**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 2015, 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 IIA

## Inorganic Chemistry

**Monday 12th January 2015, 09:30-11:00**

**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.**

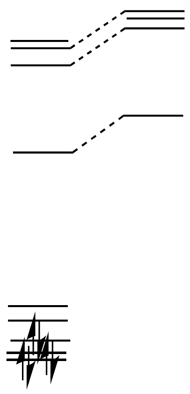
**Year 2/0115** **Turn Over**

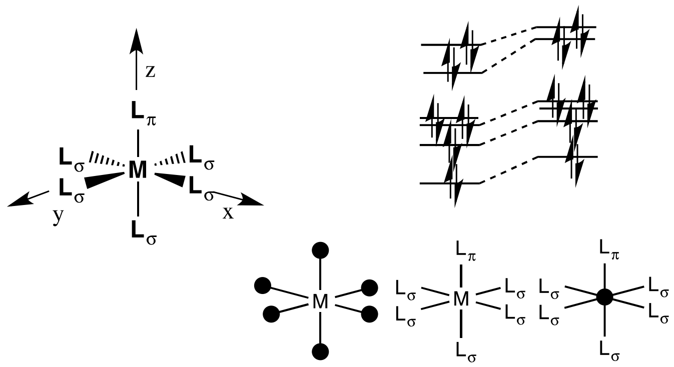
## 2I1 – Molecular Orbitals in Inorganic Chemistry

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

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

i) Complete a valence energy diagram for a $C_{4v}$ point group TM complex $M(L_\sigma)_5L_\pi$ where $L_\sigma$ is a $\sigma$-donor ligand and $L_\pi$ is a $\pi$-acceptor ligand. Note that the ligand FOs for a $M(L_\sigma)_6$ complex of $O_h$ symmetry have $a_{1g}$, $t_{1u}$ and $e_g$ symmetry.






(6 marks)

ii) Identify the metal based MOs and the ligand based MOs on your diagram.

(2 marks)

iii) Draw the strongly interacting bonding and anti-bonding MOs for a TM-CO bond (only one orbital of each degenerate set is required).

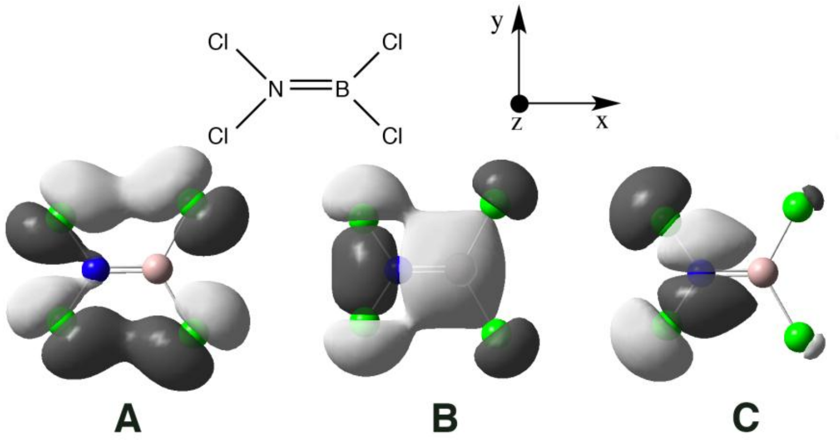
(3 marks)

iv) Explain using MO theory and appropriate diagrams why M-CO bonds are stronger than $M\text{-}N_2$ bonds in TM complexes.

(4 marks)

QUESTION CONTINUED OVERLEAF

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




i) Considering only atomic orbitals in the xy plane, **draw** a linear combination of atomic orbitals (LCAO) diagram for each MO.

(4 marks)

ii) Annotate diagrams of MOs **A** and **B**, identify and explain features that are important in evaluating the overall bonding or anti-bonding character of these MOs.

(4 marks)

iii) Identify the symmetry and molecular fragments it would be best to employ in constructing a MO diagram for this molecule.

(2 marks)

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

i) Derive the formula:

$$E_{\pm} = \frac{e_{aa} \pm 2H_{ab} + e_{bb}}{2(1 \pm S_{ab})}$$

(4 marks)

ii) Modify the formula for the case of two degenerate fragment orbitals that do not directly overlap and illustrate the effects of this approximation on a MO diagram.

(3 marks)

iii) Describe a situation where the above approximation is a good one.

