THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. & B. Ed. DEGREE / STAND ALONG COURSE IN SCIENCE - LEVEL 5
ASSIGNMENT TEST II (NBT) 2017/2018
CYU5300/CMU3122 – Organometallic Chemistry

20th July 2018 (Friday) 4.15 – 5.15 p.m.

ANSWER ALL QUESTIONS

Select the most correct answer/choice 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 (45 marks)

1. Which one of the following statements is **true** about $[Co_2(CO)_8]$?
   1) There is no Co-Co bond in the complex.
   2) It has bridging carbonyl ligands when it is dissolved in an organic solution.
   3) Co centre does not obey the 18e rule.
   4) Reduction of $Co(OAc)_2$ with CO/H_2 gives $[Co_2(CO)_8]$.
   5) In solid state it does not have bridging carbonyl ligands.

2. Which one is an example of an **insertion reaction**?
   1) $[Os(CO)_5] + 2\ CF_2{=}CF_2 \rightarrow [(OC)_4Os(C_4F_8)] + CO$
   2) $[PtH(CO)_3]I + CH_2{=}CH_2 \rightarrow [PtH(\eta^2\text{-}C_2H_4)(CO)_3]I$
   3) $[(\eta^5\text{-}C_5H_5)MnPh(H)(CO)] + CH_2{=}CH_2 \rightarrow [(\eta^5\text{-}C_5H_5)MnPh(Et)(CO)]$
   4) $[(\eta^5\text{-}C_5H_5)Mn(CO)_3] + LiMe \rightarrow Li[(\eta^4\text{-}C_5H_5Me)Mn(CO)_3]$
   5) $[Pd(PPh_3)_4] + PhI \rightarrow [Pd(Ph)(I)(PPh_3)_2] + 2\ PPh_3$

3. The **correct** statement regarding oxidative addition reaction is
   1) Valence electron count of the metal is always increased by 2 electrons.
   2) Coordination number of the metal is always reduced by 2 units.
   3) Oxidation number of the metal is always increased by 2 units.
   4) Oxidation number of the metal is increased by 2 units and the Coordination number of the metal is decreased by 2 units.
   5) None of the above statements is true.

4. Which statement is **not true** about $[RhCl(PPh_3)_3]$?
   1) It is a square planar complex.
   2) It is a catalyst for hydrogenation of olefins.
   3) Its IUPAC name is tris(triphenylphosphine)rhodium chloride.
   4) It reacts with O_2 to give $[RhCl(\eta^2\text{-}O_2)(PPh_3)_3]$.
   5) It is called "Wilkinson's Catalyst".

5. Most **likely** reaction that would take place is
   1) $[(\eta^6\text{-}C_6H_6)Rh(\eta^5\text{-}C_5H_5)]^+ + Ph^- \rightarrow [(\eta^6\text{-}C_6H_6)Rh(\eta^4\text{-}C_5H_5Ph)]$
   2) $[(\eta^5\text{-}C_5H_5)_2TiCl_2] + AlMe_3 \rightarrow [(\eta^5\text{-}C_5H_5)_2TiMe_2] + AlCl_2Me$
   3) $[Ni(PEt_3)_3] + PhCl \rightarrow [Ni(Ph)(Cl)(PEt_3)_2] + PEt_3$
   4) $Ni + 4\ NH_3 \rightarrow [Ni(NH_3)_4]$
   5) $[MnCF_3(CO)_5] + CO \rightarrow [Mn(COCF_3)(CO)_5]$

6. Consider the following statements,

(i) The nucleophilicity of R^- group decreases as NaR > RMgX > LiR > ZnR_2

(ii) $[CoH(CO)_4]$ is a H^+ donor.

(iii) $[CoH(PEt_3)(CO)_3]$ is more basic than $[CoH(CO)_4]$.

The **correct** statement/s is/are

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

7. β-Hydride abstraction occurs in

1) compound where the metal is coordinatively unsaturated.
2) compound having a metal-carbene group.
3) compound having a metal-methyl group.
4) compound having a metal-benzyl group.
5) compound having a PPh_3 ligand.

