



THE OPEN UNIVERSITY OF SRI LANKA  
B.Sc. & B. Ed. DEGREE / STAND ALONG COURSE IN SCIENCE - LEVEL 5  
ASSIGNMENT TEST II (NBT) 2012/2013  
CMU3122/CME5122 – Organometallic Chemistry

28<sup>th</sup> February 2013 (Thursday)

4.00 – 5.30 p.m.

**ANSWER ALL QUESTIONS**

Select the most correct answer to each question given below. Mark a cross (X) over the most suitable answer on the **given answer script**. Any answer with more than one cross will not be counted.

**PART A (60 marks)**

1. Consider the following statements about  $[\text{Fe}(\text{CO})_5]$ .

- (i) It shows the trigonal bipyramidal geometry in the solid state.
- (ii) It can be prepared by reacting iron with CO at high temperatures and pressures.
- (iii) It reacts with NaH to give  $\text{Na}[\text{FeH}(\text{CO})_5]$ .

The correct statement/s is/are

- 1) (i) only
- 2) (i) & (ii) only
- 3) (i) & (iii) only
- 4) (ii) & (iii) only
- 5) (i), (ii) & (iii).

2. Pick the **correct** statement regarding an **oxidative addition** reaction.

- 1) Oxidative addition of coordinated dihydrogen is *trans*.
- 2) Oxidative addition is facile if the metal centre is coordinatively saturated.
- 3) Coordinatively saturated metal centres cannot undergo oxidative addition reaction.
- 4) Coordination number of the metal is always increased by 2 units.
- 5) None of the above statements is true.

3. Electrophilic attack on a coordinated ligand is facilitated if

- 1) the metal is in a higher oxidation state.
- 2) the metal is coordinatively unsaturated.
- 3) the metal coordinated to good  $\sigma$ -donor ligands.
- 4) the metal is positively charged.
- 5) electron withdrawing groups are on coordinated ligands.

4. Consider the following statements regarding **reductive elimination**.

- (i) Coordination number of the metal is reduced by two units.
- (ii) It is facile if the metal centre is positively charged.
- (iii) Coordinatively saturated compounds prefer to undergo reductive elimination.

The correct statement/s is/ are

- 1) (i) only.
- 2) (i) & (iii) only.
- 3) (i) & (ii) only.
- 4) (ii) & (iii) only.
- 5) (i), (ii) & (iii).

5. What is the most **stable** product formed, when  $[\text{Fe}(\text{CO})_5]$  is reacted with 1,3-butadiene ( $\text{C}_4\text{H}_6$ )?

- 1)  $[\text{Fe}(\text{CO})_4(\eta^4\text{-C}_4\text{H}_6)]$
- 2)  $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_6)]$
- 3)  $[\text{Fe}(\text{CO})_5(\eta^2\text{-C}_4\text{H}_6)]$
- 4)  $[\text{Fe}(\text{CO})_2(\eta^4\text{-C}_4\text{H}_6)_2]$
- 5)  $[\text{Fe}(\text{CO})_3(\eta^2\text{-C}_4\text{H}_6)]$

