A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

www.angewandte.org

Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202014310

Link to VoR: https://doi.org/10.1002/anie.202014310

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10.1002/anie.202014310

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Cu-mediated Dichotomic Borylation of Alkyne Carbonates: Stereoselective Access to (*E*)-1,2-Diborylated 1,3-Dienes versus Traceless Monoborylation affording α-Hydroxyallenes

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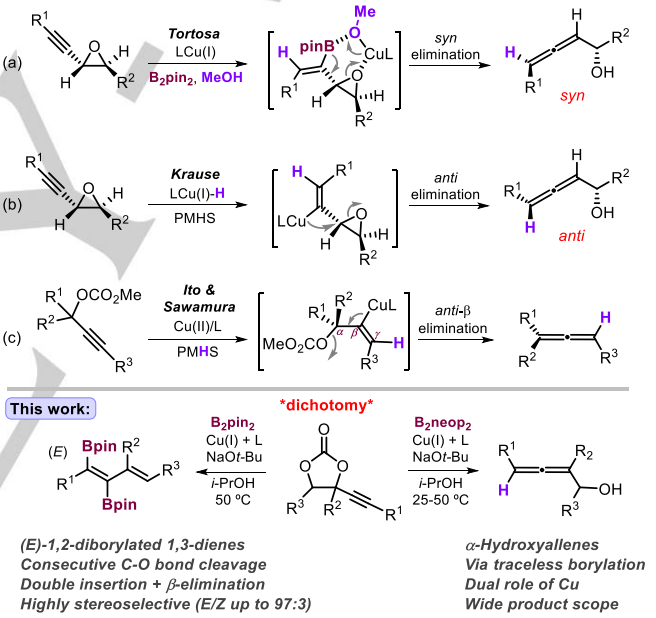
Abstract: A mild copper mediated borylation protocol of alkynyl cyclic carbonates has been developed. Depending on the nature of the borylating reaction partner, either stereoselective diborylation of the propargylic surrogate takes place providing convenient access to (*E*)-1,2-borylated 1,3-dienes, or traceless mono-borylation that leads to α-hydroxyallenes as the principal product. The dichotomy in this borylation protocol has been scrutinized by several control experiments illustrating that a relatively small change in the diboron(4) reagent allows for competitive alcohol-assisted protodemetalation to forge an α-hydroxyallene product under ambient conditions.

Organoboronate compounds play a privileged role in organic synthesis representing benchmark-stable synthons featuring C–B bonds that can be utilized to create a wide range of complex molecules.[1] In particular, bis(pinacolato)diboron (B_2pin_2) and its congeners are versatile borylating agents which have enabled the preparation of a great diversity of (un)saturated boron derivatives including allyl, allenyl, propargyl, vinyl and alkyl/aryl boronates through well-established catalytic carbon-boron bond formation processes.[2] Many elegant strategies have been developed over the years, and in this context the borylation of propargyl substrates displays a particular diversity of reactivity patterns that can be controlled by an appropriate transition metal catalyst.

Pioneering work reported by Ito and Sawamura in 2008 illustrated the regio- and stereoselective borylation of linear propargyl carbonates under Cu catalysis affording a variety of mono-borylated, tri- and tetrasubstituted allenes.[3] In 2017, Tortosa *et al.* demonstrated that propargylic epoxides can be conveniently transformed into their formally reduced α-hydroxyallenes by Cu-catalysis in the presence of B_2pin_2 and methanol (Scheme 1a),[4a] with a *syn*-elimination of the Bpin group playing a pivotal role in this process. The combination of B_2pin_2 and an alcohol as a reducing medium mimics the utilization of copper hydride chemistry reported independently by Krause (Scheme 1b)[5] and Ito/Sawamura (Scheme 1c).[6] Both groups demonstrated that Cu-mediated formal reduction of propargylic epoxides and propargylic linear carbonates could be accomplished, respectively, by PMHS (polymethylhydrido-siloxane) as the stoichiometric hydride source offering a straightforward synthetic route towards allenes.

