

CHUKA

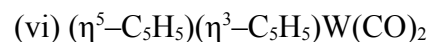
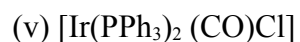


UNIVERSITY

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**UNIVERSITY EXAMINATIONS**
**EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN  
CHEMISTRY AND BACHELOR OF EDUCATION SCIENCE**
**CHEM 416: COMPARATIVE STUDY OF D – AND F- BLOCK ELEMENTS**
**STREAMS:****TIME: 2 HOURS****DAY/DATE: FRIDAY 12/04/2019****8.30 A.M – 10.30 A.M****INSTRUCTIONS**Answer question **One** (Compulsory) and any other **Two** questions**QUESTION ONE [30 MARKS]**

(a) Determine the oxidation state of the metal and the total valence electron count for each of the complexes. (6 marks)



(b) Discuss the following reactions with the aid of a suitable example. (10 marks)

(i) Migratory insertion

(ii) oxidative addition

(iii) reductive elimination

(c) Explain the vibrational frequencies of the carbonyl ligand in the following complexes.

(2marks)

<b><u>Complex</u></b>	<b><u><math>\nu_{\text{CO}}</math> (cm<sup>-1</sup>)</u></b>
$[\text{Ti}(\text{CO})_6]^{2-}$	1748
$[\text{Cr}(\text{CO})_6]$	2000
$[\text{Mn}(\text{CO})_6]^+$	2100

(d) Order the following phosphines from the highest to the weakest  $\sigma$ -donor. Justify your answers (4 marks)

- (i)  $P(t\text{-Bu})_3$                       (ii)  $PF_3$                       (iii)  $PPh_3$                       (iv)  $P(Bu)_3$

(e) Discuss, with the aid of suitable examples, the pathways through which metal alkyl complexes decomposes. (8 marks)

### QUESTION TWO [20 MARKS]

(a) Compare and contrast homogeneous and heterogeneous catalysis. (6 marks)

(b) The Monsanto process is used for industrial production of acetic acid using a rhodium carbonyl iodide,  $[RhI_2(CO)_2]^-$ , catalyst.

(i) Write a balanced equation for the overall reaction (1 mark)

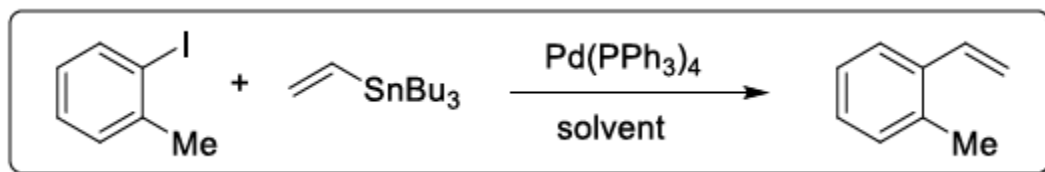
(ii) Draw the catalytic cycle for the process (6 marks)

(iii) Name the elementary steps of the reaction (3 marks)

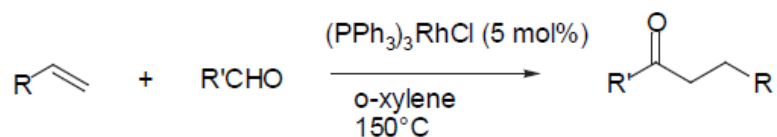
(iv) Explain the advantages of the Monsanto process over the cobalt-catalyzed BASF process for industrial production of acetic acid. (4 marks)

### QUESTION THREE [20 MARKS]

(a) Draw a well labelled catalytic cycle for the Pd-catalyzed Stille cross-coupling of 2-iodotoluene and tributyl(vinyl)stannane shown below. The rate of migration of groups from  $R_3SnX$  compounds is alkenyl > aryl > allyl > alkyl (7 marks)



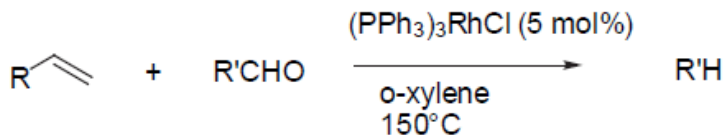
(b) Consider the following hydroacylation reaction:



(i) Draw the catalytic cycle for the reaction indicating the oxidation states and the electron count of all species. (5 marks)

(ii) Name the elementary reaction steps of the reaction. (2½ marks)

(iii) Draw the catalytic cycle for the following by-product of the reaction. (4½ marks)



(iv) Explain how the formation of the by-product in (iii) minimized? (1 mark)

#### **QUESTION FOUR [20 MARKS]**

(a) Describe the production (reaction conditions, mechanisms, etc.) of propylene using Ziegler-Natta catalysts. (8 marks)

(b) Consider the following reaction:

(i) Draw the catalytic cycle for the reaction indicating the oxidation states and the electron count of all species. (7 marks)

(ii) Name the elementary reaction steps of the reaction. (3 marks)

(iii) Explain the advantages of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  over cobalt catalysts. (2 marks)