Copper catalyzed borocarbonylation of benzylidenecyclopropanes through selective proximal C–C bond cleavage: synthesis of γ-boryl-γ,δ-unsaturated carbonyl compounds†

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A copper catalyzed borocarbonylation of BCPs via proximal C–C bond cleavage for the synthesis of γ-boryl-γ,δ-unsaturated esters has been developed. Using substituted benzylidenecyclopropanes (BCPs) and chloroformates as starting material, a broad range of γ-boryl-γ,δ-unsaturated esters were prepared in moderate to excellent yields with excellent regio- and stereoselectivity. Besides, when aliphatic acid chlorides were used in this reaction, γ-boryl-γ,δ-unsaturated ketones could be produced in excellent yields. When substituted BCPs were used as substrates, the borocarbonylation occurred predominantly at the proximal C–C bond trans to the phenyl group in a regio- and stereoselective manner, which leads to the Z-isomers as the products. This efficient methodology involves the cleavage of a C–C bond and the formation of a C–C bond as well as a C–B bond, and provides a new method for the proximal C–C bond difunctionalization of BCPs.

Introduction

Organoboron compounds have emerged as versatile building blocks in organic synthesis owing to their unique reactivity and divergent synthetic applications.† They have also found wide utility in materials science‡ and medicinal chemistry.§ Thus, continued research efforts have been made for their synthesis,¶ while the most prevalent synthetic route for their preparation proceeds via metal-catalyzed borylation of organohalides, hydroboration of alkenes, and borylation of C–H, C–Het and C–C bonds. Recently, impressive progress has been made in copper catalyzed borylative difunctionalization of π-systems, which provides a promising strategy for rapid generation of molecular complexity to install a boron and unique groups across π-systems.¶ These processes are particularly valuable since the resulting C–B bond could be transformed into various functional groups via C–C and C–heteroatom bond-forming reactions through stereospecific transformations.¶ The key step in these reactions is the addition of Cu–Bpin species to C–C π-bonds to give the corresponding β-borylalkylcopper intermediates, which could be captured by various electrophiles to give the difunctionalized products (Scheme 1a). A range of π-systems including alkynes, allenenes, dienes, and alkynes as well as some carbon–heteroatom systems such as ketones, aldehydes and imines have been examined and found to react with a copper-boryl species. These reactions employed borometalation of π-bonds to give 1,2- or 1,4-difunctionalized products. However, borylative difunctionalization via C–C σ-bond cleavage has rarely been reported.⁷

The introduction of strained small rings, which can make σ-bonds behave like π-bonds, as molecular building blocks has recently emerged as a powerful tool in organic synthesis.⁴

Scheme 1  Difunctionalization of π-systems and BCPs.
Among them, methylenecyclopropanes (MCPs) and benzylidene-
cyclopropanes (BCPs), containing a highly strained cyclo-
propane ring with an exo-methylene group, are valuable
building blocks in organic synthesis owing to their unique
structure and high reactivity. The reactions of MCPs and BCPs
under transition metal catalysis have been extensively explored
in the past few decades, and have been frequently used in
a range of reactions, such as cycloaddition reactions, ciclo-

ering reactions.18 The cleavage of a proximal or a distal C–C
accompanied by the addition of an E1

