Faculty News

Robert K. Boeckman, Jr.

Marshall D. Gates, Jr. Professor of Chemistry and Chair — Ph.D. 1971, Brandeis University

RESEARCH INTERESTS

Total synthesis of alkaloids, terpenes, antibiotics, and antitumor agents; development of new synthetic methodology including the asymmetric synthesis methods involving the Diels-Alder reaction, the Claisen-retro-Claisen and other reactions; applications of conformational theory to the development of stereocontrolled organic reactions.

CONTACT

rkb@rkbmac.chem.rochester.edu

During the 2010-2011 academic year, **ROBERT K. BOECKMAN, JR.** completed his eighth year as the chair of the chemistry department. Professor Boeckman is continuing as chair for the 3rd year of a 3-year term in 2011-2012. He also continues his duties as associate editor of the *Journal of Organic Chemistry*, and as vice president and member of the Board of Directors of Organic Syntheses, Inc.

Bob Boeckman's research group continues their efforts directed toward the development of new synthetic methodology and the application of that methodology to problems of current interest in complex molecule synthesis, particularly molecules possessing important biological activity. Significant progress has been made in the past year toward FK-506, as well as projects directed toward Apoptolidin. New aza-[3,3]-sigmatropic rearrangement methodology has been developed, which has now been published, and attention is now focused on application of this chemistry to the antitumor Manzamine class alkaloid Nakadomarin A. Work is continuing toward an asymmetric variant of a shelf stable chromium(III) complex that serves as a precatalyst for Nozaki-Hiyama and Takai type chromium mediated allylations of aldehydes and for a wide variety of chromium(II) mediated reactions and on asymmetric vinylogous Mukiayama aldol reactions catalyzed by chiral oxazaborolidines. The group has also completed their first efforts in organocatalysis with the development of catalytic systems for hydroxymethylation of aldehydes. Studies in this area are continuing

Rush Rhees Library

toward asymmetric α oxidation of aldehydes and other applications. New collaborative projects have been initiated with Professors David Goldfarb of the biology department and Damian Krysan of Department of Pediatrics URMC whose goals are 1) the identification of the biological target(s) of a novel series of small molecules which mimic the effects of caloric restriction on lifespan in yeast and in small mammals and 2) the development of PDK-1 inhibitors showing specificity for the fungal enzymes for use in antifungal therapy against invasive fungal infections of neonatals and young infants.

GREG FRATTINI (PH.D. '10) defended his thesis and continues as a postdoctoral associate in the group working on the Goldfarb (biology) collaboration. **JOHN R. MILLER (PH.D. '10) AND YAN MILLER (PH.D. '10)** defended their theses in March of 2010 and moved on to Stanford University, where they both began work as postdoctoral associates in Barry Trost's group. John will join the law firm of Hodgson Russ LLP in Buffalo, NY in July 2011 as a scientific advisor and Yan Miller is currently seeking employment in the Buffalo area. **NATHAN E. GENUNG (PH.D. '10)** continues as a postdoctoral associate with Larry Overman at UC Irvine. **XINYI SONG (PH.D. '07)** was married in July 2011 and is currently employed as a research chemist with J&W Pharmlab in Levittown, PA. Matt Betush continues his research in the group on various aspects of asymmetric catalysis. George Arab and Brian Ohman are completing their 4th year and continue working on FK-506 and Apoptolidin, respectively. Part-time scientist Dr. Dennis Savage, retired from Kodak, continues his work in the group on several projects with the Goldfard (biology) and Krysan groups (pediatrics URMC). **CHRISTOPHER WONG (B.S. '11)** completed his B.S. thesis in the group in Spring 2011 and will begin graduate studies in chemistry at Boston University in the fall. During the summer of 2010, one undergraduate worked in the group as part of the NSF REU program along with two new graduate students, Doug Tusch from RIT and Kyle Biegasiewicz from Niagara U. Both joined the group permanently in December 2010. Doug and Kyle are collaborating on an organocatalysis project and helping out with FK-506 and Apoptolidin when time allows. David Kaphan, a UR senior, has worked in the group since his freshman year and will do his B.S. thesis in the group during the 2011 academic year after having spent the summer of 2010 working at Novartis in Cambridge, MA. Two new graduate students Gil Ryenders (Lake Forest College) and Adam Feinberg (RIT) and three undergraduates, Wil Ksander (Beloit College, WI), Emily Vogt (Ohio U.), and Peter Jaenike (U. Buffalo) are working in the group during the Summer of 2011. **CHRISTINA COLLISON (PH.D. '04)** recently was promoted to associate professor with tenure in the chemistry department at RIT and **JEREMY CODY (PH.D. '04)** continues as assistant professor of chemistry also at RIT. **JOSEPH PERO (PH.D. '05)** continues as a research scientist with Merck in West Point, PA. **XIAORONG LIU (PH.D. '04)** recently joined AstraZeneca in Waltham, MA as research scientist.

Meliora Medallion

Kara L. Bren

Professor of Chemistry

Ph.D. 1996, California Institute of Technology

RESEARCH INTERESTS

Bioinorganic and biophysical chemistry: heme protein structure and function, protein folding and dynamics, NMR of paramagnetic biomolecules, solar energy conversion.

