Privileged Chiral Ligands and Catalysts

During the last decade, the field of asymmetric catalysis has continued to evolve at an accelerating pace. Despite significant advances, the field still lacks predictive tools that could facilitate the discovery and optimization of new reactions. It was in this very context that the term "privileged chiral catalysts" was first coined by Yoon and Jacobsen in 2003 in a *Science* viewpoint article (which has already accumulated over 350 citations!). In analogy with pharmaceuticals that are active towards specific biological targets, the expression refers to ligands and catalysts that are highly enantioselective for mechanistically unrelated catalytic asymmetric transformations. Because there is still no general recipe for the ab initio design of efficient chiral catalysts, the search for a new catalytic asymmetric reaction generally begins with an evaluation of these privileged or universal structures. The identification of a lead candidate from this pool of special molecules is then followed by further structural optimization.

The book *Privileged Chiral Ligands and Catalysts*, edited by Qi-Lin Zhou, provides an overview of a selection of 11 of the most often used privileged scaffolds for asymmetric catalysis. The book is divided into 11 independent chapters written by an impressive list of world-renowned experts. Each chapter is essentially devoted to an exhaustive description of the various catalytic asymmetric transformations for which a particular privileged chiral catalyst has been successfully applied. The originality of the book resides in the fact that the editor has chosen to present a series of results from the catalyst point of view rather than—as is usually the case in review articles—from the reaction point of view. Most (but unfortunately not all) chapters begin with a description of the historical context at the time of the discovery of the catalyst in question, followed by a brief presentation of the synthetic route(s) for its preparation. It should be particularly noted that Chapters 3 and 5 have been enriched with extremely instructive discussions of the structural aspects of transition metal complexes bearing Josiphos-type and Box-type ligands respectively. When appropriate, rationales based on intuition or experimental evidence are also provided for several catalytic transformations. It is striking to note the general lack of theoretical calculations performed so far in this context.

The editor's choice of the 11 ligands and catalysts presented in this book is, of course, inherently subjective, and some readers might have views about the arbitrary selection. However, perhaps it is more interesting to note the relatively low proportion of organocatalysts compared with ligands for transition metals (2 examples out of 11 structures), despite the emergence of the former as a highly competitive field of research in the last decade. Similarly, the absence of chiral N-heterocyclic carbene ligands (NHCs) may be indicative of the difficulty of adding new classes of privileged scaffolds to the current repertoire.

In conclusion, thanks to its well-organized structure, the book *Privileged Chiral Ligands and Catalysts* provides a rapid and innovative entry into the field of asymmetric catalysis, and will certainly be useful to both experts and novices, whether these are students or experienced academics. Worthy of note, from a didactic point of view, is the overall high quality of the text and the figures, and the exhaustiveness of the references, topped with an indispensable comprehensive index.

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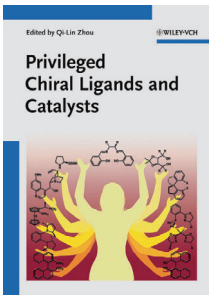
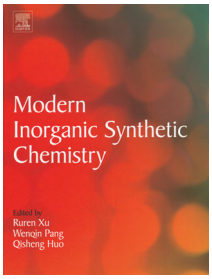


Privileged Chiral Ligands and Catalysts
Edited by Qi-Lin Zhou. Wiley-VCH, Weinheim, 2011. 462 pp., hardcover, € 139.00.—ISBN 978-3527327041

Modern Inorganic Synthetic Chemistry

During the last few years there has been enormous progress in the development of modern synthetic methods and techniques for the preparation of new inorganic solids that exhibit advanced properties. Synthetic chemistry is in the main focus of chemists, and is the central tool for preparing materials to solve future challenges such as energy generation, energy storage, and energy conversion. The prosperity of mankind is directly related to progress in the synthesis and development of new and advanced materials. Review articles describing special synthetic methods appear quite frequently, but up to now there has not been a textbook presenting the various facets of the synthesis of inorganic solids in a comprehensive way. The book *Modern Inorganic Synthetic Chemistry* is an attempt to fill that gap. Ruren Xu, Wenqin Pang, and Qisheng Huo have edited a book that consists of 24 chapters in which various authors present and discuss modern synthetic methods and preparation techniques for inorganic solids. Most chapters include brief descriptions of the equipment needed for the preparations.



