ACS Catalysis

Copper-Catalyzed Regioselective Formation of Tri- and Tetrasubstituted Vinylboronates in Air

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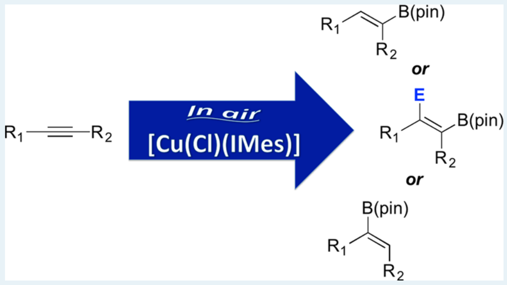
Supporting Information

ABSTRACT: The first “in air” copper-catalyzed method for the selective synthesis of tri- and tetrasubstituted vinylboronate derivatives is presented. Three different variants of the borylation of internal alkynes (α-hydroboration, β-hydroboration, and carboboration) are described using a single catalyst: [Cu(Cl)(IMes)] (IMes = *N,N′*-bis-[2,4,6-(trimethyl)phenyl]-imidazol-2-ylidene) without taking any precaution to avoid the presence of air. Bis(pinacolato)diboron was used to afford β-hydroborated products in the presence of methanol. Adding instead another electrophile allowed the formation of tetrasubstituted vinylboronate species. Finally, the α-products were obtained using pinacolborane as the boron source. All compounds were obtained in high yield with excellent regioselectivity at low catalyst loading (0.04−2 mol %). The protocol constitutes a very convenient route to access these highly valuable molecules.



KEYWORDS: *hydroboration, carboboration, copper, alkynes, N-heterocyclic carbenes*

INTRODUCTION

Vinylboronates are extremely versatile building blocks and highly valuable reagents in the synthesis of more complex molecules. They play a prevalent role in organic chemistry as partners for C−C bond formation reactions, including the widely used Suzuki−Miyaura cross-coupling process,[1] other transition metal-catalyzed transformations,[2] and metal-free conjugate additions.[3]

Several methodologies have been developed to generate such intermediates, which explains the significant attention they have recently received.[4] Among all these synthetic methods, the use of copper(I) as catalyst for hydroboration of terminal and internal alkynes has generated renewed interest in the area. The pioneering work carried out by Miyaura[5a] in 2001 was followed by several investigations in the past few years, especially involving terminal alkynes.[5b−f] Recently, Hoveyda and co-workers have published a method leading to the highly selective α- and β-hydroboration of terminal alkynes, showcasing copper as a metal of choice for such transformations.[6] So far, only a few systems based on internal alkynes have been reported, mainly because of the low reactivity of such substrates compared with their terminal analogues.[7−12] As mentioned above, the success story of copper-catalyzed synthesis of vinylboronates has recently attracted much attention. Early work on acetylenic esters reported by Aue[7] has been improved by Tsuji, who generalized the synthetic method to obtain selectively α- and β-products, depending on the choice of boron reagents for various unsymmetrical alkynes.[8] The Carretero group developed a regiocontrolled hydroboration of propargylic functionalized internal alkynes,[9] and McQuade published an α- and β-selective methodology for such propargylic species (ethers and alcohols) by matching substrates and copper(I) catalysts.[10] Recent advances in this area have also given birth to several variations of this reaction,[11] such as the first Cu-catalyzed syn carboboration of alkynes developed by Tortosa and co-workers and then investigated by Takaki.[12] However, the control of the selectivity remains a challenge, especially when dealing with unsymmetrical internal alkynes.

Phosphines have been ligands of choice in copper-catalyzed formation of vinylboronates. In-situ-generated catalysts have been favored[5b,d−f,9,12a] compared with well-defined counterparts.[7] Interestingly, systems based on N-heterocyclic carbenes (NHCs) are scarce for such reactions and limited to hydroboration.[5c,6,8,10] Considering that NHCs often lead to more active and robust catalytic systems,[13] we investigated their potential in selective α-, β-hydroboration and carboboration of unsymmetrical alkynes in air.

