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Nickel Catalysis |*Hot Paper*|

Ni-Catalyzed Cyclization of Enynes and Alkynylboronates: Atom-Economical Synthesis of Boryl-1,4-dienes

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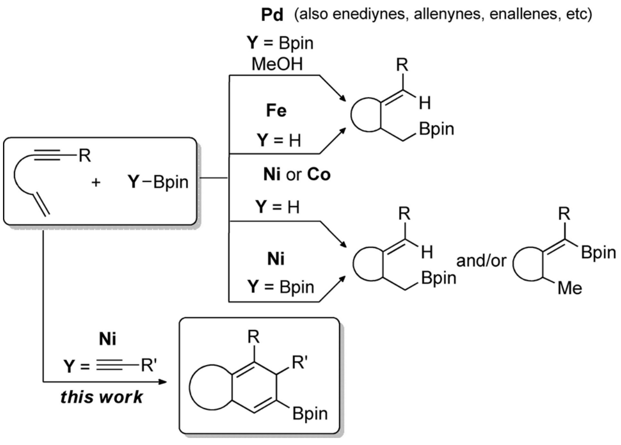
Abstract: We report a novel atom-economical Ni-catalyzed cyclization reaction of enynes with alkynylboronates. The reaction employs a non-expensive Ni salt, a phosphine-based ligand and easy-handling alkynylboronates as boron–carbon source. The reaction provides complex fused-bicyclic compounds containing borylated 1,4-cyclohexadienes in high yields in short reaction times, involving the formation of two C–C bonds in one step. A reasonable reaction mechanism is proposed based on mechanistic experimental results.

The development of practical, simple and highly efficient synthetic methods is one of the priorities of novel organic chemistry. We are witnessing an increasing interest in the improvement of conventional methodologies to describe useful and efficient synthetic procedures, since economic and environmental aspects cannot be ignored nowadays.[1] This is one of the reasons why the use of the first-row transition-metals has increased during the last decades.[2] Catalytic reactions based on these metals have opened up new perspectives since they provide novel activation pathways and surprising reaction mechanisms, accessing to a unique chemical space.

On the other hand, organoboron compounds have been widely employed as powerful building blocks both in synthetic organic chemistry and medicinal chemistry, that is, alkenylboronates find application as electronic materials and bioactive natural products.[3] They can also be considered as green compounds since they are non-toxic and allow reactions in water. Organoboronates usually show a good stability to molecular oxygen and moisture, facilitating their synthesis, purification, isolation and storage, on top to their high functional group compatibility. Despite their stability, organoboron compounds still exhibit reasonable reactivity as nucleophilic partners in the Suzuki–Miyaura cross-coupling reaction or[4] the Petasis reaction,[5] among others, showing less side reactions in comparison to other organometallic compounds, such as organomagnesium or organolithium reagents. Although there are many commercially available organoboron compounds, those with more structural complexity need to be prepared. Therefore, the development of new, mild and efficient synthetic routes based on inexpensive and atom-economical catalytic systems are still required.

Among the different described methods for the synthesis of organoboronates, hydroboration,[6] diboration,[7] and carboborations,[8] are the most commonly used. In particular, the latter leads to the simultaneous formation of C–C and C–B bonds in a single step. Especially interesting is the report published by Suginome in 2003, which describes the first regioselective Ni-catalyzed carboboration of alkynes with alkynylboronates, in which a C–B bond activation by oxidative addition is proposed.[8d] On the other hand, our group has focused its efforts on the development of novel borylative cyclization reactions of polyunsaturated species, allowing the concomitant formation of a C–B and one or more C–C bonds using Pd catalysis and diboron reagents.[9] More recently, we have succeeded at developing full atom-efficient Fe-,[10] and Ni-catalyzed[11] hydroborylative cyclizations, using pinacolborane as the boron source (Scheme 1). To the best of our knowledge, carboborylative cyclization reactions have no precedent in the literature.



Scheme 1. Metal-catalyzed borylative cyclization reactions of enynes.

