Facile Arylation of Four-Coordinate Boron Halides by Borenium Cation Mediated Boro-desilylation and -destannylation

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ABSTRACT: The addition of AlCl₃ to four-coordinate boranes of the general formula (C−N-chelate)BCl₂ results in halide abstraction and formation of three-coordinate borenium cations of the general formula [(C−N-chelate)BCl]⁺. The latter react with both arylstannanes and arylsilanes by boro-destannylation and -desilylation, respectively, to form arylated boranes. Catalytic quantities of AlCl₃ were sufficient to effect high-yielding arylation of (C−N-chelate)BCl₂. Boro-destannylation is more rapid than boro-desilylation and leads to double arylation at the boron center, whereas in reactions with arylsilanes either single or double arylation occurs dependent on the nucleophilicity of the arylsilane and on the electrophilicity of the borenium cation. The electrophilicity of the borenium cation derived from 2-phenylpyridine was greater than that of the benzothiadiazole analogues, enabling the boro-desilylation of less nucleophilic silanes and the direct electrophilic borylation of 2-methylthiophene.

INTRODUCTION

Four-coordinate boron compounds containing a chelating π-conjugated C/N donor and two exocyclic aromatic moieties, termed (C−N-chelate)BAr₂ (e.g., 1-BAr₂ right Scheme 1), have been extensively studied for application in optoelectronic devices.¹,² Changing the exocyclic aryl groups in 1-BAr₂ significantly modulates the key optoelectronic properties including the frontier orbital energies and the photoluminescence quantum yield.²,³ Therefore, efficient and versatile routes to libraries of these compounds are important to optimize the materials properties and deliver improved device performance. A particularly attractive approach is the arylation of (C−N-chelate)BX₂ (e.g., 1-BX₂, X = Cl or Br) to form a wide range of (C−N-chelate)BAr₂ compounds, as the starting compounds are readily accessed by electrophilic C−H borylation (Scheme 1).³,⁴

Installation of aromatic moieties at three-coordinate boron species is generally achieved by reaction with either arylithium or aryl Grignard reagents.⁵ However, reaction of these reagents with Lewis base adducts of boranes often gives the desired product in poor yield.⁴ Instead functionalization of borane-Lewis adducts such as (2-phenylpyridyl)BBr₂ (1-BBr₂, Scheme 1) requires organozinc or organoaluminum reagents to achieve high-yielding transmetalation.³,⁴ Unfortunately these nucleophiles are highly sensitive to protic species (ROH), and the synthesis of organozinc reagents often results in mixtures containing ionic species (termed zincates) and coordinated etherate solvent, which can complicate transmetalation.⁶ Alternative nucleophiles are required that are readily synthesized, are well-defined, can be handled in air, and enable the boron-containing products to be easily isolated, preferably without column chromatography. Arylsilanes and arylstannanes meet these criteria; however, while three-coordinate boranes (e.g., ArBBr₂) undergo transmetalation with arylsilanes and arylstannanes, four-coordinate boranes do not due to the Lewis acidity at boron being effectively quenched by the dative bond.⁵ We hypothesized that conversion of (C−N-chelate)BX₂ into borenium cations,⁷ [(C−N-chelate)BX]⁺, using a halophilic Lewis acid (e.g., AlCl₃) will enable transmetalation using arylstannanes and arylsilanes. The process is potentially catalytic in the halophile, as the byproduct from transmetalation will react as a functional equivalent of [R₃Si]⁺ or [R₃Sn]⁺, abstracting halide to generate further equivalents of borenium cations for subsequent transmetalation (Scheme 2). Related, albeit stoichiometric in halophile, approaches have been
reported for activating chloro-boron subphthalocyanine and F$_2$B-dipyromethenes toward substitution of B–X with chalcogen-based nucleophiles.\textsuperscript{8} In contrast, the use of borenium cations in boro-desilylation has extremely limited precedence,\textsuperscript{9} while their use in boro-destannylation has not been reported to date to the best of our knowledge. Herein is reported catalytic (in AlCl$_3$ activator) borenium cation mediated borylation as a simple method to functionalize (C–N-chelate)BCl$_2$ species based on benzo[4]diazole (BT) and pyridyl with aryl and heteroaryl groups.

**RESULTS AND DISCUSSION**

Our initial attempts to access new 2-BAr$_2$ compounds used an isolated organozinc reagent synthesized from ZnBr$_2$ and p-tolylMgBr in THF, but this led to low yields of the desired arylated product. The low conversion was attributed to the “Zn(p-tolyl)$_2$” formed under these conditions actually being the zinicate [Mg(THF)$_2$]$_2$ indicated by multinuclear NMR spectroscopy\textsuperscript{1, 10} in $^{13}$C or $^{27}$Al NMR spectrum), indicating the feasibility of borenium-mediated transmetalation with organo-destannylation reactions with PhSnBu$_3$ consistent with the enhanced nucleophilicity of the thienylzinc.

