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Prof. Akinyele's Part

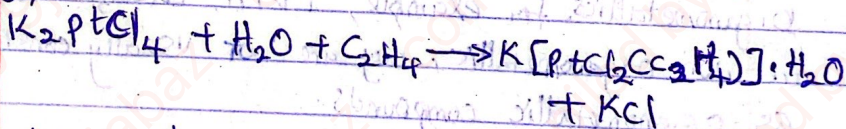
13th April, 2026

Prof. Arinyele

Organometallic Chemistry

Organometallic compounds are compounds whose carbon atoms are directly bonded to the metal atoms. The

first organometallic compound was prepared by Liebig in 1827, when $K_2PtCl_4(C_2H_4) \cdot H_2O$ was prepared by bubbling ethylene through a aqueous solution of potassium tetrachloroplatinate (II) according to;



and compound was analyzed using X-ray chromatography. The synthesis of this compound was closely followed by ~~the synthesis of this compound was closely followed by~~ Mond et al. in 1890 the synthesis of $Ni(CO)_4$ by Mond et al. in 1890 and later, $Fe(CO)_5$ in 1891. synthesized

Organo

An organometallic compound is defined as a compound in which a direct bond occurs between the metal atoms and the carbon ^{atoms} of the ^{organic} ~~organic~~ group.

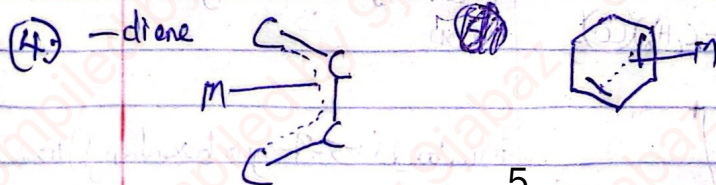
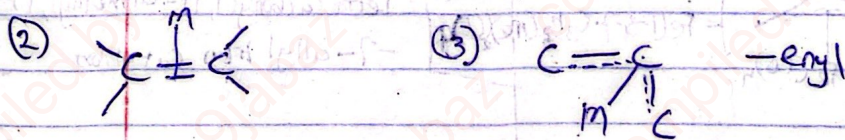
~~Carbon~~ Although, the term organometallic indicates a compound containing a metal and an organic group (carbon containing specie). Those compounds in which a direct metal carbon bond is not in operation are not classified as organometallics. For example, EDTA, CaCO_3 , Na_2CO_3 are non organometallic, they are not usually considered as organometallic compounds.

Classification of Organometallic Compound

Organometallic compounds are classified according to the number of carbon atom from the organic group, ligands, that are directly bonded to the metal.

No. of C atom	Nomenclature of complex formed	Example
1	-yl	Alkyl e.g. CH_3 , C_2H_5
2	-ene	C_2H_4
3	-enyl, allyl	C_3H_5
4	-diene	C_4H_6 , 
5	-dienyl	C_5H_8 ,  only 5 C atoms are bonded to the metal
6	-triene	C_6H_8
7	-tri-enyl	C_7H_9 , C_8H_9
8	tetraene	

① Alkyls: $\text{M}-\text{CH}_3$, metal carbonyls e.g. $\text{Fe}(\text{CO})_5$, $\text{Ni}(\text{CO})_4$

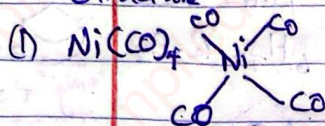


(5) -diene)

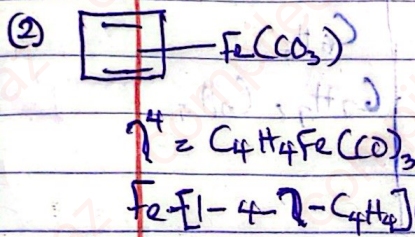
Examples of Organometallic compounds

Structure

Name

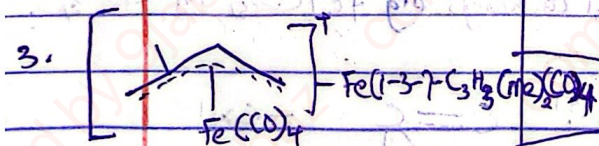


Nickel tetracarbonyl

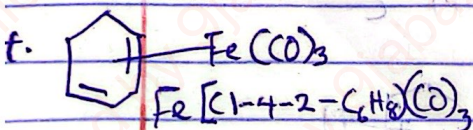


1,5-cyclooctadiene-1-iron tricarbonyl

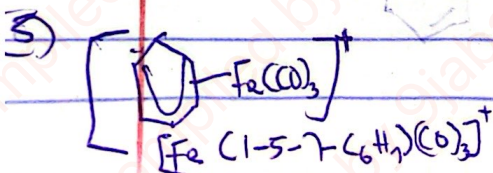
It is referred to as tricarbonyl cycloocta (1,3) diene iron



Tetra carbonyl (1,1)-dimethyl, (1,3) -7-allyl iron cation

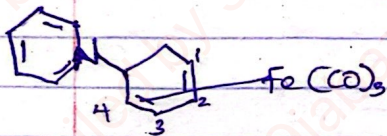


tricarbonyl [1-4-2 cyclohexa-1,3-diene] iron



tricarbonyl (1-5-7 cyclohexadienyl) iron cations

The symbol η is called haptic number or hapticity and it represents carbon atoms from the organic functions that are directly bonded to the metal atom. The position of attachment of the added nucleophile to the organometallic compound must be indicated in the nomenclature eg



tricarbonyl (1-4-9-cyclohexa-1,3-diene η 5



The effective atomic no. rule. (EAN)

All organic compounds must obey 18e⁻

The effective atomic no. rule, otherwise referred to as 18 electron rule or Sidgwick-Bailey's rule states that all stable organometallic compounds should have 18 electrons within metal valence shell. The rule was first proposed by Sidgwick and later extended by Bailey that is why this sometimes referred to as Sidgwick-Bailey's rule or 18e⁻ rule.

The rule arises mainly from the kinetic stability of d metal complex which may be associated with the Sidgwick-Bailey's rule.

With full occupancy or complete filling of all lying available bonding and non-bonding (the top of an octahedral complex) orbitals of d metal there are 1s 3p 5(n-1)d. The numbers 1s and 5 simply refer to orientation in space or the number of orbitals of d s, p and d orbitals respectively. While n is the principal quantum number or subshell. n must not be less than 4. If u have an organometallic compound proper. i.e. $n \geq 4$. $(4-1)d = 3d$ $(5-1)d = 4d$ $(6-1)d = 5d$ etc.

$s=2e$ $p=6$ $d=10$ max. $2+6+10 = 18$ electrons (full occupancy).

According to rule of max. multiplicity, each suborbital must have 2e⁻ so that each have a better 18e⁻ from all d, p available orbitals. Full occupancy of these valence orbitals ensures max. no. of bonding electrons and hence, stability of d complex.

If we have less than 18e⁻ in d valence orbital of d metal atom, this clearly leads to creation of empty low lying orbital into which electrons may be promoted to initiate thermal decomposition of d complex.

On the other hand, d presence of more than 18e⁻ will create antibonding orbitals whose creating effect with d bonding orbitals leads to kinetic instability. This complete filling of all 9 available ^{valence} orbitals is d molecular orbital explanation of d 18e⁻ rule.

* Explain the term effective atomic no. rule.

All stable organometallic -----

Application of 18 electron rule.

In applying 18 electron rule to an organometallic compound, d no. of electrons in d valence shell of this compound obey 18e⁻ rule? If yes how, if no how? state d reason!!!
Firstly, d uncomplexed metal (i.e. metal in d zero oxidation state) is added to those donated by d ligands provided by addition of negatively charged or subtracted (if positively charged) of electrons in accordance with d overall charge and compare d no. of electrons donated by d ligands are as follows:

Ligand directly bonded to d metal	no of electrons donated to d metal.
1. Carbon	1
2. Hydrogen	1
3. Halogens $\langle F, Cl, Br, I \rangle$ Terminal Bridging	Terminal 1, 3 (Bridging).
4. CO (Carbonyl)	2
5. NO (Nitrosyl)	3
6. CN	1
7. Nitrogen and its compounds	2
8. Sulphur " " "	2
9. Phosphorus " " "	2

In working out d no of electron in d uncomplexed metal, i.e metal with zero oxidation state. It is important to remember d zero oxidation state electronic config. of the first row transition metals. Once this is known, we can very easily state d config. of other metals in d same first. (class 6 metals)

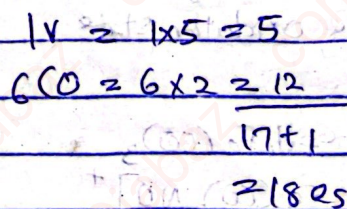
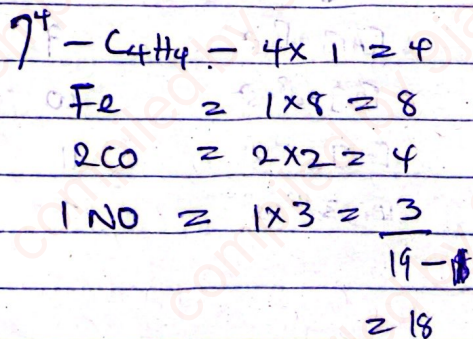
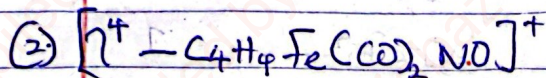
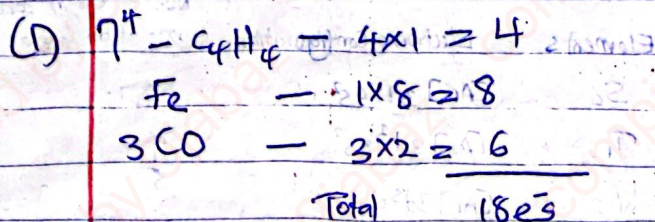
20th April, 2026

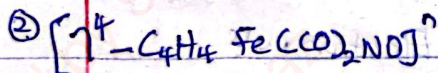
Atomic NO	Elements	Electronic Configuration	No. of e ^s in zero oxidation state.
21	Sc	[Ar] 3d ¹ 4s ²	3
22	Ti	[Ar] 3d ² 4s ²	4
23	V	[Ar] 3d ³ 4s ²	5
24	Cr	[Ar] 3d ⁵ 4s ¹	6
25	Mn	[Ar] 3d ⁵ 4s ²	7
26	Fe	[Ar] 3d ⁶ 4s ²	8
27	Co	[Ar] 3d ⁷ 4s ²	9
28	Ni	[Ar] 3d ⁸ 4s ²	10
29	Cu	[Ar] 3d ¹⁰ 4s ¹	11
30	Zn	[Ar] 3d ¹⁰ 4s ²	12

Examples

We want to look at the following compounds whether they obey the rule of 18 oxidation state.

- 1) $\text{C}_4\text{H}_4\text{Fe}(\text{CO})_3$
- 2) $[\text{C}_4\text{H}_4\text{Fe}(\text{CO})_2\text{NO}]^+$
- 3) $[\text{V}(\text{CO})_6]^-$
- 4) $\text{Co}(\text{CO})_3(\text{NO})$
- 5) $[\text{Co}(\text{CO})_2(\text{NO})_2]^{2-}$





Determine the value of n

$$7^+ - 4 \times H_4 = 4 \times 1 = 4$$

$$Fe = 1 \times 8 = 8$$

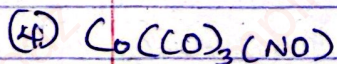
$$2CO = 2 \times 2 = 4$$

$$1NO = 1 \times 3 = 3$$

$$\underline{19}$$

$$n + 18 = 19$$

$$n = 19 - 18 \Rightarrow n = +1$$

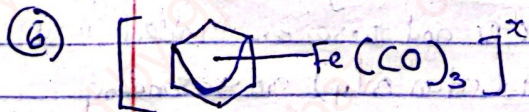


$$Co - 1 \times 9 = 9$$

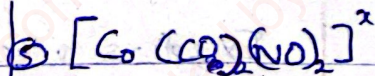
$$3CO - 3 \times 2 = 6$$

$$1NO = 1 \times 3 = 3$$

$$\underline{18}$$



$$1 C_5H_5$$



$$1Co - 1 \times 9 = 9$$

$$2CO - 2 \times 2 = 4$$

$$2NO \rightarrow 2 \times 3 = 6$$

$$\underline{19}$$

$$n + 18 = 19$$

$$n = +1$$

Exceptions to the 18 Electron rule

Although a wide variety of organometallics obey the 18 electron rule, notable exceptions to this rule include; 4-coordinate d^8 system, i.e., complexes of ~~thorium~~ ^{Rhodium}, Iridium, Nickel (II), Palladium (II) and Aurum (III) ($Rh(I)$, $Ir(I)$, $Ni(II)$, $Pd(II)$, $Au(III)$)

Examples are organometallic with bulky ligands, such as;
 $[Rh(CO)_2Cl]_2$, $[Ni\{P(cyclohexyl)_3\}_2(CH_2CH_2)]$

Metal Carbonyl and Metal's Nitrosyls

The carbonyl ligands CO acts as two electron donor; a number of transition metal to form metal carbonyls that can be grouped into three main types

- 1.) Binary metal carbonyls: The binary metal carbonyls, the only ligand present is CO and these are divided into primary (involving one metal atom only) and secondary (involving two or more metal atoms)
- 2.) Metal carbonyl Halides: It contains both the carbonyl and halide group. Example is iodotris(η⁵-cyclopentadienyl)iridium $[Ir(CO)_5I]$

NO is stronger than CO

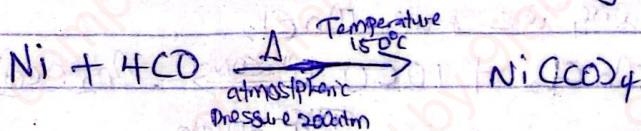
OS before = OS after

(3) Metal carbonyl Nitrosyls: Eg, $M(CO)_x(NO)_y$,

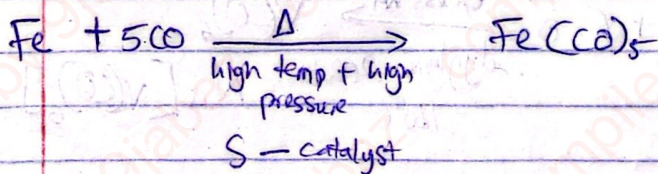
Synthesis

(1) Direct reaction between metal and carbon monoxide: This is a useful method only when the oxidation state of the uncomplexed metal is to be maintained in the metal carbonyl formed

Nickel tetracarbonyl is synthesized by ^{heating} ~~reacting~~ Nickel in an atmospheric pressure of CO under high temperature



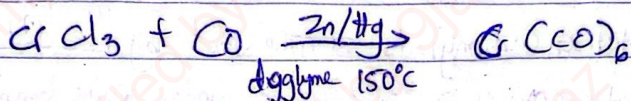
Ironpentacarbonyl is synthesized under high temperature and pressure in the presence of sulphur as catalyst



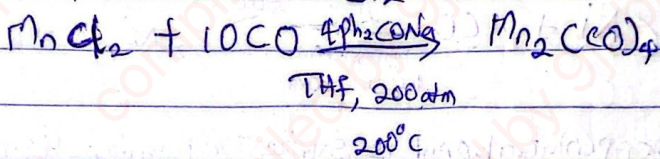
(2) Direct reaction of metal salt with carbon monoxide

This is useful when the oxidation state of the metal in the starting salt ~~needs~~^{is} to be reduced.

