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Reactivity of Lewis Acid Activated Diaza- and Dithiaboroles in Electrophilic Arene Borylation

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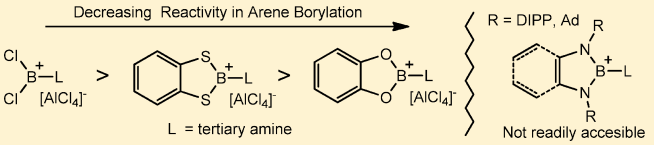
Supporting Information

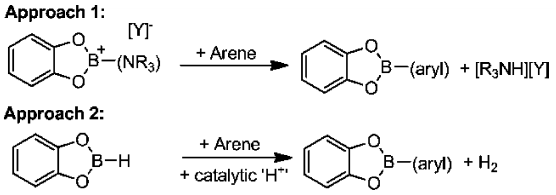
ABSTRACT: Hydride abstraction from *N,N′*-bis(adamantyl)-1-hydrido-1,3,2-benzodiazaborole with catalytic $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$ resulted in a low yield of arene borylation and a major product derived from migration of both adamantyl groups to the arene backbone. In contrast, the related aryl-substituted diazaborole *N,N′*-(2,6-diisopropylphenyl)-1-bromo-1,3,2-diazaborole did not borylate benzene or toluene, being resistant to halide abstraction even with strong halide acceptors: e.g., $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$. The reactivity disparity arises from greater steric shielding of the boron p_z orbital in the 2,6-diisopropylphenyl-substituted diazaboroles. Boron electrophiles derived from 1-chloro-1,3,2-benzodithiaborole ($(CatS_2)BCl$) are active for arene borylation, displaying reactivity between that of catecholato- and dichloro-boron electrophiles. $[(CatS_2)B(NEt_3)][AlCl_4]$ is significantly less prone to nucleophile-induced transfer of halide from $[AlCl_4]^-$ to boron compared to catecholato and dichloro borocations, enabling it to borylate arenes containing nucleophilic $-NMe_2$ moieties in high conversion (e.g., *N,N,*4-trimethylaniline and 1,8-bis(dimethylamino)naphthalene). Calculations indicate that the magnitude of positive charge at boron is a key factor in determining the propensity of chloride transfer from $[AlCl_4]^-$ to boron on addition of a nucleophile.



INTRODUCTION

Intermolecular direct borylation is an highly efficient method for the generation of synthetically ubiquitous aryl boronates,[1] particularly using iridium catalysis.[2,3] An alternative direct arene borylation route which represents a boron analogue of the Friedel−Crafts reaction has been recently reported using molecular[4−7] and polyhedral boron electrophiles.[8] This proceeds under electronic control, complementing iridium-catalyzed direct borylation, which operates predominantly under steric control. A key step in electrophilic borylation is sequestering the Brønsted acidic byproduct from electrophilic aromatic substitution to prevent protodeboronation and provide an additional energetic driving force for the reaction.[9−14] We have reported two distinct approaches to ultimately sequester the protic byproduct from direct electrophilic arene borylation with catecholboranes (CatBH and CatBCl): (1) "H^+" is trapped by a good Lewis base, and (2) "H^+" is combined with an hydrically polarized B−H to evolve H_2.[4−6] Both of these approaches currently have limitations; the former requires stoichiometric Lewis acid and base and is restricted in substrate scope to activated arenes. In contrast, the second approach is effective for deactivated arenes (e.g., 1,2-dichlorobenzene) and is catalytic in Lewis acid activator. However, it has poor turnover frequencies (due to the slow regeneration of the active electrophile and poor solubility of ionic species in low dielectric solvents) and alkylated arenes undergo extensive alkyl migration during borylation.

Herein we report on (i) our studies into the factors determining the stability of borocations derived from diaza- and dithia-ligated boroles and (ii) the borylating ability of these



alternative boron electrophiles following approaches 1 and 2. It was envisaged that diazaborole derivatives, $(R_2N)_2BH$, while less electrophilic (due to enhanced N→B π donation)[15,16] would undergo H_2 loss and regeneration of the active electrophile more readily due to the weaker B−H bond relative to that in the catechol analogue. Furthermore, the Brønsted acid byproduct from electrophilic borylation would more strongly coordinate to aza functionalities (relative to the oxygen moiety in CatBH),[15,17] reducing the Brønsted acidity and preventing alkyl migration. In contrast, 1,2-benzenedithiol-ligated boron electrophiles will have enhanced electrophilicity relative to the catechol analogues, increasing the arene nucleophile substrate scope via approach 1.[18] The Lewis acidities of $B(SR)_3$ species have been calculated to be significantly greater (toward hydride) than that of BF_3,[19] suggesting that the arene substrate scope of 1,2-dithiol-ligated boron electrophiles may be comparable to or even broader than that reported for electrophiles derived from BCl_3.[6]

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RESULTS AND DISCUSSION

(1). Diazaboroles. 1-Hydrido-1,3,2-benzodiazaborole, $(C_6H_4(NH)_2)BH$, was readily synthesized by reaction of 1,2-diaminobenzene with $H_3B{\cdot}SMe_2$.[20] Attempts to access the base-stabilized borenium cation (a three-coordinate borocation using the Nöth terminology)[15] $[(C_6H_4(NH)_2)B(NEt_3)]^+$ were not successful by sequential addition of a Lewis base adduct of $B(C_6F_5)_3$ to $(C_6H_4(NH)_2)BH$ (a route previously used to synthesize $[CatBP^tBu_3][HB(C_6F_5)_3]$);[21] this instead formed $Et_3NB(C_6F_5)_3$ as the only new product. In the absence of an amine nucleophile, abstraction of a hydride from $(C_6H_4(NH)_2)BH$ by $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$[22] proceeded at 20 °C in benzene and toluene (Ph_3CH observed by ^1H NMR spectroscopy). The arene borylation product, $(C_6H_4(NH)_2)$-BAr, was not observed; instead, a solid insoluble in common organic solvents was formed. The insoluble material may be due to the formation of oligomeric amine-bridged cationic species, $[\{(C_6H_4(NH)_2)B\}_n]^{n+}$, as previously proposed by Parry et al.[23] and as intermediates after protonation and H_2 loss from ammonia–borane.[24] N–H was exchanged for N–adamantyl to enhance the steric bulk at nitrogen and preclude both oligomerization after hydride abstraction and the coordination of Lewis acids larger than a proton to nitrogen. *N,N′*-Diadamantyl-1-hydrido-1,3,2-benzodiazaborole (**1**; Figure 1) was readily synthesized, and IR spectroscopy confirmed a

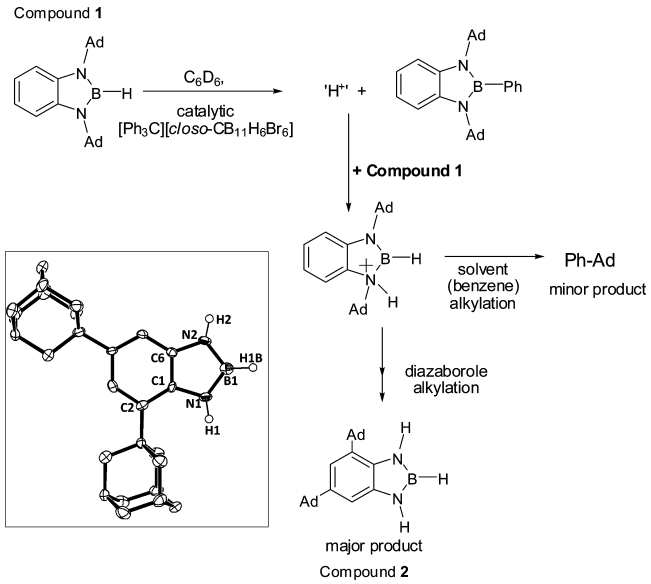
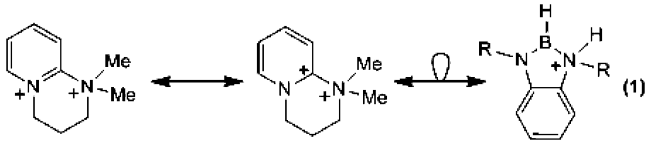


