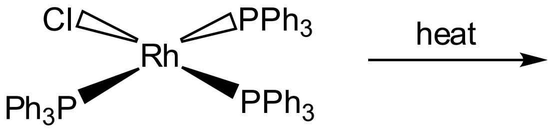
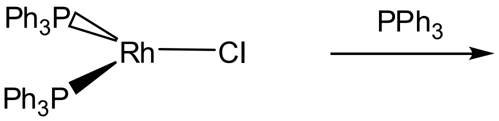
Organometallic Chemistry Basics

Ligand dissociation – is the loss of a ligand from a transition metal centre which does not involve a change in the oxidation state.

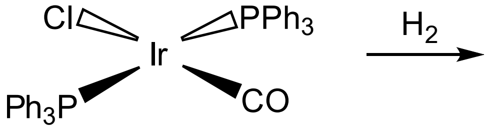


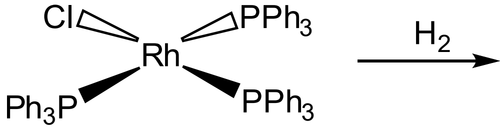
Ligand association– is the addition of a ligand to a transition metal centre that does not involve a change in the oxidation state at the metal centre.



Rh( ), VE

Oxidative addition – involves addition of a substrate to a complex with a **two** electron oxidation at the metal. The more reduced a metal centre, the greater its reactivity towards oxidative addition.



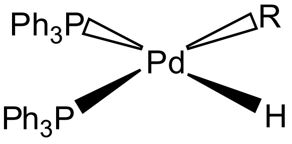


Which of the following will be **more** reactive towards oxidative addition?

$[Co(dppe)_2]^+$ $[Ir(dppe)_2]^+$

dppe = bis(diphenylphosphino)ethane

Reductive elimination – is the reverse of oxidative addition, combining ligand loss with a two electron reduction at the metal centre. The groups being eliminated must be in a *cis* orientation. Reductive elimination is more likely for compounds in high a oxidation state.



R = alkyl, aryl etc

Which of the following is **least** likely to undergo reductive elimination?

$Cp_2Ti(n\text{-}Bu)(H)$ $[(CO)_2I_3Rh(COMe)]^-$

cis-$(P\text{-}iPr_3)_2Pt(H)_2$ $Cp^*{}_2Nb(H)(C_2H_4)$

If a complex $L_nM(A)(B)$ undergoes facile reductive elimination to give AB and L_nM, then what can we say about the reverse reaction, oxidative addition of AB to L_nM?

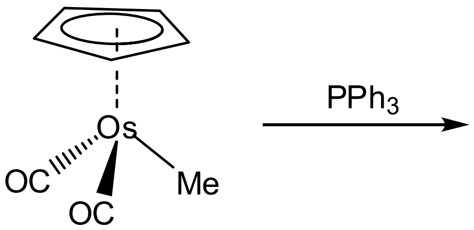
i. L_nM must oxidatively add AB with the same ease.

ii. L_nM cannot undergo oxidative addition of AB.

iii. Whether L_nM can undergo oxidative addition depends on both L_nM and AB.

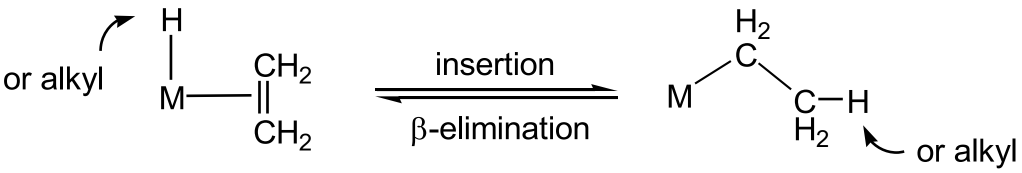
iv. The oxidative addition will be slow compared to the reductive elimination reaction.

Migratory insertion – involves a coordinated nucleophile such as an alkyl, aryl, alkoxide or amide , *cis* to a ligand, insert into the M-ligand bond. The oxidation state of the metal does not change.

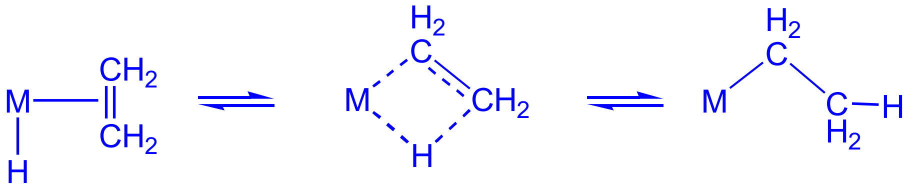


β-Hydride transfer: olefin insertion and β-elimination

The generic example of olefin insertion is into a metal-alkyl or metal-hydride bond:



The transition state involves an **agostic interaction** of the β-hydrogen of the new alkyl:

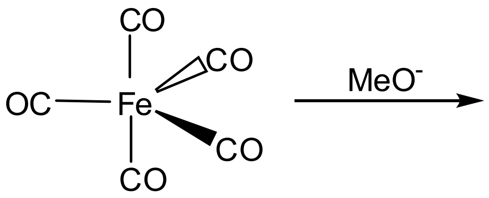


The formation of **metallacycles** is a very important step in many catalysed reactions.

