Chem 309 - 2009 Final Exam Solutions

Question 1. 2 marks for definition
1 mark for example

(a) <u>Chemisorption</u> - is characterized by a strong interaction between an adsorbate and a substrate surface, e.g. cleavage of H_2 bond by a Pt surface.

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(b) <u>Isolobacity</u> - of molecular fragments results if they have similar frontier orbitals in terms of shape and symmetry, e.g. BH_3 and CH_3^+.

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(c) <u>Hypervalency</u> - is exhibited by a molecule in which the central atom appears to expand its octet of valence electrons, e.g. PF_5, SF_6. (3)

(d) ⇒ <u>pi complex</u> - contains a ligand that binds by donation of its π-bonding electrons to the metal, e.g. $(\eta^2\text{-}C_2H_4)\text{-}M$. (3)

(e) ⇒ <u>secondary kinetic isotope effect</u> - is observed when an isotopic substitution does not involve the bond that is breaking or forming, (3)

e.g. $k_H/k_D = 1$ for $H_3C\text{-}M\text{-}^{H}_{H}$ $(D)_3$

$\rightarrow$ $H_3C\text{-}M + H_2$ $(D)_3$

(f) Electron-deficient bonding - results when there are insufficient

3 electrons to form 2c-2e⁻ bonds between all bonded atoms, e.g. B_2H_6.

QUESTION 2. 3 marks for each part.

(a) Polysilanes exhibit σ-conjugation whereas polyethylene does not, i.e.

3 

(b) CH_4 is kinetically stable whereas SiH_4 is kinetically unstable because

3 of weaker Si-H bonds and low-lying vacant d orbitals. - that lower E_a.

(c) BF_3 exhibits B - F $p\pi - p\pi$ bonding whereas BBr_3 and BCl_3 do not.

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(d) The more electronegative oxygen atom in H_2O pulls electrons in bonding pairs more strongly toward itself. This causes the bonding pairs to repel each other more strongly, thereby increasing the bond angle.

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(e) Lone-pair lone-pair repulsions in  are 109° apart - hence diminish N-N bond strength relative to P-P with less repulsions.

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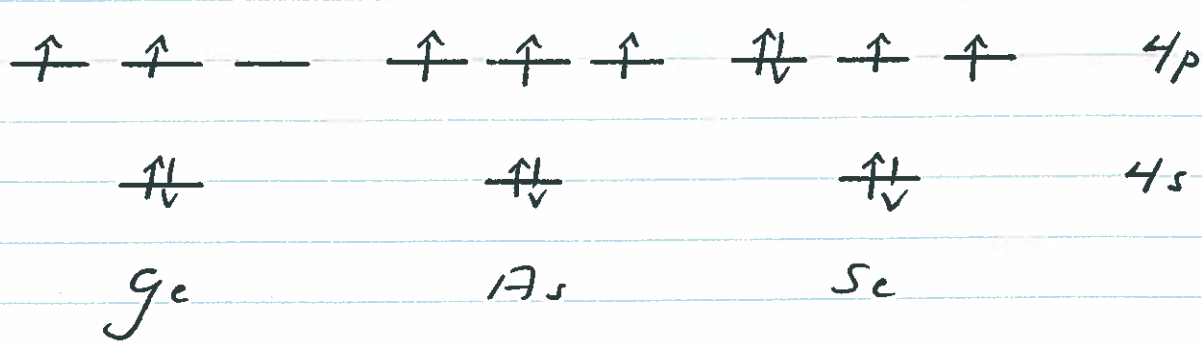
(f) 

3

Electron affinity increases across the periodic table – hence expect Se to have a higher electron affinity than As. By adding an electron to Ge, a half-filled orbital results – but adding an electron to As requires electron pairing. This pairing requires energy and thus makes the addition of an electron to As less favourable and less exothermic.

QUESTION 3.