Mixing 2-BCl$_2$ (readily formed from the unborylated precursor 2 (F8-BT-F8) and BCl$_3$)\textsuperscript{3} with 2 equiv of PhSnBu$_3$ in CH$_2$Cl$_2$ at room temperature led to no reaction until catalytic (ca. 5 mol %) AlCl$_3$ was added to the reaction mixture. Compound 2-BCl$_2$ then slowly transformed into diphenylated 2-BPh$_2$ at 20 °C (Scheme 3). Heating of the reaction resulted in a more rapid reaction and good conversion to 2-BPh$_2$ (89% isolated yield after 16 h at 60 °C in CH$_2$Cl$_2$ in a sealed tube). The addition of AlCl$_3$ results in chloride abstraction from 2-BCl$_2$ and borenium cation formation (indicated by downfield shifts in the $^1$H NMR spectrum and formation of [AlCl$_4$]$^-$ in the $^{27}$Al NMR spectrum), consistent with previous studies on related compounds.\textsuperscript{3} The borenium cation [2-BCl]$^+$ is then sufficiently electrophilic to boro-destannylation PhSnBu$_3$. An alternative mechanism where AlCl$_3$ and PhSnBu$_3$ react to form Al-Ph species (which have been previously reported to transmetalate to four-coordinate boron halides)\textsuperscript{3} is precluded based on previous work where the combination of these reagents (in the absence of 2-BCl$_2$) in haloalkane solvents (such as CH$_2$Cl$_2$) leads to solvent activation via C–Cl···AlCl$_2$ interactions (Friedel–Crafts-type reactivity) and carbodestannylation to form R$_3$C-Ph.\textsuperscript{11} Friedel–Crafts products are not observed in the reaction with 2-BCl$_2$, which is attributed to AlCl$_3$ reacting rapidly to form the borenium cation, thus disfavoring solvent activation. The ability to form 2-BPh$_2$ in high conversion using catalytic AlCl$_3$ confirmed that the electrophilic [Bu$_3$Sn]$^+$ (or a functional equivalent thereof) byproduct can react with further 2-BCl$_2$ directly or via initial reaction with [AlCl$_4$]$^-$ to provide access to additional equivalents of borenium cations.

The installation on boron of heteroaryl substituents using 5-Bu$_3$Sn-2-Me-thiophene, 3 (prepared by lithiation of 2-methylthiophene and quenching with Bu$_3$SnCl) was also explored. Mixing 2-BCl$_2$ with 2.2 equiv of 3 gave no reaction, but addition of catalytic AlCl$_3$ (ca. 5 mol %) resulted in rapid arylation at 20 °C (complete within 10 min), and facile isolation simply by filtration through silica allowed 2-B(MeT)$_2$ to be isolated in 67% yield. It is noteworthy that arylation using 3 is considerably more rapid at 20 °C than reactions with PhSnBu$_3$, consistent with the enhanced nucleophilicity of the thienylzinc.

Borenium cation mediated transmetalation with organo-stannanes is effective for tetaarylation of [4-(BCl)$_2$]$^{2+}$. The diborenium cation [4-(BCl)$_2$]$^{2+}$ (Scheme 4) is produced by double borylative fusion of the unborylated precursor 4 (BT-F8-BT)\textsuperscript{3} as previously reported. With a slight excess of PhSnBu$_3$ (4.2 equiv) [4-(BCl)$_2$]$^{2+}$ forms the previously characterized teta-arylated product 4-BPh$_2$ as the major boron-containing complex after 72 h at 20 °C or 24 h at 60 °C (by multinuclear NMR spectroscopy) in 1,2-Cl$_2$C$_6$H$_4$. Transmetalation with ZnP$_2$ to form 4-(BPh$_2$)$_2$ required prior conversion of [4-(BCl)$_2$]$^{2+}$ to neutral 4-BCl$_2$, by addition of NMe$_4$Cl for acceptable conversion.\textsuperscript{4} In contrast, the borodestannylation methodology requires the borenium for transmetalation; therefore it proceeds directly from [4-(BCl)$_2$]$^{2+}$.

