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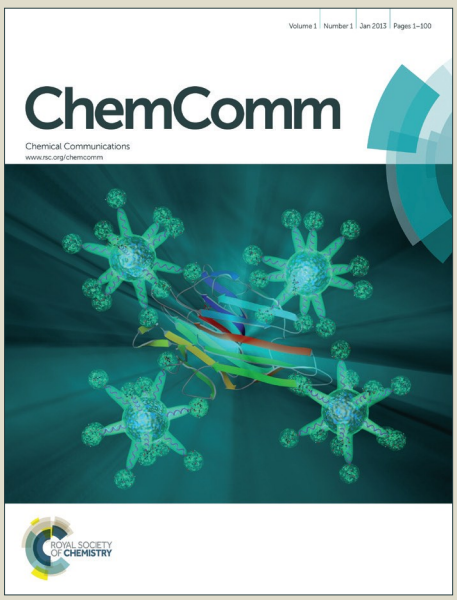

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Regioselective Electrophilic Borylation of Haloarenes.

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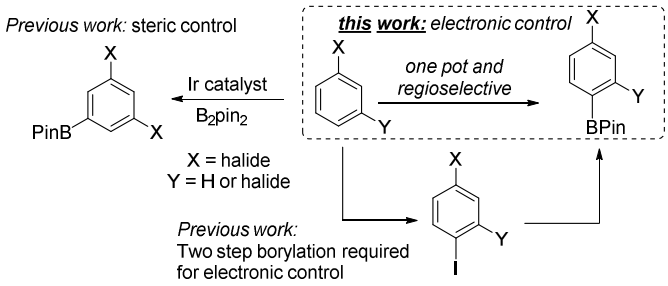
Haloarenes undergo direct borylation using amine:BCl_3:$AlCl_3$ in the ratio of 1:1:2. After esterification the pinacol boronate esters are isolated in good yield with regioselectivity controlled by steric and electronic effects. Regioselectivity is maximised using [(2,6-Cl_2-C_5H_3N)BCl_2][Al_2Cl_7].

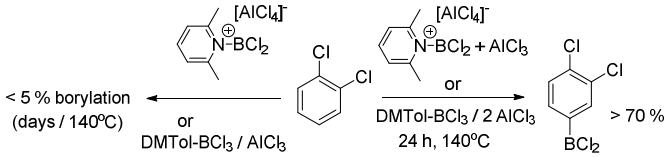
Aryl boronic acids and aryl boronate esters are valuable intermediates in synthesis, materials and pharmaceuticals.[1] Their importance arises mainly from their general and efficient use in the Suzuki-Miyaura reaction,[2] but they can also be converted into many other functional groups.[1] Numerous processes have been developed for forming C-B bonds on aromatic frameworks; however, these generally require pre-functionalised arenes (e.g. aryl halides).[1] Direct C-H borylation represents a straightforward method to prepare aryl boronic compounds in one step. Significant progress has been made in this area using iridium catalysts with which direct borylation of arenes proceeds predominantly under steric control.[3] For example, the borylation of 1,3-dichlorobenzene occurs exclusively at the 5 position.[4] However, under iridium catalysis mono-halobenzenes produce mixtures containing significant quantities of both *meta* and *para* borylated products.[5] An alternative direct borylation of haloarenes that proceeds under electronic control would be desirable as it would provide access to the complementary regioisomers, e.g., the 1,3,4 isomer on borylation of 1,3-dihalobenzenes. Furthermore, direct borylation of mono-halobenzenes under electronic control would yield only *para* borylated products (with *ortho* borylation sterically disfavoured). These borylated haloarenes are extremely important not only as highly functionalised and versatile synthetic intermediates but also due to the ubiquity of such moieties in established drugs (e.g., Crestor, Diflunisal, Atorvastatin and Sertraline) and in current pharmaceutical research programmes.[6]

Electrophilic direct arene borylation was pioneered by Lappert and Muetterties who employed highly electrophilic boron species, although these systems were limited in arene scope.[7] More recently, heteroarene and more functional group tolerant electrophilic borylation methodologies have been developed. These combine strong boron electrophiles with amine bases to sequester the protic by-product from S_EAr.[8] Previously we have reported the combination of B-chlorocatecholborane (and subsequently BCl_3) with an aprotic amine and $AlCl_3$ to borylate a broad range of electron rich heteroarenes, polyaromatic compounds and activated benzenes.[9]