Contact
bren@chem.rochester.edu

The **KARA BREN** group had a busy year pursuing projects in heme protein structure-function relationships, in protein folding, and in solar energy conversion. A highlight was celebrating the graduation of **SARAH BOWMAN (PH.D. '10)**, who left for her postdoc at MIT with Professors Cathy Drennan and Collin Stultz. We also were thrilled to hear Sarah's recent news that she was awarded an NIH Postdoctoral Fellowship.

The studies of cytochrome electronic structure and function have moved forward well, led by postdoc Matt Liptak and graduate students, Jesse Kleingardner and Mehmet Can. Matt published an interesting paper in *JACS* reporting the effect of interactions with heme propionates on electron transfer activity and on pro-apoptotic activity of human cytochrome *c*. Jesse also had a publication in *Metallomics* on the requirements for heme attachment in mitochondrial cytochromes *c*. He is following up that result by performing studies of the conformation of the heme in cytochromes with unsual modes of heme attachment with the assistance of incoming first-year graduate student Rebecca Smith. Mehmet Can has new results linking heme conformation to its EPR spectrum in collaborative work with Prof. Kristoffer Andersson (University of Oslo) now submitted for publication. Mehmet is also studying high-spin cytochrome *c* variants with the assistance of U of R undergraduate Ben Snyder, who is doing his senior thesis project in the Bren lab. Jesse and Mehmet gave talks on their results in a symposium on heme modification and regulation at the ACS National Meeting in Anaheim (March, 2011). Jesse won a travel award from the ACS Division of Biological Chemistry to present this work. In summer 2011, Matt will be departing for a faculty position in the Department of Chemistry at the University of Vermont. We will miss his contributions to the project but are thrilled to see him strike out on his own.

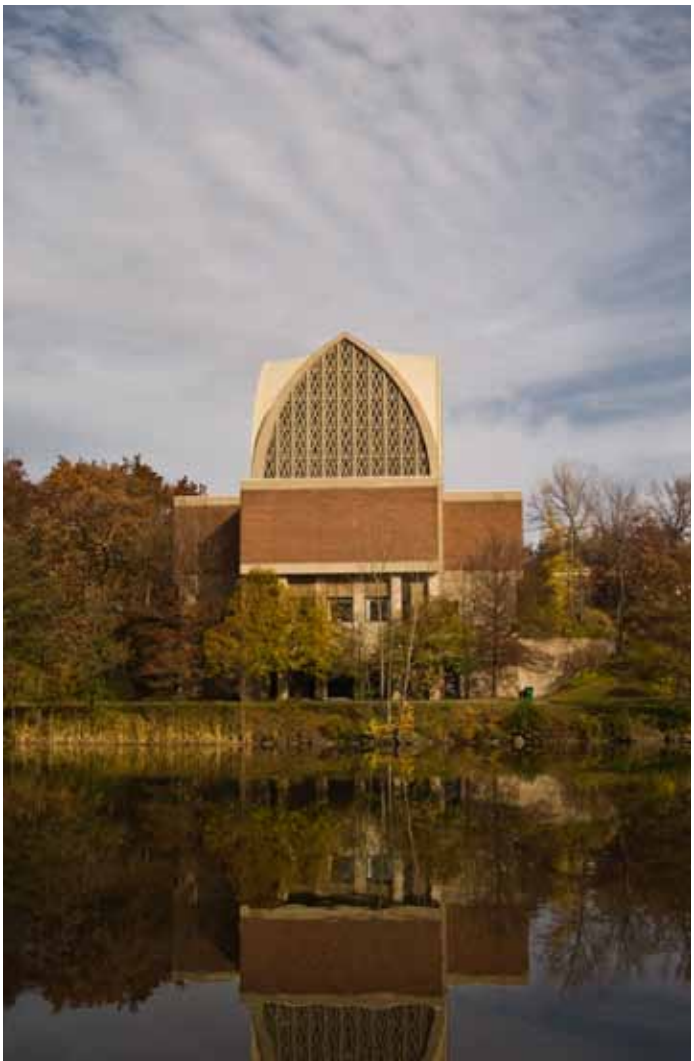
The group's efforts, pursued jointly with the Krauss group, to study cytochrome *c* folding on the single-molecule level

Carlson Library and Computer Studies Building

have continued to move forward. Postdoc Andrea Lee and graduate student Wesley Asher have exciting new data. Wes won a travel award from the ACS Division of Biological Chemistry to present his results at ACS in Denver (August, 2011), and Andrea was invited to present her results at the 2011 Aspen Meeting on Single Molecule Biophysics where she was the only non-faculty member to give a talk. Wes also has continued to pursue his work on heme-tagged proteins with the assistance of UR undergraduate Emily Redman. We congratulate Andrea who will be taking a research position at the University of Vermont starting this summer.

