Organometallic compounds-l PG Semester I Gauhati University

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What is organometallic compound?

- ♦ Organometallic compound: contains at least one metal-carbon (M-C) bond
- Includes ligands like CO, NO, N₂, PR₃, H₂ (no C-atom), does not include cyano complexes due to its conventional coordination chemistry
- A common platform for organic and inorganic chemists (organic synthesis, industrial catalyst, material chemistry)
- ✤ Edward Frankland was known as the father of organometallic chemistry
- Vitamin B_{12} (cyanocobalamin) is naturally available organometallic compound (Co-C bond).
- \diamond Zeise's Salt, K[Pt(C₂H₄)Cl₃]H₂O (1827), bearing H₂C=CH₂ ligand is the first synthesized organometallic compound.
- Solution Different bonding modes viz. σ- and π-bonding, sometime even δ-bonding.
- ✤ Organometallic chemistry of s- and p-block metals are simple
- Organometallic chemistry of d and f-block metals are complex and much more recent.

Nobel-Prize Winners

- Ehrlich (1908) (Organo-arsenic compounds)
- Victor Grignard and Paul Sabatier (1912) Grignard reagent
- ➢ K. Ziegler, G. Natta (1963) Ziegler-Natta catalyst
- E. O. Fisher, G. Wilkinson (1973) Sandwich compounds
- ▶ W. Lipscomb (1976) -boranes illuminating problems of Chem. Bonding
- → Herbert Brown and G. Wittig (1979) hydroboration reaction
- ≻ K. B. Sharpless, R. Noyori (2001) Hydrogenation and oxidation
- Yves Chauvin, Robert H. Grubbs, Richard R. Schrock (2005) Metal catalyzed alkene metathesis
- Suzuki, Heck and Negishi (2010) Pd-catalysed C-C bond formation

Nomenclature of organometallic compounds

- > Naming/writing formula of an organometallic compounds is **similar to coordination compounds**
- Ligands are listed in alphabetical order followed by the name of the metal with its oxidation number in parentheses, all of which is written as one word.
- > Ligands with multiple bonding modes are indicated with hapticity (η)
- IUPAC recommendation for formula: The symbol for the metal is written first, followed by the ligands, listed in alphabetical order based on their symbol.
- Ligands like hydride, CO can bond to more than one metal atom in the same complex, and are then referred to as bridging ligands (μ)

Some examples

Q. 1 Give the formal names of (a) ferrocene and (b) $[RhMe(PMe_3)_4]$.

Answer

- (a) Ferrocene contains two cyclopentadienyl groups that are both bound to the metal atom through all five carbon atoms, thus both groups are designated η^5 . The full name for ferrocene is thus bis(η^5 -cyclopentadienyl)iron(II).
- (b) The rhodium compound contains one formally anionic methyl group and four neutral trimethylphosphine ligands, therefore the formal name is methyltetrakis-(trimethylphosphine)rhodium(I).
- Q. 2 What is the formal name of $[Ir(Br)_2(CH_3)(CO)(PPh_3)_2]$?

Ligands in organometallic compounds

- \succ Ligands in organometallic complexes are many, have different bonding modes viz. σ -and π -bonding and even δ -bonding
- > The reactivity of the metal atom and the ligands is affected by the M-L bonding.

| Ligand | Name | Ligand | Name |
|----------------------------|--|------------------|---|
| СО | Carbonyl | \bigcirc | |
| =c | Carbene (alkylidene) | \bigcirc | Benzene |
| $\equiv c -$ | Carbyne (alkylidyne) | | 1,5-cyclooctadiene (1,5-COD) |
| ∇ | Cyclopropenyl (<i>cyclo</i> -C ₃ H ₃) | $H_2C = CH_2$ | Ethylene |
| \bigvee | | НС≡СН | Acetylene |
| \land | | | π -Allyl (C ₃ H ₅) |
| $\langle \bigcirc \rangle$ | Cyclobutadiene ($cyclo$ -C ₄ H ₄) | -CR ₃ | Alkyl |
| $\tilde{\bigcirc}$ | Cyclopentadienyl ($cyclo$ -C ₅ H ₅) (Cp) | | Acyl |