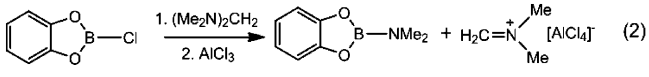
Figure 1. Formation of **2** proceeding via the proposed protonated 1-hydrido-1,3,2-benzodiazaborole intermediates. Inset bottom left: ORTEP representation of **2**, with thermal ellipsoids at the 50% probability level (N–H and B–H were located in the penultimate Fourier difference map and freely refined).

weaker B–H bond relative to CatBH (ν(B–H): **1** at 2607 cm^{-1}, CatBH at 2656 cm^{-1}, both in toluene solution). The addition of 10 mol % of $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$ to **1** in C_6D_6 resulted in a slow reaction (incomplete after 7 days at 20 °C) that could be accelerated by moderate heating. **1** is completely consumed within 2 days (at 50 °C), with the ^1H NMR spectrum confirming the formation of the Ph_3CH byproduct from hydride abstraction. However, the expected arene borylation product, $(C_6H_4\{NAd\}_2)BPh$, was only a minor component (observed as a broad ^{11}B resonance centered at δ 28 ppm). The major boron-containing species, **2**, had low symmetry and contained B–H and N–H resonances. Increasing the loading of $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$ to 33 mol % relative to **1** increased the amount of $(C_6H_4\{NAd\}_2)BPh$ formed compared to the resonance of **2** (δ 23.8 ppm). Repeated recrystallization attempts from saturated arene solutions of **2** afforded only small single crystals of **2** which diffracted weakly (maximum 2θ of 42°). Nevertheless, X-ray diffraction analysis unambiguously revealed this species to be derived from the formal exchange of aryl C–H protons with the *N*-adamantyl groups (Figure 1). The angles at boron in **2** sum to 360°, while the short B–N distances (N1–B1 = 1.413(7) Å, N2–B1 = 1.401(7) Å) are indicative of N→B π donation.

The repeated observation of Ph_3CH and $(C_6H_4\{NAd\}_2)BPh$ indicates that both hydride abstraction from **1** and borylation of the solvent (e.g., benzene) take place. Arene borylation generates a Brønsted acid byproduct that in weakly basic media will protonate an additional molecule of **1** at nitrogen (Figure 1). Previous work by Nöth and Corey has demonstrated that strong Lewis acids (e.g., H^+ and $AlBr_3$) will coordinate to the nitrogen of a diazaborole (or an oxazaborole) in weakly basic media, generating an extremely strong boron Lewis acid.[15,25] Instead of the desired H_2 loss from this intermediate (Figure 1 center) to regenerate an active arene borylating electrophile, cleavage of the N–C bond occurs. N–C cleavage would initially generate an adamantyl cation, $[Ad]^+$, active for electrophilic aromatic substitution of the benzodiazaborole arene backbone. Arene alkylation then forms a new C–C bond and regenerates the Brønsted superacid, enabling further $[Ad]^+$ loss and ultimately complete formal H/Ad exchange. This mechanism is supported by the identification of phenyladamantane as a minor product (by GC-MS) formed by reaction of the adamantyl cation with the solvent benzene instead of a diazaborole. Protonated 1-hydrido-1,3,2-benzodiazaboroles are isoelectronic with amidine dications that are stronger methylating agents than MeI and Me_2SO_4 (eq 1).[26] Therefore, the formal alkyl migration



converting **1** to **2** and the alkylation of benzene are both consistent with the formation of a highly electrophilic intermediate that evolves a carbocation. Amidine dications and protonated diazaboroles are both gitonic superelectrophiles, using Olah's formalism, where related alkyl migration and skeletal rearrangements by carbocation shifts are well precedented.[27] The susceptibility of borenium cations to N–C cleavage is not restricted to **1**; attempts to generate the borenium cation $[CatB(\kappa^1\text{-}N(Me_2)CH_2N(Me_2))][AlCl_4]$ also resulted in the formation of products from N–C cleavage, namely $CatBNMe_2$ and the iminium cation $[H_2C{=}NMe_2]$-$[AlCl_4]$ (by NMR spectroscopy; eq 2). In this case the



developing positive charge on the methylene CH_2 is stabilized by N→C π donation.[28] Thus, highly electrophilic borocations

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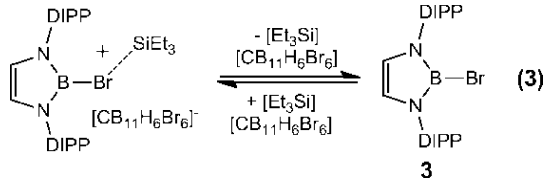
are not accessible when a relatively stable carbocation leaving group (e.g., tertiary alkyl or heteroatom stabilized carbocations) can be formed. The generation of a carbocation from a borenium cation (also observed in the C−O cleavage on reaction of pinacolborane with strong electrophiles)[4] emphasizes the necessity for aryl substituents (or other poor cationic leaving groups) on the pnictogen or chalcogen boron substituents to successfully access strongly electrophilic boron species.

To preclude N−C cleavage, *N,N*′-(2,6-diisopropylphenyl)-1-bromo-1,3,2-diazaborole (**3**) was synthesized following the procedure of Nozaki et al.[29] The diisopropylphenyl (DIPP) substituents and the alkenyl backbone of **3** were chosen to disfavor analogous carbocation deactivation routes, while still providing sufficient steric bulk at nitrogen to prevent borocation oligomerization. Addition of the silicenium cation $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ (made in situ by addition of Et_3SiH to $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$) to **3** led to a broadening of the ^{1}H NMR resonances of **3**, suggesting a fluxional process. However, attempts to reach the slow-exchange regime failed to −40 °C in 1/1 d_8-toluene/$C_6H_4Cl_2$ (to enhance the solubility of the ionic species at low temperature). We attribute the broadening of the ^{1}H resonances to an interaction between the silicenium cation and the bromine of **3** (eq 3) analogous to that



(3)

3

observed in halide-bridged $[(R_3Si)_2X]^+$ cations.[30] On standing, equimolar **3**/$[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ did not borylate benzene or toluene even at raised temperatures. In contrast, CatBBr/$Et_3Si[closo\text{-}CB_{11}H_6Br_6]$ rapidly borylates these arenes even at −10 °C.[4] Furthermore, when the reaction is repeated in the presence of excess Et_3SiH, the CatBBr/$Et_3Si[closo\text{-}CB_{11}H_6Br_6]$ combination rapidly forms CatBH, while **3**/$Et_3Si[closo\text{-}CB_{11}H_6Br_6]$ does not react (24 h at 80 °C). We attribute this reactivity disparity and the contrasting behavior of **1** and **3** toward Lewis acids to the significant steric shielding of the boron p_z orbital by the DIPP groups in **3**. The DIPP phenyl and diazaborole rings are orientated orthogonally in DIPP-substituted diazaboroles (e.g., Figure 2, left).[29] This arrangement results in significant axial steric bulk that prevents the interaction of Lewis bases with the p_z orbital of boron in **3**. Nucleophile coordination to the p_z orbital of boron in Y_2BX systems (X = H, halide, Y = chelating bis-amido or bis-alkoxide) appears to be vital to facilitate abstraction of X by a Lewis acid. The alternative, proceeding via initial abstraction of X, would involve a two-coordinate chelate restrained borinium cation that would be extremely high in energy. The inability of bases to coordinate to **3** is further demonstrated by the absence of Py→**3** adduct formation (by ^{11}B NMR). The lack of adduct formation precludes borenium cation formation by sequential addition of pyridine and $AlCl_3$ to **3**, with the only observed products being **3** and pyridine adducts of $AlCl_3$. The requirement in these chelated systems for base coordination to boron prior to abstraction of X by a Lewis acid is also consistent with the observed reactivity of **1** with $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$. The axial steric bulk in **1** is significantly lower relative to **3** (while we have been unable to obtain suitable single crystals of **1**, it will be structurally related to the previously reported N-heterocyclic carbene, Figure 2 right), enabling interaction of a Lewis base with the p_z orbital during abstraction of the hydride.