The exploration of the reactivity of both allylic[7] and alkynyl cyclic carbonates and similar heterocycles[8] as modular substrates in transition metal catalyzed stereoselective transformations has significantly expanded over the last five years. In particular, we found that Cu-catalyzed decarboxylative silylation of cyclic carbonates functionalized with alkyne groups is feasible affording a library of tetrasubstituted 2,3-allenols.[9]



Scheme 1. Formal reduction of propargylic substrates (a-c) and dichotomic reactivity observed in the Cu-mediated conversion of alkynyl cyclic carbonates in the presence of borylating reagents (**This Work**).

Inspired by the pioneering work described in Scheme 1[4a,5-6] and the structural versatility of alkynyl cyclic carbonates,[8a-e,9] we envisioned that borylation of a new type of propargylic surrogate could significantly expand the diversity of functional and highly substituted α-hydroxyallene scaffolds, which are useful building blocks for heterocyclic chemistry and natural product synthesis.[10] In the course of these studies, we discovered an unexpected though unique dichotomic behavior of the borylating agent providing selective pathways leading either to an (*E*)-diborylated 1,3-diene or α-hydroxyallene product with the same catalytic system. Apart from the synthetic utility of the modular alkynyl cyclic carbonates to serve as common substrates for product diversion, the reasons for this remarkable dichotomic reactivity

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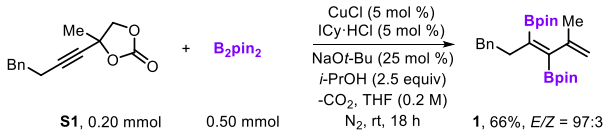
has also been studied through a series of mechanistic control reactions.

First, cyclic carbonate **S1** and B_2pin_2 were combined to examine the influence of various reaction parameters on the selectivity of the borylation process (Table 1). We initially pre-screened a wide series of ligands, bases and solvents using a high-throughput experimentation approach (see the Supporting Information, SI). From this first screening phase, we selected the carbene precursor ICy·HCl (1,3-dicyclohexylimidazolium hydrochloride), NaO*t*-Bu as base and THF/*i*-PrOH as medium on the basis of the selectivity and yield (66%) for 1,2-diborylated 1,3-diene product **1** and the overall stereoinduction (*E*/*Z* = 33:1). [11]

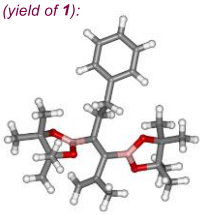
Table 1. Cu-mediated transformation of alkynyl cyclic carbonate **S1** and B_2pin_2 under various reaction conditions leading to diborylated product **1**.[a]



