

**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 2017, for Internal Students  
of the Imperial College of Science, Technology and Medicine**

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

**CHEM60001 ADVANCED CHEMISTRY**

**Paper 1**

**Tuesday 10<sup>th</sup> January 2017, 14:00-16:15**

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

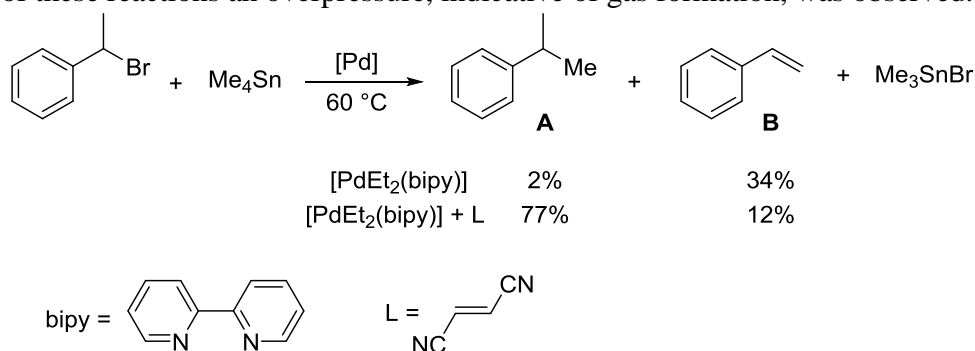
**USE A SEPARATE ANSWER BOOK FOR EACH  
QUESTION. WRITE YOUR CANDIDATE NUMBER ON  
EACH ANSWER BOOK.**

## Q1: Advanced Transition Metal Chemistry

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

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

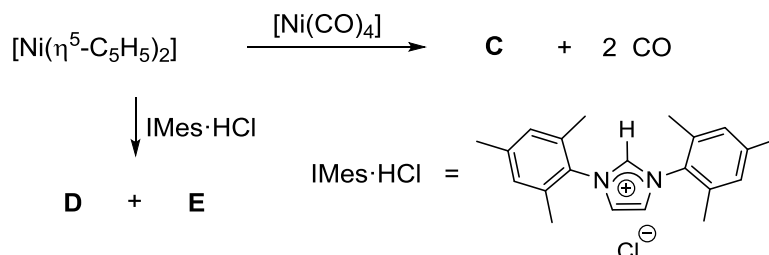
The cross-coupling reaction of 1-bromoethylbenzene and tetramethyltin produces isopropylbenzene **A** in low yield, since styrene **B** is the main reaction product. However, in the presence of alkene **L**, **A** is formed preferentially and in good yield. In both of these reactions an overpressure, indicative of gas formation, was observed.



- i) What is the catalytically active complex in these reactions and how does it form? (2 marks)
- ii) Draw all the mechanistic steps required to form both **A** and **B** in the scheme above, showing all the intermediates in these catalytic cycles. Explain the origin of the observed overpressure. (9 marks)
- iii) Explain the effect of alkene **L** in the product distribution. (2 marks)
- iv) Propose two structurally different electrophilic reagents that would ensure the formation of cross-coupled products only. (2 marks)

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

Two reactions of nickelocene are shown below. Compound **C** shows absorptions in the infrared spectrum at around  $1780\text{ cm}^{-1}$ . Compound **D** shows a singlet integrating to 5 protons at 4.61 ppm in the  $^1\text{H}$  NMR spectrum and gives a molecular ion in the mass spectrum of  $m/z$  463 as well as a fragment at  $m/z$  428. Compound **E** is an organic compound of formula  $\text{C}_5\text{H}_6$ . All equations are balanced.



QUESTION CONTINUED OVERLEAF

i) Draw structures for compounds **C**, **D** and **E**.

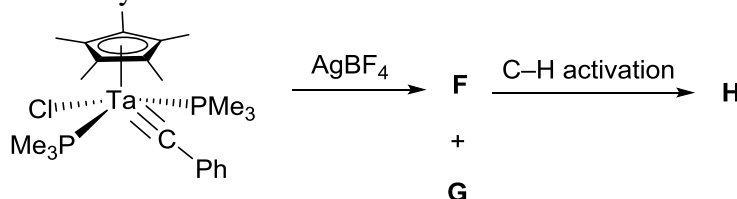
(3 marks)

ii) Would you expect  $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$  to be paramagnetic or diamagnetic? Explain your answer.

(2 mark)

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

When the tantalum alkylidyne complex shown below is reacted with  $\text{AgBF}_4$  a new complex **F**, and inorganic solid **G** are obtained. Compound **F** is extremely reactive and able to activate one of its phosphine ligands through a C–H activation process leading to the formation of **H**. The  $^1\text{H}$  NMR spectrum of **H** did not show any resonance attributable to a metal hydride.



i) Draw the structures of **F** and **H** and identify solid **G**.

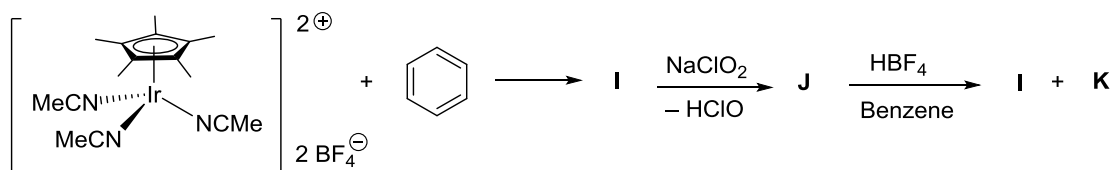
(3 marks)

ii) Propose two characterisation techniques that would help to confirm the structure of complex **H**.