Herein, the first “one catalyst, three reaction” system used toward the synthesis of tri- and tetrasubstituted vinylboronates employing well-defined copper(I) NHC (NHC = N-heterocyclic carbene) complexes in air (Scheme 1) is reported.

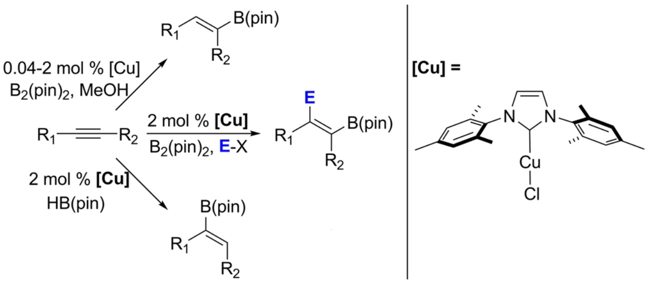
RESULTS AND DISCUSSION

We undertook the exploration of the catalytic performances of well-defined NHC−copper(I) complexes (Figure 1) in the regioselective β-hydroboration of internal alkynes.

Initial experiments leading to optimized reaction conditions for each tested copper catalyst were performed under inert atmosphere using 1-phenyl-1-butyne **1** as the benchmark substrate (Table 1).

Received: January 28, 2014
Revised: March 18, 2014
Published: April 18, 2014

Scheme 1. Selective Hydro- and Carboboration Using a Single Precatalyst



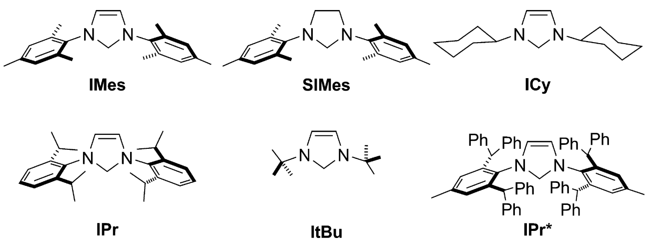
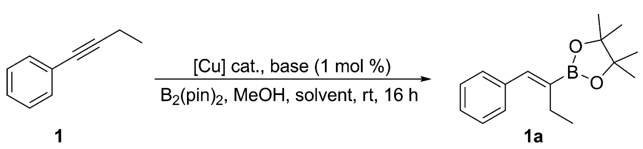


Figure 1. NHC ligands used in this study.

Table 1. Optimization of Reaction Conditions (β-Hydroboration)[a]



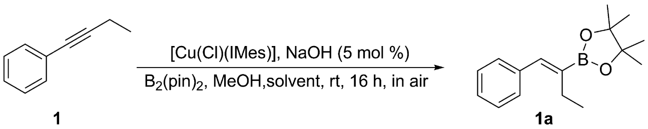
entry	catalyst (loading/mol %)	solvent	base	conv (%)[b]
1	[Cu(Cl)(IPr)] (0.025)	^{i}PrOH	NaO^{t}Bu	34
2	[Cu(IPr)(ItBu)]BF_4 (0.025)	MTBE		18
3	[Cu(IPr)(P^{t}Bu$_3$)]BF_4 (0.025)	MTBE		15
4	[Cu(Cl)(ItBu)] (0.025)	1,4-dioxane	NaO^{t}Bu	67
5	[Cu(Cl)(ICy)] (0.025)	DCM	NaO^{t}Bu	76
6	[Cu(Cl)(SIMes)] (0.005)	MTBE	NaOH	95
7	**[Cu(Cl)(IMes)] (0.005)**	**MTBE**	**NaOH**	**96**
8	[Cu(Cl)(IMes)] (0.0025)	MTBE	NaOH	35
9	[Cu(Cl)(IMes)] (0.0025)	MTBE	NaOH	50[c]

[a] **1** (2.0 mmol), $B_2(pin)_2$ (2.2 mmol), base (0.2 mmol, 1 mol %), Cu catalyst, MeOH (4.0 mmol, 0.18 mL), solvent (2.4 mL), rt, 16 h. [b] Conversion determined by GC, based on alkyne, average of two runs. [c] Using 5 mol % of base.