S1, 0.20 mmol | 0.50 mmol | N_2, rt, 18 h | **1**, 66%, *E*/*Z* = 97:3

*variations from the reaction conditions (yield of **1**):*

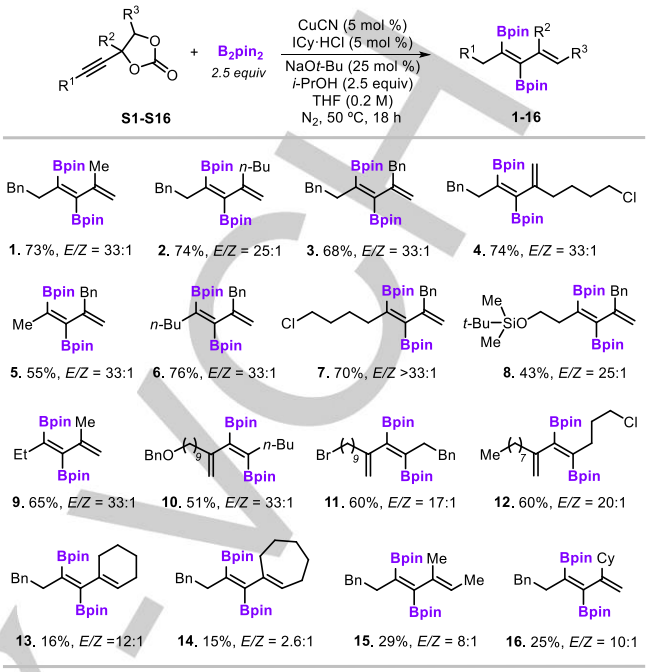
1. No Cu (0%)
2. No base (0%)
3. No ligand (0%)
4. No *i*-PrOH (32%, *E*/*Z* = 1.6:1)
5. 10 mol% Cu (50%)
6. Concentration 0.4 M (46%)
7. Concentration 0.1 M (54%)
8. 1.8 equiv B_2pin_2 (57%)
9. 3 equiv B_2pin_2 (59%)
10. reaction at 0 °C (60%)
11. reaction at 50 °C (62%)
12. No *i*-PrOH but HFIP (0%)[b]
13. No *i*-PrOH but *t*-amyl-OH (54, *E*/*Z* = 5:1)
14. DCM as solvent (0%)
15. ACN as solvent (0%)
16. Et_2O as solvent (44%)



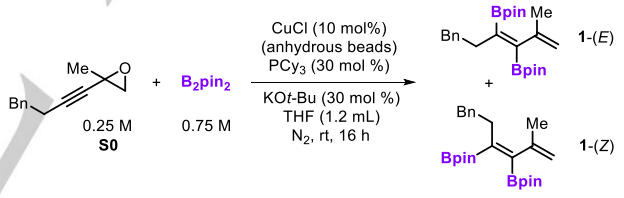
17. Cs_2CO_3 as base (51%)
18. NaOMe as base (20%)
19. CuBr/CuOAc (50/4%)
20. $CuCl_2$/$CuOTf_2$/$CuOAc_2$ (48/15/36%)
21. CuCN (60%), CuCl (66%)
22. 50 °C: CuCN (73%)
23. Mes-Cu: 47% (25 °C), 62% (50 °C)

[a] The comparative reaction conditions are shown in the scheme. If not stated otherwise, the *E*/*Z* ratio of **1** is similar to the one observed using CuCl/ ICy·HCl as catalyst, NaO*t*-Bu as base, and *i*-PrOH/THF as medium. [b] A complex product mixture was obtained.

Then we set out to screen the influence of the amount of B_2pin_2, base additive, solvent and reaction temperature. As can be judged from Table 1, the reaction proved to be inadequate in the absence of either the Cu precursor, base additive or the carbene ligand (entries 1-3). The protic additive (*i*-PrOH) also plays an important role as its presence significantly improves the yield of **1** and the stereoinduction (entry 4). Lowering or increasing the amount of CuCl, concentration, the amount of B_2pin_2 or the reaction temperature did not positively affect the reaction efficiency (entries 5-11). Replacing the protic additive by HFIP (hexafluoroisopropanol, entry 12) gave an intractable reaction mixture whereas the use of *t*-amyl-alcohol (entry 13) demonstrated somewhat lower catalytic potential in terms of yield of **1** and its *E*/*Z* ratio. Further changes in solvent and base (entries 14-18) did also not improve the outcome of this conversion. Finally, several Cu(I) and Cu(II) precursors were scrutinized (entries 19-22) showing that both types of precursors allow for effective catalysis. Compared to CuCl, the utilization of CuCN at room temperature produced a slightly lower yield of **1** (entry 21), though at 50 °C the presence of this precursor led to the best catalytic performance furnishing the diborylated product in 73% isolated yield and maintaining high stereocontrol (entry 22 versus entry 11). The identity of the main stereoisomer (*E*) was confirmed by X-ray analysis (see the inset in Table 1).[12]



Scheme 2. Scope of 1,2-diborylated 1,3-dienes (**1**-**16**) using various alkynyl cyclic carbonates **S1**-**S16** and B_2pin_2 as reagents under the optimized catalytic conditions (Table 1, entry 22). All yields are of the isolated product, *E*/*Z* ratios were determined by ^1H NMR.



