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Amides as modifiable directing groups in electrophilic borylation†

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Amide directed C–H borylation using ≥two equiv. of BBr₃ forms borenium cations containing a R₂N(R′)C=O→B(Ar)Br unit which has significant Lewis acidity at the carbonyl carbon. This enables reduction of the amide unit to an amine using hydrosilanes. This approach can be applied sequentially in a one-pot electrophilic borylation–reduction process, which for phenyl-acetylamides generates *ortho* borylated compounds that can be directly oxidised to the 2-(2-aminoethyl)-phenol. Other substrates amenable to the C–H borylation–reduction sequence include mono and diamino-arenes and carbazoles. This represents a simple method to make borylated molecules that would be convoluted to access otherwise (*e.g. N*-octyl-1-BPin-carbazole). Substituent variation is tolerated at boron as well as in the amide unit, with diarylborenium cations also amenable to reduction. This enables a double C–H borylation–reduction–hydrolysis sequence to access B,N-polycyclic aromatic hydrocarbons (PAHs), including an example where both the boron and nitrogen centres contain functionalisable handles (N–H and B–OH). This method is therefore a useful addition to the metal-free borylation toolbox for accessing useful intermediates (ArylBPin) and novel B,N-PAHs.

Introduction

Directed C–H borylation is a powerful methodology to install boron moieties onto arenes with high regioselectivity.[1] This conversion is desirable as organo-boronate esters are powerful intermediates in synthesis.[2] In this area, notable advances have been made using metal based (principally iridium) catalysts to generate pinacol boronate esters (Ar-BPin).[3] Recently, it has been demonstrated that directed electrophilic C–H borylation using BX₃ (X = Cl, Br or I) is a viable metal-free route to install useful boron units, such as BPin, onto arenes.[1a,4] However, this area is less developed than metal-catalysed directed C–H borylation, particularly regarding the utilisation of the directing group (DG) post borylation. To date, the DG is kept intact in the product post electrophilic borylation (Fig. 1(i)) or is removed (Fig. 1(ii)). An attractive alternative is to convert the DG into a new functional group post borylation (Fig. 1(iii)), here it is fulfilling two roles: (a) a DG and (b) a reactive handle for further

functionalisation.[5] Outcome (iii) is significantly underexplored in electrophilic borylation despite its potential to access otherwise challenging to make molecules. To our knowledge, approach (iii) has only been used to make B-doped polycyclic aromatic hydrocarbons (PAHs) in very limited examples (*e.g.*
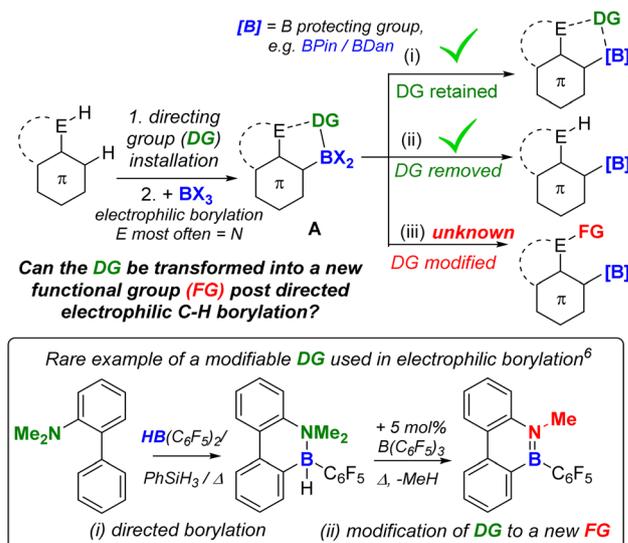

Fig. 1 (Top) Three possible fates of DGs post directed borylation. (Bottom) A rare example of a modifiable DG in directed electrophilic borylation to make a B-doped PAH.

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bottom Fig. 1).[6] Furthermore, approach (iii) has not been used to our knowledge to access synthetically useful organoboranes, such as functionalised ArylBPin species.

In directed electrophilic borylation, the Lewis basic DG binds the boron Lewis acid (*e.g.*, BX_3) enabling subsequent access to a borenium cation (a three coordinate borocation) that then effects C–H borylation.[1a,4] Several DGs used in electrophilic borylation contain unsaturated units, *e.g.*, C=O, and in the primary product formed post C–H borylation, *e.g.* **A** (Fig. 1) or **B** (Fig. 2), the DG remains bound to a Lewis acidic boron centre.[4] Thus, the DG will be activated, *e.g.* at the carbonyl carbon in **B**, towards reaction with nucleophiles. For example, Lewis acid–carbonyl adducts are effectively reduced by silanes or boranes.[7] These reductions can be selective, for example using silanes and $B(C_6F_5)_3$ as Lewis acid activator, amides are reduced to amines *via* a hemi-aminal (Fig. 2 top).[8] Therefore, the primary products from amide directed electrophilic borylation (*e.g.* **B**) should be amenable to reduction to the amine. This would be notable if the C–B unit remained intact as it would generate a new set of borylated compounds from a common intermediate (*e.g.* **B**).