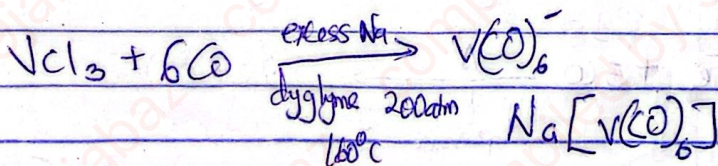
Therefore, a reducing agent is required for the preparation. Chromium hexacarbonyl is synthesized by reacting CrCl_3 with atmospheric CO in the presence of Zn/Hg.



Likewise we have MnCl_2



Also, we have

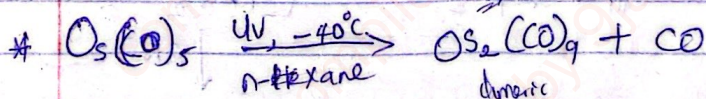


(B) The (1) and (2) reactions earlier mentioned are by thermolysis reaction.

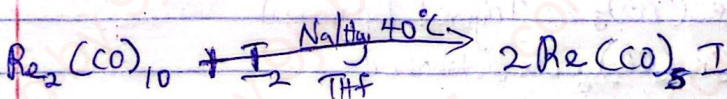
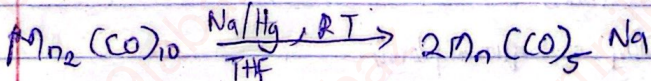
* Synthesis of metal carbonyl

This is a useful ^{route} ~~route~~ to the synthesis of secondary metal Carbonyl. For instance, $\text{Fe}(\text{CO})_5$ in *n*-Hexane is irradiated at room temperature to give $\text{Fe}_2(\text{CO})_9$, under UV radiation.

This is also the same for Os, but at a temperature of -140°C , $\text{Os}(\text{CO})_5$ gives $\text{Os}_2(\text{CO})_9$.



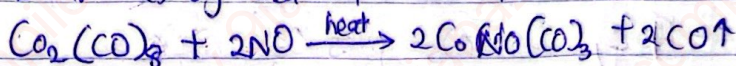
This is a good route to anion metal carbonyls and in the presence of a halide to give metal carbonyl halides.



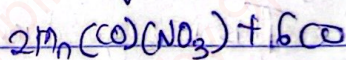
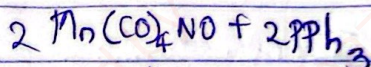
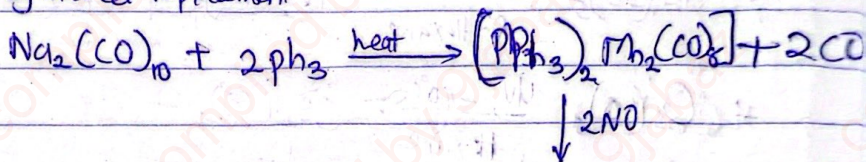
(5) Synthesis of Carbon Metal Nitrosyls

Metal carbonyl nitrosyls are best synthesized from dimeric metal carbonyls, either by direct replacement of the CO group by the nitrosyl ligand or indirectly via some of the two electron donor ligands

Example: (i) by direct replacement of CO



(ii) by indirect replacement

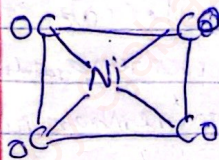


Structures

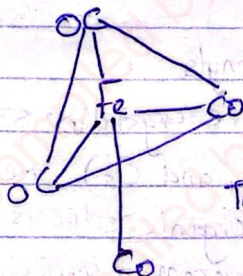
$\text{Ni}(\text{CO})_4$ - square planar

$\text{Fe}(\text{CO})_5$ - trigonal bipyramidal

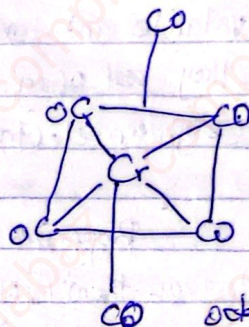
$\text{Cr}(\text{CO})_6$ - octahedral



square planar

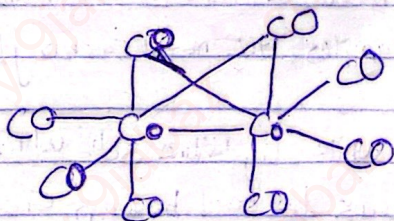
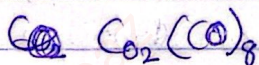


Trigonal bipyramidal



octahedral

There are other dimeric carbonyl with bridging CO



$Ni(CO)_4$ is a toxic colourless gas, $Fe(CO)_5$ is a volatile and toxic yellow liquid at room temperature. They ~~will~~ ^{effectively} obey the ~~18~~ ^{carb} atomic number rule (eighteen electron rule)

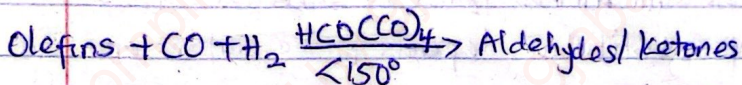
Properties of Metal Carbonyls

- ① Most of them (metal carbonyls) are crystalline solids, while some, e.g. $M(CO)_5$, ($M=Fe, Ru$ and Os) are liquids
- ② Most of them are soluble in organic solvents
- ③ They are fairly air stable, except a few such as $V(CO)_6^-$ (a 17 electron species)
- ④ They are toxic if swallowed
- ⑤ Most of them obey the 18 electron rule, those that do not obey are stored under dinitrogen
- ⑥ Their stability appears to be kinetic rather than ~~thermo~~ ^{thermodynamic}. For examples, the metal carbonyl bond, $Cr(CO)_6$, $Fe(CO)_5$.

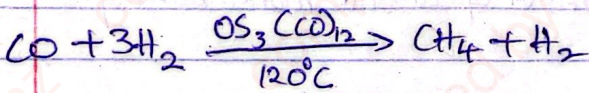
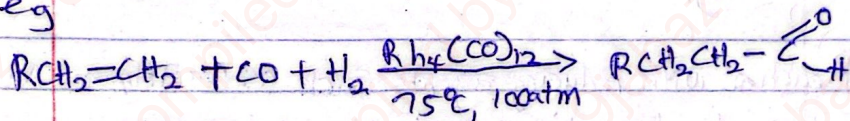
$Cr(CO)_6$ is a red stable white crystalline solid which requires 13 kJ/mol of energy to break the bond between Cr and CO . This value compared with the dissociation energy of 180 kJ/mol required for the $Fe-CO$ bond in $Fe(CO)_5$, which is ~~180~~ ¹³⁰ kJ a volatile yellow liquid.

Thermodynamically, the most higher dissociation energy of the $M-CO$ bond is envisaged for the most stable $Cr(CO)_6$ and the higher dissociation energy observed for the $Fe(CO)_5$ complex must therefore be attributed to kinetic stability.

(7) Some of these metal carbonyls act as catalyst in industrial processes. For example olefin (alkenes)

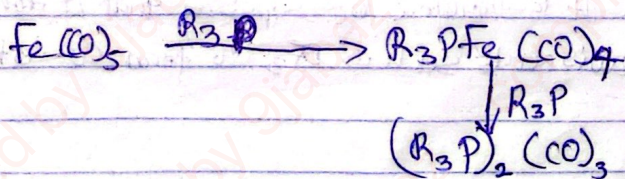


e.g.



This tells us that some of the metal carbonyls acts as catalyst.

(8) The Carbonyl ligands may be replaced by 2 electron donor ligands such as π -phosphines



Reactivity of Metal Carbonyl

- (1) Some metal carbonyls react with unsaturated organic molecules to form organometallic derivatives. This is achieved either by photolysis or thermolysis.
- (2) Reaction with Lewis base (electron pair donor) such as phosphines and amines leads to substituted product. The degree of substitution depends on the nature and the reaction type.
- (3) Reaction with reducing agents such as NaBH_4 and NaNH_2 leads to the formation of anionic metal carbonyls.

Nature of Bonding in Metal Carbonyl

Principally, there are 5 bonding and π -bonding scheme. CO is known to be a very weak ligand, it is not a good electron donor and therefore expected to be a very weak σ -donor. It is therefore not surprising that it doesn't react with Lewis acids such as BF_3 to form CO-BF_3 .

Nature of bonding in metal carbonyls.

Princip Carbon monoxide is known to be a very weak ligand, it is not a good electron donor - and thus expected to be a very weak π -acceptor. It is therefore not surprising that it does not react with Lewis acids such as BF_3 to form $CO-BF_3$.
A question as to why it forms stable complexes such as metal carbonyls lies in its π -bonding ability i.e. it readily accepts electrons from a metal center thus forming a weak sigma bond formed by σ electron donation from the filled sp orbital of the carbonyl carbon to the empty T_{2g} orbitals of the metal.

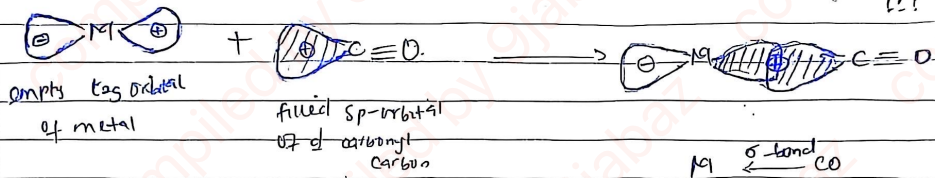
As well as a strong π -bond, resulting from the back donation of electrons from the filled t_{2g} orbital of the metal to the empty π^* orbital of the carbonyl carbon.

The important features resulting from such a bonding scheme are: first of symmetry of the overlapping orbitals must match and the metal must have filled d-orbitals of the π type. These synergically related bonding scheme σ and π effect was first reported by Dewar and then followed closely by Chatt. This is why it is sometimes called Dewar Chatt model of bonding.

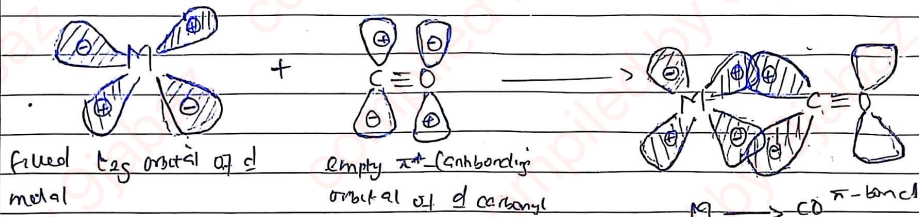
Decorar-Ogatt model for bonding in metal carbonyls.

σ bonding scheme.

* d overlapping -- must be of same phase !!!



π bonding scheme.



The overall result of such bonding scheme i.e. movement of electron density from a filled d orbital of metal into a π^* antibonding orbital of d carbonyl can be seen. This must thereby weaken the carbon oxygen bond since increase in electron density will increase the C-O bond length and consequently slow down its vibrational frequency. Its IR stretching frequency must therefore decrease and a shift to a lower wavenumber results when CO is coordinated to a metal compared to a free CO group. Free CO gas exhibits a sharp IR Nco band (frequency band) at 2143 cm^{-1} . But on coordination to a metal, this band decreases sharply to between 2120 and 1600 cm^{-1} depending on the mode of coordination which may be terminal, double bridging or triple bridging.

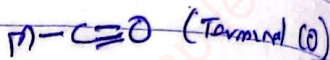
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Types of Metal Carbonyl Bond

① Terminal: It is linear, ~~with~~ a slightly bent,
IR - 2130, 1850.