1. No change: **1**, 80%, *E*/*Z* = 3.7:1
2. With 50 mol% of Cu: **1**, 75%, *E*/*Z* = 4.4:1
3. CuCl (powder): **1**, 29%, *E*/*Z* = 3.8:1
4. As for 3, *i*-PrOH: **1**, 20%, *E*/*Z*>20:1
5. Using conditions from entry 22, Table 1: **1**, 50%, *E*/*Z*>20:1

*Isolated yields of **1***
E/Z ratios determined by ^1H NMR

Scheme 3. Influence of propargylic epoxide **S0** and supporting ligand in the Cu-catalyzed diborylation process leading to **1**.

The scope of this stereoselective diborylation process (Scheme 2) was further investigated using a more ample set of alkynyl cyclic carbonate precursors (**S1**-**S16**: for their synthesis, see the SI).[9] Diborylated compounds **1–12** were produced with a high degree of stereocontrol, appreciable yields and reasonable skeletal variation useful in post-synthetic operations.[11b] Products **13**–**16**, however, were isolated in low yields and with substantially lower levels of stereoinduction which is ascribed to the increasing steric impediment exerted by the R^2 and R^3 substituents of the cyclic carbonate precursor. These combined results (Schemes 2 and 3) clearly show that rather different reactivity and chemoselectivity is observed in the conversion of the alkynyl-substituted cyclic carbonates versus epoxides in the presence of B_2pin_2 and a protic additive (cf., Scheme 1a).

