THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION-2014/2015
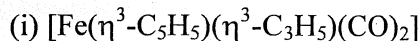
CMU3122/CHU3127 ORGANOMETALLIC CHEMISTRY

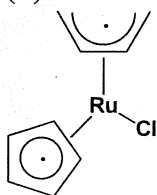Date: 12th May 2015 (Tuesday)   Time 1.00 – 3.00 p.m.

Answer any **FOUR** (04) questions. If more than four questions are answered, **only the first four answers will be marked.**

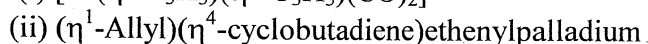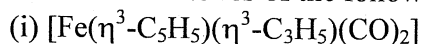1. (a) Give the IUPAC name for each of the following complexes.
    (i) $[Fe(\eta^3-C_5H_5)(\eta^3-C_3H_5)(CO)_2]$
    (ii)   (20 marks)

   (b) Draw the **structures** of the following complexes.
    (i) $[Fe(\eta^3-C_5H_5)(\eta^3-C_3H_5)(CO)_2]$
    (ii) $(\eta^1\text{-Allyl})(\eta^4\text{-cyclobutadiene})$ethenylpalladium   (20 marks)

   (c) Determine the valence electron count (**VEC**) of the complex
    $[CoCl(\eta^1-C_3H_5)(\eta^3-C_5H_5)(\eta^2-C_2H_4)]$ using the **ionic model**.
    (Indicate in your workout, the electron contribution made
    by each ligand, Co is a Group 9 metal).   (15 marks)

   (d) What is the **active catalyst** used in
    (i) Monsanto process and (ii) Shell process   (12 marks)

   (e) (i) Arrange CN^-, NH_3, CS and CO in the increasing order of π-acceptability.
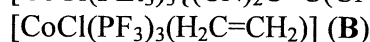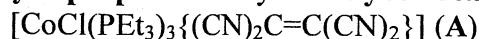   (ii) Give one **anion** which is isoelectronic with PH_3.   (15 marks)

   (f) Using an orbital diagram, explain the bonding between
    a metal (M) and an alkynyl ($-C\equiv CR$) ligand.   (18 marks)
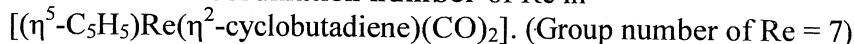
2. (a) Which one of the following compounds is **more likely** to have a
    metallacyclopropane moiety? **Give your reasons.**
    $[CoCl(PEt_3)_3\{(CN)_2C=C(CN)_2\}]$ **(A)**
    $[CoCl(PF_3)_3(H_2C=CH_2)]$ **(B)**   (20 marks)

   (b) (i) Determine the **coordination number** of Re in
        $[(\eta^5-C_5H_5)Re(\eta^2-cyclobutadiene)(CO)_2]$. (Group number of Re = 7)
        (ii) Determine the **coordination geometry** of the Fe-NO fragment in the
        18e-complex $[FeCl(NO)(PF_3)_4]$.   (20 marks)

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

Compound	$v(CO)$ in cm^{-1}
free CO	2143
$[Pd(CO)(PF_3)_3]$	2100
$[Pd(CO)(PMe_3)_3]$	2050

                                                                         (20 marks)

   (d) **Draw** and **identify** the structures of all **geometrical** isomers of $[FeI_2(CO)_2(dppe)]$.
       dppe = $PPh_2CH_2CH_2PPh_2$ and it is a bidentate ligand.
       Comment on **optical isomerism** of above isomers.   (20 marks)

   (e) Give **four** main differences between Fischer-carbenes and Schrock-carbenes. (20 marks)

3. (a) Briefly discuss the **geometry** and the **nature of bonding** in the anion
    of the Ziese's salt $K[PtCl_3(\eta^2-CH_2=CH_2)]$.   (20 marks)

   (b) (i) What is an agostic interaction?
        (ii) Assume that cis-$[CoI(CO)_2(PPh_3)]$ **(C)** shows **square-pyramidal** arrangement
        with one agostic type interaction in the **apical position.** Draw the **structure**
        of **(C)** and identify the type of agostic interaction associated with it?
        (iii) **(C)** undergoes cyclometallation to give a Co(III) hydride **(D).**
        Draw the **structure** of **(D).**   (32 marks)

   (c) $[Ni(PEt_3)_3]$ undergoes an 2e-oxidative addition reaction with allyl bromide
       $CH_2=CHCH_2Br$ to give a **five coordinate** neutral Ni(II) complex **(E). (E)** looses
       one neutral ligand to give a Ni(II) complex with two geometrical isomers **(F)** and **(G).**
       Removal of **another** neutral ligand from **(F)** and/or **(G)** gives a neutral, **four coordinate**
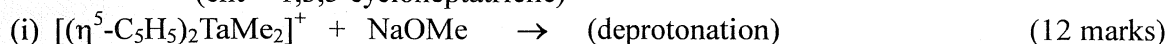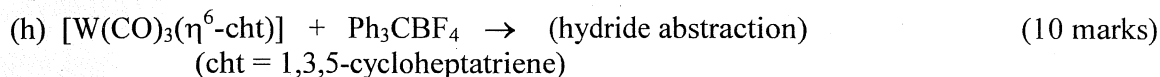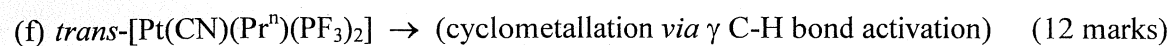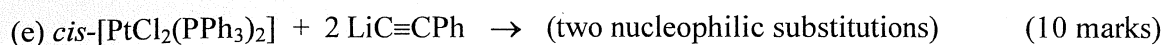 π-allyl-complex **(H)**. Identify **(E), (F), (G)** and **(H).** (32 marks)

