ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

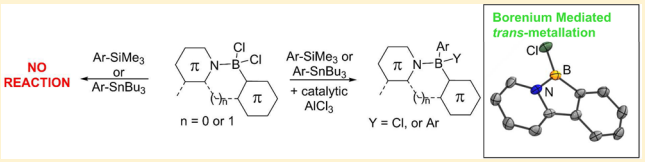
Facile Arylation of Four-Coordinate Boron Halides by Borenium Cation Mediated Boro-desilylation and -destannylation

Daniel L. Crossley, Jessica Cid, Liam D. Curless, Michael L. Turner, and Michael J. Ingleson*

School of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom

Supporting Information

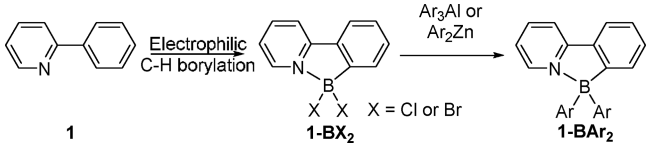
ABSTRACT: The addition of $AlCl_3$ to four-coordinate boranes of the general formula (C−N-chelate)BCl_2 results in halide abstraction and formation of three-coordinate borenium cations of the general formula $[(C-N\text{-chelate})BCl]^+$. The latter react with both arylstannanes and arylsilanes by boro-destannylation and -desilylation, respectively, to form arylated boranes. Catalytic quantities of $AlCl_3$ were sufficient to effect high-yielding arylation of (C−N-chelate)BCl_2. 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-desilyation of less nucleophilic silanes and the direct electrophilic borylation of 2-methylthiophene.



INTRODUCTION

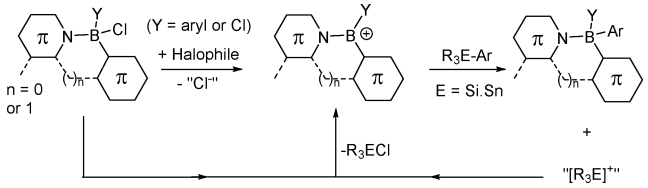
Four-coordinate boron compounds containing a chelating π-conjugated C/N donor and two exocyclic aromatic moieties, termed (C−N-chelate)BAr_2 (e.g., **1-BAr$_2$** right Scheme 1), have been extensively studied for application in optoelectronic devices.[1,2] Changing the exocyclic aryl groups in **1-BAr$_2$** 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)BX_2 (e.g., **1-BX$_2$**, X = Cl or Br) to form a wide range of (C−N-chelate)BAr_2 compounds, as the starting compounds are readily accessed by electrophilic C−H borylation (Scheme 1).[3,4]

Scheme 1. Electrophilic C−H Borylation Followed by Previously Reported High-Yielding Arylation Methodologies



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)BBr_2 (**1-BBr$_2$**, 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., $ArBBr_2$) 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.[4] We hypothesized that conversion of (C−N-chelate)BX_2 into borenium cations,[7] $[(C-N\text{-chelate})BX]^+$, using a halophilic Lewis acid (e.g., $AlCl_3$) 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 $[R_3Si]^+$ or $[R_3Sn]^+$, abstracting halide to generate further equivalents of borenium cations for subsequent transmetalation (Scheme 2). Related, albeit stoichiometric in halophile, approaches have been

Scheme 2. Borenium Cation Mediated Transmetalation



Received: October 12, 2015

DOI: 10.1021/acs.organomet.5b00857
Organometallics XXXX, XXX, XXX−XXX

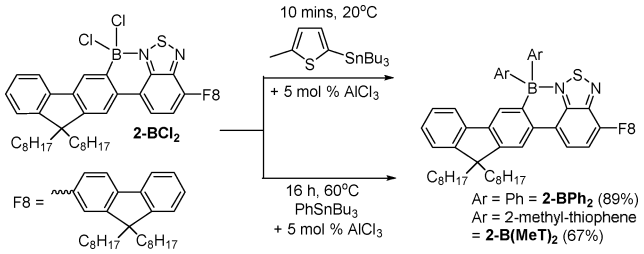
reported for activating chloro-boron subphthalocyanine and F_2B-dipyrromethenes toward substitution of B−X with chalcogen-based nucleophiles.[8] In contrast, the use of borenium cations in boro-desilylation has extremely limited precedence,[9] while their use in boro-destannylation has not been reported 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 benzothiadiazole (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 zincate $[Mg(THF)_4(\mu\text{-}Br)_2(Zn(p\text{-}tol)_2)_2]_n$.[10] Due to the significant challenge presented in forming etherate-free arylzinc reagents,[10] $ArylSiMe_3$ and $ArylSnBu_3$ nucleophiles were investigated for expanding the exocyclic boron substituents.

Mixing **2-BCl$_2$** (readily formed from the unborylated precursor **2** (F8-BT-F8) and BCl_3)[3] with 2 equiv of $PhSnBu_3$ in CH_2Cl_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

Scheme 3. $AlCl_3$-Catalyzed Transmetalation from Arylstannanes to 2-BCl$_2$, with Isolated Yields in Parentheses

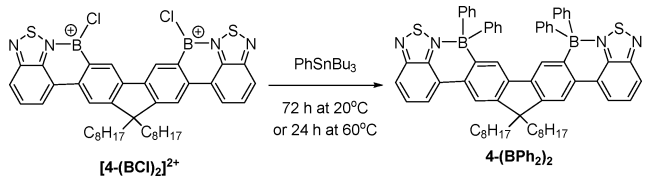


in a more rapid reaction and good conversion to **2-BPh$_2$** (89% isolated yield after 16 h at 60 °C in CH_2Cl_2 in a sealed tube). The addition of $AlCl_3$ results in chloride abstraction from **2-BCl$_2$** and borenium cation formation (indicated by downfield shifts in the ^1H NMR spectrum and formation of $[AlCl_4]^-$ in the ^{27}Al NMR spectrum), consistent with previous studies on related compounds.[3] The borenium cation **[2-BCl]$^+$** is then sufficiently electrophilic to boro-destannylate $PhSnBu_3$. 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)[4] 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_2Cl_2) leads to solvent activation via C−Cl···$AlCl_3$ interactions (Friedel−Crafts-type reactivity) and carbodestannylation to form R_3C-Ph.[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 $[Bu_3Sn]^+$ (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_3Sn-2-Me-thiophene, **3** (prepared by lithiation of 2-methylthiophene and quenching with Bu_3SnCl) 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 thienylstannane. Furthermore, the use of **3** indicates that transmetalation occurs via direct boro-destannylation, as the α C-Me in **3** precludes an alternative mechanism involving C−H borylation followed by proto-destannylation, as determined by Jäkle and co-workers for the borylation of a stannylated ferrocene.[12]