Herein we report that hydrosilanes reduce the primary products from amide directed electrophilic borylation to amine containing borylated products. The amide to amine reduction process is applicable to a range of substrates including phenylacetyl, arylamine, and carbazole based amides along with more complex doubly borylated systems. This process is a rare example of using a modifiable directing group in electrophilic

borylation and represents a new route to access synthetically useful arylboranes and novel *ortho*-B,N-containing PAHs (an area of significant current interest).[9]

Results and discussion

Borylation–reduction of phenyl-acetyl derivatives

The formation of $[\mathbf{1}]^+$ (Fig. 3) as the $[BBr_4]^-$ salt by directed electrophilic C–H borylation has been previously reported.[10] Borenium $[\mathbf{1}][\mathbf{BBr_4}]$ was selected to start the reduction studies as the product from amide to amine reduction would form an *ortho* borylated $PhCH_2CH_2NMe_2$ species predisposed to form a six-membered boracycle (by $N \rightarrow BY_2$ dative bond formation, Y = H or Br, *e.g.* **2a**, Fig. 4). This boracycle should be bench stable based on previous work,[11] thereby facilitating isolation and identification of the exocyclic Y substituents on boron (note the identity of Y will control the equivalents of reductant needed). The identity of Y is challenging to predict *a priori*, as in $[\mathbf{1}]^+$ both boron and the carbonyl carbon are electrophilic and could accept hydride. To assess Lewis acidity the hydride ion affinity (HIA) relative to BEt_3 was calculated using the previously reported methodology (at M06-2X/6-311G(d,p)/PCM(DCM) level, this level is used throughout this work).[12] This revealed (Fig. 3) that both positions have comparable Lewis acidity towards hydride, thus hydride transfer is feasible to both carbon and boron. Note, these HIAs are high, being greater than $B(C_6F_5)_3$,[12] and comparable to the carbon based Lewis acid *N*-methyl-2-phenyl benzothiazolium cation,[13] with both these Lewis acids able to activate hydrosilanes.[13,14]

While a range of boranes/borohydrides gave complex mixtures in the reduction of $[\mathbf{1}][\mathbf{BBr_4}]$, the use of hydrosilanes resulted in more selective reduction, with $SiHEt_3$ providing good results (note modification in the hydrosilane provided limited change in outcome, see Table S1†). The addition of one equiv. of $SiHEt_3$ to $[\mathbf{1}][\mathbf{BBr_4}]$ at ambient temperature resulted in three major new resonances in the *in situ* ^{11}B NMR spectrum at $\delta_{11B} = 40.4, 4.5$ and -2.7, the latter was a doublet with a $^1J_{B-H} = 156$ Hz. The ^{1}H NMR spectrum contained a diagnostic doublet of doublets ($\delta_{1H} = 5.60, J = 12.2, 3.3$ Hz) assigned to the hemi-aminal C–H in **3** (Fig. 4) in addition to resonances further upfield for the diastereotopic $PhCH_2$ protons. However, the aromatic region showed there are two new products formed under these conditions along with significant $[\mathbf{1}][\mathbf{BBr_4}]$ remaining. Additional studies (*vide infra*) revealed the second product to be the amine borane **2a**. The complete consumption
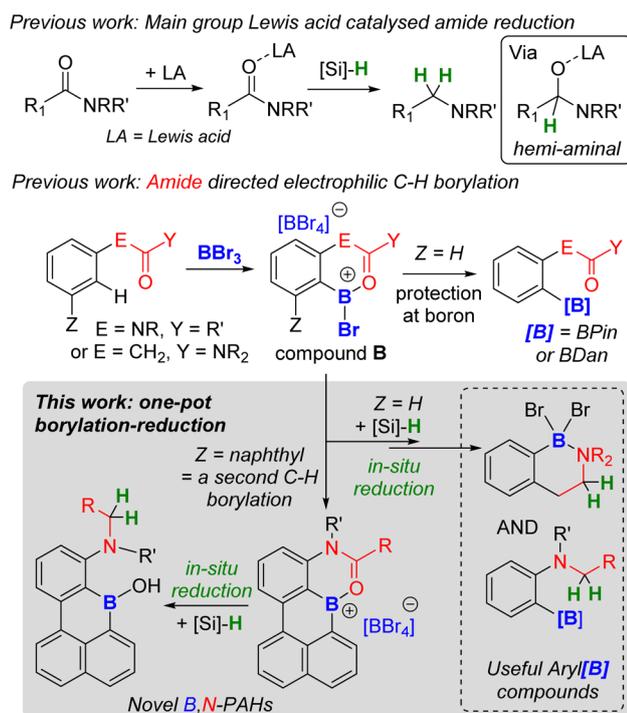

Fig. 2 Previous work on: Lewis acid catalysed amide reduction (top); amide directed borylation (middle); and this work (bottom) combining amide directed electrophilic borylation and amide reduction to make novel borylated compounds.
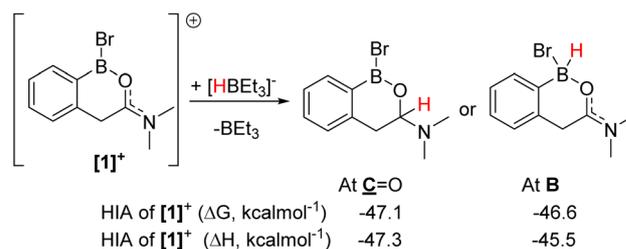

