Chemistry 579: Coordination Chemistry Applied to Catalysis

Special Topics in Inorganic Chemistry, Spring 2021, Rutgers University-Newark

Instructor: Prof. Demyan Prokopchuk
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Class Time and Location: Thursdays 6:00 – 8:50 PM via Cisco WebEx https://rutgers.webex.com
Class Material: Available on Canvas https://canvas.rutgers.edu/
Office Hours: by appointment (WebEx), please email me to arrange a time.

Overview

This course will range from classical to modern aspects of coordination chemistry and catalysis using transition metals surrounded by ligands. Fundamental ligand design principles such as coordination number, binding mode, charge, spin state, and sterics will be presented. The coordination of different ligand classes to transition metals will be correlated with reactivity trends and catalytic activity. Students are expected to develop a rational approach in assessing the reactivity of metals/ligands using electronic structure and thermodynamic arguments. Particular emphasis will be placed on hydrogenation, small molecule activation, "non-innocent" ligands, and (electro)catalysis.

Class Schedule (Thursdays 6:00-8:50 PM ET)

Week	Date	Lecture #	Topic
1	Jan 21	1	Metals, Ligands, and Bonding
2	Jan 28	2	Important Ligands in Catalysis
3	Feb 4	3	Reaction Mechanisms
4	Feb 11	4	Reaction Mechanisms; Sterics and Electronics
5	Feb 18	5	Cross-Coupling and Olefin Metathesis **(Assignment 1 Due)**
6	Feb 25	6	Non-Innocent Ligands
7	Mar 4	7	Hydrogenation of Nonpolar Bonds
8	Mar 11	8	Hydrogenation of Polar Bonds **(Assignment 2 Due)**
9	Mar 18		**Spring Break – No class**
10	Mar 25	9	Thermodynamics of M-H Bonds **(Essay Topic Due)**
11	Apr 1	10	N2 Reduction
12	Apr 8		Inorganic echem, electrocatalysis; Selected Recent Papers
13	Apr 15		Presentations **(All Essays Due)**
14	Apr 22		Presentations
15	Apr 29		Presentations; Literature Discussion – Selected Recent Papers
Final	**TBD**		**Date TBD**

Course Objectives

During this course, you will:

- identify major ligand classes coordinated to transition metals
- study transition metal complexes and their reactivity by evaluating a ligand sterics, electronic structure, coordination geometry, acidity/basicity, redox potential

- establish general trends of ligand coordination and reactivity across the transition metal series
- identify how ligand(s) affect the product outcome for important reactions catalyzed by homogeneous transition metal complexes
- prepare an essay summarizing an important reaction/process catalyzed by homogeneous transition metal compounds (**choosing a suggested essay topic is strongly recommended**)
- build your presentation skills by summarizing your essay in a clear and concise manner
- discuss and critique recent literature in the field of coordination chemistry and ligand design

Lectures and Course Material

Real-time (synchronous) lectures will occur virtually at the scheduled time via Cisco WebEx Meetings – **everyone is expected to attend lectures at the scheduled class times. If this is not possible due to technical issues or a situation beyond your control, please notify me as soon as possible.** Lectures will be recorded and all other course material (assignments, exams, grades) will be managed through Canvas. Lectures will be recorded and posted online to Canvas after each class. If a real-time lecture is not possible due to technical difficulties with WebEx, lectures will be recorded offline and posted to Canvas as soon as possible.

Please remember that:
Lectures and materials utilized in this course, including but not limited to videocasts, podcasts, visual presentations, assessments, and assignments, are protected by United States copyright laws as well as Rutgers University policy. As the instructor of this course, I possess sole copyright ownership. You are permitted to take notes for personal use or to provide to a classmate also currently enrolled in this course. Under no other circumstances is distribution of recorded or written materials associated with this course permitted to any internet site or similar information-sharing platform without my express written consent. Doing so is a violation of the university's Academic Integrity Policy (https://policies.rutgers.edu/sites/default /files/10.2.13%20-%20current.pdf). Similarly, these copyright protections extend to original papers you produce for this course. In the event that I seek to share your work further, I will first obtain your written consent to do so.

