



THE OPEN UNIVERSITY OF SRI LANKA B.Sc. & B. Ed. DEGREE / STAND ALONG COURSE IN SCIENCE - LEVEL 5 ASSIGNMENT TEST II (NBT) 2016/2017

CMU3122/CME5122 - Organometallic Chemistry

15th May 2017	(Monday)
13" IVIAY 2017 ((Wonday)

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 is the most likely substitution reaction?
 - 1) $[Pd(PPh_3)_4] + CH_2=CHI \rightarrow [PdI(CH=CH_2)(PPh_3)_2] + 2PPh_3$
 - 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) $[(OC)_4Fe(C_4F_8)] \rightarrow [Fe(CO)_4] + C_4F_8$
 - 5) $[(\eta^1-C_3H_5)Mn(CO)_5] \rightarrow [(\eta^3-C_3H_5)Mn(CO)_4] + CO$
- 2. Which one of the following reactions would not take place?
 - 1) $Na_2[Fe(CO)_4] + HC1 \rightarrow Na[HFe(CO)_4] + NaC1$
 - 2) $[Pt(PPh_3)_3] + HCN \rightarrow [PtH(CN)(PPh_3)_2] + PPh_3$
 - 3) $[Cp_2TiCl_2] + AlMe_3 \rightarrow [Cp_2TiMe_2] + AlMeCl_2$
 - 4) $[Pd(PPh_3)_4] + CH_2 = CHI \rightarrow [PdI(CH = CH_2)(PPh_3)_2] + 2PPh_3$
 - 5) $[Pt(PPh_3)_3] + I_2 \rightarrow [PtI_2(PPh_3)_2] + PPh_3$
- 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 center is positively charged.
 - (iii) Coordination number of the metal is reduced by two units during reductive elimination. 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).
- 4. Which one of the following statements is **not true** about $[W(\eta^2-H_2)(CO)_3(PPr^i_3)_2]$ (A)?
 - 1) (A) is a divalent complex.
 - 2) (A) has the octahedral geometry.
 - 3) In (A), H-H bond distance is larger than that of free H₂.
 - 4) In (A), H_2 can be replaced by N_2 by bubbling nitrogen.
 - 5) (A) has the *mer*, trans arrangement.
- 5. What is the product of the reaction, $[PtCl_2(PMe_3)_2] + excess LiMe \rightarrow ?$
 - 1) Li₂[PtCl₂Me₂(PMe₃)₂]
- 2) $[PtMe_2(PMe_3)_2]$
- 3) $[PtCl(Me)(PMe_3)_2] + LiCl$
- 4) Li[PtCl₂Me(PMe₃)₂]
- 5) $[PtCl_2Me_2(PMe_3)_2]$
- 6. Which one of the following metal carbonyls has not got a bridging carbonyl ligand?
 - 1) $[Fe_2(CO)_9]$
- 2) $[Fe_3(CO)_{12}]$
- 3) $[(\eta^5-C_5H_5)_2Fe_2(CO)_4]$

- 4) $[Ir_4(CO)_{12}]$
- 5) [Co₂(CO)₈]

 7. Which one is an example for one-el 1) [Os(CO)₅] + I₂ → [OsI₂(CO)₅] 2) 2[Co(CN)₅]³⁻ + H₂ → 2[HOO)₅ + H₂ → 2[HOO)₅ + H₂ → [Os(CO)₅] + I₂ → [OsI(CO)₅] + I₂ → [OsI(CO)₅] + I₂ → [PtB₁ 5) Pt(PPh₃)₄] + Br₂ → [PtB₁ 	$O)_4] + CO$ $Co(CN)_5]^{3-}$ $I \rightarrow [IrMeI_2(CO)(PFO)_5]I$	
8. Consider the following statements. (i) Oxidative addition of MeI t (ii) [Os(CO) ₅] is coordinatively reaction with I ₂ to form [Os (iii) Oxidative addition of O ₂ to The correct statement/s is/are 1) (i) only 4) (ii) & (iii) only	y saturated and it does it sI(CO) ₅]I. [IrCl(CO)(PPh ₃) ₂] is a 2) (i) & (ii) only.	not undergo oxidative addition
9. Consider the following statements. (i) Dihydrogen can act as a general field of the contract of the correct statement of the correct statement of the correct of the correct statement of the correct of the correct statement of the correct of t	ood π-acceptor. coordinated H ₂ depend o [IrCl(CO)(PPh ₃) ₂] giv & (ii) only. 3) (i)	
10. β-Agostic interaction could be seer 1) [Pt(PPh ₃) ₃] 2) [Ni 4) [(η ⁵ –C ₅ H ₅)Rh(Me)(PPh ₃)I]	$(PEt_3)_3$ 3) [1	MeCo(CO)3] PhCH2Co(CO)3]
 Nucleophilic attack on a coordinate The metal is coordinatively s the metal is coordinated to g the metal carries a positive c electron withdrawing groups the metal is coordinated to g 	saturated. ood σ-donor ligands. harge. are on coordinated lig	ands
12. Consider the following statements a (i) The carbonyl stretchin higher than those of the statement (ii) CO stabilizes the met (iii) The back bonding income The correct statement/s is/are 1) (ii) only 4) (ii) & (iii) only	ng frequencies of doub riply bridging ones. al centres in lower oxid reases the M-C bond s 2) (i) & (ii) only	
13. Consider the olefins propene (A), <i>th</i> The ease of hydrogenation of the ab 1)(A) > (B) > (C)	pove olefins is $>(C)>(B)$ 3) (C	cis-2-butene (C).
14. Some metals react directly with alk The order of reactivity of organic h 1) RCl > RBr > RI 4) RBr > RI > RCl		σ-bonds. 3) RBr > RCl > RI

