

**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 2012, for Internal Students of  
the Imperial College of Science, Technology and Medicine**

**This paper is also taken for the relevant examination for the  
Associateship**

**ADVANCED CHEMISTRY THEORY IIIA**

**Inorganic Chemistry**

**Monday 09<sup>th</sup> January 2012, 09:30-12:30**

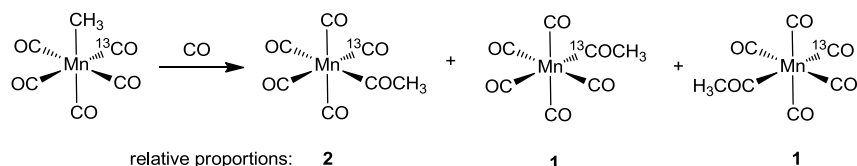
**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT  
THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING  
OF ANY PRIOR CORE COURSE.**

**USE A SEPARATE ANSWER BOOK FOR EACH  
QUESTION. WRITE YOUR CANDIDATE NUMBER ON  
EACH ANSWER BOOK.**

### 3. I1 – Inorganic Mechanisms and Catalysis

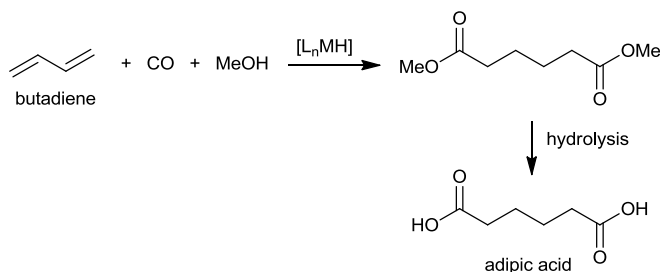
Answer part a) **AND** part b) and **EITHER** part c) **OR** part d) of this question.

- a) The reaction of CO with the labeled manganese complex  $[\text{Mn}(\text{CO})_4(^{13}\text{CO})\text{CH}_3]$  results in the formation of three isomeric products, with relative proportions shown below. Explain the mechanism of the reaction and the product distribution.



(5 marks)

- b) The methoxycarbonylation of butadiene is a potential new route to adipic acid. The initial reaction of butadiene with CO and methanol would produce the methyl ester of adipic acid, which is subsequently hydrolysed to adipic acid, as shown in the Scheme below. Starting from a generic metal catalyst  $\text{L}_n\text{MH}$ , draw a catalytic cycle for the methoxycarbonylation of butadiene and explain each step in the cycle. What side reactions could occur and what side products may be formed? Explain your reasoning.

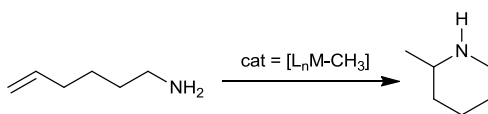


(12 marks)

- c) Describe the iridium-catalysed carbonylation of methanol to acetic acid (BP-Cativa Process) and the differences between this process and the related rhodium-catalysed Monsanto Process.

(8 marks)

- d) In recent years, several examples of metal-catalysed hydroamination of alkenes have been reported. Starting from a metal alkyl catalyst precursor, propose a catalytic cycle for the intramolecular hydroamination of 6-amino-1-hexene to give 2-methylpiperidine, as shown below.



(8 marks)

### 3I2 – Advanced Main Group Chemistry

Answer part a) and any **TWO** parts from b), c) and d) of this question.

a) Answer **ALL** parts of this question.

i) What problems are encountered when trying to prepare transition metal complexes of disilenes?  
(2 marks)

ii) Give three different methods by which transition metal disilene complexes may be prepared, illustrating each method with a particular example.  
(9 marks)

iii) How can the structure of a complex that is thought to contain a disilene ligand be investigated in order to determine the extent of disilene versus disilametallacyclopropane nature?  
What structural/spectroscopic features are expected for a disilene complex?  
(4 marks)

b) Draw the structure of  $\text{ClF}_3$  and use a simple molecular orbital diagram to account for any differences in bond length present in the structure.  
(5 marks)

c) Give balanced equations to show the synthesis of  $\text{XeF}_6$  and  $\text{XeO}_3$  starting from Xe.  
Why is  $\text{XeF}_6$  not used in glass apparatus?  
(5 marks)

d) Show a specific example of how a sila-aromatic compound can be made.  
When the substituents on the silicon and the ring are relatively small, give equations to show what reactions the sila-aromatic compound undergoes, under the following conditions:

i) in the absence of any other external compounds.  
ii) upon addition of EtOH.  
(5 marks)

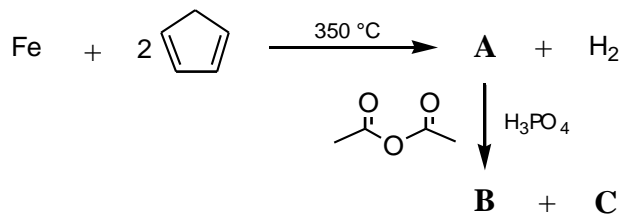
### 3.I3 – Advanced Transition Metal Chemistry

Answer part a) **AND** part b) and **EITHER** part c) **OR** part d) of this question.

a) Answer **ALL** parts of this question.