Classification of Organometallic compound based on M-C bond

- \succ σ -bonded: It is the classical 2c-2e M-C bond, mostly found in organometallics of main group elements
- \succ Examples: CH₃MgBr, Zn(C₂H₅)₂
- \succ σ -donor and π -acceptor: It involves the σ -donation of the ligand followed by π -acceptance by the ligand
- Examples: Metal carbonyls, metal nitrosyls
- > π -donor and π -acceptor: It involves the σ -donation of the carbocyclic, acyclic unsaturated ligand followed by π acceptance by the ligand
- Examples: Organometallic complexes of alkene, benzene
- > Non-classically bonded: Sometimes alkyl group may act as the bridging groups. In such cases, instead of normal 2c-2e

M-C bonds, electron deficient multicentered M-C bonds are formed.

- \succ Example: Li₄(CH₃)₄ 4c-2e bond
- \succ Usually, π -acceptor organometallics are more stable than σ -donor organometallics.

Hapticity of ligands

- The number of C-atoms (unsaturated organic ligands) bound to metal center is expressed in terms of 'hap' to nomenclature (η^x)
- The superscripts x provides a topological description by indicating the connectivity between ligand and the central atom.
- Example, a CH_3 group attached by a single M-C bond is monohapto, η^1 , and, if the two C atoms of an ethene ligand are both within bonding distance of the metal, the ligand is dihapto, η^2 .
- > Thus, three cyclopentadienyl complexes might be described as having η^1 , η^3 , or η^5 cyclopentadienyl groups
- ➢ However, the concept of hapticity also been extended to non carbon ligand



n¹-Cyclopentadienyl



η³-Cyclopentadienyl



η⁵-Cyclopentadienyl

Stable electronic configuration: 18-Electron Rule

- ✤ Irwing Langmuirin (1921) first formulated this rule (extension of octet theory) rule of thumb
- It states that 'Thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d-electrons and the electrons conventionally considered as being supplied by the surrounding ligands equals 18'
- Applicable for organometallics with metals (transition) in low oxidation state bearing strong π -acceptor character.
- In octahedral complexes, six bonding interactions are possible. In presence of π -acceptor ligands, bonding combinations with three t_{2g} orbitals also possible leading to nine bonding MOs, and space for a total of 18e.
- Square-planar complex has only eight bonding MOs, thus a 16-electron configuration is energetically favorable
- ✤ Complexes with 17e and 19e are paramagnetic in nature

| Usually fewer than 18e | Usually 18e | 16 or 18e |
|------------------------|-------------|-----------|
| Sc, Ti, V | Cr, Mn, Fe | Co, NI |
| Y, Zr, Nb | Mo, Tc, Ru | Rh, Pd |
| La, Hf, Ta | W, Rep Os | Ir, Pt |

Electron counting and oxidation states

- Dominance of 16- and 18-electron configurations in organometallic chemistry makes it suitable to count the number of valence electrons on a central metal atom.
- ✤ Number of electrons allows us to predict the stabilities of compounds.
- Complexes with 17 e are strong oxidising agent and complexes with 19 e are strong reducing agent
- Two models are used viz. neutral-atom method (covalent method) and the donor-pair method (oxidation state/ionic method).
- ✤ Donor-pair method is more convenient (oxidation numbers can be assigned) to use.

Donor-pair method/Oxidation state method

- Ligands are considered to donate electrons in pairs (treated as neutral and/or charged)
- Oxidation number of an element is calculated as that for coordination compounds.
- > Number of electrons contributed by ligand depend on its nature. CO and PPh₃, are neutral two-electron donors (ON=0),

X⁻, H⁻, and CH₃⁻ are mono-negative and two-electron donors. Cp treated as $C_5H_5^-$ (ON= -1) a six-electron donor

- \blacktriangleright Oxidation number of the metal = total charge of complex charges of ligands.
- ➤ Number of electrons the metal provides = Group number oxidation number.
- > TEC is the sum of electrons contributed by metal and all ligands.
- > Advantage: Both the electron count and the oxidation number may be determined.
- > **Disadvantage**: It overestimates the charge on the metal atom

Neutral-ligand method

- > All ligands are treated as neutral and are categorized according number of electrons they donate.
- ➤ Metal atom is also treated as neutral, considers all valence electrons of the metal.
- ➢ For charged complex, add/subtract the appropriate number of electrons to the total
- Count 1e for every covalent bond to another atom and count 2e for every dative bond from another atom. Three- and fourcenter bonds need special treatment
- Delocalized carbon fragments: usually 1e per C-atom (hapticity)
- \succ TEC is the sum of electrons contributed by metal and all ligands.
- * Advantage: It is trivial to establish the electron count.
- ✤ Disadvantage: It overestimates the degree of covalence (underestimates charge).

