Academic Year	AY20/21	**Semester**	1
Course Coordinator	Leong Weng Kee (Assoc Prof), Jason England (Asst Prof)		
Course Code	CM3021		
Course Title	Organometallic Chemistry		
Pre-requisites	CM2021 or by permission		
Mutually Exclusive	nil		
No of AUs	3		
Contact Hours	Lectures/reflections: 26, Tutorials: 12		

Course Aims

The aim of this course is to introduce to you some of the basic concepts in Organometallic Chemistry. You will be introduced to some fundamental ideas that are useful to understanding the subject, including an overview of the various types of ligands, some of their properties, and the reaction mechanisms, that are encountered in organometallic chemistry.

Intended Learning Outcomes (ILO)

At the end of the course, you should be able to:

Introductory concepts

1. Use the "ionic" and "covalent" methods to count valence electrons in organometallic complexes
2. Work out the formal oxidation state of an organometallic complex
3. Apply the isolobal analogy to relate or construct related complexes
4. Use the EAN rule to assess if an organometallic complex is likely to be stable

The carbonyl and phosphine ligands

5. Construct a qualitative MO diagram for carbon monoxide (CO)
6. Describe the orbital interactions between the metal atom and CO
7. Quote experimental evidence for the metal-to-ligand π-back bonding
8. Correlate the shift in the CO vibrational frequencies in terms of its bonding mode, electronic properties of the complex, and the geometry
9. Describe the bonding between the metal atom and a phosphine ligand
10. Describe the stereoelectronic effects of phosphine ligands in terms of Tolman's parameters
11. Extrapolate the bonding descriptions and effects to similar ligands such as CS and CN^-

Hydride, dihydrogen, alkyl and related monohapto ligands

12. Describe the various bonding modes of a transition metal hydride ligand
13. Describe the bonding interaction between a metal atom and a dihydrogen ligand (H_2)
14. State some of the more useful characterization methods for such ligands, such as, the minimum T_1 in ^1H NMR spectroscopy
15. Describe the primary steps in β-H elimination and its association with the instability of transition metal alkyls
16. State the requirements for β-H elimination and hence illustrate approaches to stable transition metal alkyls

Transition metal carbenes

17. List the characteristics such as ligand type, substituents and nature of the metal centre, of Schrock- and Fischer-type transition metal carbenes
18. Describe the bonding interactions between the metal atom and the carbene ligand for the two types of transition metal carbenes
19. Describe the differences between the two types of transition metal carbenes in terms of their reactivity pattern, correlate them with their organic counterparts, and illustrate them with examples
20. Describe the bonding in N-heterocyclic carbenes (NHC)

Ligands employing π-electrons

21. Identify π-electron ligands as open (acyclic) or closed (cyclic), and even (ene) or odd (enyl) number of π-electron systems
22. Use simple Hückel theory to describe the π molecular orbitals of both open and closed π-systems
23. Describe the metal-ligand interaction in an open π-system using an example such as an alkene or allyl
24. Describe the metal-ligand interaction in a closed π-system using an example such as cyclopentadienyl (Cp) or an arene
25. Describe the effects on the chemistry of these organic ligands on binding to a metal, such as, the change in their susceptibility towards nucleophilic and electrophilic attacks, NMR chemical shifts and steric hindrance
26. State that ligands such as Cp increases the basicity of the metal centre
27. Describe hapticity shifts
28. State the relative stability of ene and enyl ligands
29. Explain and construct the qualitative MO diagram for the metal-ligand bonding in metallocenes
30. Describe the chemical behavior and redox properties of ferrocene

2nd half semester

31. Identify different types of elementary reaction that occur on transition metals, explain the factors that control them, and provide the products formed
32. Provide a mechanism for and discuss the catalytic cycles of selected major industrial homogeneous catalytic processes
33. Propose a feasible mechanism, built from elementary reactions, for any given transition metal centred transformation of an organic fragment/molecule
34. Devise a short synthesis for a given organic molecule using organometallic reactions as key steps, including control of some aspects of regioselectivity, chemoselectivity and stereoselectivity