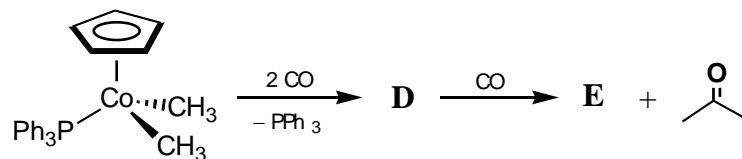
- i) Draw structures for organometallic compounds **A** - **C**. Compound **B** displays a singlet in the  $^1\text{H}$  NMR spectrum at 4.2 ppm. Only multiplets are observed in the region between 4 - 5 ppm in the  $^1\text{H}$  NMR spectrum of compound **C**.

N.B. Not all side products are shown in the formation of **B** and **C**.



(3 marks)

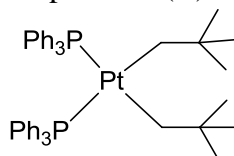
- ii) Draw structures for the organometallic compounds **D** and **E** and describe the mechanism for the formation of **E** and acetone. Compound **D** shows absorptions at 1680 and 1990  $\text{cm}^{-1}$  in the infrared spectrum, while compound **E** displays absorptions at 1960 and 2017  $\text{cm}^{-1}$ . Assign these absorptions to functional groups in your structures.



(5 marks)

b) Answer **ALL** parts of this question.

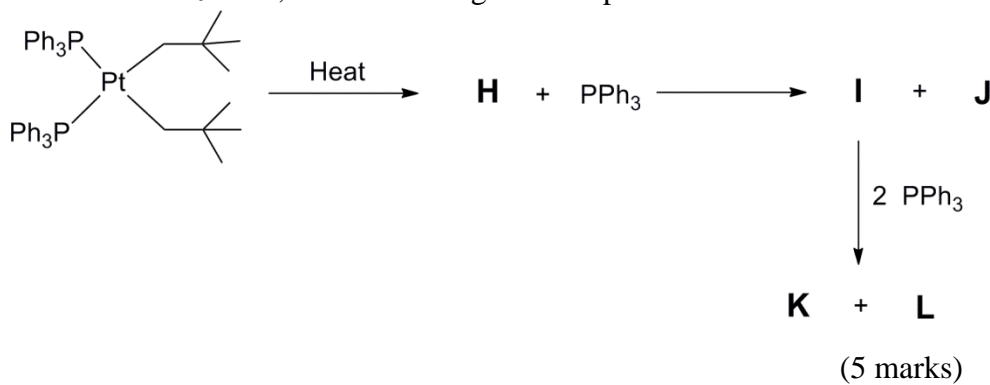
- i) Propose a plausible preparation of the platinum(II) complex shown below.



(1 mark)

QUESTION CONTINUED OVERLEAF

- ii) Draw structures for compounds **H** - **L**. Compound **H** is highly unstable and its  $^1\text{H}$  NMR spectrum would be expected to show a signal at around -10 ppm. The mixture of **H** and  $\text{PPh}_3$  readily convert into a di-phosphine metal complex **I** and an organic compound **J**. The  $^{13}\text{C}$  NMR spectrum of **J** presents only two signals and a single signal can be found in its  $^1\text{H}$  NMR spectrum. **K** displays a molecular ion at  $m/z$  1243, and **L** is an organic compound.



- iii) Propose an intermediate showing an agostic interaction in the formation of **H**.  
(1 mark)

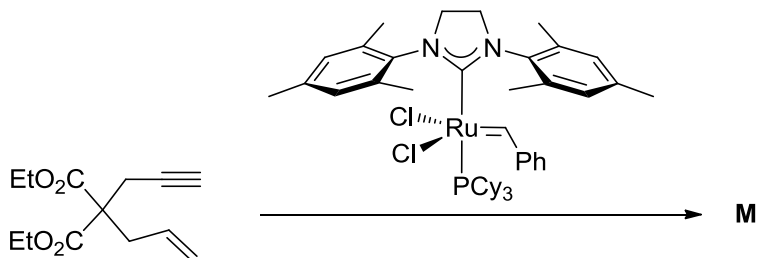
c) Answer **ALL** parts of this question.

- i) Using  $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2$  as the pre-catalyst, discuss the Cossee-Arlman mechanism for the polymerisation of ethene, including initiation and propagation steps. Explain the role played by methylaluminoxane (MAO).  
(7 marks)
- ii)  $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2$  can be used to prepare high-density polyethylene (HDPE) from ethene. If propene was used with this pre-catalyst, what polymer would result and why?  
(3 marks)

QUESTION CONTINUED OVERLEAF

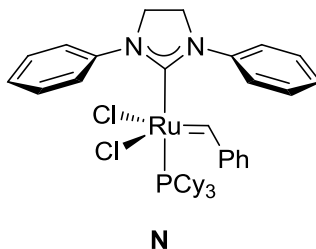
d) Answer **ALL** parts of this question.

- i) For the following metathesis reaction, catalysed by the second generation Grubbs catalyst, give the structure of the organic product **M**, and propose a mechanism for its formation.



(5 marks)

- ii) Complex **N** tends to decompose by a standard organometallic reaction. Propose a plausible decomposition product, taking into account that such decomposition cannot take place in the 2<sup>nd</sup> generation Grubbs catalyst. Briefly rationalise your proposal.



(5 marks)