

THE OPEN UNIVERSITY OF SRI LANKA
 B. Sc. & B. Ed. DEGREE/STAND ALONE
 COURSES IN SCIENCE Level 5
 ASSIGNMENT TEST I (NBT)
 CMU3122/CME5122 – Organometallic Chemistry



DURATION : 1.5 hours

DATE: 29 September 2011 (Thursday)

TIME : 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 and 1/6th of the mark will be deducted for each **incorrect** answer.

PART A (60 marks)

1. Consider the following organic ligands,

(i) π -allyl (ii) C_4H_4 (iii) benzene

The possible *trihapto* ligand/s is/are

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

2. The possible **coordination mode(s)** of $C_5H_5^-$ is/are?

- 1) η^1 only. 2) η^1 and η^2 only 3) η^1 and η^3 only
 4) η^2 and η^4 only. 5) η^1 , η^3 and η^5 only.

3. What is the **Valence Electron Count (VEC)** of Co in $[CoBr_2(CO)_2(\eta^1-C_5H_5)]$?
 (Group number of Co is 9)

- 1) 16 2) 17 3) 18 4) 19 5) 20

4. The IUPAC name of $[CoBr_2(CO)_2(\eta^1-C_5H_5)]$ is

- 1) Dibromodicarbonyl(monohaptocyclopentadienyl)cobaltate
 2) Dibromodicarbonyl(η^1 -cyclopentadienyl)cobalt(II)
 3) Dibromodicarbonyl(η^1 -cyclopentadienyl)cobalt
 4) Cobalt dibromodicarbonyl(monohaptocyclopentadiene)
 5) Dibromodicarbonyl(η^1 -cyclopentadiene)cobalt(III)

5. An L_2X type ligand is

- 1) $\eta^1-C_5H_5^-$ 2) $\eta^3-C_3H_5^-$ 3) $\eta^5-C_5H_5^-$ 4) $\eta^6-C_6H_6$ 5) $\eta^2-C_4H_3Cl$

6. The **coordination number** of Ru in $[RuBr(\eta^4-C_4H_4)(\eta^3-C_3H_5)]$ is

- 1) 4 2) 5 3) 6 4) 7 5) 8

7. According to **ionic model**, which one of the following is **not** a 4e-donor ligand?

- 1) $\eta^3-C_3H_5^-$ 2) $\eta^3-C_3H_5^-$ 3) $\eta^4-C_4H_4$ 4) $\equiv CPh$ 5) $\eta^4-C_4H_6$

8. Which one of the following statements is true about Fischer carbenes?
- 1) Metal is in a higher oxidation state.
 - 2) Carbene carbon is nucleophilic.
 - 3) Carbene carbon contains a + δ charge.
 - 4) These carbenes are formed with early transition metal.
 - 5) Carbene carbon is attacked by electrophiles.
9. The strongest π -acceptor ligand among the following ligands is
- 1) NH_3
 - 2) PMe_3
 - 3) MeCN
 - 4) CS
 - 5) CN^-
10. What is true about the C_5H_5^- ?
- 1) It cannot form a sandwich complex with iron.
 - 2) According to LX classification, it can act as a L-type ligand.
 - 3) It is a good π -acceptor.
 - 4) It is a poor σ -donor.
 - 5) None of the above statements is true.
11. Consider the following statements regarding the symmetrical molecule $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mn}(\mu\text{-Cl})_2\text{Mn}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]$. (Group number of Mn is 7)
- (i) According to ionic model, oxidation number of each Mn is +2.
 - (ii) It does not form geometrical isomers.
 - (iii) It is a paramagnetic complex.
- The correct statement/s is/are
- 1) (i) only.
 - 2) (i) and (ii) only.
 - 3) (i) and (iii) only.
 - 4) (ii) and (iii) only.
 - 5) (i), (ii) and (iii).
12. Consider the following statements about carbynes.
- (i) Carbyne ligand is a 3e-donor.
 - (ii) It forms one σ -bond and two π -bonds with a metal.
 - (iii) Carbyne carbon is sp^2 hybridized.
- The correct statement/s is/are
- 1) (ii) only.
 - 2) (i) and (ii) only.
 - 3) (i) and (iii) only.
 - 4) (ii) and (iii) only.
 - 5) (i), (ii) and (iii).
13. In metal carbonyls, what is true about back donation?
- 1) the carbonyl frequency increases as back donation increases.
 - 2) the bond strength of $\text{C}\equiv\text{O}$ decreases as back donation decreases.
 - 3) the $\text{M}-\text{CO}$ bond order increases as back donation decreases.
 - 4) the $\text{M}-\text{CO}$ bond length decreases as back donation decreases.
 - 5) None of the above is true.
14. According to the ionic model, the d^n electron configuration and the coordination number of Co in $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)(\text{CO})]$ are (Group number of Co is 9)
- 1) $d^9, 5$
 - 2) $d^7, 5$
 - 3) $d^7, 3$
 - 4) $d^6, 3$
 - 5) $d^5, 4$

