Spring Semester 2013
(Due 4 / 10 / 12)

This problem set will take longer than the last one in the sense that you will almost certainly need to submit some jobs, leave, and check your results later. **Get started early***.*

Some mechanical reminders: To run a G09 job, you must have the `gaussian` module loaded. After login, type `module list`—if you don't see `gaussian/g09.c01` listed, type `module load gaussian`, and then `module list` again, and now you should see it. Next, remember that your input files should be named, for example `myfile.com`. Issue the command `qg09 myfile.com` and the script will submit a 5 hour job to the batch queue to run on one 8-processor node using local scratch space. You can look at the output from `qg09 -h` if you want to include flags that will send you an email on completion, ask for more (or less) time, ask for more nodes, etc. (note that asking for more than 8 nodes will not generally be helpful). If you want to look at an output deck while a job is running, you can either `vi myfile.out` or `more myfile.out`. To examine the queue on itasca, the command is `qstat -a`; you may find that `qstat -a | egrep cm8021##` (where cm8021## is your userid (or the analogous cm4021##)) is also convenient. Links to `vi` commands and a unix primer are provided on the class webpage.

A nomenclature reminder: the notation *x*/*y*//*w*/*z* means level of theory *x* using basis set *y* at a geometry optimized at level of theory *w* with basis set *z*. E.g., MP4/6-311G(d,p)//MP2/6-31G(d) means that the geometry was optimized at the MP2/6-31G(d) level but the energy (and/or other properties) are being calculated at the MP4/6-311G(d,p) level. The notation *x*/*y* in the absence of a trailing //*w*/*z* implies optimization and energy evaluation were performed with the same level of theory.

Some quick notes/reminders with respect to *Gaussian 09*:

1) Some files have been provided in my directory `~cm8021pr/templates` — feel free to study them carefully to ensure that you have proper file formats, e.g., checkpoint naming conventions (`%chk=myfile.chk`).

2) If you are entering geometric or basis set data in a G09 input deck (as opposed to reading it from the checkpoint file) you *must* end the input file with a blank line.

3) To find transition states *in the absence of a symmetry constraint*, use `opt=(ts,calcfc)`. If you have a symmetry constraint, you need to decide whether the reaction coordinate for the TS structure *breaks* the symmetry (in which case, use neither `ts` nor `calcfc` as keywords, because

the symmetry will hold you at the TS structure) or preserves it (in which case use both keywords). If you are looking for a TS, you may often find it helpful to do `opt=(ts,calcfc,noeigentest)`. The other keywords besides `ts` request calculation of analytic force constants on the first step (`calcfc`), and that the job not die if other than exactly one negative force constant is found at some step (`noeigentest`).

4) You can save a *lot* of time by using useful information from previous calculations stored in the checkpoint file. *Plan* your calculations to try to save time. You can also save a lot of time by using *symmetry* when appropriate.

    a) Keywords `guess=read` and `geom=checkpoint` get the wave function and the geometry, respectively, from the last completed calculation. So, if you have just done an optimization, and want to follow-up with a frequency calculation, for instance, you will certainly want to use these keywords. **Note: Frequencies *must* be calculated using the same level of theory with which the geometry was optimized to correspond to true IR frequencies!** (Note that if you know ahead of time that you will want frequencies after a given optimization, you can simply include the `freq` keyword in the same job as `opt`).

    b) If you just optimized a geometry at one level of theory, and want to repeat that optimization at a different level, include `readfc` in the `opt=()` keyword, e.g., `opt=(ts,readfc)` for a second pass at a transition-state optimization. This causes the program to start with the force constants from the previous calculation, which is efficient. **It's usually a good idea to work your way up in a geometry optimization so you don't waste a lot of computer time because of a bad initial guess.**

5) Serving GaussView across the local network can be slow owing to the massive amounts of graphics data being transferred. It will often be more convenient to transfer readable files to a local machine (e.g., a computer in Chemistry's Computer Lab) and run GaussView locally. In particular, output files (which are text) can be transferred easily. For inspection of molecular orbitals, it is convenient to transport a formatted checkpoint file. To generate such a file, the command is `formchk myfile.chk`, where `myfile.chk` is the name of the (binary) checkpoint file. A text formatted checkpoint file `myfile.fchk` will be created and can be moved in the same fashion as an output file. GaussView accepts .fchk as an option for file types to be opened.

********** THE PROBLEMS **********

1. Let's return to our favorite natural products from the first problem set. In the templates subdirectory of my cm8021pr account, you will find two files, A_isomer.pcm and B_isomer.pcm, which contain the lowest energy structures that I found from my GMMX

searches for these two structures. Convert these files to Gaussian input format and optimize the structures at the M06-L level of theory using the 6-31G(d,p) basis set together with an auxiliary density fitting basis set. In addition, specify an ultrafine integration grid. If you look at the file tmsopt.com in my templates subdirectory, you will see what keywords it takes to accomplish that.

