THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. & B. Ed. DEGREE / STAND ALONG COURSE IN SCIENCE - LEVEL 5
ASSIGNMENT TEST II (NBT) 2008/2009
CHU 3127/CHE 5127 – *Organometallic Chemistry*

02nd October 2008 **Duration: 1 ½ hours** **3.30 – 5.00 pm.**

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 1/5th of the mark will be deducted for each incorrect answer.

PART A (60 marks)

1. Which one is an example of an **insertion reaction**?
   1) $[Fe(CO)_5] + 2\ CF_2{=}CF_2 \rightarrow [(OC)_4Fe(C_4F_8)] + CO$
   2) $[(\eta^1\text{-}C_3H_5)Mn(CO)_5] \rightarrow [(\eta^3\text{-}C_3H_5)Mn(CO)_4] + CO$
   3) $[Pd(PPh_3)_4] + PhI \rightarrow [Pd(Ph)(I)(PPh_3)_2] + 2\ PPh_3$
   4) $[HMn(CO)_5] + CF_2{=}CF_2 \rightarrow [Mn(CF_2CF_2H)(CO)_5]$

2. Which one is the most likely **substitution reaction**?
   1) $[(\eta^1\text{-}C_3H_5)Mn(CO)_5] \rightarrow [(\eta^3\text{-}C_3H_5)Mn(CO)_4] + CO$
   2) $[Ni(PEt_3)_3] + PhI \rightarrow [Ni(Ph)(I)(PEt_3)_2] + PEt_3$
   3) $[Os(CO)_5] + I_2 \rightarrow [OsI_2(CO)_4] + CO$
   4) $[(OC)_4Fe(C_4F_8)] \rightarrow [Fe(CO)_4] + C_4F_8$

3. Consider the following statements regarding **reductive elimination**.
   (i) Coordination number of the metal is reduced by one unit during reductive elimination.
   (ii) Reductive elimination is facile if the metal centre is negatively charged.
   (iii) Coordinatively saturated compounds prefer to undergo reductive elimination.
   The correct statement/s is are
   1) (i) only 2) (iii) only
   3) (i) & (iii) only 4) (i), (ii) & (iii).

4. What is **not true** for a **2e-oxidative addition** reaction?
   1) Oxidation number of the metal is increased by 2 units.
   2) Coordination number of the metal is increased by 2 units.
   3) Valence electron count of the metal is always increased by 2 electrons.
   4) Oxidative addition is facile if the metal centre is coordinatively unsaturated.

5. Consider the following statements about $[Cr(CO)_6]$.
   (i) It shows the octahedral geometry in the solid state.
   (ii) It shows one carbonyl band in its IR spectrum.
   (iii) It can be prepared by reducing $CrCl_3$ with Al in the presence of CO at high temperatures and pressures.
   The correct statements are
   1) (i) & (ii) only 2) (i) & (iii) only
   3) (ii) & (iii) only 4) (i), (ii) & (iii).

6. Which one is an example for **one-electron** oxidative-addition reaction?
   1) $[Os(CO)_5] + I_2 \rightarrow [OsI_2(CO)_4] + CO$
   2) $2[Co(CN)_5]^{3-} + H_2 \rightarrow 2[HCo(CN)_5]^{3-}$
   3) $[Pd(PPh_3)_4] + PhI \rightarrow [Pd(Ph)(I)(PPh_3)_2] + 2\ PPh_3$
   4) $[HMn(CO)_5] + CF_2{=}CF_2 \rightarrow [Mn(CF_2CF_2H)(CO)_5]$

7. β-Agostic interaction could be seen in
   1) $[Pd(PPh_3)_4]$
   2) $[Ni(PEt_3)_3]$
   3) $[MeMn(CO)_5]$
   4) $[(\eta^5\text{-}C_5H_5)Rh(Me)(PPh_3)(CO)]I$

8. Consider the following statements about **metal carbonyls,**
   (i) CO stabilizes the metal centres in lower oxidation states.
   (ii) The back bonding decreases the M–C bond strength.
   (iii) The carbonyl stretching frequencies of doubly bridging metal carbonyls are higher than those of triply bridging ones.

