THE UNIVERSITY OF TEXAS AT TYLER

FALL 2023 RBS 2015, 6-8:45 PM

Dr. Jason Smee

Contact Info

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Office Hours

- MWF 10:30-11:30 am
- TR 9–10 am
- and by appointment
- Zoom link for office hours (please email me in advance so I can get Zoom running)

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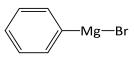
CHEM 4399.002 Ind. Study: Organometallic Chemistry

Course Description

Synthesis, bonding, and reactivity of transition metal and main group organometallic compounds and their applications in organic synthesis, catalysis, and nature. A list of topics is provided later in the syllabus. A few example compounds, prepared in ChemDraw, are shown below.







<u>Organometallic</u> (adjective): of, relating to, or being an organic compound that usually contains a metal or metalloid bonded directly to carbon

- Merriam-Webster dictionary

Required & Recommended Materials



The **recommended** text is *The Organometallic Chemistry of the Transition Metals*, 7/e by Crabtree (ISBN: 9781119465867)

(Image from https://www.wiley.com.)



A scientific calculator (capable of exponents and logarithms) is **required**.

(Image from https:// www.schoolspecialty.com/ casio-scientific-calculator-035399.)

Other Useful References

- Inorganic Chemistry 4/e by Miessler and Tarr; ISBN 13:9780136128663
- Inorganic Chemistry 4/e by Housecroft and Sharpe; ISBN-13: 9780273742753
- Inorganic Chemistry 7/e by Weller et al. ISBN-13: 9780198768128.
- The Organometallic Hyper Textbook http://www.ilpi.com/organomet/index.html
- We also look at some "classic papers" of organometallic chemistry. You will also give a 15-minute
 presentation on a current journal article of your choosing. Therefore, you will need to be able access,
 among others, the ACS journals through the UT Tyler library website (<u>library.uttyler.edu</u>). If you need
 to access the library while off campus please visit the <u>Connecting from Off-Campus: Welcome page</u>

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Cacodyl, also known as tetramethyldiarsine, is widely considered the first organometallic compound; prepared by Cadet de Gassicourt in 1757. (Image from Wikipedia.)

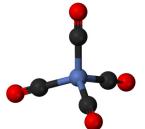
Recording of Class Sessions

I will not be recording my lectures unless student accommodations or extenuating circumstances require it. Please note that some recordings may contain personally identifiable information or other information subject to FERPA. They shall not be shared with individuals not enrolled in this course unless appropriate consent is obtained from all relevant students. Class recordings are reserved only for the use of students enrolled in the course and only for educational purposes. Course recordings should not be shared outside of the course in any form without express permission.

Student Learning Outcomes

By the end of this course, students should be able to

- 1) Count electrons according to the neutral ligand and donor pair methods
- 2) Use Molecular Orbital (MO) theory to explain the bonding in a variety of transition metal complexes
- 3) Propose syntheses of organometallic complexes
- 4) Recognize fundamental organometallic reactions (e.g. β elimination)
- 5) Predict products of reactions catalyzed by organometallic complexes
- 6) Extract key concepts from classical and current journal articles
- 7) Effectively present a summary of the results of a journal article relating to organometallic chemistry.



Tetracarbonylnickel(0), Ni(CO)₄, was discovered by Mond in 1890. It is one of the first "carbonyl" compounds and is a gas at room temperature. The Mond process is used to purify crude nickel ore. (Image from Wikipedia.)

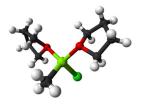
Course Requirements

- 1) One semester of undergraduate inorganic chemistry similar to CHEM 3320 and/or CHEM 4330 is strongly suggested.
- 2) We meet Mondays from Aug 21 to November 27, except Thanksgiving week (Nov 20th-24th). Attendance will be taken and class participation will be sought to nurture student communication and presentation skills.
- 3) You will be required to give a 15-minute presentation over a journal article obtained from such journals as *Organometallics* (ACS), *The Journal of Organometallic Chemistry* (Elsevier), and *Applied Organometallic Chemistry* (Wiley).
- The cumulative final exam will be on Monday, December 4th from 6-8 pm and must be taken to pass the course.

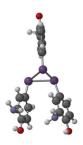


Zeise's salt, potassium trichloro(ethene)platinate (II) (the anion is shown) is the first organometallic complex containing a transition metal; prepared by Zeise in 1827. (Image from Wikipedia.)

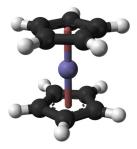
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Grignard reagents, such as CH₃MgCl (shown above as the bis-tetrahydrofuran adduct) were developed in the late 1890s. (Image from Wikipedia.)



