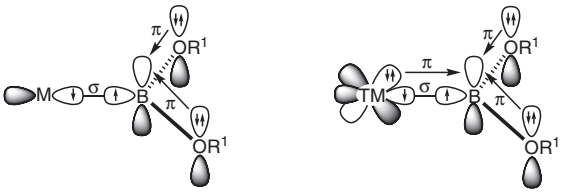
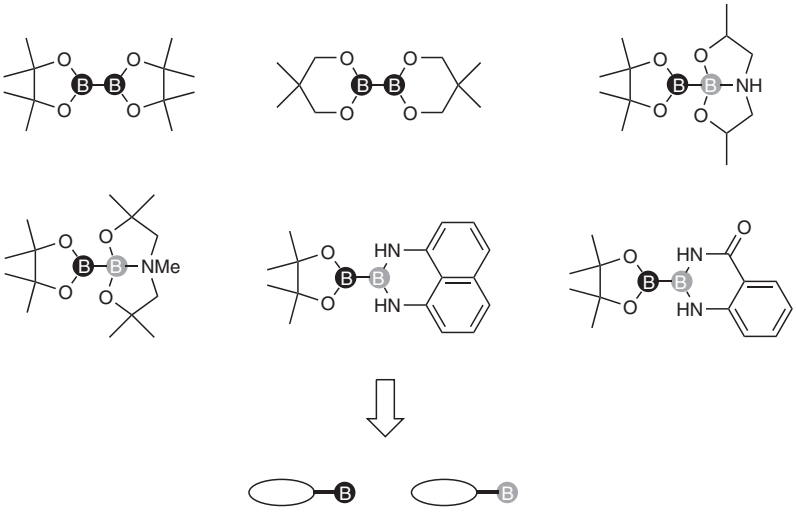
Abstracts

Mechanisms for the selective formation of carbon—boron bonds under mild reaction conditions can be better understood with the help of computational studies, either alone or in collaboration with experimental research. There is a diversity of reaction mechanisms, many of which can be effectively characterized with currently available techniques.



Keywords: carbon—boron bonds · hydroboration · borylation · nucleophilic substitution · electrophilic substitution · Lewis base catalysts · computational studies

This chapter describes the synthesis of symmetrical and unsymmetrical diboron compounds, and their synthetic applications for installing boron into organic molecules via activation of the boron—boron σ-bond under transition-metal/transition-metal-free catalysis. Because of the vast scale of these diboron-based boron-installing reactions, this chapter focuses mainly on the reactions with unsaturated carbon—carbon bonds such as alkynes and alkenes, α,β-unsaturated carbonyl compounds, organic halides, and C_{aryl}—H bonds. A discussion of the regio-, stereo-, and enantioselectivities of the boron-installing reactions is also included.



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Keywords: symmetrical diboron compounds · unsymmetrical diboron compounds · transition-metal-catalyzed borylation · non-transition-metal-catalyzed borylation · diborylation · hydroboration · borylstannylation · aminoboration · carboboration · boron conjugate addition · borylative substitution · C—H borylation

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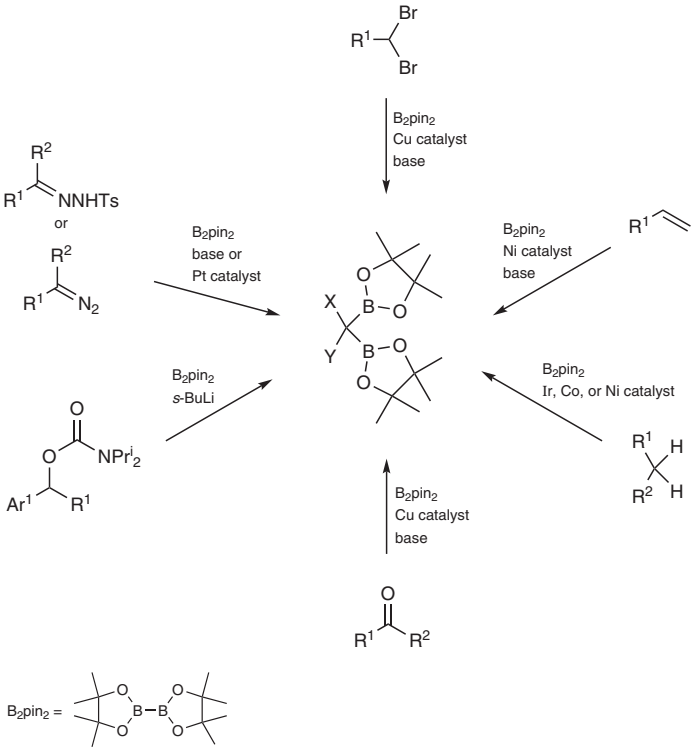
gem-Diboron compounds are important intermediates in organic synthesis. In recent decades, a variety of methods for the preparation of *gem*-diboron compounds have been developed, among which, insertion into B—B bonds represents a unique approach. This chapter summarizes the synthesis of *gem*-diboron compounds based on insertion reactions into diboron compounds. These reactions include the diborylation of *gem*-dibromides, alkenes, benzylic C—H bonds, carbonyls, carbamates, and diazo compounds.



