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Synthesis of arylboronates via Cp*RuCl-catalyzed cycloaddition of alkynylboronates

Yoshihiko Yamamoto,* Kozo Hattori, Jun-ichi Ishii and Hisao Nishiyama

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan

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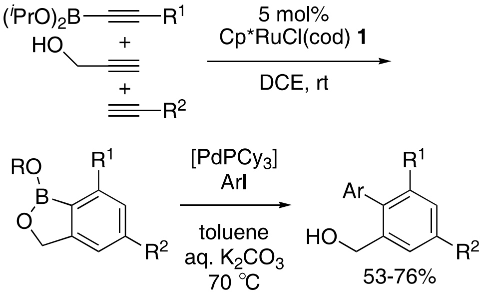
Abstract—In the presence of 5–10 mol% Cp*RuCl(cod), 1,6- and 1,7-diynes were allowed to react with an ethynylboronate at ambient temperature to give rise to bicyclic arylboronates in 64–93% isolated yields. 1,6-Diynes bearing a boronate terminal also underwent cycloaddition with monoalkynes to give the corresponding bicyclic arylboronates.

1. Introduction

Arylboronic acids and their congeners have become indispensable reagents in modern organic synthesis. In fact, they are now used for a wide variety of significant organic transformations including Suzuki–Miyaura cross coupling,[1] homo coupling,[2] rhodium-catalyzed asymmetric 1,2- and 1,4-additions to carbonyl compounds,[3,4] Heck-type reaction,[5] Petasis–Mannich condensation,[6,7] and others.[8] Arylboronic acid derivatives have been conventionally prepared by the reactions of arylmagnesium or -lithium reagents with trialkylborates, although reactive functional groups are incompatible with this method.[9] To address this issue, transition-metal-catalyzed couplings of arylhalides, -triflates, or -diazoniums with tetraalkoxydiboranes or dialkoxyboranes have been developed by several research groups.[10] Furthermore, transition-metal-catalyzed direct borylation of aromatic C–H bonds has emerged as an environmentally benign process.[11] In addition to these methods utilizing aromatic precursors, benzannulation or cycloaddition involving unsaturated organoboron reagents realized the assembly of highly substituted arylboronic acid frameworks, which are otherwise difficult to be prepared.[12,13] In this context, we recently developed the ruthenium-catalyzed cyclotrimerization of alkynylboronates, propargyl alcohol, and a terminal alkynes giving rise to arylboronates, which were subjected to one-pot Suzuki–Miyaura coupling to afford highly substituted biaryls as single regioisomers (Scheme 1).[14] As an extension of this study, we also explored the Cp*RuCl-catalyzed cycloaddition of α,ω-diynes with an ethynylboronate, yielding polycyclic arylboronates.[15] Herein, we wish to report the full details of our study on the catalytic partially intramolecular cycloaddition of alkynylboronates and diynylboronates.



Scheme 1.

2. Results and discussion

Aubert and co-workers recently reported the cycloaddition of the $Co_2(CO)_6$-complexed alkynylborates with α,ω-diynes bearing various tether lengths.[16] Although their protocol efficiently afforded various bicyclic arylboronates, the direct cycloaddition of diynes with alkynylboronates in the presence of appropriate catalyst is highly desirable in terms of atom economy.[17] Thus, our Cp*RuCl-catalyzed alkyne cyclotrimerization protocol would serve this purpose well.[14,18] In a recent work of Dixneuf and co-workers, Cp*RuCl(cod) also proved to be a competent precatalyst for [2+2] dimerization of an allenylboronate.[19]

Keywords: Ruthenium catalysis; Cyclotrimerization; Alkynylboronate; Arylboronate; Suzuki–Miyaura coupling.

* Corresponding author. Tel.: +81 52 789 3337; fax: +81 52 789 3209; e-mail: yamamoto@apchem.nagoya-u.ac.jp

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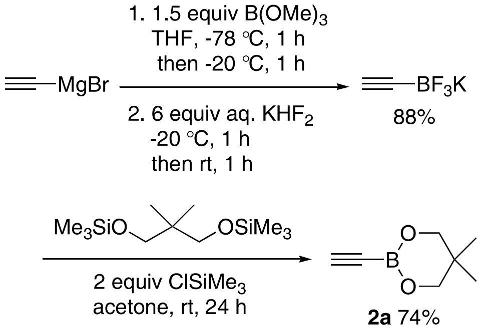
2.1. Preparation of ethynylboronate