The thiophene analogue of 2-BCl$_2$, S-BCl$_2$ (Scheme 5), can be readily prepared from the unborylated precursor 5 as previously reported.\textsuperscript{4} Again while arylation with ethereate-free diaryl zinc reagents proceeds with high fidelity, the addition of [Mg(THF)$_2$]$_2$Zn(p-tol)$_2$ to 2-BCl$_2$ led to an extremely low conversion to 5-B(p-tol)$_2$. As the major product of the reaction with $^{1}$H NMR resonances and the observation of [AlCl$_4$]$^-$ in the $^{27}$Al NMR spectrum), indicating the feasibility of borenium-mediated transmetalation with organostannanes. The addition of stannane 3 to 5-BCl$_2$ again resulted in no reaction until addition of catalytic AlCl$_3$ (ca. 5 mol %), at which point double arylation proceeded rapidly (complete within 10 min at 20 °C) to form 5-B(MeT)$_2$. This product could be isolated by column chromatography in 51% yield (Scheme 5). It should be noted that both 2-B(MeT)$_2$ and 5-B(MeT)$_2$ undergo slow proto-deboronation of the exocyclic thiényl groups on standing in wet solvents but are stable in the solid state under ambient conditions.

**Scheme 3. AlCl$_3$-Catalyzed Transmetalation from Arylstannanes to 2-BCl$_2$, with Isolated Yields in Parentheses**

**Scheme 4. Tetaarylation of [4-(BCl)$_2$]$^{2+}$ with PhSnBu$_3$**

![Scheme 4. Tetaarylation of [4-(BCl)$_2$]$^{2+}$ with PhSnBu$_3$](image-url)
atmosphere for at least three months. An alternative synthesis of 5-B(MeT)₂ by electrophilic C–H borylation was explored based on our previous success using PhBCl₂ to form 5-B(Ph(Cl)) directly from 5. However, (5-(2-methylthiophene))₂BCl ((MeT)₂BCl) does not react with 5 (Scheme 5, right), presumably due to the reduced Lewis acidity at boron (relative to BCl₂ and PhBCl₂). Furthermore, (MeT)BCl₂ also fails to borylate 5. Thus, C–H borylation using BCl₂ followed by transmetalation is necessary to access this compound.

The boro-destannylation reaction was extended to 2-B₆Sn-9,9-diocetylfluorene (6), synthesized by standard procedures. The reaction of 5-BCl₂ with 2.2 equiv of 6 and catalytic AlCl₃ (ca. 5 mol %) proceeded at room temperature, but required 18 h for formation of 5-(F₈)₂ in high conversion. The longer reaction time compared to transmetalation with 3 is attributable to the variation in arene nucleophilicity. Attempts to selectively form the monoarylated product by addition of 1 equiv of 6 to 5-BCl₂ (with catalytic AlCl₃) led to a mixture of 5-BCl₂/5-BCl(F₈) and 5-(F₈)₂. 5-(F₈)₂ also can be synthesized from 5 in a two-step, one-pot reaction without the use of a glovebox in 88% yield. Compound 5-BCl₂ is prepared by reaction of 5 with BCl₃, followed by degassing (removing excess BCl₃ and the HCl byproduct from C–H borylation) and subsequent addition of catalytic AlCl₃ and 2.2 equiv of 6 (both weighed and handled under ambient atmosphere). The product, 5-(F₈)₂, is then simply isolated by filtering through silica.

The use of arylsilanes in place of arylstannanes is preferable from a toxicity perspective. However, reacting PhSiMe₃ and 2-BCl₂ with a range of AlCl₃ loadings and reaction conditions (at 20 and 60 °C) consistently resulted in minimal transmetalation. It is well documented that silicon–boron exchange only proceeds with highly electrophilic boranes, in contrast with tin–boron exchange. This suggests that the borenium cation [2-BCl]⁺ is insufficiently electrophilic to effect boro-desilylation of PhSiMe₃. A more nucleophilic silane, 2-Me-5-Me₃Si-(MeT)₂, was therefore utilized. Compound 2-BCl₂ was combined with an excess (2.2 equiv) of 7, resulting in no reaction. Addition of AlCl₃ (ca. 5 mol %) to the reaction mixture initiated transmetalation, leading to only one transmetalation per boron, producing 2-BCl(MeT) (Scheme 6), even after long reaction times. As the borenium cation [2-B(MeT)]⁺ formed after the first transmetalation and subsequent halide abstraction contains a thienyl π donor, its Lewis acidity is presumably reduced relative to [2-BCl]⁺, disfavoring boro-desilylation of 7. Analogous trends have been previously observed when comparing the Lewis acidity of [PhBCl(amine)]⁺ and [Cl₄B(amine)]⁺ borocations. Compound 2-BCl(MeT) then can be further arylated using other organometallic reagents; for example reaction with Zn(C₆F₅)₂ gave the mixed arylated complex 2-B(MeT)(C₆F₅) (85% isolated yield). This provides a simple route to mixed arylated compounds, (C–N-precate)BAr²(Ar²). It is notable that current routes to unsymmetrically substituted borane derivatives are challenging and require multiple steps and purifications. This is due to the formation of Ar₁Ar₂BX (for reaction with lithiated C–N-precursors), often leading to mixtures generally necessitating purification by fractional distillation.

