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α-Chloro alkylboronic (α-CAB) esters are a class of stable bifunctional molecules wherein the intrinsic differences of a carbon–chlorine and carbon–boron bond can be used to unlock distinct reactivity through carbon-electrophile, carbon-nucleophile, and carbon-centered radical intermediates. Despite their apparent utility, complex variants are not trivial to prepare via established methods. We present a new visible-light-mediated dual catalytic process for the multicomponent coupling of diaryliodonium salts, alkenes, and a simple metal chloride. The broad scope of the reaction combined with the capacity of their synthetic diversification will make this transformation attractive for practitioners of synthetic and medicinal chemistry in academic and industrial environments.
Multicomponent synthesis of α-chloro alkylboronic esters via visible-light-mediated dual catalysis

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SUMMARY
α-Chloro alkylboronic (α-CAB) esters are a class of stable bifunctional molecules wherein the intrinsic differences of a carbon–chlorine and carbon–boron bond can be used to unlock distinct reactivity through carbon-electrophile, carbon-nucleophile, and carbon-centered radical intermediates. Despite their apparent utility, complex variants are not trivial to prepare via established methods. We present a new visible-light-mediated dual catalytic process for the multicomponent coupling of diaryliodonium salts, alkenes, and a simple metal chloride. The broad scope of the reaction combined with the capacity of their synthetic diversification will make this transformation attractive for practitioners of synthetic and medicinal chemistry in academic and industrial environments.

INTRODUCTION
Stable molecules displaying inherent multifaceted reactivity at the same carbon atom are valuable intermediates in organic synthesis.1–4 Sequential leveraging of their orthogonal reactivities via discrete activation modes can enable the programmable bond formation to append multiple new substituents at a single position, streamlining complex molecule synthesis. Despite their apparent utility, readily available and user-friendly variants of such molecules remain rare, with the notable exception of precursors to carbene-like species.5–7 α-Chloro alkylboronic (α-CAB) esters, however, represent a class of stable bifunctional molecule wherein the intrinsic differences of a carbon–chlorine and carbon–boron bond can be used to unlock reactivity through carbon-electrophile, carbon-nucleophile, and carbon-centered radical intermediates (Figure 1).8–12 The pioneering work of Matteson and co-workers provides the most straightforward means through which to prepare α-CAB esters,13–15 wherein lithiated dichloromethane is added to an alkyl- or aryl-boronic ester to form a boronate complex from which the alkyl- (or -aryl) group undergoes a boron-to-carbon migration through the internal nucleophilic attack at one of the carbon–chlorine bonds (Figure 1B). Although this method has underpinned many of the syntheses of α-CAB esters, fully substituted α-CAB esters cannot be accessed via this method because the corresponding lithiation chemistry of more substituted dichloroalkanes is difficult and the boron-to-carbon migration is hindered by the additional alkyl substituent. Notably, Aggarwal and co-workers have developed a wide range of alternative methods to direct Matteson chemistry that involves 1,2-rearrangements through boronate intermediates, and they have evolved as powerful tools for the synthesis of complex molecules.16–22 We reasoned that a modular catalytic method for the synthesis of α-CAB esters that draws from readily available starting materials would enable a facile synthesis of a range of these versatile synthetic intermediates and provide a means for the rapid assembly of complex molecules through reactions that can exploit their inherent multifaceted reactivity.

THE BIGGER PICTURE
Organic molecules that can react selectively in many different ways are valuable intermediates in chemical synthesis. α-chloro alkylboronic esters contain two functional groups that can be activated, sequentially, to form new bonds, which makes them useful in complex molecule synthesis. We report a method for their synthesis from three readily available components. The combination of visible light with two different metal catalysts brings about the union of an aryl radical, vinyl-boronic acid, and chloride ion to form α-chloro alkylboronic esters in a single step. The multifaceted reactivity of the α-chloro alkylboronic ester products can be exploited through established transformations to provide access to compounds that would be non-trivial to prepare by conventional means. We believe this transformation will help to streamline the synthesis of molecules of function, such as pharmaceuticals and agrochemicals.
Here, we report a visible-light-mediated dual catalytic system for aryl-chlorination of vinyl-boronic esters to form $\alpha$-chloro, $\beta$-aryl alkylboronic esters. The multicomponent reaction of diaryliodonium salts, substituted vinyl-boronic esters, and potassium chloride is orchestrated by visible light through a photocatalyst, which brings about aryl-radical formation and leads to aryl-radical addition to the vinyl-boronic ester. A group transfer catalyst then affects a chloride-group transfer step to the newly formed $\alpha$-boryl radical, forming an $\alpha$-CAB ester (Figure 1C). The reaction displays a broad scope in the vinyl-boronic ester and diaryliodonium salt components, and we show that the latent multifaceted reactivity of the $\alpha$-CAB ester motif can be leveraged by orthogonal activation modes toward diverse and complex products.

