

**Department of Chemistry
Cumulative Examinations
April 1, 2006**

You may choose to answer any exam from any area covered in the examination booklet. Each exam may contain multiple parts. You may answer more than one exam but each exam is scored separately and is treated as an individual examination result. Thus, answering parts of two exams with a score of 50% *would not* yield a 100% grade for this cumulative exam. Instead you would receive 50% on each examination attempted.

This booklet contains *five* examinations.

- 1) Analytical Cumulative Examination, Pages 1-2
- 2) Biochemistry Cumulative Examination, Page 3
- 3) Inorganic Cumulative Examination, Page 4
- 4) Organic Cumulative Examination, Page 5
- 5) Physical Cumulative Examination, Page 6-7

On your examination booklet:

- 1) Print your student ID number.
- 2) Print this Exam Booklet number: _____
- 3) Print the question number you are answering.
- 4) Print the Exam Date.

Do not write your name anywhere on the examination booklet. Each exam will be scored anonymously. If you attempt more than one exam, you must use a separate examination booklet for each examination.

When you complete the examination, return the examination and your answer booklet to the proctor. Exam results will be posted on bulletin board #2B on the north side of the hall near BRWN 2124.

PURDUE
U N I V E R S I T Y

Analytical Cume April 2006

NMR Spectroscopy

1. (40 pts) Define the 8 of the following 10 terms. Be Brief!

Most of these terms have numbers associated with them, or a range. Put down a reasonable value or range and the unit associated with that value for full credit (some quantitative hints are given in parentheses).

- A. Larmor Frequency
- B. J coupling
- C. Chemical Shift Anisotropy
- D. Magic Angle Spinning (speed)
- E. Deuterium channel (frequency)
- F. Probe resonant Q factor
- G. Solvent suppression (for quantitation, mention dynamic range)
- H. Apodization
- I. T_2 relaxation
- K. dipolar coupling

2. (10 pts) Give two reasons why larger magnetic fields are preferable. Be quantitative, as in "if the magnetic field strength is doubled the _____ changes by a factor of _____."

3. (20 pts) Name 2 different multidimensional NMR experiments and briefly explain how they work and what they measure.

4. (10 pts) What are the advantages and disadvantages of the ^1H - ^{13}C heteronuclear HSQC experiment as compared to ^1H or ^{13}C NMR?

5. (10 pts) How does a cryoprobe work? (In a cryoprobe, the detection coil operates at 20K improve the signal to noise).

6. (10 pts) The combination of NMR and multivariate statistical analysis of complex samples such as urine or serum is gaining attention as a possible method for early disease detection. What properties of the NMR experiment do you think are desirable to this end? What are some undesirable qualities of NMR and what would you do as an analytical chemist to get around these problems?

1. The catabolite activator protein (CAP) plays a central role in the control of a subset of genes in *E. coli* cells.

Provide a concise overview of mechanisms through which CAP regulates gene expression.

2. Experimental data support a strong role for chromatin structure in the regulation of gene expression in cells of higher organisms.

To probe the structure of chromatin, a researcher treated a sample of nuclei preparation with micrococcal nuclease. Subsequently, she examined the digestion product by gel electrophoresis.

Provide the expected result, based on the finding that the DNA is chromatin is organized into nucleosomes.

3. What are the components of nucleosomes, and why nucleosomes would contribute to the control of gene expression?
4. Steroid receptors provide examples of inducible transcription factors.
 - A. Provide two examples of steroid receptors.
 - B. Choose one of the examples and describe concisely how it regulates gene expression.
5. Give an example of gene regulation through cAMP signaling in eukaryotic cells.

Inorganic Chemistry Cume Exam

April 1, 2006

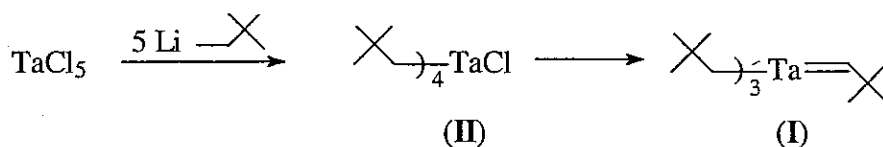
100 points will be assigned

Give an authentic example of each of the following that involves a transition metal from Groups IV-VII. For each example you have given, 1) provide a reaction to show how you would prepare the compound, 2) sketch its molecular structure, and 3) give brief details of the electronic structure of the metal core that is present in the compound.