8. Which statement is **not true** about $Na[Fe(CO)_4]$?

1) Its IUPAC name is sodium tetracarbonylferrate.
2) The coordination number of iron is 4.
3) According to ionic model, the oxidation number of iron is zero.
4) Reduction of $Na[Fe(CO)_4]$ with Na gives $Na_2[Fe(CO)_4]$.
5) $Na[Fe(CO)_4]$ is an 17e complex.

9. 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 σ-donor ligands.
4) the metal is positively charged.
5) electron withdrawing groups are on coordinated ligands.

10. What is the product of the reaction, $[Mn_2(CO)_{10}] + Na \rightarrow ?$

1) $Na[Mn(CO)_4]$ 2) $Na[Mn_2(CO)_{10}]$ 3) $Mn_2[Na(CO)_5]$
4) $Na[Mn(CO)_5]$ 5) Both $Na[Mn(CO)_4]$ and $Na[Mn(CO)_5]$ are formed.

11. Consider the following statements,

(i) Addition of MeI to *trans*-$[IrCl(CO)(PPh_3)_2]$ is *cis*.

(ii) Basic metal centres can be protonated by acids such as HCl, CH_3CO_2H and CF_3CO_2H to give metal hydrides.

(iii) D_2O can be used to distinguish a metal hydride from a metal carbonyl.

*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).

12. Consider the following statements about the Vaska's complex, *trans*-$[IrCl(CO)(PPh_3)_2]$.

(i) It reacts with H_2 to give $[Ir\ H_2Cl(CO)(PPh_3)_2]$.

(i) It reacts with N_2 to give $[trans\text{-}IrCl(N_2)(PPh_3)_2]$.

(iii) It reacts with NaI to give *trans*-$[IrI(CO)(PPh_3)_2]$.

*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).

13. Consider the following statements about $[RhH(CO)_3]$. (Group number of Rh is 9)

(i) It shows only one carbonyl band in its IR spectrum.

(ii) It is a tetrahedral complex.

(iii) It reacts with styrene to give $[Rh(CH_2CH_2Ph)(CO)_3]$.

*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).

14. Consider the following statements about metal carbonyls.

(i) The carbonyl stretching frequencies of doubly bridging metal carbonyls are higher than those of triply bridging ones.

(ii) CO stabilizes the metal centres in lower oxidation states.

(iii) $[Ni(CO)_4]$ shows two carbonyl bands in its IR spectrum.

The **correct** statement/s is/are

1) (ii) only 2) (i) & (ii) only 3) (i) & (iii) only

4) (ii) & (iii) only 5) (i), (ii) & (iii)

15. Consider the following statements.

(i) $[HCo(CO)_4]$ is a strong acid than acetic acid.

(ii) The oxidative addition of coordinated H_2 does not depend on the strength of the back donation.

(i) Metal hydrides cannot act as H^+ donors.

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).

THE OPEN UNIVERSITY OF SRI LANKA
B. Sc DEGREE PROGRAMME 2017/2018
CYU5300/CMU3122 – ORGANOMETALLIC CHEMISTRY- LEVEL 5
ASSIGNMENT TEST-II (Part A)

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

Reg. No. | | | | | | | | | |

For Examiners Use

Part A	
Part B	
Total %	

Marks

Correct Answers		
Wrong Answers		
Total		

1.	1	2	3	4	5	2.	1	2	3	4	5	3.	1	2	3	4	5
4.	1	2	3	4	5	5.	1	2	3	4	5	6.	1	2	3	4	5
7.	1	2	3	4	5	8.	1	2	3	4	5	9.	1	2	3	4	5
10.	1	2	3	4	5	11.	1	2	3	4	5	12.	1	2	3	4	5
13.	1	2	3	4	5	14.	1	2	3	4	5	15.	1	2	3	4	5

Part B (55 marks)

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

1. (a) (i) What is the **molecular formula** of the product (**A**) formed due to oxidative addition of PhI to $[PtI_2(PMe_3)_2]$? .....

(ii) Draw and identify the structures of the **three** isomers of (**A**).