Recently, we reported a visible-light-driven anion-gated dual catalysis process for the multicomponent assembly of $\alpha$-chloro alkylboronic esters from alkenes, diaryliodonium salts, and sodium azide. Key to the success of this process was the deployment of two discrete copper catalysts that could promote carbon–carbon and carbon–nitrogen bond formation via catalyzed aryl-radical formation and azide-group transfer to the alkene component. A key feature of the mechanism of this transformation is the role of the azide anion, which not only acts as the nucleophile but also gates the redox balancing of the reaction via a process that proceeds catalytically-generated aryl radical readily available vinyl boronic esters simple chloride source $\alpha$-chloro, $\beta$-aryl alkylboronic esters versatile synthetic intermediates.

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through an inner-sphere electron transfer (ISET) pathway between the two discrete copper catalysts. Guided by this reaction blueprint, we questioned whether aryl-radical addition to a vinyl-boronic ester could be coupled with a chloride group to transfer the resulting α-boryl-radical, providing the basis of a modular catalytic synthesis of α-chloro, β-aryl alkylboronic esters, which would represent a streamlined and operationally straightforward preparation of these versatile synthetic intermediates (Figure 1C). The successful realization of this idea would require the alignment of several new mechanistic features. Naturally, the accommodation of vinyl-boronic esters and the chloride anion to the multicomponent process is a fundamental requirement, but their use also poses questions to the anion-gated dual catalysis platform. Our mechanistic understanding dictates that a simple metal chloride should function both as a nucleophile and as a mediator of the photocatalytic system via the putative ISET. Although chloride ions have been well documented as bridging ligands in ISET processes between metal centers, it was not known whether chloride could facilitate redox balancing between the photocatalytic and group transfer phases of our anion-gated dual catalysis platform that would be required for the aryl-chlorination of vinyl-boronic esters. However, related to this, we also questioned whether the intrinsic mechanistic requirements could be influenced by exploring a wider range of different metal complexes capable of the aryl-radical formation and chloride-group transfer steps. As a result, the kinetically controlled ISET step could be replaced by a thermodynamically driven redox balancing process to close the dual catalytic cycles, thereby extending the versatility of the dual catalysis platform.

RESULTS AND DISCUSSION

Guided by our previous work on visible-light-mediated alkene aryl-azidation, we began exploring the desired reaction using the aryl-radical source, diphenyliodonium triflate (A-i) as the limiting reagent in combination with four equivalents of vinyl-boronic ester (B-i) and two equivalents of potassium chloride in the presence of [Cu(I)(dpp)2]PF6 (as a photocatalyst, A-i) and BQA•Cu(OTf)2 (as a precursor to the chloride-group transfer catalyst, B-i) in acetonitrile and irradiation with a 30 W compact fluorescent lamp (Figure 2A). We were pleased to observe a 71% assay yield of the desired α-CAB ester (3a) from this initial reaction. According to our previous mechanistic studies, the redox balancing and closure of the two copper catalytic cycles are affected by an ISET process wherein an azide-anion bridges the oxidized photocatalytic species [Cu(II)(dpp)2] and the reduced group transfer complex, thought to be BQA•Cu(0)N3. One of the compelling aspects of this dual catalysis platform is the capacity to introduce different photocatalysts and group transfer catalysts, providing a flexible parameter through which to modulate the empirically required redox balancing step. Although a system exploiting two discrete copper complexes had served the needs of the alkene aryl-azidation, we realized that they may not be matched to the proposed aryl-chlorination of vinyl-boronic esters, which prompted us to consider whether different metals could be leveraged to close the catalytic cycles. To test this, the group transfer catalyst was first changed from a copper-based complex to an iron-based catalyst, (bpmen)Fe(II)Cl2 (B-ii): iron(II)-catalysts have been capable of affecting carbon–chloride bond formation as part of atom transfer-based reactions. We observed that the combination of [Cu(I)(dpp)2]PF6 (A-i) as photocatalyst and (bpmen)Fe(II)Cl2 (B-ii) as group transfer catalyst led to an assay yield of 64% of the desired product. Next, the photocatalyst was changed to [Ru(II)(bpy)3](PF6)2 (A-ii), which can still enable single electron reduction of the diphenyliodonium salt (1a) to the aryl radical, and the resulting [Ru(III)(bpy)3] species has an oxidation potential (E(1/2) (Ru(III)/R(II)) = +0.82 V versus...
Figure 2. The evolution of visible light-driven, dual catalytic ary1-chlorination of vinyl-boronic esters

