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Synthesis of Fused Arylboronic Esters via Cobalt(0)-Mediated Cycloaddition of Alkynylboronates with α,ω-Diynes

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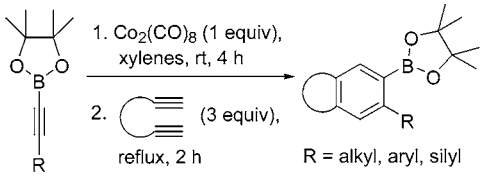
ABSTRACT



$Co_2(CO)_6$-complexed alkynyl pinacolborane derivatives are readily transformed with functional group tolerance into fused arylboronates via the [2 + 2 + 2]cycloaddition to α,ω-diynes.

The transition-metal-mediated cyclotrimerization of alkynes is a general and powerful method for constructing polysubstituted benzenes.[1] In this context, the cobalt(I)-catalyzed [2 + 2 + 2]cycloaddition of α,ω-diynes to alkynes constitutes a straightforward approach to the synthesis of fused arenes.[2] Of particular interest are alkynes bearing heteroatoms which might give rise to subsequent transformations after the cyclization step (Scheme 1). For example, alkynylsilanes[2,3] and alkynylstannanes[4] have been used to produce "metalated" benzene derivatives allowing for electrophilic substitutions or metal−halogen exchanges. Along these lines, it would seem that boron-substituted alkynes, such as alkynylboronates, should also be promising candidates for co-cyclization partners. One notes that such compounds function as efficient dienophiles in Diels−Alder reactions, a system employing cobalt catalysis being particularly relevant.[5] If successful in cyclotrimerizations, the resulting arylboronic esters could be subject to the plethora of known functional group transformations[6] and coupling reactions.[7] The synthesis of arylboronic esters is normally accomplished by metal−halogen exchange of haloarenes followed by addition of trialkoxyborates.[8] However, this strategy is not compatible with many

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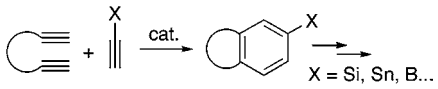
Scheme 1

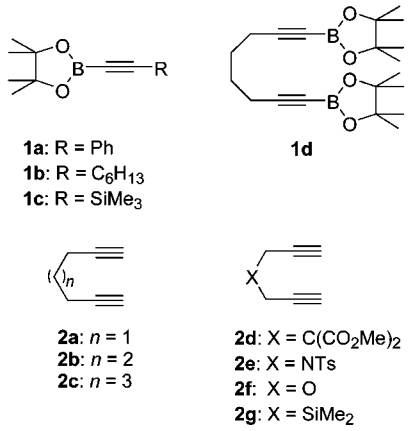


functional groups. To address this issue, new methods involving alkynylboronic esters are emerging. Thus, the Dötz benzannulation with Fischer carbenes allows the preparation of quinone boronic esters.[9] Recently, and complementary to our investigations, the [2 + 2 + 2]co-cyclotrimerization of tethered alkynylboronic esters with alkynes catalyzed by Ru(II) was reported.[10] In this work, the product arylboronates could not be isolated but were converted directly by Suzuki−Miyaura coupling reactions. Similarly relevant, Siebert et al. observed the cyclization of catechol-substituted mono- and diborylalkynes to oligoborylarenes catalyzed by cobalt and nickel complexes.[11]

As part of efforts directed toward the assembly of complex polycyclic molecules by cobalt-catalyzed oligomerizations,[12] we turned our attention to the preparation of isolable fused arylboronic esters. To achieve our goal, we envisaged the new two-component cyclization of alkynylboronic esters with α,ω-diynes, as in Scheme 1. Guided by the literature on the conversion of catechol-substituted borylalkynes,[11] we chose pinacol-substituted monoborylalkynes **1a**−**d** as the new reagents (Scheme 2).

Preliminary experiments using 5 mol % of $CpCo(CO)_2$ proved difficult. Thus, autocyclization of **1a**−**d** did not occur at appreciable rates and, unlike alkynylsilanes and -stannanes, their reaction with α,ω-diynes was poor. For example, irradiating a refluxing toluene solution containing alkyne **1a** and diyne **2b** in the presence of catalytic amounts of $CpCo(CO)_2$ failed to provide the corresponding cycloadduct **3b**. Under

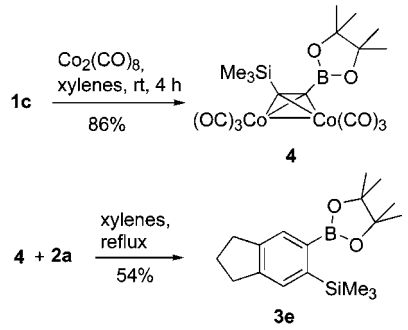
Scheme 2



the same conditions, the silylated alkyne **1c** and **2b** furnished **3f**, albeit in only 6% yield. In both cases, the oligomers of 1,7-octadiyne were also generated.[2] Relatively extreme conditions were necessary to reach a 38% yield of **3e**: 20 equiv of **1c**, 1 equiv of **2a**, and 1.0 equiv of $CpCo(CO)_2$ in irradiated refluxing toluene. In addition to the desired product, GC/MS revealed the presence of 1,4-bis(trimethylsilyl)-1,3-butadiyne, resulting from the homocoupling of **1c**.[13]

Faced with these difficulties, we next turned to $Co_2(CO)_8$.[11] Indeed, mixing the borylalkynes with a stoichiometric amount of cobalt carbonyl in xylenes at room temperature led to the corresponding dicobaltatetrahedrane derivatives, such as **4**, in good yields after column chromatography (Scheme 3). Gratifyingly, treatment of complex **4** (1 equiv)

Scheme 3



with diyne **2b** (1 equiv) in refluxing xylenes gave the cycloadduct **3f** in an improved isolated yield of 50%. Compared to the initial $CpCo(CO)_2$ protocol, this unusual $Co_2(CO)_8$-mediated cycloaddition represents a major improvement, since only 1 equiv of each reagent is required.

