ORGANOMETALLIC AND CATALYSIS

Dr. Malay Dolai,

Assistant Professor,

Department of Chemistry,

Prabhat Kumar College, Contai,

Purba Medinipur-721404, WB, India.

1.Introduction

Organometallic chemistry is the study of organometallic compounds, chemical compounds containing at least one chemical bond between a carbon atom of an organic molecule and a metal, including alkaline, alkaline earth, and transition metals, and sometimes broadened to include metalloids like boron, silicon, and tin, as well. Aside from bonds to organyl fragments or molecules, bonds to 'inorganic' carbon, like carbon monoxide (metal carbonyls), cyanide, or carbide, are generally considered to be organometallic as well. Some related compounds such as transition metal hydrides and metal phosphine complexes are often included in discussions of organometallic compounds, though strictly speaking, they are not necessarily organometallic. The related but distinct term "metalorganic compound" refers to metal-containing compounds lacking direct metal-carbon bonds but which contain organic ligands. In 1827, Zeise's salt is the first platinum-olefin complex: $K[PtCl_3(C_2H_4)].H_2O$, the first invented organometallic compound.

Organometallic compounds find wide use in commercial reactions, both as homogeneous catalysis and as stoichiometric reagents For instance, organolithium, organomagnesium, and organoaluminium compounds, examples of which are highly basic and highly reducing, are useful stoichiometrically, but also catalyze many polymerization reactions. Almost all processes involving carbon monoxide rely on catalysts, notable examples being described as carbonylations. The production of acetic acid from methanol and carbon monoxide is catalyzed via metal carbonyl complexes in the Monsanto process and Cativa process. Most synthetic aldehydes are produced via hydroformylation. The bulk of the synthetic alcohols, at least those larger than ethanol, are produced by hydrogenation of hydroformylation-derived aldehydes. Similarly, the Wacker process is used in the oxidation of ethylene to acetaldehyde. Almost all industrial processes involving alkene-derived

polymers rely on organometallic catalysts. The world's polyethylene and polypropylene are produced via both heterogeneously via Ziegler–Natta catalysis and homogeneously, e.g., via constrained geometry catalysts.

2. Definition of Organometallics

The compounds that contain a metal-carbon bond, R-M, are known as "organometallic" compounds. Organometallic compounds of Li, Mg (Grignard reagents) are amongst some of the most important organic reagents. In general, organometallic compounds (metal organyls, organometallics) are defined as materials which possess direct, more or less polar bonds $M^{\delta+}\!-\!C^{\delta-}$ between metal and carbon atoms i.e covalent character and follow the chemical behavior of organometallic compounds. It encompasses a wide variety of chemical compounds and their reactions, including compounds containing both σ and π bonds between metal atoms and carbon, many cluster compounds, containing one or more metal-metal bonds. Aside from their intrinsically interesting nature, many organometallic compounds form useful catalysts and consequently are of significant industrial interest.

Examples: CH_3-MgBr, Ph-Li, [$Ni(CO)_4$], Ferrocene, organo-borane compounds such as triethyl-borane (Et_3B). etc. Metal-cyano complexes are not considered as organometallic compounds while metal carbonyl complexes are this type compounds.

2.1 Classification of organometallic compounds

Classification based on the nature of Metal-Carbon bond. The following five types of organometallic compounds can be distinguished depending upon the nature of metal-carbon bond.

[1] Ionic organometallic compounds

[2]Organometallic compounds containing metal-carbon sigma (σ) bond.

[3] Ylides.

[4] Organometallic compounds with multicentre bonds.

[5] Organometallic compounds with pi(π) bonded ligands.

Ionic organometallic compounds:

Most of the organometallic compounds of alkali metals fall in this category. They have short life because of their high reactivity. Examples are $Na^+(CH_2=CH-CH_2)^-$,$Na^+(CH_2-C_6H_5)^-$,$Na^+(C_6H_5)^-$, $Na^+(C_5H_5)^-$, etc

Organometallic compounds containing metal-carbon sigma (σ) bond:

Metallic elements of Group II, III, IV and V as well as transition metals form organometallic compounds in which the metal atoms are bonded to carbon atoms by sigma bond. Organometallic compounds of transition metals: Very few examples of alkyl compounds of transition metals are known because of their greater reactivity. The alkynyl compounds [M-C≡C-R] are more stable than alkyl or aryl complexes. The first genuine organometallic compound containing a metal — carbon σ bond, C_2H_5ZnI was prepared in 1849 by Frankland. In 1952, when the first compound containing a covalent Ti-C-bond was isolated, was the characterization of the first organo-metallic compound containing a carbon —metal σ bond accomplished.

Ylides:

A ylide or ylid is a neutral dipolar molecule containing a formally negatively charged atom (usually a carbanion) directly attached to a hetero atom (usually nitrogen, phosphorus or sulphur), with a formal positive charge and in which both atoms have full octets of electrons. Ylides are thus 1,2-dipolar organometallic compounds. One of the most celebrated reactions for converting aldehydes and ketones to alkenes employs phosphorus ylides ($RC^-H-P^+Ph_3$) in the Wittig reaction.

Organometallic compounds with multicentre bonds:

Organometallic compounds are of multicentre bonds seen in metal carbonyl complexes where metal carbonyls contain two or more metal atoms, such as decacarbonyldimanganese {$Mn_2(CO)_{10}$} and octacarbonyldicobalt {$Co_2(CO)_8$}. In all these structures carbon monoxide is connected to the metal through its carbon atom. When more than one metal atom is present, as in octacarbonyldicobalt, the carbon of the carbonyl ligand may bridge between metal atoms.

Organometallic compounds with pi(π) bonded ligands:

An alkene ligand contains a π bond between carbon atoms, C=C, which can serve as an electron pair donor in a metal complex, as in the case of Zeise's salt. This complex may be prepared by bubbling ethylene, C_2H_4, through an aqueous solution of $[PtCl_4]^{2-}$ in the presence of divalent tin, Sn(II), which aids in the removal of the chloride ion (Cl^-) from the coordination sphere of the divalent platinum, Pt(II).

$$K_2[PtCl_4] + H_2C=CH_2 \xrightarrow{\text{SnCl}_2} K[PtCl_3(\eta^2\text{-}C_2H_4)] + KCl$$
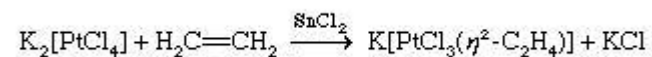
The alkene ligand bonds to the metal centre by both electron donation and acceptance, similar to the situation with carbon monoxide. Electron donor-and-acceptor character between the metal and the alkene ligand appear to be fairly evenly balanced in most ethylene complexes of the *d* metals.

3. Hapticity of ligands

The number of atoms in the ligand which are directly coordinated to the metal or to describe how a group of contiguous atoms of a ligand are coordinated to a central atom. Hapticity is denoted as η i.e a ligand is indicated by the Greek character 'eta', η.

η^n: n = the number of contiguous atoms of the ligand that are bound to the metal.

The term is usually employed to describe ligands containing extended π-systems or where agostic bonding is not obvious from the formula.

i) Ferrocene: bis(η^5-cyclopentadienyl)iron

ii) Zeise's salt: $K[PtCl_3(\eta^2\text{-}C_2H_4)].H_2O$

iii) Uranocene: bis(η^8-1,3,5,7-cyclooctatetraene)uranium

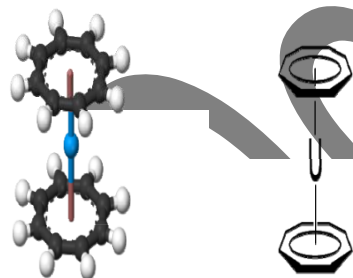iv) $W(CO)_3(PPr^i_3)_2(\eta^2\text{-}H_2)$

v) $IrCl(CO)[P(C_6H_5)_3]_2(\eta^2\text{-}O_2)$

TABLE 1.Electrons donated by "π-ligands" vs. hapticity

	(neutral counting)	(ionic counting)
η^1-Allyl	1	2
η^3-Allyl, cyclopropeny	3	4
η^3-Allenyl	3	4
η^2-Butadiene	2	2
η^4-Butadiene	4	4

η^1-cyclopentadienyl	1	2
η^5-cyclopentadienyl	5	6
cyclohexadienyl		
η^2-Benzene	2	2
η^6-Benzene	6	6
η^7-Cycloheptatrienyl	7	6
η^8-Cyclooctatetraenyl	8	10

4. 18-electron rule and its applications

The 18-electron rule is a rule of thumb used primarily in transition metal chemistry for characterizing and predicting the stability of metal complexes. The rule states that thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d electrons and the electrons conventionally considered as being supplied by the surrounding ligands equals to 18.   The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs. This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding. When a metal complex has 18 valence electrons, it is said to have achieved the same electron configuration as the noble gas in the period. The rule and its exceptions are similar to the application of the octet rule to main group elements.

4.1 Applications

The rule usefully predicts the formulas for low-spin complexes of the Cr, Mn, Fe, and Co. Well-known examples include ferrocene, iron pentacarbonyl, chromium carbonyl, and nickel carbonyl.

Ligands in a complex determine the applicability of the 18-electron rule. In general, complexes that obey the rule are composed at least partly of π-acceptor ligands (also known as π-acids). This kind of ligand exerts a very strong ligand field, which lowers the energies of the resultant molecular orbitals so that they are favorably occupied. Typical ligands include olefins, phosphines, and CO. Complexes of π-acids typically feature metal in a low-oxidation state. The relationship between oxidation state and the nature of the ligands is rationalized within the framework of π back-bonding.

The ligands in a complex play an important role in determining whether or not it obeys the 18-electron rule. Generally, complexes that do obey the rule have ligands that are π-acids. This kind of ligand typically exerts very strong carbonyls. Metals form the best complexes with π-acids when the metal is in a low-oxidation state (because then you get good overlap of metal and ligand orbitals, and the metal can donate electrons back to the ligand in a synergic fashion), so complexes that obey the 18-electron rule generally have the metal in a low-oxidation state too.

This is not to say that all complexes with low oxidation-state metal and π-acidic ligands have 18 electrons - see below for counterexamples. It is also not to say that if a metal is in a high oxidation state or does not have π-acidic ligands it cannot have 18 electrons.

Compounds that obey the 18-electron rule are typically "exchange inert". Examples include $[Co(NH_3)_6]Cl_3$, $Mo(CO)_6$, and $[Fe(CN)_6]^{4-}$. In such cases, in general ligand exchange occurs via dissociative substitution mechanisms, wherein the rate of reaction is determined by the rate of dissociation of a ligand. It can, however, be compared to the octet rule for carbon, which equally makes enough covalent bonds to fill its valence orbitals. On the other hand, 18-electron compounds can be highly reactive toward electrophiles such as protons, and such reactions are associative in mechanism, being acid-base reactions.

4.2 Using the 18-electron rule

The usefulness of the 18-electron rule becomes more apparent when one considers what chemical transformations or derivatives might be readily accessible. Using the ionic approach, removing one cyclopentadienyl anion yields a cationic fragment containing one cyclopentadienyl (Cp) fragment and 12 valence shell electrons. Since each carbon monoxide

ligand contributes 2 electrons (3 CO ligands give the requisite 6 electrons), it should be possible to create an iron-containing complex cation containing one cyclopentadienyl group, one iron atom, and 3 carbon monoxide ligands:

$CpFe(CO)_3^+$
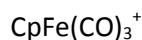
What one finds is that the iron complex satisfies the 18 electron count another way, by forming a dimer with an Fe-Fe bond (see Cyclopentadienyliron dicarbonyl dimer). Counting electrons for just one iron center can be done by considering the other iron as contributing 1 electron to the count:

$[CpFe(CO)_2]_2$
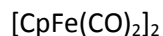
neutral counting: Cp 5 + Fe 8 + 2 CO 4 + Fe 1 = 18

Another stable compound is obtained, when one small monoanionic ligand is used:

$CpFe(CH_3)(CO)_2$
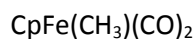
Neutral counting: Cp 5,Fe 8e, CH_3 1e, CO 2e, 5+8+1+4 = 18

Other stable compounds are obtained follow the 18-electron counts $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$.
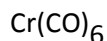
$Cr(CO)_6$

Neutral counting: Cr 6e, CO 2e, 6 + 2(6) = 18 valence electrons
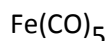
$Fe(CO)_5$

Neutral counting: Fe 8e, CO 2e, 8 + 2(5) = 18 valence electrons

$Ni(CO)_4$

Neutral counting: Ni 10e, CO 2e, 10+ 2(4) = 18 valence electrons

Since these are the 18-electron compounds, so $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$ are stable compounds.

4.3 16-electron complexes

Important classes of complexes that violate the 18e rule are the 16-electron complexes with metal d^8 configurations. All high-spin d^8 metal ions are octahedral (or tetrahedral), but the low-spin d^8 metal ions are all square planar. Important examples of square-planar low-spin d^8 metal Ions are Rh(I), Ir(I), Ni(II), Pd(II), and Pt(II). At picture below is shown the splitting of the d subshell in low-spin square-planar complexes. Examples are especially prevalent for derivatives of the cobalt and nickel triads. Such compounds are typically square-planar. The most famous example is Vaska's complex (IrCl(CO)(PPh$_3$)$_2$), $[PtCl_4]^{2-}$, and Zeise's salt $[PtCl_3(\eta^2-C_2H_4)]^-$. In such complexes, the dz^2 orbital is doubly occupied and nonbonding.

Square Planar d^8 Tetrahedral d^8
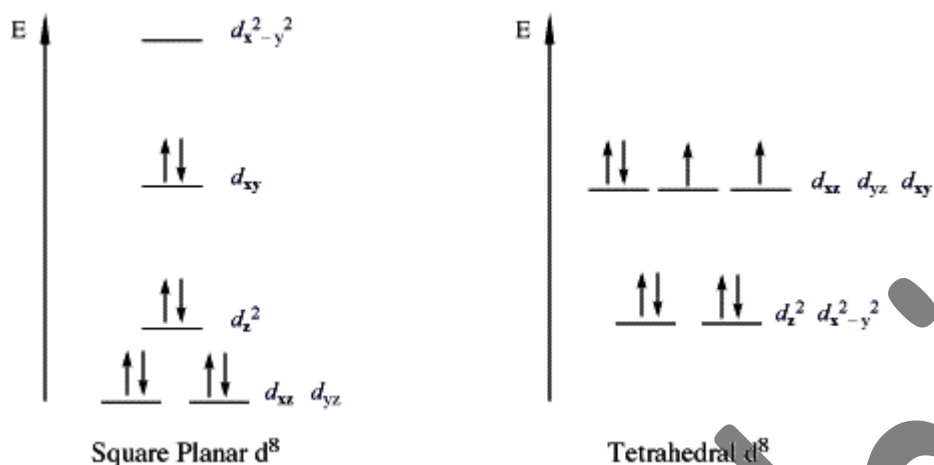
Many catalytic cycles operate via complexes that alternate between 18-electron and square-planar 16-electron configurations. Examples include Monsanto acetic acid synthesis, hydrogenations, hydroformylations, olefin isomerizations, and some alkene polymerizations. The sterically demanding bulky ligands force complexes to have less than 18 electrons. The coordination number around the metal normally remains six or lesser species such as $Mn(CO)_5$, $Co(CO)_4$ dimerize to gain 18 electrons to $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ respectively.

5. Metal carbonyls of 3d series

Metal carbonyls are coordination complexes of transition metals with carbon monoxide ligands. Metal carbonyls are useful in organic synthesis and as catalysts or catalyst precursors in homogeneous catalysis, such as hydroformylation and Reppe chemistry. In the Mond process, nickel tetracarbonyl is used to produce pure nickel. In organometallic chemistry, metal carbonyls serve as precursors for the preparation of other organometalic complexes.

Metal carbonyls are the transition metal complexes of carbon monoxide containing metal-carbon bond. Lone pair of electrons are available on both carbon and oxygen atoms of carbon monoxide ligand. However, as the carbon atoms donate electrons to the metal, these complexes are named as carbonyls.

A variety of such complexes such as mono nuclear, poly nuclear, homoleptic and mixed ligand are known. These compounds are widely studied due to industrial importance, catalytic properties and structural interest.
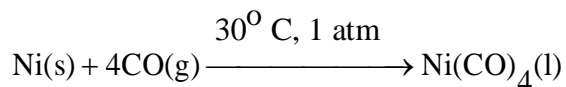
Carbon monoxide is one of the most important π- acceptor ligand. Because of its π- acidity,

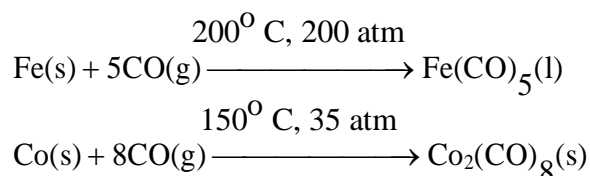carbon monoxide can stabilize zero formal oxidation state of metals in carbonyl complexes.