Despite these recent advances, the electrophilic borylation of arenes is currently limited to arenes more nucleophilic than benzene. Herein we report the extension of electrophilic borylation to deactivated arenes, specifically a range of mono- and di-substituted haloarenes. Borylation proceeds in one step, under electronic control to give, in most cases, a single aryl boronate esters complementary in regioselectivity to that obtained from iridium catalysis.

As previously reported, the reaction of [2,6-lutidine-BCl_2][$AlCl_4$], **1**, with *ortho*-dichlorobenzene (o-DCB) at 140 °C for 27 hours resulted in the formation of no borylated products by ^{11}B NMR spectroscopy.[10] Furthermore, only trace borylated o-DCB was observed using an equimolar mixture of DMTol-BCl_3 (DMTol = *N*,*N*-dimethyl-*p*-toluidine) and $AlCl_3$ at 140 °C and 46 h. Surprisingly, the combination of **1** and $AlCl_3$ in a 1 : 1 ratio, or DMTol-BCl_3 and $AlCl_3$ in a 1 : 2 ratio, borylated o-DCB at 140 °C and gave, after esterification, 2-(3,4-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane regioselectively in 71 % and 80 % yield after 72 hours and 24 hours, respectively (Scheme 1).



Scheme 1: Contrasting borylation outcomes depending on equivalents of $AlCl_3$.

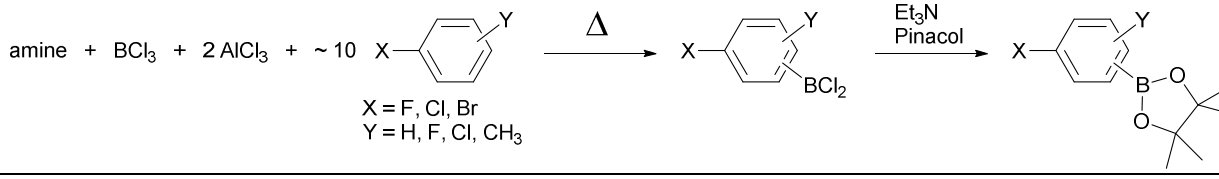
Following this unexpected discovery the borylation of the more challenging (with respect to producing a single product regioisomer) haloarene, bromobenzene, was investigated. Bromobenzene was borylated with 1 equivalent of DMTol-BCl_3[11] and 2 equivalents of

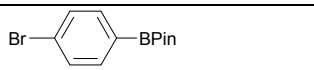
$AlCl_3$ at 140 °C in 2 hours yielding, after esterification, a mixture of *meta* and *para* products in 1 : 8 ratio (Table 1). The use of 1 equivalent of Et_3N-BCl_3 or 2,6-lutidine-BCl_3 and 2 equivalents of $AlCl_3$ resulted in a lower selectivity (*meta:para* ratios of 1 : 1 and 1 : 5, respectively). Furthermore, formation of benzene and consequently borylated benzene was also observed using these two amines. The formation of benzene is attributed to the disproportionation of bromobenzene under the action of $AlCl_3$, as previously reported.[12] Due to this side reaction and the inferior regioselectivity, these amines were excluded from further borylation studies. The effect of temperature using DMTol was next explored as an alternative route to improve regioselectivity. A significantly improved regioselectivity for the borylation of bromobenzene was achieved simply by carrying out the reaction at a lower temperature, (at 100 °C for 6 hours, after esterification with pinacol the *meta*:*para* ratio was 1 : 23 by ^{1}H NMR spectroscopy). Finally, the optimal ratio of DMTol-BCl_3 : $AlCl_3$ was determined to be 1 : 2, with the use of less than two equivalents of $AlCl_3$ resulting in a decreased reaction rate and no significant change in selectivity.