(C–N-precate)BAr₂ compounds based on 2-arylpyridyls and derivatives have been more extensively studied than the benzothiadiazole systems for a range of optoelectronic applications. Therefore, the borenium cation mediated boro-destannylation/borosilylation reactions of these species were explored. 2-Phenylpyridine, 1, was readily borylated by a modification of a literature method using BCl₃, 2,4,6-triisobutylpyridine (TBP), and AlCl₃ to form 1-BCl₂. Compound 1-BCl₂ was stable to ambient conditions and could be readily isolated in air simply by sequential washing with H₂O/MeOH and pentane. In contrast BT derivatives (e.g., 2-BCl₂) are sensitive to water and column chromatography. The enhanced stability of 1-BCl₂ is attributed to a stronger N–B dative bond in the pyridyl congener. The addition of an equivalent of AlCl₃ to 1-BCl₂ led to formation of the borenium salt [1-BCl][AlCl₄], as indicated by a signal at +39.0 ppm in the ¹¹B NMR spectrum and further confirmed by X-ray diffraction studies (crystallized by cooling a saturated CH₂Cl₂ solution to 4 °C, Figure 1).

The solid-state structure of [1-BCl][AlCl₄] reveals a planarized tricyclic structure and a trigonal planar environment at boron (Σ = 359.8°). Although two [AlCl₄]⁻ anions are proximal, the four Al–Cl (two participating in Al–Cl–B bridges and two not) distances are all identical (within 3σ), suggesting that these close contacts are principally due to electrostatic forces and packing effects. The ability of the borenium cation [1-BCl]⁺ to mediate boro-destannylation was investigated. Addition of 2.2 equiv of PhSnBu₃ to 1-BCl₂ resulted in no reaction until addition of ca. 5 mol % of AlCl₃, which resulted in rapid boro-destannylation at 20 °C to form 1-BPh₂. This compound has been previously synthesized by Murakami and co-workers via 1-BBr₂ and AlPh₃. The synthesis of 1-BPh₂ in one pot in two steps from 2-
phenylpyridine via electrophilic C–H borylation and subsequent AlCl₃-catalyzed boro-destannylation can be performed without use of a glovebox in high conversion (72% isolated yield).

The rapid room-temperature double boro-destannylation observed on combination of 1-BCl₂, catalytic AlCl₃, and PhSiBu₃ is in contrast to the BT congener 2-BCl₂ (which requires heating to 60 °C). This suggests an enhanced electrophilicity of the boron center in [1-BY⁺] (Y = Cl and Ph) relative to that in [2-BY⁺]. This was confirmed by the observation that addition of 2.2 equiv of PhSiMe₃ to 1-BCl₂ in the presence of catalytic (ca. 5 mol %) AlCl₃ rapidly led to monoarylation (<10 min) and complete double arylation of boron within 10 h at 20 °C to form 1-BPh₂. Thus, with 1-BCl₂ double transmetalation is possible using the less toxic arylsilane reagent. This methodology can also be performed without the aid of a glovebox with no significant loss in yield, and the doubly arylated products can be isolated simply by filtration through a short plug of silica followed by drying in vacuo.

The electronically deactivated silane (meta-Br-C₆H₄)SiMe₃ was also a viable reagent for transmetalation to boron; however, at 20 °C this led only to a single arylation of 1-BCl₂ (using ca. 5 mol % AlCl₃), with no further arylation proceeding at 20 °C (Scheme 7). Double arylation of 1-BCl₂ can be realized with (meta-Br-C₆H₄)SiMe₃ by heating 1-BCl₂/catalytic AlCl₃ in 1,2-Cl₂C₆H₄. The change in solvent is essential, as in this case heating a mixture of AlCl₃, CH₃Cl₂, and an arylsilane for prolonged periods of time led to Friedel–Crafts alklyation reactions. Analogous conditions enabled the synthesis of the spiro complex 1-B(biphenyl) (Scheme 7, bottom) in good yield (82%) from the commercially available 9,9-dimethyl-9-fluorene. Spiro complexes such as 1-B(biphenyl) have been extensively explored as electron transport materials in electroluminescent devices. It is notable that attempts to make the analogous spiro compound from 2-BCl₂ using catalytic AlCl₃ failed with no reaction observed at 20 or 60 °C, again indicating the lower electrophilicity of the [2-BCI⁺]⁺ boronium cation relative to [1-BCI⁺].