15. Consider the following statements.

- (i) PMe_3 is a weak π -acceptor than PPh_3 .
- (ii) PF_3 can stabilise metal centres in lower oxidation states.
- (iii) PPh_3 has a higher cone angle than PF_3 .

The correct statement/s is/are

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

16. Which one of the following ligands is isoelectronic with N_2 ?

- 1) C_2H_4
- 2) $\text{HC}\equiv\text{CH}$
- 3) NO
- 4) CS
- 5) C_2^-

17. What is not true about the carbene ligand?

- 1) It can form a metal carbon double bond.
- 2) It can act as a 2e-donor.
- 3) Carbene carbon is *sp* hybridized.
- 4) It can act as a monodentate ligand.
- 5) It can form Schrock carbenes with Group 6 metals.

18. According to the Ionic Model, what is the oxidation number of Mn in

$\text{Na}[\text{Mn}(\text{CO})_5]$ (Group number of Mn is 7)?

- 1) +1
- 2) +2
- 3) 5
- 4) 0
- 5) -1.

19. Consider the following statements,

- (i) Ammonia is a stronger σ -donor than NF_3 .
- (ii) PPh_3 is a stronger σ -donor than CO
- (iii) NF_3 is a weaker π -acceptor than NO^+ .

The correct statement/s is/are

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

20. Consider the complex $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]$. Which one of the following statements is not true about the above complex? (Group number of Cr is 6)

- 1) Cr centre has 18 valence electrons.
- 2) It is an unsymmetrical molecule.
- 3) The oxidation number of Cr is 0.
- 4) It has the piano-stool geometry.
- 5) The coordination number of Cr is 6.

Part B (40 marks)

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

1. (a) Give IUPAC names for the following complexes.

i. $[\text{FeCl}(\eta^2\text{-C}_2\text{H}_4)(\eta^3\text{-C}_3\text{H}_5)]$

ii. $[\text{CoF}(\eta^4\text{-C}_4\text{H}_4)(\text{CO})]$

(b) Draw the structures of the following complexes.

i. $[\text{RuCl}(\eta^3\text{-C}_3\text{H}_5)(\eta^4\text{-C}_4\text{H}_6)(\text{CO})]$

ii. $(\eta^3\text{-Allyl})(\eta^6\text{-benzene})\text{bromocarbonyltungsten}$

(c) (i) Determine the **VEC** of Ru in $[\text{RuCl}(\eta^3\text{-C}_3\text{H}_5)(\eta^4\text{-C}_4\text{H}_6)(\text{CO})]$ using **ionic model**. (Indicate your break down; Group number of Ru is 8)

(ii) Determine the **VEC** of Co in $[\text{CoBr}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_4\text{H}_4)]$ using **covalent model**. (Indicate your break down; Group number of Co is 9)

(d) Determine the **coordination number** of Mo in $[\text{MoBr}_2(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-C}_2\text{H}_4)(\text{CO})_2]$. Group number of Mo is 6.

(20 marks)

2. (a) What is meant by an “**agostic interaction**”? Draw the structure of $[\text{PdCl}_3(\text{PPh}_3)]^-$ indicating an agostic interaction. **Hint:** Think about square pyramidal geometry.

(b) Draw the **orbital diagram** between a metal (M) and a PPh_3 ligand, indicating the σ - and π -overlap.

(c) (i) Arrange PPh_3 , MeO^- , CO and CS in the order of increasing **π -acceptability**.

.....

(ii) Arrange NMe_3 , $\text{CF}_2=\text{CF}_2$ and $\text{CH}_2=\text{CH}_2$ in the order of increasing **σ -donor ability**.

.....

(d) (i) What are the possible **geometries** for a metal centre with **five** coordinated ligands?

.....

(ii) Draw the structures of three **geometrical isomers** of the Co(III) complex $[\text{CoCl}_2\text{Br}(\text{PF}_3)_3]$.

(iii) $[(\eta^5\text{-Cp})_2\text{V}(\text{NO})]$ has a **linear** V–NO fragment. Determine the Valence Electron Count (**VEC**) of V. V is a Group 5 metal.

