



080

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc/ B.Ed DEGREE PROGRAMME/ STAND ALONE COURSES IN SCIENCE

FINAL EXAMINATION- LEVEL 5- 2006/2007

CHU 3127/ CHE 5127- ORGANOMETALLIC CHEMISTRY

(2 ½ hours)

*Friday 24th November 2006**1.30 a.m.- 4.00 p.m.*

ANSWER ANY FOUR QUESTIONS.

IF MORE THAN FOUR QUESTIONS ARE ANSWERED, ONLY THE FIRST FOUR ANSWERS WILL BE MARKED.

1.(a) Give IUPAC names of the following complexes.

- i. $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^1\text{-CH=CH}_2)(\text{CO})_2]$
- ii. $\text{K}[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$
- iii. $[(\eta^5\text{-C}_5\text{H}_5)\text{CoMc}(\text{CO})(\text{PPh}_3)]\text{Cl}$ (30 marks)

(b) Draw the structures of the following complexes.

- i. Trichloro(η^2 -ethene)platinate ion
- ii. Bis(η^3 - allyl)palladium
- iii. (η^1 - allyl)tricarbonyl(η^5 -cyclopentadienyl)molybdenum
- iv. Carbonyl(η^3 -cyclopropenyl)hydrido(η^1 -phenylethynyl)iridium (40 marks)

(c) Determine the Valence Electron Count (VEC) of the following complexes using the covalent model. (Indicate, in your work out, the electron contribution made by each ligand)

- i. $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\eta^3\text{-C}_5\text{H}_5)(\text{CO})_2]$ (W is a Group 6 metal)
 - ii. $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^1\text{-CH=CH}_2)(\text{CO})(\text{N}_2)]]$ (Fe is a Group 8 metal)
 - iii. $[\text{Ru}(\equiv\text{CPh})\text{Cl}(\text{CO})_2(\text{PPh}_3)]$ (Ru is a Group 8 metal)
- (30 marks)

2. (a) Using a suitable diagram, describe the bonding between Pt and $-\text{C}\equiv\text{CMe}$ group. (20 marks)
- (b) $[(\eta^5-\text{C}_5\text{H}_5)_2\text{Fe}_2(\mu_2-\text{CO})_2(\text{CO})_2]$ is a coordinatively saturated complex. Deduce the structure of this complex. (25 marks)
- (c) Work out the Group number of Nb. Write the d^n representation for Nb^{3+} . (Atomic number of Nb is 41) (15 marks)
- (d) Determine the coordination number of Tc (group 7 metal) in $[(\eta^5-\text{C}_5\text{H}_5)\text{Tc}(\eta^2\text{-cyclooctatetraene})(\text{CO})_2]$. (20 marks)
- (e) List three ligands which are isoelectronic with CO. Arrange them in the order of increasing π -acceptor ability. (20 marks)
3. (a) Draw all the possible isomers of $[\text{RuBr}_2(\text{en})(\text{NH}_3)_2]$. (20 marks)
- (b) What are the main differences between Fischer-carbenes and Schrock-carbenes? (20 marks)
- (c) How do you account for the variation in carbonyl stretching frequencies of the following compounds? (ν_{CO} of free CO is 2143 cm^{-1})
- | <u>Compounds</u> | <u>$\nu_{\text{CO}}/\text{cm}^{-1}$</u> |
|------------------------------|--|
| $[\text{Cr}(\text{CO})_6]$ | 2000 |
| $[\text{V}(\text{CO})_6]^-$ | 1860 |
| $[\text{Mn}(\text{CO})_6]^+$ | 2090 |
- (30 marks)
- (d) E-Acetophenone dimethylhydrazone, $\text{Ph}(\text{Me})\text{C}(=\text{NNMe}_2)$ reacts with Na_2PdCl_4 to give a chloride bridged Pd(II) dimer containing a five-membered ring. Draw the structure of this dimer. (20 marks)
- (e) Metal carbonyls are very common in nature compared to dinitrogen compounds. Explain this observation. (10 marks)
4. Draw the structure(s) of the major product(s) of each of the following reactions using the hint given in brackets.
- (a) $\text{trans} [\text{IrCl}(\text{CO})(\text{PPh}_3)_2] + \text{O}_2 \rightarrow$
(oxidative addition)
- (b) $\text{cis} [\text{PtCl}(\text{Et})(\text{PMe}_3)_2] \xrightarrow{\Delta}$
(β -H abstraction)