Initial experiments focused on the use of [Cu(Cl)(IPr)][14] (IPr = *N,N′*-bis-[2,6-(di-isopropyl)phenyl]imidazol-2-ylidene) (Table 1, entry 1) which displayed promising catalytic activity because the complex remained active even at 0.025 mol % loading, far below reported work using monodentate phosphorus-based ligands.[5d] Recently, reported heteroleptic bis-N-heterocyclic carbenes copper and mixed NHC−phosphine copper complexes[15] (Table 1, entries 2 and 3) provided similar activity without a base but with lower conversion. Switching to *N*-alkyl-substituted NHC−Cu complexes such as [Cu(Cl)(ItBu)] (I^{t}Bu = *N,N′*-(di-*tert*-butyl)imidazol-2-ylidene)[14a] and [Cu(Cl)(ICy)] (ICy = *N,N′*-(dicyclohexyl)-imidazol-2-ylidene)[14a] (Table 1, entries 4 and 5) leads to a dramatic increase in the conversion and the formation of the β-borylated product (67 and 76%, respectively). Gratifyingly, copper complexes bearing IMes (IMes = *N,N′*-bis-[2,4,6-(trimethyl)phenyl]imidazol-2-ylidene) and its saturated analogue SIMes (*N,N′*-bis[2,4,6-(trimethyl)phenyl]imidazolidin-2-ylidene) were highly active, giving almost complete conversion, even with a mere 0.005 mol % loading (Table 1, entries 6 and 7). Decreasing the amount to 0.0025 mol % showed that [Cu(Cl)(IMes)] was the most efficient catalyst (Table 1, entries 8). Using 5 mol % of sodium hydroxide proved to enhance the conversion to 50% with only 0.0025 mol % of catalyst, leading to turnover numbers (TONs) of up to 20 000. It is noteworthy that all tested systems proved to be highly selective toward the formation of the desired species **1a** with an α/β ratio better than 2:98 (see the Supporting Information for details about optimization).

[Cu(Cl)(NHC)] complexes are usually air-stable species as a result of the stabilizing effect of NHCs induced by their steric, electronic and bonding properties.[13b,16] So far, hydroboration of alkynes has been carried out under inert atmosphere because intermediates in the reaction, such as copper alkoxides, are air- and moisture-sensitive. Considering the constraints of working under inert atmosphere and the robustness of NHC−Cu complexes, using our optimized reaction conditions (Table 1), the β-hydroboration of **1** was carried out in air (Table 2). At very low catalyst loading, the conversion of **1** is moderate, presumably because of decomposition.[17] Increasing the catalyst loading to 0.04 mol % and using the greener solvent CPME (cyclopentyl methyl ether) instead of MTBE (methyl *tert*-butyl ether)[18] led to quantitative formation of **1a** at room temperature (Table 2, entry 5).

Table 2. β-Hydroboration Optimization in Air[a]



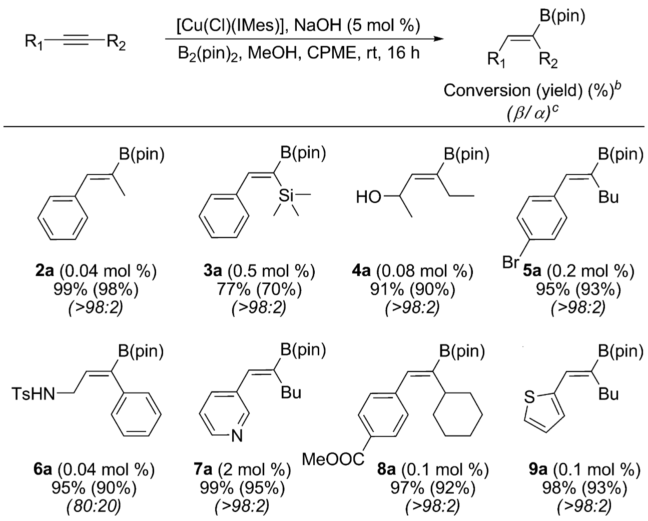
entry	loading (mol %)	solvent	conv (%)[b]
1	0.0025	MTBE	25
2	0.0025	CPME	36
3	0.01	CPME	45
4	0.02	CPME	55
5	**0.04**	**CPME**	**99 (98)**[c]

