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Regio- and Stereoselective 1,2-Carboboration of Ynamides with Aryldichloroboranes

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In memoriam Klaus Hafner

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Abstract: Catalyst-free 1,2-carboboration of ynamides is presented. Readily available aryldichloroboranes react with alkyl- or arylsubstituted ynamides in high yields with complete regio- and stereoselectivity to valuable β -boryl- β -alkyl/aryl α -aryl substituted enamides which belong to the class of trisubstituted alkenylboronates. The 1,2-carboboration reaction is experimentally easy to conduct, shows high functional group tolerance and broad substrate scope. Gram-scale reactions and diverse synthetic transformations convincingly demonstrate the synthetic potential of this method. The reaction can also be used to access 1-boraphenalenes, a class of boron-doped polycyclic aromatic hydrocarbons.

Organoboron compounds are versatile reagents in organic synthesis that also play an important role in materials science and medicinal chemistry. Particularly, alkenylboronates are highly useful building blocks in organic synthesis because of their broad application as substrates in the Suzuki-Miyaura cross-coupling^[1], conjugate additions,^[2] Zweifel olefination^[3] and other interesting transformations that proceed via their alkenylboronate complexes.^[4] To date, many methods for the preparation of alkenylboronates have been developed; however, regio- and stereoselective construction of α,β,β -trisubstituted alkenylboronates, which can be used as precursors in the stereoselective synthesis of tetrasubstituted alkenes, is challenging.^[5] The carboboration of internal alkynes with organoboron compounds, in which a C-C and a C-B bond are formed, offers a straightforward approach towards α,β,β trisubstituted alkenylboronates. Along these lines, metalcatalyzed^[6] (Scheme 1a) and phosphine-catalyzed^[7] (Scheme 1b) 1,2-carboboration of internal alkynes have been disclosed. Recently, atom economic environmentally benign catalyst-free direct carboboration, which offers an alternative pathway to α,β,β trisubstituted alkenylboronates, has received growing attention. For example, Uchiyama and Hirano reported a 1.2alkynylboration of alkynes enabled by intramolecular activation of alkynylboronates by propargylic alcohols (Scheme 1c).^[8] Highly

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electrophilic boranes can directly be used for alkyne carboboration. However, in contrast to the well-studied 1,1-carboboration, the "Wrackmeyer" reaction,^[9] only a few reports on catalyst-free direct 1,2-carboboration have appeared to date, and these procedures suffer from specific boron species or low yields, which limits their applicability in organic synthesis.^[10,11] Therefore, the development of an efficient and practical catalyst-free direct 1,2-carboboration with readily available boron reagents, which would expand the scope and the synthetic utility of boron-mediated organic transformations, is highly desirable.

a) Transition-metal-catalyzed direct 1,2-carboboration of internal alkynes

$$R^1 = R^2 + R^3 - BXY \xrightarrow{\text{Ni or Pd cat}} R^3 = R^3 R^3 R^3$$

b) Phosphine-catalyzed direct 1,2-carboboration of alkynoates



c) 1,2-Carboboration enabled by intramolecular activation of alkynylboronates



d) Dichloroborane induced direct 1,2-carboboration of ynamides (*this work*)



Scheme 1. Synthesis of α , β , β -trisubstituted alkenylboronates via direct 1,2carboboration of internal alkynes (EWG = electron withdrawing group).

Encouraged by our recent work on catalyst-free boration,^[12] we decided to study the electrophilic 1,2-carboboration of ynamides, that are versatile N-containing alkyne synthons in organic synthesis,^[13] with readily available boron reagents for the preparation of highly substituted β -boryl-enamides. Such enamides are valuable in organic chemistry as they can be readily further transformed to various highly substituted enamides. Moreover, they can also serve as substrates for the preparation of boron-doped polycyclic aromatic hydrocarbons. On the basis of the inherent nature of the polarized ynamide triple bond,^[13] we assumed that ionic 1,2-carboboration would be feasible with readily available boron reagents in the absence of any catalyst (Scheme 1d). Thus, reaction of an electrophilic boron reagent with an ynamide should generate the corresponding keteniminium-type zwitterion, which upon stereoselective intramolecular 1,3-

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migration of the R³-substituent of the boron ate complex moiety from boron to carbon would deliver the targeted α,β,β trisubstituted alkenylboron derivative with complete regio- and stereoselectivity.

We first explored the reaction of the ynamide 1a with various readily available phenylboronic acid derivatives that differ in electrophilicity at ambient temperature in CH₂Cl₂. To our delight, commercially available dichlorophenylborane 2a (3 equiv) gave after treatment of the crude product with pinacol the targeted trisubstituted alkenylpinacol boronate 3a in good yield (76% NMR yield; for the structure of 3a, see Scheme 2).[14] Other common boron reagents, including phenyl boronic acid (2b), phenyl pinacol boronic ester (2c), phenyl catechol boronic ester (2d), and triphenylboroxine (2e) did not engage in the 1,2-carboboration, because their boron Lewis acidity is too low for the initial electrophilic borylation step (see the Supporting Information, SI). Solvent screening revealed CHCl₃ to be superior to all other solvents tested. Decreasing the amount of boron reagent 2a from 3 to 1.5 equivalents did not influence reaction outcome to a large extent and the best result was obtained with 2 equivalents of 2a (74% isolated vield, see SI for details on the optimization study).