\[
[X₂BL]⁺ + [HBEt₃]⁻ \rightarrow X₁HBL + BEt₃ \quad (1)
\]

The greater reactivity of [1-BCI⁺] relative to [2-BCI⁺] suggested an enhanced electrophilicity at boron; to assess if this was due to the change in the aromatic moiety (i.e., thienyl/fluorenyl vs phenyl), calculations comparing [1-BCI⁺] with the model BT analogue [8-BCI⁺] were performed at the M06-2X/6311G(d,p) (PCM DCM) level (Figure 2). The optimized structure of [1-BCI⁺] was in excellent agreement with the solid-state structure of [1-BCI⁺][AlCl₄]. Using a previously reported approach the hydride ion affinity (HIA, eq 1) relative to BEt₃ was assessed and found to be 6.7 kcal mol⁻¹ greater for [1-BCI⁺] compared to [8-BCI⁺]. This indicates a greater Lewis acidity for the pyridyl congener toward soft nucleophiles (such as π systems) consistent with the relative reactivity observed. The nitrogen sites in BT are weakly basic relative to that in pyridine; however examination of the calculated structure of [8-BCI⁺] indicates a greater N→B π donation than in [1-BCI⁺] (B–N in [8-BCI⁺] = 1.474 Å; B–N in [1-BCI⁺] = 1.514 Å). Furthermore, the N–S distances in [8-BCI⁺] are different with a longer S–N bond involving the nitrogen bound to boron (N₁–S = 1.69 vs N₂–S = 1.59 Å, Scheme 8). Natural bond orbital analysis also indicates a significant positive charge on sulfur (+1.073e) and a greater negative charge on N₁ in [8-BCI⁺] (−0.757e for N₁ vs −0.511e for N₂) relative to that of the nitrogen in [1-BCI⁺] (−0.588e). This indicates a significant contribution from a resonance form where sulfur is formally in the +4 oxidation state for [8-BCI⁺] (Scheme 8, right). Presumably this effect combined with the preference for the
activated arenes. This would remove the requirement for AlCl₃, leading to the new NMR resonance varying between 18 and 115.7° in [8-BCl]⁺ leads to the observed Lewis acidity and reactivity trend.

The significant electrophilicity of [1-BCI]⁺ suggested it may be sufficiently reactive to directly borylate C–H bonds of activated arenes. This would remove the requirement for preinstallation of RₓE⁻ groups on the desired aryl moiety. The addition of 1.1 equiv of 2-methylthiophene and TBP (to sequester the proton) to [1-BCI][AlCl₄] (generated in situ) resulted in full consumption of [1-BCI][AlCl₄], to form two new resonances in the ¹¹B NMR spectrum. However, multinuclear NMR spectroscopy showed that ca. 0.6 equiv of 2-methylthiophene and 0.5 equiv of TBP and 1-BCI were present in the reaction mixture. The observations are consistent with the second new boron resonance being [1-B(MeT)]⁺. Minor variations in starting stoichiometry (between 1-BCI and AlCl₃) led to the new ¹¹B NMR resonance varying between 18 and 40 ppm. This is attributed to a fast exchange between differing quantities of [1-B(MeT)]⁺ and 1-B(MeT)Cl (Scheme 9). [1-B(MeT)]⁺ does not react with further 2-methylthiophene (presumably due to insufficient Lewis acidity) and is less chlorophilic than [1-BCI]⁺, resulting in the consumption of 0.5 equiv of the latter by rapid halide transfer from the expected initial product 1-B(MeT)Cl. The addition of a second equivalent of AlCl₃ to this reaction mixture led to consumption of all 1-BCI₂ and full conversion to [1-B(MeT)]⁺ (45 ppm in ¹¹B NMR spectrum, Scheme 9). With only a single C–H borylation of 2-methyl thiophene possible using the 2-phenylpyridyl-chelated borenium cation double arylation at boron requires addition of an organometallic nucleophile, e.g., an arylsilane or arylstannane reagent. Alternatively, conversion of [1-B(MeT)]⁺ to form 1-BCI(MeT)Cl is achieved by addition of a halide source to form 1-BCI(MeT).

