

THE UNIVERSITY OF BRITISH COLUMBIA
Department of Chemistry

Chemistry 309 - “Foundations of Inorganic Chemistry”

FINAL EXAMINATION

Instructor: Professor P. Legzdins

December 11, 2009 (3:30 PM)
Maximum Time: 2.5 hours

THIS EXAMINATION HAS 7 QUESTIONS WITH A TOTAL OF 120 MARKS AVAILABLE.

ANSWER ALL QUESTIONS IN THE ANSWER BOOKLETS – PROVIDED SEPARATELY.

This examination consists of 5 numbered pages.

PLEASE CHECK THAT YOU HAVE A COMPLETE PAPER.

A PERIODIC TABLE, CALCULATORS, TEXTBOOKS, FORMULAE PAGES, AND
CELLPHONES ARE NOT PERMITTED.

THE USE OF A MODEL KIT IS PERMITTED.

REQUISITE SUPPLEMENTARY MATERIALS ARE PROVIDED AS A SEPARATE PACKAGE
ACCOMPANYING THIS EXAMINATION PAPER.

The following are the rules governing formal examinations:

1. Each candidate must be prepared to produce, upon request, a Library/AMS card for identification.
2. Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
3. No candidate shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination.
4. Candidates suspected of any of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action.
 - a. Having at the place of writing any books, papers or memoranda, calculators, computers, audio or video cassette players or other memory aid devices, other than those authorized by the examiners.
 - b. Speaking or communicating with other candidates.
 - c. Purposely exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.
5. Candidates must not destroy or mutilate any examination material; must hand in all examination papers; and must not take any examination material from the examination room without permission of the invigilator.

Question 1. [18 marks]

Clearly define and provide one example of each of the following:

- (a) Chemisorption.
- (b) Isolobality.
- (c) Hypervalency.
- (d) A pi complex.
- (e) A secondary kinetic isotope effect.
- (f) Electron-deficient bonding.

Question 2. [18 marks]

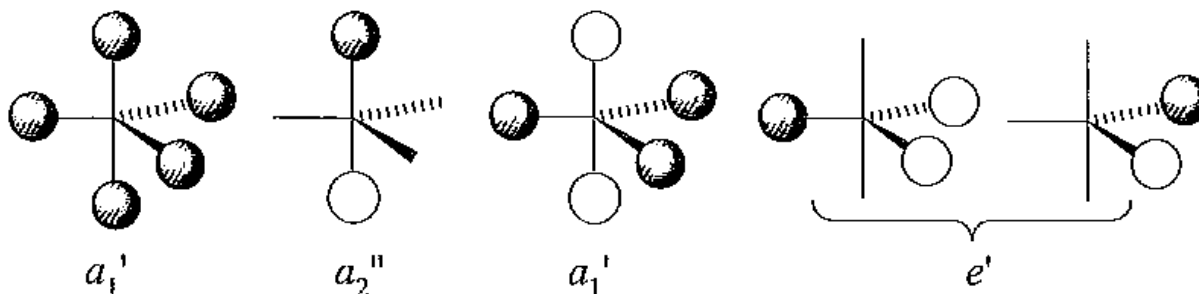
Provide a rationale for the following experimental observations.

- (a) Polysilanes are semiconductors whereas polyethylene is an electrical insulator.
- (b) Silane explodes immediately upon contact with oxygen whereas methane requires a spark to ignite it.
- (c) BBr_3 and BCl_3 are stronger Lewis acids than BF_3 .
- (d) The bond angle in H_2O is 104.5° whereas that in H_2S is 92° .
- (e) The average bond dissociation enthalpy of an N-N single bond is 167 kJ/mol whereas that for a P-P single bond is 201 kJ/mol.
- (f) The electron affinities of both germanium and selenium are larger than that of arsenic.

Question 3. [24 marks]

As a research project you have been assigned the synthesis of the still unknown PH_5 molecule which is expected to have a trigonal bipyramidal molecular structure.

- (a) Write two balanced chemical equations for transformations by which you will try to prepare PH_5 .
- (b) The sigma LGO's for a trigonal bipyramidal molecule are as shown below:



Provide a molecular-orbital description of the bonding in PH_5 . Assume that the phosphorus uses only its 3s and 3p valence orbitals to form bonds with the hydrogen atoms. For this description construct a qualitative energy-level diagram that shows clearly how the various orbitals interact to form molecular orbitals. Assign group-theory symmetry labels to each of the molecular orbitals and indicate the electron occupancies of the various molecular orbitals.

