



IV Semester M.Sc. Degree Examination, June 2015  
(NS)  
CHEMISTRY  
C-401-IC : Organometallic Chemistry

Time : 3 Hours

Max. Marks : 80

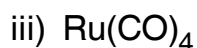
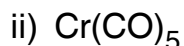
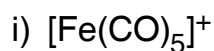
**Instruction :** Answer question 1 and **any five** of the **remaining**.

Answer **any ten** of the following :**(2×10 = 20)**

1. a) Write the IUPAC nomenclature for the following organometallic complexes :
  - i)  $(\eta^5 - \text{Cp}_2) \text{Ti} (\text{Me})\text{Cl}$
  - ii)  $(\eta^3 - \text{C}_3\text{H}_5) \text{CO} [\text{P}(\text{OMe})_3(\text{CO})_2]$
- b) Predict the number of M – M bonds in the following stable organometallic compounds and write their plausible structures.
  - i)  $(\mu - \text{CO}) - [\eta^5 - \text{CpRe}(\text{CO})_2]_2$
  - ii)  $(\mu - \text{H})_2 - [\eta^5 - \text{Cp}(\text{CO})\text{WH}_2]_2$
- c) Trimetallic complexes of phosphido bridges are well known. Assuming that the 18 e rule is followed, write the structure of  $[\text{Mn}(\mu - \text{PH}_2) (\text{CO})_4]_3$ .
- d) What is insertion reaction ? Explain with an example.
- e) Illustrate with figures, the possible modes of bonding of alkyne ligand to metals.
- f) What is Heck reaction ? Give one example each for intermolecular and intramolecular coupling reaction.
- g) Illustrate the use of Grignard reagent in organic synthesis with any two reactions.



h) Give the corresponding organic isolobal fragments of the following species :



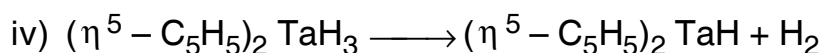
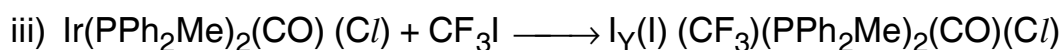
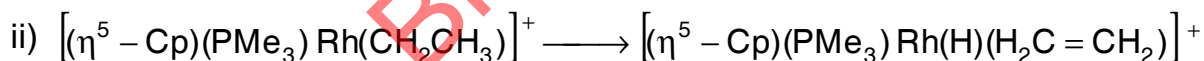
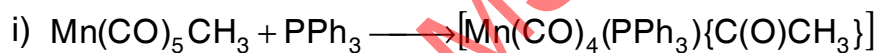
i) Between  $\eta^5\text{-Cp}_2\text{Mn}(\text{CO})_3$  and Ferrocene, which will undergo electrophilic substitution faster and why ?

j) Among  $\text{Cr}(\text{CO})_5(\text{PF}_3)$  and  $\text{Cr}(\text{CO})_5(\text{PMe}_3)$ , which one do you think will have

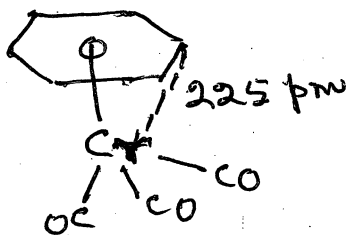
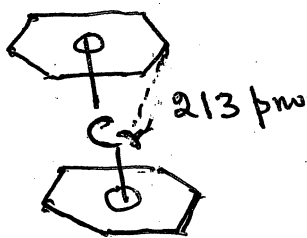
i) the stronger C – O bond and

ii) the stronger Cr – C bonds ? Justify your answer.

k) Classify the following reactions as oxidative addition, reductive - elimination, migratory insertion and  $\beta$  - elimination;



l) Based on the following data, comment on the reactivity order of the following compounds towards electrophilic substitution reaction into the  $\eta^6$  - arene ring and justify your answer.





2. a) What is 18-e rule ? Deduce the total electron count for the following organometallic complexes by both neutral and ionic modules :
- $[(\eta^5 - \text{Cp}) (\text{CO})_2 \text{Fe} (\text{PhC} \equiv \text{CH})]^+1$
  - $[(\eta^6 - \text{C}_6\text{H}_6) \text{Mn} (\text{CO})_2\text{CH}_3]$
- b) Write the structure of solid methyl lithium and explain the nature of bonding in it.
- c) Why do alkyls of beryllium exhibit predominantly covalent character ? Comment on the structure of beryllocene. **(5+4+3=12)**
3. a) Write the structure of trimethyl aluminium and indicate the bond parameters. Why is Al – C bond considered as dynamic in nature ?
- b) Why are transition metal alkyls unstable ? What strategy you would adopt for the synthesis of inert transition metal alkyls ?
- c) Give two methods for the synthesis of cyclobutadiene complexes. Discuss the bonding in them. **(4+4+4=12)**
4. a) How is ferrocene obtained ? Discuss the structure and bonding in ferrocenes.
- b) What is isolobal concept ? Why is  $\text{Os}(\text{CO})_4$  considered isolobal with  $\text{CH}_2$  radical ? Explain.
- c) The compound  $(\eta^1 - \text{allyl}) \text{Mn}(\text{CO})_5$  -on heating releases a gas and forms a new compound which obeys 18-e rule. Identify the compound and schematically draw its room temperature  $\text{H}^1 - \text{NMR}$ . Will there be any change in its  $\text{H}^1 - \text{NMR}$  spectrum when measured at high temperature ? Explain. **(5+4+3=12)**
5. a) Explain the nature of bonding in transition metal carbenes. Illustrate their reactivity with an example each.
- b) What are the factors which favour the formation of metal-metal bonds ? Using Wade's-Mingos-Leuhev rules, predict the structure of a cluster  $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{OMe})_3]_3$ .
- c) What is meant by activation of C – H bond ? Discuss the different types of cyclometallation reactions with examples. **(4+3+5=12)**



6. a) Discuss the utility of organolithium and organomercurials in organic synthesis with suitable examples.
- b) What is Gilman reagent and how it is prepared ? Give any two applications of the reagent in organic synthesis.
- c) What are DGM rules ? Illustrate the rules with suitable examples. **(5+4+3=12)**
7. a) Illustrate the uses of iron carbonyls in organic synthesis with specific reactions.
- b) Write an explanatory note on the photochemical substitutions at metal carbonyls.
- c) What is fluxional behaviour in organometallic complexes ? Discuss the fluxionality in  $[\text{CpFe}(\text{CO})_2]_2$ . **(4+4+4=12)**

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