Herein, we report a Ni-catalyzed cyclization of enynes using easy-handling and readily accessible alkynylboronates,[12] and a simple and inexpensive Ni-based catalytic system. The reaction furnishes 1,4-cyclohexadienes, proceeds with complete atom-

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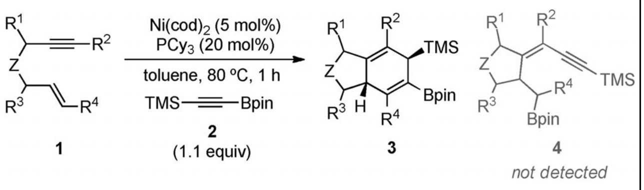
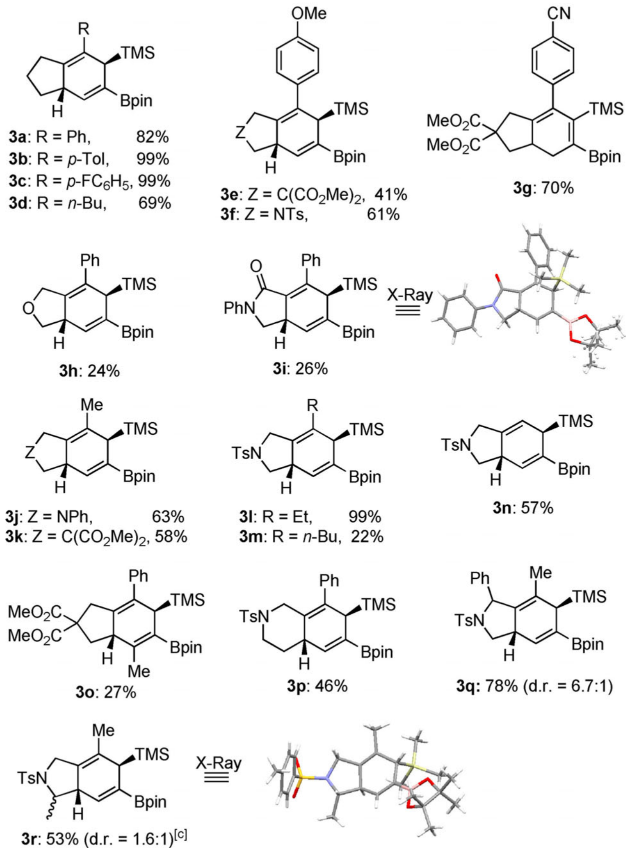
economy and shows a broad scope. As it is shown below, the formation of the observed products does not seem to proceed through the expected mechanism, and the reactivity of enynes contrast with that of simple akynes.[8d]

We intended to develop a carboborylative reaction analogous to the hydroborylative cyclization of enynes mentioned above,[11] by taking advantage of the previously proposed C–B oxidative addition of alkynylboronates to Ni. Thus, enyne **1a** was initially treated with alkynylboronate **2** (1.1 equiv), Ni(cod)$_2$ (5 mol%) and PCy$_3$ (20 mol%), in toluene at 80 °C. When the enyne was present in the reaction medium from the beginning, or when it was rapidly added to the mixture of the rest of the reagents, only oligomerization products derived from the enyne were observed. This was already observed by Suginome in the boryl-alkynylation of alkynes.[8d] In contrast, slow addition of enyne **1a** by a syringe pump for 1 h, led to complete suppression of oligomerization, and surprisingly afforded the unexpected compound **3a** in 82% yield (Table 1). The expected isomer, which would result from a carboborylative cyclization similar to those already described (**4**), was not observed in any case. Further experimentation using different reaction conditions was carried out, but neither the yield of **3a** increased nor other borylation products were observed (see Supporting Information for details). Formation of **3a** involves the formation of two C–C bonds in just one synthetic operation, affording a complex fused-bicyclic structure with boryl and silyl groups and two non-conjugated double bonds. Control experiments show that the reaction does not take place in the absence of Ni(cod)$_2$ or PCy$_3$.