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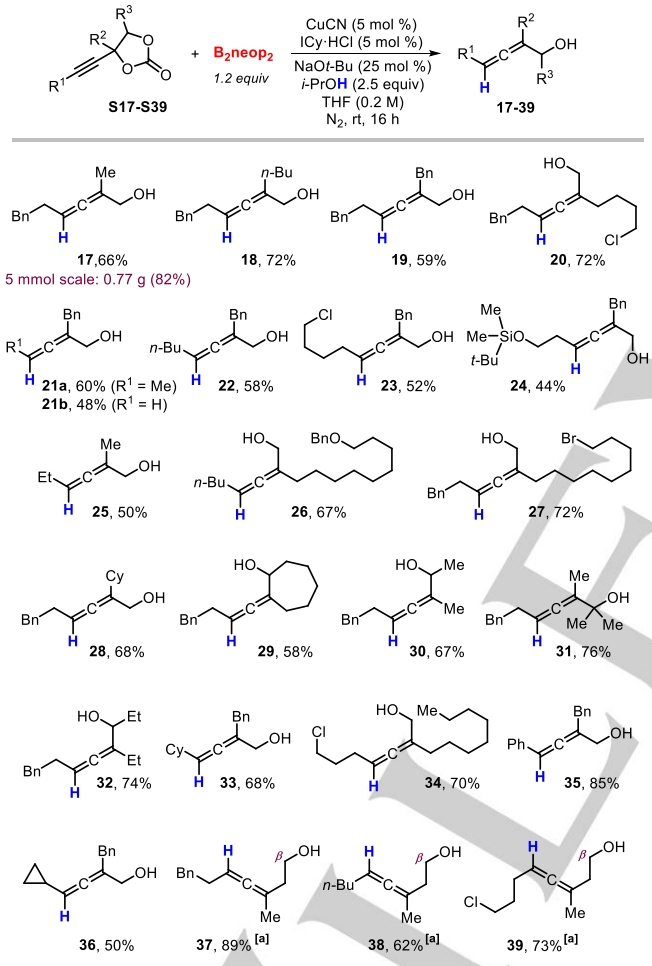
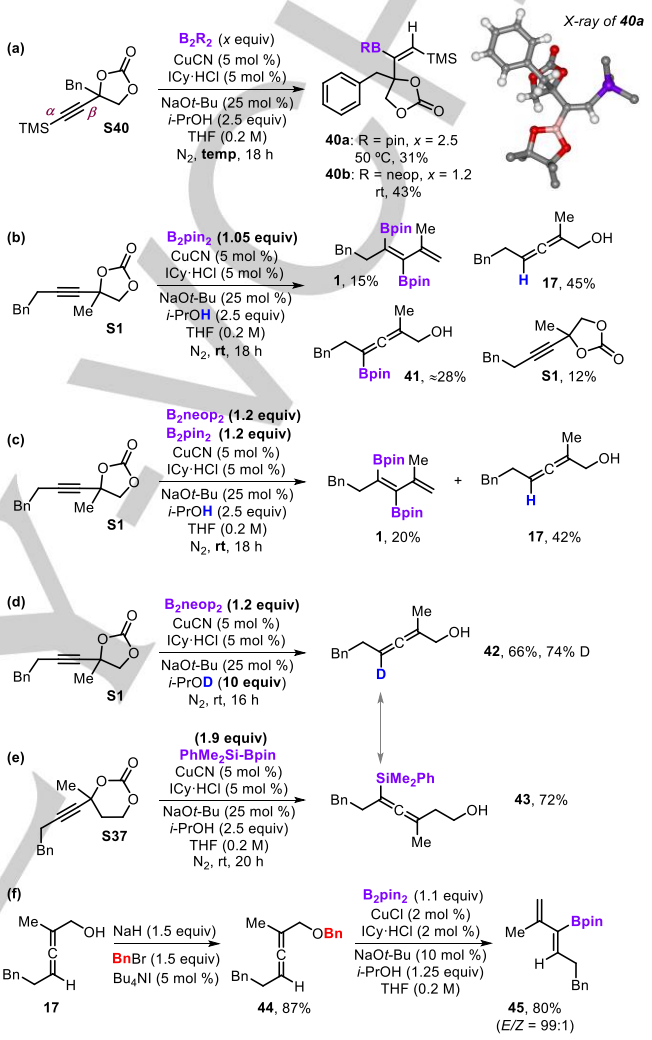
The nature and influence of the propargylic precursor and the supporting ligand was further examined (Scheme 3, entry 1). We were able to reproduce the outcome of the diborylation procedure reported by Szabó et al.[11a] using a propargylic epoxide (**S0**) providing a rather similar yield of **1** (80%) and *E*/*Z* ratio for the isolated product (4:1). The nature of the Cu precursor (entries 3 and 4) had a significant impact on the yield of **1**, whereas the presence of *i*-PrOH gave **1** in low yield though with high stereofidelity (entry 4, *E*/*Z*>20:1). By applying the optimized conditions from Table 1 (entry 22: CuCN/ICy·HCl), propargylic epoxide **S0** was converted into diborylated product **1** (50%) with an *E*/*Z* ratio of >20:1 (entry 5). These control experiments demonstrate that a Cu-carbene catalyst with a protic additive is able to produce 1,2-diborylated 1,3-dienes with significantly higher levels of stereoinduction.



Scheme 4. Formal reduction of alkynyl cyclic carbonates **S17**-**S39** in the presence of B_2neop_2 under similar reaction conditions used in Table 1, entry 22. All yields are of the isolated product. [a] Reaction time was 20 h.

We next wondered whether the scope of 1,2-diborylated 1,4-dienes could be further amplified by variation of the diboron(4) compounds. We considered the use of B_2neop_2 [bis(neopentyl glycolato)diboron], as this reagent is commercially available and has frequently been used in other types of organic transformations.[2i,13] By applying the same catalyst and reaction conditions reported for the synthesis of diborylated compounds **1**-**16** (Scheme 2), we observed the primary formation of a different product from alkynyl cyclic carbonate **S1**, which was identified as the formally reduced α-hydroxyallene **17** (67%, Scheme 4). The yield of **17** did not change (66%) when lowering the reaction temperature from 50 to 25 ºC, and furthermore only a slight excess (1.2 equiv) of B_2neop_2 was required. The reaction could be easily scaled up (*i.e.*, using 5 mmol of starting carbonate) delivering **17** in 82% yield (0.77 g).



