IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2016, 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

Paper 1

Wednesday 13th January 2016, 14:00-16:15

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

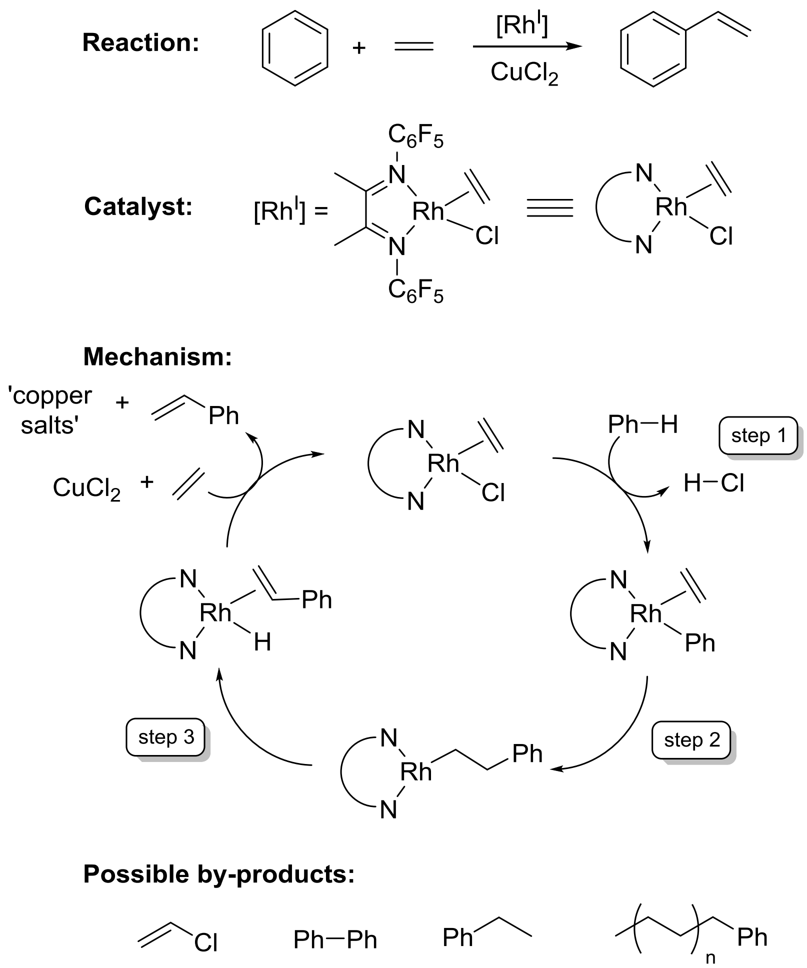
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

3.I3 – Advanced Transition Metal Chemistry

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

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

The rhodium(I) complex shown below is an excellent catalyst for the preparation of styrene from benzene and ethylene. In this reaction $CuCl_2$ is used as a stoichiometric oxidant. The proposed catalytic cycle for this transformation is also shown below.



i) State what type of chemical reaction occurs in steps 1, 2 and 3 of the catalytic cycle and propose a rhodium intermediate for each of the first two steps.

(3 marks)

ii) Starting from any of the species shown in the mechanism, rationalise the formation of each of the four possible by-products provided.

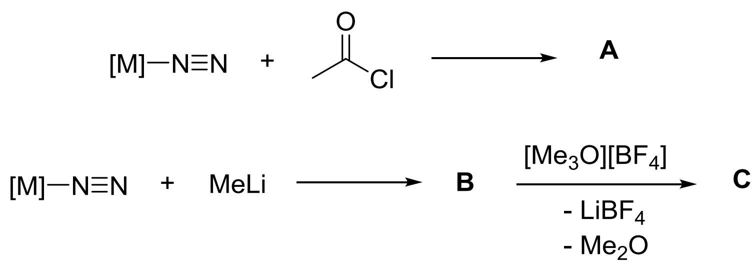
(12 marks)

QUESTION CONTINUED OVERLEAF

b) The activation of N_2 by coordination of a transition metal can be used not only to protonate N_2 (ammonia production), but also to form nitrogen–carbon bonds. Indeed, dinitrogen complexes can react with either electrophiles or nucleophiles to form new metal complexes.

Draw the structures of **A**, **B** and **C** (remember: N_2 is isoelectronic with CO).

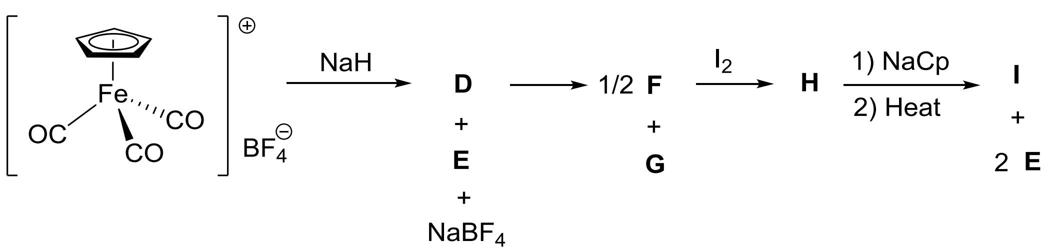
(5 marks)



c) $[Fe(\eta^5\text{-}C_5H_5)(CO)_3]BF_4$ reacts with NaH to give compound **D** and a colourless gas **E**. Compound **D** has a resonance signal at -15 ppm in the ^{1}H NMR spectrum and it rapidly rearranges at room temperature to form a solid compound **F** and a colourless gas **G**. Compound **F** has two strong IR absorption bands, one at 1850 cm^{-1} and the other at 2000 cm^{-1}. Treatment of **F** with iodine generates solid compound **H**. The reaction of **H** with NaC_5H_5 followed by heating leads to the formation of an orange, sublimable compound **I** and gas **E**.