   The correct statements are
   1) (i) & (ii) only.
   2) (i) & (iii) only.
   3) (ii) & (iii) only.
   4) (i), (ii) & (iii).

9. How many IR bands does $[Ni(CO)_4]$ show?
   1) 1 2) 3 3) 2 4) 4

10. Consider the following statements regarding ligands,
   (i) CO is a better π-acceptor than CS.
   (ii) CO is a weaker σ-donor than CN^-.
   (iii) PMe_3 is a better π-acceptor than PPh_3.

   The correct statement/s is/are
   1) (ii) only.
   2) (i) & (ii) only.
   3) (i) & (iii) only.
   4) (ii) & (iii) only.

11. Nucleophilic attack on a coordinated ligand is **not** facilitated if
   1) metal is in a higher oxidation state
   2) the metal is coordinatively saturated.
   3) the metal is coordinated to good π-acceptor ligands.
   4) the metal carries a positive charge.

12. Which one of the following metal carbonyls has a **bridging** carbonyl ligand?
   1) $[Fe_3(CO)_{12}]$
   2) $[Ru_3(CO)_{12}]$
   3) $[Ir_4(CO)_{12}]$
   4) $[Re_2(CO)_{10}]$

13. Which statement is **true** about $Na[Fe(CO)_4]$?
   1) The coordination number of iron is 5.
   2) The oxidation number of iron is –1.
   3) The IUPAC name of the compound is sodium tetracarbonyliron.
   4) It cannot be prepared by reacting Na with $[Fe(CO)_5]$.

14. A metal carbonyl contains a **doubly bridging** carbonyl ligand. What would be the CO stretching frequency of the bridging ligand?
   1) 2150 2) 1980 3) 1800 4) 1650

15. Consider the following statements regarding metal hydrides:

(i) Metal hydrides can act as H^- donors.
(ii) Metal hydrides react with CCl_4 to give $CHCl_3$.
(iii) $LiAlH_4$ and $NaBH_4$ can be used to reduce aldehydes into alcohols.

The correct statements are

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

16. Consider the following statements about hydrogen:

(i) Hydrogen is a good π-acceptor.
(ii) H_2 can act as a dihapto ligand.
(iii) Addition of H_2 to $[Co(CN)_5]^{3-}$ gives $[HCo(CN)_5]^{2-}$.

The correct statement/s is/are

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

17. Consider the following statements about benzene,

(i) It can act as L_3 type ligand.
(ii) It can act as a dihapto or tetrahapto ligand.
(iii) The coordination number of Cr in $[Cr(\eta^6\text{–}C_6H_6)(CO)_3]$ is 6.

The correct statements are

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

18. Consider the following statements,

(i) Addition of dioxygen to Vaska's compound is *trans*.
(ii) Addition of HCl to Vaska's compound gives a metal hydride.
(iii) D_2O can be used to distinguish metal hydrides from metal carbonyls.

The correct statements are

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

19. What is the most stable **product** of the reaction, $[Co_2(CO)_8] + H_2 \rightarrow$?

1) $[Co_2(\mu\text{-}H)_2(CO)_6]$
2) $[CoH(CO)_5]$
3) $[CoH_2(CO)_4]$
4) $[CoH(CO)_4]$

20. What is the most stable **product** formed, when you reflux $[Mo(CO)_6]$ in toluene?

1) $[Mo(CO)_5(toluene)]$
2) $[Mo(CO)_4(toluene)]$
3) $[Mo(CO)_3(toluene)]$
4) $[Mo_2(CO)_8]$

Part B (40 marks)

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

1. (a) (i) *fac*-[$PdMe_3I(dppe)$] undergoes **reductive elimination** to give the complex (**A**) and an organic molecule (**B**). Write the molecular formulae of (**A**) and (**B**).

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

(ii) What **structural** change would you expect for this **reductive elimination** process?

.....

(b) $[PtH(CO)_3]I$ reacts with $CH_2{=}CH_2$ to give $[Pt(CH_2CH_3)(CO)_3]I$.
Write the mechanism of the above reaction.