Fig. 3 HIA at boron and the carbonyl carbon of $[\mathbf{1}]^+$.
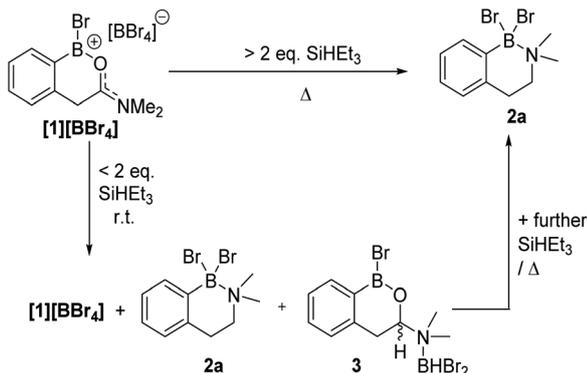
Fig. 4 Formation of amine-borane **2a** using silanes *via* hemi-aminal **3**.

of **[1][BBr4]** required at least two equiv. of $SiHEt_3$ and produced a mixture of **2a** and **3** at ambient temperature (Fig. S7†).

Compound **2a** could be formed as the sole soluble product starting from **[1][BBr4]** by using >2 equiv. $SiHEt_3$ and heating. **2a** displays an ^{11}B NMR singlet at δ_{11B} = +4.5 (precluding a BH_2 formulation as the BH_2 congener of **2a** is a triplet at δ_{11B} −5.2),[11] while the ^1H NMR spectrum showed two aliphatic triplets consistent with an $ArCH_2CH_2$ unit formed from reduction of amide to amine. Further confirmation of the formation of an amine→BBr_2 species was forthcoming from the reduction of previously reported **4** (ref. 10) with $SiHEt_3$ (Fig. 5). On heating this formed compound **5**, displaying a δ_{11B} = 5.0, and a singlet at δ_{1H} = 3.5 for the CH_2 unit. **5** could be isolated as a crystalline solid which enabled X-ray diffraction studies to corroborate the formulation. Coordination of the amine to the boron centre in **5** (N–B = 1.604(3) Å) results in a pyramidalised boron centre ($\Sigma Br2$–B1–C1/Br1–B1–C1/Br1–C1–Br2 = 329.72(3)°), with this strong dative bond allowing the amine boranes **2a** and **5** to be handled on the bench for short periods. Finally, it should be noted the formation of a BBr_2 unit during reduction is consistent with a 2 : 1 Si–H : **[1][BBr4]** stoichiometry leading to complete amide to amine reduction.
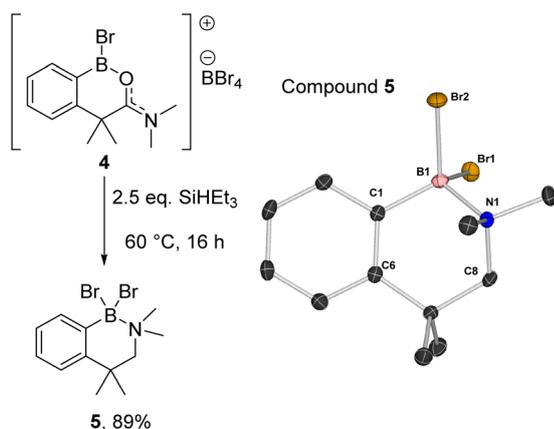

Fig. 5 (Left) Formation of amine borane **5**. (Right) The solid-state structure of **5**, ellipsoids at the 50% probability and hydrogens omitted for clarity.

The amine boranes also can be formed in a one-pot borylation–reduction process, and starting from N,N-Me_2-phenylacetylamide compound **2a** was formed in 81% isolated yield (Scheme 1). To determine if this process tolerated electron donating (Me) and electron withdrawing groups (F and Br) three derivatives each functionalised at a different arene position were explored. These led to the formation of **2b–2d** in good yield (Scheme 1), albeit requiring modified borylation reaction times (see ESI Section 3†) due to the different electronic effects of the substituents consistent with our previous report.[10] To determine if the N–B dative bond in **2a** prohibits subsequent transformations, the oxidation of **2a** was explored. Shi and co-workers have reported that $ArylBBr_2$ units that are chelated by amide directing groups can be oxidised using $NaBO_3 \cdot 4H_2O$.[15] Analogous conditions were applied for the oxidation of **2a** and this led to the full consumption of **2a** and formation of the corresponding phenol, **6**, as the only new species observed by NMR spectroscopy (Fig. S29†). This indicates that despite the N→B dative bond, these amine boranes are useful intermediates. This is noteworthy as (2-aminoethyl)-phenols are common motifs found in bioactives (*e.g.* psilocin),[16] while **6** represents an *ortho*-tyramine derivative that can be accessed in just two steps from simple precursors.