Modern Inorganic Synthetic Chemistry
Edited by Ruren Xu, Wenqin Pang and Qisheng Huo. Elsevier, Amsterdam, 2010. 610 pp., hardcover, € 230.00.—ISBN 978-0444535993

The first chapter, "Frontiers in Modern Inorganic Synthetic Chemistry", provides an introduction to new types of reactions, reaction pathways, and technologies. In Chapter 2, classical high-temperature syntheses, spark plasma sintering, self-propagating high-temperature syntheses (SHS), and high-temperature electrolysis of molten salts are discussed. Here several sub-chapters are devoted to the preparation of different classes of solids and of precursors.

Chapter 3, "Synthesis and Purification at Low Temperature", starts with technical details of these techniques followed by a discussion of fractional condensation and distillation, selective desorption and separation, and syntheses of volatile inorganic substances. Methods for the preparation of noble gas compounds and reactions in liquid ammonia are also presented. Hydrothermal and solvothermal syntheses of solids such as zeolites, hybrid materials, metal–organic frameworks (MOFs), and nanoparticles are in the focus of Chapter 4. Some comments are made concerning hydrothermal biochemistry, reactions in supercritical water, and ionothermal syntheses. In "High Pressure Synthesis and Preparation of Inorganic Materials" (Chapter 5) the focus is on the behavior of gases, solids, and water under high pressure. Changes of the electronic and crystal structure of solids are also discussed.

Chapter 6, "Inorganic Photochemical Synthesis", deals with the synthesis of organometallic compounds, photoisomerization reactions, cleavage of metal–metal bonds, the syntheses of some selected compounds, and the preparation of thin films. The preparation of nanoparticles and the photochemical production of hydrogen are also described briefly. Several methods based on chemical vapor deposition (CVD), including PECVD, PCVD, ALD, etc., are introduced in Chapter 7, entitled "CVD and its Related Theories in Inorganic Synthesis and Materials Preparations". Kinetic and thermodynamic models are illustrated both theoretically and practically using the example of the formation of diamond. Some further examples are also presented. In "Microwave-assisted Inorganic Syntheses" (Chapter 8), the synthesis of microporous and mesoporous materials is discussed, as also are aspects of sol–gel syntheses. Further sub-chapters describe microwave-assisted production of nanomaterials, and solid–solid, solid–gas, and SHS reactions. Plasma-assisted reactions are also mentioned briefly.

Only eight pages are devoted to the synthesis of coordination polymers (Chapter 9). Some basic reaction types and synthetic techniques are discussed. Structural aspects of coordination polymers and binding modes of suitable linker molecules are discussed in detail in Chapter 10, "Assembly Chemistry of Coordination Polymers". The influence of variations in the synthesis parameters is discussed, and special reaction types such as the in situ formation of ligands are addressed.

Synthetic aspects of cluster chemistry are the focus of "Synthetic Chemistry of Cluster Compounds" (Chapter 11). In addition to polyoxometalate chemistry, the chapter discusses structural and synthetic aspects of lanthanoid oxoclusters, borates, borogermanates, aluminoborates, and thiometalate clusters. In the following chapter, "Synthetic Chemistry of Fullerenes", the chemistry of fullerenes is introduced, and free-radical, cycloaddition, and halogenation reactions are described. At the beginning of Chapter 13, "Synthesis of Organometallic Compounds", typical reaction mechanisms are presented. Strategies for the synthesis of different organometallic compounds are described in the following pages.

Inorganic polymers as a class of compounds are treated in Chapter 14, "Synthesis and Assembly Chemistry of Inorganic Polymers", by using the example of polyphosphazenes. A further two pages are devoted to silicone chemistry. A prominent example of a non-stoichiometric compound is the high-temperature superconductor $YBa_2Cu_3O_{7-x}$. Chapter 15, "Synthetic Chemistry of Non-stoichiometric Compounds", discusses the definition and classification of non-stoichiometric solids, and describes selective methods for synthesizing them. Some thermodynamic aspects concerning the formation of such solids are also discussed.

