

Organometallic Chemistry

GALGOTIAS
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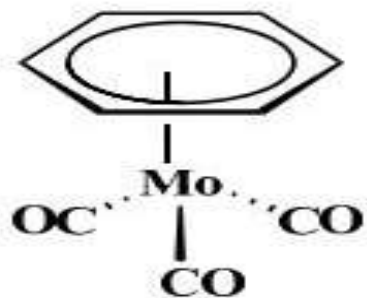
School of Basic and Applied Science

Course Code : BSCC3003

Course Name: Organometallic Chemistry

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



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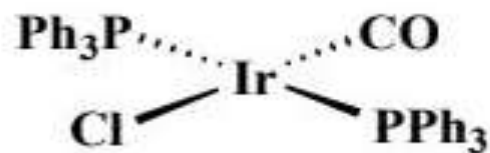
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Organometallic compounds:

Ligands such as CO, benzene are treated as neutral

Alkyl groups and hydrogen are treated as anions

Cyclopentadienyl is treated as an anion



Oxidation state of Iridium is +1

PPh₃ and CO contribute 2 electrons each

Cl contributes one electron

Ir contributes 9 electrons

Total = 16 electrons

Ni(CO)₄ – Ni(0) compound

V(CO)₆⁻ - V(-I) compound

W(Me)₆ – W(VI) compound

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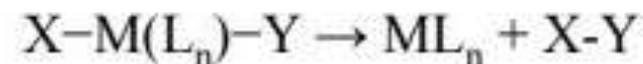
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The transferring of the two electrons from the metal to the incoming ligand breaks a bond in that ligand forming two new anionic ligands. At least one of these new anionic ligands ends up bonded to the metal center.



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

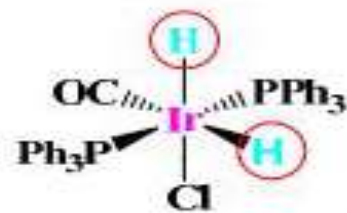
A cisoidal anionic and neutral ligand on a metal complex couple together to generate a new coordinated anionic ligand.

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 $2e^-$.



Reductive Elimination

two cisoidal anionic ligands that can form a bond between them



Ir(III)
18e⁻



Ir(I)
18e⁻
rarely observed intermediate

A neutral ligand is eliminated



Ir(I)
16e⁻

Generally the eliminated molecule is not a very reactive compound

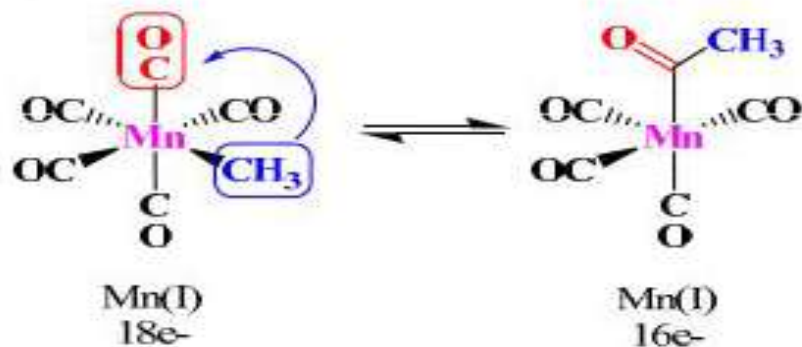
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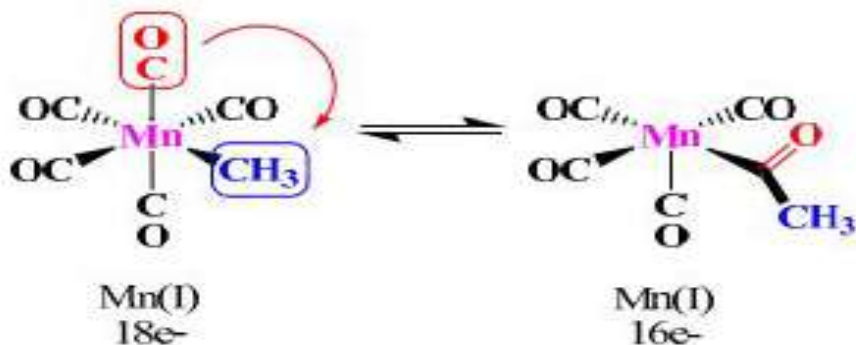
Migration vs. Insertion

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.

