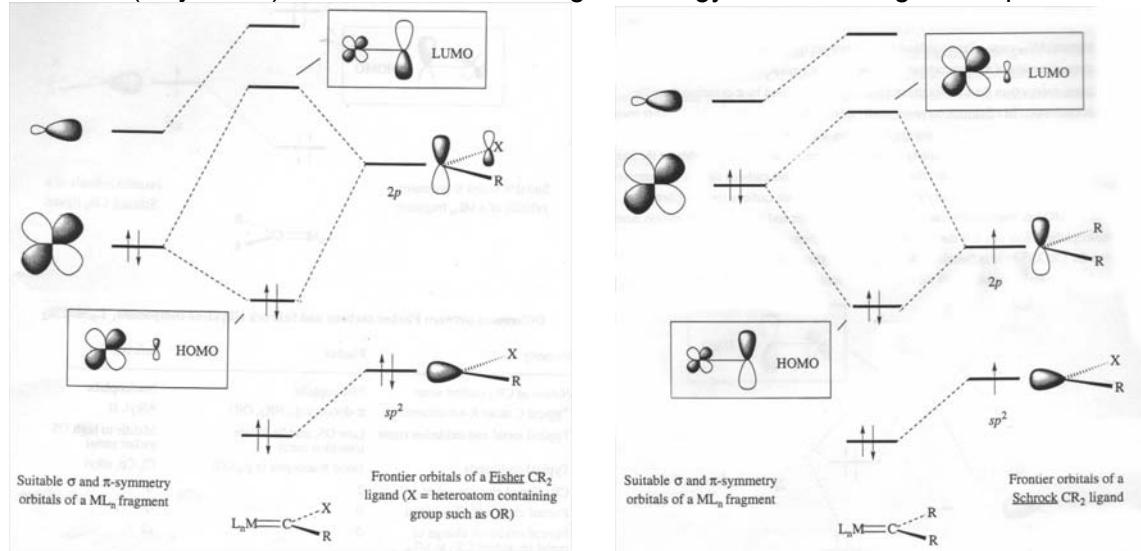
Carbenes

Of the form $L_nM=CR_2$.

ML_n must have 2 d electrons to donate for the π component of the bond.

Fischer – metal d π -donor orbitals are lower energy than the CR_2 fragment's p-orbital. This is usually the case for metals stabilised by CO ligands.

Schrock (alkylidene) – metal orbitals are higher energy than CR_2 fragment's p-orbitals.



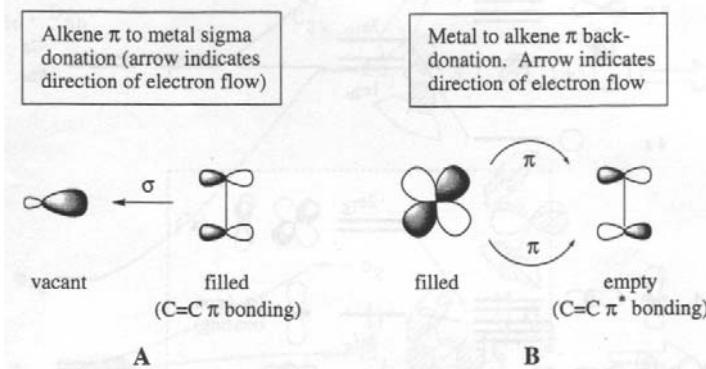
Difference affects polarity of the $M=C$ bond. Fischer => carbene is electrophilic (LUMO has carbon character) while for Schrock => carbene is nucleophilic (HOMO has carbon character).

<i>Property</i>	<i>Fischer</i>	<i>Schrock</i>
<i>Nature of CR₂ carbon</i>	Electrophilic	Nucleophilic
<i>Typical C atom R substituents.</i>	π-donor	Alkyl, H
<i>Typical metal and Ox St.</i>	Low OS, middle to late TM	Middle to high OS, early TM
<i>Typical co-ligands</i>	π-acceptor (CO)	Cl, Cp, alkyl
<i>CR₂ ligand e-count</i>	2	2
<i>Formal charge of ligand</i>	0	-2
<i>Formal oxidation change of metal on adding ligand</i>	0	+2

Metal-Alkene Complexes

The alkene HOMO (carbon-carbon π -bonding) and LUMO (carbon-carbon π^* -antibonding) are the important ligand orbitals involved.

Principal bonding features described by the Dewar-Chatt-Duncanson model:



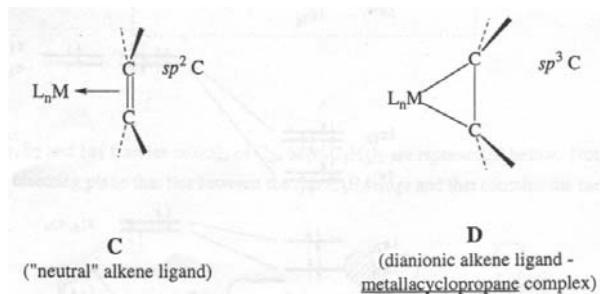
A = electrons from the alkene HOMO are formally donated into empty transition metal d-type hybrid orbital.

B = electrons from a filled metal d function are transferred by π -back-bonding to the vacant alkene LUMO.

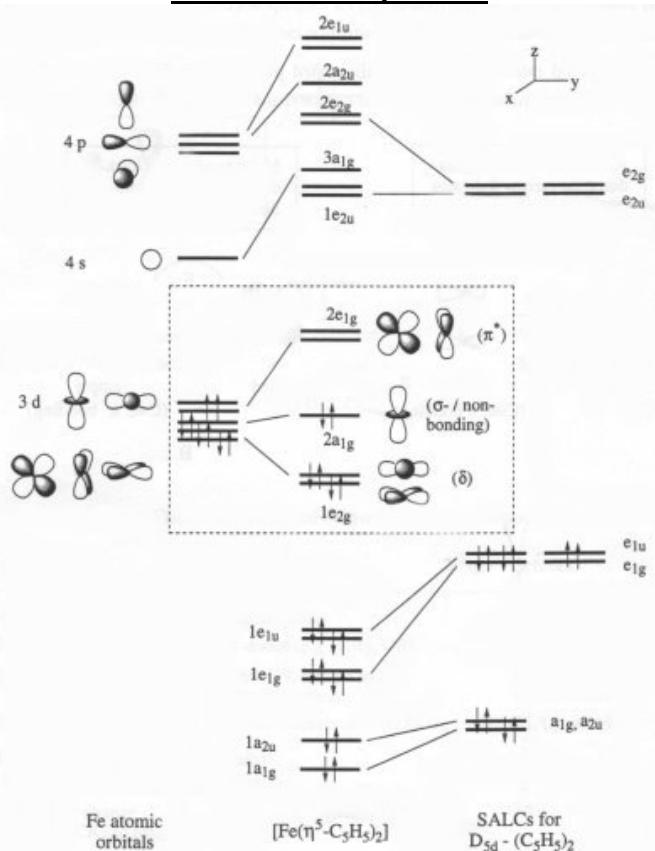
This is synergic bonding (as for carbonyls).

