



THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION-2017/2018

ORGANOMETALLIC CHEMISTRY CYU5300
ORGANOMETALLIC CHEMISTRY CMU3122

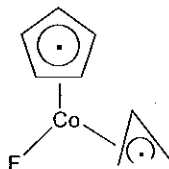
26th September 2018

Time 1.30 – 3.30 p.m.

Answer **only FOUR (04)** questions.

Questions 1, 2, 3 and 4 are **COMPULSORY** for students registered for CYU5300. Questions 5 and 6 are **ONLY** for students registered for CMU3122.

1. (a) Give the IUPAC name of the following complexes. (20 marks)
- (i) $[\text{CrCl}(\eta^3\text{-C}_5\text{H}_5)(\eta^2\text{-C}_2\text{H}_4)(\text{NO})]$
- (ii)



- (b) Draw the structures of the following complexes. (20 marks)
- (i) $[\text{FeCl}(\eta^1\text{-C}_3\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)(\eta^2\text{-C}_4\text{H}_6)]$
- (ii) dicarbonyl(η^5 -cyclopentadienyl)ethenyl(η^2 -ethyne)molybdenum
- (c) Determine the valence electron count (VEC) of the complex $[\text{Fe}(\text{CN})(\text{CO})(\eta^3\text{-C}_5\text{H}_5)(\eta^4\text{-C}_4\text{H}_4)]$, using the **covalent model**. (Indicate in your work out, the electron contribution made by each ligand). (14 marks)
- (d) What is the **active catalyst** used in
 (i) Union Carbide process and (ii) Wacker Process (16 marks)
- (e) Using an orbital diagram explain the bonding between a metal (M) and a ligand in $[\text{Pt}(\text{PPh}_3)_4]$ (20 marks)
- (f) Arrange NO^+ , N_2 , C_2H_4 and CO in the increasing order of π -acceptability. (10 marks)

2. (a) How would you account for the variation in the CO stretching frequency in the following compounds ?

Compound	$\nu(\text{CO})$ in cm^{-1}	
free CO	2143	
$[\text{Cr}(\text{CO})_6]$	2000	
$[\text{V}(\text{CO})_6]^-$	1860	(20 marks)

- (b) In the presence of CO, *cis*- $[\text{MeMn}(\text{CO})_4(^{13}\text{CO})]$ (A) undergoes migratory insertion reaction to give an octahedral complex (B). Draw the structures of the isomers of (B). (20 marks)

- (c) Give a **binary metal carbonyl** which is isoelectronic with $[\text{FeH}_2(\text{CO})_4]$. (10 marks)

- (d) MeBr oxidatively adds to $[\text{RhBr}_2(\text{CO})_2]^-$ to give (C). In the presence of CO, (C) gives the 18e acetyl complex (D). (D) reductively eliminates (E) to regenerate $[\text{RhBr}_2(\text{CO})_2]^-$. Identify (C), (D) and (E). (30 marks)

- (e) (i) Aniline PhNH_2 reacts with acetyl chloride to give the amide (F). Draw the structure or write the molecular formula of (F).
 (ii) (F) undergoes **orthometallation** with $[\text{PdCl}_2(\text{NCPH})_2]$ to give the chloride-bridged Pd(II) dimer (G) with an **6-membered chelate ring**. Draw the **structure** of (G). (20 marks)

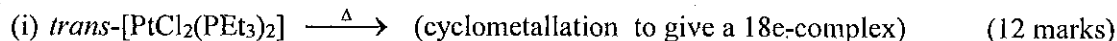
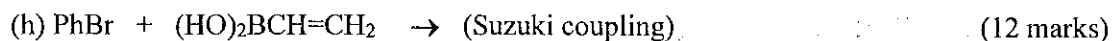
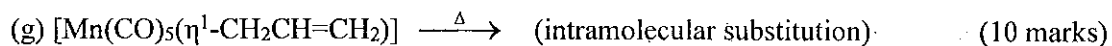
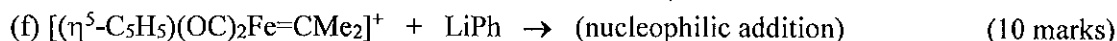
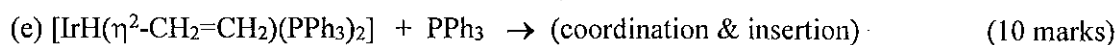
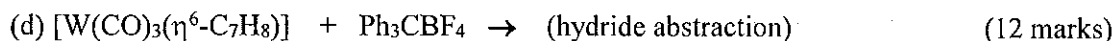
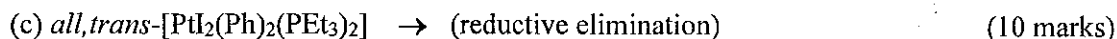
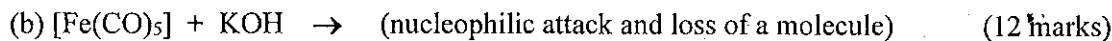
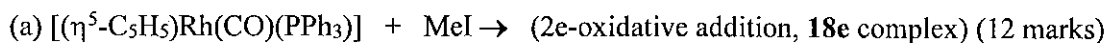
3. (a) (i) Determine the **coordination geometry** of the Co-NO fragment in the 18e-complex $[\text{Co}(\text{NO})(\text{CO})_3]$ (H). Co is a Group 9 metal.
 (ii) Draw the **orbital diagram** showing the π -overlap of orbitals of CO and the metal in (H). (20 marks)