2. M_2 -Bridging

3. μ_3 Centered Carbonyl



① Terminal metal carbonyl bonds: It is usually linearly bonded to the metal (bond angle: 180°). There are cases where the angle is not exactly 180° , but varies between $165^\circ - 179^\circ$. The IR Visible band is very sharp and strong with neutral species absorbing in the range $2130 + 1850 \text{ cm}^{-1}$

② ~~M_2 -bridging~~

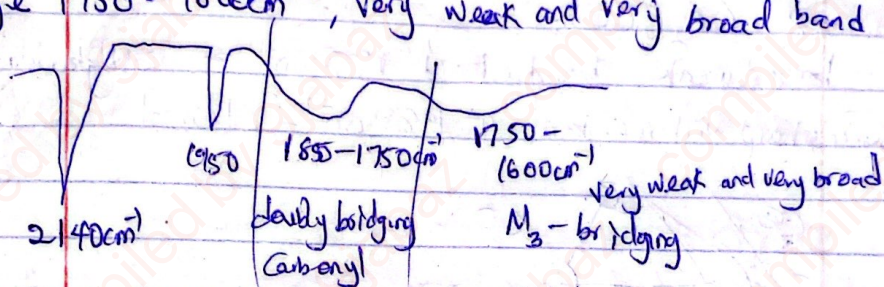
② M_2 -Bridging or doubly bridging metal carbonyl: The IR ~~2130~~ band are usually weak and broad, with neutral species absorbing in the range $1850 - 1750 \text{ cm}^{-1}$
e.g. $M-CO-M$, 

③ Triply bridging or M_3 -Bridging Carbonyl: Metal carbonyl bonded to three metals. The three metals have the same

Example of M_3 -bridging carbonyl



distance to the metal. The IR ν_{CO} bands absorb in the range $1750 - 1600\text{ cm}^{-1}$, very weak and very broad band



Question

A metal carbonyl has an empirical formula $\text{Co}(\text{CO})_n$. It shows a parent peak 342 amu in its mass spectral. In addition IR study reveals a broad weak band around 1860 cm^{-1} and several sharp intense band at 1980 cm^{-1} . (1) Suggest the structure of the metal carbonyl

(1) Does the compound obey effective atomic number rule?
If yes, how? (Co - 59, C - 12, O - 16)

Solution

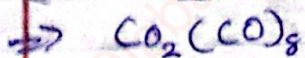
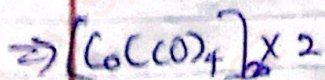
Let $\frac{x}{n}$ represent the molecular M

$$[\text{Co}(\text{CO})_n]_n = 342$$

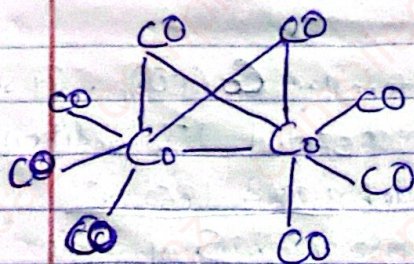
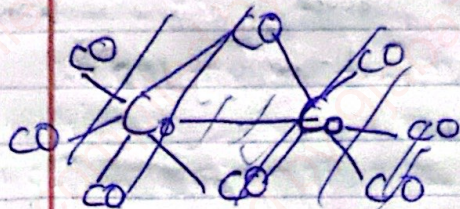
$$[59 + (12 + 16)4]_n = 342$$

$$n \mid n = 342$$

$$n = 2$$



broad weak band around 1850 cm^{-1} - doubly bridging
 several sharp intense band at 1980 cm^{-1} - terminal



$$\text{Co}-\text{Co}-|\times| = 1$$

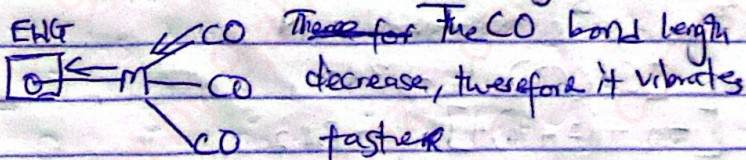
$$1 \text{ Co} = 1 \times 9 = 9$$

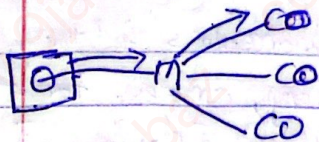
$$3 \text{ CO} = 3 \times 2 = 6$$

$$2 \text{ H}-\text{Co} = 2 \times 1 = 2$$

$$\underline{\underline{18e^-}}$$

Factors Influencing the position of IR Bands of
 Coordinated CO (Carbonyls)





CO bond length increases, vibration is slower.

(f) Nature of Other ligands coordinated to the central metal

~~with~~

When the complex is charged, we assume that the charge whether + or - is at the metal center. When "+", the metal is electron deficient and it attracts electron from CO, making the bond length decrease and vibration will be faster.

When the charge is "-", it means the metal has excess electrons and sends it to the CO bond, increasing the CO bond length, making vibration slower.

Factors

(i) Nature of other ligands coordinated to the central metal.

Substitution of CO in a metal carbonyl by ligand which are stronger sigma donor than CO encourages back donation of electrons from the metal to the remaining CO groups which must accept this extra electrons. In order to avert ^{accumulation} of negative charge on the metal atom.

The CO bond length is thus increased, and its stretching band consequently shifts to lower wave number.

Strong sigma donors are weak π -acceptors and this includes halides, phosphines, cyclopentadienyl, amines. For example, replacement of 3 CO groups in Chromium hexacarbonyl with phosphine and a CO group in $1-5-7-C_6H_7Fe(CO)_3I]^+$ with the iodide ligand gives products with much lower IR ν_{CO} bands:

$$Cr(CO)_6 = \nu_{CO} = 2100, 2000, 1980 \text{ cm}^{-1}$$

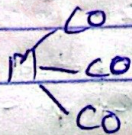
$$W(CO)_3 = \nu_{CO} = 1935, 1855 \text{ cm}^{-1}$$

$$[1-5-7-C_6H_7Fe(CO)_3]^+ = \nu_{CO} = 2110, 2065 \text{ cm}^{-1}$$

$$[1-5-7-C_6H_7Fe(CO)_3I] = \nu_{CO} = 2030, 1980 \text{ cm}^{-1}$$

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Conversely, a weaker sigma donor than CO is a stronger π -acceptor which will cause depletion of electron and reduce the number of electrons in the metal's d-orbital. These electrons are regained from the remaining coordinated CO groups leading to a reduction in the $Cr-C$ bond length and consequently increasing its vibrational frequency. The IR ν_{CO} band shifts to a higher wave number.



② Overall charge on the complex: Addition of a negative charge to the complex will increase back donation of the electrons from the metals to the carbonyl group. Thereby increasing the C-O bond length. This will decrease the frequency of vibration of the C-O bond leading to a shift of IR ν_{CO} band to lower wave number.

Conversely, a positive charge will decrease the back bonding capacity of the metal thereby decreasing the C-O bond length. This will increase the frequency of vibration of CO leading to a shift of IR ν_{CO} band to higher wave number (higher frequency).

In essence, increase in overall positive or negative charges on the complex will cause further increase shift to higher wavenumber or (decrease shift to lower cm^{-1}) respectively of the coordinated ~~ligand~~ carbonyl ligand.

Arrange the carbonyls in order of increasing frequency

③ $[Ni(CO)_4]$, $[Fe(CO)_4]^{2-}$ ①, $[Co(CO)_4]^+$ ②, $[Cu(CO)_4]^+$ ④, $[Fe(CO)_6]^{2+}$ ⑤

This fact is illustrated by
 $[\text{Fe}(\text{CO})_5]^{2-}$, $[\text{Co}(\text{CO})_4]$, $[\text{Ni}(\text{CO})_4]$, $[\text{Cu}(\text{CO})_4]^+$, $[\text{Fe}(\text{CO})_5]$
 1790cm^{-1} 1890cm^{-1} 2060cm^{-1} 2180cm^{-1} 2230cm^{-1}

Metal Nitrosyls

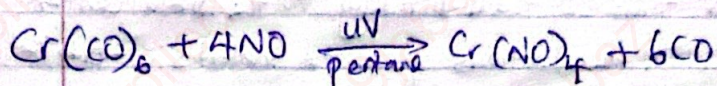
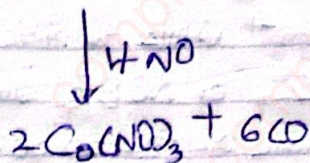
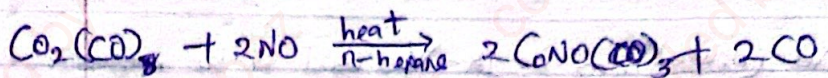
Nitric oxide (NO) is a paramagnetic species and has electron in an antibonding orbital. The latter electron is readily lost to form the 10 electron species NO^+ . This is called Nitrosonium ion, and it is in this form that NO is found in most nitrosyl complexes.

The Nitrosyl ligand acts as a three electron donor and it is a better π acceptor ligand than CO .

Synthesis of Metal Nitrosyls

Only two metal nitrosyls have been fully characterized till date. The two metal nitrosyls are; (1) Chromium tetranitrosyl $\text{Cr}(\text{NO})_4$ and $[\text{Co}(\text{NO})_5]$.

Metal nitrosyls are generally prepared by the replacement of CO in metal carbonyl with NO , either thermally or by photolysis.



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Stronger σ -donor — Weak π -acceptor

Weak σ -donor — Strong π -acceptor (withdraws electron)

Properties of Metal Nitrosyls

- (1) They are usually low melting point solids or low boiling point liquid.
- (2) They are all poisonous.
- (3) They are thermally unstable and air sensitive.

Types of Metal

Metal nitrosyls are of three types, which are;

- (i) linear (ii) bridging internal ($\text{M}_2\text{-NO}$), (iii) Triply bridging $\text{NO}(\text{M}_3\text{-NO})$

Free NO (neutral) has its IR-~~No~~ band in the range $1880 - 1860 \text{ cm}^{-1}$ while the nitrosonium ion (isolated for example, NOHSO_4 or NOBF_4 such) has π IR $\nu(\text{NO}^+)$ bands in the range $2400 - 2200 \text{ cm}^{-1}$. Since NO is a stronger π -acceptor than CO, then bonding to the metal center cause depletion of electrons from the metal's d-orbitals, so that the net effect is weakening of the NO bond length and a consequent decrease in its vibrational frequency.

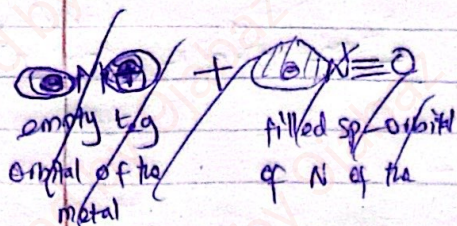
The IR bands of the coordinated NO therefore shifts to much lower ^{wavenumber} ~~frequency~~ than the ~~As a general guide~~ corresponding CO bands.

As a general guide, for linear N-O bonding $\text{M}-\text{NO}$, the IR $\nu(\text{NO})$ band occurs in the range $1900 - 1800 \text{ cm}^{-1}$, doubly bridging NO occurs with the range $1540 - 1480 \text{ cm}^{-1}$ while triply bridging NO have their IR band in the range $1350 - 1300 \text{ cm}^{-1}$.

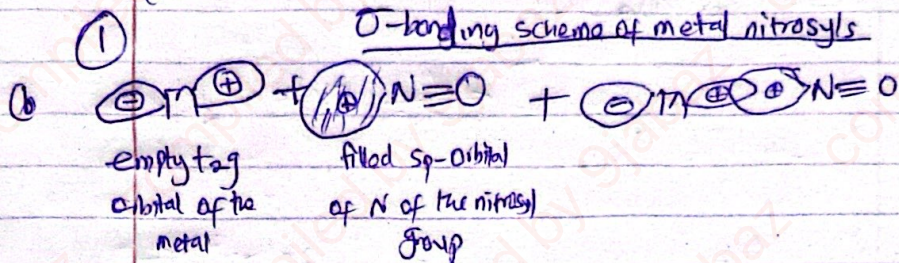
Most of the above IR-bands were established from studies of mixed nitrosyl carbonyl

Bonding in Metal Nitrosyl

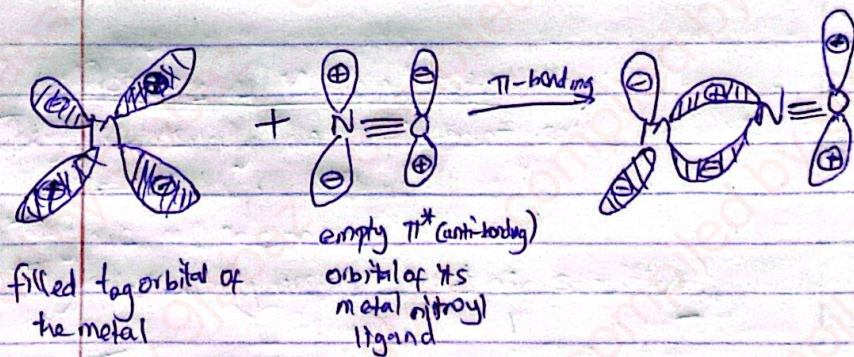
* Describe the nature of bonding in metal nitrosyls



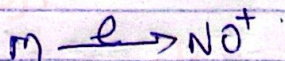
σ -bonding scheme of metal nitrosyls



(2) π -bonding scheme



$\xrightarrow{e}$



Dewar-Chauffe model of metal bonding in metal nitrosyls

$$Co = 59, C = 12, O = 16$$

Solution

let n represent molecule n
 $[Co(CO)_4]_n = 342$

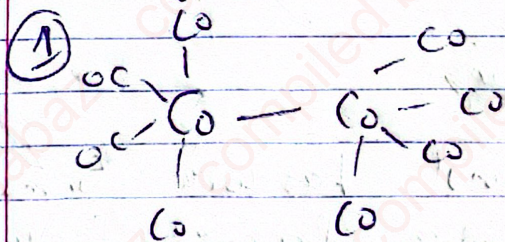
$$[59 + (12 + 16)4]_n = 342$$

$$(59 + 112) \cdot n = 342$$

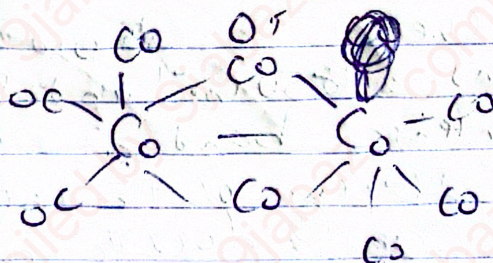
$$171n = 342$$

$$n = \frac{342}{171} = 2$$

Hence, the molecular formula for the complex $Co_2(CO)_8$



(2)



$$\text{Co} = 9e^-$$

$$4\text{Co} = 36e^-$$

$$1\text{M} - \text{M} = 1e^-$$

$$\underline{18e^-}$$

Yes, it obeys the rule.