Borenium cation mediated transmetalation with organostannanes is effective for tetraarylation of **[4-(BCl)$_2$]$^{2+}$**. The diborenium cation **[4-(BCl)$_2$]$^{2+}$** (Scheme 4) is produced by

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

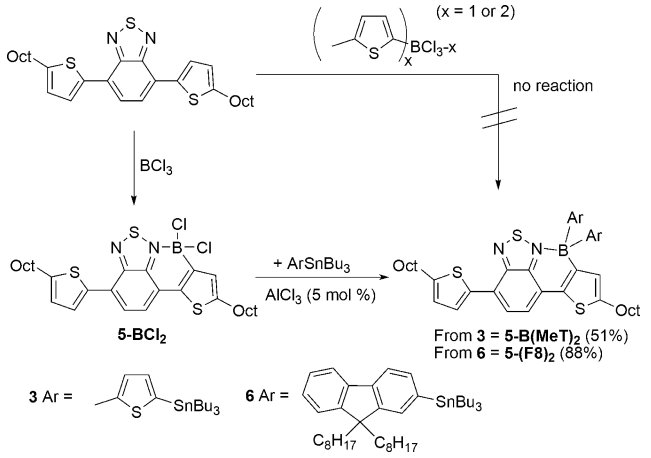


double borylative fusion of the unborylated precursor **4** (BT-F8-BT)[3] as previously reported. With a slight excess of $PhSnBu_3$ (4.2 equiv) **[4-(BCl)$_2$]$^{2+}$** forms the previously characterized tetra-arylated product **4-(BPh$_2$)$_2$** as the major boron-containing complex after 72 h at 20 °C or 24 h at 60 °C (by multinuclear NMR spectroscopy) in 1,2-$Cl_2C_6H_4$. Transmetalation with $ZnPh_2$ to form **4-(BPh$_2$)$_2$** required prior conversion of **[4-(BCl)$_2$]$^{2+}$** to neutral **4-(BCl$_2$)$_2$** by addition of NMe_4Cl for acceptable conversion.[4] In contrast, the boro-destannylation methodology requires the borenium for transmetalation; therefore it proceeds directly from **[4-(BCl)$_2$]$^{2+}$**.

The thiophene analogue of **2-BCl$_2$**, **5-BCl$_2$** (Scheme 5), can be readily prepared from the unborylated precursor **5** as previously reported.[4] Again while arylation with etherate-free diaryl zinc reagents proceeds with high fidelity, the addition of $[Mg(THF)_4(\mu\text{-}Br)_2(Zn(p\text{-}tol)_2)_2]_n$ to **2-BCl$_2$** led to an extremely low conversion to **5-B(*p*-tolyl)$_2$** (isolated in only 13% yield). Analogous to the fluorene congener **2-BCl$_2$**, the addition of stoichiometric $AlCl_3$ to **5-BCl$_2$** resulted in halide abstraction and formation of the borenium cation **[5-BCl]-[AlCl$_4$]** (based on the significant downfield chemical shift of aryl ^1H 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 thienyl groups on standing in wet solvents but are stable in the solid state under ambient

DOI: 10.1021/acs.organomet.5b00857
Organometallics XXXX, XXX, XXX−XXX

Scheme 5. Transmetalation to 5-BCl_2 with Isolated Yield in Parentheses

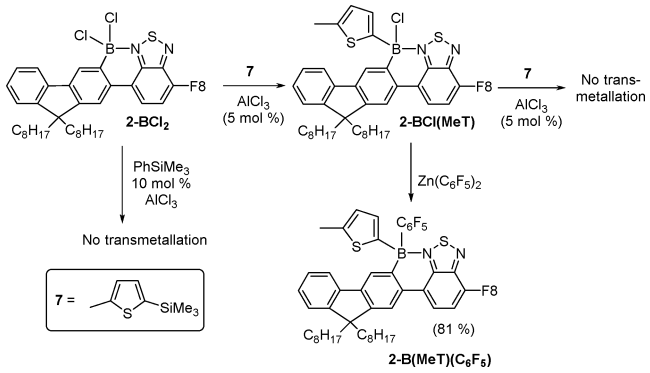


atmosphere for at least three months. An alternative synthesis of **5-B(MeT)$_2$** by electrophilic C−H borylation was explored based on our previous success using $PhBCl_2$ to form **5-B(Ph(Cl))** directly from **5**.[4] However, (5-(2-methylthiophene))$_2$BCl ((MeT)$_2$BCl) does not react with **5** (Scheme 5, right), presumably due to the reduced Lewis acidity at boron (relative to BCl_3 and $PhBCl_2$). Furthermore, (MeT)BCl_2[13] also fails to borylate **5**. Thus, C−H borylation using BCl_3 followed by transmetalation is necessary to access this compound.

