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63/2 (SEM-4) CHM 406

2023

CHEMISTRY

(Theory Paper)

Paper Code : CHM 406

(Organometallics and Photoinorganic Chemistry)

Full Marks – 80

Pass Marks – 32

Time – Three hours

The figures in the margin indicate full marks
for the questions.

1. Choose the correct answers (any *four*) : $1 \times 4 = 4$

(a) Wilkinson's catalyst is used in Polymerization

(i) Condensation (ii) Hydrogenation

(iii) Halogenation (iv) None of these

[Turn over

(b) Which of the following is an organo-metallic compound ?

- (i) Lithium ethoxide
- (ii) Ethyl Lithium
- (iii) Lithium carbide
- (iv) Lithium acetate

(c) The fact that the fluorescence wavelength is often much longer than the irradiation wavelength (Stokes shift) is a consequence of which phenomenon ?

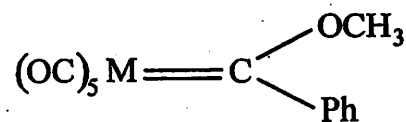
- (i) low extinction coefficients (Lambert-Beer law)
- (ii) vertical transitions (Kasha's rule)
- (iii) high ISC rates (El Sayed rule)
- (iv) the Franck-Condon principle

(d) What is the oxidation state of Pd in $\text{Pd}(\text{OAc})_2$?

- (i) 0
- (ii) 1
- (iii) 2
- (iv) 4

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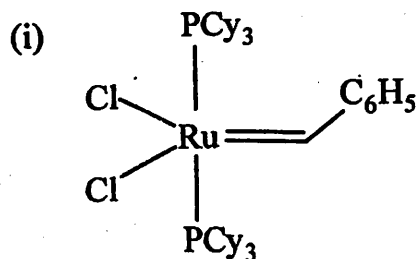
(e) The molecule



Obeys 18e rule. The two 'M' satisfying the conditions are

- (i) Cr.V
- (ii) V.Re⁺
- (iii) Mo.V
- (iv) Cr.Re⁺

(f) The catalyst involved in carrying out the metathesis of 1-butene to give ethylene and 3-hexene is



- (ii) Na_2PdCl_6
- (iii) $\text{CO}_2(\text{CO})_8\text{H}_2$
- (iv) $\text{RhCl}(\text{PPh}_3)_3$

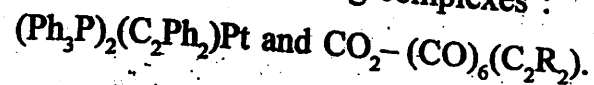
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2. Answer any *two* of the following questions :

8×2=16

- (a) Draw the modes of ligation of alkynes to single-metal atom and clusters of two, three and four metal atom. Discuss the bonding of alkynes in the following complexes :

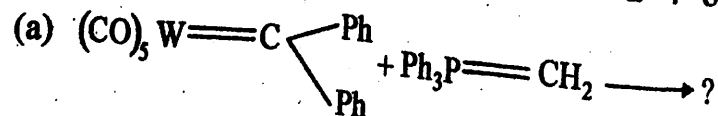


- (b) The complex $[\text{Fe}(\text{CO})_4(\eta^2-\text{C}_2\text{H}_4)]$ may have two limiting orientations of the ethylene ligand-perpendicular to the equatorial plane or in that plane. Discuss with MO theory which structure will be preferred.

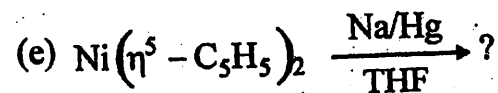
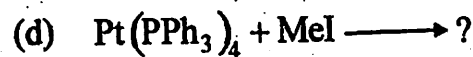
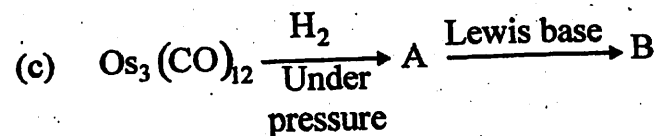
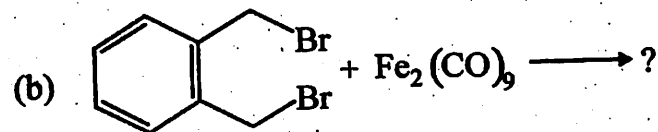
- (c) Explain with MO theory the bonding in agostic methyl group of the complex $[\text{TiH}_5\text{CH}_3]^{2-}$.

3. Predict the product of the following reactions (any *four*) :

2×4=8

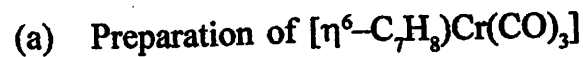


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4. Answer any *four* of the following questions :

1×4=4



(b) Write down the preparation of Fisher type carbene.

(c) Write down the preparation of $\text{Ni}(\text{CP}_3)^+$

(d) Write down the preparation of CH_3OH from CO and H_2 .

(e) Preparation of Benzyne complex.

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[Turn over

5. Answer any *four* of the following questions :

4×4=16

- (a) Indenyl complexes are more reactive than their cyclopentadienyl analogues. Explain.
- (b) The product from HCl addition to $\text{IrMe}(\text{CO})(\text{PMe}_3)_2$ and $\text{IrPh}(\text{CO})(\text{PMe}_3)_2$ are unstable, but the addition product to $\text{IrCl}(\text{Co})(\text{PPh}_3)_2$ and $\text{IrCl}(\text{CO})(\text{PMe}_3)_2$ are stable. Explain and state how first two will decompose.
- (c) Explain catalytic C-H activation.
- (d) Explain the mechanism of C-H activation of $\text{Tp}\cdot\text{Rh}(\text{CO})_2$ [$\text{Tp}=\text{HB}(2,4\text{-Me}_2\text{Pyr})_3$]
- (e) Explain how IR spectra may be used to distinguish
 - (i) the cis-and trans- octahedral dicarbonyl and
 - (ii) fac- and mer-octahedral tricarbonyls.

6. Answer any *two* of the following questions :

8×2=16

- (a) The use of cobalt catalyst was replaced by Rhodium catalyst in the hydroformylation of unsaturated alkene. Explain the disadvantage of cobalt catalysed reaction and advantages of Rhodium catalysed hydroformylations.

- (b) What is metathesis of olefins ? Describe all the types of metathesis of olefins.

- (c) Discuss in brief :

- (i) Ziegler-Natta Polymerization of olefins.
- (ii) Wilkinson's Catalyst.

7. Answer any *two* of the following questions :

8×2=16

- (a) Once chemists expected to split water with photo-excited $\text{Ru}(\text{bip})_3^{2+}$. Explain the proposed redox reaction and its causes, of failures.
- (b) Discuss the photochemical pathways in metal complexes.
- (c) Explain the following :
 - (i) Thexi-state
 - (ii) Actinometer