



THE OPEN UNIVERSITY OF SRI LANKA

B.Sc./B.Ed. DEGREE /STAND ALONE COURSES IN SCIENCE- LEVEL 5

FINAL EXAMINATION-2012/2013

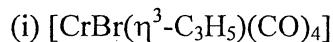
CMU3122/CME5122 ORGANOMETALLIC CHEMISTRY  
 CHU3127/CHE5127 ORGANOMETALLIC CHEMISTRY

Date: 08th June 2013 (Saturday)

Time 1.00 – 3.00 p.m.

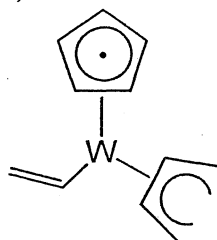
Answer any **FOUR** (04) questions. If more than four questions are answered, **only the first four answers will be marked.**

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

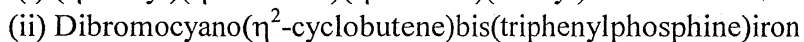
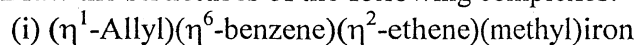


(20 marks)

(ii)



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



(20 marks)

(c) Determine the valence electron count (VEC) of the complex  $[\text{CoCl}(\eta^1\text{-C}_3\text{H}_5)(\eta^1\text{-CH=CH}_2)(\eta^4\text{-C}_4\text{H}_4)]$  using the **ionic model**. (Indicate in your workout, the electron contribution made by each ligand, Co is a Group 9 metal).

(15 marks)

(d) Give four characteristics of Schrock carbenes.

(20 marks)

(e) Name three reducing agents that could be used for the preparation of binary metal carbonyls from metal salts.

(10 marks)

(f) Arrange  $\text{PF}_3$ ,  $\text{PMe}_3$ ,  $\text{PCl}_3$ , and  $\text{PPh}_3$  in the increasing order of their  $\sigma$ -donor ability. (Reasons not required)

(15 marks)

2. (a) Briefly describe the geometry and the nature of bonding in  $[\text{Pt}(\eta^2\text{-CH}_2\text{=CH}_2)_3]$ . (20 marks)

(b) Explain why  $[\text{Ni}(\text{CO})_4]$  is stable at room temperature, but  $[\text{Ni}(\text{NH}_3)_4]$  does not exist. (20 marks)

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

Compound	$\nu(\text{C}=\text{C})$ in $\text{cm}^{-1}$	
Free $\text{CH}_2=\text{CH}_2$	1620	
$[\text{Au}(\eta^2\text{-CH}_2\text{=CH}_2)_2]^+$	1590	
$[\text{CpIr}(\eta^2\text{-CH}_2\text{=CH}_2)_2]$	1490	(20 marks)

(d) The ruthenium(II) complex  $[\text{RuCl}(\text{CN})(\text{CO})_3]$  shows four isomers with the square-pyramidal geometry. Draw the structures of them (20 marks)

(e)  $[\text{CpFe}(\text{CO})_2]_2$  reacts with K to give (P). (P) with MeI gives (Q). (Q) can be prepared by reacting (R) with MeMgBr. Identify (P), (Q) and (R). (20 marks)

3. (a) List three ligands which are isoelectronic with  $\text{NO}^+$ . Arrange all four in the order of increasing  $\pi$ -acceptability. Give your reasons. (20 marks)

(b) What factors promote metallacyclopropane character in alkene-metal complexes? (15 marks)

(c) (i) What is an agostic interaction?

(ii) If the complex  $[\text{W}(\text{CO})_3(\text{PCy}_3)_2]$  has an octahedral arrangement with one agostic type interaction. Note that two phosphine ligands are *trans* to each other. Draw the structure of the complex and identify the type of agostic interaction associated with it ? (Cy = cyclohexyl,  $\text{C}_6\text{H}_{11}$ )

(iii)  $[\text{W}(\text{CO})_3(\text{PCy}_3)_2]$  reacts with dihydrogen to give the dihydrogen complex known as Kubas complex. Draw structure of this complex. (30 marks)

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

(e) Draw and name three coordination modes of the hydride ion. Give an example for each. (15 marks)

