

Chemistry 423/523

Advanced Organometallic Chemistry

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Monday 2:00-3:00 pm; Wednesday 3:00-4:00 pm or by appointment

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Useful texts:

'Organometallic Chemistry', Spessard and Miessler
'Organometallic Chemistry', Elschenbroich and Salzer
'Organometallic Chemistry', Powell
'Organometallic Chemistry', Crabtree

Grades: The total percentage mark will be made up as follows for Chem 423 and 523:

Chem 423:	Midterm 1	Friday, Oct 21	25 %
	Midterm 2	Friday, Nov 18	25 %
	Final		50 %
Chem 523	Midterm 1	Friday, Oct 21	25 %
	Midterm 2	Friday, Nov 18	25 %
	In-class special topics presentation		10%
	Term paper/proposal		40%

Examinations:

Midterms 50 minutes
Final 3 hours

Syllabus

The following outline is intended as a study guide only, to complement the material presented in the lectures. The lectures are your best guide to the level of detail required.

A Basic bonding concepts and M.O. theory.

- ◆ review of basic M.O. theory
- ◆ ligand bonding and metal-ligand interactions
- ◆ π -donors: alkoxides and amides
- ◆ π -acceptors: CO and ethylene
- ◆ alkynes and cyclic π -systems: both π -donors and acceptors
- ◆ allylic and cyclopentadienyl ligands

B Organometallic concepts, terminology and nomenclature.

- ◆ electron counting and the 18 e⁻ (EAN) rule
- ◆ neutral vs. charged counting schemes
- ◆ formal oxidation states
- ◆ relationship to M.O. theory
- ◆ exceptions to the 18 e⁻ rule: stable d^8 16 e⁻ complexes
- ◆ organometallic nomenclature

C General synthetic strategies.

- ◆ methathesis
- ◆ protonolysis (hydrogenolysis)
- ◆ reductive routes
- ◆ insertions

D NMR spectroscopy and fluxional processes.

- ◆ chemical shift norms
- ◆ heteronuclear NMR
- ◆ fluxional processes: coalescence temperature and energy barriers
- ◆ examples of fluxional processes: hapticity changes and rotational barriers

E Organometallic Reactions I: Reactions at the metal.

- ◆ ligand substitution
- ◆ oxidative-addition
- ◆ reductive-elimination

F Organometallic Reactions II: Reactions involving the ligands.

- ◆ insertion and deinsertion of unsaturated substrates
- ◆ nucleophilic addition
- ◆ electrophilic reactions

G Industrial homogeneous catalysis.

- ◆ basic principles
- ◆ hydroformylation
- ◆ hydrogenation/isomerization of alkenes
- ◆ Monsanto process
- ◆ Wacker process
- ◆ Ziegler-Natta polymerizations

H Alkylidenes (carbenes) and alkylidynes (carbynes).

- ◆ bonding and formation
- ◆ nucleophilic vs. electrophilic alkylidenes
- ◆ alkene metathesis

Note on problem sets: Problem sets will be assigned periodically and answer sets will be available on the course web site approximately one week later. Although these assignments are not graded, it is **strongly recommended** that students attempt each set.