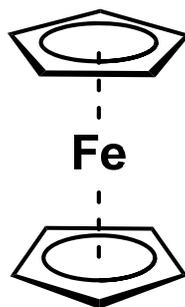


Organometallic Compounds

In simpler terms these are compounds containing metal-carbon bonds

Examples: $\text{CH}_3\text{-MgBr}$, Ph-Li , $[\text{Ni}(\text{CO})_4]$, Ferrocene etc.



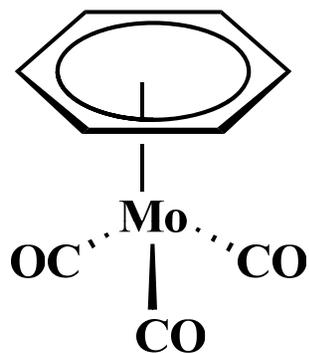
These compounds can be seen as having covalent bonds between the metal and the carbon atom(s).

In general, compounds having a metal-ligand bond of considerable covalent character have similar chemistry and follow the chemical behavior of organometallic compounds

Metal-cyano complexes are not considered as organometallic compounds, while metal carbonyl complexes are.

18-electron Rule

Having 18 electrons in the outer shell consisting of s , p and d orbitals is considered as an indication of stability as in inert gases. The rule suggests that compounds that can attain 18 electrons within the bonding orbitals of the metal show increased stability



Mo contributes 6 electrons

Benzene contributes 6 electrons

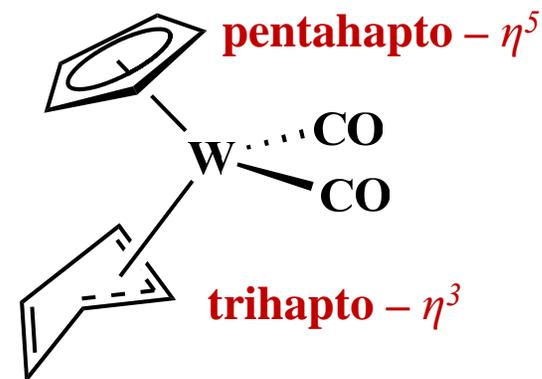
Three CO contribute 6 electrons

The compound follows 18-electron rule and is stable

Hapticity: The number of atoms in the ligand which are directly coordinated to the metal.
Hapticity is denoted as η

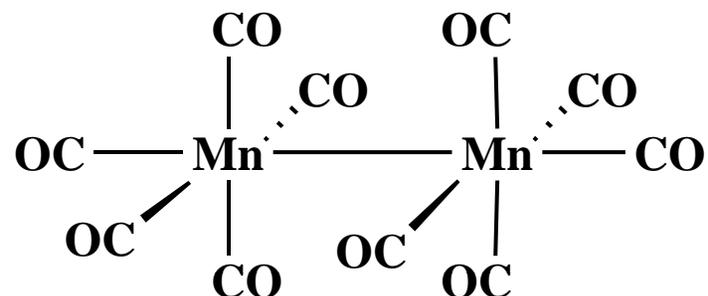
W contributes 6 electrons
One cyclopentadiene contributes 5 electrons
The other contributes 3 electrons
Two CO contribute 4 electrons

The compound follows 18-electron rule and is stable



18-electron Rule

Metals with odd number of electrons form metal-metal bonds in their carbonyl complexes to satisfy the 18-electron rule



Carbonyl groups can also bridge between two metals, where they can be seen as contributing one electron each to the two metals

Scope of 18-electron rule for *d*-block organometallic compounds

Usually less than 18 electrons			Usually 18 electrons			16 or 18	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

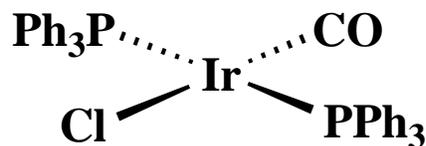
Oxidation Numbers

Oxidation numbers are important in predicting and understanding the reactivity of organometallic compounds.

Ligands such as CO, benzene are treated as neutral

Alkyl groups and hydrogen are treated as anions

Cyclopentadienyl is treated as an anion



PPh₃ and CO contribute 2 electrons each

Cl contributes one electron

Ir contributes 9 electrons

Total = 16 electrons

Oxidation state of Iridium is +1

Ni(CO)₄ – Ni(0) compound

V(CO)₆⁻ - V(-I) compound

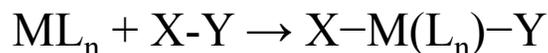
W(Me)₆ – W(VI) compound

Common Reactions

Oxidative Addition

A reaction in which (usually) a neutral ligand adds to a metal center and in doing so oxidizes the metal, typically by $2e^-$.

