This summer the Carleton Chemistry Department will offer its continuing summer research program for Carleton students. We expect to offer research positions to between 13 and 15 new students. For the most part, the new student researchers will come from the sophomore and junior classes. Professors Kohen, Whited, Gross, Drew, Chihade, and Alberg/Hofmeister (jointly), will offer projects that reflect their research interests. The research projects offered by each faculty member are described at the end of this document. In addition, a summer research recruiting seminar will be offered on Wednesday, January 18 in Olin 04 at 4:00 pm. General information on summer research in the chemistry department will be presented along with brief introductions to the science each research group is pursuing.

**Dates of the Program:** Monday, June 11, through Friday, August 17, for a total of 10 weeks. Each student will arrange starting and ending dates and summer vacation with his or her professor; these dates are usually flexible.

**Stipend:** $4,200 for 10 weeks (subject to final Board of Trustee approval in February).

**Expectations of Students by the Chemistry Department:**
A research position in our summer research program is a full-time position. You should not plan on taking a second job during the same period.

Each week you will be expected to attend a research conference with all of our summer researchers. Each student will give an oral presentation on his or her project at this weekly research conference. You may have the opportunity to give a presentation on your research at a state or national research meeting. Following the summer of research, you will prepare a comprehensive written report and give a poster on your research at the fall All Science/Math Student Poster Session at Carleton.

**Deadlines and How to Apply:** Submit an electronic application using the form titled “Summer 2012 Research Application” available at the Chemistry Department’s web site. Follow the directions on the electronic application form and rank order your preferences for research projects. Also tell us how strong your preferences are and how flexible you are in accepting a position in the other research groups you list. Before submitting your application, you should talk to individual professors in order to explore your interest in their research project. Keep in mind that some professors will not invite a student to join their research group unless the student has taken the time to stop by, meet the professor, and discuss the research project. Email the completed electronic application form to Steven Drew by Wednesday, February 15.

On Tuesday, February 28, offers will go out to individual students in campus mail. We will ask for your decision on our offer by Friday, March 9.

**Reasons to Participate in the Summer Research Program:** Research is considered by many to be at the pinnacle of intellectual endeavors as it is the main vehicle by which new knowledge is created. Research requires a demanding combination of intellect, creativity, endurance, and curiosity. Many valuable skills are developed in the research laboratory. Some examples include the ability to work as a member of a team, to operate sophisticated instrumentation, and to use available resources to become a life-long learner. Research is also excellent preparation for graduate school, a career in the medical sciences, or a career in other scientific or quantitative fields.

Choosing to do research at Carleton offers a number of advantages. First of all, you will have the chance to get to know your professors much better. In addition, you can start preparing for your summer research experience during spring term. This additional preparation will improve the quality of the research you can perform during the short ten-week summer. Furthermore, if you wish, your
research project can be continued as an independent study during the following academic year. Some students at Carleton who have had the most positive research experiences have worked on their research projects over the course of two years. Unlike the experience at a larger institution, colleges like Carleton offer research opportunities exclusively for undergraduate students. At a larger institution, you would probably work most directly with a graduate student or post-doc, which is a good, yet different kind of experience. At Carleton you are guaranteed to work closely with a professor and to have your peers as research colleagues.

Life at Carleton and in Northfield is much different during the summer than during the academic year. You will be surprised by the pace, and you will be pleased to know that you will not need your down jacket and warm hat (you may want to buy a fan). Many of the facilities (such as the gym, pools, weekly movies, etc.) at Carleton are open for summer programs. We will have at least two expeditions; canoe trips, baseball games, Valley Fair, and tubing have been popular choices in the past.
INDIVIDUAL FACULTY RESEARCH PROGRAMS

Professor Dani Kohen: Atomistic Simulations of Small Gas Molecules on Molecular Sieves

Positions for 2 new students

I am a theoretical and computational physical chemist. I am interested in the general area of dynamics in condensed phase (how atoms and molecules move and interact when they're not by themselves). Currently, I am using atomistic simulations to understand and characterize at the molecular level how small gas molecules interact with pure CO$_2$ on molecular sieve's pores, and how this interaction changes in the presence of other gases that are present in our atmosphere. The goal of these studies is to provide a basic understanding of the use of molecular sieves as filters to remove CO$_2$ from the atmosphere. In recent years the power of computational research has been shown to provide scientific insight that might not result from experimental research alone.

This research introduces students to the study of chemistry through the lens of molecular simulations, which provide a powerful tool in giving new meaning to familiar concepts. It also serves as a reference point to understand not only the computational chemistry literature but also why the importance of this field as a tool for studying many problems keeps growing.