With the identity of Y and utility of the amine-boranes **2** confirmed our attention turned to the hemi-aminal, assigned as **3**. Multiple attempts to form **3** as the sole boron containing species using a range of silanes/conditions failed, with varying quantities of **2a/[1][BBr4]** always present, furthermore **2a** and **3** proved intractable. However, the identity of **3** is supported by comparison to Me_3N→$BHBr_2$ which displays a δ_{11B} = −0.7 doublet with an identical $^1J_{B-H}$ coupling constant (156 Hz) to that observed in **3**.[17] Furthermore, the −2.7 and 40.4 ppm ^{11}B resonances increased in intensity concomitant with each other and with the δ_{1H} = 5.60 doublet of doublets. The δ_{11B} = 40.4 is consistent with boron in an $ArB(OR)Br$ environment.[18] Finally, it should be noted that leaving mixtures containing **3** for longer reaction times led to the conversion of **3** into **2a**, suggesting **3** is an intermediate in the production of **2a**.

Based on these observations a mechanism for the formation of **2a** can be proposed (Scheme 2, note only a single new
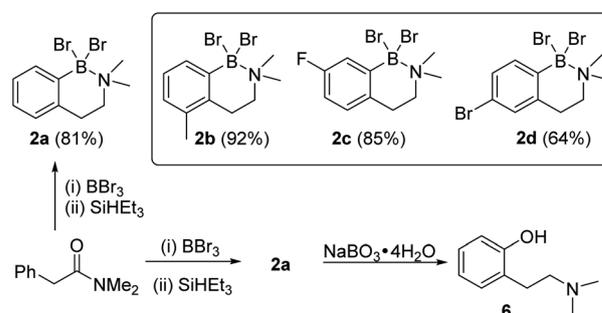
Scheme 1 (Top) Borylation reduction tolerating both electron donating and withdrawing groups and substituents at *ortho*, *meta* and *para* positions in the starting material (isolated yields in parentheses). (Bottom) Conversion of N,N-Me_2-phenylacetylamide into 2-(2-Me_2N-ethyl)phenol **6**.
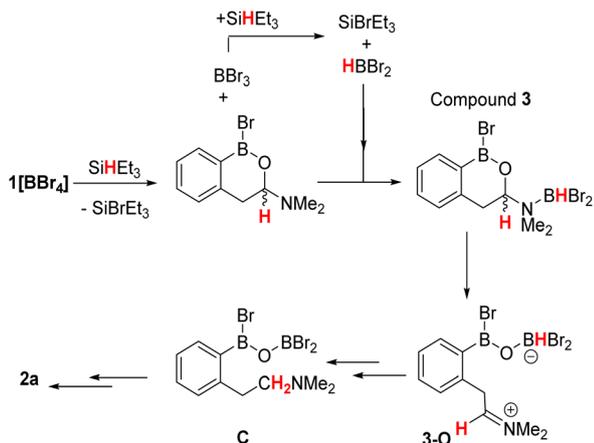
Scheme 2 Proposed pathway for the reduction of [1]$^+$ to **2a** via **3**, **3-O** and **C**.

resonance in the ^{29}Si NMR spectrum was observed at $\delta_{29\text{Si}} = 37.9$ consistent with SiBrEt$_3$). The initial reduction of **[1][BBr$_4$]** would produce the hemi-aminal, with SiBrEt$_3$ and BBr$_3$ the by-products. BBr$_3$ would then react rapidly with SiHEt$_3$ producing SiBrEt$_3$ and HBBr$_2$,[19] the latter is observed bound to the hemi-aminal nitrogen in compound **3** by NMR spectroscopy (*vide supra*). In the absence of additional silane, the only reducing equivalent now present is HBBr$_2$ and we propose this can form the O-bound isomer of **3**, termed **3-O** (Scheme 2, bottom right). Compound **3-O** was calculated to be more stable than **3** by $\Delta G = 8.4$ kcal mol^{-1}, thus **3** is the kinetic product. The calculated structure of **3-O** has the C–O bond already cleaved and instead contains an iminium moiety that is primed for reduction by the B–H unit to furnish **C**. Support for formation of an ArylB–O–BBr$_2$ unit (as shown in **C**) comes from studies on other related substrates (*vide infra*). Finally, boron substituent scrambling and N→B dative bond formation then will convert **C** into **2a**.

During attempts to isolate the hemi-aminal the boron enolate **7** was isolated (Scheme 3), with related boron enolates previously shown to be useful intermediates.[20] However, under a range of conditions **7** could only be formed in low (max. 26%) conversion from **[1][BBr$_4$]**. In an attempt to form a hemi-aminal selectively the bulk around N was increased by replacing NMe$_2$ with N^{i}Pr$_2$ (**[8][BBr$_4$]**, Scheme 4), hypothesising that the extra bulk may preclude HBBr$_2$ coordination to N and O and thus prevent the second hydride transfer step. However, using this bulkier amide led to initial hydride transfer to boron, confirming that reduction can occur at boron as well as at carbon, consistent with the HIA calculations. The only reduced product
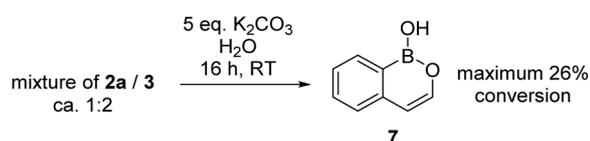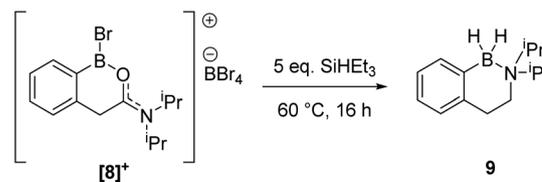
Scheme 4 Reduction of **[8][BBr$_4$]** to form compound **9**.

