THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. & B. Ed. DEGREE / STAND ALONG COURSE IN SCIENCE - LEVEL 5
ASSIGNMENT TEST II (NBT) 2013/2014
CMU3122/CME5122 – *Organometallic Chemistry*

07th April 2014 (Monday) 10.30 – 11.30 a.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. *Pick the **incorrect** statement regarding an **oxidative addition** reaction.*
   1) Oxidative addition of chlorine is *cis*.
   2) Oxidative addition is facile if the metal centre is coordinatively unsaturated.
   3) Coordinatively saturated metal centres can undergo oxidative addition reaction.
   4) Oxidation number of the metal is increased by 1 or 2 unit(s).
   5) Coordination number of the metal is always increased by 2 units.

2. Consider the following statements regarding **reductive elimination**.
   (i) Coordination number of the metal is reduced by two units.
   (ii) Oxidation number of the metal is reduced by one unit.
   (iii) Coordinatively unsaturated 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).

3. 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) $[MnCF_3(CO)_5] + CO \rightarrow [Mn(COCF_3)(CO)_5]$
   4) $Ni + 4\,NH_3 \rightarrow [Ni(NH_3)_4]$
   5) $[MeMn(CO)_5] + CO \rightarrow [Mn(COMe)(CO)_5]$

4. Which one is an example of a **1,1-insertion reaction**?
   1) $[Fe(CO)_5] + CF_2{=}CF_2 \rightarrow [(OC)_4Fe(CF_2{=}CF_2)] + CO$
   2) $[(\eta^1\text{-}C_3H_5)Mn(CO)_5] + \text{heat} \rightarrow [(\eta^3\text{-}C_3H_5)Mn(CO)_4] + CO$
   3) $[Fe(CO)_5] + 2\,CF_2{=}CF_2 \rightarrow [(OC)_4Fe(C_4F_8)] + CO$
   4) $[(\eta^3\text{-}C_3H_5)PtMe(CO)] + CO \rightarrow [(\eta^3\text{-}C_3H_5)Pt(CO)(COMe)]$
   5) $[MeMn(CO)_5] + CF_2{=}CF_2 \rightarrow [Mn(CF_2CF_2Me)(CO)_5]$

5. Which statement is **not true** about $[IrCl(PPh_3)_3]$?
   1) The IUPAC name of it is chlorotris(triphenylphosphine)iridium.
   2) It forms two geometrical isomers.
   3) It is a d^8 complex.
   4) PPh_3 is a poor π-acceptor than CO.
   5) It reacts with H_2 to give $[IrClH_2(PPh_3)_3]$.

6. Consider the following complexes.

(i) $[EtRh(CO)_3]$ (ii) $[MeOCo(CO)_3]$ (iii) *trans*-$[NiCl_2(PPh_3)_2]$

β-Agostic (beta agostic) interaction could be seen in

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

7. What is the **most stable product** formed, when $[Mo(CO)_6]$ is reacted with KOH?

1) $K[Mo(OH)(CO)_5]$ 2) $[Mo(OH)_2(CO)_4]$ 3) $K[Mo(CO)_5(CHO)]$
4) $K[MoH(CO)_5]$ 5) $K[Mo(CO)_5]$

8. Pick the **incorrect** statement regarding metal hydrides.

1) $\nu(M–D) = \nu(M–H) \times \sqrt{2}$.
2) Dihydrogen can act as a η^2-ligand.
3) Oxidative addition of coordinated H_2 depends on the strength of the back donation.
4) $K_2[ReH_9]$ is a fluxional molecule.
5) Metal hydrides show a weak IR band around 2200 cm^{-1}.

9. Consider the following statements on catalysis.

(i) An active catalyst increases the rate of a reaction.
(ii) A catalyst does not alter the activation energy of a reaction.
(iii) A catalyst involved in a reaction is regenerated at the end of each catalytic cycle.

*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).

10. 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 square planar complex.
(iii) It reacts with ethene to give $[Rh(Et)(CO)_3]$.

