



THE OPEN UNIVERSITY OF SRI LANKA
B.Sc./B.Ed DEGREE IN SCIENCE-LEVEL 5
FINAL EXAMINATION-2013/2014

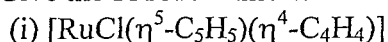
CMU3122/CHU3127 ORGANOMETALLIC CHEMISTRY

Date: 18th June 2014 (Wednesday)

Time 1.00 – 3.00 p.m.

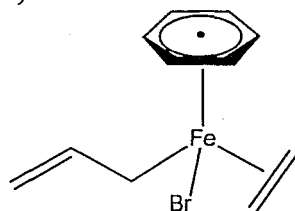
Answer any **FOUR** (04) questions. If more than four questions are answered, **only the first four answers will be marked.**

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

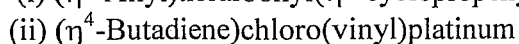
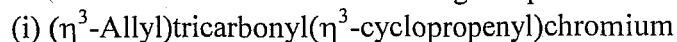


(20 marks)

(ii)

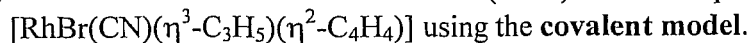


(b) Draw the **structures** of the following complexes.



(20 marks)

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



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

(15 marks)

(d) Using an orbital diagram(s), explain the bonding between a metal (M) and a PPh_3 ligand.

(18 marks)

(e) What is the active catalyst or catalytic system used in

(i) Wacker process, and (ii) Roelen process

(12 marks)

(f) (i) Arrange NO^+ , PMe_3 and CO in the increasing order of π -acceptability.

(ii) Give one molecule which is isoelectronic with NH_3 .

(15 marks)

2. (a) $[\text{MeMn}(\text{CO})_5]$ reacts with ^{13}CO to give *cis*- $[\text{Me}(\text{O}=\text{C})\text{Mn}(^{13}\text{CO})(\text{CO})_4]$.
Write the mechanism of the above reaction. (20 marks)

(b) (i) $[\text{Co}_2(\text{CO})_8]$ is a coordinatively saturated symmetrical compound.

Using valence electron count, show that there is a metal-metal bond.

(ii) In the solid state it shows bridging carbonyl ligands, draw the structure of solid $[\text{Co}_2(\text{CO})_8]$.

(iii) Arrange the following compounds in the increasing order of carbonyl stretching frequency. Explain your answer.

$[\text{Co}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2]$, $[\text{CoMe}(\text{CO})(\text{PPh}_3)_2]$ and $[\text{CoI}(\text{CO})(\text{PPh}_3)_2]$. (24 marks)

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

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

(20 marks)

(d) Draw and identify the structures of all geometrical isomers of $[\text{RhH}_3(\text{CO})(\text{PPh}_3)_2]$.

Comment on optical isomerism of above isomers (20 marks)

(e) What are the **two** aldehydes formed due to hydroformylation of $\text{EtCH}=\text{CH}_2$? (16 marks)

3. (a) What is a **carbene** ligand? Explain the bonding between a carbene ligand and a metal centre using orbital diagrams. (20 marks)

(b) (i) What is meant by β -agostic interaction?

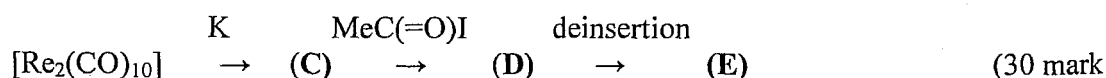
(ii) The alkyl-complex $[\text{RhCH}_2\text{CH}_3(\text{CO})_3]$ (**A**) shows a **square pyramidal** arrangement with an β -agostic interaction in the axial position.

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

(iii) Upon gentle heating (**A**) undergoes C-H bond activation to give a **square pyramidal** 18e-complex (**B**) with a hydride in the axial position.

Draw the structure of (**B**). (30 marks)

(c) Identify the metal complexes (**C**), (**D**) and (**E**) of the following reaction scheme.



(d) (i) Explain why dinitrogen complexes are rare when compared to metal carbonyls?.

(ii) Draw and name three coordination modes of dinitrogen.