isolable clean starting from **[8][BBr$_4$]** was compound **9** (formed as the major species when using 5 equiv. silane), with no hemi-aminal observed at any point by *in situ* NMR spectroscopy. Compound **9** is formed from hydride transfer to boron, and then slower amide reduction to the amine. Similar amine-borane products were reported by Vedejs and co-workers and were also made by electrophilic borylation of PhCH$_2$CH$_2$N(R)$_2$-BH$_3$, however this required stoichiometric amounts of the expensive reagent [Ph$_3$C][B(C$_6$F$_5$)$_4$].[11]

Borylation–reduction of aniline derivatives

With a borylation–reduction process in hand its applicability to other substrates was investigated. N-Pivaloyl anilines also produce primary products from directed electrophilic borylation using BBr$_3$ that contain a boron Lewis acid coordinated to the amide carbonyl (such as **10-Br/[10][BBr$_4$]**, Fig. 6).[21] It should be noted that as reported for the phenylacetyl derivatives,[10] **10-Br** and **[10][BBr$_4$]** exist in equilibrium, with the position of the equilibrium favouring **[10][BBr$_4$]** when two equiv. of BBr$_3$ are used in the C–H borylation step. This is important as it was found that conditions where borocations, *e.g.* **[10][BBr$_4$]**, are the dominant species (over neutral species *e.g.* **10-Br**) give better amide reduction outcomes using SiHEt$_3$ (see Fig. S32†). This is attributed to the carbonyl carbon in borenium cations such as **[10][BBr$_4$]** being more electrophilic than that in neutral derivatives (*e.g.* **10-Br**) which will facilitate reduction. Attempts to monitor the reduction of **[10][BBr$_4$]** by *in situ* NMR spectroscopy were not informative as these reactions formed complex mixtures from which no intermediate borane could be identified. However, the addition of pinacol or 1,8-diaminonaphthalene (Dan) to these mixtures formed **11-Pin** and **11-Dan**,

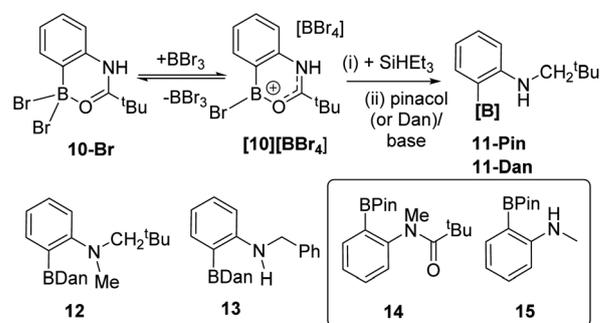**Scheme 3** Formation of boron-enolate **7** from **3**.

Fig. 6 Top, reduction of **[10][BBr$_4$]**. Bottom left, additional substrates isolated as Dan derivatives. Inset, substrate **14** used in Zn catalysed amide reduction, and **15** one of the products from that process.

respectively (Fig. 6), as the major boron compounds (by NMR spectroscopy *versus* an internal standard, Fig. S33†). Other aniline derivatives, including a tertiary amide and an *N*-benzoyl congener, also were amenable to this borylation/reduction process. The products were protected and isolated as the Dan derivatives, **11-Dan**, **12** and **13**, due to the enhanced stability of these BDan congeners relative to the BPins (the latter proved sensitive to column chromatography). The ability to vary the protecting group installed on boron (*e.g.* Pin or Dan) is an attractive feature of this approach and is distinct to iridium-catalysed routes which are limited generally to BPin due to the use of B_2Pin_2.[22] Furthermore, attempts to access these products cleanly by amide reduction of the BPin containing arylamide **14** (Fig. 6 inset), was not effective. The reduction of **14** under mild conditions $(Zn(OAc)_2/(EtO)_3SiH)$[23] led to the formation of multiple ArylBPin species, with their ratios dependent on the equiv. of silane used. The major products were the desired **12-Pin** and **15** (by *in situ* NMR spectroscopy, Fig. S34†), but conditions leading to clean formation of **12-Pin** or **15** were not identified.

To expand the borylation–reduction scope it was applied in the previously reported *N*-benzoyl directed C1 borylation of carbazole.[21] This one pot borylation–reduction process enabled formation of **16** in 61% yield (Fig. 7, inset), with **16** containing an *N*-benzyl group that can be readily removed. Carbazoles, including C1-functionalised derivatives,[24] are prevalent in organic electronics where they are often *N*-substituted with alkyl chains to enhance solubility. Therefore, the applicability of borylation–reduction to access *N*-alkyl-1-borylated-carbazoles was assessed. N–H-carbazole was functionalised to form **17** and this derivative underwent acyl directed borylation with BBr3 and protection at B to afford **18** in 93% isolated yield. This in itself is notable as it is the first report of an enolisable acyl unit being successfully used in amide directed electrophilic C–H borylation to our knowledge. Applying borylation–reduction to **17** afforded **19** in 53% yield. The formation of **19** from **17** in one-pot represents a streamlined route to access useful C1-bory-lated-*N*-alkylated carbazoles compared to previous methods (which proceed *via* formation of the C1-brominated precursor and then lithiation–borylation).[24]