Because the dicobaltatetrahedrane complexes derived from our substrates proved to be very light sensitive and therefore hard to handle, we decided to avoid their isolation and to

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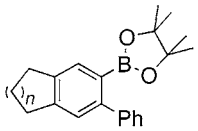
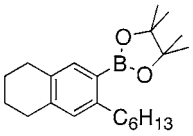
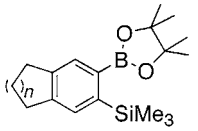
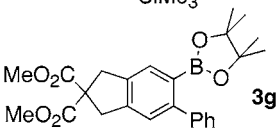
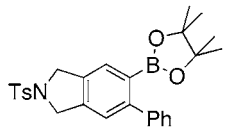
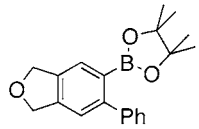
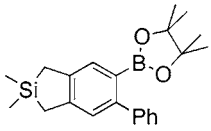
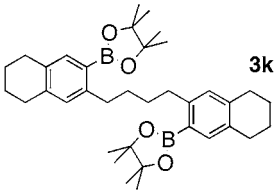
Table 1. Cycloaddition Reactions[a,b]

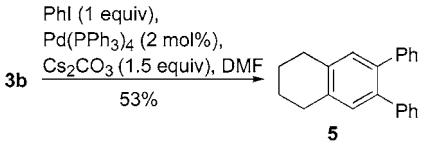
entry	alkyne/diyne	[2+2+2]cycloadduct (yield %)
1 2 3	**1a/2a** **1a/2b** **1a/2c**	 **3a**: n = 1 (61) **3b**: n = 2 (60) **3c**: n = 3 (45)
4	**1b/2b**	 **3d** (55)
5 6	**1c/2a** **1c/2b**	 **3e**: n = 1 (54) **3f**: n = 2 (50)
7	**1a/2d**	 **3g** (63)
8	**1a/2e**	 **3h** (71)
9	**1a/2f**	 **3i** (62)
10	**1a/2g**	 **3j** (75)
11	**1d/2b**	 **3k** (51)

[a] $Co_2(CO)_8$ (342 mg, 1 mmol), alkynyl pinacolborane (1 mmol), diyne (3 mmol). [b] Isolated yields are given in parentheses.

treat them in situ with α,ω-diynes, leading to the results compiled in Table 1. Using this sequence, an excess of diyne is needed to reach the same yields as those obtained in the stepwise procedure. Unreacted cobalt−carbonyl might be responsible for some depletion of diyne by oligomerization, affecting the yields of cycloaddition.

Alkyl-, aryl-, and silyl-substituted alkynylboronic esters were successfully converted into arylboronates following this one-pot procedure: a xylenes solution of $Co_2(CO)_8$ is added at once to the alkyne in the same solvent. The dark solution is stirred in the absence of light until no more CO evolution is visible (∼4 h). The neat diyne is then added, and the mixture is refluxed until the conversion is complete (∼2 h). The product is then purified by column chromatography on silica gel.

Scheme 4



In this way, a variety of indan, tetralin, and benzocycloheptene derivatives become accessible starting with 1,6-hepta-, 1,7-octa-, and 1,8-nonadiyne (entries 1−6). The ester function of diyne **2d** was tolerated perfectly, as exemplified by the synthesis of **3g** (entry 7). Heterodiynes **2e**−**g** allowed the preparation of heterocycles **3h**−**j** (entries 8−10) in good yields. Finally, a double cycloaddition was performed successfully with compound **1d**, using 2 equiv of $Co_2(CO)_8$ (entry 11).

The authenticity of the products was ascertained by their spectral data (see the Supporting Information). In all cases, the quaternary carbon attached to boron gave rise to a barely observable, broad (200 Hz) ^{13}C NMR signal. The presence of boron was confirmed by means of ^{11}B NMR, with chemical shifts of about +31 ppm, in good agreement with the reported values for dialkoxyarylboranes.[11,14]

To demonstrate the utility of the products and also provide an example of chemical structural proof, compound **3b** was treated with phenyl iodide in the presence of 2 mol % of $Pd(PPh_3)_4$[15] to furnish the cross-coupling product **5**[16] in unoptimized 53% yield (Scheme 4).

In summary, we have developed a novel one-pot method for the preparation of arylboronic esters via Co(0)-mediated cycloaddition of alkynylboronates to α,ω-diynes. We are now extending this method to the construction of mixed "metalated" benzene derivatives allowing for differing cross-coupling reactions on the same substrate.

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Supporting Information Available: Experimental details and characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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