Give an example for each. (20 marks)

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

- (a) $\text{trans-}[\text{Ir}(\text{CO})(\text{PPh}_3)_2] + \text{MeI} \rightarrow$ (2e-oxidative addition) (10 marks)
- (b) $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{Fe}=\text{CH}(\text{Me})]^+ + \text{LiPh} \rightarrow$ (nucleophilic attack) (12 marks)
- (c) $[\text{Fe}(\text{CO})_5] + 1,3\text{-butadiene} \rightarrow$ (disubstitution) (10 marks)
- (d) $\text{fac-}[(\text{dppe})\text{PdI}(\text{Me})_3] \rightarrow$ (reductive elimination) (12 marks)
- (e) $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2] + \text{LiCH}_2\text{CH}_2\text{CH}_2\text{Li} \rightarrow$ (two nucleophilic substitutions) (10 marks)
- (f) $[\text{Ir}(\text{CH}_2\text{COCH}_3)(\text{PCl}_3)_3] \rightarrow$ (cyclometallation via γ C-H bond activation) (12 marks)
- (g) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CO})_2] + 2 \text{H}_2\text{C}=\text{C}=\text{CH}_2 \rightarrow$ (oxidative coupling) (12 marks)
- (h) $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{Ru}(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2)] + \text{Br}_2 \rightarrow$ (electrophilic addition) (10 marks)
- (i) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrH}(\text{Br})] + \text{HC}\equiv\text{CH} \rightarrow$ (coordination & insertion) (12 marks)

5. (a) $[\text{Co}_2(\text{CO})_8]$ reacts homolytically with H_2 to give the 18e-cobalt hydride (**K**). (**K**) loses a gas molecule to give the 16e complex (**L**). Coordination of $\text{CH}_3\text{CH}=\text{CH}_2$ to (**L**) gives the 18e olefin-complex (**M**). Migration of hydride on to the coordinated olefin gives two 16e alkyl-complexes (**N**) and (**O**). Identify (**K**), (**L**), (**M**), (**N**) and (**O**). (40 marks)
- (b) Oxidative addition of MeI to $[\text{RhI}_2(\text{CO})_2]^-$ gives (**P**). (**P**) with CO gives (**Q**). (**Q**) reductively eliminates (**R**) to regenerate $[\text{RhI}_2(\text{CO})_2]^-$. Identify (**P**), (**Q**) and (**R**). (30 marks)
- (c) $[\text{Mo}(\text{CO})_6]$ reacts with two moles of PPh_3 to give a molybdenum(0) complex (**S**). (**S**) shows only one IR band in the carbonyl region, draw the structure of (**S**). (10 marks)
- (d) Suggest reagent(s) which can be used to carry out the following conversions.
- (i) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2] \rightarrow [(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{Me})]$
- (ii) $[\text{Fe}(\text{CO})_5] \rightarrow [\text{HFe}(\text{CO})_4]^-$
- (iii) $[\text{WCl}_6] \rightarrow [(\eta^5\text{-C}_5\text{H}_5)_2\text{WH}_2]$
- (iv) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TaMe}_2]^+ \rightarrow [(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta}(\text{=CH}_2)\text{Me}]$ (20 marks)

6. (a) The Ni(II) complex $[(\text{CH}_3\text{CH}_2)\text{Ni}(\text{OCH}_2\text{CF}_3)(\text{dppe})]$ decomposes to give an alkane (**T**), alkene (**U**), alcohol (**V**) and aldehyde (**W**) when it is heated in toluene at 100 C.. Identify (**T**), (**U**), (**V**), and (**W**). $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (30 marks)
- (b) $[\text{RhCl}(\text{PPh}_3)_3]$ catalyses the hydrogenation of ethene *via* the hydride mechanism. Draw the catalytic cycle for this process and identify the catalytic intermediates formed. (40 marks)
- (c) (i) Define the terms turnover number (TON) and turnover frequency (TOF).
(ii) In the presence of PdCl_2 (0.000005 mmol), bromobenzene (2.0 mmol) reacts completely with styrene (2.0 mmol) to give stilbene. The reaction time is 20 min. Calculate TON and TOF for this reaction. (20 marks)
- (d) The following molecule undergoes an intramolecular Heck reaction to give an indole derivative (**Z**). Draw the structure of (**Z**). (10 marks)