Keywords: *gem*-diboron compounds · borylation · diborylation · alkenes · carbonyl compounds · carbamates · hydrazones · diazo compounds · *gem*-dibromides · transition-metal catalysis

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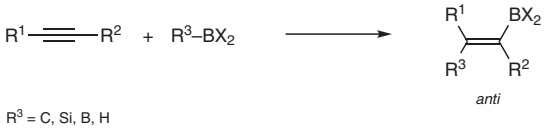
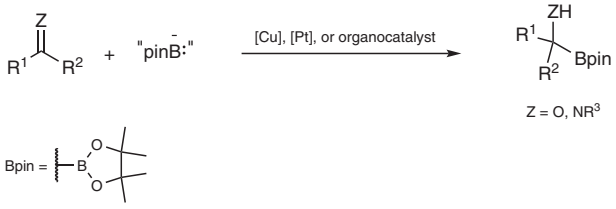
Boron additions, such as carboboration, silaboration, diboration, or hydroboration of alkynes, offer efficient strategies for the synthesis of alkenylborons, which are versatile synthetic intermediates. Most of the reported reactions occur in *syn* addition mode. Accordingly, *anti*-selective boron addition to alkynes is an important challenge in modern organic synthesis. This chapter describes successful examples of *anti*-selective boron additions.



Keywords: *anti* selectivity · alkynes · vinylboranes · alkenylboranes · carboboration · silaboration · diborylation · hydroboration

The nucleophilic borylation of carbonyl groups and imines provides α-oxy and α-amino boronate esters, respectively, under a variety of metal-catalyzed and metal-free reaction conditions. The resulting boronate esters, which can be accessed in high enantiopurity, have been utilized in a variety of transformations based on the reactivity of the carbon—boron bond. For α-oxy boronate esters, the oxygen or boron is often protected for increased stability. Formation of carbon—carbon bonds by homologation reactions and Suzuki–Miyaura-type coupling reactions provides advanced intermediates in synthesis. A variety of methods have been developed for the asymmetric synthesis of α-amino boronate esters, a key precursor to the α-amino boronic acid pharmacophore. Application of these methods to the synthesis of bortezomib and a precursor to (*R*)-cetirizine have been demonstrated.



Keywords: borylation · aldehydes · ketones · imines · homogeneous catalysis · asymmetric catalysis · organocatalysis · homologation · 1,2-metalate rearrangement · Suzuki–Miyaura coupling · bortezomib · cetirizine · α-hydroxy boronate esters · α-amino boronate esters · trifluoroborate salts