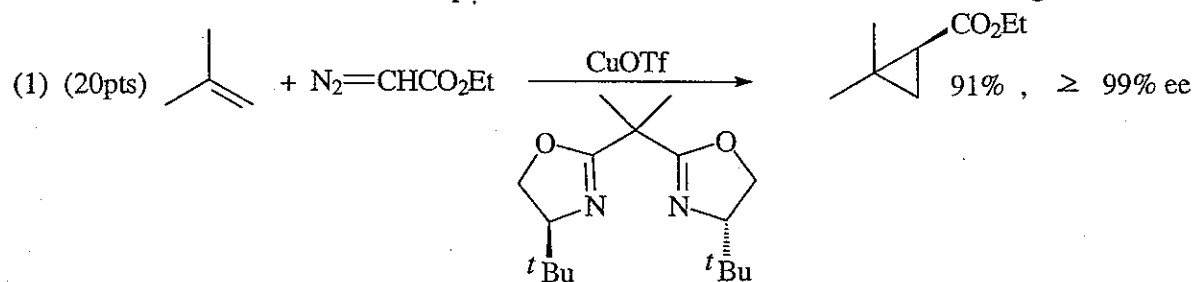
- (i) A mononuclear transition metal tetrabromide MBr_4 .
- (ii) A transition metal pentachloride MCl_5 .
- (iii) The product from a reaction between a metal halide and an alcohol (specify the alcohol).
- (iv) An acetylacetonate complex of the type $MCl_2(acac)_2$.
- (v) A complex that contains an imido ligand (NR^{2-} ; specify the R group).
- (vi) A complex of the type $MCl_2(tmeda)_2$ (where $tmeda = Me_2NCH_2CH_2NMe_2$).
- (vii) A complex that contains a carbonyl dianion of the type $[M(CO)_6]^{2-}$.
- (viii) A simple metallocene of the type $M(\eta^5-C_5R_5)_2$ (specify the R group) that contains a ferrocene-like sandwich structure.
- (ix) A compound of composition $(C_5H_5)_2M$ that does not contain a ferrocene-like sandwich structure.
- (x) A mixed-sandwich compound of the type $(\eta^5-C_5R_5)M(\eta^n-C_xH_x)$ that contains a seven or eight membered ring.

[1] (60pts) The 2005 Nobel Prize in Chemistry was given to R.H. Grubbs (California Inst. of Technology), R.R. Schrock (MIT), and Y. Chauvin of France for their development of olefin metathesis reactions and chemistry of metal-carbene complexes.

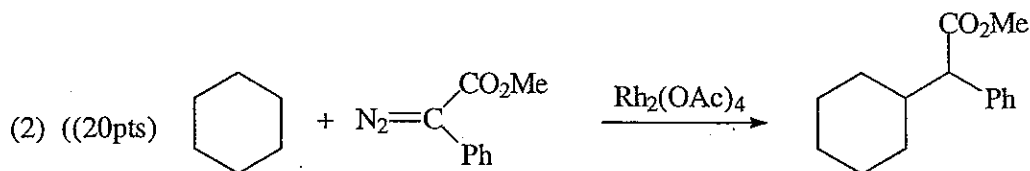
- (1) ²⁰(15pts) What is meant by olefin metathesis? Show a general equation for olefin metathesis using RuL_n as a generalized structure for a Ru-containing catalyst.
- (2) ²⁰(15pts) What is meant by the Chauvin mechanism for olefin metathesis reactions?
- (3) ²⁰(15pts) Shown below is an example of the ring-closing metathesis reaction using $PhCH= Ru(P(\text{cyclohexane}))_2Cl_2$ as a catalyst. Show a plausible mechanism for the reaction. Just use $PhCH= RuL_n$ for an active catalyst. *We failed to show an example.*
- (4) ²⁰(15pts) Schrock reported the formation of (I) from $TaCl_5$ and 5 equivalent of neopentyl lithium. tetraneopentyltantalum chloride (II) was a key intermediate. Show a plausible mechanism for the conversion of (II) into (I).



[2] (40pts) Metal-carbene complexes have been shown to play key roles in many reactions other than olefin metathesis as well. Show a plausible mechanism for each of the following reactions.



Note: You do not need to rationalize the details of asymmetric induction. Just provide a mechanism for the overall transformation disregarding the absolute stereochemistry.



Note: Use RhL_n to represent an active catalyst generated from $Rh_2(OAc)_2$.

Bonus Question (10pts)

Olefins and certain transition metal complexes (represented here as ML_n) can interact each other to generate metal carbene complexes ($R^1R^2C=ML_n$) via metallacyclopropanes and metallacyclobutanes. Provide a plausible mechanism for the entire transformation.