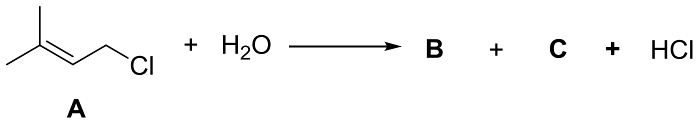
(3 marks)

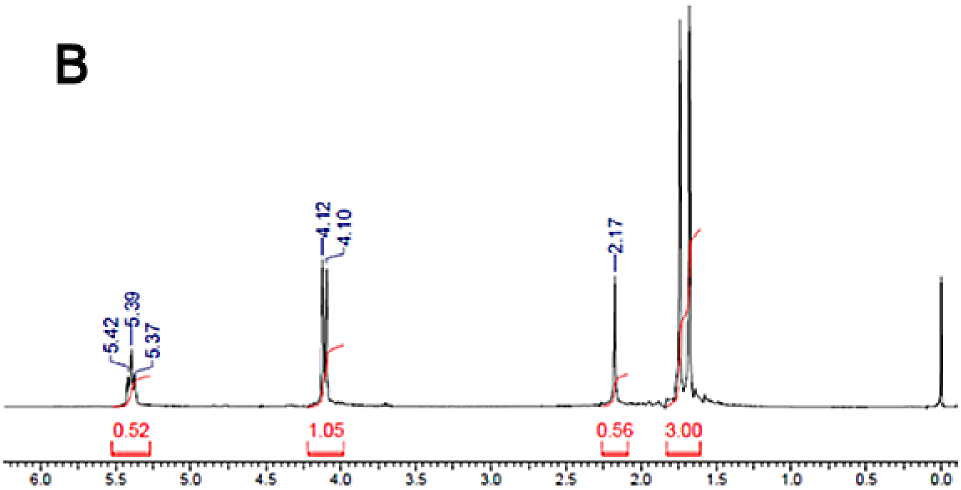
## 2.I5 – NMR Spectroscopy

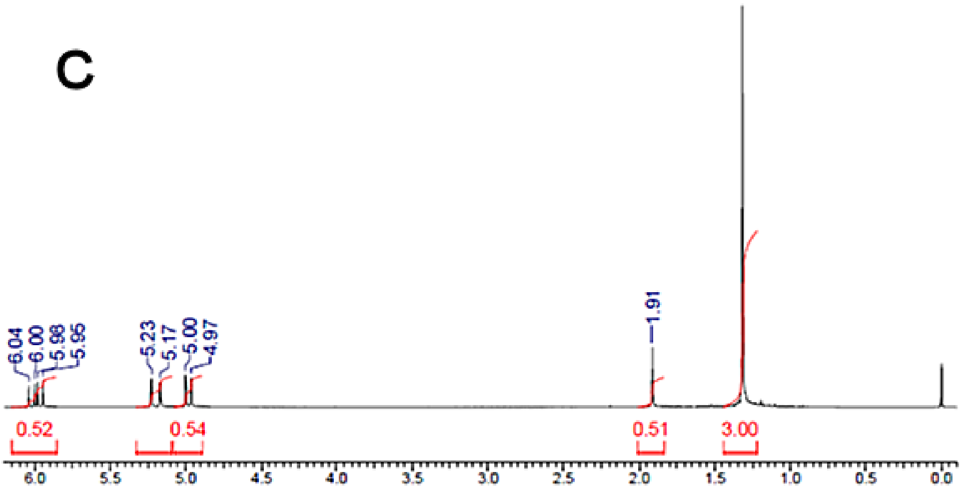
Answer part a) and **EITHER** part b) or part c) of this question.

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

The allylic halide **A** undergoes reaction with water to yield a mixture of two isomeric organic products, **B** and **C**. The proton NMR spectra of **B** and **C** (recorded at 300 MHz, peak picking made in ppm) are given below (singlet at 0 ppm = TMS reference).




i) Identify the molecular structures of **B** and **C**.

(2 marks)

ii) Provide a mechanism for the formation of **B** and **C**.

(2 marks)

QUESTION CONTINUED OVERLEAF

iii) Assign all the resonance signals observed in the spectrum of **C** Include in your answer the values of the chemical shifts and *J* coupling constants.

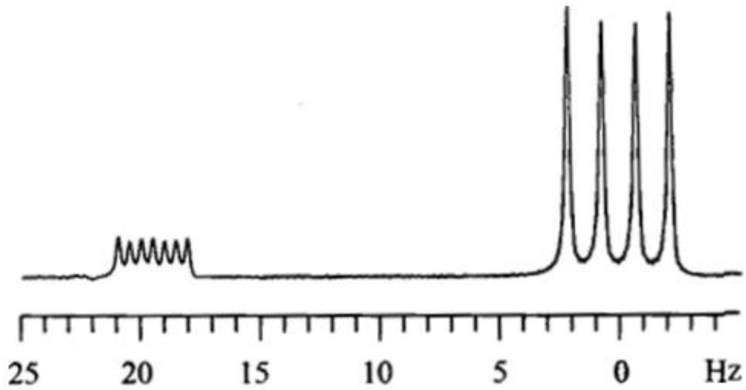
(5 marks)

iv) Use any of the molecules **A**, **B** and **C** to explain the following terms: Enantiotopic protons; ABX spin system.