The way my research group works is that I mostly write the programs (software), my student collaborators use and modify these to investigate chemical systems; and then, together, we use the results to learn about the chemical processed that occur in the systems we study. In doing this kind of research the learning curve is steep, but the results are very satisfying and my student collaborators made significant progress in their own projects enjoying doing research. I anticipate that I will be able to invite two students to join my group. If you are interested in joining us, please stop by to talk to and even better, ask a member of my group (Katie Deeg (’12) and Diane Walters (’12)) about their experience as their thoughts will be the best introduction to our work.
Research in my laboratory addresses problems related to energy and organic synthesis by focusing on reaction chemistry of late transition metals (Group 8–10). All of the projects look for new ways to generate and utilize highly reactive complexes containing metal–element single, double, or even triple bonds (where element = carbon, nitrogen, silicon, boron, oxygen). This summer, research projects in the Whited lab will be split into 2 subgroups, which use similar techniques but address different problems, as described below.

**Ambiphilic Metal Complexes for Cooperative Small-Molecule Activation**

Ambiphilic molecules are ones that have both Lewis acidic and Lewis basic sites, such as the (aluminoamino)phosphine shown at the left in the figure below (phosphorus has a nucleophilic lone pair and aluminum is electrophilic since it only has 6 valence electrons). These sorts of molecules are quite useful for activating small molecules (such as CO and CO$_2$).

We are interested in extending the idea of “ambiphilicity” to metal complexes, such as the one shown at right below, containing bonds between electron-rich transition metals and electropositive main-group elements such as silicon, carbon, and boron. Since transition metals can access a greater range of coordination numbers and oxidation states than organic molecules, we expect that these types of complexes will exhibit a rich variety of cooperative reactivity with simple organic and energy-relevant molecules (a few possibilities are shown below; atoms not directly involved in the reaction have been removed).
New Routes to Metal Phosphinidene (M=PR) and Imido (M=NR) Complexes

A second project is focused on the development of new synthetic routes to complexes containing metal–nitrogen and metal–phosphorus multiple bonds (metal imides and phosphinidenes, respectively). These complexes are important reactive intermediates for the incorporation of nitrogen and phosphorus into organic molecules, but most synthetic routes involve either involve high-energy starting materials (which are undesirable for catalytic applications, Route A) or laborious multi-step syntheses (which are incompatible with catalysis, Route B).

An alternative possible route to these complexes is shown at the bottom of the above figure. Fluoride can be used to cleave a Si–N bond, and concomitant oxidation of the metal center affords the same M=NR species in a single step using mild reagents. We are interested in developing this route with a variety of metals, especially those for which traditional approaches (such as Routes A and B) are ineffective. The ultimate goal of this research is to lead to new mild ways of incorporating nitrogen and phosphorus groups into organic molecules.

What Will You Do?

Both projects involve some amount of organic synthesis in order to prepare the desired ligands (such as the mixed phosphorus/silicon ligand shown in the first project above). You will also become (intimately) familiar with methods for manipulation of air-sensitive organic and inorganic compounds in our inert-atmosphere glove box and Schlenk manifold (don’t worry if you don’t know what these are yet).

Multinuclear NMR ($^1$H, $^{11}$B, $^{13}$C, $^{15}$N, $^{29}$Si, and $^{31}$P) will be our primary characterization technique, though we will also use X-ray crystallography, IR and UV-Vis spectroscopies, and GC or LC/MS.

**NOTE:** You do not need a background in inorganic chemistry to work on these projects. Familiarity with organic chemistry (through Chem 234) is sufficient, and we’ll cover the rest as we go.

If you are interested in working in my laboratory, please do the following:

- Set up an appointment to meet with me and discuss my research (I will not accept anyone as a summer research assistant who has not talked with me ahead of time).
- Plan to enroll in an independent study (Chem 394) in Spring 2012 in order to do some background work to prepare for your research project.
**Positions for 1-2 new students**

The air around us is full of aerosol particles (small droplets or chunks of solids), which impact our lives in many ways. These particles come from natural as well as anthropogenic (human) sources. They nucleate cloud droplets, they decrease visibility by scattering sunlight, and they impact our health when we inhale them. Our research group works with an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS), code-named “Gromit,” to obtain size and chemical composition information about the aerosol population in real time. With this data, we hope to try to increase our understanding of some of the complex issues in the atmosphere.

I hope to have two students (of which one might be a returning student) work with me this summer. Students working in my lab will get an opportunity to acquire ambient data in the Northfield area as well as to analyze ATOFMS data sets obtained in collaboration with groups at the University of Minnesota, University of Wisconsin, St. Louis University, and the Paul Scherrer Institute in Switzerland. We have long-standing collaborations with these groups, and have a number of complex data sets to work with. Our analysis is done using software development by Dave Musicant’s group in the CS Department at Carleton. Our work in Summer 2012 will also include laboratory studies to characterize the chemical composition of lab-generated particles based on those emitted by a variety of household activities (meat cooking, air-freshener use, etc.).