Required Textbooks (see Reading List on Canvas)

1. Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 6th Edition; John Wiley and Sons Inc., 2014. (selected chapters)
2. Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books, 2010. (selected chapters)
3. *Ligand Design in Chemistry: Reactivity and Catalysis*; Stradiotto, M.; Lundgren, R. J., Eds.; John Wiley and Sons Inc., 2016 (selected chapters)

Additional Resources (see Reading List on Canvas)

Although not required, this textbook will be useful for the course:

1. Jean, Y. *Molecular Orbitals of Transition Metal Complexes*; Oxford University Press, 2005. (digital version available)

Grading and Evaluation

Assignments: 30%
Essay: 30%
Presentation: 20%
Final Exam: 20%

Assignments (30%)

Hand-written assignments can be submitted to me in person (LSC 200) or digitally submitted through Canvas. For example, you can take high-resolution photos or scan your assignment pages and upload them to Canvas before the deadline. Assignment questions will broadly cover topics related to coordination chemistry, ligand design, and catalysis taught throughout the course. ***Assignments must be hand written and submitted before the beginning of class on the due date. Late assignments will be penalized by 20% for every 24 h they are overdue (5 days overdue = 0%!).***

Essay (30%)

Each student will write an essay (10-15 pages, Times New Roman 11 pt, double spaced, 2.54 cm margins). If using ChemDraw (available for free at software.rutgers.edu), use "ACS Document 1996" formatting (File → Apply Document Settings From… → ACS Document 1996). See suggested essay topics on the next page. You should:

- identify the unique features of the ligand(s)
- how metal/ligand combinations are suited for the reactions they facilitate
- describe reaction trends with metal/R-group variations.
- mechanisms for catalyzed reactions should also be presented and discussed (e.g. rate-determining step(s), resting state(s), possible deactivation pathways).

Essays must be submitted online before the due date along with a paper copy submitted before class. Late submissions will be penalized by 5% for every 24 h they are overdue.

Suggested Essay Topics (key researchers shown in **bold**)

- complexes containing phosphine ligands with pendant amines (PNP, P_2N_2) for electrocatalytic H_2 oxidation or H^+ reduction (**Bullock, DuBois**)
- metalloporphyrin complexes for the following electrocatalytic reactions (pick only one):
    - CO_2 reduction (**Saveant**, **Costentin**)
    - H_2 production (**Nocera**)
    - O_2 reduction (**Mayer**)
- *N,N'*-bis(salicylidene)ethylenediamine (salen) ligands for the asymmetric epoxidation of olefins (i.e., **Jacobsen-Katsuki** epoxidation)
- Fe and Ru cyclopentadienone complexes in catalysis (**Shvo, Casey**)
- impact of organophosphine vs. and N-heterocyclic carbene ligands on ruthenium-catalyzed olefin metathesis (i.e., **Grubbs** catalysts)

- bidentate phosphine ligand design for the hydroformylation of alkenes (**van Leeuwen, Reek**)
- aerobic oxidation catalysis of organic molecules using late transition metals (**Stahl**)
- C-C coupling reactions with open-shell 1st row transition metal catalysts (i.e., α-diimine or bis(imino)pyridine ligands; **Chirik**)
- Fe- and Ni-catalyzed olefin polymerization catalyzed by diimine ligands (**Brookhart**)
- recent advances in ligand design for the catalytic reduction of N_2 to NH_3/N_2H_4 (**Peters, Nishibayashi**)
- catalytic alkane dehydrogenation using pincer (PCP) ligands (**Goldman, Goldberg**)
- Activation of E-H bonds (E = H, N, O) by aromatization-dearomatization of pincer ligands (PNP, PNN, CNN, etc.) (**Milstein**)

If you really wish to prepare an essay on a different subject, please speak with me.

Presentation (20%)

The presentation will be based upon your essay topic (25 min. presentation with 5 min. for questions). You should:

- introduce the field of study (motivation, challenges, goals, etc.) to the audience in a clear and concise manner
- compare and contrast the effects of different variables (metal, charge, spin state, oxidation state, electronics, sterics) for the reaction(s) under investigation
- show a general reaction mechanism and highlight important reaction steps (rate determining, selectivity determining, deactivation, etc.)
- select one or two papers from the recent literature (< 5 yrs. old) to inform the audience with cutting-edge work in the area

Final (20%)

This will be an "open book" exam with a limited timeframe for completion. *The academic integrity policies described below still apply!* Exam distribution and submission will be through Canvas. **The exam must be hand-written and then digitally submitted through Canvas.** For example, you can take high-resolution photos or scan your pages and upload them to Canvas before the deadline. The final exam will cover lecture material from the course. **Makeup exams will not be allowed unless there is a legitimate written reason in accordance with University Policy.**

Important Dates

Last day to drop without "W" Grade: **Mar 22nd, 2021**
Last day to drop course and receive "W" Grade: **Apr 19th, 2021**

Attendance and Academic Integrity Policy

Please review the Rutgers University Attendance Policy:
https://policies.rutgers.edu/view-policies/academic-—-section-10

