

The course will deal in general with transition metal organometallic chemistry with emphasis on topics related to homogeneous catalysis. The text for the course is "The organometallic chemistry of the transition metals, 5th edition" by Robert H. Crabtree (Wiley, 2009), but the 4th edition (2005) of the book will be adequate. An important aspect of the course will, however, be reading of significant journal articles that provide the underlying basis for the "principles" of organotransition metal chemistry.

The course grade will be determined on the basis of problem sets (40%) (see back of this page for policy on problem sets) and two "take-home" exams (30% each). There will also be regular in-class exercises. While no grade will be assigned, full participation is expected and individual participation will be used to resolve final grades that are "on the bubble".

A tentative outline for the course is given below. The actual content and order of discussion of topics may be somewhat different depending upon how the course evolves. Reading assignments from the text related to each of the topics are shown below. References to papers from the literature will be given prior to discussion in class.

1. Metal ligand interactions - **Chapter 1**
Effective atomic number concept (EAN) - **Chapter 2**
Physical methods commonly used in organometallic chemistry - **Chapter 10**
2. Kinetics of organometallic reactions and determination of mechanism - **Chapter 4, sections 3-7 plus handouts**
3. General syntheses of important classes of organometallics - **portions of Chapters 3-5 dealing with syntheses**
4. Reactions essential to homogeneously catalyzed processes.
 - a. Ligand exchange - **Chapter 4, sections 3-7**
 - b. Intramolecular rearrangements in metal complexes - **Chapter 10.5, 10.6**
 - c. Oxidative-addition/reductive elimination (including C-H activation and molecular hydrogen complexes) - **Chapter 6, Chapter 12.4**
 - d. Insertion/deinsertion - **Chapter 7**
 - e. Nucleophilic addition/electrophilic abstraction to/from coordinated ligands - **Chapter 8**
5. Catalytic cycles
 - a. Isomerization - **Chapter 9.1**
 - b. HX addition
 - i. Hydrogenation including asymmetric processes - **Chapter 9.2**
 - ii. Hydrosilation - **Chapter 9.5**
 - iii. Hydrocyanation - **Chapter 9.4**
 - c. Hydroformylation and other reactions of carbon monoxide - **Chapter 9.3, 12.3**
 - d. Olefin polymerization - **Chapter 12.2**
 - e. Formation and reactions of complexes of multiply-bonded ligands, i.e., carbene/alkylidene, carbyne, imido, nitrido - **Chapter 11, sections 1-2**
 - f. Olefin metathesis - **Chapter 12.1**
6. Carbon-carbon and carbon-heteroatom bond forming reactions utilized in modern synthetic organic chemistry. **Chapter 9.6, portions of Chapter 14**

Policy on Problem Sets

You may (and are encouraged to) work in groups in developing general outlines for responses to questions on problem sets; however, the specific answers to all questions must be done on an individual basis

You may consult the textbook, assigned readings and reference materials on electronic and molecular structure or spectroscopy in developing your answers.

Many problems are based upon literature precedent, sometimes an exact compound or reaction. You **may not** conduct literature searches for specific compounds or reactions as part of your effort to develop answers to problem sets.

Some problems may have been used on problem sets or exams in previous offerings of this course. You **may not** consult solutions to problems done by others.

Work Load

There were ten problem sets assigned in spring 2010 with a total of 40 problems plus a one page summary of a full paper from the recent literature. The first exam had 6 problems and the second exam had 8 problems.

Write/print on only one side of any paper to be turned in for grading.