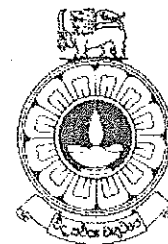




The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc/ B. Ed Degree Programme



Department	: Chemistry
Level	: 5
Name of the Examination	: Final Examination
Course Code and Title	: CYU5300/CMU3122 Organometallic Chemistry
Academic Year	: 2019/2020
Date	: 04-01-2020
Time	: 1.30 – 3.30 p.m.
Duration	: 2 hours
Index number	:

General Instructions

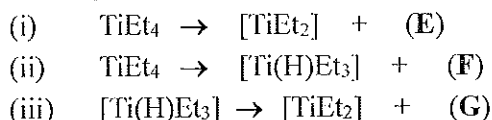
1. **Read all instructions carefully** before answering the questions.
 2. This question paper consists of 06 questions in 05 pages.
 3. Answer 04 questions only. All questions carry equal marks.
 4. Answer for each question should commence from a new page.
 5. Draw fully labelled diagrams where necessary
 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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Questions 1, 2, 3 and 4 are **COMPULSARY** for students registered for CYU5300. Questions 5 and 6 are **ONLY** for students registered for CMU3122.

1. (a) (i) Give the IUPAC name of $[\text{PtCl}(\text{Me})(\eta^2\text{-C}_2\text{H}_4)(\text{CO})]$ (**A**).
 (ii) Draw the structures of three geometrical isomers of (**A**). (20 marks)
- (b) Draw the structures of the following complexes.
 (i) $[\text{Fe}(\text{CN})(\text{CO})(\eta^3\text{-C}_5\text{H}_5)(\eta^4\text{-C}_4\text{H}_4)]$
 (ii) $(\eta^1\text{-allyl})\text{tricarbonyl}(\eta^5\text{-cyclopentadienyl})\text{molybdenum}$ (20 marks)
- (c) (i) Determine the valence electron count (VEC) of the complex $(\eta^1\text{-allyl})\text{tricarbonyl}(\eta^5\text{-cyclopentadienyl})\text{molybdenum}$, 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) $\text{K}_3[\text{Co}(\text{CN})_5]$ activates H_2 homolytically. Write a balanced equation for this reaction. (10 marks)
- (e) Using an orbital diagram explain the bonding between a metal (M) and the ligand in $[\text{M}-\text{C}\equiv\text{CMe}]$. (16 marks)
- (f) Suggest **reagent(s)** or **active catalyst(s)** which can be used to carry out the following conversions.
 (i) $\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{CO}_2\text{H}$
 (ii) $[\text{Fe}(\text{CO})_5] \rightarrow [\text{HFe}(\text{CO})_4]^-$
 (iii) $\text{CH}_2=\text{CH}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{CHO}$
 (iv) $[\text{TiCl}_4] \rightarrow [\text{TiCl}_3(\text{Me})]$ (20 marks)
2. (a) (i) $[\text{Co}_2(\text{CO})_8]$ is a coordinatively saturated symmetrical compound. Using valence electron count, show that there is a metal-metal bond.
 (ii) In the solid state it shows bridging carbonyl ligands, draw the structure of the solid $[\text{Co}_2(\text{CO})_8]$. (Group no. of Co = 9)
 (iii) Arrange the following compounds in the increasing order of carbonyl stretching frequency. **Explain** your answer.
 $[\text{Rh}(\text{CF}_3)(\text{CO})(\text{PEt}_3)_2]$, $[\text{RhMe}(\text{CO})(\text{PEt}_3)_2]$ and $[\text{RhI}(\text{CO})(\text{PEt}_3)_2]$. (25 marks)
- (b) Draw the structures of four isomers of $[\text{RuBr}_2(\text{dppe})(\text{CO})_2]$.
 $\text{dppe} = \text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ is a **bidentate** ligand. (20 marks)
- (c) Reduction of the carbonyl-bridged dimer $[(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2]_2$ with K gives the mononuclear 18e-salt (**B**). (**B**) reacts with allyl iodide ($\text{CH}_2=\text{CHCH}_2\text{I}$) to give the neutral 18e-complex (**C**) and KI. Upon heating, (**C**) is converted into an 18e-complex (**D**) with a loss of carbonyl ligand. Identify (**B**), (**C**) and (**D**). (30 marks)

- (d) (i) What is a carbene ligand?
 (ii) Give an example each for **Fischer** and **Schrock** carbenes.
 (iii) Write a short account on Fischer carbenes. (25 marks)

3. (a) TiEt_4 decomposes as shown below. (20 marks)



Identify the type of each reaction (i), (ii) and (iii); and the molecules **(E)**, **(F)** and **(G)**.

