

Cite this: *Chem. Sci.*, 2021, 12, 15765

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Three-component 1,2-carboamination of vinyl boronic esters *via* amidyl radical induced 1,2-migration†

Cai You and Armido Studer

Three-component 1,2-carboamination of vinyl boronic esters with alkyl/aryl lithium reagents and *N*-chloro-carbamates/carboxamides is presented. Vinylboron ate complexes generated *in situ* from the boronic ester and an organo lithium reagent are shown to react with readily available *N*-chloro-carbamates/carboxamides to give valuable 1,2-aminoboronic esters. These cascades proceed in the absence of any catalyst upon simple visible light irradiation. Amidyl radicals add to the vinylboron ate complexes followed by oxidation and 1,2-alkyl/aryl migration from boron to carbon to give the corresponding carboamination products. These practical cascades show high functional group tolerance and accordingly exhibit broad substrate scope. Gram-scale reaction and diverse follow-up transformations convincingly demonstrate the synthetic potential of this method.

Received 21st October 2021
Accepted 16th November 2021

DOI: 10.1039/d1sc05811h

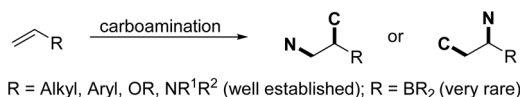
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Alkenes are important and versatile building blocks in organic synthesis. 1,2-Difunctionalization of alkenes offers a highly valuable synthetic strategy to access 1,2-difunctionalized alkanes by sequentially forming two vicinal σ -bonds.^{1a-h} Among these vicinal difunctionalizations, the 1,2-carboamination of alkenes, in which a C–N and a C–C bond are formed, provides an attractive route for the straightforward preparation of structurally diverse amine derivatives (Scheme 1a).^{2a-c} Along these lines, transition-metal-catalyzed or radical 1,2-carboaminations of activated and unactivated alkenes have been reported.^{3a-p} However, the 1,2-carboamination of vinylboron reagents, a privileged class of olefins,^{4a-h} to form valuable 1,2-aminoboron compounds which can be readily used in diverse downstream functionalizations,^{5a-c,6a-d} has been rarely investigated. To the best of our knowledge, there are only two reported examples, as shown in Schemes 1b and c. In 2013, Molander disclosed a Rh-catalyzed 1,2-aminoarylation of potassium vinyltrifluoroborate with benzhydroxamates *via* C–H activation (Scheme 1b).⁷ Thus, the 1,2-carboamination of vinylboron reagents is still underexplored but highly desirable.

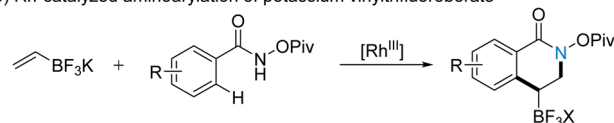
1,2-Alkyl/aryl migrations induced by β -addition to vinylboron ate complexes have been shown to be highly reliable for 1,2-difunctionalization of vinylboron reagents (Scheme 1c).^{4d-h} In 1967, Zweifel's group developed 1,2-alkyl/aryl migrations of vinylboron ate complexes induced by an electrophilic halogenation.⁸ In 2016, the Morken group reported the electrophilic palladation-induced 1,2-alkyl/aryl migration of vinylboron ate

complexes.^{9a-k} Shortly thereafter, we,^{10a-c} Aggarwal,^{11a-c} and Renaud¹² developed alkyl radical induced 1,2-alkyl/aryl migrations of vinylboron ate complexes. In these recent examples, the

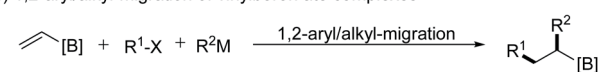
a) Carboamination of alkenes



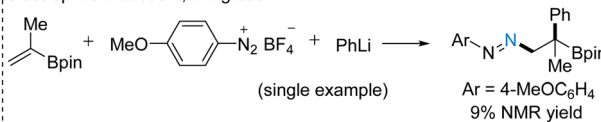
b) Rh-catalyzed aminoarylation of potassium vinyltrifluoroborate



c) 1,2-aryl/alkyl-migration of vinylboron ate complexes

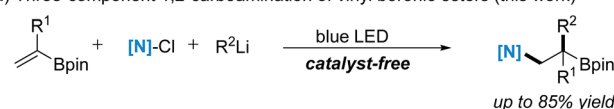


electrophile-induced 1,2-migration



Pd or Ni-catalyzed conjunctive cross-coupling $R^1 = C$ (established); $R^1 = N$ (unknown)
radical-induced 1,2-migration $R^1 = C$ (established); $R^1 = N$ (unknown)

d) Three-component 1,2-carboamination of vinyl boronic esters (this work)