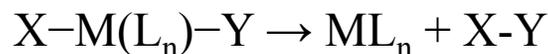
The transferring of the two electrons from the metal to the incoming ligand breaks a bond in that ligand forming two new anionic ligands. At least one of these new anionic ligands ends up bonded to the metal center.



Reductive Elimination

A reaction in which two cisoidal anionic ligands on a metal center couple together.

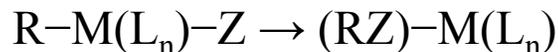
Each anionic ligand pushes one electron back onto the metal center to reduce it by $2e^-$. The coupled anionic ligands then usually fall off the metal center as a neutral molecule.



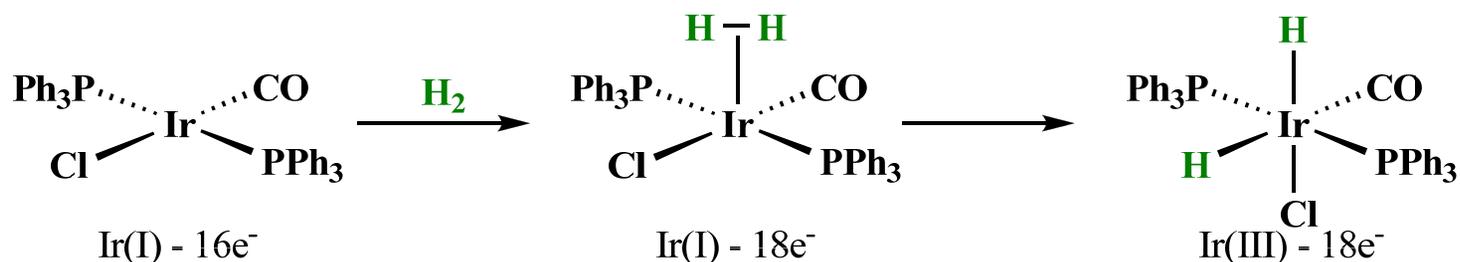
Migratory Insertion

A cisoidal anionic and neutral ligand on a metal complex couple together to generate a new coordinated anionic ligand.

There is no change in the oxidation state or d electron-count of the metal center. But the overall electron-count on the metal decreases by $2e^-$.



Oxidative Addition



Non-electrophilic: Such molecules do not contain electro-negative atoms and/or are not good oxidizing agents. They are often considered to be “non-reactive” substrates. These molecules generally require the presence of an empty orbital on the metal center in order for them to pre-coordinate prior to being activated for the oxidative addition reaction.