Fluoro- and chloro-benzene underwent borylation with DMTol-BCl_3 and $AlCl_3$ in a 1 : 2 ratio at 100 °C, predominately at the *para* position (< 5 % of *meta* isomer observed in both cases by ^{1}H NMR spectroscopy). Regioselective borylation was also achieved for 1,3-dihalobenzenes. 1,3-difluoro- and 1,3-dichloro-benzene yielded almost exclusively products from borylation at the 4 position (< 2 % of other isomers observed by ^{1}H NMR spectroscopy). Remarkably, the borylation of 1-chloro-3-fluorobenzene and 1-bromo-3-fluorobenzene also proceeded predominantly at the 4 position in both cases (< 5 % of other isomers observed by ^{1}H NMR spectroscopy), consistent with this position being the sterically less encumbered site (*e.g.* relative to *ortho* to chloro or bromo and *ortho* to both halides) between the less electronically deactivated site. Less regioselective borylation outcomes were obtained with the mixed *ortho*-dihalobenzenes and 2-fluorotoluene. Borylation of 1-chloro-2-fluorobenzene, 1-bromo-2-fluorobenzene and 2-fluorotoluene occurred competitively at the 4 and 5 position. The regioisomer deriving from the electrophilic substitution at 5 position (*para* to fluoro) was the major product as expected from the relative Hammett-Brown σ^+_{arene} parameters.[13]

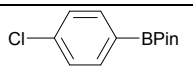
The regioselectivity observed in the borylation of bromobenzene was related to amine nucleophilicity (DMTol > 2,6-lutidine > Et_3N) analogous to our previous report, where the least nucleophilic amine gave the highest regioselectivity in the borylation of toluene.[9d] Thus in an attempt to improve regioselectivity during the borylation of mixed 1,2-dihalobenzenes the use of the less nucleophilic amine (relative to DMTol) 2,6-dichloropyridine (Cl_2Py) was examined. Due to variability in the molarity of commercial BCl_3 a crystalline source of $[(Cl_2Py)BCl_2]^+$ was targeted to enable borylation studies using known stoichiometries. Previous attempts at synthesising $[(Cl_2Py)BCl_2][AlCl_4]$, **2**, by mixing equimolar amounts of Cl_2Py, BCl_3 and $AlCl_3$ in o-DCB produced ^{11}B NMR spectra dominated by BCl_3 from which no borocations species could be isolated.[14] However, the borenium salt **2** proved isolable using dichloromethane as the reaction solvent. The ^{11}B NMR spectrum of the equimolar mixture of BCl_3, 2,6-dichloropyridine and $AlCl_3$ (0.5 M) in dichloromethane showed a sharp resonance at 45.9 ppm consistent with free BCl_3 and a low intensity broad signal at 43.1 ppm consistent with a borenium salt. Notably the ^{27}Al NMR spectrum of this reaction displayed two overlapping broad

Table 1. Direct electrophilic borylation of haloarenes.[a]

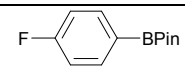




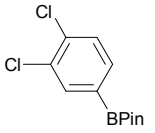
DMTol 140 °C 2 h[b] 3:4 ratio 1:8 90 %[c]
DMTol 100 °C 6 h[b] 3:4 ratio 1:23 59 %[c]
DMTol[d] 100 °C 24 h[b] 3:4 ratio 1:30 72 %[c]



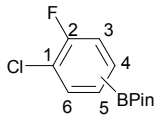
DMTol 100 °C 7 h[b] 78 %[c]
DMTol[d] 100 °C 24 h[b] 81 %[c]
DMTol[e] 100 °C 7 h[b] 73 %[c]



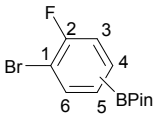
DMTol 100 °C 2 h[b] 53 %[c]



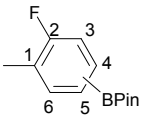
DMTol 140 °C 24 h[b] 80 %[c]



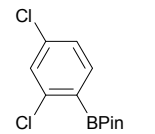
DMTol 140 °C 21 h[b] 4:5 ratio 1:3.2[f] 75 %[c]
Cl$_2$Py 140 °C 41 h[b] 4:5 ratio 1:4.4[f] 74 %[c]



