



THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION-2012/2013

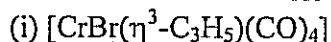
CMU3122/CMES122 ORGANOMETALLIC CHEMISTRY
CHU3127/CHE5127 ORGANOMETALLIC CHEMISTRY

Date: 08th June 2013 (Saturday)

Time 1.00 – 3.00 p.m.

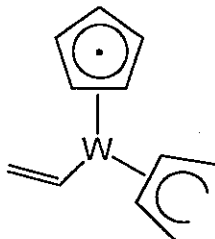
Answer any **FOUR** (04) questions. If more than four questions are answered, **only the first four answers will be marked.**

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

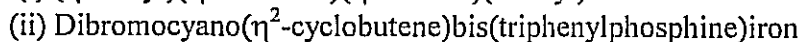
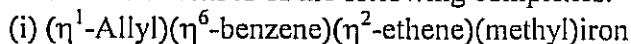


(20 marks)

(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 PF_3 , PMe_3 , PCl_3 , and PPh_3 in the increasing order of their σ -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 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 NO^+ . Arrange all four in the order of increasing π -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, C_6H_{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 H_2 to give the octahedral M(III) dihydride (A). Replacement of PR_3 by $\text{MeCH}=\text{CH}_2$ of (A) gives the olefin-complex (B). In the presence of 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 (H^-) to give the neutral 18e complex (P) which in the presence of PPh_3 gives the 18e complex (Q) and ethane (C_2H_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 CO gives the acyl-complex (L) (with two insertions). (L) reacts with 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 (C_5H_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 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)