(ii) (iii)	r the folloy Metal hyd [HCo(CO] ν(M–H) = rect staten	rides cam)₃(PPh₃)] · ν(M–D)	not act is a stro x √2.	as H ⁺ do onger aci	nors. id than [I	HCo(CO)4].		
1) (i	ii) only i) & (iii) o		2) (i) 8	& (ii) on! (ii) & (ii	ly i)	3) (i) &	t (iii) only		
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MCQ ANSW	ER SHEE	Γ: Mark a	cross (X) over (the most	suitable :	answer.	Part A	
Reg. No.		n 1484		Fo	r Exami	norg I	Inc	Part B	
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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 HCl to [CoH(CO) ₃]?	formula of the product (A) for	ormed due to oxidative addition of
(ii) Draw the structures of t		
•		
		·
(b) [IrCl ₃ (PPh ₃) ₃] reacts with an eliminates an alkane (Q) to g give another 16e-complex (S)	excess of MeLi to give the 186 ive the 16e-complex (R). Und 1. Identify (P), (Q), (R) and (S)	er pressure. (R) reacts with CO to
(P)	(Q)	
(R)	(S)	
(c) Arrange PF ₃ , PMe ₃ , P(OMe)		_
(d) Identify the product(s) of the	following reactions using the	hint given in the brackets.
(i) $[(\eta^5-Cp)(Ph_3P)_2FeC=CI$	Ph] + Me ₃ O ⁺ \rightarrow 18e-comp	lex (K) (electrophilic attack)
(ii) $[Fe(PMe_3)_4] \rightarrow 18e^{-\frac{1}{2}}$	-complex (L) (cyclometallat	ion)
(iii) cis-[PtCl(Et)(PPh ₃) ₂]	$\xrightarrow{\Delta}$ 16e-complex (M)	(β-H abstraction)
(K)	(L)	(M)

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

- (i) $[Cp_2TiCl_2] \rightarrow [Cp_2TiCl(Me)]$ -----
- (ii) $[Cr(CO)_6] \rightarrow [HCr(CO)_5]$ ------
- (f) [Mo(CO)₆] reacts with two moles of PPh₃ to give a molybdenum(0) complex (**Z**). (**Z**) shows only one IR band in the carbonyl region, draw the structure of (**Z**).

Registration ?	lo:	
Name & Add	ress:	• • • • • • • •
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CMU 3122 ORGANOMETALLIC CHEMISTRY CAT 02 (ANSWER GUIDE)

Part A (45 marks)

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

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 HCl to [CoH(CO)₃]? [CoH₂Cl(CO)₃]

(ii) Draw the structures of the three isomers of (A).

CI CO H CO

fac-[CoH2CI(CO)3]

mer, trans-[CoH2CI(CO)3] mer, cis-[CoH2CI(CO)3]

(b) [IrCl₃(PPh₃)₃] reacts with an excess of MeLi to give the 18e-complex (P). (P) reductive eliminates an alkane (Q) to give the 16e-complex (R). Under pressure, (R) reacts with CO to give another 16e-complex (S). Identify (P), (Q), (R) and (S).

(P) [IrMe₃(PPh₃)₃]

(Q) CH₃CH₃

(R) [IrMe(PPh₃)₃]

(S) [Ir(COMe)(PPh₃)₃]

(c) Arrange PF₃, PMe₃, P(OMe)₃, and NMe, in the order of increasing π -acceptability.

 $NMe_3 < PMe_3 < P(OMe)_3 < PF_3$

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

(i) $[(\eta^5-Cp)(Ph_3P)_2FeC\equiv CPh] + Me_3O^+ \rightarrow 18e$ -complex (K) (electrophilic attack)

(ii) [Fe(PMe₃)₄] → 18e-complex (L) (cyclometallation)

(iii) cis-[PtCl(Et)(PPh₃)₂] $\xrightarrow{\Delta}$ 16e-complex (M) (β -H abstraction)

- (e) Write on the dotted line, the **compound/reagent(s)** which can be used to carry out the following conversions.
 - (i) $[Cp_2TiCl_2] \rightarrow [Cp_2TiCl(Me)]$ ----- AlMe₃
 - (ii) $[Cr(CO)_6] \rightarrow [HCr(CO)_5]^-$ -----NaOH or KOH
- (f) [Mo(CO)₆] reacts with two moles of PPh₃ to give a molybdenum(0) complex (**Z**). (**Z**) shows only one IR band in the carbonyl region, draw the structure of (**Z**).

trans-[Mo(PPh₃)₂(CO)₄] (Z)