(b) The alkyl Pt(II) complex $[CH_3CH_2Pt(OMe)(dppe)]$ gives an alkane (**C**), alkene (**D**), alcohol (**E**) and aldehyde (**F**) when it is heated in toluene at 100 °C.
Identify (**C**), (**D**), (**E**), and (**F**). (dppe = $PPh_2CH_2CH_2PPh_2$ is a bidentate ligand).

(**C**) ..... (**D**) .....

(**E**) ..... (**F**) .....

(c) Arrange the complexes $[Ni(CO)_3PX_3]$ in the decreasing order of their carbonyl frequencies $\upsilon(C\equiv O)$. X varies from Cl, Me, OMe, F.

.....

(d) **Identify** the product(s) of the following reactions using **the hint given in the brackets**.

(i) $[RhH(\eta^2\text{-}CH_2{=}CH_2)(PPh_3)_2]$ + PPh_3 → 16e-complex (**K**) (association & insertion)

(ii) $[(X_3P)_3IrCH_2C(=O)CH_3] \xrightarrow{\Delta}$ 18e-complex (**L**) (cyclometallation)

(iii) $[(\eta^5\text{-}Cp)Fe(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_2]$ + I_2 → 18e-complex (**M**) (electrophilic addition)

(**K**) (**L**) (**M**)

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

(i) $[Cr(CO)_5]$ → $[(OC)_4Cr\text{-}C(=O)H]^-$ ----------

(ii) $[Cp_2ZrCl_2]$ → $[Cp_2Zr(C\equiv CPh)_2]$ ----------

(f) Methane and a Ir-complex (**P**) are produced when $[MeIr(PPh_3)_3]$ is heated in an atmosphere of H_2. Identify the Ir-complex (**P**) and the write the molecular formula of the probable octahedral intermediate (**Q**).

THE OPEN UNIVERSITY OF SRI LANKA
B. Sc. DEGREE PROGRAMME 2017/2018
CYU5300/CMU3122 – ORGANOMETALLIC CHEMISTRY
ANSWER GUIDE FOR ASSIGNMENT TEST-II

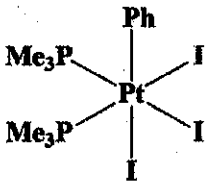
Part A

(1) 4 (2) 3 (3) 5 (4) 3 (5) 3 (6) 4 (7) 1 (8) 3 (9) 3
(10) 4 (11) 3 (12) 2 (13) 1 (14) 2 (15) 1

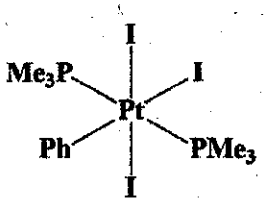
Part B

1. (a) (i) $[PtI_3(Ph)(PMe_3)_2]$

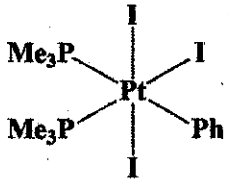
(ii)



fac-$[PtI_3(Ph)(PMe_3)_2]$



mer,trans-$[PtI_3(Ph)(PMe_3)_2]$

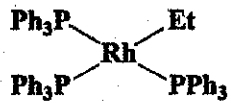


mer,cis-$[PtI_3(Ph)(PMe_3)_2]$

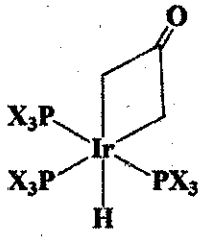
(b) (C) CH_3CH_3 **(D)** $CH_2{=}CH_2$ **(E)** MeOH **(F)** HCHO

(c) F > Cl > OMe > Me

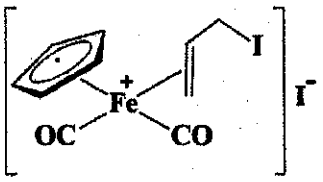
(d)



(K)



(L)



(M)

(e) (i) NaH / $LiAlH_4$

(ii) 2 MC≡CPh M = Na, K, Li

(f) (P) $[IrH(PPh_3)_3]$ **(Q)** $[IrMe(H)_2(PPh_3)_3]$