Extreme case – metal to alkene π^* orbital back-bonding is very extensive, the alkene may be considered to be a dianionic “di-alkyl” type ligand (**D**). This occurs for very e-deficient alkenes and/or very e-rich metals.

Otherwise, alkenes are usually considered to be neutral ligands (**C**).

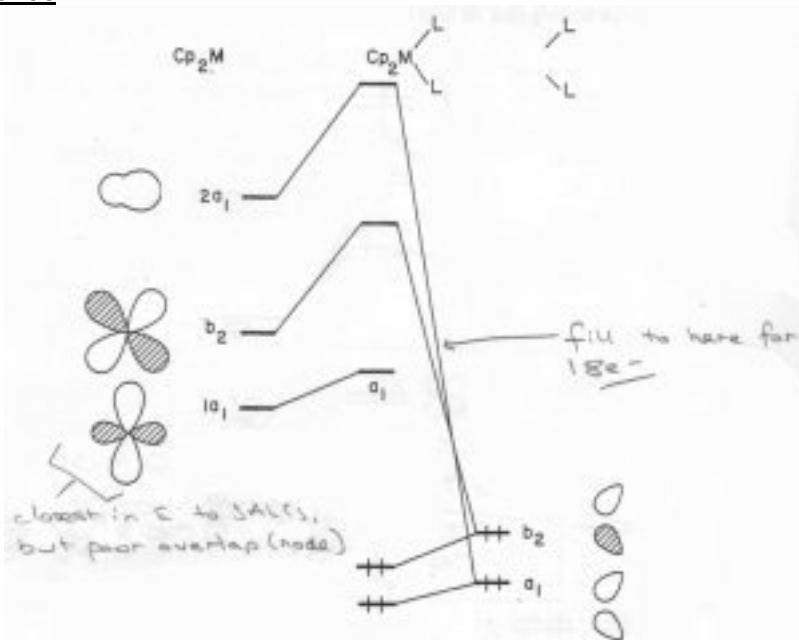


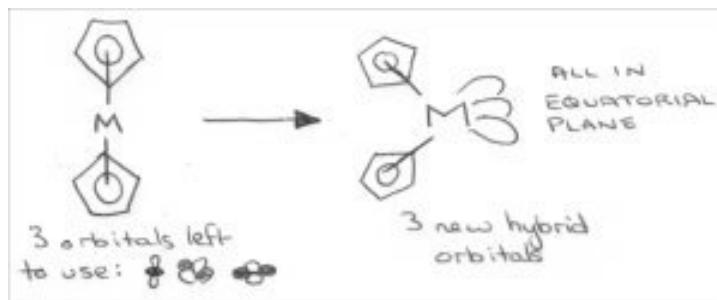
Sandwich Compounds



M-C bond length is expected to decrease across the series (as radius of M decreases with Z_{eff} increasing). Increase in $r(\text{M-C})$ (i.e. weakening of the bond – against the trend) occurs when population of the π^* orbitals occurs.

Bent Sandwiches

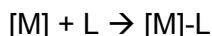




The consequence of this is that all bonding interactions are in the equatorial plane.

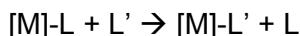
Mechanisms and Reaction Types

Association and Dissociation:



Typically results in the valence electron count increasing by 2, but Oxidation State and d-count remain the same.

Substitution:

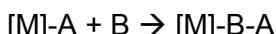


Net no change in valence electrons, d-count or Oxidation State. Typically proceeds via first Dissociation, since a 20e intermediate would be highly unstable (occupation of σ^* orbitals required).

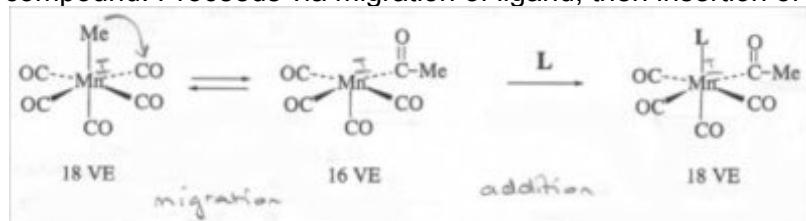
Oxidation and Reduction:

Gain or loss of electrons. For oxidation, leads to change in valence electron count (-1), oxidation state (+1) and d-count (-1).

Migratory Insertion

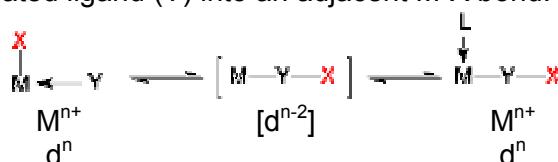


No net change in electron counts or oxidation states. Classic Example: Me insertion into Mn carbonyl compound. Proceeds via migration of ligand, then insertion of B.



Formal Definition:

Insertion of an unsaturated ligand (Y) into an adjacent M-X bond.



Y = CO, C₂H₄, C₂H₂, Benzene, Cyclopentadienyl

X = H, R, Ar, C(O)R

L = Lewis Base, Solvent, PR₃, NR₃, R₂O

Contrast with:



(Intermolecular nucleophilic attack on M-Y bond).