Draw the structures of **D**, **F**, **H** and **I** and identify gases **E** and **G**.

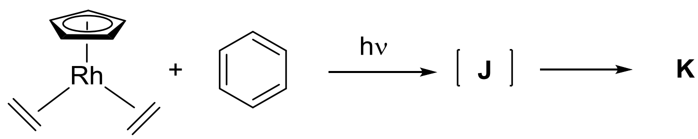
(5 marks)



QUESTION CONTINUED OVERLEAF

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

Photolysis of $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)_2]$ in the presence of benzene yields compound **K** of formula $Rh_2C_{16}H_{16}$, via intermediate **J**. **K** follows the 18-electron rule and has a metal–metal bond. Furthermore, its ^1H NMR spectrum presents three resonance signals of relative intensities 5:2:1.



Note: these equations are NOT balanced

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

(3 marks)

ii) Provide the electron count for compound **K** and rationalise the spectroscopic information provided.

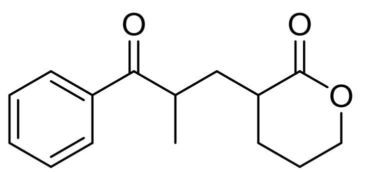
(2 marks)

3.O11 – Organic synthesis

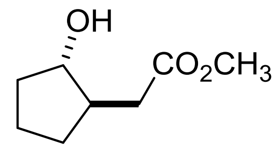
Answer **ALL** parts of this question.

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)



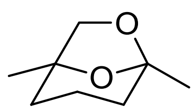
A



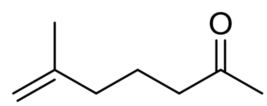
B

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

(5 marks)



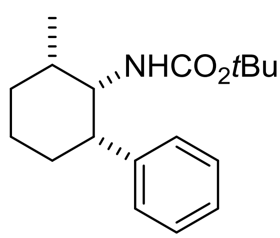
C



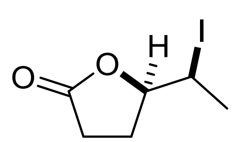
D

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 the stereoselectivity of the reactions you propose.

(10 marks)



E



F

3.P15 – Electronic Properties of Solids

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

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

Consider a ring that contains N=3 atoms of type i. The distance between two neighbouring atoms is equal to 1.

i) Write down the molecular wavefunction Ψ, in terms of a basis set of hydrogen 1s atomic orbitals ϕ_i. Assume that the ϕ_i are orthonormal and that only nearest-neighbour interactions need to be considered.

(2 marks)

ii) Write down the Hamiltonian matrix for this system. Denote the on-site matrix element by α and the hopping integral by β in Dirac notation. Simplify the Hamiltonian matrix as much as possible.

(3 marks)

iii) Calculate the energy spectrum in terms of α and β. During the derivation you will encounter a third-order polynomial, the solutions of which you should be able to guess (i.e. they are small numbers). Remembering the relation between ring geometry and energy level distribution, how many numerically different solutions do you expect?

(6 marks)

iv) Now let N grow to infinity. Write down an equation for the energy spectrum. Comment on the expected change in band width ΔE and level spacing dE as N increases. How does dE compare to thermal energy at room temperature and what does that mean for the electronic properties of the material?

(4 marks)

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

Consider an infinitely long, one-dimensional chain of atoms. The bond distance is a, the atoms are placed along the z-axis.

i) Using a basis set of p_z-orbitals, draw the two molecular orbitals that correspond to the highest and the lowest energy within the band, and specify the k-values in each case.

(3 marks)

QUESTION CONTINUED OVERLEAF

ii) How does the electronic structure change, when the bond distance a is increased to infinity? Use the on-site matrix element α and the hopping integral β in your explanation, and draw the electronic structure diagram E(k) for the two cases.

(4 marks)

iii) Explain why, in principle, any insulating material can become metallic when the pressure is sufficiently high.

(3 marks)

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

i) Write down the probability distribution function that describes electrons in extended solids and define all terms. What is the name of this probability distribution function?

(3 marks)

ii) Sketch this function for different temperatures, namely for $T_0 = 0$ K as well as T_1 and T_2, where $T_2 > T_1 > T_0$. Comment on the result.

(4 marks)

iii) Use the probability distribution from part ii) to calculate the specific heat capacity, C_V, of copper at 298 K; assume that the Fermi energy of copper is 7.00 eV. Compare your computed value to C_V for an ideal gas of classical particles ($1.5 \cdot R$) and explain the difference.

(3 marks)