The boro-destannylation reaction was extended to 2-Bu_3Sn-9,9-dioctylfluorene (**6**), synthesized by standard procedures. The reaction of **5-BCl_2** with 2.2 equiv of **6** and catalytic $AlCl_3$ (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-BCl_2** (with catalytic $AlCl_3$) led to a mixture of **5-BCl_2**/**5-BCl(F8)** and **5-B(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-BCl_2** is prepared by reaction of **5** with BCl_3, followed by degassing (removing excess BCl_3 and the HCl byproduct from C−H borylation) and subsequent addition of catalytic $AlCl_3$ 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 $PhSiMe_3$ and **2-BCl_2** with a range of $AlCl_3$ 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.[14] This suggests that the borenium cation [**2-BCl**]$^+$ is insufficiently electrophilic to effect boro-desilylation of $PhSiMe_3$. A more nucleophilic silane, 2-Me-5-Me_3Si-thiophene, **7**, was therefore utilized. Compound **2-BCl_2** was combined with an excess (2.2 equiv) of **7**, resulting in no reaction. Addition of $AlCl_3$ (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**]$^+$,

Scheme 6. Transmetalation Outcomes Using Varying Arylsilanes and 2-BCl_2



disfavoring boro-desilylation of **7**. Analogous trends have been previously observed when comparing the Lewis acidity of [PhBCl(amine)]$^+$ and [Cl_2B(amine)]$^+$ borocations.[15] Compound **2-BCl(MeT)** then can be further arylated using other organometallic reagents; for example reaction with $Zn(C_6F_5)_2$ gave the mixed arylated complex **2-B(MeT)(C_6F_5)** (in 81% isolated yield). This provides a simple route to mixed arylated compounds, (C−N-chelate)$BAr^1(Ar^2)$. 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 Ar_1Ar_2BX (for reaction with lithiated C−N-precursors), often leading to mixtures generally necessitating purification by fractional distillation.[16]

(C−N-chelate)BAr_2 compounds based on 2-arylpyridyls and derivatives have been more extensively studied than the benzothiadiazole systems for a range of optoelectronic applications.[2,6a,17] Therefore, the borenium cation mediated boro-destannylation/boro-desilylation reactions of these species were explored. 2-Phenylpyridine, **1**, was readily borylated by a modification of a literature method[4] using BCl_3, 2,4,6-tri-tBu-pyridine (TBP), and $AlCl_3$ to form **1-BCl_2**. Compound **1-BCl_2** was stable to ambient conditions and could be readily isolated in air simply by sequential washing with H_2O/MeOH and pentane. In contrast BT derivatives (e.g., **2-BCl_2**) are sensitive to water and column chromatography. The enhanced stability of **1-BCl_2** is attributed to a stronger N→B dative bond in the pyridyl congener. The addition of an equivalent of $AlCl_3$ to **1-BCl_2** led to formation of the borenium salt [**1-BCl**][**$AlCl_4$**], as indicated by a signal at +39.0 ppm in the ^{11}B NMR spectrum and further confirmed by X-ray diffraction studies (crystallized by cooling a saturated CH_2Cl_2 solution to 4 °C, Figure 1).

The solid-state structure of [**1-BCl**][**$AlCl_4$**] reveals a planarized tricyclic structure and a trigonal planar environment at boron ($\sum$ = 359.8°). Although two $[AlCl_4]^-$ 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 $PhSnBu_3$ to **1-BCl_2** resulted in no reaction until addition of ca. 5 mol % of $AlCl_3$, which resulted in rapid boro-destannylation at 20 °C to form **1-BPh_2**. This compound has been previously synthesized by Murakami and co-workers via **1-BBr_2** and $AlPh_3$.[4] The synthesis of **1-BPh_2** in one pot in two steps from 2-

DOI: 10.1021/acs.organomet.5b00857
Organometallics XXXX, XXX, XXX−XXX

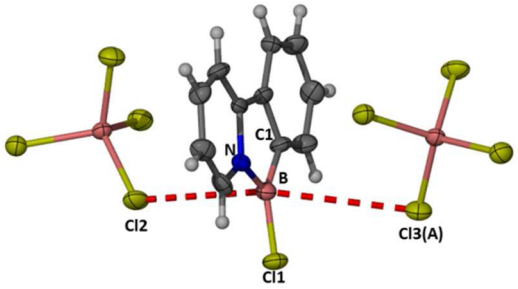


Figure 1. Structure of [**1-BCl**][$AlCl_4$] showing the two closest $[AlCl_4]^-$ anions in the extended structure. Thermal ellipsoids at the 50% probability level. Selected bond lengths and angles: B−N = 1.525(9); B−C1 = 1.522(9); B−Cl1 = 1.708(7); B−Cl2 = 3.223 Å; B−Cl3(A) = 3.737 Å; N−B−C1 = 105.0(5)°.

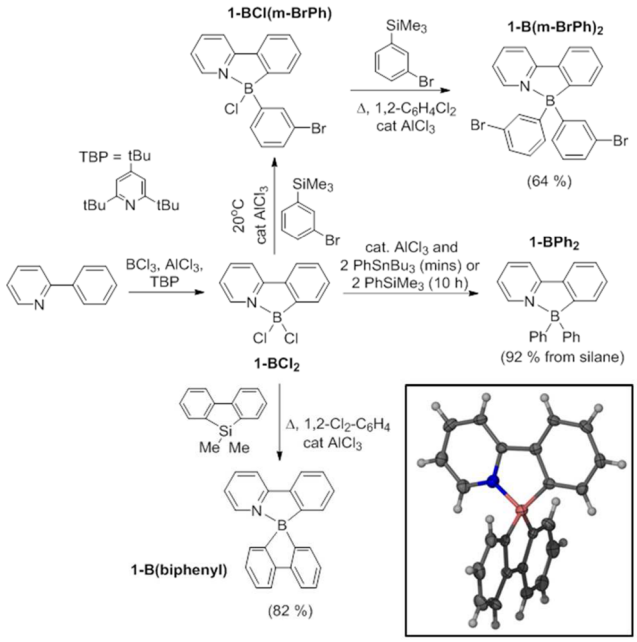
phenylpyridine via electrophilic C−H borylation and subsequent $AlCl_3$-catalyzed boro-destannylation can be performed without use of a glovebox in high conversion (72% isolated yield).