5.1 SYNTHESIS OF METAL CARBONYLS

Following are some of the general methods of preparation of metal carbonyls.
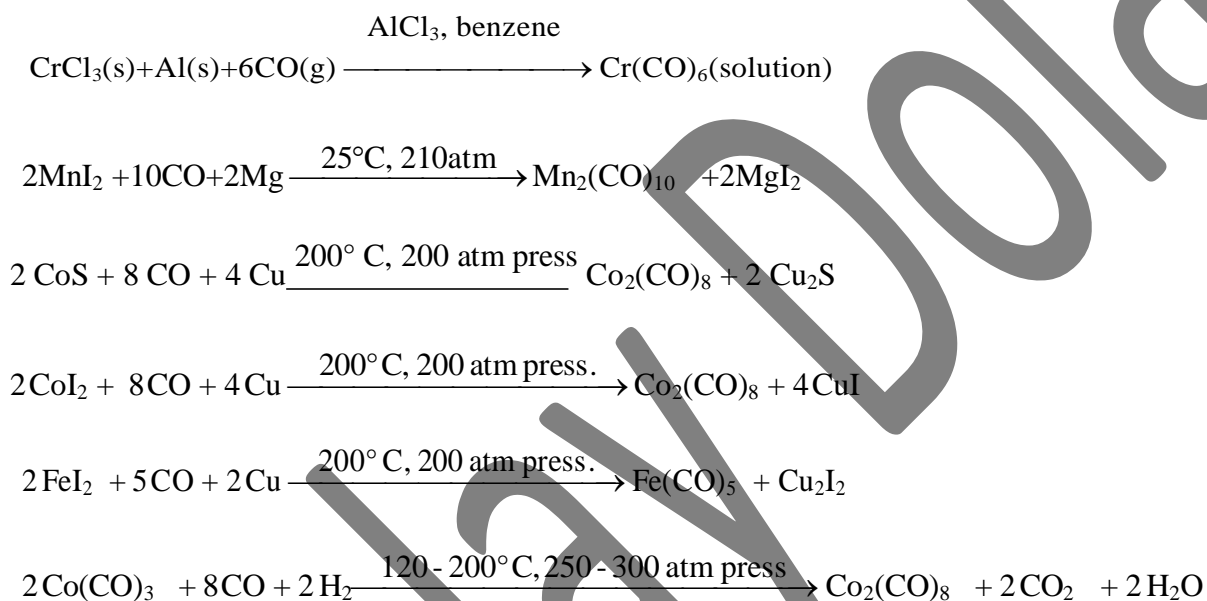
Direct Combination:

Only $Ni(CO)_4$ and $Fe(CO)_5$ and $Co_2(CO)_8$ are normally obtained by the action of carbon monoxide on the finely divided metal at suitable temperature and pressure.

$$Ni(s) + 4CO(g) \xrightarrow{\quad 30^O\ C,\ 1\ atm \quad} Ni(CO)_4(l)$$

$$\text{Fe(s)} + 5\text{CO(g)} \xrightarrow{\quad 200^O \text{ C, 200 atm} \quad} \text{Fe(CO)}_5\text{(l)}$$

$$\text{Co(s)} + 8\text{CO(g)} \xrightarrow{\quad 150^O \text{ C, 35 atm} \quad} \text{Co}_2\text{(CO)}_8\text{(s)}$$

Reductive carbonylation:

Many metallic carbonyls are obtained when salts like $CrCl_3$, VCl_3, CoS, $Co(CO)_3$, CoI_2 etc. are treated with carbon monoxide in presence of suitable reducing agent like Mg, Ag, Cu, Na, H_2, $AlLiH_4$ etc.

$$CrCl_3\text{(s)} + Al\text{(s)} + 6CO\text{(g)} \xrightarrow{\quad AlCl_3,\ \text{benzene} \quad} Cr(CO)_6\text{(solution)}$$

$$2MnI_2 + 10CO + 2Mg \xrightarrow{\quad 25°C,\ 210atm \quad} Mn_2(CO)_{10} + 2MgI_2$$

$$2\ CoS + 8\ CO + 4\ Cu \xrightarrow{\quad 200°\ C,\ 200\ \text{atm press} \quad} Co_2(CO)_8 + 2\ Cu_2S$$

$$2CoI_2 + 8CO + 4Cu \xrightarrow{\quad 200°C,\ 200\ \text{atm press.} \quad} Co_2(CO)_8 + 4CuI$$

$$2FeI_2 + 5CO + 2Cu \xrightarrow{\quad 200°C,\ 200\ \text{atm press.} \quad} Fe(CO)_5 + Cu_2I_2$$

$$2Co(CO)_3 + 8CO + 2H_2 \xrightarrow{\quad 120\text{-}200°C,\ 250\text{-}300\ \text{atm press} \quad} Co_2(CO)_8 + 2CO_2 + 2H_2O$$

5.2 Preparation of dinuclear carbonyls from mononuclear carbonyls:

When a cold solution of $Fe(CO)_5$ in glacial CH_3COOH is irradiated with ultra-violet light, $Fe_2(CO)_9$ are obtained.

$$Fe(CO)_5 \xrightarrow{\quad h\nu \quad} Fe_2(CO)_9 + CO$$

$$Os(CO)_5 \xrightarrow{\quad h\nu \quad} Os_2(CO)_9 + CO$$
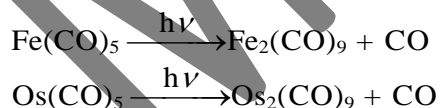
5.3 PHYSICAL PROPERTIES

State:

Majority of the metallic carbonyls are liquids or volatile solids.

Colour:

Most of the mononuclear carbonyls are colourless to pale yellow. $V(CO)_6$ is a bluish-black solid. Polynuclear carbonyls exhibit are dark in colour.

Solubility:

Metal carbonyls are soluble in organic solvents like glacial acetic acid, acetone, benzene, carbon tetrachloride and ether.

Toxicity:

Due to low melting points and poor thermal stability, they show toxicity related to the corresponding metal and carbon monoxide. Exposure to these compounds can cause damage to lungs, liver, brain and kidneys. Nickel tetracarbonyl exhibits strongest inhalation toxicity. These compounds are carcinogenic over long-term exposure.

Magnetic Property:

All the metal carbonyls other than vanadium hexacarbonyl are diamagnetic. The metals with even atomic number form mononuclear carbonyls. Thus, all the electrons in the metal atoms are paired. In case of dinuclear metal carbonyls formed by metals with odd atomic number, the unpaired electrons are utilized for the formation of metal-metal bonds.

Thermal Stability:

Most of the metal carbonyls melt or decompose at low temperatures. Solid carbonyls sublime in vacuum but they undergo some degree of degradation.

Thermodynamic Stability:

Metal carbonyls are thermodynamically unstable. They undergo aerial oxidation with different rates. $Co_2(CO)_8$ and $Fe_2(CO)_9$ are oxidized by air at room temperature while chromium and molybdenum hexacarbonyls are oxidized in air when heated.

5.4 CHEMICAL PROPERTIES

The metal carbonyls give a variety of chemical reactions.

Ligand substitution reactions:

Substitution of carbon monoxide ligand by various mono dentate and bidentate ligands can be carried out using thermal and photochemical reactions. Monodentate ligands like isocyanides (CNR), cyanide (CN^-), phosphine (PR_3) and ethers can partially or completely replace the carbonyl group.

$$Fe(CO)_5 + 2\,CNR \rightarrow Fe(CO)_3(CNR)_2 + 2\,CO$$
$$Ni(CO)_4 + 4\,CNR \rightarrow Ni(CNR)_4 + 4\,CO$$
$$Mn_2(CO)_{10} + PR_3 \rightarrow 2\,Mn(CO)_4(PR_3) + 2\,CO$$
$$2\,Fe_2(CO)_{12} + 3\,py \rightarrow Fe_3(CO)_9(py)_3 + 3\,Fe(CO)_5$$
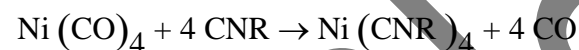
Bidentate ligands like o-phenylene-bis(dimethyl arsine) (diars) and o-phenanthroline(o-phen) can replace carbonyl groups in the multiple of two.

$$Ni(CO)_4 + \text{o- phen} \rightarrow Ni(CO)_2(\text{o- phen})_2 + 2\,CO$$
$$Cr(CO)_6 + 2\,\text{diars} \rightarrow Cr(CO)_2(\text{diars})_2 + 4\,CO$$
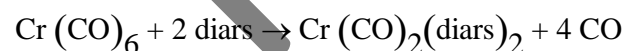
Reaction with metallic sodium:

Metallic sodium and its amalgam can be used to reduce the metal carbonyls.

$$Cr(CO)_6 + 2\,Na \rightarrow Na_2[Cr(CO)_5] + CO$$

$$Mn(CO)_{10} + 2\,Na \rightarrow 2\,Na[Mn(CO)_5\,] + CO$$
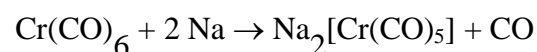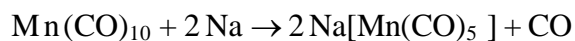
In the above two reactions, the Cr and Mn atoms in their zero oxidation states are reduced to -2 and -1 oxidation states respectively.

5.5 BONDING IN METALLIC CARBONYLS

In order to understand the bonding in metal carbonyls, let us first see the MO diagram of carbon monoxide.
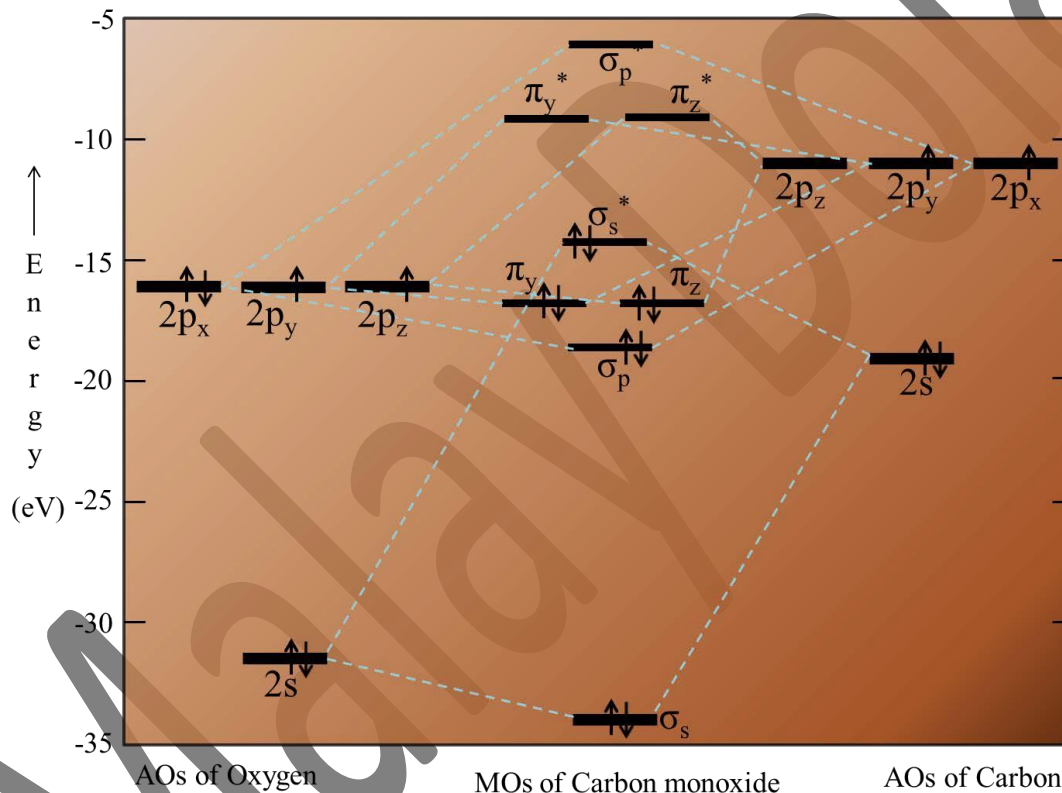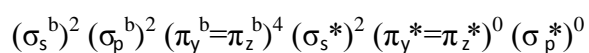

Figure: Molecular Orbital Energy Level Diagram of Carbon Monoxide

The order of energy of the molecular orbitals and the accommodation of ten electrons of the carbon monoxide can be shown as:

$(\sigma_s{}^b)^2\ (\sigma_p{}^b)^2\ (\pi_y{}^b{=}\pi_z{}^b)^4\ (\sigma_s{*})^2\ (\pi_y{*}{=}\pi_z{*})^0\ (\sigma_p{*})^0$

$(\sigma_s{*})$ is the highest occupied molecular orbital (HOMO) which can donate the lone pair of

electrons for the formation of a OC→M σ bond.

$(\pi_y^* = \pi_z^*)$ are the lowest unoccupied molecular orbitals (LUMO) which can accept the electron density from an appropriately oriented filled metal orbital resulting into formation of a M→CO π bond.

The nature of M-CO bonding in mononuclear carbonyls can be understood by considering the formation of a dative σ-bond and π-bond due to back donation.

5.6 Formation of dative σ-bond:

The overlapping of empty hybrid orbital (a blend of d, s and p orbitals) on metal atom with the filled hybrid orbital (HOMO) on carbon atom of carbon monoxide molecule results into the formation of a M←CO σ-bond.
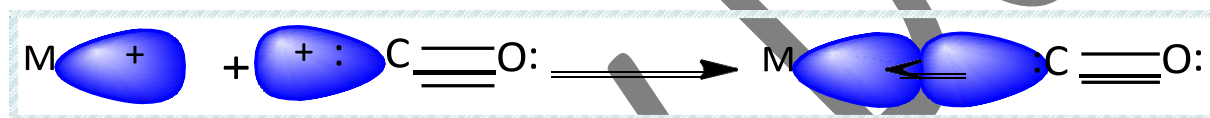
Figure: Formation of a M←CO σ-bond in metal carbonyls.

5.6.1 Formation of π-bond by back donation:

This bond is formed because of overlapping of filled dπ orbitals or hybrid dpπ orbitals of metal atom with low-lying empty (LUMO) orbitals on CO molecule. i.e. M $\xrightarrow{\pi}$ CO
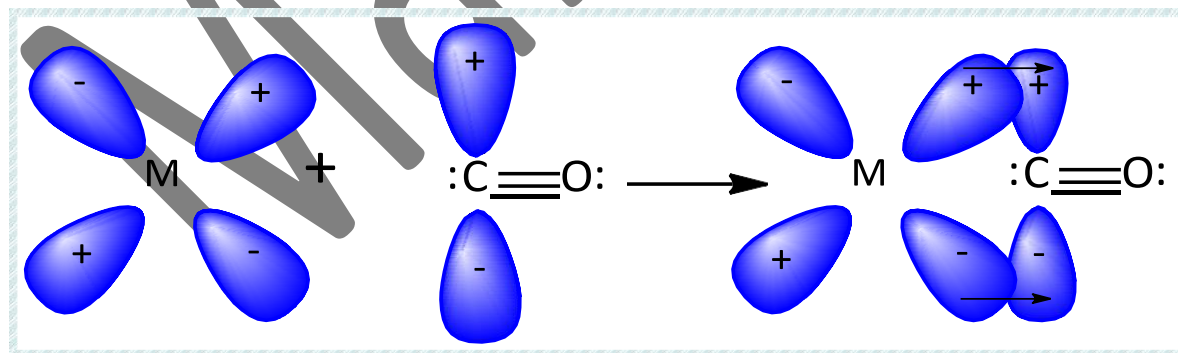
Figure: Formation of M $\xrightarrow{\pi}$ CO bond by back donation in metal carbonyls.

5.6.2 Bridging CO groups:

In addition to the linear M-C-O groups, the carbon monoxide ligand is also known to form bridges. This type of bonding is observed in some binuclear and polynuclear carbonyls. It is denoted by μ_n–CO, where n indicates the number of metals bridged. While n=2 is the most common value, it reaches to be 3 or 4 in certain less common carbonyls.

In a terminal M-C-O group, the carbon monoxide donates two electrons to an empty metal orbital, while in μ_2–CO group, the M-C bond is formed by sharing of one metal electron and one carbon electron.

5.7 Structure of mono nuclear carbonyls

Ni(CO)$_4$, Nickel tetracarbonyl:

Structure:

Nickel tetracarbonyl has a tetrahedral geometry with Ni-C bond lengths of 1.5 Å. It is also found to be diamagnetic.
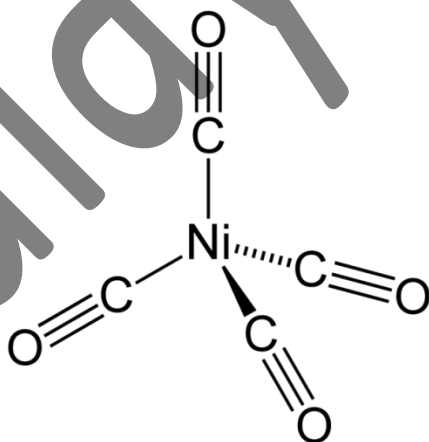
Figure: Tetrahedral structure of nickel tetracarbonyl

The structure of Ni(CO) $_4$ can be explained by considering sp^3 hybridization of Ni atom. Since it is diamagnetic, all the ten electrons present in the valence shell of Ni atom (Ni = 3d^8 4s^2) get paired in 3d orbitals. Thus the valence shell configuration of Ni atom in Ni(CO) $_4$ molecule becomes 3d^{10} 4s^0.

OC→Ni bond results by the overlap between the empty sp^3 hybrid orbital on Ni atom and the HOMO on C atom in CO molecule as shown below.

Acceptance of four electron pairs by nickel in zero oxidation state severely increases the electron density on the nickel atom. According to the electro neutrality principle given by Pauling, the atoms in a molecule share the electron pairs to the extent such that charge on each of the atom remains close to zero. Thus, the nickel atom donates back some electron density from the filled d-orbitals to the low-lying empty (LUMO) orbitals on CO molecule resulting into formation of a double bond.

$Fe(CO)_5$, Iron pentacarbonyl:

Structure:

The structural studies have suggested trigonal bipyramidal geometry for iron pentacarbonyl. The Fe-C distances are found to be 1.80 Å and 1.84 Å for axial and equatorial bonds respectively. The molecule is also found to be diamagnetic.
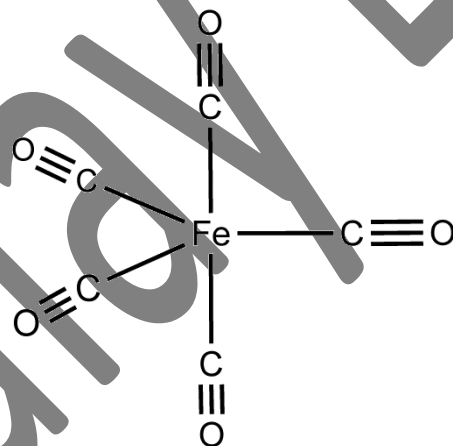
Figure: Trigonal bipyramidal structure of iron pentacarbonyl.

The structure can be explained using dsp^3 hybridization in Fe atom. All eight electrons present in the valence shell of Fe atom ($Fe:3d^64s^2$) get paired in four 3d orbitals. Thus the valence shell configuration of Fe in $Fe(CO)_5$ becomes $3d^84s^0$. The OC→Fe bond results by the overlap between the empty dsp^3 hybrid orbitals on Fe atom.

Cr(CO)₆, Chromium hexacarbonyl:

Structure:

The structural studies have suggested an octahedral geometry for chromium hexacarbonyl. The Cr-C distance is found to be 1.92 Å while the C-O bond length is 1.16 Å. The molecule is also found to be diamagnetic.
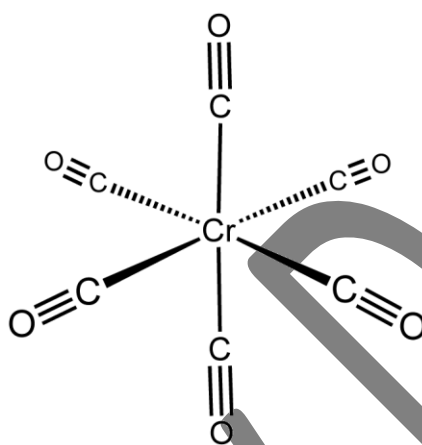

Figure: Octahedral structure of chromium hexacarbonyl.

The structure can be explained using d^2sp^3 hybridization in Cr atom. All six electrons present in the valence shell of Cr atom (Cr: $3d^54s^1$) get paired in three 3d orbitals. Thus the valence shell configuration of Cr in Cr(CO)₆ becomes $3d^64s^0$. The OC→Cr bond results by the overlap between the empty d^2sp^3 hybrid orbitals on Fe atom and the HOMO on C atom in CO molecule as shown below. The MO energy diagram for Cr(CO)₆ is shown in the figure below. For the molecular orbitals, 12 electrons are contributed from the lone pairs on the carbon atoms of the six carbon monoxide ligands. The metal contributes six electrons while 24 electrons come from the π system of the six ligands. The MOs are occupied by these 42 electrons and the t_{2g} level becomes the highest occupied molecular orbital (HOMO) of the metal carbonyl.

The net effect of the π^* orbitals is to increase the magnitude of 10 Dq (the splitting between the t_{2g} and e_g levels by lowering t^* to a level lower in energy than when no π^* orbitals are involved. Consequently, the complexes are predicted to be more stable when the ligands have π and π^* orbitals

available for bonding. The ligand CO may be predicted to bond increasingly strongly with electron releasing metal atoms. The bond order of CO decreases progressively as the π^* orbitals are increasingly populated by $d \rightarrow \pi^*$ donation.

As discussed above, the low-lying empty π^* orbitals on CO allow back bonding from the metal d electrons to the ligand. It has a very pronounced effect on the coordinated C-O bond order.

5.8 Structure of dinuclear Carbonyls
$Mn_2(CO)_{10}$, Dimanganese decacarbonyl:
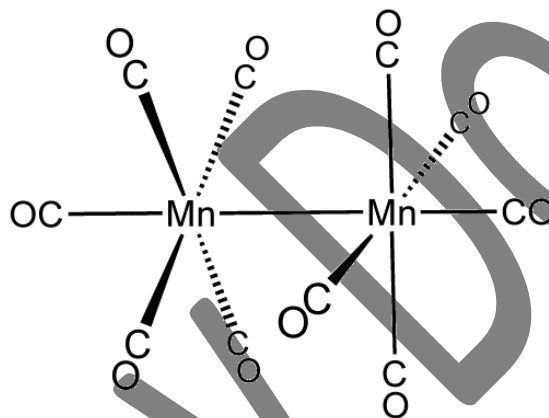
Figure: Structure of dimanganese decacarbonyl.

