5.03 Final Exam

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May 21, 2009

9am – 12pm

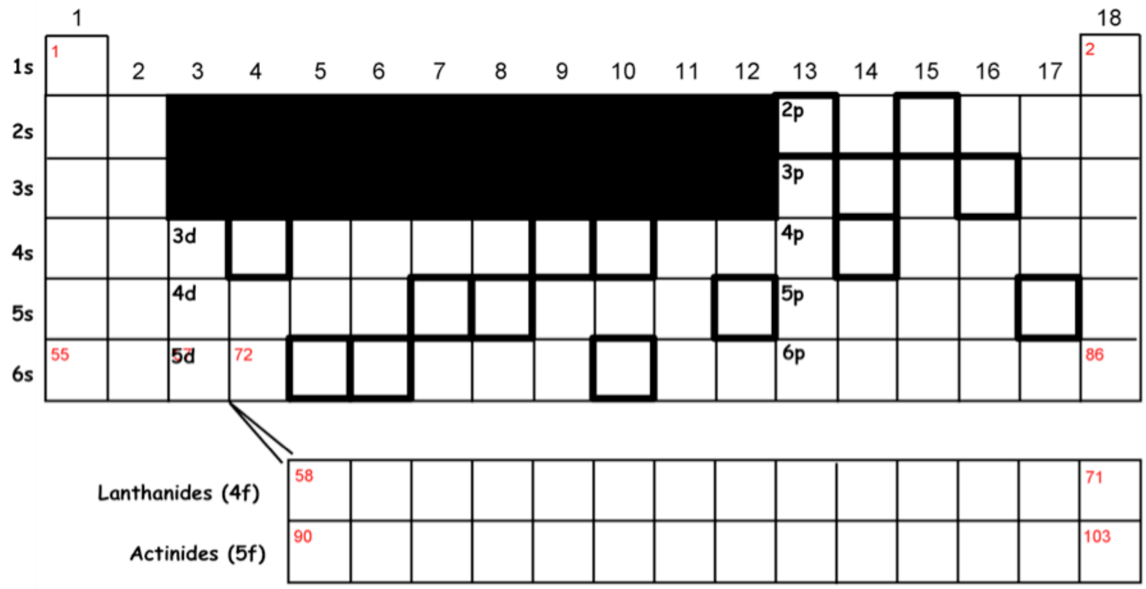
Instructions: write your name and that of your TA clearly in the lower left hand corner of this front page. Read over the test questions carefully before writing down any answers. Answer all questions to the best of your ability to receive partial credit.

Problem	Possible Points	Points Earned
1	20	
2	20	
3	20	
4	20	
5	20	
6	20	
7	20	
8	20	
9	20	
10	20	
11	20	
12	20	
13	20	
14	20	

Total:

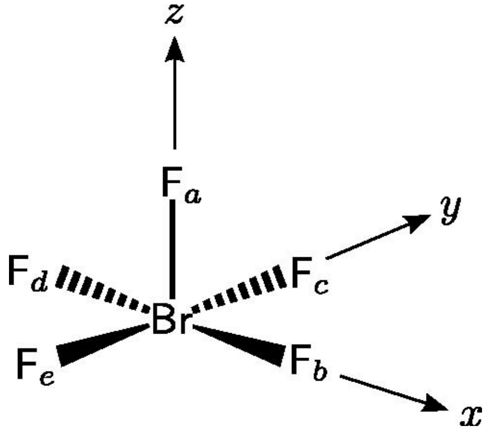
1. The periodic Table

Below is a blank periodic table, with 15 boxes highlighted by a heavy line. Fill in the appropriate element formula for each box indicated. Two points will be deducted for every box is that is not correctly labeled from the maximum points you would receive assuming all boxes were correctly labeled.



2. Symmetry Elements and Operations

Answer the following questions pertaining to the BrF_5 molecule, drawn in Figure 1 with the coordinate system specified.



The BrF_5 molecule drawn with Cartesian axes specified.

1. What is the symbol for the principal axis of rotation for the BrF_5 molecule?

2. Reflection through the xz plane interchanges which pair of fluorine atoms?

3. Which of the Cartesian planes is *not* a σ plane?

4. Are there *n* C_2 axes located ⊥ to the principal *n*-fold axis of rotation?

5. How many C_2 axes are present?

6. How many σ planes are present?

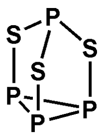
7. What is the symbol for the symmetry operation that interchanges F_a with F_b?