As per the University's Course Attendance policy (10.2.7), students are responsible for communicating with their instructors regarding absences. *As an academic community dedicated to the creation, dissemination, and application of knowledge, Rutgers University is committed to fostering an intellectual and ethical environment based on the principles of academic integrity. Academic integrity is essential to the success of the University's educational and research missions, and violations of academic integrity constitute serious offenses against the entire academic community. The entire Academic Integrity Policy can be found at http://academicintegrity.rutgers.edu/academic-integrity-policy.* This policy applies to all Schools and Colleges of Rutgers, the State University of New Jersey, including the Ernest Mario School of Pharmacy and the Rutgers College of Nursing.

Special Accommodations

Rutgers University Newark (RU-N) is committed to the creation of an inclusive and safe-learning environment for all students and the University as a whole. RU-N has identified the following resources to further the mission of access and support:

For Individuals with Disabilities: The Office of Disability Services (ODS) is responsible for the determination of appropriate accommodations for students who encounter barriers due to disability. Once a student has completed the ODS process (registration, initial appointment, and submitted documentation) and reasonable accommodations are determined to be necessary and appropriate, a Letter of Accommodation (LOA) will be provided. The LOA must be given to each course instructor by the student and followed up with a discussion. This should be done as early in the semester as possible as accommodations are not retroactive. More information can be found at ods.rutgers.edu. Contact ODS at (973)353-5375 or via email at ods@newark.rutgers.edu.

For Individuals who are Pregnant: The Office of Title IX and ADA Compliance is available to assist with any concerns or potential accommodations related to pregnancy. Students may contact the Office of Title IX and ADA Compliance at (973) 353-1906 or via email at TitleIX@newark.rutgers.edu.

For Absence Verification: The Office of the Dean of Students can provide assistance for absences related to religious observance, emergency or unavoidable conflict (e.g., illness, personal or family emergency, etc.). Students should refer to University Policy 10.2.7 for information about expectations and responsibilities. The Office of the Dean of Students can be contacted by calling (973) 353-5063 or emailing deanofstudents@newark.rutgers.edu.

For Individuals with temporary conditions/injuries: The Office of the Dean of Students can assist students who are experiencing a temporary condition or injury (e.g., broken or sprained limbs, concussions, or recovery from surgery). Students experiencing a temporary condition or injury should submit a request using the following link: https://temporaryconditions.rutgers.edu.

For English as a Second Language (ESL): The Program in American Language Studies (PALS) can support students experiencing difficulty in courses due to English as a Second Language (ESL) and can be reached by emailing PALS@newark.rutgers.edu to discuss potential supports.

For Gender or Sex-Based Discrimination or Harassment: The Office of Title IX and ADA Compliance can assist students who are experiencing any form of gender or sex-based discrimination or harassment, including sexual assault, sexual harassment, relationship violence,

or stalking. Students can report an incident to the Office of Title IX and ADA Compliance by calling (973) 353-1906 or emailing TitleIX@newark.rutgers.edu. Incidents may also be reported by using the following link: tinyurl.com/RUNReportingForm. For more information, students should refer to the University's Student Policy Prohibiting Sexual Harassment, Sexual Violence, Relationship Violence, Stalking and Related Misconduct located at http://compliance.rutgers.edu/title-ix/about-title-ix/title-ix-policies/.

For support related to interpersonal violence: The Office for Violence Prevention and Victim Assistance can provide any student with confidential support. The office is a **confidential resource** and does ***not*** have an obligation to report information to the University's Title IX Coordinator. Students can contact the office by calling (973) 353-1918 or emailing run.vpva@rutgers.edu. There is also a confidential text-based line available to students; students can text (973) 339-0734 for support.

For Crisis and Concerns: The Campus Awareness Response and Education (CARE) Team works with students in crisis to develop a support plan to address personal situations that might impact their academic performance. Students, faculty and staff may contact the CARE Team by using the following link: tinyurl.com/RUNCARE or emailing careteam@rutgers.edu.

For Stress, Worry, or Concerns about Well-being: The Counseling Center has confidential therapists available to support students. Students should reach out to the Counseling Center to schedule an appointment: counseling@newark.rutgers.edu or (973) 353-5805. If you are not quite ready to make an appointment with a therapist but are interested in self-help, check out *TAO at Rutgers-Newark* for an easy, web-based approach to self-care and support: https://tinyurl.com/RUN-TAO.

For emergencies, call 911 or contact Rutgers University Police Department (RUPD) by calling (973) 353-5111.