Manganese pentacarbonyl does not exist as Mn (Z=25) has an odd atomic number. However, the structure of dimanganese decacarbonyl consists of two manganese pentacarbonyl groups joined through a Mn-Mn (2.79 Å) bond. The formation of this inter metallic bond effectively adds one electron to each of the manganese atoms. Thus, manganese, an element with odd atomic number forms a binuclear carbonyl. Since the molecule does not have any unpaired electrons, it is diamagnetic.

$Co_2(CO)_8$, Dicobalt octacarbonyl:

Structure:
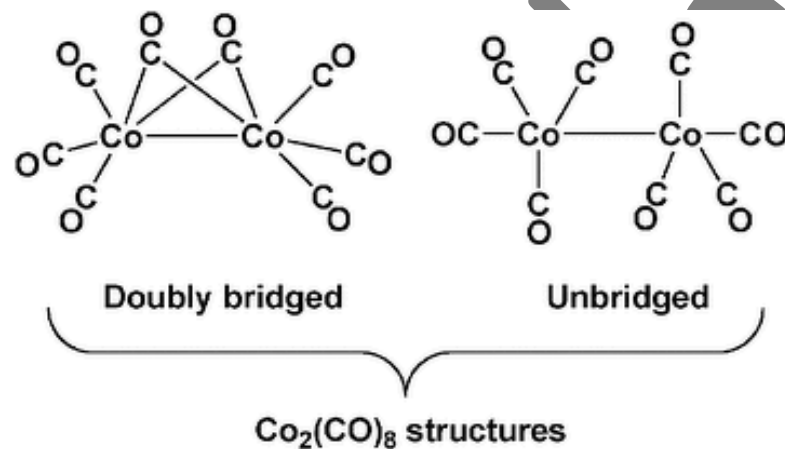
Figure: Structure of dicobalt octacarbonyl (without bridge and with bridge).

Dicobalt octacarbonyl is known to exist in two isomeric forms. A bridged structure of this molecule is observed in the solid state as well as solution state at a very low temperature. A non - bridged structure predominates in a solution at temperatures above ambience.

In the bridged structure, the cobalt atoms are in d^2sp^3 hybrid state. Three such hybrid orbitals on each cobalt atom accept lone pair of electrons from three carbon monoxide molecules to form total six Co←CO coordinate bonds. A Co-Co bond is formed by the overlapping of two half-filled d^2sp^3 hybrid orbitals on the cobalt atoms. Remaining two half–filled hybrid orbitals on each Co atom overlap with appropriate orbital on carbon atom of the carbonyl to form two bridging CO groups. Thus, all electrons in this molecule are paired and it is diamagnetic.

In the structure without bridge, the cobalt atoms are in dsp^3 hybrid state. Out of the five hybrid orbitals on each cobalt atom, four orbitals on each cobalt atom accept a lone pair of electrons from the carbon monoxide molecules to form eight Co←CO coordinate bonds. One half–filled orbitals on each cobalt overlap to form a Co-Co bond.

$Fe_2 (CO)_9$, Diiron nonacarbony

Structure:

Each of the iron atoms in diiron nonacarbonyl has three terminal carbonyl groups. The remaining three carbon monoxide ligands act as μ_2–CO groups. In addition to this, there is a weak Fe-Fe bond (2.46 Å) formed by sharing of two unpaired electrons present in the 3d orbitals of iron atoms. Thus, both the iron atoms in the molecule are identical with coordination number seven. Since the molecule does not have any unpaired electron, it is diamagnetic.
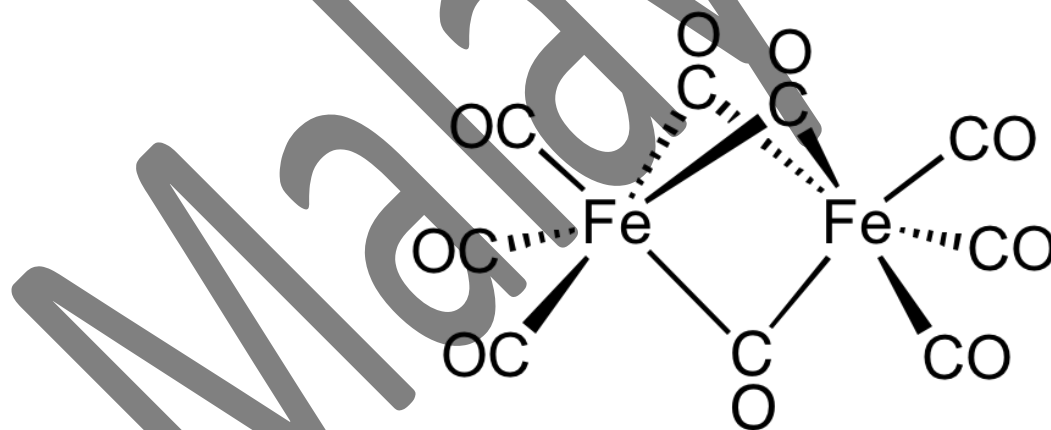
Figure: Structure of diiron nonacarbonyl.

6. Synergic effect of CO

A description of the bonding of π-conjugated ligands to a transition metal which involves a synergic process with donation of electrons from the filled π-orbital or lone electron pair orbital of the ligand into an empty orbital of the metal (donor–acceptor bond), together with release (back donation) of electrons from an nd orbital of the metal (which is of π-symmetry with respect to the metal–ligand axis) into the empty π^*-antibonding orbital of the ligand.

In case of carbonyls compounds, the π- bonding of CO ligands to a transition metal which involves the donation of electrons from the filled π-orbital of CO into an empty orbital of the metal, release (back donation) of electrons from an d orbital of the metal into the empty π^*-anti-bonding orbital of the ligand is called Synergic effect of CO.

π -Backbonding(π -backdonation): electrons move from an atomic orbital on one atom to a π^* anti-bonding orbital on another atom or ligand, in the process relieving the metal of excess negative charge.
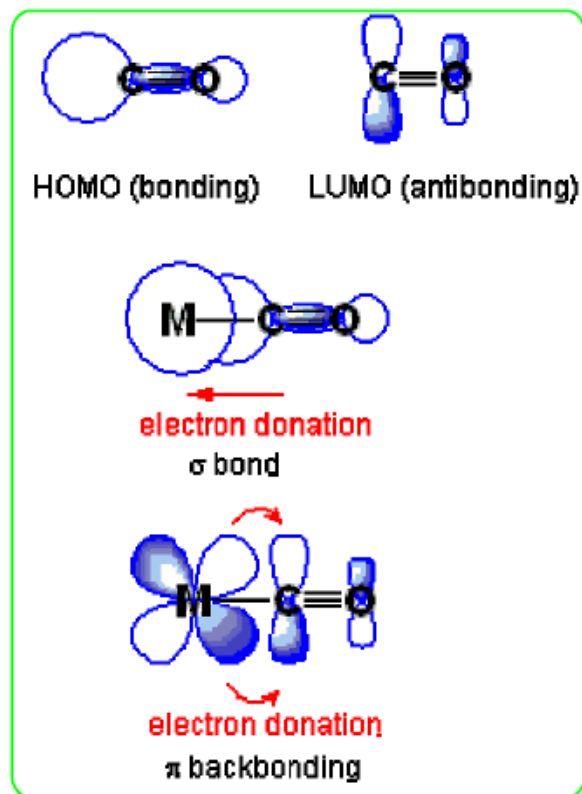
Figure: Top: the HOMO and LUMO of CO. Middle: a sigma bonding orbital in which CO donates electrons to a metals center from its HOMO. Bottom: the metal center donates electron through a d orbital to CO's

7. Infrared (IR) data to explain extent of back bonding of metal carbonyls

CO is a dative, L-type ligand that does not affect the oxidation state of the metal center upon binding, but does increase the total electron count by two units. We've recently seen that there are really two bonding interactions at play in the carbonyl ligand: a ligand-to-metal n → dσ interaction and a metal-to-ligand dπ → π* interaction. The latter interaction is called back-bonding, because the metal donates electron density back to the ligand. To remind myself of the existence of back-bonding, I like to use the right-hand

resonance structure whenever possible; however, it is important to remember to treat CO as an L-type ligand no matter what resonance form is drawn.

$$^{\ominus}M-\!\!\!\equiv\!\!\!O^{\oplus} \longleftrightarrow M=C=O$$

σ-type orbital interaction

π-type orbital interaction

Electron   Electron
donor!   acceptor!
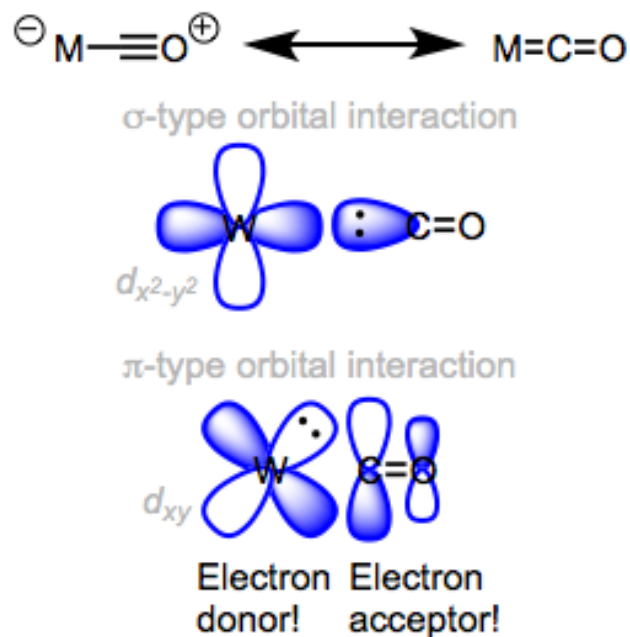
Orbital interactions in M=C=O

CO is a strong σ-donor (or σ-base) and a good π-acceptor (or π-acid). The properties of ligated CO depend profoundly upon the identity of the metal center. More specifically, the electronic properties of the metal center dictate the importance of back-bonding in metal carbonyl complexes. Most bluntly, more electron-rich metal centers are better at back-bonding to CO.

Infrared spectroscopy has famously been used to empirically support the idea of back-bonding. The table below arranges some metal carbonyl complexes in "periodic" order and provides the frequency corresponding to the C=O stretching mode. Notice that without exception, every complexed CO has a stretching frequency lower than that of free CO. Back-bonding is to blame! The C–O bond order in complexed carbon monoxide is (almost always) lower than that of free CO.

Free CO
2143 cm^{-1}

$V(CO)_6$ $Cr(CO)_6$ $Mn_2(CO)_{10}$ $Fe(CO)_5$ $Co_2(CO)_8$ $Ni(CO)_4$
1976 cm^{-1} 2000 cm^{-1} 2013 cm^{-1} 2023 cm^{-1} 2044 cm^{-1} 2057 cm^{-1}

$[Ti(CO)_6]^{2-}$
1747 cm^{-1}

$$^{\ominus}M\!-\!\!\equiv\!\!O^{\oplus} \longleftrightarrow M\!=\!C\!=\!O$$
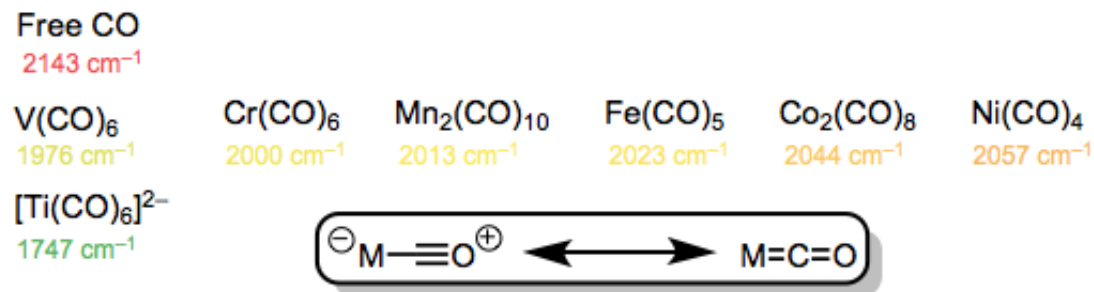
C=O stretching frequencies in metal-carbonyl complexes.

The figure above depicts a clear increase in frequency (an increase in C–O bond order) as we move left to right across the periodic table. This finding may seem odd if we consider that the number of d electrons in the neutral metal increases as we move left to right. Recall the periodic trend in orbital energy. As we move left to right, the d orbital energies decrease and the energies of the dπ and π* orbitals separate. As a result, the back-bonding orbital interaction becomes worse (remember that strong orbital interactions require well-matched orbital energies) as we move toward the more electronegative late transition metals.

Logically, electron-donating ligands will tend to make the back-bond stronger (they make the metal a better electron donor), while electron-withdrawing ligands will worsen back-bonding. Adding electron-rich phosphine ligands to a metal center, for instance, decreases the CO stretching frequency due to improved back-bonding.

Carbonyl ligands are famously able to bridge multiple metal centers. Bonding in bridged carbonyl complexes may be either "traditional" or delocalized, depending on the structure of the complex and the bridging mode. The variety of bridging modes stems from the different electron donors and acceptors present on the CO ligand (and the possibility of delocalized bonding). Known bridging modes are shown in the figure below.
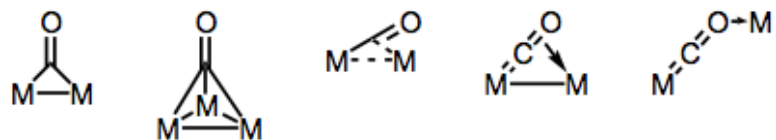
Building bridges with carbonyl ligands

The carbonyl groups can have two modes of stretching. They are Symmetric and asymmetric stretching. Since both of these modes result in change in dipole moment, two bands are expected in the infrared spectra of a terminally ligated carbon monoxide.

The infrared and Raman spectroscopy together can be used to determine the geometry of the metallic carbonyls. A mono nuclear pentacarbonyl can exist both in square pyramidal and trigonal bipyramidal geometry. Performing infrared spectra after calculating the IR active and Raman active bands in both the possible geometries can provide information about the actual geometry of the molecule.

Infrared spectroscopy of metallic carbonyls helps in determining the bond order of ligated carbon monoxide. The C-O bond order and the frequency related to its absorption are directly proportional. Thus, it can be predicted that the frequencies of absorption will be in the order shown below:

Free CO > metal carbonyl cation > neutral metal carbonyl > metal carbonyl anion.

Table: Comparison C-O stretching in representative metal carbonyls

Carbonyl	Type	C-O stretching frequency (cm^{-1})
Carbon monoxide	Free	~2150
$Mn(CO)_6^+$	Cation	~2090
$Cr(CO)_6$	Neutral	~2000

V(CO)₆⁻	Anion	~1850

It is also used to distinguish the terminal and bridging carbonyl groups.
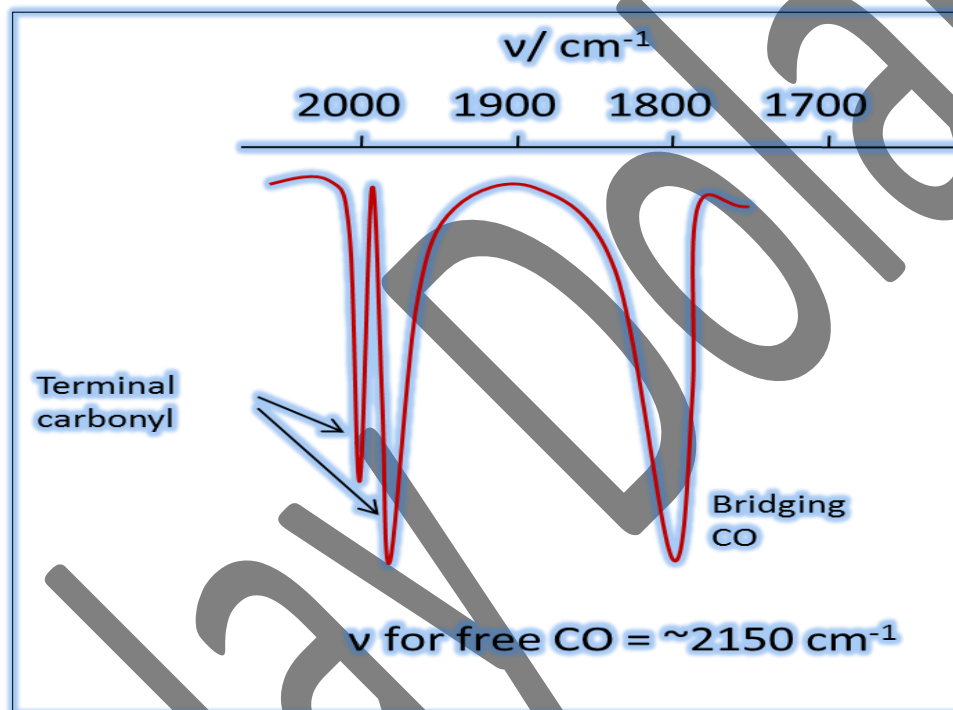
Figure: A partial infrared spectrum showing terminal and bridged carbonyl.

The C-O bonding in terminal carbonyl groups is stronger than the bridged carbonyl groups. Therefore, it is possible to differentiate the terminal carbonyls which absorb in the region of 2050–1900 cm^{-1} from the bridged carbonyls absorbing below 1900 cm^{-1}.

The change in the intensity of bands related to carbonyl group can provide information for the kinetic studies of the substitution

reactions involving replacement of carbonyls.

8. General methods of preparation of metal-carbon σ-bonded complexes

Ligands play a vital role in stabilizing transition metal complexes. The stability as well as the reactivity of a metal in its complex form thus depends upon the number and the type of ligands it is bound to. In this regard, the organometallic carbon based ligands come in diverse varieties displaying a wide
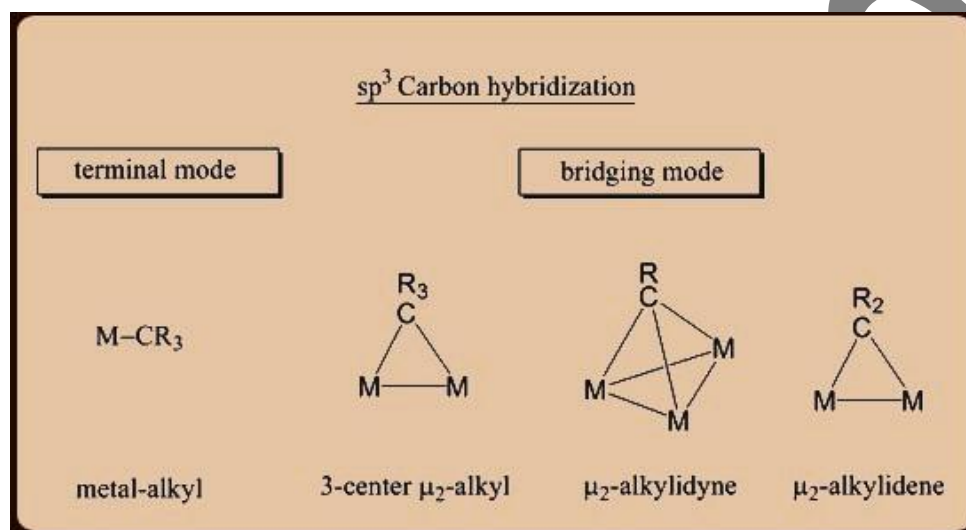
range of binding modes to a metal. In general, the binding modes of the carbon-derived ligands depend upon the hybridization state of the metal bound carbon atom. These ligands can thus bind to a metal in many different ways as depicted below. Lastly, these ligands can either be of (a) purely σ−donor type, or depending upon the capability of the ligand to form the multiple bonds may also be of (b) a σ−donor/π −acceptor type, in which the σ−interaction is supplemented by a varying degree of π−interaction.