8. How many operations are present that interchange F_b with F_d?

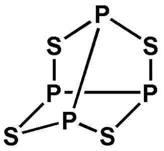
9. Give the symbols for the operations from part 8 of this problem.

3. Point Groups

a.



b.



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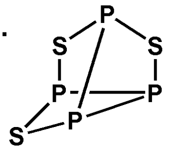

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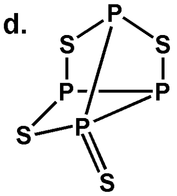
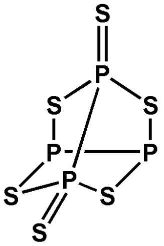
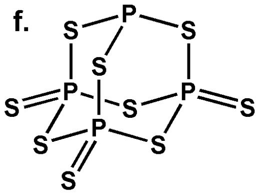


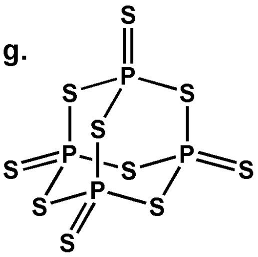
e.



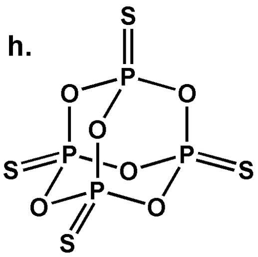
f.



g.



h.



Structures to be considered as part of problem 2.

1. Assign each of the structures depicted above to a point group:

(a)________(b)________(c)________(d)________(e)________(f)________(g)________(h)

2. Draw the structure and assign the point group of PF_5.

3. Draw the structure and assign the point group of ferrocene.

4. A perfect cube belongs to what point group?

4. Hypervalent molecules

For this problem we will consider the SH_6 molecule as a model for the SF_6 molecule. The latter is a known, stable molecule, whereas SH_6 is not known and stable but is useful as a theoretical model because it has only 10 valence atomic orbitals total, while the real system SF_6 has 28. To answer the questions, it will be helpful to refer to the figure below, containing the O_h character table, as is appropriate to either SF_6 or SH_6.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

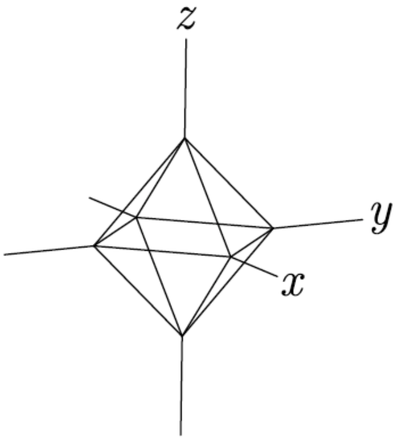
1. Take the six hydrogen 1s atomic orbitals of octahedral SH_6 as a basis for a reducible representation, Γred and find the irreducible representations that are the components of Γred.

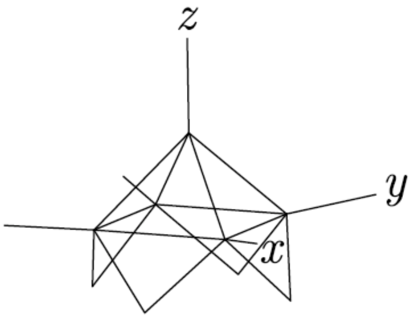
2. To which of the irreducible representations do the valence orbitals of sulfur belong?

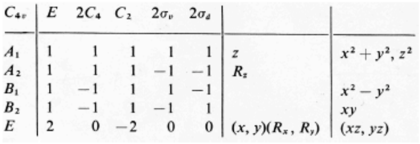
3. Looking at your answer to part 1 of this question, do any of the irreducible representations generated from the set of six hydrogen 1s atomic orbitals *not* find a symmetry match among the set of sulfur valence atomic orbitals (see part 2)? Which one(s)?

4. A typical line-drawing of SF_6 or SH_6 shows the sulfur with lines drawn between S and each of the six atoms to which S is connected, implying perhaps that there are six two-electron bonds and thus a total of 12 electrons in the valence shell of the sulfur atom, in violation of the octet rule. According to your symmetry analysis (parts 1-3), is there really a violation of the octet rule? Explain, giving as part of your explanation the labels for the irreducible representations of all of the symmetry-allowed bonds in SH_6.