Methods of counting: Oxidation state (A) & Neutral atom (B) method

| Ligand | Method A | Method B |
|---|--|----------|
| Н | 2 (H ⁻) | 1 |
| Cl, Br, I | 2 (X ⁻) | 1 |
| OH, OR | 2 (OH ⁻ , OR ⁻) | 1 |
| CN | 2 (CN ⁻) | 1 |
| CH ₃ , CR ₃ | $2(CH_3^-, CR_3^-)$ | 1 |
| NO (bent M — N — O) | 2 (NO ⁻) | 1 |
| NO (linear M — N — O) | 2 (NO ⁺) | 3 |
| CO, PR ₃ | 2 | 2 |
| NH ₃ , H ₂ O | 2 | 2 |
| = CRR' (Carbene) | 2 | 2 |
| $H_2C = CH_2$ (Ethylene) | 2 | 2 |
| CNR | 2 | 2 |
| =0, =S | $4 (O^{2-}, S^{2-})$ | 2 |
| η^3 -C ₃ H ₅ (π -allyl) | $4(C_{3}H_{5}^{-})$ | 3 |
| \equiv CR (Carbyne) | 3 | 3 |
| ≡N | 6 (N ³⁻) | 3 |
| Ethylenediamine (en) | 4 (2 per nitrogen) | 4 |
| Bipyridine (bipy) | 4 (2 per nitrogen) | 4 |
| Butadiene | 4 | 4 |
| η^5 -C ₅ H ₅ (Cyclopentadienyl) | $6 (C_5 H_5^{-})$ | 5 |
| η^{6} -C ₆ H ₆ (Benzene) | 6 | 6 |
| η^7 -C ₇ H ₇ (Cycloheptatrienyl) | $6 (C_7 H_7^+)$ | Draft 7 |

 $Fe(CO)_5$ acquires 18 electrons from the eight valence electrons on the Fe atom and the 10 electrons donated by the five CO ligands.

Comparison of two methods

| | Metho | od A | Metho | d B |
|---|--------------------------------|--------------------------|---|-------------------|
| ClMn(CO) ₅ | Mn(I) | 6 e ⁻ | Mn | 7 e ⁻ |
| | Cl^{-} | $2 e^{-}$ | Cl | 1 e ⁻ |
| | 5 CO | <u>10 e</u> ⁻ | 5 CO | $10 e^{-}$ |
| | | 18 e ⁻ | | 18 e ⁻ |
| $(\eta^5 - C_5 H_5)_2 Fe$ | Fe(II) | 6 e ⁻ | Fe | 8 e ⁻ |
| (Ferrocene) | $2 \eta^{5} - C_{5} H_{5}^{-}$ | $12 e^{-}$ | $2 \eta^{5}$ -C ₅ H ₅ | $10 e^{-}$ |
| | | 18 e ⁻ | | 18 e ⁻ |
| $[\text{Re}(\text{CO})_5(\text{PF}_3)]^+$ | Re(I) | 6 e ⁻ | Re | 7 e ⁻ |
| | 5 CO | $10 e^{-}$ | 5 CO | $10 e^{-}$ |
| | PF ₃ | $2 e^{-}$ | PF ₃ | $2 e^{-}$ |
| | + charge | * | + charge | $-1 e^{-1}$ |
| | | 18 e ⁻ | | 18 e ⁻ |
| [Ti(CO) ₆] ²⁻ | Ti(2-) | 6 e ⁻ | Ti | 4 e ⁻ |
| | 6 CO | 12 e ⁻ | 6 CO | $12 e^{-}$ |
| | 2- charge | * | 2- charge | $2 e^{-}$ |
| | | 18 e ⁻ | | 18 e ⁻ |