Preparation of transition metal-alkyl and transition metal-aryl complexes
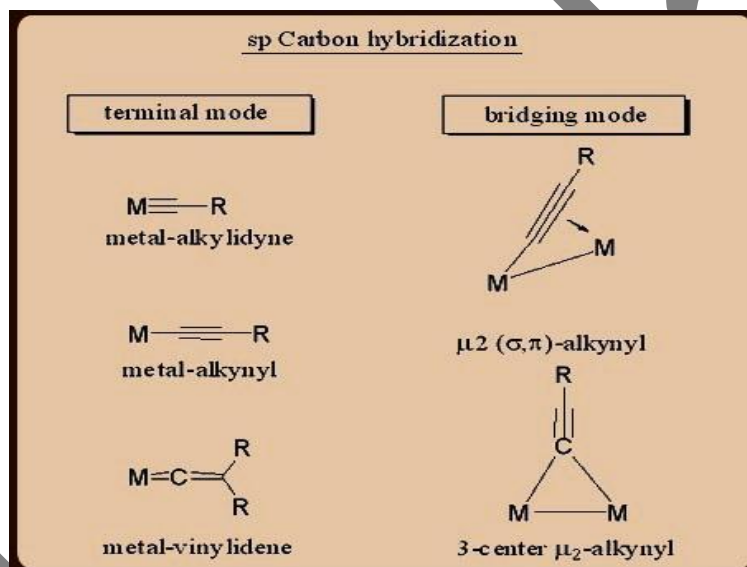
The transition metal–alkyl and transition–metal aryl complexes are usually prepared by the following routes discussed below,

a.Metathesis

This involves the reactions of metal halides with organolithium, organomagnesium, organoaluminium, organotin and organozinc reagents.

$$\text{ZrCl}_4 \xrightarrow[\text{Et}_2\text{O}]{4\ \text{PhCH}_2\text{MgCl}}$$
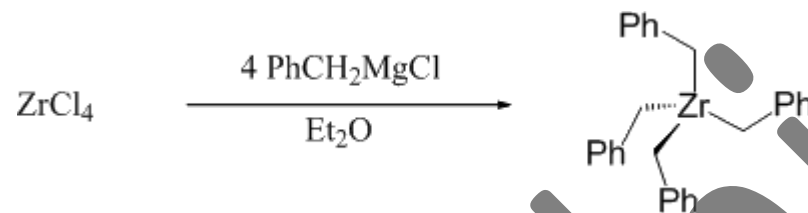
Of the different organoalkyl compounds listed above, the organolithium and organomagnesium compounds are strongly carbanionic while the remaining main group organometallics like the organoalkyl, organozinc and organotin reagents are relatively less carbanionic in nature. Thus, the main group organometallic reagents have attenuated alkylating power, that can be productively used in partial exchange of halide ligands.

$$\text{TiCl}_4 \xrightarrow{\text{Al}_2\text{Me}_6} \text{MeTiCl}_3$$

$$\text{NbCl}_5 \xrightarrow{\text{ZnMe}_2} \text{Me}_2\text{NbCl}_3$$
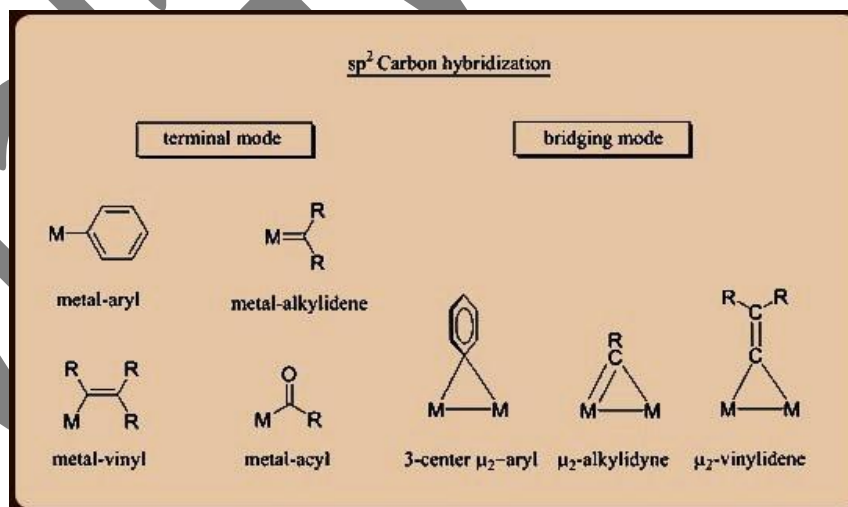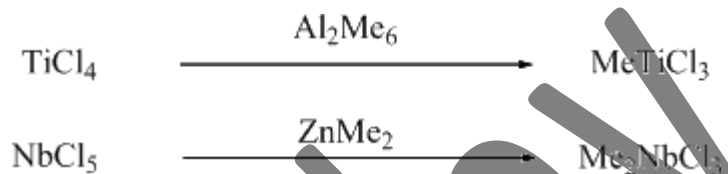
b.Alkene insertion or Hydrometallation

As the name implies, this category of reaction involves an insertion reaction between metal hydride and alkene as shown below. These type reactions are relevant to certain homogeneous catalytic processes in which insertion of an olefin to M−H bond is often observed.
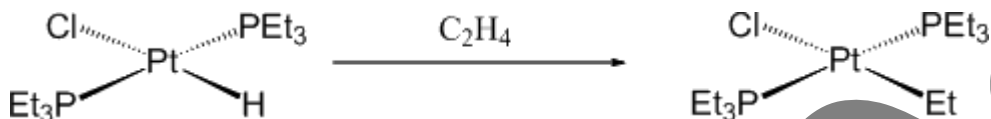
c. Carbene insertion

This category represents the reaction of metal hydrides with carbenes.
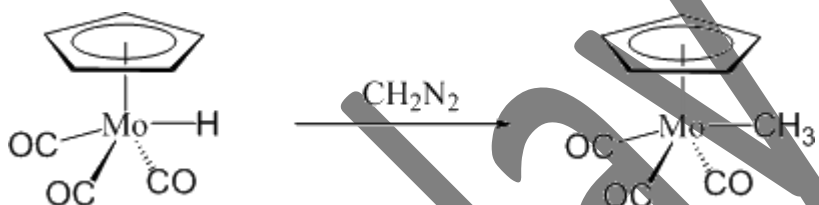
d.Metallate alkylation reaction

This category represents the reaction of carbonylate anions with alkyl halides as shown below.
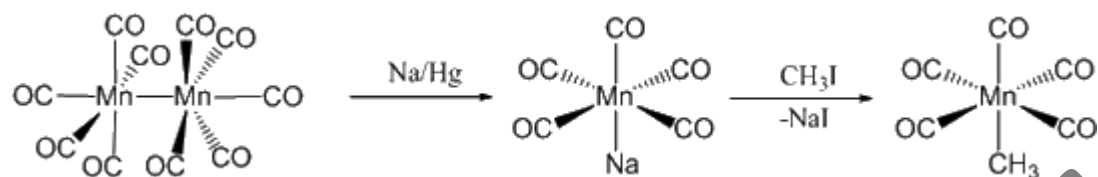
e. Metallate acylation reaction

This category involves the reaction of carbonylate anions with acyl halides.
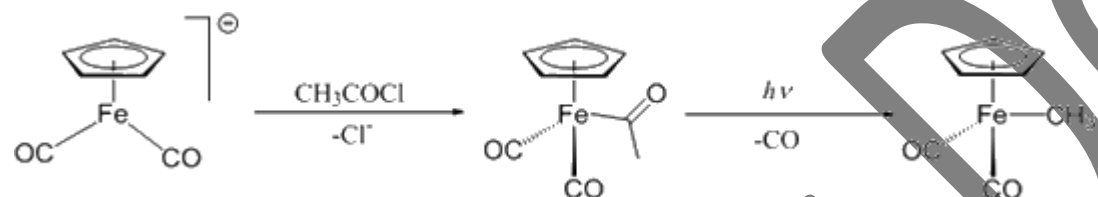
f. Oxidative addition reaction

Many unsaturated 16 VE transition metal complexes having *d* or *d* configuration undergo oxidative addition reactions with alkyl halides. The oxidative addition reactions proceed with the oxidation state as well as coordination number of the metal increasing by +2.
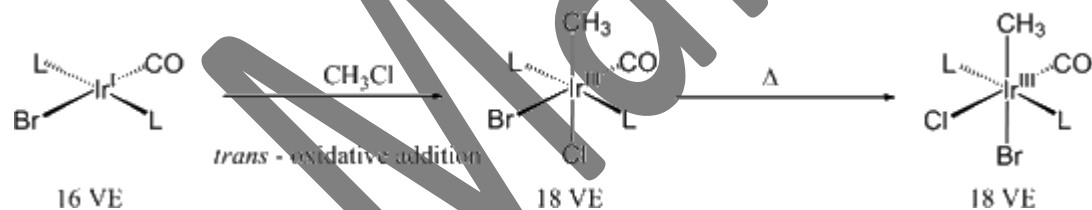

g. Addition reaction

This category involves the reaction of an activated metal bound olefin complex with a nucleophile as shown below.
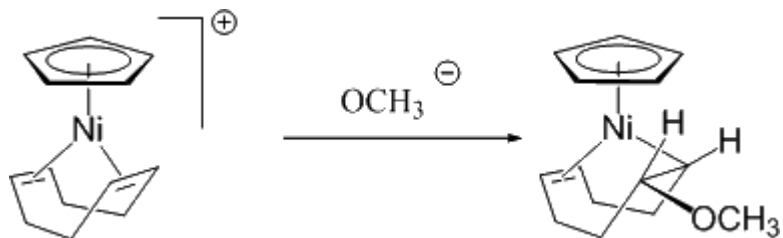
Thermodynamic Stability and Kinetic Lability

The transition metal organometallic compounds are often difficult to synthesize under ordinary laboratory conditions and require stringent experimental protocols involving the exclusion of air and moisture for doing so. As a consequence, many homoleptic binary transition metal–alkyl and transition metal–aryl compounds like, Et_2Fe or Me_2Ni cannot be made under normal laboratory conditions. More interestingly, most of the examples of transition metal–aryl and transition metal–alkyl compounds, known in the literature, invariably contain additional ligands like η^5-C_5H_5, CO, PR_3 or halides.

For example,
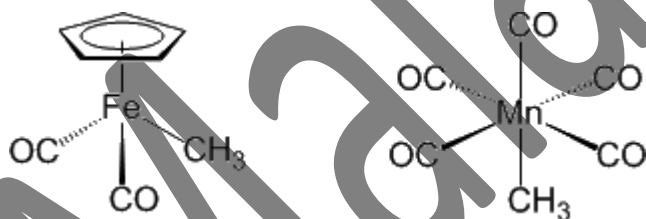
Transition metal–carbon (TM–C) bond energy values are important for understanding the instability of transition metal organometallic compounds. In general, the TM–C bonds are weaker than the transition metal–main group element (TM–MGE) bonds (MGE = F, O, Cl, and N) and more interestingly so, unlike the TM–MGE bond energies, the TM–C bond energy values

increase with increasing atomic number. The steric effects of the ligands also play a crucial role in influencing the TM–C bond energies and thus have to be given due consideration.

Contrary to the popular belief, the difficulty in obtaining transition metal–aryl and transition metal–alkyl complexes does primarily arise from the thermodynamic reasons but rather the kinetic ones. β
–elimination is by far the most general decomposition mechanism that contributes to the instability of transition metal
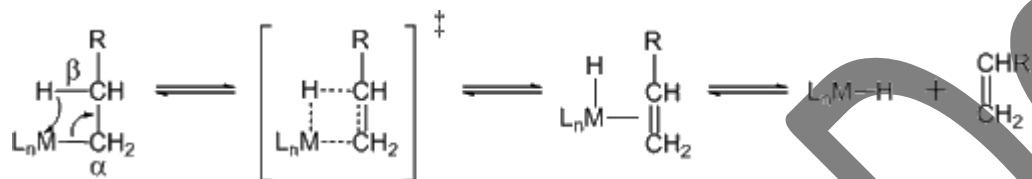
organometallic compounds. β–elimination results in the formation of metal hydrides and olefin as shown below.

β–elimination can also be reversible as shown below.
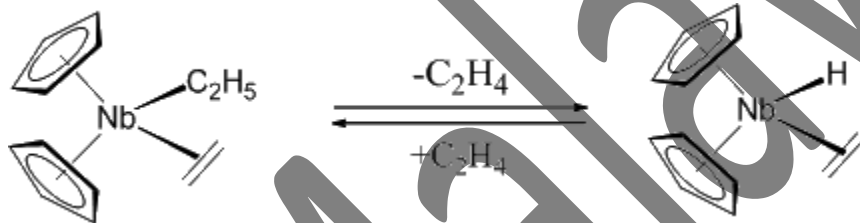
The instability of transition metal organometallic compounds can arise out of kinetic lability like in the case of the β–elimination reactions that trigger decomposition of these complexes. Thus, the suppression of the decomposition reactions provides a viable option for the stabilization of the transition metal organometallic complexes. The β–elimination reactions in transition metal organometallic complexes may be suppressed under any of the following three conditions.

9. Zeise's salt

Zeise's salt, potassium trichloro (ethene) platinate(II), is the chemical compound with the formula $K[PtCl_3(C_2H_4)]\cdot H_2O$. The anion of this air-stable, yellow, coordination complex contains an η^2-ethylene ligand. The anion features a platinum atom with a square planar geometry. The salt is of historical importance in the area of organometallic chemistry as one of the first examples of a transition metal alkene complex and is named for its discoverer, William Christopher Zeise.

9.1 Preparation

This compound is commercially available as a hydrate. The hydrate is commonly prepared from $K_2[PtCl_4]$ and passing through ethylene gas in the presence of a catalytic amount of $SnCl_2$. In another way, $K_2[PtCl_4]$ is reacted with ethanol in presence of heat to form $K[PtCl_3(C_2H_4)]\cdot H_2O$. The water of hydration can be removed *in vacuo*.
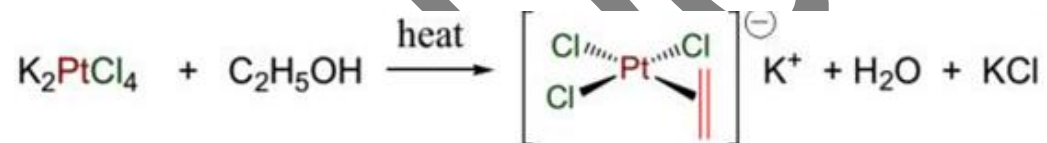
9.2 Structure

The alkene C=C bond is approximately perpendicular to the $PtCl_3$ plane. In Zeise's salt and related compounds, the alkene rotates about the metal-alkene bond with a modest activation energy. Analysis of the barrier heights indicates that the π-bonding between most metals and the alkene is weaker than the σ-bonding. In Zeise's anion, this rotational barrier has not been assessed.
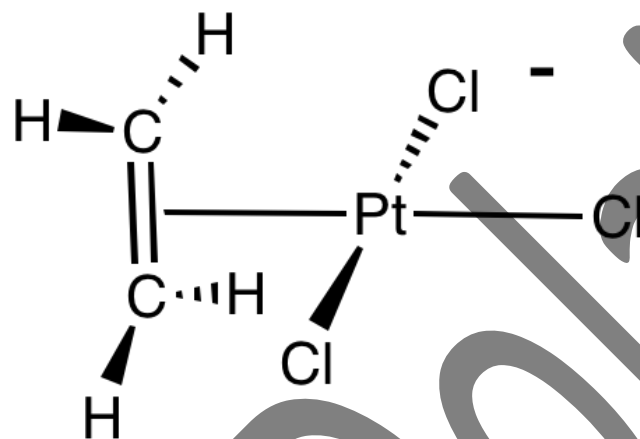
Structure of Zeise's anion

10. Metal-carbon multiple bonding

An importance of metal-carbon multiple bonds is the carbenes. Carbenes contain metal-carbon double bonds. They are often divided into two classes: Fischer carbenes and Schrock carbenes or alkylidenes. Fischer carbenes were developed by E.O. Fischer, who shared a Nobel Prize with Geoff Wilkinson in 1973 for other work. Fischer carbenes have a hetero-atom attached to the double bonded carbon, such as an oxygen or nitrogen. They can be somewhat more stable than alkylidenes, which have only hydrogens or carbons attached to the double bonded carbon.