The Bren group is continuing our efforts to develop porphryin peptides for energy conversion in a collaborative project with the Eisenberg, Holland, and Krauss groups. The two new members who joined the group this year are focusing on this project. First-year student Shaun Shahan joined as a joint student with the Krauss lab and is developing porphyrin peptides for use in photoinduced charged transfer. He also is utilizing fluorescent zinc-substituted cytochromes to probe intermolecular interactions and, with the assistance of NSF-REU student Lisa Richter from Luther College, expressing a photosynthetic cytochrome c for further study. In addition, Anni Siitonen, a postdoc joint with the Krauss lab who also started in the past year, is engineering porphryin-

Interfaith Chapel



nanotube structures for long-range photoinduced charge transfer. Graduate student Lenore Kubie, also a Bren/Krauss joint group member, is studying protein-nanotube and peptide-nanotube interactions. Lenore is supported by an NSF IGERT grant in Distributed Renewable Energy and this summer is pursuing an internship at the National Renewal Energy Lab (NREL) in Colorado. Finally, Erin Knappen-Kleingardner is continuing her development of heme peptide expression and is writing her first manuscript resulting from the work. Erin and Anni also are mentoring an incoming biophysics student, Tom Hilimire, who is conjugating cytochromes and quantum dots for charge transfer. The group is enjoying seeing this work develop as we expand the collaborative aspects of the project.

A group alumnus, **LINGHAO ZHONG (PH.D. '03)**, informed us that that he has been awarded tenure at Penn State Mont Alto, making him the first graduate of the Bren lab to receive tenure. Although this news makes Kara feel old, she was thrilled to hear of his continued success.

Kara had another busy year, taking on the directorship of the Biological Chemistry Cluster and also chairing the Graduate Recruiting Committee. She also organized a symposium on Heme Modification, Transport, and Regulation at ACS in Anaheim (March 2011) along with Prof. Eric Hegg of Michigan State. This past year saw a lot of travel for Kara who gave invited talks at five conferences as well as at seven colleges and Universities.

Esther M. Conwell

Research Professor

Ph.D. 1948, University of Chicago

RESEARCH INTERESTS

Transport along the base stack in DNA; proton transfer in DNA; electrical and optical properties of organic semiconductors, particularly conjugated polymers.

CONTACT

conwell@chem.rochester.edu

An interesting finding obtained in our recent simulations for DNA with the code CP2K was the rapid contraction of a hole injected into the DNA. Immediately after injection, the hole wavefunction was spread over 5 adenines, the extent of the QM region. Within 20 to 25 femtoseconds the wavefunction was almost entirely contained on a single adenine. At 300K, the hole stays on this adenine for the length of the simulation, typically a few hundred femtoseconds. We considered three possible reasons for the contraction: (1) An electronegative nitrogen on adenine (N7 or N3) forming hydrogen bonds with water and in the process repelling the hole from all but one adenine; (2) a concentration of water molecules around one adenine, forming a stable region for the hole; (3) polarization of the surrounding water by the positive charge of the hole.

Carrying out our simulation, we found that, around the adenine with the hole, during the time the wavefunction contraction was taking place, the closest water molecules were still at least 4A away, a distance too great to allow the formation of a hydrogen bond. With time, diffusion brings water molecules closer to the adenine with the hole, but the earliest any appropriately oriented water molecule is seen to come within bonding distance is ~ 150 fs, well beyond the time scale in which the contraction occurs. The finding of such a low concentration of water near the adenines also rules out the possibility of the contraction mechanism being the elimination of the hole wavefunction from all but one adenine by the formation of hydrogen bonds between the electronegative nitrogens and water hydrogens on all the other adenines.

We found several types of evidence that the polaron contraction is due to the polarization of the water by the hole. The very short time required for the polarization can be attributed to the very rapid librational motion of the water, which allows correspondingly rapid rotation of the water dipoles. The time dependence we found for the size of the hole is consistent with there being two different librational modes with different frequencies, as is known to be the case for water. We showed also that localization of the hole on a single site led to the lowest energy of the system. Our work is significant in establishing that the steady state hole wavefunction, rather than extending over several adenines, is localized on one, a proposition that is still being debated by those working in the field.

Esther enjoyed working with her two undergraduate students: **COLIN KINZ-THOMPSON (B.S. '10)** who went on to Columbia for graduate studies, and Shane Kravec who is currently a senior in physics.

Esther with student Shane Kravec

Joseph P. Dinnocenzo

Professor of Chemistry

Ph.D. 1983, Cornell University

RESEARCH INTERESTS

Chemistry of organic ion radicals; mechanistic and physical organic chemistry.

CONTACT

jpd@chem.rochester.edu

JOE DINNOCENZO and his group continue to pursue a variety of problems in photoinduced electron transfer and related chemistry. As part of an ongoing collaboration with Samir Farid, we discovered that ground state electron transfers between neutrals and cation radicals have a rate constant/driving force dependence that surprisingly follows a simple Sandros-Boltzmann dependence. We also found that the charge shift, electron transfer quenching of excited pyrylium cations by neutral donors also had the same dependence. Most surprisingly, we found that excited state quenching of neutral cyanoaromatics by neutral electron donors had a Sandros-Boltzmann dependence on the driving force for electron transfer. Our results contrast with the well-known Rehm-Weller description of excited state electron transfer quenching (k_q) involving neutral donors and acceptors ($A^* + D \rightarrow A^{-\bullet} + D^{+\bullet}$), where a gradual fall off in log k_q vs ΔG is reported. This caused us to carefully reexamine all of the original Rehm-Weller data. Remarkably, when accurate redox potentials are used for the electron donors and acceptors, and when one excludes data points in the highly endergonic region that are not due to electron transfer, the quenching constants for the experiments described by Rehm and Weller were found to follow a Sandros-Boltzmann dependence on driving force! Perhaps more important from a mechanistic perspective, all of the reinvestigated Rehm-Weller reactions were found to proceed through exciplex intermediates. Historically, the Rehm-Weller reaction and numerous other similar reactions have been quantitatively modeled with electron transfer theories that all assume one-step complete transfer of an electron from a donor to an acceptor in contact. This is not the mechanism of the Rehm Weller reactions, which involve partial electron transfers from A^*/D to the exciplex and from the exciplex to $A^{-\bullet}/D^{+\bullet}$. Thus, it seems likely that our results will lead to the reinterpretation of a large body of previously published data, and will require the development of new theories to fit partial electron transfer reactions.