5. Polyhedral Boranes and Wade's Rules







C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

The questions for this problem pertain to $[B_6H_6]^{2-}$ and to B_5H_9, sketched above as unlabeled line drawings, and with the latter to be considered in C_{4v} point group symmetry.

1. Calculate the total number of valence electrons in the $[B_6H_6]^{2-}$ ion.

2. Calculate the total number of valence electrons for the B_5H_9 molecule.

3. How many electrons are there in $[B_6H_6]^{2-}$ for framework/cluster bonding?

4. According to the accepted nomenclature, $[B_6H_6]^{2-}$ is referred to as "closo". What is the corresponding term with reference to B_5H_9?

5. The four *bridging* H atoms in B_5H_9 serve to replace an axial $[H—B]^{2-}$ unit in $[B_6H_6]^{2-}$. What are the three irreducible representations of the C_{4v} point group for which the four *bridging* H atom valence orbitals in B_5H_9 serve as a basis? **Show your work**.

6. Which of the irreducible representations from part 5 corresponds to the *tangential* orbitals of the $[\text{H—B}]^{2-}$ unit that has been replaced?

7. Which of the irreducible representations from part 5 finds no counterpart among the valence orbitals of a H—B unit?

6. MLXZ Plots

To figure out where a particular organometallic molecule should be located in a MLXZ plot for a particular *d*-block element, the molecule must be first assigned to its correct $ML_lX_xZ_z$ class. Make such an assignment for each molecule listed below and for each molecule give the valence number VN, the electron count EN, and the d^n count, and indicate whether you think the molecule is likely to be stable enough to be isolated.

1. $Cr(\eta^6\text{-}C_6H_6)_2$

2. $(^tBuO)_3Mo{\equiv}C^tBu$

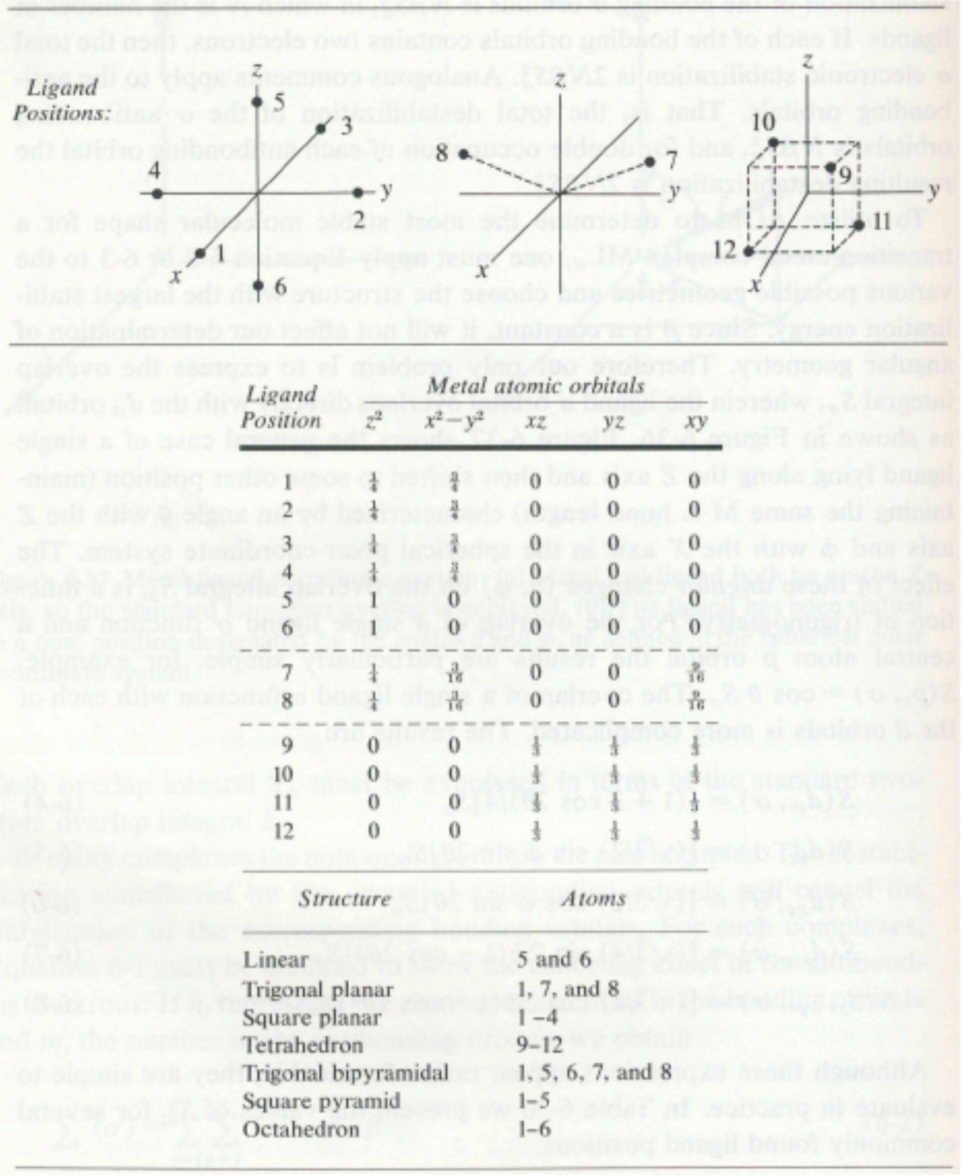
3. $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$