A large number of such Fischer type complexes are now known for d^5 — d^8 metals (usually in 0 or + 1 formal oxidation states, assuming the carbene to be a neutral two electron ligand). These Fischer type complexes are 18 electron species with the metal in formally 0 or + 1 oxidation state, these are also characterized by having at least one stabilizing resonance form and in showing reactivety at C-carbene with necleophiles.
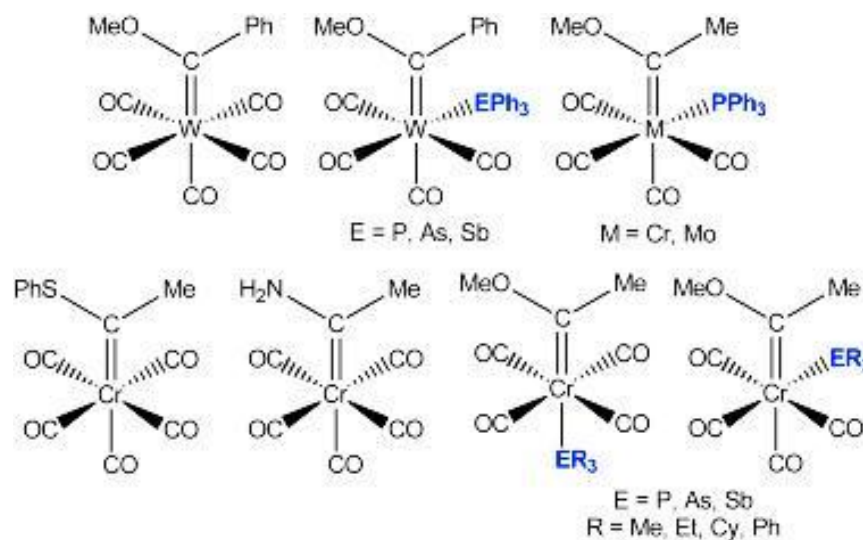
Fischer type carbene complexes

Alkylidenes were discovered by Dick Schrock, in the early 1970's. While trying to place some bulky alkyl groups on tantalum, he noticed spectroscopic evidence that suggested a double bond. Years later, Schrock and other workers, including Bob Grubbs were able to develop new alkylidene-based catalysts useful in polymer chemistry and organic synthesis. For their contributions in this area, Schrock, along with Bob Grubbs, shared the Nobel Prize in chemistry in 2005.
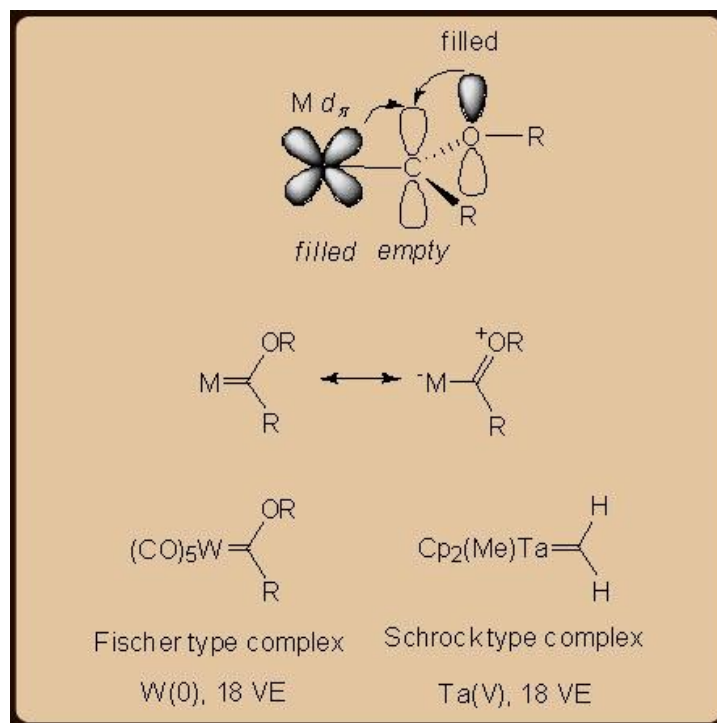
Fischer and Schrock carbene complexes type
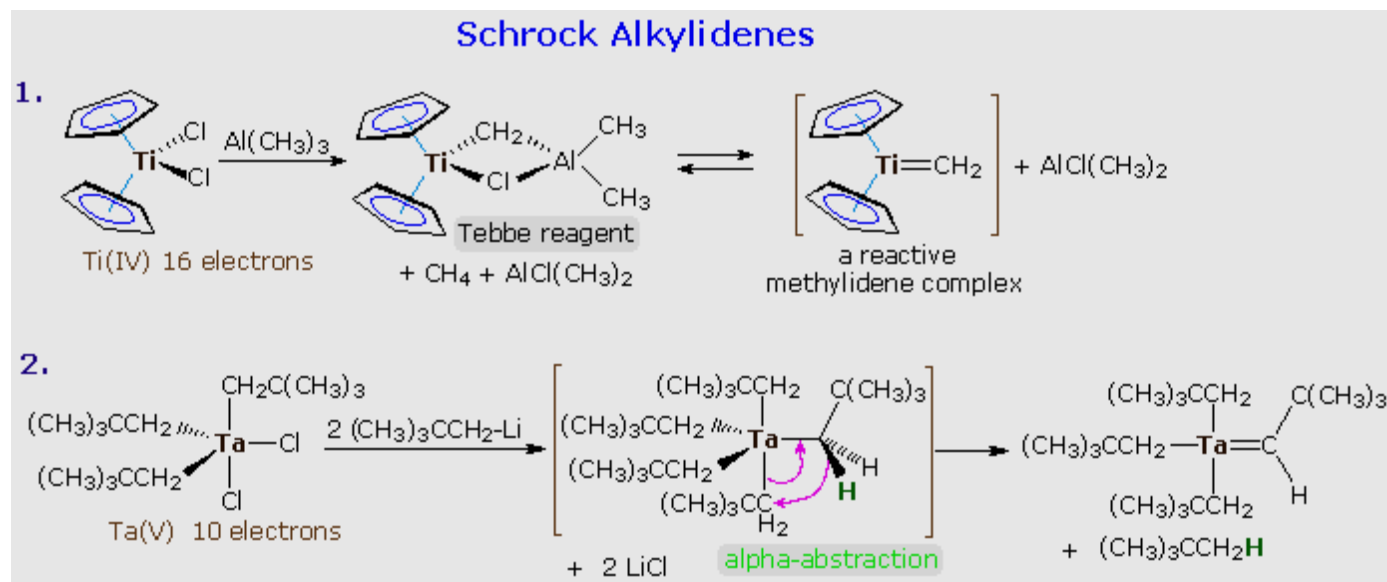
Schrock carbene complex type

11. Preparation, structures, properties and reactions of ferrocene

Ferrocene was accidently discovered in 1951 at Duquesne University in Pittsburgh, Pennsylvania by T.J. Kealy and P.L.Paulson. Cyclopentadienyl magnesium bromide (CpMgBr) was reacted with iron (II) chloride in attempt to create a fulvalene. When an orange complex formed instead, the chemists hypothesized that the iron was bound to one carbon in each ring. A year later, in 1952, G. Wilkinson and R. B. Woodward correctly deduced the sandwich structure: two anionic cyclopentadienyl (Cp) rings each donating 6 π electrons to the Fe^{2+} cation between them. Ferrocene is an organometallic compound with the formula $Fe(C_5H_5)_2$. The molecule consists of two cyclopentadienyl rings bound on opposite sides of a central iron atom. It is an orange solid with a camphor-like odor, that sublimes above room temperature, and is soluble in most organic solvents. It is remarkable for its stability: it is unaffected by air, water, strong bases, and can be heated to 400 °C without decomposition. In oxidizing conditions it can reversibly react with strong acids to form the ferrocenium cation $Fe(C_5H_5)_2^+$. The structure of ferrocene was discovered by G. Wilkinson and E. O. Fischer, were awarded the Nobel Prize in Chemistry in 1973 for their pioneering work on the chemistry of this sandwich complex.

11.1 Structure

Ferrocene's cyclopentadienyl rings are aromatic – each containing 6 delocalized π electrons like benzene. If a strong base is used to deprotonate cyclopentadiene (Cp), the H^+ is removed from the only sp^3 (tetrahedral) carbon in the structure. A lone pair of electrons is then formally assigned to a nonbonding p orbital of that carbon (which is now sp^2 hybridized). Mössbauer spectroscopy indicates that the iron center in ferrocene should be assigned the +2 oxidation state. Each cyclopentadienyl (Cp) ring should then be allocated a single negative charge. Thus ferrocene could be described as iron(II) biscyclopentadienide, $Fe^{2+}[C_5H_5]_2$.

The number of π-electrons on each ring is then six, which makes it aromatic according to Hückel's rule. These twelve π-electrons are then shared with the metal via covalent bonding. Since Fe^{2+} has six d-electrons, the complex attains an 18-electron configuration, which accounts for its stability. In modern notation, this sandwich structural model of the ferrocene molecule is denoted as $Fe(\eta^5-C_5H_5)_2$.

The carbon–carbon bond distances around each five-membered ring are all 1.40 Å, and the Fe–C bond distances are all 2.04 Å. From room temperature down to 164K, X-ray crystallography yields the monoclinic space group; the cyclopentadienide rings are a staggered conformation, resulting in a centrosymmetric molecule, with symmetry group D_{5d}. However, Below 110 K, ferrocene crystallizes in an orthorhombic crystal lattice in which the Cp rings are ordered and eclipsed, so that the molecule has symmetry group D_{5h}. In the gas phase, electron diffraction and computational studies show that the Cp rings are eclipsed.

The Cp rings rotate with a low barrier about the $Cp_{(centroid)}–Fe–Cp_{(centroid)}$ axis, as observed by measurements on substituted derivatives of ferrocene using ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy. For example, methylferrocene ($CH_3C_5H_4FeC_5H_5$) exhibits a singlet for the C_5H_5 ring.

Conformations of ferrocene

Eclipsed (D_{5h})   Staggered (D_{5d})
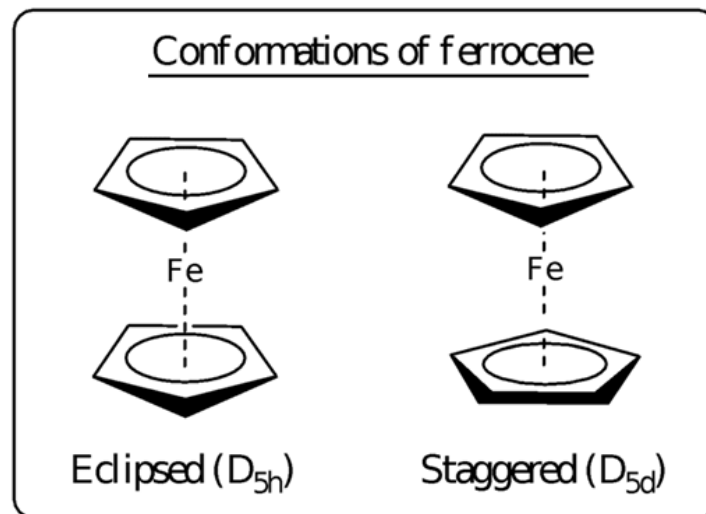
11.2 Syntheses

The first reported syntheses of ferrocene were nearly simultaneous. Pauson and Kealy synthesised ferrocene using iron(III) chloride and a Grignard reagent, cyclopentadienyl magnesium bromide. Iron(III) chloride is suspended in anhydrous diethyl ether and added to the Grignard reagent. A redox reaction occurs, forming the cyclopentadienyl radical and iron(II) ions. Dihydrofulvalene is produced by radical-radical recombination while the iron(II) reacts with the Grignard reagent to form ferrocene. Oxidation of dihydrofulvalene to fulvalene with iron(III), the outcome sought by Kealy and Pauson, does not occur.
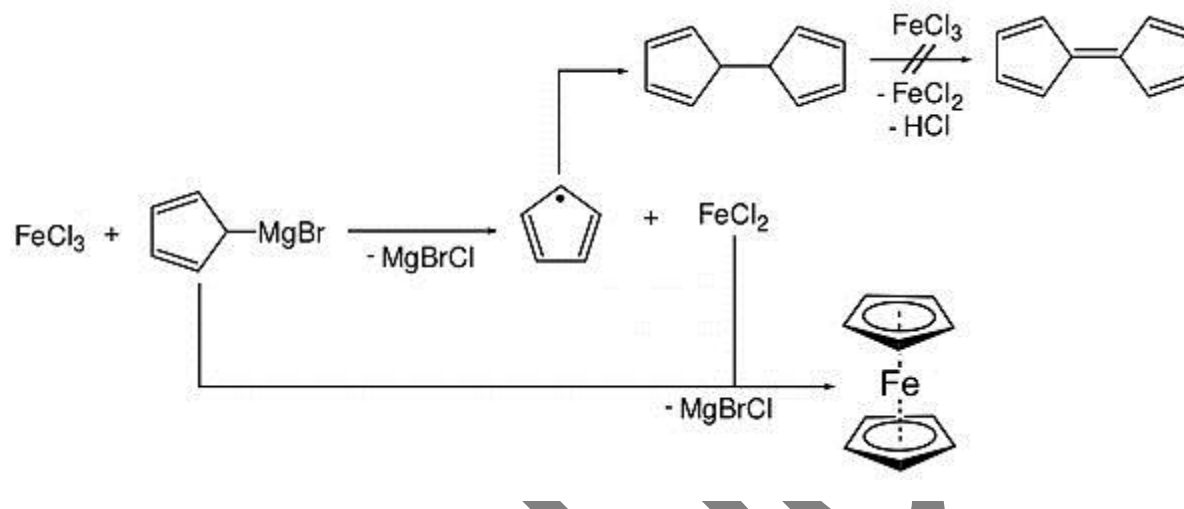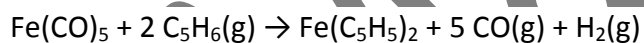
Gas-metal reaction
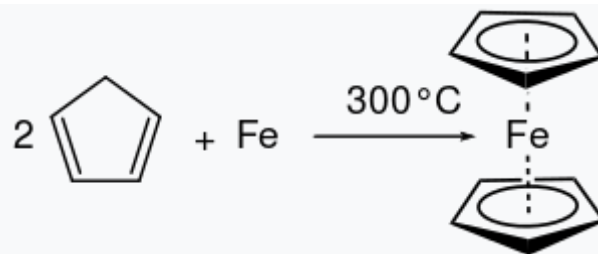
The Miller approach to ferrocene

The other early synthesis of ferrocene was by Miller who reacted metallic iron directly with gas-phase cyclopentadiene at elevated temperature. An approach using iron pentacarbonyl was also reported.

$$Fe(CO)_5 + 2\ C_5H_6(g) \rightarrow Fe(C_5H_5)_2 + 5\ CO(g) + H_2(g)$$

Via alkali cyclopentadienide

More efficient preparative methods are generally a modification of the original transmetalation sequence using either commercially available sodium cyclopentadienide or freshly crackedcyclopentadiene deprotonated with potassium hydroxide and reacted with anhydrous iron(II) chloride in ethereal solvents.

Modern modifications of Pauson and Kealy's original Grignard approach are known:

- Using sodium cyclopentadienide: $2 \, NaC_5H_5 \; + \; FeCl_2 \; \rightarrow \; Fe(C_5H_5)_2 \; + \; 2 \, NaCl$

- Using-freshly-cracked cyclopentadiene: $FeCl_2 \cdot 4H_2O \; + \; 2 \, C_5H_6 \; + \; 2 \, KOH \; \rightarrow \; Fe(C_5H_5)_2 \; + \; 2 \, KCl \; + \; 6 \, H_2O$

- Using an iron(II) salt with a Grignard reagent: $2 \, C_5H_5MgBr \; + \; FeCl_2 \; \rightarrow \; Fe(C_5H_5)_2 \; + \; 2 \, MgBrCl$

Even some amine bases (such as diethylamine) can be used for the deprotonation, though the reaction proceeds more slowly than when using stronger bases:

$2 \, C_5H_6 \; + \; 2 \, (CH_3CH_2)_2NH \; + \; FeCl_2 \; \rightarrow \; Fe(C_5H_5)_2 \; + \; 2 \, (CH_3CH_2)_2NH_2Cl$
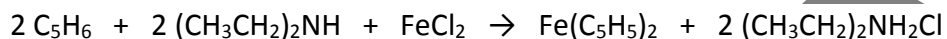
Direct transmetalation can also be used to prepare ferrocene from other metallocenes, such as manganocene:

$FeCl_2 \; + \; Mn(C_5H_5)_2 \; \rightarrow \; MnCl_2 \; + \; Fe(C_5H_5)_2$
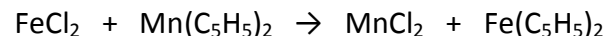
11.3 Properties

Ferrocene is an air-stable orange solid with a camphor-like odor. As expected for a symmetric, uncharged species, ferrocene is soluble in normal organic solvents, such as benzene, but is insoluble in water. It is stable to temperatures as high as 400°C.

Ferrocene readily sublimes, especially upon heating in a vacuum. Its vapor pressure is about 1 Pa at 25°C, 10 Pa at 50 °C, 100 Pa at 80 °C, 1000 Pa at 116 °C, and 10,000 Pa (nearly 0.1 atm) at 162°C

Reactions

Ferrocene easily undergoes acylation resulting in the addition of acetyl groups to one or both cyclopentadienyl rings. While conditions can be optimized so that more of one product is formed over the other, the crude product always has to be purified by column chromatography to separate the acetylated products from each other and from any unreacted ferrocene.

With electrophiles

Ferrocene undergoes many reactions characteristic of aromatic compounds, enabling the preparation of substituted derivatives. A common undergraduate experiment is the Friedel–Crafts reaction of ferrocene with acetic anhydride (or acetyl chloride) in the presence of phosphoric acid as a catalyst.
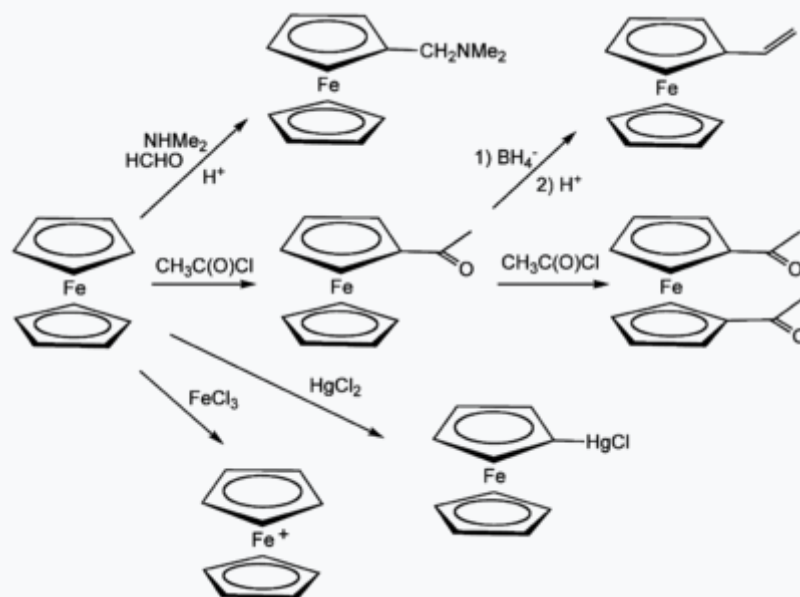
Important reactions of ferrocene with electrophiles and other reagents.

Protonation of ferrocene allows isolation of $[Cp_2FeH]PF_6$

In the presence of aluminium chloride Me_2NPCl_2 and ferrocene react to give ferrocenyl dichloro phosphine, whereas treatment with phenyl dichloro phosphine under similar conditions forms P,P-diferrocenyl-P-phenyl phosphine.

Ferrocene reacts with P_4S_{10} forms a diferrocenyl-dithiadiphosphetane disulfide.

Lithiation

Ferrocene reacts with butyl lithium to give 1,1'-dilithioferrocene, which is a versatile nucleophile. Tert-Butyllithium produces mono-lithio-ferrocene. Dilithioferrocene reacts with S_8, chlorophosphines, and chlorosilanes. The strained compounds undergo ring-opening polymerization.
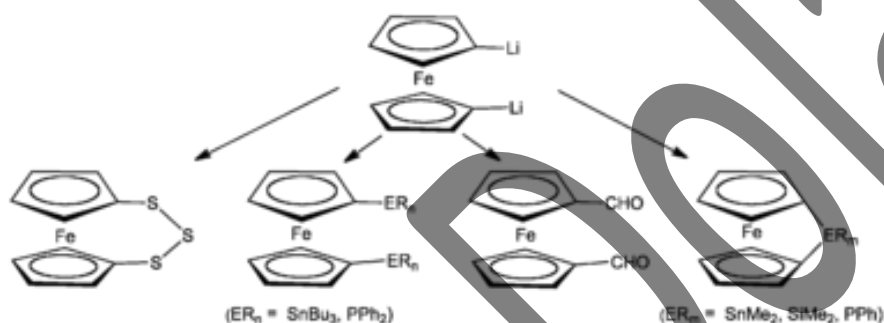
Some transformations of dilithio ferrocene.

The phosphine ligand 1,1'-bis(diphenyl phosphino) ferrocene (dppf) is prepared from dilithio ferrocene.

12. Oxidative addition, Reductive elimination and insertion reactions

12.1 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. Actually, when addition of ligands is accompanied by oxidation of the metal, it is called an oxidative addition reaction

$$ML_n + X\text{-}Y \rightarrow X-M(L_n)-Y$$

Requirements for oxidative addition

• availability of nonbonded electron density on the metal,

• two vacant coordination sites on the reacting complex (LnM), that is, the complex must be coordinatively unsaturated,

• a metal with stable oxidation states separated by two units; the higher oxidation state must be energetically accessible and stable.

12.2 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.

$$X{-}M(L_n){-}Y \rightarrow ML_n + X\text{-}Y$$
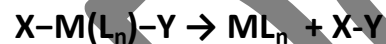
Factors which facilitate reductive elimination

- a high formal positive charge on the metal,
- the presence of bulky groups on the metal, and
- an electronically stable organic product.