Two Main Types:

(A) 1,1 Insertion



e.g. X = Me, AB = CO

(B) 1,2 Insertion



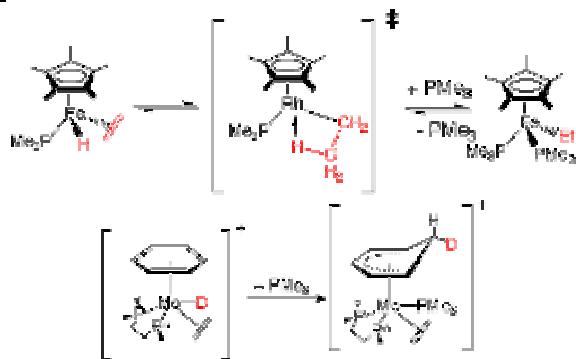
e.g. X = H, AB = H₂C=CH₂

General Features of Insertion Reactions

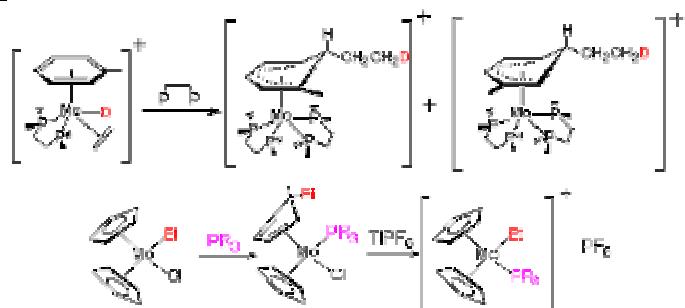
1. No change in formal oxidation state of metal centre, except if inserting ligand (Y) is M=C or MC.
2. Groups must be adjacent (cis) to each other.
3. Vacant coordination site is created during the forward reaction.
4. When the X ligand is chiral, the reaction generally proceeds with retention of configuration.
5. Examples of X-migration and Y-insertion are known.
6. Position of equilibrium depends upon the strength of M-X, M-Y, and M-(XY) bonds.
7. 1-electron oxidation often speeds up reaction.

Specific Examples of Migration Reactions

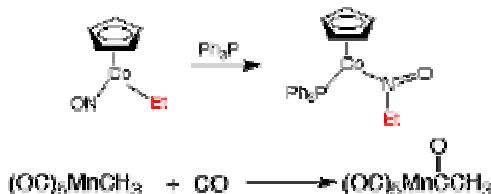
(1) Hydride Migrations



(2) Alkyl Migration



(3) Other Examples



"Case Study" of a Carbonylation Reaction

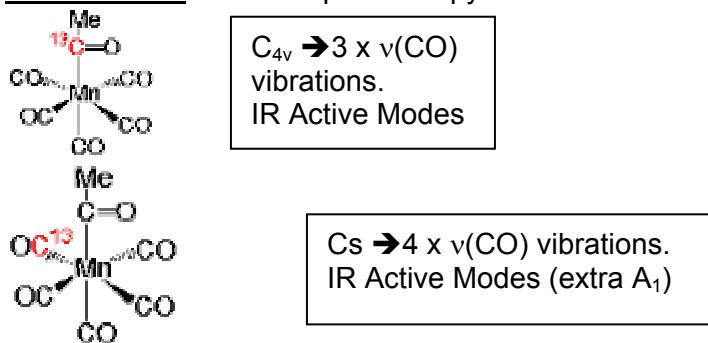


Three Possible Mechanisms

- Direct Insertion
- "Knock-on" Insertion
- Alkyl Migration

Use ^{13}CO to examine stereochemistry of products to elucidate mechanism

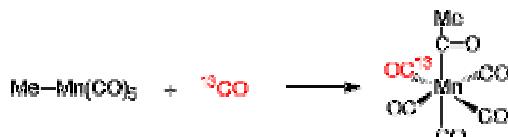
TECHNIQUE: Infrared Spectroscopy



Acetyl derivative has separate band $v(\text{CO}) = 1664 \text{ cm}^{-1}$

Position of entry/exit of ^{13}CO can be deduced from intensity changes and band positions.

Experiment 1



I.R Data:

Intensity at 1970 cm^{-1}

Intensity at 1963 cm^{-1}

Intensity at 1625 cm^{-1}

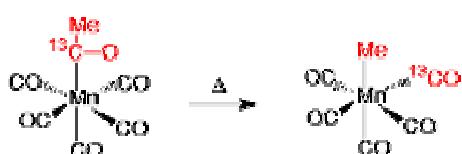
Thus:

Acetyl group is cis to ^{13}CO

^{13}CO cannot be directly inserted

No scrambling takes place in the product

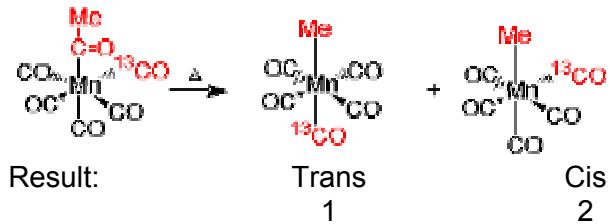
Experiment 2



Result 100% cis product

Does not prove either carbonyl insertion or methyl migration.

Experiment 3

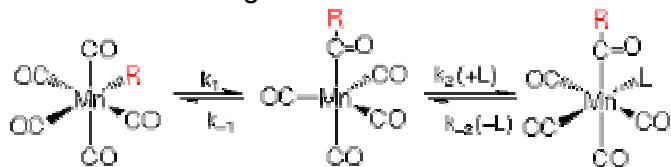


Proved using intensities of 1976 cm^{-1} (cis) and 1949 cm^{-1} (trans) in I.R. spectrum

- Only migration can give correct product distribution.
- Cannot get trans isomer by de-insertion of CO.

Rate Law for Carbonylation Reaction

Under Normal conditions the following rates are observed



k_1 is rate determining, i.e. 1st Order in alkyl-Mn

0^{th} Order in L (incoming ligand)

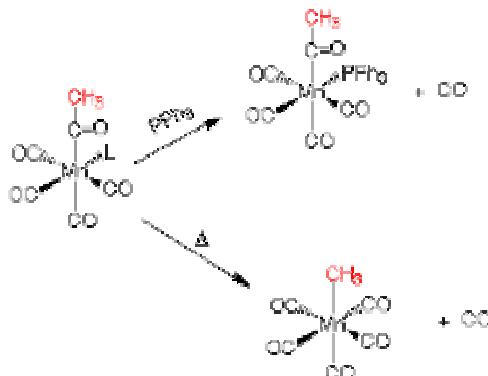
if k_2 is $\gg k_{-2}$, then,

$$\text{RATE} = \frac{k_1 k_2 [\text{Mn}(\text{CO})_5\text{R}] [\text{L}]}{k_{-1} + k_2 [\text{L}]}$$

High [L]: First order in starting material

Low [L]: Mixed order kinetics

Rate constants are found to be identical for the substitution of CO in $\text{Me}-\text{CO}-\text{Mn}(\text{CO})_5$ and for the decarbonylation of the acetyl compound, i.e. they have the same rate determining step.