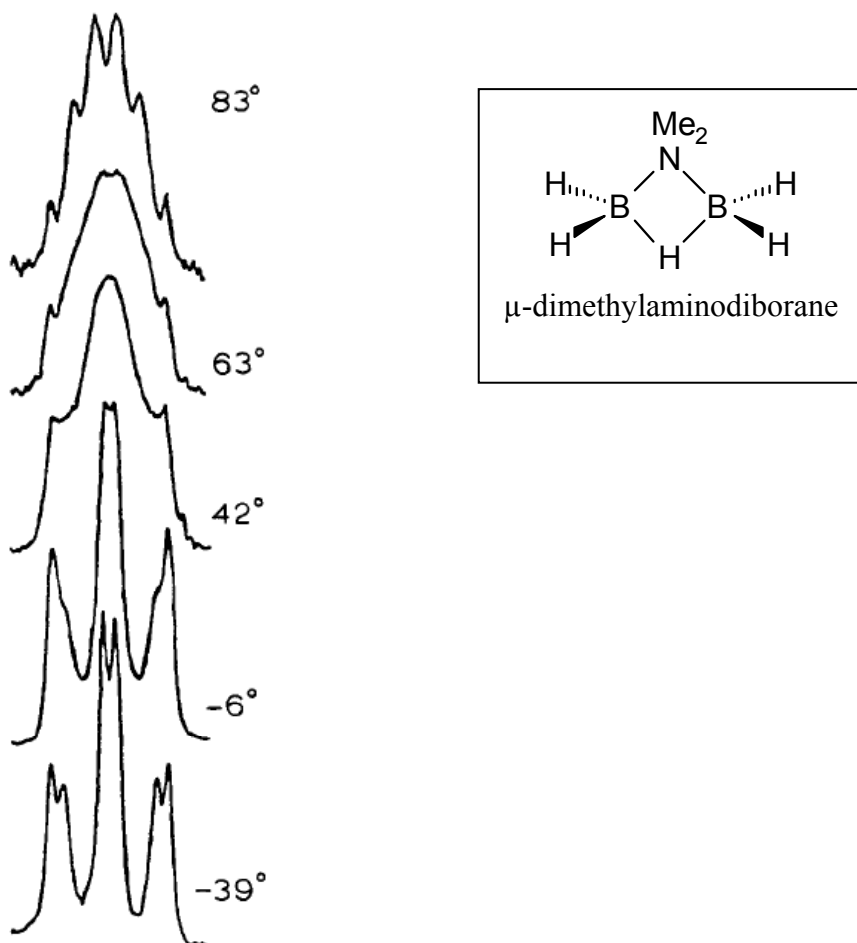
- (c) Provide a sketch of the HOMO of PH_5 . What is its physical significance?
- (d) What is the overall bond order of PH_5 ? Would you therefore expect it to be more or less thermally stable than PH_3 ?
- (e) What ^1H and ^{31}P NMR spectra would you expect PH_5 to exhibit if it is fluxional?

Question 4. [12 marks]

- (a) Use Wade's rules to determine the number of skeletal electron pairs, number of vertices, and the cluster type for $\text{C}_2\text{B}_4\text{H}_6$.
- (b) How many cage isomers are possible for $\text{C}_2\text{B}_4\text{H}_6$?
- (c) Write balanced equations for the reactions of $\text{C}_2\text{B}_4\text{H}_6$ with (i) one equivalent of methyl chloride in the presence of AlCl_3 and (ii) two equivalents of potassium hydride.

Question 5. [15 marks]

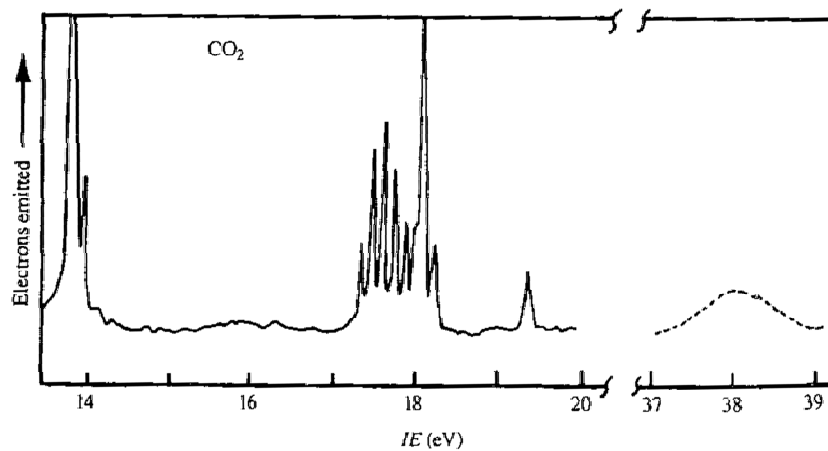
Several ^{11}B NMR spectra of μ -dimethylaminodiborane dissolved in ethylene glycol have been recorded at different temperatures. The spectra are shown below along with the temperatures in $^{\circ}\text{C}$. The coupling constants are $^1J_{^{11}\text{B}-^1\text{H}_{\text{terminal}}} = 130\text{Hz}$; $^1J_{^{11}\text{B}-^1\text{H}_{\text{bridging}}} = 30\text{Hz}$; and $^2J_{^1\text{H}_{\text{terminal}}-^1\text{H}_{\text{bridging}}} = 6\text{Hz}$



- (a) Provide an explanation for the splitting pattern observed at: (i) $+83^{\circ}\text{C}$ and (ii) -39°C . Why do these spectra have such different appearances?
- (b) Predict the ^1H NMR spectra you would expect to observe for μ -dimethylaminodiborane at both -39°C and above 83°C . Draw stick diagrams showing relative intensities to illustrate your answers at both temperatures. Assume that the μ -dimethylaminodiborane sample is 100% enriched in ^{11}B .

Question 6. [12 marks]

The photoelectron spectrum of carbon dioxide is as shown below. Explain.

**Question 7.** [21 marks]

Draw the molecular structures for the expected product(s) in each of the following reactions. The equations all indicate the stoichiometry, but they may not be balanced.

- (a) 1,2-dihydro-1,2-azaborine (C_4BNH_6) + HCl \rightarrow
- (b) H_3NBH_3 + Proton Sponge \rightarrow
- (c) $PbCl_4$ \rightarrow
- (d) $RBr_2Si-SiBr_2R + 4 KC_8 \rightarrow$ A silicon compound (**1**)
 Then, **1** + 2 Me_3SiCN (in hexane) \rightarrow
 (R = a bulky alkyl group)
- (e) $PCl_5 + NH_4Cl$ (gentle warming) \rightarrow Compound **2**
 Then, heat compound **2** at 250 °C \rightarrow

THE END