Borylation

DOI: 10.1002/anie.201006196

Pinacol Boronates by Direct Arene Borylation with Borenium Cations**

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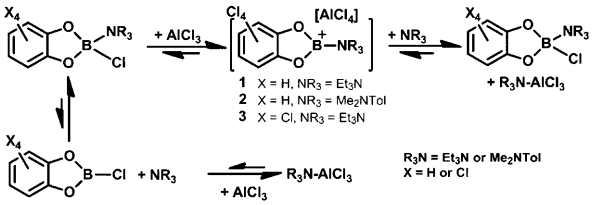
Aryl boronate esters are essential synthetic building blocks, their ubiquity arising from ease of handling combined with high efficacy in C–X (X = C, N, O) bond-forming reactions.[1] Aryl boronate esters are commonly synthesized from arenes by a multistep process involving haloarene intermediates and either stoichiometric hard organometallic reagents or metal-catalyzed cross-coupling (e.g., Cu, Ni, Co, or Pd).[1–7] Recent alternative approaches avoiding haloarenes include: [4+2] cycloadditions,[8] aryl-CH deprotonation,[9,10] diazonium ions,[11] and direct arene borylation with sterically hindered iridium catalysts.[12–14] The latter represents a considerable advance, being highly generic and proceeding in one step from the parent aryl CH. It is however still subject to a number of restrictions: 1) borylation is dominated by steric factors;[4,15] 2) in low steric environments regioselectivities are poor, e.g., anisole reacts with 74% *meta* and 25% *para* borylation;[4] 3) iridium catalysts are required making larger scale syntheses uneconomical.

The development of a generic direct arene borylation route by electrophilic aromatic substitution is highly desirable, with the potential to provide complementary selectivities to iridium catalysis (electronic compared to steric control) and enhanced reaction efficiency (to traditional multistep borylation). In contrast to Friedel–Crafts chemistry, direct intermolecular arene borylation by electrophilic substitution is rare,[16–19] requiring directing groups to pre-coordinate boron (making the process intramolecular) and forcing conditions.[20–23] We recently reported intermolecular arene borylation using borocations,[16] with borylation regioselectivity controlled by arene electronic effects. However, the active boron electrophile was poorly defined due to its high reactivity. A related intramolecular arene borylation was shown to proceed through a three-coordinate borocation intermediate,[24] termed a borenium cation.[25,26] Borenium cations are well documented to be strong electrophiles,[27] a key prerequisite for electrophilic aromatic substitution.[17] It is plausible that borenium cations will be active electrophiles in intermolecular borylation, though there have been no definitive examples published to date.[28] Herein we report new catecholato-ligated borenium cations that are sufficiently electrophilic to intermolecularly borylate a range of arenes. This is a boron analogue of classic Friedel–Crafts chemistry, and represents an inexpensive methodology for the formation of synthetically desirable pinacol boronate esters under electronic control direct from the parent arene.

B-chlorocatecholborane (CatBCl) does not react with $AlCl_3$ at 20 °C.[16] In contrast, the addition of 1 equivalent of $AlCl_3$ to the amine adducts CatBCl(L) resulted in a rapid reaction. Multinuclear NMR spectroscopy suggested the formation of $[CatB(L)][AlCl_4]$ (L = Et_3N (**1**) and L = *N*,*N*-dimethyl-*p*-toluidine (**2**); Scheme 1) with ^{11}B chemical shifts



Scheme 1. Equilibria involved in the formation of borenium cations by halide abstraction with $AlCl_3$.

