Advanced Inorganic Synthesis Laboratory
Chem 1140, Spring 2013

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Class Period: Monday, 12:00-12:50, CSC 135

Lab Periods: Tuesday (NK), Thursday (NK) and Friday (JA), 8:00-11:50, CSC 410

Course Objectives: This course has three objectives. The first objective for this course is your demonstrated proficiency, gained by "hands-on" experience, with a range of techniques and spectroscopic tools used in the synthesis and characterization of inorganic, organic and organometallic compounds. The second objective for this course is your demonstrated intellect of the techniques and processes involved in the preparation, analysis, characterization and implementation of various inorganic, organic and organometallic compounds. The third objective is your demonstrated skill as a scientific writer.

Textbook: All experiments and techniques will be taken from the primary literature and the internet, so a textbook purchase is not required. However, a spiral bound Chemistry Student Lab Notebook, Publisher Hayden McNeil, **ISBN-10:** 1429275995 is required. This notebook is available from Amazon for ca. $17.00. Please make sure to get the notebook with 100 pages. Last year students who bought the 50-page notebook had to buy a second notebook later in the semester. Your lab report should make use of a drawing program, ChemDraw Ultra 12 that is now available to you for $5 at http://technology.pitt.edu/software/for-students-software/chemdraw-st.html.

Course Organization: The experiments for this course fall into two different categories, main-group chemistry and organotransition metal chemistry. All experimental work will be carried out as teams! This means that in most cases the experimental data will need to be pooled and shared. [Solving scientific problems often involves working in teams, often multi-disciplinary teams; this is especially true in industry. Moreover, group experiences may capture an individual's areas of expertise, which in turn may result in a stronger final product than would have been possible through independent work; the whole may actually be greater than the sum of the parts. You should be able to lead portions of an activity or be an effective follower as dictated by the activity.] Given the time requirements for each of the experiments it is important that you use your lab time efficiently, this is a process that involves coming to lab on time and prepared. For example, the lab starts at 8:00 A.M., you should not only arrive a few minutes before but you should also be acquainted with the sequence of manipulations for each experiment and also the reason for each of the manipulations. You should anticipate potential hazards and how you will respond to them, if encountered. I will assist you with your preparedness for the laboratory by providing handouts, videos, lectures and references. You must always keep in mind a suitable stopping point, the laboratory will close at 11:50 sharp, but not before all laboratory benches have been cleaned off and all equipment stored in the proper place.

Grading: Your grade in this course will be based upon: 1) your laboratory notebook (4 sets of notebook pages x 50 points each = 200 points); 2) your lab report (3 reports x 50, 100 points and 150 each = 300 points. Only three lab reports will be required even though we will be performing four laboratory experiments. For the first experiment, only an abstract will be required and this will count as one of the homework assignments.); 3) homework assignments including, pre and post lab answers to questions and writing assignments (5 x 50 = 250 points); 4) and your laboratory attendance-you will need to arrive by 8:00 AM to receive credit for attendance (13 labs, 20 points per lab for a total of 260 points). Sets of questions related to specific projects will be assigned to be turned in at pre-announced times. The instructor will collect notebooks and compounds for completed projects at pre-announced times. Grades for late notebooks and lab reports will be reduced. Yields of compounds are not as important as purity. Samples of compounds synthesized and not used in further steps or characterization will be submitted to the instructor at the end of the semester in vials clearly labeled with your name, notebook number and the structure of the compound. Your notebook should account for any difference between the amount you hand in and the yield that you report.

Students who complete the required projects, reports, questions and writing assignments and keep their laboratory notebook at a minimum level can expect to receive a C for the course. Those who complete the required projects, reports, questions and writing assignments, and keep their laboratory notebook at a good level can expect to receive a B. Students who complete the required projects and keep their laboratory notebook at a high level can expect to receive an A. Other factors that can help your grade are a positive attitude towards the work and completing more than the required projects.

Laboratory Notebook: A laboratory notebook is a written record of a scientist's experimental procedures, observations, data, calculations and conclusions during a research project. It must be clear, concise and complete. *Entries should be made as the work is being performed and written in enough detail that another scientist could use the notebook to duplicate the experiments.* The practice of writing on loose sheets of paper for later transcription into the notebook is not acceptable.

A properly kept notebook is essential to establish a claim of scientific priority or patent rights to discovery. The notebook required for this course is Chemistry Student Lab Notebook, Publisher Hayden McNeil, **ISBN-10:** 1429275995. The only pages that are to be torn out from this notebook are the duplicated copies that will be handed in for grading during the semester. The final version of your notebook will be handed in at the end of the semester and grades for the notebook will be reduced if any of the original pages are torn out. The table of contents should be kept up to date. The top of each page should be dated and a brief title of the project provided. All notebook entries must be made in permanent blue or black ink. Corrections should be made by crossing out the error with a single line to leave it legible. A single-line should be accompanied by your initials and the date that the change was made.

