M.Sc. Chemistry Sem III EC-2

Inorganic Special Set-1

FM-70

Time-3hr.

(i) Identify the 18e⁻ species in the following complex
(a) $Ni(H_2O)_6^{2+}$ (b) $Fe(CO)_5$ (c) $(\eta^6-C_6H_6)_2Ru$ (d) $V(CO)_6$

(ii) Hydroformylation reaction are catalyzed by—
(a) $TiCl_4$ and $AlEt_3$ (b) $CaCl_2$ and NaOEt
(c) $Ni(CO)_4$ (d) $Co_2(CO)_8$

(iii) The Product (s) of the rx: $[Fe(\eta^5-C_5H_5)(CH_3)(CO)_2]$ and PPh_3 is/are
(a) $[Fe(\eta^5-C_5H_5)(CH_3)(CO)_2(PPh_3)]$
(b) $[Fe(\eta^5-C_5H_5)(COCH_3)(CO)(PPh_3)]$
(c) $[Fe(\eta^5-C_5H_5)(CH_3)(CO)(PPh_3)] + CO$
(d) $[Fe(\eta^5-C_5H_5)(CH_3)(H)(CO)(PPh_3)] + CO$

(iv) The ~~hapti~~ haptacity of nitrosyl in $[Mo(\eta^3\text{-allyl})(\eta^3\text{-allyl})NO]$ is
(a) 1 (b) 2 (c) 3 (d) 0

(v) Calculate z in the complex $[CP_3Ni_3(\mu_3CO)_2]^z$
(a) -2 (b) -1 (c) -3 (d) +1
Given the complex has 3 Ni-Ni bond,

(vi) The catalyst used for polymerisation of olefin is.
(a) $Rh(PPh_3)_3Cl$ (b) $TiCl_4/AlEt_3$ (c) $PdCl_2$ and $CuCl_2$
(d) $Co_2(CO)_8$ and Na

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(vii) Schrock Carbene are!

• (a) Triplets and nucleophilic (b) Triplets and electrophilic
(c) Singlets and " (d) Singlet and "

(viii) The correct order of energy levels of d-orbital in ferrocene is.

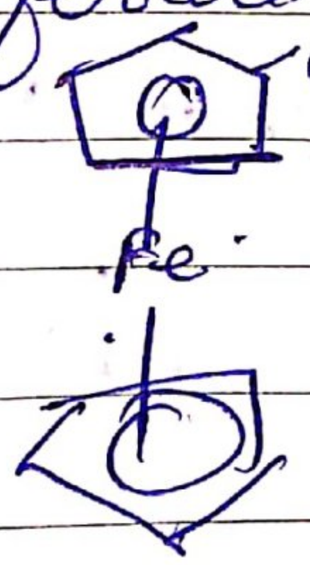
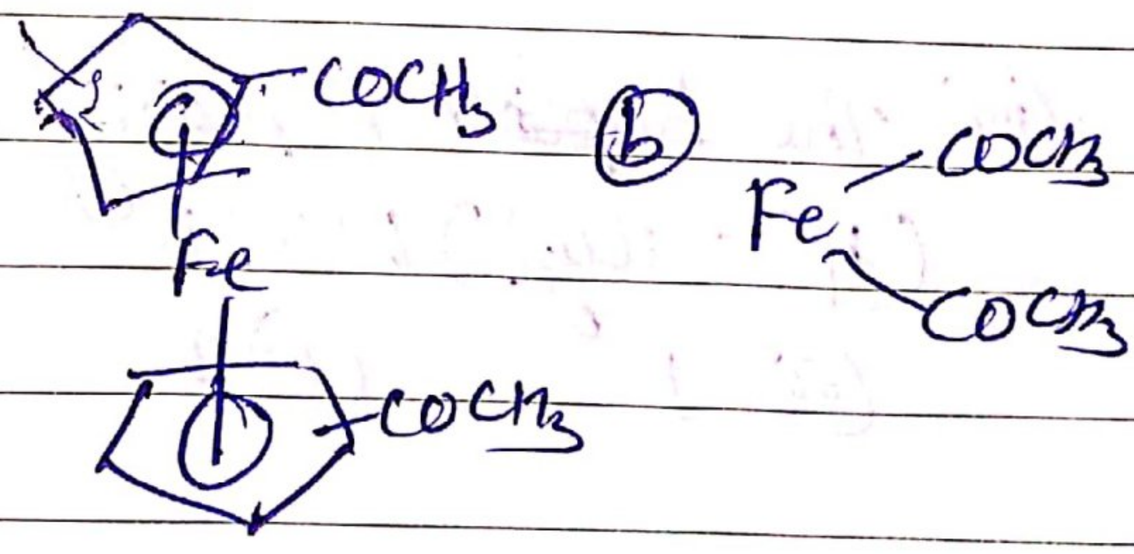
• (a) $a_{1g} < e_{1g} < e_{2g}$ (b) $e_{1g} > e_{2g} > a_{1g}$
(c) $a_{1g} > e_{1g} > e_{2g}$ (d) $e_{1g} < e_{2g} < a_{1g}$