(c) $[(PPh_3)_3RhCH(Me)CH_2CH_3]$ undergoes β-hydride abstractions to give the metal complex (**P**) and **two** olefins (**Q**) and (**R**). Identify (**P**), (**Q**) and (**R**).

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

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

(d) How would you account for the variation in $\underline{\nu_{CO}}$ of the following compounds?

Compounds	ν_{CO}/cm^{-1}
Free CO	2143
$[Ni(CO)_3(PF_3)]$	2111
$[Ni(CO)_3(PMe_3)]$	2064

(e) Name **three** coordination modes of the carbonyl ligand. **Give an example each.**

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

(i) $[MeMn(CO)_5]$ + ^{13}CO →

(insertion)

(ii) $[W(CO)_5(THF)]$ + PPh_3 →

(substitution)

(iii) $[Fe(PMe_3)_4]$ + heat →

(cyclometallation)

(iv) $[(\eta^5\text{-Cp})Mo(CO)_3(\eta^1\text{-}CH_2CH{=}CH_2)]$ + H^+ →

(electrophilic attack on coordinated ligand)

(v) $[(\eta^5\text{-}C_5H_5)Rh(PPh_3)(CO)]$ + MeI →

(2e-oxidative addition)

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

(i) $[Fe(CO)_5] \rightarrow [HFe(CO)_4]^-$ ----------

(ii) $[(\eta^5\text{-Cp})_2TiCl_2] \rightarrow [(\eta^5\text{-Cp})_2TiCl(Me)]$ ----------

(iii) $Na[Mn(CO)_5] \rightarrow [MeMn(CO)_5]$ ----------

(iv) $[Re_2(CO)_{10}] \rightarrow Na[Re(CO)_5]$ ----------

(v) $[Mo(CO)_3(\eta^6\text{-}C_7H_8)] \rightarrow [Mo(CO)_3(\eta^7\text{-}C_7H_7)]BF_4$ ----------

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B.Sc. DEGREE PROGRAMME 2008/2009
CHU3127/CHE 5127 – ORGANOMETALLIC CHEMISTRY- LEVEL 5
ASSIGNMENT TEST II - MCQ TEST

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

Name:- .....

Reg.No/Index No.

	Marks
Part A	
Part B	
Total %	

FOR EXAMINER'S USE	
Unanswered	
Correct Answers	
Wrong Answers	
Total	

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

ASSIGNMENT TEST II – ANSWER GUIDE
CHM 3127 / CHE 5127

PART (A)

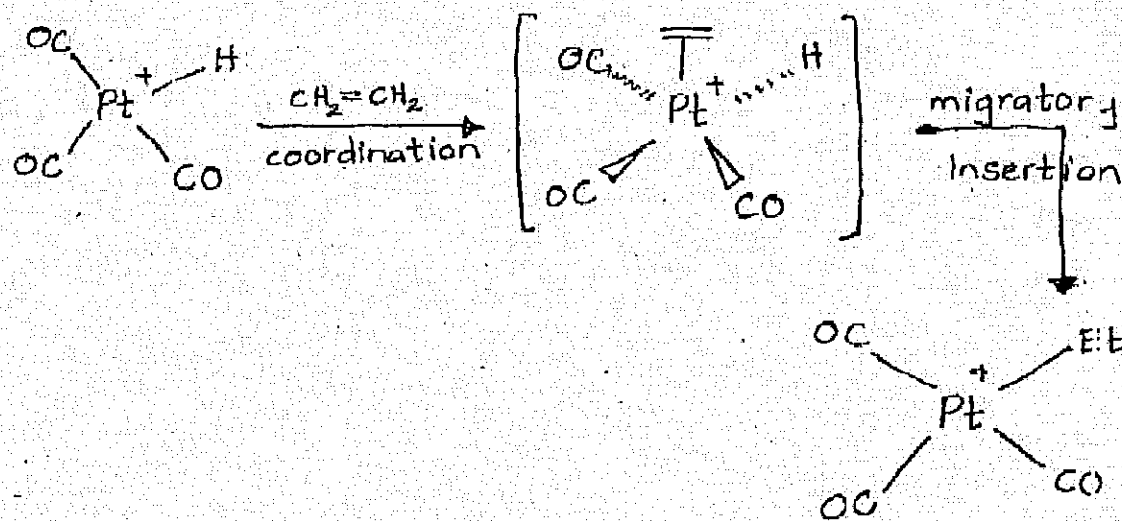
1. (4) 2. (1) 3. (2) 4. (3) 5. (4) 6. (2)
7. (2) 8. (2) 9. (1) 10. (1) 11. (2) 12. (1)
13. (2) 14. (3) 15. (4) 16. (1) 17. (4) 18. (4)
19. (4) 20. (3)