(A) Selected optimization exploring photocatalysts and group transfer catalysts. (B) Proposed mechanism for dual (Ru/Fe)-catalytic ary1-chlorination of vinyl-boronic esters.

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Ru-photocatalyst (A-ii) resulted in a 6% assay yield of product, most likely due to inefficient aryl radical formation facilitated by the Fe(II)-catalyst,\textsuperscript{36,37} and no product was observed when the group transfer catalyst, (bpmen)Fe(II)Cl\textsubscript{2} (B-ii), was removed from the reaction.

Under the optimal reaction conditions, the mechanism is proposed to proceed via visible-light excitation of the [Ru(II)(bpy)]\textsubscript{2+} photocatalyst (A-ii), which is oxidatively quenched by the diphenyliodonium triflate 1a to form the aryl-radical int-I and an oxidized [Ru(III)(bpy)]\textsuperscript{3+} species (Figure 2B). The aryl radical can undergo addition to vinyl-boronic ester 2a to form the β-aryl, α-boro-alkyl radical int-II.\textsuperscript{38–44} The group transfer pre-catalyst, (bpmen)FeCl\textsubscript{2} (B-ii), \(E_{1/2}[LFe(III)/LFe(II)] = \pm 0.08\) V versus Fc*/Fc in MeCN requires oxidation to its active Fe(III) form by the oxidized photocatalyst [Ru(III)(bpy)]\textsuperscript{3+} (\(E_{1/2}[Ru(III)/Ru(II)] = \pm 0.82\) V versus Fc*/Fc in DMA). Based on our initial hypothesis of the dual copper catalysis system used in the alkene azidoarylation reaction, this oxidation would proceed through chloride-mediated ISET between the Fe(II) and Ru(III) centers to form the active group transfer species [(bpmen)Fe(III)Cl\textsubscript{2}]\textsuperscript{+} (confirmed by X-ray diffraction of a single crystal), while regenerating the [Ru(II)(bpy)]\textsuperscript{2+} to close the photocatalytic cycle. However, the coordinately saturated nature of the oxidized photocatalyst [Ru(III)(bpy)]\textsuperscript{3+} suggests that the bridging chloride anion to the Fe(II) complex required for ISET is unlikely to be able to bind to the Ru(III) center, thereby precluding reduction by this pathway. Instead, we surmise that redox balancing to close the catalytic cycles of the Ru and Fe complexes proceed through a more thermodynamic single electron transfer pathway accounted for by the oxidation potentials of the Fe(II) \(E_{1/2}[Fe(III)/LFe(II)] = \pm 0.08\) V versus Fc*/Fc in MeCN and Ru(III) \(E_{1/2}[Ru(III)/Ru(II)] = \pm 0.82\) V versus Fc*/Fc in DMA species. In order to complete the group transfer catalytic cycle, [(bpmen)Fe(III)Cl\textsubscript{2}]\textsuperscript{+} transfers a chlorine atom to the β-aryl, α-boro-alkyl radical int-II to form the desired β-aryl-α-chloro-α-boro-alkane 3a and regenerates the group transfer pre-catalyst, completing the transformation.

