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Preface

Abstract

In principle, chiral catalysis is the best method to introduce stereochemistry into pharmaceutically active molecules. This is reflected by the fact that papers and reviews have appeared at an ever increasing rate since the end of the 1960s when the first papers using chiral metal catalysts were published. However, to be economical and friendly, the catalytic system must fit many constraints. Tremendous new chiral catalysts which offer phenomenal scope and selectivity are being developed in laboratories around the world. In this special issue, we bring together various review articles dealing with recent research activity on chiral catalysis covering novel metal catalyst design in organic solvents, supported-catalytic systems and chiral catalysis in water using artificial or natural enzymes.

Keywords: Chiral catalysis; Metal catalyst; Asymmetric synthesis; Enzymes

The first eight papers in this special issue are primarily focused on metal catalyst design. Four papers describe advances in asymmetric hydrogenation. The synthesis of β-aminoacid derivatives (Bruneau and co-workers) via enantioselective hydrogenation of unsaturated compounds is a very interesting system, especially as, in this case, these substrates are building blocks of choice for the preparation of β-peptides. The synthesis and application of chiral monodentate phosphines in asymmetric hydrogenations is reviewed by Beller and co-workers. After years of neglect, these ligands have recently found a new renaissance. Chiral iridium catalysts (Andersson and Church) have been used in the asymmetric hydrogenation of largely unfunctionalized olefins for nearly a decade. This review discusses several classes of new substrates, outlines the progress that has been made toward their selective hydrogenation, and highlights the role of iridium complexes in this emerging field. As a nice complement to the previous review, Xiao and co-workers will describe the chemistry of chiral half-sandwich complexes and the general application of these complexes in catalysis, in particular asymmetric hydrogenation. Since the initial work in the 1970s, asymmetric metal–carbenoid reactions have undergone many important developments, particularly in terms of the additives that have been applied within this general technique. The use of dirhodium paddlewheel complexes as catalysts for carbene transfer has been described by Davies and Hansen. This review will highlight that many of these catalysts have higher symmetry than the individual ligands themselves. Metalbis(oxazoline) complexes and their application in asymmetric catalysis are reviewed by Reiser and Rasappan. Based on the most common complex geometries, the authors proposed a mechanistic picture that allows one to control the enantioselectivities of the reactions focusing mainly on the relationship between the geometry of the complexes. Various methods for the catalytic asymmetric synthesis of cyanohydrins derived from aldehydes or ketones are discussed by Khan and co-workers. The emphasis is given to chiral Lewis acid metal complexes as efficient catalysis for cyanation reaction. Important achievements in the field of stereoselective reactions catalyzed by hypervalent silicate compounds, silicate-generated by the addition of chiral Lewis bases, is described by Benaglia and co-workers, with a special focus on the most recent contributions in this area.

Transition metal catalytic complexes attached to insoluble supports have an important role in the development of heterogeneous catalysis. Various methods are available for the heterogeneization of homogeneous chiral catalysts, two examples are given in this special review. As a complement of the bis(oxazoline) complex in solution reviewed by Reiser, recent advances in the immobilization of chiral catalysts containing bis(oxazolines) are first described by Mayoral and co-workers. A second aspect, reported by Herrmann and co-workers, will focus on the catalytic applications of chiral monomeric organomolybdenum(VI) and organorhenium(VII) oxides in homogeneous and heterogeneous phases.

A considerable amount of current work is directed towards the chiral catalysis of different types of reactions in water. In view of the environmental aspect, organic reactions in protic or aqueous media have recently gained importance and this topic is covered in the remaining eight papers of this special issue. The general catalytic asymmetric formation of carbon-carbon bonds, in the presence of water, is reviewed by Wang and Pan, and the more specific asymmetric catalytic cyclopropanation reactions in water are described by Simonneaux and co-workers. Distinct methodologies have been presented for carbene transfer such as the use of water-soluble metal catalysts or micelles in water.

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Artificial metalloenzymes (Ward and co-workers) based on the non-covalent attachment of rhodium complexes in protein as hosts, combines the advantages of both catalytic strategies. The concept of deracemization has been introduced in recent times to indicate methods which allow one to transform a racemate into one single enantiomer in 100% yield, thus overcoming the limitation of the traditional kinetic resolution. Two papers are related to a combination of lipases with transition metals or some other racemizing agents which resulted in high yields of single enantiomers, with acylation and in situ racemization occurring simultaneously. In the first one, the roles of the transition metal, in particular, ruthenium, as racemization catalyst, is emphasized by Park and co-workers. In the second paper, a combination of enzymes with transition metals or other related racemizing agents is described by Kamal and co-workers, with respect to types of organic reactions. This review thoroughly highlights the recent trends on these chiral catalyses in the last decade.

Three other articles review useful methods employing pure chemo-enzymatic systems for the preparation of optically active molecules. They are a nice complement of the previous systems in which a combination of metal and enzymes was used. The first one (Servi and co-workers) will focus on the deracemization of *rac*-amino acids to yield non-natural amino acids, either proteinogenic amino acids of D-configuration or non-proteinogenic amino acids of L- or D-configuration. The second paper (Wimmer and co-workers) selects synthetic ways of preparation of chiral alcohols with special attention to the preparation of enantiomerically pure cycloalkanols. Finally, a general review, written by Patel, on the synthesis of chiral pharmaceutical intermediates by biocatalysis emphasizes applications of chiral catalysis in drug production.

I express my thanks to all the contributors for accepting the offer to submit a review and especially to Professor Barry Lever for allowing a special issue to be devoted to chiral catalysis.

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