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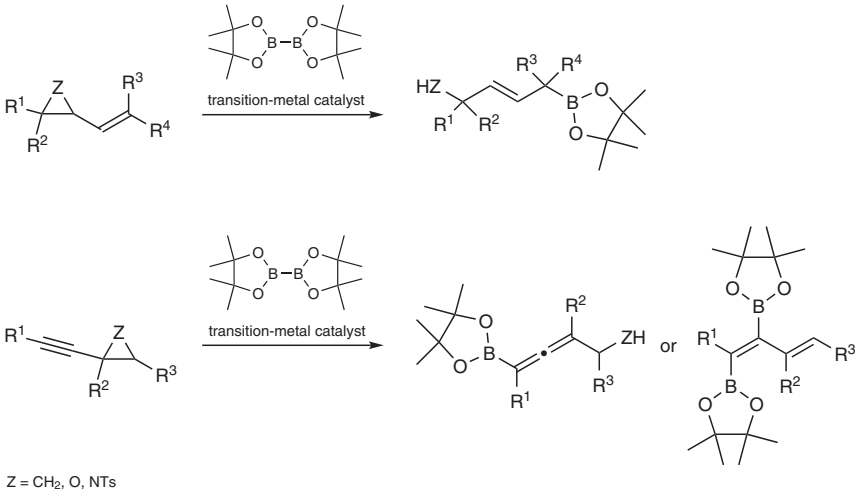
7 Borylative Ring Opening

M. Pineschi and C. Boldrini

This review describes published methods for the direct introduction of a boron atom into organic molecules by ring opening of strained cyclic systems using nucleophilic diboron species. Considering the synthetic versatility of functionalized organoboron derivatives, the newly formed carbon—boron bond thus installed paves the way for a wide range of useful subsequent transformations.



Keywords: borylation · nucleophilic diboron species · boronic esters · ring-opening reactions · vinyl epoxides · vinyl aziridines · vinylcyclopropanes · propargylic epoxides · propargylic aziridines · propargylic oxetanes · epoxides · aryl aziridines · transition-metal catalysis

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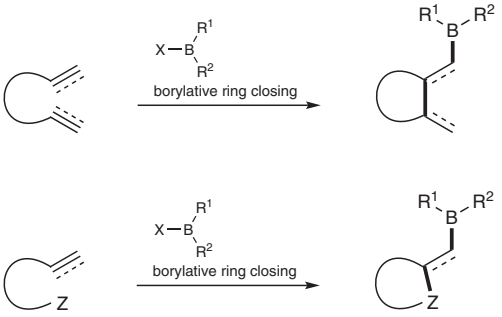
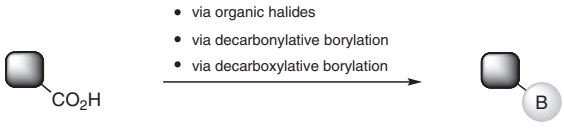
This chapter reviews metal-catalyzed and boron-mediated borylative ring-closing reactions of unsaturated substrates that offer efficient routes to a wide variety of boron-functionalized carbo- and heterocyclic compounds.



Keywords: boron · borylation · cyclization · ring-closing reactions · catalysis · cyclic compounds

Organoboron species are versatile building blocks and have been widely used in the synthesis of bioactive molecules, natural products, and organic materials. Accordingly, approaches to access such compounds have been widely explored. Carboxylic acids, which are ubiquitous and abundant organic feedstocks, can be transformed into their borylated counterparts via several different catalytic or stoichiometric approaches. In this review, decarboxylative borylation reactions, which form a carbon—boron bond with elimination of carbon dioxide, are detailed in terms of reaction conditions, substrate scope, and experimental procedures.



Keywords: decarboxylative borylation · decarbonylative borylation · decarboxylation · borylation · carboxylic acids · boronic acids · boronic acid esters · boronates · light-induced reaction · photoredox catalysis · nickel catalysis · copper catalysis · redox-activated esters · *N*-hydroxyphthalimides

