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Digest paper

Geminal bis(boron) compounds: Their preparation and synthetic applications

Chaoqiang Wu, Jianbo Wang *

Beijing National Laboratory of Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

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ABSTRACT

Geminal bis(boron) compounds have recently emerged as valuable building blocks for the synthesis of molecules with structural diversity. They have advantages of unique stability, operational simplicity and can be engaged in several kinds of transformations. This review covers the synthetic methods of geminal bis(boron) compounds and their applications in organic synthesis.

Contents

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* Corresponding author.
E-mail address: wangjb@pku.edu.cn (J. Wang).

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Introduction

Organoboron compounds are highly important synthetic intermediates in transition-metal-catalyzed or transition-metal-free cross-coupling reactions and other functional-group transformations.[1] Particularly, geminal bis(boron) compounds as novel alkylboron nucleophiles have gained great attentions recently as they are air- and moisture-stable compounds of which diverse substituted derivatives can be easily prepared and operated. Moreover, they can be applied in versatile C–C bonds formation reactions via deprotonation or deborylation pathway for the synthesis of molecules with complex structures. Due to the easy availability and extensive applications in organic synthesis, reports regarding the synthesis and transformations of geminal bis(boron) compounds have arisen over the past decade. In this review, progress on the preparation and synthetic applications of geminal bis(boron) compounds are summarized.

Synthetic methods for geminal bis(boron) compounds

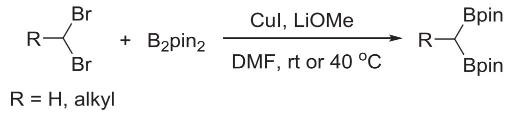
Several practical methods for the synthesis of geminal bis(boron) compounds have been reported in recent years. Most of these methods utilize commercially available or easily prepared starting materials and afford the desired geminal bis(boron) compounds in limited steps with satisfactory yields. Herein we summarized the typical methods for the synthesis of geminal bis(boron) compounds.

Borylation of geminal dibromides

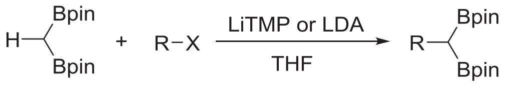
Geminal bis(boron) compounds can be prepared from the corresponding geminal dibromides with copper-catalyzed borylation reaction using bis(pinacolato)diboron (B_2pin_2) as the boron source (Scheme 1).[2] Both the simplest bis[(pinacolato)boryl]methane and alkyl group substituted geminal bis(boron) compounds can be prepared with this method in moderate to good yields. However, the limited commercially availability of substituted geminal dibromides restricts its practicability for the synthesis of geminal bis(boron) compounds.

Deprotonation and alkylation of bis(boryl)methane

As mentioned above, bis[(pinacolato)boryl]methane can be easily prepared by borylation of dibromomethane and is now commercially available. Therefore, it can be used as the precursor for the synthesis of many substituted geminal bis(boron) compounds by deprotonation with strong bases such as LiTMP or LDA followed by alkylation with alkyl halides (Scheme 2).[2] Both primary and secondary alkyl halides can be used and dialkyl substituted geminal bis(boron) compounds can be achieved by sequential deprotonation and alkylation.



Scheme 1. Borylation of geminal dibromides for the synthesis of geminal bis(boron) compounds.

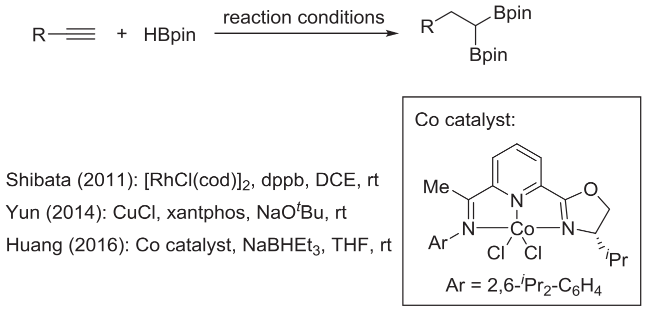


Scheme 2. Deprotonation and alkylation of bis(boryl)methane for the synthesis of geminal bis(boron) compounds.

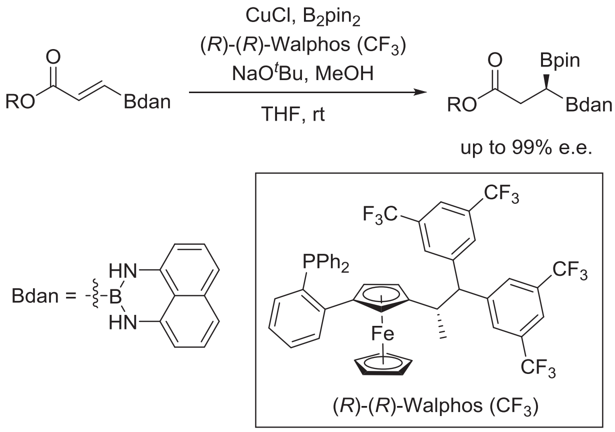
Hydroboration of alkynes and vinylboronates

Transition-metal-catalyzed sequential hydroboration of terminal alkynes and hydroboration of vinylboronates are also important methods for the synthesis of geminal bis(boron) compounds. In 2009, Shibata and co-workers reported a Rh(I)-catalyzed sequential regioselective hydroboration of terminal alkynes with pinacolborane (HBpin) to afford geminal bis(boron) compounds with high regioselectivity (Scheme 3).[3a] However, the yields were low to moderate as monoborylalkanes were formed as noticeable by-products via reduction of the alkenylboronate intermediates. Later in 2014, Yun and co-workers reported a Cu(I)-catalyzed selective sequential hydroboration of alkyl alkynes with HBpin to form geminal bis(boron) compounds, but the reactions of aryl alkynes afforded mixtures (Scheme 3).[3b] More recently, Huang and co-workers described similar reactions using iminopyridine-oxazoline (IPO) Co complex as catalyst (Scheme 3).[3c] Both alkyl and aryl alkynes can afford the desired products under mild conditions with high yields, high regioselectivity and wide functional group tolerance.

Hydroboration of vinylboronates is another way to synthesize geminal bis(boron) compounds. In 2011, Hall and co-workers disclosed a copper-catalyzed enantioselective conjugate borylation of boronylacrylates, furnishing highly optically enriched geminal bis(boron) compounds that feature two distinct boronyl units (Scheme 4).[4] Sequential transformations of these optically enriched geminal bis(boron) compounds were also explored in their work.



Scheme 3. Metal-catalyzed hydroboration of alkynes for the synthesis of geminal bis(boron) compounds.



Scheme 4. Copper-catalyzed hydroboration of vinylboronates for the enantioselective synthesis of geminal bis(boron) compounds.