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CONCLUSIONS

The catalytic (in AlCl₃) borenium cation mediated arylation of four-coordinate boron compounds using aryl stannanes and aryl silanes represents a simple route to (C–N-chelate)B(aryl)₂ species, which are useful for optoelectronic applications. The methodology proceeds with a range of arylstannanes and arylsilanes without the requirement for a glovebox or isolation of the (C–N-chelate)BCl₂. Single and double arylation of each boron center can be selected by appropriate choice of reagents, thus enabling facile access to unsymmetrically substituted four-coordinate boron compounds that are challenging to access via other methodologies.

EXPERIMENTAL SECTION

Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques under argon or in an MBraun UniLab glovebox, under an atmosphere of argon (<0.1 ppm of O₂/H₂O). Unless otherwise indicated, solvents were distilled from appropriate drying agents: tetrahydrofuran (potassium); toluene (potassium); n-hexane (NaK); and dichloromethane (CaH₂). Tetrahydrofuran and dichloromethane were stored over activated 3 Å molecular sieves, while toluene and n-hexane were stored over potassium mirrors. [2-BCI]⁺ was prepared according to previously published procedures. All other compounds were purchased from commercial sources and used as received. NMR spectra were recorded on Bruker AvanceIII-400 or Bruker Ascend-400 spectrometers. Chemical shifts are reported as dimensionless δ values and are referenced relative to residual protio-impurities in the NMR solvents for H and Cl⁺(¹H), respectively, while B and F(¹H) shifts are referenced relative to external BF₃-etherate and hexafluorobenzene, respectively. Coupling constants J are given in hertz (Hz) as positive values regardless of their real individual signs. The multiplicities of the signals are indicated as “s”, “d”, “t”, “m”, “pent”, “sept”, or “m” for singlet, doublet, triplet, pentet, septet, or multiplet, respectively. Carbon atoms directly bonded to boron are not always observed in the ¹³C(¹H) NMR spectra due to quadrupolar relaxation leading to considerable signal broadening. In a number of compounds individual carbon resonances are not observed for all inequivalent protons (particularly in the octyl chains) due to resonance coincidence. High-resolution mass spectra (HRMS) were recorded on a Waters QTOF mass spectrometer. Microanalysis was performed by Stephen Boyer at the London Metropolitan University microanalytical service. For the arylated compounds accurate combustion data were not obtainable with consistently low %C content observed. This is attributed to boron carbide formation and persisted even when V₂O₅ was used as an oxidant. For these compounds NMR spectra are included in the SI to support compound purity.

Synthesis of 2-B(MeT)Cl. BCl₃ 1 M in DCM (0.3 mL, 0.3 mmol), was added to a solution of 2 (95 mg, 0.10 mmol) in DCM (3 mL), and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL), and AlCl₃ (1 mg) was added to the solution. 2-Methyl-5-tributylstannylthiophene, trimethyl(5-methyl-thiophen-2-yl)silane, tributyl(9,9-dioctyl-9H-fluoren-2-yl)stannane, and [Mg(TTHF)(µ-Br),Zn(p-tol)]. were prepared according to previously published procedures. All other compounds were purchased from commercial sources and used as received. NMR spectra were recorded on Bruker AvanceIII-400 or Bruker Ascend-400 spectrometers. Chemical shifts are reported as dimensionless δ values and are referenced relative to residual protio-impurities in the NMR solvents for H and Cl⁺(¹H), respectively, while B and F(¹H) shifts are referenced relative to external BF₃-etherate and hexafluorobenzene, respectively. Coupling constants J are given in hertz (Hz) as positive values regardless of their real individual signs. The multiplicities of the signals are indicated as “s”, “d”, “t”, “m”, “pent”, “sept”, or “m” for singlet, doublet, triplet, pentet, septet, or multiplet, respectively. Carbon atoms directly bonded to boron are not always observed in the ¹³C(¹H) NMR spectra due to quadrupolar relaxation leading to considerable signal broadening. In a number of compounds individual carbon resonances are not observed for all inequivalent protons (particularly in the octyl chains) due to resonance coincidence. High-resolution mass spectra (HRMS) were recorded on a Waters QTOF mass spectrometer. Microanalysis was performed by Stephen Boyer at the London Metropolitan University microanalytical service. For the arylated compounds accurate combustion data were not obtainable with consistently low %C content observed. This is attributed to boron carbide formation and persisted even when V₂O₅ was used as an oxidant. For these compounds NMR spectra are included in the SI to support compound purity.
131.3, 131.2, 130.0, 128.7, 128.4, 128.2, 127.9, 127.5, 127.3, 126.3, 126.1, 125.2, 124.3, 123.6, 123.5, 120.9, 120.6, 120.5, 117.0, 55.7, 55.5, 41.1, 40.7, 32.4, 32.4, 30.6, 29.6, 29.8, 29.8, 24.5, 24.4, 23.2, 15.6, 14.4 ppm. \(^{11}B\) NMR (128 MHz, CDCl\(_3\)): \(\delta = -2\) (v br). HRMS (APCI): calculated for C\(_{3}H_{6}BN_{2}S_{2}\)\(^{+}\) (M + H) 577.2177, found 577.2186.