Table 1. Scope of the Ni-catalyzed carboborylative cyclization reaction.[a–b]





3a: R = Ph, 82%
3b: R = *p*-Tol, 99%
3c: R = *p*-FC$_6$H$_5$, 99%
3d: R = *n*-Bu, 69%

3e: Z = C(CO$_2$Me)$_2$, 41%
3f: Z = NTs, 61%

3g: 70%

3h: 24%

3i: 26%

3j: Z = NPh, 63%
3k: Z = C(CO$_2$Me)$_2$, 58%

3l: R = Et, 99%
3m: R = *n*-Bu, 22%

3n: 57%

3o: 27%

3p: 46%

3q: 78% (d.r. = 6.7:1)

3r: 53% (d.r. = 1.6:1)[c]

[a] Conditions: enyne **1** (0.4 mmol) was slowly added by syringe pump for 1 h to a mixture of Ni(cod)$_2$ (5 mol%), PCy$_3$ (20 mol%) and **2** (1.1 equiv) in toluene (2 mL) at 80 °C. [b] Isolated yields. [c] We could not assign the crystal structure to the major or minor isomers.

The scope of the reaction was evaluated under the optimized reaction conditions (Table 1). Several 1,6-enynes with both aryl and alkyl-substituted alkynes effectively performed the carboborylative cyclization reaction (see Supporting Information for enynes that failed to give the reaction). The best results were obtained with enynes containing simple alkyl tethering chains (**3a**–**c**) bearing different substituents in the aromatic ring in *para* position (Me and F). Nitrogen- and malonate-tethered substrates also gave the desired products in good yields (**3e**,**f**), albeit worse results were obtained for the oxygen derivative **3h** and for the preparation of lactam **3i**. The structure of **3i** was confirmed by single-crystal X-ray crystallography (see Crystallographic data for details). Interestingly, these compounds, which present two stereogenic centers in the positions 1 and 4, are formed as single diastereoisomers, which suggests a highly stereoselective reaction mechanism. Substrates containing internal alkynes with different distal substituents, such as Me, Et and Bu, led to the desired products in poor to excellent yields (**3d, 3j**–**m**) regardless of the enyne connector. It is noteworthy that the longer chain (Bu) derivative affords lower yield in comparison with the ethyl-substituted analogue (22% for **3m** vs. 99% for **3l**). Enyne **1n**, bearing a terminal alkyne in the structure gave the reaction in moderate yield (**3n**). An internal alkene was also evaluated, affording the expected compound **3o**, albeit in low yield. This method could be also extended to a 1,7-enyne, leading to the formation of two fused 6-membered rings in moderate yield (**3p**). Finally, substitution in the allylic and propargylic positions was evaluated. Thus, enynes **1q** and **1r** afforded the corresponding compounds **3q** and **3r**, respectively, in good yields as diastereomeric mixtures. Again, compound **3r** was successfully crystallized, which allowed the confirmation of the proposed structure for the fused-bicycle.

Noticeably, enyne **1g**, bearing a *p*-CN substituent on the aryl ring, exclusively afforded the conjugated 1,3-diene **3g** in high yield. In fact, we have observed that compounds **3** are not very stable and tend to evolve through different pathways, involving aromatization and deborylative-aromatization of the 6-membered ring, which made difficult their purification and characterization. However, it was possible to identify and characterize some of these products such as **3a**′ and **3f**′ (Figure 1). The latter was obtained when we tried to crystallize compound **3f** under air. Formation of compound **3f**′ involves de-