(2). Dithiaboroles. 1-Chloro-1,3,2-benzodithiaborole (**4**; $(CatS_2)BCl$)[32] forms the 1/1 Lewis acid/base adduct $(CatS_2)BCl(NEt_3)$ (**5**) with 1 equiv of triethylamine in dichloromethane. The borenium cation $[(CatS_2)B(NEt_3)][AlCl_4]$ (**6**$[AlCl_4]$) is then readily accessed by addition of stoichiometric aluminum trichloride. While attempts to obtain single crystals failed, **6**$[AlCl_4]$ could be readily obtained analytically pure (by elemental microanalysis) simply by solvent removal in vacuo. Multinuclear NMR spectroscopy on this isolated material was fully consistent with an ionic formalism for **6**$[AlCl_4]$. Addition of 1 equiv of *N*-methylindole or *N*-TIPS-indole to **6**$[AlCl_4]$ resulted in rapid (complete within 3 and 4 h, respectively) arene borylation. The reaction time for the borylation of *N*-TIPS-indole with **6**$[AlCl_4]$ was considerably reduced compared to borylation of this substrate with $[CatB(NEt_3)][AlCl_4]$ (**7**$[AlCl_4]$),[5] indicating that **6**$[AlCl_4]$ is a more reactive electrophile (Table 1).[18] Standard pinacol transesterification conditions were applicable to the (1,3,2-benzodithiaborol-2-yl)aryl products.[5] For example, the 3-indolyl boronic ester 1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indole could be isolated in 70% yield (unoptimized; Table 1, entry 2).

The borylation of the less activated heteroarene 2-methylthiophene (N = 1.26 on the Mayr scale)[33] with **6**$[AlCl_4]$ was extremely slow, with no borylation observed after 24 h at 20 °C. In an attempt to generate a more reactive borylating agent, NEt_3 was replaced with the less nucleophilic amine *N,N*-4-trimethylaniline (Me_2NTol). $[(CatS_2)B(Me_2NTol)][AlCl_4]$ (**8**$[AlCl_4]$, characterized by resonances at δ 60.0 ppm, ^{11}B; δ 104 ppm, ^{27}Al; and downfield-shifted aliphatic ^{1}H resonances at δ 3.90 and 2.44 ppm) was only the minor product (∼20%) from sequential addition of equimolar Me_2NTol and $AlCl_3$ to **4**. The major species present in solution were **4** and Me_2NTol−$AlCl_3$ (the latter has a broad ^{27}Al resonance centered at δ 109 ppm). The amine-dependent

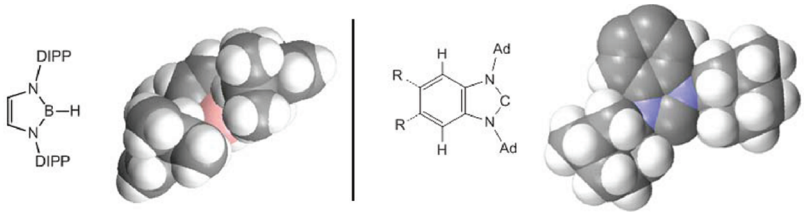


Figure 2. Steric comparison of a DIPP-substituted diazaborole (left) and an adamantyl-substituted N-heterocyclic carbene, R = N(Ad)C:[31] (right), both at 100% van der Waals radii. Views are perpendicular to the heterocyclic rings.

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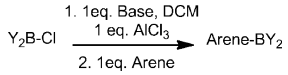
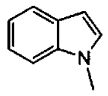
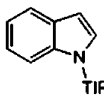
Table 1. Variation in Borylation Times for a Range of Boron Electrophiles



Entry	Arene Substrate	Boron Precursor	Base	Time (h)[a]	Yield (%)[b]
1		CatBCl	NEt_3	4	>99
2		4	NEt_3	3	>99
3		CatBCl	NEt_3	48	>99
4		4	NEt_3	4	>99
5		CatBCl	NEt_3	24	<5
6		CatBCl	Me_2NTol	24	<5
7		4	NEt_3	24	<5
8		4	Me_2NTol	96[c]	60
9		BCl_3	Me_2NTol	2	90

[a]Time for full consumption of starting materials by ^1H and ^{11}B NMR spectroscopy. [b]In situ yield by ^1H NMR versus an internal standard. [c]Maximum thiophene borylation of 60% (by ^1H NMR spectroscopy) reached after 96 h; no further borylation of thiophene is observed at longer reaction times.

reactivity is due to the relative amine nucleophilicities producing different equilibrium positions, with Me_2NTol favoring the free species **4** and Me_2NTol over the adduct $(CatS_2)BCl(Me_2NTol)$. This disparity is exemplified by the ^{11}B NMR spectra of equimolar mixtures of **4** and Et_3N or Me_2NTol (δ 16.0 or 38.7 ppm, respectively). Equilibria between borocations and neutral species are well documented,[34−36] including for $BCl_3/AlCl_3/Me_2NTol$, which is a highly active combination, rapidly borylating 2-methylthiophene in excellent yield despite the borocation being a minor component (Table 1, entry 9).[6] In contrast, an equimolar $4/Me_2NTol/AlCl_3$ mixture (where the borocation is also the minor component) only resulted in partial borylation of 2-methylthiophene, which did not proceed beyond a maximum of 60% thiophene borylation after 96 h (by ^1H NMR). The comparatively slow borylation indicates that the reactivity of thiocatechol-ligated boron electrophiles is intermediate between that of catechol- and dichloro-ligated congeners. This we attribute to the lower reactivity of electrophiles derived from **4** compared to BCl_3 analogues, a conclusion indirectly supported by the competition reactions between $4/(Me_2NTol)BCl_3$ (no reaction) and $BCl_3/(CatS_2)BCl(Me_2NTol)$ (amine transfer forming (Me_2NTol)-BCl_3 and **4**).

The reasons for incomplete thiophene borylation using the equimolar $4/Me_2NTol/AlCl_3$ mixture were found to be as follows: (i) base-induced disproportionation of **4** and (ii) competitive borylation of Me_2NTol. These were both indicated by the ^1H and ^{11}B NMR spectra, which after 96 h revealed that all $8[AlCl_4]$ is consumed yet 2-methylthiophene is still present in a ratio of 2/3 to the expected product 2-methyl-5-B(S_2Cat)-thiophene. Compound **4**, $(CatS_2)_3B_2$ (from disproportionation of **4**), and minor resonances at δ +59 and +57 ppm were also present in the ^{11}B NMR spectrum. Additional resonances were also observed in the ^1H spectra attributable to $[HMe_2NTol]$-$[AlCl_4]$ and one other minor Me_2NTol-containing product. The minor "Me_2NTol" product (1/3 ratio relative to $[HMe_2NTol]^+$) contained a singlet of relative intensity 1 in the aromatic region of the ^1H NMR spectrum, which in combination with the additional ^{11}B resonances suggested borylation of Me_2NTol (Figure 3, bottom). As borylation of Me_2NTol had not been previously observed with catecholato- and dichloro-ligated boron electrophiles, confirmation was sought that this was viable with thiocatecholato−borenium cations. The addition of 1 equiv of Me_2NTol to $6[AlCl_4]$ led to the complete regioselective borylation of Me_2NTol ortho to NMe_2 in 24 h, forming *N,N*,4-trimethyl-2-(1,3,2-benzodithioborolan-2-yl)aniline as the only boron-containing product (Figure 3, top right). The relatively slow borylation of the highly activated Me_2NTol substrate can be attributed to steric

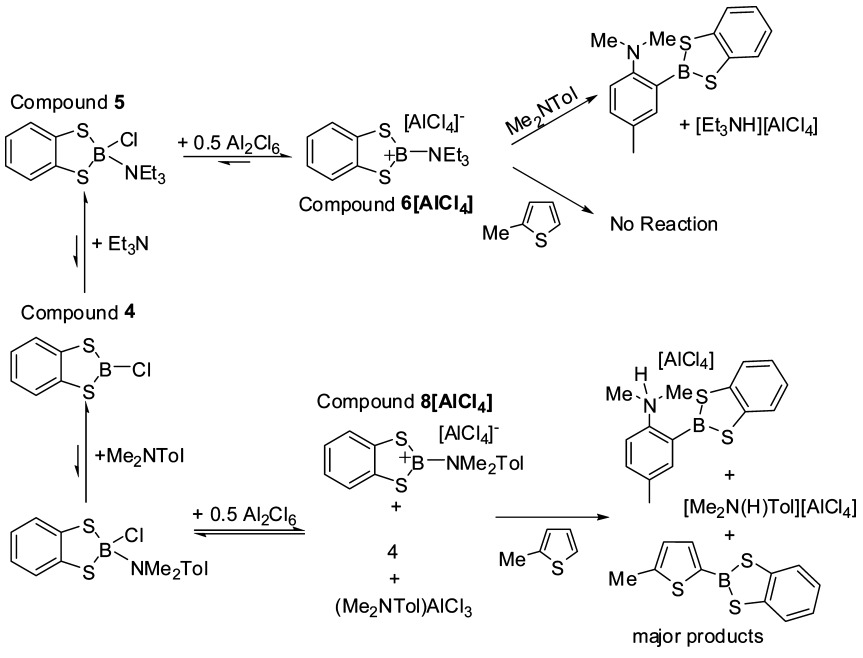


Figure 3. Scheme for the reaction of $6[AlCl_4]$ and $8[AlCl_4]$ with 2-methylthiophene and Me_2NTol.

