UNIVERSITÀ
DEGLI STUDI DI MILANO-BICOCCA

COURSE SYLLABUS

Coordination and Metallorganic Chemistry

2425-1-F5401Q017

Aims

To know electronic configuration, properties, structures, spectroscopy, reactivity and uses of coordination and organometalic compounds.

The student must be able to understand the formulae of coodination compounds, predict geometries, recognize the ligands and describe the metal-ligand bonding and to predict reactivity.

The student must be able to sinthesize, isolate and purify inorganic compound, must be able to prepare a sample for spectroscopy and obtain structural informations

Contents

The course will deal with properties of the coordination compounds of the transition metals , which will be classifed according to the electronic configuration, the donor atom of the ligand, the geometry. The course will then describe synthesis, structure and reactivity of the organometaalic compounds, explaining the different types of M-C bonds, and their peculiar properties. Applications in catalysis, in stoichiometric organic synthesis and for the production of materials will be illustated.

Detailed program

Introduction -The crystal field theory in octahedral, tetrahedral and square planar complexes - Ligand field theory - Spectrochemical series - ? and ? donation, ? * and ? * backdonationj

Electronic counting d? configuration of the metal ion - UV-vis spectra and magnetism in the complexes. The

18-electron rule (Ionic and covalent approch). The isolobal principle

Classification of the complexes according to coordination and geometry numbers. Classification of ligands according to the donor atom. Relations between geometry and d? configuration of the metallic ion.

Isomerism in complexes - conformational, geometric, optical, bonding, spin isomerism.

Reactions of transition metal complexes - Kinetic equations, Activation parameters

a) Substitution inert and labile complexes. Associative (A), dissociative (D) and interchange (I) mechanisms. Associative substitutions in square-planar complexes: effect of the solvent, of the incoming ligand (nucleophilicity), leaving ligand. Trans effect and trand influence. Dissociative and interchange substitutions in octahedral complexes. Linear free energy relationship (LFER). Base- and redox catalyzed substitutions (the SN?CB mechanism).

b) redox reactions Outer sphere mechanism, the Marcus theory. Inner sphere mechanism, the Taube experiment. Effect of the bridging ligand. Adjacent and remote attack. Intervalence complexes.

c) Isomerization Geometrical and optical somerization in tetra-, penta, and hexacoordinated complexes racemizations. Bonding isomerizations.

Organometallic complexes. Historical Background.

a) Carbonyl complexes - The metal-CO bond. Terminal and bridging carbonyls Synthesis of carbonyl metal complexes. CO reactions: substitutions, nucleophilic and electrophilic attack, insertion.

b) Alkyl complexes - Synthesis of alkyl complexes. Alkyl reactions: ? elimination.

c) Hydride complexes - Synthesis of the hydride complexes. Spectroscopic characterization methods. Hydrides reactions. Non-classical hydrides, agostic bonds

d) CO analogues: isonitriles, dinitrogen, nitrosyl, substituted phosphines

e) Complexes of **alkenes, alkynes and polyenes** (the Dewar-Chatt model)

f) Allylic complexes and carbocyclic ligands: pentadienyl complexes, metallocenes, metalloarenes fullerene complexes

g) Carbines and carbines

Reactions of organometallic complexes: CO substitutions, elimination, migration, oxidative addition, reductive elimination, isomerizations, fluxionality.

Homogeneous catalytic cycles: hydrogenation, hydroformylation, carbonylation of alcohols, Wacker and Heck reactions, metathesis.

Prerequisites

Theories on Chemical bonds, Molecular Orbital (MO) theories, Chemistry of Main Grop Elements, Molecular Spectroscopy

Teaching form

24 two-hour lectures, in person, Delivered Didactics

6 four-hour lab activities, in person, Interactive Teaching

Textbook and teaching resource

Suggested textbooks:

Atkins Overton - Chimica Inorganica - Zanichelli

Huheey - Chimica Inorganica - Piccin

Text for documentation:

Ribas - Coordination chemistry - Wiley

Elschenbroich - Organometallics - Wiley

Rankin - Structural Methods in Molecular Inorganic Chemistry - Wiley

Power point containing images of lectures.Book chapters and scientific paper (mainly on spectroscopic structural methods)

Semester

First semester

Assessment method

Oral examination.

The interviews are used mainly to evaluate the knowledge of the subject, but also the ability to connect with subjects of the other courses, within the LT and the LM.

The final judgment is expressed in numeric marks, where 30/30 means full experties and 18 means just sufficiency

Office hours

Any hour, after phone or Email appointment

Sustainable Development Goals

AFFORDABLE AND CLEAN ENERGY | RESPONSIBLE CONSUMPTION AND PRODUCTION | CLIMATE ACTION