

THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION-2010/2011

CHU3127/CHE5127 - ORGANOMETALLIC CHEMISTRY

Date: 31st December 2010 (Friday)

Time 1.30 – 4.00 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.
- (i) $[\text{Cr}(\eta^3\text{-C}_3\text{H}_5)(\eta^4\text{-C}_4\text{H}_4)(\text{CO})_2]$
- (ii) $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-CH=CH}_2)(\text{PPh}_3)_2]$ (20 marks)
- (b) Draw the **structures** of the following complexes,
- (i) $(\eta^4\text{-Butadiene})\text{methyl(vinyl)platinum.}$
- (ii) $(\eta^3\text{-Allyl})(\eta^6\text{-benzene})\text{carbonyl(ethyl)chromium.}$
- (iii) $\text{Cyano}(\eta^5\text{-cyclopentadienyl})(\eta^3\text{-cyclopropenyl})\text{iron}$ (30 marks)
- (c) (i) Determine the valence electron count (VEC) of the complex $[\text{CrBr}(\eta^1\text{-CH=CH}_2)(\eta^3\text{-C}_3\text{H}_5)(\eta^4\text{-C}_4\text{H}_4)]$ using the **ionic model**. (Indicate in your workout, the electron contribution made by each ligand, Cr is a Group 6 metal).
- (ii) Determine the valence electron count (VEC) of the complex $[\text{FeCl}(\text{Me})(\text{CO})_2(\text{PPh}_3)(\eta^2\text{-CH}_2=\text{CH}_2)]$ using the **covalent model**. (Indicate in your workout, the electron contribution made by each ligand, Fe is a Group 8 metal). (20 marks)
- (d) Draw and identify all the **geometrical** and **optical** isomers (altogether four) of $[\text{FeCl}_2(\text{CO})_3(\text{PPh}_3)]$. (20 marks)
- (e) List the following ligands in the **increasing order** of π -acceptability. PH_3 , NH_3 , CS and CO (10 marks)

2. (a) Describe the bonding between a metal (M) and a phosphine ligand. (20 marks)

(b) What are the factors which facilitate oxidative addition reactions? (20 marks)

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

Compound	$\nu(\text{CO})$ in cm^{-1}	
free CO	2143	
$[\text{Mo}(\text{CO})_6]$	2005	
$[\text{Mo}(\text{CO})_6]^+$	2090	(20 marks)

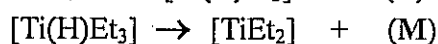
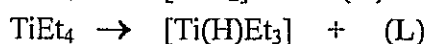
(d) $[\text{Cr}(\text{CH}_2\text{SiMe}_3)_3]$ is an isolable crystalline solid, but $[\text{CrMe}_3]$ is unknown. Explain. (20 marks)

(e) How would you prepare the acyl compound $[\text{Pt}\{\text{C}(=\text{O})\text{Et}\}(\text{CO})_3]^+$ from $[\text{PtH}(\text{CO})_3]^+$. (20 marks)

3. (a) (i) $[(\eta^5\text{-Cp})_2\text{V}(\text{NO})]$ has a linear V–NO fragment. Determine the Valence Electron Count (VEC) of V. V is a Group 5 metal.

(ii) Determine the coordination number of Rh in $[(\eta^5\text{-Cp})\text{RhCl}_2(\text{CO})]$. Rh is a Group 9 metal. (20 marks)

(b) TiEt_4 decomposes *via* reductive elimination and β -hydride elimination as shown below.