4. $Ru(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)$

5. Cp*Ni≡N—O, where Cp* = $\eta^5\text{-}C_5Me_5$ and the bond angle at nitrogen is linear.

7. D Orbitals and Coordination Chemistry

For this problem we will utilize the information provided in the Figure below. The requested d-orbital splitting diagrams should be σ-only in nature.

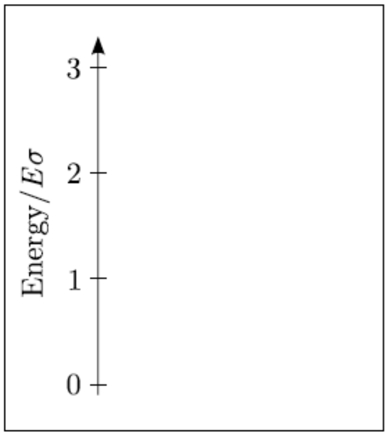


Ligand Position	Metal atomic orbitals				
	z^2	x^2-y^2	xz	yz	xy
1	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	1	0	0	0	0
6	1	0	0	0	0
7	$\frac{1}{4}$	$\frac{3}{16}$	0	0	$\frac{9}{16}$
8	$\frac{1}{4}$	$\frac{3}{16}$	0	0	$\frac{9}{16}$
9	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
10	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
11	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
12	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$

Structure	*Atoms*
Linear	5 and 6
Trigonal planar	1, 7, and 8
Square planar	1–4
Tetrahedron	9–12
Trigonal bipyramidal	1, 5, 6, 7, and 8
Square pyramid	1–5
Octahedron	1–6

Angular Overlap Model (AOM)

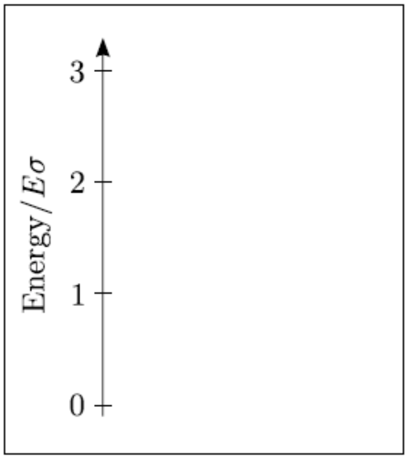
1. In the box provided, draw in the d-orbital splitting diagram for $Cr(CO)_6$ and populate with the correct number of electrons. Chromium is in group 6. Any degenerate orbitals should be drawn in side-by-side.



2. In your answer to part 1, did you represent $Cr(CO)_6$ as high spin (HS) or as low spin (LS)? Explain your choice.

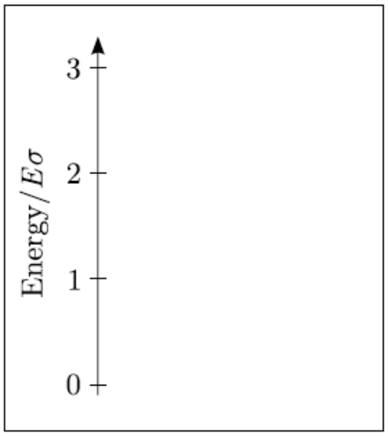
3. Based on your answer to part 1, how many unpaired electrons does $Cr(CO)_6$ have?