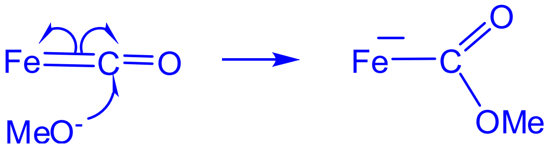
For β-hydride elimination an open coordination site on the metal complex is required.

Nucleophilic attack on coordinated ligands

Metals withdraw electron density from a ligand making the ligand electropositive and susceptible to nucleophilic attack. Nucleophilic attack at CO is involved in many catalytic processes where carbon monoxide is present as a substrate.

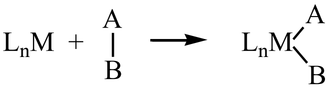
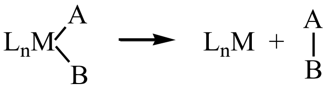
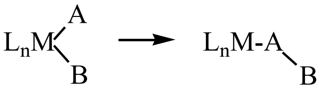
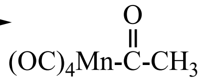
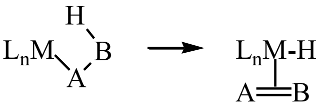


Fe( ), VE



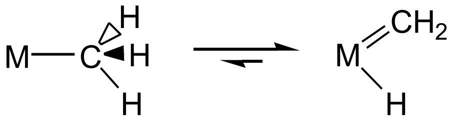
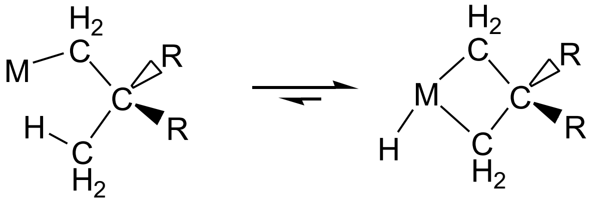
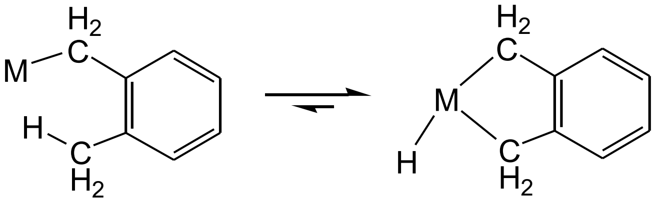
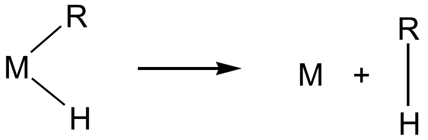
When pushing arrows with carbonyls the M=C=O valence bond form should be used.

Summary of main organometallic reactions

	ΔVE	**ΔOS**	**ΔCN**	
Ligand association				
$L_nM + L' \longrightarrow L_nM\text{-}L'$	+2	0	+1	$Pt(PPh_3)_3 + PPh_3 \longrightarrow Pt(PPh_3)_4$
Ligand dissociation				
$L_nM\text{-}L' \longrightarrow L_nM + L'$	-2	0	−1	$Cr(CO)_6 \longrightarrow Cr(CO)_5 + CO$
Oxidative addition				
	+2	+2	+2	$IrCl(CO)(PPh_3)_2 + H_2 \longrightarrow$ $IrCl(H)_2(CO)(PPh_3)_2$
Reductive elimination				
	-2	−2	−2	$IrCl(H)_2(CO)(PPh_3)_2 \longrightarrow$ $IrCl(H)_2(CO)(PPh_3)_2 + H_2$
Migratory insertion				
	-2	0	−1	$(OC)_5Mn\text{-}CH_3 \longrightarrow$  $(OC)_4Mn\text{-}\overset{\overset{\displaystyle O}{\Vert}}{C}\text{-}CH_3$
β-Elimination				
	+2	0	+1	$Cp_2Ta\text{-}CH_2\text{-}CH_3 \longrightarrow$ $Cp_2Ta(H)(\eta^2\text{-}CH_2{=}CH_2)$

Decomposition of alkyl complexes

Although β-hydride transfer is the most important process for the decomposition of alkyl complexes (see lecture notes), many other processes are also known, and they are shown below:

α-Hydrogen transfer (α-elimination)	
Cyclometallations:	
γ-hydrogen transfer	
δ-hydrogen transfer	
intramolecular elimination of hydrocarbon (reductive elim)	 (R can be an alkyl or H)
Binnuclear (intermolecular elimination)	$M{-}R + H{-}M \longrightarrow M{-}M + R{-}H$
Free radical (homolytic fission)	$M{-}R \longrightarrow M^{\bullet} + R^{\bullet}$