The rapid room-temperature double boro-destannylation observed on combination of **1-BCl$_2$**, catalytic $AlCl_3$, and $PhSnBu_3$ is in contrast to the BT congener **2-BCl$_2$** (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 $PhSiMe_3$ to **1-BCl$_2$** in the presence of catalytic (ca. 5 mol %) $AlCl_3$ rapidly led to monoarylation (<10 min) and complete double arylation of boron within 10 h at 20 °C to form **1-BPh$_2$**. Thus, with **1-BCl$_2$** 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-C_6H_4)$SiMe_3$ was also a viable reagent for transmetalation to boron; however, at 20 °C this led only to a single arylation of **1-BCl$_2$** (using ca. 5 mol % $AlCl_3$), with no further arylation proceeding at 20 °C (Scheme 7). Double arylation of **1-BCl$_2$** can be realized with (*meta*-Br-C_6H_4)$SiMe_3$ by heating **1-BCl$_2$**/catalytic $AlCl_3$ in 1,2-$Cl_2C_6H_4$. The change in solvent is essential, as in this case heating a mixture of $AlCl_3$, CH_2Cl_2, and an arylsilane for prolonged periods of time led to Friedel−Crafts alkyation reactions.[11] 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*H*-9-silafluorene. Spiro complexes such as **1-B(biphenyl)** have been extensively explored as electron transport materials in electroluminescent devices.[18] It is notable that attempts to make the analogous spiro compound from **2-BCl$_2$** using catalytic $AlCl_3$ failed with no reaction observed at 20 or 60 °C, again indicating the lower electrophilicity of the [**2-BCl**]$^+$ borenium cation relative to [**1-BCl**]$^+$.

$$[X_2BL]^+ + [HBEt_3]^- \xrightarrow{\Delta H_{HIA}} X_2HBL + BEt_3 \qquad (1)$$

The greater reactivity of [**1-BCl**]$^+$ relative to [**2-BCl**]$^+$ 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-BCl**]$^+$ with the model BT analogue [**8-BCl**]$^+$ were performed at the M06-2X/6311G(d,p) (PCM DCM) level (Figure 2). The optimized

Scheme 7. Boro-destannylation and Boro-desilylation Reactions Using 1-BCl$_2$ Activated by $AlCl_3$ (Isolated Yields in Parentheses)[a]



[a]Inset bottom right: structure of **1-B(biphenyl)**, thermal ellipsoids at 50% probability.

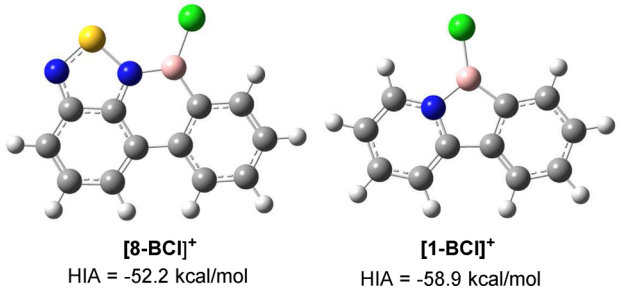
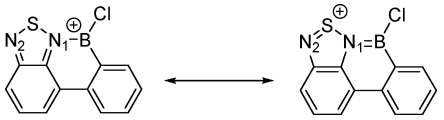


Figure 2. Hydride ion affinity of [**1-BCl**]$^+$ and [**8-BCl**]$^+$ relative to BEt_3 (at the M06-2X/6311G(d,p) (PCM DCM) level).

structure of [**1-BCl**]$^+$ was in excellent agreement with the solid-state structure of [**1-BCl**][$AlCl_4$]. Using a previously reported approach the hydride ion affinity (HIA, eq 1)[15] relative to BEt_3 was assessed and found to be 6.7 kcal mol^{-1} greater for [**1-BCl**]$^+$ compared to [**8-BCl**]$^+$. 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 pyridyl; however examination of the calculated structure of [**8-BCl**]$^+$ indicates a greater N→B π donation than in [**1-BCl**]$^+$ (B−N in [**8-BCl**]$^+$ = 1.474 Å; B−N in [**1-BCl**]$^+$ = 1.514 Å). Furthermore, the N−S distances in [**8-BCl**]$^+$ are different with a longer S−N bond involving the nitrogen bound to boron (N_1−S = 1.69 vs N_2−S = 1.59 Å, Scheme 8). Natural bond orbital analysis also indicates a significant positive charge on sulfur (+1.073*e*) and a greater negative charge on N_1 in [**8-BCl**]$^+$ (−0.757*e* for N_1, −0.511*e* for N_2) relative to that of the nitrogen in [**1-BCl**]$^+$ (−0.588*e*). This indicates a significant contribution from a resonance form where sulfur is formally in the +4 oxidation state for [**8-BCl**]$^+$ (Scheme 8, right). Presumably this effect combined with the preference for the

DOI: 10.1021/acs.organomet.5b00857
Organometallics XXXX, XXX, XXX−XXX

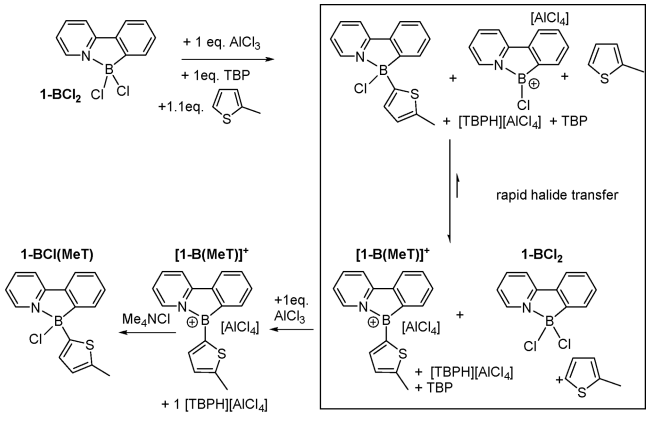
Scheme 8. Resonance Structures of [8-BCl]$^+$



five-membered boracycle to pyramidalize relative to the six-membered boracycle (N−B−C angles of 104.8° in [**1-BCl**]$^+$ and 115.7° in [**8-BCl**]$^+$) leads to the observed Lewis acidity and reactivity trend.