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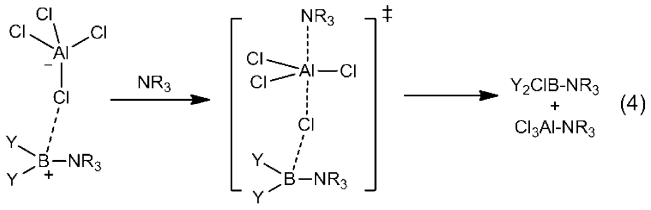
crowding of the positions ortho to $-NMe_2$. Subsequent pinacol esterification produced *N,N*,4-trimethyl-2-(4,4,5,5-tetramethyl-dioxaborolan-2-yl)aniline in a moderate unoptimized yield of 51%.

Previous attempts to borylate Me_2NTol by using stoichiometric $[Cl_2B(NR_3)][AlCl_4]$ or $[CatB(NR_3)][AlCl_4]$ borenium cations had resulted in Al−Cl bond cleavage and formation of predominantly $(NR_3)AlCl_3$ and $(Me_2NTol)B(Cl)Y_2$ (Y = catecholato, Cl). This contrasting reactivity suggested either a lower chloride ion affinity for **6**$[AlCl_4]$ (relative to dichloro and catecholato analogues) or a more significant kinetic barrier to halide transfer. The latter can be precluded, as addition of 1 equiv of Et_3N to **6**$[AlCl_4]$ did induce rapid Al−Cl cleavage and formation of **5** and $(Et_3N)AlCl_3$ (Et_3N is more bulky with a cone angle of 150° compared to 140° for Me_2NTol).[37] The dependence of Al−Cl cleavage on amine nucleophilicity indicates the concerted nature of chloride transfer from $[AlCl_4]^-$ to boron, which we propose will proceed via a S_N2 type mechanism via a five-coordinate aluminum, as observed in bis-amine-$AlCl_3$ adducts (eq 4).[38] The other key variable in this

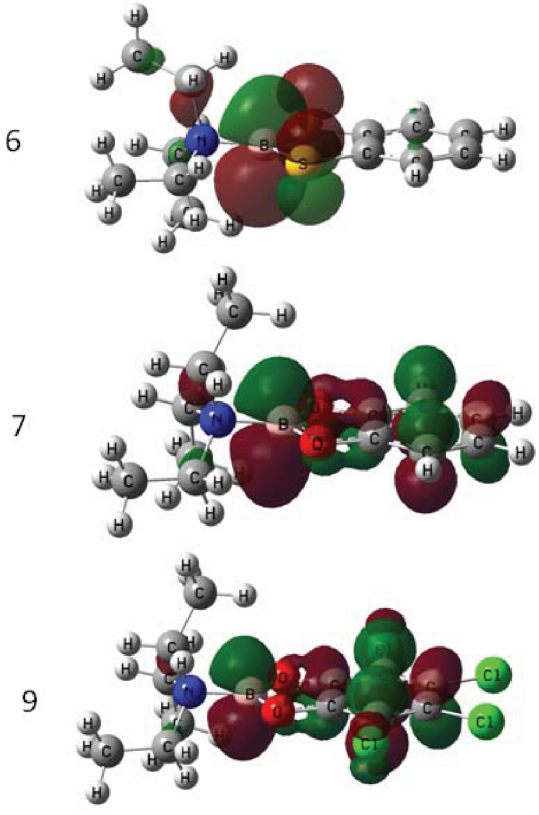


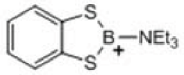
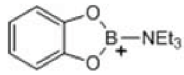
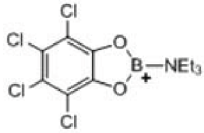
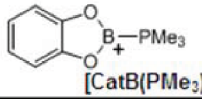
(4)

halide transfer process is the strength of the interaction between the cationic boron center and the anion $[AlCl_4]^-$. This interaction will have a considerable electrostatic component, which will be strongly affected by the charge on boron. To determine the origin of the disparity to halide transfer observed between catechol- and benzene-1,2-dithiol-ligated borenium cations, the charge at boron and the nature of the LUMO were probed computationally for the relevant borenium cations. The results (Table 2) are at the DFT MPW1K/6-311++G(d,p) level for comparison to those previously reported for $[CatBPMe_3]^+$,[21] and at this level the crystallographic geometry of $[Cl_4CatBNEt_3]^+$ (**9**) is in good agreement with that determined computationally.[5]

The character of all three LUMOs is grossly similar, with a considerably increased boron contribution to the LUMO in **6** (54% boron contribution in **6**, 33% in **9**, and 20% in **7**). Cations **7** and **9** have extremely similar LUMOs, the only significant difference being their relative energies, with the LUMO of **9** being 0.6 eV lower. Despite this difference, both **7**$[AlCl_4]$ and **9**$[AlCl_4]$ undergo Al−Cl cleavage on addition of a range of amines, including Me_2NTol. The LUMO of **6** is 0.87 eV lower in energy than that of **7**, yet **6**$[AlCl_4]$ does not undergo halide transfer to boron on addition of Me_2NTol. The calculated natural bond order (NBO) charges at boron correlate with the observed reactivity toward chloride transfer. The similar degrees of NBO positive charge localized at boron in **7** and **9** are consistent with their comparable reactivities. The replacement of oxygen for the less electronegative sulfur in **6** results in a significant decrease in the overall charge at boron

Table 2. Calculated (at the DFT MPW1K/6-311++G(d,p) level) LUMOs and NBO Charges for Cations 6 (LUMO, Top Left), 7 (LUMO, Middle Left) and 9 (LUMO, Bottom Left), All at the 0.04 Isosurface



Cation	B	O or S	P or N
 6	+0.396	+0.203, +0.193	-0.638
 7	+1.338	-0.693, -0.691	-0.609
 9	+1.348	-0.677, -0.675	-0.616
 [CatB(PMe3)]+a	+0.847	-0.650	+1.181

[a]Values taken from ref 21.

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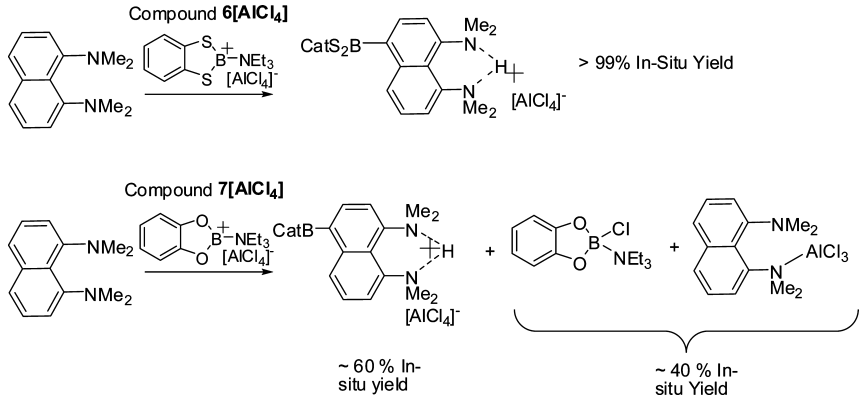

Figure 4. Borylation of 1,8-bis(dimethylamino)naphthalene with **6**[$AlCl_4$] (top) and with **7**[$AlCl_4$] (bottom).