Scheme 5. Mechanistic control experiments.

With these conditions in hand, we explored the scope of this unusual borylation driven dichotomy.[14] Various alkynyl cyclic carbonates (**S17**-**S39**) could be conveniently converted into their (reduced) α-hydroxyallenes (Scheme 4, **18**–**36**) with ample diversity in the substitution and functional groups in the presence of B_2neop_2 and the same catalyst employed to access the diborylated 1,3-dienes (Scheme 2, **1**–**16**). Most of the allene products were isolated in appreciable yields. Unlike in the case of diborylation, the presence of more rigid or more sterically demanding substituents in the carbonate substrate did not pose a restriction to the formation of the α-hydroxyallenes (cf., **28**–**32**) and the developed protocol allows for the presence of various fragments in the final product including alkyl halides (**20**, **23**, **27** and **34**), protected alcohols (cf., **24** and **26**) and cycloalkane rings (**29** and **36**). Gratifyingly, six-membered alkynyl cyclic carbonate

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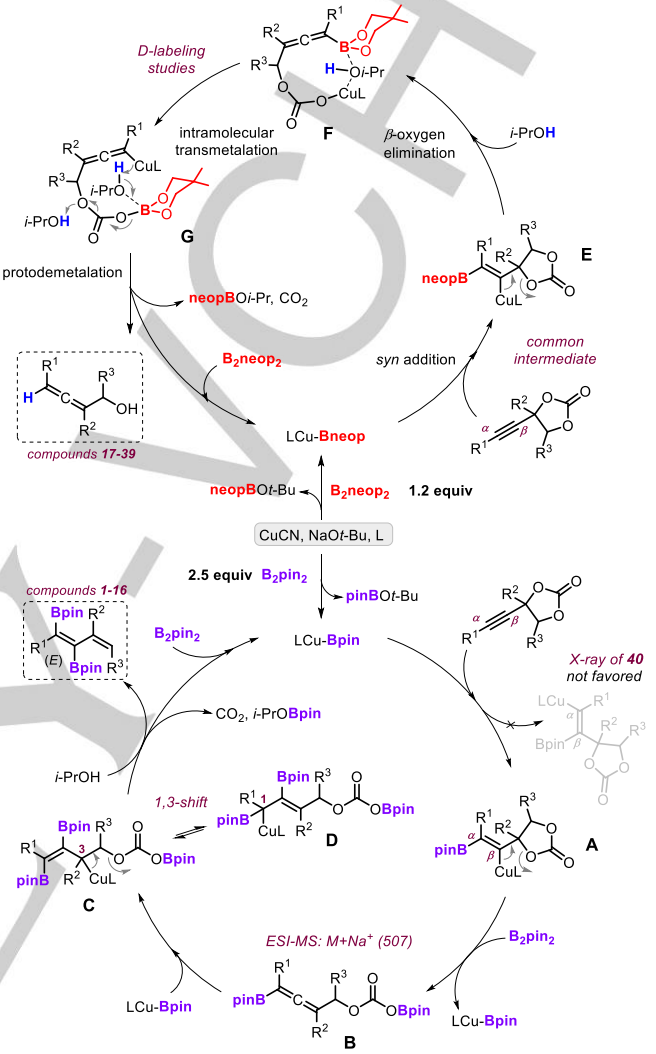
precursors (see the SI for more details) were also productive substrates in this catalytic methodology giving straightforward access to β-hydroxyallenes **37–39** in good yields. The use of six-membered alkynyl carbonates further expands the repertoire of hydroxyallene scaffolds and validates the great versatility and synthetic potential of these functionalized cyclic carbonates compared to the significantly less modular propargylic epoxides.