Porous materials with pore diameters of different sizes are used in various applications. "Synthetic Chemistry of Inorganic Porous Materials" (Chapter 16) covers the preparation of zeolites, MOFs, aluminophosphates, organic–inorganic hybrid zeolites, and materials such as MCM-41 and SBA-15. Several synthetic strategies are presented and discussed. Post-synthetic modifications, nanocasting, and the preparation of films and of nanoparticles are introduced in sub-chapters.

Chapter 17, "Assembly Chemistry of Anion-Intercalated Layered Materials", begins by describing the structural properties of layered double hydroxides (LDHs). Several synthetic strategies and methods for the fabrication of LDH films are presented. In addition, the use of LDHs as molecular reactors is discussed. In "Host–Guest Functional Materials" (Chapter 18), the materials that are synthesized include, for example, zeolites in which the normally empty spaces are occupied by metal clusters or dye molecules. Other examples based on MCM-41 or SBA-15 are also discussed.

Various synthetic methods for the preparation of ceramics are described in Chapter 19, "Chemical Preparation of Advanced Ceramic Materials". These involve CVD, precipitation reactions, sol–gel processes, microemulsions, and hydrothermal approaches. A special focus is concentrated on

composite materials with carbon fibers, SiC whiskers, or carbon nanotubes as reinforcing components.

Amorphous materials, selected properties, and relevant synthetic strategies are in the focus of Chapter 20, "Amorphous Materials". Some semi-empirical rules for the formation of metallic glasses are discussed, and the preparation of amorphous alloys under high-pressure conditions is also described. Nanomaterials are currently a very active research area, and Chapter 21, "Synthetic Chemistry of Nanomaterials", presents the most important synthetic strategies of the top-down and bottom-up approaches. Techniques of preparation in ionic liquids and electrochemical methods are also described. Sub-chapters also deal with nanowires, hollow nanostructures, and core–shell particles. Inorganic membranes are thermally, chemically, and mechanically much more stable than polymer membranes, and permeation selectivity is also significantly higher. Preparative techniques for silica membranes and membranes based on zeolites, MOFs, or mesoporous materials are described in Chapter 22, "Preparation Chemistry of Inorganic Membranes".

Natural mechanisms of biomineralization, biomimetic syntheses of inorganic chiral materials using bio-templates, bio-inspired surface modifications, and nacreous organic–inorganic composites are discussed in Chapter 23, "The Frontier of Inorganic Synthesis and Preparative Chemistry: (I)—Biomimetic Synthesis". The book is completed by the chapter "The Frontier of Inorganic Synthesis and Preparative Chemistry: (II)—Inorganic Crystalline Porous Materials", where the focus is on different theoretical approaches for the prediction of structures of microporous solids and the identification of suitable structural directors.

The title of the book is a little bit misleading, because several important classes of compounds are not covered, and the focus is directed towards inorganic materials. Moreover, I expected to find in it several highly topical research areas of solid state chemistry, such as Zintl and intermetallic phases and clathrates, as well as techniques for the handling of radioactive substances. But one should keep in mind that inclusion of these topics would lead to a bulkier book. As mentioned above, the present book aims to complete the range of textbooks available for many different areas of chemistry. Unfortunately, the book does not fulfill that claim in all details. The chapters differ in overall quality and in their graphic representations. The impression arises that in some chapters little attention was devoted to the graphical layout. For example, Chapter 18 contains only four figures. The numbers of literature references, the up-to-date quality of the citations, and also the styles, vary widely. For the intensively studied coordination polymers, only 49 references are provided, whereas the authors of Chapter 17 include 449 citations. Some chapters leave the impression that papers of Chinese colleagues are in the focus, while those of scientists of other countries are only cited sporadically. Also, the keyword and compound indexes do not meet the high standards required for a good textbook. Overall, it is not fully clear what advantages the chapters of the book offer compared to good review articles.

Finally, the question arises: for whom can the book be recommended? For students of chemistry the content seems to be too specialized. It is also questionable whether PhD students working in the area of inorganic materials chemistry want to spend so much on a book. But in a faculty library the book should be available as a reference source.

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