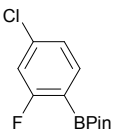
DMTol 140 °C 24 h[b] 4:5 ratio 1:3.8[f] 80 %[c]
Cl$_2$Py 140 °C 24 h[b] 4:5 ratio 1:6.3[f] 78 %[c]



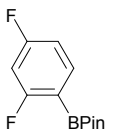
DMTol 140 °C 1 h[b] 4:5 ratio 1:5.0[f] 75 %[c]
Cl$_2$Py 140 °C 1 h[b] 4:5 ratio 1:6.6[f] 76 %[c]



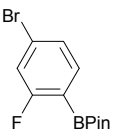
DMTol 140 °C 40 h[b] 50 %[c]



DMTol 140 °C 39 h[b] 75 %[c]



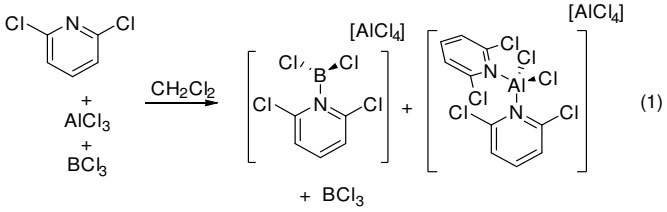
DMTol 140 °C 17 h[b] 45 %[c]



DMTol 140 °C 1 h[b] 67 %[c]

[a] Unless otherwise stated borylation reactions run with 0.8 mmol of amine and BCl_3, 1.6 mmol of $AlCl_3$ and 0.8 ml of haloarene. [b] Time before esterification. [c] Isolated yield. [d] performed using non-purified haloarene and without a glovebox. [e] Using 5 equivalents of chlorobenzene [f] regioisomer ratios are the average of two runs.

resonances, one at 103 ppm attributable to $[Al_xCl_{3x+1}]^-$ anions, and a second species at 99 ppm. The reaction of equimolar $AlCl_3$ and Cl_2Py in the absence of BCl_3 led to the assignment of this resonance as due to $[(Cl_2Py)_2AlCl_2]^+$, whose formulation was confirmed by X-ray crystallography (Figure 1, right). The solid state structure of $[(Cl_2Py)_2AlCl_2][AlCl_4]$, **3**., contains N-Al bonds *ca.* 0.1 Å longer than other reported four coordinate at aluminium $(pyridyl)_2Al$ cations,[15] indicating steric destabilisation of these bonds in **3**. Dissolution of crystals of **3** produced two broad resonances in the ^{27}Al NMR spectrum comparable to that observed on equimolar combination of BCl_3, $AlCl_3$ and Cl_2Py in CH_2Cl_2. Therefore the latter reagent combination leads to a mixture containing BCl_3, the four coordinate aluminium cation **3** (Equation 1) and a species giving rise to a resonance at 43.1 ppm in the ^{11}B NMR spectrum.



(1)