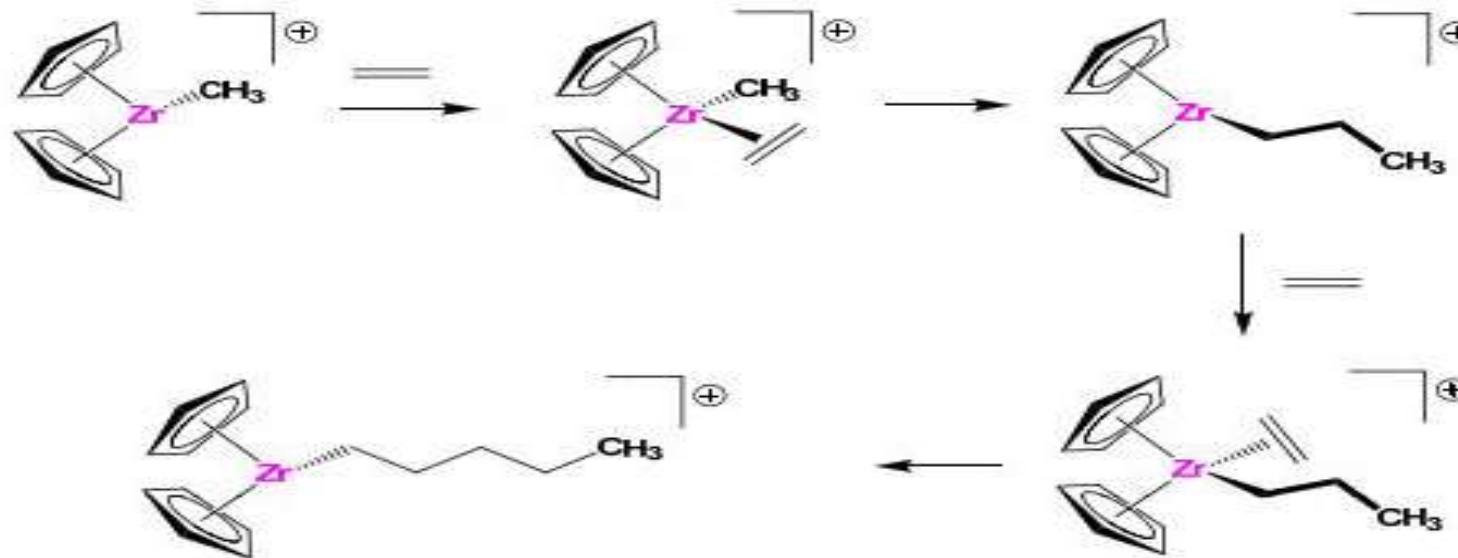
Insertion:



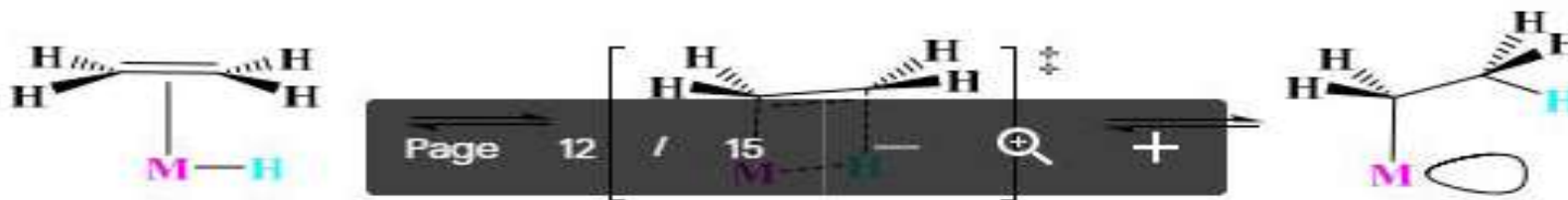
The neutral ligand moves over to where the anionic ligand is coordinated and "inserts" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind where the neutral ligand originally was located.

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



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

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2.3 CLASSIFICATION OF ANIONS (ACIDIC RADICALS)

The anions are provided by the acids in the process of salt formation; hence these are generally referred to as acidic radicals. These radicals cannot be divided in the systematic groups as has been done in the case of the cations. However, for the sake of simplicity, these have roughly been divided into three groups depending upon their reactions with certain reagents.

Classification of acidic radicals or anions:

Group	Name and formula of the Radical	Group Reagent	Inference of the group
Class I anions (First group)	Carbonate (CO_3^{2-}) Sulphite (SO_3^{2-}) Sulphide (S^{2-}) Acetate (CH_3COO^-) Nitrite (NO_2^-) Thiosulphate ($\text{S}_2\text{O}_3^{2-}$)	Dil. HCl or H_2SO_4 (Cold or hot.)	Gases of different colours and smells are evolved.
Class II anions (Second group)	Chloride (Cl^-) Bromide (Br^-) Iodide (I^-) Nitrate (NO_3^-) * Oxalate ($\text{C}_2\text{O}_4^{2-}$) * Borate (BO_3^{3-}) * Fluoride (F^-)	Conc. H_2SO_4 (hot.)	Gases of different colours and smells are evolved.
Class III anions	Sulphate (SO_4^{2-}) * Phosphate (PO_4^{3-})	Barium chloride (BaCl_2) m	A white precipitate

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Chloroform	Organic compound; often used as CDCl ₃ (deuterated chloroform) as a solvent for NMR spectroscopy and as a general solvent.
Chromic acid	A strong and corrosive oxidising agent; an intermediate in chromium plating
Chromium trioxide	The acidic anhydride of chromic acid; mainly used in chrome-plating .
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Collins reagent	Used to selectively oxidize primary alcohols to an aldehyde
Copper(I) iodide	Useful in a variety of applications ranging from organic synthesis to cloud seeding
Dess-martin periodinane	Chemical reagent used to oxidize primary alcohols to aldehydes and secondary alcohols to ketones
Diborane	The central organic synthesis reagent for hydroboration
Diethyl azodicarboxylate	A valuable reagent but also quite dangerous and explodes upon heating
Diethyl ether	Organic compound; a common laboratory solvent
Dihydropyran	A heterocyclic compound; used as a protecting group for alcohols in organic synthesis.
Diisobutylaluminum hydride	An organoaluminum compound; a reducing agent; converts esters and nitriles to aldehydes
Diisopropyl azodicarboxylate	The diisopropyl ester of azodicarboxylic acid; a

School of Media and Communication Studies

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Reference Books:

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