Oxidative addition(OA)
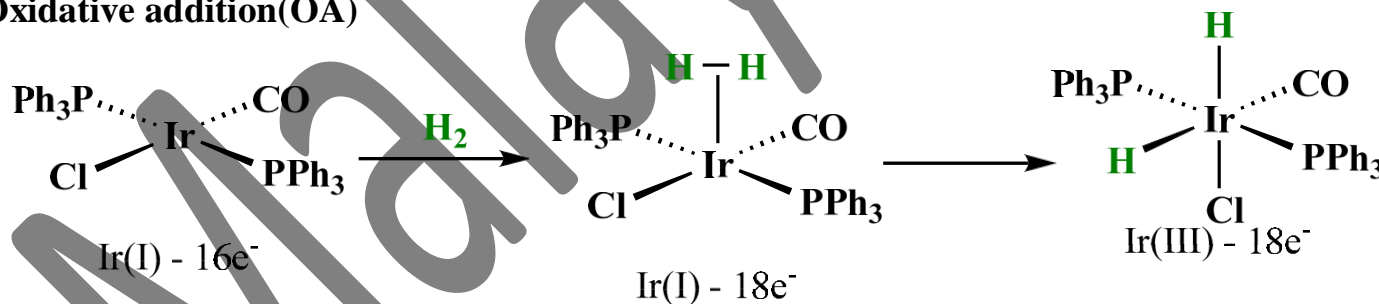
Such molecules do not contain electro-negative atoms and/or are not good oxidizing agents. They are often considered to be
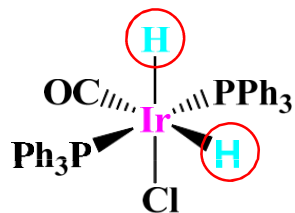
"non-reactive" substrates. These molecules generally require the presence of an empty orbital on the metal center in order for them to pre-coordinate prior to being activated for the oxidative addition reaction. Examples: H_2, C-H bonds, Si-H bonds, S-S bonds, C-C bonds.
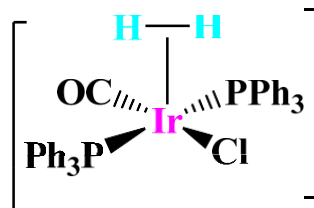
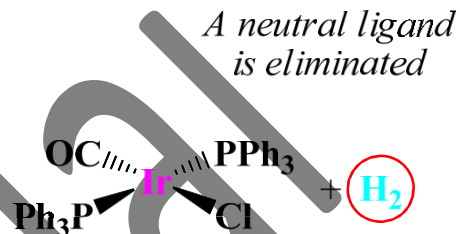**Oxidative Addition with a Reactive Substrate**
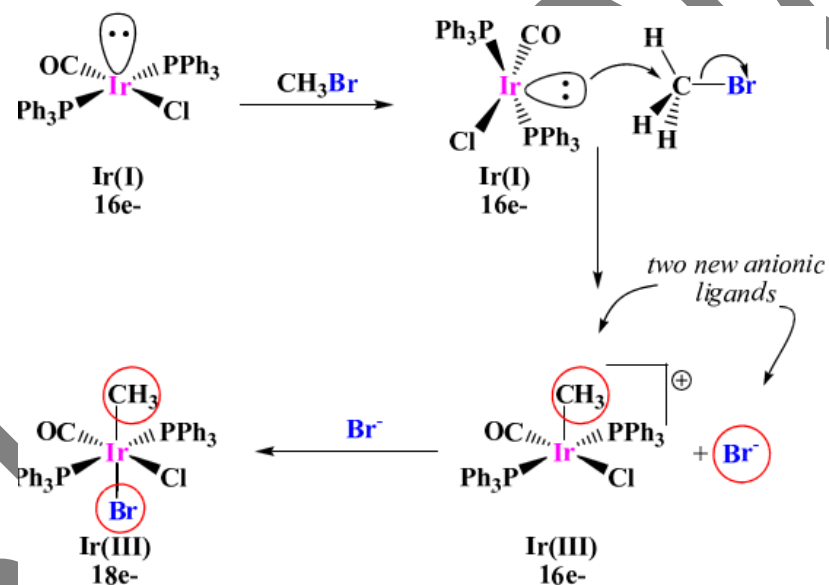
Reductive Elimination (RE)

two cisoidal anionic ligands that can form a bond between them

A neutral ligand is eliminated

OC//,,,——Ir——PPh₃ with H (circled), Ph₃P, H (circled), Cl

Ir(III)
18e⁻

[H—H, OC//,,,——Ir——PPh₃, Ph₃P, Cl]

Ir(I)
18e⁻
rarely observed intermediate

OC//,,,——Ir——PPh₃, Ph₃P, Cl + H₂

Ir(I)
16e⁻

In the OA, we break the (2-electron) A—B bond and form two (2-electron) bonds to the metal, i.e. M—A and M—B. Hence, there are some requirements for OA to occur.

(i) A vacant coordination site must be available on the metal complex, and

(ii) the metal must have an accessible oxidation state 2 units higher.

Conversely, for RE to occur, there must be a stable oxidation state 2 units lower than that in the starting complex. The resulting complex will necessarily have a free coordination site which may make it reactive or perhaps unstable. The position of the OA/RE equilibrium is determined by the overall thermodynamics of the system, i.e. the relative stabilities of the two oxidation states, the relative bond strengths of A—B, M—A and M—B, and entropy terms.

12.3 Insertion reactions

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-.

$$R-M(L_n)-Z \rightarrow (RZ)-M(L_n)$$

No change in the formal oxidation state of the metal.

A vacant coordination site is generated during a migratory insertion (which gets occupied by the incoming ligand). The groups undergoing migratory insertion must be cis to one another. Althought the oxidative addition of X–Y to M gives a complex that formally results from the insertion of a metal atom into the covalent X–Y-bond, the term "insertion" is reserved for reactions in which a molecule (which must possess a multiple bond) is inserted into a metal-ligand bond.

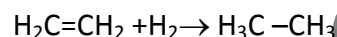**CO-Insertion into an M–C-Bond**
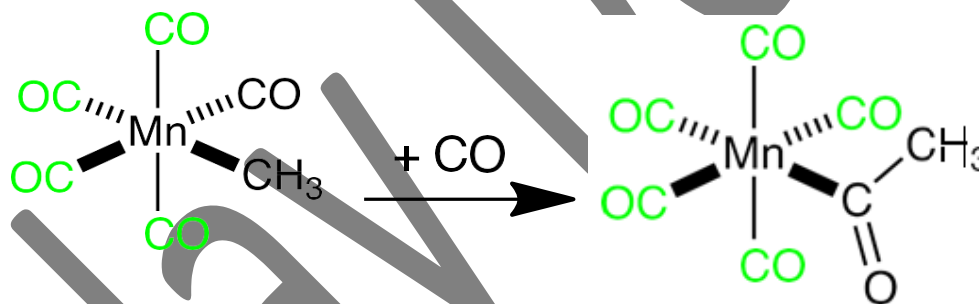
Mechanism
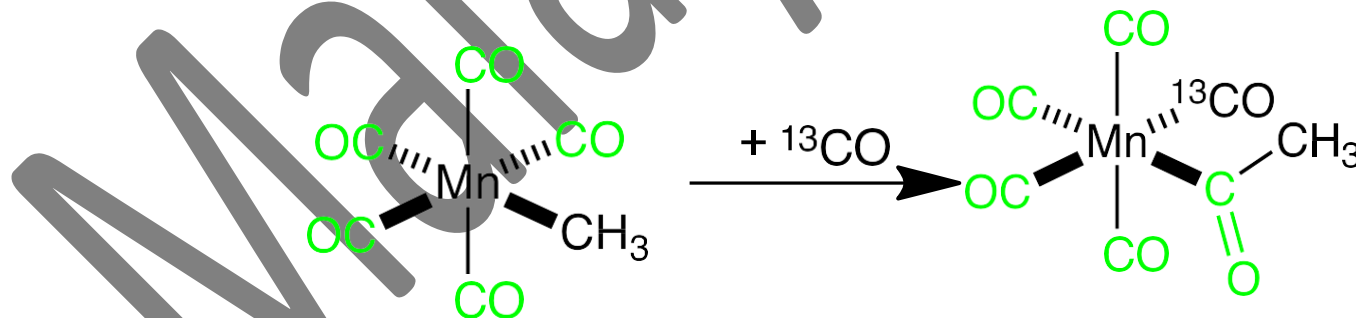
is the only product

No ^{13}C is incorporated into the acetyl group. No ^{13}CO *trans* to the acetyl group.

13. Study of the few important catalytic processes

13.1. Hydrogenation of Alkenes (Wilkinson's Catalyst)

$$H_2C=CH_2 + H_2 \rightarrow H_3C - CH_3$$

Although the above reaction is highly exothermic (ΔH^O = +136.8 kJ/mole) ethane (ethylene) does not react with hydrogen at an appreciable rate without an appropriate catalyst; the high activation energy corresponds to negligibly slow reaction rate.

The uncatalyzed hydrogenation of alkenes could theoretically occur by conceptually simple, "four-centre" mechanism (path 'p' in scheme) or a stepwise process (path 'p'). However, both the paths are unfavorable, the concerted path ('p') is "forbidden" by the Woodward-Hoffman orbital symmetry rules i.e. electron can't flow from hydrogen (H_2) to the empty π^* orbital of ethane as there is no net overlap, whereas the stepwise process (π) would necessarily involve high energy hydrogen atoms.

However, a large number of transition metal ions of electronic configurations varying from d^5 to d^{10} {Ru(III)d^5, Ru(II)d^6, Co(II)d^7, Co(I)d^8,Rh(I)d^8, Ir(I)d^8, Pd(II)d^8, Pt(II)d^8, Ag(II)d^9, Cu(I)d^{10}, Ag(I)d^{10}} are known to promote the above hydrogenation reaction by lowering the activation energy barrier for the process. The d-orbitals of a transition metal have the correct symmetry to interact directly with hydrogen molecule, the flow of electrons from the filled metal d-orbitals into the anti-bonding molecular hydrogen orbital causes H-H bond dissociation and leads to the formation of two metal-hydride bonds. The hydrogen atoms can now be transferred to the alkene.

The hydrogenation of naturally occurring materials/products (general or at selected specific sites of unsaturation) with double bonds often leads to very useful materials. In this direction, hydrogenation of vegetable oils to solid facts can be cited as an important example. These hydrogenation reactions are assuming ever-increasing importance due to their newer and novel applications in petrochemical and drug industries. In these directions, useful heterogeneous catalysts for specific purposes are Adams catalyst (platinum black oxide): Pd/C'. Pd/BaSO$_4$, Raney nickel, rhodium, ruthenium, and copper-chromium oxide. Typical hydrogenations (using

heterogeneous catalysts) have to be carried out at moderately high pressures of hydrogen (~1000/psi) and generally at elevated temperatures. Any catalysts capable of facilitating hydrogenation reactions at ambient conditions, therefore, are obviously very attractive propositions and in more recent years, homogeneous catalytic systems have proved highly successful in these directions.

$$CH_3CH_2R \qquad H_2$$

$L = PPh_3$

$CH_2 = CHR$

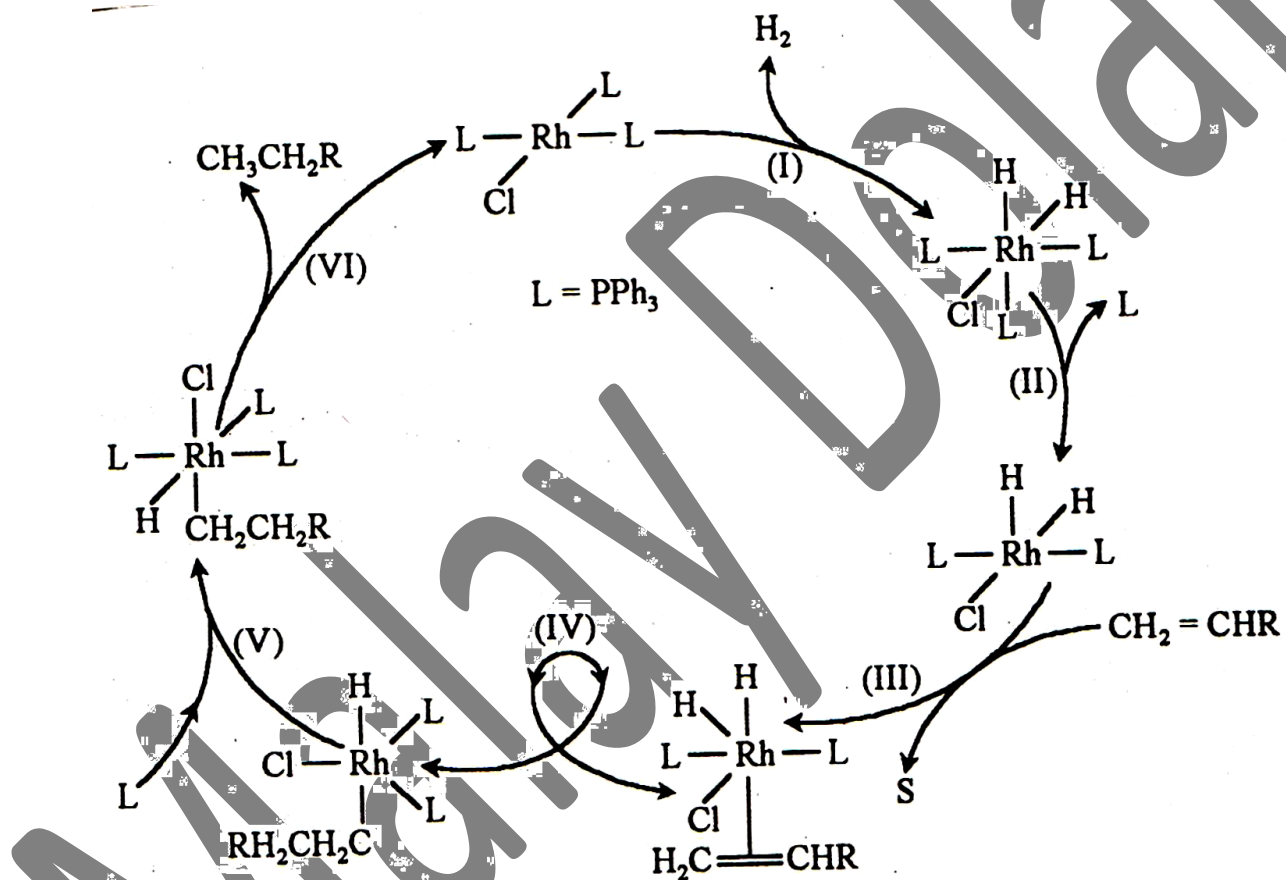(I), (II), (III), (IV), (V), (VI)

$H_2C = CHR$

Figure: Catalytic loop for alkene hydrogenation (Wilkinson's catalyst).

The mechanism of homogeneously catalyzed hydrogenations is rather complicated and has been the subject of much speculation and

controversy, but the accumulated evidence reveals that metal-hydrogen bond (either present in the parent transition metal complex itself or formed during the catalytic process) appears to be an essential step in the catalytic cycle, followed by the coordination and insertion of the alkenes and reductive elimination, the full cycle is illustrated in above Figure.

For example, the chemistry of hydrogenation involving RhCI $(PPh_3)_3$ catalyst can be understood in terms of the following steps (numbered according to their sequence in the cycle illustrated in above Figure, triphenylphosphine PPh_3 is for convenience symbolized by (P').


d^8, square planar, red d^6, octahedral, yellow
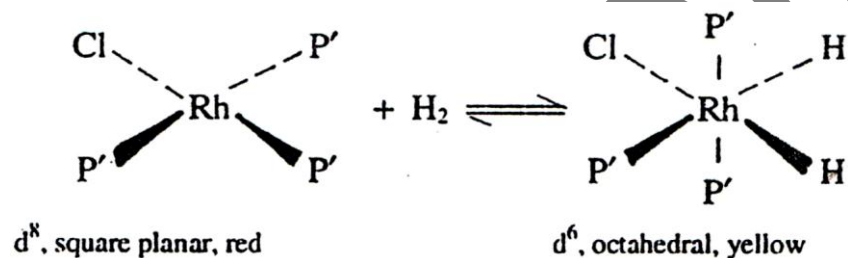
(the above indicates cis hydrogen addition and the same has been established by 'H and ^{31}P N.M.R spectroscopy; the coordination number of rhodium increases from 4 to 6 and its oxidation state from +1 to + 3 and hence, the process is known as 'oxidative addition' of hydrogen).
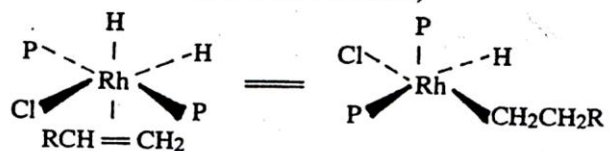
This type of 'heterolytic' activation of hydrogen is more likely with metal complexes in higher oxidation states, which makes the oxidative addition path less feasible :
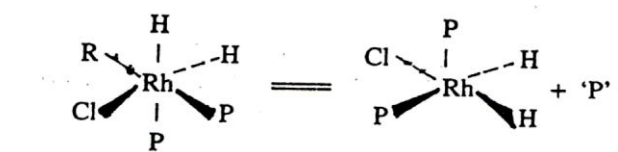
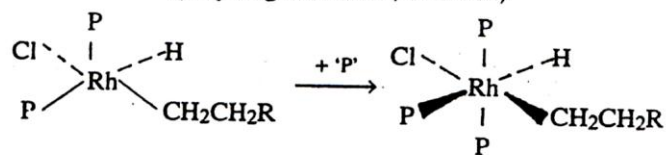(Phosphine ligand dissociation)
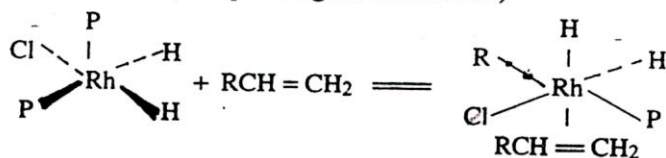
(alkene coordination)

(β-hydrogen transfer; insertion)

(Phosphine coordination)

In view of the catalyst being regenerated after a cycle of reactions, it should be possible to represent a catalytic process by a closed loop incorporating various steps of reactions involved. For example, the above reactions can be combined in a loop form as represented in above first Figure.

(reductive elimination)
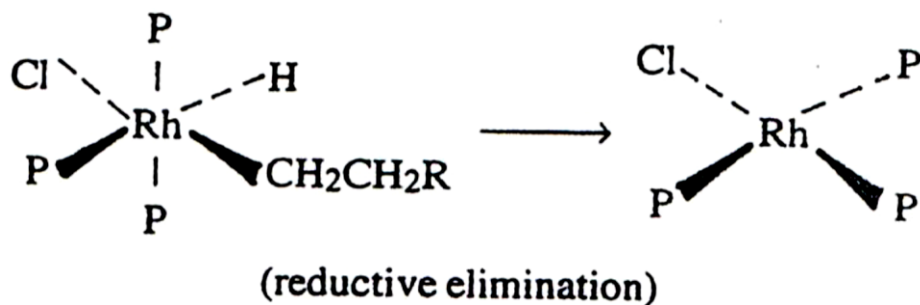
13.2. Hydroformylation of Alkenes ('Oxo' Process)

The original process (1930s) used $[Co_2(CO)_8]$ and this is still the most popular. There some problems with this system

- HCo(CO)4, which is the active species, is volatile and unstable

- it is also a good hydrogenation catalyst

- large amount of branched aldehydes produced (linear aldehydes are the most valuable)

- no spectroscopic "handle" except IR \ mechanistic studies difficult.

