**THE OPEN UNIVERSITY OF SRI LANKA**
**FACULTY OF NATURAL SCIENCES**
**B. Sc. Degree Programme - Level 5**
**FINAL EXAMINATION – 2023/2024**
**Organometallic Chemistry CYU5300**

Date: 15-10-2023 (Sunday) Time: 1.30-3.30 p.m. (Two hours)

**Answer all 04 questions.**

1. (a) Give the IUPAC name of $[RuCl(CO)(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4H_4)]$. (10 marks)

   (b) Draw the structures of the following complexes.
   (i) $[Ru(CH{=}CH_2)(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4H_4)(CO)]$.
   (ii) Dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^2$-ethene)vinylmolybdenum (20 marks)

   (c) (i) Determine the valence electron count (VEC) of the complex $[RuCl(CO)(\eta^3\text{-}C_5H_5)(\eta^4\text{-}C_4H_4)]$, using the **ionic model**.
   (Indicate the electron contribution made by each ligand)
   (ii) What is the coordination number of Ru in this complex?
   (Group no. of Ru = 8) (15 marks)

   (d) Draw the **structures** of the **geometrical** isomers of
   $[Mo(NO)(CO)_3(\mathbf{Me_2P}CH_2CH_2\mathbf{PPh_2})]$.
   $Me_2PCH_2CH_2PPh_2$ is a bidentate ligand. (15 marks)

   (e) $[MeMn(CO)_5]$ reacts with $^{13}CO$ to give *cis*-$[(OC)_4Mn\text{-}C(=O)Me(^{13}CO)]$.
   Write the mechanism of the above reaction. (20 marks)

   (f) Na reduces $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ to give the **mononuclear** salt (**A**).
   (**A**) with MeI gives (**B**). (**B**) can be prepared by reacting (**C**) with LiMe.
   Identify (**A**), (**B**) and (**C**). (20 marks)

2. (a) Arrange $NO^+$, $NMe_3$ and MeCH=CHMe in the order
   of increasing **$\pi$-acceptability**. (10 marks)

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

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

| **Compound** | **$\nu$(C=C) in $cm^{-1}$** |
|---|---|
| Free $CH_2{=}CH_2$ | 1623 |
| $[Ag(\eta^2\text{-}CH_2{=}CH_2)_2]BF_4$ (**D**) | 1584 |
| $[CpRh(\eta^2\text{-}CH_2{=}CH_2)_2]$ (**E**) | 1493 |

(20 marks)

(d) Suggest **starting material** or the **active catalyst** used or the **product** formed regarding the following reactions/conversions.

(i) $CH_2{=}CH_2 + \frac{1}{2} O_2 \rightarrow CH_3CHO$

(ii) $[Fe(CO)_5] + NaH \rightarrow ?$

(iii) Give the active catalyst formed during the Roelen Process?

(iv) $? + H_2 \rightarrow [HCo(CO)_4]$ (20 marks)

(e) (i) What is meant by "hydroformylation of olefins"?

(ii) Write the molecular formulae of the two products formed due to hydroformylation of $CH_3CH{=}CHCH_2CH_3$. (20 marks)

(f) Briefly comment on the electronegativity of 3*d*-series. (10 marks)

3. (a) The reaction of two equivalents of $PhCH_2NMe_2$ with $Na_2[PdCl_4]$ in methanol gives the **orthometallated** chloride-bridged palladium(II) **dimer (F)** and sodium chloride. Draw the **structure** of (**F**). (10 marks)

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

(ii) Assume that $[PtCl_3(PMe_3)]^-$ shows square-pyramidal arrangement with one agostic type interaction *via* the apical position. Draw the **structure** of this complex and **identify** the type of agostic interaction associated with it? (20 marks)

(c) Using an **orbital diagram**, explain the bonding between the metal and ligand in $[CuPPh_3]^+$. (20 marks)

(d) The alkoxy Rh(I) complex $[(OC)_3RhOCH_2CF_3]$ undergoes β-hydride abstraction to give the aldehyde (**G**) and the 16e Rh(I) complex (**H**). (**H**) reacts with $CH_2{=}CH_2$ to give the 16e alkyl-complex (**I**). In the presence of carbon monoxide, (**I**) undergoes migratory insertion reaction to give the acyl complex (**J**). Identify the compounds (**G**), (**H**), (**I**) and (**J**). (40 marks)

(e) What is the major product (**K**) formed due to cross-coupling of PhMgBr with 2-bromopyridine ($C_5H_4NBr$) with the active catalyst $[Pd(PPh_3)_2]$. (10 marks)

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

(a) $2\ [Rh(CN)_5]^{3-} + MeI \rightarrow$ (1e-oxidative addition) (12 marks)

(b) $[Cr(CO)_6]$ + cyclobutadiene $\rightarrow$ (di-substitution) (10 marks

(c) $[Co(CH_2CH_2Me)(PMe_3)_3] \rightarrow$ (β-H abstraction gives 18e-complex) (12 marks)

(d) $[IrBr(PPh_3)_3] \rightarrow$ (cyclometallation) (10 marks)

(e) *cis*-$[PdMe_2(PPh_3)_2] + CH_2{=}CH_2 \rightarrow$ (coordination + 1,2-insertion) (12 marks)

(f) *fac*-$[PtIMe_3(dppe)] \rightarrow$ (reductive elimination, dppe = $Ph_2PCH_2CH_2PPh_2$) (10 marks)

(g) $[CpFe(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_2] + Br_2 \rightarrow$ (electrophilic addition) (12 marks)

(h) $[Cp(OC)_2Fe{=}CH(Me)]^+ + LiMe \rightarrow$ (nucleophilic addition) (10 marks)

(i) $[Fe(CO)_5] + 2\ H_2C{=}C{=}CH_2 \rightarrow$ (oxidative coupling) (12 marks)