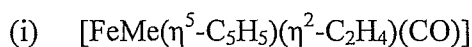THE OPEN UNIVERSITY OF SRI LANKA

B.Sc./B.Ed DEGREE IN SCIENCE-LEVEL 5

FINAL EXAMINATION-2016/2017

CMU3122/CHU3127 ORGANOMETALLIC CHEMISTRY

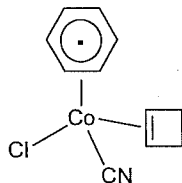Date: 30th July 2017   Time: 1.00 – 3.00 pm

Answer any **FOUR** (04) questions. If more than four questions are answered, **only the first four answers will be marked.**
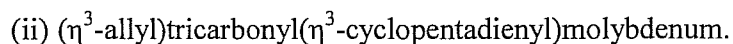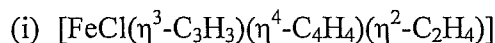
1. (a) Give the IUPAC name of the following complexes.   (20 marks)
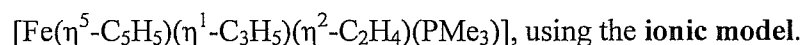
      (i) $[FeMe(\eta^5-C_5H_5)(\eta^2-C_2H_4)(CO)]$

      (ii)

  (b) Draw the structures of the following complexes.   (20 marks)

      (i) $[FeCl(\eta^3-C_3H_3)(\eta^4-C_4H_4)(\eta^2-C_2H_4)]$

      (ii) (η^3-allyl)tricarbonyl(η^3-cyclopentadienyl)molybdenum.

  (c) Determine the valence electron count (VEC) of the complex

      $[Fe(\eta^5-C_5H_5)(\eta^1-C_3H_5)(\eta^2-C_2H_4)(PMe_3)]$, using the **ionic model**.

      (Indicate in your work out, the electron contribution made by each ligand) (15 marks)

  (d) What is the **active catalyst** used in

      (i) Roelen Process and (ii) Shell Process   (12 marks)

  (e) Using an orbital diagram explain the bonding between a metal (M)

      and a -C≡CR group.   (18 marks)

  (f) (i) Arrange CN^-, NMe_3, CS, and CO, in the increasing order of π-acceptability.

      (ii) Give an **atom** which is isoelectronic with BH_4^- (15 marks)

2. (a) (i) Give an example **each** for a Fischer-carbene and a Schrock-carbene.

(ii) Give **three** main differences between Fischer-carbenes and Schrock-carbenes.

(25 marks)

(b) List the following compounds in the **increasing order** of the IR frequency of the carbonyl band. **Explain.**

$[Fe(CO)_4(PPh_3)]$, $[Fe(CO)_4(PF_3)]$ and $[Fe(CO)_4(PMe_3)]$ (20 marks)

(c) (i) Draw the structures of the **four geometrical** isomers with the **tetragonal pyramidal** geometry for $[FeBr_2(CO)(dppe)]$.

dppe = $PPh_2CH_2CH_2PPh_2$ and it is a bidentate ligand.

(ii) Draw the structures if there are optical isomers.   (24 marks)

(d) The presence of Rh-H group in a metal hydride is confirmed by converting the Rh-H group into Rh-D (D = deuterium, $_1^2H$) group and recording the infra-red spectrum.

(i) How would you convert Rh-H into Rh-D?

(ii) Calculate the $v(Rh-D)$ value if $v(Rh-H)$ is 2200 cm^{-1}.   (16 marks)

(e) Give **three** main differences between M–(alkene) and M–alkyl bonds.   (15 marks)

3. (a) Write the possible pathways for the decomposition of $[TaEt_4]$.

Group number of Ta is 4.   (20 marks)

(b) How would you prepare the **acyl complex** $[(\eta^5\text{-}Cp)(PPh_3)_2RuC(=O)Et]$ from $[(\eta^5\text{-}Cp)RuH(PPh_3)_2]$?   (20 marks)

(c) The **chelating** diphosphine complex $[PdMe_2(PPh_2CH_2CH_2PPh_2)]$ (**A**) undergoes reductive elimination 100 times slower than the analogous complex with the monodentate phosphine ligands, cis-$[PdMe_2(PPh_3)_2]$ (**B**). **Explain.**   (20 marks)

(d) (i) What is an agostic interaction?

(ii) **Assume** that $[RhCl(PPh_3)_3]$ (**P**) shows **trigonal bipyramidal** arrangement with the chloride ligand in the **equatorial plane.** Draw the **structure** of (**P**) and identify the type of agostic interaction associated with it?