**Synthesis of 2-BPh\(_{2}\).** BCl\(_{3}\), 1 M in DCM (0.1 mL, 0.1 mmol), was added to a solution of 2 (50 mg, 0.055 mmol) in DCM (3 mL), and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was subsequently removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL), and AlCl\(_{3}\) (1 mg) was added to the solution. Tributylphenylstannane (0.15 mL, 0.456 mmol) was then added to the solution. The solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure, and the purification was performed under ambient atmosphere using nonpurified solvents thereon. The residue was dissolved in hexane and was passed through a short plug of base-treated silica gel (5% NEt\(_{3}\)/hexane) [eluent chloroform/hexane (2:8)] to a solution of HCl (8M) (50 mg, 0.5 mmol) in DCM (3 mL), and AlCl\(_{3}\), 1 M solution in DCM (0.7 mL). After inverting the reaction mixture, it was then stirred overnight. The solvent was then removed under reduced pressure, and the resulting residue was dissolved in DCM (3 mL), and 10% DCM/90% hexane as eluent) a short plug of base-treated silica gel (5% NEt\(_{3}\)/hexane) [eluent DCM/hexane (1:9)] to a solution of BC\(_{3}\)N\(_{2}\)Cl\(_{2}\) (50 mg, 0.055 mmol) in DCM (3 mL), and AlCl\(_{3}\), 1 M solution in DCM (0.30 mL, 0.3 mmol), was added to a bright yellow solution of 4 (50 mg, 0.076 mmol) and 2,4,6-tri-tert-butylpyridine (38 mg, 0.154 mmol) in DCM (3 mL). The solution rapidly changed color to a dark red. AlCl\(_{3}\) (20 mg, 0.15 mmol) was then added to the reaction mixture. After rotating for 16 h, an additional portion of AlCl\(_{3}\) (20 mg, 0.15 mmol) was added to the reaction mixture. The solution was rotated for a further 16 h, whereupon the solution turned dark green. The DCM was removed under reduced pressure, and the reaction mixture was dissolved in o-DCB (4 mL). Tributylphenylstannane (0.15 mL, 0.456 mmol) was added to the reaction mixture, which was then stirred at 20 °C for 48 h and heated at 40 °C for 16 h. NM\(_{2}\)Cl (50 mg, 0.046 mmol) was then added to the reaction mixture, and after 1 h the solution was removed under reduced pressure. The purification was performed under ambient atmosphere using nonpurified solvents thereon. The residue was purified via column chromatography on base-treated silica gel (5% NEt\(_{3}\)/hexane) [eluent chloroform/hexane (2:8)] to afford a purple residue. Yield: 24 mg, 32%. The spectra agree with that previously reported.\(^3\)

**Synthesis of 4-B(BPh\(_{2}\))\(_{2}\).** BCl\(_{3}\), 1 M solution in DCM (0.2 mL, 0.20 mmol), was added to a solution of 5 (95 mg, 0.18 mmol) in DCM (3 mL), and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL), and AlCl\(_{3}\) (1 mg) was added to the solution. 2-Methyl-5-tritylstannyliophene (154 mg, 0.40 mmol) was then added to the reaction mixture, which was then stirred overnight. The solvent was then removed under reduced pressure, and the purification was performed under ambient atmosphere using nonpurified solvents thereon. The residue was purified via column chromatography on base-treated silica gel (5% NEt\(_{3}\)/hexane) [eluent chloroform/hexane (2:8)] to afford a dark blue residue. Yield: 67 mg, 51%.

**Synthesis of 5-B(Me)Tet\(_{2}\).** BCl\(_{3}\), 1 M in DCM (0.2 mL, 0.20 mmol), was added to a solution of 5 (95 mg, 0.18 mmol) in DCM (3 mL), and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL), and AlCl\(_{3}\) (1 mg) was added to the solution. 2-Methyl-5-tritylstannyliophene (154 mg, 0.40 mmol) was then added to the reaction mixture, which was then stirred overnight. The solvent was then removed under reduced pressure, and the purification was performed under ambient atmosphere using nonpurified solvents thereon. The residue was purified via column chromatography on base-treated silica gel (5% NEt\(_{3}\)/hexane) [eluent chloroform/hexane (2:8)] to afford a dark blue residue. Yield: 67 mg, 51%.