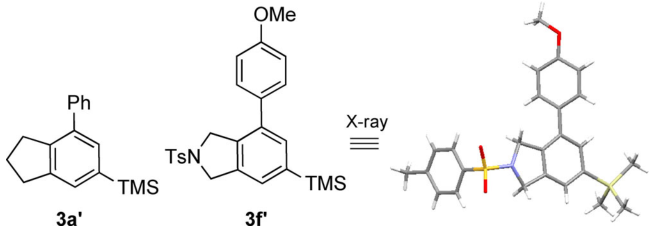
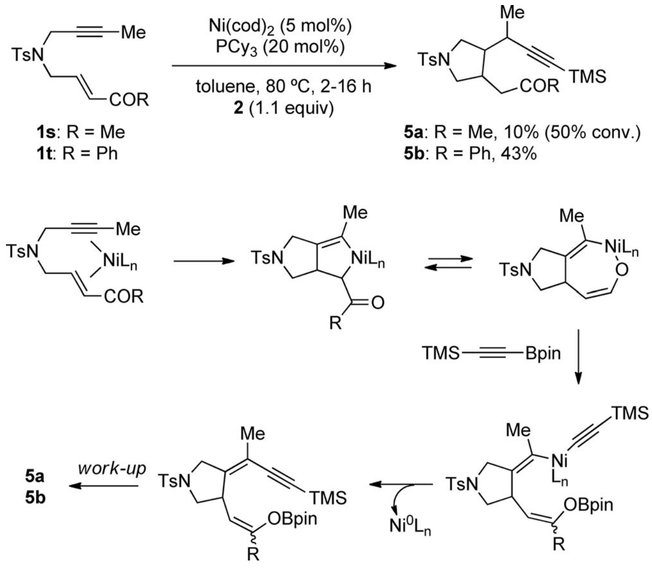


Figure 1. Compounds isolated after decomposition.

borylation (probably by hydrolysis) followed by 1,2-migration of TMS. This process has been previously reported in other arylsilanes, and it is proposed to take place through a cationic pathway triggered by protonation of the aromatic ring, which is favored by the stabilizing effect of Si, and driven by the release of steric hindrance.[12]

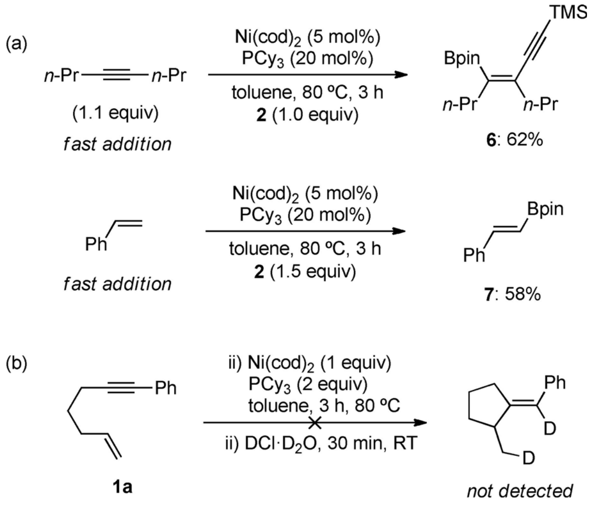
In contrast to the reactivity observed for the enynes shown above, the reaction of enones **1s** and **1t** under similar conditions led to cyclic ketones **5a** and **5b**, respectively, in which only the alkyne moiety from the alkynylboronate was incorporated to the structure (Scheme 2). Although we have no experimental evidence, formation of compounds **5** might take place by generation of a Ni-enolate complex, followed by transmetalation of alkynyl to the metal, insertion of the alkyne into the alkynyl–Ni bond and reductive elimination.[13] An alternative initial C–B bond activation, two subsequent consecutive insertions of the alkyne and alkene, and a final hydrolysis of an intermediate boron enolate during the reaction work-up would also explain these structures. Nevertheless, C–B oxidative addition to Ni is not probably operating in this case (see below).[11]



Scheme 2. Ni-catalyzed carbocyclization of enones, and possible reaction pathway.

We tried to extend the reaction to other alkynylboronates, bearing Ph, *p*-Tol or *n*-Hex instead of TMS group. Unfortunately, the desired products were not obtained. Although boron and alkyne moieties seem to be incorporated, we observed the formation of complex mixtures of several isomers as well as decomposition products.

With the aim of getting preliminary insight into the reaction mechanism, and to propose a reasonable pathway for the formation of compounds **3**, additional experiments were performed (Scheme 3).



