

**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JUNE 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**

**CHEM50001 INORGANIC CHEMISTRY 2**

**Thursday 29<sup>th</sup> June 2017, 14:00-16:15**

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

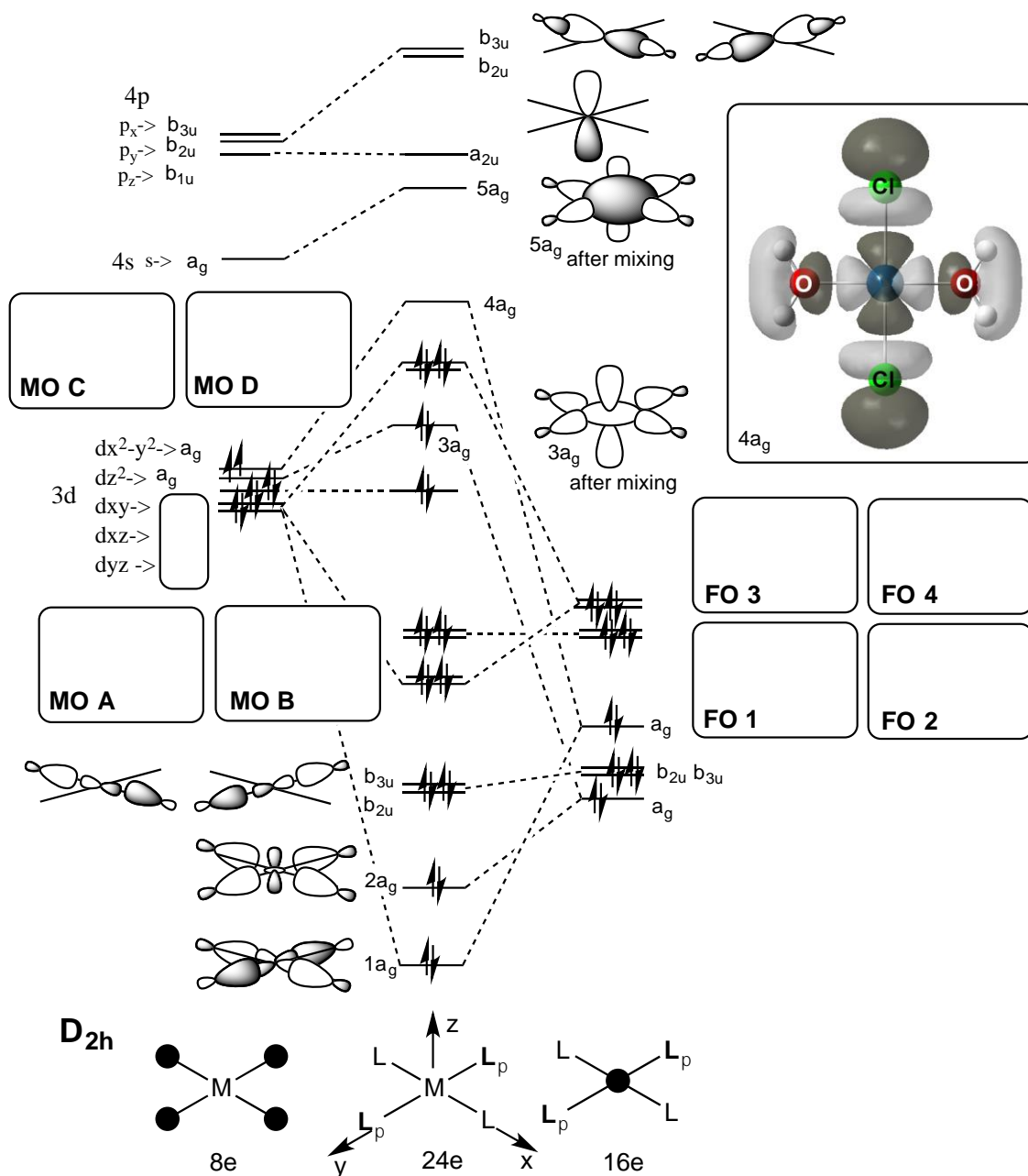
**USE A SEPARATE ANSWER BOOK FOR EACH QUESTION.  
WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER  
BOOK.**

1. Answer **ALL** parts of this question.

- a) Write a reaction scheme for the sequential hydration of  $[\text{PtCl}_4]^{2-}$ . What reactions will occur on the addition of  $2\text{NH}_3(\text{aq})$  or  $2\text{AgNO}_3$ ?