| | <u> </u> | ionic | | coval | covalent | |
|------|------------------|---------------------|-------|--------|----------|--|
| | l Co | $_{\rm Co}\pi$ | 7 e- | Co | 9 e- | |
| | - <u> -</u> | 2 Cp- | 12 e⁻ | _2 Cp• | 10 e- | |
| | | Total | 19 e- | Total | 19 e- | |
| | | | | | | |
| | 7 | Ti ^{IV} | Oe⁻ | Ti | 4 e- | |
| | Ti on Cl | 2 CI- | 4 e⁻ | 2 Cl• | 2 e⁻ | |
| | Ç, cı | 2 Cp- | 12 e- | 2 Cp• | 10 e- | |
| | \tilde{S} | Total | 16 e- | Total | 16 e- | |
| | | | | | | |
| Cl | PPh ₃ | ${	t Rh^{	ext{I}}}$ | 8 e- | Rh | 9 e⁻ | |
| न | n | Cŀ | 2 e⁻ | Cl• | 1 e- | |
| PhaP | PPha | 3 PPh3 | 6 e- | 3 PPh3 | 6 e- | |
| 2 | | Total | 16 e- | Total | 16 e- | |
| | | W_0 | 6 e- | w | 6 e- | |
| | | 6 CO | 12 e⁻ | 6 CO | 12 e⁻ | |
| OC 🚩 | ™ co | Total | 18 e- | Total | 18 e⁻ | |
| C | CO | | | | | |

Some examples

Q.1 Assign the oxidation number and count the valence electrons on the metal atom in (a) $[IrBr_2(CH_3)(CO)(PPh_3)_2]$ and (b) $[Cr(\eta^5-C_5H_5)(\eta^6-C_6H_6)]$ and (c) $[Mn(CO)_5]^-$.

Answer: (a) Two Br groups and the CH_3 as three singly negatively charged two-electron donors. CO and the two PPh₃ ligands as three two-electron donors, providing 12 electrons in all. Because neutral, the Group 9 Ir atom must have a charge of +3 to balance the charge of the three anionic ligands, and thus contributes 6 electrons, TVE = 18. (b) η^5 -C₅H₅ ligand is treated as C₅H₅⁻ and thus it donates six electrons, and η^6 -C₆H₆ ligand donates another six. To maintain neutrality, the Group 6 Cr atom must have a charge of 1 and contributes 5 electrons, TVE = 17. This complex does not obey the 18-electron rule and is unlikely to be stable.

(c) Each CO ligand contributes two electrons, giving 10 electrons. The charge of the complex -1 and the ligands are neutral, the charge should reside Mn atom, giving an OS -1. Thus, Group 7 Mn atom thus contributes 7+1 = 8 electrons, TVE = 18 (Mn -1 complex). 16

Q. 3 Which of the following compounds have 18 electrons: (a) the agostic Pd compound and (b) [Re(i-Pr-Cp)(CO)(PF3)Xe]?



Answer

(a) Both the η^1 -alkenyl and the bromide ligands are two-electron singly negatively charged donors, with PPh3 ligands as twoelectron neutral donors. Thus, the compound is a complex of Pd(II), which provides eight further electrons. Finally, agostic interaction is also a two electron donor. Thus, TEC = 18

(b) The iPr-Cp ligand is considered a six-electron donor with a single negative charge, the CO, PF3, and Xe ligands are each considered to be two-electron neutral donors, implying that the Re must have oxidation number +1, so providing a further six electrons. TEC = 18.

Problems for practice

Q.1 Confirm that the Cr center in $[(\eta^6-C_6H_6)Cr(CO)_3]$ obeys the 18-electron rule, but Rh in $[(CO)_2Rh(\mu - Cl)Rh(CO)_2]$ does not.

Q. 2 Confirm that the Fe centers in $H_2Fe(CO)_4$ and $[(\eta^5-C_5H_5)Fe(CO)_2]^-$ obey the 18-electron rule.

Q. 3 Show that $Fe(CO)_4(\eta^2-C_2H_4)$, $HMn(CO)_3(PPh_3)_2$ and $[\eta^5-(C_6H_5Br)Mn(CO)_3]^+$ contain 18-electron metal centres.