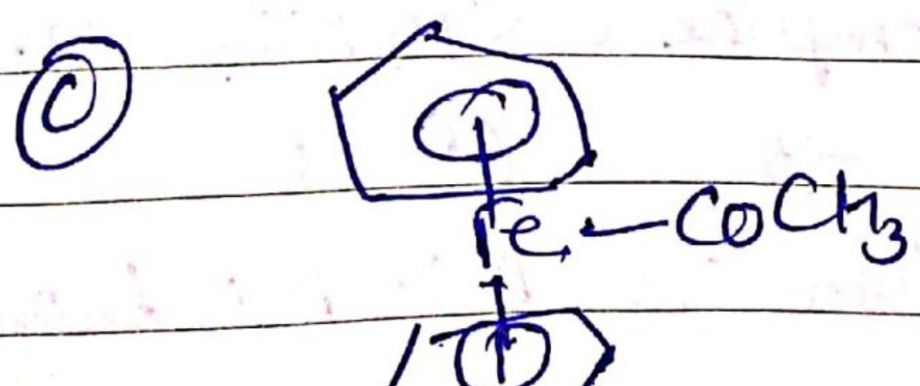
(ix) The number of M-M bonds is following complex.

$(\mu\text{-CO})_2[\eta^5(Cp\ Ir)]_3$ ~~PEt3~~ PEt_3

(a) 2 (b) 3 (c) 4 (d) 1

(x) The reaction of acetyl chloride and $AlCl_3$, with ferrocene.

(a)  and (b) 

(c)  (d) $FeCl_3$ and $Al(COCH_3)_3$

(2) (a) Discuss the method of preparation, properties and bonding of metal alkyl complexes (10)

(b) Write down the method of preparation and some synthetic application of organo copper complex (5)

(3) (a) Proton NMR of $(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})_2Ti$ shows two peaks at $-35^\circ C$ and one peak at $62^\circ C$. Explain the stm. (5)

(b) Discuss the ^{1}HNMR spectra of: $Mn(CO)_4(\eta^3\text{-}C_3H_5)$ and $Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ 5+5 = (10)

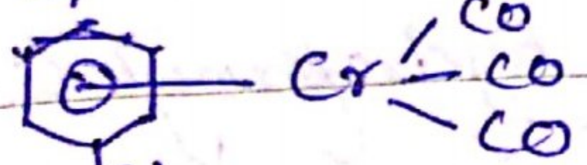
(4) (a) Propose a mechanism for the polymerization of propene to polypropene by a Ziegler–Natta catalyst. (10)

(b) What are advantage of this catalyst over other available catalyst. (3)

(c) Which alkenes are polymerized by this catalyst (2)

(5) (a) Complete the following rxn: 5×2 = (10)