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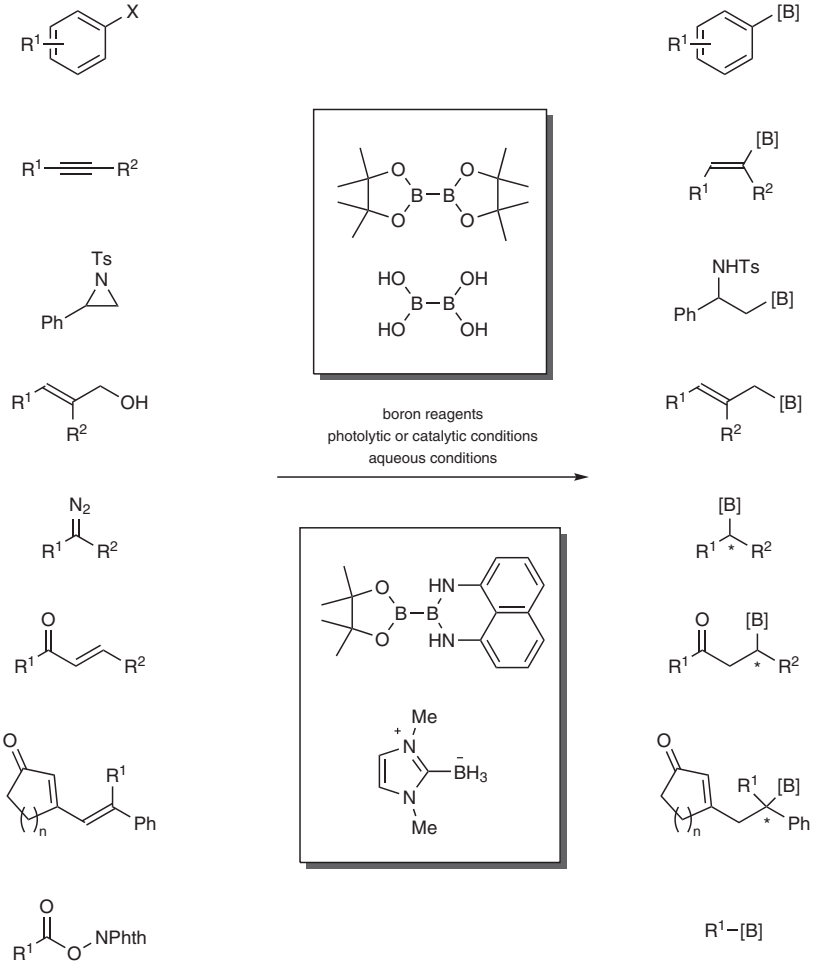
10 Borylation Reactions in Water

T. Kitanosono and S. Kobayashi

Organoboron compounds are integral to modern synthetic organic chemistry as their C—B linkages undergo a range of chemical transformations. Their privileged position is underpinned by their versatile transformability with retention of stereochemistry, as well as their non-toxic nature and excellent functional-group tolerance. Although water has become a common medium in the reaction of organoboron compounds, such as Suzuki–Miyaura couplings, C—B bond formations in aqueous media have emerged only recently. This chapter offers an overview of recent developments across the broad landscape of organoboron chemistry, using solvent amounts of water and covering a range of C—B bond-formation processes, including enantioselective reactions.



Keywords: water · aqueous · bis(pinacolato)diboron · tetrahydroxydiboron · Miyaura borylation · photolysis · photoredox · visible light · arenediazonium salts · diazo compounds · arylboronates · vinylboronates · allylboronates · alkylboronates · boranes · reductive borylation · hydroboration · ring opening · decarboxylation · photopolymerization · conjugate addition · 1,6-addition · asymmetric synthesis · palladium · copper · photocatalysis · N-heterocyclic carbenes (NHC) · porphyrins · directed evolution · cytochrome · surfactants · heterogeneous catalysis · continuous flow

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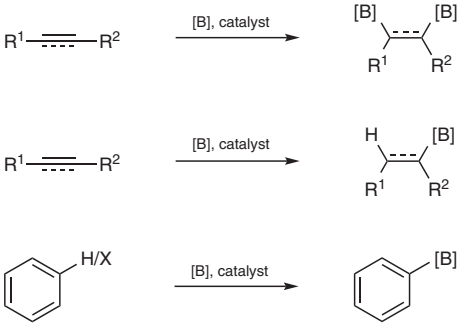
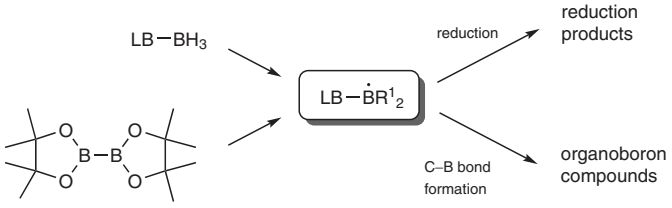
Nanocatalyzed organoboron synthesis is currently a topic of significant interest as it overcomes some of the limitations of homogeneous catalyst systems. This chapter focuses on the use of nanoparticles to catalyze carbon—boron bond-formation reactions via different approaches including diboration and hydroboration of C—C multiple bonds as well as C—H and C—X (X = Br, I) borylation reactions.



