



FINAL EXAMINATION-2021/2022

CYU5300 ORGANOMETALLIC CHEMISTRY

Date: 21st October 2022 (Friday)

Time 2.00 – 4.00 p.m.

Answer ALL FOUR (04) questions.

1. (a) Give the IUPAC name of $[\text{FeBr}(\text{CH}=\text{CH}_2)(\eta^6\text{-C}_6\text{H}_6)(\text{CO})]$. (10 marks)
- (b) Draw the structures of the following complexes.
 (i) $[\text{FeBr}(\text{CH}=\text{CH}_2)(\eta^6\text{-C}_6\text{H}_6)(\text{CO})]$
 (ii) Tricarbonyl(η^3 -cyclopentadienyl)(η^2 -ethene) (20 marks)
- (c) (i) Determine the valence electron count (VEC) of the complex tricarbonyl(η^3 -cyclopentadienyl)(η^2 -ethene)methylmolybdenum using the **covalent model**. (Indicate in your work out, the electron contribution made by each ligand).
 (ii) What is the coordination number of Mo in this complex? (Group no. of Mo = 6) (14 marks)
- (d) Draw all possible isomers of $[\text{FeBr}_2(\text{CO})_2(\text{PPh}_3)_2]$ (20 marks)
- (e) Using an orbital diagram explain the bonding between the metal (Mo) and $\text{C}\equiv\text{O}$ in $[\text{Mo}(\text{CO})_6]$. (16 marks)
- (f) Oxidative addition of MeBr to $[\text{IrBr}_2(\text{CO})_2]^-$ gives (A). (A) with CO gives (B). (B) reductively eliminates (C) to regenerate $[\text{IrBr}_2(\text{CO})_2]^-$. Identify (A), (B) and (C). (20 marks)
2. (a) Arrange $\text{H}_2\text{C}=\text{CH}_2$, $\text{FCH}=\text{CHF}$ and $\text{MeCH}=\text{CHMe}$ in the order of increasing π -acceptability. Give your reasons. (10 marks)
- (b) Explain why $[\text{Ni}(\text{CO})_4]$ is stable at room temperature, but $[\text{Ni}(\text{NH}_3)_4]$ does not exist. (15 marks)
- (c) How would you account for the variation in the CO stretching frequencies in the following compounds?
- | Compound | $\nu(\text{CO})$ in cm^{-1} |
|---|--------------------------------------|
| free CO | 2143 |
| <i>fac</i> - $[\text{Mo}(\text{CO})_3(\text{PCl}_3)_3]$ | 2040, 1991 |
| <i>fac</i> - $[\text{Mo}(\text{CO})_3(\text{PET}_3)_3]$ | 1937, 1841 |
- (20 marks)
- (d) Suggest starting material(s) used or active catalyst(s) or the product formed regarding the following reactions/conversions.
 (i) ? + NaOEt \rightarrow $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(=\text{CH}_2)\text{Me}]$
 (ii) $[\text{Fe}(\text{CO})_5] + \text{LiMe} \rightarrow$?
 (iii) Give the active catalyst formed during Monsanto acetic acid synthesis?
 (iv) $[\text{Co}_2(\text{CO})_8] + \text{H}_2 \rightarrow$? (20 marks)

- (e) Reaction of azobenzene, PhN=NPh, with $[\text{PdCl}_2]$ gives the cyclometallated chloride-bridged palladium(II) dimer containing two 5-membered chelate rings. Draw the structure of this dimeric complex. (15 marks)
- (f) If $[\text{Ni}(\text{PR}_3)_2]$ catalyzes the hydrocyanation of $\text{CH}_2=\text{CH}_2$ to give $\text{CH}_3\text{CH}_2\text{CN}$. Give the intermediates formed in terms of (i) oxidative addition, (ii) olefin coordination and (iii) migratory insertion. (20 marks)
3. (a) What is the major product formed due to cross-coupling of PhBr with $\text{CH}_2=\text{CHSnBu}_3$ in the presence of the catalyst $[\text{Pd}(\text{PPh}_3)_4]$. (10 marks)
- (b) (i) What is meant by "agostic interaction"?
 (ii) $[\text{W}(\text{CO})_3(\text{PCy}_3)_2]$ has an octahedral **mer-arrangement** with one agostic type interaction. Draw the structure of the complex and identify the type of agostic interaction associated with it? (20 marks)
- (c) (i) Define the terms Turnover number (TON) and Turnover frequency (TOF).
 (ii) In the presence of a palladium catalyst (0.00001 mmol), MeI (8.0 mmol) reacts completely with $\text{MeCH}=\text{CH}_2$ (8.0 mmol) to give butene. The reaction time is 20 min. Calculate the Turnover number (TON) and Turnover frequency (TOF). (20 marks)
- (d) Methane and a Ir-complex (**D**) is produced when $[\text{MeIr}(\text{PMe}_3)_3]$ is heated in an atmosphere of H_2 . Identify the Ir-complex (**D**) and write the molecular formula of probable octahedral intermediate (**E**). (15 marks)
- (e) The active catalyst $[\text{RuHCl}(\text{PPh}_3)_3]$ coordinates with $\text{CH}_2=\text{CH}_2$ to give the olefin-complex (**P**). (**P**) undergoes migratory insertion to give the alkyl-complex (**Q**). (**Q**) reacts with H_2 to give the dihydrogen-complex (**R**) which eliminates (**S**) to regenerate $[\text{RuHCl}(\text{PPh}_3)_3]$. Identify (**P**), (**Q**), (**R**) and (**S**). (20 marks)
- (f) Calculate the $\nu(\text{Pt-D})$ value if the $\nu(\text{Pt-H})$ value is 2200 cm^{-1} . (15 marks)
4. Predict the major product(s) formed of each of the following reactions, using the hint given in the brackets.
- (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CH}_2\text{CH}_3)(\text{CO})_3] + \text{Ph}_3\text{CBF}_4 \rightarrow$ (proton abstraction) (10 marks)
- (b) $[\text{Mo}(\text{CO})_6] + \text{Toluene} \rightarrow$ (tri-substitution) (10 marks)
- (c) $\text{cis-}[\text{PtCl}(\text{CH}_2\text{CH}_2\text{Me})(\text{PMe}_3)_2] \xrightarrow{\Delta}$ (β -H abstraction) (10 marks)
- (d) $[\text{Fe}(\text{PMe}_3)_4] \rightarrow$ (cyclometallation) (10 marks)
- (e) $\text{cis-}[\text{IrH}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{PPh}_3)_2] + \text{PPh}_3 \rightarrow$ (association & then insertion) (12 marks)
- (f) $[(\eta^5\text{-C}_5\text{H}_5)\text{WMe}(\eta^2\text{-CH}_2=\text{CH}_2)]^+ + \text{Me}^- \rightarrow$ (nucleophilic addition) (12 marks)
- (g) $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{FeC}\equiv\text{CPh}] + \text{Me}_3\text{O}^+ \rightarrow$ (electrophilic attack) (12 marks)
- (h) $[(\eta^5\text{-Cp})\text{Rh}(\text{CO})_2] + \text{MeI} \rightarrow$ (2e-oxidative addition) (12 marks)
- (i) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}]^+ + \text{LiMe} \rightarrow$ (nucleophilic addition) (12 marks)