PART (B)

(b) (a) (i) (A) $[PdI(Me)(dppe)]$ (B) CH_3-CH_3

(ii) octahedral ⟶ square planar

(b)



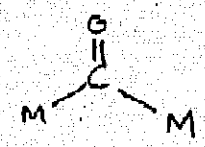
(c) (P) $[RhH(PPh_3)_3]$ (Q) $CH_2=CHCH_2CH_3$

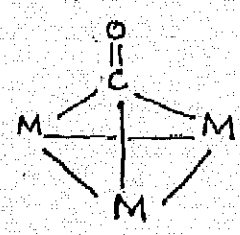
(R) $MeCH=CHMe$

(d) The strength of the C≡O bond $\propto \nu_{CO}$.
Back donation weakens the bond strength of CO.
Complexes show low ν_{CO} values due to back donation
donar ability $PMe_3 > PF_3$

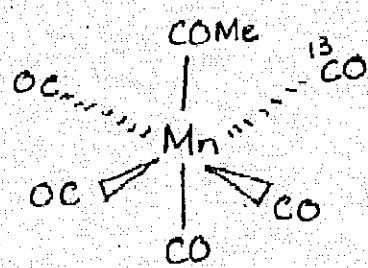
The lowest value ($2064\ cm^{-1}$) shown by $[Ni(CO)_3(PMe_3)]$ as Ni centre has more electron density ; thereby it exerts more back donation.

1. Terminal M – CO $[Mo(CO)_6]$

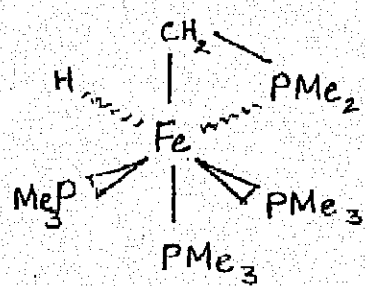
2. Doubly bridging  $[Co_2(CO)_8]$

3. Triply bridging  $[Rh_6(CO)_{16}]$

(a) (i) $[Mn(COMe)(CO)_4(^{13}CO)]$ OR

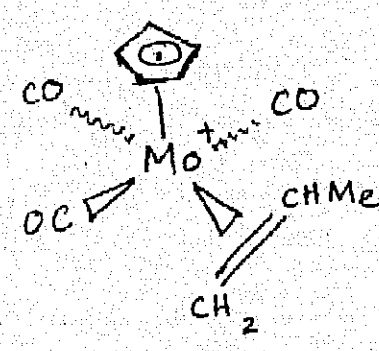


(ii) $[W(CO)_5(PPh_3)] + THF$

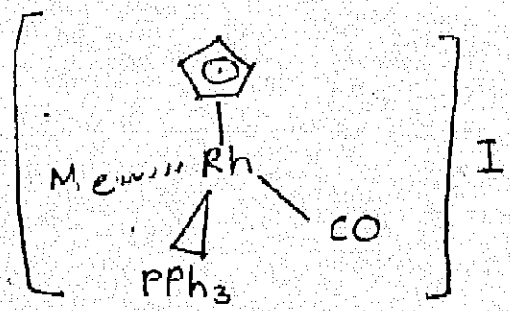
(iii) 

(iv) $\left[(\eta^5\text{-}Cp)(OC)_3Mo\text{—}\overset{CH_2}{\overset{\|}{CHMe}}\right]^+$

OR



v) $[Rh(Me)(\eta^5\text{-}C_5H_5)(PPh_3)(CO)]I$



(i) NaOH or OH^-

(ii) $AlMe_3$

(iii) MeI.

(iv) Ph_3CBF_4