

The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc/B.Ed Degree Programme



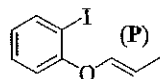
Department	: Chemistry
Level	: 5
Name of the Examination	: Final Examination
Course Code and Title	: CYU5300 Organometallic Chemistry
Academic Year	: 2020/2021
Date	: 16-12-2021
Time	: 1.30 – 3.30 p.m.
Duration	: 2 hours

General Instructions

1. **Read all instructions carefully** before answering the questions.
 2. This question paper consists of **04** questions in 03 pages.
 3. **Answer all 04 questions**. All questions carry equal marks.
 4. Answer for each question should commence from a new page.
 5. Draw fully labelled diagrams where necessary.
 6. Having any unauthorized documents/mobile phones in your possession is a punishable offense.
 7. Use **blue** or **black** ink to answer the questions.
 8. Circle the number of the questions you answered in the front cover of your answer script.
 9. Clearly state your **index number** in your answer script.
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1. (a) Give the IUPAC name of $[\text{Fe}(\text{CN})(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_4\text{H}_6)]$. (10 marks)
- (b) Draw the structures of the following complexes.
 (i) bromocarbonyl(η^4 -cyclobutadiene)(η^2 -ethyne)methyltungsten
 (ii) dicarbonyl(η^5 -cyclopentadienyl)(η^2 -ethene)ethenylmolybdenum (20 marks)
- (c) (i) Determine the Valence Electron Count (VEC) of the complex $[\text{RhF}(\text{CN})(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-C}_4\text{H}_4)]$ using the **covalent model**. (Indicate in your workout, the electron contribution made by each ligand, Rh is a Group 9 metal).
 (ii) What is the coordination number of Rh in this complex? (15 marks)
- (d) Determine the coordination geometry of the Fe-NO fragment in the 18e-complex $[\text{FeCl}(\text{NO})(\text{CO})_4]$, Atomic number of Fe is 26. (15 marks)
- (e) $[\text{CoH}(\text{CO})_4]$ is a stronger acid than $[\text{CoH}(\text{CO})_3(\text{PPh}_3)]$. Explain. (10 marks)
- (f) Arrange CN^- , NH_3 , NO^+ and CO in the order of **increasing** π -acceptability. (10 marks)
- (g) (i) Draw and name **three** coordination modes of a hydride ligand. Give an example each.
 (ii) What are polyhydrides? (20 marks)
- (h) Using an orbital diagram explain the bonding between Ag and PPh_3 in $[\text{AgCl}(\text{PPh}_3)]$ (15 marks)
2. (a) (i) Draw the **three** isomers of $[\text{Mo}(\text{CO})_3(\text{CS})(\text{PPh}_3)_2]$.
 (ii) Comment on the optical isomerism of above isomers. (20 marks)
- (b) What structural changes would you expect for an 2e-oxidative addition process of a d^8 metal center? Explain giving an example. (20 marks)
- (c) $[(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2]_2$ is reduced with Na to afford (A). (A) with methyl iodide affords (B). (B) can be prepared by reacting (C) with LiMe . Identify (A), (B) and (C). (15 marks)
- (d) What are the two **alkenes** formed due to decomposition of $[(\text{OC})_3\text{RhCH}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2\text{CF}_3]$? (10 marks)
- (e) Suggest reagent(s) used to carry out the following conversions.
 (i) $[\text{TiCl}_4] \rightarrow [\text{TiCl}_3(\text{Me})]$
 (ii) $[(\eta^5\text{-C}_5\text{Me}_5)\text{W}(\text{CO})_3] \rightarrow [(\eta^5\text{-C}_5\text{Me}_5)\text{W}(\eta^2\text{-H}_2)(\text{CO})_3]^+$
 (iii) $[\text{Ru}(\text{CO})_5] \rightarrow [(\text{OC})_4\text{Ru-C}(=\text{O})\text{H}]^+$ (15 marks)
- (f) Palladium complexes are widely used in catalysis. Explain giving reasons. (10 marks)

- (g) The following molecule (**P**) undergoes an intramolecular Heck reaction to give the derivative (**Q**). Draw the structure of (**Q**). (10 marks)



3. (a) What is an agostic interaction?
Assume that *trans*-[PdI₂(CO)(PPh₃)] (**D**) shows square-pyramidal arrangement with **one agostic type interaction via the apical position**. Draw the structure of complex (**D**) and identify the type of agostic interaction associated with it? (20 marks)
- (b) *cis*-[PtI₂(NMe₃)₂] reacts with one mole of AlMe₃ to give a Pt(II) complex (**E**).
(**E**) reacts with MeMgBr to give another 16e Pt(II) complex (**F**).
(**F**) undergoes a disubstitution reaction with **dppe** to yield the 16e Pt(II) complex (**G**).
In the presence of another mole of **dppe**, (**G**) reductively eliminates an alkane (**H**) to generate the 18e Pt(0) complex (**I**). **Identify (E), (F), (G), (H) and (I)**.
(dppe = PPh₂CH₂CH₂PPh₂ and it is a bidentate ligand) (40 marks)
- (c) The active catalyst [Pd(PPh₃)₂] reacts with PhI to give the *cis*-Pd(II) complex (**X**). (**X**) reacts with CH₂=CH₂ to give the 5-coordinate intermediate (**Y**). Migratory insertion of the phenyl group gives the 16e-complex (**Z**). **Identify (X), (Y) and (Z)**. (20 marks)
- (d) Reaction of *E*-Pinacolone oxime, Bu^tC(=NOH)Me, with [PdCl₂(NPh)₂] and NaOAc gives the cyclometallated chloride-bridged palladium(II) dimer, which contains a 5-membered chelate ring.
Draw the **structure** of this dimeric complex. (10 marks)
- (e) What are the **two** isomeric organic molecules that can be formed due to hydroformylation of the olefin CF₃CH₂CH=CH₂ using a metal catalyst? (10 marks)
4. Predict the **major product(s)** formed by each of the following reactions, using the hint given in the brackets.
- (a) [(η⁵-C₅Me₅)Co(CO)(PMe₃)] + MeI → (2e-oxidative addition) (10 marks)
- (b) [(acac)Ni(Ph)(PPh₃)] + PhC≡CPh → (coordination + insertion) (10 marks)
- (c) [(η⁵-C₅H₅)Ru(η⁶-C₆H₆)]⁺ + LiMe → (nucleophilic addition) (12 marks)
- (d) [Re(CH₂CH=CH₂)(CO)₅] → (loss of molecule + coordination) (10 marks)
- (e) [(η⁵-Cp)(Ph₃P)₂FeC≡CPh] + Me₃O⁺ → (electrophilic attack) (12 marks)
- (f) *cis*-[PtCl(Et)(PMe₃)₂] $\xrightarrow{\Delta}$ (β-H abstraction) (12 marks)
- (g) [(C₅Me₅)(OC)₂Fe(η¹-CH₂CH=CH₂)] + HBr → (electrophilic addition) (12 marks)
- (h) 3-Bromothiophene + PhB(OH)₂ → (Suzuki coupling) (12 marks)
- (i) *cis*-[NiCN(CH₂CH₃)(PPh₃)₂] → (reductive elimination) (10 marks)