The significant electrophilicity of [**1-BCl**]$^+$ suggested it may be sufficiently reactive to directly borylate C−H bonds of activated arenes.[7c,d] This would remove the requirement for preinstallation of R_3E− groups on the desired aryl moiety. The addition of 1.1 equiv of 2-methylthiophene and TBP (to sequester the proton) to [**1-BCl**][**AlCl$_4$**] (generated *in situ*) resulted in full consumption of [**1-BCl**][**AlCl$_4$**], to form two new resonances in the ^{11}B NMR spectrum. However, multinuclear NMR spectroscopy showed that ca. 0.6 equiv of 2-methylthiophene and 0.5 equiv of TBP and **1-BCl$_2$** 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-BCl$_2$** and $AlCl_3$) led to the new ^{11}B NMR resonance varying between 18 and 40 ppm. This is attributed to a fast exchange between differing quantities of [**1-B(MeT)**][**AlCl$_4$**] and **1-B(MeT)Cl** (Scheme 9). [**1-B(MeT)**]$^+$ does not react with further 2-

Scheme 9. C−H Borylation of 2-Me-thiophene with [1-BCl]$^+$



methylthiophene (presumably due to insufficient Lewis acidity) and is less chlorophilic than [**1-BCl**]$^+$, resulting in the consumption of 0.5 equiv of the latter by rapid halide transfer from the expected initial product **1-B(MeT)Cl**.[19] The addition of a second equivalent of $AlCl_3$ to this reaction mixture led to consumption of all **1-BCl$_2$** and full conversion to [**1-B(MeT)**]$^+$ (45 ppm in ^{11}B 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-BCl(MeT)** is achieved by addition of a halide source to form **1-BCl(MeT)**.

CONCLUSIONS

The catalytic (in $AlCl_3$) 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)BCl_2. 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 O_2/H_2O). Unless otherwise indicated, solvents were distilled from appropriate drying agents: tetrahydrofuran (potassium); toluene (potassium); *n*-hexane (NaK); and dichloromethane (CaH_2). Tetrahydrofuran and dichloromethane were stored over activated 3 Å molecular sieves, while toluene and *n*-hexane were stored over potassium mirrors. **2**, **2-BCl$_2$**, **4**, **5**, 2-methyl-5-tributylstannylthiophene, trimethyl(5-methylthiophen-2-yl)silane, tributyl(9,9-dioctyl-9*H*-fluoren-2-yl)stannane, and $[Mg(THF)_4(\mu\text{-}Br)_2(Zn(p\text{-}tol)_2)_2]_n$ were prepared according to previously published procedures.[3,10] 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 ^{1}H and ^{13}C{^{1}H}, respectively, while ^{11}B and ^{19}F{^{1}H} shifts are referenced relative to external BF_3-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", "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 ^{13}C{^{1}H} 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 V_2O_5 was used as an oxidant. For these compounds NMR spectra are included in the SI to support compound purity,

Synthesis of 2-B(MeT)$_2$. BCl_3, 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 $AlCl_3$ (1 mg) was added to the solution. 2-Methyl-5-tributylstannylthiophene (90 mg, 0.22 mmol) was 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 non-purified solvents thereon. The residue was dissolved in hexane and was passed through (using hexane initially and then 10% DCM/90% hexane as eluent) a short plug of base-treated silica gel (pretreated with 5% NEt_3/hexane), and only the purple-colored solution was retained. The solvent was removed to afford a purple residue. Yield: 78 mg, 67%.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.50 (d, *J* = 7.7 Hz, 1 H), 8.15 (s, 1 H), 8.09 (d, *J* = 7.6 Hz, 1 H), 8.04−7.96 (m, 3 H), 7.93−7.87 (m, 1 H), 7.82 (d, *J* = 2.3 Hz, 1 H), 7.76−7.69 (m, 1 H), 7.48−7.27 (m, 6 H), 6.82 (d, *J* = 3.3 Hz, 2 H), 6.69 (d, *J* = 3.1 Hz, 2 H), 2.44 (s, 6 H), 2.20−2.01 (m, 8 H), 1.27−1.04 (m, 40 H), 0.89−0.67 (m, 20 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 155.1 (br), 154.4, 152.0, 151.9, 150.8 (br), 150.1, 148.0, 142.5, 142.5, 142.2, 141.4, 140.9, 134.7, 133.2,

DOI: 10.1021/acs.organomet.5b00857
Organometallics XXXX, XXX, XXX−XXX

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, 55.8, 55.5, 41.1, 40.7, 32.4, 32.4, 30.6, 30.6, 29.8, 29.8, 29.8, 24.5, 24.4, 23.2, 15.6, 14.4. ppm. ^{11}B NMR (128 MHz, CD_2Cl_2): δ = −2 (v br). HRMS (APCI): calcd for $C_{74}H_{94}BN_2S_3^+$ (M + H) 1117.6667, found 1117.6664.

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 then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL), and $AlCl_3$ (1 mg) was added to the solution. Tributylphenylstannane (40 mg, 0.121 mmol) was added to the solution, and the reaction mixture was stirred and heated overnight at 60 °C. 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 (using hexane initially and then 10% DCM/90% hexane as eluent) a short plug of base-treated silica gel (pretreated with 5% NEt_3/hexane), and only the purple-colored solution was retained. The solvent was removed to afford a purple residue. Yield: 53 mg, 89%. The spectra agree with that previously reported.[3]

Synthesis of 4-(BPh$_2$)$_2$. BCl_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-tritbutylpyridine (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. NMe_4Cl (50 mg, 0.456 mmol) was added to the reaction mixture, and after 1 h the solvent 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 5-B(MeT)$_2$. 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-tributylstannylthiophene (154 mg, 0.40 mmol) was 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 DCM/hexane (1:9)] to afford a dark blue residue. Yield: 67 mg, 51%.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.71 (d, J = 3.7 Hz, 1 H), 7.58 (d, J = 7.6 Hz, 1 H), 7.35 (d, J = 7.6 Hz, 1 H), 6.94−6.83 (m, 1 H), 6.82−6.77 (m, 1 H), 6.76 (d, J = 3.2 Hz, 2 H), 6.71−6.64 (m, 2 H), 2.87 (q, J = 7.1 Hz, 4 H), 2.45 (s, 6 H), 1.83−1.68 (m, 4 H), 1.51−1.22 (m, 20 H), 1.00−0.82 (m, 6 H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 158.7 (br), 153.8 (br), 151.9, 149.4, 148.8, 147.0, 142.3, 135.8, 131.6, 131.3, 130.9, 128.1, 128.1, 126.4, 126.1, 124.5, 124.4, 122.8, 32.5, 32.5, 32.2, 31.0, 30.8, 29.9, 29.9, 29.9, 29.8, 29.8, 23.3, 15.5, 14.5. ^{11}B NMR (128 MHz, CD_2Cl_2): δ = −2 ppm (v br). HRMS (APCI): calcd for $C_{35}H_{44}BN_2S_4^+$ (M − C_5H_5S) 631.2486, found 631.2477.