(6 marks)

- b) Consider the partial MO diagram of square planar  $D_{2h}$   $[\text{PtCl}_2(\text{OH}_2)_2]$  below. Do NOT redraw the whole MO diagram.



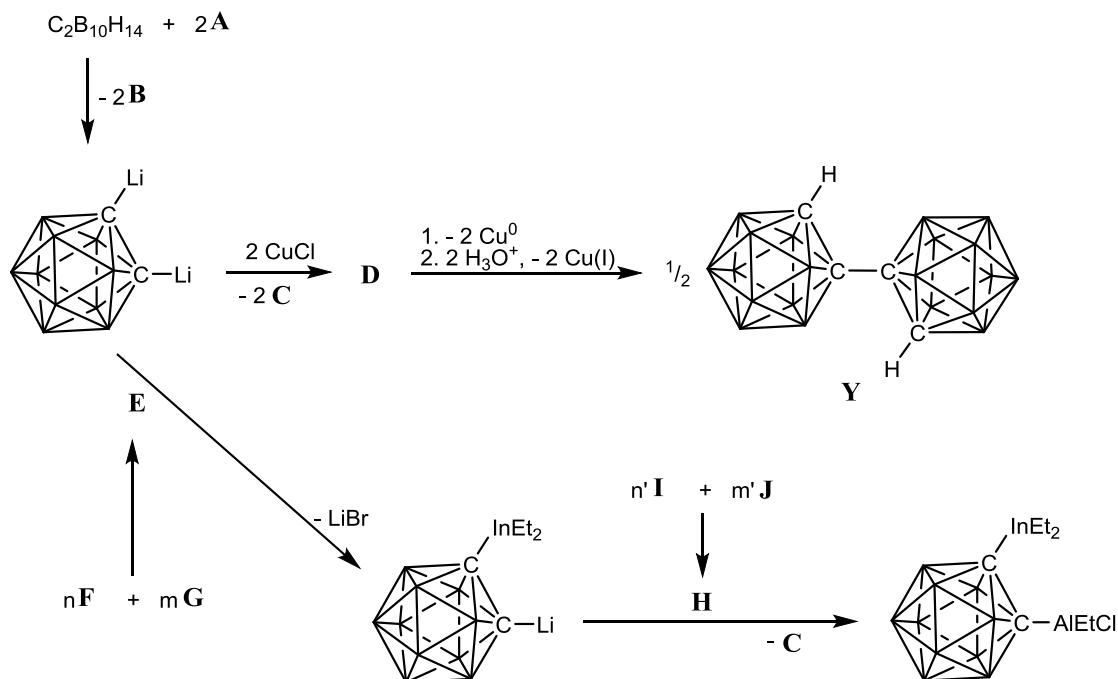
QUESTION CONTINUED OVERLEAF

- i) Identify the symmetry labels of the dxy, dxz and dyz AOs. Draw and identify the symmetry labels of the missing fragment orbitals **FO 1- 4** and the missing molecular orbitals **MOs A-D**. Provide 2 annotations related to these orbitals.  
(9 marks)
- ii) What **differentiates**  $\pi$ -donor and  $\pi$ -acceptor ligands? What does the label " $\pi$ -" refer to in this case?  
(5 marks)
- iii) Draw a linear combination of atomic orbitals (LCAO) diagram for the real  $4a_g$  MO (depicted above). **Identify** the water FO that contributes to this MO and explain how this relates to the water MO diagram.  
(5 marks)

2. Answer **ALL** parts of this question

Welch *et al*<sup>1</sup> report the synthesis of ruthenium and cobalt complexes of *bis*(carborane) **X**<sup>4-</sup> formed by double deboronation of a conjuncto-carborane **Y**.

- a) **Y** can be prepared by coupling of two C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> units *via* a di-lithiated intermediate which is a precursor for a wide range of carborane reactions.



- i) Propose identities of compounds **A** and **B** and identify compounds **C** – **J**. Give balanced equations for the formation of **E** from **F** and **G**, and **H** from **I** and **J** (all other reactions are balanced).