6.  $\gamma$ -Agostic (gamma agostic) interaction could be seen in
- 1)  $[\text{MeMn}(\text{CO})_5]$
  - 2)  $[(\text{OC})_3\text{Pt}\{\text{P}(\text{OPh})_3\}]$
  - 3)  $[\text{Mn}(\text{CF}_2\text{CF}_2\text{Me})(\text{CO})_4]$
  - 4)  $[\text{MeOMn}(\text{CO})_5]$
  - 5) None of the above
7. Which one is an example of an **reductive elimination** reaction?
- 1)  $[\text{Fe}(\text{CO})_5] + \text{CF}_2=\text{CF}_2 \rightarrow [(\text{OC})_4\text{Fe}(\text{CF}_2=\text{CF}_2)] + \text{CO}$
  - 2)  $[(\eta^3\text{-C}_3\text{H}_5)\text{PtMe}(\text{CO})_2] \rightarrow [(\eta^3\text{-C}_3\text{H}_6)\text{Pt}(\text{CO})(\text{COMe})]$
  - 3)  $[\text{Fe}(\text{CO})_5] + 2 \text{CF}_2=\text{CF}_2 \rightarrow [(\text{OC})_4\text{Fe}(\text{C}_4\text{F}_8)] + \text{CO}$
  - 4)  $[\text{Pt}(\text{Ph})(\text{H})(\text{PPh}_3)_2] + 2 \text{PPh}_3 \rightarrow [\text{Pt}(\text{PPh}_3)_4] + \text{C}_6\text{H}_6$
  - 5)  $[\text{MeMn}(\text{CO})_5] + \text{CF}_2=\text{CF}_2 \rightarrow [\text{Mn}(\text{CF}_2\text{CF}_2\text{Me})(\text{CO})_5]$
8. Which statement is **not true** about  $[\text{Fe}(\text{PPh}_3)_2(\text{CO})_3]$ ?
- 1) The IUPAC name is tricarbonylbis(triphenylphosphine)iron.
  - 2) CO is a good  $\pi$ -acceptor ligand.
  - 3) It shows only two geometrical isomers.
  - 4) The coordination number of iron is 5.
  - 5) The  $\nu(\text{CO})$  of  $[\text{Fe}(\text{PPh}_3)_2(\text{CO})_3]$  is higher than that of  $\text{K}[\text{Fe}(\text{PPh}_3)_2(\text{CO})_3]$ .
9. Consider the following statements regarding ligands,
- (i)  $\text{CH}_2=\text{CH}_2$  is a weaker  $\pi$ -acceptor than  $\text{CHMe}=\text{CHMe}$ .
  - (ii)  $\text{PMe}_3$  is a better  $\sigma$ -donor than  $\text{PH}_3$ .
  - (iii) CO is a better  $\pi$ -acceptor than cyclopentadienyl ligand.
- The correct statement/s is/are
- 1) (ii) only.
  - 2) (i) & (ii) only.
  - 3) (ii) & (iii) only.
  - 4) (i) & (iii) only.
  - 5) (i), (ii) & (iii).
10. What is the **product** formed, when  $[\text{Fe}(\text{CO})_5]$  is reacted with NaOH?
- 1)  $\text{Na}[\text{Fe}(\text{CO})_4]$
  - 2)  $\text{Na}[\text{FeH}(\text{CO})_4]$
  - 3)  $\text{Na}[\text{Fe}(\text{CO})_4\{\text{C}=\text{O}\text{H}\}]$
  - 4)  $[\text{FeH}_2(\text{CO})_4]$
  - 5)  $\text{Na}[\text{Fe}(\text{OH})(\text{CO})_5]$
11. Consider the following statements.
- (i) Dihydrogen is a weaker  $\sigma$ -donor than dinitrogen.
  - (ii)  $\nu(\text{M}-\text{D}) \times \sqrt{2} = \nu(\text{M}-\text{H})$
  - (iii) The oxidative addition of coordinated  $\text{H}_2$  depends on the strength of the back donation.
- The correct statement/s is/are
- 1) (i) only.
  - 2) (i) & (ii) only.
  - 3) (ii) & (iii) only.
  - 4) (i) & (iii) only.
  - 5) (i), (ii) & (iii).
12. What are the most likely IR frequency or frequencies of *fac*- $[\text{Mo}(\text{PCl}_3)_3(\text{CO})_3]$ ?
- 1) 2040 & 1990
  - 2) 2040 only
  - 3) 1990 & 1650
  - 4) 1850 only
  - 5) 1850 & 1650
13. Consider the following statements about metal carbonyls,
- (i) Back bonding weakens the CO bond strength.
  - (ii) Back bonding increases the M-C bond strength.
  - (iii) CO stabilizes the metal centers in higher oxidation states.
- The correct statement/s is/are
- 1) (i) only.
  - 2) (i) & (ii) only.
  - 3) (ii) & (iii) only.
  - 4) (i) & (iii) only.
  - 5) (i), (ii) & (iii).