Scheme 1 Intermolecular 1,2-carboamination of alkenes.

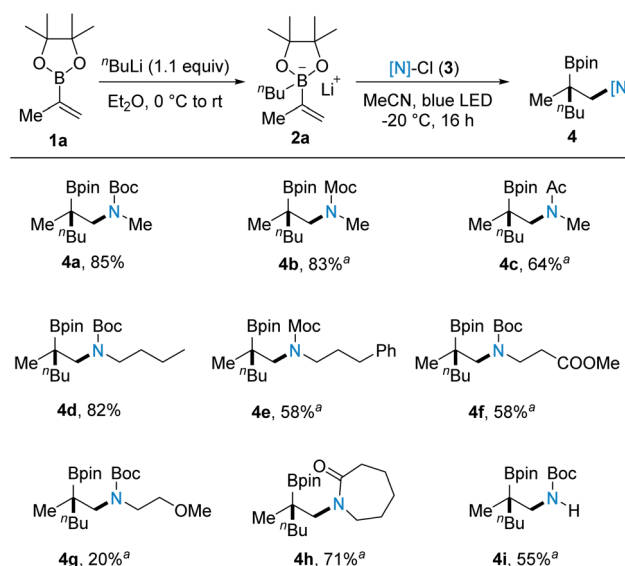
Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstraße 40, 48149 Münster, Germany. E-mail: studer@uni-muenster.de

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1sc05811h

migration is induced by a C-based radical/electrophile, halogen and chalcogen electrophiles.^{13a,b}

In contrast, N-reagent-induced migration of vinylboron ate complexes proceeding *via* β -amination is not well investigated. To our knowledge, as the only example the Aggarwal laboratory described the reaction of a vinylboron ate complex with an aryldiazonium salt as the electrophile, but the desired β -aminated rearrangement product was formed in only 9% NMR yield (Scheme 1c).^{13a} No doubt, β -amino alkylboronic esters would be valuable intermediates in organic synthesis. Encouraged by our continuous work on amidyl radicals^{14a-i} and 1,2-migrations of boron ate complexes,^{10a-c,15a-f} we therefore decided to study the amidyl radical-induced carboamination of vinyl boronic esters for the preparation of 1,2-aminoboronic esters. *N*-chloroamides were chosen as N-radical precursors,^{16a-c} as these *N*-chloro compounds can be easily prepared from the corresponding N-H analogues.¹⁷ Herein, we present a catalyst-free three-component 1,2-carboamination of vinyl boronic esters with *N*-chloroamides and readily available alkyl/aryl lithium reagents (Scheme 1d).

We commenced our study by exploring the reaction of the vinylboron ate complex **2a** with *tert*-butyl chloro(methyl)carbamate **3a** applying photoredox catalysis. Complex **2a** was generated *in situ* by addition of *n*-butyllithium to the boronic ester **1a** in diethyl ether at 0 °C. After solvent removal, the photocatalyst *fac*-Ir(ppy)₃ (1 mol%) and THF were added followed by the addition of **3a**. Upon blue LED light irradiation, the mixture was stirred at room temperature for 16 hours. To our delight, the desired 1,2-aminoboronic ester **4a** was obtained, albeit with low yield (26%, Table 1, entry 1). Solvent screening revealed acetonitrile to be superior to all other solvents tested, and a 56% yield was achieved (Table 1, entries 1–3). With Ru(bpy)₃Cl₂·6H₂O in place of *fac*-Ir(ppy)₃, yield of **4a** increased to 69% (Table 1, entry



Scheme 2 1,2-Carboamination of **1a** with various amidyl radical precursors. Reaction conditions: **1a** (0.20 mmol, 1.0 equiv.), *n*-BuLi (0.22 mmol, 1.1 equiv.), in Et₂O (2 mL), 0 °C to rt, 1 h, under Ar; then [N]-Cl (0.24 mmol, 1.2 equiv.), –20 °C, 16 h, in MeCN (4 mL). Yields given correspond to yields of isolated products. ^aA solution of [N]-Cl (0.30 mmol, 1.5 equiv.) in MeCN (1 mL) was used. See the ESI† for experimental details.