With an optimal set of reaction conditions and a preliminary hypothesis for the mechanism of the dual catalytic aryl-chlorination of vinyl-boronic ester, the scope of the new transformation was next explored. Using methyl-substituted vinyl-boronic ester 2a as a representative substrate, the scope of the reaction in the aryl component was examined using a range of substituted diaryliodonium salts that can be prepared in a straightforward fashion from the corresponding aryl iodides (Figure 3). In most cases, the symmetrical diaryliodonium salts were used because aryl transfer through a radical species displays modest selectivity amidst differentially substituted aryls (see supplemental information for details).\textsuperscript{45} Beyond the transfer of phenyl (3a, Figure 2A), we found that a wide range of para-, meta-, and ortho-substituted benzenes were successfully added to vinyl-boronic ester as part of the aryl-chlorination (3b–3m). There appears to be little difference in the reactivity of aryl transfer, in terms of both steric and electronic properties of the diaryliodonium salts, with yields of isomeric products consistently high. The transfer of a ketone-containing aryl group (to 3f) is noteworthy because the presence of the enolizable carbonyl functionality would likely preclude its incorporation using classical Matteson chemistry. We were pleased to find that some heterocyclic aryl groups also worked effectively and although the yield for the transfer of the electron-rich thiophene was modest (3p), a reaction transferring a pyridyl unit (3q) was unaffected by its intrinsic properties.

Next, the scope of the vinyl-boronic ester component was assessed, wherein the α-substituent was varied. A selection of common functional groups appended to the alkene could be accommodated in the reaction to form the corresponding fully substituted α-CAB esters (3r-v), which produced molecules with versatile orthogonal
functionality to the core α-chloro-alkylboronic ester motif (Figure 4). The increased steric bulk of branched alkyl substituents on the vinyl-boronic ester did not adversely affect the process with the α-cyclohexyl substituted, leading to a reasonable yield of the desired product (3v). Conversely, the unsubstituted vinyl-boronic ester was also converted to the desired product 3w although the yield was lower, likely due to the poorer stabilization afforded by the unsubstituted α-borono-alkyl radical, which resulted in the formation of arene-related side products resulting from the hydrogen atom transfer, Sandmeyer-type chlorination, and vinylation at the site of the aryl radical as the mass balance (see supplemental information for details). Vinyl-boronic esters containing α-aryl groups adorned with electronically diverse substituents (3x-3ad) were good substrates for the aryl-chlorination reaction and delivered the desired products with generally good yields. The reaction also worked well when more hindered ortho substituents were incorporated into the aromatic ring of the α-aryl vinyl-boronic esters (3ac, 3ad). Unfortunately, vinyl-boronic esters substituted with a 4-methoxy phenyl group could not be formed using this aryl-chlorination reaction, and it was also observed that trisubstituted vinyl-boronic esters were unreactive. We were, however, pleased to find that phthalimide- and allylic ether-substituted vinyl-boronic esters were accommodated by the reaction conditions and produced densely functionalized α-CAB esters displaying a protected amine and hydroxymethyl features (3ae-f).

Having established a broad scope in each component of the dual catalytic aryl-chlorination of vinyl-boronic esters, we next investigated leveraging the orthogonal reactivities of the α-chloro, α′,α″-dialkylboronic ester products through different
activation modes. For example, simple S_N2 displacement at the electrophilic carbon–chlorine bond in 3w with a thiolate nucleophile forms a-thioether alkylboronic ester 4a and an amination reaction using LiHMDS as a source of nucleophilic amine forms the corresponding a-amino alkylboronic ester 4b (Figure 5 A).46,47

The functional pattern of a-heteroatom substituted alkylboronic acids, which can be derived from boronic esters 4a and 4b, are important in several pharmaceutically relevant molecules.48–51 The S_N2 displacement only proceeds with less substituted a-CAB esters, presumably due to steric hindrance in the fully substituted systems (such as 3a). To exploit the electrophilic reactivity of a-CAB esters with neutral nucleophiles, we treated 3w with an indole derivative in the presence of AgSbF_6, which facilitated the cationic C3-alkylation of the indole motif to form a highly functionalized a-tertiary-Bpin ester (4c) in 44% yield (Figure 5 B).52 Moreover, the reaction of a-CAB ester 3a with vinyl-MgBr and butyl-lithium furnished the fully substituted alkyl-Bpin esters 4d,e in 65% and 55%, respectively, reflecting the powerful carbon–carbon bond forming capacity of 1,2-metallate rearrangements on alkyl-Bpin esters displaying a-leaving groups.53 In the case of 4e, we advanced the complex alkyl-Bpin esters to the corresponding tertiary alcohol (5a) and a-tertiary amine (5b), using established oxidation methods (Figure 5 C).54,55