The remarkable difference in chemoselectivity between the catalytic experiments performed in the presence of B_2pin_2 or B_2neop_2, despite of their structural similarity, was then scrutinized in detail through several control experiments and synthetic extensions (Scheme 5). First, the diborylation of the TMS-protected alkynyl cyclic carbonate **S40** (Scheme 5a) was attempted. However, the major constituent of the product mixture turned out to be a mono-β-borylated cyclic carbonate product using either B_2pin_2 or B_2neop_2. The identity and atom connectivity of **40a** was unambiguously established by X-ray crystallography.[12] This β-regioselectivity is believed to be driven by electronic control, as previously Sun and coworkers described that silyl substituents act as strong β-regio-controlling substituents in propargylic borylations.[15] This precedent not only allows to rationalize the β-borylation of **S40**, but also points at the α-borylation being the productive pathway towards 1,3-diborylation.

Intrigued by this observation, we then performed the borylation of substrate **S1** under the optimized reaction conditions using a slight excess (1.05 equiv) of B_2pin_2 (Scheme 5b). Four major components were identified by ^{1}H NMR spectroscopy in the reaction mixture being unreacted starting material **S1** (12%), diborylated 1,4-diene **1** (15%), α-hydroxyallene **17** (45%) and the mono-borylated allene **41** (~28%, cf. α-borylation of the alkyne unit; see SI for details).[16] These data illustrate that an excess of B_2pin_2 is required to favor the formation of the diborylated diene, and that the mono-borylated allene **41** is a likely precursor to **1**. In the absence of a sufficiently large excess of B_2pin_2 alternative parasitic pathways may be favored. The formation of α-hydroxyallene **17** as the major compound under these reaction conditions suggest that alcohol-promoted protodeborylation of **41** is competitive.

Next a competition experiment was carried out adding both B_2pin_2 and B_2neop_2 to a mixture of **S1** and the Cu-carbene catalyst (Scheme 5c). No scrambling of boronate groups was observed for **1**, and both **1** (20%) and **17** (45%) could be isolated pointing to similar order of magnitude kinetics of the first borylation step in both manifolds. This suggests that the origin of the observed dichotomy in the process is related to the relative kinetics of the second borylation step versus protodeborylation. Since the B–C bond in the Bneop functionalized allene intermediate reminiscent to **41** is sterically more susceptible for transmetalation followed by protonation, the preferred formation of the formally reduced α-hydroxyallenes (Scheme 4) in the presence of B_2neop_2 and the Cu-carbene complex can be rationalized.

The proposed proto-demetalation step induced by the alcohol additive was examined converting substrate **S1** into α-hydroxyallene **42** (Scheme 5d) in the presence of *i*-PrOD providing the product with 74% deuterium incorporation being in line with our mechanistic hypothesis. Finally, the six-membered alkynyl cyclic carbonate **S37** was converted into the silylated β-hydroxyallene **43** in 72% yield demonstrating a useful amplification of this type of building block,[9] and α-hydroxyallene **17** was transformed via a two-step process into the mono-2-borylated 1,3-diene **45** in good yield and with high stereoselectivity.[17] Interestingly, for these latter conversions virtually the same catalytic process was effective as the one leading to the diborylated synthons (Scheme 2) and α-hydroxyallenes (Scheme 4).



Scheme 6. The proposed manifolds for 1,2-diborylated 1,3-diene (bottom half) and α-hydroxyallene formation (upper part). L stands for the carbene ligand ICy.