During the past year we have also solved a long standing puzzle in cation radical reactivity, namely understanding the unusual chemistry of aryltrimethylstannane cation radicals, which are unique amongst known Group 14 cation radicals in that they undergo Sn-C bond fragmentation to preferentially give the less stable aryl radical rather than a methyl radical. Our experiments show that the stannane cation radicals fragmentations are not unimolecular, as previously thought, but are nucleophile-assisted. This new reaction mechanism can readily explain the otherwise perplexing chemistry of these stannane cation radicals. Along similar lines, the group also continues to investigate new aspects of organosilane and organogermane cation radical chemistry.

Joe is also enjoying a pedagogical research project to introduce Peer Led Team Learning (aka Workshops) into CHM210 (Honors Organic Laboratory II). Joe is working with graduate student Terrell Samoriski, whose Ph.D. studies will involve design of the Workshop program and evaluation of its impact.

Campus Winter Scene

Richard Eisenberg

Tracy H. Harris Professor of Chemistry

Ph.D. 1967, Columbia University

RESEARCH INTERESTS

Inorganic and organometallic chemistry; artificial photosynthesis and light-to-chemical energy conversion; complexes of the platinum group elements (PGE's) and gold; homogeneous catalysis; photochemistry and photophysical properties of metal complexes; oxidative addition and bond activation chemistry; use of luminescent complexes in light emitting diodes; parahydrogen induced NMR effects in hydrogen addition reactions.

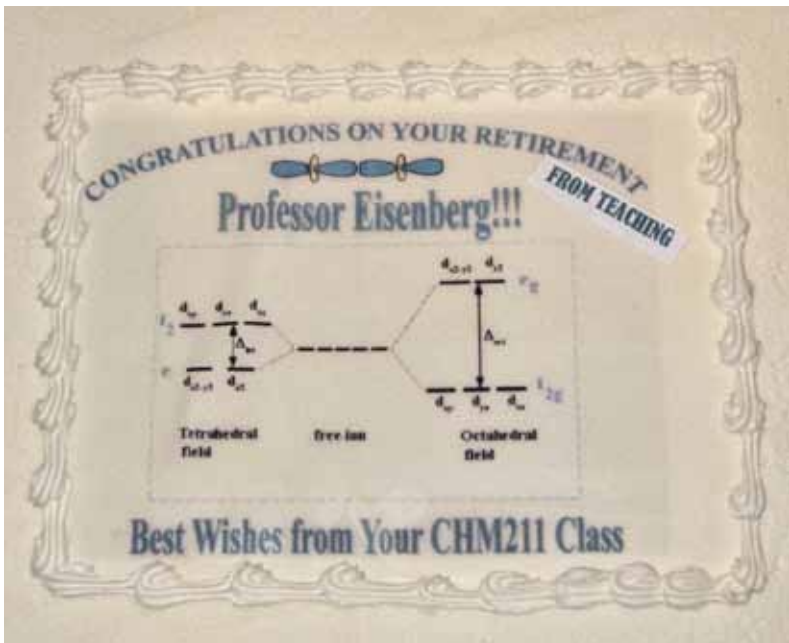
CONTACT

eisenberg@chem.rochester.edu

Another momentous year and one that **RICH EISENBERG** was happy to share with past and present students, colleagues and friends at "Richfest" in May. The celebration in honor of Rich's career (see p. 16) also marked a transition from full-time faculty member to research professor. Rich's formal teaching ended in the Fall 2010 semester with CHM 211, Advanced Inorganic Chemistry, an upper level undergraduate course he has taught for many years. The final lecture was marked with a student-designed cake and a champagne toast. While Rich loves the course and its material, he is also happy with no more tests and grading. Formal teaching aside, Rich and the Eisenberg group remain active and vigorous in the pursuit of science.

In July 2010, Rich was a plenary lecturer at the International Conference on Coordination Chemistry in Adelaide, Australia. The trip afforded Rich and Marcia the chance to snorkel on the Great Barrier Reef, see kangaroos, wallabies and koalas in the wild, and enjoy the beauty and vibrance of Sydney. After several trips to the west coast in January for the annual ACS Editors meeting and the NSF Center for Chemical Innovation on Solar Fuels (Rich is a Scientific Advisory Board member), the activities in 2011 ramped up. In March at the ACS Meeting in Anaheim, former student Pingwu Du and Rich were honored with the ACS Nobel Laureate Award for Graduate Education. The award symposium featured talks by Dan Nocera, **CLIFF KUBIAK (PH.D. '80)**, Phil Castellano and Harry Gray, in addition to the award address given mainly by **PINGWU DU (PH.D. '09)**. Interesting science and great fun was enjoyed by all. Also at the meeting, Rich participated in other symposia honoring long-time friends Alan Balch and Pete Wolczanski who were also award recipients. In April, Rich was formally inducted into the National Academy of Sciences, "one of the highest honors to which we can aspire." The induction ceremony was attended by Rich's immediate family. The subsequent NAS annual meeting included talks and workshops (Rich moderated one on sustainable energy), and ended with a black-tie ball (great music and dancing). In May, there was the special "Richfest" celebration, and the day after it was over, Rich and Marcia were off to Prague for a Conference on Solar Fuels, after which they journeyed to Florence and the Cinque Terra for vacation. For the latter, they met up with Maurice Brookhart and his wife to hike from town to town in one of the most charming locales