14. Which metal carbonyl has got **bridging** carbonyl ligands?
- 1)  $[\text{Os}_3(\text{CO})_{12}]$
  - 2)  $[\text{Ir}_4(\text{CO})_{12}]$
  - 3)  $[\text{Ru}_3(\text{CO})_{12}]$
  - 4)  $[\text{Re}_2(\text{CO})_{10}]$
  - 5)  $[\text{Fe}_3(\text{CO})_{12}]$
15. The nucleophilicity of the  $\text{R}^-$  group varies in the following order,
- 1)  $\text{LiR} > \text{NaR} > \text{RMgX} > \text{HgR}_2$
  - 2)  $\text{LiR} > \text{NaR} > \text{HgR}_2 > \text{RMgX}$
  - 3)  $\text{NaR} > \text{LiR} > \text{HgR}_2 > \text{RMgX}$
  - 4)  $\text{NaR} > \text{LiR} > \text{RMgX} > \text{HgR}_2$
  - 5)  $\text{HgR}_2 > \text{RMgX} > \text{LiR} > \text{NaR}$
16. Most likely reaction that would take place is?
- 1)  $\text{Ni} + 5 \text{CO} \rightarrow [\text{Ni}(\text{CO})_5]$
  - 2)  $\text{TiCl}_4 + \text{AlMe}_3 \rightarrow \text{MeTiCl}_3 + \text{AlClMe}_2$
  - 3)  $[\text{Mo}(\text{CO})_6] + \text{NaCp} \rightarrow \text{Na}[(\eta^3\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_4] + 2 \text{CO}$
  - 4)  $[\text{MnCF}_3(\text{CO})_5] + \text{CO} \rightarrow [\text{Mn}(\text{COCF}_3)(\text{CO})_5]$
  - 5)  $[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\eta^5\text{-C}_5\text{H}_5)]^+ + \text{Me}^- \rightarrow [(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\eta^4\text{-C}_5\text{H}_5\text{Me})]$
17. Which statement is **not true** about  $[\text{Fe}_2(\text{CO})_9]$ ?
- 1) There are three bridging carbonyl ligands.
  - 2) It can be prepared by photochemical irradiation of  $[\text{Fe}(\text{CO})_5]$ .
  - 3) There is a Fe-Fe bond in the complex.
  - 4) Fe centre does not obey 18e rule.
  - 5) Fe is a Group 8 metal.
18. Consider the following statements about  $[\text{HCo}(\text{CO})_4]$ .
- (i) It is a  $\text{H}^+$  donor.
  - (ii) It is a weaker acid than  $[\text{HCo}(\text{CO})_3(\text{PPh}_3)]$ .
  - (iii) It shows a negative proton chemical shift (in ppm) with respect to  $\text{SiMe}_4$  (TMS).
- The correct statement/s is/are
- 1) (iii) only.
  - 2) (i) & (iii) only.
  - 3) (i) & (ii) only.
  - 4) (ii) & (iii) only.
  - 5) (i), (ii) & (iii).
19. Consider the following statements about  $[\text{W}(\text{CO})_4(\text{dppe})]$ ,  
(dppe =  $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$  is a bidentate ligand).
- (i) It shows the octahedral geometry.
  - (ii) It shows only one carbonyl band in its IR spectrum.
  - (iii) It can be prepared by reacting  $[\text{W}(\text{CO})_6]$  with dppe.
- The correct statement/s is/are
- 1) (i) only
  - 2) (i) & (ii) only.
  - 3) (i) & (iii) only.
  - 4) (ii) & (iii) only.
  - 5) (i), (ii) & (iii).
20. What is the **most stable product** of the reaction,  $[\text{Os}(\text{CO})_5] + \text{I}_2 \rightarrow ?$
- 1)  $[\text{OsI}(\text{CO})_4]$
  - 2)  $[\text{OsI}(\text{CO})_4]\text{I}$
  - 3)  $[\text{OsI}_2(\text{CO})_5]$
  - 4)  $[\text{OsI}_2(\text{CO})_4]$
  - 5) *fac*- $[\text{OsI}_3(\text{CO})_3]$