(a) $PCl_5 + 5\,LiAlH_4 \rightarrow PH_5$

(2) METATHESIS $+ 5\,LiAlH_3Cl$

(2) $PH_3 + H_2 \rightarrow PH_5$ $\Delta H = -212$ kJ/mol.

OXIDATIVE ADDITION

(6)

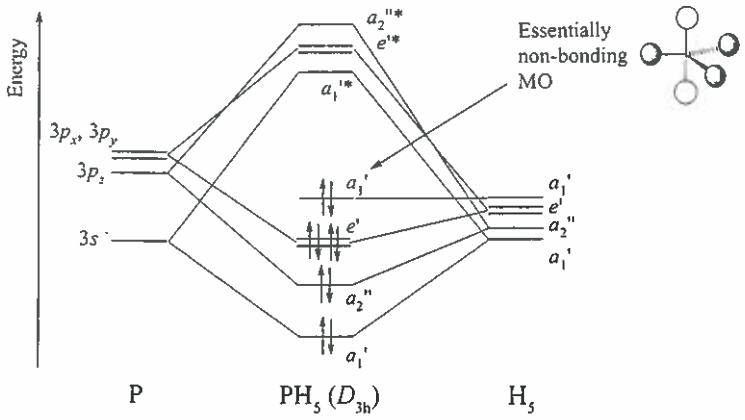


Figure 4.5 A qualitative MO diagram for the formation of the hypothetical molecule PH_5 from P and an H_5 fragment.

(10)

A qualitative MO diagram for the formation of the hypothetical molecule PH_5 is shown in Figure 4.5. Although there are two LGOs with the correct symmetry to interact with the phosphorus 3*s* (a_1') orbital, only one of the interactions will lead to a bonding MO. There are 10 electrons (5 from P, 1 from each H) and these occupy one non-bonding and four bonding MOs. The P–H bond order in hypothetical PH_5 is therefore $^4/_5$.

(c) The HOMO is the non-bonding LGO of a_1' symmetry shown on the previous page. It has no physical significance. (4)

(d) The overall bond order of PH_5 is four. Hence, you would expect it to be less thermally stable than PH_3 (overall B.O. = 3). (3)

(e) The ^1H NMR spectrum would be a doublet, reflecting coupling with ^{31}P. (3)

The ^{31}P NMR spectrum would be a 1 : 5 : 10 : 10 : 5 : 1 sextet, reflecting coupling with five ^1H's.

QUESTION 4.

(a) $C_2B_4H_6$

4 H-B = 4 x 2
2 H-C = 2 x 3

∴ 14 electrons available for cluster bonding ⇒ 7 electron pairs

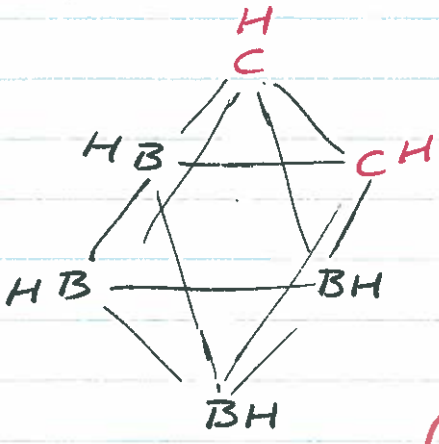
vertices = 6 (based on O_h)

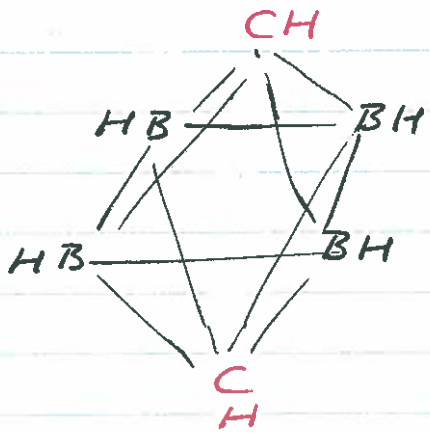
n = 6 (4B and 2C atoms)

∴ n + 1 structure, a closo cage,

i.e. an octahedron. 5

(b) There are two cage isomers:





3

(c) $C_2B_4H_6 + MeCl \xrightarrow{AlCl_3}$

(2) $C_2B_4H_5Me + HCl$

Friedel-Crafts alkylation.