Table 1 Optimization of the reaction conditionsa

| Entry | Cu        | Ligand | Base    | Solvent | Yield (%) |
|-------|-----------|--------|---------|---------|-----------|
| 1     | IMesCuCl  | PPh3   | LiO'Bu  | Toluene | 58        |
| 2     | IPrCuCl   | PPh3   | LiO'Bu  | Toluene | 26        |
| 3     | CuBr      | PPh3   | LiO'Bu  | Toluene | No reaction |
| 4     | IMesCuCl  | —      | LiO'Bu  | Toluene | Trace     |
| 5     | IMesCuCl  | BINAP  | LiO'Bu  | Toluene | 67        |
| 6     | IMesCuCl  | PCy3   | LiO'Bu  | Toluene | 29        |
| 7a    | IMesCuCl  | BINAP  | LiO'Bu  | Toluene | 57        |
| 8g    | IMesCuCl  | BINAP  | LiO'Bu  | Toluene | 69        |
| 9d    | IMesCuCl  | BINAP  | KO'Bu   | Toluene | 58        |
| 10d   | IMesCuCl  | BINAP  | NaOMe   | Toluene | 42        |
| 11df  | IMesCuCl  | BINAP  | LiO'Bu  | Toluene | 89        |
| 12df  | IMesCuCl  | BINAP  | LiO'Bu  | PhCl    | 76        |
| 13df  | IMesCuCl  | BINAP  | LiO'Bu  | MeCN    | 43        |
| 14df  | IMesCuCl  | BINAP  | LiO'Bu  | Toluene | 91        |

a Reaction conditions: 1a (0.1 mmol), B2pin2 (0.15 mmol), 2a (0.15
mmol), catalyst (5 mol%), ligand (10 mol% for monodentate ligand,
5 mol% for bidentate ligand), base (1.5 equiv.), solvent (1 mL), 90 °C,
12 h. b Isolated yields. c BINAP (2.5 mol%). d BINAP (7.5 mol%). e 2a
(0.35 mmol). f 100 °C.

Results and discussion

Initially, 2-(cyclopropyldenemethyl)naphthalene 1a and phenyl
chloroformate 2a were selected as model substrates to react with
B2pin2 to evaluate the feasibility of the borocarbonylation
reaction. To our delight, using IMesCuCl as a catalyst, PPh3 as
the ligand and LiO’Bu as a base, when a solution of 1a, B2pin2
and 2a in toluene was stirred at 90 °C for 12 h, the desired
borocarbonylation product 3aa was successfully obtained in
58% yield (Table 1, entry 1). This reaction turned out to be
highly regio- and stereoselective, and only the Z-isomer was
obtained. Then, we examined a range of copper catalysts for this
reaction. When the precatalyst was substituted with IPrCuCl,
a much reduced conversion was observed and a decreased yield
of 26% was obtained (Table 1, entry 2). No reaction was
observed when CuBr was used (Table 1, entry 3); other copper
catalysts such as CuTc and Cu(CH3CN)PF6 lead to the forma-
tion of the hydroboration products (see details in the ESIf).19
The phosphine ligands were reported to be able to affect the β-
carbon elimination step.20 Thus, we then screened a series of ligands.
Indeed, a phosphine or a pyridyl ligand is essential for this
reaction. Only a trace amount of product 3aa was observed in
the absence of ligand (Table 1, entry 4). The yield of 3aa was
improved to 67% when BINAP was used (Table 1, entry 5). Other
ligands such as PCy3, BuPAd2 and dbbpy were also effective and
produced the desired product 3aa (Table 1, entry 6, see details
in the ESI†). The ratio of the ligand to the catalyst also played an
important role in this reaction. Decreased yield was obtained
when the reaction was performed at a lower ligand/Cu ratio
(Table 1, entry 7). A ligand/Cu ratio of 1.5 : 1 was found to be
optimal and produced 3aa in 69% yield (Table 1, entry 8). Then,
a series of bases were tested and it was found that alkali metal
alkoxides including KO’Bu and NaOMe were effective and
provided the desired product 3aa in 58% and 42% yields,
respectively (Table 1, entries 9 and 10). The bisborylated
product of 1a and small amounts of hydroboration products
were observed as the by-products in these reactions. However,
when NaO’Bu was used as a base, no desired product 3aa was
obtained, only the bisborylated product was observed.12 Other
bases such as K2CO3, Na2CO3 and Et3N were ineffective and no
reaction was observed (see details in the ESI†). The yield of 3aa
could be further improved to 89% when 3.5 equivalents of
phenyl chloroformate 2a were used (Table 1, entry 11, see
details in the ESI†). Screening of the solvent revealed that
toluene is the optimal solvent. When PhCl and MeCN were used
as the solvents, the yields decreased to 76% and 43%, respec-
tively (Table 1, entries 12 and 13). Finally, the reaction
temperature affected the efficiency of this reaction as well, and
an excellent yield of 91% was obtained when the reaction was
performed at 100 °C (Table 1, entry 14).