(2 marks)

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

The iridium complex shown below readily reacts with benzene to form a new compound **I**. Reaction of **I** with sodium chlorite leads to **J** upon elimination of  $\text{HClO}$ . **J** has a stretching band at  $1633\text{ cm}^{-1}$  in its IR spectrum. An acidic treatment in the presence of benzene regenerates compound **I** and leads to a new organic compound **K**. All these reactions are carried out at room temperature in acetonitrile as solvent.



i) Draw the structures of **I**, **J** and **K**.

(3 marks)

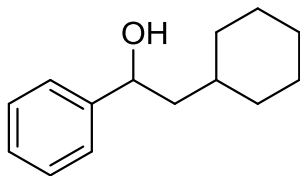
ii) Propose an intermediate in the formation of **J**. What is the role of the metal in these reactions?

(2 marks)

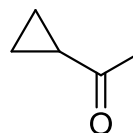
## Q2: Organic Synthesis 2

Answer **ALL** parts of this question.

- a) For **BOTH** of the compounds **A AND B** shown below show a simplifying C–C bond disconnection. Identify the synthons implied by your disconnections, and write down the synthetic equivalents of the synthons. (2 x 5 marks)

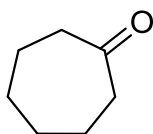


**A**

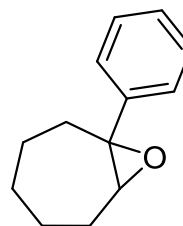


**B**

- b) Explain how compound **D** below may be synthesised from compound **C**; more than one step will be required. Give mechanisms for the transformations you propose. (5 marks)

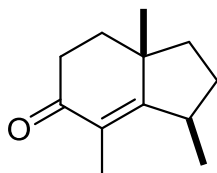


**C**

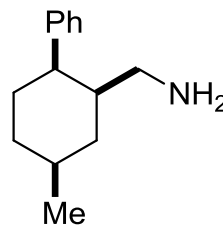


**D**

- c) Devise a synthesis of **EITHER** compound **E OR** compound **F** shown below. Show clearly your retrosynthetic analysis, identifying synthons and synthetic equivalents where necessary. Propose reagents for your forward synthesis, and comment on any stereoselectivity in the reactions you propose. (10 marks)



**E**



**F**

### Q3: Electronic Properties of Solids

Answer part a) and **EITHER** part b) or part c) of this question.

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

Silicene is the silicon analogue of graphene and individual sheets have a similar, hexagonal two-dimensional lattice.

- i) Draw the structure of silicene in real space and indicate the two lattice vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  given below. 'a' is the nearest-neighbour Si-Si distance. Explain why a hexagonal lattice (or net) is not a Bravais lattice.

(2 marks)

$$\mathbf{a}_1 = \frac{a}{2} \cdot \begin{pmatrix} 3 \\ \sqrt{3} \end{pmatrix} \quad \mathbf{a}_2 = \frac{a}{2} \cdot \begin{pmatrix} 3 \\ -\sqrt{3} \end{pmatrix}$$

- ii) Calculate the reciprocal lattice vectors  $\mathbf{b}_1$  and  $\mathbf{b}_2$  using the appropriate formula. The required rotational matrix R is given below.

(3 marks)

$$R = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

- iii) Draw the reciprocal lattice based on  $\mathbf{b}_1$  and  $\mathbf{b}_2$ , and indicate both vectors in your drawing. Construct the Brillouin zone.

(4 marks)

- iv) Add the symmetry points  $\Gamma$ , M, K and K' given below to the drawing in part iii). Calculate their respective energies using the dispersion relation, in terms of  $\alpha$  and  $\beta$ . Draw the energy diagram based on these symmetry points (take  $\beta > 0$ ).

(6 marks)

$$\Gamma = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad \mathbf{M} = \frac{2\pi}{3a} \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \mathbf{K} = \frac{2\pi}{3a} \cdot \begin{pmatrix} 1 \\ 1/\sqrt{3} \end{pmatrix} \quad \mathbf{K}' = \frac{2\pi}{3a} \cdot \begin{pmatrix} 1 \\ -1/\sqrt{3} \end{pmatrix}$$

$$E_{\pm}(\mathbf{k}) = \alpha \pm \beta \cdot \sqrt{3 + f(\mathbf{k})}$$

$$\text{where } f(\mathbf{k}) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right)$$

QUESTION CONTINUED OVERLEAF

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

Consider a simple metal such as sodium at finite temperature, i.e.  $T > 0$  K.

- i) Write down the probability distribution for the electrons as a function of energy  $E$  and specify all terms. Draw the function and label the drawing as accurately.  
(3 marks)
- ii) Calculate the specific heat capacity  $C_V$  for a metal with a Fermi energy  $E_F = 3.2$  eV at  $T = 298$  K and compare your result with the value for an ideal gas.  
(3 marks)
- iii) Estimate the absolute number of electrons in a cube of Na that are affected by thermal broadening. The mass of the cube is  $m = 0.5$  g, the molar mass of Na is 23 g/mol and the temperature  $T = 298$  K.  
(4 marks)

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

- i) What is the difference between a direct and an indirect bandgap semiconductor material? Define both terms and illustrate your definition with suitable  $E(k)$  diagrams.  
(3 marks)
- ii) Give a simple proof why optical transitions from the valence band to the conduction band in a semiconducting material normally occur at effectively the same  $k$ -value.  
(3 marks)
- iii) Write down an expression for the electric conductivity  $\sigma$  of a semiconducting material and define all terms. Explain how each parameter in the expression for  $\sigma$  changes with increasing temperature. Rationalize why the temperature dependence of  $\sigma$  is different for a semiconducting material, compared to a metal.  
(4 marks)