

Register Number:

DATE:

St. Joseph's College (Autonomous), Bengaluru – 27 End Semester Examination, October 2019 III Semester M.Sc. Chemistry

CH 9218 – Organometallic Chemistry and Inorganic Reaction Mechanisms

Time: 21/2 hours

Max. Marks: 70

Note: This question paper has three pages and three sections

PART A

Answer any SIX of the following:

6 X 2 = 12

1. Give a pictorial representation of the stereochemistry of nucleophilic substitution in square planar complexes.

2. Distinguish between remote attack and adjacent attack in the inner sphere mechanism of electron transfer.

3. Explain why cyclopropene binds strongly to transition metals.

4. Depict two important mode of binding of an allyl group to transition metals.

5. Draw the structure of AI_2Me_6 specifying the bond angles and bond lengths.

6. Give two reactions for the synthesis of organoberyllium compounds.

7. Arrive at the total valence electron count of $W(CO)_6$. [Hint: outer electronic configuration of W is: $5d^4 6s^2$]

8. Give any two methods of synthesis of organoselenium compounds.

PART B

Answer any FOUR of the following:

9. a) Why is the excited state [Ru(bpy)₃]²⁺ a better oxidizing and reducing agent than the ground state complex? Draw a catalytic cycle involving [Ru(bpy)₃]²⁺ and a reductive quenching agent, methyl viologen for the photocatalytic reduction of water.

 $4 \times 12 = 48$

b) Discuss the various mechanisms of oxidative addition. (6+6)

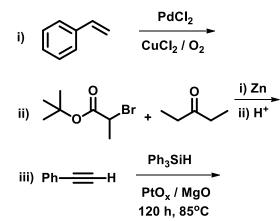
- 10. a) Give the mechanisms of the following reactions:
 - (i) Acid hydrolysis of $[Cr(H_2O)_5F]^{2+}$
 - (ii) Base hydrolysis of [Co(NH₃)₅Cl]²⁺

b) Explain the salient features of two extreme modes of binding of ethene to transition metals. (6+6)

11.a) List out the important characteristics of Fischer carbenes. Explain these characteristics based on the bonding in these compounds.

b) Discuss the various dissociation pathways in transition metal alkyls. What are the conditions under which each of these pathways is promoted? (6+6)

12. a) Identify the major organic product in the following organic reactions:



- b) Outline the catalytic cycle of Monsanto acetic acid process. (6+6)
- 13. a) Discuss the structure of Grignard Reagents by Schlenk equilibrium. Give any two evidences in favor of this interpretation.

b) Distinguish between thermodynamic and kinetic stability of organometallic compounds taking decomposition of $Pb(CH_3)_4$ as an example. (6+6)

14. a) How does the nature of the metal and ligand affect 18-electron rule in organometallic complexes?

b) Outline the catalytic cycle of hydrogenation by Wilkinson's catalyst? Suggest two catalysts for asymmetric hydrogenation of organic compounds with respective reactions. (6+6)

PART C

Answer any TWO of the following:

2 X 5 = 10

15. Show the steps of the electron-transfer mechanism that accounts for the following reaction. Note that one of the reactant metal ion is labeled making its identification in the products possible.

 $[*Co(NH_3)_5 - NCS]^{2+} + 5 CN^{-} + Co^{2+}(aq) \rightarrow [Co(CN)_5 - SCN]^{3-} + 5 NH_3 + *Co^{2+}(aq).$ (5)

- 16.a) With proper explanation find the organic fragment that is isolobal with [Fe(CO)₂(PPh₃)]⁻
 b) Comment on the IR and mass spectra of CH₃Li. (3+2)
- 17. Can we synthesize a co-polymer of isotactic ethylene and propylene with alternating units? Suggest a method using your knowledge of catalytic polymerization. (5)

-----End of questions-----