Examples: H₂, C-H bonds, Si-H bonds, S-S bonds, C-C bonds

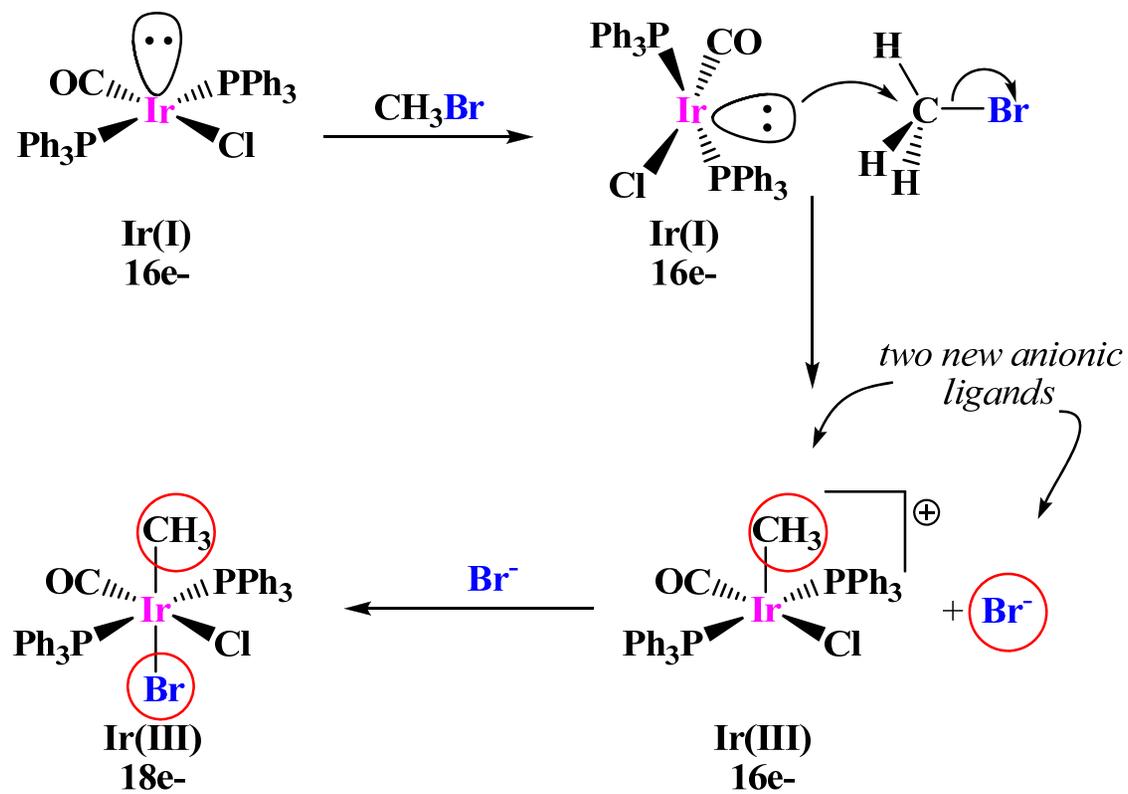
Electrophilic: Such molecules do contain electro-negative atoms and are good oxidizing agents. They are often considered to be “reactive” substrates. These molecules do not require the presence of an empty orbital (18e⁻ is OK) on the metal center in order to perform the oxidative addition reaction.

Examples: X₂ (X = Cl, Br, I), R-X, Ar-X, H-X, O₂

The most common substrates used are

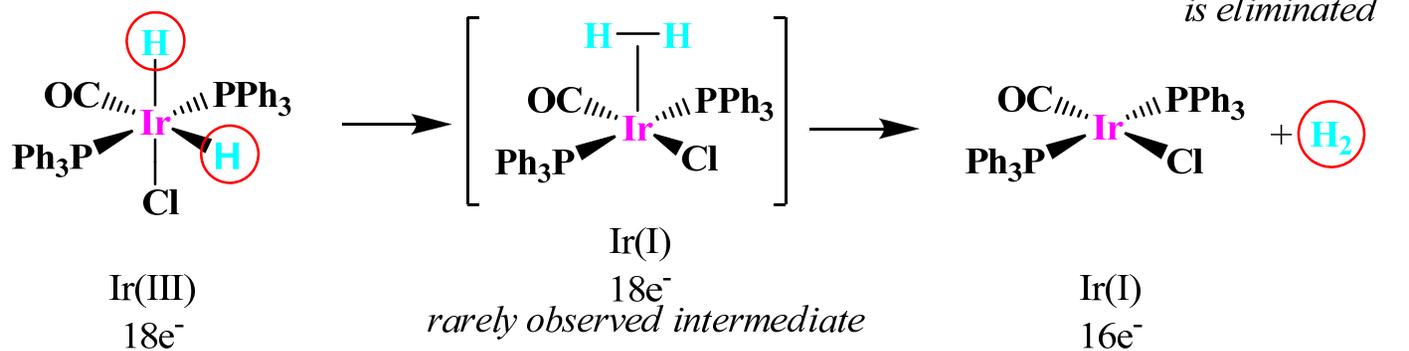
R-X (alkyl halides), Ar-X (aryl halides), and H-X.

