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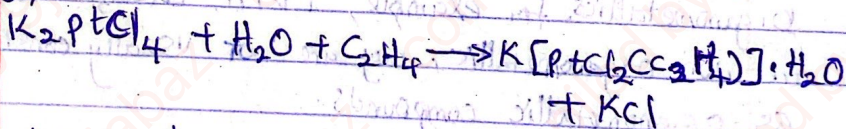
13th April, 2026

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.

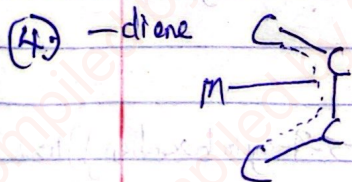
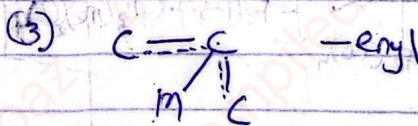
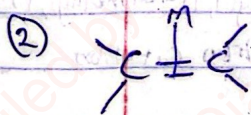
~~Carbon~~ Although, the term organometallic indicates a compound containing a metal and an organic group (carbon containing specie). Those compounds in which a direct metal carbon bond is not in operation are not classified as organometallics. For example, EDTA, CaCO_3 , Na_2CO_3 are non organometallic, 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_7 , C_5H_5  only 5 C atoms are bonded to the metal
6	-triene	C_6H_8 
7	-tri-enyl	C_7H_9 , C_7H_7
8	tetraene	

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

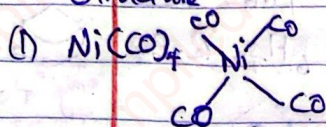


⑤ -diene)

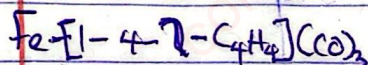
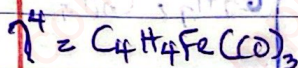
Examples of Organometallic compounds

Structure

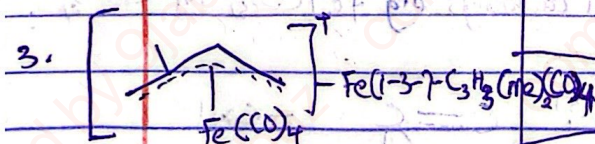
Name



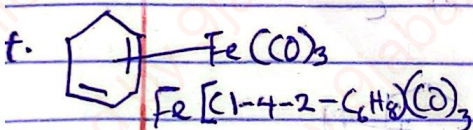
Nickel tetracarbonyl



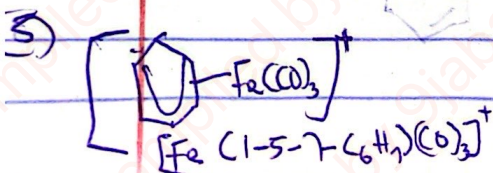
It is referred to as tricarbonyl cyclobuta (1,3) diene iron



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

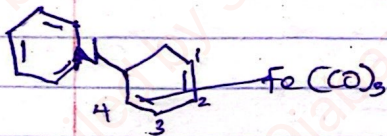


tricarbonyl [1-4-2 cyclohexa-1,3-diene] iron



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-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 18e⁻ 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 3np 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 lower 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 (i.e. negatively charged) or subtraction (i.e. 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 transition d same first. (class 6 metals)

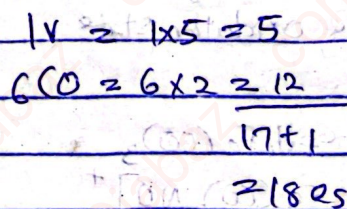
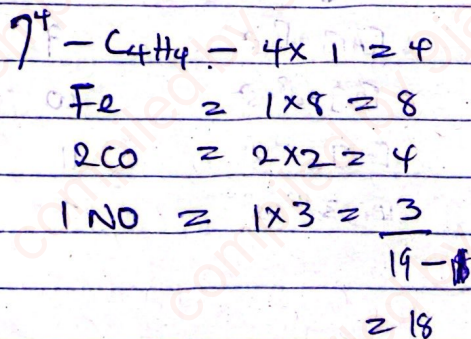
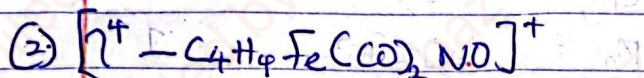
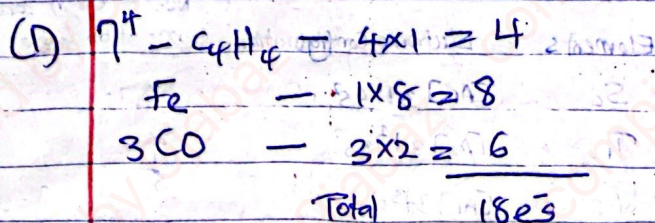
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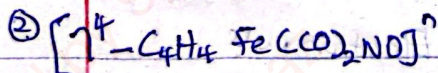
Atomic NO	Elements	Electronic Configuration	No. of e ^s in zero oxidation state.
21	Sc	[Ar] 3d ¹ 4s ²	3
22	Ti	[Ar] 3d ² 4s ²	4
23	V	[Ar] 3d ³ 4s ²	5
24	Cr	[Ar] 3d ⁵ 4s ¹	6
25	Mn	[Ar] 3d ⁵ 4s ²	7
26	Fe	[Ar] 3d ⁶ 4s ²	8
27	Co	[Ar] 3d ⁷ 4s ²	9
28	Ni	[Ar] 3d ⁸ 4s ²	10
29	Cu	[Ar] 3d ¹⁰ 4s ¹	11
30	Zn	[Ar]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

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

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

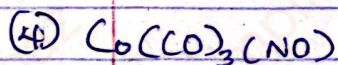
$$2CO = 2 \times 2 = 4$$

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

$$\underline{19}$$

$$n + 18 = 19$$

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

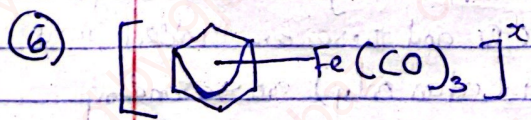


$$Co - 1 \times 9 = 9$$

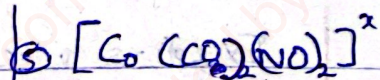
$$3CO - 3 \times 2 = 6$$

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

$$\underline{18}$$



$$1 C_5H_5$$



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

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

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

$$\underline{19}$$

$$n + 18 = 19$$

$$n = +1$$

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;
 $[Rh(CO)_2 Cl]_2$, $[Ni\{P(cyclohexyl)_3\}_2 (CH_2CH_2)]$

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 $[Ir(CO)_5 I]$

NO is stronger than CO

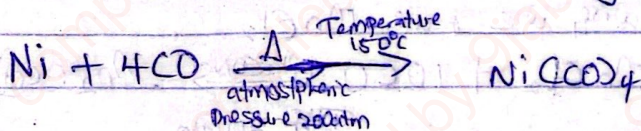
OS before = OS after

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

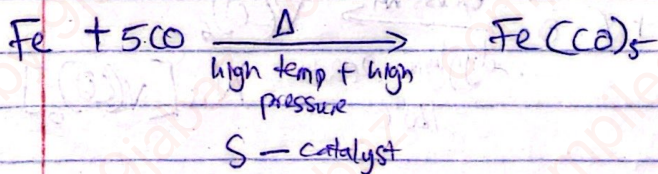
Synthesis

(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



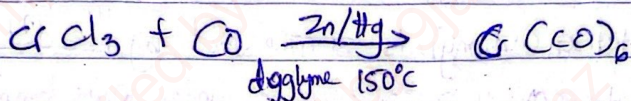
Ironpentacarbonyl is synthesized under high temperature and pressure in the presence of sulphur as catalyst



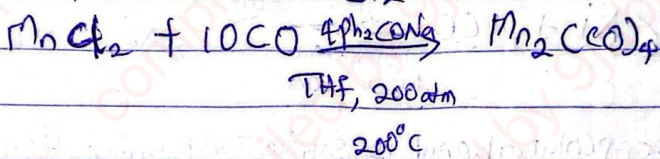
(2) Direct reaction of metal salt with carbon monoxide

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

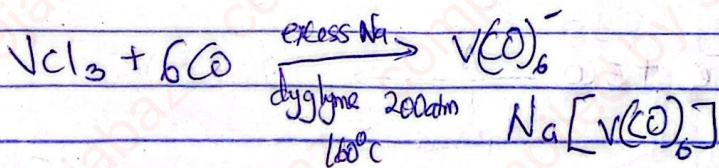
Therefore, a reducing agent is required for the preparation. Chromium hexacarbonyl is synthesized by reacting CrCl_3 with atmospheric CO in the presence of Zn/Hg.