**IF YOU ARE INTERESTED IN JOINING THESE PROJECTS, YOU SHOULD DO ALL OF THE FOLLOWING THINGS:**

- Come talk to me as soon as possible, to discuss the details of the research and to see the ATOFMS instrument. Email to make an appointment. I won’t accept anyone into the group unless we’ve talked about your interests, the projects, etc.
- Be prepared to spend part of the summer away from Carleton. While we are not sure yet of our specific plans, fieldwork could be included. Your expenses for fieldwork would be paid.
- Plan to enroll in independent studies (Chem 394) in Spring, 2012.
- Be aware of the fact that I will be on sabbatical during 2012-2013 academic year, so the opportunities to continue your research during the year (or the summer of 2013) will be limited or non-existent.

![Image 1: Particle types emitted from combustion of ethanol/gasoline mixtures, measured with the ATOFMS](image1.png)

![Image 2: The Carleton College ATOFMS](image2.png)
Positions for 2 new students

I will be hiring two students this summer to work in the research lab and help me teach a three-week enrichment program for high school students called the Carleton Summer Science Institute (CSSI). Because of my commitment to the CSSI program I will be offering students in my lab 5-6 weeks of summer research followed by 3 weeks working in the CSSI program. Briefly, CSSI responsibilities will include helping with a short course on materials chemistry that will be taught every morning for three weeks, helping students work on research projects in the afternoon, and interacting with the students outside the laboratory in informal settings. More information about the CSSI program can be found at: http://apps.carleton.edu/summer/science/

In the research lab I am interested in the application of materials chemistry to analytical chemical measurements. Currently, I am studying platinum(II) square planar extended linear chain (ELC) materials and their application in gas sensing. Many of these platinum(II) ELC materials are crystalline, luminescent solids that selectively absorb gas phase molecules to form solvates. Formation of the solvates leads to changes in solid-state luminescence, a feature that can potentially be used as the basis for a gas sensor.

This summer my research group will be working on two varieties of platinum(II) ELC materials, Pt(II)(CNR)₂(CN)₂ where R = CH(CH₃)₂ (1) or CH₂CH₂CH₃ (2), to determine their solid-state reactivity in the presence of benzene vapor. We have already studied some aspects of benzene solvate formation at 1 and have structural data on both the benzene-solvated and unsolvated versions (see

**Figure 1.** Crystal structures of 1 (A) and the benzene solvate of 1 (B) viewed looking down the Pt···Pt interaction axis.
Figure 1). I am interested in determining if 2 has benzene sensing characteristics similar to 1. This will provide some insight into whether benzene solvate formation is a general feature of Pt(II)(CNR)$_2$(CN)$_2$ type ELC materials or only specific to 1.

Students working on this research project will have the opportunity to improve their skills in chemical synthesis and synthetic characterization techniques like NMR, ATR-IR, and ESI-MS. In addition, the college recently purchased a new X-ray diffractometer capable of studying crystalline thin films samples in a controlled atmosphere. This instrument will allow us to examine the diffraction patterns of our platinum(II) ELC materials as they form benzene solvates. These diffraction patterns will provide insight into the structural changes that accompany solvate formation. Solid-state luminescence studies of platinum(II) ELC material thin films will also be performed to determine benzene sensing characteristics and benzene uptake solid-state kinetics.
Converting the information stored in DNA into functional proteins requires a set of enzymes that are common to all organisms, from bacteria to humans. Among the most important of these enzymes are the aminoacyl-tRNA synthetases (aaRSs). aaRSs enforce the genetic code by catalyzing the formation of ester linkages between amino acids and particular transfer RNAs (tRNAs), so that each of the twenty amino acids is only linked to the tRNAs that match the corresponding DNA codons. So, for example, alanine is only linked to tRNAs that match the codons GCU, GCC, GCA, and GCG. In most organisms, there are twenty aaRSs, one for each amino acid. Each one of these enzymes must differentiate between several potential amino acid and tRNA substrates, recognizing subtle differences between them. Some of the enzymes use error-correcting “editing” domains to ensure that only correctly aminoacylated tRNAs are produced.

For the several years, students in my lab have worked on understanding one particular aaRS, the enzyme that links alanine to its corresponding tRNA in human mitochondria. This enzyme, human mitochondrial alanyl-tRNA synthetase, is of interest because even though it is quite similar to alanyl-tRNA synthetases from other organisms, it recognizes and binds to its tRNA substrate in a very unique way. By making a series of changes to the tRNA substrate and seeing how they affect the rate of aminoacylation, we are trying to understand how this tRNA recognition works.