4). The use of the photocatalyst Na₂Eosin Y gave a similar result (Table 1, entry 5). Decreasing the concentration led to an improvement of the yield with Na₂Eosin Y as the photocatalyst (70%, Table 1, entry 6). Surprisingly, a control experiment run in the absence of any photocatalyst under irradiation with blue LED afforded the aminoboronic ester **4a** in 45% yield (Table 1, entry 7). Upon lowering the temperature, the yield of **4a** under such catalyst-free conditions further improved, and the best result was obtained when the reaction was conducted at –20 °C (85% yield of isolated product; Table 1, entries 8 and 9). Very little product was formed upon conducting the reaction in the dark, which showed that light was essential (Table 1, entry 10).

With optimal conditions in hand, we then investigated the scope of this new 1,2-carboamination protocol keeping **2a** as the N-radical acceptor (Scheme 2). This transformation turned out to be compatible with various primary amine reaction partners bearing carbamate (**4a**, **4b** and **4d–4g**) or acyl protecting groups (**4c**) (20–85%). Notably, *N*-chlorolactams can be used as N-radical precursors, as shown by the successful preparation of **4h** (71%). Moreover, Boc-protected ammonia was also tolerated, delivering **4i** in an acceptable yield (55%).

We continued the studies by testing a range of vinylboron ate complexes (Scheme 3). To this end, various vinylboron ate complexes were generated by reacting the vinyl boronic ester **1a** with methylolithium, *n*-hexyllithium, isopropyllithium and *tert*-butyllithium. For the *n*-alkyl-substituted vinylboron ate complexes, the 1,2-carboamination worked smoothly to afford **4j** and **4k** in good yields. However, the vinylboron ate complex derived from isopropyllithium addition provided the desired products in much lower yield (**4l**, 18% yield). When *tert*-

Table 1 Reaction optimization^a

Entry	Photocatalyst	Solvent	T (°C)	Yield ^b (%)
1	<i>fac</i> -Ir(ppy) ₃	THF	rt	26
2	<i>fac</i> -Ir(ppy) ₃	DMSO	rt	2
3	<i>fac</i> -Ir(ppy) ₃	MeCN	rt	56
4	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	MeCN	rt	69
5	Na ₂ Eosin Y	MeCN	rt	69
6 ^c	Na ₂ Eosin Y	MeCN	rt	70
7 ^c	None	MeCN	rt	45
8 ^c	None	MeCN	0	78
9 ^c	None	MeCN	–20	88 (85)
10 ^{c,d}	None	MeCN	–20	2

^a Reaction conditions: **1a** (0.20 mmol), *n*-BuLi (0.22 mmol), in Et₂O (2 mL), 0 °C to rt, 1 h, under Ar. After vinylboron ate complex formation, solvent exchange to the selected solvent (2 mL) was performed. ^b GC yield using *n*-C₁₄H₃₀ as an internal standard; yield of isolated product is given in parentheses. ^c 4 mL MeCN was used. ^d Reaction carried out in the dark.