– a boron atom being the probable site of attachment of the methyl group. BONUS (1)

$C_2B_4H_6 + 2KH \longrightarrow$

(2) $2K^+[C_2B_4H_4]^{2-} + 2H_2$

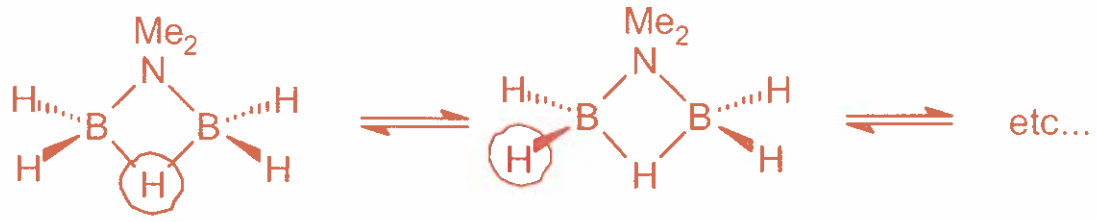
– the carbon atoms being the probable sites of deprotonation.

BONUS (1)

10 marks total

QUESTION 5.

(a) Provide an explanation for the splitting pattern observed at: (i) +83 °C and (ii) –39 °C. Why do these spectra have such different appearances?



This system is fluxional (i.e. stereochemically nonrigid): at high T, $H_{bridging}$ and $H_{terminal}$ exchange rapidly on the NMR timescale. (* NMe_2 group is always bridging).

At High T (+83 °C)

- All H's are exchanging rapidly.
- ^{11}B couples to all H's equivalently
- # lines = 2nI + 1
  = 2x5x(1/2) + 1
  = 6
- Relative Intensities: 1:5:10:10:5:1

2

At Low T (-39 °C)

- Spectrum due to static structure is observed.
- ^{11}B couples to 2 $H_{terminal}$
  2nI+1 = 3 lines in 1:2:1 ratio (^1J = 130 Hz)
- ^{11}B couples to 1 $H_{bridging}$
  2nI+1 = 2 lines in 1:1 ratio (^1J = 30 Hz)

Observe a triplet of doublets

2

2

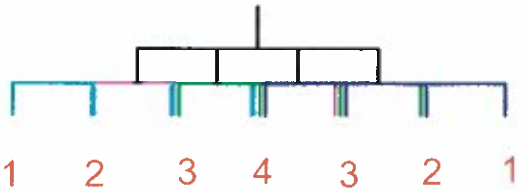
(b) Predict the ^{1}H NMR spectra you would expect to observe for μ-dimethylaminodiborane at both -39 °C and above 83 °C. Draw stick diagrams showing relative intensities to illustrate your answers at both temperatures. Assume that the μ-dimethylaminodiborane sample is 100% enriched in ^{11}B.

At + 83 °C, all H's are equivalent; each couple to 2 x ^{11}B equivalently.

lines = 2nI+1 = 2x2x(3/2) + 1 = 7 lines

Intensities:

3



$^{1}J_{BH}$ will be between 130 and 30 Hz

1 Elsewhere in the spectrum there will also be a singlet of relative intensity 6 for the NMe_2 protons.

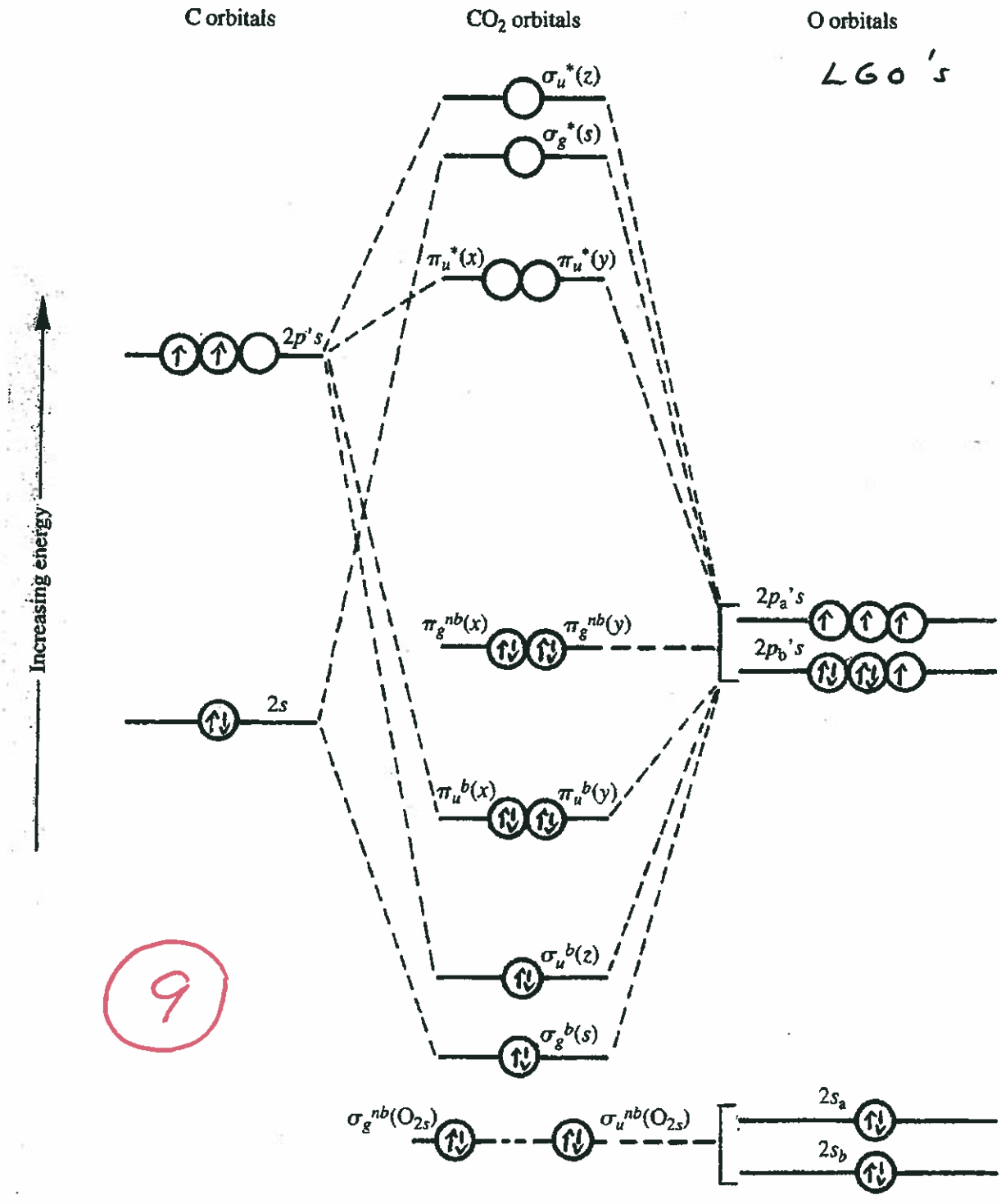
At -39 °C, there will be three sets of signals of relative intensities 6:4:1 corresponding to the NMe_2 protons, the terminal H's and the bridging H.

1 The NMe_2 proton signal is still a singlet.

2 The terminal proton signal is first split into a 1:1:1:1 quartet by one ^{11}B atom, and then each signal is further split into a doublet by coupling to the bridging H. In other words, it is a quartet of doublets with coupling constants of 130 and 6 Hz, respectively.