Rich & Marcia at the National Academy of Sciences Award meeting with family and friends



they have ever visited. The wine and food were great too! After Italy, Rich continued his travels onto Israel where he is chairing a committee of the Council for Higher Education to evaluate chemistry programs and research for all institutions which grant Ph.D.'s in Israel. The trip lasted 12 days with another planned in December. After returning home in late June, Rich returned to Europe a week later for the International Symposium on the Photochemistry and Photophysics of Coordination Compounds in Strasbourg, France, where he was a plenary lecturer. Rich reflects that this is hardly what he thought his transition would be - he now calls it "refirement."

This year marks the 50th volume of *Inorganic Chemistry*. The journal is doing well with special events planned to commemorate the golden anniversary year. One of these is a special symposium to be held at the ACS Meeting in Denver in August, while another is a series of interviews hosted by Rich that are on the web with leaders in the field (http://pubs.acs.org/page/inocaj/multimedia/voices.html). The interviews have been well received with favorable comments coming in from all over the world. Rich says the interviews are best enjoyed with a glass of wine and some time to ponder why chemists do what they do. He is especially gratified by teachers who say they will use the interviews in their courses (without the wine). Rich is also deeply appreciative of the tireless efforts put in by Arlene Bristol, Kirstin Campbell and spouse Marcia in the Editor-in-Chief's office, as well as by the Associate Editors, their assistants, and the many staff who keep the journal running so successfully.

The Eisenberg group continues to make progress developing and analyzing new systems for the photogeneration of H_2 from water which is the reductive side of water splitting and one of the key reactions for light-to-chemical energy conversion. Research on this problem is spear-headed by postdoctoral researcher Bill McNamara and graduate student Zhiji Han. Both Bill and Zhiji are co-advised with colleague Pat Holland under a DOE grant to Kara Bren, Todd Kraus, Pat Holland and Rich for a multi-pronged approach to the solar hydrogen challenge. Graduate student Randy Sabatini, who is co-advised with Dave McCamant, has also made significant progress in looking at ultra-fast processes involving dye sensitizers for H_2 generation. On iridium catalysis of electrocyclization reactions in a joint project with Alison Frontier, several articles were published on research by graduate student Tulaza Vaidya who has made presentations at the last two ACS Meetings and continued her streak in Denver in August.

Group comings and going for the year include the departure of postdoc Theresa McCormick who did wonderful research for two years as an NSERC Fellow on the photogeneration of hydrogen and the arrival of postdoc Will Eckenhoff from Duquesne who will also work on this problem. Undergraduate researcher Paul Alperin also carried out a notable senior research project and will start Ph. D. studies this Fall at Stanford University. Finally, as this article is being written, Jerry Manbeck, Rich's last solely advised graduate student, has defended his thesis on new luminescent Cu and bimetallic Cu/Au complexes, including an impressively bright one that contains a steroid derivative as a ligand. Jerry will be leaving shortly to assume a postdoctoral research position at Virginia Polytechnic Institute with Professor Karen Brewer.

Rich with students in his last class, Dec 2010

Samir Farid

Research Professor

Ph.D. 1967, Göttingen University

RESEARCH INTERESTS

Mechanisms and kinetics of photoinduced electron transfer reactions; fundamental aspects of ion pair dynamics and the kinetics of radiative and nonradiative electron transfer processes.

CONTACT

farid@chem.rochester.edu

The focus of **SAMIR FARID'S** research continues to be on electron transfer reactions and kinetics. Rate constants for thermal and photochemical electron transfer reactions were found not to follow a model that has been universally accepted for over 40 years. Instead, the new data, published in two papers in *JACS,* showed that the rate constants follow a simple Boltzmann-type dependency on the reaction free energy. Thanks to current work by Pu Luo, an exceptional graduate student in Joe Dinnocenzo's lab, the scope and limitations of the new model have been significantly expanded. For example, we now know that steric hindrance has a profound effect on thermal electron transfer reactions.

James M. Farrar

Professor of Chemistry

Ph.D. 1974, University of Chicago

RESEARCH INTERESTS

Dynamical studies of low energy ion-molecule reactions in the gas phase; imaging studies of collisions; photochemistry of size-selected ionic clusters.

CONTACT

farrar@chem.rochester.edu

JIM FARRAR continues to study low energy ion-molecule reactions, with special emphasis on ion-radical reactions using imaging techniques. He has been joined by postdocdoctoral fellow Linsen Pei, who received his Ph.D. degree from the University of Science and Technology of China, and most recently worked with Professor Chunlei Guo in the Institute of Optics. Linsen's superb experimental skills have been vital in bringing the new detection system up to speed.

