2016

M.Sc. 2nd Seme. Examination

CHEMISTRY

PAPER—CEM-203

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

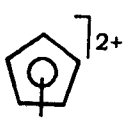
(*Inorganic*)

Group—A

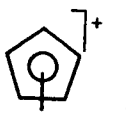
Answer any *one* question.

1. (a) Arrange the following compounds in the increasing order of ethylene C – C bond length with proper explanation.

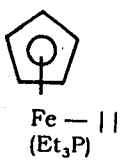
(A)



(B)



(C)



(D)

(b) "IR-Spectroscopy of olefin complexes is a less useful probe of π-bonding than IR spectrocopy of CO-complexes" — justify.

(c) The Pt – C and C – C bond length data are give for complex 1 and 2.

$Pt(Ph_3P)_2(\eta^2 - C_2H_4)$	$Pt(Ph_3P)_2\{\eta^2 - C_2(CN)_4\}$
(1)	(2)
d_{C-C} : 1.43 Å	d_{C-C} : 1.49 Å
d_{Pt-C} : 2.11 Å	d_{Pt-C} : 2.11 Å

Draw the structure of complex 1 and 2 and discuss their bonding.

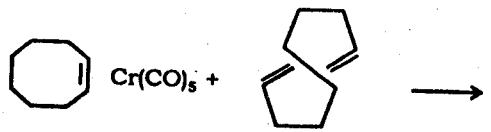
(d) Predict the product in the following reactions :

(i) $W(CO)_6 + CH_3L_i \xrightarrow{Et_2O} (A) \xrightarrow{[Me_3O]BF_4} (B)$

(ii) $Re(CO)_5Cl + C_2H_4 \xrightarrow{AlCl_3} (C)$

3+2+2+3

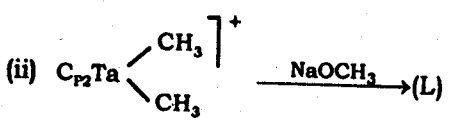
2. (a) Complete the following reaction and discuss the formation of the product :

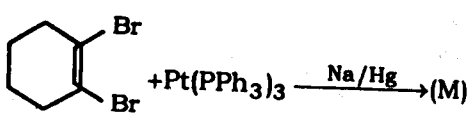


(b) "NMR-Spectroscopy is applied to detect / monitor stereochemical non rigidity" — justify.

(c) Predict the product of the following reaction :

(i) $C_PFe(CO)_2I + AgBF_4 + C_2H_4 \longrightarrow (K)$

(ii) 

(iii) 

(d) Schematically present the possible orbital interaction in Fischer's and Schrock's carbene complexes.

2+2+3+3

Group—B

Answer any *one* question.

3. (a) Complete the following reactions :

(i) $B_4H_{10} + N(CH_3)_3 \rightarrow$

(ii) $B_5H_9 + Li(CH_3) \rightarrow$

(iii) $5K[B_9H_{14}] + 2B_5H_9 \rightarrow$

(iv) $B_5H_9 + CH_3Cl \xrightarrow{AlCl_3}$

(v) $B_4H_{10} + C_2H_2 \xrightarrow{50^\circ C}$

(vi) $B_{10}C_2H_{12} + 2LiC_4H_9 \longrightarrow$

(vii) $Al_2(CH_3)_6 + 2[B_{11}H_{13}]^{2-} \xrightarrow{\Delta}$

(viii) $2\ C_4H_9Li + C_2H_2B_{10}H_{10} \rightarrow$

(b) Classify the following compounds with respect to closo, nido, arachno and hypo

$B_3H_6^+$, B_4H_8, $B_2H_7^-$ and C_8H_8 (1×8)+2

4. (a) What do you mean by carborane and metallo carborenes ?

(b) Calculate the styx number of $[B_4H_8]$, $[B_3H_8^-]$ and established the most probable structure.

(c) With the help of styx number 3100 draw the probable structure of the boron hydride. 2+5+3

Group—C

Answer any *one* question.

5. (a) Establish the relation

$$a_i = \frac{1}{h}\sum_R X(R)\, X_i(R)$$

where the terms have usual significance.

(b) Determine the characters of the irreducible representations of C_{3v} point group. Write the appropriate Mulliken Symbols for these irreducible representations. Show that p_x and p_y orbitals, as a pair, provide basis for the E representation of C_{3v} point group.

Investigate whether an A_1 electron in NH_3 make an electric dipole transition to a E orbital. What polarized radiation will emitted or absorbed during this transition ?

2+(1+1+3+3)

6. (a) The energy integral $\int \psi_i H \psi_j d\tau$ may be non-zero only if Ψi and Ψj belong to the same irreducible representation of the molecular point group. Explain.

(b) The ground state of trans-N_2F_2 is Bg. To what excited states may it be excited by electric dipole transitions, and what polarization of light is necessary to use ? Given below the character table for C_{2h} point group.

C_{2h}	E	C_2	i	σ_n		
Ag	1	1	1	1	R_z	x^2, y^2, z^2, xy
Bg	1	−1	1	−1	R_x, R_y	xz, yz
Au	1	1	−1	−1	z	
Bu	1	−1	−1	1	x, y	

(c) Show that the representation of a direct product, $\overline{\Gamma_{AB}}$ will contain the totally symmetric representation only if the irreducible $\overline{\Gamma_A}$ = the irreducible $\overline{\Gamma_B}$.

(d) Write short note on "spectral transition probabilities".

1+4+2+3

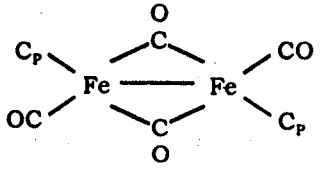
Group—D

Answer any *five* questions : 5×2

7. (i) What do you mean by 'Agostic interaction'?

(ii) What is 'Tebbe's reagent'? How it is synthesized?

(iii) Cite the possible binding modes of alkyne complexes and allyl complexes in organometallic chemistry.

(iv) "In 

complex, the 'CO' molecules move from one direction to other" — justify with mechanism.

(v) Explain why the splitting pattern of f-orbitals and F states should be same in octahedral environment.

(vi) Explain why the polarization effect is not observed in cubic or higher symmetry molecule.

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