[a] **1** (2.0 mmol), $B_2(pin)_2$ (2.2 mmol), NaOH (0.1 mmol, 5 mol %), [Cu(Cl)(IMes)], MeOH (4.0 mmol, 0.18 mL), solvent (2.4 mL), rt, 16 h. [b] Conversion determined by GC analysis, based on alkyne, average of two runs. [c] Isolated yield.

The β-hydroboration of various internal alkynes was next examined in air using these optimized reaction conditions (Scheme 2). Regioselectivity in the crude mixtures was excellent (>98:2), except for **6a**, in which a ratio of 80:20 was found. However, the system showed excellent tolerance toward a protected amine, **6a**, being obtained in high yield. Interestingly, **2a** was obtained quantitatively and regioselectively, which is in contrast with the results of Son and coworkers.[5c]

The β-hydroboration was also successful in the presence of silyl (**3a**), alcohol (**4a**), halide (**5a**), and carbonyl (**8a**) groups, without loss of selectivity. Conjugated heteroaromatic substituted internal alkynes were also examined, and the reaction proceeded with high yield and regioselectivity (**7a** and **9a**). [Cu(Cl)(IMes)] appeared to be a suitable catalyst in promoting β-hydroboration for all substrates in high yields

Scheme 2. Scope of the β-Hydroboration in Air[a]

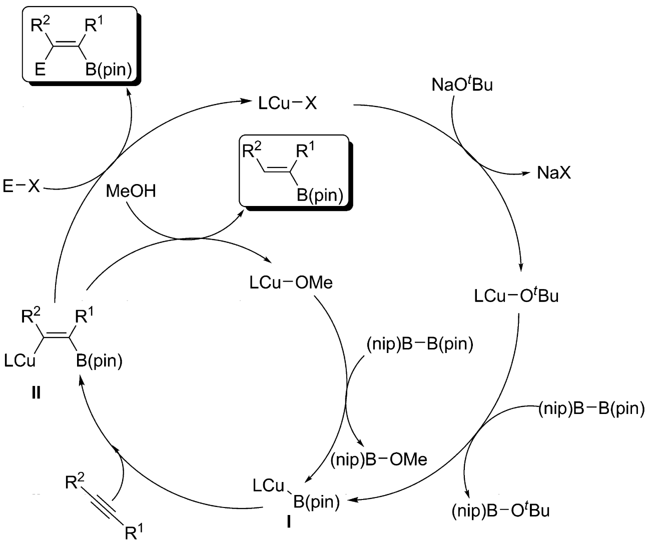


[a]Reaction conditions: alkyne (0.50 mmol), B$_2$(pin)$_2$ (0.55 mmol), NaOH (0.025 mmol, 5 mol %), [Cu(Cl)(IMes)], MeOH (1.0 mmol, 0.05 mL), CPME (0.6 mL), rt, 16 h. [b]Conversion determined by GC based on alkyne, isolated yield in parentheses, average of two reactions. [c]Ratio (β/α) regioisomers determined by GC.

and excellent selectivity, using a lower catalyst loading than previously reported, and *in air!*

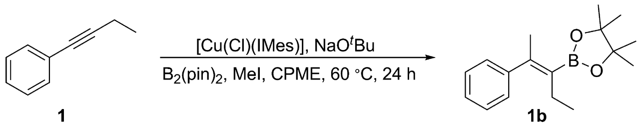
Carboboration and hydroboration catalytic cycles are very similar, both involving the same intermediate species **I** reacting with the substrate to give the vinylcopper intermediate **II** (Scheme 3). Logically, these similarities led us to investigate this reaction using our Cu–NHC system. Because hydroboration occurred with high efficiency in air, the carboboration reaction was directly examined in air.