$$\text{Co} = 9e^-$$

$$3\text{Co} = 27e^-$$

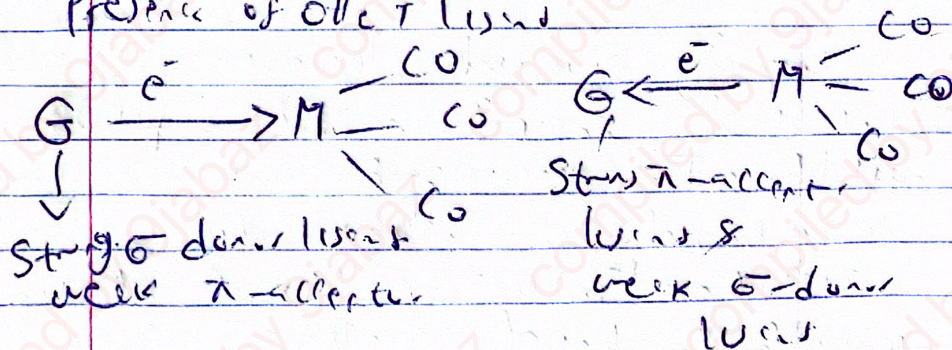
$$1\text{M} = 1$$

$$2\text{Co} = 2 \times 9 = 18e^-$$

$$\underline{18e^-}$$

(2) Factors affecting the IR values from carbonyl

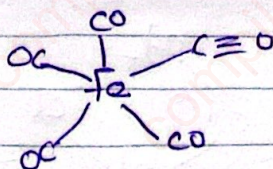
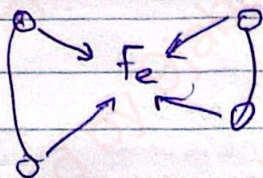
Presence of other ligands



Dr. Ajayeoba's Part

Mo	Tu	We	✓Th	Fr	Sa	Su
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Date 10/06/26

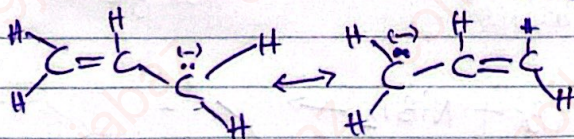


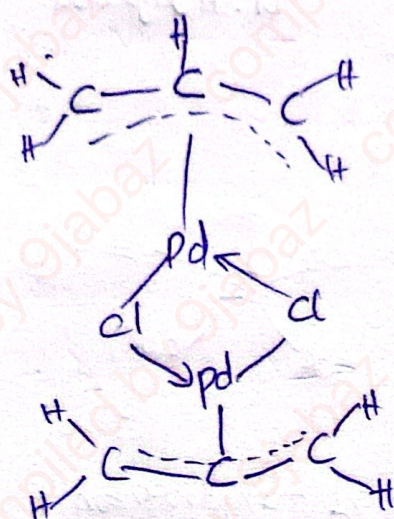
Synthesis and Reactivity of π -hydrocarbon metal Complexes

A wide variety of ~~wide~~ hydrocarbon coordinated to the metal center are known and their synthesis and reactivity are of special interest

Example

Allyl $\rightarrow$ $-\text{CH}_2-\text{CH}=\text{CH}_2$, consists of methylene bridge attached to a vinyl group.





each carbon is donating two

$$3C = 6$$

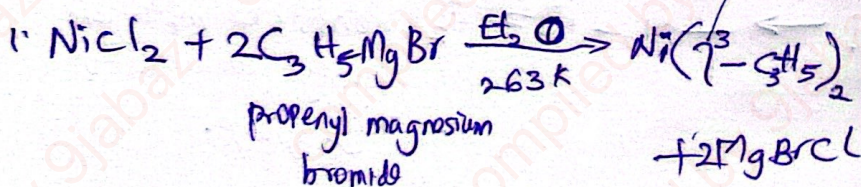
$$Ni = 10$$

pd is under the group of Ni

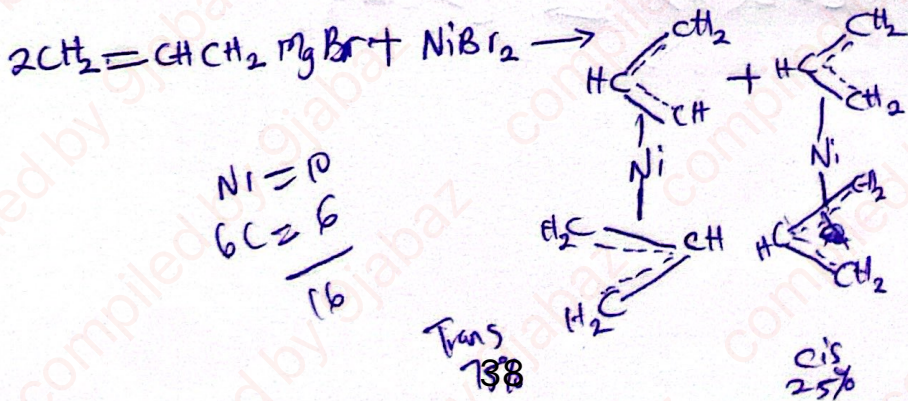
we can also have stable $16e^-$ especially square planar compounds

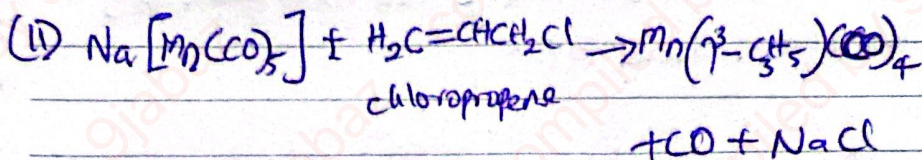
Preparation of the Allyl

η^3 -allyl and related complexes can be prepared by reaction such as

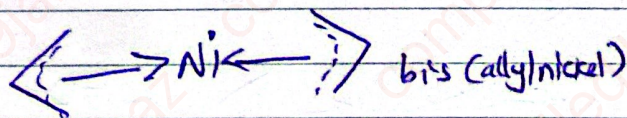
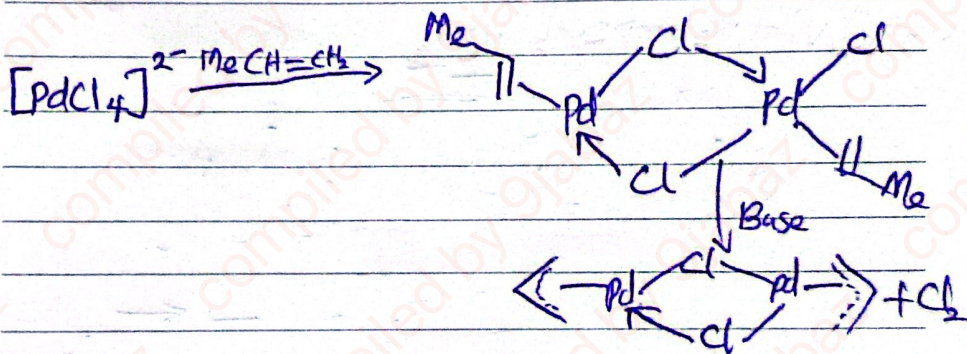


or





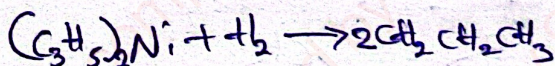
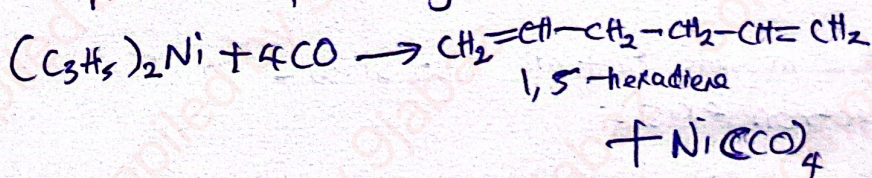
* compounds that are also stable at 16 electron exists.



bis(allyl)nickel is one of the best known allyl complexes, but it is pyrophoric and decomposes above 293 K. Bulky substituents can be used to stabilize analogs of $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2$

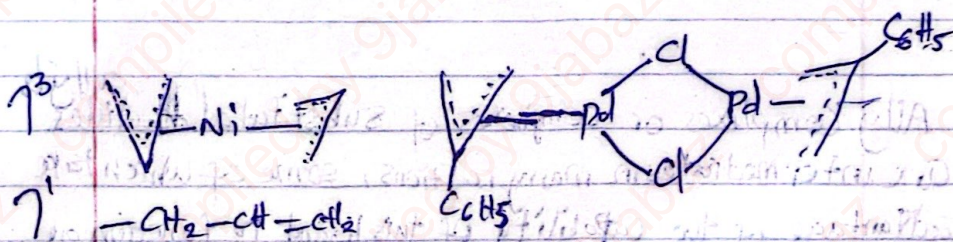
Thus, $\text{Ni}[\eta^3-1,3-(\text{Me}_3\text{Si})_2(\text{C}_3\text{H}_3)_2]$ is kinetically stable in air for several days and decomposes only when heated above 373 K.

Reactions of Bis(allyl)nickel include:



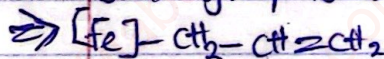
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3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

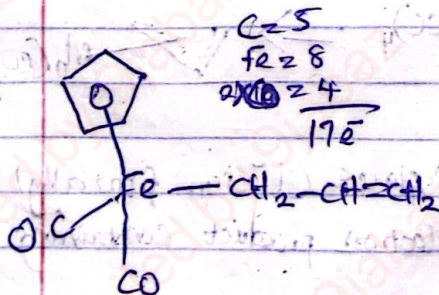


Sigma-allyl ligands

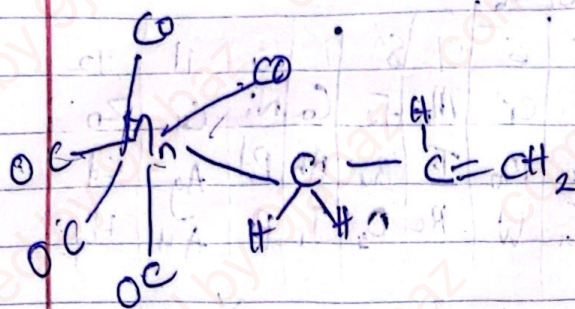
Complexes with η^1 -allyl ligands (classified as X-type ligands) are also known e.g. $\text{CpFe}(\text{CO})_2(\eta^1\text{-C}_3\text{H}_5)$, in which only the methylene group is attached to the Fe centre.



The monohaplicity here is enforced by $18e^-$ rule



$$\begin{array}{r}
 \text{C} \approx 5 \\
 \text{Fe} \approx 8 \\
 2 \times \text{CO} \approx 24 \\
 \hline
 17e^-
 \end{array}$$



$$Mn = 7$$

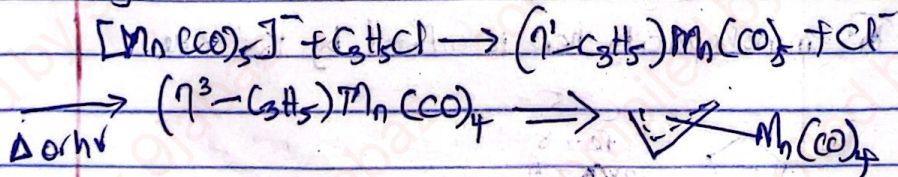
$$5 \times CO = 2 \times 5 = 10$$

$$\begin{array}{r} C = 1 \\ \hline 18e \end{array}$$

Allyl complexes or complexes of substituted ~~aldehydes~~ ^{allyls} are intermediates in many reactions, some of which take advantage of the capability of this ligand to function as η^3 and η^1 fashion.

Loss of Carbonyl (CO) from carbonyl complexes containing η^1 -allyl ligands often results in conversion of η^1 -allyl to η^3 -allyl.

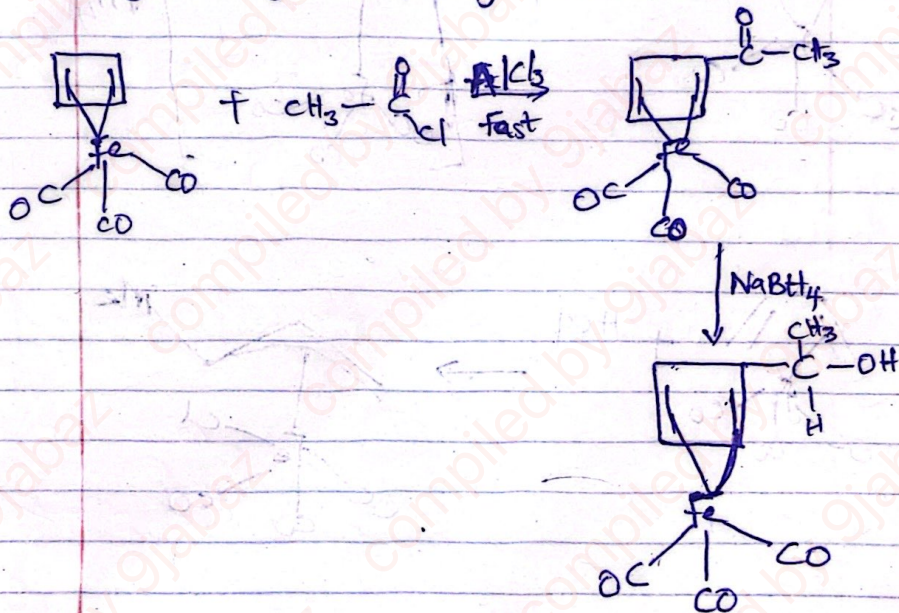
e.g.



The $[Mn(CO)_5]^-$ ion displaces Cl^- ion from allyl chloride to give an 18-electron product containing $\eta^1-C_3H_5$.

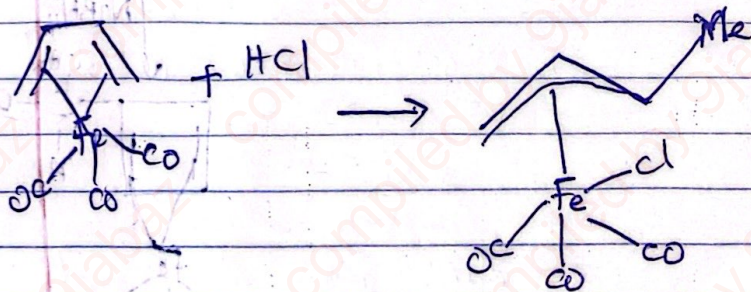
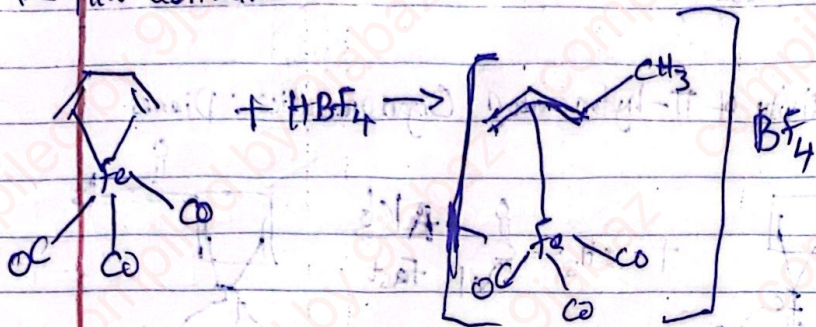
The ligand switches to trihapto when a CO is lost, preserving the $18e^-$ count.