Jim continues to work with the Kearns leadership center, along with the Office of Minority Student Affairs, to provide academic assistance to minority students interested in pursuing careers in science. This activity, supported by several dedicated, talented graduate students, has established a strong connection between Chemistry and University efforts to support minority student success in the sciences. Earlier this year, an NSF S-STEM grant for $598,000, for which Jim served as PI along with Beth Olivares from the Kearns Center, was awarded to the University in support of this work.

With support and encouragement of our late colleague Jack Kampmeier, Jim introduced Peer-Led Team Learning (PLTL) workshops into freshman chemistry over a decade ago. Based on the success of that initial effort, PLTL workshops have become an integral component of all of Jim's teaching. He has enjoyed working with many talented undergraduate and graduate student workshop leaders, and has particularly enjoyed collaborating with Dr. Catherine Perez from the Center for Teaching and Learning to help leaders become more effective peer mentors. The large number of students who volunteer to be workshop leaders is a strong testimony to the success of the program.

Rudi Fasan

Assistant Professor of Chemistry

Ph.D. 2005, University of Zürich, Switzerland

RESEARCH INTERESTS

Bioorganic chemistry and chemical biology; Synthesis and directed evolution of macrocyclic peptides and organo-peptide hybrids for molecular recognition and catalysis; Protein-protein interactions; P450 engineering and chemo-enzymatic C-H functionalization.

CONTACT

fasan@chem.rochester.edu

It has been a productive year for the **FASAN** group with a series of important achievements being realized in the lab, both in our P450-centered projects and within our efforts directed at constructing and evolving macrocyclic organo-peptidic structures for targeting protein-protein interactions. The year started well with a paper by post-doc Kaidong Zhang and UR undergraduate and McNair fellow Shady El Damaty being published in *Journal of the American Chemical Society*. This work introduced a method for mapping the active site of cytochrome P450s ('P450 fingerprinting') in order to rapidly assess and predict the reactivity of these enzymes. We found that through analysis of the P450 fingerprints, reliable predictions can be made regarding the catalytic activity of these enzymes toward substrates structurally related to the fingerprint probes and information can be obtained also regarding their regioselectivity properties. The group is currently investigating the potential of P450 fingerprinting and fingerprint analysis to enable the engineering of P450 C-H oxidation catalysts with tailored regio- and stereoselectivity, with first exciting results being obtained both in the context of the antimalarial artemisinin and the anticancer parthenolide. In the artemisinin project, Kaidong has been joined during the year by two talented UR undergraduates, Brian Shafer and Matthew Demars II. First-year graduate student Josh Kolev joined the group this year and he has been focusing on P450-mediated oxidation and chemoenzymatic functionalization of parthenolide, getting off to a great start in this project, which involves a collaboration with Professor Craig Jordan at the UR Medical Center.

During the past year, we also had a series of breakthroughs in our efforts toward developing chemo-biosynthetic strategies for generating macrocyclic organo-peptide hybrids. A first paper in this area, coauthored by Jessica Smith (third-year student) and Francesca Vitali (postdoc), appeared in *Angewandte Chemie* earlier this year and it was highlighted as a "Hot paper" in the same journal. UR undergraduate and McNair fellow Steven

Fasan Group, Summer 2011

Archer also contributed to the project. In a parallel study, Maragani Satyanarayana (postdoc), Francesca, and John Frost (second-year student) were successful in developing a highly efficient and catalyst-free method for constructing organo-peptide macrocycles via an oxime/intein-mediated dual ligation, which will be published in *ChemComm*. Building on these studies, John and his valuable undergraduate collaborator Nick Jacob succeeded in developing a strategy for synthesizing lariat and cyclic peptides in living bacteria cells, while another milestone was achieved by Jessica by implementing a bacterial display system for ultrahigh-throughput screening of our macrocyclic ligands against protein targets. John completed his second year oral exam in July and his outstanding performance as teaching assistant for CHM131 and CHM207 was recognized with a Walters Teaching Award in 2010 and the Peck Curtis Award earlier this year.

Other exciting news concerns the influx of funds to support the group's research. In spring, Rudi was selected as a recipient of the 2011 Provost's Multidisciplinary Research Award along with Prof. Craig Morrell (School of Medicine and Dentistry) and Prof. David Goldfarb (Biology) for a collaborative project related to the synthesis and bioactivity evaluation of chemoenzymatic artemisinin derivatives. The group was also awarded a grant from the National Science Foundation, which will support a three-year project aimed at developing and investigating macrocyclic organo-peptide ligands for selective recognition of oncoproteins Hdm2 and HdmX and disruption of their interaction with tumor suppressor p53.

The group has welcomed a number of motivated and enthusiastic UR undergraduate students to the lab this year: Brian Shafer, Matthew Demars II, Yick Chong Lam, Micah Brown, and Hojun Lee, who have helped in a variety of synthetic and protein engineering projects. Matt and Yick will continue work through the summer of 2011, with Matt being supported by a De Kiewiet fellowship from UR Department of Biology and Yick receiving support from the REU program. Jabari Henriques from North Carolina A&T State University will also join us for the summer as McNair Summer Research fellow. **JACQUELINE ZAENGLE (B.S. '11)** graduated in May, receiving the Merk Index Award in recognition of her academic and research accomplishments. Jacqueline carried out a senior thesis research project in the lab studying the effect of unnatural amino acid incorporation on P450 function. Rajesh Ravikumar, who worked elbow-to-elbow with Jacqueline on this project, will start graduate school at Carnegie Mellon in the fall. Shady El Damaty and Steven Archer, two former members of the group, will join the graduate program at Drexel University. Finally, the group wishes best of luck to **MARAGANI SATYANARAYANA (POSTDOC '10)**, who moved to a postdoctoral position at the University of Massachusetts Lowell.