4. In the box provided, draw in the *d*-orbital splitting diagram for $[PtCl_4]^{2-}$ and populate with the correct number of electrons. Platinum is in group 8. Any degenerate orbitals should be drawn in side-by-side.



5. Go back to your diagram from part 4 of this question and label each of the orbitals in the splitting diagram. Is the complex expected to have any unpaired electrons?

6. In the box provided, draw in the *d*-orbital splitting diagram for $MoCl_5$ and populate with the correct number of electrons. Molybdenum is in group 6. Any degenerate orbitals should be drawn in side-by-side.



7. Go back to your diagram from part 6 of this question and label each of the orbitals in the splitting diagram. How many unpaired electrons is the complex expected to have?

8. Microstates and Tanabe-Sugano

1. Identify the ground term of the following gas-phase ions:

(i) Mn^{2+} (ii) W^{3+} (iii) Pd^{2+}

2. What is the largest M_L value a gas phase $3d^4$ ion can have?

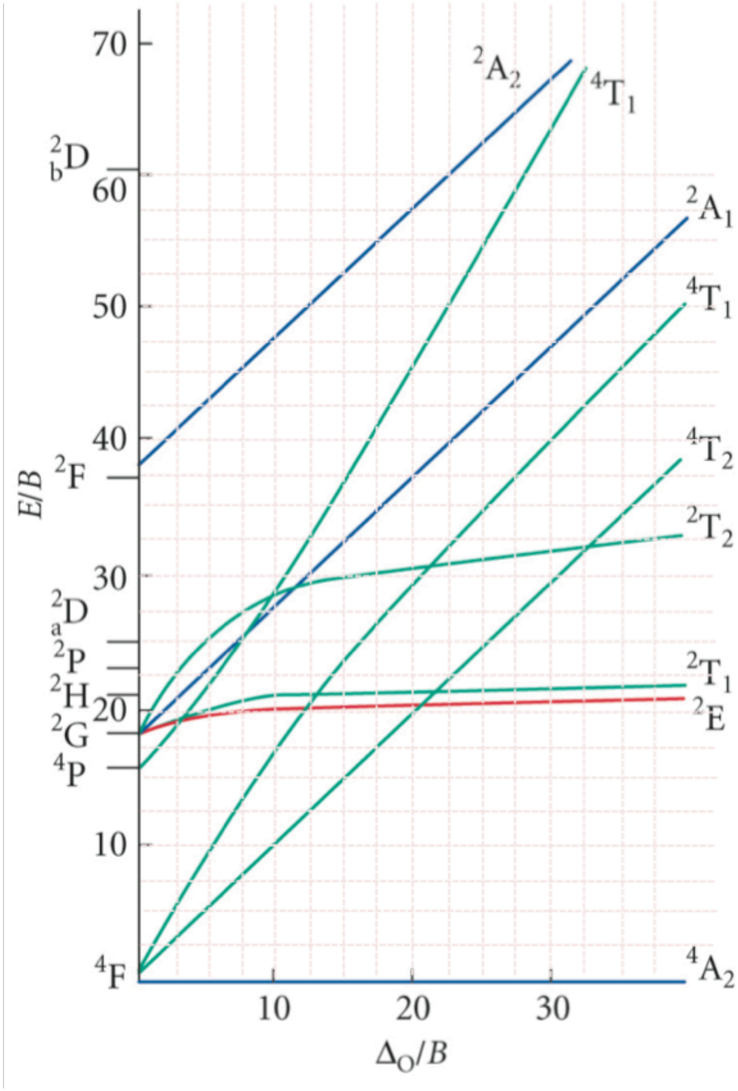
Density Functional Theory (DFT) is now frequently used to predict/rationalize the electronic structure of inorganic complexes. Assume you have run DFT calculations on the complex $Cr(H_2O)_6^{3+}$ to obtain the Ligand Field (LF) parameters of Δ_o = 17,600 cm^{-1} and B = 700 cm^{-1}.

3. Sketch a d-orbital splitting diagram for $Cr(H_2O)_6^{3+}$, label each d-orbital and fill in the appropriate number of d-electrons, and define the term Δ_o in your diagram.