Reactivity of π -hydrocarbon: Organometallics: Dienes



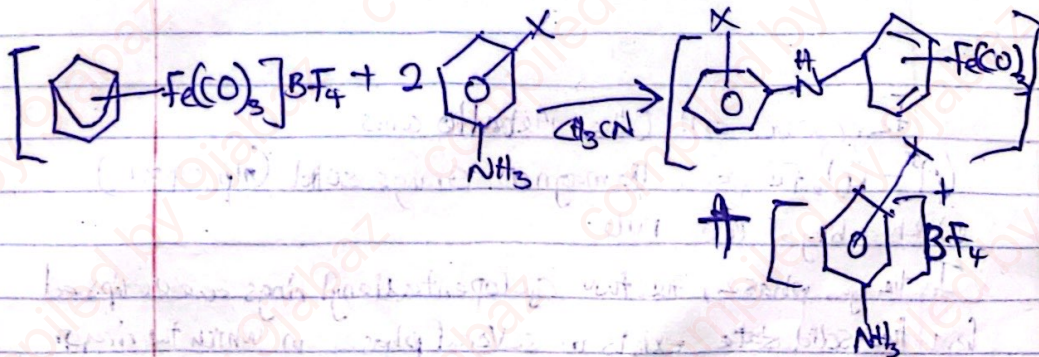
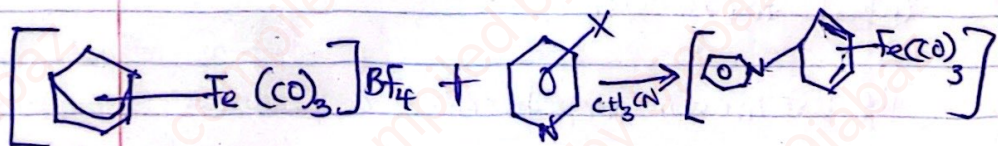
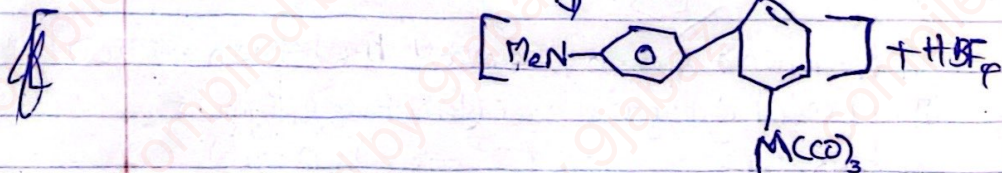
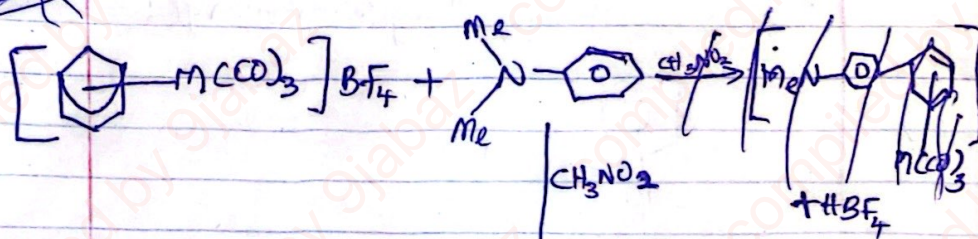
Tricarbonyl (cyclobuta-1,3-diene) Iron behaves as a very reactive organic molecule by undergoing Friedel-Crafts alkylation. The resulting product is rapidly reduced to the alcohol derivative with NaBH_4 .

Fluoroboration of tricarbonyl (Cbuta-1,3-diene) Iron affords the following derivative



Diene (Five-electron ligands)

The reaction of dienylium organometallics with N,N -dimethylaniline, pyridines, anilines, amides and aryltrimethylsilanes and stannanes afford the 1,3-diene substituted derivatives



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Complexes containing η^6 -cyclopentadienyl ligand

In a sandwich complex, the metal lies between the two π -bonded hydrocarbon or (derivatives) ligands. Complexes of the type $(\eta^5-Cp)_2M$ are called metallocenes.

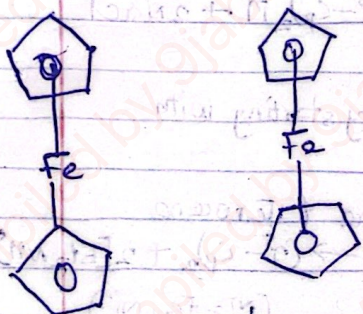
The best known metallocenes is ferrocene.

Ferrocene and Other Metallocenes

$(\eta^5-Cp)_2Fe$ is a diamagnetic orange solid (mp 393K) which obeys 18e rule.

In the gas phase, the two cyclopentadienyl rings are eclipsed but the solid state exists in several phases in which the rings are coparallel but in different orientation.

Structure of Ferrocene

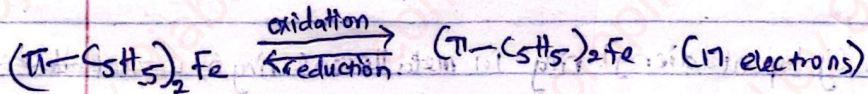


eclipsed

332 pm

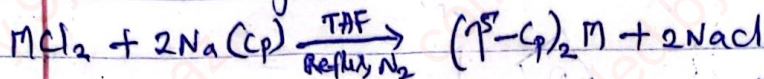
The bonding in $(\eta^5\text{-Cp})_2\text{Fe}$ can be described in terms of the interactions between the π molecular orbitals of the ligands and the 3d atomic orbitals of the metals.

Ferrocene is oxidized (e.g. by I_2 or FeCl_3) to the paramagnetic blue ferrocenium ion $[(\eta^5\text{-Cp})_2\text{Fe}]^+$



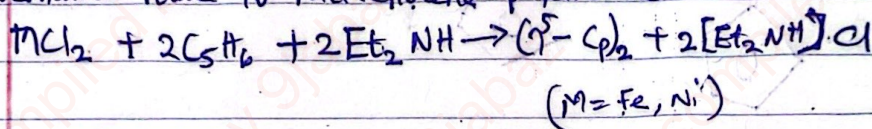
Metallocenes of the first row transition metals are known for V(II) , Cr(II) , Mn(II) , Fe(II) , Co(II) , Ni(II) and Zn(II) .

General Synthetic Route



For $(\eta^5-Cp)_2V$, it is prepared by starting with Vanadyl trichloride ($VOCl_3$)

* Alternative route to Nickelocene & Ferrocene



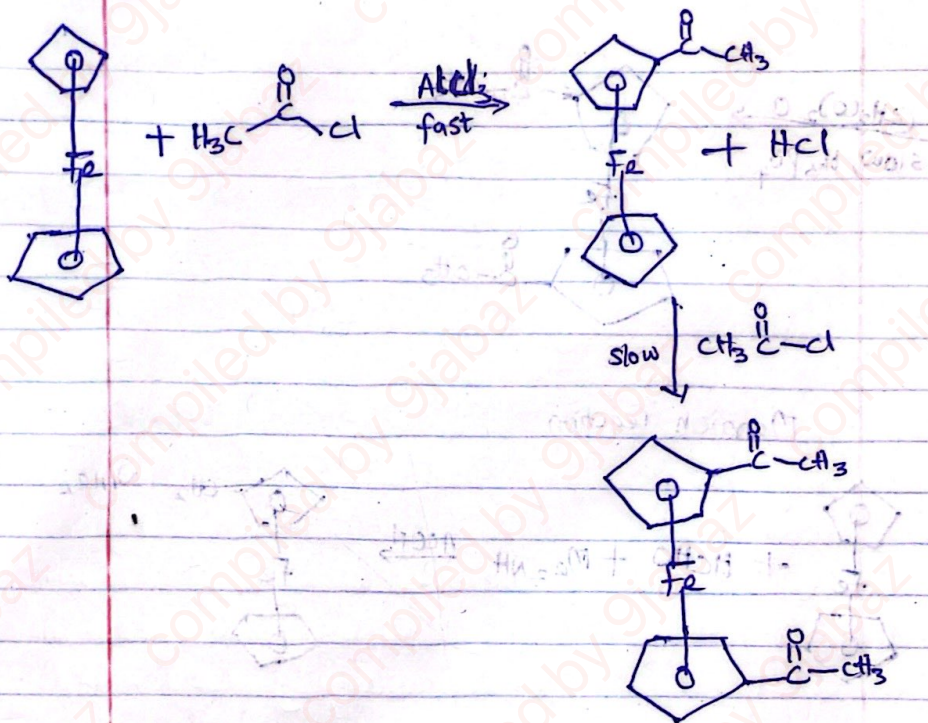
React



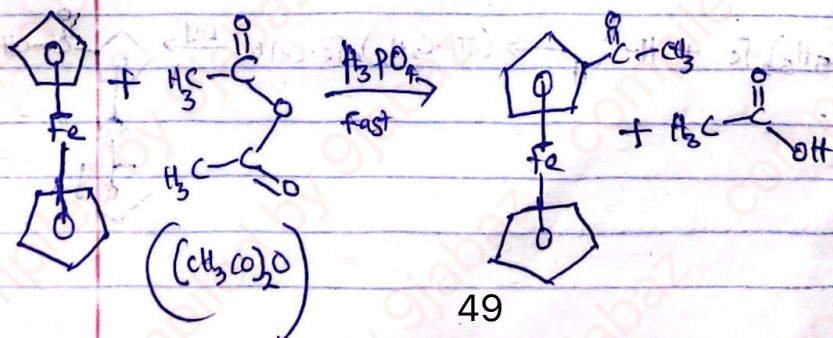
Ruthenocene

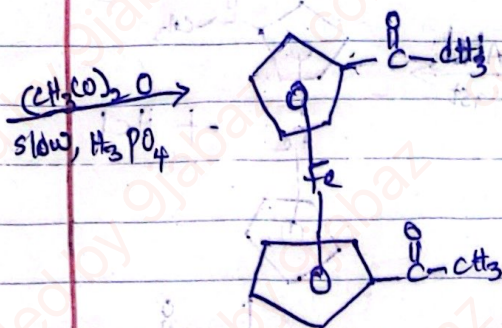
The Cyclopentadienyl ring in metallocene rings, ~~in metallocenes~~, particularly ferrocene are ~~usually~~ aromatic and behaves like benzene in most reactions; they are reactive towards electrophiles.

Electrophilic addition occurs at the dienyl fragment of metallocene e.g. Simple Friedel-Crafts acylation, using acetyl chloride occurs to give the ketonic ^{or} acetyl product

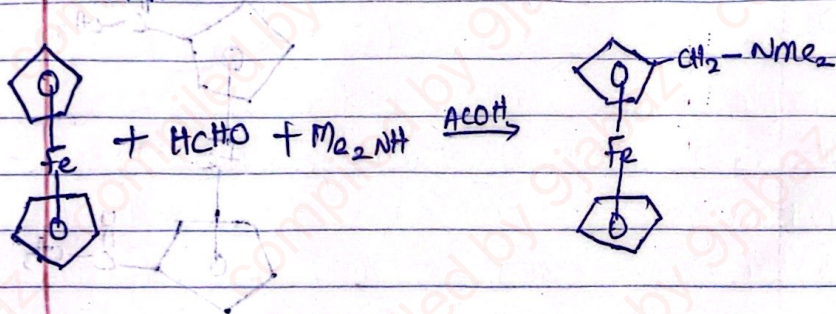


The ~~product~~ ^{same} product are obtained when acetylation is carried out using acetic anhydride in the presence of phosphoric acid as a catalyst.

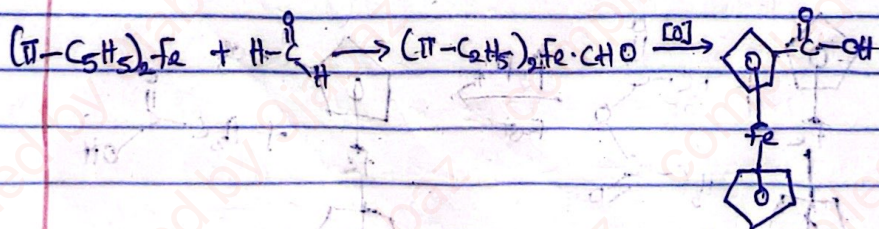


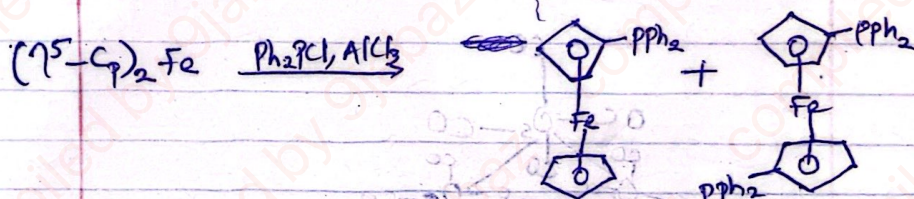
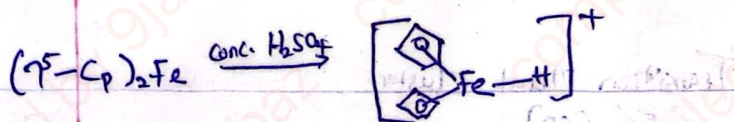


Mannich reaction

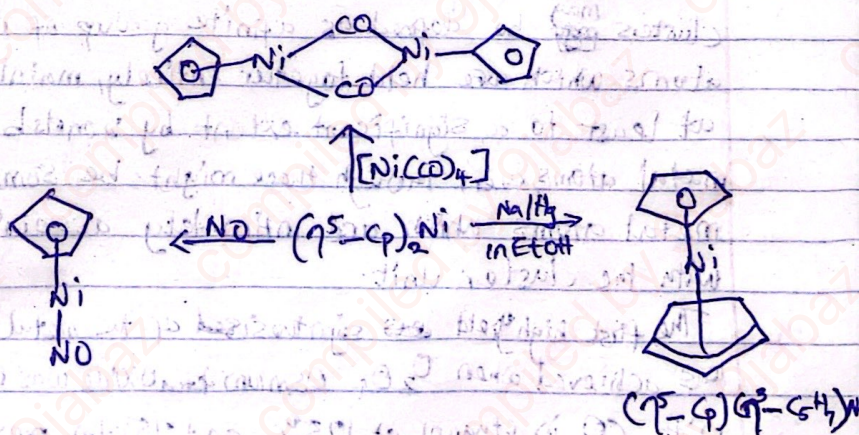


Formylation also occurs at the diene ring to form the aldehyde derivative which is oxidized to give ferrocenic acid. It is a weaker acid than benzoic acid.