of $\delta = 27.9$ and 28.1 ppm, respectively, comparable to the related borenium cations $[PinB(NMe_2Ph)]^+$ and $[CatB(PtBu_3)]^+$ ($\delta = 26.4$ and 29.9 ppm).[29,30] A sharp ^{27}Al resonance at $\delta = 104$ ppm confirmed the formation of $[AlCl_4]^-$. The amine proton resonances in **1** were well defined, but in **2** they were significantly broadened at 20 °C indicating fluxionality. On cooling to −20 °C new ^{11}B resonances were resolved; the two major products corresponded to CatBCl and the borenium cation $[CatB(Me_2NTol)]^+$, whilst a minor resonance was attributed to $[CatBCl(Me_2NTol)]$.[31] Attempts to reach the slow exchange regime for **1** failed (to −40 °C, CD_2Cl_2), but reactivity studies support the presence of analogous equilibria, that is, addition of CatBCl to preformed Et_3N-$AlCl_3$ resulted in approximately 20% conversion to **1** after 15 h. Furthermore, the addition of 1 equivalent of Et_3N to **1** produced the neutral adducts $CatBCl(Et_3N)$ and Et_3N-$AlCl_3$ and not the boronium cation, $[CatB(Et_3N)_2]^+$, expected in the absence of reversible halide transfer. These equilibria (Scheme 1) are analogous to the reaction of (9-BBN)BCl (BBN = borabicyclo[3.3.1]nonane) and BCl_3 with pyridines and strong Lewis acids.[32–34] Borenium cations **1** and **2** are therefore highly electrophilic, with a Lewis acidity towards chloride comparable to $AlCl_3$, important for applications in electrophilic aromatic substitution where a strong boron electrophile is essential.

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[**] This work was supported by the Royal Society (University Research Fellowship to M.J.I.).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201006196.

Whilst attempts to crystallize compounds **1** and **2** were unsuccessful, their formulation as borenium cations was supported by X-ray diffraction on a related compound derived from tetrachlorocatecholato (Cl_4-Cat) [Cl_4-CatB-(NEt_3)][$AlCl_4$] (**3**; Figure 1). Crystallization of **3** is facilitated

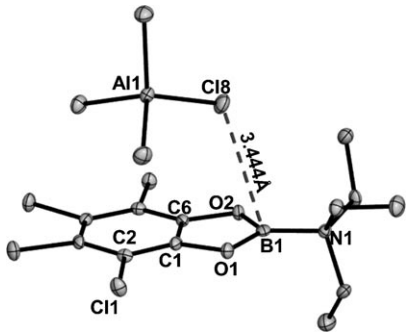


Figure 1. ORTEP drawing of compound **3** (thermal ellipsoids at 50% probability and hydrogen atoms omitted for clarity). Selected bond lengths [Å]: B1–N1 1.505(3), B1–O1 1.364(3), B1–O2 1.370(3).

by intermolecular CCl···H_2CN hydrogen bonding.[35] The boron center in **3** is trigonal planar (angles sum to 360°), with the closest B···$ClAlCl_3$ contact long at 3.444 Å, consistent with an ionic species. The short B–N bond (1.505(3) Å) is comparable to the borenium cations [$(aryl)_2$B(DMAP)]$^+$ (e.g., B–N 1.500(6) Å; DMAP = 4-dimethylaminopyridine).[36] The B–O bonds in **3** (1.364(3) Å and 1.370(3) Å) are short, shorter than in CatBCl (both 1.381(2) Å) and comparable with [CatB($PtBu_3$)]$^+$ (1.369(6) Å and 1.373(5) Å), indicative of significant O→B π donation in **3**.[30,37] Despite this π donation from the catecholato moiety compounds **1**–**3** are still highly electrophilic, presumably a direct consequence of their cationic character.