Statue of George Eastman on the Eastman Quadrangle

Alison J. Frontier

Associate Professor of Chemistry

Ph.D. 1999, Columbia University

RESEARCH INTERESTS

Synthetic organic chemistry; synthesis of bioactive natural products; pericyclic reactions; asymmetric catalysis; discovery of new reactions catalyzed by transition metal complexes.

CONTACT

frontier@chem.rochester.edu

Professor **ALISON FRONTIER'S** research program is devoted to the planning and execution of syntheses of biologically and structurally interesting natural products. The study of Nazarov cyclization continues, as more and more variations on the cyclization are uncovered. The development of rearrangement chemistry gets more and more interesting, as have efforts to discover alternative starting points for the 4π electrocyclization. Work on asymmetric cyclizations and applications of Nazarov cyclization toward total synthesis of natural products continues. The study of diastereoselective hydrogenation of pyrroles is also underway, as well as efforts toward the synthesis of the natural products phomactin A, and cyanthawigins U and AC.

Tulaza Vaidya (fourth-year student, working jointly with Rich Eisenberg) has developed remarkably active Ir(III) complexes as Nazarov cyclization catalysts. This year she discovered and developed a new reaction pathway of furans and benzofurans, that only occurs using the reactive Ir(III) complexes. We continue to study rearrangement chemistry that occurs during Nazarov cyclization (Eric Theiste, fourth-year student; and Dr. David LeBoeuf), which is not only stereospecific but also highly chemoselective in most cases. The products have adjacent stereocenters, and also adjacent quaternary centers. Two additional interesting versions of the Nazarov cyclization were developed in the group this year: Bill Spencer (third-year student) studied initiation of Nazarov cyclization by oxidation of vinyl alkoxyallenes, and Josh Brooks (third-year student) has developed efficient Nazarov cyclization initiated by addition of nucleophiles to unsaturated diketones. All three of these variations give cyclopentane-containing products that are quite different from the cyclopentenone products of conventional Nazarov cyclization. Steven Jacob is continuing to develop methodology for the synthesis of complex pyrrolidines via diastereoselective and enantioselective hydrogenation of pyrroles,

In our natural product synthesis studies, Jen Ciesielski (fourth-year student) is getting closer and closer to the bridged oxadecalin structure of phomactin A, and Peter Carlsen (second-year student) has built a tetracyclic precursor to tetrapetalone A using interesting and efficient chemistry. Yu-Wen Huang is working on a streamlined and enantioselective synthesis of the potent antiproliferative roseophilin.

Frontier Group, Summer 2011

Joshua L. Goodman

Professor of Chemistry — Ph.D. 1984, Yale University

RESEARCH INTERESTS

Organic chemistry: use of two complementary techniques, nanosecond laser flash absorption spectroscopy and pulsed time-resolved photoacoustic calorimetry to observe transient reaction intermediates produced following an initial photochemical event.

CONTACT

goodman@chem.rochester.edu

The **JOSH GOODMAN** group has continued to investigate organic reaction mechanisms using a variety of time-resolved techniques such as pico- and nanosecond absorption spectroscopy and photoacoustic calorimetry. In particular, we have been examining processes in which electron transfer is coupled to bond breaking, and/or bond making. These bond-coupled electron transfer (BCET) reactions have the potential to drive chemical reactions using light. We have focused primarily on dissociative return electron transfer (DRET) reactions that involve cleavage of C-C, Si-Si and Ge-Ge bonds.

Memorial Art Gallery

Patrick L. Holland

Associate Professor of Chemistry — Ph.D. 1997, University of California, Berkeley

RESEARCH INTERESTS

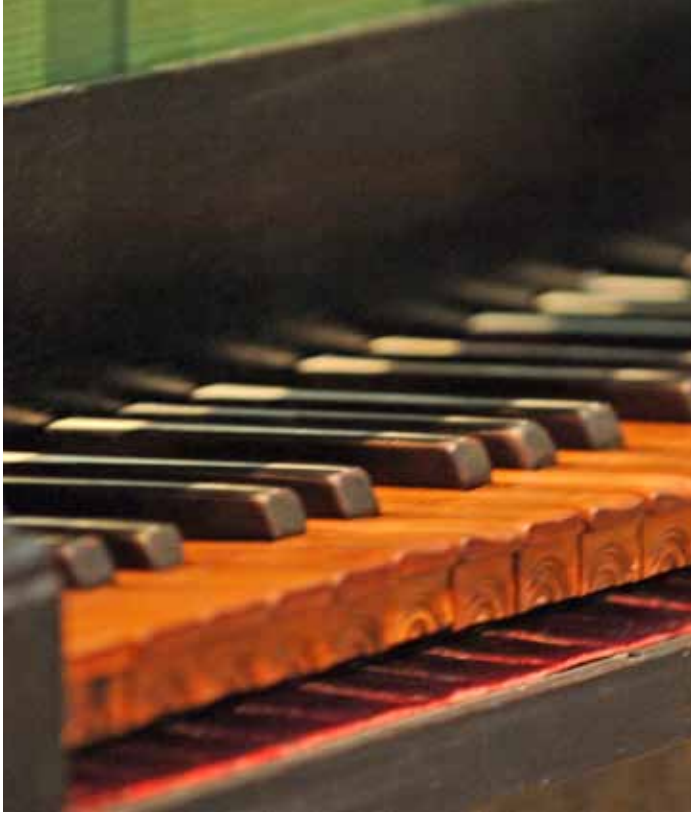
Synthetic inorganic chemistry: structure and function of models for metalloproteins, mechanisms of catalytic reactions, bioorganometallic chemistry.

