



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: 2½ 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

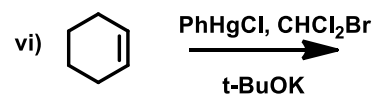
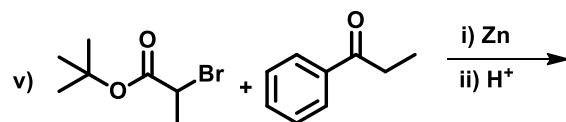
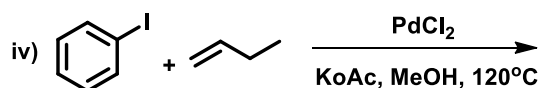
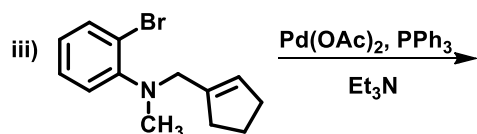
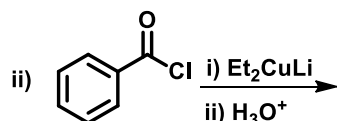
1. Ni(II) is more labile than Pt(II) even though both are d^8 metal ions. Why?
2. What is meant by 'C-H activation'?
3. Give the orbital overlap picture of Schrock carbenes.
4. Draw the electronic arrangement in the d- orbitals of cobaltocene.
5. i) What is the hybridization of Al in Al_2Me_6 ?
ii) The catalyst used in Wacker process is
6. Give a method for the synthesis of organolithium compounds.
7. What are π -bonded organometallic compounds? Give an example with structure.
8. Give any two uses of organosilicon compounds.

PART B

Answer any FOUR of the following:

4 X 12 = 48

9. Identify the major organic product in the following organic reactions:



10. a) Discuss the theories of *trans* effect.

(b) What are the criteria for molecular fragments to be isolobal? Using suitable MO diagrams explain why CH₂ is isolobal with Fe(CO)₄. (6+6)

11. a) Give the mechanism of the base hydrolysis of [Co(NH₃)₅Cl]²⁺. Explain its rate law. Give an evidence for this mechanism.

b) Give the mechanism of the inner sphere electron transfer reaction between [Co(NH₃)₅Cl]²⁺ and [Cr(H₂O)₆]²⁺. Give an evidence for this mechanism. (6+6)

12. a) Explain the bonding in transition metal- alkene complexes with the help of an orbital overlap diagram. Explain the phenomenon of *umpolung* in these complexes.

(b) Discuss ring slippage in cyclopentadienyl complexes with a suitable example.

(c) Explain the changes that happen to cyclobutadiene once it binds to a transition metal. (6+3+3)

- 13.a) Discuss the structure of Grignard Reagents by Schlenk equilibrium. Give any two evidences in favor of this interpretation.
 b) How does the nature of the metal and ligand affect 18-electron rule in organometallic complexes? (6+6)
- 14.a) What do you mean by kinetic and thermodynamic stability of organometallic compounds. Discuss homolytic dissociation and β -elimination in organometallic complexes.
 b) Outline the catalytic cycle of hydroformylation process. (6+6)

PART C

Answer any TWO of the following:

2 X 5 = 10

- 15.a) For $[\text{PtX}_4]^{2-}$ complexes both ligand exchange rate and thermodynamic stability increase in the order $\text{X} = \text{Cl} < \text{Br} < \text{I} < \text{CN}$. Explain why these observations are not inconsistent.
 (b) With proper reasoning arrange the following in the decreasing order of ligand exchange rates: $[\text{SiF}_6]^{2-}$, $[\text{PF}_6]^-$, $[\text{AlF}_6]^{3-}$. (3+2)
- 16.a) Why is the existence of a series of entering groups with different rate constants evidence for an associative mechanism (A or I_a)?
 b) Suggest two methods to prevent oligomerization of CH_3Li . (2+3)
17. A heap of plastic bags (LDPE) at Bellandur was burnt at $t^\circ\text{C}$. The resulting gaseous product was subjected to a reaction with $\text{TiCl}_4/\text{Et}_3\text{Al}$ at a moderate temperature. The resulting product was now stronger and did not get affected at $t^\circ\text{C}$. Explain the chemical transformations involved with mechanism. (5)

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