Likewise we have MnCl_2



Also, we have

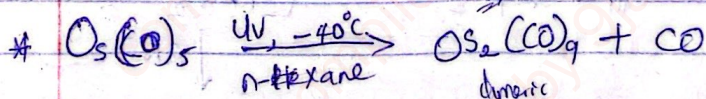


(B) The (1) and (2) reactions earlier mentioned are by thermolysis reaction.

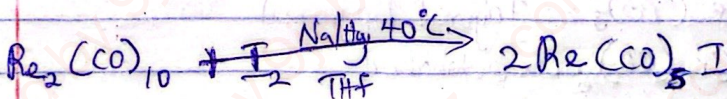
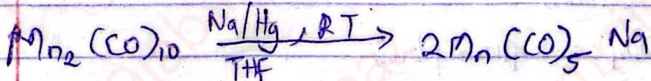
* Synthesis of metal carbonyl

This is a useful ^{route} ~~rate~~ 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 $\text{Os}_2(\text{CO})_9$.



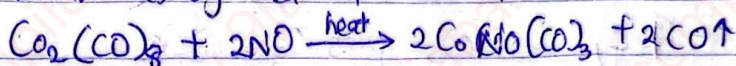
This is a good route to anion metal carbonyls and in the presence of a halide to give metal carbonyl halides.



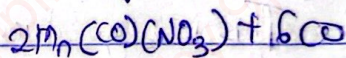
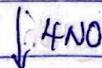
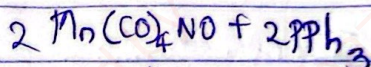
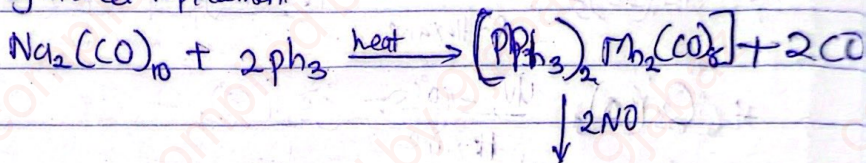
(5) Synthesis of Carbon Metal Nitrosyls

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

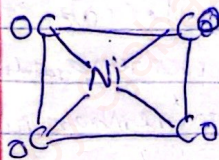


Structures

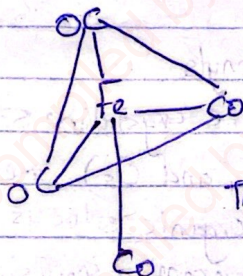
$\text{Ni}(\text{CO})_4$ - square planar

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

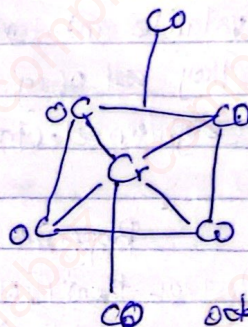
$\text{Cr}(\text{CO})_6$ - octahedral



square planar

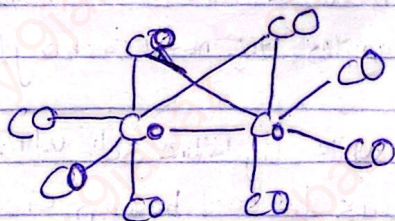


Trigonal bipyramidal



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)

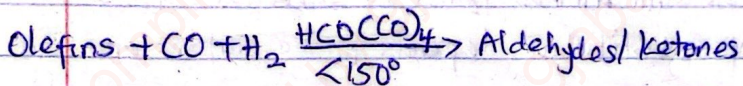
Properties of Metal Carbonyls

- 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 thermodynamic. For examples, the metal carbonyl bond, $Cr(CO)_6$, $Fe(CO)_5$.

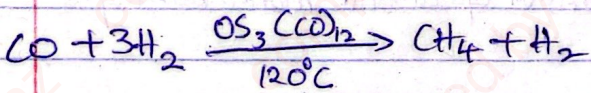
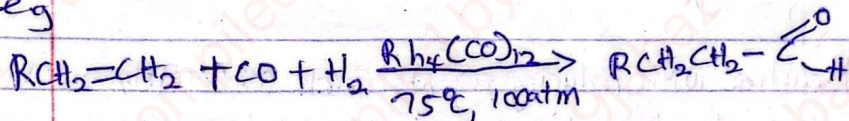
$Cr(CO)_6$ is a red stable white crystalline solid which requires 13 kJ/mol of energy to break the bond between Cr and CO . This value compared with the dissociation energy of 180 kJ/mol required for the $Fe-CO$ bond in $Fe(CO)_5$, which is ~~180~~ ¹³⁰ kJ a volatile yellow liquid.

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)

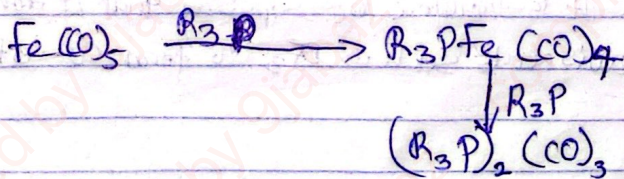


e.g.



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.

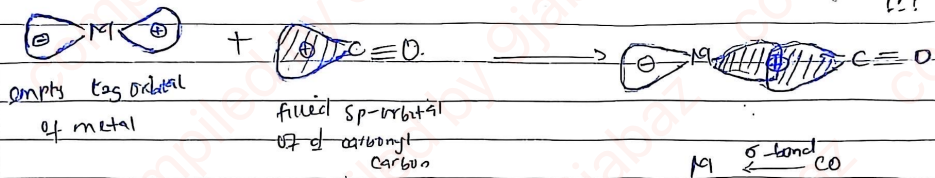
As well as a strong π -bond, resulting from the back donation of electrons from the filled t_{2g} orbital of the metal to the empty π^* orbital of the carbonyl carbon.

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.

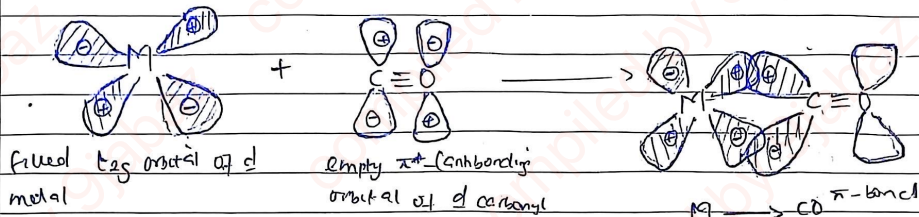
Decorar-Ogatt model for bonding in metal carbonyls.

