APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 732
Published online in Wiley InterScience (www.interscience.wiley.com)

Book Review

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Titanium and zirconium in organic synthesis

Wiley–VCH, Weinheim, 2002
xxv + 512 pp. Price £95.
ISBN 3-527-30428-2

From the standpoint of organic synthesis, the use of the early transition metals titanium and zirconium lags far behind that of the ubiquitous palladium, although titanium-mediated reactions such as Sharpless epoxidation and McMurry reduction are established synthetic methods. Despite the tremendous importance of these elements in the context of olefin polymerization catalysis, and despite the dramatic progress in the organometallic chemistry of these prototypical early transition metals, the practical use of titanium and zirconium is still not widely popular because of the apparent lack of truly catalytic, rather than stoichiometric, reactions, and because of the bewildering variety of often unfamiliar reaction patterns.

The introduction of the bis(η^5-cyclopentadienyl) ligand template, however, clearly allowed a more systematic approach to this area, and the editor of this well-compiled volume is to be congratulated for bringing together 29 international authors to write 14 mostly superbly focused as well as structured chapters on specific reaction types of organo-zirconium and -titanium reagents and catalysts. As to be expected from the general literature, the main focus of this book is on the synthetic utilization of zirconocene-based reagents. Out of 14 chapters, nine more or less exclusively deal with the methods based on zirconocene units.

The fundamental characteristics and reactivity patterns are summarized in the first chapter, along with general information, including the historical development of chemistry of di- and tetra-valent zirconocenes. This is followed by a chapter covering the use of zirconacyclopentadienes, which probably belong to one of the most successful zirconium-based reagents to date. With the discovery of various transmetalation methods, a new dimension in versatility and applicability has been added, allowing, for example, the synthesis of soluble pentacenes, which are important as superconductors in materials chemistry.

Chapter 3 describes the insertion chemistry of carbenoid species (α-halo-α-lithio reagents) into zirconacycles, including application to natural product synthesis. An update on the most useful method of the classic hydrozirconation is provided in Chapter 4, followed by discussion on the reactivity of acylzirconocenes in Chapter 5. The synthetically most important aspect of stereoselectivity is covered in Chapter 6, in which an admirably systematic overview of zirconium-catalyzed stereoselective organic reactions is given. Heterobimetallic zirconocenes, so-called *gem*-metallozirconocenes, are treated, with some emphasis on structural aspects, in Chapter 7. Chapter 8 deals with the use of cationic zirconocene reagents that find application in formation of glycoside bonds.

Chapter 9 introduces the low-valent titanium alkoxo reagent $Ti(O^iPr)_4/^iPrMgX$. This exhibits similar reactivity to divalent zirconocenes. The reactivity of acetylene titano- and zirconocene complexes is summarized in the following chapter. One of the recently recognized, most intriguing low-valent titanium reagents is $Ti(O^iPr)_4/^iPrMgX$, which allows efficient two-carbon–carbon bond formations in esters to give cyclopropanols and cyclopropylamines (Chapter 11). The usefulness of titanocene-catalyzed epoxide opening processes in organic synthesis is described in Chapter 12, while Chapter 13 summarizes the chemistry of allyltitanium reagents. The final chapter of the volume describes the chemistry of titanocene alkylidenes, which, following the seminal discovery by Tebbe, have found their place in certain useful organic transformations, including ester olefination reactions. Of course, the important role of the Tebbe reagent in the development of olefin metathesis should not be overlooked.

The present volume is a truly masterly edited monograph on the recent developments of organo-zirconium and -titanium chemistry for organic synthesis. I am convinced that it will help accelerate the synthetic use of the early transition metals, whose merits not only lie in their new exciting chemistry, but in their low cost and negligible toxicity.

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DOI:10.1002/aoc.371