

Syllabus: CHEM 5620
Selected Topics in Inorganic Chemistry:
Transition Metal Organometallic Chemistry and Catalysis
Spring Semester 2017 (3 credit hours)

- Instructor:** Dr. LeGrande M. Slaughter
Chemistry Building Rm. 307E
Office phone: 565-4350; legrande.slaughter@unt.edu
- Lecture:** Tues, Thurs 11:00 am-12:20 pm, CHEM 331D
- Required Text:** *Organotransition Metal Chemistry: From Bonding to Catalysis*
John Hartwig, University Science Books, 2010.
- Office Hours:** Monday and Wednesday, 1:30 – 3:00 pm; other times by request
- Prerequisites:** Permission of the instructor. CHEM 4610/5560 is recommended but not required. Familiarity with elementary molecular orbital theory is expected.
- Objectives:** The course provides an introduction to the synthesis, structure, bonding, reactivity, and catalytic applications of transition metal organometallic compounds. The primary emphasis will be on the fundamental reaction types of organometallic compounds, their mechanisms, methods for studying them, and their relevance to important processes in industrial catalysis and organic synthesis.
- Grades:**
- | | | |
|---------------------|-------------|------------------|
| Problem sets: | 150 points | (10 X 15 points) |
| Oral paper summary: | 50 | |
| Examination #1: | 250 | |
| Examination #2: | 250 | |
| Final Examination: | 300 | |
| | <hr/> | |
| | 1000 points | |
- Letter grade scale:**
- | | |
|---|-----------------|
| A | 880-1000 points |
| B | 750-879 |
| C | 620-749 |
| D | 500-619 |
| F | 0-500 |

Topic Outline (subject to adjustments)

| | <u>Text Sections</u> |
|---|----------------------|
| I. Introduction and Background | |
| A. Features of Organometallic Complexes | Ch. 1.1 |
| B. Periodic Trends of Transition Metals | <u>Ch. 1.2</u> |
| C. Electronic Structure and Bonding | <u>Ch. 1.3</u> |
| D. Electron Counting and the 18 e ⁻ Rule | <u>Ch. 1.3</u> |
| II. Organometallic Complexes & Ligands | |
| A. Ligand Types; σ - and π -Bonding | <u>Ch. 2, 3, 4</u> |
| B. Metal-Ligand Multiple Bonds | <u>Ch. 13</u> |
| III. Fundamental Reactions of Organometallic Compounds | |
| A. Ligand Substitution | <u>Ch. 5</u> |
| B. Oxidative Addition | <u>Ch. 6, 7</u> |
| C. Reductive Elimination | <u>Ch. 8</u> |
| D. σ -Bond Metathesis | <u>Ch. 6.5</u> |
| E. Migratory Insertion and Elimination | <u>Ch. 9, 10</u> |
| F. Nucleophilic/Electrophilic Attack on Coordinated Ligands | <u>Ch. 11, 12</u> |
| IV. Catalysis | |
| A. Hydrogenation & Related Reactions | <u>Ch. 15, 16</u> |
| B. Hydroformylation, CO Activation | <u>Ch. 17</u> |
| C. Olefin and Alkyne Metathesis | <u>Ch. 21</u> |
| D. Olefin Polymerization/Oligomerization | <u>Ch. 22</u> |
| E. Coupling Reactions | <u>Ch. 19</u> |
| F. Allylic Substitution | <u>Ch. 20</u> |
| G. C-H Activation & Functionalization | <u>Ch. 18</u> |

Lecture Materials:

Lectures will be based on a variety of sources, including classic and recent organometallic literature. The goal will be to bridge the gap between basic inorganic/ organometallic concepts and current research. The Hartwig text is an excellent supplementary and reference text, but reading the text is not a substitute for attending lectures.

Problem Sets:

Approximately 10 problem sets will be assigned. These are intended to help you learn the material, and each student should work on them individually. It is acceptable to discuss problems with other students, but sharing or copying answers is unacceptable and may result in penalties. Problem sets will be due at the beginning of class one week after they are assigned. Solutions will be provided after the due date. Any late assignments will receive a grade penalty of 10% for each day until turned in.

Midterm Examinations:

Two midterm exams will be given during regular class hours (Tentatively February 23 and April 13; 80 min each). Exams will be closed book, i.e. no notes or textbooks may be used. Students may miss exams only with valid excuses (e.g. death in the family, serious illness with note from doctor). No make-up exam will be given; the final grade will be calculated based on the other components (e.g. a point total of 750 will correspond to a grade of 100%).

Oral Paper Summary:

Because acquainting students with current organometallic research is one goal of this course, students will be asked to present a short summary (~20 min) of a recent communication or short article (≤6 pages) from the literature near the end of the course. The presentation should briefly cover the background, highlight the key results, and critically analyze the importance of the work.