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.

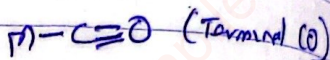
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Types of Metal Carbonyl Bond

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

2. M_2 -Bridging

3. Face 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~~

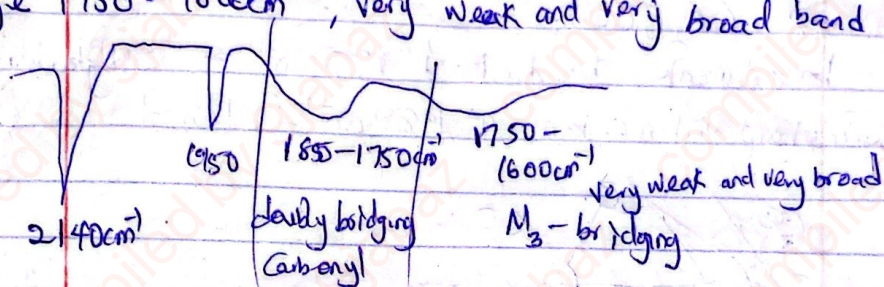
② M_2 -Bridging or doubly bridging metal carbonyl: The IR ~~2130~~ band are usually weak and broad, with neutral species absorbing in the range $1850 - 1750 \text{ cm}^{-1}$
e.g. $M-CO-M$, 

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 $\text{Co}(\text{CO})_4$. 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} . Suggest the structure of the metal carbonyl

- (i) Does the compound obey effective atomic number rule?
If yes, how? ($\text{Co} = 59$, $\text{C} = 12$, $\text{O} = 16$)

Solution

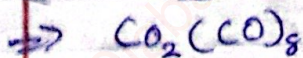
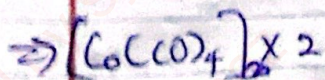
Let $\frac{x}{n}$ represent the molecular M

$$[\text{Co}(\text{CO})_4]_n = 342$$

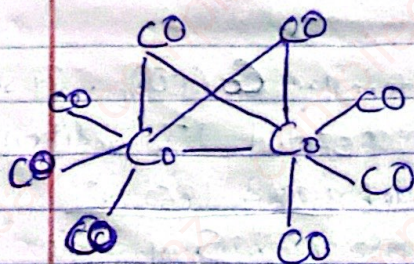
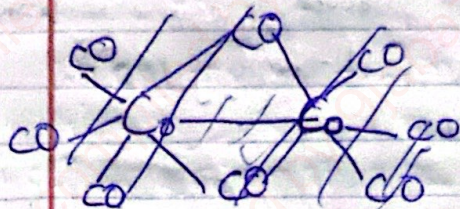
$$[59 + (12 + 16)4]_n = 342$$

$$n \mid n = 342$$

$$n = 2$$



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



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

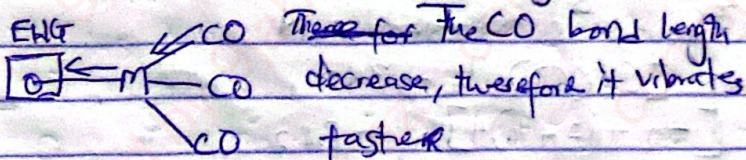
$$1 \text{ Co} = 1 \times 9 = 9$$

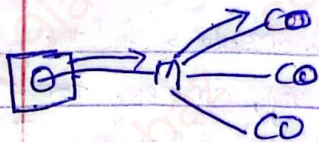
$$3 \text{ CO} = 3 \times 2 = 6$$

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

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

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} 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 $1-5-7-C_6H_7Fe(CO)_3]^+$ with the iodide ligand gives products with much lower IR ν_{CO} bands:

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

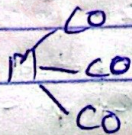
$$W(CO)_3 = \nu_{CO} = 1935, 1855 \text{ cm}^{-1}$$

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

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

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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 $C \equiv O$ 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

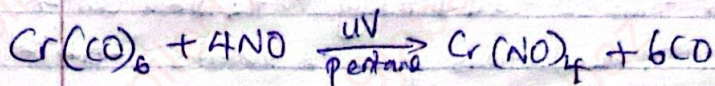
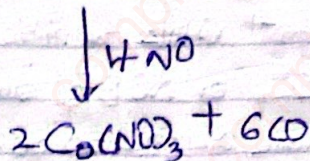
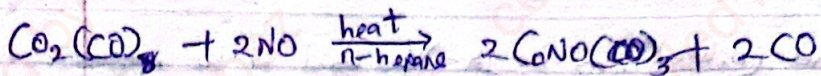
Nitric oxide (NO) is a paramagnetic species and has electron in an antibonding orbital. The latter electron is readily lost to form the 10 electron species NO^+ . This is called Nitrosonium ion, and it is in this form that NO is found in most nitrosyl complexes.

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 interval ($\text{M}_2\text{-NO}$), (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.

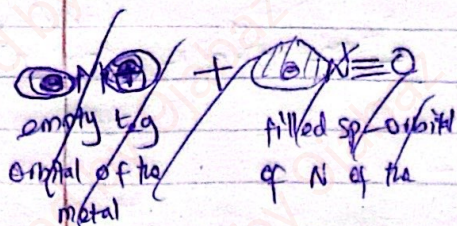
The IR bands of the coordinated NO therefore shifts to much lower ^{wavenumber} ~~frequency~~ than the ~~As a general guide~~ corresponding CO bands.

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 $1350 - 1300 \text{ cm}^{-1}$.

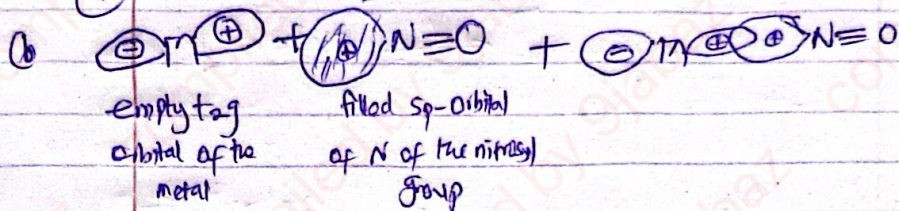
Most of the above IR-bands were established from studies of mixed nitrosyl carbonyl

Bonding in Metal Nitrosyl

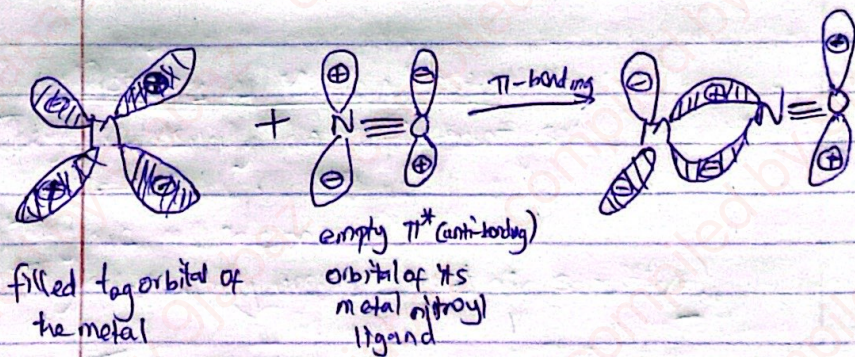
* Describe the nature of bonding in metal nitrosyls



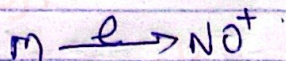
σ -bonding scheme of metal nitrosyls



(2) π -bonding scheme



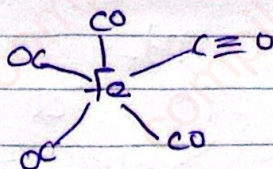
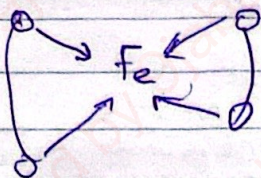
$\xrightarrow{e}$