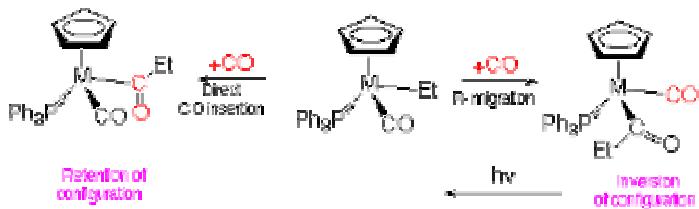
Rate accelerated by Lewis Acid catalysis, e.g. H^+ , AlCl_3 , BF_3 .

Lewis acids are presumed to stabilise Transition state as shown:

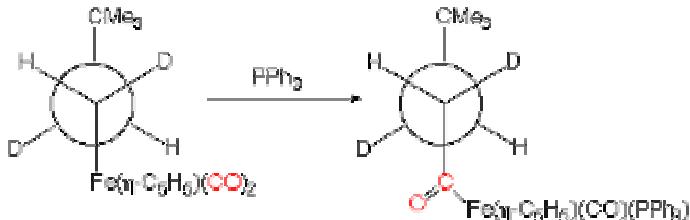


General Observations of Stereospecificity

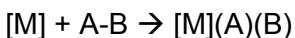
Metal Centre



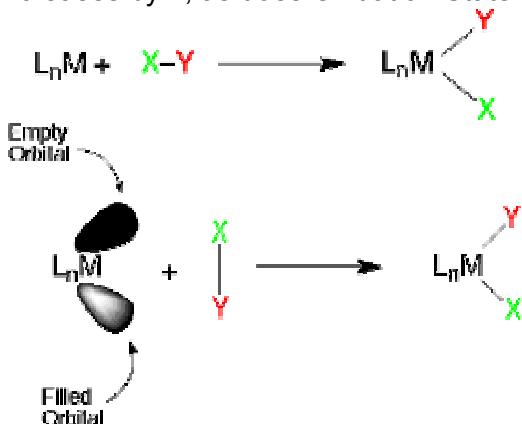
Carbon Centre



Oxidative Addition



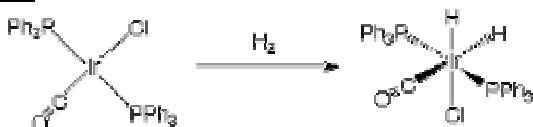
Valence electron count increases by 2, as does Oxidation State. d-count reduces by 2.



Requirements for the Metal Complex

- Metal centre must be d² or greater.
- Metal centre must be coordinatively unsaturated.
- Metal must have appropriate both empty and vacant orbitals.

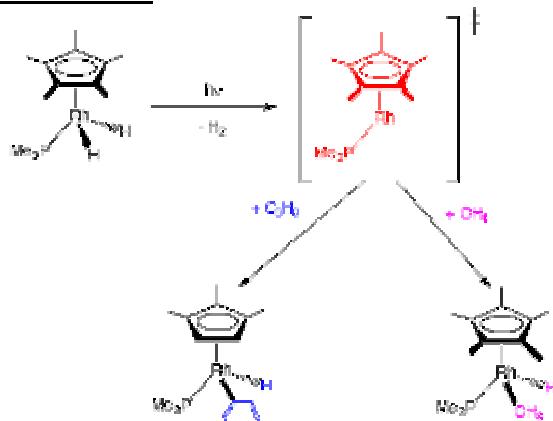
Transition Metal Example:



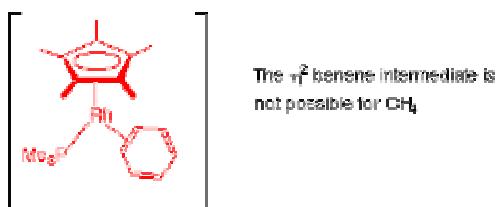
Non-transition Metal Examples:

- Me—Br + Mg → Me—Mg—Br
- PF₃ + F₂ → PF₅
- SnCl₂ + Cl₂ → SnCl₄

Carbon-Hydrogen Bond Activation



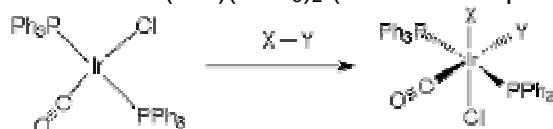
Note: Reaction proceeds faster for C_6H_6 versus CH_4 but $Ph-H$ bond stronger than CH_3-H bond



Kinetic Rate Laws for Oxidative Addition Reactions

(1) d^8 Square planar Complexes

e.g. Oxidative addition of XY to $IrCl(CO)(PPh_3)_2$ (Vaska's complex)



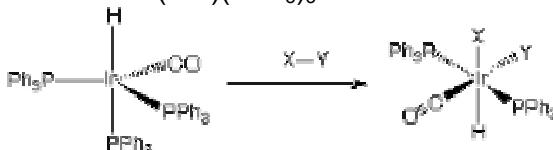
we observe:

$$\text{Rate} = k_2[\text{Ir(I)}][\text{XY}]$$

- Simple 2nd Order Kinetics
- Characteristic of Coordinatively Unsaturated systems

(2) d^8 Trigonal Bipyramidal Complexes

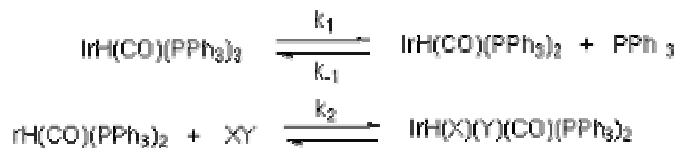
e.g. Oxidative addition of XY to $IrH(CO)(PPh_3)_3$



we observe:

$$\text{RATE} = \frac{k_1 k_2 [\text{Ir(I)}][\text{XY}]}{k_{-1} [\text{PPh}_3] + k_2 [\text{XY}]}$$

- Characteristic of Coordinatively Saturated complexes
- consistent with the following scheme:



Note: Reaction is retarded by extra phosphine.

Mechanisms of Oxidative Addition Reactions

- No single mechanism holds for all oxidative-addition reactions.
- 3 main mechanism have been observed depending on the reactants, and conditions.

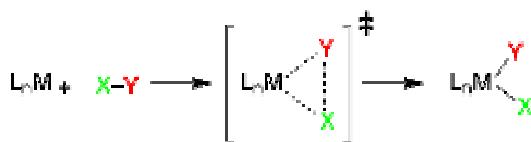
Types:

- (a) Concerted.
- (b) (i) Nucleophilic Attack ($\text{S}_{\text{N}}2$).
(ii) Ionic Mechanism.
- (c) Radical Reaction.