Your notebook does not need to look pretty but it must be legible and the organization should be clear. Sign your name after the entries for each day's work. Keep space in the margins for later notes and corrections and for the instructor's comments. Spectral and other data printouts from instruments should be labeled with the notebook page reference and either permanently attached to a blank page in the notebook or in a separate folder. Your notebook should contain descriptions and or drawings of experimental apparatus. You should also record actual observations like weighings, quantities of reagents and calculations, order and manner of addition of reagents, time and temperatures of the reaction, color changes…

Samples of compounds must be clearly labeled with the compound structure, and notebook page identifying the procedure used and the history of the sample. For example, KMB-I-25b, would be used to indicate Kay M. Brummond's notebook, volume I, page 25 and compound b (if more than one compound is reported on that page).

Entries in your notebook related to a single project should be contiguous. So if you begin a second experiment before completing the first, make sure to leave a sufficient number of blank pages. You should include a section following your entries for each project that states your conclusions concerning the project, a table that summarizes your principle results and data and answers to assigned questions.

Lab Report: Most scientific research reports, irrespective of the field, parallel the method of scientific reasoning. That is: 1) the problem is defined, 2) a hypothesis is created, 3) experiments are devised to test the hypothesis, 4) experiments are conducted, and 5) conclusions are drawn. This framework is consistent with the following organization of a research report:

Title page. This should include the title of your experiment (the title should reflect the content and emphasis of the project described in the report. It should be as short as possible and include the essential key words), your name, date and an abstract of less than 150 words. The abstract should summarize the report concisely. A primary objective of the abstract is to communicate to the reader the essence of the lab report. The reader then will be able to judge whether to read the full report or not. It is best to include specific important results. For example, if you perform an olefin metathesis reaction and isolate none of the desired product, but instead recover only starting material, your abstract should state this in no uncertain terms.

Introduction. A brief statement of the purpose and scope of the experiment is presented. "A good introduction is a clear statement of the problem or project and why you are studying it." (The ACS Style Guide. American Chemical Society, Washington, DC, 1986). It is appropriate to include some background from the literature.

Experimental: This section should describe what was actually done. It is a *succinct* exposition of the laboratory notebook, describing procedures, techniques, instrumentation, special precautions, weights of reagents and so on. It should be sufficiently detailed that other experienced researchers would be able to repeat the work and obtain comparable results.

Results: In this section, relevant data, observations and findings are summarized. Tabulation of data, equations, charts, and figures can be used to present results clearly and concisely. Schemes to show reaction sequences may be used here or elsewhere in the report.

Discussion: The crux of the report is the analysis and interpretation of results. What do the results mean? How do they relate to the objectives of the project? To what extent have they resolved the problem? Because the "results" and "discussion" sections are interrelated, they can often be combined into one section.

Conclusions and Summary: A separate section outlining the main conclusions of the project is appropriate if conclusions have not already been stated in the discussion section. Directions for future work are also suitably expressed here.

References: Literature references should be collated at the end of the report and cited in one of the formats described in The ACS Style Guide. Do not mix formats. All references should be checked against the original literature.

Supplementary Material. Attach original spectra and other appropriate data to your report.

Safety: A high degree of safety awareness begins with your first laboratory course and continues throughout your college career. The chemicals and equipment used in this course can be hazardous if handled improperly. Hazards can results from uncontrolled reactivity, toxicity, and the extremes of temperatures and pressures used in the experiments. Many of the compounds and techniques that you will encounter are currently unfamiliar to you. Some chemicals react violently with water or spontaneously inflame in air. It is most important that you become completely familiar with the experiment before you begin. If you have any questions about the proper use and handling of the chemicals or equipment, read about them or ask about them before using them. Material Safety Data Sheets (MSDS) can be obtained online. Unsupervised experiments are not permitted.

Try to anticipate where hazards could occur and anticipate how you would respond to them. Be aware of what other students are doing around you and how it may affect you and your experiment. Know where the safety equipment (fire extinguishers, eye wash, fire blanket, gas cut off switch…) is located and be familiar with how to use it.

Safety hazards can be reduced by proper use of protective equipment and clothing. Goggles or approved safety glasses are required at all times in the laboratory. Contacts are not recommended because they can trap corrosive volatile materials that may damage the eye. The use of gloves, safety shields, and other protective measures will be mandated in certain instances. Shorts and sandals are not safe laboratory attire because they provide no protection from splashed or spilled materials. To avoid possible entanglement with lab equipment, necklaces and bracelets should not be worn and long hair must be tied back. Backpacks and all personal belongings should be placed in the coat-rack area and not on the laboratory benches or floor.