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(iii) **(P)** undergoes cyclometallation to give a Rh(III) hydride **(Q)**.

Draw the **structure** of **(Q)**. (30 marks)

(d) $K_3[Rh(CN)_5]$ activates H_2 homolytically.

Write a balanced equation for this reaction. (10 marks)

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

(a) *trans*-$[IrBr(CO)(PMe_3)_2]$ + MeBr $\rightarrow$ (2e-oxidative addition) (10 marks)

(b) *cis*-$[PtCl_2(PEt_3)(\eta^2\text{-}CH_2=CH_2)]$ + pyridine $\rightarrow$ (nucleophilic addition
on coordinated ligand) (12 marks)

(c) *mer,trans*-$[IrI_2(Me)(CO)_3]$ $\rightarrow$ (reductive elimination) (10 marks)

(d) $[(\eta^5\text{-}C_5Me_5)_2TiMe_2]^+$ + KOEt $\rightarrow$ (deprotonation) (12 marks)

(e) $[(\eta^5\text{-}C_5H_5)_2Zr(H)CF_3]$ + $CF_3CH=CHCF_3$ $\rightarrow$ (coordination & insertion) (12 marks)
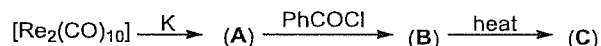
(f) $[(dppe)PtCl_2]$ + $LiCH_2CH_2CH_2CH_2Li$ $\rightarrow$ (nucleophilic di-substitution) (10 marks)
(dppe = $PPh_2CH_2CH_2PPh_2$)

(g) $[Ru(CO)_5]$ + cyclobutadiene $\xrightarrow{\Delta}$ (di-substitution) (10 marks)

(h) $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]^+$ + NaH $\rightarrow$ (nucleophilic addition) (12 marks)

(i) *trans*-$[Pt(PEt_3)_2Me_2]$ $\xrightarrow{\Delta}$ (cyclometallation and loss of methane) (12 marks)

5. (a) Identify **(A)**, **(B)** and **(C)** of the following reaction scheme. (24 marks)

$$[Re_2(CO)_{10}] \xrightarrow{K} (A) \xrightarrow{PhCOCl} (B) \xrightarrow{heat} (C)$$

(b) The Pt(II) complex $[PhCH_2CH_2Pt(OCH_2CF_3)(dppe)]$ gives an alkane **(E)**,
alkene **(F)**, alcohol **(G)** and aldehyde **(H)** when it is heated in toluene at 100 C.
Identify (E), (F), (G) and **(H)**. (32 marks)

(c) (i) Acetophenone $PhC(=O)CH_3$ reacts with hydroxyl amine NH_2OH to give
the oxime **(J)**. Draw the structure of **(J)**.

(ii) **(J)** reacts with $[PdCl_2(NCPh)_2]$ to give the cyclometallated chloride-bridged
Pd(II) dimer **(K)**. Draw the **structure** of **(K)**. (14 marks)

(d) [Pt(PPh₃)₃] undergoes an 2e-oxidative addition reaction with allyl iodide to give
four coordinate neutral Pt(II) complex with two geometrical isomers **(L)** and **(M)**.
Removal of neutral ligand from **(L)** and/or **(M)** gives **another** neutral,
four coordinate Pt(II) complex **(N)**. Identify **(L)**, **(M)** and **(N)**.   (21 marks)

(e) Hydrogenation of olefins gives alkanes. Arrange the following olefins in the
order of increasing ease of hydrogenation.

        trans-PhCH=CHPh, *cis*-PhCH=CHPh and $Ph_2C=CH_2$ (09 marks)

6. (a) (i) What is the **active catalyst** of the Monsanto process ?

    (ii) Write the balanced equations for the following reactions found in the,
Monsanto process:-

      α. formation of MeI

      β. catalytic carbonylation of MeI

      γ. formation of acetic acid   (25 marks)

(b) (i) Define the terms turnover number (TON) and turnover frequency (TOF).

    (ii). Hydrogenation of styrene (20 mmol) by a rhodium catalyst (1×10^{-6} mmol) is
complete within 0.5 hours.
Calculate the TON and TOF for this process.   (20 marks)

(c) (i)   What is meant by the 'Wacker Process'?

    (ii) What is the **catalyst-system** used in this process?

    (iii) What is the **active catalyst**?

    (iv) The Wacker process is based on a combination of **three** reactions,
write chemical equations for these **three** reactions.   (45 marks)

(d) The following molecule **(Y)** undergoes an intramolecular Heck reaction to give the
derivative **(Z)**. Draw the structure of **(Z)**.   (10 marks)

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