To further demonstrate the multifaceted reactivity inherent to these a-CAB esters, we showed that 3u can undergo a Ni-catalyzed stereoconvergent Negishi coupling to afford secondary alkylboronic ester 4f in 55% yield and with a 91:9 enantiomeric ratio.10 After treatment with 2-furyllithium, to form nucleophilic “boronate” complex, 4e can undergo 1,2-metallate rearrangement upon treatment with N-bromosuccinimide to afford enantioenriched functionalized alkane 6 in 75% yield, which is reported to
proceed with complete stereoretention (Figure 5D).56–58 This cross-coupling sequence demonstrates the orthogonality between the electrophilic carbon–chlorine bond and its nucleophilic carbon–Bpin bond in α-CAB esters that can be exploited, sequentially, to form complex products.
CONCLUSIONS

In summary, we have developed a new method for the multicomponent synthesis of versatile α-CAB esters. Key to the success of this work was the leveraging of a new visible-light-mediated dual catalysis system that combines an aryl radical, alkene, and chloride to form this versatile class of stable molecules displaying intrinsic multifaceted reactivity at the same carbon atom. The reaction displays broad scope in both components and we showed that the orthogonal reactivity of α-CAB esters can be exploited through a number of discrete activation modes, appending multiple new substituents at a single position. As such, we believe the generation of complex molecules using this new dual catalytic aryl-chlorination of vinyl-boronic esters to form complex α-CAB esters in combination with established transformations of carbon–chlorine and carbon–boron bonds will be of substantial interest to practitioners of synthetic and medicinal chemistry in academic and industrial settings.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled, where possible, by the lead contact, Matthew Gaunt (mjg32@cam.ac.uk).

Materials availability

Full experimental details, including methods, optimization studies, experimental procedures, mechanistic studies, and 1H NMR, 13C NMR and 19F NMR spectra, HRMS, IR, and UV-vis data are available in the supplemental information for all unique compounds. Crystallographic data are available free of charge from the Cambridge Crystallographic Data Centre: (CCDC) 2209089. There are restrictions to the availability of all reagents and products because of limitations on our capacity to store compounds. Raw data are available from the corresponding author upon reasonable request.

Data and code availability

All data supporting this study are available in the manuscript and supplemental information.

General experimental procedure

A 4.0 mL PTFE/silicone-lined septa screw cap (PP) clear glass vial equipped with magnetic stirrer bar (10 mm, cylindrical) was charged with all non-volatile reagents (typically Ru11(bpy)3(PF6)2 [1.7 mg, 0.002 mmol, 1.0 mol %], (bpmen)FeIICl2 [4.0 mg, 0.010 mmol, 5.0 mol %], diaryliodonium salt 1a [0.200 mmol, 1.0 equiv], and KCl [30.0 mg, 0.400 mmol, 2.0 equiv]) under air. The vial was closed and evacuated/backfilled with N2 (3 cycles). Anhydrous MeCN (1.0 mL, c = 0.200 M) was added via syringe under N2, followed by vinyl-boronic ester 2a (76.0 μL, 0.400 mmol, 2.0 equiv). The vial was sealed with additional parafilm, whereas the punctures on the septum were sealed with vacuum grease. The sealed vial was then secured to a stirrer/hotplate, 5 cm from the Kessil lamp, along with an overhead desk fan for cooling. The vial was irradiated overnight with vigorous stirring (1,000 rpm). Upon completion, the reaction mixture was concentrated in vacuo and added with 10% Et2O/PE (2.0 mL) to induce precipitation. The mixture was filtered through a pad of celite to remove all the insoluble and then the filtrate was concentrated in vacuo. The residue was purified via flash chromatography (0%–95% MeCN/H2O over 10 min on C18-coated SiO2) to isolate the desired product 3a.
SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.chempr.2022.10.010.

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AUTHOR CONTRIBUTIONS
A.B., B.L., and M.J.G. conceived the project. B.L. conducted the experiments. B.L., A.B., and M.J.G. analyzed and interpreted the results. B.L., A.B., and M.J.G. wrote the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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