School of Physical and Chemical Sciences

UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

General Course Information

CHEM335
Organometallic Chemistry and Catalysis

0.125 EFTS 15 Points
Semester Two 2022

Description
A selection of the following will typically be presented:

INORGANIC MATERIALS FOR CATALYSIS: introduction into heterogeneous catalysis; synthesis, characterization and applications of high surface area materials; with specific focus on the selected porous solids and nanoparticles and their applications. Selected industrial processes will be covered in-depth.

ORGANOMETALLIC CHEMISTRY: Introduction to organometallic chemistry, electron counting, valence, oxidation states, review of ligand classes, oxidative addition and reductive elimination; insertion and elimination reactions; nucleophilic and electrophilic addition and abstraction reactions;

HOMOGENEOUS CATALYSIS: Selected catalytic processes involving homogeneous catalysts of both fundamental and industrial importance will be covered in-depth building up on the foundations laid in the previous block of lectures. Highlights of several Nobel Prizes awarded in early 21st century for organometallic catalytic processes, such as asymmetric hydrogenation, polymerization and coupling reactions will help to cement appreciation of the importance of this area of Chemistry.

Timetable
Two and a half or three contact hours a week. Typically, four lectures followed by a tutorial/workshop each fortnight or two lectures and a tutorial/workshop each week.
Students should note that in the Science Faculty that the average student is responsible for approximately 4.5 hours of additional study for each hour of lecture at the 300-level.
Please, check most recent timetable using "My Timetable" online.

Course Coordinator
Associate Professor Vladimir Golovko, School of Physical and Chemical Sciences
email: vladimir.golovko@canterbury.ac.nz

Email Vladimir if you have any queries about the course.

Examination and Formal Tests
In order, with course component indicated:

Test (1st Block of Lectures)	30%	1.5 hours, Ernest Rutherford 141, 6.30pm on 19/09/2022. (please, double check closer to the date)
Assignment	10%	will be set by Vladimir Golovko. See below.
Final Examination	60%	3 hours, details to be advised.

Assignment
This 10% assignment will be set by Vladimir Golovko and should be uploaded on Learn as per instructions provided. Extensions will be granted only in exceptional circumstances (such as illness or bereavement). If necessary, you should seek an extension **before** the due date.

Recommended Textbooks
Standard resources on Learn, plus course textbook(s) and handouts.
- C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry*, 3rd or 4^{th} Ed
- R. A. Henderson, *The Mechanisms of Reactions at Transition Metal Sites*
- C.H. Bartholomew and R.J. Farrauto, *Fundamentals of Industrial Catalytic Processes*, 2nd Ed, J. Wiley & Sons, 2006, ISBN-13 978-0-471-45713-8, UC Library QD 505.F37 2005

Pre-requisites
CHEM251 or CHEM241

Response to Student Feedback
As this is a new course, constructive feedback will be especially valuable.

Goal of the Course
To build on prior study in chemistry and develop an advanced understanding of inorganic, organometallic and (nano)materials chemistry as well catalysis as outlined in the course description.

Some Expected Learning Outcomes

General:
You will be able to:

- Develop the ability to apply scientific principles and concepts by engaging with chemistry related to organometallic chemistry and catalysis in lectures and problem-solving workshops
- Develop scientific problem-solving skills through analysing chemical processes in organometallic chemistry and catalysis in lectures and problem-solving workshops
- Understand, evaluate, access and critically use new chemical information by completing a literature-based assignment which will build lifelong learning skills
- Demonstrate the ability to think independently about chemical concepts via assignments and examination work
- Develop a more in-depth knowledge of organometallic chemistry and catalysis
- Develop a critical understanding of the challenges and significance of applying chemistry to industrial contexts in an assignment and test.
- Communicate effectively in written English and chemical diagrams.

Course-specific:
You will be able to:

- Develop appreciation of the importance of catalysis for our civilization, and a critical understanding of the industrial context of catalysis in contemporary life;
- Explain role and mode of action of a catalyst and discuss in depth its key properties;
- Compare and contrast heterogeneous and homogeneous catalysts as well as discuss major advantages and disadvantages for each class of catalysts;
- Reflect on the evolution of knowledge about active sites in heterogeneous catalysts;
- Discuss modern approaches to fabrication of model nanoparticle-based heterogeneous catalysts and contrast these with a simpler ones used in industry;
- Develop appreciation for importance of development of novel characterisation methods for heterogeneous catalysts; discuss selected relevant characterization methods and difficulties arising when using these to study heterogeneous catalysts;
- Explain, giving examples, what is meant by geometric effects in the case of heterogeneous catalysts;
- Classify porous materials and discuss in detail properties, synthesis and applications of two major classes of microporous materials (zeolites and aluminophosphates).
- Discuss in detail applications of heterogeneous catalysts in selected industrially-important reactions.
- Develop an appreciation of how the nature of the reaction affects the choice of conditions used within industrially-implemented catalytic reactors.