Concerted Mechanism

Characteristics:

- Involves a 3-centre Transition State, with side on approach of the incoming molecule.
- Molecule X—Y attaches to the reaction centre and simultaneously or subsequently undergoes electron rearrangement from X—Y bond to M—X and M—Y bonds.
i.e.

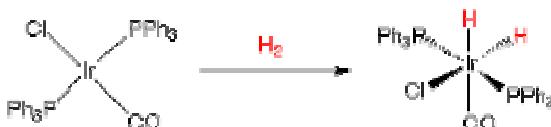


- In Transition State there is synergistic electron-flow



Features of Concerted Mechanism

- Coordinatively unsaturated molecule
- Common when X—Y group has low bond polarity, e.g. H_2 , $\text{R}_3\text{Si}-\text{H}$
- Stereospecific and cis-addition
e.g.



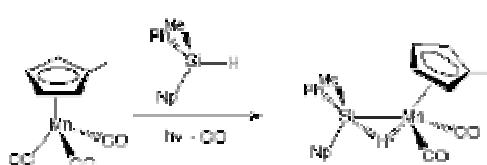
Cis-addition shown by Infrared Spectroscopy.

Observe 2 M—H stretching bands (symmetric and asymmetric)

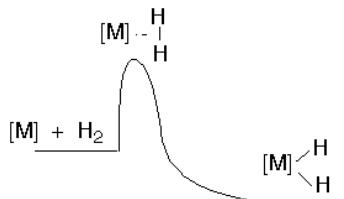
Note: Only one asymmetric if Trans.

- If X—Y is chiral then reaction proceeds with retention

e.g.



- Side on addition of H₂ has low activation energy.

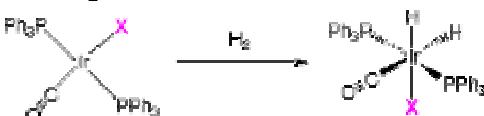


Considering the strength of H—H bond (420 kJ mol⁻¹) suggests "early T.S." with little H—H stretching.

Thus Kinetic isotope effect small:

$$\frac{K_H}{K_D} = 1.09$$

- Rates for Vaska's complex + H₂



X = I > Br > Cl (Ratios of Rate = 100:4:0.9).

Electron density on the metal centre is crucial in determining ΔG.

Donation into H₂(σ*) appears to be the most important factor.

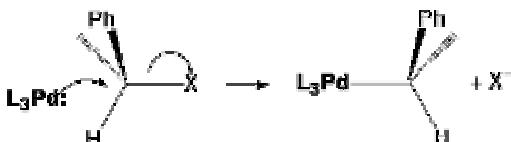
Note: If replace CO by CS (better π-Acceptor) get no reaction with H₂.

Nucleophilic Attack

- Favoured when X—Y bond is polar, e.g. RX, HX, HgCl₂.
- Dipolar Transition State expected.

Metal centre acts as electron pair donor (nucleophile).

For reactions involving R—X, inversion of stereochemistry at the α-carbon, analogous to S_N2 reactions, e.g.

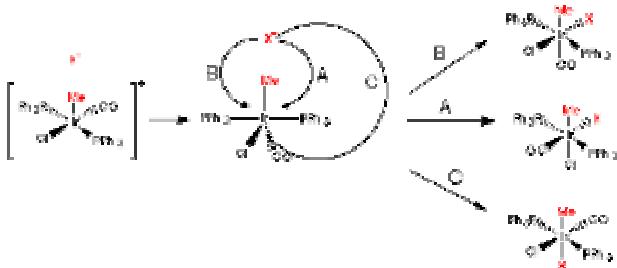


Features of nucleophilic Attack

- Trans addition.
- Rates faster in polar solvents.
- Large –ve ΔS[‡], due to solvent organisation around the dipolar Transition State.
- Rates sensitive to nature of other ligands (L) – more electron donating the ligands, faster the rate of addition.
- Hammett plots indicate increased ligand basicity leads to increased nucleophilicity of M-centre.
- Steric effects, increasing size of ligands decreases the rate of oxidative addition; due to crowding of Transition State.

Ionic Mechanism

- In polar solvents (eg. MeOH) sometimes addition less stereospecific.
- In polar solvents the lifetime of the +ve charged 5-coordinate intermediate drawn for the nucleophilic mechanism is enhanced.



Polar solvents (DMF, MeOH, H₂O, MeCN) → cis + trans

Non-polar solvents (C₆H₆, CHCl₃) → cis only

Gas phase → cis only

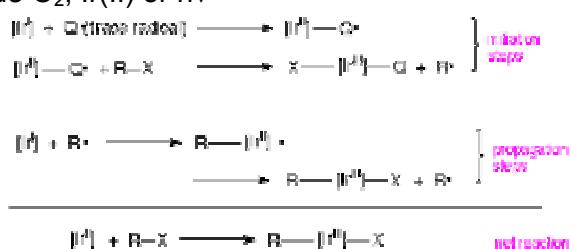
Radical Reactions

1 Alkyl (not methyl), vinyl, aryl halides react with Vaska's complex by radical chain reaction.

RATE depends on:

- (1) initiators
- (2) inhibitors
- (3) radical spin traps

Typical initiators include O₂, Ir(II) or hν



Features of chain mechanism

Complete loss of stereochemistry of R in R—X

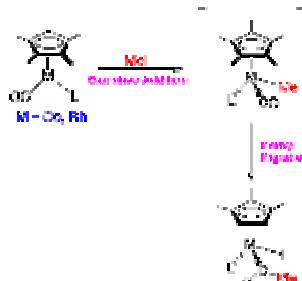
2 17-electron ML₅ complexes such as Co(II)-d⁷ undergo stepwise free radical addition.