Salvarsan, shown above as the trimer of 2-amino-4arsanylphenol, was developed in 1914 by Erlich as a treatment for syphilis and was one of the earliest chemotherapeutics. (Image created from Spartan '10.)



Ferrocene, $[Fe(C_6H_5)_2]$, was first isolated by Pauson in 1951 after a failed attempt to make fulvalene. This "sandwich" compound was the "catalyst" that really got organometallic chemistry going. (Image from Wikipedia.)

Exams (17.65% per exam, 35.3% total)

- Two mid-term exams will be given during class time and are collectively worth 30% of your overall grade. They will be mostly short answer/calculation questions and some multiple choice. I will inform you where the material will be cutoff at least one week before the exam.
- Missed exams due to an unexcused absence will result in a grade of zero. In the event of an excusable situation, please give me at least two days' notice (if possible) to schedule an alternate time.
- 3) Cell phones, smart watches, and any similar electronic devices must be turned off and put away during exams. If they observed out in a visually accessible place (i.e. between legs, on the floor, etc.), it will be assumed that they are being used to cheat; your exam will taken away, you will receive a zero score (0 points) for the test, and you will be referred to the Office of Judicial Affairs.

In-Class Presentation (not required for undergrad students)

Towards the end of the semester you will be asked to give a 10-15 minute presentation (15% of your overall grade) summarizing the results of an article or communication (i.e. a mini-article) relating to a topic in this class. The paper, published within the last 5 years, should involve either the synthesis of an organometallic compound or the use of such a compound as a catalyst. If you are unsure of whether a paper is suitable, please ask me. Good journals to look through are *Organometallics* (ACS), *The Journal of Organometallic Chemistry* (Elsevier), and *Applied Organometallic Chemistry* (Wiley); although there are others as well. <u>NO-RE-</u> *VIEW ARTICLES!*

Your paper must be pre approved by me, no later than two weeks before the date of the presentations. The grade will be based primarily on organization, style, clarity, and the ability to answer questions related to this course. A full rubric will be provided later in the semester to help with the planning of your presentation.

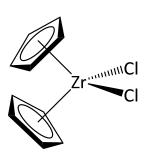
Homework (35.3%)

Homework (30% of your overall grade) is comprised of 1) problem sets; and 2) questions regarding assigned reading of classic and some contemporary papers. Each assignment will be due at the beginning of class.

Final Exam (29.4%)

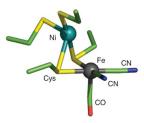
The final exam (25% of your overall grade) is an instructor-written exam that is comprehensive over all the semester's material.

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Dichlorobis (cyclopentadienyl) zirconium(IV) is an example of a homogeneous catalyst used for the polymerization of polypropylene. (Image prepared in ChemDraw.)

Cobalamin, also known as vitamin B12 (shown here as the cyano complex), was the first known bioinorganic compound. It plays a significant role in many biological processes. (Image from Wikipedia.)



Using isotopic labeling, IR studies confirmed that the iron-only and nickel-iron hydrogenase (shown above) enzymes required "toxic" ligands such as CO and CN⁻ to function. (Image from Shriver 6/e.)

Grading

- All grades will be shown on Canvas
- Grades will be tentatively based on a 90/80/70 scale, but may be adjusted based upon my evaluation of the class's overall performance.

Total	100%
Cumulative final exam	29.4%
Homework	35.3%
2 In-class exams	35.3%

Canvas

I will utilize Canvas to post the following items

canvas

- syllabus
 lecture notes
- 3) grades (my Excel grade book has the official grades)

You may be asked to submit portions of homework assignments through Canvas as well.

Important Dates

(Note: exam and presentation dates are tentative; final exam date and time is fixed)

- September 1 (Friday): Census Date; last day to file for grade replacement
- October 2: Exam 1
- Oct 30 (Monday): Last Day to Drop with a "W"
- November 13: Exam 2
- November 20-24: Thanksgiving, no classes
- November 27: Presentations
- December 4 (Monday): Final Exam, 6-8 pm

Topics to Be Covered (Chapter Numbers are from Crabtree)

- Review: quantum numbers, electron configurations, and molecular orbital (MO) Theory
- Chapter 1: Introduction (review of nomenclature, geometric and stereo isomers, Lewis acid-base theory, hard-soft acid-base theory, and crystal/ligand field theory)
- Chapter 2: Making Sense of Organometallic Complexes
- Chapter 3: Alkyls and Hydrides
- Chapter 4: Carbonyls, Phosphines, and Substitution
- Chapter 5: Pi-Complexes
- Chapter 6: Oxidative Addition and Reductive Elimination
- Chapter 7: Insertion and Elimination
- Chapter 8: Addition and Abstraction
- Chapter 9: Homogeneous Catalysis
- Chapter 11: M–L Multiple Bonds
- Chapter 12: Applications