

CHEMISTRY 401: ORGANOMETALLIC CATALYSIS SEMINAR

Thursday, 1:10 – 4:00 pm, Tomsich 206

Prof. Yutan Getzler
Office: Tomsich Hall 308
Office hours: Tue – Thurs 9:40 am – 11 am, or by appointment
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Texts:

There is no required text for this course. There is one relatively inexpensive text for sale at the bookstore (*Catalysis* by Rothenberg). You may find an undergraduate inorganic text to be a useful reference. Other texts you may find useful can be located in the library in QD. 411 and include the following classics:

Principles and Application of Organotransition Metal Chemistry, 2nd ed. by Colman, Hegedus, Norton & Fink

The Organometallic Chemistry of the Transition Metals by Crabtree

Goals:

In this course we will study the formalisms of contemporary organometallic chemistry, focusing on the subfield of homogeneous catalysis. Our understanding will be built through close, critical reading of the primary literature.

Schedule:

Student-led discussions will begin on the fifth week of class, September 25th. Since you best know your schedules, I leave it up to you to decide who goes when. You will inform me by the beginning of class on September 4th. The specific topics of the last four classes will be determined by the class. This decision will be made by October 23rd, and responsibilities for those discussions will be divided up among all members of the class, myself included.

August 28th – historical overview, effective atomic number, ligand classifications, oxidation state, electron counting

September 4th – orbital topology, ligand field theory, common coordination numbers, common coordination geometries

September 11th – basic reaction steps; ligand substitution, oxidative addition, reductive elimination, insertion, extrusion, attack on coordinated substrate, others

September 18th – Prof. Schmidt visit; papers linked on website

September 25th – quiz (≤ 1 hr); catalysis: TON, TOF, selectivities, cycle, intermediates, pre-catalysts, initiators, kinetics

October 2nd – **Cooley/Hofferberth**: K. Noack, F. Calderazzo “Carbon Monoxide Inertion Reactions V. The Carbonylation of Methylmanganese Pentacarbonyl with ¹³CO” *J. Organometallic Chem.* **1967**, 10, 101

October 9th – No Class; October Reading Days

October 16th – **Getzler**: A. S. C. Chan, J. J. Pluth, J. Halpern “Identification of the Enantioselective Step in the Asymmetric Catalytic Hydrogenation of a Prochiral Olefin” *J. Am. Chem. Soc.* **1980**, 102, 5952

October 23rd – **Cooley**: G. W. Coates, R. M. Waymouth “Oscillating Stereocontrol: A Strategy for the Synthesis of Thermoplastic Elastomeric Polypropylene” *Science*, **1995**, 267, 217

October 30th – **Hofferberth**: D. Forster “On the Mechanism of a Rhodium-Complex-Catalyzed Carbonylation of Methanol to Acetic Acid” *J. Am. Chem. Soc.* **1976**, 98, 846

November 6th – whole class, topic to be determined

November 13th – whole class, topic to be determined

November 20th – individual: J. P. Collman, K. M. Kosydar, M. Bressan, W. Lamanna, T. Garrett “Polymer Bound Substrates: A Method to Distinguish Between Homogeneous and Heterogeneous Catalysis” **1984**, 106, 2569

December 4th – individual: L. E. Martinez, J. L. Leighton, D. H. Carsten, E. N. Jacobsen “Highly Enantioselective Ring Opening of Epoxides Catalyzed by (salen)Cr(III) Complexes” *J. Am. Chem. Soc.* **1995**, 117, 5897

December 11th – whole class, topic to be determined

Responsibilities:

Each member of the class will lead a discussion of two papers. These papers have been chosen because of their importance in the fields of organometallics or catalysis. These experimental works variously provided strong evidence consistent with a particular theory of bonding or reactivity, were early indications of what grew into important catalytic processes or were realizations of long held goals of the field. These papers feature a range of experimental techniques and theoretical assumptions, but all share clever design and close observation. This is consistent with the maxim that extraordinary claims require extraordinary evidence and while the ideas presented in these papers is now accepted as fact, there was a time when they were new and, in some cases, controversial. We will barely be scratching the surface of this rich, dynamic field, but hopefully this course will prepare you to pursue your interests wherever they lead you.