The reactions involved in the process are in principle the addition of hydrogen (-H) and the formyl (-CHO) group to alkenes leading to the formation of aldehydes, which are generally precursors for the production of higher alcohols (usually C_6-C_9): Earlier, the reactions used to be catalyzed by cobalt carbonyl $CO_2(CO)_8$, which was not so effective a catalyst as the reaction had to be carried out at high (150-180°C) temperature and pressure (~200 atmospheres).

$$CH_3CH=CH_2 + H_2 + CO \rightarrow CH_3CH_2CH_2CHO \qquad \Delta G = -42 \text{ kJ/mol}$$

The hydroformylation reaction is highly exothermic but less exergonic due to the decreasing entropy.

Further the products were generally mixtures of linear and branched-chain isomers in roughly 3 : 1 ratio. The role of the cobalt catalyst, $CO_2(CO)_8$ can be illustrated by a catalytic cycle shown in below Figure

$$[Co_2(CO)_8] \xrightarrow{H_2} [CoH(CO)_4]$$

$$[CoH(CO)_4] \xrightarrow{-CO} [CoH(CO)_3]$$
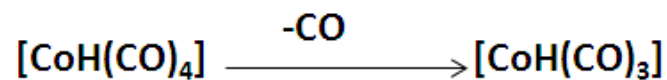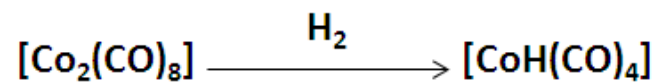
Active species (CO dissociation: negative order in CO)
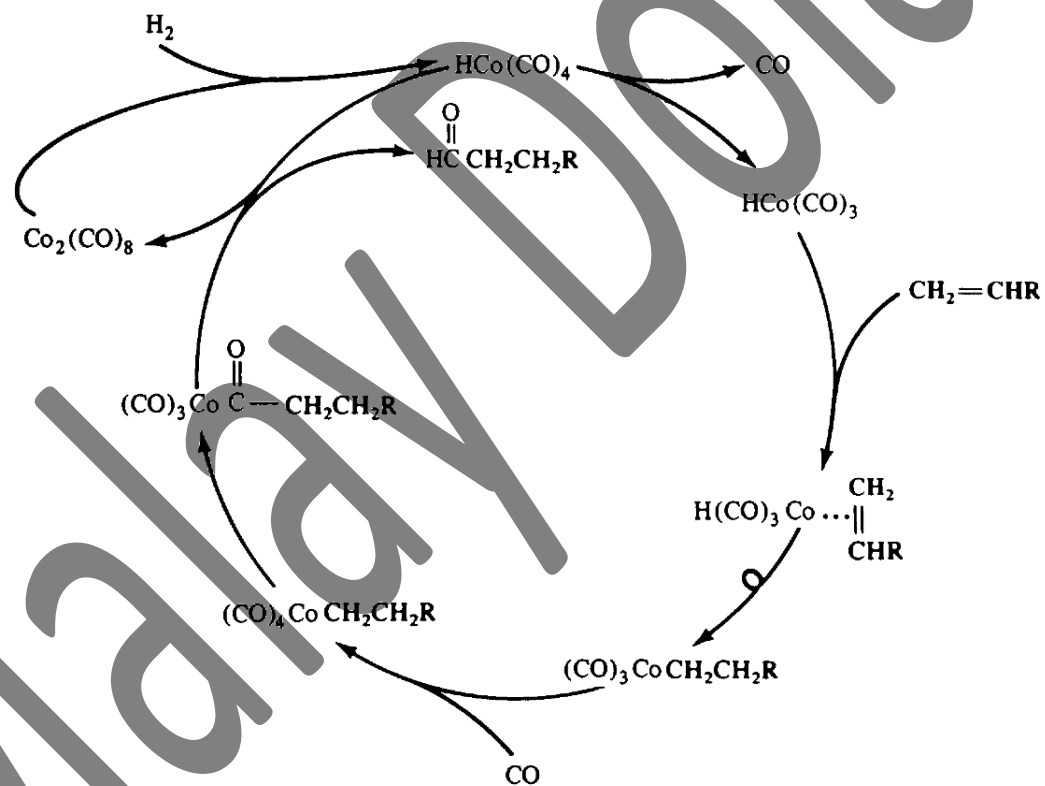
Catalytic Cycle for hydroformylation of alkenes by cobalt catalyst.

The cobalt process thus suffers from a number of disadvantages such as :

- Volatile nature of $CoH(CO)_4$ leading to its loss along with the product aldehyde and requiring its separation which is generally done in the form CoSO4.

- loss (-15%) of the alkene by a side hydrogenation reaction,

- a small amount of the conversion of aldehydes into alcohols by hydrogenation.

- production of generally less useful branched chain aldehydes and

- drastic conditions (high temperature and pressure).

More recently it has been found that the platinum group complexes such as $RhCl(CO)(PPh_3)_3$, $RhH(CO)(PPh_3)_3$ and $Ru(CO)_3(PPh_3)_2$ are much more effective than cobalt complexes. These new complexes facilitate the reactions much more effectively to proceed at lower temperatures and pressures.

For example, with $RhH(CO)(PPh_3)_3$ as catalyst, the hydroformylation reactions can proceed under ambient conditions (25°C and atomspheric pressure) yield aldehydes almost quantitatively.

For example, the hydroformylation of propene in the presence of $Co_2(CO)_8$ yields a mixture of normal and isobutyraldehyde. The ratio of normal to iso-isomers is increased with the rhodium catalyst and in presence of excess phosphine mainly the normal butyraldehyde is obtained.

13.3. Oxidation of Alkere (Oxo Palladation), Wacker process

One of the first processsses to highlight the importance of alkenes in the production of a wide variety of organic compounds was the Wacker process developed in Germany in the early 1960's this is an important large scale industrial process for the production of acetaldehyde, acetone, and methlyl ethyl ketone. It has been stated that "the invention of the Wacker process was a triuph of common sense". It may be noted that the oxidation of ethylene to acetaldehyde with the help of platinum group metals had been known as for

back as 1894: ketone. It has been stated that "the invention of the Wacker process was a triuph of common sense".

$$[PtCl_3(C_2H_2)] + H_2O \xrightarrow{\text{heat}} CH_3CHO + Pt\,(O) + 3Cl^-$$
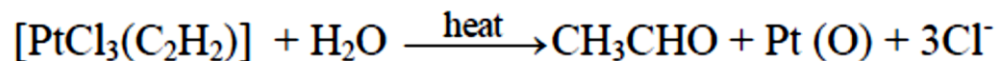
Zeise's salt

It was, however, more than six decades later that Smidt working at Wacker Chemie laboratories discovered a practical process for the oxidation of ethylene to acetaldehyde using $PdCl_2$ as a catalyst.

Complexes of alkenes often undergo nucleophilic attack to give metal alkyls which may then rearrange to give other products.
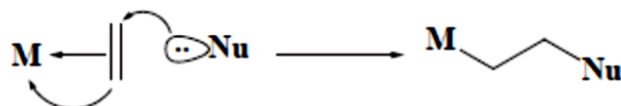
This is used as the basis for production of millions of tons of aldehydes *p.a.* in the Wacker Process.

It was established in the 19th century that aqueous $PdCl_2$ oxidises ethylene to acetaldehyde. The reaction consumes the $PdCl_2$ (and is thus hideously expensive) and deposits black Pd metal. The key discovery that made this reaction catalytically feasible is that acidified Cu(II) will oxidise the Pd(0) before it has a chance to precipitate.

As the Pd(II) is reduced by the ethylene (mechanism later) it is quickly re-oxidised by two moles of Cu(II). The Cu(I) product is airsensitive and is reoxidised itself to Cu(II). Pd(0) is not oxidised by air at a significant rate under these conditions.
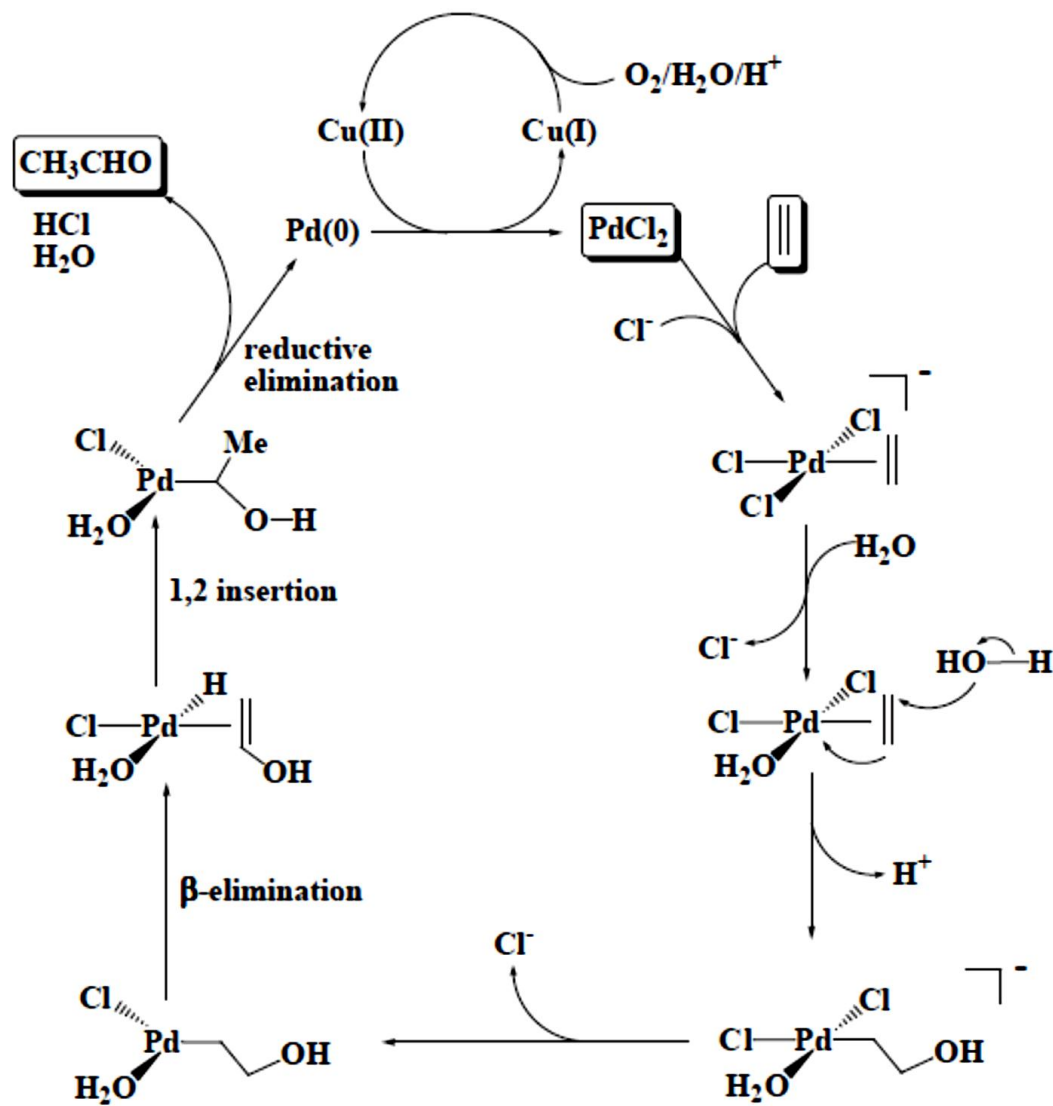
$$C_2H_4 \xrightarrow{PdCl_2/O_2/H_2O/Cu(II)} CH_3CHO$$
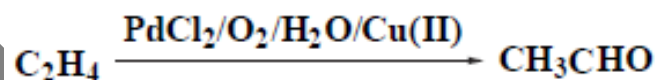
Mechanistic work on the process suggested the following rate equation:

$$\text{Rate} = \frac{k[PdCl_4{}^{2-}][C_2H_4]}{[Cl^-]^2[H^+]}$$

Because the reaction takes place in water, it is not feasible to determine the order of reaction with respect to $[H_2O]$.

Proposed Catalytic Cycle for the Wacker Process

13.4. Synthetic gasoline (Fischer Tropsch reaction)

The "reformation" of natural gas (see below) provides a C1 feedstock called variously "water-gas" or "synthesis gas" or plain "syngas" which is used in the production of a variety of chemicals. Synthesis gas can be converted to methanol or long-chain alkanes and alcohols via the Fischer Tropsch reaction.

$$CH_4 + H_2O \xrightarrow{\text{heat}} \boxed{\begin{array}{c} CO + 3H_2 \\ \textbf{Synthesis Gas} \end{array}} \xrightarrow{\text{het. cat.}} CH_3OH$$

Fischer-Tropsch

$$CH_3(CH_2)_nCH_3$$
$$+$$
$$CH_3(CH_2)_nCH_2OH$$
$$+$$
$$H_2O$$

homogeneous F.-T.

$$HOCH_2CH_2OH$$
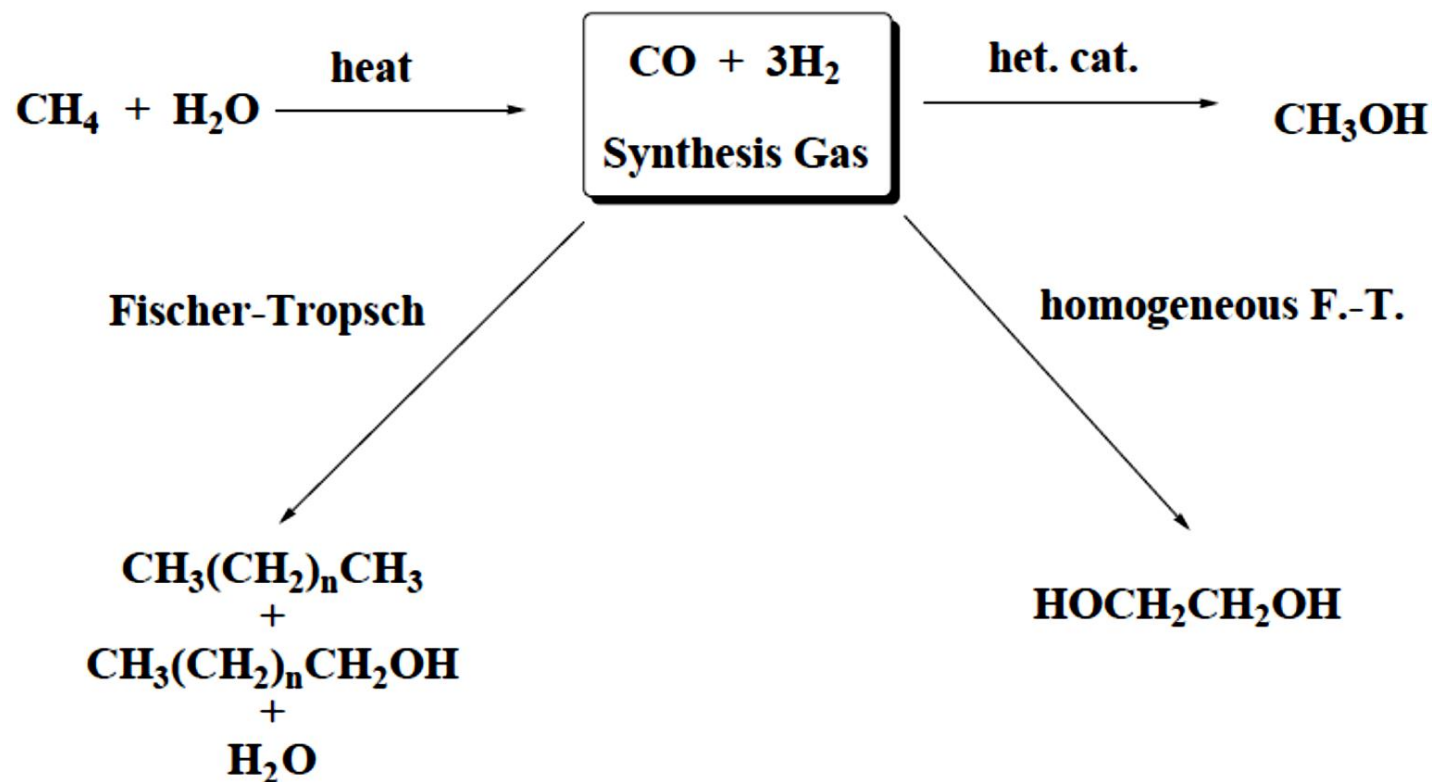
A wide variety of heterogeneous catalysts are used, but perhaps the most common is Fe or Fe oxides. Some "models" of what is occurring at the surface of the catalyst in this reaction have been developed in homogeneous systems, but it is hard to relate these systems to the real heterogeneous catalyst.

13.5. Alkene Polymerization (Ziegler-Natta Catalysis)

Ziegler and Natta shared the Nobel Prize in 1963 for their earlier work on the heterogeneous polymerization of ethene and propene. The catalysts used are similar to those active as metathesis catalysts, the earliest and most popular is a mixture of $TiCl_3$ and the alkylating agent $AlEt_2Cl$. Homogeneous analogues of the Ziegler-Natta system have been very widely studied. The parent complex of several generations of catalyst, zirconocene dichloride, was popularised by Sinn and Kaminski in 1976.

The polymerization of alkenes to give commercially useful fibres, resign, and plastics is a thermodynamically favored process. However, the alkene must first be activated by a catalyst, so that the polymerization reaction may proceed at a reasonable rate. A variety of organometallic compounds have been frequently used for this activation or catalytic process and the reactions in their presented generally lead to stereoregular polymers.

$$nC_2H_4 \xrightarrow[\text{and pressure}]{\text{high tempeature}} [C_2H_4]_n$$
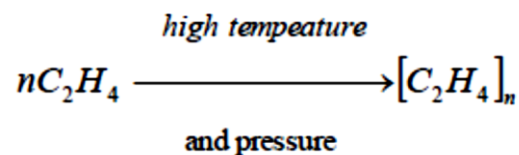
The origional uncatalyzed industrial process for polythene involved the use of high temperatures and pressures and the product was atactic, amorphous, and of low density. However, K.Ziegler (Germany) and G. Natta (Italy) achieved low pressure and room temperature stereoregular catalytic polymerization of ethane and propane in the presence of organometallic mixed catalysts (1955) to give isotactic, high density, harder and tougher, higher melting crystalline polyethylene ("Polythene") and other plastics on an industrial scale. A typical Ziegler-Natta catalyst can be made by mixing $TiCl_4$ and Al_2Et_6 in heptane. In Ziegler-Natta type of catalytic system consists of a reducing and/or alkylating agent from Group I-III such as an aluminium alkyl (usually Al_2Et_6 or $AlClEt_2)_2$, and a transition metal compound (usually a halide of early transition metal series, e.g. $TiCl_4$, $TiCl_3$, or VCl_4).