Gas cylinders should be chained and clamped at all times. Cylinders should only be moved on proper cylinder carts.

Check glassware for small cracks or "star-cracks" before use. Such glassware may break, explode or implode when subject to increased pressure, vacuum or rapid temperature changes. Broken glassware should be turned over to the instructor or TA for replacement.

Never isolate a cold trap cooled with liquid nitrogen from the vacuum pump to which it is attached, Also, any operation involving liquid nitrogen should be done carefully to ensure that liquid oxygen, which has a slightly higher boiling point than nitrogen, is not condensed into the apparatus. Upon warming, liquid oxygen will rapidly vaporize and cause an explosion. This is especially true if organic material is present.

Clean up chemical and water spills immediately. This includes areas surrounding balances and other equipment. Water on the floor can cause slips and falls. Some chemicals can be highly corrosive to equipment that it is left in contact with or to skin that unknowingly contacts it. Some chemicals spills need to be cleaned up using a spill kit, this is located underneath the sink in the lab.

Eating, drinking, smoking, and noisy disruptive behavior (cell phones, ipods, ipads…) are strictly forbidden in the laboratory.

Safety considerations, prudent practice, and the environmental protection agency (EPA) mandate that all compounds, samples and reaction mixtures generated during the course must be clearly labeled with the name of the compound (or possible contents, if unknown), your initials and a notebook page reference. Do not delay labeling containers; you will forget what they contain. Unlabelled containers can result in significant fines levied by the EPA.

All wastes must be disposed of in the proper manner. Many metals and organic solvents are toxic and must not be disposed of down the drain. Receptacles for the solid and liquid waste will be provided. Please try to minimize the volume of waste. Waste should be segregated by categories such aqueous vs. organic vs. halogenated organic… If you are in doubt, ask.

Ethics: Chemistry, like any discipline, has a social structure with a code of practices that govern acceptable and unacceptable behaviors. Progress in chemistry, as in all sciences, relies on complete honesty, openness, and trustworthiness of chemists, and on reproducibility of experimental results. Students should display high personal standards and integrity, conduct themselves responsibly, and be aware of contemporary issues related to chemistry.

Chemical Information Retrieval Skills: Students who intend to become a practicing chemist, or who will use chemistry in an allied field of science or medicine should know how to use the chemical literature effectively and efficiently. Students should be able to retrieve specific information from the chemical literature and use the peer-reviewed scientific literature effectively. For example, you should be able to locate chemical and physical properties of substances, including their spectra, locate references for the synthesis or reactions of desired compounds, locate references to desired chemical transformations, and identify CAS registry numbers. Margarete Bower, the Chemistry Librarian has developed a website for this course, please see: http://pitt.libguides.com/content.php?pid=300520&sid=2463340.

Listing of Experiments and Advanced Techniques:

1) Grubbs' cross metathesis of eugenol with cis-2-butene-1,4-diol to make a natural product: A Nobel Prize winning illustration of olefin metathesis. This experiment will require that you work with: an air-sensitive organometallic catalyst, flash chromatography to purify product, thin layer chromatography for monitoring the progress of the reaction and chromatography, recrystallization, compound characterization by ^{1}H NMR, ^{13}C NMR, melting point and x-ray crystallography. You will work individually, not in teams, for this reaction, see: *Journal of Chemical Education* **2006**, *83*, 283.

2) MCPBA epoxidation/acetylation and Sharpless epoxidation/acetylation of geraniol: A Nobel Prize winning illustration of asymmetric synthesis. This experiment will require that you work under anhydrous conditions, purify product mixtures by flash column chromatography, use chiral NMR shift analysis to determine ee's. Students will work in teams, one team member will perform the asymmetric epoxidation/acetylation and the other team member will perform the racemic epoxidation/acetylation. The lab reports must include the results from each team member. Each student will write a detailed lab procedure of the experiment to be performed. A copy of this procedure will be handed in to the instructor prior to the lab. For experimental details, see: *Journal of Chemical Education* **1997**, *74*, 1336.

3) Preparation and Characterization of (η^6-mesitylene)Mo(CO)$_3$ and Cyclocarbonylation Reaction using (η^6-mesitylene)Mo(CO)$_3$. The product is characterized by NMR and IR. Molecular modeling will be performed to calculate the number of IR-active CO stretching modes and the number of IR bands to which they will give rise. The use of this complex in a cyclocarbonylation reaction will illustrate the importance of transition metals in multi-component cycloaddition reactions.

4) Copper-catalyzed Huisgen dipolar cycloaddition of azides and alkynes using a well defined copper catalyst, Cu(IMes)Cl, 1,3-bis(2,4,6-trimethylphenyl)-imidazolium copper(I) chloride. The synthesis of the N-heterocyclic carbene will involve the use microwave irradiation and is performed in the absence of solvent. The 1,3 dipolar cycloaddition allows for a discussion of many of the concepts of green chemistry and catalysis such as: atom economy, e-factors, turns over numbers (TONs), and turn over frequency (TOF), and catalytic cycles.