THE OPEN UNIVERSITY OF SRI LANKA  
 B. Sc DECREE PROGRAMME 2012/2013  
 CMU3122/CMES122 – ORGANOMETALLIC CHEMISTRY- LEVEL5  
 ASSIGNMENT TEST-II (Part A)



MCQ ANSWER SHEET: Mark a cross (X) over the most suitable answer.

Reg. No.

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For Examiners Use

Part A	
Part B	
Total %	

Marks

Correct Answers		
Wrong Answers		
Total		

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**Part B (40 marks)**

*Answer the questions in the space provided. Attached sheets will not be graded.*

1. (a) (i)  $[\text{PtI}_2(\text{dppe})]$  undergoes oxidative addition with  $\text{PhI}$  to give the octahedral complex (Z).  
(dppe =  $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ )

Write the **molecular formula** of (Z) .....

(ii) **Draw and identify** the two isomers of (Z).

- (b) Reduction of the **dimer**  $[(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2]_2$  with K gives the salt (P), which reacts with  $\text{PhBr}$  to give the complex (Q) and  $\text{KBr}$ . (Q) in the presence of CO gives the acyl complex (R). Identify (P), (Q) and (R).

(P) ..... (Q).....

(R) .....

- (c) The alkoxy complex  $[(\text{OC})_3\text{RhOCH}_2\text{CH}_2\text{CH}_3]$  undergoes  $\beta$ -hydride abstraction to give the Rh(I) complex (A) and organic molecule (B). Upon heating (A) with  $\text{CH}_2=\text{CH}_2$  gives the alkyl complex (C). Identify (A), (B) and (C).

(A)

(B)

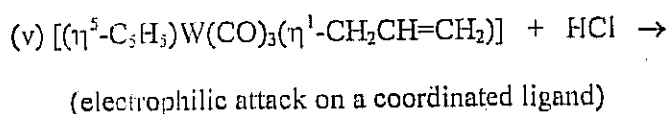
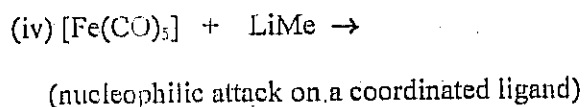
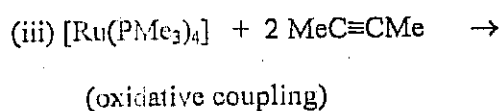
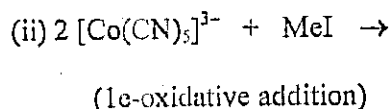
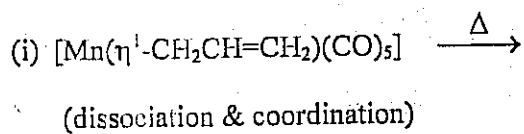
(C)

- (d) How would you account for the variation in  $\nu(\text{CO})$  of the following compounds?

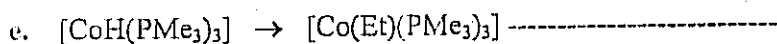
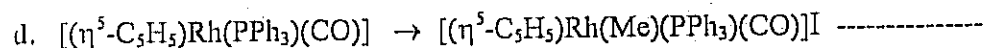
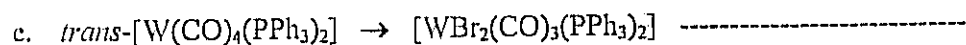
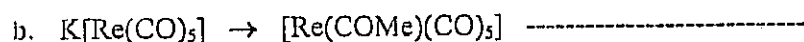
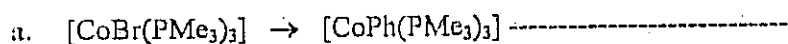
Compound	$\nu(\text{CO})$ in $\text{cm}^{-1}$
Free-CO	2143
$[\text{Mo}(\text{CO})_6]$	2005
$[\text{Mo}(\text{CO})_6]^+$	2090

- (e) What is meant by "cyclometallation"? Give an example (a reaction).

