

PG - 605

## IV Semester M.Sc. Examination, June 2017 (Repeaters) (NS 2010 - 11 Scheme) **CHEMISTRY**

C-401-IC: Organometallic Chemistry

Time: 3 Hours Max. Marks: 80

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

1. Answer any ten of the following:

 $(10 \times 2 = 20)$ 

- a) What does the term 'metal' signify in organometallic compounds?
- b) Complete the following reactions

i) 
$$(C_6H_5)_3CH + LiC_2H_5 \rightarrow ?+?$$

ii) 
$$3LiR + AICI_3 \xrightarrow{heptane} \rightarrow ?+?$$
.

- c) What are ring slippage reactions? Give an example.
- d) Write the organic fragments which are isolabal with the following:

i) 
$$C_nC_o$$
 (CO)

- e) Predict the haptocity of the two C<sub>p</sub> rings in [Cp<sub>2</sub> W(CO)<sub>2</sub>] assuming 18-electron configuration.
- f) Ensure the following conversion using IR spectroscopic technique.

$$\label{eq:ch2} \text{CH}_2 = \text{CH} - \text{CH}_2 - \text{Mn (CO)}_5 \, \rightarrow (\, \eta^{\, 3} - \text{C}_3\text{H}_5) \, \, \text{Mn (CO)}_4 + \text{CO}.$$

- g) Hydroformylation of 1-pentene is catalysed by CO2(CO)8. It is observed that, an increase in the partial pressure of CO, above a certain threshold decreases the rate of the reaction. Account for this observation.
- h) Predict the product in the following reaction

i) Complete the reaction  $Zn Me_2 \xrightarrow{LiAlH} ?$ 



-2-



- j) Benzene resists nucleophilic substitution where as dibenzene chromium does not. Give reason.
- k) What is a reductive-elimination reaction? Give an example.
- I) Complete the following reaction

- 2. a)  $[M(\eta^3 C_3H_5)(CO)_5]$  is a stable, first row transition metal complex. Predict 'M' in it.
  - b) Predict the products

i) 
$$2EtI + 2Hg/Na \xrightarrow{EtOAc} ? + ?$$

ii) 
$$2 \text{Li} + \text{MgR}_2 \rightarrow ? + ?$$

iii) 
$$Me_3$$
 sicl + LiSH  $\rightarrow$  ? + ?

- c) Electrophilic attack on transition metal olefins is relatively uncommon. Give reasons. (3+6+3=12)
- 3. a) How  $^1$ H-NMR helps in distinguishing ( $\eta$   $^1$   $C_3H_5$ ) Mn (CO) $_5$  from ( $\eta$   $^3$   $C_3H_5$ ) Mn (CO) $_4$ .
  - b) Explain the structure and bonding in

c) Complete the following reactions and comment on the products formed

ii) 
$$\xrightarrow{\text{CH}_{S}\text{COCl}}$$
 ?  $\xrightarrow{\text{CH}_{S}\text{COCl}}$  ?  $\xrightarrow{\text{AICl}_{S}}$  ?  $\xrightarrow{\text{CH}_{S}\text{COCl}}$  ?



- 4. a) Explain the structure and bonding in transition metal cyclooctatetraene complex.
  - b) Derive the isolobal organic hydrocarbon fragment for the following molecules.

- c) What are Wade-Mingos-Lauher rules and how are they useful in predicting the structures of carbonyl clusters? (4+3+5=12)
- 5. a) Discuss fluxionality in dienyl complexes.
  - b) Discuss the activation of CF by transition metal organometallics.
  - c) Complete the following reactions

i) 
$$\xrightarrow{Pd, base}$$
?

ii)  $\xrightarrow{Pd, base}$ ?

$$\xrightarrow{Pd, base}$$
?

$$(4+4+4=12)$$



- 6. a) Explain the synthesis of aromatic compounds using chromium carbonyls citing specific examples.
  - b) Write briefly on the utility of BuLi in the synthesis of organic compounds.
  - c) Predict the products

i) 
$$\frac{\text{Hg}(\text{OAC})_{2}}{\text{H}_{2}\text{O}, \text{ THF}} ?$$

$$25^{\circ}\text{C}$$
ii) 
$$\frac{\text{Hg}(\text{OAC})_{2}}{\text{H}_{2}\text{O}, \text{ THF}}} ?$$

$$\frac{\text{Hg}(\text{OAC})_{2}}{\text{2) NaBH}_{4}/\text{OH}^{-}} ?$$

$$(4+4+4=12)$$

- 7. a) Write a note on photochemical cleavage of Metal-Hydrogen bonds in organotransition metal complexes.
  - b) Compare the nucleophilic and electrophilic attack on coordinated ligands with that of uncoordinated ligands.
  - c) What are insertion and de-insertion reactions? Give any two examples each.

(4+4+4=12)