Scheme 3. Proposed Catalytic Cycles (Hydroboration and Carboboration)



To avoid any nucleophilic substitution from the base on iodomethane, sodium *tert*-butoxide was preferred to sodium hydroxide.[19] Starting with 1 mol % of catalyst, 1.1 equiv of base, and 1.3 equiv of the boron source, the reaction occurred efficiently, giving the desired product **1b** in 82% conversion (Table 3, entry 1). Increasing the amount of base or electrophile did not enhance the reactivity (Table 3, entries 2 and 3). **1b** was finally obtained in high yield as a single regioisomer when increasing the catalyst loading to 2 mol % (Table 3, entry 4). Under inert conditions, a similar result is obtained using only 0.5 mol % of catalyst (Table 3, entry 5).

Table 3. Copper-Catalyzed Methylboration of 1 in Air[a]

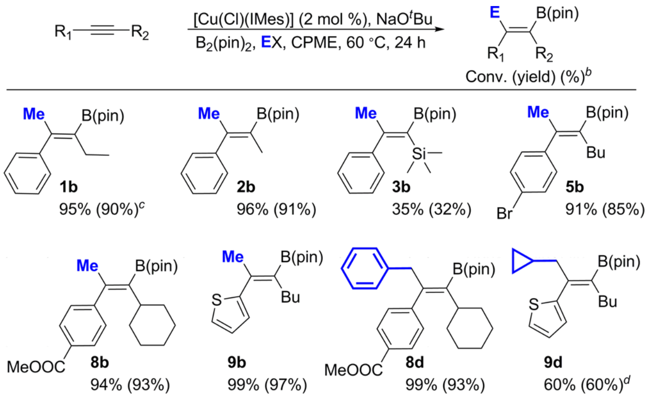


entry	catalyst loading (mol %)	base (equiv)	MeI (equiv)	conv (%)[b]
1	1	1.1	4	82
2	1	1.5	4	85
3	1	1.1	8	77
4	**2**	**1.1**	**4**	**95 (90)**[c]
5	**0.5**	**1.1**	**4**	**96 (93)**[c,d]

[a]**1** (0.50 mmol), B$_2$(pin)$_2$ (0.65 mmol), NaO^{t}Bu, [Cu(Cl)(IMes)], MeI, CPME (1.4 mL), 60 °C, 24 h, air atmosphere. [b]Conversion determined by GC, based on alkyne, average of two runs. [c]Isolated yield. [d]Under argon.

These optimized "in air" reaction conditions were then applied to various aryl- and alkyl-substituted internal alkynes (Scheme 4). Products were obtained in moderate to excellent yields at relatively low catalyst loading (2 mol %). These conditions are in contrast with the results recently published by Tortosa and co-workers (10 mol % of both CuCl and xantphos).[12] Iodomethane was first used as a reference for electrophilic species. The exclusive formation of the single regioisomer bearing the methyl moiety at the most substituted position was observed even when modifications were brought to the alkyl group or the aryl/heteroaryl substituent. The method proves highly compatible with many functional groups. Aryl bromide bonds remained untouched (**5b**), and ester groups appear compatible with the reaction conditions. The carboboration using different electrophiles was also examined. Products were obtained in good yield using alkyl bromide (**9d**) and chloride (**8d**). Remarkably, the formation of **3b** bearing a

Scheme 4. Scope of the Carboboration in Air[a]