- (c) $\text{Trans-}[\text{IrCl}(\text{CO})(\text{PPh}_3)_2] + \text{H-C}\equiv\text{C-H} \rightarrow$
(association)
- (d) $[\text{Ni}(\text{PEt}_3)_3] + \text{PhCl} \rightarrow$
(oxidative addition)
- (e) $2[\text{Co}(\text{CN})_5]^{3-} + \text{MeI} \rightarrow$
(1e oxidative addition)
- (f) $\text{Fe}(\text{PMe}_3)_4 + 2\text{MeC}\equiv\text{CMe} \rightarrow$
(oxidative coupling)
- (g) $\text{PtCl}_2(\text{pyridine})(\eta^2\text{-CH}_2=\text{CH}_2) + \text{pyridine} \rightarrow$
(nucleophilic addition)
- (h) $\text{Fe}(\text{PMe}_3)_4 \xrightarrow{\Delta}$
(cyclometalation)
- (i) $\text{Mn}(\text{CO})_5(\eta^2\text{-CH}_2\text{CH}=\text{CH}_2) \rightarrow$
(loss of CO and coordination)
- (j) $\text{MeMn}(\text{CO})_5 + \text{PPh}_3 \rightarrow$
(insertion and association) (100 marks)

5. (a)(i) Arrange, giving reasons, the phosphines PX_3 ($\text{X} = \text{Me, OMe, OAr, Cl, F}$) in the increasing order of their σ -donor ability and π -acceptor ability.
- (ii) Explain the bonding between a metal and a phosphine ligand PX_3 .
- (iii) Arrange the ν_{CO} of $[\text{Ni}(\text{CO})_3\text{PX}_3]$ with varying X from $\text{Me, OMe, OAr, Cl, F}$ with respect to CO . (25 marks)
- (b)(i) $[\text{TiEt}_4]$ does not exist at room temperature whereas $[\text{PbEt}_4]$ is stable at temperatures below 100°C . Explain why this is so.
- (ii) Write possible pathways for the decomposition of $[\text{TiEt}_4]$, giving the products in each case. (20 marks)
- (c) *fac*- $[\text{Pd}(\text{Me})_3(\text{NMe}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]$ undergoes reductive elimination to give the square planar complex $[\text{Pd}(\text{Me})(\text{NMe}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]$.
- (i) What is the molecule that is eliminated?
- (ii) Write the changes in the Valence Electron Count (VEC), oxidation number and the coordination number of the metal. (20 marks)

- (d) $[\text{Co}(\text{CO})_4]^\cdot$ radical dimerizes to give $[\text{Co}_2(\text{CO})_8]$, which in the solid state has one Co-Co bond and two bridging carbonyls. In solution, however, it has no bridging carbonyl ligand.
- Calculate the Valence Electron Count (VEC) of the species $[\text{Co}(\text{CO})_4]^\cdot$ and $[\text{Co}_2(\text{CO})_8]$.
 - Draw the structures of the complex $[\text{Co}_2(\text{CO})_8]$ in solid state and in solution.
 - How are these distinguished from one another using spectroscopic method(s)?

Write a method of synthesis of $[\text{Co}_2(\text{CO})_8]$ starting from $\text{Co}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$, giving only the reagents and conditions used. (35 marks)

- 6.(a) $[\text{Mo}(\text{CO})_6]$ reacts with two moles of PPh_3 to give a tetracarbonyl Mo(0) complex A, which shows only one infra-red band in the carbonyl region. (20 marks)
- Deduce the structure of A.

- (b) The presence of M-H group in a metal hydride is confirmed by converting the M-H group to M-D (D = deuterium, ^2_1H) group and recording the infra-red spectrum. Where will the new M-D stretching appear with respect to the position of M-H stretching?

Give reason(s) for your answer.

Calculate the $\nu(\text{Ir-D})$ value if $\nu(\text{Ir-H})$ is 2240 cm^{-1} . (20 marks)

- (c) Give **three** reasons as to why transition metal complexes are used as catalyst. Distinguish between homogeneous catalyst and heterogeneous catalyst, giving **one** example of each. (20 marks)

- (d)(i) The monohydride $[\text{RuHCl}(\text{PPh}_3)_3]$ is coordinately unsaturated and catalyses hydrogenation of olefins. Write a possible mechanism for the hydrogenation of ethene by $[\text{RuHCl}(\text{PPh}_3)_3]$.

- (ii) Draw the catalytic cycle for the hydroformylation of $\text{RCH}_2=\text{CH}_2$ to $\text{RCH}_2\text{CH}_2\text{CHO}$ using $[\text{RhH}(\text{CO})(\text{PPh}_3)_2]$ as active catalyst (Union Carbide Process). (40 marks)

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