A   **B**
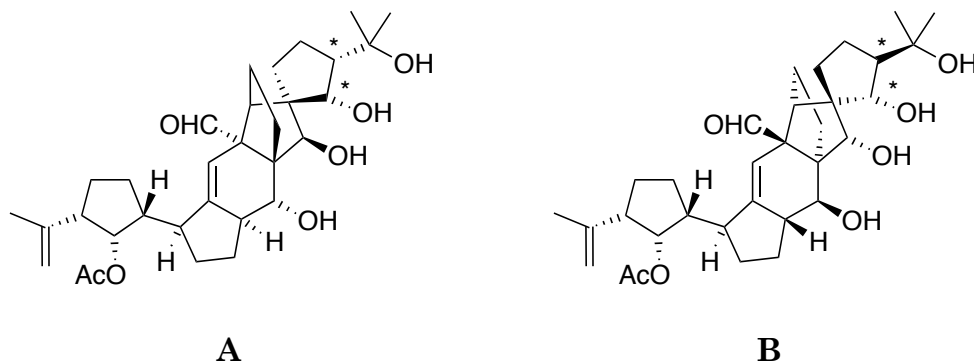
Once your structures are optimized, report their absolute energies. In kcal/mol, which is more stable and by how much compared to the other? If they were interconverting isomers (which they most certainly are not, but *if* they were) what percentage would each contribute to a total population at 298 K? How does the DFT value compare to those computed from steric energies at the MMX, MM3, and MMFF levels in PCModel, when reoptimizing the provided structures?

Now, compute ^{13}C NMR chemical shifts for both isomers as a single-point calculation on your optimized geometries at the M06-2X/6-31+G(d,p) level, i.e., ***do not reoptimize at this level***. The experimental data for the natural product are 201.9, 172.1, 157.4, 144.8, 114.8, 111.4, 78.1, 76.9, 75.7, 72.2, 71.2, 68.8, 62.5, 58.6, 57.9, 52.7, 52.1, 51.4, 50.7, 45.2, 39.0, 33.7, 31.0, 29.9, 29.4, 29.0, 26.6, 24.5, 24.4, 24.0, 23.2, 21.0 ppm relative to TMS. Which of **A** or **B** is the natural product? Explain how you came to your conclusion.

2.   In ring-opening metathesis polymerization, a metal-carbene undergoes a [2+2] cycloaddition with a cycloalkene to form a metallacyclobutane-containing bicyclic intermediate. Subsequently, a retro-[2+2] reaction (that breaks the 4-membered ring in the opposite manner as its formation) leads to lengthening of the growing polymer and a new, reactive metal carbene. The process is illustrated below in general.
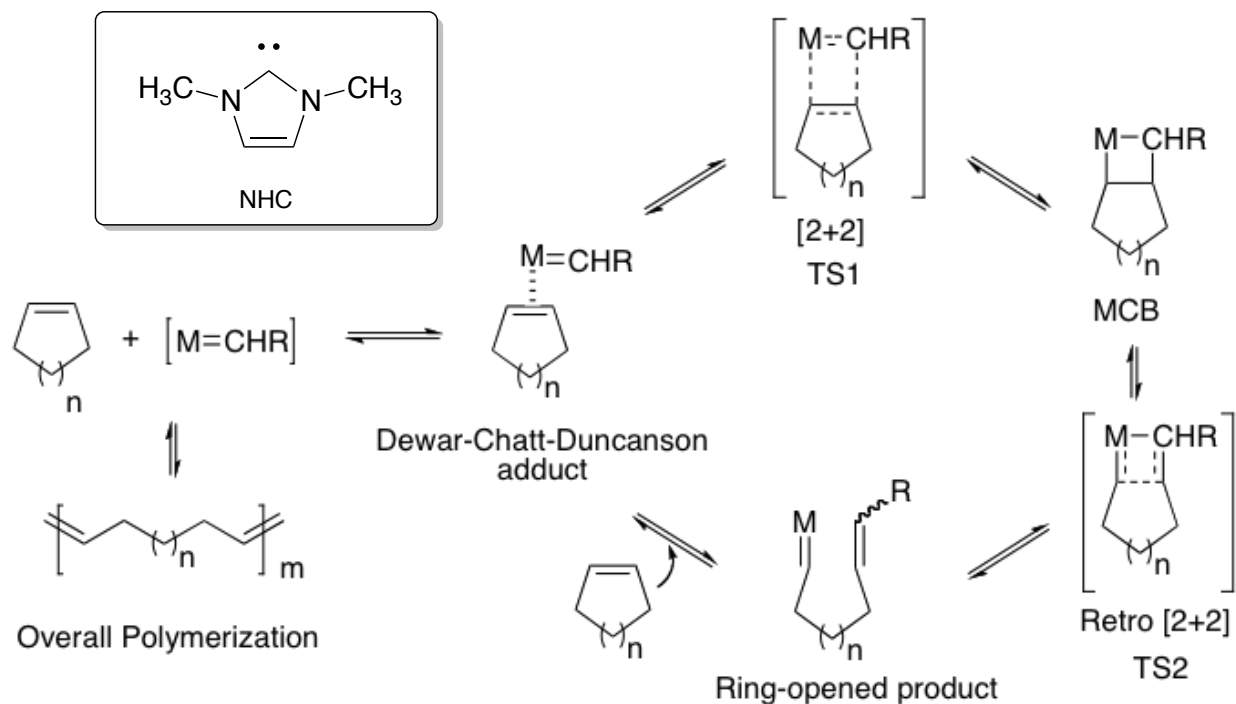
Your task is to characterize all 5 stationary points (the initial adduct, the intermediate, the final product, and the two transition-state structures; note that the final product has the terminal olefin coordinated to the metal) at a variety of levels for M = $Ru^{II}(NHC)Cl_2$ where NHC is the N-heterocyclic carbene shown in the inset to the figure above. The reaction is between $M=CH_2$ and cyclopentene (so, just as a check, all of your molecular formulas should be $C_{11}H_{18}N_2Cl_2Ru$).