   (d) $[Cr(CH_2SiMe_3)_3]$ is an isolable crystalline solid, but $[CrMe_3]$ does not exist.
   Explain.   (16 marks)

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

(a) cis-[NiBr(Et)(PPh$_3$)$_2$] $\xrightarrow{\Delta}$ (β-H abstraction) (10 marks)

(b) [(η^5-C$_5$H$_5$)Fe(η^2-CH$_2$=CH$_2$)(CO)$_2$]$^+$ + NMe$_3$ → (nucleophilic addition) (12 marks)

(c) [MnBr(CO)$_5$] + cyclobutadiene → (substitution with loss of two CO) (10 marks)

(d) [IrMe(PPh$_3$)$_3$] → (cyclometallation and then reductive elimination) (12 marks)

(e) cis-[PtCl$_2$(PPh$_3$)$_2$] + 2 LiC≡CPh → (two nucleophilic substitutions) (10 marks)

(f) $trans$-[Pt(CN)(Pr^n)(PF$_3$)$_2$] → (cyclometallation via γ C-H bond activation) (12 marks)

(g) [(η^5-C$_5$H$_5$)(OC)$_2$Ru(η^1-CH$_2$CH=CH$_2$)] + MeBF$_4$ → (electrophilic addition) (12 marks)

(h) [W(CO)$_3$(η^6-cht)] + Ph$_3$CBF$_4$ → (hydride abstraction) (10 marks)
(cht = 1,3,5-cycloheptatriene)

(i) [(η^5-C$_5$H$_5$)$_2$TaMe$_2$]$^+$ + NaOMe → (deprotonation) (12 marks)

5. (a) A **neutral mononuclear** 18e-complex (**J**) contains a Co(I) centre coordinated **only** to hydride and carbon monoxide ligands. (**J**) can be prepared by the reaction between the binuclear Co(0) complex (**K**) and H$_2$. (**J**) looses a gas molecule to give the 16e-complex (**L**). Coordination of MeCH=CH$_2$ to (**L**) gives the 18e olefin-complex (**M**). In the presence of CO, (**L**) undergoes hydride migration to give the 16e-complex (**N**). (**L**) reacts with H$_2$ to give the 18e-cobalt(III) hydride (**O**). Identify (**J**), (**K**), (**L**), (**M**), (**N**) and (**O**). (42 marks)

(b) The active catalyst [RuHCl(PPh$_3$)$_3$] coordinates with CH$_2$=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 [RuHCl(PPh$_3$)$_3$]. Identify (**P**), (**Q**), (**R**) and (**S**). (28 marks)

(c) Reaction of the E-oxime, Me$_3$CC(=NOH)CF$_3$, with [PdCl$_2$(NCPh)$_2$] gives the cyclometallated chloride-bridged Pd(II) dimer which contains a 5-membered chelate ring. Draw the **structure** of this dimeric complex. (10 marks)

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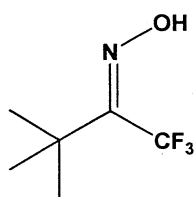
(d) Suggest **reagent(s)** or **active catalyst(s)** which can be used to carry out the following conversions.

(i) $CH_2=CHCH=CH_2 + 2\,HCN \rightarrow NC(CH_2)_4CN$

(ii) $[Mo(CO)_6] \rightarrow [(CO)_5MoC(=O)H]^-$

(iii) $[(\eta^5\text{-}Cp)_2Zr(H)Cl] \rightarrow [(\eta^5\text{-}Cp)_2Zr(CH=CH_2)Cl]$

(iv) $[(\eta^5\text{-}Cp)WMe(\eta^2\text{-}CH_2=CH_2)]^+ \rightarrow [(\eta^5\text{-}Cp)W(CH_2CH_2CH_3)Me]$ (20 marks)

6. (a) (i) Give **three** reasons as to why palladium complexes are used widely in catalysis.

    (ii) $[Pd(PPh_3)_4]$ catalyses the reaction of ethene with bromobenzene to give Styrene ($PhCH=CH_2$) and HBr. Write a mechanism for this process.   (35 marks)

(b) (i) What is meant by "Hydrosilation of an olefin"?

    (ii) What is the Speier's catalyst?

    (iii) What is the main product obtained if $CH_2=CHCN$ is reacted with $PhMe_2SiH$ in the presence of the catalyst $[RhH(CO)(PPh_3)_3]$?   (25 marks)

(c) How would you prepare $MeTiCl_3$, Me_2TiCl_2 and $TiMe_4$ from $TiCl_4$.   (15 marks)

(d) Identify the two molecules formed due to the **ring closed metathesis** of 1,7-octadiene (C_8H_{14}).   (15 marks)

(e) The following molecule undergoes an intramolecular Heck reaction to give a benzofuran derivative (**X**). Draw the structure of (**X**).   (10 marks)