Q. 4 Show that $[Rh(PMe_3)_4]^+$ contains a 16-electron metal center. Comment on whether violation of the 18-electron rule is expected

Q. 5 Metal-metal bonding in multinuclear species is not always clear-cut. Solely on the basis of the 18-electron rule, suggest whether $(\eta^5-Cp)Ni$ $)(\mu-PPh_2)_2Ni(\eta^5-Cp)$ might be expected to contain a metal-metal bond

Q. 6 Show that an M-M single bond is expected in $M_2(CO)_{10}$ (M = Mn, Tc, Re) on the basis of the 18-electron rule.

Q. 7 The presence of an Fe-Fe bond in the compound $(\eta^5-Cp)(CO)Fe(\mu-CO)_2Fe(CO)(\eta^5-Cp)$ has been a controversial topic.

Solely on the basis of the 18-electron rule, show that an Fe-Fe bond is expected. What does your conclusion depend on? Are your assumptions infallible?

Q. 8 What is the electron count for and oxidation number of platinum in the anion of Zeise's salt, $[Pt(CH_2CH_2)Cl_3]$? Treat

 CH_2CH_2 as a neutral two-electron donor.

Q. 9 Show that both (a) $[Mo(\eta^6-C_7H_8)(CO)_3]$ and (b) $[Mo(\eta^7-C_7H_7)(CO)_3]$ are 18-electron species.

Q.10 Is $[Mo(CO)_7]$ likely to be stable?

| Determine the valence electron | counts for the transition metals in the following |
|---|--|
| complexes: | |
| a. $[Fe(CO)_4]^{2-}$ | c. $(\eta^3 - C_5 H_5)(\eta^5 - C_5 H_5) Fe(CO)$ |
| b. $[(\eta^5 - C_5 H_5)_2 Co]^+$ | d. $Co_2(CO)_8$ (has a single Co — Co bond) |

| Identify the first-row transition | metal for the following 18-electron species: |
|-----------------------------------|--|
| a. $[M(CO)_3(PPh_3)]^-$ | c. $(\eta^4 - C_8 H_8) M(CO)_3$ |
| b. $HM(CO)_5$ | d. $[(\eta^5 - C_5 H_5)M(CO)_3]_2$ (assume single M — M bond) |

Q. 11 Which of the following complexe is strong reducing and strong oxidizing

(a) $Fe(CO)_5$ (b) $V(CO)_6^{2-}$ (c) $Co(CO)_4^{-}$ (d) $Mn(CO)_{-}$

Q. 12 On the basis of 18e rule, find the value of n

(a) $\text{TcBr}(\text{CO})_n$ (b) $\text{Na}_2[\text{Fe}(\text{CO})_n]$ (c) $[\text{Rh}(\text{CO})_3]^n$ (d) $[\text{IrCl}_2(\text{CS})_n(\text{PPh}_3)_2\text{H}]$ (e) $[\text{Mn}(\text{CO})_n]^-$

Q. 13 On the basis of 18e rule, find the value of M and identify it if M=3d series metals

(a) $(CO)_5M = C(OCH_3)(Ph)$ (b) $[(\eta^4 - C_4H_4)(\eta^5 - C_5H_5)M]^+$ (c) $[(\eta^3 - allyl)(\eta^5 - C_5H_5)M(CO)]^-$

Q. 14 Organometallic compound $[Mo(Cp)_2(CO)_2]$ follows 18e rule; calculate the heptacity of two Cp groups?

Q. 15 On the basis of 18e rule, find the value of z

(a) $[Ni(CO)_3(NO)]^z$ (b) $[(\eta^5 - C_5H_5)Fe(CO)2(PhC_2H)]^z$ (c) $[Co(CO)_3]^z$

MO approaches of 18e rule

- \succ To accommodate more than 18e in an O_h-complex with strong-field ligands, it should be on antibonding orbital.
- Such complexes are unstable, loose electron and act as reducing agents.
- Compounds with fewer than 18e will not necessarily be unstable, but it is energetically favorable to acquire extra electrons to populate their bonding MOs fully.
- Ligands in square-planar complexes are 2e donor and to reach 16e, the metal (usually Gr 9 and 10) ions must provide 8e.