- (b) (i) What is an agostic interaction?
 (ii) Assume that *trans*- $[\text{IrCl}(\text{CO})_2(\text{PMe}_3)]$ shows square-pyramidal arrangement with one agostic type interaction *via* the apical position. Draw the **structure** of this complex and **identify** the type of agostic interaction associated with it? (20 marks)

- (c) The catalyst $[\text{IrBr}(\text{PPh}_3)_3]$ oxidatively adds dihydrogen to give the octahedral Ir(III) complex (K). Substitution of PPh_3 of (K) by $\text{CH}_2=\text{CH}_2$ gives the 18e olefin-complex (L). In the presence of PPh_3 , (L) undergoes migratory insertion to give the 18e alkyl-complex (M). (M) reductively eliminates an alkane (N) to regenerate the catalyst $[\text{IrBr}(\text{PPh}_3)_3]$. Write the molecular formulae of (K), (L), (M) and (N). (40 marks)

- (d) (i) What is meant by hydroformylation of olefins?
 (ii) What are the compounds formed due to hydroformylation of $\text{PhCH}=\text{CF}_2$? (20 marks)

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

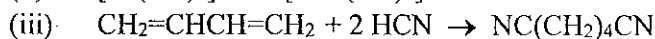
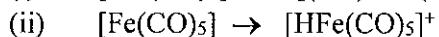
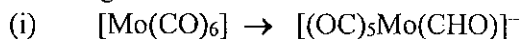


Questions 5 and 6 are ONLY for Students registered for CMU3122

5. (a) Describe the bonding between Pt and $\text{CH}_2=\text{CH}_2$ in $[\text{Pt}(\eta^2\text{-CH}_2\text{=CH}_2)_3]$. (20 marks)

(b) *trans*- $[\text{NiBr}_2(\text{PPh}_3)_2]$ reacts with AlMe_3 to give 16e Ni(II) complex (P). (P) reacts with LiMe to give another 16e Ni(II) complex (Q). (Q) undergoes a substitution reaction with dppe to give the 16e Ni(II) complex (R). In the presence of PPh_3 , (R) reductively eliminates an alkane (S) to generate the 16e Ni(0) complex (T). Identify (P), (Q), (R), (S) and (T). (dppe = $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ and it is a bidentate ligand) (50 marks)

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



(d) $[\text{CoH}(\text{CO})_4]$ is a stronger acid than $[\text{CoH}(\text{CO})_3(\text{PMe}_3)]$. Explain. (10 marks)

6. (a) Write the reaction mechanism for the conversion of the 18e-complex $[(\eta^5\text{-Cp})\text{FeH}(\text{CO})_2]$ to **acyl complex** $[(\eta^5\text{-Cp})(\text{OC})_2\text{FeC}(=\text{O})\text{Et}]$. Identify the steps involved in this process. (35 marks)
- (b) $\text{ArX} + \text{RMgX} \rightarrow \text{Ar-R} + \text{MgX}_2$ is catalyzed by the active catalyst $[\text{Ni}(\text{PPh}_3)_2]$. Draw the catalytic cycle for this reaction. Identify the steps involved in this process. (35 marks)
- (c) $[(\eta^5\text{-Cp})\text{Rh}(\text{PMe}_3)_2]$ undergoes oxidative addition reactions more readily than $[(\eta^5\text{-Cp})\text{Rh}(\text{CO})_2]$. Explain. (15 marks)
- (d) The following molecule (**Y**) undergoes an intramolecular Heck reaction to give the derivative (**Z**). Draw the structure of (**Z**). (15 marks)