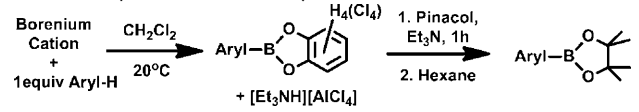
For arene borylation studies **1** and **3** were chosen as the boron electrophiles due to the neutral adducts, (e.g., CatBCl-(Et_3N)) not undergoing complicating disproportionation reactions in contrast to **2**.[37] Initial confirmation that **1** is viable for arene borylation came on addition of 1 equivalent of the activated arene *N*,*N*-dimethylaniline in CD_2Cl_2 at 20 °C. This rapidly and quantitatively (by NMR spectroscopy) led to regioselective arene borylation in the *para* position of *N*,*N*-dimethylaniline, simultaneously producing 1 equivalent of [Et_3NH][$AlCl_4$]. The sequestering of the proton by-product from electrophilic aromatic substitution by Et_3N prevents formation of Brønsted superacidic H[$AlCl_4$] which would otherwise lead to competitive protodeboronation of the boronate ester,[18] as observed in the analogous electrophilic arene silylation.[38] In the previously reported intermolecular arene borylation using BCl_3/$AlCl_3$ mixtures, activated aluminium metal was required to consume the H[$AlCl_4$] by-product and prevent protodeboronation.[18,19] Therefore high-yielding arene borylation by electrophilic aromatic substitution requires both a strongly electrophilic boron source and a proton scavenger that does not deactivate the electrophile. These requirements are fulfilled by **1** where, despite ligation by two π-donating alkoxy groups, the boron center is sufficiently electrophilic for electrophilic aromatic substitution of *N*,*N*-dimethylaniline, which releases the base, Et_3N, necessary for proton scavenging. Electrophilic borylation of *N*,*N*-dimethylaniline occurs exclusively in the *para* position due to synergic electronic (*meta* deactivating) and steric effects (*ortho* deactivating). Borenium cation borylation therefore provides complimentary selectivity to iridium-catalyzed borylation, which for mono-substituted arenes gives predominantly *meta*-borylated products.[4]

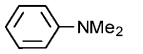
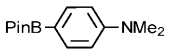
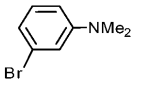
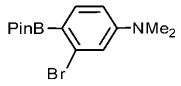
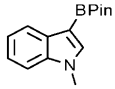
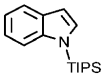
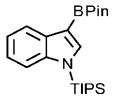
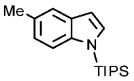
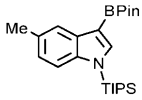
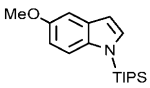
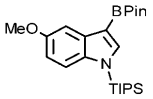
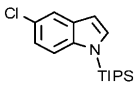
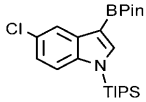
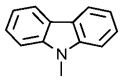
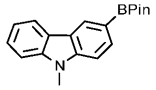
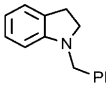
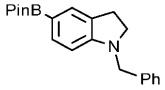
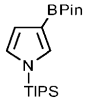
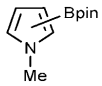
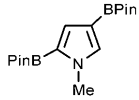
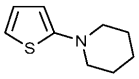
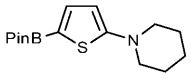
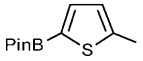
This complementary behavior is further emphasized by the electrophilic borylation of 3-bromo-*N*,*N*-dimethylaniline that proceeds under electronic control to provide only the 1,3,4- borylated isomer, in high yield. In contrast, iridium-catalyzed borylation of 1,3-disubstituted arenes gives the 1,3,5-trisubstituted isomer.[15] Whilst the borylation of 3-bromo-*N*,*N*-dimethylaniline was extremely slow with **1** (only ca. 50% after seven days), borylation proceeded to completion within 32 h using **3**. This reactivity disparity can be attributed to the greater electrophilicity of **3** relative to **1**, engendered by the inferior electron-donor ability of the tetrachlorocatecholato ligand.

