**Chemistry 234** *Organometallic Chemistry* spring 2013

---

**Instructor**: Rory Waterman
Cook A-129
656-0278
rory.waterman@uvm.edu

**Lecture**: TR 8:30–9:45, Angell B-203

**Office hours**: Stop by as needed or feel free to make an appointment.

**Course outline**: I. A skirmish with kinetics
II. Transition metals and ligands
III. Reaction types
IV. Synthetic considerations
V. Catalysis

**Text**: (Optional) *Organotransition Metal Chemistry* by John Hartwig, ISBN = 9781891389535.

**Grading**: There will be two mid-term exams (20% each), a final exam (20%), problem-based homework (20%) and essays (ca. 2 pages/each; 20%).

**Homework**: Homework will be assigned approximately weekly and is due at the *beginning* of class on the date noted. Homework turned in within 24 hours of the due date will be given 50% credit and after 48 hours no credit. I will accept and correct homework after 48 hours: Practicing the concepts presented in class is more important than the grade on an individual assignment.

**Essays**: There will be 4–5 short written assignments (ca. 2–4 pages) dealing with fundamental topics in organometallic chemistry. Further details supplied in class. No homework or a limited problem set will be due on the weeks of an essay assignment.

**Web content**: Course materials are available at Blackboard (bb.uvm.edu)

**Important dates**:
Thursday February 26, exam 1
Tuesday April 16, exam 2
Tuesday April 30, last class
Tuesday May 3 at 1:30 pm, final exam

**No lectures**: Thursday 1/31
Monday – Friday 3/7–3/11

*The instructor reserves the right to make changes, with notice*

**Course description**: Organometallics, rigorously defined, deals with the interactions between metals and carbon-based molecules. The rich chemistry associated with metal complexes and main-group ligands has widened this description, and the editorial score of the journal *Organometallics* summarizes (albeit not concisely) the breadth of the field:

> For the purposes of this journal, an "organometallic" compound will be defined as one in which there is a bonding interaction (ionic or covalent, localized or delocalized) between one or more carbon atoms of an organic group or molecule and a main group, transition, lanthanide, or actinide metal atom (or atoms). Following longstanding tradition, organic derivatives of the metalloids (boron, silicon, germanium, arsenic, and tellurium) will be included in this definition. Furthermore, manuscripts dealing with metal-containing compounds which do not contain metal-carbon bonds will be considered as well if there is a close relationship between the subject matter and the principles and practice of organometallic chemistry. Such compounds may include, inter alia, representatives from the following classes: molecular metal hydrides; metal alkoxides, thiolates, amides, and phosphides; metal complexes containing organo-group 15 and 16 ligands; metal nitrosyls. Papers dealing with certain aspects of organophosphorus, organoselenium, and organosulfur chemistry also will be considered. In considering submissions that deal with subject matter that is peripheral to mainstream organometallic chemistry, our primary concern will be that the manuscript be of interest to our readers.

Our principal interest will be in organometallic complexes of the transition-series elements (groups 3–10). The elements of the *s*, *p*, and *f*-block certainly have interesting organometallic chemistry. The limits of time force us to largely ignore these elements. However, application of transition-metal complexes in catalysis and organic synthesis makes this course more topical. Of course, this class is conceptual in nature, and the fundamental principals we investigate are widely applicable throughout organometallic chemistry.

**Supplemental texts** (many on reserve in Bailey-Howe Library)

*Principles and Applications of Organotransition Metal Chemistry* by J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke; University Science Books, Mill Valley, California, 1987. ISBN: 0935702512.

*Organometallic Chemistry* by G. O. Spessard, G. L. Miessler; Prentice Hall, 1997. ISBN: 0136401783. Second edition: 978-0-19-533099

*Organometallics* (Third edition) by Christoph Elschenbroich; Wiley-VCH, Weinheim, 2006. ISBN: 3527293906

*The Organometallic Chemistry of the Transition Metals, 4th Ed.* by R. H. Crabtree; Wiley-Interscience, 2005. ISBN: 0471662569.

*Oxford Primer No. 12: Organometallics 1 – Complexes with Transition Metal-Carbon σ-Bonds* by M. Bochmann, Oxford University Press, Toronto, 2002. ISBN: 0198557507.

*Oxford Primer No. 13: Organometallics 2 – Complexes with Transition Metal-Carbon π-Bonds* by M. Bochmann; Oxford University Press, Toronto, 2001. ISBN: 0198558139.

Selected standard inorganic chemistry texts:

*Inorganic Chemistry* by Huheey, Keiter, and Keiter
*Inorganic Chemistry* by Shriver, Atkins, and Langford
*Inorganic Chemistry* by Meissler and Tarr
*Inorganic Chemistry* by Housecroft and Sharpe

## Course Outline

I. A skirmish with kinetics
- A. Definitions
- B. Integrated rate laws
- C. Activation parameters
- D. Key concepts

II. Fundamentals of transition metals and ligands
- A. Basics of metals
  1. Definitions and periodic trends
  2. Oxidation state and d-electron count
  3. Valence electron count
  4. 16/18 Electron rule
- B. Ligand types
  1. Pure σ-donors (alkyls, aryls, hydrides, hydrogen, silyls)
  2. π-Acceptors (CO, NO, $PR_3$, NHC, $BR_2$)
  3. π-Bound ligands (aklenes, alkynes, arenes, dienes, cyclopentadienyl)
  4. Multiple bonding (carbenes, nitrene/imido)
- C. Properties of metal-ligand complexes

III. Key reaction types
- A. Ligand exchange processes
  1. Dissociation/association
  2. Oxidative addition/reductive elimination
  3. σ-Bond metathesis
- B. Nucleophilic/electrophilic reactivity
- C. Insertions/eliminations
- D. Alkene and olefin metathesis

IV. Building organometallic complexes
- A. Reagents
- B. Synthetic methods

V. Catalysis
- A. Hydrogen-catalysis
- B. Polymerizations
- C. “Pd-catalysis” (cross-couplings, Ar–Ar, Heck, etc.)
- D. High energy processes
  1. C–H bond activation
  2. $N_2$ activation
  3. Water-splitting
- E. Olefin metathesis
- F. Other hot topics (Au catalysts, Cu, etc)