- Develop an appreciation of the role of characterization techniques and methodology for handling of organometallic materials in the evolution of organometallic chemistry;
- Compare and contrast organometallic complexes with Werner-type complexes, highlighting the specific chemical nature of organometallic complexes;
- Discuss in detail the bonding, synthesis and properties of organometallic complexes, for example, of metal carbonyls;
- Reflect on the origin of the 18-electron rule and perform electron counting for selected classes of organometallic complexes;
- Define electronic and steric factors in organometallic complexes using the example of Tolman factors for phosphine complexes;
- Explain in detail which specific changes can be expected within an organometallic complex when one ligand is substituted for another;
- Discuss binding and activation of hydrogen within organometallic complexes and factors affecting this phenomenon;
- Account for the stability or lack of stability of alkyl complexes;
- Describe the manner in which alkenes bind to metals;
- Rationalise barriers to propeller rotation in transition metal-alkene complexes;
- Rationalise and explain the bonding modes of allyl ligands;
- Rationalise and explain the bonding modes of carbene ligands and how these differences affect reactivity of corresponding species;
- Account for the stability of ferrocene and other metallocenes
- Discuss in detail how organometallic catalysts could be tailor made and studied in situ;
- Identify intermediate species for each of the catalytic cycles involving organometallics;
- Explain how selectivity is achieved for selected examples of catalytic processes involving organometallic catalysts, using concepts of electronic and steric effects;
- Define the characteristics and requirements of an OA reaction;
- Appreciate that RE is the reverse of an OA and describe the factors affecting the direction of an OA/RE reaction;
- Define the characteristics and requirements of a migratory insertion reaction;
- Describe the factors affecting the reversibility of a migratory insertion;
- Distinguish between the various classes of nucleophilic and electrophilic addition and abstraction reactions;
- Be able to analyse and describe the individual steps of a catalytic cycle;
- Understand the methods used to characterise and investigate the mechanisms in a catalytic cycle such as olefin metathesis and polymerisation.
- Be able to discuss and analyse in depth selected organometallic catalytic processes

Summary of the Course Content

The topics coved by this course are:

INTRODUCTION TO CATALYSIS, ADVANCED INDUSTRIAL AND NANOCATALYSIS
(9 lectures and 3 problem-solving workshops)

This course will start with an introduction into catalysis, with an aim to develop appreciation of the importance of catalysis for modern civilization. Key properties of catalysts will be discussed in detail. We will then lay down a foundation by considering the evolution of knowledge about the active site of heterogeneous catalysts while highlighting contrast with the case of homogeneous catalysts. Detailed discussion of the properties, synthesis, characterization and applications of high surface area nanostructured materials will conclude subsection of this block dedicated to heterogeneous catalysts. Particular attention will be paid to selected classes of porous solids and nanoparticles as well as applications of these materials in catalysis. Industrially important reactions, such as CO oxidation (automobile emissions control), ammonia synthesis (fertilizers) and hydrogen production from natural gas (steam methane reforming) will be used as illustrations in this section of the course.

Lecturer: Associate Professor Vladimir Golovko,
email: vladimir.golovko@canterbury.ac.nz

INTRODUCTION TO ORGANOMETALLIC CHEMISTRY
(9 lectures and 3 problem-solving workshops)

Part I: This part will start with a brief overview of the history of organometallic chemistry. Classical Werner-type complexes will be contrasted and compared with organometallic complexes in order to instil appreciation of special nature of the latter. Bonding, synthesis, and properties of transition-metal carbonyl compounds will be discussed next, leading to the discussion of the origin and use of the 18-electron rule. The variety of possibilities to tune properties of organometallic complexes will be introduced by example of metal phosphine complexes leading to appreciation of the role of steric and electronic factors. We will finish with a discussion of hydrogen-containing complexes leading to better understanding of factors affecting hydrogen activation and achieving appreciation of a toolkit for the organometallic chemist in developing and optimizing novel catalysts.

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Part II: Next, we will focus our attention on the complexes containing carbon-based ligands such alkyl, alkene, allyl, carbene and cyclopentadienyl ligands.

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REACTION MECHANISMS AND SELECTED HOMOGENEOUS CATALYTIC PROCESSES
(9 lectures and 3 problem-solving workshops)

We will start by considering elemental steps in reactions involving organometallic catalysts, such as oxidative addition (OA) and reductive elimination (RE), insertion and elimination reactions, including metathesis, nucleophilic and electrophilic addition and abstraction reactions. Building up on the detailed case-study of hydrogen activation by organometallic complexes, including experimental techniques to study such a system, will proceed to our study of hydrogenation of alkenes, highlighting a case study of the Nobel Prize winning asymmetric hydrogenation. Selected other catalytic processes, such as alkene isomerisation, hydroformylation, selected Nobel Prize winning coupling reactions and several polymerization processes will be also be covered.

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GENERAL INFORMATION 2022

Policy on 'Dishonest Practice'
The University has strict guidelines regarding 'dishonest practice' and 'breach of instructions' in relation to the completion and submission of examinable material. In cases where dishonest practice is involved in tests or other work submitted for credit a department may choose to not mark such work ('Academic Integrity and Breach of Instruction Regulations').