(Table 2). The lower magnitude of charge at boron in **6** entails a relatively weaker electrostatic interaction with the anion, preventing chloride transfer initiated by the addition of a poor nucleophile (e.g., Me_2NTol). While **6** has a significantly lower LUMO energy and is more reactive in arene borylation than **7**, the degree of positive charge localized at boron is a key factor in nucleophile-induced halide transfer.

Comparison of amine- and phosphine-ligated catecholato borocations reveals a related ligand electronegativity (χ_N = 3.0, χ_P = 2.2) controlled variation in NBO charge at boron, with [CatBPMe_3]$^+$ having a significantly lower positive charge than **7** (Table 2). For reactivity comparison purposes [CatBP^{t}Bu$_3$][$AlCl_4$] (**10**[$AlCl_4$]) was synthesized and recrystallized from CH_2Cl_2/pentane (the structure of the cation is identical within 3σ with that previously reported for **10**[HB(C_6F_5)$_3$]).[21,39] Dissolution of this recrystallized material showed only resonances attributable to **10**[$AlCl_4$] with B−P coupling observed in the $^{31}P\{^1H\}$ and ^{11}B NMR spectra (at 20 °C in CD_2Cl_2). The observation of B−P coupling precludes halide transfer equilibria in the absence of additional base. Were halide transfer to occur, this would form CatBCl(P^{t}Bu$_3$) and result in loss of B−P coupling due to rapid phosphine dissociation, as previously reported.[40] In contrast to the reactivity of **7**[$AlCl_4$], the addition of 1 equiv of Me_2NTol to **10**[$AlCl_4$] resulted in no Al−Cl cleavage of [$AlCl_4$]$^-$ (^{27}Al NMR spectrum showed only a sharp resonance for [$AlCl_4$]$^-$). Instead a mixture of **10**[$AlCl_4$] and resonances attributable to the boronium cation [CatB(P^{t}Bu$_3$)(Me_2NTol)][$AlCl_4$] were observed as the major products. The absence of [$AlCl_4$]$^-$ cleavage is consistent with the lower magnitude of NBO positive charge at boron in [CatBPMe_3]$^+$ compared to **7**.

An obvious alternative that would also preclude halide transfer would be to utilize weakly coordinating anions in place of [$AlCl_4$]$^-$. However, the vast majority of classic weakly coordinating anions are either oxo based (e.g., triflate, [ClO_4]$^-$), which coordinate too strongly to boron for arene borylation purposes,[15] or are Lewis acid/anion adducts vulnerable to analogous anion transfer.[41] The latter is exemplified by attempts to form **7**[SbF_6] from CatBCl(NEt_3) and $AgSbF_6$, instead producing multiple B−F-containing products. Therefore, the borenium cation **7** has a higher fluoride ion affinity than SbF_5, which is itself extremely fluorophilic.[41] Furthermore, **7**[$AlCl_4$] activates C−F bonds in aryl-CF_3 compounds, precluding other common weakly coordinating anions. Vedejs et al. previously reported the C−F activation of [B($C_6H_3(CF_3)_2$)$_4$]$^-$ with a less stabilized aryl hydrido ligated borenium cation.[42] The fact that C−F activation is observed with **7**[$AlCl_4$] indicates that catechol ligation and its associated O→B π donation does little to attenuate the reactivity of borenium cations toward fluoride anion sources.

For the borylation of arenes that contain coordinating functionalities (without resorting to relatively expensive weakly coordinating anions such as [B(C_6F_5)$_4$] and *closo*-carboranes), it is essential to decouple borylation reactivity from rapid chloride transfer by minimizing the positive charge at boron and thus enabling [$AlCl_4$]$^-$ to be used as the anion. This is demonstrated by the borylation of 1,8-bis(dimethylamino)-naphthalene using **6**[$AlCl_4$], which was highly effective, leading to the 4-borylated product as the only boron-containing product within 1 h (as a mixture of protonated at nitrogen and nonprotonated species, Figure 4 top). Combination of 1,8-bis(dimethylamino)naphthalene with equimolar **7**[$AlCl_4$] also resulted in an equally rapid reaction (all **7**[$AlCl_4$] is consumed within 1 h); however, this produced the aryl boronate ester in only ~60% yield (by in situ ^1H and ^{11}B NMR spectroscopy). The other major products were CatBCl(Et_3N) and the 1,8-bis(dimethylamino)naphthalene adduct of $AlCl_3$ (Figure 4, bottom). This indicates that arene borylation and chloride transfer are kinetically competitive when borylating 1,8-bis(dimethylamino)naphthalene with **7**[$AlCl_4$]. In contrast, in the borylation of 1,8-bis(dimethylamino)naphthalene with **6**[$AlCl_4$] no products derived from halide transfer are observed, due to the relatively lower charge localized at boron.

■ CONCLUSIONS

The generation of highly electrophilic borenium cations requires a judicious choice of anion and neutral ligands to prevent anion or cation decomposition. Borenium cations, [$(RY)_2BL$]$^+$ (Y = O, S, RN; L = neutral two-electron-donor ligand, e.g., NR_3), can be designed to prevent decomposition by C−Y bond cleavage by using R groups that can only generate high-energy carbocations on C−Y cleavage (e.g., R = Me$^+$, Ph$^+$). Only once all decomposition routes have been removed can the electrophilicity of borenium cations be directed toward external substrates. The order of reactivity of borenium cations with constant L in direct electrophilic arene borylation is [$(halide)_2BL$]$^+$ > [$(CatS_2)BL$]$^+$ > [CatBL]$^+$. Our attempts to place a number of chelate restrained diazaboroles ($(R_2N)_2BX$) in this series have failed to date. Stable Lewis base/acid adducts between $(R_2N)_2BX$ (X = H, halide) and L are not observed, due to the low Lewis acidity and significant steric bulk of the $(R_2N)_2BX$ species investigated herein. The inability to form stable adducts prevents abstraction of X$^-$ and formation of the borenium cation on addition of a Lewis acid. Finally, we have

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demonstrated that halide transfer from $[AlCl_4]^-$ to boron in borenium cations is dependent on the charge at boron. This enables borenium cations that are highly electrophilic (possessing a low-lying LUMO) but have a low degree of positive charge localized at boron to borylate arenes containing nucleophilic substrates (e.g., $-NMe_2$) with no evidence for $[AlCl_4]^-$ decomposition by Al−Cl cleavage.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed using standard glovebox or Schlenk line techniques, unless otherwise specified. Solvents used were either purified by an Innovative Technology PS-MD-5 solvent purification system or distilled from appropriate drying agents and degassed. Deuterated solvents were distilled from appropriate drying agents and degassed. $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$,[22] 1-hydrido-1,3,2-benzodiazaborole,[20] *N,N′*-(adamantyl)$_2$-1,2-diaminobenzene,[43] *N,N′*-(2,6-diisopropylphenyl)-1-bromo-1,3,2-diazaborole (**3**),[29] and 1-chloro-1,3,2-benzodithiaborole ($(CatS_2)BCl$, **4**)[32] were synthesized according to published routes. All other materials were purchased from commercial vendors and used as received. NMR spectra were recorded with a Bruker AV 400 spectrometer (400 MHz; ^1H, 100 MHz; ^{13}C. 100 MHz; ^{11}B, 128 MHz; ^{31}P, 162 MHz; ^{19}F, 376.5 MHz; ^{27}Al, 104.3 MHz; ^{29}Si, 79.5 MHz). ^1H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents, and ^{13}C NMR shifts are reported using the center line of the $CDCl_3$ (or CD_2Cl_2 as appropriate) triplet as an internal standard. ^{11}B NMR spectra were referenced to external $BF_3{\cdot}Et_2O$, ^{31}P to H_3PO_4, ^{19}F to Cl_3CF, and ^{27}Al to $Al(NO_3)_2$ in D_2O ($Al(D_2O)_6^{3+}$).Unless otherwise stated, all NMR spectra were recorded at 293 K. Elemental analysis of air -sensitive compounds was performed by London Metropolitan University. For borylation conditions using borenium cations derived from CatBCl, see ref 5.