Dewar-Chauffe model of metal bonding in metal nitrosyls

Mo	Tu	We	✓Th	Fr	Sa	Su
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Date 10/06/26

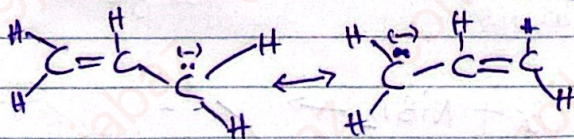


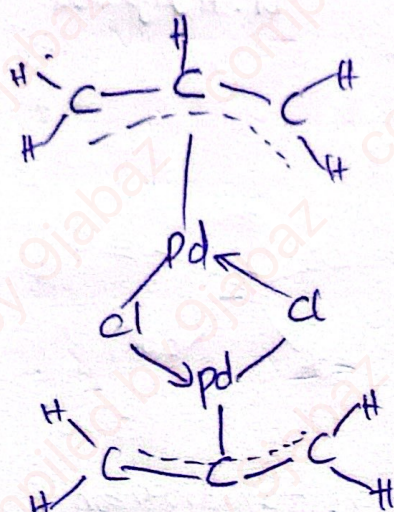
Synthesis and Reactivity of π -hydrocarbon metal Complexes

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

$$3C = 6$$

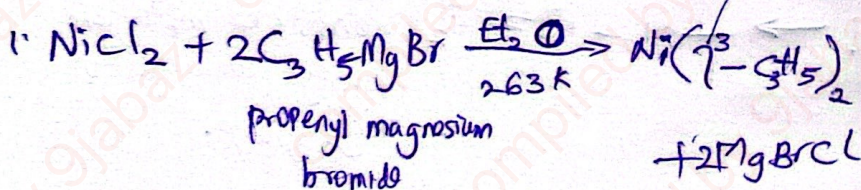
$$Ni = 10$$

pd is under the group of Ni

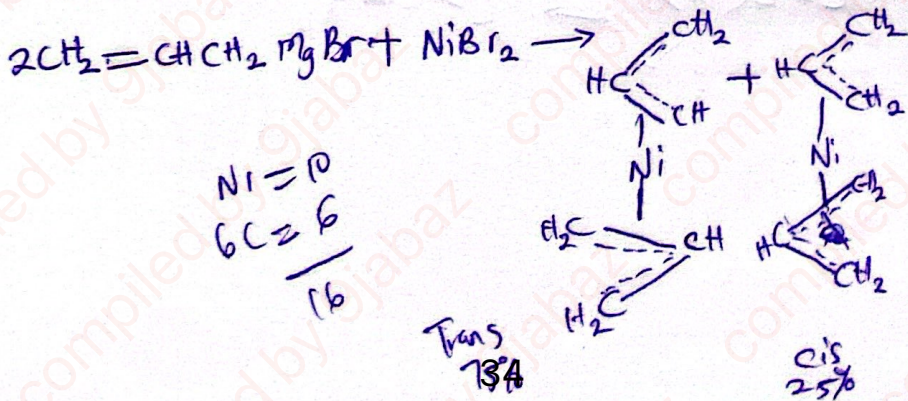
we can also have stable $16e^-$ especially square planar compounds

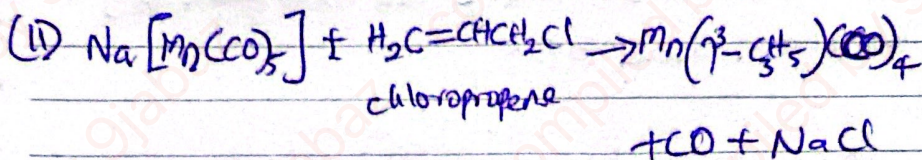
Preparation of the Allyl

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

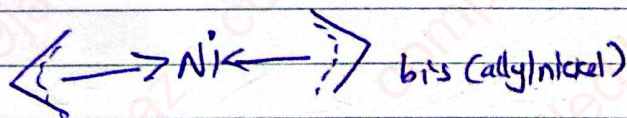
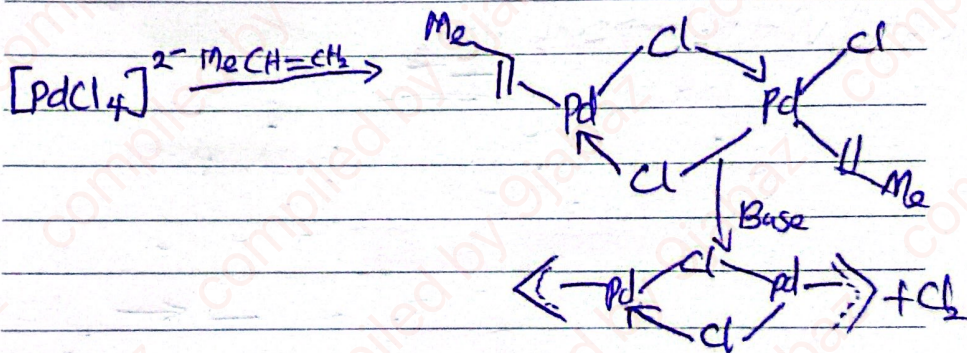


or





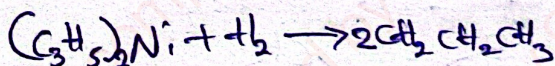
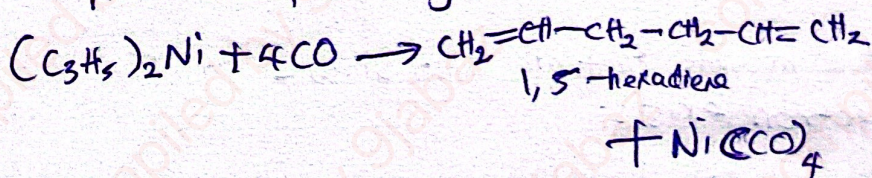
* compounds that are also stable at 16 electron exists.



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 $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2$

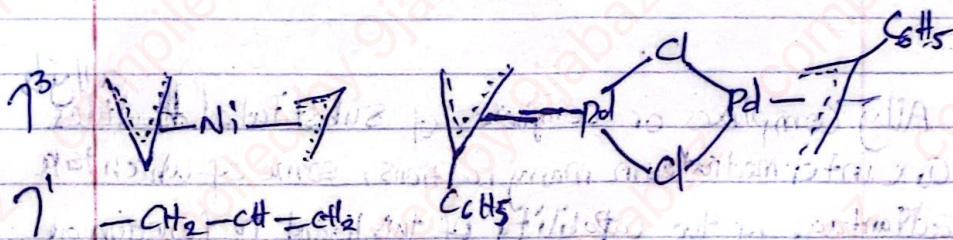
Thus, $\text{Ni}[\eta^3-1,3-(\text{Me}_3\text{Si})_2(\text{C}_3\text{H}_3)_2]$ is kinetically stable in air for several days and decomposes only when heated above 373 K.