Oxidative Addition with a Reactive Substrate



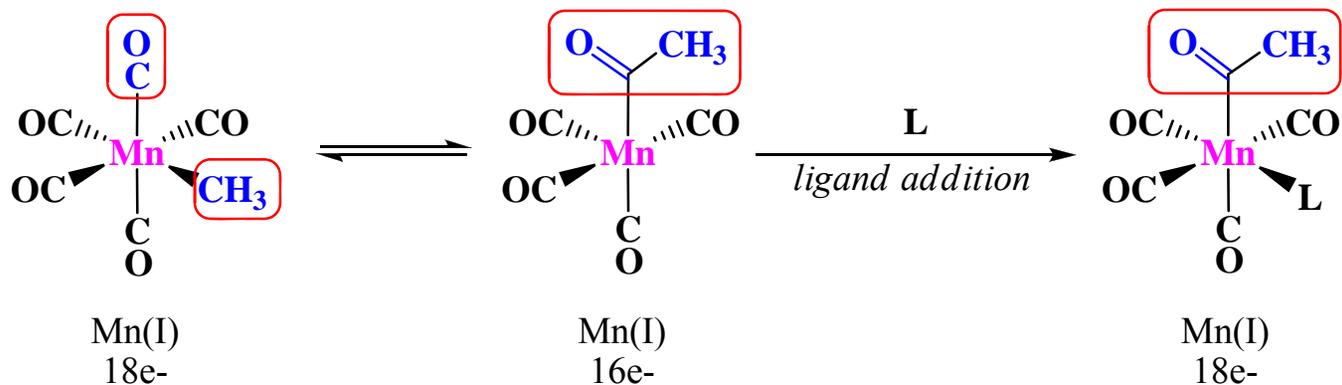
Reductive Elimination

two cisoidal anionic ligands that can form a bond between them



Generally the eliminated molecule is not a very reactive compound

Migratory Insertion



The opposite of a migratory insertion is sometimes referred to as an elimination

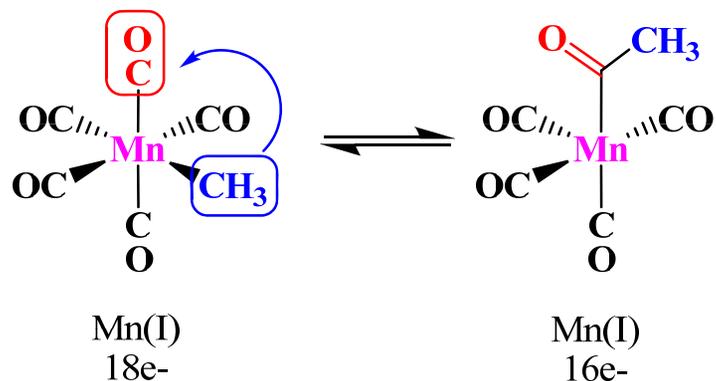
Common anionic and neutral ligands that undergo migratory insertions with one another:

Anionic: H⁻, R⁻ (alkyl), Ar⁻ (aryl), acyl⁻, O²⁻ (oxo)

Neutral: CO, alkenes, alkynes, carbenes

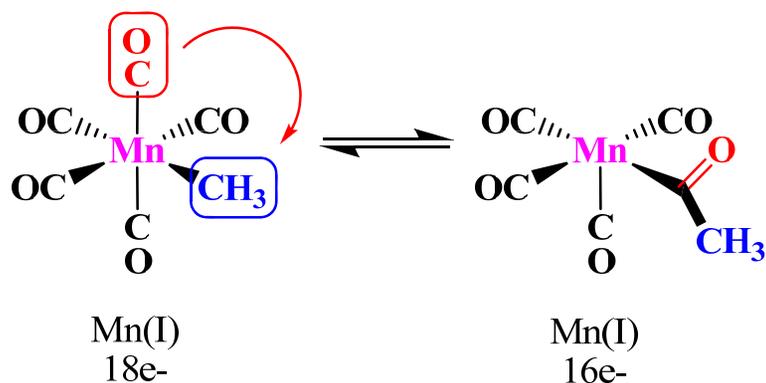
Migration vs. Insertion

Migration:



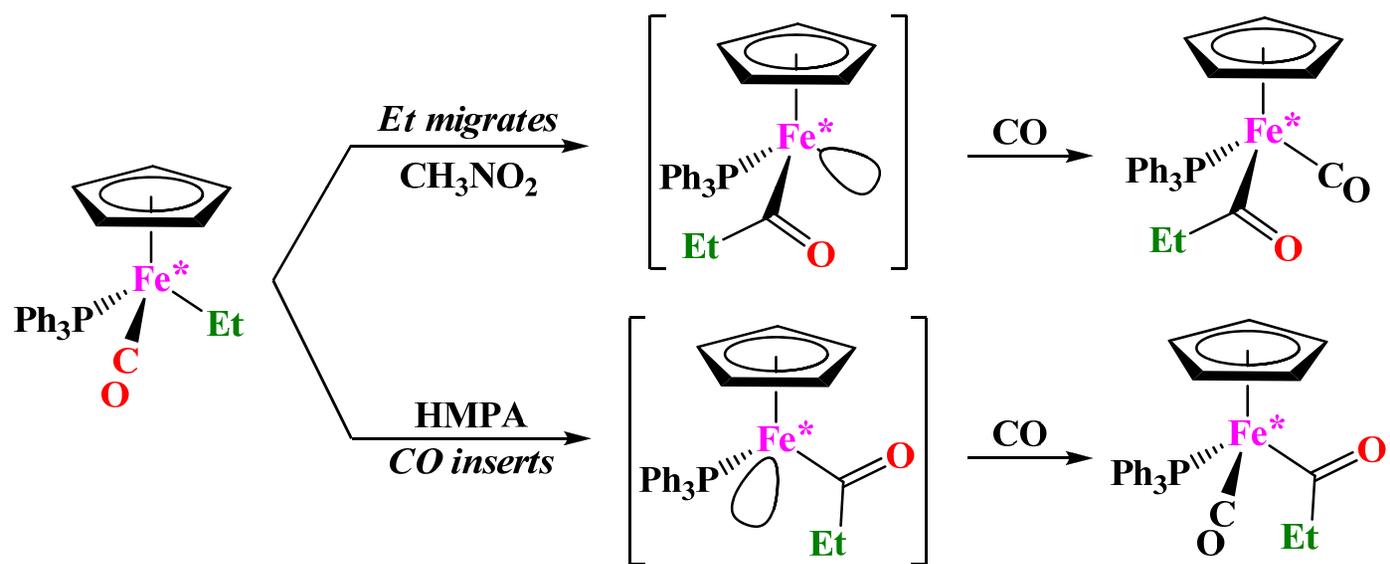
The anionic ligand does a nucleophilic-like attack on the neutral ligand. This involves the anionic ligand moving to the site where the neutral ligand is coordinated. An empty coordination site is left behind.

Insertion:



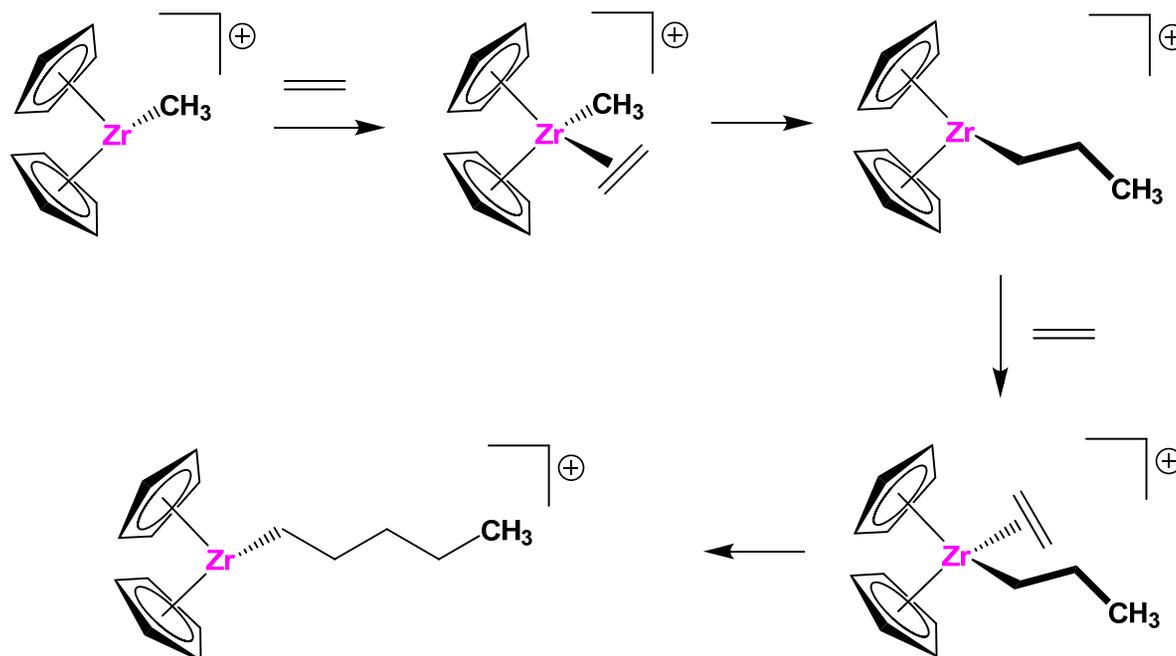
The neutral ligand moves over to where the anionic ligand is coordinated and "inserts" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind where the neutral ligand originally was located.