2 The bridging H signal is first split into a 1:2:3:4:3:2:1 septet by coupling to two ^{11}B atoms, and then each line is further split into a 1:4:6:4:1 quintet by coupling to four terminal H's. In other words, it is a septet of quintets with coupling constants of 30 and 6 Hz, respectively.

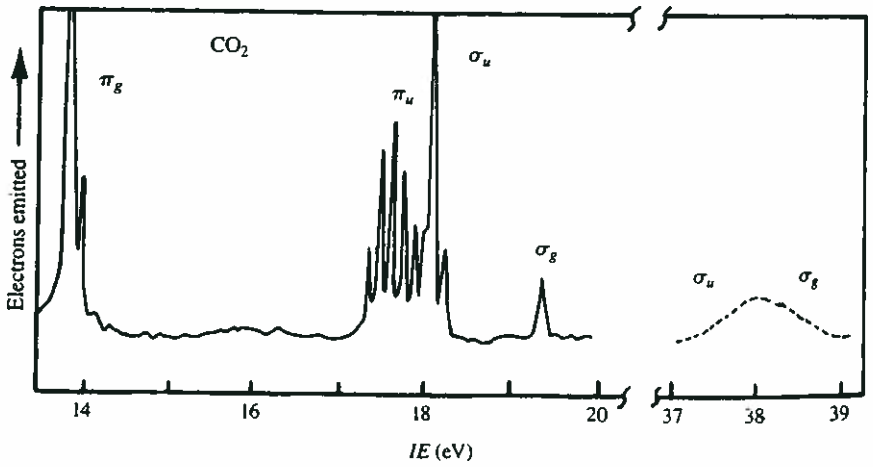
QUESTION 6.



9

This MO diagram for CO_2 leads to ....

the assigment of the features in the photoelectron spectrum as shown below.

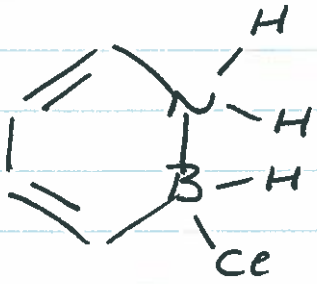


3

Question 7.

(a)

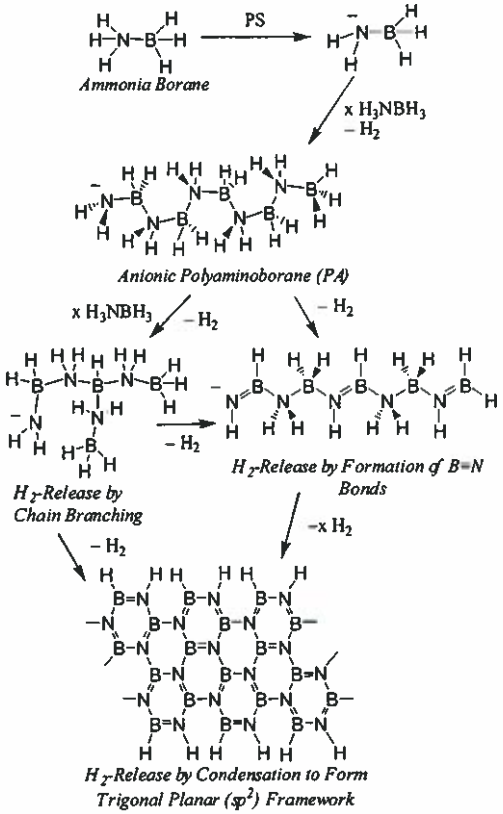
2



non-planar.