Course Content

Introductory concepts
The carbonyl and phosphine ligands
Hydride, dihydrogen, alkyl and related monohapto ligands
Transition metal carbenes
Ligands employing π-electrons
Elementary Reactions
Cross-Coupling Reactions
Oxidative Functionalization of Alkenes
Catalytic Carbonylation
Catalytic Hydrogenation of Alkenes
Alkene Polymerization and Metathesis

Assessment (includes both continuous and summative assessment)

Component	Course ILO Tested	Related Programme LO or Graduate Attributes	Weighting	Team/Individual	Assessment rubrics
1. Mid-term Test	1-30	Competence, Creativity, Character	30%	Individual	See appendix
2. Mid-term Test	31-34	Competence (a-c), creativity (a,b), communication (a), character (a,b), and civic-mindedness (a-c)	20%	Individual	See appendix
3. Tutorials (weeks 9-13)	31-34	Competence (a-c), creativity (a,b), communication (a), character (a,b), and civic-mindedness (a-c)	10%	Team	See appendix
4. Final Examination	1-34	Competence, Creativity, Character	40%	Individual	See appendix
Total			*100%*		

Formative feedback

Formative feedback: The online quizzes will allow you to monitor your learning of the concepts on a weekly basis. During the weekly workshop sessions, there will also be clicker-type questions to allow you to assess your understanding although it will not be formally assessed. Through the weekly reflections, you will be able to test your own learning. The lecturer will have read through your reflections and offer a summative feedback to the class weekly. Tutorial classes provide another avenue for you to assess the status of your learning. Along with regular consultation hours, tutorial classes also provide a point of contact with the lecturers. Model answers are provided throughout.

Summative Feedback: Summative feedback will be in the form of the mid-term and the final examinations, the former of which will be reviewed in class.

Learning and Teaching approach

First half semester

Directed self-learning (~6 hours)	This course involves directed self-learning and peer learning. The first component will involve a list of the concepts to be learned on your own each week. The supporting material available include: **Bite-sized videos** – these are about 5-10 min long each. A list of the currently available ones for each week's lesson is provided, and they have also been set up in a LAMS environment on NTULearn. You can watch any of them at any time and for any number of times. Each presentation is on one or a couple of concepts. They are not meant to cover everything that you can learn about a topic or concept, but as a springboard for you to explore your books and the internet for more. **Internet and ebooks**. **List of recommended textbooks** **Concept questions** – these are meant to prompt you on what you will need to learn. We will go through them during the key points sessions.
Key point lectures (5 hours)	During these sessions, we will begin with (a) feedback from the previous reflections session, (b) revision of the key points for the previous week's lesson, together with (c) some clicker-based questions. The concept question for the week will then be discussed, using clicker-based questions. This is followed by the key points to be learned for the week, reinforced with another series of clicker-based questions. Reproductions of the Powerpoint slides for the lectures are already available from NTULearn so that you can focus on learning rather than on copying things down.
Tutorials (6 hours)	The tutorial sessions provide a peer teaching and learning environment. You will have already been provided with a list of tutorial questions, one for each tutorial session. The tutorial class sizes are kept small (<25) deliberately, in order that it will not inhibit discussion. All tutorial classes will be facilitated by the lecturer. In each tutorial session, you will self-assemble into groups of up to six to discuss the tutorial question which you already have on hand. This will be followed by a class-level discussion. After that, a second tutorial question will be provided to the class for discussion.
Reflections (5 hours)	During these sessions, you will be given a set of questions based primarily on the concepts to be learned for the week. This is to allow you to ponder over the concepts and allow you to determine if you have understood the lesson or not. It is also a chance for you to explore connected ideas, and perhaps come up with new queries, all of which can be jotted down. The lecturer will go through all the reflection papers and any misconception, etc, from the class will be noted and discussed at the next key point lecture session.

Second half semester

Lectures (16 hours)	Core course content for the second half of the course will be delivered via traditional lectures. To allow the students of focus on listening and learning, rather than note taking, slides will be posted on NTULearn prior to the lectures. This half of the course provides an introduction to reactivity of organometallic complexes via consideration of industrially relevant homogeneous catalysis. Thus, it focusses on real-world examples.

