

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc./B.Ed DEGREE IN SCIENCE-LEVEL 5

FINAL EXAMINATION-2015/2016

CMU3122/CHU3127 ORGANOMETALLIC CHEMISTRY

Date: 11th July 2016 (Monday) 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. (a) Give the IUPAC name for each of the following complexes. (i) [CoCl₂(η^1 -C₅H₅)(η^6 -C₆H₆)] (20 marks) (b) Draw the structures of the following complexes. (i) $[RhHBr(\eta^3-C_5H_5)(CS)(\eta^2-C_4H_4)]$ f(i) Dicarbonyl(η^5 -cyclopentadienyl)(η^2 -ethene)ethenylchromium (20 marks) (Uz-Cb) ((O)2 (c) Determine the valence electron count (VEC) of the complex [FeMe(H)(η^4 -C₆H₆)(η^2 -C₄H₄)] using the ionic model. (Indicate in your workout, the electron contribution made by each ligand, Fe is a Group 8 metal). (15 marks) (d) What are the active catalysts used in (i) Hydrocyanation, and (ii) Union Carbide process (12 marks) Arrange PH₃, PF₃, NMe₂H and NMe₃ in the increasing order of σ -donor ability. Give one cationic ligand which is isoelectronic with the ethynyl group as in sodium acetylide. (15 marks) HC ECH Using an orbital diagram, explain the bonding between

(18 marks)

the metal and ligand in [CuPPh₃]⁺.

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

(a)
$$TiCl_4 + ZnMe_2 \rightarrow (Nucleophilic Substitution)$$
 (10 marks)

(b)
$$2 \left[\text{Rh}(\text{CN})_5 \right]^{3-} + \text{CH}_3 \text{CH}_2 \text{I} \rightarrow \text{(1e-oxidative addition)}$$
 (12 marks)

(c)
$$[Fe(CO)_5] + Ph_2PCH_2CH_2 CH_2PPh_2 \rightarrow (disubstitution with loss of CO)$$
 (10 marks)

(d) [IrMe(PPh₃)₃] + BrCH=CH₂
$$\rightarrow$$
 (2e-Oxidative addition) (10 marks)

(e)
$$[(\eta^5 - C_5H_5)_2 \text{WMe}(\eta^2 - \text{CH}_2 = \text{CH}_2)]^+ + \text{Me}^- \rightarrow \text{(nucleophilic addition)}$$
 (12 marks)

(f)
$$[CF_3CF_2Rh(PPh_3)_3] \rightarrow (cyclometallation via γ C-H bond activation) (12 marks)$$

(g)
$$PhBr + (Bu^n)_3SnCH=CH_2 \rightarrow (Stille Coupling)$$
 (10 marks)

(h)
$$[(\eta^5 - C_5 H_5)_2 Zr H(Br)] + MeC \equiv CMe \rightarrow (coordination \& insertion)$$
 (12 marks)

(i) [NiBr(CF₂CH₂Me)(dppe)]
$$\xrightarrow{\Delta}$$
 (β -H abstraction to give an 18e-complex) (12 marks) (dppe = PPh₂CH₂CH₂PPh₂ and it is a bidentate ligand)

5. (a) Iodobenzene oxidatively adds to [RhEt(PPh3)3] to give the 18e-complex (J).

(J) reductively eliminates an aromatic hydrocarbon (K) while forming an 16e-complex (L). With MeLi, (L) gives the alkyl-complex (M). Coordination of CH₂=CH₂ to (M) gives the 18e alkene-complex (N). (N) undergoes 1,2-insertion reaction to give the alkyl-complex (O). In the presence of CO,

(O) undergoes 1,1-insertion reaction to give the 16e-complex (P).

Identify
$$(J)$$
, (K) , (L) , (M) , (N) , (O) and (P) . (42 marks)

(b) (i) What is meant by hydroformylation of olefins?

(ii) Write the molecular formulae of the two products formed due to hydroformylation of MeCH=CHEt.

(20 marks)

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

Compound
$$v(N\equiv N)$$
 in cm⁻¹ free N₂ 2330 [Ni(N₂)] 2088 [Ni(N₂)₂] 2187 (20 marks)

- (d) Suggest reagent(s) or active catalyst(s) which can be used to carry out the following conversions.
 - CH₃OH + CO $\xrightarrow{\checkmark}$ CH₃CO₂H [Fe(CO)₅] $\xrightarrow{\checkmark}$ [HFe(CO)₅]
 - (ii)
 - (iii)
 - $cis-[PtCl₂(PMe₃)₂] \rightarrow cis-[PtClMe(PMe₃)₂]$ $[(\eta^{5}-Cp)WH(PPh₃)₃] \rightarrow [(\eta^{5}-Cp)W(\eta^{2}-H₂)(PPh₃)₃]BF₄$ (20 marks)
- 6. (a) [RhCl(PPh₃)₃] catalyses the hydrogenation of ethene via the hydride mechanism. Draw the catalytic cycle for this process and identify the catalytic intermediates formed. (45 marks)
 - (b) Draw the structure of the polymer (X) formed due to the ring opening metathesis polymerization of norbornadiene.



Norbornadiene

(10 marks)

- (c) (i) Identify the two olefins formed due to the ring closed metathesis of 1,6-heptadiene (C_7H_{12}).
 - (ii) 1,6-heptadiene undergoes an oxidative coupling reaction with $[(\eta^5-Cp)_2Zr(CO)_2]$ to give a 16e-complex (Y) with a fused 5-membered metallacycle. Draw the structure of (Y). (25 marks)
- (d) (i) What is meant by "Heck reaction"?
 - (ii) The following molecule undergoes an intramolecular Heck reaction to give an indole derivative (Z). Draw the structure of (Z).

(20 marks)