- (b) (i) What is an agostic interaction?
 (ii) $[(\eta^5\text{-C}_5\text{H}_5)\text{Co(Et)(PMe}_3\text{)}]^+$ (**K**) has an agostic ethyl group. Draw the structure of **(K)**.
 Draw the structure of expected 18e-cobalt hydride (**L**) that would be formed due to the cleavage of this agostic C–H bond. (20 marks)

- (c) The alkoxyCo(I) complex $[(\text{OC})_3\text{CoOCH}_2\text{Ph}]$ undergoes β -hydride abstraction to give the aldehyde (**M**) and the 16e Co(I) complex (**N**). (**N**) reacts with $\text{CH}_2=\text{CH}_2$ to give the 16e alkyl-complex (**O**). In the presence of carbon monoxide, (**O**) undergoes migratory insertion reaction to give the acyl complex (**P**).
 Identify the compounds **(M)**, **(N)**, **(O)** and **(P)**. (40 marks)

- (d) (i) **Define** the terms Turnover number (TON) and Turnover frequency (TOF).
 (ii) In the presence of the catalyst $[\text{Pd}(\text{PPh}_3)_4]$ (2×10^{-5} mmol), iodoethane (24 mmol) reacts **completely** with $\text{CH}_2=\text{CH}_2$ (24 mmol) to give 1-butene. The reaction time is 5 min. Calculate TON and TOF for this process. (20 marks)

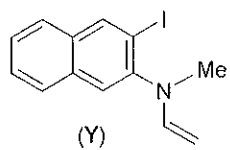
4. Predict the **major product(s)** formed of each of the following reactions, **using the hint given in the brackets**.

- (a) $[\text{Fe}(\text{CO})_5] + 1,3\text{-butadiene} \rightarrow$ (disubstitution) (10 marks)
 (b) $2[\text{Co}(\text{CN})_5]^{3-} + \text{CH}_3\text{CH}_2\text{I} \rightarrow$ (1e-oxidative addition) (10 marks)
 (c) $\text{fac-}[\text{RhI}_3(\text{COMe})(\text{CO})_2]^- \rightarrow$ (reductive elimination) (12 marks)
 (d) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TaMe}_2]^{\dagger} + \text{NaOMe} \rightarrow$ (deprotonation) (10 marks)
 (e) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr(H)Cl}] + \text{MeC}\equiv\text{CMe} \rightarrow$ (coordination + insertion) (12 marks)
 (f) $[\text{CpFe}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{CO})_2]^{\dagger} + \text{NMe}_3 \rightarrow$ (nucleophilic attack on olefin) (10 marks)
 (g) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{N}_2)_2] + 2 \text{CH}_2=\text{C}=\text{CH}_2 \rightarrow$ (substitution + oxidative coupling) (12 marks)

- (h) 2-Bromopyridine + PhMgBr \rightarrow (Grignard coupling) (12 marks)
- (i) $[(\eta^5\text{-Cp})\text{Fe}(\eta^1\text{-CH}_2\text{CH=CH}_2)(\text{CO})_2] + \text{HCl} \rightarrow$ (electrophilic addition) (12 marks)

Questions 5 and 6 are ONLY for students registered for CMU3122.

5. (a) Iodobenzene oxidatively adds to $[\text{RhH}(\text{PPh}_3)_3]$ to give the 18e-complex (**J**). (**J**) reductively eliminates an aromatic hydrocarbon (**K**) while forming an 16e-complex (**L**). With PhLi, (**L**) gives the phenyl-complex (**M**). Coordination of $\text{CH}_2=\text{CH}_2$ 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) The 18e-cation $[(\eta^2\text{-Cp})_2\text{MoH}(\eta^2\text{-CH}_2=\text{CH}_2)]^+$ reacts with hydride ion (H^-) to give the **neutral** 18e complex (**Q**) which in the presence of PPh_3 gives the 18e-complex (**R**) and eliminates an organic molecule. Identify (**Q**) and (**R**).
 (ii) *trans*- $[\text{PdMe}_2(\text{PPh}_3)_2]$ does not form ethane easily. **Explain.** (28 marks)
- (c) Acetophenone $\text{Ph}(\text{C}=\text{O})\text{Me}$ reacts with hydrazine (NH_2NH_2) to give the E-hydrazone (**X**). The reaction of (**X**) with $[\text{PdCl}_2(\text{NCPH}_2)_2]$ activate the methyl group to give the chloride-bridged Pd(II) dimer (**Y**) containing a 5-membered chelate ring. Draw the **structures** of (**X**) and (**Y**). (20 marks)
- (d) What are the **two** aldehydes formed by hydroformylation of $\text{PhCH}_2\text{CH}=\text{CH}_2$? (10 marks)
6. (a) How would you prepare the **acyl** cation $[\text{Pt}\{\text{C}(=\text{O})\text{Et}\}(\text{CO})_3]^+$ from $[\text{PtH}(\text{CO})_3]^+$. (20 marks)
- (b) $[\text{NiH}(\text{CN})(\text{PPh}_3)_2]$ catalyzes the hydrocyanation of $\text{PhCH}=\text{CH}_2$ to give $\text{PhCH}_2\text{CH}_2\text{CN}$. Draw the catalytic cycle for this process. (30 marks)
- (c) How would you account for the variation in the $\text{N}\equiv\text{N}$ stretching frequency of the following compounds?
- | Compound | $\nu(\text{N}\equiv\text{N})$ in cm^{-1} |
|-----------------------------|---|
| free N_2 | 2330 |
| $[\text{Ni}(\text{N}_2)]$ | 2088 |
| $[\text{Ni}(\text{N}_2)_2]$ | 2187 |
- (15 marks)
- (d) The following molecule (**Y**) undergoes an intramolecular Heck reaction to give the derivative (**Z**). Draw the structure of (**Z**). (15 marks)



- (e) (i) **Draw and name** three coordination modes of hydride ligand.
Give an example each.
- (ii) What are polyhydrides?

(20 marks)

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