

M.Sc. 2nd Semester Examination, 2012**CHEMISTRY***(Inorganic)*

PAPER – CEM- 203

*Full Marks : 40**Time : 2 hours*

Answer any four questions

The figures in the right hand margin indicate marks

1. (a) Using valence bond theory derive the expression for the energy of symmetric and antisymmetric states of H_2 molecule. 7
- (b) What do you mean by " direct product" ? 1
- (c) Establish the relation

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$$

where the term have usual significance. 2

2. (a) Show that for $[\text{Mo}_2\text{Cl}_8]^{4-}$ species, the $\delta \rightarrow \delta^*$ transition is electric-dipole allowed with z -polarization and forbidden for radiation with its electric vector in the xy plane. Given below the character table for D_{4h} point group.

6

D_{4h}	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

- (b) Is $p_y - p_x$ an allowed transition in a tetrahedral molecule? Explain. Given below the character table for T_d point group.

2

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

- (c) The ground state of NO_2 is A_1 in the group C_{2v} . 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_{2v} point group.

2

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

3. (a) Which among the following alkenes will bind most strongly to a metal ? Give reasons. 2

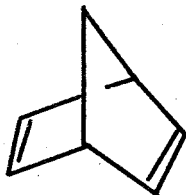
(i)



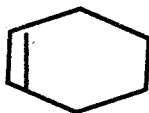
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(iii)



(iv)

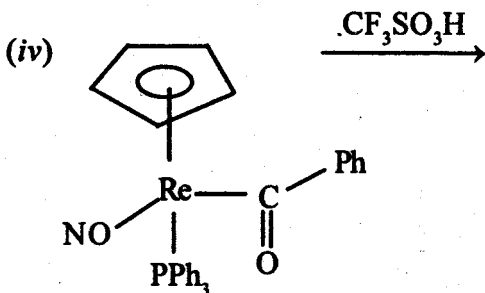
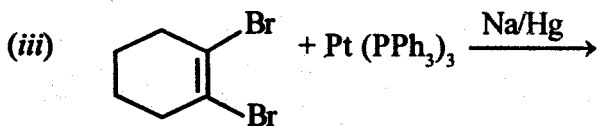
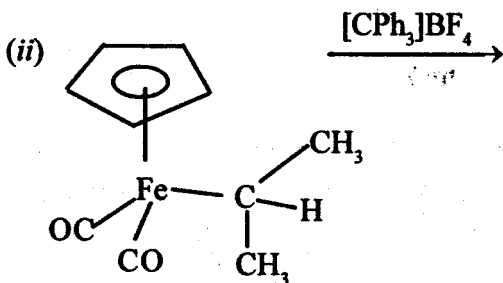
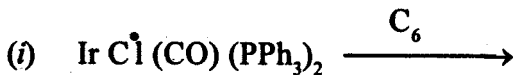


- (b) Comment on the following observation.

"In the IR spectrum of free $\text{MeCH}=\text{CH}_2$, $\bar{\nu}_{\text{C}=\text{C}} \sim 1652 \text{ cm}^{-1}$, but in the complex $\text{K}[\text{PtCl}_3(\eta^2-\text{CH}_3\text{CH}=\text{CH}_2)]$, the corresponding absorption band is $\sim 1504 \text{ cm}^{-1}$.

2

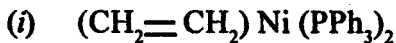
(c) Predict the products of the following reaction : 4



(d) Write down the probable binding modes of alkynes in transition metal alkyne complex. 2

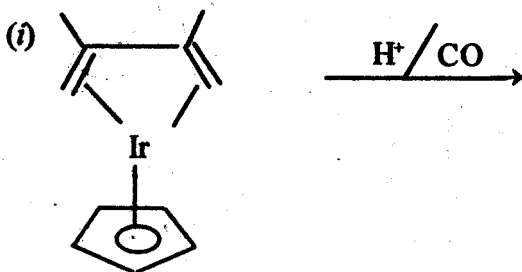
4. (a) If an olefin has to bind to a transition metal, say Cr, which of the olefins, Cis-Cyclooctene or trans-cyclooctene will form the stronger complex and why? 2

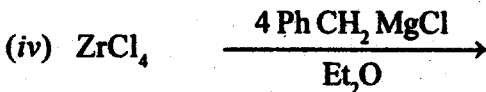
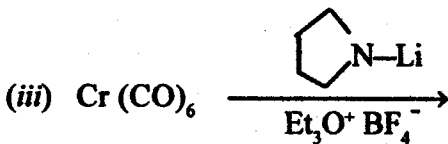
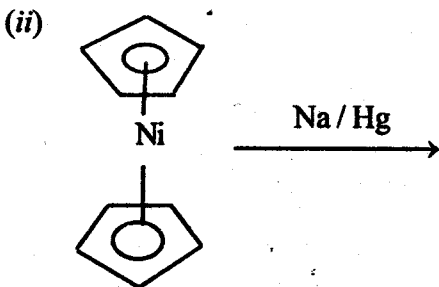
(b) Which of the following metal alkene complexes do you think will look most like a metallacyclopropane? Explain your answer: 2



(c) How will you synthesize a transition-metal allyl complex starting from a carbonylate ion? 2

(d) Complete the following reaction 4





5. (a) Discuss "Nonflame AAS technique". 3
- (b) What is the application of cyclic voltammetry? 2
- (c) Explain why fluorescence intensity of $\text{C}_6\text{H}_5\text{NH}_2$ is 20 whereas in case of $\text{C}_6\text{H}_5\text{NO}_2$ that is nil? 2
- (d) Define molar absorptivity. What is its unit? 3

6. (a) Discuss about photoemissive phototube. 3
- (b) Zinc complex of 8-hydroxyquinoline show higher grade of fluorescence but 8-hydroxyquinoline does not— why? 2
- (c) Why is oxygen to be removed from the polarographic cell before experiment? 3
- (d) What is the basic difference between a calorimeter and a spectrophotometer? 2
7. (a) What do you mean by "Irving William Order"? 2
- (b) Write statistical and non-statistical factors which control the stability of a complex in solution. 2
- (c) Discuss the determination of composition and stability constant of a complex by spectrophotometric method. 3
- (d) Give an example of cyclic neutral ionophores. 1
- (e) What do you mean by labile and inert complexes? Give example of each. 2
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