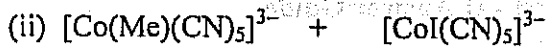
2. (a) Predict the product(s) of the following reactions using the hint given in the brackets.



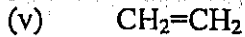
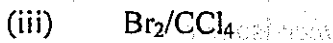
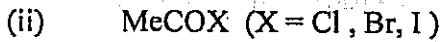
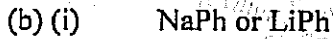
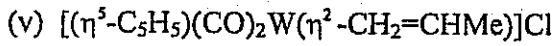
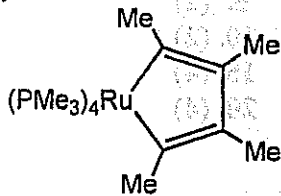
(b) Write on the dotted line, the reagent(s) which can be used to carry out the following conversions.



(2) (a)



(iii)



The Open University of Sri Lanka  
 B.Sc. Degree Program 2012/2013  
 CMU3122/CME5122 – Organometallic Chemistry - Level 5  
 Assignment Test - II Answer Guide

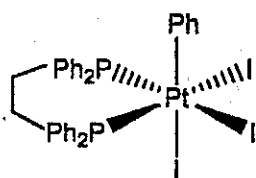
**Part A – MCQ ANSWERS**

1. (2)	2. (5)	3. (3)	4. (5)	5. (2)
6. (3)	7. (4)	8. (3)	9. (3)	10. (2)
11. (5)	12. (1)	13. (2)	14. (5)	15. (4)
16. (2)	17. (4)	18. (2)	19. (3)	20. (4)

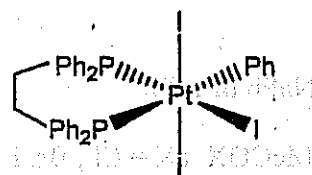
**Part B**

(1)(a)(i)  $[\text{PtI}_3(\text{Ph})(\text{dppe})]$

(ii)



*fac-isomer*



*mer-isomer*

(b) (P) =  $\text{K}[(\eta^5\text{-C}_p)\text{Fe}(\text{CO})_2]$     (Q) =  $[(\eta^5\text{-C}_p)\text{Fe}(\text{Ph})(\text{CO})_2]$     (R) =  $[(\eta^5\text{-C}_p)\text{Fe}(\text{COPh})(\text{CO})_2]$

(c) (A) =  $[\text{RhH}(\text{CO})_3]$     (B) =  $\text{CH}_3\text{CH}_2\text{CHO}$     (C) =  $[\text{Rh}(\text{Et})(\text{CO})_3]$

(d) There is no back donation when  $\text{C}\equiv\text{O}$  is not bonded to a metal therefore it shows the highest frequency.  $\nu(\text{CO})$  is directly proportional to the strength of  $\text{C}\equiv\text{O}$  bond.  $[\text{Mo}(\text{CO})_6]$  has a lower frequency than that of  $[\text{Mo}(\text{CO})_6]^+$  because back donation in the cation complex is lower due to low electron density on the metal. Therefore the  $\text{C}\equiv\text{O}$  bond strength of  $[\text{Mo}(\text{CO})_6]^+$  is higher than that of  $[\text{Mo}(\text{CO})_6]$ , as Mo in  $[\text{Mo}(\text{CO})_6]$  has a higher back donation ability.

(e) Cyclometallation is a process where a new M-C bond is formed due to activation of a C-H or C-X bond in a coordinated ligand. e.g., see the cover page of Unit II