The wider borylation substrate scope using **1** was subsequently investigated. At 20 °C in CH_2Cl_2 *N*-methylindole was readily borylated exclusively at the 3-position, consistent with the electrophilic aromatic substitution of indoles.[39] However, attempts to isolate the catechol boronate ester were hampered by protodeboronation to *N*-methylindole and *B*-hydroxycatecholborane. This susceptibility to protodeboronation can be attributed to the low steric environment and the electron deficiency of boron in catechol boronate esters, which allows coordination of protic species (e.g., H_2O) to boron, the first step in protodeboronation in weakly acidic media.[40] The bulkier and more electron-donating diol, pinacol, forms analogous pinacol boronate esters that are significantly more resistant to protodeboronation in the presence of H_2O. Therefore, in situ transesterification of catechol for pinacol was performed, eliminating the undesirable protodeboronation and enabling product isolation in high yield. The use of pinacolato-ligated borenium cations would conceptually enable the single-step synthesis of pinacol boronate esters. This approach was initially complicated by the instability of PinBCl,[41] and then precluded by the failure of [PinB(amine)]$^+$, synthesized from PinBH (amine = *N*,*N*-dimethylaniline or 2,6-lutidine), to borylate *N*,*N*-dimethylaniline and *N*-methylpyrrole.[31] This is attributable to the reduced electrophilicity of boron on replacing catechol for the more electron-donating pinacol.

A broad range of electron-rich N-heterocycles[42] were amenable to borylation using this methodology (Table 1), which proceeded effectively quantitatively (by in situ ^{1}H and ^{11}B NMR spectroscopy). Borylation is highly regioselective and subsequent transesterification to the synthetically desirable pinacol derivatives is facile allowing for isolation of pinacol boronate esters in high yield. Longer reaction times were required for borylation of TIPS-protected indole, compared to the alkyl-protected analogue, due to the weaker electron-donating ability of trialkylsilyl groups, relative to alkyl groups (as indicated by σ_p^+ values of −0.09 and −0.31 for Me_3Si and Me, respectively).[43] Borylation of

Table 1: One-pot, direct arene borylation with borenium cations.[a]



Substrate		Product		Cation	*t* [h]	Yield [%][b]
	**4a**		**4b**	**1**	1	85
	**5a**		**5b**	**3**	32	93
	**6a**		**6b**	**1**	4	92
	**7a**		**7b**	**1** **3**	48 4	78 >95[c]
	**8a**		**8b**	**1**	24	86
	**9a**		**9b**	**1**	30	88
	**10a**		**10b**	**3**	4	84
	**11a**		**11b**	**3**	24	71
	**12a**		**12b**	**1**	1	96
	**13a**		**13b**	**1** **3**	72 3	89 >95[c]
	**14a**		**14b**	**1**	20	91[d]
	**15a**		**15b**	**1**[e]	192	73[f]
	**16a**		**16b**	**1**	0.5	62
	**17a**		**17b**	**3**	72	69

[a] Borenium cations made in situ in CH_2Cl_2 from 1 equiv CatBCl (or Cl_4CatBCl), 1.05 equiv Et_3N, and 1.1 equiv $AlCl_3$. 1 equiv of arene substrate is then added. Reaction time refers to consumption of all borenium cation. TIPS = triisopropylsilyl. [b] Yield of isolated products. [c] Yield >95% by in situ ^{11}B and ^1H NMR spectroscopy. [d] This is a mixture of the 2- and 3-regioisomers, with individual yields at 39% and 52%, respectively. [e] 2.1 equiv of borenium cation used. [f] Other products are regioisomers of **14b**.

indoles is effective with both electron-donating and electron-withdrawing groups on the phenyl ring. 5-Methyl-*N*-TIPS-indole and 5-MeO-*N*-TIPS-indole were efficiently borylated by **1**. It is particularly noteworthy that there was minimal ether cleavage observed during borylation of the latter, in contrast to the reactivity of other strong boron electrophiles with ethers (e.g. BBr_3). Whilst attempts to borylate 5-Cl-*N*-TIPS-indole failed with **1**, due to reduced arene nucleophilicity, borylation was successful using **3**, proceeding in excellent yield. Compound **3** also borylated *N*-methylcarbazole regioselectively in the 3-position in good yield, again in contrast to **1** where no arene borylation was observed (*N*-methylcarbazole is a poorer nucleophile than *N*-methylindole). One-pot transesterification of tetrachlorocatechol for pinacol is also facile, producing compounds **10b** and **11b** in good isolated yields. Compound **1** is sufficiently reactive to borylate *N*-benzylindoline, with borylation occurring exclusively at the 5-position of indoline (**12b**), with no benzyl borylation observed. This highlights the high degree of electronic discrimination between inequivalent arene rings achievable with borenium cation arene borylation: only one position out of seven inequivalent aryl C–H sites in **12a** is borylated.