Reactions of Bis(allyl)nickel include:



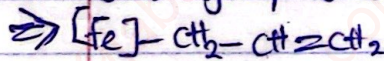
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3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

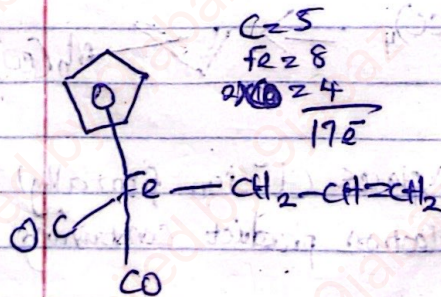


Sigma-allyl ligands

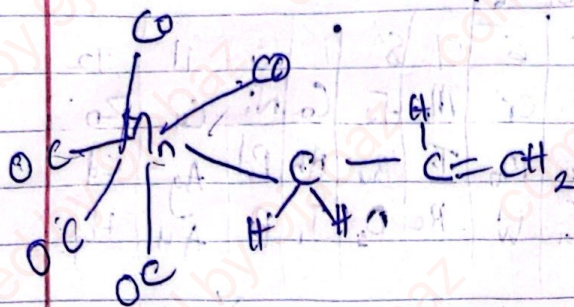
Complexes with η^1 -allyl ligands (classified as X-type ligands) are also known e.g. $\text{CpFe}(\text{CO})_2(\eta^1\text{-C}_3\text{H}_5)$, in which only the methylene group is attached to the Fe centre.



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



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



$$Mn = 7$$

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

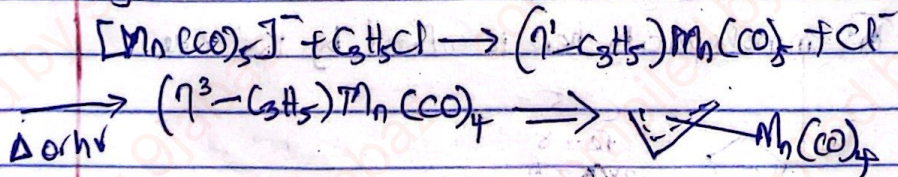
$$C = 1$$

$$18e^-$$

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.

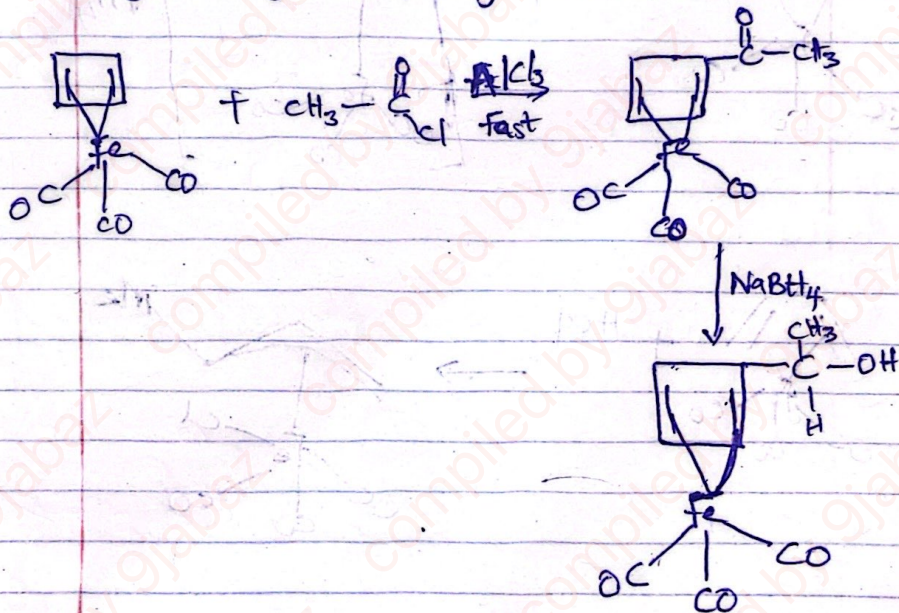
e.g.



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

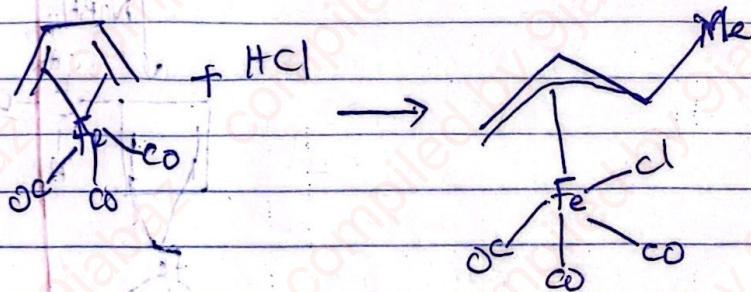
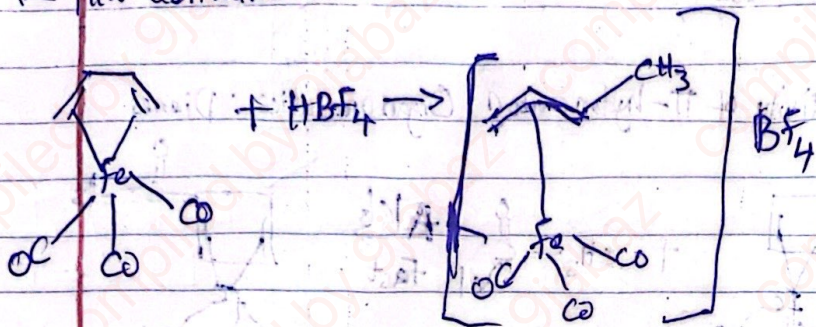
The ligand switches to trihapto when a CO is lost, preserving the $18e^-$ count.

Reactivity of π -hydrocarbon: Organometallics: Dienes



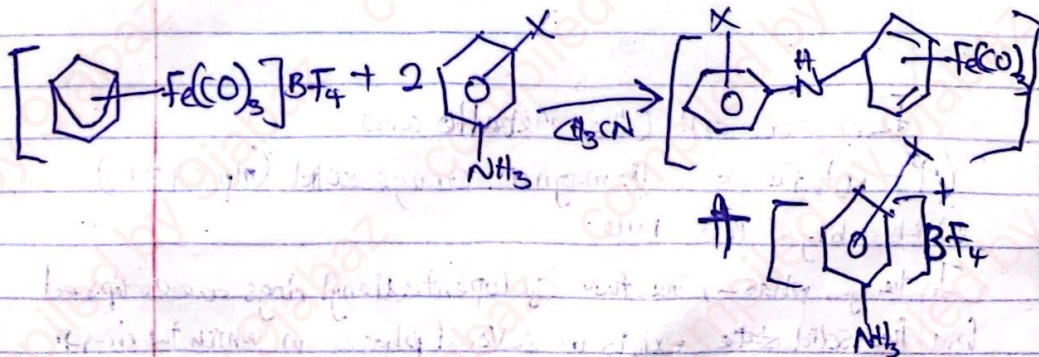
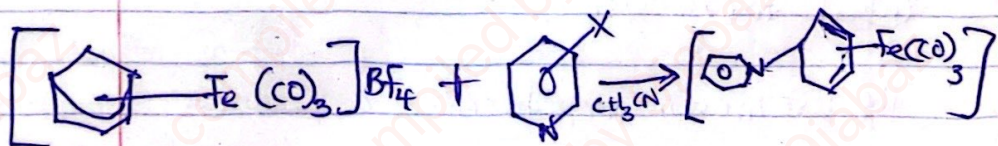
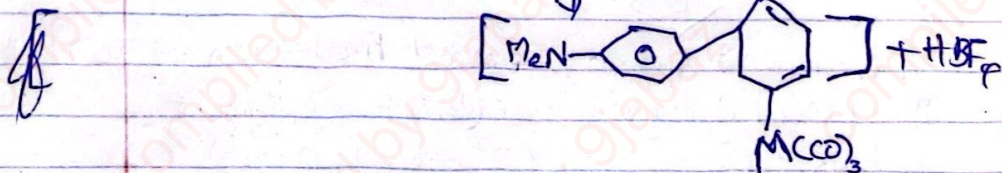
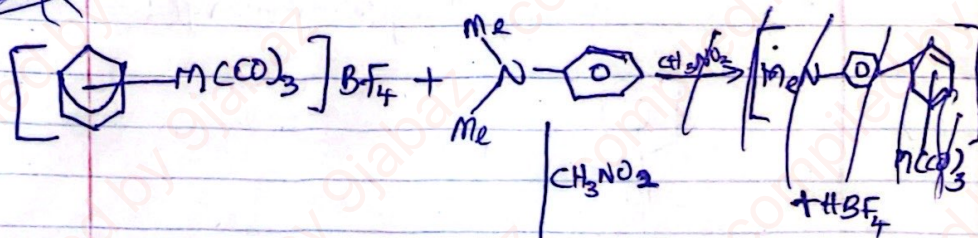
Tricarbonyl (cyclobuta-1,3-diene) Iron behaves as a very reactive organic molecule by undergoing Friedel-Crafts alkylation. The resulting product is rapidly reduced to the alcohol derivative with NaBH_4 .

