UNIVERSIDADE DA CORUÑA USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA Universidade de Vigo

MÁSTER UNIVERSITARIO
INDUSTRIA E INVESTIGACIÓN QUÍMICA

Organometallic Compounds in Synthesis and Catalysis

Teaching Guide

Teaching Guide

1. Descriptive data

Character: Opcional
Call: Annual
Credits: 3 ECTS (12h classroom + 7h seminars + 2h tutorials)

Faculty USC:

Carlos Saá Rodríguez
Professor of Organic Chemistry
Department of Organic Chemistry
Faculty of Chemistry
Classroom: 6h
Tutorials: 1h

José Manuel Vila Abad
Professor of Inorganic Chemistry
Department of Inorganic Chemistry
Faculty of Chemistry
Classroom: 6h
Tutorials: 1h

Dolores Pérez Meirás
Associate Professor of Organic Chemistry
Department of Organic Chemistry
Faculty of Chemistry
Seminars: 7h

Faculty UDC:

Luis Sarandeses da Costa
Professor of Organic Chemistry,
Department of Fundamental Chemistry
Faculty of Sciences
Seminars: 7h
Tutorials: 2h

Faculty UVigo:

Rosana Álvarez Rodríguez
Professor of Organic Chemistry,
Department of Organic Chemistry
Faculty of Chemistry
Seminars: 7h
Tutorials: 2h

Languages: Spanish and English

2. Situation, significance and importance of the subject in the Master's degree

2.1. Block to which the subject belongs in the Curriculum. Related subjects

Block 2: Synthetic Chemistry. Mainly related with the subject "Metal complexes" of the same block (devoted to coordination metal complexes). Both subjects are basic for the speciality of Synthetic Chemistry.

2.2. Role of this course in this training block and throughout the Curriculum

This course is key in the Block Synthetic Chemistry, for studying the structure and reactivity of organometallic complexes and their catalytic applications in chemical synthesis. Also, this area contains basic concepts to understand other subjects belonging to Blocks concerning Biological Chemistry and Nanochemistry and New Materials.

2.3. Prior knowledge (recommended / required) that students must possess to take the subject

It is mandatory to have completed before all subjects of Chemistry's Degree.

3. Learning objectives and competencies to be achieved by the student with the subject

3.1. Learning objectives

- Predict the reasons for the stability and reactivity of organometallic complexes based on their electronic properties.
- Propose reasonable mechanisms, based on the basic organometallic reactions, for reactions catalyzed by organometallic complexes.
- Use of knowledge based on steric and electronic effects to predict how changes in the reactants, metals and ligands influence the course of the reactions.
- Design modern synthetic routes involving the use of organometallic complexes in the key steps.
- Read and critically interpret current scientific papers, with understanding and explanation of its content and significance.

3.2. General skills

- Possess knowledge and understanding to provide a basis or opportunity for originality in developing and / or applying ideas, often within a research context.
- That the students can apply their knowledge and ability to solve problems in new or unfamiliar environments within broader contexts (or multidisciplinary) related to their field of study.
- Students should be able to integrate knowledge and handle complexity, and formulate judgments based on information that was incomplete or limited, include reflecting on social and ethical responsibilities linked to the application of their knowledge and judgments.
- Identify information from scientific literature using appropriate channels and integrate such information to raise and contextualize a research topic.
- Use scientific terminology in English to argue the experimental results in the context of the chemical profession.
- Ensure proper implementation of new technologies to capture and organize information to solve problems in professional activity.

3.3. Specific skills

- Define concepts, principles, theories and facts of the various specialized areas of chemistry.
- Suggest alternatives for solving complex chemical problems of various specialty chemicals.
- Apply materials and biomolecules in innovative fields of industry and chemical engineering.
- Operate with advanced instrumentation for chemical analysis and structural determination.

• *4. Course contents*

4.1. Sections of the course:

Theoretical contents:

Topic 1. General characteristics of organometallic complexes

Topic 2. Mechanisms of organometallic reactions

Topic 3. Cross-coupling reactions. Heck reaction

Topic 4. Carbonylation and decarbonylation reactions

Topic 5. Metal-carbene complexes

Topic 6. Metal-alkyne complexes

Topic 7. Metal-alkene, metal-diene and metal-dienyl complexes. Reactions via η3-allyl complexes. Metal-arene complexes

Topic 8. Metal-catalyzed C-H activation

4.2. Recommended bibliography

4.2.1. Basic (reference manuals)

- Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules* 3rd Ed., University Science Books, 2009.
- Bates, R. *Organic Synthesis using Transition Metals*, Wiley, 2012.