(4 marks)

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

The $^{19}$F NMR spectrum of a solution of $NaBF_4$ in $D_2O$ is given below (note: the scale is plotted in Hz). [$^{19}$F, I = ½, 100% abundant; $^{10}$B, I = 3, 19.58% abundant, $\gamma$ = 2.874, $^{11}$B, I = 3/2, 80.4% abundant, $\gamma$ = 8.6]




i) Predict the structure of the $BF_4^-$ anion.

(1 mark)

ii) Explain the appearance of the spectrum and assign the resonance signals, including their multiplicity and all the observable J coupling constants.

(6 marks)

iii) Comment on the relative sizes of the *J* values.

(2 marks)

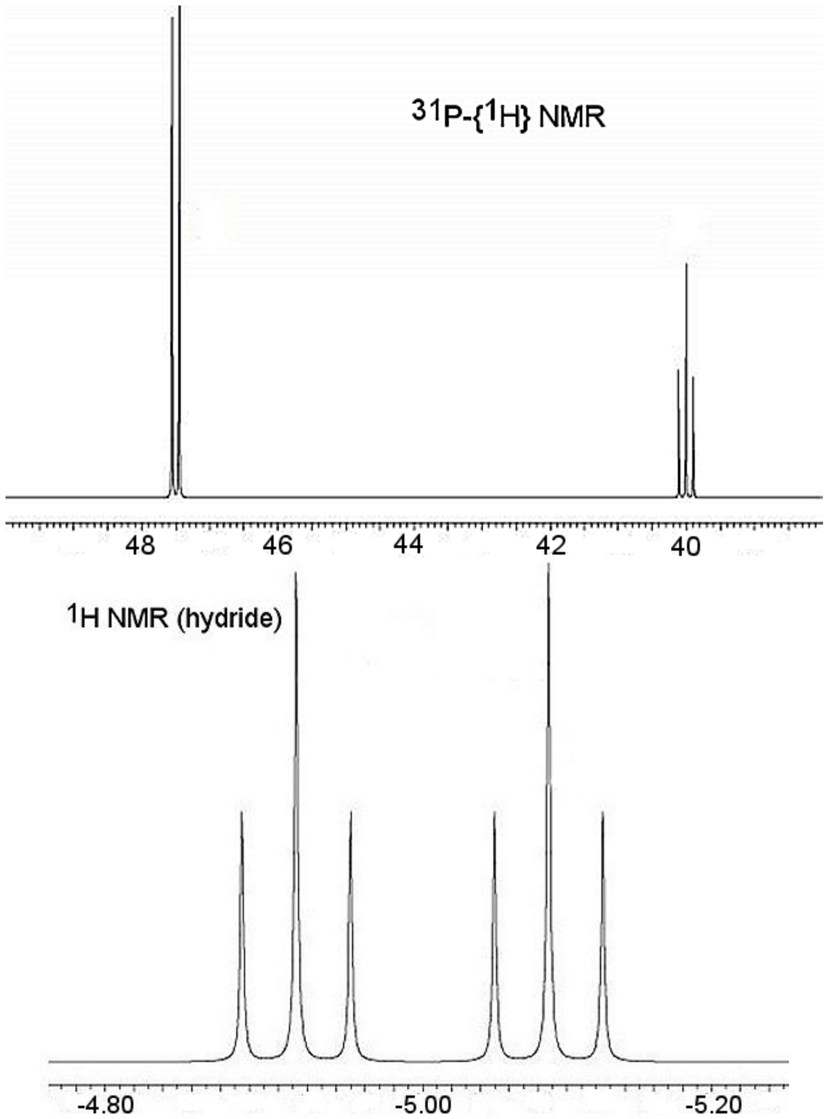
iv) Provide a sketch of the corresponding $^{11}$B NMR spectrum.

(3 marks)

QUESTION CONTINUED OVERLEAF

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

The $^{31}P$-{$^{1}H$} and $^{1}H$ (hydride region only) NMR spectra of an iridium complex [Ir($PPh_3$)$_3$(H)] are given below. [$^{31}P$, $^{1}H$, $^{103}Rh$, all I = ½; 100% natural abundance; Ir, I = 0]




i) Predict and draw the structure of the iridium complex. Comment on its oxidation state and d-occupancy.

(2 marks)

ii) Reproduce these spectra in your answer booklet and assign the resonance signals. Identify the multiplicity observed for each of these resonance signals and label all the observable coupling constants (precise values not necessary). Comment on the relative <u>*J*</u> values.

(6 marks)

iii) Produce a sketch of the $^{31}P$-{$^{1}H$} NMR spectrum of the corresponding Rh complex: [Rh($PPh_3$)$_3$(H)]. Comment on the key features of your spectrum.

(4 marks)