Features of stepwise reaction:

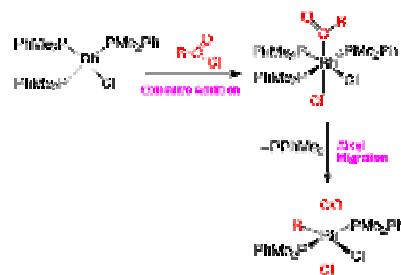
- 2nd order kinetics
- Reactants extracts a radical fragment from X—Y
- Racemisation at C-based radicals

Combined Oxidative Addition and Alkyl Migration Reactions

(A) Alkyl → Acyl

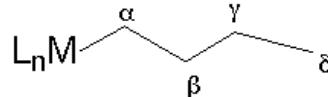


(B) Acyl \rightarrow Alkyl

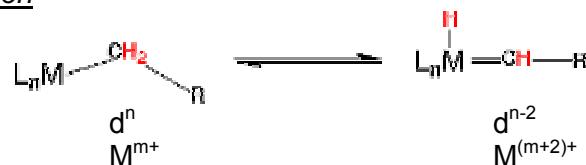


Elimination Reactions

Hydrogen Elimination Reactions



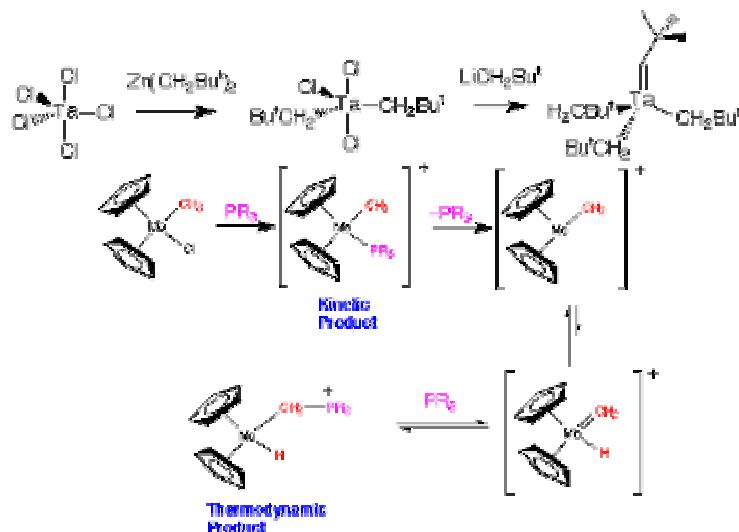
α -Hydrogen Elimination



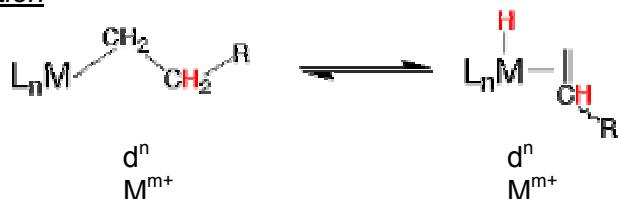
Previously α -elimination reactions were thought to be much less common than β -elimination.

Probably due to the fact that M(Carbene)Hydrides are very reactive.

Examples:

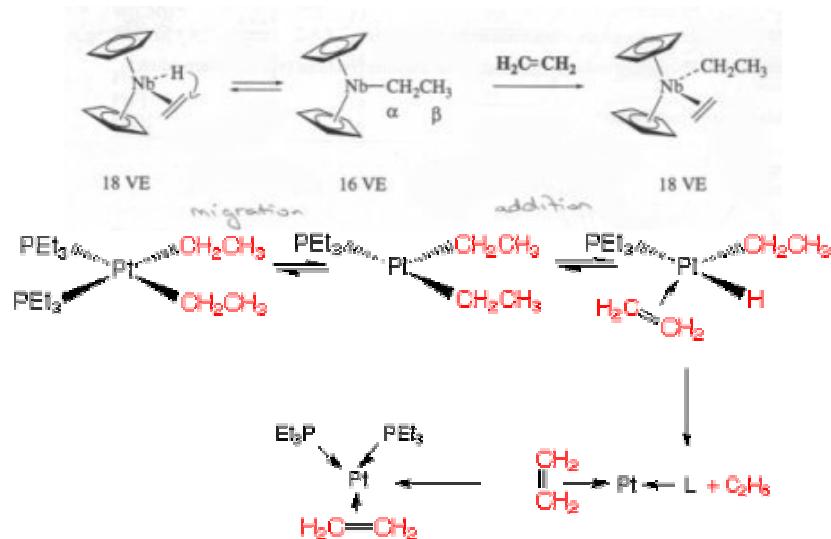


β -Hydrogen Elimination



Traditionally been assumed that the presence or absence of β -hydrogens is the most important single factor determining the stability of an alkyl ligand coordinated to a transition metal centre.

Examples:

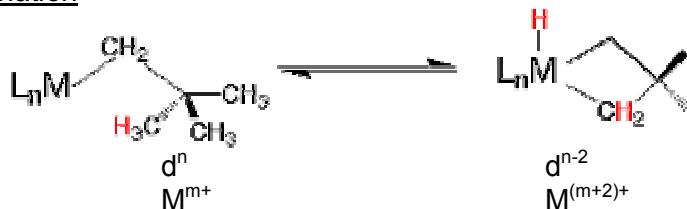


Extra Stability associated with ligands containing **no** β -hydrogens

For example: Me , CH_2Ph , CH_2Bu^t

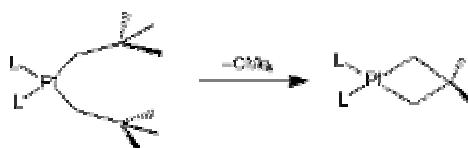


γ -Hydrogen Elimination

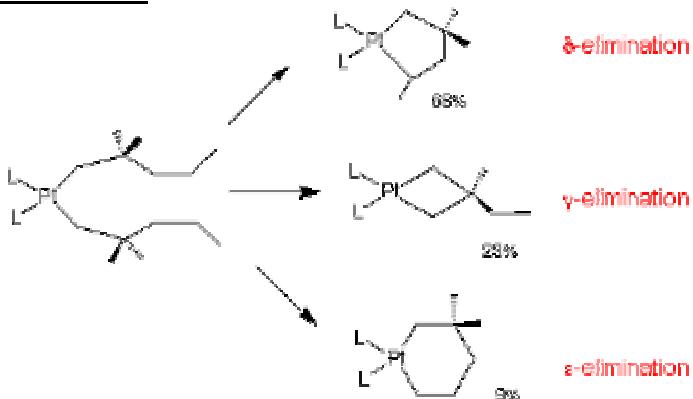


- Strong M-C bond needed (late TM's, e.g. Pt).
- Neopentyl platinum alkyls compounds tend to decompose by γ -elimination, in contrast to α -elimination which is favoured by Ta.
- May imply a different mechanism operating in each case.
- Ta case one alkyl may be deprotonated at α -carbon by another alkyl group.
- Whereas oxidative addition mechanism more likely for Pt(II).

