



THE OPEN UNIVERSITY OF SRI LANKA
 B.Sc./B.Ed DEGREE IN SCIENCE-LEVEL 5
 FINAL EXAMINATION-2014/2015

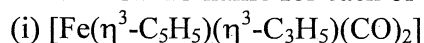
CMU3122/CHU3127 ORGANOMETALLIC CHEMISTRY

Date: 12th May 2015 (Tuesday)

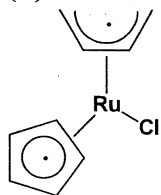
Time 1.00 – 3.00 p.m.

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.

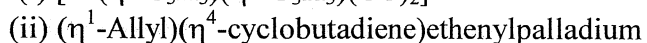
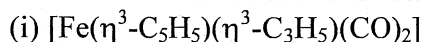


(ii)



(20 marks)

(b) Draw the **structures** of the following complexes.



(20 marks)

(c) Determine the valence electron count (VEC) of the complex $[\text{CoCl}(\eta^1\text{-C}_3\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)(\eta^2\text{-C}_2\text{H}_4)]$ using the **ionic model**.

(Indicate in your workout, the electron contribution made by each ligand, Co is a Group 9 metal).

(15 marks)

(d) What is the **active catalyst** used in

(i) Monsanto process and (ii) Shell process

(12 marks)

(e) (i) Arrange CN^- , NH_3 , CS and CO in the increasing order of π -acceptability.

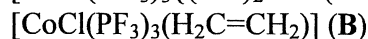
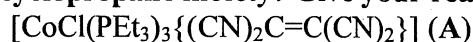
(ii) Give one **anion** which is isoelectronic with PH_3 .

(15 marks)

(f) Using an orbital diagram, explain the bonding between a metal (M) and an alkynyl ($\text{-C}\equiv\text{CR}$) ligand.

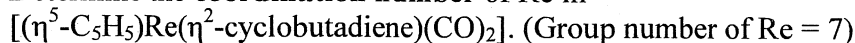
(18 marks)

2. (a) Which one of the following compounds is **more likely** to have a **metallacyclopropane** moiety? **Give your reasons.**



(20 marks)

- (b) (i) Determine the **coordination number** of Re in



- (ii) Determine the **coordination geometry** of the Fe-NO fragment in the 18e-complex $[\text{FeCl}(\text{NO})(\text{PF}_3)_4]$.

(20 marks)

- (c) How would you account for the variation in the CO stretching frequencies in the following compounds?

Compound	$\nu(\text{CO})$ in cm^{-1}	
free CO	2143	
$[\text{Pd}(\text{CO})(\text{PF}_3)_3]$	2100	
$[\text{Pd}(\text{CO})(\text{PMe}_3)_3]$	2050	(20 marks)

- (d) **Draw and identify** the structures of all **geometrical** isomers of $[\text{FeI}_2(\text{CO})_2(\text{dppe})]$.
dppe = $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ and it is a bidentate ligand.

Comment on **optical isomerism** of above isomers.

(20 marks)

- (e) Give **four** main differences between Fischer-carbenes and Schrock-carbenes. (20 marks)

3. (a) Briefly discuss the **geometry** and the **nature of bonding** in the anion of the Ziese's salt $[\text{PtCl}_3(\eta^2\text{-CH}_2=\text{CH}_2)]^-$.

(20 marks)

- (b) (i) What is an agostic interaction?

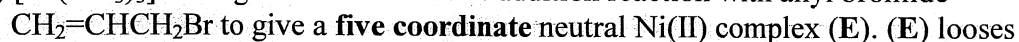
- (ii) Assume that *cis*- $[\text{CoI}(\text{CO})_2(\text{PPh}_3)]$ (C) shows **square-pyramidal** arrangement with one agostic type interaction in the **apical position**. Draw the **structure** of (C) and identify the type of agostic interaction associated with it?

- (iii) (C) undergoes cyclometallation to give a Co(III) hydride (D).

Draw the **structure** of (D).

(32 marks)

- (c) $[\text{Ni}(\text{PEt}_3)_3]$ undergoes an 2e-oxidative addition reaction with allyl bromide



one neutral ligand to give a Ni(II) complex with two geometrical isomers (F) and (G).

Removal of **another** neutral ligand from (F) and/or (G) gives a neutral, **four coordinate** π -allyl-complex (H). Identify (E), (F), (G) and (H).