(i) $(\eta^6\text{-}C_6H_6)Cr + Cr(CO)_6 \rightarrow$

(ii)  $\xrightarrow[MeOH]{NaOMe}$

(iii) $(\eta^5 C_5H_5)_2Fe + CH_2O + R_2NH \xrightarrow[CH_3COOH]{H_3PO_4}$

(iv) $(\eta^5 C_5H_5)_2Fe \xrightarrow[(ii)\ N_2O_4]{(i)\ n\text{-}BuLi}$ ~~$\xrightarrow{N_2}$~~

(v) $(\eta^5 C_5H_5)_2Fe \xrightarrow{CH_3CH_2}$

(b) What is heptotropic shift, Explain with example. (5)

(6) (a) Explain oxo process with suitable example. Give an example of a catalyst which work more efficient for this purpose at 25°C and 1 atm pressure. (10)

(b) Explain role of $CuCl_2$ in wacker process. (5)

(7) (a) What are alkyne complexes ? Discuss bonding in such complex. (10)

(b) $Co(\eta^5 - C_5H_5)_2$ is more readily oxidised than ferrocene. Explain (5)

(8) Discuss preparation, properties and nature of bonding in metal alkylidenes. (15)

M.Sc Chemistry Sem III EC-2

Inorganic special set-1 Answer

(i) b (ii) d (iii) b (iv) d (v) a

(vi) b (vii) a (viii) b (ix) b (x) a

M.Sc. Chemistry Sem III EC2

Inorganic Special Set 2

FM-70
Time-3hr.

Q.1.

(i) The Complex which obey 18e rule
(a) $Fe(CO)_4$ (b) $Ni(CO)_3(PPh_3)$ (c) $Cr(CO)_5$ (d) $Cr(C_5H_5)_2$

(ii) Predict the product of the reaction of $[IrCl(CO)(PC_6H_5)_3)_2]$ and CH_3I is/are
(a) $[IrCl(COCH_3)I(PPh_3)_2]$ (b) $[IrCl(CO)(CH_3)I(PPh_3)_2]$
(c) $[Ir(CO)(PPh_3)_2] + CH_3Cl$ (d) $[IrCl(CO)CH_3I(PPh_3)] + PPh_3$

(iii) The rxn of H_2 with Wilkinson catalyst result in
(a) cis addition of H_2 and metal Oxidation state change of -2
(b) trans " " " " " "
" " +2
(c) trans " " " " " "
" " -2
(d) cis " " " " " "
" " +2

(iv) Active catalytic species for hydroformylation is
(a) $Ru_4Cl_2(PPh_3)_3$ (b) $HCo(CO)_3$
(c) $RhCl(PPh_3)_3$ (d) K_2PtCl_6.

(v) Which one of following IR frequency is the closest to that of a triply bridged CO group?
(a) 1700 cm^{-1} (b) 1810 cm^{-1} (c) 1920 cm^{-1} (d) 2140 cm^{-1}

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(VI) The hapticity of nitrosyl in $[Mo(\eta^1\text{allyl})(\eta^3\text{allyl})NO]$ is

(a) 1 (b) 2 (c) 3 (d) 0

(VII) Calculate z in the following complex $[Cp_3Ni_3(\mu_3CO)_2]^z$

(a) -2 (b) -1 (c) -3 d) +1

Given the complex has 3 Ni-Ni bond.

(VIII) Schrock carbene are

(a) Triplets and nucleophilic

(b) " and electrophilic

(c) Singlet and "

(d) " and nucleophilic

(IX) The correct order of energy & level of d-orbital of ferrocene is

(a) $a_{1g} < e_{1g} < e_{2g}$ (b) $e_{1g} > e_{2g} > a_{1g}$

(c) $a_{1g} < e_{1g} > e_{2g}$ (d) $e_{1g} < e_{2g} < a_{1g}$

(X) The incorrect statement about Zeise's salt is:

(a) Zeise salt is diamagnetic

(b) The oxidation state of Pt in Zesise's salt is +2

(c) All Pt-Cl bond length are equal

(d) C-C bond of ethylene moiety is longer than that of free ethylene molecule.

