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

23/24

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

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 d2. 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 reations
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 β-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

Type	Required
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.

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 D4

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

- 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

Availability

Post-requisite modules

If you pass this module, you can take:

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

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)