**Synthesis of 5-BPh\(_{2}\)Tet\(_{2}\).** BCl\(_{3}\), 1 M in DCM (0.2 mL, 0.20 mmol), was added to a solution of 5 (95 mg, 0.18 mmol) in DCM (3 mL), and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL), and AlCl\(_{3}\) (1 mg) was added to the solution. 2-Methyl-5-tritylstannyliophene (154 mg, 0.40 mmol) was then added to the reaction mixture, which was then stirred overnight. The solvent was then removed under reduced pressure, and the purification was performed under ambient atmosphere using nonpurified solvents thereon. The residue was purified via column chromatography on base-treated silica gel (5% NEt\(_{3}\)/hexane) [eluent chloroform/hexane (2:8)] to afford a dark blue residue. Yield: 67 mg, 51%.
solution (~4 mL), which was then filtered via cannula, and the solution transferred to a 10 mL Young's ampule. The sample was then held at 2 °C for 16 h, whereupon amber-colored crystals formed. The crystals were isolated via filtration. Yield: 93 mg, 60%.

1H NMR (400 MHz, CDCl3): δ = 8.76 (d, J = 5.6 Hz, 1 H), 8.62–8.50 (m, 1 H), 8.09 (d, J = 8.1 Hz, 1 H), 7.94 (d, J = 7.1 Hz, 1 H), 7.90–7.79 (m, 2 H), 7.75 (t, J = 8.1 Hz, 1 H), 7.69–7.59 (m, 1 H). 13C NMR (101 MHz, CDCl3): δ = 158.8, 153.0, 144.6, 140.4, 137.2, 135.8, 135.0, 127.0, 124.8, 124.8, 121.3. 23Al (104 MHz, CDCl3): δ = 104 (br) ppm. 11B NMR (128 MHz, CDCl3): δ = 39 (v br). Anal. Calc'd for C13H8BNAlCl5: C, 35.78; H, 2.18; N, 3.79. Found: C, 35.84; H, 2.32; N, 3.82.

Synthesis of 1-BPh via Tributlyphenylstannane. AlCl3 (2 mg) was added to a suspension of 1-BCl2 (31 mg, 0.13 mmol) and tributylphenylstannane (106 mg, 0.286 mmol) in DCM (4 mL). 1-BCl2 dissolved almost instantly upon the addition of AlCl3. The reaction mixture was stirred overnight, and the solution was passed through a short plug of silica gel. The purification was performed under ambient atmosphere using nonpurified solvents thereon. The reaction mixture was evaporated to dryness under reduced pressure, and the resulting residue was washed with hexane to yield the desired product as a white crystalline solid. Yield: 30 mg, 72%

1H NMR (400 MHz, CDCl3): δ = 8.43 (d, J = 5.7 Hz, 1 H), 8.13–8.00 (m, 2 H), 7.88 (d, J = 7.6 Hz, 1 H), 7.69 (d, J = 7.3 Hz, 1 H), 7.48 (t, J = 7.3 Hz, 1 H), 7.44–7.33 (m, 2 H), 7.33–7.27 (m, 2 H), 7.23 (s, 2 H), 7.16 (d, J = 7.5 Hz, 2 H), 7.09 (t, J = 7.6 Hz, 2 H). 13C NMR (101 MHz, CDCl3): δ = 161.3 (br), 158.4, 153.2 (br), 143.8, 141.1, 135.8, 135.2, 131.6, 130.6, 129.3, 128.9, 126.5, 122.6, 122.3, 121.9, 118.5. 11B NMR (128 MHz, CDCl3): δ = 3 (v br) ppm. HRMS (APCI): calc'd for C13H8BNAlCl5+: [M + H]+ 318.1447, found 318.1449.

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The research leading to these results has received funding from Cambridge Display Technology (CDT/EPSC Case Award to D.L.C.), the EPSRC (EP/K03099X/1), and the European Research Council (FP/2007-2013/ERC Grant Agreement 305868). M.J.I. acknowledges the Royal Society (for the award of a University Research Fellowship), and M.L.T. thanks InnovateUK for financial support of the Knowledge Centre for Material Chemistry. The authors would also like to acknowledge the use of the EPSRC UK National Service for Computational Chemistry Software (NSCCS) at Imperial College London in carrying out this work. Dr. Martin Humphries at CDT is also thanked for useful discussions.

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