Pyrroles were also effectively borylated. Borylation of TIPS-protected pyrrole with **1** proceeded in excellent yield in 72 h, generating only the 3-substituted product, **13b**, due to steric deactivation of the 2-position.[44] The use of the more electrophilic cation **3** significantly reduced the overall reaction time to 3 h for full borylation (by ^{11}B and ^1H NMR spectroscopy). Thus, borenium cation electrophilicity is not only important for controlling substrate scope but also for ensuring reasonable rates of reaction. This is further emphasized by the borylation of *N*-TIPS-indole being complete within 4 h using **3** whilst requiring 48 h when borylated with **1**. Borylation of pyrroles containing less bulky nitrogen substitutents, e.g., *N*-methylpyrrole, produced mixtures of 2 and 3-borylated regioisomers as expected,[39] along with trace amounts of the 2,4-diborylated product (**15b**). The latter could be synthesized in good yield by use of 2.1 equivalents of **1** and *N*-methylpyrrole, albeit requiring extended reaction times due to the reduced arene nucleophilicity of the monoborylated intermediates, **14b**.

Thiophenes are less aromatic and nucleophilic than their *N*-heterocyclic analogues, but they are also amenable to electrophilic aromatic substitution with borenium cations **1** and **3**. 2-Piperidyl- and 2-methyl-substituted thiophenes are borylated and subsequently transesterified to give the expected 2,5-substituted products, **16b** and **17b**, respectively, with no observable borylation at the 3-position, due to combined electronic and steric deactivation. Whilst borylation of both **16a** and **17a** is essentially quantitative (by in situ ^{11}B NMR spectroscopy) the yields are somewhat lower as these arenes are extremely sensitivity to protodeboronation on exposure to protic oxo species necessary to effect transesterification. Attempts to borylate furans, the least aromatic of the common five-membered heterocycles, with **1** or **3** failed (for furan, 2-methylfuran, and benzofuran). Instead insoluble materials were formed, presumably from Lewis acid initiated polymerization, consistent with the instability of furans towards $AlCl_3$.[39]

In conclusion, we have demonstrated that catecholato-ligated borenium cations are strong Lewis acids, possessing

sufficient electrophilicity to react with arenes in a boron analogue of Friedel–Crafts chemistry. The new borenium cations can be readily synthesized using inexpensive, commercially available reagents and subsequently used in situ. They are effective for the direct borylation of a range of anilines, N-heterocycles, and thiophenes at room temperature. Subsequent same-pot transesterification provides the synthetically useful, and more robust to protodeboronation, pinacol boronate esters in excellent yield. The direct borylation proceeds with outstanding regioselectivity, generating products controlled by arene electronic effects. Overall this work represents a new, inexpensive one-pot direct arene borylation methodology for producing pinacol boronate esters. Furthermore, it eliminates undesirable haloarene intermediates and offers complimentary selectivities to iridium-catalyzed direct borylation, which operates predominantly under steric control or at the carbon *ortho* to the heteroatom in five-membered heterocycles (e.g., indoles are borylated at the 2-position under iridium-catalyzed borylation).[45,46] Borenium cation-based borylation also displays remarkable functional-group tolerance for a boron based strong Lewis acid, with weak bases (e.g., $-NMe_2$), ether, and halogen groups all compatible. The full substrate scope of this new methodology for direct arene borylation is currently under investigation. Rational variation in borenium cation electrophilicity is expected to be essential for maximizing both substrate scope and high regioselectivity.