Taking the initial adduct as the zero of energy, report the relative energies, enthalpies, and free energies along the reaction coordinate at the PM6 level. Then, repeat the process with full optimization and frequency calculations at the ωB97X-D/SDD|6-31G(d) level of theory. Finally, do *single point* calculations on the ωB97X-D structures at the MP2/SDD|6-311+G(2df,p) level of theory and report the HF and MP2 relative *energies* at that level of theory as well.

Comment on the results, both energetic and structural, from the various levels of theory. **Note that while it is usually a good idea to use information from a lower level of theory to make more efficient a subsequent calculation, this is *not* true if the lower level of theory is ill suited to the problem.** Thus, if you plan to read geometries or wave functions from checkpoint files for this exercise, you should always visualize the structures first to ensure that they seem reasonable. In addition, note that there is a very useful subkeyword to `opt`, namely, `modredundant`, that allows one to freeze certain degrees of freedom so that other degrees of freedom can be relaxed first, and then the frozen coordinates can be unfrozen to permit, say, a TS optimization to start with most of the molecule relaxed but certain bonds stretched (for

example…) However, the online manual has not caught up to a change in the code. Thus, if you try to freeze a bond using a line like: `1 2 2.0 f`, it will *not* work. You can no longer specify the distance (`2.0`); instead, you can freeze whichever coordinate you like at the specific distance that is already in the structure you provide, e.g., `1 2 f` is allowed and *will* freeze the bond length between atoms 1 and 2 (see the G09 manual for more details, noting this one difference).

3.　　Consider the two pairs of isomeric iminium ions below. In each pair, compute which is more stable (both energy and free energy) at the HF/6-31G(d), MP2/6-311+G(2df,p)//HF/6-31G(d), and M06-2X/6-31+G(d,p). Note (i) there are likely boat-like and chair-like ring forms for each structure that should be separately averaged and (ii) for the MP2 level you will be computing only energies, not free energies.

1　　　　**2**　　　　**3**　　　　**4**
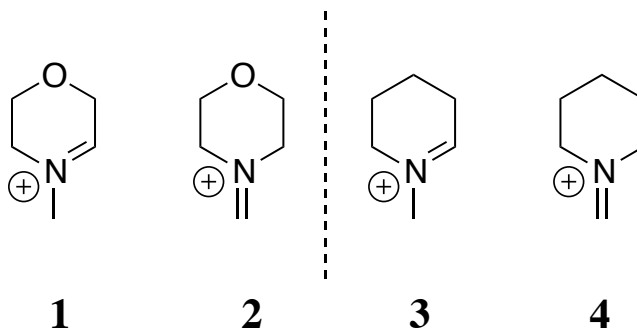
　　　　Discuss the theoretical variations (as a function of level) and the chemical differences (as a function of O vs. CH_2 substitution).

　　　　Next, it is observed that refluxing **1** in aqueous solution leads to **2**. Is that consistent with your calculations? Find a transition-state structure for the necessary proton transfer at the M06-2X/6-31G(d) level and report its energy relative to the two minima. Next, find a water-catalyzed transition-state structure for the same process using a single water molecule. By how much are the energy and free energy of activation lowered? Why is there a substantial difference between energy and free energy? For your various structures, perform a single-point calculation at the MP2/6-311+G(2df,p) level and compare the HF and MP2 energies of activation to the DFT values. (For purposes of this problem set, do *not* use a continuum solvent model for these calculations.)