

# CH267-15 Transition Metal Chemistry: Structure, Reactivity & Organometallic Chemistry

**22/23**

**Department**

Chemistry

**Level**

Undergraduate Level 2

**Module leader**

Paolo Coppo

**Credit value**

15

**Module duration**

10 weeks

**Assessment**

20% coursework, 80% exam

**Study location**

University of Warwick main campus, Coventry

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## Description

### Introductory description

N/A

[Module web page](#)

### Module aims

- To develop a formal understanding of bonding in transition metal complexes, as a platform for understanding the spectroscopy and reactivity of such complexes
- To develop a systematic knowledge of organometallic chemistry, and thereby explore some of the conceptual links between organic and inorganic

### Outline syllabus

This is an indicative module outline only to give an indication of the sort of topics that may be covered. Actual sessions held may differ.

## Group theory

Recognition of symmetry elements. Identification of point groups. Elementary uses of character tables such as assigning appropriate symmetry labels to molecular orbitals.

## d-d spectroscopy of cubic metal complexes

d-d interelectron repulsion. Microstates and many-electron term symbols for  $d^2$ . Term symbols for remaining d configurations. Term splittings in cubic symmetry. Qualitative electric-dipole selection rules. Selected examples.

## Compound formation: thermodynamic considerations

Stepwise and overall formation constants; extension of concepts developed in CH160

## Substitution reactions

Classification scheme, A, D, I. Activation parameters and reaction profiles. Solvent exchange rates and relationships to d configurations/spin states/LFSE. Ligand substitution at octahedral complexes – Eigen-Wilkins mechanism and its associated rate law. Ligand substitution at square planar centres. Rate laws. Trans effects and trans influence. Stereospecific synthesis.

## Redox reactions

Outer sphere processes and simple Marcus theory. Inner sphere reaction. Diagnostic tests for inner versus outer sphere.

## Main group organometallics

Systematic review. Reactivity (source of R- etc). Oxidative addition as applied to Grignard synthesis.

## d-Block organometallics – the 18 electron rule

MO diags for octahedral complexes: sigma and pi bonding. Electron counting, co-ordination compounds vs organometallics. Exceptions to the 18 electron rule, including 16 electron square planar complexes.

Bonding of ligands to metal centres.

Carbon monoxide: sigma donation, pi backbonding, effect on IR spectra

Phosphines: bonding and steric effects

Hydrides and dihydrogen: bonding, backbonding and transformation to dihydride. Recognition that is oxidative addition.

Organic molecules as ligands, exemplified through systems such as: 1 bonding with alkyls; 2 with alkenes; 3 with allyls; 4 with cyclobutadiene; 5 with cyclopentadienyl; 6 with benzene

Carbenes: Fischer, Schrock and NHC

Alkanes, agostic hydrogens and noble gases.

## Reactions of organometallics

Ligand substitution exemplified by carbonyl replacement, the differences between 16e and 18e complexes (associative vs dissociative substitution). Masked dissociative pathways.

Oxidative Addition and Reductive Elimination.

1,1-Migratory insertion reactions, as exemplified by migration onto carbonyl ligands.

1,2-Insertions and  $\beta$ -hydride elimination. Brief discussion.

## Learning outcomes

By the end of the module, students should be able to:

- Use group theory to assign a point group to a molecule and understand the key features of the associated character table.
- Understand why d-d repulsion leads to multiple transitions in electronic spectroscopy.

- Understand the thermodynamics of complex formation and how it leads to an appreciation of the kinetics of ligand substitution (as exemplified by associative, interchange and dissociative processes).
- Understand the difference between inner and outer sphere redox reaction, and how to tell them apart. Use the Marcus cross-relation to approximate reaction rates.
- Understand basic reactivity of TM organometallic complexes, exemplified by ligand substitution, oxidative addition, reductive elimination and migratory insertion reactions.
- Understand and describe the factors affecting reactivity of s and p block alkyls and aryls. Explain successes and limitations of synthetic methods.
- Describe the MO basis for understanding the 18e rule Explain why classical complexes and square-planar organometallics do not follow the 18e rule Count electrons in organometallic complexes.
- Use an MO bonding description to describe the bonding of common ligands to transition metals. Appreciate synthetic methods to make simple complexes.
- Key Skills: Information retrieval, critical analysis, written communication

### **Indicative reading list**

Inorganic Chemistry 6ed by Weller, Overton, Rourke and Armstrong (OUP)

### **Subject specific skills**

Numeracy  
 Problem solving  
 Critical thinking

### **Transferable skills**

Numeracy  
 Problem solving  
 Critical thinking

## **Study**

### **Study time**

<b>Type</b>	<b>Required</b>
Lectures	30 sessions of 1 hour (20%)
Tutorials	3 sessions of 1 hour (2%)
Private study	117 hours (78%)
Total	150 hours

### **Private study description**

Self-study/revision.

## Costs

No further costs have been identified for this module.

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## Assessment

You do not need to pass all assessment components to pass the module.

Students can register for this module without taking any assessment.

### Assessment group D3

	Weighting	Study time
Team Video project See Moodle page for details.	20%	
In-person Examination	80%	

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- Answerbook Green (8 page)
- Students may use a calculator
- Graph paper
- Periodic Tables

### Feedback on assessment

The feedback for the assessed work will be in the form of a mark (summative) with a commentary (formative). Cohort level examination feedback provided via Moodle.

[Past exam papers for CH267](#)

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## Availability

### Post-requisite modules

If you pass this module, you can take:

- CH3F0-15 Advanced Inorganic Chemistry and Laboratory
- CH3F3-30 Advanced Chemistry (Organic, Inorganic and Physical)
- CH3G3-30 Advanced Chemistry (Organic, Inorganic and Physical) Industrial Placement
- CH3F8-15 Advanced Coordination and Bio-Inorganic Chemistry

## Courses

This module is Core for:

- UCHA-4 Undergraduate Chemistry (with Intercalated Year) Variants
  - Year 2 of F101 Chemistry (with Intercalated Year)
  - Year 2 of F122 Chemistry with Medicinal Chemistry (with Intercalated Year)
- UCHA-3 Undergraduate Chemistry 3 Year Variants
  - Year 2 of F100 Chemistry
  - Year 2 of F100 Chemistry
  - Year 2 of F121 Chemistry with Medicinal Chemistry
- UCHA-F110 Undergraduate Master of Chemistry (with Industrial Placement)
  - Year 2 of F100 Chemistry
  - Year 2 of F110 MChem Chemistry (with Industrial Placement)
  - Year 2 of F112 MChem Chemistry with Medicinal Chemistry with Industrial Placement
- Year 2 of UCHA-F107 Undergraduate Master of Chemistry (with Intercalated Year)
- UCHA-F109 Undergraduate Master of Chemistry (with International Placement)
  - Year 2 of F109 MChem Chemistry (with International Placement)
  - Year 2 of F111 MChem Chemistry with Medicinal Chemistry (with International Placement)
- UCHA-4M Undergraduate Master of Chemistry Variants
  - Year 2 of F100 Chemistry
  - Year 2 of F105 Chemistry
  - Year 2 of F110 MChem Chemistry (with Industrial Placement)
  - Year 2 of F109 MChem Chemistry (with International Placement)
  - Year 2 of F126 MChem Chemistry with Med Chem (with Prof Exp)
  - Year 2 of F125 MChem Chemistry with Medicinal Chemistry
  - Year 2 of F106 MChem Chemistry with Professional Experience
- Year 2 of UCHA-F127 Undergraduate Master of Chemistry with Medicinal Chemistry (with Intercalated Year)