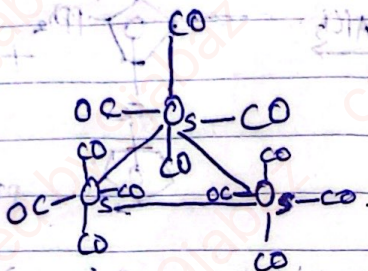
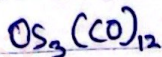




Selected reactions of Nickel(II)ocene $(\eta^5\text{-Cp})_2\text{Ni}$



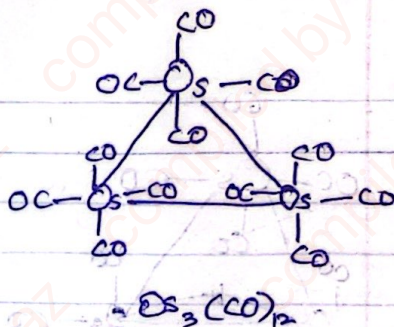
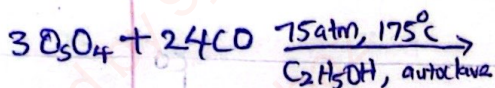
Transition Metal Clusters



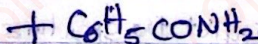
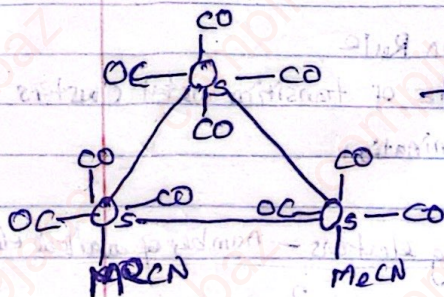
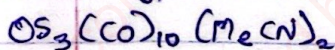
clusters ~~may~~ be defined as a finite group of metal atoms which are held together entirely, mainly or at least to a significant extent by bonds between metal atoms, even though there might be some non metal atoms which are intimately associated with the cluster unit.

The first high yield ~~was~~ ~~synthesised~~ synthesis of the metal cluster was achieved when OsO_4 Osmium tetroxide was reacted with CO in ethanol at 175°C and 15 atm pressure in an autoclave triosmiumdodecacarbonyl in 85% yield.

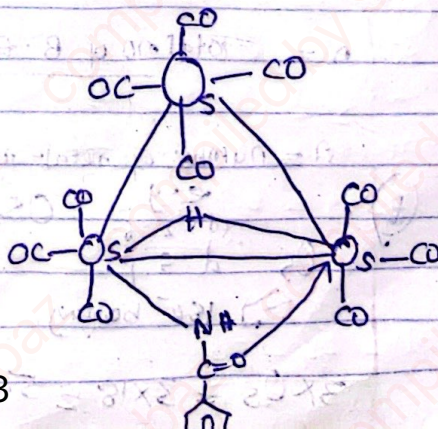
X-ray Crystallographic Studies showed that there was a triangular array of metal atoms ~~terminally~~ with four Carbonyl groups terminally bonded with each metal.

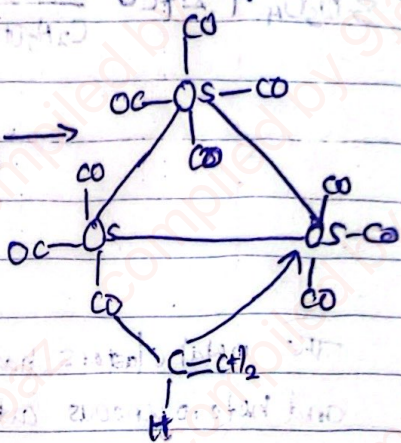
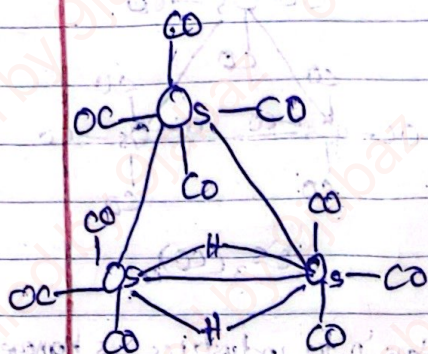


The metal clusters have applications in the industries as homogeneous and heterogeneous catalyst. Some other examples includes



Reflux
 N_2 / Cyclohexane





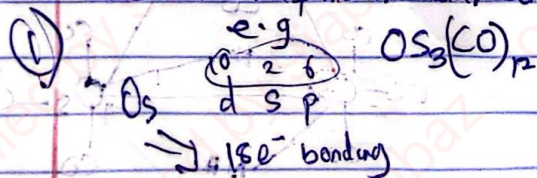
Generalized 18 electron Rule

It is used to predict the structures of transition metal clusters before X-ray structural determination

$$n = \frac{\text{total number of bonding electrons} - \text{number of available electrons}}{2}$$

$$n = \frac{\text{Total no of B.E} - \text{no of available e}^-}{2}$$

$$n = \text{number of metal-metal bonds in the cluster unit}$$



$$3 \times \text{Os} = 3 \times 18 = 54 \text{ bonding electrons}$$

No of available electrons

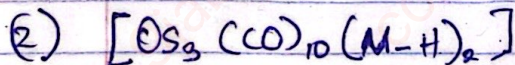
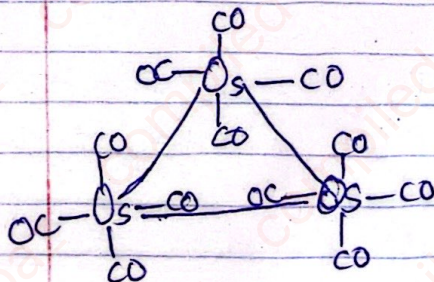
$$3 Os = 3 \times 8 = 24$$

$$12 CO = 12 \times 2 = 24 = 48 \text{ available electrons}$$

$$n = \frac{54 - 48}{2} = \frac{6}{2} = 3$$

$$n = 3$$

Number of metal-metal bonds = 3



Bonding electrons

$$3 Os = 3 \times 8 = 24$$

Available electrons

$$3 Os = 3 \times 8 = 24$$

$$10 CO = 10 \times 2 = 20$$

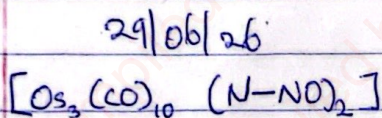
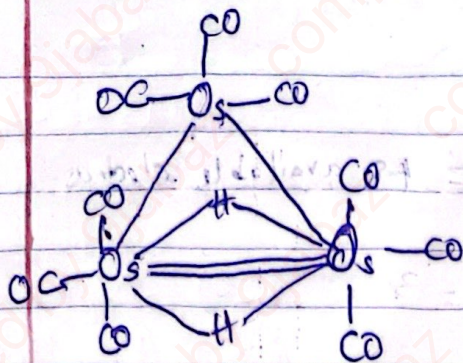
$$2 H = 2 \times 1 = 2$$

$$\underline{46}$$

$$n = \frac{BE - A \cdot E}{2}$$

$$n = \frac{54 - 46}{2} = \frac{8}{2} = 4$$

Number of metal-metal bonds = 4



$$n = \frac{B-E - A-E}{2}$$

Bonding Electrons

$$2 \times \text{Os} = 3 \times 16 = 54$$

Available Electrons

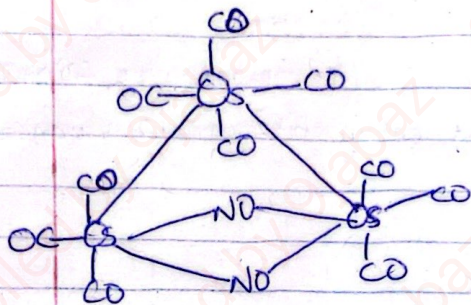
$$3 \text{ Os} = 3 \times 8 = 24$$

$$10 \text{ CO} = 2 \times 10 = 20$$

$$2 \text{ NO} = 2 \times 3 = 6$$

$$24 + 20 + 6 = 50$$

$$+ n = \frac{54 - 50}{2} = 2$$



$$\begin{aligned}
 \text{Os} &= 8 \\
 3 \text{ CO} &= 6 \\
 n - m &= 1 \\
 \text{NO} &= 3 \\
 \hline
 18e^-
 \end{aligned}$$

Wade's Rule

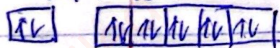
The rule applies to higher nucleant metal clusters, such as $\text{Os}_5(\text{CO})_{16}$ and $\text{Os}_6(\text{CO})_{18}$

$$n + 1 = \frac{\text{total number of available electrons} - \text{number of valence electrons}}{2}$$

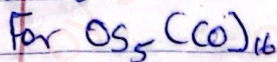
n describes the stereochemistry or orientation in space of the metal.

In order to determine the number of valence electrons within the metal clusters. Only the s and d outermost orbitals are involved.

s and d that is we have $1 + 5 = 6$ valence orbitals for each metal atom



Since each orbital must contain two electrons, which are spinally opposed, then each metal must contain 6×2 or 12 valence electrons.



$$n+1 = \frac{\text{A.E.} - \text{Valence } e^-}{2}$$

$$5\text{Os} = 5 \times 8 = 40$$

$$16\text{CO} = 2 \times 16 = 32$$

$$72$$

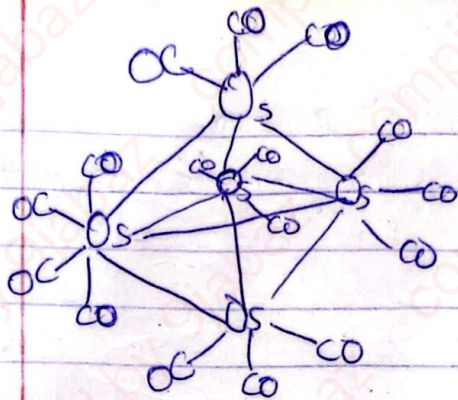
Valence e^-

$$5\text{Os} = 5 \times 12 = 60$$

$$n+1 = \frac{72 - 60}{2} \Rightarrow n+1 = 6$$

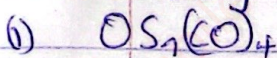
$$\Rightarrow n = 5$$

The best way we can arrange the metal cluster whose metal atoms have 5 orientation in space is to have a trigonal bipyramidal structure.



01/07/26

Find the number of M-M bond and the orientation in space or the stereochemistry



(a) No of metal-metal bond

$$\frac{B.E - A.E}{2}$$

B.E

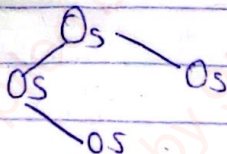
$$7\text{Os} = 12 \times 7 = 126$$

A.E

$$7\text{Os} = 7 \times 8 = 56$$

$$21\text{CO} = 21 \times 2 = 42$$

$$n = \frac{B.E - A.E}{2} = \frac{126 - 98}{2} = 14$$



(b) Orientation in space

$$n+1 = \frac{A.E - \text{Valence}}{2}$$

Valence

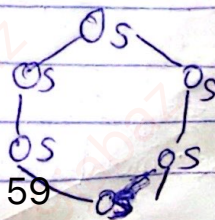
$$7\text{Os} = 12 \times 7 = 84$$

Valence

$$A.E = 98$$

$$n+1 = \frac{98 - 84}{2}$$

$$n+1 = 7, n = 7 - 1 = 6$$



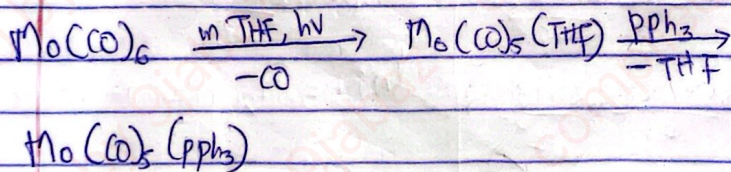
Types of Organometallic Reaction

The types of ligand transformation that takes place at the metal center are include

- (1) Ligand substitution
- (2) Oxidative addition
- (3) Reductive elimination
- (4) β -hydrogen elimination
- (5) α -hydrogen

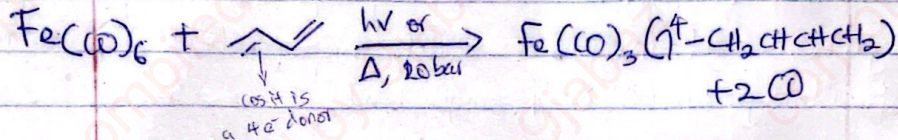
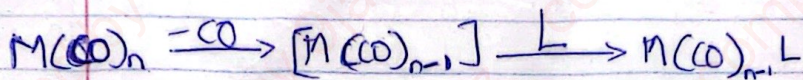
(1) Ligand substitution

The substitution of a CO ligand by another ~~two~~ electron donor e.g. trialkyl phosphine may occur by photochemical or thermal activation either by direct reaction of the metal carbonyl and incoming ligand or by first replacing a carbonyl by a more labile ligand such as THF or acetonitrile. An example is the formation of $\text{Mo}(\text{CO})_5(\text{PPh}_3)$

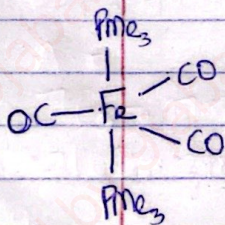
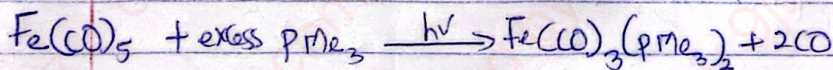


The substitution steps are dissociative, the outgoing ligand leaves creating a $16e^-$ metal center, which is coordinatively unsaturated.

