THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. & B. Ed. DEGREE / STAND ALONG COURSE IN SCIENCE - LEVEL 5
ASSIGNMENT TEST II (NBT) 2011/2012
CMU3122/CME5122 – Organometallic Chemistry

29th October 2011 (Saturday) 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. Pick the **correct** statement regarding an **oxidative addition** reaction.
   1) Oxidation number of the metal is **always** increased by 2 units.
   2) Coordination number of the metal is **always** increased by 2 units.
   3) Coordinatively saturated metal centres cannot undergo oxidative addition reaction.
   4) Oxidative addition is facile if the metal centre is coordinatively unsaturated.
   5) None of the above statements is true.

2. Which one is an example for **2e-oxidative-addition reaction**?
   1) $[Co_2(CO)_8] + H_2 \rightarrow 2\,[HCo(CO)_4]$
   2) $2\,[Co(CN)_5]^{3-} + MeI \rightarrow [MeCo(CN)_5]^{3-} + [CoI(CN)_5]^{3-}$
   3) $[(\eta^1\text{-}C_3H_5)Mn(CO)_5] \rightarrow [(\eta^3\text{-}C_3H_5)Mn(CO)_4] + CO$
   4) $[Ni(PEt_3)_3] + PhI \rightarrow [Ni(Ph)(I)(PEt_3)_2] + PEt_3$
   5) $[MeMn(CO)_5] + CF_2{=}CF_2 \rightarrow [Mn(CF_2CF_2Me)(CO)_5]$

3. Consider the following statements regarding **reductive elimination**.
   (i) Coordinatively unsaturated compounds prefer to undergo reductive elimination.
   (ii) Reductive elimination is facile if the metal centre is negatively charged.
   (iii) Coordination number of the metal is reduced by two units during reductive elimination.

   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).

4. Consider the following statements about $[Ni(CO)_4]$.
   (i) It is a square planar complex.
   (ii) It shows four carbonyl bands in its IR spectrum.
   (iii) It is a coordinatively unsaturated complex.

   The correct statement/s is/ are

   1) (i) only. 2) (i) & (iii) only. 3) (i) & (ii) only.
   4) (ii) & (iii) only. 5) None of the above

5. α-Agostic (alpha agostic) interaction could be seen in
   1) $[(OC)_3Pt\{P(OPh)_3\}]$ 2) $[MeMn(CO)_5]$
   3) $[RhI(OMe)(PPh_3)(CO)]$ 4) $[Ni(PEt_3)_3]$
   5) $[(EtO)Mn(CO)_5]$

6. Which one is the most likely **substitution reaction**?

1) $[Ni(CO)_4] \rightleftharpoons [Ni(CO)_3] + CO$
2) $[Ni(PEt_3)_3] + PhI \rightarrow [Ni(Ph)(I)(PEt_3)_2] + PEt_3$
3) $[PtH(CO)_3]I + CH_2{=}CH_2 \rightarrow [Pt(CH_2CH_3)(CO)_3]I$
4) $[Fe(CO)_5] + CF_2{=}CF_2 \rightarrow [(OC)_4Fe(CF_2{=}CF_2)] + CO$
5) $[Os(CO)_5] + H_2 \rightarrow [OsH_2(CO)_4] + CO$

7. How many IR bands does *trans*-$[Mo(CO)_4(PF_3)_2]$ show?

1) 1 2) 2 3) 3 4) 4 5) 5

8. Nucleophilic attack on a coordinated ligand is facilitated if

1) the metal is coordinatively unsaturated.
2) the metal is in a lower oxidation state.
3) the metal carries a negative charge.
4) the metal is coordinated to good σ-donor ligands.
5) None of the above statements is true.

9. Which one is an example of an **insertion reaction**?

1) $[Fe(CO)_5] + CF_2{=}CF_2 \rightarrow [(OC)_4Fe(CF_2{=}CF_2)] + CO$
2) $[MeMn(CO)_5] + CF_2{=}CF_2 \rightarrow [Mn(CF_2CF_2Me)(CO)_5]$
3) $[Fe(CO)_5] + 2\,CF_2{=}CF_2 \rightarrow [(OC)_4Fe(C_4F_8)] + CO$
4) $[Pt(PPh_3)_4] + PhI \rightarrow [Pt(Ph)(I)(PPh_3)_2] + 2\,PPh_3$
5) $[(\eta^1\text{-}C_3H_5)Mn(CO)_5] \rightarrow [(\eta^3\text{-}C_3H_5)Mn(CO)_4] + CO$

10. Consider the following statements regarding the preparation of *cis*-$[OsH_2(CO)_4]$.

(i) It can be prepared by reacting $[Os(CO)_5]$ with dihydrogen.
(ii) Dihydrogen addition is always *cis*.
(iii) $[Os(CO)_5]$ shows only one carbonyl band in its IR spectrum.