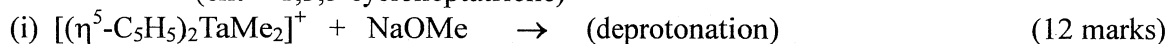
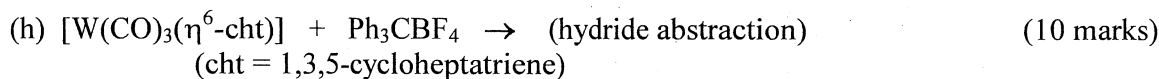
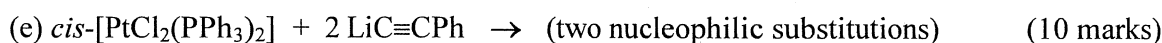
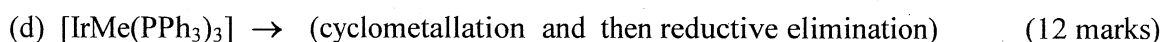
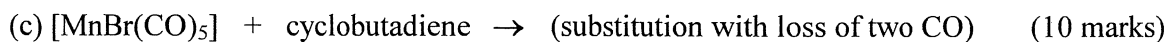
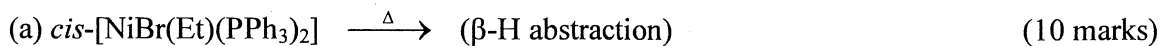
(32 marks)

- (d) $[\text{Cr}(\text{CH}_2\text{SiMe}_3)_3]$ is an isolable crystalline solid, but $[\text{CrMe}_3]$ does not exist.

Explain.

(16 marks)

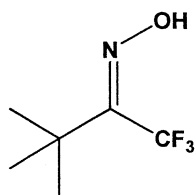
4. Predict the major product(s) of each of the following reactions, using the hint given in the brackets.



5. (a) A **neutral mononuclear** 18e-complex (**J**) contains a Co(I) centre coordinated **only** to hydride and carbon monoxide ligands. (**J**) can be prepared by the reaction between the binuclear Co(0) complex (**K**) and H_2 . (**J**) loses a gas molecule to give the 16e-complex (**L**). Coordination of MeCH=CH_2 to (**L**) gives the 18e olefin-complex (**M**). In the presence of CO, (**L**) undergoes hydride migration to give the 16e-complex (**N**). (**L**) reacts with H_2 to give the 18e-cobalt(III) hydride (**O**). Identify (**J**), (**K**), (**L**), (**M**), (**N**) and (**O**). (42 marks)

(b) The active catalyst $[\text{RuHCl}(\text{PPh}_3)_3]$ coordinates with $\text{CH}_2\text{=CH}_2$ to give the olefin-complex (**P**). (**P**) undergoes migratory insertion to give the alkyl-complex (**Q**). (**Q**) reacts with H_2 to give the dihydrogen-complex (**R**) which eliminates (**S**) to regenerate $[\text{RuHCl}(\text{PPh}_3)_3]$. Identify (**P**), (**Q**), (**R**) and (**S**). (28 marks)

(c) Reaction of the E-oxime, $\text{Me}_3\text{CC(=NOH)CF}_3$, with $[\text{PdCl}_2(\text{NCPh})_2]$ gives the cyclometallated chloride-bridged Pd(II) dimer which contains a 5-membered chelate ring. Draw the **structure** of this dimeric complex. (10 marks)



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

- (i) $\text{CH}_2=\text{CHCH}=\text{CH}_2 + 2 \text{HCN} \rightarrow \text{NC}(\text{CH}_2)_4\text{CN}$
 (ii) $[\text{Mo}(\text{CO})_6] \rightarrow [(\text{CO})_5\text{MoC}(\text{=O})\text{H}]^-$
 (iii) $[(\eta^5\text{-Cp})_2\text{Zr}(\text{H})\text{Cl}] \rightarrow [(\eta^5\text{-Cp})_2\text{Zr}(\text{CH}=\text{CH}_2)\text{Cl}]$
 (iv) $[(\eta^5\text{-Cp})\text{WMe}(\eta^2\text{-CH}_2=\text{CH}_2)]^+ \rightarrow [(\eta^5\text{-Cp})\text{W}(\text{CH}_2\text{CH}_2\text{CH}_3)\text{Me}]$ (20 marks)

6. (a) (i) Give **three** reasons as to why palladium complexes are used widely in catalysis.
 (ii) $[\text{Pd}(\text{PPh}_3)_4]$ catalyses the reaction of ethene with bromobenzene to give Styrene ($\text{PhCH}=\text{CH}_2$) and HBr . Write a mechanism for this process. (35 marks)
- (b) (i) What is meant by “Hydrosilation of an olefin”?
 (ii) What is the Speier’s catalyst?
 (iii) What is the main product obtained if $\text{CH}_2=\text{CHCN}$ is reacted with PhMe_2SiH in the presence of the catalyst $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$? (25 marks)
- (c) How would you prepare MeTiCl_3 , Me_2TiCl_2 and TiMe_4 from TiCl_4 . (15 marks)
- (d) Identify the two molecules formed due to the **ring closed metathesis** of 1,7-octadiene (C_8H_{14}). (15 marks)
- (e) The following molecule undergoes an intramolecular Heck reaction to give a benzofuran derivative (**X**). Draw the structure of (**X**). (10 marks)