The entry of a new two-electron ligand restores the $18e^-$ count. There may be competition between ligands for coordination to the $16e^-$ center if the ligands are in excess

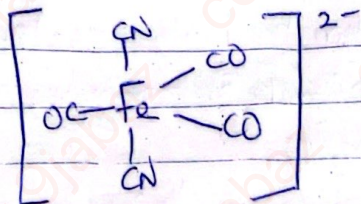


In the above reaction, the incoming ligand provides $4e^-$ and displaces 2 carbonyl ligand.



photolysis of $Fe(CO)_5$ with $(Et_4N)CN$ leads to substitution reaction and introduces cyano ligands in the axial position

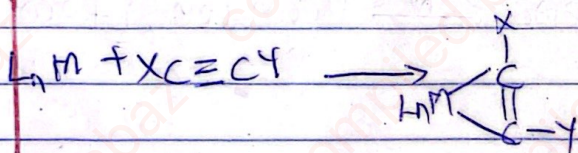




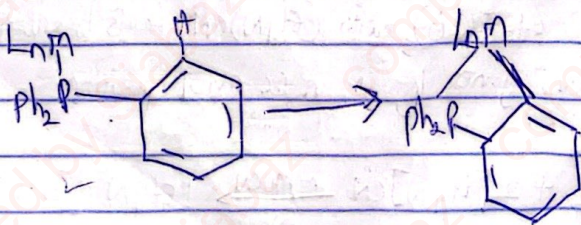
Oxidative Addition Reactions are very important in organometallic synthesis. It involves the addition of a molecule X-Y with ~~not~~ cleavage of the X-Y single bond



To addition of a multiple bonded species, (e.g. alkene, alkyne) and formation of a metallocycle



Addition of a C-H bond in the orthometallation step or a similar addition



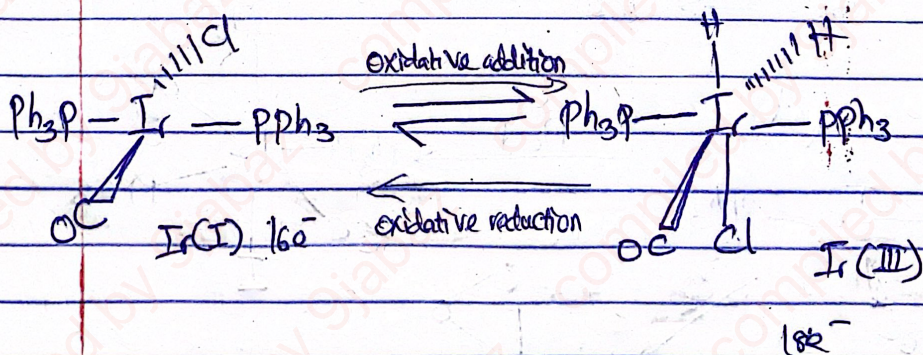
Each addition above occurs as a $16e^-$ metal center taking it to an $18e^-$ center in the product most commonly, the precursor has a d^8 or d^{10} configuration

e.g. Rh(I), Ir(I), Pd(0), Pd(II), Pt(II) and the metal must have an accessible higher oxidation state e.g. Rh(III)

22nd July, 2026

A representative Vaska's complex $\xrightarrow{\text{Phenyl}}$
 $\text{trans-IrCl(CO)(P(C}_6\text{H}_5)_3)_2$

In this transformation Iridium changes its formal oxidation from +1 to +3. The product is formally bonded to three anions which 1 chloride and 2 hydride ligands



reactant	product
$\text{Ir} - 9e^-$	$\text{Ir} = 9e^-$
$\text{Cl} - 1e^-$	$\text{Cl} = 1e^-$
$2\text{PPh}_3 - 4e^-$	$2\text{PPh}_3 = 4e^-$
$\text{CO} - 2e^-$	$\text{CO} = 2e^-$
<u>$16e^-$</u>	$2\text{H} = 2 \times 1 = 2e^-$
	<u>$18e^-$</u>

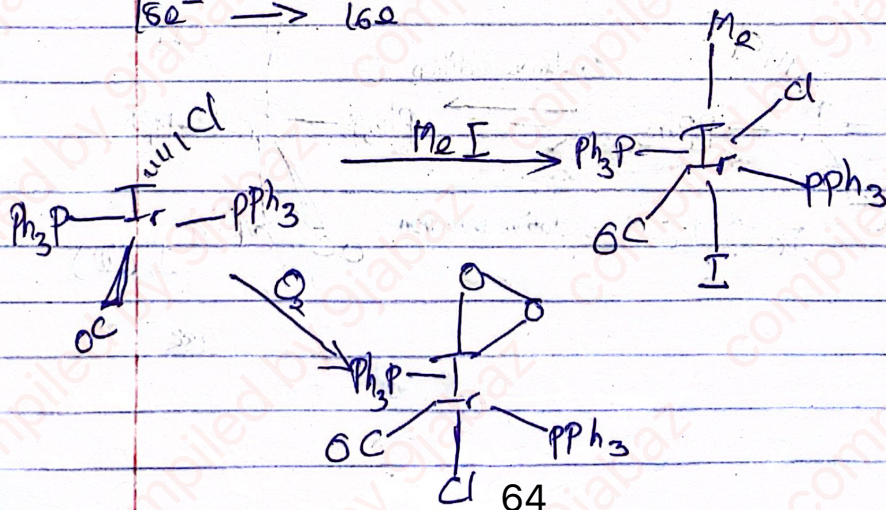
For oxidative addition this takes place;
 4 coordinate $\rightarrow$ 6 coordinate
 Also change in oxidation state;
 $16e^- \rightarrow 18e^-$

For reductive elimination

6 coordinate $\rightarrow$ 4 coordinate

change in o.s

$18e^- \rightarrow 16e^-$



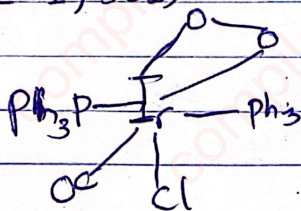
O_2 is acting as peroxide and the oxidation state will be -2 like H_2O_2

$$2(+1) + O_2 = 0$$

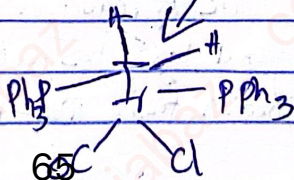
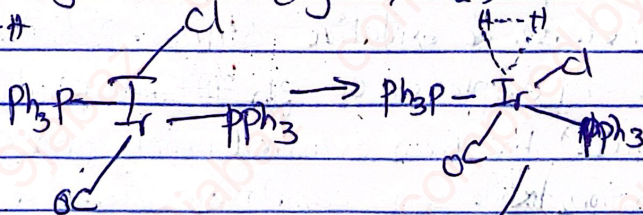
$$O_2 = -2$$

How do these reactions occur?

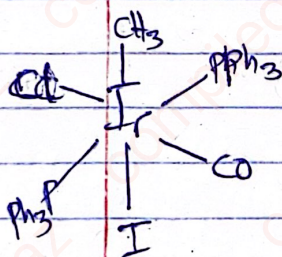
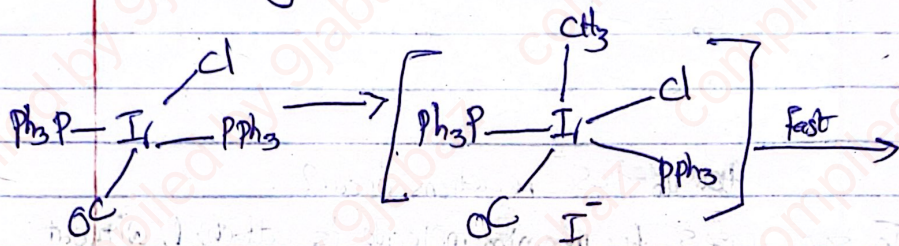
In some cases, the incoming molecule is attached, without breaking up the integrity of the molecule concerned
eg. (O_2 , SO_2)



While in some cases, the concerted addition is followed by breaking up of the original molecule (eg. H_2 , Cl_2)



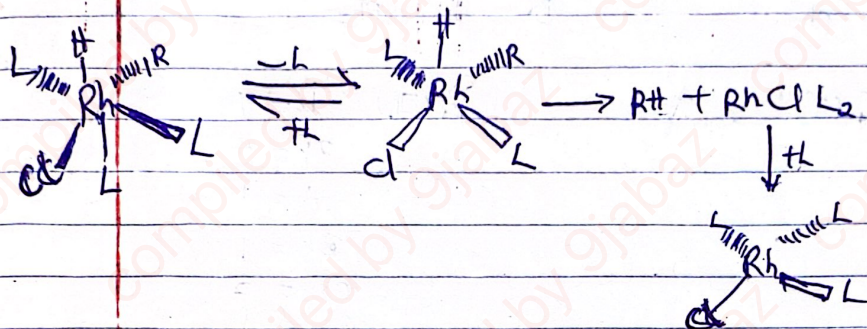
The addition of methyl Iodide proceeds by S_N2 reaction, with slow step involving a 5-coordinate cationic species



Reductive Elimination

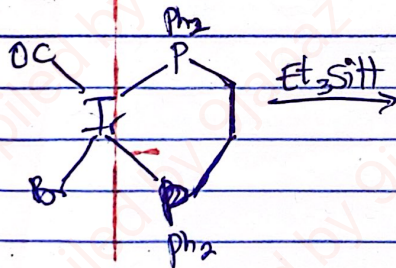
It is the reverse of oxidative addition. Reductive elimination from octahedral complexes of ~~Ir(III)~~ and Rhodium (III) and Iridium (III) has been examined mainly from C-H bond formation, while some complexes undergo a dissociative mechanism, direct reductive elimination without preliminary ligand loss has also been documented. In the alkane elimination from $\text{Mer-Rh H(R) Cl (PMe}_3)_3$ in

~~the attack of~~
It involves preliminary dissociation of pmc_3 ligand

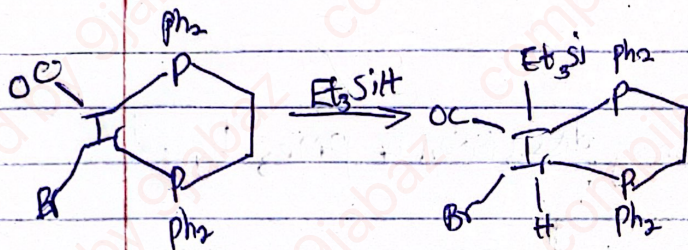


Reductive elimination is simply the reverse of oxidative addition, the former valence state of the metal is reduced by 2 (or 1 in a bimetallic reaction) and the total electron count of the complex is reduced by 2.

While oxidative addition can also be observed from a main group element, the reaction is more typical of the transition elements.



If the reactant produces a d^8 product, what can the changes in OS and coordination compound? write the four possible products



Ir(I)

Ir(III)

$1r = 9$

$2P = 4$

$H = 1$

$Br = 1$

$CO = 2$

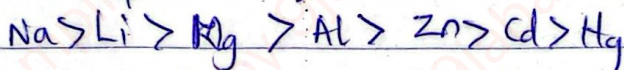
$C = 1$

18e⁻

Prof. Durosimi's Part

Organometallic compounds are organic compound that have the carbon atom directly linked to a metal atom or a metal directly linked to a carbon.

The Ionic Character of the Carbon metal bond depends on the electropositivity of the metal



The larger the difference in the electronegativity between metal and carbon, the greater the ionic character of the C-M bond.

Example of Organometallic compounds; metal carbonyl, Grignard reagent ($RMgX$), metalloenzymes

Catalysts

A catalyst is a substance that ^{in the process} increases the rate of reaction but it is not itself consumed. ①

② The catalyst is usually added in small amount to alter the reaction rate and ^{it can increase} ~~they can continue~~ the rate of reaction repeated.

How it works. ③ Catalyst forms an unstable intermediate which transforms back to the catalyst after the end of the process. ④ It lowers activation energy

⑤ It is recovered at the end of reaction

We have positive and negative catalyst
The negative catalysts are called inhibitors or poison. They retard the reaction.

Properties of a Catalyzed Reaction

A Catalyzed reaction is faster and more specific in some reactions than other reactions ^{with} because of a lower activation energy.

Requirement for a Successful Catalytic Process

- (1) The reaction being catalyzed must be thermodynamically favourable
- (2) The reaction must be fast enough when catalyzed
- (3) The catalyst must have an appropriate selectivity towards a desired product
- (4) The catalyst must be economical, i.e. it must have a lifetime long enough to be economical

Types of catalyst: Homogeneous and heterogeneous catalyst

Homogeneous Catalyst: It is the catalyst that is in the same phase of the molecule of the catalyst are dispersed in the same phase as the molecule of the reactant

They can both in the gaseous phase or the liquid phase.

Heterogeneous catalyst: It is the ~~catalyst~~ ^{Catalyst} that are of different phase from the reactant. The reactant can be liquid or gases. The heterogeneous catalyst are usually in the solid phase: hydrogenation of fat to give butter, Ni is used as catalyst.

They are of more economic importance because they can easily be separated from the reacting mixture.

Primitive Catalytic processes

- (i) Fermentation of wine to acetic acid
- (ii) The manufacture of soap from fat to alkalies
- (iii) Formation of ether to alcohol and Sulphuric acid
- (iv) The Le Chatelier process of the manufacture of ~~Sulphur dioxide~~ Sulphuric acid in which SO_2 is oxidized by the addition of oxide of nitrogen

which catalyst is being used?

Catalysis

It is a cyclic process in which a specific catalyst increases the rate of conversion of reactant to products and is constantly regenerated.

The Study of Catalysts is very important because many industrial processes depends of ~~caty~~ catalyst for their process.