With the optimized reaction conditions in hand (Table 1,
entry 14), we began to investigate the substrate scope of this
borocarbonylation reaction with emphasis being placed first on
BCPs (Scheme 2). A wide range of substituted BCPs were tested

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and delivered the corresponding products in moderate to excellent yields with excellent regio- and stereoselectivities. When substituted BCPs were used as substrates, the borocarbonylation occurred selectively at the proximal C–C bond *trans* to the aryl group, leading to the formation of *Z*-isomers selectively. Only *Z*-isomers were obtained in these reactions. Both electron-donating (3ca–3ma) and electron-withdrawing groups (3na–3qa) were tolerated. Functional groups such as ether (3ja, 3ka and 3ma), fluoro- (3na), chloro- (3oa) and cyano (3qa) groups were compatible in this reaction. In addition, heteroaryl-substituted BCPs were tolerated as well. For example, 3-thiophenyl and 5-benzofuranyl substituted substrates reacted successfully with B2pin2 and phenyl chloroformate 2a and provided the corresponding products 3ra and 3sa in 70% and 75% yields, respectively. When a 1-naphthyl substituted substrate was used in this reaction, the corresponding product 3ta was produced in 34% yield. Moreover, ferrocene can be tolerated as well, and the corresponding product 3ua was isolated in 57% yield. However, when diphenyl substituted methylenecyclopropane was used in this reaction, the desired product 3va was obtained in a low yield of 24%, which might have resulted from the steric effect.

Then, we began to explore the substrate scope of this borocarbonylation reaction with a series of chloroformates. As shown in Scheme 3, phenyl chloroformates with substitution of either electron-withdrawing (3ab and 3ac) or electron-donating groups (3ad) on the phenyl ring reacted smoothly to provide the corresponding products in good yields. Alkyl chloroformates were also suitable substrates: primary and secondary alkyl chloroformates reacted smoothly and afforded the corresponding γ-boryl-γ,δ-unsaturated esters in good to excellent yields (3ae–3am). Moreover, when chloroformate 2n derived from natural cholesterol was treated with B2pin2 and 1a under the standard conditions, the target product 3an was obtained in 33% yield. However, when tert-butyl chloroformate was used in this reaction, no desired borocarbonylation product was obtained, only the bisborylated product was observed as the main by-product.11a

In addition to chloroformates, acid chlorides were also tested in this reaction (Scheme 4). Aliphatic acid chlorides were tolerated well in this reaction. Although low yields were obtained when primary alkanoyl chlorides were used under the standard conditions, the desired products could be obtained in acceptable yields at a lower reaction temperature.15 When *n*-butyric chloride and *n*-dodecanoyl chloride were used in this reaction, the desired products 3ao and 3ap were obtained in 47% and 52% yields, respectively. Secondary and tertiary alkanoyl chlorides showed good reactivity and provided the desired products in good to excellent yields. For instance, iso-butyryl chloride, cyclohexanecarbonyl chloride, pivaloyl chloride and 1-adamantanecarbonyl chloride reacted with B2pin2 and 1-(cyclopropylidenemethyl)naphthalene 1a under the standard conditions and produced the corresponding γ-boryl-γ,δ-unsaturated ketones 3ar–3at in 86–93% yields. However, aromatic acid chlorides failed to give the desired products, inseparable mixtures of by-products were obtained when aroyl chlorides were used.
To understand the reaction pathway and to illustrate the synthetic versatility of the borocarbonylated products, the following reactions were conducted. First, when cyclopropyl substituted substrate $1w$ was treated with B$_2$pin$_2$ and phenyl chloroformate $2a$ under the optimal reaction conditions, a 1,5-borocarbonylated product ($4$) was obtained in 62% yield. This observation indicates that the reaction proceeds via an addition of Cu–Bpin to the C–C double bond followed by a $\beta$-C elimination and a carboxylation process (Scheme 5a). As mentioned above, the borocarbonylated products could be used in various transformations. For example, the C–B bond could be easily oxidized by NaBO$_3$·4H$_2$O to give the 1,4-diketone $5$ in 95% yield from $3as$ (Scheme 5b). In another instance, treatment of $3aa$ with aqueous KHF$_2$ delivered the corresponding potassium trifluoroborate $6$ in 87% yield (Scheme 5c). Moreover, the Suzuki–Miyaura cross-coupling reaction of $3aa$ with iodobenzene worked smoothly to produce $7$ in 92% yield (Scheme 5d).