Doubly functionalised diamino-arenes also are useful building blocks,[25] therefore the extension of this process to double amide directed C–H borylation products was investigated. Substrates **20** and **21** (Scheme 5) were synthesised *via*
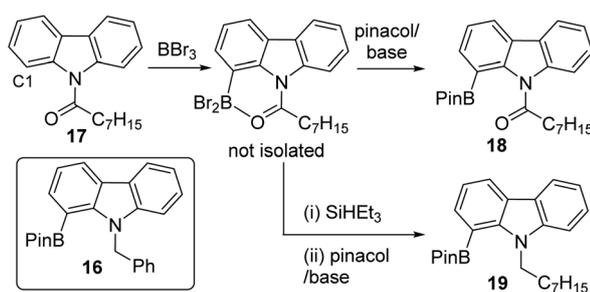
Scheme 5 (i) Borylation with BBr3 followed by protection at boron; (ii) borylation with BBr3, reduction with SiHEt3 and then protection.

standard methodologies and found to undergo double directed electrophilic borylation using BBr3 to afford **22** and **23** in good isolated yields (80 and 83%, respectively). Incorporating a reduction step prior to protection at boron enabled formation of **24** and **25** in moderate yields (24 and 40%, respectively). The double borylation of the naphthyl derivative **21** at the C2/6 positions in preference to the *peri*-positions was confirmed by single crystal X-ray diffraction studies on compound **25** (see Fig. S119†). The solid-state structure of **25** is unremarkable, excluding the fact that the nitrogen atoms are pyramidalised (*e.g.* C–N–C = 115.14(7)°), something we attribute to pyramid-alisation being required to permit the N–H···OB_Pin intra-molecular hydrogen bond (2.024(9) Å) that is present in the structure of **25**. The selective formation of the 2,6-diborylated isomers (**23** and **25**) is consistent with the preference for forming six membered boracycles over seven membered during electrophilic borylation (the latter would be required to borylate at the *peri* position of **21**).[1a]

Borylation–reduction of diaryl borane derivatives

While a range of substituents on the amide are tolerated in borylation–reduction all the examples above have very similar substituents at boron in the borenium cation being reduced, specifically in each case boron is substituted with an aryl, a bromine and a carbonyl. We were interested in determining if altering one substituent at boron in the borocation was compatible with selective amide to amine reduction. Therefore, a directed C–H borylation was targeted where a single boron centre performs two C–H borylations to generate a borocation substituted with two aryl groups (*e.g.* compound **D**, Fig. 8 left). If reducible this amide would form species **E** (right, Fig. 8) and compounds related to **E** are of current interest as they are B,N containing PAHs that have a reactive site at B and at N thus would facilitate further reactivity *e.g.* for making rigid "pre-organized" intramolecular FLPs[26] or emissive B,N-PAHs.[27]

However, embedding Lewis acidic centres into rigid PAHs can dramatically alter their reactivity.[28] Therefore the HIA was calculated at boron and carbon for **D**. This revealed the HIA at

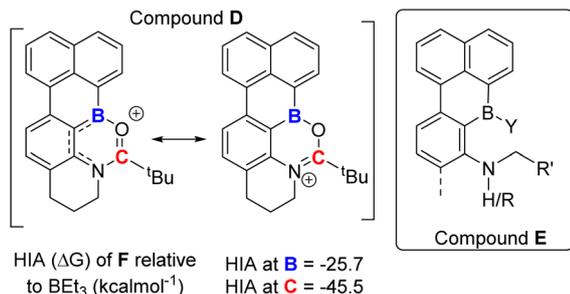**Fig. 7** The C1 borylation–reduction of *N*-acyl carbazoles.

Fig. 8 Lewis acidity of diaryl-borane derived cations.

boron in **D** is significantly reduced relative to that in **1**[+] (Fig. 3), while the carbonyl carbon possesses a high HIA (Fig. 8), comparable to that in **1**[+]. The disparity between the HIA values at boron and carbon in **D** is attributed to the *N*-(alkyl)aryl amide structure (in contrast to the *N*-dialkyl amide unit in **1**[+]) which will result in the N lone pair being delocalised to some extent into the extended π system (Fig. 8, left-hand resonance structure). This is supported by the calculated structures, which revealed a longer (O)C–N bond and a shorter aryl–B bond in **D** relative to that in **1**[+], consistent with the relative Lewis acidity at boron and carbon in **D**. Regardless, the high HIA at carbon in **D** indicates reduction of amide to amine is feasible.

Two precursors, **26-THQ** and **26-Me** (top, Fig. 9), were synthesised in two steps from commercial precursors. Both are designed so that amide directed C–H borylation can only incorporate the boron centre in the correct position for a second C–H borylation at the naphthalene *peri* position. The latter step is expected to be facile based on our previous work.[29] Indeed, the addition of two equiv. BBr$_3$ to **26-THQ** in DCM at room temperature led to the precipitation of **27-THQ**, with the formulation supported by single crystal X-ray diffraction analysis (*vide infra* for discussion). Similarly, the addition of two equiv. BBr$_3$ to **26-Me** led to precipitation of a yellow solid, assigned as **27-Me**. Both **27-THQ** and **27-Me** were sufficiently soluble in CD$_2$Cl$_2$ to produce weak NMR spectra that displayed resonances consistent with their formulation, *e.g.* δ_{11B} = +36.5 (broad) and −24.4 for **27-THQ** and +36.0 (broad) and −24.4 for **27-Me**. The sharp −24.4 ppm resonance is due to [BBr$_4$]$^-$ and confirms borenium ion formation, as expected based on the low (relative to **1**[+]) Lewis acidity calculated at boron in **D**. The ^{1}H NMR spectra for both compounds **27** contained eight 1H integral resonances in the aromatic region as expected.

