



THE OPEN UNIVERSITY OF SRI LANKA

B.Sc./B.Ed DEGREE IN SCIENCE-LEVEL 5

FINAL EXAMINATION-2015/2016

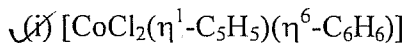
CMU3122/CHU3127 ORGANOMETALLIC CHEMISTRY

Date: 11th July 2016 (Monday)

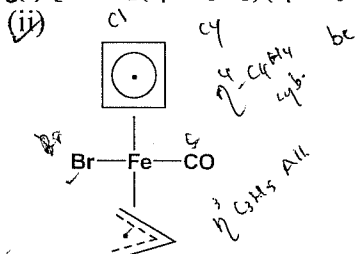
Time 1.00 – 3.00 p.m.

Answer any **FOUR** (04) questions. If more than four questions are answered, **only the first four answers will be marked.**

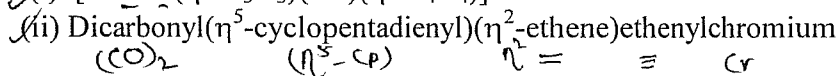
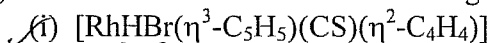
1. (a) Give the IUPAC name for each of the following complexes.



(20 marks)



(b) Draw the structures of the following complexes.



(20 marks)

(c) Determine the valence electron count (VEC) of the complex



(Indicate in your workout, the electron contribution made

by each ligand, Fe is a Group 8 metal).

(15 marks)

(d) What are the **active catalysts** used in

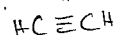
(i) Hydrocyanation, and (ii) Union Carbide process

(12 marks)

(e) (i) Arrange PH_3 , PF_3 , NMe_2H and NMe_3 in the **increasing order of σ -donor ability**.

(ii) Give one **cationic ligand** which is isoelectronic with the ethynyl group as in sodium acetylide.

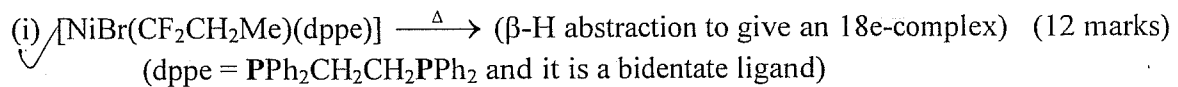
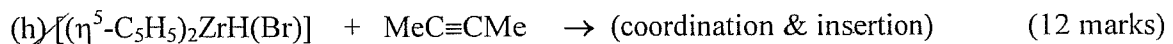
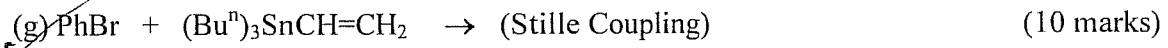
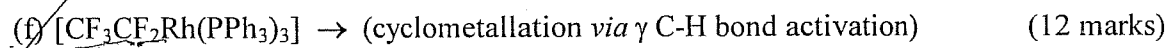
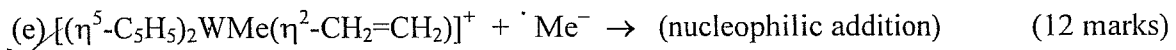
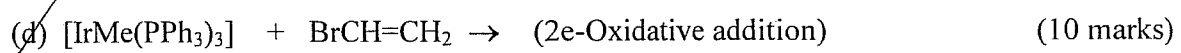
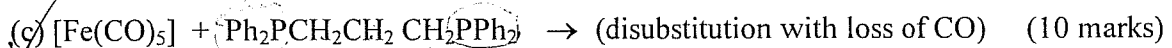
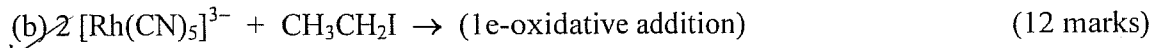
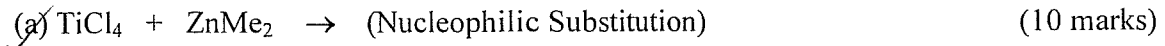
(15 marks)



(f) Using an **orbital diagram**, explain the bonding between the metal and ligand in $[\text{CuPPh}_3]^+$.

(18 marks)

4. Predict the major product(s) of each of the following reactions, using the hint given in the brackets.



5. (a) Iodobenzene oxidatively adds to $[\text{RhEt}(\text{PPh}_3)_3]$ to give the 18e-complex (J). (J) reductively eliminates an aromatic hydrocarbon (K) while forming an 16e-complex (L). With MeLi, (L) gives the alkyl-complex (M). Coordination of $\text{CH}_2=\text{CH}_2$ to (M) gives the 18e alkene-complex (N). (N) undergoes 1,2-insertion reaction to give the alkyl-complex (O). In the presence of CO, (O) undergoes 1,1-insertion reaction to give the 16e-complex (P). Identify (J), (K), (L), (M), (N), (O) and (P). (42 marks)

(b) (i) What is meant by hydroformylation of olefins?

(ii) Write the molecular formulae of the two products formed due to hydroformylation of $\text{MeCH}=\text{CHEt}$. (20 marks)

(c) How would you account for the variation in the $\text{N}\equiv\text{N}$ stretching frequency of the following compounds?

Compound	$\nu(\text{N}\equiv\text{N})$ in cm^{-1}
free N_2	2330
$[\text{Ni}(\text{N}_2)]$	2088
$[\text{Ni}(\text{N}_2)_2]$	2187

(20 marks)



(d) Suggest **reagent(s)** or **active catalyst(s)** which can be used to carry out the following conversions.

- (i) $\text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CO}_2\text{H}$
- (ii) $[\text{Fe}(\text{CO})_5] \xrightarrow{\text{H}^+} [\text{HFe}(\text{CO})_5]^+$
- (iii) $\text{cis-}[\text{PtCl}_2(\text{PMe}_3)_2] \rightarrow \text{cis-}[\text{PtClMe}(\text{PMe}_3)_2]$
- (iv) $[(\eta^5\text{-Cp})\text{W}(\text{PPh}_3)_3] \rightarrow [(\eta^5\text{-Cp})\text{W}(\eta^2\text{-H}_2)(\text{PPh}_3)_3]\text{BF}_4$ (20 marks)

6. (a) $[\text{RhCl}(\text{PPh}_3)_3]$ catalyses the hydrogenation of ethene *via* the **hydride mechanism**. Draw the catalytic cycle for this process and identify the catalytic intermediates formed. (45 marks)

(b) Draw the **structure** of the polymer (X) formed due to the ring opening metathesis polymerization of norbornadiene.



(10 marks)

- (c) (i) Identify the two olefins formed due to the **ring closed metathesis** of 1,6-heptadiene (C_7H_{12}).
- (ii) 1,6-heptadiene undergoes an oxidative coupling reaction with $[(\eta^5\text{-Cp})_2\text{Zr}(\text{CO})_2]$ to give a 16e-complex (Y) with a fused 5-membered metallacycle. Draw the structure of (Y). (25 marks)

- (d) (i) What is meant by "Heck reaction"?
- (ii) The following molecule undergoes an intramolecular Heck reaction to give an indole derivative (Z). Draw the structure of (Z). (20 marks)