Identify the molecules (K), (L) and (M). (20 marks)

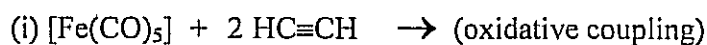
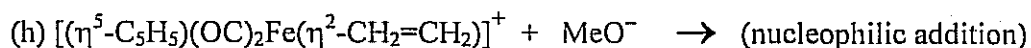
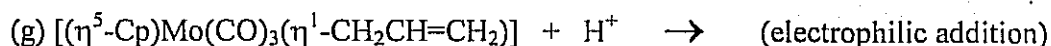
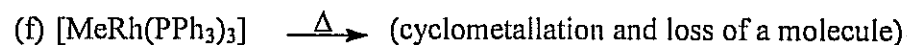
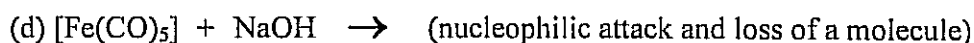
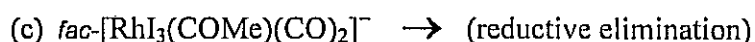
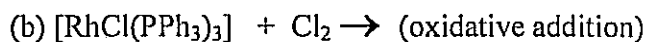
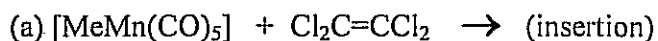
(c) (i) What is an agostic interaction?

(ii) Assume that $[\text{PtCl}_3(\text{PMe}_3)]^-$ 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)

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

(e) Draw and name coordination modes of dinitrogen. (20 marks)

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



(10 x 10 marks)

5. (a) The active catalyst $[\text{Pd}(\text{PPh}_3)_2]$ reacts with PhI to give the *cis*-Pd(II) complex (A). (A) reacts with $\text{CH}_2=\text{CH}_2$ to give the 5-coordinate intermediate (B). Migratory insertion of the phenyl group gives the alkyl-complex (C). β -Hydride abstraction followed by dissociation of the organic molecule (D) gives the Pd(II) complex (E). Identify (A), (B), (C), (D) and (E).

(40 marks)

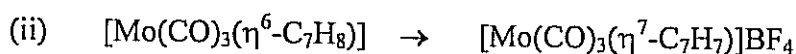
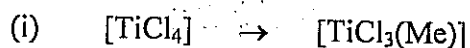
(b) Reduction of the carbonyl-bridged dimer $[(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2]_2$ with Na gives the mononuclear 18e-salt (X). (X) reacts with allyl bromide ($\text{CH}_2=\text{CHCH}_2\text{Br}$) to give the neutral 18e-complex (Y) and NaBr. Upon heating, (Y) is converted into an 18e-complex (Z) with a loss of carbonyl ligand. Identify (X), (Y) and (Z).

(30 marks)

(c) The reaction of two equivalents of $\text{PhCH}_2\text{NMe}_2$ with $\text{Na}_2[\text{PdCl}_4]$ in methanol gives the orthometallated chloride-bridged palladium(II) dimer (J) and sodium chloride. Draw the structure of (J).

(15 marks)

(d) Suggest reagent(s)/compound(s)/ions which can be used to carry out the following conversions.



6. (a) Replacement of the solvent molecule of the active catalyst

$[\text{RhCl}(\text{solvent})(\text{PPh}_3)_2]$ by ethene ($\text{CH}_2=\text{CH}_2$) gives the 16e-complex (P). (P) reacts with H_2 to give the 18e-octahedral Rh(III) dihydride (Q). In the presence of PPh_3 , (Q) undergoes migratory insertion to give the octahedral alkyl-complex (R). (R) reductively eliminates the alkane (S) to regenerate the pre-catalyst $[\text{RhCl}(\text{PPh}_3)_3]$.

Write the molecular formulae of (P), (Q), (R) and (S).

(40 marks)

(b) Nucleophilic attack of water on coordinated ethene in the complex

$[\text{PdCl}_2(\text{H}_2\text{O})(\eta^2\text{-CH}_2=\text{CH}_2)]$ resulted in the formation of the palladate(II) ion (X). Loss of a Cl^- ion followed by β -hydride abstraction gives the neutral complex (Y). Reductive elimination of HCl and dissociation of the organic molecule (Z) gives zerovalent palladium.

Write the molecular formulae of (X), (Y) and (Z).

(30 marks)

(c) (i) What is meant by "Hydroformylation of olefins"? Give an example.

(ii) Draw the structure of the polymer formed due to the ring opening metathesis polymerization of cyclopentene (C_5H_8)

(iii) What is the product formed due to metathesis of cyclobutene (C_4H_6) and $\text{Me}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{Me}$?

(30 marks)