Most Ziegler Natta catalytic systems are heterogeneous, although several homogenoeous catalytic procedures have also been developed (e.g. from $TiCl_2(n^5\text{-}C_5H_5)$ or $TiClEt(n_5\text{-}C_5H_5)_2$. Recetnt studies appear to show that the polymerization site is generally the transition metal in an

activated form, which is brought about by its reaction with aluminium alkyl (an initiator acting as reducing and alkylating agent). The initiating step, according to Cossee, consists in the replacement of one of the chloride ions coordinated to a titanium(III) ion {which has been initially generated in situ from the parent titanium (IV) chloride by reduction with $Al_2(CH_2CH_3)_6$, at the surface by an alkyl "Group of the aluminum alkyl.
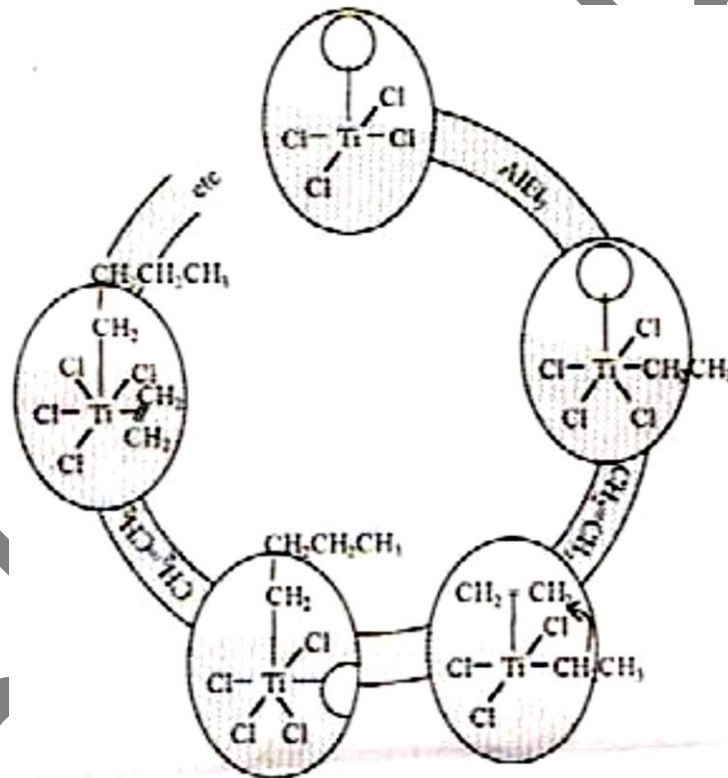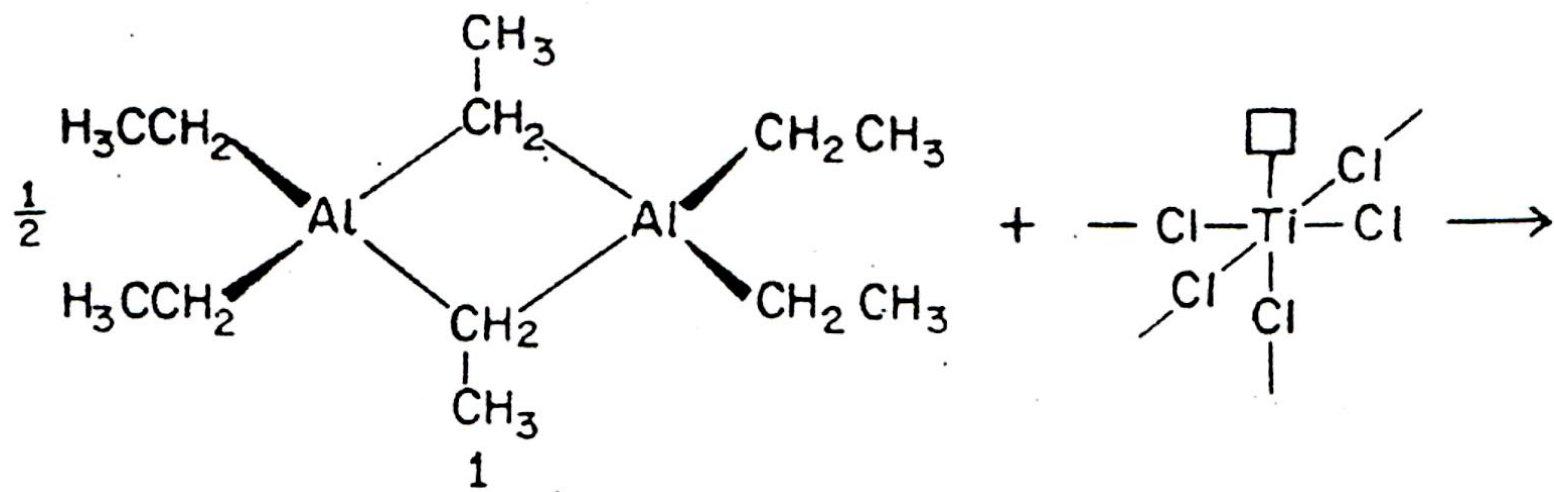
Due to the formation of an empty coordination site exposed at the surface of the alkylated titanium (III) halide, a molecule of propylene (propene) can bind itself to it through it π-electrons (step 2):
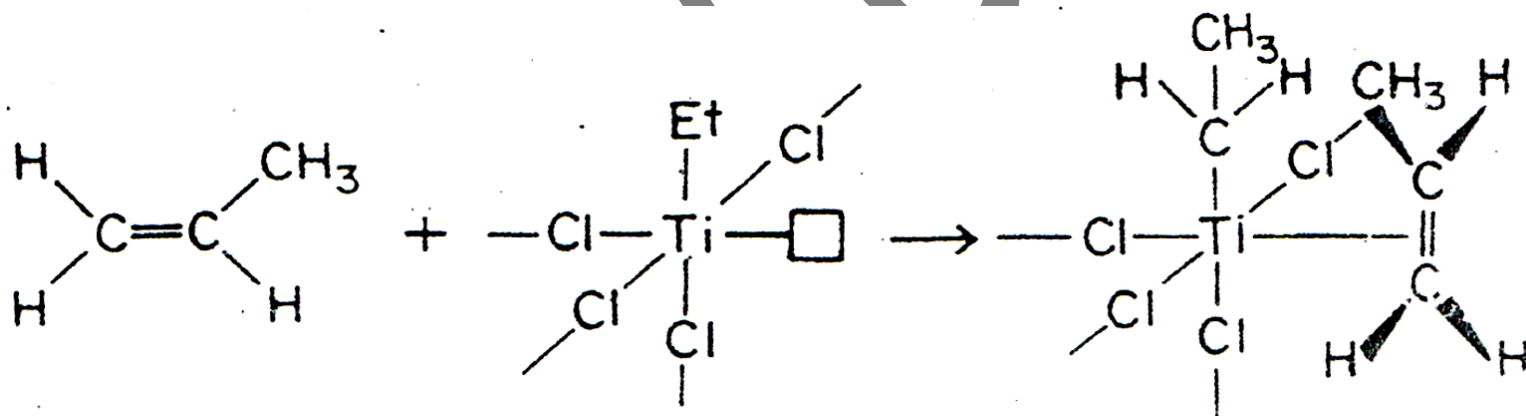
This reaction brings the alkyl group and the alkene in proper stereochemical arrangement to facilitate migration of the alkyl group to alkene (i.e., cis-insertion in the neighboring metal-alkyl bond), giving a longer chain (i.e., growing polymer chain) of the alkyl derivative; this results in a fresh vacant site at the surface (step 3):

This vacant site can be occupied by another propene molecule and the insertion process is repeated and steps (2) and (3) continued until a chain termination process occurs by the severing of the titanium-alkyl bond:
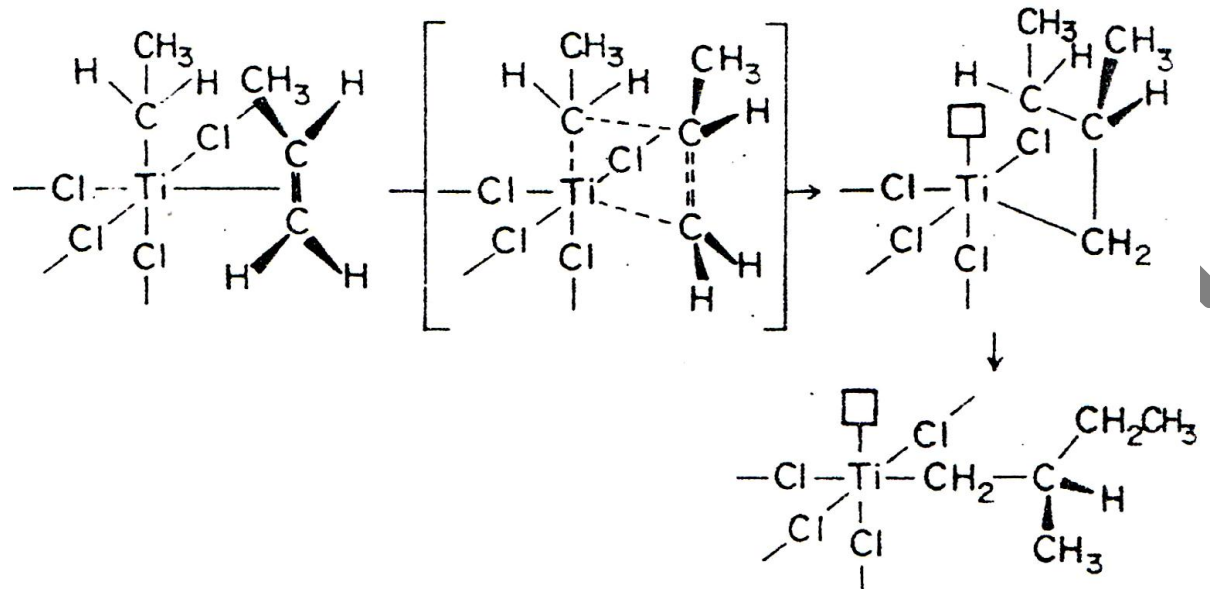
The vacant site can be occupied by another propene molecule and the insertion process is repeated and steps (2) and (3) continued until a chin termination process occurs y the serving of titanium-alkyl bond:

$$-Cl-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle \square}{|}}{Ti}}\overset{Cl}{-}CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}}-H \qquad \underset{H}{\overset{H}{>}}C=C\underset{H}{\overset{CH_3}{<}} \longrightarrow$$

$$\cdots\overset{CH_2}{\underset{\underset{Me}{\diagup}\ \ \underset{H}{\diagdown}}{C}}\cdots\overset{CH_2}{\underset{\underset{Me}{\diagup}\ \ \underset{H}{\diagdown}}{C}}\cdots\overset{CH_2}{\underset{\underset{Me}{\diagup}\ \ \underset{H}{\diagdown}}{C}}\cdots\overset{CH_2}{\underset{\underset{Me}{\diagup}\ \ \underset{H}{\diagdown}}{C}}\cdots\overset{CH_2}{\underset{\underset{Me}{\diagup}\ \ \underset{H}{\diagdown}}{C}}\cdots$$

14. Problems

1. How many lone pairs are there in the CO molecule?

   Ans: Three (one from carbon and two from oxygen).

2. Despite O being more electronegative than C, the dipole moment of CO is almost zero. Explain.

   Ans: Because of the electron donation from oxygen to carbon.

3. What type of metal centers form metal carbonyl complexes?

   Ans: Low–valent metal centers.

4. What are the two main modes of binding exhibited by CO ligand?

   Ans: Terminal and bridging modes of binding.

5. Predict the product of the reaction?

   Ni+ CO(excess) →

Ans: Ni(CO)$_4$

6. Upon binding to a metal center the C–O stretching frequency increases/decreases with regard to that of the free CO?

Ans: Decreases.

7. Explain why do low–valent metal centers stabilize CO binding in metal carbonyl complexes?

Ans: Because metal to ligand π–back donation.
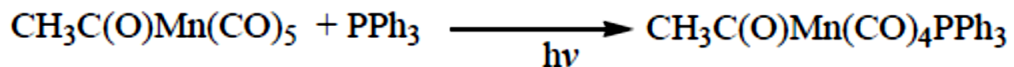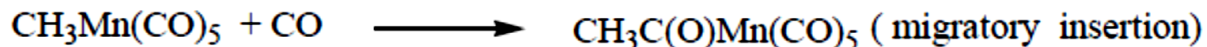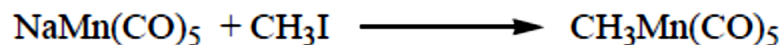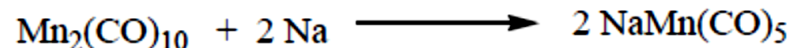
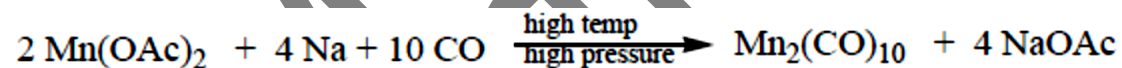8. Give an example of a good σ–donor and π–donor ligand?

Ans: Alkoxides (RO-).

9. A metal complex having the empirical formula FeC$_9$H$_7$O$_3$Cl, has one ligand as a substituted cyclopentadienyl group. It is an ionic compound and has poor solubility in hydrocarbon solvents. The compound gives a white precipitate on treatment with AgNO3 solution. Assuming that it obeys the 18 electron rule, suggest its structure.

Ans.
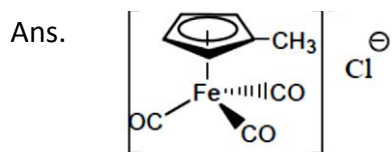
10. Give a scheme for the synthesis of Mn(CO)$_4$(PPh$_3$)[C(O)CH$_3$] starting from Manganese acetate, Mn(OAc)$_2$.

Ans.

$$2\ Mn(OAc)_2\ +\ 4\ Na\ +\ 10\ CO\ \xrightarrow[\text{high pressure}]{\text{high temp}}\ Mn_2(CO)_{10}\ +\ 4\ NaOAc$$

$$Mn_2(CO)_{10}\ +\ 2\ Na\ \longrightarrow\ 2\ NaMn(CO)_5$$

$$NaMn(CO)_5\ +\ CH_3I\ \longrightarrow\ CH_3Mn(CO)_5$$

$$CH_3Mn(CO)_5\ +\ CO\ \longrightarrow\ CH_3C(O)Mn(CO)_5\ (\text{migratory insertion})$$

$$CH_3C(O)Mn(CO)_5\ +\ PPh_3\ \xrightarrow{hv}\ CH_3C(O)Mn(CO)_4PPh_3$$

11. Mark against each statement the appropriate type of reaction or reactions from the list (oxidative addition, reductive elimination, migratory insertion and β-H transfer)

(a) *cis* orientation of the participating ligands is a must.

(b) This reaction does not occur for $d0$ metal complexes.

(c) This reaction is enthalpy favoured and entropy prohibited.

(d) A vacant coordination site on the metal centre is a prerequisite.

(e) The more electron rich the metal centre, the more facile is the reaction.

(f) There is an increase in the electron count of the metal complex by two units during this reaction.

Ans:

(a) Red elimination and migratory insertion

(b) Oxidative addition

(c) Migratory insertion

(d) Oxidative addition and β-H transfer

(e) Oxidative addition

(f) Oxidative addition and β-H transfer

12. Which among the following compounds will not undergo oxidative addition of methyl iodide ? Give reasons

(a) $Ir(PPh_3)_2(CO)Cl$ (b) $[RhI_2(CO)_2]^-$ (c) $\eta^5\text{-}Cp_2Ti(Me)Cl$

Ans: (c) As titanium is already in its highest oxidation state of +4 and therefore no d electrons present for further oxidation

13. An organometallic bond is defined as the bond between which?

Ans: Metal- carbon direct bond.

14. In the Ziegler Natta catalyst, which metal is used?

Ans: Ti, $TiCl_3(Et)$.

15. Summary

CO is a hallmark ligand of organometallic chemistry. The metal carbonyl complexes have been studied for a long time. The CO ligands bind tightly to metal center using a synergistic mechanism that involves σ–donation of the ligand lone pair to metal and followed by the π–back donation from a filled metal d orbital to a vacant σ* orbital of C–O bond of the CO ligand. The metal carbonyl complexes are prepared by several methods. The metal carbonyl complexes are usually stabilized by metal centers in low oxidation states. Metal carbonyl catalysts may be attached to solid supports which, in principle, facilitate their separation from the reactions products, which can be a problem with homogeneously catalyzed reactions. It has been discussed on the topics of hepticity, ferrocene and Ziese's salt elaborately and their importance in society. Infrared spectroscopy is also discussed with the effect of synergic back bonding formation which helps to determine the structures of carbonyls compounds. The elementary idea about oxidative addition, reductive elimination, insertion reactions have been written and exclusive study on the catalytic processes: alkene hydrogenation (Wilkinson's catalyst), hydroformylation, Wacker process, Synthetic gasoline (Fischer Tropsch reaction) and Olefin polymerization reaction (Ziegler-Natta catalyst) have been described in this chapter.

16. Questions

1. Spectroscopy (IR) which is very useful in identifying the structures suggests the C– O bond order in M CO complexes is less than in free CO? Hints: (2143 cm^{-1} is the C-O stretch is free CO).In most CO complexes they range from 1850–2150 cm^{-1}.

2. In the catalytic cycle of hydroformylation starting with active catalysts $HCo(CO)_3$ or trans $Rh(PPh_3)_2(CO)(H)$, the first step is the coordination of the alkene on the metal. If instead, one proposes oxidative addition of H_2 as the first step (followed by removal of a spectator ligand and then alkene coordination) will it make any difference in the product composition of the reaction? If yes, give

reasons. See the Hydroformylation sections.

3. How many unpaired electrons, if any, are in each of the following complexes? Indicate whether either complex would be an oxidizing or a reducing agent.

 Cp_2Co,

 Cp_2Fe^+. See the ferrocene section.

4. Infra-red spectral analysis of the following three complexes showed a set of two IR bands for the νCO stretching frequencies. Match the correct set of IR bands to the given compounds and justify your reason for the assignment. See the IR section.

5. The complex $[M(\eta^6\text{-}C_6H_6)(CO)_2]_2$ obeys 18 electron rule and has one metal- metal double bond. Predict M and sketch the probable structure of the complex.

6. Determine the unknown quantity

 a) $[CpW(CO)x]_2$ [has W-W single bond]

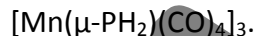 $[(CO)_3Ni\text{-}Co(CO)_3]_2$
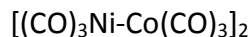
 $[CpMn(CO)x]_2$ (has Mn = Mn double bond]

 $[(Cp)_3Ni_3(\mu_3\text{-}CO)_2]z$ (no metal metal bonds) (hint: consider unit as a whole)

 $[CpM(CO)_3]_2$ (has a single M-M bond; M = Ist row TM]

7. Trimetallic complexes of phosphido bridges are well known. Assuming that the 18e rule is followed, postulate the structure of

 $[Mn(\mu\text{-}PH_2)(CO)_4]_3$.

8. Arrange the following in the decreasing order of back donation

 $Cr(CO)_6$; $[Ti(CO)_6]^{-2}$; $[Mn(CO)_6]^+$; $[Ir(CO)_6]^{3+}$; $[V(CO)_6]^-$

9. The compound (η5-C_5H_5)Co(CO)$_2$ (A) upon UV irradiation, resulted in the evolution of equimolar amount of a gas and formation of a new compound B. While the infrared spectrum of A showed absorptions around 1988 cm^{-1}, the spectrum of B showed absorptions only around 1798 cm^{-1}. Compounds A and B both obey 18 electron rule and both has the cyclopentadienyl group in the η^5 mode. Draw the structure of compound B. See IR section.

10. Ferrocene is thermally stable and not air sensitive but cobaltocene is readily oxidized to cobaltocenium ion. Why ?

11. Although the 17 electron species V(CO)$_6$ has not been found to dimerize to give V$_2$(CO)$_{12}$, the latter has been found to form along with V(CO)$_6$ and remain stable at extremely low temperatures when a V/CO mixture in the ratio 1:102 was condensed into a pure CO matrix at 6-12 K. Infrared spectral analysis of V$_2$(CO)$_{12}$ showed three bands at 2014, 2050 and 1850 cm^{-1} . Given that this dimer obeys the 18 electron rule and vanadium has a coordination number of eight, propose a structure for the same. See IR section.

12. Why is the carbon metal bond in organometallic compounds unusual in organic chemistry? (hint: consider unit as a whole)

13. What does hapticity (η) refer to in organometallic chemistry? See hepticity section.

14. Why is the vibrational wavenumber of CO in M-CO complexes than in free CO? See IR section.

15. Wilkinson's catalyst is commonly employed in what reaction? See Wilkinson's catalyst.

16. What is the oxidation state of Iron in Ferrocene?