Last spring, researchers in Finland discovered that two mutations in the human mitochondrial alanyl-tRNA synthetase cause severe infantile cardiomyopathy and early death. (Götz, et al., Am. J. Hum. Genet. 88, 635, 2011). We have begun to characterize these mutations at the molecular level. One mutation appears to cause protein misfolding, which results in a completely non-functional and mostly insoluble enzyme. The second mutation does not disrupt protein folding and does not even affect aminoacylation rates much. This summer we will explore the possibility that the mutation is lethal because it causes defects in editing.

Work in my lab involves protein purification, in vitro transcription of tRNAs, creation of new RNA and protein mutants using site-directed mutagenesis and other molecular biology techniques, enzymatic assays to measure charging ability, and probing of tRNA structures to determine regions of protein-RNA interactions. I plan to take one to two new students in my lab this summer.
Positions for 1-2 new students

This year we are continuing a collaborative research program in organocatalysis. Organocatalysis involves the use of small organic molecules to catalyze organic reactions that are valuable in synthesis. Of primary interest is the use of chiral organocatalysts to control the stereochemical outcome of these reactions.

Project 1: Transition State Analogs of Asymmetric Desymmetrization Reactions

In connection to a recent project that we are finishing up, which involves the desymmetrization of a derivative of citric acid (equation below), we are initiating a new project that is focused on developing a better understanding of the basis for enantioselectivity in this and related transformations. Specifically, we plan to prepare stable transition state analogs (TSAs) of the likely transition state for asymmetric desymmetrization reactions, related to the reaction in the box below, and use NMR to study their interactions with the chiral catalysts for this reaction.

This reaction is catalyzed by derivatives of the cinchona alkaloids, like quinine (3), and the catalyst is thought to act as a general base by hydrogen-bonding to the alcohol, activating it for nucleophilic attack on the anhydride (Scheme 1). The rate-limiting step in this mechanism is expected to be formation of the high energy tetrahedral intermediate 1. The Hammond postulate suggests that the transition state for this step should resemble the intermediate, and we plan to mimic this tetrahedral transition state with stable tetrahedral phosphorus derivatives, such as 2 (Scheme 1).

Under the conditions employed in the catalytic desymmetrization reactions, TSAs such as 2 will form an ionic complex with the alkaloid catalyst. The solution conformations and interactions of the resultant alkaloid-TSA complexes can be evaluated by NMR spectroscopy. By resolving our proposed TSAs into their component enantiomers, we can investigate each enantiomer’s interactions with the catalyst separately. Differences in these interactions can provide insight into the mechanism by which these alkaloids achieve their impressive enantioselective catalysis. We also hope to collect quantitative measurements of the differential binding of TSA enantiomers to the catalyst, by measuring association constants ($K_a$) though NMR methods. We can then compare the relative binding constants of the two TSA enantiomers to a particular catalyst ($K_a/K_{a(cm)}$) with the enantiomeric excess for the catalyzed reaction. A correlation between these values
would indicate that our TSAs are reasonable mimics for the ASD reaction.

**Project 2: Organocatalytic Transamination**

The asymmetric introduction of an amine functional group is a critical transformation in organic synthesis, particularly for the preparation of many amino-functionalized pharmaceutical agents. Nature accomplishes this transformation, for example in the synthesis of chiral amino acids, by using amino transferase enzymes that rely on a pyridoxal phosphate (PLP) cofactor. The net transformation interconverts α-keto-acids with α-amino acids (eq 1), via tautomerization of an imine that is generated from PLP and an amino functional group. The enzyme first catalyzes the transfer of an amino functional group from an amino acid to PLP, generating PMP (in box). This species then transfers the amine to the α-keto-acid substrate, regenerating PLP.

![Reaction Scheme](image)

In our initial studies, we investigated the second half of the catalytic cycle, which involves transferring the amino group from PMP (or a suitable analog) to the ketone. We did this by combining molar equivalents of 1 or 2 and a substrate ketone with 10-30 mol % of bifunctional organocatalysts (3-5) in a variety of solvents (equation below). We found the reaction to be highly dependent on the nature of R and R' on the ketone. For example, acetophenone resulted in no reaction, but p-nitroacetophenone resulted in formation of ketimine but no aldimine product. Importantly, when R' is an ester, conversion to the aldimine results. This can then be hydrolyzed to release the desired amine product and the aldehyde analog of the starting amine.

Shortly after we began our investigations, Shi and coworkers published an organo-catalytic asymmetric transamination methodology that employs 2-chlorobenzylamine (among other substituted benzylamines) as the amine source and α-keto-esters as substrates.² Their strategy, as well as our initial plan, relies on formation of a stable aldimine as the thermodynamic driving force for the organocatalytic transformation. We now plan to explore this transformation in more detail and develop methods to extend it to other ketone substrates.

Students working on these projects will gain experience in synthesis, methodologies for performing and analyzing organocatalytic reactions, NMR spectroscopy, and chiral chromatography.

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