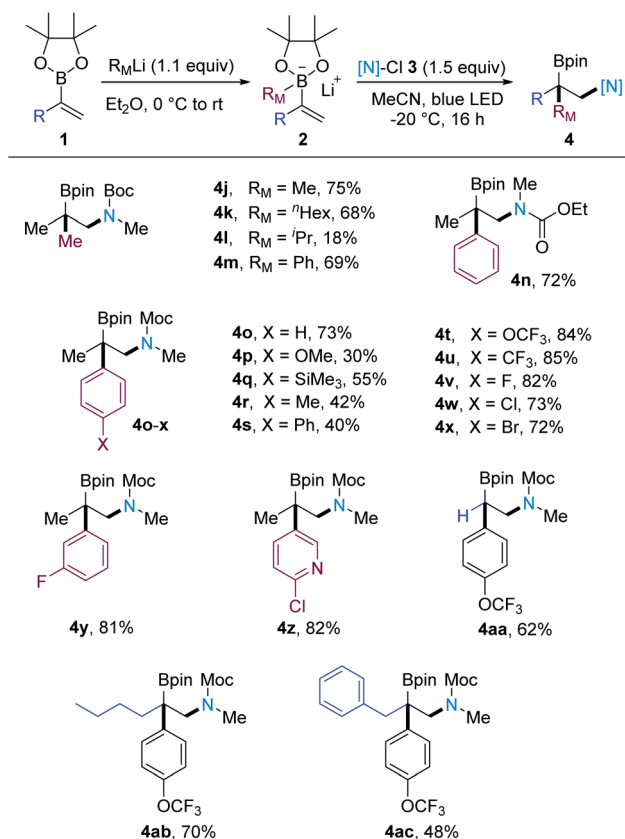
butyllithium was employed, only a trace of the targeted product was detected (see ESI†). As expected, cascades comprising a 1,2-aryl migration from boron to carbon worked well. Thus, by using PhLi for vinylboron ate complex formation, the 1,2-aminoboronic esters **4m–4o** were obtained in 69–73% yields with the Boc (*t*-BuOCONClMe), ethoxycarbonyl (EtOCONClMe) and methoxycarbonyl (Moc)-(MeOCONClMe) protected *N*-chloromethylamines (for the structures of **3**, see ESI†) as radical amination reagents. Keeping **3b** as the *N*-donor, other aryllithiums bearing various functional groups at the *para* position of the aryl moiety, such as methoxy (**4p**), trimethylsilyl (**4q**), methyl (**4r**), phenyl (**4s**), trifluoromethoxy (**4t**), trifluoromethyl (**4u**), and halides (**4v–4x**) all reacted well in this transformation. Aryl groups bearing *meta* substituents are also tolerated, as documented by the preparation of **4y** (81%). To our delight, a boron ate complex generated with a 3-pyridyl lithium reagent engaged in the cascade and the carboamination product **4z** was isolated in high yield (82%).

The reason for the dramatic reduction in yield when α -branched alkyl lithium or electron-rich aryllithium reagents were used might be that the corresponding vinylboron ate complexes could be oxidized by *N*-chloroamides *via* a single-electron oxidation process.^{18a–e} Furthermore, the α -unsubstituted vinyl boronic ester and vinyl boronic ester bearing various α -

substituents are suitable *N*-radical acceptors and the corresponding products **4aa–4ac** were obtained in 48–70% yield.

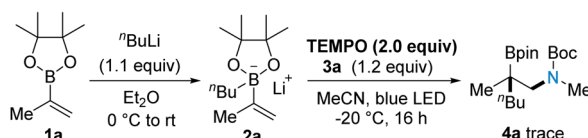
To gain insights into the mechanism of this 1,2-carboamination, a control experiment was conducted. The reaction could be nearly fully suppressed when the reaction was carried out in the presence of a typical radical scavenger (2,2,6,6-tetramethyl piperidine-*N*-oxyl, TEMPO), indicating a radical mechanism (Scheme 4a). Further, considering an ionic process, the *N*-chloroamides would react as Cl⁺-donors that would lead to Zweifel-type products, which were not observed under the applied conditions. The proposed mechanism is shown in Scheme 4b. As chloroamides have been recently proposed to undergo homolysis under visible light irradiation,^{19a,b} we propose that initiation proceeds *via* homolytic N–Cl cleavage generating the electrophilic amidyl radical **A**, which then adds to the electron-rich vinylboron ate complex **2a** to give the adduct boronate radical **B**. The radical anion **B** then undergoes single electron transfer (SET) oxidation with **3a** in an electron-catalyzed process^{20a,b} or chloride atom transfer with **3a** to provide **C** or **D** along with the amidyl radical **A**, thereby sustaining the radical chain. Intermediates **C** or **D** can then react *via* a boronate 1,2-migration^{10c,11c,21} to eventually give the isolated product **4a**.

