Register Number:
Date:

St. Joseph's College (Autonomous), Bangalore-27
M.Sc. Chemistry - IV Semester
End Semester Examination: April 2022
(Examination conducted in July 2022)
CH 0216 – Organometallic Chemistry and Inorganic Reaction Mechanisms

Time- 2 hrs. 30 min. Max Marks-70

This paper contains ***three*** printed pages and ***three*** parts

PART – A

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

1. $[Cr(H_2O)_6]^{2+}$ is labile but $[Cr(H_2O)_6]^{3+}$ is inert. Explain.
2. What is 18-electron rule? Give any one of its limitations.
3. Write the structures of the following:
   (i) (Butane-1,4-diyl)bis(triphenylphosphane)platinum
   (ii) 1,1-Diacetylosmocene
4. Give two applications of zinc dialkyls.
5. Write the Marcus equation for a cross reaction and explain the terms therein.
6. $Be(t\text{-}Bu)_2$ undergoes decomposition at 100 ^oC, whereas $Be(Me)_2$ decomposes above 200 ^oC. Why?
7. What is fluxional structure? Explain with an example of a metallocene.
8. Me_3B is inert towards hydrolysis, whereas Me_3Al undergoes hydrolysis readily. Give reason.

PART - B

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

9. (a) What are outer sphere electron transfer reactions? Give an example. Write and explain the steps of outer sphere mechanism of electron transfer in complexes.

   (b) Illustrate S_N1CB mechanism in octahedral complexes using a suitable example. Write and explain the rate law of this reaction. (6+6)

10. (a) Based on d-orbital splitting in metallocenes explain the following:

(i) Ferrocene is the most stable among all the metallocenes of first row transition metals.

(ii) Cobaltocene is paramagnetic and more reactive than ferrocene.

(b) Interpret the rate law and enumerate the evidences in favour of associative mechanism for the nucleophilic substitution in square planar complexes. (6+6)

11. (a) Give a general equation for the β-elimination in transition metal alkyls. Citing suitable examples explain under which all conditions β-elimination does not occur in these complexes.

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

12. (a) Outline the catalytic cycle of hydroformylation of an alkene.

(b) Give any two applications of the following in organic synthesis (chemical reactions needed):

i) organoselenium compounds ii) trialkylsilyl derivatives iii) organomercury compounds (6+6)

13. a) Discuss the structure and bonding in CH_3Li solid.

b) Give the systematic nomenclature of

i) $H_3C\text{-}Zn\text{-}C_2H_5$ ii) $(C_2H_5)_3As$ iii) $H_5C_6\text{-}Hg\text{-}C_6H_5$.

c) Discuss the structure in $(CH_3)_3Al$. (6+3+3)

14. a) Discuss the structure of Grignard reagents by Schlenk equilibrium. Give any two evidences in favor of this interpretation.

b) Despite being thermodynamically unstable, $Pb(CH_3)_4$ can be isolated. Comment on the thermodynamic and kinetic stabilities of $Pb(CH_3)_4$.

c) Arrive at the total valence electron count of $(PPh_3)_3RhCl$ using ionic or covalent model of electron counting. (Hint: Rh: $[Kr]4d^85s^1$). (6+3+3)

PART - C

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

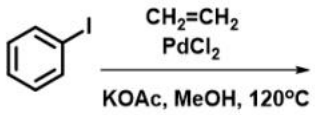
15. a) Predict the products **A, B, C** and **D** in the following reactions:

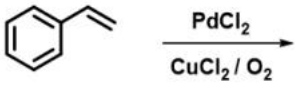
$[PtCl_3NH_3]^-$ + NO_2^- ------> **A** + NO_2^- ------> **B**

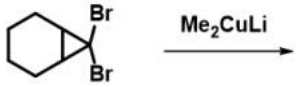
$[PtCl(NH_3)_3]^+$ + NO_2^- ------> **C** + NO_2^- ------> **D**

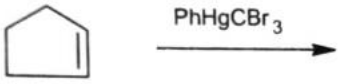
(Hints: The trans effects are in the order NO_2^- > Cl^- > NH_3. Cl^- is the best leaving group among the three).

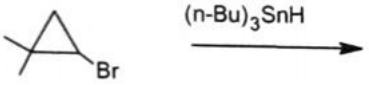
15. Predict the products of the following reactions:

i) 

ii) 

iii) 

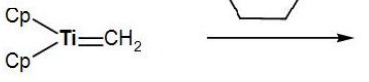
iv) 

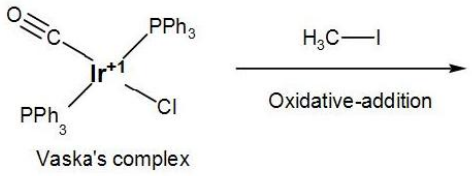
v) 

17. (a) Match the following isolobal fragments based on frontier orbitals:

S.No.	Organic isolobal fragment	Inorganic isolobal fragment
i	CH	(a) MnL_5
ii	CH_2	(b) CoL_3
iii	CH_3	(c) FeL_4

(b) Predict the products of the following reactions:

(i) 

(ii) 

Vaska's complex

(3+2)

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