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

- (a)  $2 [\text{Co}(\text{CN})_5]^{3-} + \text{MeI} \rightarrow$  (1e oxidative addition) (10 marks)
- (b)  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^5\text{-C}_5\text{H}_5)]^+ + \text{Me}^- \rightarrow$  (nucleophilic attack on coordinated ligand) (12 marks)
- (c)  $[\text{Mo}(\text{CO})_6] + \text{PhMe} \rightarrow$  (substitution) (10 marks)
- (d)  $\text{fac-}[\text{RhI}_3(\text{COMe})(\text{CO})_2]^- \rightarrow$  (reductive elimination) (10 marks)
- (e)  $[\text{IrH}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{PPh}_3)_2] + \text{PPh}_3 \rightarrow$  (coordination & insertion) (12 marks)
- (f)  $[\text{Cp}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\text{FeC}\equiv\text{CPh}] + \text{Me}_3\text{O}^+ \rightarrow$  (electrophilic attack) (12 marks)
- (g)  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CO})_2] + 2 \text{PhC}\equiv\text{CPh} \rightarrow$  (oxidative coupling) (12 marks)
- (h)  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2] + \text{O}_2 \rightarrow$  (2e-oxidative addition) (10 marks)
- (i)  $[\text{Cp}_2\text{Zr}(\text{H})\text{CH}_2\text{CH}_3] + 2 \text{PPh}_3 \rightarrow$  (coordination & reductive elimination)(12 marks)

5. (a) The catalyst  $[\text{MCl}(\text{PR}_3)_3]$  reacts with  $\text{H}_2$  to give the octahedral M(III) dihydride (A). Replacement of  $\text{PR}_3$  by  $\text{MeCH}=\text{CH}_2$  of (A) gives the olefin-complex (B). In the presence of  $\text{PR}_3$ , (B) undergoes migratory insertion to give the octahedral alkyl-complex (C). (C) reductively eliminates the alkane (D) to regenerate the catalyst  $[\text{MCl}(\text{PR}_3)_3]$ . Write the molecular formulae of (A), (B), (C) and (D). (40 marks)

- (b) (i) The 18e cation  $[\text{Cp}_2\text{MoH}(\eta^2\text{-CH}_2=\text{CH}_2)]^+$  reacts with hydride ion ( $\text{H}^-$ ) to give the **neutral** 18e complex (P) which in the presence of  $\text{PPh}_3$  gives the 18e complex (Q) and ethane ( $\text{C}_2\text{H}_6$ ). Identify (P) and (Q).  
 (ii)  $\text{trans-}[\text{PdMe}_2(\text{PPh}_3)_2]$  does not form ethane easily. Explain. (30 marks)

(c) Reaction of azobenzene,  $\text{PhN}=\text{NPh}$ , with  $\text{Na}_2[\text{PdCl}_4]$  gives the cyclometallated chloride-bridged palladium (II) **dimer** containing two 5-membered chelate rings. Draw the structure of this **dimeric** complex. (15 marks)

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

- (i)  $\text{CH}_2=\text{CH}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_3\text{CHO}$   
 (ii)  $[\text{Mo}(\text{CO})_6] \rightarrow [(\text{OC})_5\text{MoC}(\text{=O})\text{H}]^-$   
 (iii)  $[\text{C}_p\text{WH}(\text{CO})_3] \rightarrow [\text{C}_p\text{W}(\text{H}_2)(\text{CO})_3]\text{BF}_4$  (15 marks)

6. (a) The active catalyst  $[\text{CoH}(\text{CO})_3]$  reacts with  $\text{CH}_2=\text{CH}_2$  to give the olefin-complex (**K**), which in the presence of  $\text{CO}$  gives the acyl-complex (**L**) (with two insertions). (**L**) reacts with  $\text{H}_2$  to give the octahedral compound (**M**) which eliminates (**N**) to regenerate  $[\text{CoH}(\text{CO})_3]$ . Identify (**K**), (**L**), (**M**) and (**N**). (40 marks)

(b)  $[\text{NiH}(\text{CN})(\text{PPh}_3)_2]$  catalyses the hydrocyanation of  $\text{CH}_2=\text{CH}_2$  to give  $\text{CH}_3\text{CH}_2\text{CN}$ . Draw the catalytic cycle for this process. (30 marks)

(c) (i) What is the main product formed due to metathesis of cyclopentene ( $\text{C}_5\text{H}_8$ ) and  $\text{Me}(\text{CH}_2)_{10}\text{CH}=\text{CH}(\text{CH}_2)_6\text{CO}_2\text{Et}$ ?

(ii)  $[\text{Pd}(\text{PPh}_3)_4]$  catalyses the cross coupling between styrene ( $\text{PhCH}=\text{CH}_2$ ) and bromobenzene to give (**Y**) and  $\text{HBr}$ . Identify (**Y**).

(iii)  $[\text{Pd}(\text{PPh}_3)_4]$  catalyses intramolecular Heck reactions. Draw the structure of the product formed by the intramolecular Heck reaction of the compound (**Z**). (30 marks)