The addition of two equiv. of SiHEt$_3$ to suspensions of **27-THQ** led to gradual dissolution and formation of a single major product containing a three and a four-coordinate boron centre (by NMR spectroscopy). This species was isolated by crystallisation, and analysis by X-ray diffraction revealed formation of **28-THQ**. In **28-THQ** the amide has been reduced to an amine, but the product has not undergone B–O cleavage. Instead the B and N centres are bridged by a [O–BBr$_2$]$^-$ moiety, presumably derived from an O–BHBr$_2$ intermediate (as proposed in the conversion from **3** to **C**, Scheme 2). The formulation as **28-THQ** from X-ray diffraction studies is fully consistent with the ^{11}B
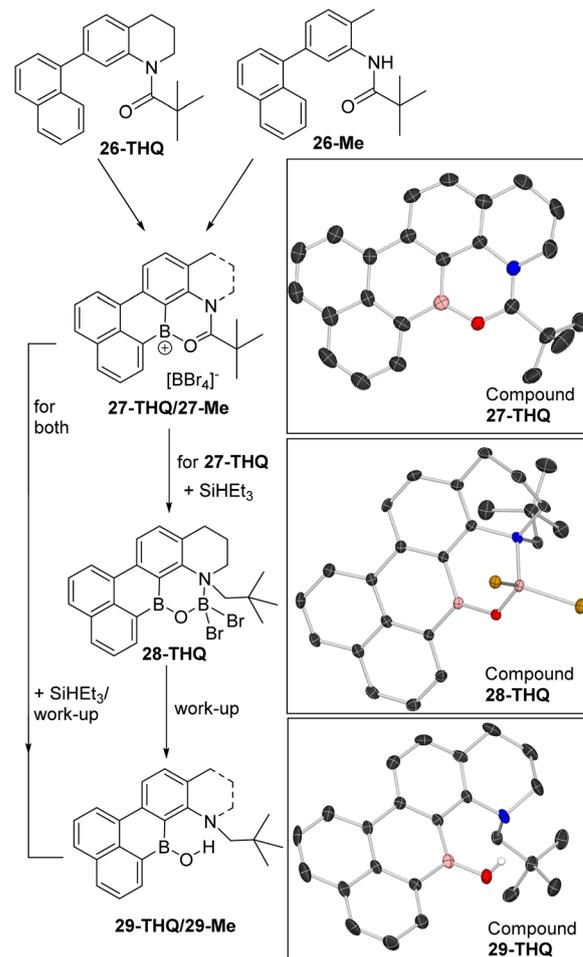

Fig. 9 Double borylation–reduction–hydrolysis to form B,N-containing PAHs **29-THQ** and **29-Me**. Right, solid state structures, ellipsoids at 50% probability and most hydrogens omitted for clarity.

NMR spectrum which contained resonances at +40.6 and +6 ppm, for a three and a four coordinate boron centre, respectively. Due to the chiral N in **28-THQ** the methylene protons are diastereotopic in the ^{1}H NMR spectrum, while there remain eight aromatic resonances.

Starting from **27-Me**, *in situ* NMR spectroscopy revealed a complex mixture is formed post reduction with SiHEt$_3$, but the mixture can be converted into the borinic acid **29-Me** in 78% yield by treatment with aqueous base. Compound **29-Me** displayed a δ_{11B} at +41.1 in the expected region, while a δ_{1H} singlet at +11.95 was observed for the B–OH which is consistent with a borinic acid O*H* in a rigid environment containing a BO···H–N hydrogen bond.[30] **29-THQ** can be accessed analogously from **28-THQ** by aqueous basic work up, or in a one pot process directly from **27-THQ** in 67% isolated yield. **29-THQ** has a comparable δ_{11B} (+40.9 broad) and δ_{1H} (+11.92) for the B–OH unit. The formation of compounds **29** demonstrates that it is possible to access B/N containing PAHs using the directed borylation–reduction methodology, including an example containing the modifiable groups, N–H and a B–OH as in **29-Me**.
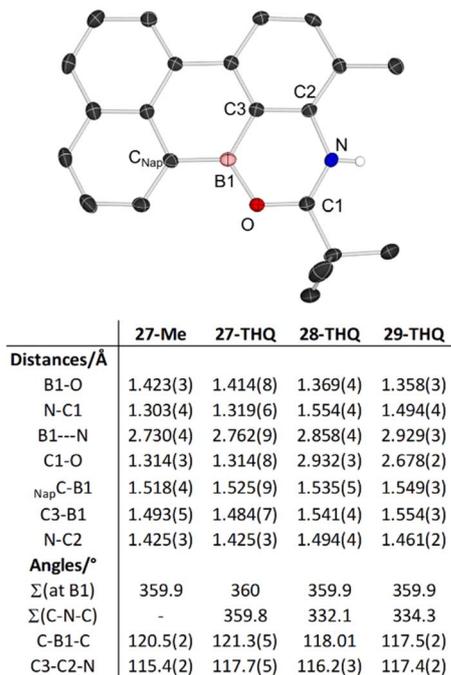
	27-Me	27-THQ	28-THQ	29-THQ
Distances/Å				
B1-O	1.423(3)	1.414(8)	1.369(4)	1.358(3)
N-C1	1.303(4)	1.319(6)	1.554(4)	1.494(4)
B1---N	2.730(4)	2.762(9)	2.858(4)	2.929(3)
C1-O	1.314(3)	1.314(8)	2.932(3)	2.678(2)
$_{Nap}$C-B1	1.518(4)	1.525(9)	1.535(5)	1.549(3)
C3-B1	1.493(5)	1.484(7)	1.541(4)	1.554(3)
N-C2	1.425(3)	1.425(3)	1.494(4)	1.461(2)
Angles/°				
Σ(at B1)	359.9	360	359.9	359.9
Σ(C-N-C)	-	359.8	332.1	334.3
C-B1-C	120.5(2)	121.3(5)	118.01	117.5(2)
C3-C2-N	115.4(2)	117.7(5)	116.2(3)	117.4(2)