Synthesis of 5-B(F8)$_2$. BCl_3, 1 M in DCM (0.1 mL, 0.1 mmol), was added to a solution of **5** (30 mg, 0.057 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. Tributyl(9,9-dioctyl-9*H*-fluoren-2-yl)stannane (85 mg, 0.125 mmol) was 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 dissolved in hexane and was passed through a short plug of base-treated silica gel (5% NEt_3/hexane), and only the dark blue colored solution was retained. The solvent was removed to afford a purple residue. Yield: 66 mg, 88%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 3.7 Hz, 1 H), 7.84 (d, J = 7.6 Hz, 1 H), 7.66 (dd, J = 1.3, 6.2 Hz, 2 H), 7.61−7.50 (m, 5 H), 7.37−7.22 (m, 7 H), 7.04 (dd, J = 0.9, 7.6 Hz, 2 H), 6.86 (d, J = 3.7 Hz, 1 H), 2.89 (t, J = 7.6 Hz, 2 H), 2.81 (t, J = 7.7 Hz, 2 H), 2.07−1.85 (m, 8 H), 1.81−1.64 (m, 4 H), 1.42−0.98 (m, 60 H), 0.97−0.83 (m, 18 H), 0.68 (dt, J = 6.0, 13.8 Hz, 8 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.0 (br), 153.3 (br), 151.9, 150.9, 149.9, 149.0, 147.9, 147.6, 141.7, 139.3, 135.5, 132.0, 130.9, 130.2, 128.2, 127.4, 126.5, 126.4, 125.5, 125.2, 123.9, 122.8, 121.6, 119.3, 118.9, 54.9, 40.5, 31.9, 31.9, 31.8, 31.6, 30.7, 30.3, 30.3, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 24.1, 24.1, 22.7, 22.7, 14.2, 14.2. ^{11}B NMR (128 MHz, $CDCl_3$): no ^{11}B NMR peak was observed at 20 °C. HRMS (APCI): calcd for $C_{88}H_{122}BN_2S_3^+$ (M + H) 1313.8858, found 1313.8862.

Synthesis of 2-B(MeT)(C$_6$F$_5$). $AlCl_3$ (1 mg) was added to a solution of **2-BCl$_2$** (50 mg, 0.5 mmol) and trimethyl(5-methylthiophen-2-yl)silane (20 μL, 0.1 mmol) in DCM (0.7 mL). After inverting for 14 h at room temperature NMR investigation showed only one arylation had occurred. The reaction mixture was then evaporated to dryness, and the residue was dissolved in DCM (0.7 mL). $Zn(C_6F_5)_2$ (24 mg, 0.6 mmol) was added to the reaction mixture. After stirring for 3 h the reaction mixture was filtered through a plug of base-treated silica gel (5% NEt_3/hexane). The reaction mixture was then purified via column chromatography on base-treated silica gel (5% NEt_3/hexane) [eluent DCM/hexane (1:9)] to afford a dark purple residue. Yield: 48 mg, 81%.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.51 (d, J = 7.7 Hz, 1 H), 8.19−8.03 (m, 3 H), 8.01 (s, 1 H), 7.98 (d, J = 7.9 Hz, 1 H), 7.90 (d, J = 7.8 Hz, 1 H), 7.85−7.77 (m, 1 H), 7.74 (dd, J = 3.4, 5.1 Hz, 1 H), 7.47−7.27 (m, 6 H), 6.78 (d, J = 3.2 Hz, 1 H), 6.70−6.64 (m, 1 H), 2.44 (s, 3 H), 2.20−1.94 (m, 8 H), 1.26−1.01 (m, 42 H), 0.86−0.58 (m, 20 H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 154.4, 152.0, 151.9, 150.7, 148.1, 142.9, 142.7, 142.5, 141.2, 140.9, 134.6, 133.4, 131.3, 130.9, 130.1, 128.5, 128.5, 128.2, 128.1, 127.5, 127.4, 126.6, 125.8, 125.5, 124.4, 123.6, 123.6, 120.8, 120.6, 120.5, 117.2, 55.9, 55.6, 41.1, 40.9, 40.8, 32.4, 32.4, 32.3, 30.6, 30.6, 30.6, 29.8, 29.8, 24.6, 24.5, 24.5, 23.2, 23.1, 15.6, 14.4, 14.4. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = −131.7 (dd, J = 9.0, 24.8 Hz, 2 F), −158.6 (t, J = 20.7 Hz, 1 F), −164.0 (m, 2 F). ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta \approx -3$ ppm. HRMS (APCI): calcd for $C_{75}H_{89}BN_2S_2^+$ (M + H) 1187.6475, found 1187.6471.

Synthesis of 1-BCl$_2$. BCl_3, 1 M in DCM (4.0 mL, 4 mmol), 2,4,6-tri-*tert*-butylpyridine (0.8 g, 3.2 mmol), and 2-phenylpyridine (0.5 g, 3.2 mmol) were dissolved in DCM (40 mL). $AlCl_3$ (0.854 mg, 6.4 mmol) was added to the reaction mixture, whereupon a color change from colorless to yellow was observed. After stirring for 4 h the reaction mixture was degassed under vacuum and NMe_4Cl (0.351 g, 3.2 mmol) was added, whereupon the reaction mixture changed color from yellow to colorless. The reaction mixture was evaporated to dryness and washed with water (3 × 100 mL) and hexane (100 mL). The resulting white powder was dried under reduced pressure. Yield: 0.584 g, 77%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 5.8 Hz, 1 H), 8.18 (dt, J = 1.5, 7.8 Hz, 1 H), 7.98−7.91 (m, 1 H), 7.86 (d, J = 7.3 Hz, 1 H), 7.77 (d, J = 7.8 Hz, 1 H), 7.62−7.53 (m, 2 H), 7.47−7.39 (m, 1 H). Carbon NMR data are not reported due to the extremely low solubility of the product in a range of common organic solvents. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 7 (v br) ppm. Anal. Calcd for $C_{11}H_8BNCl_2$: C, 56.01; H, 3.43; N, 5.94. Found: C, 56.09; H, 3.32; N, 5.88.