To document the synthetic utility of the method, a larger-scale reaction and various follow-up transformations were conducted. Gram-scale reaction of **2a** with **3a** afforded the desired product **4a** in good yield, demonstrating the practicality of this transformation (Scheme 5a). Oxidation of **4a** with NaBO₃ provided the β -amino alcohol **5** in 89% yield (Scheme 5b). The *N*-Boc homoallylic amine **6** was obtained by Zweifel-olefination with a commercially available vinyl Grignard reagent and elemental iodine in good yield (79%).²² Heteroarylation of the C–B bond in **4a** was realized by oxidative coupling of **4a** with 2-thienyl lithium to provide **7**.²³

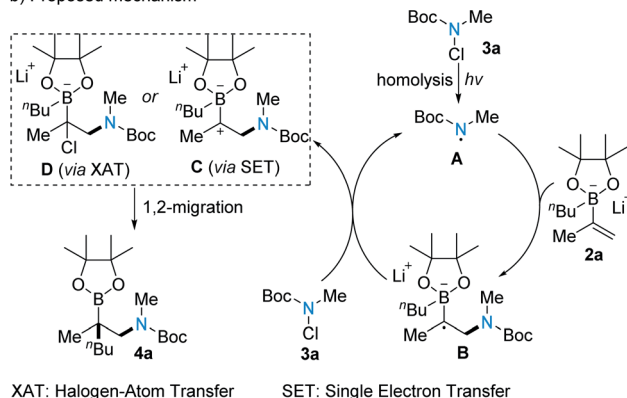


Scheme 3 Scope of vinylboron ate complexes. Reaction conditions: **1** (0.20 mmol, 1.0 equiv.), R_MLi (0.22 mmol, 1.1 or 1.3 equiv.), Et₂O or THF, under Ar; then [N]-Cl (0.30 mmol, 1.5 equiv.), –20 °C, 16 h, in MeCN. Yields given correspond to yields for isolated products. See the ESI† for experimental details.

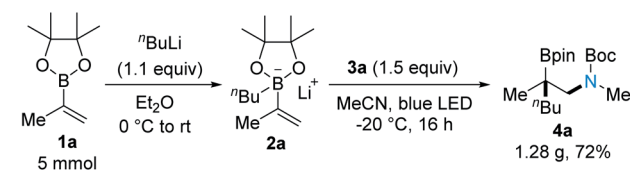
a) Control experiment



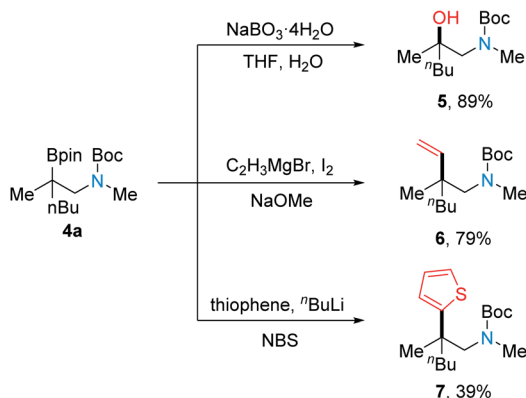
b) Proposed mechanism



Scheme 4 Control experiment and proposed mechanism.

a) Gram-scale synthesis of **4a**

b) Follow-up chemistry



Scheme 5 Gram-scale reaction and follow-up chemistry.

In summary, we have described an efficient method for the preparation of 1,2-aminoboronic esters from vinyl boronic esters *via* catalyst-free three-component radical 1,2-carboamination. Readily available *N*-chloro-carbamates/carboxamides, which are used as the *N*-radical precursors, react efficiently with *in situ* generated vinylboron ate complexes to afford the corresponding valuable 1,2-aminoboronic esters in good yields. The reaction features broad substrate scope and high functional group tolerance. The value of the introduced method was documented by Gram-scale reaction and successful follow-up transformations.

Data availability

The data that support the findings of this study are available in the ESI† or on request from the corresponding author.

Author contributions

C. Y. conducted all experiments and characterized the novel compounds. C. Y and A. S. designed the experiments and wrote the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

We thank the European Research Council (ERC Advanced Grant Agreement No. 692640) for financial support.

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