A listing of topics that will be covered in lecture during the semester in addition to lectures pertaining to the experiments:

Lecture Schedule

January 7	Syllabus and Safety
January 14	Writing in a laboratory notebook
January 21	Holiday
January 28	Olefin Metathesis
February 4	Writing an Abstract
February 11	NMR Spectroscopy-Abstract due for olefin Metathesis experiment
February 18	Sharpless Epoxidation
February 25	Writing a Lab Report (part 1)
March 4	(η^6-Mesitylene)Mo(CO)$_3$ and Cyclocarbonylation Chemistry-Lab Report Due for Epoxidation Experiment
March 11	Springbreak
March 18	Writing a lab report (part 2)
March 25	NHC Ligands/Click Chemistry-Lab Report Due Pauson-Khand Experiment
April 1	Writing a lab report (part 3)
April 8	Ethics
April 15	Lab Clean-up- Lab Report Due for Click Chemistry Experiment

◄ December | **~ January 2013 ~** | February ►

Sun	Mon	Tue	Wed	Thu	Fri	Sat
		1	2	3	4	5
6	7 Syllabus and Safety	8	9 No lab	10 No lab	11 No Lab	12
13	14 Writing in a laboratory notebook	15 Safety @ 9:00 AM & NMR Training Sage Bowser Group 1 10:00-11:00AM Group 2 11:00-12:00 AM	16	17 Safety @ 9:00 AM & NMR Training Sage Bowser Group 1 10:00-11:00AM Group 2 11:00-12:00 AM	18 Safety @ 9:00 AM & NMR Training Sage Bowser Group 1 10:00-11:00AM Group 2 11:00-12:00 AM	19
20	21 Holiday	22 Olefin Cross Metathesis	23	24 Olefin Cross Metathesis	25 Olefin Cross Metathesis	26
27	28 Olefin Metathesis	29 Complete Olefin Cross Metathesis	30	31 Complete Olefin Cross Metathesis	Notes:	

◄ January ~ February 2013 ~ March ►

Sun	Mon	Tue	Wed	Thu	Fri	Sat
					1 Complete Olefin Cross Metathesis	2
3	4 Writing an Abstract	5 MCPBA Epoxidation	6	7 MCPBA Epoxidation	8 MCPBA Epoxidation	9
10	11 NMR Spectroscopy & Abstract due for Olefin Metathesis Experiment	12 Acetylation	13	14 Acetylation	15 Acetylation	16
17	18 Sharpless Epoxidation	19 Chiral Shift Analysis & Tricarbonyltripyridine molybdenum	20	21 Chiral Shift Analysis & Tricarbonyltripyridine molybdenum	22 Chiral Shift Analysis & Tricarbonyltripyridine molybdenum	23
24	25 Writing a lab report (part 1)	26 Propargylation Reaction & Tricarbonyl (η^6-mesitylene) molybdenum	27 Propargylation Reaction & Tricarbonyl (η^6-mesitylene) molybdenum	28	Notes:	

◄ February ~ March 2013 ~ April ►

Sun	Mon	Tue	Wed	Thu	Fri	Sat
					1 Propargylation Reaction & Tricarbonyl (η^6-mesitylene) molybdenum	2
3	4 Pauson-Khand Reaction Lab Report Due for Epoxidation Experiment	5 Pauson-Khand Reaction	6	7 Pauson-Khand Reaction	8 Pauson-Khand Reaction	9
10	11 Spring Break	12 Spring Break	13	14 Spring Break	15 Spring Break	16
17	18 Writing a lab report (part 2)	19 NHC Ligand	20	21 NHC Ligand	22 NHC Ligand	23
24	25 NHC Ligands & Click Chemistry Lab Report Due for Pauson-Khand Experiment	26 NHC Ligand & Azide Preparation	27	28 NHC Ligand & Azide Preparation	29 NHC Ligand & Azide Preparation	30
31	Notes:					

◀ March | ~ April 2013 ~ | May ▶

Sun	Mon	Tue	Wed	Thu	Fri	Sat
	1 Writing a lab report (part 3)	**2** NHC Ligand	**3**	**4** NHC Ligand	**5** NHC Ligand	**6**
7	**8** Ethics	**9** Click Reaction	**10**	**11** Click Reaction	**12** Click Reaction	**13**
14	**15** Lab Clean-up- Lab Report Due for Click Chemistry Experiments	**16** Lab Clean-up	**17**	**18** Lab Clean-up	**19** Lab Clean-up	**20**
21	**22**	**23**	**24**	**25**	**26**	**27**
28	**29**	**30**	**Notes:**			