The use of 2 equivalents of $AlCl_3$ relative to BCl_3 / Cl_2Py cleanly yielded the borenium salt $[(Cl_2Py)BCl_2][Al_2Cl_7]$, **4**, as indicated from the ^1H and ^{11}B NMR spectra (δ_{11B} = 43.0 ppm). The formation of **4** in essentially quantitative yield (by ^{11}B NMR spectroscopy) with two equivalents of $AlCl_3$ was attributed to the enhanced chloride ion affinity of Al_2Cl_6 with respect to $AlCl_3$.[16] Attempts to crystallise the borenium salt **4** were unsuccessful; however, the borenium salt **2** was repeatedly isolable as a crystalline material by equimolar combination of reagents under more concentrated conditions (1 M) than used previously. X-ray structure analysis confirmed the formation of the borenium salt **2** (Figure 1, left). Most significantly, dissolution of **2** in dichloromethane led to identical spectra to the that generated *in-situ* consistent with an equilibrium mixture favouring free BCl_3 and the aluminium salt **3** over **2**. The solid state structure of **2** is comparable to that previously reported for the 2,6-lutidine analogue **1**, with the pyridyl and BCl_2 moieties orientated orthogonally in **2**, with no close anion-cation contacts observed. The B-Cl distances in **2** are short (1.703(4) Å), consistent with significant π donation from Cl→B. However, it is notable that the distances between boron and the two pyridyl *ortho* chlorines (2.86 and 2.88 Å) are significantly shorter than the sum of the van der Waals radii (3.67 Å).[17] Previously, Yamaguchi and co-workers demonstrated the presence of 3c-4e bonding between boron and two proximal chlorines at comparable (2.727(4) Å) B-Cl distances in a neutral triarylborane, albeit in a significantly more linear Cl-B-Cl arrangement than that found in **2** (167.2° versus 128.0° in **2**).[18] Inspection of the calculations (M06-2X/6-311G(d,p) PCM CH_2Cl_2) on **2** revealed that the HOMO-8 contains a degree of bonding overlap between the *ortho* chlorines on Cl_2Py and boron. However, the major bonding component in this orbital is from B-Cl π donation (Figure 1, bottom left). This observation combined with the short B-Cl3 and B-Cl4 bonds and the absence of any significant opening of the C-C-Cl angles (123.2(2)° and 122.7(3)° in **2** versus 136.5(3)° for the $[(2\text{-DMAP})BCl_2]^+$ borocation analogue where there is a significant bonding between the *ortho* pyridyl $-NMe_2$ substituent and boron)[19] indicates a weak interaction between the boron centre and the *ortho* chlorines on Cl_2Py. This Cl---B---Cl is more comparable to that observed between boron and flanking arene rings in dihalo-borenium cations containing *ortho* mesityl substituted pyridyls.[20]

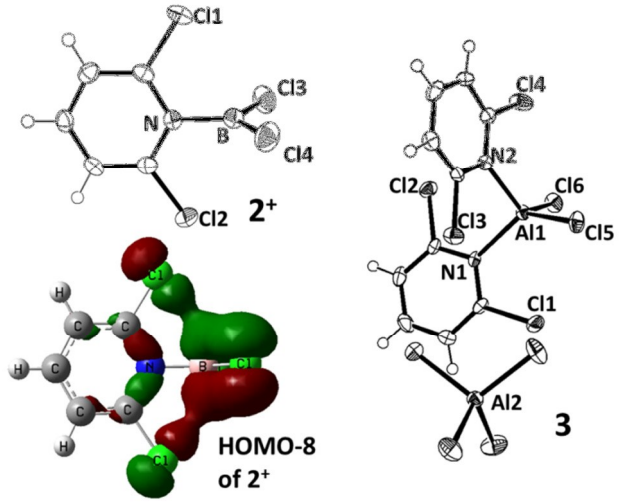


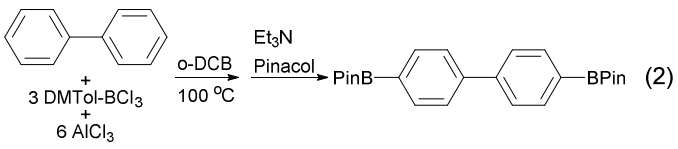
Figure 1. Top left, ORTEP representation of $[(Cl_2Py)BCl_2]^+$, $\mathbf{2}^+$ and right, ORTEP representation of $[(Cl_2Py)_2AlCl_2][AlCl_4]$, **3**, thermal ellipsoids at 50 % probability. Selected bond lengths (Å) and angles (°) for $\mathbf{2}^+$: B-N = 1.524(4), B1-Cl3 = 1.703(4) B1-Cl4 = 1.702(4), N-B-Cl3 = 117.0, N-B-Cl4 = 118.7, Cl3-B-Cl4 = 124.2. For **3**; Al1-N1 = 1.984(4), Al1-N2 = 2.007(4), Al1-Cl5 = 2.101(2), Al1-Cl6 = 2.109(2) Bottom left, the HOMO-8 of $\mathbf{2}^+$ at isovalue of 0.04.