CONTACT

holland@chem.rochester.edu

PATRICK HOLLAND and his research group continue to have fun with research on iron- and cobalt-containing compounds for catalysis. In an NSF-funded project on high-valent iron complexes with metal-ligand multiple bonds, our fundamental studies on three-coordinate complexes with Fe=N bonds led to three more papers from Ryan Cowley that appeared this past year. Sarina Bellows also succeeded in making a new supporting ligand that will lead to the next chapter in this effort! In a DOE-funded project on cobalt catalysis, Tom Dugan discovered an intriguing low-coordinate cobalt system that will soon appear in *J. Am. Chem. Soc.* Catalysis by the cobalt complexes has been the purview of postdoc Aydin Kavara, new graduate student Chi Chen, and undergraduate student Jonathan Goldberg. This grant also paid for a new X-band EPR spectrometer, which arrived in September. In an NIH-funded project on nitrogen reduction, Meghan Rodriguez discovered an iron system that is capable of breaking the N-N bond of N_2 and producing ammonia, the first time this has been done with iron in well-characterized complexes. In parallel, Karen Chiang completed the characterization of new iron complexes with hydride and thiolate ligands that help to understand nitrogenase.

In a collaborative project with the Eisenberg group, postdoc Bill McNamara and graduate students Matt McLaughlin and Zhiji Han each discovered a new photocatalytic H_2 production system. Matt's paper recently appeared in *Chemical Communi-*



cations, and Bill's and Zhiji's papers are expected to come out soon. This project is starting to incorporate biomolecules and nanoparticles from the Bren and Krauss groups, and we enjoy these collaborations within the department.

This year also saw a "labor of love" come to fruition, the publication of a chapter of Inorganic Syntheses devoted to diketiminate complexes. This chapter was co-edited by Pat together with Tim Warren (Georgetown) and Dan Mindiola (Indiana), and featured the work of many group members.

We welcomed a number of new researchers this past year. Postdoc P. M. Gurubasavaraj is our new Guru of synthetic chemistry. We were also joined by new graduate students Wenwen Yao and Chi Chen. Wenwen is expanding our N_2 reduction effort. Chi is a joint student with Dan Weix as co-advisor, and will develop practical organic transformations from our new cobalt catalysts. We also have had a number of summer visitors: Monica Boshart from Whitman College has been with us in the summers of 2010-2011, and **PROFESSOR BRIAN EDELBACH (PH.D. '99)** from Monroe Community College did research in our lab with two undergraduates these summers. Finally, we were happy to have **BEN DIBLE (POSTDOC '06-09)** back with us briefly to finish up a paper on palladium-carbene chemistry.

A number of group members were formally recognized for their achievements. These included Tom Dugan (Weissberger Memorial Fellowship), Karen Chiang (DeRight Fellowship), Ryan Cowley (Hooker Fellowship), Meghan Rodriguez (Lattimore Fellowship), and Zhiji Han (Sherman-Clarke Fellowship). Meghan and Karen also received Travel Awards to attend national ACS meetings. Ryan was chosen as the Chair for the internationally attended Gordon Research Seminar on Inorganic Chemistry that will be held in the summer of 2012. Ryan distinguished himself with a presentation in the 2010 Gordon Research Seminar, and Ryan and Karen stood out in the Gordon Conference with a special joke presentation at the end of the conference! Last but not least, Pat was proud of the group when they stepped up as a team (in his absence) to make a departmental presentation on techniques for safely disposing of spontaneously flammable compounds.

Pat has also had a successful year, with thirteen invited talks at universities and conferences. He wrote invited reviews that were published in *Dalton Transactions*, in *Angewandte Chemie*, in *Nature Chemistry*, and in a book on Nitrogen Fixation. The highlight of Pat's year was a five-month sabbatical at the University of North Carolina at Chapel Hill, where he learned about electrochemistry and electrocatalysis. This travel limited his teaching to courses on Group Theory and Inorganic Spectroscopy, which he enjoyed as always. This year, Pat was also recognized with a Volunteerism Award from the Rochester Section of the ACS in recognition of his work with the Harrison Howe Award, and received a Fulbright Scholar Award that will support a four-month trip to Germany in 2012.

In alumni news, **SALLY ROCKS (PH.D. '09)** moved to a position at FLSmidth, a mining company. **KEYING DING (PH.D. '09)** moved to a postdoctoral position with Bill Tolman and Marc Hillmyer at the University of Minnesota. **SALVADOR PEÑA (B.S. '08)** was admitted to the MD/PhD program at Rochester. **AMANDA MACK (B.S. '08)** moved to a teaching position at Phillips Andover Academy. **JEREMY SMITH (POSTDOC '00-03)** published a groundbreaking paper on a stable iron(V) nitrido complex in *Science*.

Tube Sealing in the lab