(b)

3



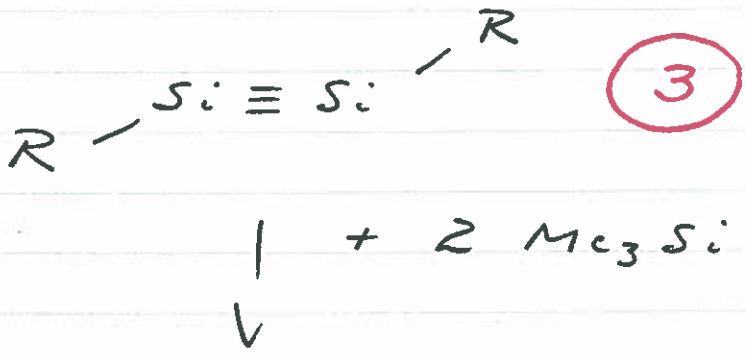
(c)

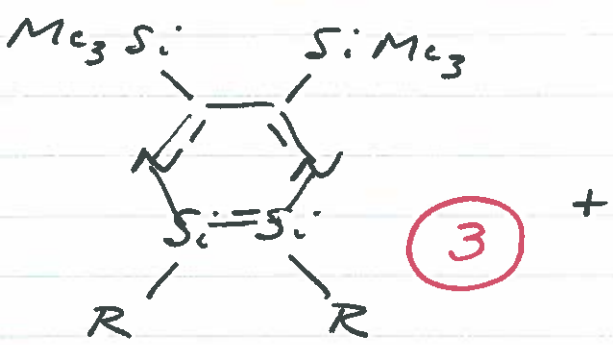
2

$Pb - Cl_2$ + Cl_2

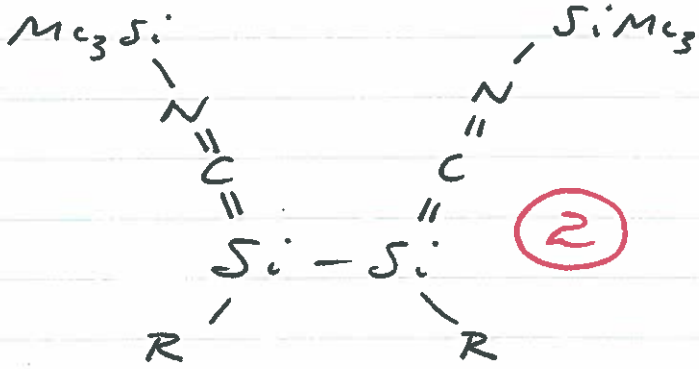
Cl ~90°

(d) 1 is non-linear



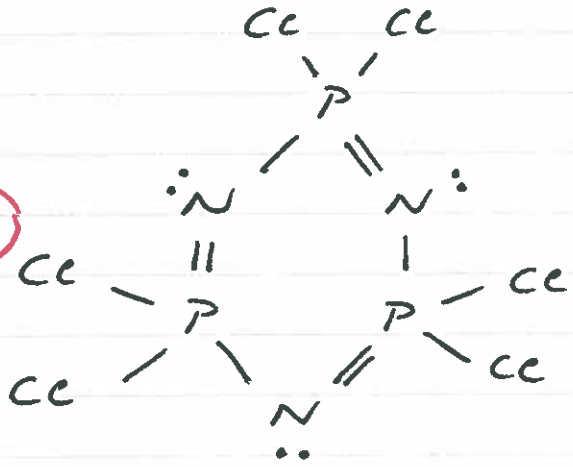


+



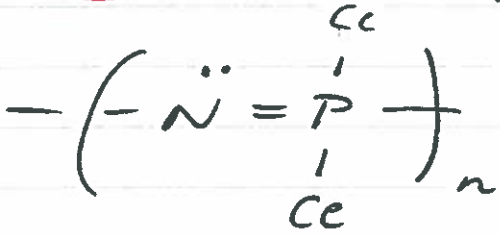
(major product) (minor product)

(e) 2 is cyclic



250 °C

3



polyphosphazene

THE END.