Final Examination:

The final exam will take place on Tuesday, May 9 from 10:30 am - 12:30 pm. The final will be a cumulative, closed book examination. Students missing the final exam who notify the instructor of the reasons for their absence by noon of the day following the scheduled time for the exam will receive a grade of incomplete ("I") for the course and must arrange a time for a make-up examination with the instructor (before the end of the first week of classes of the next semester). If there is no valid excuse for the absence, there will be a fifteen-percent penalty on the exam. Student who miss the final exam and do not notify the professor of the reason by noon of the following day will receive a score of zero on the exam.

Attendance

There is no grade for attendance, but it is in your best interest to attend all lectures given the large amount of material to be covered. If you must miss a lecture, please inform the instructor in advance and make arrangements to pick up handouts for the class you missed.

Auditing

Students who wish to sit in on the class without receiving credit may audit the course. Graduate students should obtain the approval of their research advisor before auditing the course.

Credit for CHEM 4900: Special Problems

Undergraduates may enroll for Special Problems credit with the instructor's approval. CHEM 4900 students must complete at least 600 points worth of Exams and Problem sets (for example, two Midterms and seven problem sets (605 points); or the Final plus one midterm and four problem set (610 points). In addition, a *written* summary of a current research paper, similar in content to the oral paper summaries by 5620 students, will be due at the end pre-Finals week and will earn up to 100 points. The letter grade scheme on p. 1 will be followed, with the point total determined as $[(\text{points earned})/(\text{maximum points})]*1000$. If students complete more than 600 points of Exams and Problem Sets, the "maximum points" will reflect >700 points, and/or the items with the lowest grades will be dropped – whichever gives the higher overall grade.

Important Dates

| | |
|--------------------|--|
| <u>January 30</u> | Last day to drop a course without instructor's consent |
| <u>February 23</u> | Midterm Exam #1 (tentative) |
| <u>March 13-19</u> | Spring Break (no classes) |
| <u>April 4</u> | Last day to drop course with a grade of "W" or "WF" |
| <u>April 13</u> | Midterm Exam #2 (tentative) |
| <u>May 2, 4</u> | Pre-Finals Week; Oral Paper Summaries |
| <u>May 9</u> | Final Examination 10:30 am - 12:30 pm. |

Suggested Supplemental Reading

Organometallic Introductory Text

Crabtree, R. H.. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 2005. (Newer versions available in print)

eBook available through UNT libraries:

<http://site.ebrary.com/lib/unt/docDetail.action?docID=10299695>

Excellent overview and conceptual introduction to the field; good "training wheels."

Organometallic Reference Text

Elschenbroich, Ch.; *Organometallics*, 3rd Ed.; Wiley-VCH: Weinheim, Germany, 2005.

Comprehensive survey of synthesis, structure, bonding, and reactivity, including both main group and transition metal organometallics.

Applications in Organic Synthesis

Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 2009.

Kinetics and Mechanism

Jordan, R. B. *Reaction Mechanism of Inorganic and Organometallic Systems*, 2nd Ed.; Oxford Univ. Press: New York, 1998.**

NMR Spectroscopy

Pregosin, P. S. *NMR in Organometallic Chemistry*; Wiley-VCH: Weinheim, Germany, 2012.

General Inorganic Chemistry: Concepts

Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, 3rd Ed.; Pearson: Upper Saddle River, NJ, 2004.** (Newer versions available for purchase)

General Inorganic Chemistry: Reference

Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th Ed.; Wiley: New York, 1999.**

** These books will be available for 2 hour loan at the Willis Library Services Desk. Bring your ID and give the passcode **orgmetlms**

Recommended Journals and Electronic Resources

Journals: General/High Impact

Journal of the American Chemical Society
Angewandte Chemie, International Edition
Chemical Science
Chemical Communications

Journals: Specialized

Organometallics
ACS Catalysis
Dalton Transactions
Organic Letters

Databases

SciFinder Scholar

Available from www.library.unt.edu under "Databases"
Many searching options (chemical structure, formula, keyword, author, etc.).
Includes most articles ever published (including old and out-of-print journals)

Web of Science

Available from www.library.unt.edu under "Databases"
Good for searching citations to a given article. However, only covers articles published in the past 20 years.

Cambridge Structural Database

Contains every X-ray crystal structure ever published for non-biological molecules containing at least one C-H bond (including organic and organometallic compounds).

Excellent for searching metal-ligand complexes and analyzing structural features (e.g. metal-carbon bond lengths, bond angles in ligands).

Web-based version (WebCSD; can only be accessed from on-campus computers):
<http://webcsd.ccdc.cam.ac.uk/>

Full version available on DVD for installation on UNT research computers (see Sabrina Gilbreath in the Stockroom office, CHEM 195B)