(2) (a) Write the method of preparation and properties of organo-copper compounds. — (8)

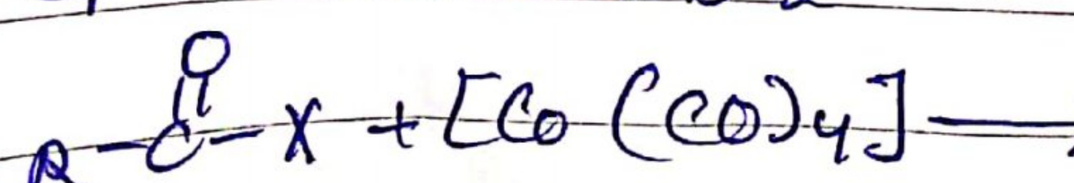
(b) Discuss the structure of organoCopper Compound and write a few synthetic application of it. 4+3 = (7)

(3) (a) Propose the mechanism for the Wacker process, when the reaction is carried out with ethylene in acetic acid solvent. (10)

(b) what is C-H activation ? Discuss few methods for C-H activation. (5)

(4) Discuss the nature of bonding and structural characteristic of metal allyl complexes. (10)

(b) Complete the following reactions :— 1X5 = (5)

(i) $Cr(CO)_6 +$  $\longrightarrow$

(ii) $+ {}^{14}CO \longrightarrow$

(iii) $Cr(CO)_6 + C_6H_6 \longrightarrow$

(iv) $Cp(CO)_3Re + Br_2 \longrightarrow$

(v)

(5) (a) What do you understand by stereochemical non rigidity ? (5)

(b) Sugest one of the method for its determination, justify it. (5)

(c) $(C_5H_5)_2Fe_2(CO)_4$ exchibits one band in its HNMR spectra, if the compound is diamagnetic drive its structure. (5)

(6) (a) $Co(\eta^5-C_5H_5)_2$ is more readily oxidised than ferrocene. Explain. (5)

(b) Discuss the nature of bonding in metal alkylidene complexes. (10)

(7) What is the basis of Zieglar-Natta Polymerization ? Is Zieglar-Natta system homogeous ? what is active species is the system ? what is the role of $Al(C_2H_5)_3$ in the catalytic system. ?

$= 8+2+2+3 = (15)$

(8) Write Notes one any two :—

(i) Difference between Fischer and Schrock carbene

(ii) Oxopalladation

(iii) Metal alkyl complexes,

(iv) Insertion reaction.

M.Sc. Chemistry, Sem III EC-2

Inorganic special. Set-2 Answer

(i) b (ii) b (iii) d (iv) b (v) a

(vi) d (vii) a (viii) a (ix) a (x) c

—x—

M.Sc Chemistry Sem III EC2

FM-70

Inorganic Special Set-3 Time-3hr

(i) For hydrogenation of alkenes involving $RhCl(PPh_3)_3$ the correct statement is:

(a) Only 18e Rh complex is involved

(b) 14, 16, and 18e Rh complexes are involved

(c) 16 and 18e " " "

(d) 14 and 16e " " "

(ii) The Complex which obey 18e⁻ rule is:

(a) $Fe(CO)_4$ (b) $Ni(CO)_3PPh_3$ (c) $Cr(CO)_5$ (d) $Cr(C_5H_5)_2$

(iii) The Catalyst used in the conversion of ethylene to acetaldehyde using Wacker process is

(a) $HCo(CO)_4$ (b) $[PdCl_4]^{2-}$ (c) V_2O_5

(d) $TiCl_4$ in presence of $Al(C_2H_5)_3$

(iv) The homogeneous catalyst that is used in the hydroformylation is based on

(a) Co (b) Cr (c) Ti (d) Y

(v) The Complex $\left[\begin{matrix} CO \\ | \\ C \leftarrow Ru - PPh_3 \\ | \\ PPh_3 \end{matrix}\right]^+$ follows

(a) 18e⁻ rule and stable (b) 16e rule and unstable

(c) 18e⁻ rule and thermodynamically unstable

(d) 16e⁻ rule and stable

(vi) The hapticity of nitrosyl in [Mo(η'allyl)(η³-allyl)(NO)] is; Given the complex has 3 Ni-Ni bond

(a) 1 (b) 2 (c) 3 (d) 0

(vii) The catalyst used for polymerization of olefins is

(a) $Rh(PPh_3)_3Cl$. (b) $TiCl_4/AlEt_3$ (c) $PdCl_2$ and $CuCl$.