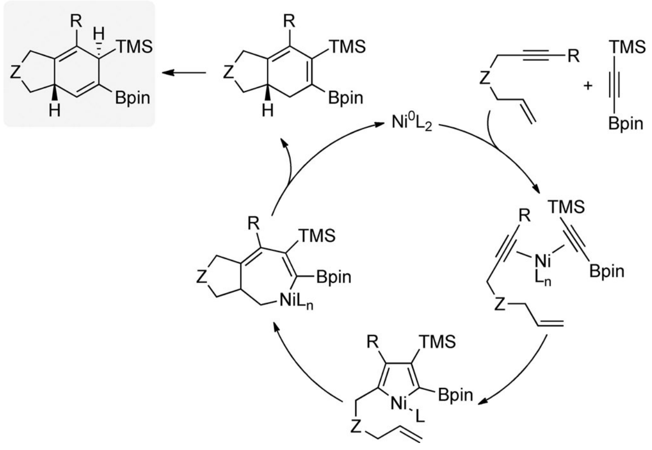
Scheme 3. Essays to probe the reaction pathway.

Thus, we tested our optimal reaction conditions with simple alkynes and alkenes (Scheme 3a). When we used 4-octyne as substrate, the previously described carboborylation compound **6** was obtained. Surprisingly, when styrene was employed, borylated compound **7** was obtained in moderate yield. Both results are consistent with an initial C–B bond activation. On the other hand, terminal alkynes such as phenylacetylene and ethynyltrimethylsilane (lacking the boryl group) only afforded oligomerization products (see Supporting Information for details). To evaluate the feasibility of an oxidative cyclometalation on a dicoordinated enyne, stoichiometric reaction between $Ni(cod)_2$, PCy_3 and enyne **1a**, without alkynylboronate, was performed. After hydrolyzing the reaction mixture with $DCl{\cdot}D_2O$, the expected dideuterated cyclic compound was not detected, and only oligomerization of enyne was observed (Scheme 3b). Therefore, oxidative cyclometalation involving both C–C multiple bonds of the enyne does not seem to take place under the reaction conditions.

In addition, the catalytic system in the absence of the enyne was also studied by ^{31}P- and ^{11}B-NMR. Comparison of the ^{31}P-NMR spectrum of a mixture of Ni/PCy_3 (1:4) in [D_8]toluene with that of a mixture of Ni/PCy_3/**2** (1:4:1) stirred at 80 °C for 5 minutes, indicated the formation of a new species showing a signal at 20.7 ppm. The same signal was observed when the mixture was stirred at 23 °C for 2 h. On the other hand, the ^{11}B-NMR spectrum of a mixture of Ni/PCy_3/**2** (1:2:1) stirred for 10 min at 23 °C, showed two signals at 21.9 and 29.5 ppm, and unreacted alkynylboronate **2** (23.5 ppm). When heating this solution for 10 min at 80 °C, only the signal at 21.9 ppm was observed (see Supporting Information for details). These results suggest that the alkyne interacts with the precatalyst affording a new species, but the small shift observed is probably due to alkyne coordination rather than oxidative addition of the C–B to Ni^0, which was proposed for the alkynylborylation of alkynes.[8d]

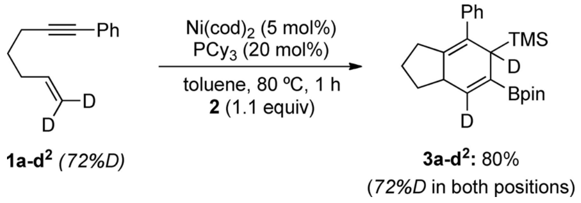
The formation of non-conjugated cyclic dienes from the reaction substrates is intriguing for a reaction taking place at 80 °C. For this reason, the thermodynamic stability of some of the observed reaction products (**3c**, **3g**, and **3l**), compared with the corresponding conjugated dienes, was studied computationally at DFT level. Interestingly, the observed 1,4-dienes are more stable (5 to 8 kcal mol^{-1} in terms of ΔG, M06/6-31G(d)), probably due to the release, upon deconjugation, of the high steric strain that exists in the conjugated diene between the coplanar SiMe$_3$, Bpin, and the substituent of the alkyne.