Fig. 10 Top, the solid-state structure of the cationic portion of **27-Me**, ellipsoids at 50% probability, most hydrogens omitted for clarity. Bottom, select metrics.

In addition to **27–29-THQ**, **27-Me** also was crystallised and analysed by X-ray diffraction studies (Fig. 10, top). Analysis of the key metrics for **27-Me** revealed them to be closely comparable to **27-THQ** (Fig. 10 bottom), therefore the structural discussion only focuses on the **27–29-THQ** series. In all the structures the boron centre is effectively trigonal planar, with the shortest anion···cation contact in **27-THQ** long at Br···B = 3.610(6) Å. **27-THQ** can be viewed as having a core that is a main group analogue of perylene and the all sp² pentacyclic core in **27-THQ** is effectively planar (max. deviation from the plane of the pentacycle = 0.12 Å), with the geometry at N effectively trigonal planar. This is in contrast to the geometry at N in **28-** and **29-THQ**, with N significantly pyramidalised in both. While this is expected for **28-THQ**, for **29-THQ** the N is pyramidalised due to the N···H–OB interaction. Other noteworthy metrics include: (i) the B–O distance being longest in the datively bonded system, **27-THQ**; (ii) significant (0.17 Å) variation in the *trans*-annular B···N distances, indicating some flexibility in this system despite its fused nature; (iii) the B1–C3 distance being significantly shorter in cationic **27-THQ**, whereas the C$_{Nap}$–B distances varies to a much lesser degree across the series. This indicates some delocalisation from the N to the Lewis acidic boron centre in **27-THQ**. Finally, the effect on stability (to protodeboronation) of embedding the boron centre into a fused amino-substituted PAH was assessed. Reactivity studies confirmed that **27-THQ** and **27-Me** are significantly more robust towards protodeboronation than the borinic acid Ph$_2$BOH and the non-fused 1-BPin-2-NR$_2$-C$_6$H$_4$ systems. For example, in contrast to the latter two compounds **27-THQ** does not react on

prolonged exposure to basic or acidic aqueous solutions (by NMR spectroscopy).

In conclusion, this work demonstrates that amides can function as modifiable directing groups in electrophilic C–H borylation. Post borylation using BBr$_3$, the addition of an hydrosilane to the crude reaction mixture enables reduction of the amide to an amine while maintaining the C–B bond(s). This process proceeds *via* borenium cations that are Lewis acidic at both boron and the carbonyl carbon, but hydride transfer occurs selectively to carbon (in the absence of significant bulk on the amide). Post reduction, the products are useful as the C–B unit can be oxidised *in situ* to the respective phenol or protected at boron to give synthetically ubiquitous aryl boronate esters (as BPin or BDan derivatives). Notably, this amide directed electrophilic borylation–reduction process represents a simple route to form aryl boranes (*e.g.* compound **19**) that can be made currently only *via* convoluted routes. By applying borylation–reduction to a range of substrates an initial mechanistic picture has emerged that indicates a stepwise reduction, where the second reduction step proceeds not from a hydrosilane, but from a HBBr$_2$ species made *in situ*. Notably, amide reduction is applicable to a range of amide→B containing borenium cations, with substituent variation tolerated at both the amide and around boron. The latter enables borylation–reduction to be used to access novel B,N-functionalised PAHs that contain reactive functionalities on both N and B. This will facilitate further functionalisation and thus enable application of these materials in FLP catalysis and as emissive organic materials, both topics currently under exploration in our laboratory.

Data availability

The data supporting this article has been uploaded as part of the ESI.†

Author contributions

MI, SI and MU conceived the research concept and aims and analysed all data. SI and MU performed the majority of the synthetic work and the majority of the analytical components of this project. IN, ZW, HJ, and CM also performed the synthesis and characterisation of a number of compounds reported in this manuscript. GN and MU collected and solved all the crystal structures. KY performed the computational analysis. Combined, MI, MU, SI and GC drafted, reviewed and edited the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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