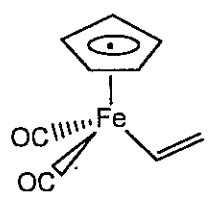
THE OPEN UNIVERSITY OF SRI LANKA

B.Sc./B.Ed. DEGREE /STAND ALONE COURSES IN SCIENCE - LEVEL 5
FINAL EXAMINATION - 2011/2012
CMU3122/CME5122 ORGANOMETALLIC CHEMISTRY
CHU3127/CHE5127 ORGANOMETALLIC CHEMISTRY

Date: 3rd January 2012 (Tuesday) 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.**

1. (a) Give IUPAC names for each of the following complexes.
   (i) $[Co(Me)(CN)(CO)(\eta^3\text{-}C_3H_5)]$
   (ii)



(20 marks)

(b) Draw the **structure** of the following complex,
Dibromo(η^4-1,3-butadiene)carbonyl(η^2-ethene)molybdenum. (15 marks)

(c) Determine the valence electron count (**VEC**) of the complex $[Co(\eta^1\text{-}C_3H_5)(CO)(\eta^4\text{-}C_4H_4)(\eta^2\text{-}C_2H_4)]$ using the **ionic model.** (Indicate in your work out, the electron contribution made by each ligand. Co is a Group 9 metal). (15 marks)

(d) $K_3[Co(CN)_5]$ activates H_2 homolytically. Write a balanced equation for this reaction. Using the ionic model, determine the oxidation numbers of both cobalt centres. (15 marks)

(e) List the following compounds/ions in the **increasing order** of π-acceptability.
MeCH=CHMe, FCH=CHF, $H_2C{=}CH_2$, NO^+ (Reasons not required) (15 marks)

(f) Explain, using orbital diagrams, the bonding between Fe and CO in $[Fe(CO)_5]$. (20 marks)

2. (a) The chelating diphosphine complex $[(PPh_2CH_2CH_2PPh_2)PdMe_2]$ undergoes reductive elimination 100 times slower than the analogous complex with the monodentate phosphine ligands, *cis*-$[(PPh_3)_2PdMe_2]$. Explain. (25 marks)

(b) Draw the structures of four isomers of $[RuBr_2(dppe)(CO)_2]$. dppe = $PPh_2CH_2CH_2PPh_2$ is a bidentate ligand. (25 marks)

(c) How would you account for the variation in the CO stretching frequencies ν(CO) in the following compounds?

Compound	**ν(CO)** in cm^{-1}
free CO	2143
fac-$[Mo(CO)_3(PCl_3)_3]$	2040, 1991
fac-$[Mo(CO)_3(PEt_3)_3]$	1937, 1841

(25 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) The tetrahedral d^{10} complex $[Pd(PPh_3)_4]$ undergoes a 2e-oxidative addition reaction with HBr to give a square planar neutral hydrido-complex (**X**).
(i) What is the molecular formula of (**X**)?
(ii) **Draw** and **identify** the two isomers of (**X**). (20 marks)

(b) (i) Define the terms Turnover number (TON) and Turnover frequency (TOF).
(ii) In the presence of the catalyst $[Pd(PPh_3)_4]$ ($2x10^{-5}$ mmol), iodoethane (12.0 mmol) reacts completely with $CH_2{=}CH_2$ (12.0 mmol) to give 1-butene. The reaction time is 10 min. Calculate TON and TOF for this process. (30 marks)

(c) What are the coordination modes of dinitrogen? Give an example for each mode. (20 marks)

(d) What is meant by an "agostic interaction"?
$[RuCl_2(PPh_3)_3]$ has an **octahedral** arrangement with **one** agostic type interaction. Draw the structure of the complex and **identify** the type of agostic interaction associated with it. (20 marks)

(e) What are the two **alkenes** formed due to decomposition of $[(OC)_3CoCH(CH_2Ph)CH_2CH_3]$? (10 marks)

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

(a) $[(\eta^5\text{-Cp})Rh(CO)_2]$ + MeI → (2e-oxidative addition) (10 marks)

(b) $[(\eta^5\text{-Cp})_2Fe]$ + NaH → (nucleophilic attack on coordinated ligand) (12 marks)

(c) $[RhCl(PPh_3)_3]$ + LiC≡CR → (substitution) (10 marks)

(d) $[(\eta^5\text{-}C_5H_5)Zr(N_2)_2]$ + 2 $CH_2{=}C{=}CH_2$ → (oxidative coupling) (12 marks)

(e) $[RhMe(PPh_3)_3] \xrightarrow{\Delta}$ (cyclometallation and loss of methane) (12 marks)

(f) $[Mn(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_5] \xrightarrow{\Delta}$ (loss of a molecule and coordination) (12 marks)

(g) $[(\eta^5\text{-}C_5H_5)_2(Ph)W(\eta^2\text{-}CH_2{=}CH_2)]^+$ + LiMe → (nucleophilic attack on a coordinated ligand) (10 marks)

(h) $[CpFe(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_2]$ + MeI → (electrophilic attack on a coordinated ligand) (10 marks)

(i) $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$ + Ph_3CBF_4 → (hydride abstraction) (12 marks)

5. (a) The alkoxy Rh(I) complex $[(OC)_3RhOCH_2CH_3]$ undergoes β-hydride abstraction to give the aldehyde (**A**) and the 16e-Rh(I) complex (**B**). (**B**) reacts with $CH_2{=}CH_2$ to give the square-planar alkyl-complex (**C**). In the presence of carbon monoxide, (**C**) undergoes migratory insertion reaction to give the acyl complex (**D**). Deduce the identity of compounds (**A**), (**B**), (**C**) and (**D**). (40 marks)

(b) (i) What are polyhydrides? Give an example of a polyhydride.

(ii) Calculate the ν(Pt–D) value if the ν(Pt–H) value is 2200 cm^{-1}. (20 marks)

(c) Suggest **reagent(s)** or **catalysts** which can be used to carry out the following conversions.

(i) $[Co_2(CO)_8]$ → $[HCo(CO)_4]$
(ii) $[W(CO)_6]$ → $[HW(CO)_5]$
(iii) $CH_2{=}CHCH{=}CH_2$ + 2 HCN → $NC(CH_2)_4CN$
(iv) $[(\eta^5\text{-Cp})_2Ta(Me)_2]^+$ → $[(\eta^5\text{-Cp})_2Ta(=CH_2)(Me)]$
(v) $[Fe(CO)_5]$ → $Na[Fe\{C(=O)H\}(CO)_4]$ (40 marks)

6. (a) $[RhCl(PPh_3)_3]$ catalyses the hydrogenation of $CH_2{=}CH_2$ *via* **hydride mechanism.** Draw the catalytic cycle for this process and identify the catalytic intermediates formed. (40 marks)

(b) Write the balanced equations for the following reactions in the "Monsanto Process".
(i) formation of MeI
(ii) catalytic carbonylation of MeI
(iii) conversion of the product formed in (ii) to the desired product. (30 marks)

(c) (i) What is the catalytic-system used in the "Wacker Process"?
(ii) The Wacker process is based on a combination of three reactions. Write chemical equations for these three reactions. (30 marks)

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