Synthesis of [1-BCl][AlCl$_4$]. $AlCl_3$ (57 mg, 0.42 mmol) was added to a suspension of **1-BCl$_2$** (100 mg, 0.42 mmol) in DCM (10 mL). This was stirred overnight, whereupon all the **1-BCl$_2$** had dissolved and the reaction mixture had changed color from colorless to yellow. The reaction mixture was then concentrated to form a saturated

DOI: 10.1021/acs.organomet.5b00857
Organometallics XXXX, XXX, XXX−XXX

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%.

^{1}H NMR (400 MHz,CD_2Cl_2): 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). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.8, 153.0, 144.6, 140.4, 137.2, 135.8, 135.0, 127.0, 124.8, 121.3. ^{27}Al (104 MHz, CD_2Cl_2): δ = 104 (br) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2): δ = 39 (v br). Anal. Calcd for $C_{11}H_8BNAlCl_5$: C, 35.78; H, 2.18; N, 3.79. Found: C, 35.84; H, 2.32; N, 3.82

Synthesis of 1-BPh$_2$ via Tributylphenylstannane. $AlCl_3$ (2 mg) was added to a suspension of **1-BCl$_2$** (31 mg, 0.13 mmol) and tributylphenylstannane (106 mg, 0.286 mmol) in DCM (4 mL). **1-BCl$_2$** dissolved almost instantly upon the addition of $AlCl_3$. 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 white residue was washed with hexane to yield the desired product as a white crystalline solid. Yield: 30 mg, 72%.

Synthesis of 1-BPh$_2$ via Trimethylphenylsilane. In a J.Young's NMR tube $AlCl_3$ (1 mg) was added to a suspension of **1-BCl$_2$** (23 mg, 0.10 mmol) and trimethylphenylsilane (33 mg, 0.21 mmol) in DCM (0.7 mL). The reaction mixture was inverted for 10 h, whereupon NMR investigation showed the reaction had gone to completion. The purification was performed under ambient atmosphere using non-purified solvents thereon The reaction mixture was then evaporated to dryness and dissolved in DCM (5 mL), and the solution was passed through a short plug of silica gel. The resulting solution was evaporated to dryness under reduced pressure to yield the desired product as a white crystalline solid. Yield: 29 mg, 92%.

The spectra agree with that previously reported.[4]

Synthesis of 1-B(*m*-BrPh)$_2$. $AlCl_3$ (15 mg, 0.11 mmol) was added to a suspension of **1-BCl$_2$** (31 mg, 0.13 mmol) and trimethyl(3-bromophenyl)silane (55 μL, 0.29 mmol) in *o*-DCB (0.7 mL). The reaction mixture was heated at 60 °C for 16 h. NMe_4Cl (15 mg, 0.14 mmol) was added to the reaction mixture, and the solvent was removed under reduced pressure. The resulting residue was purified via column chromatography on silica gel [eluent DCM/hexane (5:5)] to afford the desired product as a white crystalline solid. Yield: 38 mg, 62%.

^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (101 MHz, $CDCl_3$): 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. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 3 (v br) ppm. HRMS (APCI): calcd for $C_{23}H_{17}BBr_2N^+$ (M + H) 477.9795, found 477.9796.

Synthesis of 1-B(biphenyl). $AlCl_3$ (2 mg) was added to a suspension of **1-BCl$_2$** (30 mg, 0.13 mmol) and 9,9-dimethyl-9*H*-9-silafluorene (30 mg, 0.14 mmol) in *o*-DCB (0.7 mL). The reaction mixture was then heated overnight at 60 °C. The solvent was then removed under reduced pressure, and the purification was performed under ambient atmosphere using nonpurified solvents thereon. The resulting residue was dissolved in hexane and was filtered through a short plug of silica gel; hexane (100 mL) and then DCM (100 mL) were then passed through the silica gel, and the DCM fraction was collected and evaporated to dryness under reduced pressure to give the desired product as a white crystalline solid. Yield: 33 mg, 82%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10−8.05 (m, 1 H), 8.02−7.93 (m, 2 H), 7.85 (td, J = 1.1, 5.6 Hz, 1 H), 7.83−7.75 (m, J = 7.6 Hz, 2 H), 7.44−7.36 (m, 3 H), 7.31 (dt, J = 1.2, 7.5 Hz, 2 H), 7.14 (ddd, J = 1.2, 5.8, 7.2 Hz, 1 H), 7.05 (dt, J = 1.0, 7.2 Hz, 2 H), 6.93−6.83 (m, J = 7.1 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.3 (br), 158.8, 154.1 (br), 150.8, 143.1, 140.5, 137.5, 131.0, 130.7, 130.1, 127.2, 126.4, 126.2, 121.8, 121.4, 119.3, 117.8. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 2 (v br) ppm. HRMS (APCI): calcd for $C_{23}H_{17}BN^+$ (M + H) 318.1447, found 318.1449.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00857.

Full experimental procedures, compound characterization data, copies of NMR spectra, and coordinates for all calculations (PDF)
Crystallographic data (CCDC 1429268) (CIF)
Crystallographic data (CCDC 1429269) (CIF)
Structure model (XYZ)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Michael.ingleson@manchester.ac.uk.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The research leading to these results has received funding from Cambridge Display Technology (CDT/EPSRC 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.

■ REFERENCES

(1) For reviews of four-coordinate boranes in optoelectronics see: (a) Rao, Y.-L.; Wang, S. *Inorg. Chem.* **2011**, *50*, 12263−12274. (b) Frath, D.; Massue, J.; Ulrich, G.; Ziessel, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 2290−2310. (c) Li, D.; Zhang, H.; Wang, Y. *Chem. Soc. Rev.* **2013**, *42*, 8416−8433.

(2) For selected examples utilizing C−N-chelate substituents see: (a) Amarne, H.; Baik, C.; Murphy, S. K.; Wang, S. *Chem. - Eur. J.* **2010**, *16*, 4750−4761. (b) Matsumoto, T.; Tanaka, K.; Tanaka, K.; Chujo, Y. *Dalton Trans.* **2015**, *44*, 8697−8707. (c) Wakamiya, A.; Taniguchi, T.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3170−3173. (d) Heiden, Z. M.; Schedler, M.; Stephan, D. W. *Inorg. Chem.* **2011**, *50*, 1470−1479. (e) Rao, Y.-L.; Kusamoto, T.; Sakamoto, R.; Nishihara, H.; Wang, S. *Organometallics* **2014**, *33*, 1787−1793. (f) Smith, A. C.; Ranade, D. S.; Thorat, S.; Maity, A.; Kulkarni, P. P.; Gonnade, R. G.; Munshi, P.; Patil, N. T. *Chem. Commun.* **2015**, *51*, 16115. (g) Dou, C.; Ding, Z.; Zhang, Z.; Xie, Z.; Liu, J.; Wang, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 3648−3652.

