

# “Ruthenium Oxidation Complexes: Their Uses as Homogenous Organic Catalysts”

By W. P. Griffith (Imperial College, London, UK), Springer, Dordrecht, The Netherlands, 2011, 258 pages, ISBN: 978-1-14020-9376-0, £117.00, €129.95, US\$159.00 (Print version); e-ISBN: 978-1-4020-9378-4, doi:10.1007/978-1-4020-9378-4 (Online version)

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Professor William P. (Bill) Griffith is the world expert on the chemistry of the heavier platinum group metals (pgms), and has written definitive papers and review articles on many aspects of the chemistry of complexes of platinum, palladium, rhodium, iridium, osmium and ruthenium (1–5). Most of his professional life has been spent teaching and researching at Imperial College, London, UK. An early and abiding interest has been the use of vibrational spectroscopy, in conjunction with other techniques, to define structures of new complexes. His interests in their reactivity patterns and in the catalytic potential of the complexes grew out of this and, with his colleague Professor Steven Ley, he developed methodologies now widely used for the catalytic oxidation reactions of organic compounds (6, 7). These have been instrumental in helping workers in organic synthesis to devise new and useful catalytic oxidation reactions based on the chemistry of ruthenium and osmium.

In addition Bill Griffith has a strong interest in the history of chemistry, especially of the pgms (8, 9), and thus he is able to put the various discoveries into context. Much of his expertise he has distilled into this book, which is an immensely detailed and learned monograph despite its relatively small size. Although much of the readership of this book will be synthetic organic chemists, scientists of other backgrounds will also find much useful material in it.

## Ruthenium Complexes and Oxidation Reactions

The literature is ordered first by the reactions that are promoted and then by the types of ruthenium complexes that are used to carry them out. Within this latter category, the complexes are discussed in order of decreasing oxidation state of the ruthenium, starting

with the tetroxide ( $\text{RuO}_4$ ), Ru(VIII) in the +8 state, and going right down to the zerovalent carbonyls ( $\text{Ru}(0)$ ), emphasising the versatility of the metal. This section then brings discussions of the syntheses, the structures and the reactivities of the compounds which cause the oxidations together with some information on how the oxidations can occur.

The book begins with a brief history of the development of ruthenium chemistry in Chapter 1 and also describes the more important ruthenium complexes. As the title of the book indicates, the main emphasis is on the many and varied oxidations of organic compounds that are catalysed, mostly by higher oxidation state ruthenium compounds in solution; thus there are very helpful sections dealing with the detailed use and properties of these compounds. For example, although the most active oxidant is generally believed to be  $\text{RuO}_4$ , since that material is a strong oxidant and not easily handled as such, it is normally prepared *in situ* from standard starting materials such as hydrated ruthenium chloride, available from commercial sources.

Chapter 2 covers oxidations of alcohols, carbohydrates and diols, while the oxidations of alkenes, arenes, alkynes and alkanes are discussed in Chapters 3 and 4; Chapter 5 collects together oxidations of amines, amides, ethers, sulfides and organic compounds containing other hetero-linkages.

The oxidation reactions discussed include the conversions of primary alcohols into aldehydes or carboxylic acids, and of secondary alcohols into ketones or lactones. Alkenes are also oxidised, this can occur with C=C cleavage, giving ketones and carboxylic acids. Alternatively, under different conditions, alkene oxidation occurs without completely breaking the C—C link, to give *cis*-diols. In addition to the well-known reactions, many other oxidations, of primary amines to nitriles, of tertiary amines to *N*-oxides, of ethers to esters, and of sulfides to sulfones and sulfates, are also described.

A large number of the reactions can be run so that they are stoichiometric in the co-oxidant but catalytic in ruthenium: that way they use only small amounts of the ruthenium compound in the presence of a less expensive co-oxidant such as sodium periodate ( $\text{NaIO}_4$ ) or bromate ( $\text{NaBrO}_3$ ).

A useful touch that the author offers is the inclusion of some actual recipes such as details of a classic Sharpless procedure for the oxidation of an olefin, using ruthenium chloride hydrate and  $\text{NaIO}_4$  to generate  $\text{RuO}_4$  *in situ*, in aqueous acetonitrile

solution. The author's own classic (Griffith) procedure for making the very widely used reagent, tetra-*n*-propylammonium perruthenate (TPAP reagent) is also referenced (6).

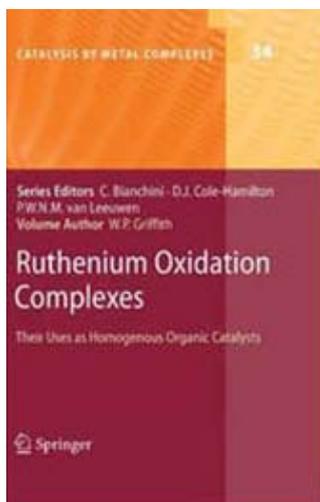
### Concluding Remarks

The book contains nearly 2000 references spanning the time from the discovery of ruthenium in Russia in 1844 (10) right up to the present explosion of interest arising from its employment as a catalyst. Thus the literature cited deals with all aspects of oxidations involving ruthenium compounds. Many of these involve reactions directed to the syntheses of complex organic products and details are provided of their use in natural product and pharmaceutical syntheses, including the oxidations of carbohydrates, amines, amides, ethers and thioethers.

The text is well illustrated with formulae to clarify the various reactions described. Inorganic and physical chemists will also find material to interest and to inspire them to learn more about the transformations that ruthenium can promote. It is a book that is warmly recommended for synthetic organic chemists and will also interest researchers of other persuasions too.

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### **The Reviewer**

*Professor Peter Maitlis FRS is an Emeritus Professor at the Department of Chemistry, University of Sheffield, UK. He holds a number of honours from UK, US, Canadian, Australian and European universities, institutions and learned societies. His research interests have been focused on synthetic and mechanistic organometallic chemistry, particularly relating to the catalysis of processes important to the chemical industry. One example is the rhodium-catalysed carbonylation of methanol to acetic acid and of methyl acetate to acetic anhydride. His group has also synthesised complexes of rhodium or ruthenium and investigated their reactions as models for stages in Fischer-Tropsch reactions.*