Open-book examinations	The course focusses upon understanding and application of knowledge, not regurgitation of information. Questions in open-book examinations reflect this and require that you think critically and learn how to apply concepts in new contexts. Given that information is readily available on the internet nowadays, but you require a basis for understanding it, the aforementioned skills are the most relevant.
Group-based tutorial classes (6 hours)	Involves solving questions/problems, provided during class, using key concepts you learned in the course. The tutorial classes are intended as a means to reinforce learning and promote creative thinking. All work is performed in groups, which encourages peer learning, collaboration, communication, and consensus building. These are key skills is most work environments. Secondary goals include familiarising you with the types of questions encountered in exams and how to approach them, common mistakes, and providing an informal avenue for discussing difficulties you have in understanding the course content.
Model answer videos	For reasons described above, you are provided with practice problems in tutorials and at the end of lectures. Short videos covering the answers to the questions are composed whilst the course is being conducted. This allows common difficulties/ misconceptions gleaned from interactions with you and your classmates to be addressed.

Reading and References

Author(s)	***Title***	***Publisher***
R H Crabtree	The Organometallic Chemistry of the Transition Metals, 5th Ed. 4th edition available as e-book ISBN: 978-1119465881	Wiley
D Astruc	Organometallic Chemistry and Catalysis Available as e-book ISBN 978-3-540-46129-6	Springer
C Elschenbroich	Organometallics, 3rd Ed. ISBN: 978-3-527-29390-2	Wiley-VCH
J Hartwig	Organotransition Metal Chemistry – From Bonding to Catalysis ISBN: 978-1891389535	University Science Books
A F Hill	Organotransition Metal Chemistry ISBN: 978-0-85404-622-5	RSC

Organometallics hypertext: http://www.ilpi.com/organomet/organometallics.html

Course Instructors

Instructor	**Office Location**	**Phone**	**Email**
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Jason England (Asst Prof)	SPMS-CBC-04-03	65922553	jengland@ntu.edu.sg

Planned Weekly Schedule

Week	Topic	Course ILO	Readings/Activities
1	**Introductory concepts** Revision • What are organometallic compounds? • Pearson's hard-soft acid-base (HSAB) concept • The Effective Atomic Number (EAN) rule The "ionic" and "covalent" models for counting electrons in organometallic chemistry The isolobal analogy	1-4	***Videos*** HSAB concept; Electron count – ionic and covalent methods; EAN rule; Isolobal analogy ***Books*** Astruc Ch 1, 2; Crabtree Ch 1, 2
2	**The carbonyl and phosphine ligands** MO diagram for CO The CO ligand in organometallic compounds • orbital interactions between the metal atom and CO • experimental evidence for metal-to-ligand □-back bonding • IR spectroscopy of transition metal carbonyls - bonding mode, electronic properties, geometry Phosphine ligands in organometallic compounds • bonding between the metal atom and phosphine ligand • steric effects • electronic effects	5-11	***Videos*** MO diagram for CO; The M-CO bond; Vibrational spectroscopy of transition metal carbonyls; Phosphine and phosphite ligands ***Books*** Astruc Ch 7; Crabtree Ch 4
3	**Hydride, dihydrogen, alkyl and related monohapto ligands** The hydride ligand (H) – bonding mode and characterization The dihydrogen ligand (H_2) – bonding interaction with a metal atom, characterization Alkyl ligands: • The reason behind instability of transition metal alkyls – β-H elimination • Requirements for β-H elimination and approaches to stable transition metal alkyls	12-16	***Videos*** Hydride ligand; Dihydrogen ligand; Transition metal alkyls (and β-H elimination) ***Books*** Astruc Ch 8; Crabtree Ch 3
4	**Transition metal carbenes** Schrock- and Fischer-type transition metal carbenes • Bonding description • Characteristics such as ligand type, substituents and metal centres • Reactivity pattern N-heterocyclic carbenes (NHC) – bonding description and applications	17-20	***Videos*** Fischer carbenes; Schrock carbenes ***Books*** Astruc Ch 9; Crabtree Ch 11
5	**Ligands employing π-electrons (I) – acyclic enes and enyls** Open, acyclic vs closed, cyclic π-systems π molecular orbitals of open π-systems: alkenes, allyls and dienes Description of the metal-ligand interaction for alkene and allyl Hapticity change in metal-allyl Effect of metal binding on reactivity of π-ligands	21-23, 25, 27, 28	***Videos*** π-MOs of polyenes and –enyls; open ene and enyl ligands ***Books*** Astruc Ch 10; Crabtree Ch 5
6	**Ligands employing π-electrons (II) – aromatic systems** π molecular orbitals of closed π-systems: cyclobutadiene, cyclopentadienyl and benzene Description of the metal-ligand interaction for closed π-systems Relative stability of ene and enyl ligands Half-sandwich complexes - hapticity change, basicity of metal centre Effect of metal binding on benzene - susceptibility to nucleophilic and electrophilic attacks, NMR chemical shifts, steric hindrance Metallocenes - Description of the bonding - Chemical and redox properties of ferrocene	21, 22, 24, 25-30	***Videos*** Cyclopentadienyl and arene ligands ***Books*** Astruc Ch 11; Crabtree Ch 5

