Register Number:

Date & Session:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU -27

M.Sc. ANALYTICAL CHEMISTRY – III SEMESTER

SEMESTER EXAMINATION: OCTOBER 2022

(Examination conducted in December 2022)

CH 9222: ORGANOMETALLIC CHEMISTRY AND INORGANIC REACTION MECHANISMS

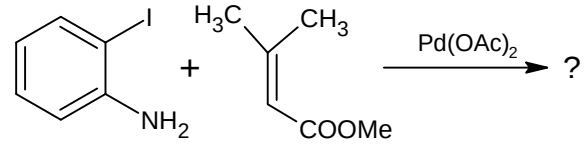
Time: 2 ½ Hours **Max Marks: 70**

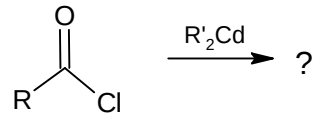
This paper contains 3 printed pages and 3 parts

PART-A

Answer any SIX of the following **(6 X 2 = 12 Marks)**

1. Give any two chemical reactions of ferrocene.
2. Name the four types of mechanisms in racemization and isomerization.
3. Give an example of template reaction. Comment on the driving force behind this reaction.
4. Write the products of the following reactions.

i) 

ii) 

5. Mention any two ways in which the reactivity of an arene is altered by complexation with $Cr(CO)_3$.
6. Carry out the valence electron counting and check whether ferrocene $Fe(C_5H_5)_2$ obeys eighteen electron rule. (Atomic number of iron = 26)
7. Give the structure of (a) Bis(η^6-benzene)chromium(0)
   (b) Tricarbonyl(η^4-cyclobutadiene)iron(0)
8. How does the reactivity of organometallic compounds of the group I metals vary down the group? Give reason.

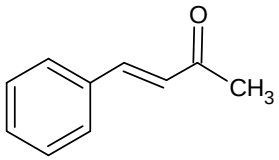
PART-B

Answer any FOUR of the following **(4 X 12 = 48 Marks)**

9. Discuss the kinetics and mechanism of nucleophilic substitution reactions in square-planar transition metal complexes. Give any two evidences in support of the mechanism.
10. a) Explain the structure and bonding in cyclopentadienyl(η^5)-ligand complexes of transition metals.

b) Give the classification of transition metal carbenes. Explain the bonding in each class. (6+6)

11. a) Explain the inner sphere mechanism of electron transfer in complexes using suitable examples.
    b) Discuss with an example each (i) cyclometallation and (ii) ring slippage reactions. (6+6)
12. a) Write the major product/s obtained when the following substrate reacts with (i) C_6H_5MgBr (ii) C_6H_5Li, followed by hydrolysis in the presence of an acid.
    b) Outline the steps in the catalytic cycle of hydroformylation reaction. (8+4)



13. a) Explain Green's rules with suitable examples.
    b) Outline any three general methods of preparation of main group organometallic compounds with suitable examples. (6+6)
14. a) Define hapticity. Sketch the structure of $[Pt(C_2H_4)Cl_3]^-$ and give the hapticity of the ligands.
    b) Discuss the structure of dimethylberyllium in gas and solid phases.
    c) Discuss the structure and bonding in $(CH_3)_3Al$. (3+3+6)

PART-C

Answer any TWO of the following (2 X 5 = 10 Marks)

15. Match the following isolobal fragments based on frontier orbitals.

Organic isolobal fragment	Inorganic isolobal fragment
i) C	(a) ML_5
ii) CH	(b) ML_3
iii) CH_2	(c) ML_6
iv) CH_3	(d) ML_2
v) CH_4	(e) ML_4

16. Predict the products **A, B, C, D** and **E** in the following reactions:

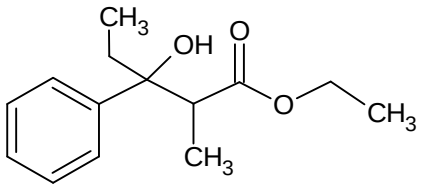
$[PtCl_3(NO_2)]^{2-} + NH_3 \longrightarrow$ **A**

$[PtCl_4]^{2-} + NH_3 \longrightarrow$ **B** $+ NH_3 \longrightarrow$ **C**

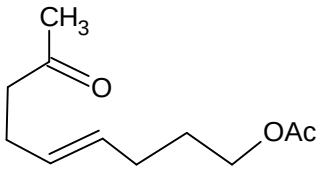
$[PtCl(NH_3)_3]^{+} + NO_2^- \longrightarrow$ **D** $+ NO_2^- \longrightarrow$ **E**

(Hints: The trans effects are in the order $NO_2^- > Cl^- > NH_3$. Cl^- is the best leaving group among the three)

17. a) What are the reactants and reagents required for the synthesis of the following compound by Reformatsky reaction?



b) Write the reaction to obtain the following compound by Wacker process. (3+2)



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