Leading an effective discussion of a paper may well involve topics not directly covered in the paper itself. Thus, while the paper at hand should be the center of any discussion, it by no means defines the boundaries. So, for example, if the paper focuses on the synthesis of stereoblock polyolefins by an oscillating metallocene catalyst, the discussion may include such related topics as polymer stereochemistry, Ziegler-Natta polymerization, catalyst activation, polymer characterization, potential commercial uses of the material, etc.

Each member of the class has responsibilities for each discussion.

Discussion Leader – To effectively lead a discussion of the paper at hand, one needs to know every aspect of the topic. This will likely involve not only thorough and repeated reading of the

paper and all supporting information, but also frequent reference to one or more of the suggested texts, reading of preceding and antecedent primary literature and one-on-one discussions with me. If you encounter material you feel the rest of the class would benefit from reading in preparation for the discussion, do not hesitate to pass it on.

You need not run the class in any particular format. However, I suggest that you avoid extensive reliance on lecturing as this tends to discourage a lively discussion. You are encouraged to experiment with how the class is run – creative class structure will be rewarded in your evaluations. As with all experiments, it may very well not go as planned. I am well aware of this and will not penalize you for well intentioned and well planned attempts which go horribly awry.

Finally, I expect that discussion leaders and I will have a fair amount of direct contact regarding the paper. At a minimum, I expect to see you in my office in the week preceding your discussion. This is an opportunity for you to discuss your plans for the class, get any last minute questions answered and go over the questions which have been received from the rest of the class.

Other course participants – You are expected to carefully study the paper to be discussed. This means multiple readings, taking notes on what you have read and sketching out molecular structures, spectra and reaction pathways. You are also quite welcome to stop by my office and discuss your studies with me. As a basic guideline, you should know the paper well enough to be able to complete the task noted below.

Starting the week of September 29^h, each week, each student will send at least two questions or comments to myself and the discussion leader by 5 pm on Tuesday. These questions are evidence of your study of the paper to be discussed and will be used to evaluate said preparation.

Point Distribution:

Discussion Leadership: 210

 Pairwise – $35 \times 1 = 35$

 Solo – $65 \times 2 = 130$

 Group – $15 \times 3 = 45$

Questions/comments – $20 \text{ pts} \times 7 = 140$

Mid-term quiz – 50

Final Exam – 100

Total – 500

Tests:

“Midterm” – This will be a closed-notes quiz on September 18th which will be one hour or less. It will test concepts such as electron counting, identification of an elementary reaction step, structure prediction based on coordination number and oxidation state, etc. You will be able to use the periodic table on the wall in Tomsich 206.

Final – The take-home final is due in my office by 4:30 pm, Friday, December 19th. For the purpose of the final you may use any material you used to prepare for the course. This includes textbooks you may have purchased or borrowed from the library, literature assigned or found on your own as background during the course, handouts, notes and your midterm exam. Any source you use must be cited. You may not in any way consult or work with any other sentient being. You may not use any websites or search engines. You may not use literature not already in your possession at the end of class on December 11th. There is no time limit, but the exam must be

completed in one sitting – once you stand up, your exam is complete. It is possible that the use of rolling chairs and adult diapers could effectively extend your exam time but seriously, do you really want to spend that much time on an exam?

Academic Honesty:

You are expected to follow the college policy for academic honesty. All materials submitted for credit must be your own work and the work must be done in accordance with the established rules of the course. The complete policy is available on the web (<http://www.kenyon.edu/x11747.xml>).

Section 504 of the Rehabilitation Act of 1973 and the Americans with Disabilities Act of 1990:

If you have a disability and need accommodation in order to fully participate in this class, please identify yourself to Erin Salva, Coordinator of Disability Services (PBX 5145, salvae@kenyon.edu). All information and documentation of disability is confidential. No accommodations of any kind will be given in this course without notification from the Coordinator of Disability Services.

This course constructed with inspiration from “A ‘Classic Papers’ Approach to Teaching Undergraduate Organometallic Chemistry” by A. P. Duncan and A. R. Johnson, *J. Chem. Ed.* **2007**, *84*, 443-446. Further thanks are due to A. P. Duncan for helpful personal communications about this course.