8	**Elementary Reactions** What is an elementary reaction? Ligand substitution: dissociative, associative and interchange mechanisms; the *trans* effect Oxidative addition and reductive elimination: mechanisms; bite angle dependence σ-bond metathesis: occurence and stereochemistry External attack on ligands: electrophilic *vs* nucleophilic; nucleophilic addition to CO, alkenes and alkynes; regioselectivity for alkenes Migratory Insertion and Elimination: 1,1-migratory insertion of CO; 1,2-migratory inserton of alkenes and alkynes, regioselectivity issues; reversibility	1-31	Supplementary questions for Week 8
9	**Cross-Coupling Reactions** General mechanistic features: oxidative addition; transmetallation; reductive elimination; side reactions; influence of ligands Prominent C-C coupling reactions and their features: Kumada, Negishi, Stille, Suzuki and Sonogashira Coupling Buchwald-Hartwig Reaction: arylation of amines; other heteroatoms Mizoroki-Heck Reaction: mechanism; reactivity trends; predicting geometry and stereoselectivity; regioselectivity patterns	1-34	Tutorial class; Supplementary questions for Week 9
10	**Oxidative Functionalization of Alkenes** Wacker Process: catalytic cycle; mechanistic details Wacker-Tsuji Oxidation of Alkenes: mechanism; regioselectivity Alternative nucleophiles: vinyl acetate production; amines and alcohols 1,3-diene substrates: mechanism; control of stereochemistry	1-34	Supplementary questions for Week 10; Tutorial class
11	**Catalytic Carbonylation** Industrial production and use of CO: generation of Syngas; conversion of Syngas to methanol Carbonylation of methanol: Monsanto and Cativa Processes; Tennessee Eastman Acetic Anhydride Process Hydrocarboxylation and hydroesterification of olefins: traditional method for producing methyl methacrylate; Lucite Alpha Process Hydroformylation: cobalt vs rhodium catalyzed; ligand control of regioselectivity and chemoselectivity	1-34	Supplementary questions for Week 11; Tutorial class
12	**Catalytic Hydrogenation of Alkenes** Dihydride complexes: hydride mechanism; alkene mechanism; reactivity trends Monohydride complexes: oxidative addition of H_2; heterolytic cleavage of H_2 Asymmetric hydrogenation; importance; ligand control	1-34	Supplementary questions for Week 12; Tutorial class
13	**Alkene Polymerization and Metathesis** Ziegler-Natta *vs* single-site catalysts Cossee-Arlman Mechanism: initiation; chain growth; termination Control of polymer architecture: chain length; chain branching; tacticity Alkene and alkyne metathesis: types of reaction; mechanism; general catalytic cycle	1-34	Supplementary questions for Week 13; Tutorial class

Course Policies and Student Responsibilities

(1) General

Your learning is your own responsibility; what has been set up is aids and an environment conducive for that. You are expected to complete all assigned pre-class readings and activities, attend all lectures punctually, and take all scheduled assignments and tests by the due dates. You are expected to take responsibility to follow up with course notes, assignments, and course related announcements for lectures that you have missed. You are expected to participate in all tutorial discussions and activities.

(2) Absenteeism

Attendance at lectures, reflection sessions and tutorial classes is strongly encouraged. For those absent, you must catch up each week and follow the recorded lectures and tutorials yourselves. Cramming the night before quizzes and the final exam to catch up is not recommended.