The correct statements are

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

11. Which statement is **not true** about $K_2[Fe(CO)_4]$?

1) The IUPAC name is dipotassium tetracarbonylferrate.
2) The coordination number of iron is 4.
3) According to ionic model, the oxidation number of iron is zero.
4) The ν(CO) of $K_2[Fe(CO)_4]$ is lower than that of $K[Fe(CO)_4]$.
5) CO is a good π-acceptor ligand.

12. Which metal carbonyl **does not** have a **bridging** carbonyl ligand?

1) $[Rh_4(CO)_{12}]$ 2) $[Fe_2(CO)_9]$
3) $[Fe_3(CO)_{12}]$ 4) $[Co_2(CO)_{18}]$
5) $[Re_2(CO)_{10}]$

13. Consider the following statements regarding ligands,

(i) $CH_2{=}CH_2$ is a weaker π-acceptor than $CF_2{=}CF_2$.
(ii) PMe_3 is a better σ-donor than PF_3.
(iii) PMe_3 is a better π-acceptor than CO.

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).

14. What is the **product** formed, when $[Fe(CO)_5]$ is reacted with NaH?

1) $Na[Fe(CO)_4]$ 2) $[FeH(CO)_4]$
3) $Na[Fe(CO)_4\{C{=}O)H\}]$ 4) $[FeH_2(CO)_4]$
5) $[Fe_2(CO)_9]$

15. Consider the following statements.

(i) Dihydrogen can act as a weak σ-donor.

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

(iii) All polyhydrides are fluxional molecules.

*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).

16. What is the **most unlikely product** that would be formed due to decomposition of $TiEt_4$?

1) n-Butane 2) Ethane 3) $[Et_2TiH_2]$
4) $[TiEt_2]$ 5) Ethene

17. A metal carbonyl contains a **doubly bridging** carbonyl ligand. What would be its IR frequency?

1) 2200 2) 2100 3) 1980 4) 1850 5) 1750

18. $[(\eta^5\text{-Cp})_2Fe_2(CO)_4]$ is a **coordinatively saturated** complex. It is a symmetrical binuclear complex. Which one of the following statements is **not true** about the above complex?

1) It does not have a Fe–Fe bond.
2) Each iron centre has two bridging carbonyl ligands.
3) Each iron centre has 18 valence electrons.
4) Fe belongs to the Group 8.
5) Each iron centre has one terminal carbonyl ligand.

19. 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 centers in lower oxidation states.

(iii) The back bonding increases the M–C bond strength.

*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).

20. Consider the following statements,

(i) Addition of dioxygen is always *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) (i) only. 2) (i) & (ii) only. 3) (ii) & (iii) only.
4) (i) & (iii) only. 5) (i), (ii) & (iii).

Part B (40 marks)

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

1. (a) (i) $[RhCl(PPh_3)_3]$ undergoes oxidative addition with Cl_2 to give the octahedral complex (**X**).

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

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

(b) What are the two **organic** products (**P**) and (**Q**) and the **metal complex** (**R**) that would be formed due to decomposition of $[L_3RhCH(Me)CH_2CH_3]$.

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

(**R**) .....

(c) The intermediate $[(OC)_4MnCH_2CH_3]$ undergoes β-hydride abstraction to give the olefin complex (**A**). Upon standing, (**A**) loses the olefin (**B**) to give the 16e-hydride (**C**). Identify (**A**), (**B**) and (**C**).

(**A**) (**B**)

(**C**)

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

Compound	ν(CO) in cm^{-1}
Free-CO	2143
$[Cr(CO)_6]$	2000
$[V(CO)_6]^-$	1860

(e) Give an example each for (i) 1,1-insertion and (ii) 1,2-insertion.