(5.5 marks)

- ii) Et<sub>3</sub>Al and Et<sub>3</sub>In show significantly different <sup>1</sup>H NMR spectra at low temperature. Sketch the spectra and account for the differences (assume Al and In are magnetically inactive).

(3.5 marks)

- iii) C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> is prepared from an *arachno*-borane adduct B<sub>10</sub>H<sub>12</sub>(SEt)<sub>2</sub>. Suggest a reagent for the synthesis of **Y** directly from B<sub>10</sub>H<sub>12</sub>.2SEt<sub>2</sub>.

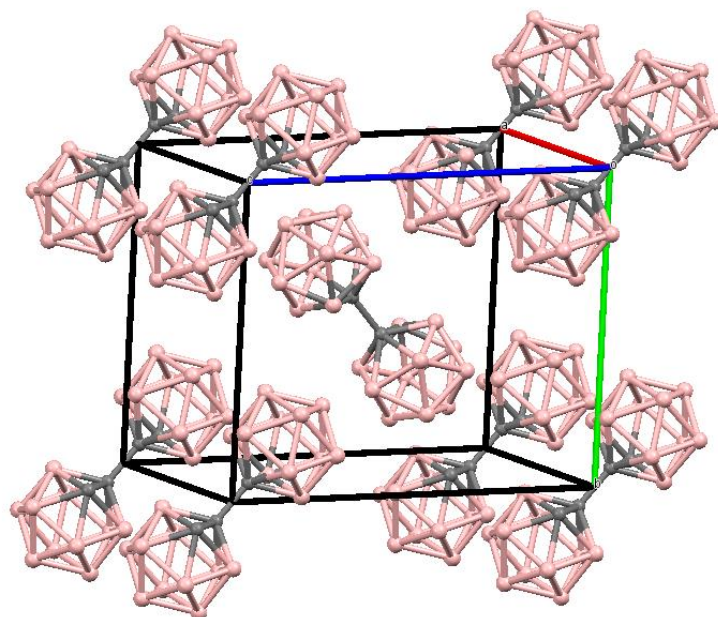
(1 mark)

- iv) Part of the crystal structure of **Y** showing the unit cell is given below. Given that the volume of the unit cell is 848 Å<sup>3</sup> and the molecular mass of **Y** is 286 g mol<sup>-1</sup>, calculate the density of **Y**.

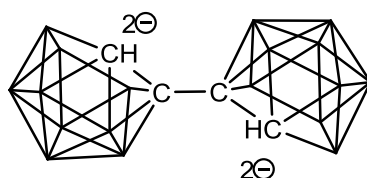
(2 marks)

QUESTION CONTINUED OVERLEAF

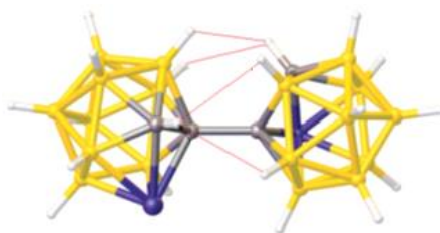
<sup>1</sup> G. Thiripuranathar, A. P. Y. Chan, D. Mandal, W. Y. Man, M. Argentari, G. M. Rosaira and A. J. Welch, Dalton Trans., 2017, 46, 1811-1821



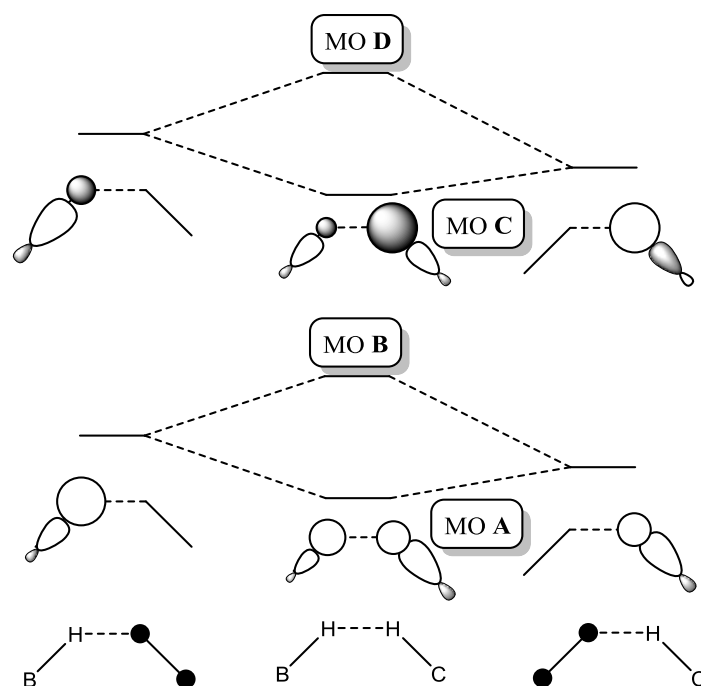
b)  $\mathbf{X}^{4-}$  has the structure shown below. Each  $\text{C}_2\text{B}_9\text{H}_{10}$  cage is dianionic.