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.

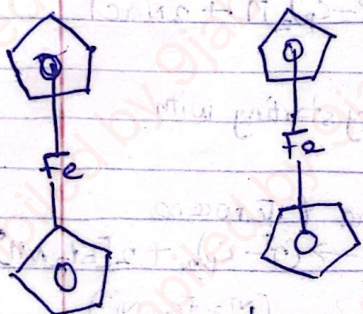
The best known metallocenes is ferrocene.

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

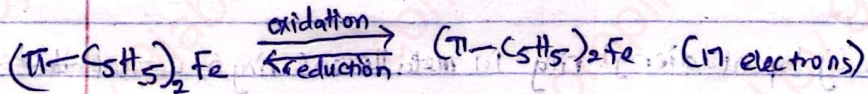


eclipsed

332 pm

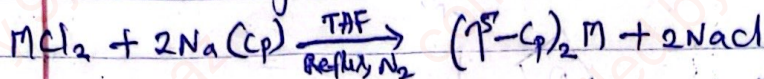
The bonding in $(\eta^5\text{-Cp})_2\text{Fe}$ can be described in terms of the interactions between the π molecular orbitals of the ligands and the 3d atomic orbitals of the metals.

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



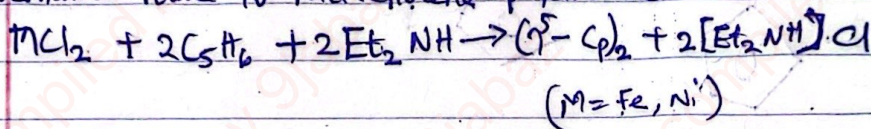
Metallocenes of the first row transition metals are known for V(II) , Cr(II) , Mn(II) , Fe(II) , Co(II) , Ni(II) and Zn(II) .

General Synthetic Route



For $(\eta^5-Cp)_2V$, it is prepared by starting with Vanadyl trichloride (VCl_3)

* Alternative route to Nickelocene & Ferrocene



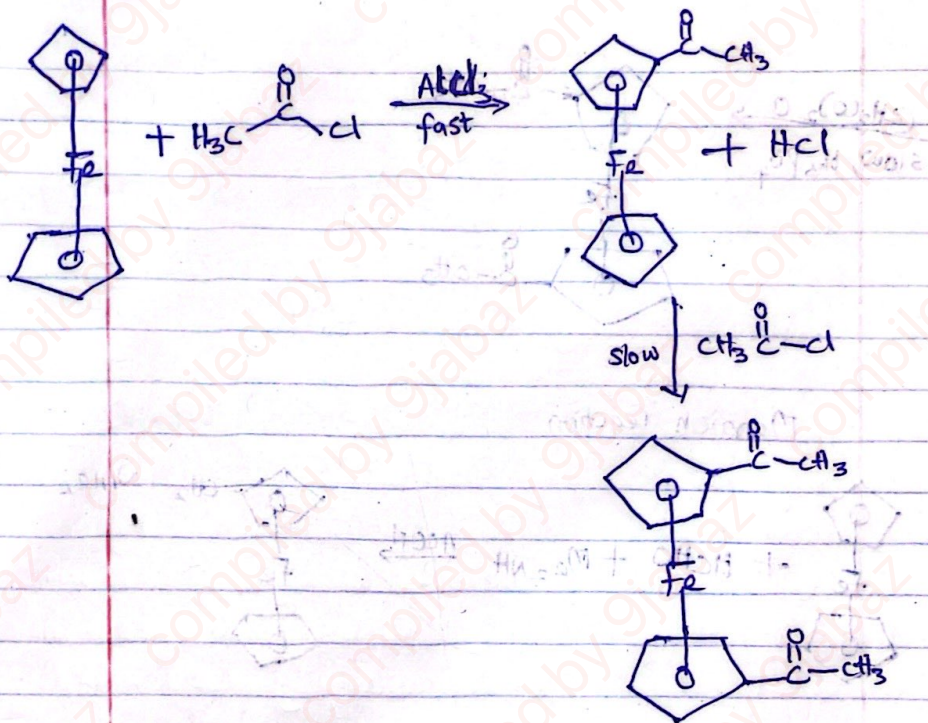
React



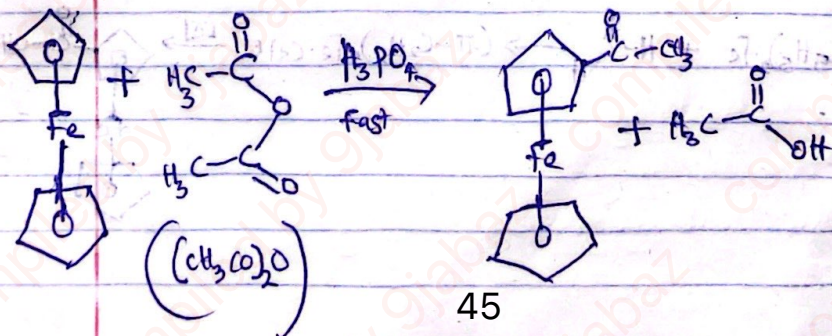
Ruthenocene

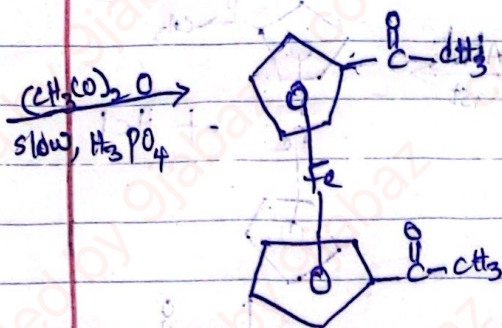
The Cyclopentadienyl ring in metallocene rings, ~~in metallocenes~~, particularly ferrocene are ~~usually~~ aromatic and behaves like benzene in most reactions; they are reactive towards electrophiles.

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

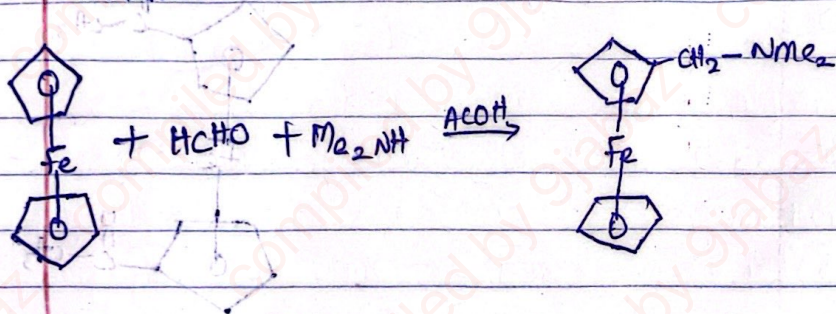


The ~~product~~ ^{same} product are obtained when acetylation is carried out using acetic anhydride in the presence of phosphoric acid as a catalyst.