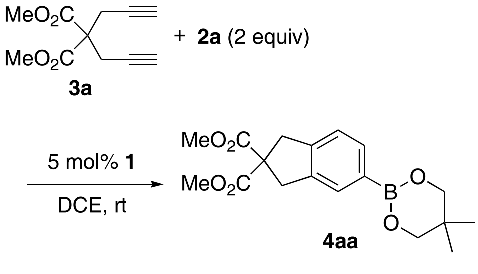
To realize an efficient catalytic protocol, we required an ethynylboronate because internal alkynes proved to be inefficient monoalkyne substrates for the ruthenium catalysis (vide infra).[18] The reaction of ethynylmagnesium bromide and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with the standard procedures of Brown and co-workers,[20] however, led to the formation of an ethynylboronate in a moderate yield with rather low purity because of its low boiling point. Thus, we turned our attention to an alternative procedure to prepare alkynylboronates reported by Vaultier and co-workers.[21] Although this method gave the desired 2-ethynyl-5,5-dimethyl-1,3,2-dioxaborinane (**2a**), commercially unavailable chlorobis(diisopropylamino)borane is required as a boron source and diaminoborane intermediates are moisture sensitive. To overcome such disadvantages, a modified route was developed by taking advantage of the ligand exchange reaction of alkynyltrifluoroborates.[22] As outlined in Scheme 2, the established procedure was applied to the synthesis of ethynyltrifluoroborate,[23] which was then treated with 2,2-dimethylpropane-1,3-diol bis(trimethylsilyl) ether in the presence of chlorotrimethylsilane in acetone at room temperature to afford ethynylboronate **2a** in a reasonable yield with high purity.



Scheme 2.

2.2. Cp*RuCl-catalyzed cycloaddition of α,ω-diynes with ethynylboronate

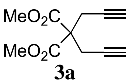
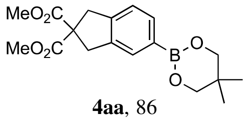
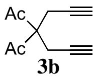
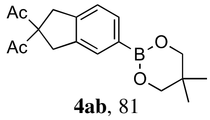
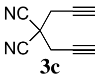
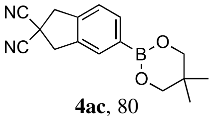
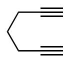
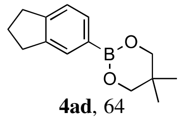
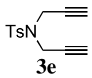
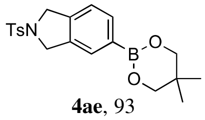
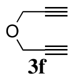
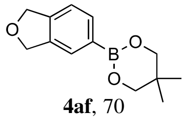
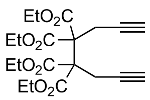
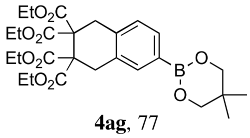
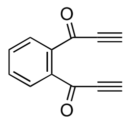
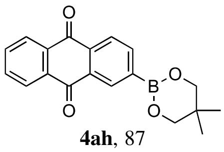
With ethynylboronate **2a** in hand, we next optimized its cycloaddition with dimethyl dipropargylmalonate (**3a**) in the presence of precatalyst Cp*RuCl(cod) (**1**) (Cp* = η^5-C_5Me_5, cod = 1,5-cyclooctadiene) as shown in Scheme 3. To suppress diyne dimerization, a solution of **3a** in 1,2-dichloroethane (DCE) was added at room temperature via syringe pump over 1 h to the DCE solution of 5 mol% **1** and 2 equiv of **2a**. As a result, the desired cycloadduct **4aa** was isolated in 77% yield after purification with silica gel column chromatography. A similar yield was obtained with increased amounts of **2a** (4 equiv). On the other hand, the yield was improved to 86%, when the reaction mixture was stirred for 1 h after the syringe-pump addition of **3a**. The obtained product was characterized as bicyclic arylboronate **4aa** by ^{1}H and ^{13}C NMR, IR, mass, and elemental analyses. This structural assignment was also confirmed by X-ray crystallography.[15]



Scheme 3.

The generality of this protocol was well demonstrated by the results obtained with various diyne substrates (Table 1). The present method well tolerated functional groups including an ester, a ketone, and a nitrile, and as a consequence, arylboronates **4aa–4ac** were obtained in 80–86% yields (runs 1–3). The quaternary center of the tether is not essential for the cycloaddition. Although an increased

Table 1. Cycloaddition of diynes **3a–h** with ethynylboronate **2a**[a]

Run	Diyne	Product, yield (%)
1	 **3a**	 **4aa**, 86
2	 **3b**	 **4ab**, 81
3	 **3c**	 **4ac**, 80
4	 **3d**	 **4ad**, 64
5	 **3e**	 **4ae**, 93
6	 **3f**	 **4af**, 70
7	 **3g**	 **4ag**, 77
8	 **3h**	 **4ah**, 87

[a] A solution of **3** in DCE was added to a DCE solution of 5 mol% (10 mol% for runs 4, 6 and 7) Cp*RuCl(cod) **1** and 2 equiv of ethynyl boronate **2a** by syringe pump over 1 h, and the solution was stirred for 1 h at room temperature.