- i) Account for the regioselectivity of the deboronation reaction to form  $\mathbf{X}^{4-}$  (*i.e.* which BH unit has been removed from  $\mathbf{Y}$ ).  
(1 mark)
- ii) Use Wade's rules to account for the structure of  $\mathbf{X}^{4-}$  including the positions of the hydrogen atoms. What structural type is each  $\text{C}_2\text{B}_9\text{H}_{10}$  cage?  
(4 marks)
- c) In the cobalt complex of  $\mathbf{X}^{4-}$ , intramolecular dihydrogen bonding is observed between the CH hydrogen atoms on one cage and BH hydrogen atoms on the other cage (shown below). Consider the simple partial MO diagram below right for the interaction of a  $\text{B}_{\text{sp}}\text{-H}$  moiety with a  $\text{H-C}_{\text{sp}}$  moiety:



QUESTION CONTINUED OVERLEAF



- i) Draw the LCAO of the highest energy MO **D**.  
(1 mark)
  - ii) Which is the HOMO?  
(1 mark)
  - iii) Draw MO **B** and use your diagram to identify and explain key features that are important in evaluating the character of this MO. Explain why this partial MO diagram suggests the absence of any net bonding H-H interaction.  
(3 marks)
- d)  $\mathbf{X}^{4-}$  is reacted with 18-electron complex  $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$  ( $p\text{-cymene}$  = 1-isopropyl-4-methylbenzene) to prepare the *bis*(ruthenacarborane).
- i) Draw the possible structures of  $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$  and suggest a characterisation method to confirm the structure.  
(2 marks)
  - ii) The structure of the ruthenium complex of  $\mathbf{X}^{4-}$  is similar to that of the cobalt complex, based on two *closo*- $\text{RuC}_2\text{B}_9$  cages linked by a C-C bond, except no intramolecular dihydrogen bonding is observed. However, two different CH signals are observed in the  $^1\text{H}$  NMR spectrum. Account for this observation.  
(1 mark)

3. Answer **ALL** parts of this question.

a) Give synthetic routes to  $\text{PEtPh}_2$  and  $\text{P(OMe)}_3$  using elemental phosphorus as the starting material in each case. (3 marks)

b) Explain, with the aid of a diagram, why  $\text{PR}_3$  species are such good ligands in transition metal chemistry. (3 marks)

c) Which of the complexes in each of the pairs below will have the lower energy CO stretching frequency in the infrared spectrum? Rationalise your choice.

- |   |    |                                     |
|---|----|-------------------------------------|
| i) $[\text{W(CO)}_5\text{Cl}]^-$        | or | $[\text{Re(CO)}_5\text{Cl}]$        |
| ii) $[\text{Mo(CO)}_6]$                 | or | $[\text{Mo(CO)}_4(\text{PPh}_3)_2]$ |
| iii) $[\text{Fe(CO)}_5]$                | or | $[\text{Fe(CO)}_4\text{Br}_2]$      |
| iv) $[\text{Mo(CO)}_4(\text{PCl}_3)_2]$ | or | $[\text{Mo(CO)}_4(\text{PPh}_3)_2]$ |

(4 marks)

d) Elements **X**, **Y** and **Z** are metals. Use the information given below to identify the three metals and the species **A** to **H**, and explain the observations.

i) Metal **X** forms a green aqua ion of formula  $[\text{X(OH}_2)_6]^{2+}$  which has a spin-only magnetic moment of 2.8 BM. When a solution of the compound  $\text{XBr}_2$  is treated with two equivalents of the phosphine  $\text{PEtPh}_2$  in ethanol, either one of two isomeric products, **A** and **B**, can be obtained by varying the crystallisation conditions. Compound **A** has no dipole moment and is diamagnetic. A peak due to X-Br stretching can be observed in its IR and Raman spectra, but the two frequencies are not the same in each spectrum. Compound **B** has a dipole moment and is paramagnetic. The IR and Raman spectra of **B** each show a peak due to X-Br stretching at the same frequency. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of **A** and **B** are both singlets, but their observed chemical shifts are different.