4. What is the physical origin of the B term?

5. Use the Tanabe-Sugano Diagram provided below to determine the energy of the *spin-allowed LF transitions* you anticipate based on the DFT calculation. Show your work.

d^3 Tanabe-Sugano diagram where C = 4.5B



9. Ligand Substitution and electronic structure

(a) Rank in order of *increasing* rate of substitution by H_2O the following complexes:

Complex	**Numerical Ranking (*1 being slowest*)**
$[Cr(H_2O)_6]^{3+}$	
$[Ir(NH_3)_6]^{3+}$	
$[Co(NH_3)_6]^{2+}$	
$[Co(NH_3)_6]^{3+}$	

(b) The complex $[Cr(H_2O)_6]^{2+}$ is substitutionally labile, whereas $[Cr(CN)_6]^{2-}$ is inert. Why?

(c) Predict whether the following complexes should be labile or inert given the magnetic data provided (*note: experimental moments often deviate from their ideal spin-only values due to spin-orbit coupling*).

Complex	**Magnetic Moment (in BM)**	**Labile or Inert?**
(i) $[Cr(O)(Cl)_5][NH_4]_2$	1.82 BM	
(ii) $[MnI_6][K]_2$	3.82 BM	
(iii) $[Fe(CN)_6][K]_3$	2.40 BM	
(iv) $[Fe(NH_3)_6][Cl]_2$	5.45 BM	

For the answers you provided above provide a brief rational using an electronic structure argument.

(i)

(ii)

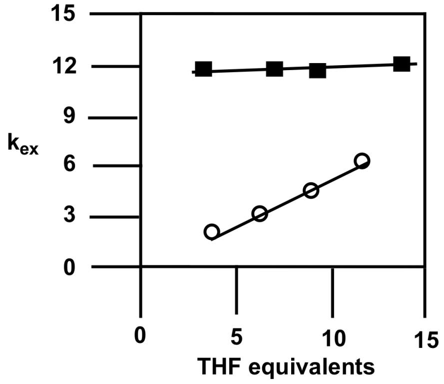
(iii)

(iv)

10. Ligand Substitution

Below is the rate data collected for THF self-exchange for the two square planar platinum complexes shown.

(a) Provide a mechanism for THF self-exchange for each complex that would account for the rate data.



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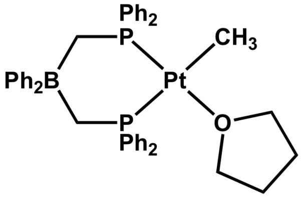

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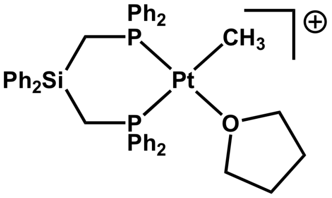


Sketch your mechanisms below:

(b) The temperature dependence of the rate of THF self-exchange provides the following activation parameters:

$[Ph_2B(CH_2PPh_2)_2]Pt(Me)(THF)$: $\Delta S^{\ddagger} = 0.1$ entropy units; $\Delta H^{\ddagger} = 16$ kcal/mol

$\{[Ph_2Si(CH_2PPh_2)_2]Pt(Me)(THF)\}^{+}$: $\Delta S^{\ddagger} = -30.2$ entropy units; $\Delta H^{\ddagger} = 1.9$ kcal/mol

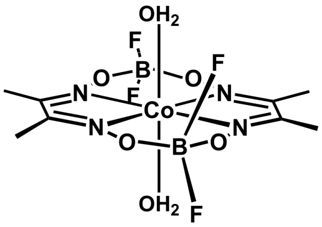
Are the mechanisms you sketched above consistent with these activation parameters? Explain.

11. Electron-transfer

In class we discussed the fact that certain tetra-imine Co(II) complexes will catalyze the reduction of protons to hydrogen by chromous chloride in aqueous solution, where chromous chloride is itself thermodynamically but not kinetically able to perform the reaction in the absence of the cobalt catalyst.

$$\mathrm{CrCl_2} + \mathrm{H^+} \xrightarrow{\substack{\mathrm{Co^{II}} \\ \text{catalyst}}} \mathrm{CrCl_2^+} + 1/2\ \mathrm{H_2}$$