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Exceptions/limitations of the 18 electron rule

- Square planar organometallic complexes of the late transition metals (16e).
- Some organometallic complexes of the early transition metals like Cp_2TiCl_2 , WMe_6 , Me_2NbCl_3 , $CpWOCl_3$ [Reason: Some of the orbitals of these complexes are too high in energy for effective interaction or the ligands are mostly σ donors
- > Some high valent d^0 complexes have a lower electron count than 18.
- Sterically demanding bulky ligands force complexes to have less than 18 electrons.
- > The 18 electron rule fails clusters of moderate to big sizes (\geq 6-metals).
- > Not applicable to organometallic compounds of main group metals as well as to those of lanthanides and actinides.
- > Unable to explain the binding mode of coordinated ligands (terminal/bridging/semibridging)

Carbon monoxide/Carbonyl

- > CO is a very common ligand, good at stabilizing very low oxidation states, sometimes even zero OS.
- ≻ Can form weak σ -bond (L → M) and strong π -bond (back bonding) (M → L).
- > Metal-CO complex is stable only with filled metal d-orbitals, suitable for back donation to CO antibonding orbital.



Phosphines

- > Phosphine complexes (not organometallic, no M-C bond). It has similarity with CO, can act as 2e-donor
- > Lone pair of P in phosphine (basic and nucleophilic) can serve as a σ -donor.
- Empty orbitals of P in phosphine can overlap with filled d-orbitals of metal ions and behave as π -acceptors (back bonding)
- > π -acceptors behavior is attributed to the P-R σ^* orbitals.
- > Reactivity of phosphine complexes is associated with its steric (bulk) and electron donating/accepting ability
- \succ Extent of σ -donation and π -acceptance depends on the substituents.
- Electron donating substituent makes it a good σ -donor while electron withdrawing substituent makes is a good π -acceptor (π -accepting ability: PF₃ > PPh₃ > PMe₃ > P^tBu₃)



Hydrides and dihydrogen complexes

- > Bonding of a hydrogen atom (referred to as hydride ligand) to a metal atom is a σ interaction, neutral 2e donor
- > Bonding of a dihydrogen ligand involves π -back bonding
- > One could also describe a back-donation of electrons from a filled metal orbital to the σ^* orbital on the dihydrogen
- Dihydrogen complexes bonding is a 3c-2e bond
- > The H_2 molecule can form bonds side-on to the metal atom (non-classical hydrides).



Alkyl, alkenyl, alkynyl and aryl ligand

- > Alkyl groups are often found as ligands in d-metal organometallic chemistry
- > The metal ligand bonding of η^1 -hydrocarbon ligands is a σ -interaction.
- > Alkyl groups with β -hydrogen undergo β -hydrogen elimination
- > Alkenyl, alkynyl and aryl groups can bond to a metal atom in η^1 -fashion.
- > Although expected, these ligand cannot accept π -electron density into their antibonding orbitals (no evidence)
- ▶ Bridging alkyl and aryl groups also exist, and the bonding is 3c-2e bonds.
- > Alkenyl, alkynyl & aryl ligands can behave as two-electron donors if they have one negative charge



η^2 -Alkene and alkyne ligands

- ► Bonding of an alkene/alkyne to a metal atom is a σ -interaction (multiple bond \rightarrow M), with a π -back bonding interaction from the metal atom to the π^* antibonding orbital on the alkene/alkyne.
- > Extent of backdonation depends primarily on the nature of substituents on the alkene/alkyne (electron withdrawing favors)





 σ -interaction

 π -back bonding

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Non conjugated diene and polyene ligands

- Bonding of nonconjugated alkenes to a metal is analogous to isolated alkene groups.
- Due to chelating effect, polyene complexes are usually more stable
- Example: $bis(\eta^4$ -cycloocta-1,5-diene)nickel(0) is more stable than the corresponding complex containing four ethene ligands



Cyclooctadiene (cod)

Norbornadiene (nbd)

 $bis(\eta^4$ -cycloocta-1,5-diene)nickel(0)

Butadiene, cyclobutadiene and cyclooctatetraene

- Bonding of butadiene and cyclobutadiene can be explained by treating them as two alkene units (4e donor)
- Molecular orbital provides better understanding. MO diagram of cyclobutadiene and butadiene is similar.
- > In butadiene, the two occupied lower energy MOs can behave as donors to the metal, the lowest one is a σ -donor and the next one is a π-donor. The next one is LUMO, can act as a π-acceptor from the metal atom.
- \triangleright δ-bonding interaction is proposed between the d_{xy} orbital of the metal atom and the most antibonding of the butadiene MOs (no evidence)
- In cyclobutadiene, two lower energy MOs are σ and π donor. The LUMO accepts two electrons from the metal and have 6π -electrons with three occupied MOs (square).
- > Cyclooctatetraene bonds in several ways; the most common mode is as an η^4 -donor, analogous to butadiene.