Migration vs. Insertion

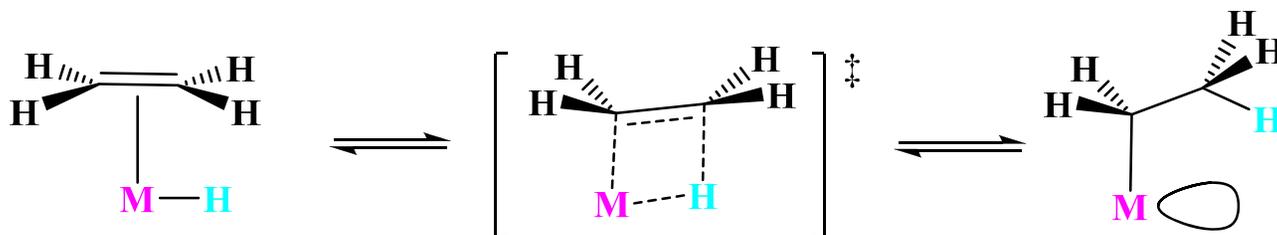


Alkene Migratory Insertions

Alkene and hydride/alkyl migratory insertions are extremely important in industry.



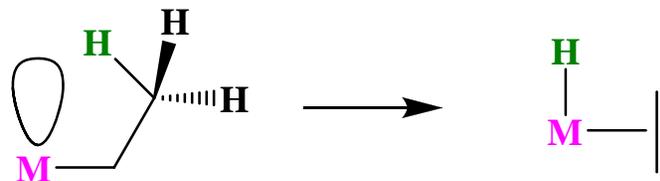
An alkene and a hydride usually react via migration of the hydride to the coordinated alkene ligand. The reverse reaction is called a β -elimination and is favored in the presence of an empty metal orbital *cis* to the alkyl ligand



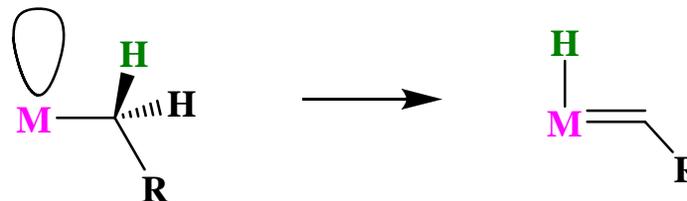
Eliminations

Elimination reactions are just the reverse of migratory insertion reactions.

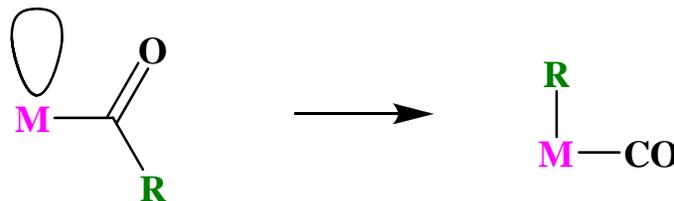
β -hydride elimination



α -hydride elimination



Carbonyl elimination or decarbonylation



One of the hardest elimination reactions is the breaking of a C-C bond.

Catalysis



Heterogeneous Catalysis: Catalyst and reactants are in different phases
95% of all chemical and petrochemical processes use heterogeneous catalysis

Homogeneous Catalysis: Catalyst is in the same phase as that of the reactants
Generally employed, when selectivity is important and isolation of products from the reaction mixture can easily be achieved.

Homogeneous catalysts are

- More selective towards the formation of a single product

- More active

- More easily studied to understand the chemical and mechanistic aspects

- More easily modifiable for optimizing selectivity

However, they

- Are more sensitive to permanent deactivation

- Lead to more difficulty in separation of products from catalyst

Terminologies in Catalysis

Turn Over (TO): Corresponds to one loop through the catalyst cycle. One equivalent of reactants is converted to one equivalent of products.

Turn Over Number (TON): The absolute number of passes through the catalytic cycle before the catalyst becomes deactivated. It is defined as the amount of reactant (moles) divided by the amount of catalyst (moles) times the percentage yield of the product. Often mol% of catalyst is used to express TON.

$$10 \text{ mol\%} = 10 \text{ TON}, 1 \text{ mol\%} = 100 \text{ TON}, 0.01 \text{ mol\%} = 10,000 \text{ TON}$$

Turn Over Frequency (TOF): The number of passes through the catalytic cycle per unit time (sec, min or h). This number is usually determined by taking the number of moles of product produced, dividing that by the number of moles of catalyst used in the reaction, and then by the time taken to produce the given amount of product. The units, therefore, are usually just time^{-1} .

For a good catalyst, TON, TOF and selectivity (chemo-, regio- and enantioselectivity) should be high.