4.2.2. Complementary

- *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals, 2nd Ed.*; Beller, M.; Bolm, C., Eds., Wiley-VCH, 2004.
- *Metal-Catalyzed Cross-Coupling Reactions, 2nd Ed.;* de Meijere, A.; Diederich, F., Eds., Wiley-VCH, 2004.
- R. H. Crabtree, E. Peris Fajarnés *Química organometálica de los metales de transición, Ed. Publicacions de la Universitat Jaume I, 1997*.

TOPIC 1. General characteristics of organometallic complexes

1. Sense theme (Introduction)

This topic describes the general characteristics of the organometallic complexes: type of ligands, number of electrons, oxidation state, dn configuration, etc. Major structural features of metal complexes will also be discussed.

2. Topic headings

1) Formalisms: a) oxidation state, b) electronic configuration, coordination number, and rule 18 e-, c) classes of ligands. 2) Bond considerations. 3) Structural considerations.

3. Bibliography

Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules* 3rd Ed., University Science Books, 2009.

Chapter 1, pag 1-12

4. Duties

Solve the exercises indicated by the teacher and deliver on the date indicated in the *schedule of activities* of the subject. During the corresponding seminar, students will solve these exercises on the blackboard.

TOPIC 2. Mechanisms of organometallic reactions

1. Sense theme (Introduction)

This topic describes the basic mechanisms of organometallic reactions. Usual series of reactions will be discussed in the most important catalytic cycles.

2. Topic headings

1) Associative and dissociative mechanism. 2) Oxidative addition and reductive elimination. 3) Insertions and eliminations. 4) Nucleophilic and electrophilic attack on ligands coordinated to the metal. 5) Transmetallation.

3. Bibliography

Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules* 3rd Ed., University Science Books, 2009.

Chapter 2, pag 13-38

4. Duties

Solve the exercises indicated by the teacher and deliver on the date indicated in the *schedule of activities* of the subject. During the corresponding seminar, students will solve these exercises on the blackboard.

TOPIC 3. Cross-coupling reactions. Heck reaction

1. Sense theme (Introduction)

This topic describes the main cross-coupling reactions between Csp3, Csp2 and Csp organometallic species catalyzed by organometallic species. Heck reaction will be discussed as a key reaction in the formation of olefins in catalytic conditions.

2. Topic headings

1) Cross-coupling reactions of organometallic species C-sp3. 2) Cross-coupling reactions of organometallic species C-sp2. 3) Cross-coupling reactions of organometallic species C-sp. 4) Heck reaction.

3. Bibliography

Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules* 3rd Ed., University Science Books, 2009.

Chapter 4, pag 65-115.

4. Duties

Solve the exercises indicated by the teacher and deliver on the date indicated in the *schedule of activities* of the subject. During the corresponding seminar, students will solve these exercises on the blackboard.

TOPIC 4. Carbonylation and decarbonylation reactions

1. Sense theme (Introduction)

The decarbonylation and carbonylation reactions catalyzed by metals and their role in reactions of industrial interest will be analyzed.

2. Topic headings

1) General reactivity of metal carbonyls. 2) Carbonylating reactions catalyzed by palladium and carbonylation of alkenes and alkynes. 3) Carbonylations of industrial interest: Monsanto process; hydroformylation (Oxo process). 4) Decarbonylation reactions.

3. Bibliography

Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules* 3rd Ed., University Science Books, 2009

Chapter 5, pag 129-146

4. Duties

Solve the exercises indicated by the teacher and deliver on the date indicated in the *schedule of activities* of the subject. During the corresponding seminar, students will solve these exercises on the blackboard.

TOPIC 5. Metal-carbene complexes

1. Sense theme (Introduction)

The nucleophilic and electrophilic reactivity of the metal-carbene complexes are analyzed. Special attention will be paid to the reaction "nobel" alkene metathesis.

2. Topic headings

1) Carbenes electrophilic (Fischer carbenes): preparation and reactivity. 2) Carbenes nucleophilic (Schrock carbenes). 3) Metathesis of alkenes: general mechanism, ROMP, and RCM.