Keywords: alkynes · alkenes · allenes · arenes · aryl halides · alkyl halides · diborylation · borylation · hydroboration · silaboration · heterogeneous catalysis · bis(pinacolato)diboron · bis(catecholato)diboron · pinacolborane · platinum · gold · copper · palladium · iron

Recent synthetic applications of boryl radical moieties, including reduction reactions and the synthesis of organoboron compounds, are reviewed in this chapter. A specific focus is given to discussion of the methodology, applicability, and experimental details.



LB = Lewis base

Keywords: boryl radicals · reduction · organoboron compounds · borylative cyclization · radical cascade reaction · hydroboration · borylation

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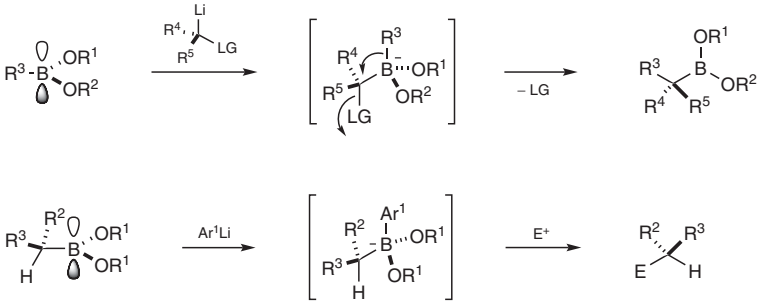
13 Boron "Ate" Complexes for Asymmetric Synthesis

S. G. Aiken, J. M. Bateman, and V. K. Aggarwal

Addition of a nucleophile to a boronic ester results in the generation of a tetravalent boronate "ate" complex. If there is a leaving group stationed on the carbon atom α to the boron atom, the boronate complex can undergo stereospecific 1,2-migration with simultaneous expulsion of the leaving group to form a homologated boronic ester. The enantioselectivity of the process is dictated by either incorporating a chiral substituent into the boronic ester component (substrate control), or by forming a boronate complex through the addition of an enantioenriched carbenoid species to a boronic ester (reagent control). Activation of a boronic ester with organolithium reagents generates a nucleophilic boronate complex that acts as a chiral organometallic-type reagent, reacting with a wide range of electrophiles with inversion of stereochemistry. This chapter discusses methodology available for the enantioselective homologation of boronic esters using both substrate- and reagent-controlled strategies, and the development of boronate complexes as chiral nucleophiles.



Keywords: Matteson reaction · substrate control · reagent control · homologation of boronic esters · asymmetric deprotonation · lithiation–borylation · 1,2-migration · 1,2-metalate rearrangement · stereospecific · assembly-line synthesis · contiguous stereocenters · chiral organometallic reagents

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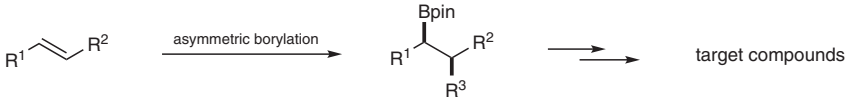
14 Application of Selective Asymmetric Borylation to Target Compounds

T.-J. Gong, E.-A. M. A. Ahmed, and Y. Fu

This chapter describes recent progress in the use of transition-metal-catalyzed asymmetric borylation (asymmetric hydroboration, diboration, and borylative difunctionalization) for the preparation of enantioenriched chiral boronate ester derivatives, and for the synthesis of α- and β-aminoboronates. Moreover, selected applications of these asymmetric borylation protocols to the synthesis of biologically active compounds and natural products are presented.



Keywords: asymmetric synthesis · borylation · hydroboration · carboboration · aminoboronates · boron compounds · natural products · transition-metal catalysis

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