(20 marks)

13/10/2011

The Open University of Sri Lanka
 B.Sc. Degree Program 2011/2012
 CMU3122 / CME3122 - Organometallic Chemistry - Level 5
 Assignment Test - I. Answer Guide

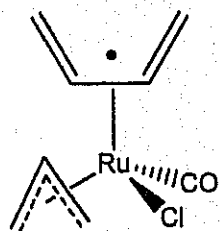
Part A – MCQ ANSWERS

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

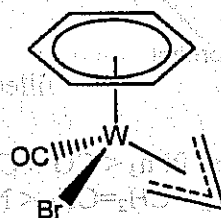
1.(a) (i) $(\eta^3\text{-Allyl})\text{chloro}(\eta^2\text{-ethene})\text{iron}$

(ii) Carbonyl($\eta^4\text{-cyclobutadiene}$)fluorocobalt

(b) i.



ii.



(c)

i. Ru^{2+}	= 6e
Cl^-	= 2e
$\eta^3\text{-C}_3\text{H}_5^-$	= 4e
CO	= 2e
$\eta^4\text{-C}_4\text{H}_6$	= 4e
VEC	= 18e

ii. Co^0	= 9e
Br	= 1e
$\eta^5\text{-C}_5\text{H}_5$	= 5e
$\eta^4\text{-C}_4\text{H}_4$	= 4e
VEC	= 19e

(d)

Electron pairs donated by two Br^- = 2

Electron pairs donated by $\eta^3\text{-C}_3\text{H}_5^-$ = 2

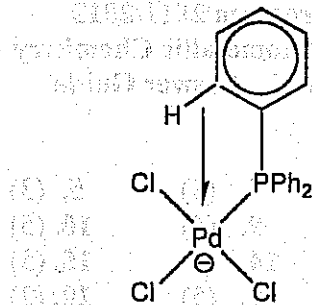
Electron pairs donated by $\eta^2\text{-C}_2\text{H}_4$ = 1

Electron pairs donated by two CO = 2

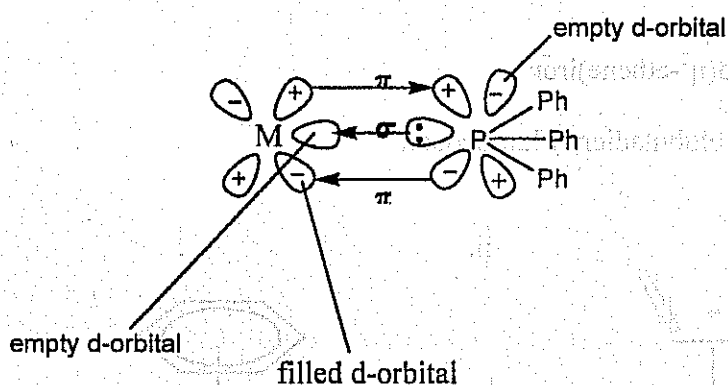
Total no. of electron pairs = 7

Therefore C.N = 7

2. (a) A weak interaction between a bonding electron pair of a C-H bond and a metal center



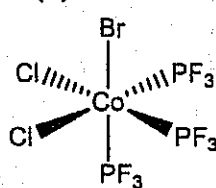
(b)



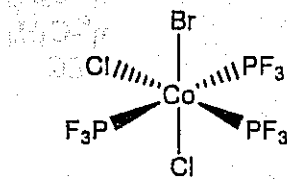
- (c) i. $\text{MeO}^- < \text{PPh}_3 < \text{CO} < \text{CS}$
 ii. $\text{CF}_2=\text{CF}_2 < \text{CH}_2=\text{CH}_2 < \text{NMe}_3$

(d) (i) trigonal bipyramidal and square-pyramidal

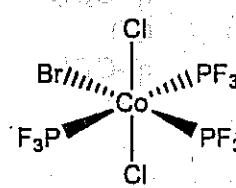
(ii)



fac



mer, cis



mer, trans

(iii)

Linear V-NO fragment

$$\begin{array}{r} \text{V}^0 = 5 \text{ e} \\ 2 \text{ Cp} = 10 \text{ e} \\ \text{NO} = \underline{3 \text{ e}} \\ \hline 18 \text{ e} \end{array}$$

NO is a 3e donor

$$\begin{array}{r} \text{V}^{2+} = 3 \text{ e} \\ 2 \text{ Cp}^- = 12 \text{ e} \\ \text{NO} = \underline{3 \text{ e}} \\ \hline 18 \text{ e} \end{array}$$