With the optimized conditions in hand, we first tested the scope with respect to the vnamide (Scheme 2). The relative configuration in selected examples were unambiguously assigned by NMR spectroscopy (see SI). Various N-tosyl vnamides bearing different R¹-N-substituents such as n-butyl (3b), benzyl (3c) and allyl (3d) were subjected to the 1,2-carboboration. The desired α,β,β -trisubstituted alkenylboronates were isolated in good yields (66-78%). Aromatic N-substituents are also tolerated, as shown by the 1,2-carboboration of the N-phenyl-tosyl ynamide 1e which gave 3e in a high yield. The N-sulfonyl protecting group can also be varied. Electronic effects exerted by the aryl group are not that pronounced, as arylsulfonyl groups bearing halides (4b-4d), trifluoromethyl (4e) and nitro (4f) all gave good yields (64-84%). Sterically more crowded ynamides also furnished the corresponding products 4g and 4h in good yields and the thienyl moiety was compatible with the electrophilic B-reagent (see 4i). β-Styrenylsulfonyl and methanesulfonyl protected ynamides engaged in the carboboration, albeit with moderate yields (4j and 4k). Next, N-tosylated N-methyl-ynamides bearing different R²substituents were tested in the reaction with 2a (5a-5p). Surprisingly, for aryl substituted ynamides with electron donating groups at the para position, lower reactivity was noted as compared to the less nucleophilic systems bearing electronwithdrawing para-substituents (see 5a-5g). Aryl-substituted ynamides with meta- and ortho-substitution at the aryl moiety were tolerated as well (5h-5j). Again, for the electron-poorer halosubstituted congeners, higher yields were obtained. Furthermore, alkyl-substituted ynamides could be employed in this 1,2carboboration and the corresponding α,β,β -trisubstituted alkenylboronates 51-5p were obtained in moderate to good yields. Of note, the β -branched alkyl substituted alkynes **10** and **1p** provided higher yields as compared to the primary alkyl substituted ynamides (see 5I-5m).

We continued the studies by varying the R-substituent at the dichloroborane 2 with the ynamide 1a as the substrate (Scheme 3). Considering the limited stability of dichloroboranes, we developed a highly practical one-pot, two-step process utilizing bench-stable trimethyl(aryl)silanes as starting materials. Dichloroboranes 2 were readily generated in situ through the reaction of the corresponding trimethyl(aryl)silanes with BCI3 in CH₂Cl₂ (volatiles were then removed in vacuo).^[15] Then, a CHCl₃ solution of 1a was added to the dichloroborane and the mixture was stirred at room temperature for 16 h. Functional groups, such as methyl (6a), phenyl (6b), phenoxy (6c), diphenylamino (6d) and halide (6e) at the para position of the phenyl group were compatible with this sequence and the corresponding alkenyl boronates were isolated in 68-86% overall yields. The sterically more hindered ortho-tolyldichloroborane also reacted well (6f). Naphthyl- and thienyl-based boron reagents engaged in the 1,2carboboration of 1a (6g-6i). Interestingly, dichloro(naphthalen-1yl)borane (from 2e') and dichloro(naphthalen-2-yl)borane (from 2f') led to the same product 6g (see SI for detailed discussion).[16] Notably, the reaction of the dichloroalkenylborane with 1a proceeded efficiently and the α,β,β -trisubstituted alkenylboronate 6i was isolated in high yield. However, reaction of cyclohexyldichloroborane with 1a provided the carboboration product in traces only (not shown).









Bpin

 R^2

EWG-N

EWG

R¹

 $-R^2$ + PhBCl₂

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 $\begin{array}{l} \label{eq:scheme 2.1,2-Carboboration of various ynamides. Reaction conditions: 1 (0.20 mmol), 2a (0.40 mmol) in CHCl_3 (2 mL), rt, 16 h, under Ar; pinacol (1.0 mmol), NEt_3 (1.0 mL), 1 h, isolated yields. [a] 2a (0.60 mmol), 50 °C. [b] 2a (0.24 mmol), 1 h. \\ \end{array}$

To demonstrate the synthetic value of the carboboration, two gram-scale reactions and four follow-up transformations were conducted (Scheme 4). First, gram-scale reaction of **1a** and **1ab** with PhBCl₂ (**2a**) under standard conditions afforded the desired products **3a** and **5I** in 72% and 57% yield, demonstrating the practicality (Scheme 4a,b). The triaryl substituted enamide **7** was obtained by Suzuki–Miyaura cross-coupling of **3a** with 4-MeC₆H₄I