MOs of the π -system in butadiene with metal d-orbitals of appropriate symmetry



MOs of π -system in cyclobutadiene with metal d-orbitals of appropriate symmetry

Allyl ligand

- Allyl ligand ($C_3H_5^-$) coordinates in an η^3 -mode, using the two occupied MOs (bonding and non-bonding) as donors and the π^* -MO as an acceptor.
- > Allyl can also be considered as C_3H_5 . η^1 -allyl binds as η^1 -alkyl group (2e donor with one negative charge).
- \triangleright Because of high reactivity, η^3 transforms to η^1 allyl complexes, facilitating them to bind another ligand.
- > The η^3 -form can be expressed as a number of resonance forms as shown (4e donor with one negative charge)



- > The allyl ligand uses three -MOs that takes part in bonding to a metal center
- Filled 1π -orbital on allyl group acts as σ -donor (to d_{z2}), 2π -orbital acts as π -donor (to d_{zx}) & empty 3π -orbital acts as a π -acceptor (from d_{yz}).
- > The interaction of metal atom with each of the terminal C-atoms is identical and gives symmetrical arrangement



Three MOs of the allyl with metal d-orbitals of appropriate symmetry

Benzene and other arenes



Cyclopentadiene and cycloheptatriene

- > The η⁵-bonding mode of a C₅H₅⁻ (most common) can be explained by both σand π-donation from the organic fragment in conjunction with δ-back bonding
- \succ C₅H₅[−] can act as a monohapto ligand (like η¹-alkyl group) and trihapto ligand (like η³-allyl group).
- ≻ Cycloheptatriene, C_7H_8 commonly forms either η^6 -complexes or η^7 complexes of the aromatic tropylium cation (C_7H_7)⁺ (hydride transfer).
- \succ η^6 -complexes is treated as three η^2 -alkene molecules bound to the metal atom





 \succ The electron donation to the metal comes from the filled 1π (σ -bonding) and 2π (π -bonding) MOs with back bonding to

the d_{xy} and d_{x2-y2} orbitals on the M-atom.

Coordinated Cp ligands behave as six-electron aromatic structure.



The molecular orbitals for the π -systems of the $\mathfrak{E}p$ with metal d orbitals of appropriate symmetry

Carbenes

- Carbene complexes possess a M=C double bond
- ➤ Carbene, CH₂ has only six electrons around its C-atom and shows two different structural arrangements.
- Linear arrangement with the two groups (4e⁻), the two remaining electrons are unpaired in two p orbitals, triplet carbene (S=1)
- ➢ Bent arrangement with the two groups, the two remaining electrons are paired and empty p orbital, singlet carbene (S=0).
- Electron pair on C-atom of singlet carbene is suitable for M-L bond formation. Empty p orbital









Alkanes and agostic hydrogen

- > Alkanes can donate the electron density from C-H σ -bond to a metal atom
- \succ It also accepts π -electron density back from the metal atom into the corresponding σ^* orbital, just like dihydrogen
- Interactions between the C-H bond of an already coordinated ligand and the metal atom are referred to as having agostic
 C-H interactions (Greek for 'to hold on to oneself'), have additional stability due to the chelate effect
- \succ Whether it be agostic or not, is known to donate two electrons to the metal.



Dinitrogen and nitrogen monoxide (none is organometallic)

Solution Bonding of N₂ to a metal atom is weak but contains both a σ -donating and a π -accepting component, have a terminal η^1 link, bonding is like CO



> NO radical (11e-) when bound, termed as nitrosyl and can form M-L bond either in a bent or in a linear fashion.

> In linear, NO is a three-electron σ -donor with strong π -acceptor ability while in bent (has LP) it behaves as one electron donor (neutral atom method)

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➤ In oxidation state method, NO behave as NO⁺ (linear) and as NO⁻ (bent), both two electron donor.

