

Book Review

**Book Review of Nitroxides: Applications in  
Chemistry, Biomedicine, and Materials Science**

Suchada Rajca, and Andrzej Rajca

*J. Am. Chem. Soc.*, **2008**, 130 (44), 14901-14902 • DOI: 10.1021/ja807722s • Publication Date (Web): 11 October 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009

**More About This Article**

---

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

**Metal Vinylidenes and Allenylidenes in Catalysis: From Reactivity to Applications in Synthesis.** Edited by Christian Bruneau and Pierre Dixneuf (CNRS-Université de Rennes I, France). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xviii + 338 pp. \$200. ISBN 978-3-527-31892-6.

This book contains 10 chapters, each contributed by a principal author with extensive experience in the chemistry of metal vinylidenes and allenylidenes. Because of the increasing importance of metal vinylidene and allenylidene intermediates in modern catalysis, its contents are highly pertinent. The authors were carefully chosen to reflect a wide array of interests in this field, ranging from the stoichiometric to catalytic generation of these organometallic complexes to their reactivity and utility in organic synthesis. The audience for the book appears to be mainly organic chemists, although it may prove to be highly useful to inorganic chemists with a strong interest in organic synthesis.

The book begins with discussions of the preparation and stoichiometric reactivity of allenylidene and vinylidene complexes (Chapters 1–3) and then launches into the theoretical aspects and physical understanding of these species (Chapter 4). This provides the strong foundation for a discussion of catalytic generation and reactivity that appears in subsequent chapters. The chemistry of vinylidenes and the chemistry of allenylidenes are generally discussed separately, and a distinction is made in some cases as to the metal used for catalysis, e.g., Cr/Mo/W versus Ru, although this is not consistently maintained.

Because of the many sets of authors that have contributed to this book, there is some overlap in terms of the material covered. Generally, each chapter is well written and incorporates recent references that make the book a pertinent reference text.

Overall, this book provides a timely compilation of information related to an emerging area of modern synthetic organic chemistry and should prove to be an excellent resource for students, faculty, and chemists in the chemical industry interested in applying or learning about this aspect of alkyne chemistry. It is offered at a price of \$200, which makes it an appropriate addition to university or other institutional libraries.

**Richmond Sarpong,**  
*University of California, Berkeley*

JA807249D

10.1021/ja807249d

**Nitroxides: Applications in Chemistry, Biomedicine, and Materials Science.** By Gertz I. Likhtenshtein (Ben-Gurion University of the Negev, Israel), Jun Yamauchi (Kyoto University, Japan), Shin'ichi Nakatsuji (University of Hyogo, Japan), Alex I. Smirnov (North Carolina State University, Raleigh, USA), and Rui Tamura (Kyoto University, Japan). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xx + 420 pp. \$215. ISBN 978-3-527-31889-6.

Nitroxide radicals are known to possess excellent stability, such that they can be prepared and functionalized to suit specific applications that take advantage of the properties associated with an unpaired electron. Some of their important, well-known applications are as spin labels/probes for studying macromolecular structure and function, as building blocks for molecular magnets, and as antioxidants and imaging contrast agents. Recently, applications of nitroxides in catalysis and in plastic batteries are rapidly emerging. This monograph is intended to cover all of these aspects, with emphasis on their theoretical and experimental background, as well as on recent advances.

The first three chapters by Yamauchi cover the fundamentals of magnetism, molecular magnetism, and electron spin resonance (ESR). These are complex subjects, for which a large number of excellent textbooks and monographs are available. Although the introductory chapters might be beneficial, the in-depth discussions of these topics—e.g., the physics of magnetism in Chapter 1 and the fundamentals of ESR in Chapter 3, which include elementary quantum and statistical mechanics with a multitude of equations throughout ~100 pages—are beyond the scope of a book on the applications of nitroxides. References cited in these chapters are limited and mostly dated. In Chapter 2, the discussion of molecular magnetism is scanty, including an error in the description of a Gomberg radical. Much of the discussion of the coordination of metal ions with nitroxides is duplicated in Chapters 8 and 9.

In Chapter 4, Smirnov reviews the biophysical applications of nitroxides using advanced ESR techniques, providing an excellent overview of key recent developments in this research field. As stated in the Preface, the main subject of Chapter 5 by Nakatsuji is the preparation and chemical properties of nitroxides. The term “functional nitroxide radicals” is defined here as “nitroxide radicals which exhibit responses to outside effects, such as light, heat, electron, proton, biological stimuli, and so on.” Nakatsuji presents a rather brief history of nitroxides and their general preparative methods and references “several excellent books and reviews” for coverage of the synthetic aspects of nitroxides. Paramagnetic properties of nitroxides in various spin systems, including charge-transfer complexes, supramolecular assemblies, and photochromic compounds, are reviewed. This chapter ends with a discussion of the biomedical applications of nitroxides and functional nitrones, duplicating the much more extensive coverage of this topic in Chapter 11.

The next three chapters by Likhtenshtein cover the topics of spin labels/probes, spin traps, and the application of nitroxides in polymer science, with the main focus being on the fundamental aspects of these subjects. A plethora of misspellings, such as “nitrone” as “nitron”, occur throughout these chapters, particularly in Chapter 7. The usage of the acronym for electron paramagnetic resonance is inconsistent, with EPR and ESR appearing randomly throughout the text. There are many other obvious mistakes throughout the text, such as misplaced or incorrect structure drawings, misplaced figures, misspellings, inconsistent or undefined acronyms, and typos.

In Chapter 9, Tamura reviews the synthesis and properties of chiral nitroxides and includes very brief sections on the applications of nitroxide in catalysis and battery developments.

Likhtenshtein covers spin labeling, emphasizing the applications of nitroxides in the study of proteins, peptides, membranes, and nucleic acids, as well as biomedical and medical applications of nitroxides in the next two chapters. Current research in these fields is at the frontier of development with a large volume of new reports in the literature accumulating rather rapidly. In the final chapter, the authors present their thoughts on future developments and summarize the applications of nitroxides.

Overall, this book reads like a series of separate “book chapters” rather than as a monograph providing an overview of nitroxides. Except for an excellent chapter on the advances in ESR spectroscopy (Chapter 4), much of the book consists of literature reviews of selected results, with sparse critical discussion and analysis. Many chapters contain duplicate material.

Reviews of some important and rapidly emerging topics, such as applications of nitroxides in catalysis and in plastic batteries, are very short and not up-to-date. The 12 chapters, written by five authors, are somewhat different in style and contain innumerable errors. A remarkably high density of misnomers, typos, and overlapping and superfluous material can be found throughout the book. In our opinion, this book could have benefited from greater editorial attention.

**Suchada Rajca and Andrzej Rajca,**  
*University of Nebraska—Lincoln*

JA807722S

10.1021/ja807722s