(6 marks)

ii) Metal **Y** forms a binary carbonyl compound **C**. The mass spectrum of **C** shows a peak due to the molecular ion at  $m/e = 390$ , and a fragmentation pattern consisting of ten sequential losses of  $m/e = 28$ . Treatment of **C** with Na/Hg in diethylether produces the ionic compound **D**. Acidification of **D** yields the neutral compound **E**. The  $^1\text{H}$  NMR spectrum of **E** shows the presence of a Y-H bond. Treatment of **D** with  $\text{CH}_3\text{I}$  affords the neutral compound **F** (Elemental analysis: **Y**, 26.2 %; **C**, 34.3 %; **H**, 1.4 %). Reaction of **D** with the compound  $[(\text{PPh}_3)\text{AuCl}]$  gives the neutral compound **G** and NaCl. The mass spectrum of **G** shows a peak due to the molecular ion at  $m/e = 654$  and a fragmentation pattern consisting of five sequential losses of  $m/e = 28$ .

(6 marks)

iii) Metal **Z** is readily soluble in hot concentrated HCl and in aqueous NaOH. When heated, **Z** reacts directly with  $\text{Cl}_2$  to give a compound of stoichiometry  $\text{ZCl}_3$ , which contains 20.2 % of **Z**. Treatment of **Z** with an excess of  $\text{Hg(CH}_3)_2$  gives the highly reactive compound **H**. The  $^1\text{H}$  NMR spectrum of **H** at low temperatures consists of two signals due to methyl groups.

(3 marks)

4. Answer **ALL** parts of this question.

- a) Ammonia borane ( $\text{BH}_3\text{NH}_3$ ) is currently receiving attention as a hydrogen storage compound. At room temperature, it forms a tetragonal **I** lattice with  $\mathbf{a} = 5.263 \text{ \AA}$ ,  $\mathbf{c} = 5.050 \text{ \AA}$ , and motif B [0, 0, 0]; N [0, 0, 0.684]; due to free rotation of the B-N bond, the hydrogen atoms are disordered.
- i) Draw a sketch of the unit cell projected along [001] (ignoring the hydrogens).  
(4 marks)
  - ii) Calculate the density of ammonia borane, at room temperature.  
(3 marks)
- b) Ammonia borane structure is often described as isoelectronic with ethane, although the melting point is  $114^\circ\text{C}$ , compared to  $-181^\circ\text{C}$  for  $\text{C}_2\text{H}_6$ .
- i) Using simple valence bond theory, describe and contrast the bonding in each case.  
(2 marks)
  - ii) Identify the shortest B-N separation and hence calculate the B-N bond length; compare your answer to the value for ethane ( $1.54 \text{ \AA}$ ).  
(2 marks)
- c) The space group has been determined to be  $I4mm$ , which indicates the presence of at least one four-fold rotational axis and two mirror planes.
- i) On a separate sketch, indicate the location of these symmetry elements.  
(3 marks)
  - ii) Rationalise how the 4-fold axis of the **crystal** can be consistent with the 3-fold axial rotational symmetry of the ammonia borane **molecule**. Suggest what might happen to the structure at low temperature.  
(2 marks)
- d) Hydrogen is released from ammonia borane on heating.
- i) Write a balanced equation for the **complete** dehydrogenation reaction, and describe a possible structure for the residue.  
(3 marks)
  - ii) Calculate the maximum volumetric hydrogen storage capacity of solid ammonia borane. Compare your value to the 2015 US Department of Energy hydrogen storage system target of  $0.081 \text{ kg hydrogen / L}$ .  
(2 marks)
  - iii) Calculate the maximum gravimetric hydrogen storage capacity of solid ammonia borane. Compare your value to the 2015 US Department of Energy hydrogen storage system target of  $9.0 \text{ wt\% hydrogen}$ .  
(2 marks)
  - iv) Briefly comment on the likely challenges to implementing ammonia borane as a hydrogen storage technology.  
(2 marks)