Academic Integrity

Good academic work depends on honesty and ethical behaviour. The quality of your work as a student relies on adhering to the principles of academic integrity and to the NTU Honour Code, a set of values shared by the whole university community. Truth, Trust and Justice are at the core of NTU's shared values.

As a student, it is important that you recognize your responsibilities in understanding and applying the principles of academic integrity in all the work you do at NTU. Not knowing what is involved in maintaining academic integrity does not excuse academic dishonesty. You need to actively equip yourself with strategies to avoid all forms of academic dishonesty, including plagiarism, academic fraud, collusion and cheating. If you are uncertain of the definitions of any of these terms, you should go to the academic integrity website for more information. Consult your instructor(s) if you need any clarification about the requirements of academic integrity in the course.

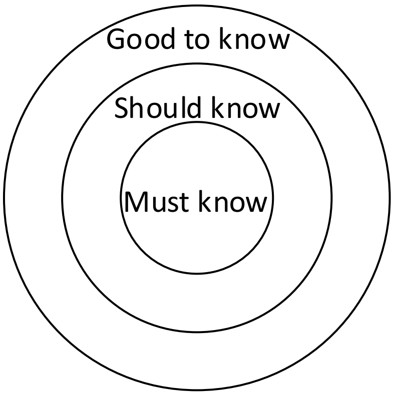
Appendix 1: Assessment Rubrics

Tutorials (10%)

The tutorial sessions and questions are to test your competence in the concepts to be learned, as well as the ability to connect ideas and concepts. It is meant also to create a peer teaching and learning environment. The questions are to be tackled individually, and as a team. The assessment is in participation and engagement.

Mid-terms (50%) and Final Examination (40%)

These constitute your summative assessments for the course. The difference being that the mid-term will be reviewed in class and hence provides formative feedback. In both assessments, you are expected to demonstrate knowledge of the course material, including the ability to utilize and extend them. The components of questions may be thought of as organized into three tiers:



Competency descriptor	**Details**
Must know	These are questions based primarily on lower-level course contents or expected prior knowledge. A demonstration of complete knowledge of these corresponds to a C grade and is required for progression of assessment beyond.
Should know	These questions will be those based directly on the course contents. Complete competency in them demonstrates mastery of the knowledge expected for the course, i.e., with organometallic chemistry. Demonstration of such competency corresponds to a B grade and is required for progression of the assessment beyond this.
Good to know	These questions require students to think beyond what has been explicitly covered in the course. It requires extension of thought beyond examples that have been encountered and may involve content knowledge of lower-level courses but not entirely new concepts. Those who can reach these will correspond to an A grade.

Appendix 2: Intended Affective Outcomes

The course serves to introduce the subject of organometallic chemistry, the bedrock to understanding metal-based catalysis, for example, as well as topics such as bioorganometallic chemistry and much of materials chemistry. Beyond this, you will develop the following "big picture" attributes:

Appreciate that inorganic and organic chemistry are not incompatible or are as distinct as you may have been led

Chemistry or Science in general, however complex some of the ideas or facts may appear, can be understood

Thinking is hard work

CBC Programme Learning Outcome

The Division of Chemistry and Biological Chemistry (CBC) offers an undergraduate degree major in Chemistry that satisfies the American Chemical Society (ACS) curricular guidelines and equips students with knowledge relevant to the industry. Graduates of the Division of Chemistry and Biological Chemistry should have the following key attributes:

1. Competence

Graduates should be well-versed in the foundational and advanced concepts of chemical science, be able to evaluate chemistry-related information critically and independently, and be able to use complex reasoning to solve emergent chemical problems.

2. Creativity

Graduates should be able to synthesize and integrate multiple ideas across the curriculum, and propose innovative solutions to emergent chemistry-related problems based on their training in chemistry.

3. Communication

Graduates should be able to demonstrate clarity of thought, independent thinking, and sound scientific analysis and reasoning through written and oral reports to audiences with varying technical backgrounds. They should also be able to effectively engage other professional chemists in collaborative endeavours.

4. Character

Graduates should be able to act in responsible ways and uphold the high ethical standards that the society expects of professional chemists.

5. Civic-mindedness

Graduates should be aware of the impact of chemistry on society, and how chemistry can be applied to benefit mankind. They should also be aware of and uphold the best chemical safety practices.