Compound 1. A Schlenk flask fitted with a J. Young valve was charged with *N,N′*-(adamantyl)$_2$-1,2-diaminobenzene (300 mg, 0.78 mmol) and dissolved in 5 mL of toluene. H_3BSMe_2 (1.2 equiv, 2 M solution in toluene, 0.5 mL) was added by syringe, resulting in rapid gas evolution. The flask was sealed under vacuum and heated to 100 °C for 1 h. Toluene was then removed in vacuo and the colorless solid dried in vacuo overnight to give 255 mg of **1** (yield 84%). ^1H NMR (C_6D_6): δ 7.61 (2H, m Ar H), 7.12 (2H, M, Ar H), 2.27 (6H, CH_2), 2.02 (3H, CH), 1.62 (6H, CH_2). $^1H\{^{11}B\}$ NMR (C_6D_6, as ^1H apart from additional resonance): δ 4.99 (br s, 1H, B−H). ^{11}B NMR (C_6D_6): δ 22.8 (s, v br), $^{11}B\{^1H\}$ NMR (C_6D_6): δ 22.8 (s, v br). IR (toluene solution): ν(B−H) 2607 cm^{-1}. Anal. Calcd for $C_{26}H_{35}BN_2$: C, 80.82; H, 9.13; N, 7.25. Found C, 79.87; H, 9.12; N, 6.87.

Compound 2. A J. Young NMR tube was charged with **1** (50 mg, 0.13 mmol) that was dissolved in C_6D_6 (0.6 mL). $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$ (10 mg, 0.012 mmol) was added as a solid and the reaction mixture subsequently heated to 50 °C with periodic monitoring by NMR spectroscopy. After 48 h all **1** had reacted and on cooling gave 23 mg of **2** as small colorless crystals (46% yield). The moderate yield is due to the partial solubility of **2** in benzene. ^1H NMR ($CDCl_3$): δ 7.03 (1H, Ar H), 6.95 (1H, Ar H), 6.63 (2H, NH, br); 2.16 (9H, CH and CH_2); 2.11 (3H, CH) 1.97 (6H, CH_2), 1.86 (6H, CH_2), 1.79 (6H, CH_2). $^1H\{^{11}B\}$ NMR ($CDCl_3$, as ^1H spectra apart from additional resonance): δ 4.58 (br s, 1H, B−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.67, 136.17, 132.55, 130.65, 112.96, 106.27, 43.88, 41.69, 37.09, 36.96, 36.82, 36.13, 28.18, 28.96. ^{11}B NMR ($CDCl_3$): δ 23.8 (s, v br), $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 23.6 (s, v br). IR (toluene solution): ν(B−H) 2593 cm^{-1}. Anal. Calcd for $C_{26}H_{35}BN_2$: C, 80.82; H, 9.13; N, 7.25. Found: C, 79.53; H, 8.82; N, 6.67.

Reactivity of CatBCl with *N,N,N′,N′*-Tetramethyldiaminomethane. Chlorocatecholborane (30 mg, 0.19 mmol) was added to a J. Young NMR tube. After dissolution in CD_2Cl_2 (1 mL) *N,N,N′,N′*-tetramethyldiaminomethane (26.5 μL, 0.19 mmol) was added, giving immediate formation of a cloudy solution. ^1H and ^{11}B NMR spectroscopy at this stage indicates the formation of *N,N*-dimethylamidocatecholborane ($CatBNMe_2$); the precipitate is attributed to autoionization and elimination of insoluble iminium chloride. The mixture was inverted repeatedly to ensure reaction, and aluminum trichloride was then added (25 mg, 0.19 mmol); dissolution of all $AlCl_3$ and the iminium chloride precipitate occurred concomitantly to form $CatBNMe_2$ and $[Me_2N{=}CH_2][AlCl_4]$ as the major products.

$[CatBNMe_2]$: ^1H NMR (CD_2Cl_2) δ 6.9−7.1 (br. m, 4 H, CatB aromatics), 2.80 (br s, 5.9 H, CatBNMe CH_3); ^{11}B NMR (CD_2Cl_2) δ 25.6 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 149.51 (broad, weak singlet, Ar O), 122.06 (s CatB Ar H), 111.74 (s, CatB Ar H), 36.58 (s, $CatBNMe_2$, CH_3).

$[Me_2N{=}CH_2][AlCl_4]$ (consistent with that previously reported by Mayr et al.[28]): ^1H NMR (CD_2Cl_2) δ 7.99 (b s, 2H, iminium CH_2), 3.87 (br s, 6H, iminium NMe_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 168.27 (1:1:1 sharp triplet, J_{CN} = 13.1 Hz, iminium CH_2), 50.82 (1:1:1 triplet, J_{CN} = 5.0 Hz, iminium NMe_2); ^{27}Al NMR (CD_2Cl_2) δ 104.1 (sharp singlet, $AlCl_4$).

Borylation of 2-Methylthiophene with Equimolar BCl_3/Me_2NTol/$AlCl_3$. A Schlenk tube containing a stirring bar was flame-dried under reduced pressure and charged in a glovebox with solid $Me_2NTol{\cdot}BCl_3$ adduct (265 mg, 1.05 mmol) and anhydrous $AlCl_3$ (140 mg, 1.05 mmol). Then anhydrous CH_2Cl_2 (3.5 mL) was added and the reaction mixture was stirred at ambient temperature for 1 h. After the $AlCl_3$ had completely dissolved, 2-methylthiophene (87 μL, 1 mmol) was added and stirring was continued at ambient temperature until an ^1H NMR spectrum of an aliquot of the reaction mixture showed no resonances attributable to 2-methylthiophene in the aromatic region (2 h). The borylated product was the major species observed in situ (>90%), with a currently unidentified minor byproduct, occurring at <10% of the major product's intensity (by ^1H NMR spectroscopy).

$(CatS_2)BCl(NEt_3)$ (5). A J. Young NMR tube was charged with triethylamine (0.21 mmol, 21 mg, 29 μL, 1.0 equiv) in anhydrous CD_2Cl_2/CH_2Cl_2 (0.7 mL). This was then treated with **4** (0.21 mmol, 40 mg, 1.0 equiv) to give a colorless solution which was sealed and rotated for 1 h. The solution was transferred via cannula to a Schlenk, the NMR tube was washed with anhydrous CH_2Cl_2 (3 × 2 mL), and the washings were transferred to the Schlenk. The CH_2Cl_2 was removed under vacuum, and the product was dried under vacuum for 2 h, to give a cream/off-white solid (27 mg, 45%). ^1H NMR ($CDCl_3$): δ 7.21 (m, 2H, ThioCatB), 6.91 (m, 2H, ThioCatB), 3.27 (q, ^3J = 8.0 Hz, 6H, 3 × NCH_2CH_3), 1.25 (t, ^3J = 8.0 Hz, 6H, 3 × NCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 10.68, 51.39, 124.3, 124.5, 140.8. ^{11}B NMR ($CDCl_3$): δ 15.95 (s, broad). Anal. Calcd for $C_{12}H_{19}Cl_4BNS_2$: C, 50.10; H, 6.66; N, 4.87. Found: C, 49.98; H, 6.75; N, 4.74.

$[(CatS_2)BNEt_3][AlCl_4]$ (6[$AlCl_4$]). A J. Young NMR tube was charged with triethylamine (0.21 mmol, 21 mg, 29 μL, 1.0 equiv) in CD_2Cl_2/CH_2Cl_2 (0.7 mL). This was then treated with **4** (0.21 mmol, 40 mg 1.0 equiv) and $AlCl_3$ (0.21 mmol, 28 mg, 1.0 equiv), resulting in immediate (<10 min) formation of **6**[$AlCl_4$]. The solution was transferred via cannula to a Schlenk, the NMR tube was washed with anhydrous CH_2Cl_2 (3 × 2 mL), and the washings were transferred to the Schlenk. The CH_2Cl_2 was removed under vacuum, and the product was dried under vacuum to produce a colorless oil. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.93 (m, 2H, ThioCatB), 7.55 (m, 2H, ThioCatB), 3.73 (q, ^3J = 8.0 Hz, 6H, 3 × NCH_2CH_3), 1.43 (t, ^3J = 8.0 Hz, 6H, 3 × NCH_2CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 9.42, 56.18, 128.3, 128.4, 137.1. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 59.84 (s, broad). ^{27}Al NMR (104.26 MHz, $CDCl_3$): δ 103.98 (s, sharp). Anal. Calcd for $C_{12}H_{19}AlBCl_4NS_2$: C, 34.23; H, 4.55; N, 3.33. Found: C, 34.35; H, 4.51; N, 3.25.