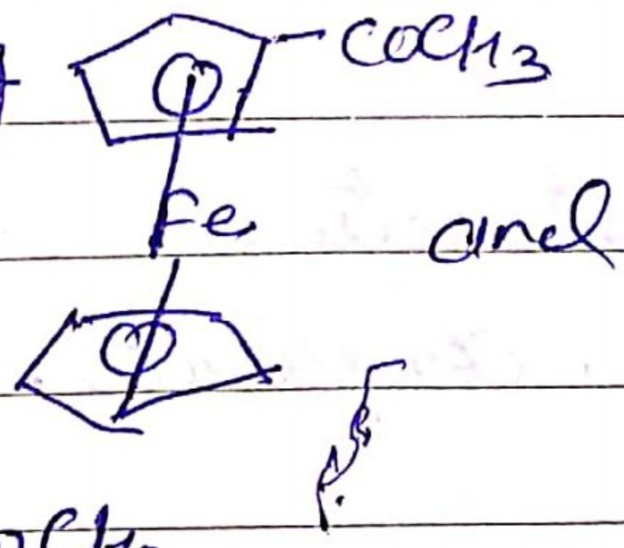
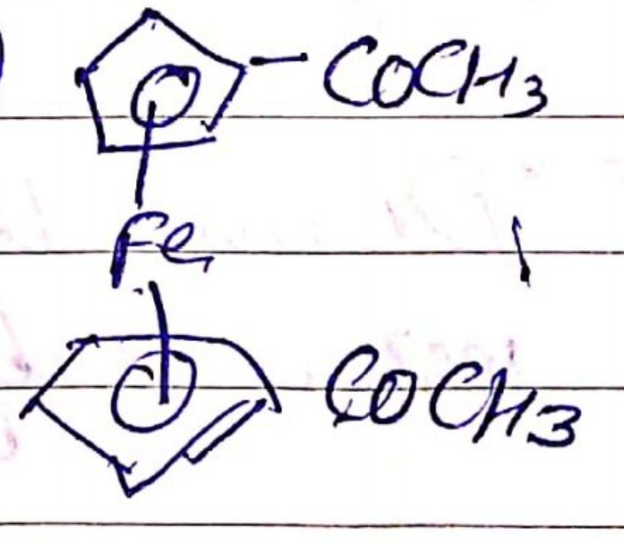
(d) $Co_2(CO)_8$ and Na.

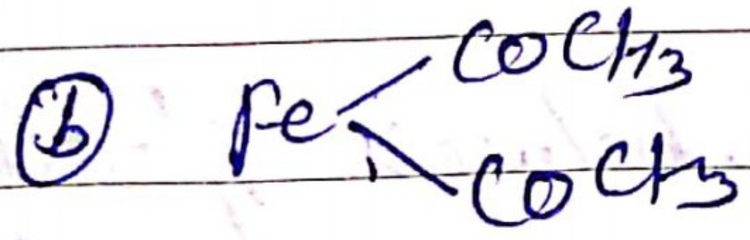
(viii) Schrock carbene are

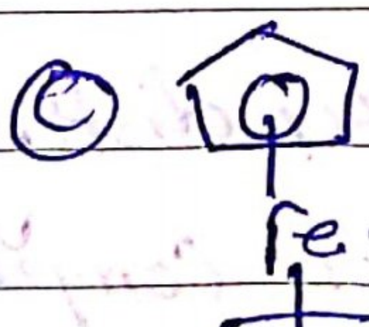
(a) Triplets and nucleophilic (b) Triplets and electrophilic

(c) Singlets and " (d) Singlets " "

(ix) The reaction of acetyl chloride and $AlCl_3$ with ferrocene gives.