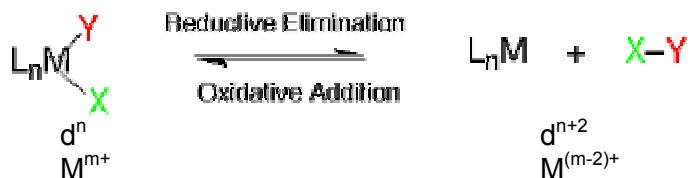
Examples:



Other Hydrogen Eliminations

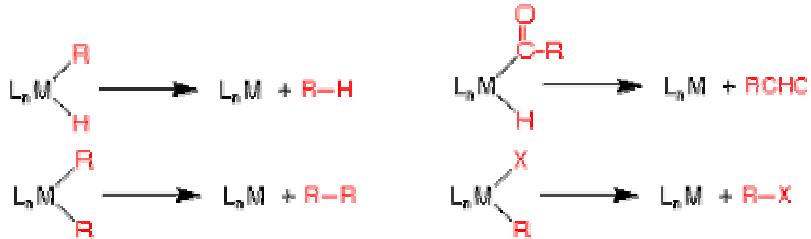


Reductive Elimination Reactions



- Reverse of oxidative addition.
- Leads to the formation of new bond between A and B groups
- Examples using a wide variety of A and B ligands are known
- Concerted reaction

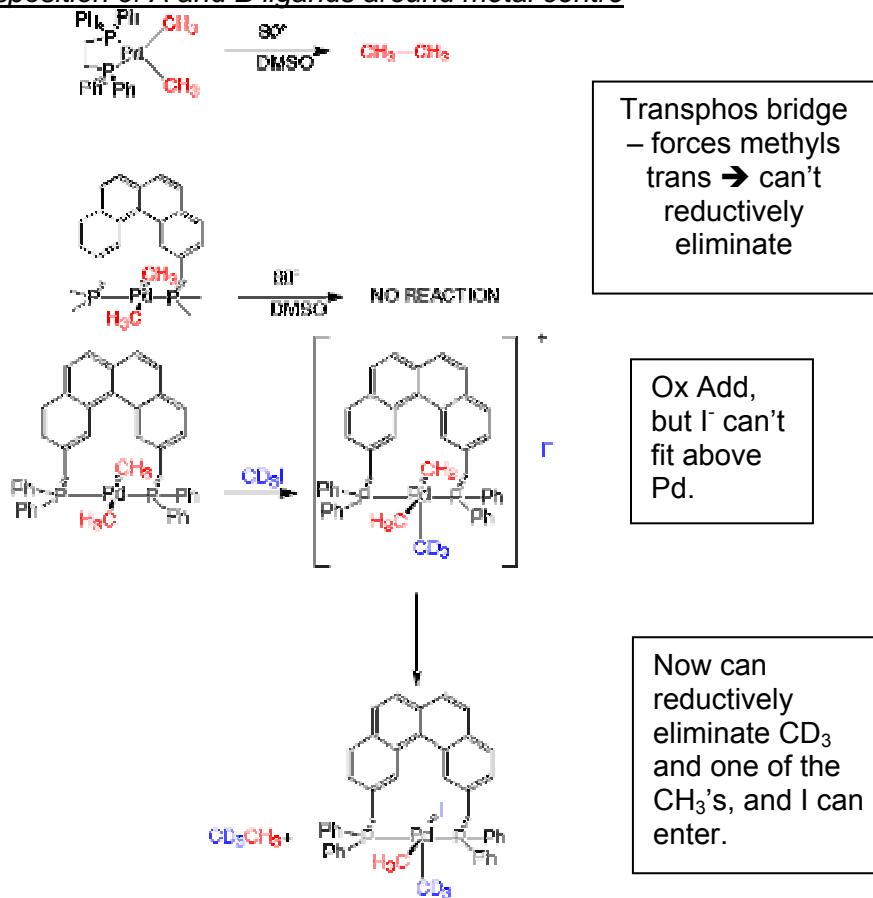
Examples:



To Enhance and/or allow intramolecular Reductive Elimination

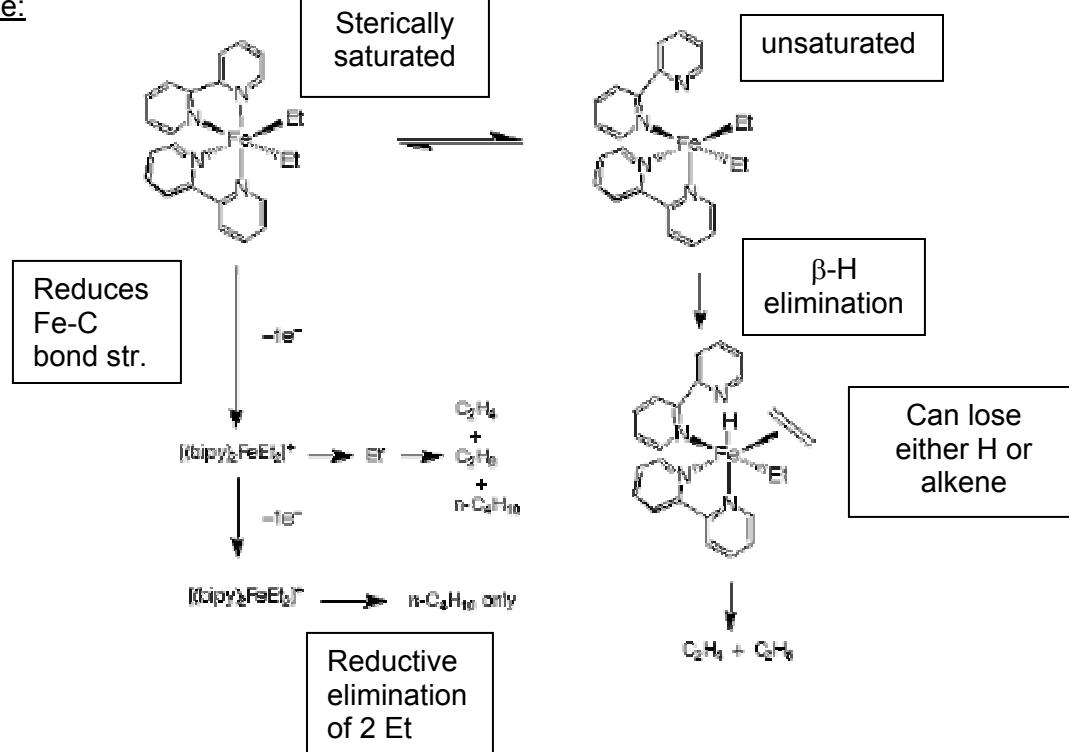
- Require **cis** disposition of A and B ligands around metal centre
- High formal charge on Metal (M)
- If the Metal centre is too electron-rich, reductive elimination will be inhibited.
- Rates of reductive Elimination
C-H > H-H > C-C
- Stereochemistry at C_α retained.