The above-mentioned experiments lead to disregard both the oxidative addition of C–B bond to Ni, and the formation of a nickelacyclopentadiene by oxidative cyclometalation of the coordinated enyne. Instead, we propose an initial oxidative cyclometalation involving the alkyne groups present in **2** and the enyne, after previous coordination to Ni^0 (Scheme 4). The resulting nickelacyclopentadiene would evolve by carbometalation of the alkene and subsequent reductive elimination to afford a 1,3-diene and regenerating the Ni^0 species. In fact, we could isolate such kind of derivative in one case (**3g**, Table 1). An off-cycle isomerization process involving a 1,3- hydrogen migration would lead to the observed products. We have no explanation for the lack of isomerization of **3g**. Thus, this reaction cannot be considered a borylative carbocyclization, but a cycloaddition involving three multiple C–C bonds. Related Fe-,[14] and Fe-catalyzed[15] processes have been previously described for the formation of pyridines and other cyclic derivatives. Although further studies are necessary to ascertain the reaction mechanism, our experimental results indicate that, noticeably, the oxidative cyclometalation involving two different alkynes seems to be faster than the oxidative addition of the C–B bond to Ni^0, which drives the observed reaction outcome. Consequently, no carboborylation of enynes takes place, in contrast to the reactivity observed for simple alkynes under similar conditions.



Scheme 4. Proposed reaction pathway.

Finally, we synthetized the dideuterated enyne **1a–d^2** (72 % D incorporation) in the terminal position of the alkene. The carboborylative cyclization reaction under the optimized conditions led to compound **3a–d^2** in 80 % yield with the expected deuterium distribution (Scheme 5). This result is in accord with the mechanistic proposal.



Scheme 5. Deuterium migration.

In conclusion, we have described the Ni-catalyzed cyclization reaction of enynes with alkynylboronates. The reaction conditions involve a simple as well as non-expensive catalytic system, and short reaction times are required to obtain good to quantitative yields. From simple structures, such as enynes and alkynylboronates, we could obtain complex fused-bicyclic structures with two non-conjugated double bonds in the structure in a complete atom-economical fashion. The reaction tolerates several functional groups affording the desired compounds in high yields. In addition, the structure contains two reactive groups, Bpin and TMS, which may be used for further transformations. Extension to other functionalized alkynes should be interesting. We have contributed to the development of a novel synthetic methodology, which extends the organic chemistry toolbox for the preparation of complex molecules.

Experimental Section

X-ray crystallographic data

CCDC 1906092 (**3i**), 1906093 (**3r**) and 1906094 (**3f′**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boron · carbocycles · homogeneous catalysis · nickel · reaction mechanism

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Nickel Catalysis

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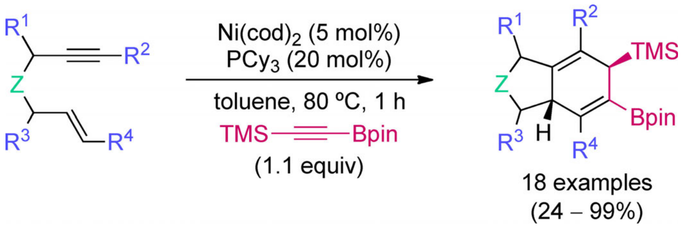
Ni-Catalyzed Cyclization of Enynes and Alkynylboronates: Atom-Economical Synthesis of Boryl-1,4-dienes



Boryl-1,4-dienes: Ni-catalyzed carboborylative cyclization reaction of enynes with alkynylboronates affords complex fused-bicyclic compounds containing borylated 1,4-cyclohexadienes. The process is fully atom-economical, and the catalytic system employs simple and inexpensive Ni salt and phosphine-based ligand.