Sample

THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. & B. Ed. DEGREE / STAND ALONG COURSE IN SCIENCE - LEVEL 5
ASSIGNMENT TEST II (NBT) 2014/2015
CMU3122/CME5122 – Organometallic Chemistry

08th March 2015 (Sunday) 4.00 – 5.00 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. Consider the following statements regarding **insertion reactions**.
   (i) Coordination number of the metal is not changed.
   (ii) Valence electron count of the metal is changed by two units.
   (iii) Migratory insertion of methyl on to a CO is called "1,1-insertion" .
   *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).

2. The component **not used** or **formed** in the Monsanto process is
   1) HOAc 2) MeCOI 3) H_2 4) CO 5) MeOH

3. Most **likely** reaction that would take place is
   1) $[(\eta^5\text{-}C_5H_5)IrCl_2(\eta^2\text{-}CH_2{=}CH_2)]^+ + Ph^- \rightarrow [(\eta^4\text{-}C_5H_5Ph)IrCl_2(\eta^2\text{-}CH_2{=}CH_2)]$
   2) $[Ni(PPh_3)_4] + 4\ NH_3 \rightarrow [Ni(NH_3)_4] + 4\ PPh_3$
   3) $[MnCF_3(CO)_5] + CO \rightarrow [Mn(COCF_3)(CO)_5]$
   4) $[(\eta^5\text{-}C_5H_5)_2TiCl_2] + AlMe_3 \rightarrow [(\eta^5\text{-}C_5H_5)_2TiClMe] + AlClMe_2$
   5) $[Fe(CO)_5] + 3\ CF_2{=}CF_2 \rightarrow [(OC)_3Fe(\eta^6\text{-}C_6F_6)] + 2\ CO$

4. Which one is an example of an **reductive elimination reaction**?
   1) $[Ni(CO)_4] + CH_2{=}CH_2 \rightarrow [(OC)_3Ni(CH_2{=}CH_2)] + CO$
   2) $[Ni(CO)_4] + 2\ CF_2{=}CF_2 \rightarrow [(OC)_2Ni(C_4F_8)] + 2\ CO$
   3) $[Pt(Ph)(H)(PPh_3)_2] + 2\ PPh_3 \rightarrow [Pt(PPh_3)_4] + C_6H_6$
   4) $[(\eta^3\text{-}C_3H_5)PtMe(CO)_2] \rightarrow [(\eta^3\text{-}C_3H_5)Pt(CO)(COMe)]$
   5) $[MeMn(CO)_5] + CF_2{=}CF_2 \rightarrow [Mn(CF_2CF_2Me)(CO)_5]$

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

6. What is the **major product** of the reaction, *cis*-$[PtCl_2(PMe_3)_2]$ + excess LiMe → ?
   1) $Li_2[PtCl_2Me_2(PMe_3)_2]$ 2) *cis*-$[PtMe_2(PMe_3)_2]$
   3) *trans*-$[PtCl(Me)(PMe_3)_2]$ 4) $Li[PtCl_2Me(PMe_3)_2]$
   5) *cis*-$[PtCl(Me)(PMe_3)_2]$

7. The product(s) of the reaction, $[Mn_2(CO)_{10}]$ + Na → is/are

1) $Na[Mn(CO)_5]$ 2) $Na[Mn_2(CO)_5]$ 3) $Na[Mn_2(CO)_{10}]$
4) $Na_2[Mn(CO)_5]$ 5) $Na_2[Mn(CO)_5]$ and $Na[Mn_2(CO)_{10}]$.

8. Consider the following statements,

(i) $[HCo(CO)_4]$ is a H^+ donor.
(ii) $[HCo(CO)_3(PPh_3)]$ is a weaker acid than $[HCo(CO)_4]$.
(iii) $[HCo(CO)_4]$ shows a negative **proton** chemical shift (in ppm) with respect to $SiMe_4$ (TMS).

*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).

9. β-Hydride abstraction could take place in

1) $[Me_3SiOMn(CO)_5]$ 2) $[Pd(PEt_3)_4]$
3) $[MeRe(CO)_5]$ 4) *trans*-$[PtBr(Me)(PPh_3)_2]$
5) $[(\eta^5\text{–}C_5H_5)Rh(Me)(PPh_3)(CO)]I$

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

(i) It reacts with Cl_2 to give $[IrCl_3(CO)(PPh_3)_2]$.
(ii) It reacts with CO to give $[IrCl(CO)_2(PPh_3)_2]$.
(iii) It reacts with NaI to give *trans*- $[IrI(CO)(PPh_3)_2]$.

*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).