Scheme 3. 1,2-Carboboration with various dichloroboranes. Reaction conditions: RSiMe₃ (0.60 mmol), BCl₃ (1.20 mmol, 1 M in CH₂Cl₂), 0 °C to rt or to 60 °C, 24 h, under Ar; then 1a (0.20 mmol) in CHCl₃ (1 mL), rt, 16 h, under Ar; pinacol (1.0 mmol), NEt₃ (1.0 mL), 1 h, isolated yields. [a] The dichloroborane was prepared in advance.





in 80% yield (Scheme 4c).^[17] AgNO₃-catalyzed protodeboration of **5I** gave stereospecifically the disubstituted enamide **8** (87%).^{[18}Treatment of **5I** with NaBO₃ provided the ketone **9** in a good yield and **5I** was successfully converted into the fully substituted cyclopropylboronate **10** using ZnEt₂/CH₂I₂ (82%).^[19]

Recently, boron-doped polycyclic aromatic hydrocarbons (B-PAHs) have attracted increasing attention because of their interesting materials properties.^[20] Among them, a 1boraphenalene scaffold is one of the minimal substructures of B-PAHs, to which several synthetic accesses have been reported.^[21] We found that our ynamide 1,2-carboboration can also be applied to the preparation of 1-boraphenalenes that furnish amino groups at the 3-position (Scheme 5). Thus, a one-pot synthesis of boraphenalene 11 was achieved via a sequence comprising the 1,2-carboboration of 1a with dichloro(naphthalen-1-yl)borane followed by an intramolecular boron-Friedel-Crafts arylation and The subsequent hydrolysis. stable hydroxy-substituted boraphenalene 11 was obtained in 71% overall yield (Scheme 5a). Upon treatment with BCl₃ in CH₂Cl₂,^[22] the boraphenalene **11** was further converted into the corresponding chloride. Removal of the solvent and reaction with mesityllithium in THF eventually provided mesityl-substituted boraphenalene 12 (78%, Scheme 5b).

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a) One-pot synthesis of polycylic aromatic borinic acid 11



b) Synthesis of B-mesityl boron-doped PAH 12



Scheme 5. Synthesis of 1-boraphenalenes.

Boraphenalenes 11 and 12 are both air and moisture stable at room temperature, and crystals suitable for X-ray crystallography were obtained from their solutions in ethyl acetate/pentane.^[23] The structural analysis of 12 revealed that not only the mesityl and phenyl groups, but also the amino plane are oriented in an orthogonal fashion against the boraphenalenyl plane (Scheme 5b). In UV-vis absorption spectrum in CHCl₃, boraphenalene 12 exhibited two broad absorption bands with the lowest energy absorption maximum (λ_{abs}) of 399 nm. In the same solvent, 12 exhibited a broad emission band with the maximum (λ_{em}) of 524 nm with a large Stokes shift of 5979 cm⁻¹ (Figure S1), where the fluorescence quantum yield ($\Phi_{\rm F}$) was 0.22. These values are comparable to those of the hitherto-known boraphenalenes.^[21d,f] Notably, the fact that both the λ_{abs} and λ_{em} values showed only subtle dependence on the solvent polarities (Table S1) suggests that the amino group does not work as an electron-donating group in this scaffold, consistent with its orthogonal orientation. The time-dependent (TD)-DFT calculation at the B3LYP/6-31+G(d) level of theory suggested that the lowest-energy absorption band can be attributed to the mixture of two electronic transitions from HOMO to LUMO and from HOMO-1 to LUMO (Table S2, Figure S3). While LUMO is delocalized over the boraphenalene skeleton, HOMO and HOMO-1 are located on the mesityl moiety or the phenylboraphenalene skeleton without contribution of the amino group. In the solid state, the fluorescence quantum yield was increased to $\Phi_{\rm F}$ = 0.41, while retaining the emission spectrum almost identical to that in solution (Figure S2). Its nonplanar molecular skeleton likely plays a role in preventing an intermolecular interaction.

In summary, we have described an efficient method for the preparation of β -boryl- β -alkyl/aryl α -aryl substituted enamides from ynamides via catalyst-free direct 1,2-carboboration. Readily available dichloroboranes react with ynamides to afford the corresponding valuable α , β , β -trisubstituted alkenylboronates in good yields with complete regio- and stereoselectivity under very

mild conditions. The reaction is operationally easy to conduct and features broad substrate scope and high functional group tolerance. The value of current methodology was documented by successful follow-up reactions and the synthesis of B-PAHs.

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Regio- and Stereoselective 1,2-Carboboration of Ynamides with Aryldichloroboranes

 $EWG_{R} + O-BCl_{2} \xrightarrow{CHCl_{3}, rt, 16 h}_{then pinacol, NEt_{3}, rt, 1 h} \xrightarrow{EWG-N_{R}}_{EWG-N_{R}} + 40 examples, up to 91% yield$ catalyst-free regioselective stereoselective broad substrate scope synthesis of B-PAHs

Catalyst-free direct 1,2-carboboration of ynamides with readily available dichloroboranes is presented. Valuable α,β,β -trisubstituted alkenylboronates are obtained in high yields with complete regio- and stereoselectivity under very mild