***N*-Methyl-2-(4,4,5,5-tetramethyldioxaborolan-2-yl)indole.** A J. Young NMR tube was charged with triethylamine (0.21 mmol, 21 mg, 29 μL, 1.0 equiv) in CH_2Cl_2/CD_2Cl_2 (0.7 mL). This was then treated with **4** (0.21 mmol, 40 mg, 1.0 equiv) and $AlCl_3$ (0.21 mmol, 28 mg, 1.0 equiv). The reaction mixture was then treated with *N*-methylindole (0.21 mmol, 28 mg, 26 μL, 1.0 equiv) and monitored by NMR spectroscopy. The reaction was 97% complete within 3 h, with ^1H NMR indicating the major product (>99%) was the borylated arene. ^1H NMR (CD_2Cl_2): δ 8.01 (m, 1H, Ar H), 7.81 (q, ^3J = 8.0 Hz, 2H, ThioCatB), 7.71 (s, 1H, Ar H), 7.42 (m, 1H, Ar H), 7.33 (m, 4H, Ar H), 3.83 (s, 3H, NCH_3). ^{11}B NMR (CD_2Cl_2): δ 53.64 (s, broad).

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Standard Workup Procedure. The solution was then treated with triethylamine (3.15 mmol, 319 mg, 0.44 mL, 15 equiv) and pinacol (0.42 mmol, 50 mg, 2.0 equiv) and rotated for 30 min to give an orange suspension. The suspension was transferred to a round-bottom flask and the NMR tube washed with dry CH_2Cl_2 (3 × 1 mL). The CH_2Cl_2 was removed under vacuum, dried for 1 h, and replaced with hexane (25 mL) to give an orange suspension. The suspension was filtered to give a colorless solution, hexane was removed under vacuum, and the product was dried overnight to give *N*-methyl-2-(4,4,5,5-tetramethyldioxaborolan-2-yl)indole (52 mg, 70% identified by comparison to our previous report).

***N*-TIPS-3-(1,3,2-benzodithioborolan-2-yl)indole.** A J. Young NMR tube was charged with triethylamine (0.21 mmol, 21 mg, 29 μL, 1.0 equiv) in CH_2Cl_2/CD_2Cl_2 (0.7 mL). This was then treated with **4** (0.21 mmol, 40 mg, 1.0 equiv) and $AlCl_3$ (0.21 mmol, 28 mg, 1.0 equiv). The reaction mixture was treated with *N*-TIPS-indole (0.21 mmol, 88 mg, 1.0 equiv) and rotated with periodic monitoring by NMR spectroscopy. The reaction was complete within 4 h, with ^{1}H NMR indicating >99% borylation. ^{1}H NMR (CD_2Cl_2): δ 8.02 (d, ^3J = 8.0 Hz, 1H, Ar H), 7.90 (s, 1H, Ar H), 7.82 (q, ^3J = 4.0 Hz, 2H, $CatS_2B$), 7.63 (d, ^3J = 8.0 Hz, 1H, Ar H), 7.31 (q, ^3J = 4.0 Hz, 2H, $CatS_2B$), 7.29 (m, 2H, Ar H), 1.78 (m, 3H, 3 × NC*H*(CH_3)$_2$), 1.18 (d, ^3J = 8.0 Hz, 18H, 3 × NCH(C*H*$_3$)$_2$). ^{11}B NMR (CD_2Cl_2): δ 53.56 (s, broad).

***N*,*N*,4-Trimethyl-2-(4,4,5,5-tetramethyldioxaborolan-2-yl)-aniline.** A J. Young NMR tube was charged with triethylamine (0.21 mmol, 21 mg, 29 μL, 1.0 equiv) in CH_2Cl_2/CD_2Cl_2 (0.7 mL). This was then treated with **4** (0.21 mmol, 40 mg, 1.0 equiv.) and $AlCl_3$ (0.21 mmol, 28 mg, 1.0 equiv). The reaction mixture was treated with Me_2NTol (0.21 mmol, 28.4 mg, 30 μL, 1.0 equiv) and monitored periodically by NMR spectroscopy. The reaction was complete within 24 h, with in situ ^{1}H NMR indicating >99% borylation. ^{1}H NMR (CD_2Cl_2): δ 7.80 (q, ^3J = 4.0 Hz, 2H, ThioCatB), 7.66 (s, 1H, Ar H), 7.30 (q, ^3J = 4.0 Hz, 2H, ThioCatB), 7.28 (dd, ^3J = 8.0, 4.0 Hz, 1H, Ar H), 7.13 (d, ^3J = 8.0 Hz, 1H, Ar H), 2.74 (s, 6H, 2 × N(CH_3)$_2$), 2.34 (s, 3H, CH_3). ^{11}B NMR (CD_2Cl_2): δ 58.3 (s, broad, peak width at half-height =339 Hz).

Esterification and isolation was as described in Standard Workup Procedure (using triethylamine (3.15 mmol, 319 mg, 0.44 mL, 15 equiv) and pinacol (0.42 mmol, 50 mg, 2.0 equiv)) and afforded *N*,*N*,4-trimethyl-2-(4,4,5,5-tetramethyldioxaborolan-2-yl)aniline (28 mg, 51%) as a colorless solid. A combination of one- and two-dimensional NMR experiments unambiguously allowed the product to be identified with the BPin group ortho to the amino group.

^{1}H NMR ($CDCl_3$): δ 1.37 (s, 12H, 4 × CH_3), 2.27 (s, 3H, CH_3), 2.83 (s, 6H, N(CH_3)$_2$), 6.79 (d, ^3J = 8.0, 1H, $Me_2NC_6H_3$-ortho), 7.13 (dd, ^3J = 4.0, 2.0, 1H, PinB-C_6H_3-para), 7.46 (s, 1H, PinB-C_6H_3-ortho). ^{13}C NMR ($CDCl_3$): δ 20.28 (CH_3), 24.74 (4 × CH_3 pinacol), 45.28 (2 × CH_3 amino group), 83.41 (quaternary C × 2, pinacol), 115.1, 128.3, 131.9, 136.9, 155.9. ^{11}B NMR ($CDCl_3$): δ 31.57 (s, broad). Accurate mass ES$^+$: calcd for MH$^+$ ($C_{15}N_{25}BNO_2$) *m*/*z* 262.1978, found *m*/*z* 262.1965.

[CatB(P^{t}Bu$_3$)][AlCl$_4$] (10[AlCl$_4$]). In an oven-dried Schlenk CatBCl (0.90 mmol, 140 mg, 1.0 equiv) was added to a stirred solution of tri-*tert*-butylphosphine (0.90 mmol, 183 mg, 1 equiv) in dry DCM (1 mL). After 3 min $AlCl_3$ (0.90 mmol, 120 mg, 1 equiv) was added to the mixture, which was stirred for 1 h and then layered with pentane. Slow diffusion of the layers yielded colorless crystals of [CatB(P^{t}Bu$_3$)][$AlCl_4$] (406 mg, 92%) suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (CD_2Cl_2): δ 1.78 (d, $^3J_{H-P}$ = 15.4 Hz, 27H, 9 × Me, *tert*-butyl), 7.42 (m, 2H, Ar H), 7.57 (m, 2H, Ar H). ^{13}C NMR (CD_2Cl_2): δ 31.07, 40.50 (d, $^1J_{C-P}$ = 23.1 Hz), 114.48, 125.85, 147.12 (d, $^3J_{C-P}$ = 4.6 Hz). ^{11}B NMR (CD_2Cl_2): δ 29.88 (d, $^1J_{B-P}$ = 184 Hz). ^{27}Al NMR (CD_2Cl_2): δ 103.74 (s, sharp). ^{31}P NMR (CD_2Cl_2): δ 26.81 (q, $^1J_{P-B}$ = 184 Hz). Anal. Calcd for $C_{18}H_{31}AlBCl_4O_2P$: C, 44.12; H, 6.38. Found: C, 44.23; H, 6.19.