Experimental Section

1: In a Schlenk tube equipped with a Young tap, Et_3N (18 μL, 1.3×10^{-4} mol) was dissolved in 1 mL of CD_2Cl_2. CatBCl (20 mg, 1.3×10^{-4} mol) was added to the solution and the reaction mixture was stirred for 5 min. Then powdered $AlCl_3$ (18 mg, 1.3×10^{-4} mol) was added and stirred until all $AlCl_3$ had dissolved. Trace quantities of CatBOH, $[Et_3NH][AlCl_4]$ (combined $<5\%$), and $AlCl_3$–NEt_3 were present. The first two derive from the reaction of borenium with trace water, the presence of the latter is due to the equilibria. These equilibria and the repeated inability to obtain crystallized **1** has prevented accurate elemental microanalysis. ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta=7.43$–7.54 (m, 2H), 7.31–7.41 (m, 2H), 3.74 (q, $J=7.3$ Hz, 6H), 1.43 ppm (t, $J=7.3$ Hz, 9H). ^{13}C NMR (CD_2Cl_2, 100 MHz): $\delta=146.9$, 126.0, 114.6, 52.9, 9.4 ppm. ^{11}B NMR (CD_2Cl_2, 128 MHz): $\delta=27.9$ ppm (br s, pwhh = 131 Hz). ^{27}Al NMR (CD_2Cl_2, 104 MHz): $\delta=103.9$ ppm (sharp s).

3: In a Schlenk tube equipped with a Young tap, Et_3N (24 μL, 1.7×10^{-4} mol) was dissolved in CH_2Cl_2 (ca. 6 mL). Cl_4CatBCl (50 mg, 1.7×10^{-4} mol) was added to the solution and the mixture was stirred, followed by addition of powdered $AlCl_3$ (23 mg, 1.7×10^{-4} mol). The reaction mixture was stirred for 2 h and filtered. The volume was reduced (to ca. 3 mL) and layered with pentane. Slow diffusion of the layers yielded colorless crystals of $[Cl_4CatB(NEt_3)][AlCl_4]$ (**3**) (76 mg, 84%), that were of sufficient quality for single-crystal X-ray diffraction analysis. ^{1}H NMR (CD_2Cl_2): $\delta=3.81$ (q, $J=7.3$ Hz, 6H), 1.49 ppm (t, $J=7.3$ Hz, 9H). ^{13}C NMR (CD_2Cl_2): $\delta=143.2$, 131.1, 119.0, 48.6, 9.6 ppm. ^{11}B NMR ($CDCl_3$): $\delta=28.1$ ppm (br s). ^{27}Al NMR (CD_2Cl_2): $\delta=103.9$ ppm (sharp s). Analysis calculated for $C_6H_{15}AlBCl_8NO_2$: C 27.37, H 2.87, N 2.66; found C 26.7, H 3.32, N 2.09.

General borylation procedure. Step 1: In a Schlenk tube equipped with a Young tap under inert atmosphere, Et_3N (1.05 equiv) was dissolved in CH_2Cl_2, followed by slow addition of CatBCl (or Cl_4CatBCl, 1 equiv). Powdered $AlCl_3$ (1.1 equiv) was added to the reaction mixture and the mixture stirred vigorously until all $AlCl_3$ had dissolved. The desired arene (1 equiv) was then added to the mixture and stirring continued until the borylation reaction was complete (by ^{11}B and ^{1}H NMR spectroscopy). Step 2: On completion of borylation, excess Et_3N (ca. 15 equiv) followed by pinacol (3 equiv) were added to the reaction mixture and stirred for 1 h. (**Caution, this is a strongly exothermic reaction.**) Volatiles were removed under vacuum and the product was extracted with 3×10 mL of hexane and filtered through a short plug of silica. Removal of the solvent yielded the desired product analytically pure.

Received: October 3, 2010
Revised: November 10, 2010
Published online: January 5, 2011

Keywords: borenium ions · borocations · boronate esters · borylation · electrophilic substitution

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