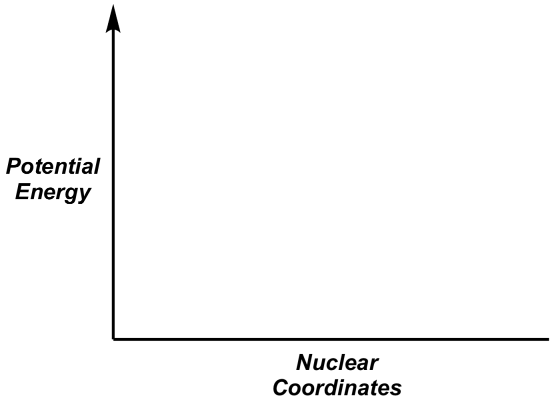
$\mathrm{Co^{II}}$ catalyst =



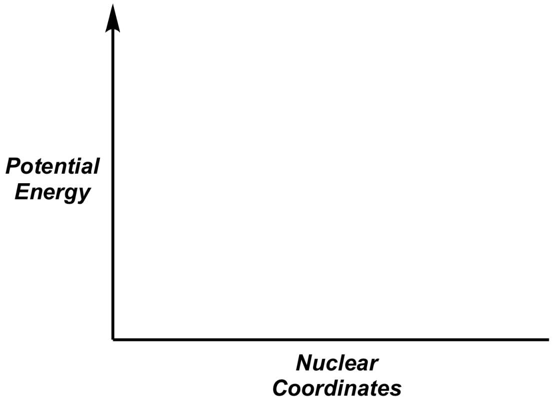
1. Do you expect this proton reduction reaction to proceed via an inner-sphere or an outer-sphere mechanism? Why?

2. Propose a plausible detailed mechanism for the cobalt-catalyzed reduction reaction.

3. As was explicitly done in class, sketch a pair of potential energy surfaces for reactants and products and illustrate on your diagram the physical meaning of $\Delta G^{\ddagger}$ and λ. What is the absolute magnitude of $\Delta G^{\ddagger}$ in units of λ?

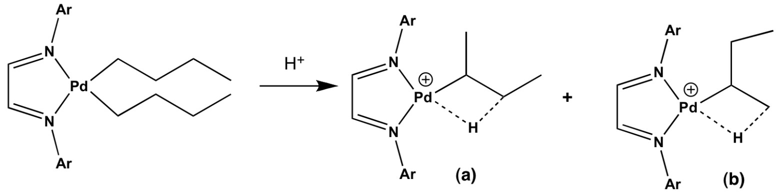


4. State in words what is meant by the 'Marcus Inverted Region', and illustrate the physical origin of the inverted region using two potential energy surfaces, as for the cases above.



12. Organometallic reaction mechanisms

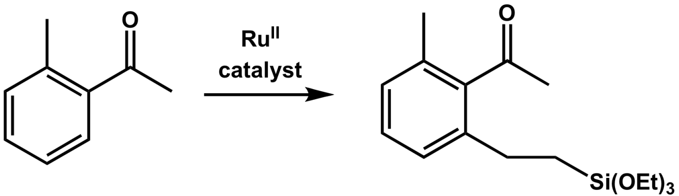
1. Low temperature protonation of the palladium dibutyl complex shown below leads to a mixture of two complexes stabilized by β-agostic interactions. Propose a mechanism that accounts for the formation of species (a) & (b).



2. Provide a *detailed* mechanism, which consists of three fundamental steps, for the $Pt^{II}Cl_2$ catalyzed transformation shown below.

$$CH_4 + H_2O + Pt^{IV}Cl_6^{2-} \rightarrow CH_3OH + 2H^+ + Pt^{II}Cl_2 + 4Cl^-$$

3. Murai has discovered catalytic systems for transformations such as that shown below. Sketch a detailed plausible mechanism for the representative transformation shown.



Ru^{II} catalyst = Ru(H)$_2$(CO)(PPh$_3$)$_3$

13. Industrial homogeneous catalysis

1. Draw a reaction below that exemplifies the ‘hydroformylation reaction.

2. Draw a reaction below that exemplifies an ‘olefin metathesis’ reaction.

3. Draw a reaction below that exemplifies the ‘Wacker’ process.

4. In the Wacker process, what is the specific role of the $CuCl_2$ additive.

5. In the Cativa process for the synthesis of acetic acid, what is the key *chemical* advantage of the iridium catalyst system as compared to the rhodium catalyst originally used by Monsanto?

14. Bioinorganic chemistry

Using the elementary inorganic chemistry concepts that you have learned in this course, please draft a scholarly paragraph that describes the chemical transformation/s known as ‘photosynthesis’ and how, in brief, the light reactions of photosynthesis are thought to work. In your paragraph, be sure to include the following concepts: *ligand substitution, electron transfer, reorganizational energy, redox shuttling, single photon coupled to multi-electron transfer, Marcus inverted region, water oxidation*.