With the crystalline borocation reagent **2** in hand the borylation of halobenzenes was investigated, with the low nucleophilicity of Cl_2Py expected to produce a stronger electrophile than **1**.[14] However, attempts to borylate o-DCB at 140 °C with **2** still led to effectively no borylation after 7 days. In contrast, adding a further equivalent of $AlCl_3$ to **2** enabled significant borylation of o-DCB under identical conditions. The borylation of mixed halide *ortho*-dihalobenzenes and 2-fluorotoluene, which using DMTol led to mixture of borylated regioisomers, was next investigated. Using an equimolar mixture of **2** and $AlCl_3$ resulted in an improvement in regioselectivity of electrophilic borylation in each case (Table 1). However, whilst more selective than the DMTol congener these conditions still produced between 10 – 18 % of the minor regioisomer. In the case of 2-fluorotoluene (the most nucleophilic arene of the series) the resultant isomer distribution using both Cl_2Py and DMTol borylating mixtures was highly dependent on the time of reaction suggesting that isomerisation of the initial borylated product (2-fluoro-5-BCl_2-toluene) occurred under these conditions. Monitoring the borylation of 2-fluorotoluene, using either Cl_2Py or DMTol as amine, by GC-MS confirmed that the 5- and 4- borylated arene ratio altered with time in both cases with higher regioselectivity (for the 5 regioisomer) at shorter reaction times, but with lower conversions.

All halobenzene borylation studies discussed above were performed using ~10 equivalents of haloarene (as solvent and reagent) with respect to BCl_3. The amount of haloarene can be reduced to 5 equivalents with no loss in yield or regioselectivity. For example with chlorobenzene this still yielded predominantly the *para* borylated isomer (along with < 5% of *meta* isomer comparable to the reaction with 10 equivalents) and a 73 % isolated yield. However, attempts using stoichiometric haloarene proved unsuccessful with minimal borylation observed. The previous borylation reactions were performed using anhydrous conditions and purified haloarene. However, it is not necessary to purify the haloarene or use a glovebox. For example, the borylation of as received chlorobenzene on a 20 mmol scale was successfully carried out using the bench stable reagent DMTol-BCl_3 and weighing all the reagents in air. Heating at 100 °C for 24 hours yielded 3.89 g of 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane post esterification (81 % yield, < 5 % of *meta* isomer by ^1H NMR

spectroscopy). The borylation of bromobenzene on a 10 mmol scale was also performed without isolating or preforming DMTol-BCl_3 adduct but instead using BCl_3 in heptanes and DMTol without purification of any reagents/solvents. The borylation proceeded efficiently giving 2.05 g of product (72 % yield of 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with < 3 % of the *meta* borylated isomer (by ^{1}H NMR spectroscopy). Finally it is also noteworthy, that the isolation of the borylated products can be accomplished without column chromatography simply by extracting the product in hexane and washing the hexane solution with HCl (6 N) to remove aluminium and protonated amine by-products.

With the utility of this direct borylation methodology towards haloarenes in hand we next sought access to other borylated compounds that were inaccessible using our previously reported electrophilic borylation conditions. DMTol-BCl_3/ 2 $AlCl_3$ was applied for the diborylation of biphenyl, a substrate that could only be monoborylated using an excess of equimolar DMTol-BCl_3 and $AlCl_3$.[9d] Pleasingly, biphenyl was diborylated regioselectively at the 4 and 4' positions on heating at 100 °C for 24 h with a 56 % isolated yield (Equation 2) using a slight excess of the 1:2 borylating reagent mixture. o-DCB was used as solvent for this reaction with minimal borylation of this dihaloarene observed due to its considerably lower nucleophilicity relative to biphenyl and 4-BCl_2-biphenyl. This indicates that this borylation methodology will be applicable to other deactivated arene nucleophiles.



(2)

In conclusion a range of synthetically important haloarenes were efficiently borylated and isolated as the pinacol boronate esters in moderate to good yields using DMTol, BCl_3 and $AlCl_3$ in a 1:1:2 ratio. The borylation of monohaloarenes and *meta*-dihaloarenes proceeded with excellent regioselectivity giving access to the highly desirable borylated products under electronic control in one step. Further substrate scope exploration and in-depth mechanistic investigations are currently ongoing.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedure, compound characterisation data, copies of NMR spectra and crystallographic data. CCDC 1038711-1038714 See DOI: 10.1039/c000000x/

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