Radical and Radical Ion Reactivity in Nucleic Acid Chemistry

This book edited by Marc Greenberg presents some very good insights into the knowledge about DNA radicals and radical anions that has been gained in the last few years. These reactive intermediates are present in humans and other organisms (oxidative stress, enzymatic reactions) and can cause damaging effects (mutations, cleavage of the DNA strand). Therefore, knowledge about the formation, stability, and reactions of these species is very important.

The state of the art is described in 14 chapters written by scientists who are working in these areas. The literature coverage extends up to 2008, and many citations come from that year. Several methods for generating these radicals and radical anions are described: 1) ionizing irradiation, 2) electron detachment, 3) electrochemistry, 4) the use of modified nucleic acids (modification at the base or the deoxyribose), and 5) the use of artificial π systems that are photoexcited. The chemical reactions that are caused by these radicals and radical anions and affect the nucleic acid bases and the deoxyribose are described in detail. This also includes the transfer of electrons and electron holes through DNA.

The reviews are mainly focused on experiments. Theoretical calculations are only rarely included. The list of authors who describe their areas of science in the book is impressive. It includes M. Sevilla, W. Bernhard, J. Cadet, C. Chatgilialoglu, M. Greenberg, H. Sugiyama, K. Kawai, T. Majima, A. Wagenknecht, L. Sanche, P. Wardman, V. Shafirovich, N. Geacintov, H. Thorp, S. Kerwin, and R. Manderville.

The text and the figures are well presented. Scientists who like to understand life sciences at a molecular level will use these reviews for at least the next 10 years.

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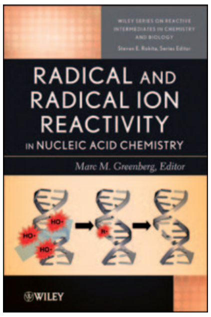


Radical and Radical Ion Reactivity in Nucleic Acid Chemistry
Reactive Intermediates in Chemistry and Biology Series. Edited by Marc Greenberg. John Wiley & Sons, Hoboken 2009. 458 pp., hardcover € 99.90.—ISBN 978-0470255582

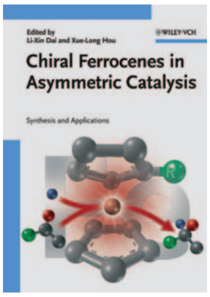
Chiral Ferrocenes in Asymmetric Catalysis

Following the earlier books *Ferrocenes*, edited by A. Togni and T. Hayashi (VCH Verlagsgesellschaft, 1995), and the now three-years-old *Ferrocenes: Ligands, Materials and Biomolecules*, edited by P. Štěpnička (John Wiley&Sons), both of which deal with applications of ferrocenes in very diverse fields of chemistry, the newly published work by Li-Xin Dai and Xue-Long Hou focuses on applications in asymmetric catalysis. This specialization appears to be reasonable in view of the plethora of successful applications of ferrocenyl ligands during the last few years. Alongside axially chiral binaphthalenes, chiral ferrocenes arguably constitute the most useful of all types of chiral ligands. In the present compendium, the problem of bringing order to the bewildering diversity of developments in the area has been solved by a skillful organization of the contents, based mainly on the structural types of the ligands.

Following an introduction in which the editors describe the special structural, chemical, and physical characteristics of ferrocenes, which form the basis for their observed efficiency in catalysis, the second chapter, by Deng, Snieckus, and Metallinos, gives an overview of the different strategies for synthesizing the ligands, with particular emphasis on stereoselective *ortho*-lithiations.

The following ten chapters describe applications in asymmetric catalysis. Xia, Jamison, and You review the use of monodentate ligands, which have become especially important in recent years, mainly because of the work on nickel-catalyzed reductive coupling reactions. Blaser and Lotz then highlight the great successes with bidentate 1,2-P,P ligands, with a focus on asymmetric hydrogenations and industrial applications. Zhou and Hou discuss the wide range of applications of 1,2-P,N ligands, based on the pioneering work by Kumada and Hayashi, who prepared the very first scalemic planar chiral ferrocenyl ligand— PPFA—also providing the synthetic basis for the Josiphos ligands described in the previous chapter.

Bolm and co-workers summarize the work with N,O ligands, mainly for 1,2 additions to aldehydes by employing organozinc or boron reagents. In Chapter 7 (by Zhang and Liu) and Chapter 8 (by You), symmetrical and asymmetrical 1,1′ bidentate ligands are discussed. It has been shown that by using a combination of many different donors and/or other substituents at the 2,2′ positions, a great variety of applications can be carried out. The area of ligands with sulfur donor moieties (such as Fesulphos) has developed rapidly in the last few years, as summarized by Carretero and co-workers.



Chiral Ferrocenes in Asymmetric Catalysis
Synthesis and Applications. Edited by Li-Xin Dai and Xue-Long Hou. Wiley-VCH, Weinheim 2009. 414 pp., hardcover € 149.00.—ISBN 978-3527322800

Coordination of a sulfur donor to a metal generates a stereocenter at the sulfur atom, which is directly connected to the catalytically active center.

Biferrocenes, the best known of which are the members of the *trans*-coordinating TRAP family, have some special applications as a result of their unique coordination behavior, and a large number of examples are described by Kuwano. The use of aza- and phosphaferrocenes in asymmetric catalysis has undergone an extraordinarily rapid development in recent years, in large part because of the work by Fu and co-workers. In their chapter these authors describe the chemical characteristics of these species and their advantages in Lewis or Brønsted base catalysis, as well as in various applications in transition-metal catalysis.

In the final chapter, Richards deals with ferrocene metallacycles, with special attention to the synthesis of the catalysts, which requires the formation of a carbon–metal bond, e.g., by C−H activation. After a discussion of some applications outside the area of catalysis, the chapter discusses the relatively new developments in asymmetric catalysis, with particular attention to rearrangements of allylic imidates.

A useful facility is the book's appendix of about 30 pages, in which the most efficient catalyst systems are summarized in a graphical form by alphabetically arranging different types of reactions. From this one can easily identify cross-links between different chapters. That is very useful, because catalysts of structurally different classes have often been successfully applied to the same types of reactions, and in this way one gets an excellent overview. However, the reader should be aware that a book about such a highly active and fast-moving field of research cannot be expected to present the very latest state of knowledge, as the most recent literature sources are already nearly two years old.

An unsatisfactory aspect of the book, in my view, is that although many applications with a high degree of stereochemical control are described, there are only a very small number of cases where the authors try to present a mechanistic rationale for the stereochemical behavior. A prime example is the case of asymmetric hydrogenations, for which the most efficient ligands—also for industrial applications—are often still identified by extensive trial-and-error screening rather than on the basis of rational catalyst design. It is only through advances in the theory and application of catalyst design that an even more rapid progress can be expected in the future.

However, that concern certainly does not detract from the great value of the book by Dai and Hou, in which all the authors have managed to transfer their enthusiasm for ferrocenes into their chapters. Characteristic of that enthusiasm is the final sentence of the introduction by Dai and Hou: "*We may be proud to say that ferrocene has played and will play a vital role in both the academic world and in the industrial world serving mankind.*"

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DOI: 10.1002/anie.201001671