(a) ~~$Ru(PPh_3)Cl$~~  and 

(b) 

(c) 

(d) $FeCl_3$ and $Al(COCH_3)_3$

(x) If $IN(cp)_2(CO)_2$ follows 18e rule. The haptiicity of the two Cp group are.

(a) 5,5 (b) 3,3 (c) 1,5 (d) 3,5

(2) (a) Discuss the metal - carbon multiple bonding in transition metal ~~carbo~~ alkylidens. (5)

(b) what are organocopper complex. Discuss some of its synthetic application. (8)

(c) Discuss the reasons for the catalytic efficiency of transition metal complexes.

(3) (a) what are transition metal carbyne complexes? Explain Fischer & Schrock carbyne complex. 2+3 = (5)

(b) Distinguish between carbyne and alkylidyne complexes. (5)

(c) Discuss the structure and bonding in metal carbyne complexes. (5)

(4) (a) How will you distinguish between η^1-allyl and η^3-allyl complexes with the help of IR spectroscopy. (5)

(b) Why free cyclobutadiene is anti aromatic while cyclobutadiene co-ordinated to metal atom is aromatic. Explain with example (5)

(c) Discuss the structure and bonding in metal alkyne complexes. (5)

(5) (a) Write a mechanism for the hydroformylation of $CH_3CH=CH_2$ (10)

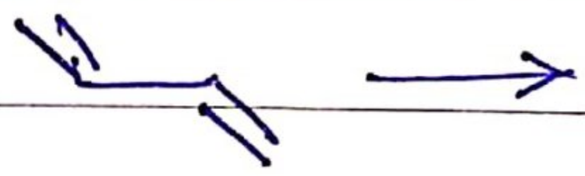
(b) Explain the term oxidative addition and reductive elimination (5)

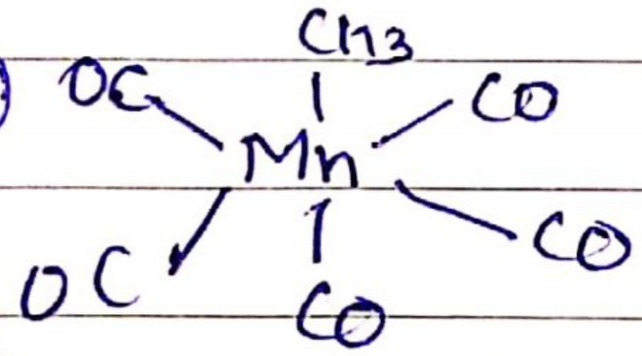
(6) (a) What do you understand by stereochemical non-rigidity? How can it be detected with help of NMR spectroscopy. Explain it with help of suitable example. 5+5+5 = 15

(7) (a) Write down the mechanism of Ethene metathesis

(7) (a) Discuss the nature of bonding and structural characteristic of metal arene complexes. (7)

(b) Complete following Reactions :— 2×4 = (8)

(i) $Cr(CO)_6 +$  $\longrightarrow$

(ii)  $+ {}^{14}CO \longrightarrow$

(iii) $Cp(CO)_3Re + Br_2 \longrightarrow$

(iv) $R-\overset{O}{\overset{\|}{C}}-X + [Co(CO)_4]^- \longrightarrow$

(8) (a) Discuss oxopalladation Catalytic reaction. (10)

(b) Using 18e rule find out the bond order in $[\eta^5Cp)Mo(CO)_3]_2$ and draw possible isomers, (5)

M.Sc. Chemistry Sem III EC-2

Inorganic Special Set – 3 Answer

(i) c (ii) b (iii) b (iv) a (v) b

(vi) b (vii) b (viii) a (ix) a (x) d