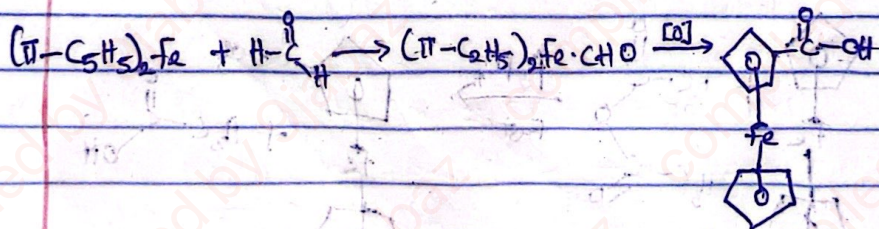


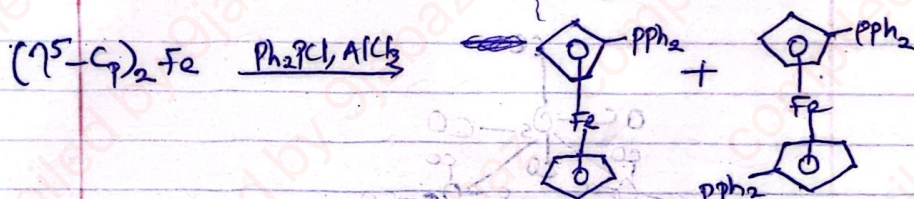
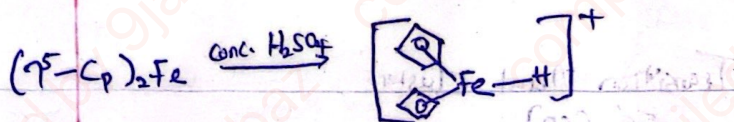


Mannich reaction

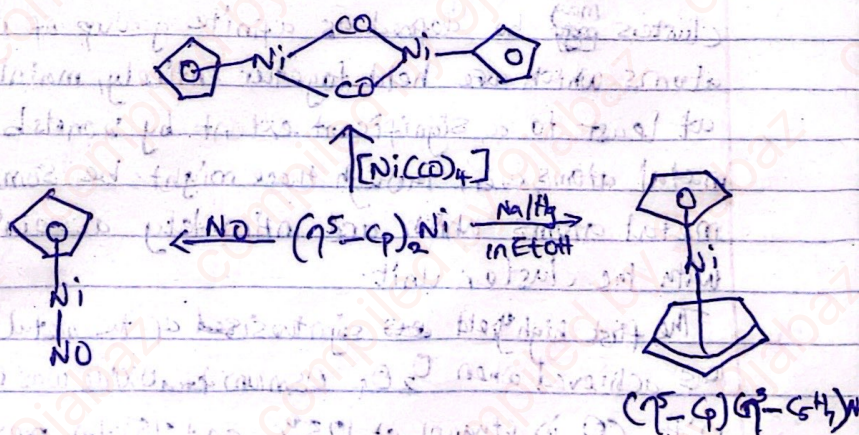


Formylation also occurs at the diene ring to form the aldehyde derivative which is oxidized to give ferrocenic acid. It is a weaker acid than benzoic acid.

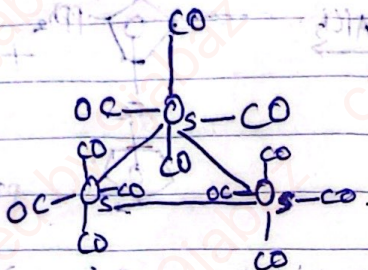
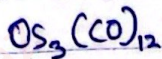




Selected reactions of Nickel(II)ocene $(\eta^5\text{-Cp})_2\text{Ni}$



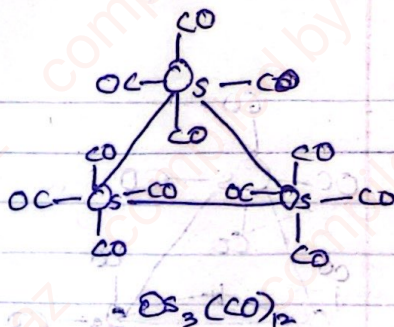
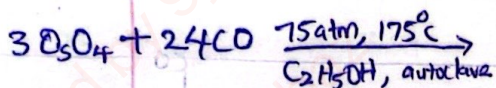
Transition Metal Clusters



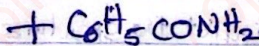
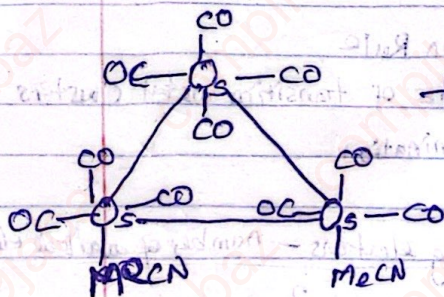
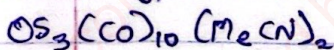
Clusters ~~may~~ be defined as a finite group of metal atoms which are held together entirely, mainly or at least to a significant extent by bonds between metal atoms, even though there might be some non metal atoms which are intimately associated with the cluster unit.

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 tris(osmium dodecacarbonyl) in 85% yield.

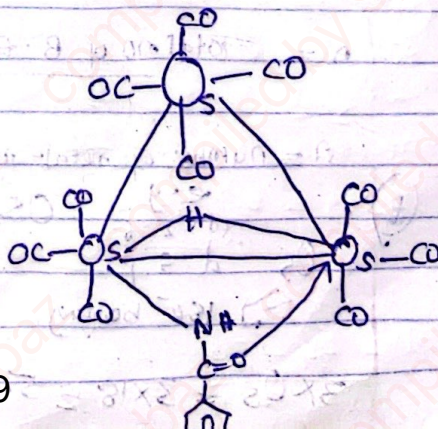
X-ray Crystallographic Studies showed that there was a triangular array of metal atoms ~~terminally~~ with four Carbonyl groups terminally bonded with each metal.

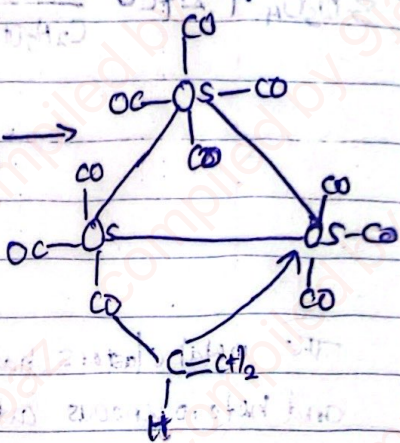
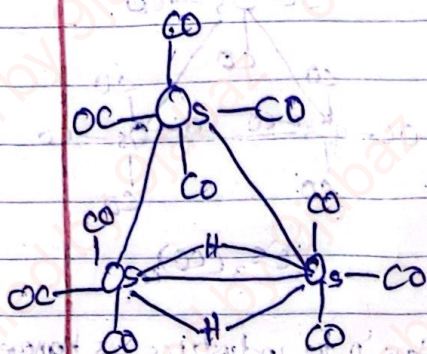


The metal clusters have applications in the industries as homogeneous and heterogeneous catalyst. Some other examples includes



