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B.Sc./B.Ed. DEGREE /STAND ALONE COURSES IN SCIENCE- LEVEL 5

FINAL EXAMINATION-2009/2010

CHU3127/CHE5127 - ORGANOMETALLIC CHEMISTRY

Date: 21th January 2010 (Thursday) Time 1.00 – 3.30 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 name for each of the following complexes.
   (i) $[CrI(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)_2]$
   (ii) $[RuCl(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4H_4)(CO)]$ (20 marks)

   (b) Draw the **structures** of the following complexes,
   (i) (η^1-Allyl)bromo(η^5-cyclopentadienyl)di(η^2-ethene)molybdenum.
   (ii) Bromodicarbonyl(η^4-cyclobutadiene)(ethyl)ruthenium.
   (iii) (η^6-Benzene)bromoethynyl(triphenylphosphine)cobalt (30 marks)

   (c) (i) Determine the valence electron count (**VEC**) of the complex $[CoCl(Me)(\eta^1\text{-}C_3H_5)(CO)_2(\eta^2\text{-}C_2H_4)]$ using the **ionic model**. (Indicate in your work out, the electron contribution made by each ligand, Co is a Group 9 metal).

   (ii) Determine the valence electron count (**VEC**) of the complex $[Ni(\eta^3\text{-}C_3H_5)Cl(CO)]$using the **covalent model**. (Indicate in your work out, the electron contribution made by each ligand, Ni is a Group 10 metal). (22 marks)

   (d) The nickel complex $[NiCl(Br)(PPh_3)_2]$ shows **three** isomers. Draw and identify the **structures** of them. (18 marks)

   (e) List the following *trans*-compounds in the **increasing order** of the IR frequency of the carbonyl band.
   $[Mo(CO)_4(PPh_3)_2]$ (**A**), $[Mo(CO)_4(PF_3)_2]$ (**B**) and $[Mo(CO)_4(PMe_3)_2]$ (**C**). (10 marks)

2. (a) Describe the bonding between a metal (M) and an alkynyl group (*e.g.* M–C≡CPh). (20 marks)

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

(c) How would you account for the variation in the N≡N stretching frequency of the following compounds ?

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Compound	ν(N≡N) in cm^{-1}
free N_2	2330
$[Ni(N_2)]$	2088
$[Ni(N_2)_2]$	2187

(20 marks)

(d) Briefly comment on the electronegativity of 3d-series (20 marks)

(e) What are the main differences between M–alkene and M–alkyl bond. (20 marks)

3. (a) (i) What factors promote metallacyclopropane character in alkene-metal complexes.
(ii) Which one of the following compound **(D)** or **(E)** is more likely to have a metallacyclopropane structure. Give your reasons.
$[IrBr(PMe_3)_3\{(NC)_2C=C(CN)_2\}]$ **(D)**
$[IrBr(CO)_3\{(MeHC=CHMe\}]$ **(E)** (20 marks)

(b) (i) Determine the **coordination geometry** of the Re-NO fragment in the 18e-complex $[Re(NO)(CO)_4(PPh_3)]$ **(F).** Re is a Group 7 metal.
(ii) Draw the **orbital diagram** showing the overlap of orbitals of NO and the metal in **(F).** (20 marks)

(c) Write the possible pathways for the decomposition of $[TiEt_4]$. (20 marks)

(d) Draw the structure of the product that you would get when you react $(CF_3)_2C=O$ with $[Pt(PEt_3)_4]$. (20 marks)

(e) Draw and name **four** coordination modes of the hydride ion. (20 marks)

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

(a) *cis*-$[(Ph_3P)_2PtCl_2]$ + $LiCH_2CH_2CH_2CH_2CH_2Li$ → (nucleophilic substitution)

(b) 2 $[Co(CN)_5]^{3-}$ + MeI → (1e oxidative addition)

(c) $[(\eta^5\text{-Cp})Rh(CO)(PPh_3)]$ + MeI → (2e-oxidative addition)

(d) $[(\eta^5\text{-}C_5H_5)(PPh_2CH_2CH_2PPh_2)FeC{\equiv}CR]$ + Me_3O^+ → (electrophilic attack)

(e) $[(\eta^5\text{-Cp})Mo(CH_2CH_3)(CO)_3]$ + Ph_3CBF_4 → (hydride abstraction)

(f) $[IrCl(PPh_3)_3]$ $\xrightarrow{\Delta}$ (cyclometallation)

(g) $[(\eta^5\text{-}C_5H_5)_2WMe(\eta^2\text{-}CH_2{=}CH_2)]^+$ + Me^- → (nucleophilic addition)

(h) $[(\eta^5\text{-Cp})_2Zr(CO)_2]$ + 2 $F_2C{=}CF_2$ → (oxidative coupling)

(i) $[(\eta^5\text{-Cp})Fe(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_2]$ + HCl → (electrophilic addition)

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

(10 x10 marks)

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5. (a) In the presence of a palladium catalyst (0.00001 mmol), MeI (8.0 mmol) reacts **completely** with $MeCH{=}CH_2$ (8.0 mmol) to give butene. The reaction time is 20 min. Calculate the Turnover number (TON) and Turnover frequency (TOF).

(20 marks)

(b) MeBr oxidatively adds $[IrBr_2(CO)_2]^-$ to give (**G**). (**G**) in the presence of CO gives the acetyl complex (**H**). (**H**) reductively eliminates (**I**) to regenerate $[IrBr_2(CO)_2]^-$. Identify (**G**), (**H**) and (**I**).

(30 marks)

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

(i) $[(\eta^5\text{-Cp})_2ZrCl_2]$ → $[(\eta^5\text{-Cp})_2Zr(C{\equiv}CPh)_2]$

(ii) $CH_2{=}CH_2$ + ½ O_2 → CH_3CHO

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

(iv) $[(\eta^5\text{-Cp})_2Ta(Me)_2]^+ \rightarrow [(\eta^5\text{-Cp})_2Ta(=CH_2)(Me)]$

(v) $[(\eta^5\text{-Cp})WH(CO)_3] \rightarrow [(\eta^5\text{-Cp})W(\eta^2\text{-}H_2)(CO)_3]BF_4$ (40 marks)

(d) What are the **two** aldehydes formed due to hydroformylation of $PhCH{=}CH_2$? (10 marks)

6. (a) The catalyst $[RhCl(PPh_3)_3]$ reacts with H_2 to give the octahedral Rh(III) dihydride (**K**). Replacement of PPh_3 by $CH_2{=}CH_2$ of (**K**) gives the olefin-complex (**L**). In the presence of PPh_3, (**L**) undergoes migratory insertion to give the octahedral alkyl-complex (**M**). (**M**) reductively eliminates the alkane (**N**) to regenerate the catalyst $[RhCl(PPh_3)_3]$.
Write the molecular formulae of (**K**), (**L**), (**M**) and (**N**). (40 marks)

(b) Reduction of $[(\eta^5\text{-Cp})Ru(CO)_2]_2$ with K gives the salt (**X**). (**X**) reacts with MeI to give the complex (**Y**) and KI. In the presence of PPh_3, (**Y**) is converted into the acetyl-complex (**Z**). Identify (**X**), (**Y**) and (**Z**). (30 marks)

(c) (i) What is meant by the "Monsanto Process"?
(ii) Write the balanced equations for
(x) formation of MeI
(y) catalytic carbonylation of MeI
(z) conversion of the product formed in (ii) to the desired product. (20 marks)

(d) What is the main product formed due to metathesis of cyclopentene and $CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2Me$ (10 marks)

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