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

(i) $[IrH(CO)(PPh_3)_2]$ + $CF_3C{\equiv}CCF_3$ →

(migratory insertion)

(ii) $[Mo(CO)_6]$ + 1,3-butadiene →

(substitution)

(iii) $[Fe(PMe_3)_5] \xrightarrow{\Delta}$

(cyclometallation)

(iv) *cis*-$[PtMe_2(PPh_3)_2]$ + MeI →

(oxidative addition)

(v) $[(\eta^5\text{-}C_5H_5)W(CO)_3(\eta^2\text{-}CH_2{=}CH_2)]^+$ + OMe^- →

(neucleophilic attack on a coordinated olefin)

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

(i) $[(\eta^5\text{-}C_5H_5)_2ZrCl_2]$ → $[(\eta^5\text{-}C_5H_5)_2ZrCl(Me)]$ ----------

(ii) $[Mo(CO)_6]$ → $Na[HMo(CO)_5]$ ----------

(iii) *trans*-$[Fe(dppe)_2Cl_2]$ → *trans*-$[Fe(dppe)_2H_2]$ ----------

(iv) $Na[Mo(CO)_5]$ → $[MeMn(CO)_5]$ ----------

(v) $[WCl_6]$ → $[(\eta^5\text{-}C_5H_5)_2WH_2]$ ----------

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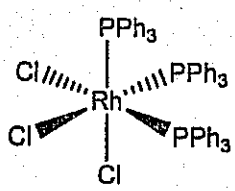
Assignment Test - II Answer Guide

Part A – MCQ ANSWERS

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

(1)(a)(i) $[RhCl_3(PPh_3)_3]$

(ii)



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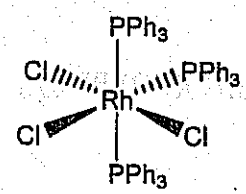

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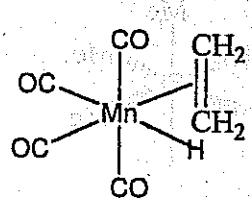
(b) **(P)** = CH_2=$CHCH_2CH_3$ **(Q)** = MeCH=CHMe **(R)** = $[L_3RhH]$

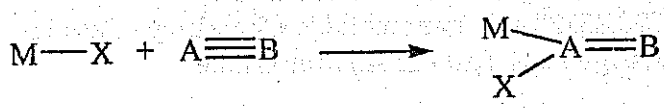
(c) **(A)** = $[Mn(CO)_4(H)(\eta^2\text{-}CH_2{=}CH_2)]$ **(B)** = $CH2{=}CH_2$



(C) = $[MnH(CO)_4]$

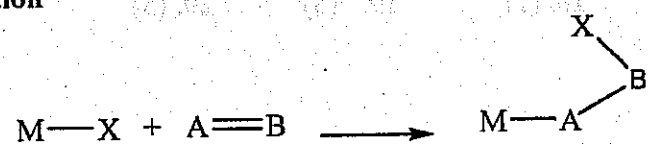
(d) ν (CO) decreases as back donation increases.
ν(CO) increases with bond strength (order) of C≡O bond. Metal complexes show lower values as there is back donation. In the case of $[V(CO)_6]^{\ominus}$, the metal is negatively charged, therefore, the back donation from the metal is higher, thus, it shows the lowest value.

(e) **1,1-insertion**



or $[MnMe(CO)_5] + CO \rightarrow [Mn(COMe)(CO)_5]$

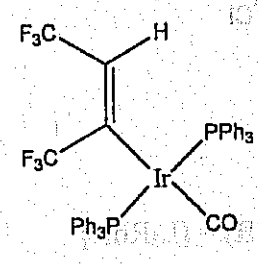
1,2- insertion

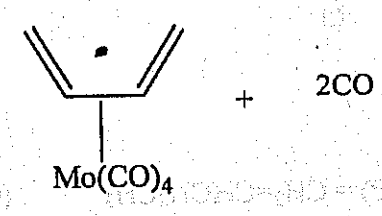


or $[PtH(PPh_3)]^+ + CH_2{=}CH_2 \rightarrow [PtEt(PPh_3)_3]^+$

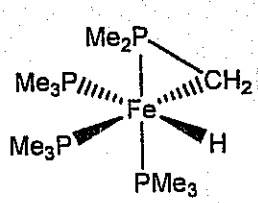
(2)

(a) (i) $[Ir(CF_3C{=}C(CF_3)H)(CO)(PPh_3)_2]$ (ii)

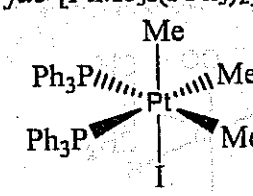




(iii)



(iv) *fac*-$[PtMe_3I(PPh_3)_2]$



(v) $[(\acute{\eta}^5\text{-}C_5H_5)W(CO)_3(CH_2CH_2OMe)]$

(b) (i) $AlMe_3$
(ii) NaOH
(iii) $NaBH_4$
(iv) MeI
(v) CpNa /$NaBH_4$