On the basis of the experimental results and the previous literature,$^{14}$ a plausible catalytic cycle is proposed in Scheme 6. Firstly, the precatalyst IMesCuCl reacts with LiO$_t$Bu to give an active (L)Cu–O$_t$Bu complex, which reacts with B$_2$pin$_2$ to generate the key (L)Cu–Bpin species. Then, the copper–boryl intermediates react with BCPs via syn-1,2-migratory insertion into the C–C double-bond to afford the borylcuprated intermediate A, which undergoes a $\beta$-carbon elimination to generate a homoallylic copper(I) complex (B). The $\beta$-carbon elimination is the stereo-determining step.$^{16}$ A $\sigma$-bond rotation should occur prior to the $\beta$-C elimination step to avoid the steric repulsion, thus favoring the formation of Z isomers. Subsequently, intermediate B reacts with acyl chloride to give Cu(III) complex C via oxidative addition. Finally, reductive elimination of C releases the product 3 and regenerates (L)CuX, which is used for the next catalytic cycle. However, the direct nucleophilic attack of acyl chloride by the homoallylic copper(I) complex B to afford product 3 cannot be excluded.

Conclusions

In summary, we have developed a copper catalyzed borocarbonylation of BCPs via proximal C–C bond cleavage for the synthesis of $\gamma$-boryl-$\gamma$,d-unsaturated carbonyl compounds. Using substituted benzylidene cyclopropanes (BCPs) and chloroformates as starting material, a broad range of $\gamma$-boryl-$\gamma$,d-unsaturated esters were prepared in moderate to excellent yields with excellent regio- and stereoselectivity. Besides, when aliphatic acid chlorides were used in this reaction, $\gamma$-boryl-$\gamma$,d-unsaturated ketones could be produced in excellent yields. When substituted BCPs were used as substrates, the borocarbonylation occurred predominantly at the proximal C–C bond trans to the phenyl group in a regio- and stereoselective manner, which leads to the Z-isomers as the products. Control experiments indicate that the reaction proceeds via a mechanism involving migratory insertion of Cu–Bpin species to the C–C double bond of BCP and subsequent $\beta$-C elimination and alylation of the intermediary homoallylic Cu(i) complex. This efficient methodology involves the cleavage of a C–C bond and

Scheme 4  Substrate scope of acid chlorides. Reaction conditions: $1a$ (0.1 mmol), B$_2$pin$_2$ (0.15 mmol), $2$ (0.35 mmol), IMesCuCl (5 mol%), BINAP (7.5 mol%), LiOBU (3.5 equiv.), toluene (1 mL), 100 °C, 12 h, isolated yields. *60 °C, 24 h.

Scheme 5  (a) Borocarbonylation of cyclopropyl substituted substrate. (b–d) Derivatization of the borocarbonylation products.

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the formation of a C–C bond as well as a C–B bond, and provides
a new method for the proximal C–C bond difunctionalization
of BCPs.

Data availability

All experimental data and detailed procedures are available in
the ESI.†

Author contributions

J.-B. P. conceived and directed the project. L.-M. Y. performed
the experiments. H.-H. Z., X.-L. L. and A.-J. M. participated in
substrate synthesis and discussions. L.-M. Y. and J.-B. P. wrote
the manuscript and ESI.†

Conflicts of interest

There are no conflicts to declare.

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