Requirement for cis disposition of A and B ligands around metal centre



High formal charge on Metal Centre

Example:

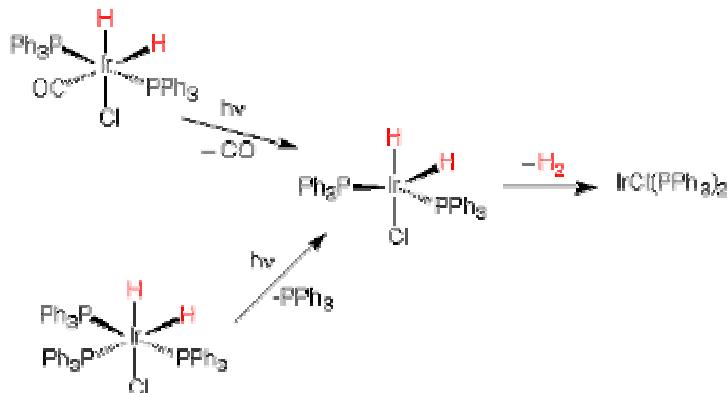


Thermolysis of neutral complex gives ethylene and ethane – result of initial β -Hydrogen elimination.

Electrochemical oxidation to the monocation gives ethylene, ethane, and butane – as a result of homolysis of Fe-Et bond, giving Et. radicals.

Further oxidation to the dication gives butane rapidly by reductive elimination.

If the Metal centre is too electron-rich, reductive elimination will be inhibited.

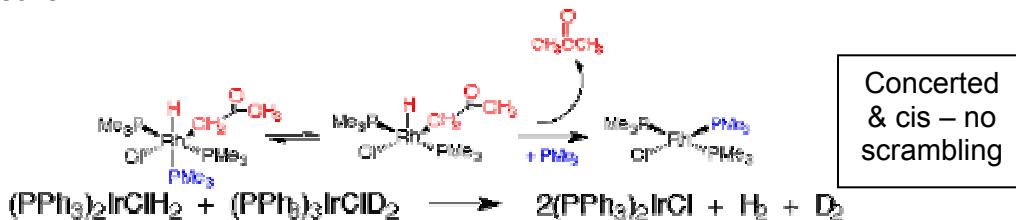


The reaction is inhibited by addition of PMe₃, implying a pre-equilibrium involving loss of PMe₃.

3 x PMe₃ make the metal centre too electron rich for elimination.

Labelling experiments show:

- Intramolecular reaction
- No crossover



Rate is 10⁷ from the coordinatively unsaturated complex above.

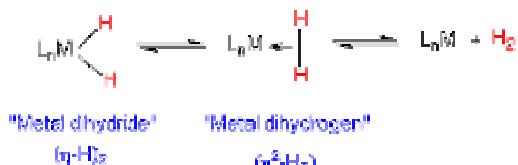
Rates of Reductive Elimination

Thermodynamic driving force ΔG^\ddagger usually increases in the order
 $H-H < C-H < C-C$

RATE: C–H > H–H > C–C

The need for reorientation of a highly directional methyl sp³ hybrid orbital leads to a substantial kinetic barrier for CH₃–CH₃ coupling.

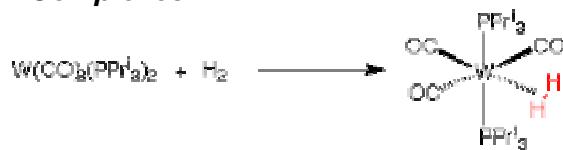
Inverse isotope effects (k_H/k_D) less than 1.0 have been observed for both C–H, and H–H elimination.



The equilibrium lies further to the right for D vs H.

Therefore $k_D > k_H$

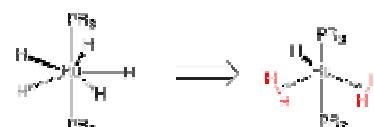
Molecular Dihydrogen Complexes



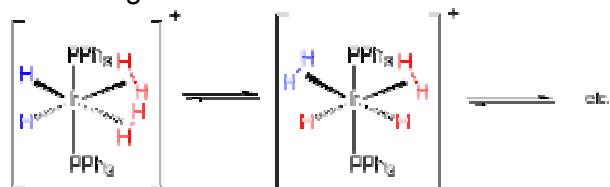
Experimental Evidence:

Neutron Diffraction (time-consuming method)	Solution NMR (modern method)
$d(\text{H}-\text{H}) = 0.84 \text{ \AA}$ compare $d(\text{H}_2) = 0.74 \text{ \AA}$	$J_{\text{HD}} \text{ ca. } 30 \text{ Hz}$ $J_{\text{HH}} \text{ ca. } 30 \times 6.66$ compare $J(\text{H}_2) \text{ ca. } 300 \text{ Hz}$

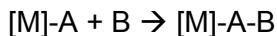
Other examples



Dihydrogen-Dihydride Exchange:



Nucleophilic Attack on Ligand



An example would be attack on Cp (complex net charged) by MeLi, or attack on an alkene (complex net charged) by H^- .

Syntheses

Alkyls –

- Transmetallation. Use Mg / Li reagents.
- Carbonylate anions, $[\text{L}_n\text{M}(\text{CO})_4]^{n-}$ act as nucleophiles to attack e.g. MeI .
- Form metal hydrides (then use these to attack alkenes and β -eliminate).
- Oxidative Addition – using e.g. MeI and 16e compound.

Carbynyls –

- metal + CO – needs low enthalpy of atomisation. Works only for Ni and Fe.
- Metal halide/salt + reducing agent + CO, e.g. $\text{CrCl}_3 + \text{Al} + 6\text{CO} \rightarrow \text{Cr}(\text{CO})_6 + \text{AlCl}_3$

Sandwich –

Arenes:

- Fischer-Hafner. Ring + $\text{MCl}_3 + \text{Al} + \text{NO}_2\text{S}_2\text{O}_4$. Works for 1st row TMs only.
- Metal atom / vapour. M(s) + electron gun, then add rings to M (atoms). Works for M = Ti, Nb, W, Mo + some lanthanides. Helps if R substituents on ring.

Cyclopentadienes:

Easier to make since Cp(-) has degree of ionic interaction. Use salt-elimination routes from $\text{NaCp} / \text{LiCp}^*$ + metal halide.