Physical Chemistry Cume

April 1, 2006

Useful Equations:

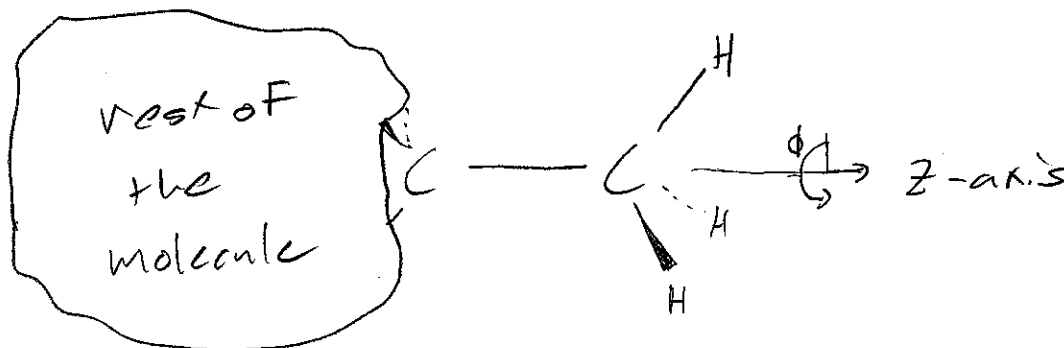
$$\int_0^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{4a}} \quad Q = \frac{q^N}{q!} \quad q = \sum_i g_i e^{-E_i/kT} \quad \langle E \rangle_V = U = NkT^2 \frac{\partial \ln q}{\partial T}$$

$$\hat{H}\psi = E\psi \quad \hbar = h/2\pi \quad e^{ix} = \cos(x) + i\sin(x) \quad e^{i\pi} = -1$$

$$\hat{H}_{trans}\psi_{trans} = \frac{\hat{p}^2}{2m}\psi_{trans} = E_{trans}\psi_{trans}; \quad \hat{H}_{vib}\psi_{vib} = \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right) \psi_{vib} = E_{vib}\psi_{vib}$$

$$\hat{H}_{rot}\psi_{rot} = \frac{\hat{L}^2}{2I}\psi_{rot} = E_{rot}\psi_{rot}; \quad \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi};$$

Note: The equations above are included to help guide your thinking through some of the questions.



1. Consider the local torsional motion of one methyl group with respect to a larger effectively fixed molecular structure (e.g., a protein) depicted above. From your chemical intuition, do you expect the barrier for torsional inter-conversion (E_a) of a free CH_3 group to be greater than, lesser than, or comparable to kT at room temperature?

2. Let's assume we are operating at a temperature high enough that $E_a \ll kT$. In this limit, the wavefunctions describing torsional motion effectively reduce down to those of a 1D rigid rotator describing the clockwise and/or counter-clockwise motions of the 3 hydrogen atoms about the C-C bond with a moment of inertia I_{CH_3} . Using typical values for bond lengths and bond angles, estimate the value of I_{CH_3} (in units of $\text{amu} \cdot \text{\AA}^2$).

3. Derive an expression for the set of normalized wavefunctions describing the pseudo-rotational motion of a single CH_3 subunit using the boundary conditions $\psi_{\text{CH}_3}(\phi) = \psi_{\text{CH}_3}(\phi + 2\pi)$ and/or $\psi'_{\text{CH}_3}(\phi) = \psi'_{\text{CH}_3}(\phi + 2\pi)$ starting from a general solution of $\psi_{\text{CH}_3}(\phi) = Ae^{im\phi}$, where A and m can each be any real rational number. Show that resulting the wavefunction is an eigenfunction of the

angular momentum operator \hat{L}_z , with the z -axis defined as the C-C bond axis. What are the eigenvalues?

4. Show that the wavefunction $\psi_{\text{CH}_3}(\phi)$ you derived in 3) leads to the following solution for the energy of the pseudo-rotational eigenstates. (hint: for a 1D rigid rotator, $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$).

$$E_m = \frac{\hbar^2 m^2}{2I_{\text{CH}_3}}; m = 0, \pm 1, \pm 2, \dots$$

5. Using this expression for the energy, prove that the partition function for this torsional motion (which is formally a vibrational motion) is given by the following expression:

$$q_\phi \cong \sqrt{\frac{2\pi I_{\text{CH}_3} kT}{\hbar^2}}$$

6. From the above expression for q_ϕ what is the contribution of this torsional motion to the molar heat capacity at constant volume C_v in terms of R (where R is the gas constant) in the limit that $E_a \ll kT$ (hint: what is the definition of heat capacity at constant volume?).

7. What would you expect the contributions to the molar heat capacity to be in the other limit of $E_a \gg kT$?

8. Is the $m = 0$ to $m = 1$ transition for this torsional mode infrared-active? Is it Raman active? Defend your answers.