Based on our observations and control experiments, a mechanistic description of the borylation process is presented in Scheme 6. After initial formation of a Cu(I)-boryl species (lower part), the reaction advances with an addition-elimination sequence that involves the first borylation step (**A**), carbonate ring-opening and elimination of the Cu complex providing a borylated allene with a pendent –OCO_2Bpin leaving group (**B**). Evidence for the intermediacy of **B** was found by ESI(+)-MS (see the SI), and its structure resembles generically the one proposed by Szabó et al.[11a] Subsequently, the allyl-OCO_2Bpin species **B** will then undergo a second Cu-catalyzed borylation via a S_N2'-type mechanism, after which the Cu-catalyst is regenerated via protodemetalation. A 1,3-sigmatropic rearrangement involving the [CuL] complex **D** allows to explain 1,2-diborylated 1,3-diene formation from the envisioned productive 3-metaled isomer **C**. The requisite for having first a borylation on the α-carbon of the

alkyne is supported by the isolation of compounds **40a** and **40b** (Scheme 5a), as β-borylation would not allow for these envisioned consecutive steps to take place. An excess (2.5 equiv) of B_2pin_2 in the proposed manifold agrees well with the experimental observation of a mixture of compounds when a virtually stoichiometric amount was present (Scheme 5b). Under these conditions, the concomitant formation of mono-borylated allenol **41** is noted being a likely precursor to the 1,2-diborylated 1,3-diene product. The whole process involves two C–O bond scission steps, with the second one leading to an (*E*)-configured diborylated alkene under steric control.

In the case of B_2neop_2 (upper part of Scheme 6), the reaction takes a different course though the first addition step (**E**) is reminiscent to the one (**A**) based on B_2pin_2. Upon β-oxygen elimination, a borylated allene carbonate copper species **F** is formed that, with the assistance of *i*-PrOH,[4,18] can undergo a directing group controlled intramolecular transmetalation (**G**).[19] The so-formed copper allene borocarbonate intermediate **G** would produce the final α-hydroxy allene via a protonation process while releasing CO_2 and neopBO*i*-Pr, and regenerating LCu(O*i*-Pr) for subsequent turnover. The competition experiment using a 1:1 molar ratio of both B_2pin_2 and B_2neop_2 (Scheme 5c) and the deuterium labeling experiment (Scheme 5d) are in line with this scenario, and the apparent easier activation of the C–Bneop bond by the Cu complex will lead preferentially to the α-hydroxyallene product.

In summary, we have discovered a new dichotomic behavior of diboron(4) reagents in the Cu-mediated catalytic conversion of alkynyl cyclic carbonates. This new process significantly expedites the synthesis of useful 1,2-diborylated 1,3-dienes, and α- and β-hydroxy allenes using a mild and simple catalytic approach. Virtually the same catalytic protocol allows for the stereoselective conversion of α-hydroxyallenes into 2-borylated 1,3-dienes, making the developed catalyst thus a privileged system for the preparation of wide range of synthetically valuable synthons.

Acknowledgements

We thank the Cerca program/Generalitat de Catalunya, ICREA, MINECO (CTQ2017-88920-P) and AGAUR (2017-SGR-232) for support. KG thanks the Chinese Research Council for a predoctoral fellowship (CSC-2017-06920025). Dr. Xisco Caldentey is thanked for assistance with the HTE screening phase and Dr. Eduardo Escudero-Adán for the X-ray crystallographic studies.

Keywords: alkyne carbonates • borylation • copper • dichotomy • homogeneous catalysis

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10.1002/anie.202014310

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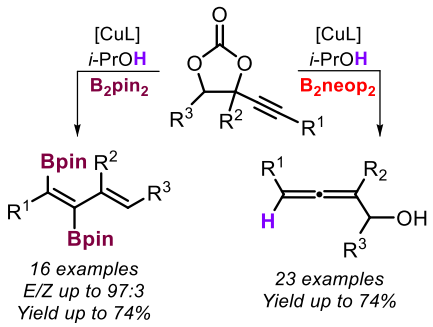

It cuts both ways: A mild copper mediated protocol has been developed that allows for dichotomic borylation of alkynyl substituted carbonates affording either 1,2-diborylated 1,3-dienes or α-hydroxy allenes as the principal products depending on the nature of the diboron(4) reagent. A mechanistic rationale is presented that corroborates with a crucial role for the relative kinetics of the second borylation step versus *i*-PrOH assisted protodemetalation.

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