

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF
BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 416: ORGANOMETALLIC CHEMISTRY

STREAMS: BSC (CHEM)

TIME: 2 HOURS

DAY/DATE: TUESDAY 14/04/2020

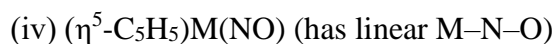
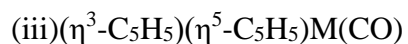
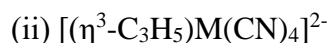
11.30 AM – 1.30 PM

INSTRUCTIONS:

Answer question One (Compulsory) and any other Two questions

QUESTION ONE [30 MARKS]

(a) Identify the first-row transition metal in the following 18-electron species (4 marks)



(b) Explain the difference in the vibrational frequencies of carbonyl ligands in the following complexes. (2 marks)

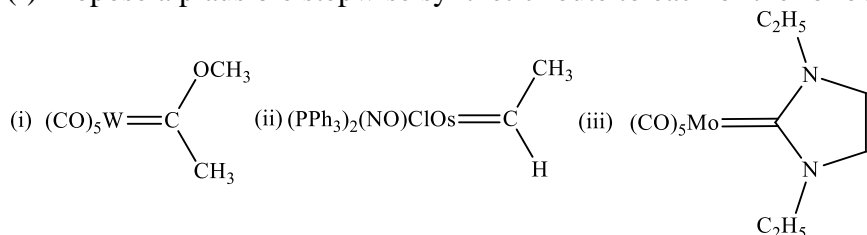
<i>Complex</i>	<i>$\nu(\text{CO}), \text{cm}^{-1}$</i>
$[\text{W}(\text{CO})_6]$	1977
$[\text{Re}(\text{CO})_6]^+$	2085
$[\text{Os}(\text{CO})_6]^{2+}$	2190
$[\text{Ir}(\text{CO})_6]^{3+}$	2254

(c) Discuss, with the aid of a CO molecular orbital diagram, bonding in metal carbonyl complexes. (5 marks)

(d) Predict the products of the following reactions. (5 marks)

- (i) $\text{Mn}(\text{CO})_6 + \text{Ph}_2\text{PCH}_2\text{PPh}_2 \xrightarrow{\text{Heat}}$
- (ii) $\text{W}(\text{CO})_5[\text{C}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)] + \text{BF}_3 \longrightarrow$
- (iii) $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_2 \xrightarrow{h\nu}$
- (iv) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2] + \text{Al}(\text{C}_2\text{H}_5)_3 \longrightarrow$
- (v) $\text{V}(\text{CO})_6 + \text{NO} \longrightarrow$
- (e) Butanal can be synthesized from an alkene having one less carbon using the $\text{HCo}(\text{CO})_4$ complex.

- (i) Write a detailed stepwise mechanism for the process and explain each catalytic step. **(5 marks)**
- (ii) Explain the limitations of the $\text{HCo}(\text{CO})_4$ complex for the process. **(3 marks)**
- (f) Propose a plausible stepwise synthetic route to each of the following complexes. **(6 marks)**

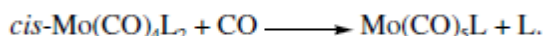


QUESTION TWO [20 MARKS]

- (a) Write the formal names of the following complexes **(4 marks)**
- (i) $[\text{Mo}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]$ (ii) $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$
- (iii) $[\text{RhMe}(\text{PMe}_3)_4]$ (iv) $\text{H}_2\text{Fe}(\text{CO})_4$
- (b) Discuss the stepwise mechanism for polymerization of ethene using the Ziegler-Natta catalyst **(8 marks)**
- (c) Draw the structures of the possible product(s) of metathesis of the following alkenes. **(6 marks)**
- (i) Propene and but-1-ene (ii) ethene and cyclohexene (iii) 1,7-octadiene
- (d) Describe one synthetic route to $\text{Fe}(\text{C}_5\text{H}_5)_2$ complex. **(2 marks)**

QUESTION THREE [20 MARKS]

- (a) Describe, with the aid of suitable examples, three methods used for laboratory synthesis of carbonyl complexes. **(6 marks)**
- (b) Discuss the catalytic cycle of the Wacker-Smith synthesis of ethanal. **(10 marks)**
- (c) In a series of experiments, the rate of phosphine dissociation from *cis*-Mo(CO)₄L₂ (L = phosphine) was determined for several phosphines. The overall reaction in each case was of the form:



The following rates were obtained:

<i>Phosphine</i>	<i>Rate constant (s⁻¹)</i>
PMe ₂ Ph	< 1.0 × 10 ⁻⁶
PMePh ₂	1.3 × 10 ⁻⁵
PPh ₃	3.2 × 10 ⁻³

Account for the trend in reaction rates **(2 marks)**

- (d) Explain the *trans influence* and *trans effect* in substitution reactions of square planar complexes. **(2 marks)**

QUESTION FOUR [20 MARKS]

- (a) Describe two synthetic routes to transition-metal alkyl complexes. **(4 marks)**
- (b) Complexes of formula Rh(CO)(phosphine)₂Cl have the C-O stretching bands shown below. Match the infrared bands with the appropriate phosphine. Justify your answers. **(4 marks)**
- Phosphines: P(*p*-C₆H₄F)₃, P(*p*-C₆H₄Me)₃, P(*t*-C₄H₉)₃, P(C₆F₅)₃; ν(CO), cm⁻¹: 1923, 1965, 1984, 2004
- (c) Propose a mechanism for the catalytic conversion of but-2-ene to butane using the RuCl₂(PPh₃)₃ complex. **(5 marks)**
- (d) Discuss the carbonylation of methanol using the [IrI₂(CO)₂]⁻ complex. **(7 marks)**
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