The School of Physical and Chemical Sciences upholds this policy. It considers plagiarism, collusion, copying, and ghost writing to be unacceptable and dishonest practices:

- ***Plagiarism*** is the presentation of any material (text, data or figures, on any medium including computer files) from any other source without clear and adequate acknowledgement of the source.
- ***Collusion*** is the presentation of work performed in whole, or in part, in conjunction with another person or persons, but submitted as if it has been completed by the named author alone. This interpretation is not intended to discourage students from having discussions about how to approach an assigned task and incorporating general ideas that come from those discussions into their own individual submissions, but acknowledgement is necessary.
- ***Copying*** is the use of material (in any medium, including computer files) produced by another person or persons with or without their knowledge and approval. **This includes copying of the lab reports (raw data may be shared within the group if permitted or required by the experiment) - data analysis and interpretation of obtained results MUST be performed individually.**
- ***Ghost writing*** is the use of other person(s) (with, or without payment) to prepare all or part of an item of work submitted for assessment.

Additional Information
Special consideration of assessment*:** If you feel that illness, injury, bereavement or any other critical extenuating circumstance beyond your control has prevented you from completing an item of assessment or affected your performance in that assessment, you may apply for special consideration. Special consideration is not available for items worth less than 10% of the course. Applications for special consideration should be made **within five days** of the due date for the work or examination. In the case of illness or injury, medical consultation should normally have taken place shortly before, or within 24 hours after, the due date for the required work or the date of the test or examination. For details on special consideration, or to make an application, refer to the Examinations Office website http://www.canterbury.ac.nz/exams/. ***You have the right to appeal any decision.

Extensions of deadlines: Where an extension may be granted for an assessment item, this will be decided by application to the course co-ordinator.

Late withdrawal from the course: If you are prevented by extenuating circumstances from completing the course after the final date for withdrawing from the course, you may apply for special consideration for late discontinuation. For details on special consideration, or to make an application, refer to the Examinations Office website http://www.canterbury.ac.nz/exams/. Applications must be submitted ***within five days*** of the end of the main examination period for the semester.

***Missing of tests*:** In rare cases a student will not be able to sit a test. In such cases, the student should consult with the course co-ordinator to arrange alternative procedures. **This must be done well in advance of the set date for the test.**

Past tests and exams: these can be found on our website using the link below:
www.chem.canterbury.ac.nz/for/undergraduate.shtml

***Submission of reports and assignments*:** **Reports (including lab reports) and assignments should be handed in on time.** Extensions will be granted only in exceptional circumstances (such as illness or bereavement). If an extension is required, as early as possible you should request it from the lecturer concerned.
Note: If you do not submit an assignment for assessment, you will be allotted zero marks, which will affect your final result. You should ensure that you pick up marked assignments and keep them until the end of the course as evidence that the work was completed and marked in the case that either is

disputed. To guard against accidental loss, it would be prudent to keep photocopies or electronic copies of anything submitted.

Late Work: Acceptance of late work will be at the discretion of the course coordinator. Please contact the coordinator if your assessment is likely to be late.

Marks and Grades: The following numbers should be considered as a guide to the expected grades under normal circumstances. The School reserves the right to adjust mark/grade conversions, if necessary.

Please note that for all invigilated assessments (tests and exams) worth 33% and above, failure to obtain a mark of at least 40% will result in a final grade no higher than an R at 100 and 200 level, and a C- at 300 level.

Grade:	**A+**	**A**	**A−**	**B+**	**B**	**B−**	**C+**	**C**	**C-**	**D**	**E**
Minimum mark %:	**90**	**85**	**80**	**75**	**70**	**65**	**60**	**55**	**50**	**40**	**0**

Reconsideration of Grades: Students should, in the first instance, speak to the course co-ordinator about their marks. If they cannot reach an agreeable solution, or have questions about their grade in a course, students should then speak to the Director of Undergraduate Studies, Assoc Prof Greg Russell (phone 3694228). Students can appeal any decision made on their final grade. You can apply at the Registry for reconsideration of the final grade within four weeks of the date of publication of final results. Be aware that there are time limits for each step of the appeals process.

Students with Disabilities: Students with disabilities should speak with someone at Equity and Disability Service, phone: 369 3334 (or ext. 93334), email: eds@canterbury.ac.nz).

***Academic Advice*:** Assoc Prof Greg Russell is the coordinator of undergraduate chemistry courses. His interest is in the academic performance and well-being of all such students. Anyone experiencing problems with their chemistry courses or requiring guidance about their B.Sc. in Chemistry should get in contact with Greg.

***Staff-Class Rep Liaison*:** Assoc Prof Greg Russell is in charge of liaison with students in chemistry courses. Your class will appoint a student representative to the liaison committee at the start of the semester. Please feel free to talk to the Academic Liaison or the student rep about any problems or concerns that you might have.

Greg Russell (greg.russell@canterbury.ac.nz, tel. 369 5129)
Director of Undergraduate Studies
School of Physical and Chemical Sciences
2022