11. Consider the following complexes.

(i) $[PhRh(CO)_3]$ (ii) $[MeCo(CO)_3]$ (iii) $[(\eta^5\text{–}C_5Me_5)Ta(CH_2Ph)_3]$

α-Agostic (alpha agostic) interaction could be seen in

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

12. The **most stable** product formed when $[Fe(CO)_5]$ is reacted with cyclopentadiene (C_5H_6) is

1) $[Fe(CO)_3(\eta^4\text{–}C_5H_6)]$ 2) $[Fe(CO)_4(\eta^2\text{–}C_5H_6)]$
3) $[(\eta^5\text{–}C_5H_5)Fe(CO)_3]$ 4) $[Fe(CO)(\eta^4\text{–}C_5H_6)_2]$
5) $[(\eta^5\text{–}C_5H_5)_2Fe]$

13. Nucleophilic attack of R^- on a coordinated alkene ligand is **not** facilitated if

1) the metal is positively charged.
2) the metal is coordinated to poor σ-donor ligands.
3) the metal is coordinatively saturated.
4) metal is in a higher oxidation state
5) none of the above choices are correct.

14. What is the **most likely** carbonyl stretching frequency in the IR spectrum of $[Ir_4(CO)_{12}]$?

1) 1660 2) 1760 3) 1860 4) 2080 5) 2250

15. Consider the following statements,

(i) Metal hydrides can be prepared by protonating metal complexes with a strong acid such as CF_3CO_2H.
(ii) Oxidative addition of H_2 to a metal centre gives a metal dihydride with the *cis*-arrangement.
(iii) CH_5^+ can be considered as the dihydrogen complex of CH_3^+.

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 2014/2015
CMU3122/CME5122 – ORGANOMETALLIC CHEMISTRY- LEVEL 5
ASSIGNMENT TEST-II (Part A)

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

Part A	
Part B	
Total %	

Reg. No. | | For Examiners Use

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 hydrogen to $[IrH(PPh_3)_3]$? .....

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

(b) $TiEt_4$ decomposes *via* reductive elimination and β-hydride elimination as shown below.

$TiEt_4 \rightarrow [TiEt_2] + (\mathbf{K})$

$TiEt_4 \rightarrow [Ti(H)Et_3] + (\mathbf{L})$

$[Ti(H)Et_3] \rightarrow [TiEt_2] + (\mathbf{M})$

Identify the molecules (**K**), (**L**) and (**M**).

(**K**) ..... (**L**) .....

(**M**) .....

(c) (i) Arrange NO^+, PH_3, NH_3 and CO in the order of increasing π-acceptability.

.....

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

(i) $[Co(CN)_5]^{3-} + MeI \rightarrow$ **?** + **?**
(1e-oxidative addition)

(ii) *trans*-$[Pt(CH_2CH_3)_2(PPh_3)_2] + CO \rightarrow$
(Migratory insertion to give a
4-coordinate 16e-complex)

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

(i) $[(\eta^5\text{-}C_5H_5)Zr(H)Cl] \rightarrow [(\eta^5\text{-}C_5H_5)Zr(Et)Cl]$ ----------

(ii) $[W(CO)_6] \rightarrow K[WH(CO)_5]$ ----------

(f) $[RhMe(PPh_3)_3]$ undergoes cyclometallation followed by reductive elimination to give a **square planar** metal complex (**R**) and an organic molecule (**S**).

Draw the **structures** of (**R**) and (**S**).

The Open University of Sri Lanka
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CMU3122/CME5122 – Organometallic Chemistry - Level 5
Answer Guide to Assignment Test-II held on 08-03-2015

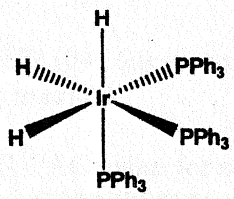
Part A – MCQ ANSWERS

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

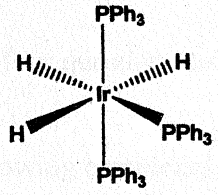
Part B

(1) (a) (i) $[IrH_3(PPh_3)_3]$

(ii)



fac- isomer



mer-isomer

(b) K = $CH_3CH_2CH_2CH_3$
L = $CH_2=CH_2$
M = CH_3CH_3

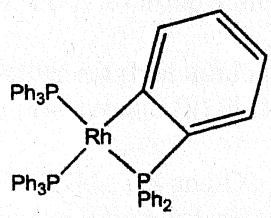
(c) $NH_3 < PH_3 < CO < NO^+$

(d) (i) $[MeCo(CN)_5]^{3-}$ + $[CoI(CN)_5]^{3-}$

(ii) $[Pt(COEt)(Et)(PPh_3)_2]$

(e) (i) $CH_2=CH_2$
(ii) KOH

(f)



R + CH_4 **S**