4-(4,4,5,5-Tetramethyldioxaborolan-2-yl)-1,8-bis-(dimethylamino)naphthalene. *Method A (Using 7[AlCl$_4$]).* A J. Young tap NMR tube was charged with triethylamine (0.34 mmol, 34 mg, 47 μL, 1.05 equiv) in CH_2Cl_2/CD_2Cl_2 (0.7 mL) and treated with CatBCl (0.32 mmol, 50 mg, 1.0 equiv), $AlCl_3$ (0.35 mmol, 48 mg, 1.10 equiv), and 1,8-bis(dimethylamino)-naphthalene (0.32 mmol, 68 mg, 1 equiv) and stirred to give a yellow solution. The reaction reached a maximum 60% conversion (by ^{11}B NMR) after stirring for 18 h. Isolation was as described above in Standard Workup Procedure (triethylamine (4.8 mmol, 0.485 g, 0.67 mL, 15 equiv) and pinacol (0.96 mmol, 114 mg, 3 equiv)) with further purification by column chromatography with hexane, followed by DCM and ethyl acetate. 4-(4,4,5,5-Tetramethyldioxaborolan-2-yl)-1,8-(dimethylamino)naphthalene was isolated as an off-white solid (62.6 mg, 57%). ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 12H, 4 × Me, pinacol), 2.67, 2.74 (2 × s, 12H, 2 × NMe_2), 6.80 (m, 2H, Ar H), 7.24 (m, 1H, Ar H), 7.84 (d, ^3J = 8.0 Hz, 1H, Ar H), 8.26 (d, ^3J = 8.0 Hz, 1H, Ar H). ^{13}C NMR ($CDCl_3$): δ 24.89 (4 × Me, pinacol), 43.66, 43.85 (2 × NMe_2), 83.06, 110.76, 111.76, 121.43, 125.86, 136.23, 141.51, 150.68, 163.48. ^{11}B NMR ($CDCl_3$): δ 32.14 (s, broad). Accurate mass ES$^+$: calcd for MH$^+$ ($C_{20}H_{29}BN_2O_2$) *m*/*z* 341.2400, found: *m*/*z* 341.2388.

Method B. A J. Young tap NMR tube was charged with triethylamine (0.113 mmol, 11.4 mg, 16 μL, 1.05 equiv) in CH_2Cl_2/CD_2Cl_2 (0.8 mL) and treated with **4** (0.107 mmol, 20 mg, 1.0 equiv), $AlCl_3$ (0.118 mmol, 16 mg, 1.10 equiv), and then 1,8-bis-(dimethylamino)naphthalene (0.107 mmol, 23 mg, 1 equiv) and stirred to give a yellow solution. The reaction reached >99% conversion (by ^{11}B NMR spectroscopy) within 1 h at room temperature. NMR data of 4-(1,3,2-benzodithioborolan-2-yl)-1,8-bis(dimethylamino)naphthalene: ^{1}H NMR (CD_2Cl_2) 2.78, 2.88 (2 × s, 2 × 6H, 2 × NMe_2), 6.88 (d, ^3J = 4.0 Hz, 1H, Ar H), 6.95 (d, ^3J = 4.0 Hz, 1H, Ar H), 7.32 (m, 2H, ThioCatB), 7.79 (m, 2H, ThioCatB), 7.87 (d, ^3J = 4.0 Hz, 1H, Ar H), 8.00 (dd, ^3J = 8.0, 4.0 Hz, 2H, Ar H); ^{11}B NMR (CD_2Cl_3) δ 58.3 (s, broad, peak width at half height 500 Hz).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables, figures, and CIF files giving full crystallographic and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hall, D. Boronic Acids: Preparation and Applications in Organic Synthesis. In *Medicine and Materials*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2011.

(2) Hartwig, J. F. *Chem. Soc. Rev.* **2011**, *40*, 1992.

(3) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.

(4) Del Grosso, A.; Muryn, C. A.; Pritchard, R. G.; Ingleson, M. J. *Organometallics* **2010**, *29*, 241.

(5) Del Grosso, A.; Singleton, P. J.; Muryn, C. A.; Ingleson, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 2102.

(6) Del Grosso, A.; Helm, M. D.; Solomon, S. A.; Caras Quintero, D.; Ingleson, M. J. *Chem. Commun.* **2011**, *47*, 12459.

(7) Prokofjevs, A.; Kampf, J. W.; Vedejs, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 2098.

(8) Bregadze, V. I.; Kosenko, I. D.; Lobanova, I. A.; Starikova, Z. A.; Godovikov, I. A.; Sivaev, I. B. *Organometallics* **2010**, *29*, 5366.
(9) Muetterties, E. L. *J. Am. Chem. Soc.* **1959**, *81*, 2597.
(10) Muetterties, E. L. *J. Am. Chem. Soc.* **1960**, *82*, 4163.
(11) Muetterties, E. L.; Tebbe, F. N. *Inorg. Chem.* **1968**, *7*, 2663.
(12) Ishida, N.; Moriya, T.; Goya, T.; Murakami, M. *J. Org. Chem.* **2010**, *75*, 8709.
(13) De-Vries, T. S.; Prokofjevs, A.; Harvey, J. N.; Vedejs, E. *J. Am. Chem. Soc.* **2009**, *131*, 14679.
(14) Hatakeyama, T.; Hashimoto, S.; Seki, S.; Nakamura, M. *J. Am. Chem. Soc.* **2011**, *133*, 18614.
(15) Koelle, P.; Nöth, H. *Chem. Rev* **1985**, *85*, 399.
(16) Piers, W. E.; Bourke, S. C.; Conroy, K. D. *Angew. Chem. Int. Ed* **2005**, *44*, 5016.
(17) Corey, E. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2100.
(18) Clegg, W.; Dai, C.; Lawlor, F. J.; Marder, T. B.; Nguyen, P.; Norman, N. C.; Pickett, N. L.; Power, W. P.; Scott, A. J. *Dalton Trans.* **1997**, 839.
(19) Mock, M. T.; Potter, R. G.; Camaioni, D. M.; Li, J.; Dougherty, W. G.; Kassel, W. S.; Twamley, B.; DuBois, D. L. *J. Am. Chem. Soc.* **2009**, *131*, 14454.
(20) Hadebe, S. W.; Robinson, R. S. *Eur. J. Org. Chem.* **2006**, 4898.
(21) Dureen, M. A.; Lough, A.; Gilbert, T. M.; Stephan, D. W. *Chem. Commun.* **2008**, 4303.
(22) Xie, Z.; Jelinek, T.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1907.
(23) Higashi, J.; Eastman, A. D.; Parry, R. W. *Inorg. Chem.* **1982**, *21*, 716.
(24) Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 746.
(25) Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 6388.
(26) Corr, M. J.; Roydhouse, M. D.; Gibson, K. F.; Zhou, S.; Kennedy, A. R.; Murphy, J. A. *J. Am. Chem. Soc.* **2009**, *131*, 17980.
(27) Olah, G. A.; Klump, D. A., *Superelectrophiles and Their Chemistry*; Wiley: New York, 2008.
(28) Mayr, H.; Ofial, A. R.; Würthwein, E.-U.; Aust, N. C. *J. Am. Chem. Soc.* **1997**, *119*, 12727.
(29) Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *314*, 113.
(30) Lehmann, M.; Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 7444.
(31) Khramov, D. M.; Boydston, A. J.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 6186.
(32) Howarth, J.; Helmchen, G.; Keifer, M. *Tetrahedron Lett.* **1993**, *34*, 4095.
(33) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66.
(34) Narula, C. K.; Nöth, H. *Inorg. Chem.* **1984**, *23*, 4147.
(35) Narula, C. K.; Nöth, H. *Inorg. Chem.* **1985**, *24*, 2532.
(36) Ryschkewitsch, G. E.; Wiggins, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 1790.
(37) Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 2520.
(38) Gelbrich, T.; Dumichen, U.; Sieler, J. *Acta Crystallogr.* **1999**, *C55*, 1797.
(39) See the Supporting Information.
(40) Coapes, R. B.; Souza, F. E. S.; Fox, M. A.; Batsanov, A. S.; Goeta, A. E.; Yufit, D. S.; Leech, M. A.; Howard, J. A. K.; Scott, A. J.; Clegg, W.; Marder, T. B. *Dalton Trans.* **2001**, 1201.
(41) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.
(42) Vedejs, E.; Nguyen, T.; Powell, D. R.; Schrimpf, M. R. *Chem. Commun.* **1996**, 2721.
(43) Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Org. Lett.* **2005**, *7*, 1991.