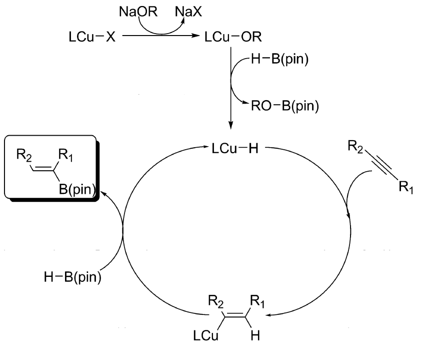
[a]Reaction conditions: alkyne (0.50 mmol), B$_2$(pin)$_2$ (0.65 mmol), NaO^{t}Bu (0.55 mmol), [Cu(Cl)(IMes)] (2 mol %), EX (2.00 mmol), CPME (1.4 mL), at 60 °C for 24 h under air. [b]Conversion determined by GC, based on alkyne, isolated yields in parentheses, average of two reactions. [c]NaO^{t}Bu (1.1 equiv). [d]3 mol % Cu.

boronic ester and a trimethylsilyl group in geminal position was also possible, although in modest yield (32%).

Recent reports have mentioned the synthesis of α-products in which bulky boryl moieties are usually added to the less bulky side of the C−C triple bond. The regioselective hydroboration carried out by McQuade relied on the choice of a very specific catalyst, applied to a narrow scope of propargylic species.[10] On the other hand, Tsuji and co-workers proposed a more general alternative derivative of Aue's early work to generate the α-product by changing the boron source to pinacolborane [HB(pin)].[7,8] In these copper-catalyzed reactions, phosphines as well as NHCs have proved to lead to efficient catalytic systems.

In such a reaction, the species entering the catalytic manifold is presumably the copper hydride species [L−Cu−H] that reacts via syn addition with the alkyne to regioselectively form an alkenyl copper intermediate. Reaction of this intermediate with HB(pin) affords the desired α-hydroborylated compound and regenerates [L−Cu−H] (Scheme 5).[8] Copper hydrides are unstable species, even under inert atmosphere and low temperature;[20] thus, performing such a reaction in the presence of air appeared a significant challenge.

Scheme 5. Proposed Catalytic Cycle for the α-Hydroboration[8]

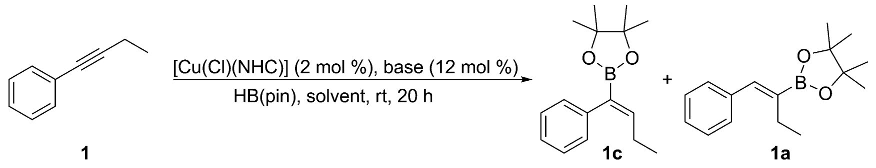


Surprisingly, no reaction occurred using [Cu(Cl)(IMes)] (2 mol %) as catalyst, in CPME and in the presence of NaO^{t}Bu under both air and inert atmosphere (Table 4, entry 1). Using toluene led to low conversion (Table 4, entry 2). Moving to sodium hydroxide as base completely changed the reactivity of the catalyst, and **1c** was obtained with 65% conversion and a 95:5 α/β ratio (Table 4, entry 3). Similar results were obtained in toluene (Table 4, entry 4). Changing the NHC to one of the bulkier congeners led to either a drop in selectivity (Table 4, entries 5 and 6, IPr* = *N*,*N*′-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene[14b,c]) or lower conversion (Table 4, entry 7), whereas a smaller ligand leads to poor conversion (Table 4, entry 8).

[Cu(Cl)(IMes)] was selected as catalyst to optimize the α-hydroboration in air (Table 5). As previously observed, a drop in conversion occurred on going from inert atmosphere to air, but the regioselectivity remained unchanged at 94:6 (Table 5, entry 1). Increasing both temperature and catalyst loading enhanced the conversion to 41 and 59%, respectively (Table 5, entries 2 and 3). At 60 °C, **1c** was formed with 83% conversion (Table 5, entry 4). The desired product was finally formed quantitatively at 80 °C with retained regioselectivity and isolated in 94% yield using 2 mol % of catalyst (Table 5, entries 5 and 6). The catalyst loading can be further decreased to 0.5 mol %, provided that the reaction is carried out under inert atmosphere (Table 5, entry 7).

