THE OPEN UNIVERSITY OF SRI LANKA

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

FINAL EXAMINATION-2007/2008

CHU3127/CHE5127 - **ORGANOMETALLIC CHEMISTRY**

Date : 24th January 2008   Duration : 2 ½ h   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) $[Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_4H_4)(CO)]Br_2$
    (ii) $[Fe(\eta^3\text{-}C_3H_5)_2(CO)(PPh_3)]$
    (iii) $Na[Mo(\eta^5\text{-}C_5H_5)_2(CO)_2]$

    (30 marks)

   (b) Draw the **structures** of the following complexes,
    (i) $(\eta^3\text{-allyl})(\eta^5\text{-cyclopentadienyl})di(\eta^2\text{-ethene})molybdenum$.
    (ii) $(\eta^1\text{-allyl})dicarbonyl(phenylethynyl)(triphenylphosphine)iron$.
    (iii) $(\eta^6\text{-benzene})bromocarbonyl(vinyl)iron$
    (iv) $(\eta^6\text{-benzene})carbonyl(\eta^4\text{-cyclobutadiene})ruthenium$

    (40 marks)

   (c) Determine the valence electron count (VEC) of the following complexes
    using the **covalent model**. (Indicate in **your work out**, the electron contribution made
    by each ligand.
    (i) $[RuBr(CH=CH_2)(\eta^6\text{-}C_6H_6)(CO)]$ (Ru is a Group 8 metal)
    (ii) $[Fe(\eta^3\text{-}C_3H_5)(\eta^3\text{-}C_5H_5)(CO)]$ (Fe is a Group 8 metal)
    (iii) $[Mo(\equiv CPh)(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)]$ (Mo is a Group 6 metal)

    (30 marks)

2. (a) Explain the bonding between Fe and CO in $[Fe(CO)_5]$.   (20 marks)

   (b) Draw the **structures** of all the isomers of $[FeBr_2(CO)_2(Ph_2PCH_2CH_2PPh_2)]$
    $Ph_2PCH_2CH_2PPh_2$ is a bidentate ligand.   (20 marks)

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

(d) Determine the coordination geometry of the Fe–NO fragment in the 18e-complex [FeCl(NO)(CO)$_4$] (20 ma

(e) Arrange PF$_3$, PMe$_3$ and P(OMe)$_3$ in the order of increasing π-**acceptability**. Give **reasons** for your choice. (20 ma

3. (a) Draw the structure of the product that you would be obtained when (CF$_3$)$_2$C=O reacts with [Pt(PEt$_3$)$_4$)]. (15 ma

(b) Reduction of [Re$_2$(CO)$_{10}$] with Na gives the salt (**A**), which reacts with MeI to give the complex (**B**) and NaI. (**B**) in the presence of CO gives (**C**). Identify (**A**), (**B**) and (**C**). (30 ma

(c) Give three ligands, which are isoelectronic with N$_2$. (15 ma

(d) Reaction of E-Pinacolone oxime , Bu^{t}C(=NOH)Me, with [PdCl$_2$(NCPh)$_2$] and NaOAc gives the cyclometallated chloride-bridged palladium(II) dimer, which contains a 5-membered chelate ring. Draw the **structure** of this dimeric complex. (20 mar

(e) What is an agostic interaction? Assume that *trans*-[PdI$_2$(CO)(PPh$_3$)] shows square-pyramidal arrangement with **one agostic type interaction *via* the apical position**. Draw the **structure** of this complex an **identify** the type of agostic interaction associated with it? (20 mark

4. **Predict** the **major product(s)** of each of the following reactions, **using the hint given in tl brackets).** (dppe = Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)

(a) [Fe(CO)$_5$] + 2 PhC≡CPh ⟶ (oxidative coupling)

(b) *cis*-[PdMe$_2$(dppe)] + PhI ⟶ (oxidative addition)

(c) [PdMe$_2$(PPh$_3$)$_2$] + CH$_2$=CH$_2$ ⟶ (coordination + 1,2-insertion)

(d) [Mn(CH$_2$CH=CH$_2$)(CO)$_5$] ⟶$^\Delta$ (loss of molecule + coordination)

(e) [CpFe(η^1-CH$_2$CH=CH$_2$)(CO)$_2$] + Br$_2$ ⟶ (electrophilic addition)

(f) [Mo(CO)$_6$] + Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$ ⟶ (substitution with loss of two molecules)

(g) *cis*-[PtCl$_2$(PPh$_3$)$_2$] + LiCH$_2$CH$_2$CH$_2$Li ⟶ (nucleophilic substitution)

(h) [IrCl(PMe$_3$)$_4$] ⟶$^\Delta$ (cyclometallation & loss of ligand or molecule)

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(i) fac-[IrI$_3$(COMe)(CO)$_2$]$^-$ $\longrightarrow$ (reductive elimination)

(j) 2 [Co(CN)$_5$]$^{3-}$ + H$_2$ $\longrightarrow$ (1e oxidative addition) (10 x 10 marks)

5. (a) How would you prepare MeTiCl$_3$, Me$_2$TiCl$_2$ and TiMe$_4$ from TiCl$_4$. (20 marks)

(b) [CoH(CO)$_4$] is a stronger acid than [CoH(CO)$_3$(PPh$_3$)]. Explain. (10 marks)

(c) The ethoxyPt(II) complex [(PhCH$_2$CH$_2$)Pt(OCH$_2$CH$_3$)(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). (dppe = Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)

(40 marks)

(d) How would you prepare the **acyl complex** [(η^5-Cp)(OC)$_2$FeC(=O)Et] from [(η^5-Cp)FeH(CO)$_2$]? (20 marks)

(e) What is the major product formed due to cross-coupling of PhI with CH$_3$CH$_2$CH=CHZnI in the presence of the catalyst [Pd(PPh$_3$)$_4$]. (10 marks)

6. (a) In the presence of a metal catalyst (0.000008 mmol), RCH=CH$_2$ (2.0 mmol) reacts **completely** with MeI (2.0 mmol) to give RCH=CHMe. The reaction time is 60 seconds. Calculate the Turnover number (TON) and Turnover frequency (TOF).

(20 marks)

(b) [NiH(CN)(PPh$_3$)$_2$] catalyses the hydrocyanation of CH$_2$=CH$_2$ to CH$_3$CH$_2$CN. Draw the catalytic cycle for this process. (30 marks)

(c) (i) What is the main product formed due to metathesis of cyclohexene and CH$_3$(CH$_2$)$_8$CH=CH(CH$_2$)$_7$CO$_2$Me?
(ii) What is the catalytic-system used in the "Wacker Process"?
(iii) The Wacker process is based on a combination of three reactions, write chemical equations for these three reactions. (40 marks)

(d) Draw the structure of the polymer formed due to the ring opening metathesis polymerization of **cyclobutene** (C$_4$H$_6$). (10 marks)