

[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 5706

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Unique Paper Code : 2172013501

Name of the Paper : BASICS OF ORGANOMETALLIC CHEMISTRY

Name of the Course : B.Sc. (H) Chemistry (NEP)

Semester : V

Duration : 3 Hours

Maximum Marks : 90

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all.
3. Question number **1** is compulsory.
4. Each question carries equal marks.

1. Complete the following :

(a) An example of a sandwich compound is

(b) An example of Schrock carbene is

(c) Number of C-O stretching vibrations observed for C-O in IR region for $\text{Fe}_2(\text{CO})_9$ are

(d) Effective atomic number of $\text{V}(\text{CO})_6^-$ is

(e) An example of a ligand with three hapticity (η^3) is

(f) The catalyst used in the hydroformylation reaction is

(g) Give an example of nucleophilic substitution reaction in organometallic chemistry.

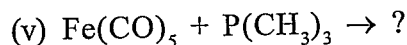
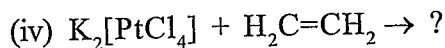
(h) Draw the structure of $\text{Mn}_2(\text{CO})_{10}$.

(i) A catalyst with a lower turnover frequency is an efficient catalyst (True/False).

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- (j) Geometry and hybridisation of $\text{Fe}(\text{CO})_5$ as per VBT is
- (k) Non bonding orbitals in MO diagram of $\text{Co}(\text{CO})_6$ are
- (l) Migratory insertion of a coordinated alkene in M-H bond leads to formation of (alkane/alkyne).
- (m) The value of x in $\text{Mn}(\text{CO})_x\text{Cl}$ is
- (n) C-C stretching frequency in $\text{H}_2\text{C}=\text{CH}_2$ is (higher/lower) than Zeise's salt.
- (o) Define metallacycles. (1×15=15)
2. (a) Based on 18 electron rule, identify the charge, x on coordination sphere for the following complexes :
- (i) $[\text{HFe}(\text{CO})_4]^x$
- (ii) $[\text{Mn}(\text{CO})_3(\text{PMe}_3)_2\text{Cl}]^x$
- (b) Giving reasons arrange the following in the order of increasing M-C bond strength
- (i) $[\text{Mn}(\text{CO})_6]^{2+}$, $[\text{Cr}(\text{CO})_6]^+$, $[\text{V}(\text{CO})_6]$
- (ii) Does the M-CO bond strength increase or decrease when L of $[\text{L}_n\text{M}-\text{CO}]$ becomes more electron withdrawing? Justify your answer.
- (c) Differentiate between metal alkene and metal alkyne compounds giving examples for each. (5×3=15)
- 3.. Provide a suitable explanation for the following statements :
- (a) Fischer carbenes are less reactive than Schrock carbenes.
- (b) For a homogeneous catalyst, the nature of ligands attached to the metal, influences its reactivity and selectivity.

- (c) $\text{Co}(\eta^5\text{-Cp})_2$ complex is much more readily oxidised than $\text{Fe}(\eta^5\text{-Cp})_2$.
- (d) Electrophilic substitution in ferrocene often occurs more readily than in benzene.
- (e) $\text{Fe}_2(\text{CO})_9$ and $\text{Mn}_2(\text{CO})_{10}$ are both dimeric carbonyls, yet their structures are not identical. (5×3=15)
4. (a) Give catalytic cycle for Monsanto acetic acid process clearly marking the type of reaction at each step.
- (b) Differentiate (giving examples) between
- (i) Hapticity and Denticity
 - (ii) Homogeneous and heterogeneous organometallic catalyst
- (c) Using VBT, deduce the structure of $\text{Mn}_2(\text{CO})_{10}$, $\text{Ni}(\text{CO})_4$. (5×3=15)
5. (a) Describe two preparative methods for metal carbonyls with the help of examples.
- (b) C-O stretching frequency for free CO is 2143 cm^{-1} while for the carbonyls $[\text{Ti}(\text{CO})_6]^{2-}$, $[\text{Cr}(\text{CO})_6]$ and $[\text{Fe}(\text{CO})_6]^{2+}$ are 1748 , 2000 and 2204 cm^{-1} respectively. Explain.
- (c) Describe Dewar-Chatt-Duncanson model of bonding in Zeise's salt. Explain its structure also. (5×3=15)
6. (a) Complete the following chemical equations :
- (i) $\text{Mn}_2(\text{CO})_{10} + \text{Na} \rightarrow ?$
 - (ii) $\text{Re}_2\text{O}_7 + \text{CO} \rightarrow ?$
 - (iii) $\text{WCl}_6 + \text{CH}_3\text{Li} \rightarrow ?$



(b) Metallocenes generally violate $18e^-$ rule and yet are stable compounds. Explain.

(c) (i) Coordinatively saturated organometallic complexes containing β hydrogen are thermally more stable towards β -elimination reactions than the unsaturated analogues. Explain

(ii) Oxidative addition to a catalyst increases its electron count. Explain giving an example. (5×3=15)

7. (a) Using MO diagram of CO, explain the synergistic bonding in M-C bond in metal carbonyls.

(b) Give one method of preparation of Ferrocene. Explain its aromatic character. Why does Ferrocene undergo acetylation reaction easily compared to benzene? Give equation and mechanism for Mannich reaction of acetylferrocene with HCHO and $(\text{CH}_3)_2\text{NH}$.

(c) What information can be drawn from cyclic voltammogram of ferrocene? (5×3=15)

8. (a) (i) Explain the role of alcohol in the synthesis of tetramminecopper(II) sulphate complex.

(ii) Why can't you obtain the crystals of the above complex by concentrating the mother liquor?

(b) Explain giving examples (i) migratory insertion of carbonyl (ii) Oxidative addition in a catalyst.

(c) Explain the mechanism of zeigler Natta polymerisation of ethene. (5×3=15)