The scope of the reaction in air was next examined (Scheme 6). All products were obtained in good to excellent yields with high regioselectivity using a relatively low catalyst loading, similar to the state-of-the-art under inert conditions.[8] Compound **2c** was isolated in 70% yield but with an α/β ratio not as high as expected (85:15). However, the regioselectivity toward the α-regioisomer remained far better than non-catalytic and titanium-catalyzed hydroborations.[21] The use of HB(pin) permitted reversal of the selectivity observed in β-hydroboration (Scheme 2) and afforded **6c** in 65% yield and 75:25 (α/β) ratio. The reaction can be efficiently carried out on challenging substrates, as exemplified in the synthesis of **3c**, which results in a high isolated yield (87%) and high selectivity (97:3, Scheme 6). Electron-donating and -withdrawing substituents on the aryl moiety were tolerated, maintaining high yield and regioselectivity (99:1) (**5c** and **8c**). Internal alkynes substituted with heteroaryls were also examined, and the reaction occurred with high yield and excellent regioselectivity (**7c** and **9c**).

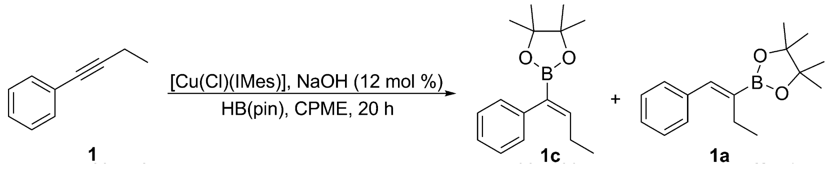
Table 4. α-Hydroboration of 1: Catalyst Screening[a]



entry	NHC	base	solvent	conv (%)[b]	**1c**α/**1a**β ratio[c]
1	IMes	NaO^{t}Bu	CPME	0	
2	IMes	NaO^{t}Bu	toluene	18	95:5
3	IMes	NaOH	CPME	65	95:5
4	IMes	NaOH	toluene	63	95:5
5	IPr	NaO^{t}Bu	toluene	99	87:13
6	IPr*	NaO^{t}Bu	toluene	99	75:25
7	I^{t}Bu	NaOH	CPME	32	96:4
8	ICy	NaO^{t}Bu	CPME	4	

[a]Alkyne (0.50 mmol), HB(pin) (0.75 mmol), base, [Cu(Cl)(NHC)], solvent (0.6 mL), rt, 20 h, inert atmosphere. [b]Conversion determined by GC, average of two runs. [c]α/β ratio determined by GC and ^{1}H NMR.

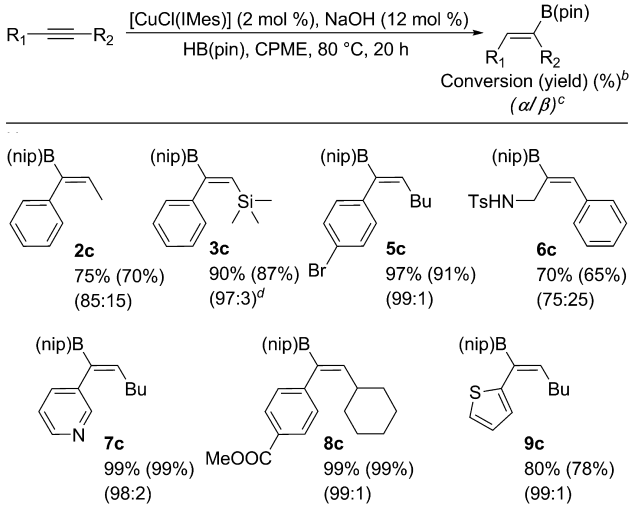
Table 5. Copper-Catalyzed α-Hydroboration of 1 in Air[a]



entry	T (°C)	catalyst loading (mol %)	conv (%)[b]	**1c**α/**1a**β ratio[c]
1	30	1	20	94:6
2	40	1	41	94:6
3	40	3	59	94:6
4	60	3	83	94:6
5	80	3	99	93:7
6	**80**	**2**	**98 (94)**[d]	**93:7**
7[e]	**80**	**0.5**	**78 (75)**[d]	**92:8**

[a] **1** (0.50 mmol), HB(pin) (0.75 mmol), NaOH (12 mol %), [Cu(Cl)(IMes)], CPME (0.6 mL), 20 h, in air. [b] Conversion determined by GC based on alkyne, average of two runs. [c] α/β ratio determined by GC and ^{1}H NMR. [d] Isolated yield. [e] Under argon.