3. Bibliography

Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules* 3rd Ed., University Science Books, 2009

Chapter 6, pag 151-191.

4. Duties

Solve the exercises indicated by the teacher and deliver on the date indicated in the *schedule of activities* of the subject. During the corresponding seminar, students will solve these exercises on the blackboard.

TOPIC 6. Metal-alkyne complexes

1. Sense theme (Introduction)

Nature and reactivity of the metal complexes with alkyne ligands will be discussed.

2. Topic headings

1) Structural aspects. 2) Stable metal-alkyne complexes: Co complexes as protecting groups and reaction of Nicholas. 3) Pauson-Khand reaction. 4) Cycloaddition reactions.

3. Bibliography

Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules* 3rd Ed., University Science Books, 2009

Chapter 8, pag 237-261.

4. Duties

Solve the exercises indicated by the teacher and deliver on the date indicated in the *schedule of activities* of the subject. During the corresponding seminar, students will solve these exercises on the blackboard.

TOPIC 7. Metal-alkene, metal-diene and metal-dienyl complexes. Reactions via η3-allyl complexes. Metal-arene complexes

1. Sense theme (Introduction)

The nature and reactivity of the metal alkenes, dienes and dienyls complexes, metal allyl complexes and metal arene complexes will be analyzed.

2. Topic headings

1) Metal-alkene complexes of palladium and iron. 2) Metal-diene complexes: stabilization of allylic cations and nucleophilic addition. 3) η5-Dienyl complexes: synthetic aplications. 6) Reactions of allylic substrates catalyzed by Pd, Ni and other metals. 7) Metal-arene complexes of groups 6 and 8 (Cr, Fe, Ru).

3. Bibliography

Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules* 3rd Ed., University Science Books, 2009

Chapters 7, 9 and 10, pag 199-229, 261-298 and 307-335.

4. Duties

Solve the exercises indicated by the teacher and deliver on the date indicated in the *schedule of activities* of the subject. During the corresponding seminar, students will solve these exercises on the blackboard.

TOPIC 8. Metal-catalyzed C-H activation

1. Sense theme (Introduction)

Different variants of catalytic functionalization (C-H activation) and its applications in chemical synthesis will be discussed.

2. Topic headings

1) Introduction. 2) Csp3-H activation of alkanes: dehydrogenation, carbonylation, borylation, oxidation and amination. 3) Csp2-H activation: borylation, carbonylation and cyclometallation. 4) Csp2-H activation catalyzed by Pd: oxygenation, arylation, halogenation, fluorination, carboxylation, oxidative Heck reaction. 5) C-H allylic activation. 6) Metal-carbene insertions.

3. Bibliography

Recent articles.

4. Duties

Solve the exercises indicated by the teacher and deliver on the date indicated in the *schedule of activities* of the subject. During the corresponding seminar, students will solve these exercises on the blackboard.

5. - Methodological indications and load allocation ECTS

5.1. ECTS Credit Allocation

LEARNING ACTIVITIES Classroom	HOURS	LEARNING ACTIVITIES No attendance	HOURS
Theoretical (master class)	12	Student dedication	54
Seminars	7		
Tutorials	2		
Subtotal	**21**	**Subtotal**	**54**
Total	**75**		

5.2. Teaching methodologies

A) Theoretical classes. Lectures (using blackboard, computer, cannon), supplemented with online teaching tools.

B) Seminars with Master's own faculty, or visiting professionals of the company, management or other universities. Interactive sessions related to different subjects with discussions and exchange of views with students.

C) Solving practical exercises (problems, multiple choice questions, interpretation and processing of information, evaluation of scientific publications, etc.).

D) Individual or small group tutorials.

E) Using specialized software and Internet. Support on-line teaching (Virtual Campus).

F) Personal study based on different sources of information.

G) Performing different tests for verification of obtaining both theoretical and practical skills and the acquisition of skills and attitudes.

6. Notes on the evaluation

6.1. Evaluation Procedure

The evaluation of this subject will be done through continuous assessment and completion of a final examination.

Continuous assessment will have a minimum weight of 25% and a maximum of 45% in the course grade and will consist of four components: a) problem solving and case studies, b) resolution of work and written reports, c) oral exposure (papers, reports, problems and case studies), d) continuous evaluation through questions and oral questions during the course.

The final exam will cover all the contents of the course and have a minimum weight of 55% and a maximum of 75%.