The term Catalysts was first employed in 1835 by a Swedish chemist, John Jacobo Berzelius, ~~a Swedish~~ ~~chem~~. It is used to corrolate a group of reaction, which includes,

08/07/26

- (1) Conversion of starch or sugar aided by acid
- (2) Hastening of Combustion of a varieties of gases by platinum,
- (3) The discovery of the stability of H_2O_2 in acid solution but its decomposition in the presence of alkali and metals such as Mn, Ag, Pt, Au.
- (4) Oxidation of alcohol to acetic acid, in the presence of finely divided platinum.

Catalytic processes in some technical acts process which involves

- (1) Fermentation of wine to acetic acid
- (2) The manufacture of Soap to fat and alkalines
- (3) Formation of ether to alcohol and Sulphonic acid

Applications/Importance/uses of Catalysts and Catalytic processes

Application of catalyst in industrial processes was first undertaken in the 19th century when an English chemist P. Phillips presented the use of Pt to oxidize SO_2 to SO_3 with air

- (2) The development of an industrial process for the oxidation of ~~hydro~~ HCl to Cl_2 in the presence of Cu(II) salt impregnated in clay bricks. The Cl_2 obtained was used in the manufacture of bleaching powder. ~~Sto~~

Studies carried out towards the end of 19th Century revealed the interaction of hydrogen with a wide variety of organic compound using various metal catalyst. This research led to the technical development of a German Patent for the hydrogenation of liquid unsaturated fat to solid saturated fat with Ni catalyst.

- (3) The contact process: catalytic reduction of H_2SO_4 from SO_2 by smelting operations
- (4) Catalytic method for the synthetic production of the Indigo dye stuffs
- (5) Catalytic combination of N_2 and H_2 for the NH_3

the Haber process. This is used for Nitrogen fixation. It is very important in the fertilizer industry and it was discovered by a German chemist Fritz Haber.

Catalysts containing d-block metal are of immense importance to the chemical industry, because they provide cost-effective synthesis, and then the specificity of the reaction. Most biochemically significant processes are catalyzed. Most industries depend on catalysts. Others include:

⊕ Energy process: such as petroleum refining which makes use of catalyst for many processes including alkylation, catalytic cracking and steam reforming.

The Exhaust from fuel burning are treated by catalysts. Bulk polymers from ethylene and propylene are prepared via Ziegler-Natta process.

- Polyesters, Polyamides and Isoocyanides are all from acid-base catalysis.
- Carbonation process requires metal catalyst.
- Catalyst and catalysis are also important in food processing especially hydrogenation of fats

using Ni catalyst to produce margarine.

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Hydroformylation (oxo) Catalysis

Hydroformylation also known as oxo synthesis / process is an important homogeneously catalyzed industrial process for the production of aldehyde from alkenes. This chemical reaction involves the addition of a formyl ($\text{C}(\text{H})\text{O}$) group and hydrogen atom to a $\text{C}=\text{C}$.

The development of hydroformylation originated within the German coal based industry, and it is considered as one of the premier achievement of 20th Century industrial chemistry because it was originate in 1938. It was discovered by Otto Roelen in 1938 in an investigation of the origin of oxygenated products, cobalt catalyzed Fischer Tropsch reaction.

Roelen noticed that CO and ~~ethylene~~^{the} were converted into diethyl ketone at higher pressures and marked the beginning of Hydroformylation.

Hydroformylation is the conversion of olefins / alkenes into aldehydes or ketones using CO and H_2 under pressure of about 100 atm and temperature of 100 - 300°C.

It is catalyzed by ~~Co~~ Co-Carbonyl complexes and related complexes such Rhodium-complexes. The Co catalysts dominate the industrial hydroformylation process until early 1970s until Rhodium catalyst were commercialized. In 2004, 75% of all hydroformylation processes are based on Rhodium trialkyl phosphine complexes, and this catalyst excel with C₈ or lower alkene or with a high regioselectivity to linear aldehyde.

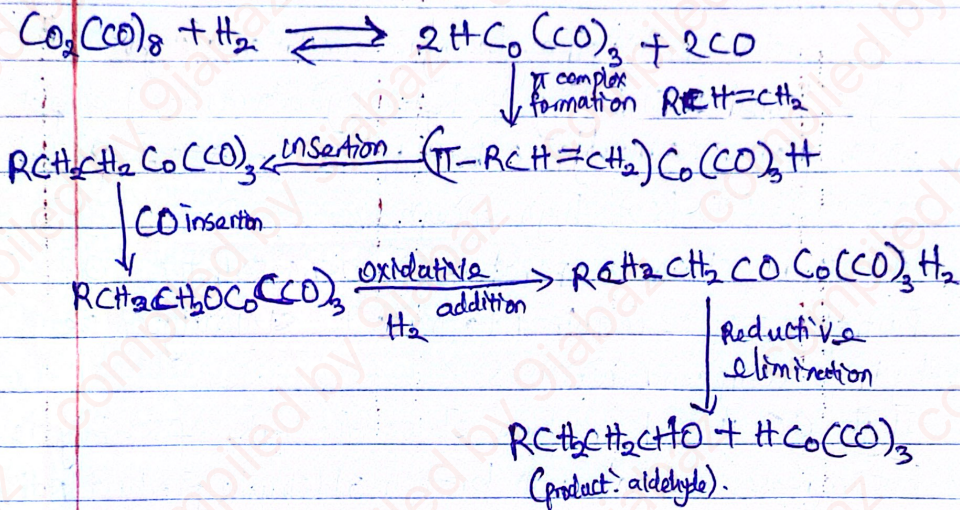
Importance of hydroformylation

- ① Most aldehydes produced are hydrogenated to alcohol or oxidized carboxylic acid. Esterification of the alcohol with ~~phthalic~~ phthalic anhydride with produce dialkyl-phthalate plasticizers which are used for PVC (polyvinyl chloride).
- ② Detergent and ~~surfactant~~ Surfactant also makes up the largest category, followed by solvents, lubricant and chemical intermediates.

The catalytic material in the system is called the hydrodocarbonyl $(HCo(CO)_3)$ which is derived from the catalyst dicobalt octacarbonyl $Co_2(CO)_8$.



Hydroformylation is the largest carbonyl rxn



Hydroformylation is the largest homogeneous catalyst

When a 1:1 ratio of H & CO is used, the reaction rate is independent of pressure due to the opposing orders of H and CO. Increasing the Hydrogen/CO (H_2/CO) ratio is of limited use for increasing the overall rate because the precursor (hydrido complex) is only stable under certain minimum carbonyl partial pressure at a given temperature

The reaction condition of the hydroformylation are governed by the thermal stability of ~~hydro~~ hydrido carbonyl complex which produces the metallic cobalt if the CO ~~present~~ partial pressure is not kept high enough.

As the reaction temperature is increased, the CO partial pressure required to make the stability of the hydrido compound increases.

High CO partial pressure slows the rate of catalysis but increases the linear to branch aldehyde product ratio (i.e. you have more linear to branched).

Higher CO partial pressure also lowers alkane isomerization side reaction.

Higher temperatures increases the reaction rate but lower the linear aldehyde product regioselectivity and also increase various undesirable side reaction.

→ One advantage of hydrido technology is that the catalyst separation is well established and also recycling.

The summary of the CO pressure is that there is careful control of the CO pressure; ~~while we need~~ which is necessary for the optimum yield of the product.

Steps

- (1) Insertion (ii) oxidative/reductive elimination

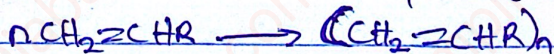
15/08/26

Ziegler-Natta Catalysts

It is named after two scientists, Karl Ziegler, a German and Giulio Natta, an Italian Chemist.

Both of them were awarded a Nobel in 1963, for the discovery of this catalyst.

Karl Ziegler is the first to discover the Titanium base catalyst while Giulio Natta used them to prepare stereoregular polymers from polyethylene or polypropylene. The catalyst are used in the synthesis of polymers of α -alkenes or α -olefins ($nCH_2=CHR$).



They are used in the commercial manufacture of ^{various} olefins since 1956. In 2010, the total volume of plastics, elastomers, rubbers produced from alkenes with these catalysts worldwide exceeds 100 billion metric tons worldwide.

The polymers represent the largest volume commodity plastics and the largest volume commodity chemicals in the world.

Ziegler discovered that a combination of Titanium tetrachloride ($TiCl_4$) and $Al(C_2H_5)_2Cl$ gave comparable ~~to~~ manufacture Polyethylene

Natta used α -Titanium trichloride [$AlCl_3$] in combination with $Al(C_2H_5)_3$ to produce isotactic polypropylene

Classes of Ziegler-Natta Catalyst

It has two broad classes which can be distinguished with their solubilities;

① Heterogeneous catalyst based on Titanium compounds.

For example, we have organoaluminium compounds such as $Al(C_2H_5)_3$ which are used in polymerization reactions in combination with co-catalyst.

This class of catalyst dominates the industry because it is more economical and they are easily separated.

② Homogeneous catalyst usually based on complexes of ~~Titanium~~ Ti , Zr , Hf

These homogeneous catalyst are used with the combination of organoaluminium catalyst called methylaluminoxane or methylaluminoxane (MAO)

This catalyst includes metallocenes and also multidentate Oxygen and Nitrogen based ligands.

and Limitations

Properties of Ziegler-Natta Catalyst

Most Ziegler-Natta Catalyst and all alkyl aluminum catalyst are unstable in air and the alkyl aluminum compound are pyrophoric. The catalyst therefore, are always prepared and handled under inert atmosphere that they do not combine with oxygen.

Limitations:

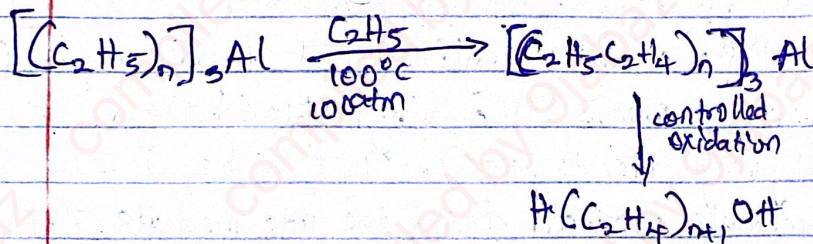
- ① Ziegler-Natta polymerization is only good to make polymers from hydrocarbons that are monomers of ethylene and propylene. It doesn't work for other monomers like vinyl chloride to give a polyvinyl chloride (PVC). This is because the radicals produced during the intermediate step can initiate free radical polymerization of the vinyl chloride monomer.
- ② It is also not good for the production of acrylates. This is also because the Ziegler-Natta Catalyst initiates an anionic vinyl polymerization in the polymer.

Industrial Applications of Organoaluminum

Triorganoaluminum compounds are of great implication in the in the preparation of alkyl derivatives

The use of these compounds avoids the employment of ethers which are necessary reagents in Grignard reagents

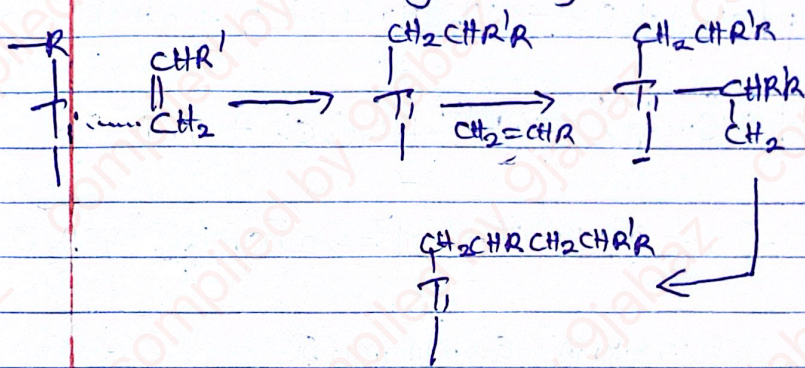
Aluminium alkyls cause dimerization, oligomerization and polymerization of olefins. These reactions are very useful in the manufacture of detergents which are often made from the long chain alcohol.



The polymers that results from this are better obtained by using the Ziegler-Natta Catalyst, because Ziegler-Natta catalyst are aluminium based catalyst

The polymers produced by these reactions are isotactic, i.e., sterically regular solids with desirable properties. This is opposed to atactic, liquids volatile substances and are oils room temperature

The mechanism probably involves an initial reduction of ~~At~~ Titanium by the aluminium alkyl followed by coordination, followed by insertion of the olefin molecules in a stereoregular way



~~The~~ WACKER PROCESS

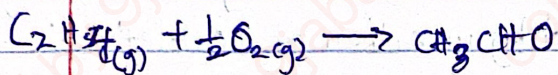
The Wacker process is an industrial process for the manufacture of ethanol by oxidizing ethene. For example, bubbling ethylene and oxygen together and treating with acidified water solution of palladium and cupric chloride will give acetaldehyde.

The reaction is catalyzed by PdCl_2 and CuCl_2 .

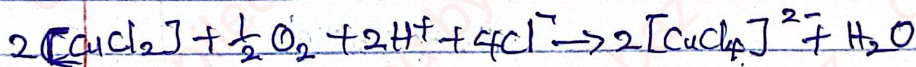
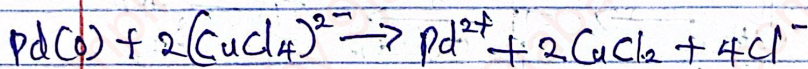
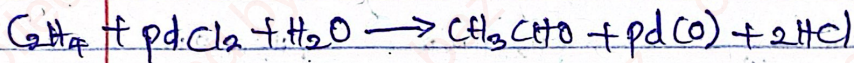
During the reaction Pd forms a complex with ethylene and is reduced to $\text{Pd}(\text{CO})$, it is then reoxidized to $\text{Cu}(\text{II})$ ion. The favourable condition of the

Know what each chemical is doing in the process and what is used for.

process is due to the abundance of ethylene.



a favourable rxn
 $\Delta = -197 \text{ kJ mol}^{-1}$



The rxn was undertaken in Germany in 1980

Platinum is not used because it is susceptible to nucleophilic attack on only Pd leads to successful completion of the reaction. It is very good in the production of acetaldehyde