CHM1258 Reactions of Ligands

Professor Robert Morris

 Ref./Acknowl.:

Objectives

- The transformations of some small inorganic and organic molecules coordinated in transition metal complexes will be examined.
- Research that explains the influence of the metal centre(s) and the ancillary ligands on the reactivity of these small molecules will be reviewed.
- Emphasis is placed on reactions found in important catalytic cycles

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Course information

Instructor: Prof. Robert Morris
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Office: DB344, 978-6962
Office hours Mon. 4-5 pm or by appt.

Lectures: Friday 2-4 pm Room SS2104; First class January 10 2019.

Evaluation:

1. *Assignment* Due Feb. 28, 2:10 pm.	20 marks
1. *Essay* (10 to 20 pages, double spaced) Due Mar. 20, 2:10 pm	30 marks
3. 15 min *oral presentation of part of the essay.* Mar. 27, Apr 3, 2:10 pm	20 marks
4. *Exam* *TBA*	30 marks

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Essay and presentation

- 10-20 pages, double spaced
- 15 minute talk, 5 minutes for questions
- compare and contrast the effect of different metals, oxidation states, bonding modes
- compare and contrast the effect of the ligands, sterics, asymmetry, electronics
- examine the rate determining step of the reaction where known and identify important factors that might be changed to alter the rate or course of the reaction
- First come, first serve choice of topic (one each)
- You can suggest your own

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Suggested essay/presentation topics

- Catalytic hydroamination- early versus late transition metals.
- Alpha-olefin polymerization- early (Sc(III), Zr(IV)) versus late transition (Ni(II), Pd(II)) metals.
- The activation of nitriles to electrophilic attack versus nucleophilic attack.
- Steric and electronic effects in the hydroformylation reaction (Cat. Sci. Techn. 2017, 7, 1404).
- Ligand effects in α-olefin polymerization catalyzed by metallocenes.
- Asymmetric oxygen atom transfer to prochiral olefins (e.g. ligand design of E. Jacobsen)
- Oxygen atom transfer reactions (e.g. JACS 2014, 136, 13845).
- Catalytic oxidations involving the activation of dioxygen.
- Olefin metathesis: molybdenum versus ruthenium (R. Schrock, R. Grubbs)
- Olefin metathesis polymerization: ligand effects on ruthenium (e.g. JACS 2005, 127, 5032; JACS 125 10103)
- Olefin metathesis polymerization: ligand effects on molybdenum (e.g. Chem. Commun. 2005 2773)

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Suggested essay/presentation topics

- Ligand effects in palladium-catalyzed C-C bond forming reactions (choose one type of reaction).
- Metal-based synthesis of phosphine ligands.
- Template synthesis of ligands.
- Catalytic reactions involving CO_2.
- Reactions of η^2-arene complexes (work of W. D. Harman – JACS 2015, 137, 3659)
- Influence of ligands and metals on the self-assembly of well-defined, functional structures.
- The catalytic arylation of olefins (see Angew. Chem. Int. Ed. 2017, 56, 7233; Nature Communications 2019, doi: 10.1038/s41467-019-11420-5).
- Ligand effects in olefin-CO copolymerization (Dalton 2003 2627).
- Changing the reactions of metal-boron bonds (J. Am. Chem. Soc. 2003, 125, 6356; J. Organometal. Chem. 2003 680, 81; J. Am. Chem. Soc. 2005, 127, 2538; ACS Catal. 2018, 8, 10606-10618)
- Similarities and differences between tris(pyrazolylborate) and cyclopentadienyl: Cp and analogous Tp complexes in reactions or catalysis.
- Ligand-based radicals in catalysis (e.g. Chem. Comm. 2017 53 4382).
- Ligands for bimetallic catalysis (e.g. J. Am. Chem. Soc. 2018, 140, 4929−4939)

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Syllabus

- Introduction
- Reactions and catalysis with dinitrogen complexes
- Reactions and catalysis with hydrides
- Reactions and catalysis with sp hybridized carbon
- Reactions and catalysis with sp^2, sp^3 hybridized carbon
- The metal and the ligand cooperating as a bifunctional unit to effect catalytic transformations
- Template reactions
- Student Presentations, Part I
- Student Presentations, Part II

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