Reflux
 N_2
Cyclohexane





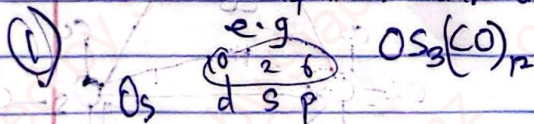
Generalized 18 electron Rule

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

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

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

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



⇒ 18e⁻ bonding

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

No of available electrons

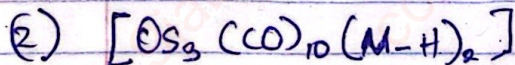
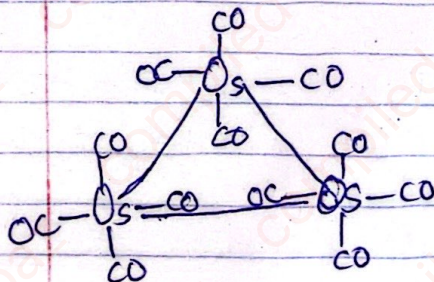
$$3 Os = 3 \times 8 = 24$$

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

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

$$n = 3$$

Number of metal-metal bonds = 3



Bonding electrons

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

Available electrons

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

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

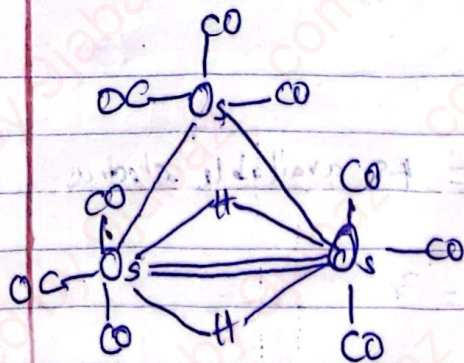
$$2 H = 2 \times 1 = 2$$

$$\underline{46}$$

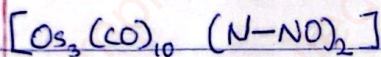
$$n = \frac{BE - A \cdot E}{2}$$

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

Number of metal-metal bonds = 4



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

Bonding Electrons

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

Available Electrons

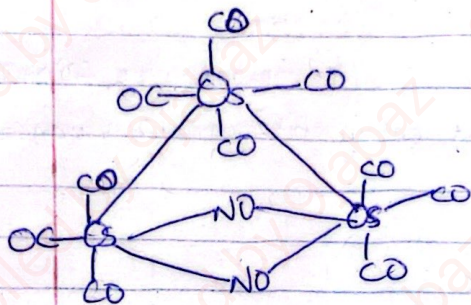
$$3 \text{ Os} = 3 \times 8 = 24$$

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

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

$$24 + 20 + 6 = 50$$

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



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

Wade's Rule

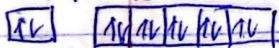
The rule applies to higher nucleant metal clusters, such as $\text{Os}_5(\text{CO})_{16}$ and $\text{Os}_6(\text{CO})_{18}$

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

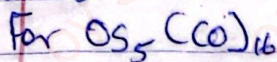
n describes the stereochemistry or orientation in space of the metal.

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.



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

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

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

$$72$$

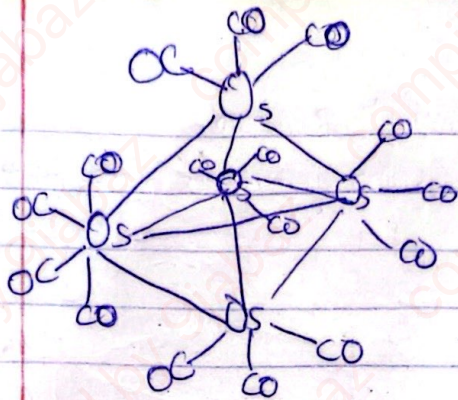
Valence e^-

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

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

$$\Rightarrow n = 5$$

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



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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

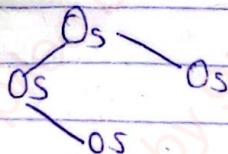
$$7\text{Os} = 12 \times 7 = 126$$

A.E

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

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

$$n = \frac{B.E - A.E}{2} = \frac{126 - 56}{2} = 14$$



(b) Orientation in space

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

Valence

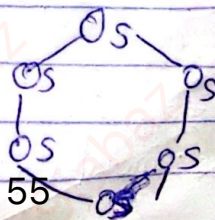
$$7\text{Os} = 12 \times 7 = 84$$

Valence

$$A.E = 98$$

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

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



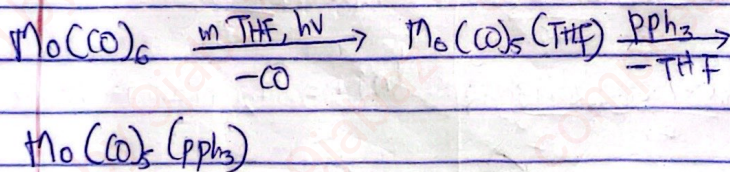
Types of Organometallic Reaction

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

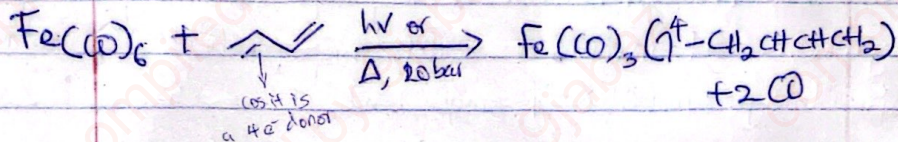
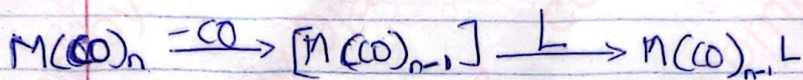
(1) Ligand substitution

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 $\text{Mo}(\text{CO})_5(\text{PPh}_3)$

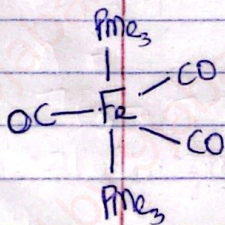
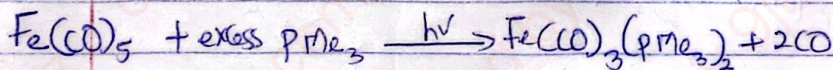


The substitution steps are dissociative, the outgoing ligand leaves creating a $16e^-$ metal center, which is coordinatively unsaturated.

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

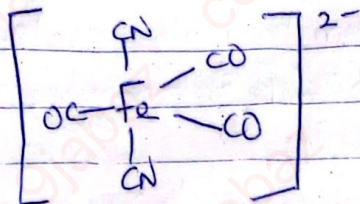


In the above reaction, the incoming ligand provides $4e^-$ and displaces 2 carbonyl ligand.



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

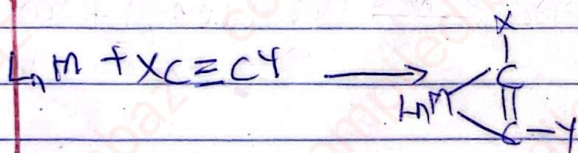




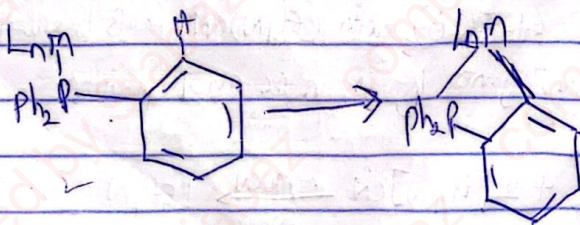
Oxidative Addition Reactions are very important in organometallic synthesis. It involves the addition of a molecule X-Y with ~~not~~ cleavage of the X-Y single bond



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