

Synthesis and Application of Organoboron Compounds

Boron chemistry is, now more than ever, an essential tool in organic synthesis. Since the pioneering contributions of H. C. Brown, D. Matteson, A. Suzuki, and N. Miyaura, new types of organoboron compounds, and new ways to produce them and exploit their considerable synthetic potential, have regularly been discovered. This volume of the series *Topics in Organometallic Chemistry* offers a selection of the most recent prominent results in this exciting area of organic chemistry. As editors of the volume, Elena Fernández and Andrew Whiting have obtained recognized experts in their respective fields as chapter authors, which contributes greatly to the interest of this book.

The first chapter deals with boryl anions, which, since the isolation of the first boryl-lithium species, have been shown to have potential for playing an important role in diverse topics of boron chemistry. M. Yamashita and K. Nozaki have structured their review in three sections: boryl anions, boryl-transition-metal complexes, and boryl-substituted main-group-element compounds derived from boryl anions. Interesting comments on the limitations of the existing chemistry in this area and desired improvements are given at the end of the chapter.

Chapter 2 is concerned with boro-cation chemistry, a field that has grown rapidly during the last five years. First, M. J. Ingleson discusses fundamental aspects of this particular class of organoboron compounds. He then describes inter- or intramolecular electrophilic aromatic borylation reactions, along with hydro- and haloboration of alkenes and alkynes. The remainder of this chapter deals with miscellaneous applications in catalysis and other areas, including a role as precursors for various products.

In Chapter 3, S. Lee and J. Yun present recent work on asymmetric borylation of activated α,β -unsaturated double bonds. Transition-metal-catalyzed reactions, mainly with copper, and to a lesser extent with rhodium, nickel, and palladium, have been successfully developed, mostly resulting in high yields and high enantioselectivities. This review is completed by a discussion of promising new approaches based on organocatalytic β -borylation and the use of water as a reaction medium.

Chapter 4 is devoted to alkynylboron compounds. N. Ishida and M. Murakami describe the synthesis and the reactive properties of alkynylboronic esters and alkynyl borates (ate complexes). Only reactions where the carbon-boron bond is

retained are treated, with an emphasis on cycloadditions and transition-metal-catalyzed reactions.

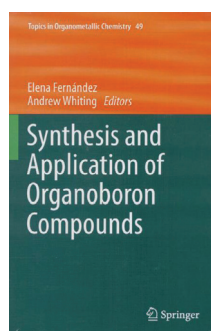
Who could be better than G. Molander to review recent advances in organotrifluoroborate chemistry? In Chapter 5, G. Molander and his co-author K. M. Traister show that these species are much more than simple protected forms of boronic acids. They often exhibit unique and useful reactive properties, illustrated here by cross-coupling reactions, free-radical processes, and various carbon-heteroatom bond-forming reactions.

Chapter 6, the longest in this volume, and probably the most difficult for a non-specialist to read, is devoted to the catalytic dehydrocoupling of amine-boranes and phosphine-boranes. These species have received considerable attention over the last ten years, in the contexts of hydrogen storage materials and polymer precursors. H. C. Johnson, T. H. Hooper, and A. S. Weller provide a panorama of the different systems used as catalysts, and describe the mechanistic scenarios that have been postulated for these processes.

Suzuki-Miyaura couplings provide one of the most straightforward methodologies for the formation of various carbon-carbon bonds. Aryl (or heteroaryl) halides, triflates, or diazonium salts and arylboronic acids and derivatives have been used extensively as coupling partners in both academia and industry. In Chapter 7, H.-Y. Sun and D. Hall describe the latest developments in the stereoselective formation of $C(sp^3)-C(sp^2)$ and $C(sp^3)-C(sp^3)$ bonds, with a particular focus on mechanistic considerations. Selected examples illustrate the synthetic potential of this strategy, as well as the steps required to improve these relatively new cross-coupling reactions of alkyl halides and boronic acids.

Chapter 8, by K. Ishihara, is concerned with boronic-acid-catalyzed reactions of carboxylic acids. Since the initial reports on Diels-Alder cycloadditions between 1,3-dienes and acrylic acids, it is in the area of condensation reactions, esterification and amidation, that the most numerous results have been obtained. The generality and the scope of these atom-economical alternative solutions to classical coupling methods are clearly defined in this review. A number of other boron-(III)-catalyzed processes, such as aldol reactions, 1,3-transposition of allylic and propargylic alcohols, and carbo- or heterocyclizations, are also reported at the end of the chapter. However, it might have been interesting to cover this area more comprehensively, as there are plenty of other examples.

In Chapter 9, V. K. Aggarwal and D. Leonori present the stereocontrolled asymmetric homologation of boronic esters, a powerful method for the synthesis of molecules with a diverse variety of substituents. Based on the fundamental work of D. Hoppe, this strategy has been widely developed by



Synthesis and Application of Organoboron Compounds
Edited by Elena Fernández
and Andrew Whiting.
Springer, New York, 2015.
331 pp., hardcover,
€ 309.00.—ISBN 978-
3319130538

the authors. Here, they discuss the application of the method according to the types of chiral lithium carbenoids involved in the lithiation–borylation process. Some mechanistic considerations and selected applications are also given, which clearly illustrates the versatility and flexibility of these approaches.

This volume ends with a chapter in which F. Jäkle summarizes recent advances in the synthesis and applications of organoborane polymers. Efficient methods that give access to boron-containing polymers are now available, either by polymerization of organoborane monomers or by functionalization of the side or the main chain of conjugated polymers. The author discusses examples of these, before focusing on selected polymers and their

applications in various areas as anion sensors, luminescent species, polyelectrolytes, or devices for the detection and immobilization of sugars. A particular emphasis is put on the architectural control of these polymeric materials.

In summary, this is really interesting book, which covers a wide range of topics and affords a good opportunity to be kept informed about the latest major advances in boron chemistry.

Bertrand Carboni

Institut des Sciences Chimiques de Rennes
UMR CNRS 6226, Université de Rennes 1 (France)

International Edition: DOI: 10.1002/anie.201509362

German Edition: DOI: 10.1002/ange.201509362