Scheme 6. Copper-Catalyzed α-Hydroboration in Air[a]



[a] Reaction conditions: alkyne (0.50 mmol), HB(pin) (0.75 mmol), NaOH (12 mol %), [Cu(Cl)(IMes)] (2 mol %), CPME (0.6 mL), 80 °C, 20 h, in air. [b] Conversion determined by GC based on alkyne, isolated yield in parentheses, average of two reactions. [c] Ratio determined by GC and ^{1}H NMR analyses. [d] 3 mol % Cu.

CONCLUSION

A convenient methodology to afford selectively and in high yields tri- and tetrasubstituted vinylboronate derivatives in air using non-anhydrous solvents and a single complex [Cu(Cl)(IMes)] has been developed. This system proved active in all three transformations: β-hydroboration, α-hydroboration, and carboboration, demonstrating the versatility of the catalyst. Moreover, these reactions were carried out at low catalyst loadings with an economically and environmentally friendly system using inexpensive base (sodium hydroxide) and relatively green solvent (CPME). This system brings a selective access to the important building blocks that are boron derivatives under mild conditions and in air.

EXPERIMENTAL SECTION

General Procedure for the β-Hydroboration of Internal Alkynes in Air. A vial was charged in air with [Cu(Cl)(IMes)] (appropriate amount using a stock solution of 0.005 mmol Cu in 3.3 mL of CH_2Cl_2. The latter was evaporated in vacuo before adding other reagents), NaOH (0.025 mmol, 1 mg), bis-(pinacolato)diboron (0.55 mmol, 140 mg), the alkyne (0.5 mmol), CPME (0.6 mL), and MeOH (1.0 mmol, 0.05 mL). The vial was closed with a screw cap, and the reaction mixture was stirred at rt for 16 h. The conversion was determined by GC analysis. The volatiles were removed in vacuo, and the product was purified by column chromatography (SiO_2).

General Procedure for the Carboboration of Internal Alkynes in Air. A vial was charged in air with [Cu(Cl)(IMes)] (4.1 mg, 2 mol %), NaO^{t}Bu (0.55 mmol, 53 mg), bis(pinacolato)diboron (0.65 mmol, 165 mg), alkyne (0.5 mmol), CPME (1.4 mL), and the electrophile (3–4 equiv). The vial was closed with a screw cap, and the reaction mixture was stirred at 60 °C for 24 h. The conversion was determined by GC analysis. The volatiles were removed in vacuo, and the product was purified by column chromatography (SiO_2).

General Procedure for α-Hydroboration of Internal Alkynes in Air. A vial was charged in air with [Cu(Cl)(IMes)], NaOH (2.5 mg, 12 mol %), the alkyne (0.50 mmol), and CPME (0.6 mL). The mixture was stirred for 5 min at rt and cooled to −30 °C. Pinacolborane [HB(pin)] was added slowly (0.75 mmol, 0.11 mL). The vial was closed with a screw cap, and the reaction mixture was stirred at 80 °C for 20 h. The conversion was determined by GC analysis. The volatiles were removed in vacuo, and the product was purified by column chromatography (SiO_2). The regioselectivity and the α/β ratio of the products were determined by ^{1}H NMR.

ASSOCIATED CONTENT

S Supporting Information

Synthesis and characterization of alkynes **5**-**9**, general procedures for catalysis, optimization of reaction conditions, ^{1}H and ^{13}C–{^{1}H} NMR spectra of all catalysis products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the Royal Society (University Research Fellowship to CSJC) and the EaStCHEM School of Chemistry for financial support. We also thank the EPSCR National Spectrometry Service Centre in Swansea for HRMS analyses and Attilio Mazzoni for assistance with substrate synthesis.

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