*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. The **most stable** product formed when $[Mo(CO)_6]$ is reacted with cyclobutadiene (C_4H_4) is

1) $[Mo(CO)_4(\eta^4–C_4H_4)]$ 2) $[Mo(CO)_4(\eta^2–C_4H_4)]$
3) $[Mo(CO)_4(\eta^2–C_4H_4)_2]$ 4) $[Mo(CO)_3(\eta^4–C_4H_4)]$
5) $[Mo(CO)_3(\eta^2–C_4H_4)]$

12. What is the **product** formed, when $[Mo(CO)_6]$ is reacted with LiMe?

1) $Li[Mo(CO)_4]$ 2) $[MoMe(CO)_5]$ 3) $Li[Mo(CO)_5(COMe)]$
4) $[MoMe_2(CO)_4]$ 5) $[MoMe(CO)_4(COMe)]$

13. The **most unlikely species** formed due to the decomposition of $PbEt_4$?

1) $CH_2=CH_2$ 2) CH_3CH_3 3) PbH_2Et_2
4) $PbEt_2$ 5) $CH_3CH_2CH_2CH_3$

14. What is the **most likely** carbonyl stretching frequency in the IR spectrum of $[Ni(CO)_4]$?

1) 2200 2) 2050 3) 1850 4) 1750 5) 1650

15. The VEC of each Ru centre in the symmetrical binuclear complex $[Cp_2Ru_2(CO)_4]$ is 18. Which one of the following statements is **true** about the above complex? (Group number of Ru is 8)

1) Hapticity of each Cp ligand is 6.
2) Each metal centre has only one bridging carbonyl ligand.
3) Each metal centre has only one terminal carbonyl ligand.
4) It does not have a Ru–Ru bond.
5) Each metal centre is coordinatively unsaturated.

THE OPEN UNIVERSITY OF SRI LANKA
B. Sc DEGREE PROGRAMME 2013/2014
CMU3122/CME5122 – 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 **structural** change or changes would you expect for **reductive eliminatio** reaction of a **octahedral** metal centre?

(ii) Give **an example** for the above reaction.

(b) (i) One mole of $[Co_2(CO)_8]$ reacts with one mole of H_2 to give two mole of (**A**). Write the chemical formula of (**A**).

(**A**) .....

(ii) (**A**) undergoes migratory insertion with $CH_2{=}CH_2$ to give the square planar complex (**B** Write the chemical formula of (**B**).

(**B**) .....

(c) How would you account for the variation in ν(CO) of the following compounds?

Compound	**ν(CO)** in cm^{-1}
Free-CO	2143
fac-$[Mo(CO)_3(PCl_3)_3]$ (**P**)	2040, 1991
fac-$[Mo(CO)_3(PEt_3)_3]$ (**Q**)	1937, 1841

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

(i) *trans*-$[IrCl(CO)(PPh_3)_2]$ + O_2 →
(oxidative addition)

(ii) *cis*-$[PtCl(CH_2CH_3)(PCl_3)_2]$ $\rightarrow$
(β-hydride abstraction to give
5-coordinate 18e-complex)

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

(i) $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \rightarrow 2\,[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ ----------

(ii) *trans*-$[FeCl_2(dppe)_2]$ $\rightarrow$ *trans*-$[FeH_2(dppe)_2]$ ----------

(f) **Ortho**cyclometallation reaction of $[IrCl(PPh_3)_3]$ gives **octahedral** iridium hydride (**R**). Draw the **structure** of (**R**).

Answer Guide for CAT-II-2013/2014
CMU3122/CME5122 – Organometallic Chemistry held on 07-04-2014

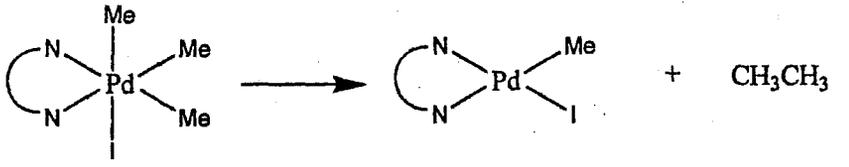
Part A – MCQ ANSWERS

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

Part B

(1)(a) (i) Octahedral $\xrightarrow{RE}$ Square Planar

(ii)



(b) (i) (**A**) = $[HCo(CO)_4]$
(ii) (**B**) = $[EtCo(CO)_3]$

(c) ν(CO) α the strength of the C≡O bond

Bond order of free CO is 3, it shows the highest value

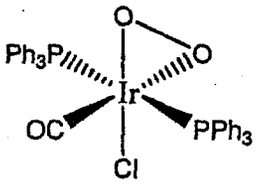
In metal complexes, ν(CO) decreases as back bonding increases

σ-donor ability of PEt_3 > PCl_3 thus Mo centre in (**Q**) is more basic than that of (**P**)

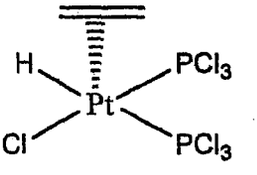
Back donation is more in (**Q**) hence it shows the lowest value

fac-geometry is expected to give two IR bands

(d) (i)



(ii)



(e) (i) Na or K
(ii) $NaBH_4$

(f)