(3) Crossley, D. L.; Cade, I. A.; Clark, E. R.; Escande, A.; Humphries, M. J.; King, S. M.; Vitorica-Yrezabal, I.; Ingleson, M. J.; Turner, M. L. *Chem. Sci.* **2015**, *6*, 5144−5151.

(4) Ishida, N.; Moriya, T.; Goya, T.; Murakami, M. *J. Org. Chem.* **2010**, *75*, 8709−8712.

(5) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988.

(6) For select recent studies on the role of zincates in transmetalation see: (a) Jin, L.; Liu, C.; Liu, J.; Hu, F.; Lan, Y.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B.; Lei, A. *J. Am. Chem. Soc.* **2009**, *131*, 16656−16657. (b) McCann, L. C.; Organ, M. G. *Angew. Chem., Int.*

DOI: 10.1021/acs.organomet.5b00857
Organometallics XXXX, XXX, XXX−XXX

Ed. **2014**, *53*, 4386−4389. (c) McCann, L. C.; Hunter, H. N.; Clyburne, J. A.; Organ, C.; Organ, M. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 7024−7027. (d) Hevia, E.; Chua, J. Z.; Garcia-Alvarez, P.; Kennedy, A. R.; McCall, M. D. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 5294−5299.

(7) For reviews on borenium cations see: (a) Koelle, P.; Noeth, H. *Chem. Rev.* **1985**, *85*, 399−418. (b) Piers, W. E.; Bourke, S. C.; Conroy, K. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5016−5036. (c) De Vries, T. S.; Prokofjevs, A.; Vedejs, E. *Chem. Rev.* **2012**, *112*, 4246−4282. (d) Ingleson, M. J. *Top. Organomet. Chem.* **2015**, *49*, 39.

(8) For select examples of Lewis acid activation for nucleophilic substitution in other four-coordinate boranes see: (a) Morse, G. E.; Bender, T. P. *Inorg. Chem.* **2012**, *51*, 6460−6467. (b) Tahtaoui, C.; Thomas, C.; Rohmer, F.; Klotz, P.; Duportail, G.; Mely, Y.; Bonnet, D.; Hibert, M. *J. Org. Chem.* **2007**, *72*, 269−272. (c) Lundrigan, T.; Cameron, T. S.; Thompson, A. *Chem. Commun.* **2014**, *50*, 7028−7031.

(9) For borocations in boro-desilylation see: (a) De Vries, T. S.; Prokofjevs, A.; Harvey, J. N.; Vedejs, E. *J. Am. Chem. Soc.* **2009**, *131*, 14679−14687. (b) Del Grosso, A.; Pritchard, R. G.; Muryn, C. A.; Ingleson, M. J. *Organometallics* **2010**, *29*, 241−249. (c) Reus, C.; Weidlich, S.; Bolte, M.; Lerner, H.-W.; Wagner, M. *J. Am. Chem. Soc.* **2013**, *135*, 12892−12907.

(10) Dunsford, J. J.; Clark, E. R.; Ingleson, M. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 5688−5692.

(11) (a) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43−57. (b) Klaukien, H.; Lehnig, M.; Reiche, T.; Reiss, S.; Such, P. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2115−2119.

(12) Chen, J.; Lalancette, R. A.; Jäkle, F. *Organometallics* **2013**, *32*, 5843−5851.

(13) For the synthesis of thienyl-BCl_2 see: Del Grosso, A.; Helm, M. D.; Solomon, S. A.; Caras-Quintero, D.; Ingleson, M. J. *Chem. Commun.* **2011**, *47*, 12459−12461.

(14) For recent examples exemplifying the disparate reactivity of arylsilanes and arylstannanes toward boranes see: (a) Li, H.; Jäkle, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 2313−2316. (b) Yin, X.; Chen, J.; Lalancette, R. A.; Marder, T. B.; Jäkle, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 9761−9765.

(15) Clark, E. R.; Del Grosso, A.; Ingleson, M. J. *Chem. - Eur. J.* **2013**, *19*, 2462−2466.

(16) For an early example of the synthesis an unsymmetric Ar_1Ar_2BCl see: Paetzold, P. I.; Habereder, P. P.; Muellbauer, R. *J. Organomet. Chem.* **1966**, *7*, 45−50.

(17) (a) Rao, Y. L.; Amarne, H.; Zhao, S. B.; McCormick, T. M.; Martic, S.; Sun, Y.; Wang, R. Y.; Wang, S. *J. Am. Chem. Soc.* **2008**, *130*, 12898. (b) Ishida, N.; Nakanishi, Y.; Moriya, T.; Murakami, M. *Chem. Lett.* **2011**, *40*, 1047−1049. (c) Wong, H.-L.; Wong, W.-T.; Yam, V. W.-W. *Org. Lett.* **2012**, *14*, 1862−1865. (d) Niu, L.; Yang, H.; Wang, R.; Fu, H. *Org. Lett.* **2012**, *14*, 2618−2612. (e) Zhao, Z.; Chang, Z.; He, B.; Chen, B.; Deng, C.; Lu, P.; Qiu, H.; Tang, B. Z. *Chem. - Eur. J.* **2013**, *19*, 11512.

(18) A patent search in Sept 2015 revealed seven separate patents filed on the use of spiro materials related to **1-B(biphenyl)** in electroluminescent devices, the earliest being: Hasegawa, M.; Morii, K.; Kuerya, T.; Akatsuka, I.; *Jpn. Kokai Tokkyo Koho*, 2013, JP2013053123.

(19) Cade, I.; Ingleson, M. J. *Chem. - Eur. J.* **2014**, *20*, 12874.

DOI: 10.1021/acs.organomet.5b00857
Organometallics XXXX, XXX, XXX−XXX