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Metal-free Selective Borylation of Arenes by a Diazadiborinine via C–H/C–F Bond Activation and Dearomatization

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Supporting Information Placeholder

ABSTRACT: A newly developed annulated 5-chlorinated 1,3,2,5-diazadiborinine derivative (**4**) selectively activates a C–H bond of benzene (C_6H_6) and 1,3-di(trifluoromethyl)benzene, as well as, a C–F bond in partially fluorinated arenes, to furnish borylation products under the catalyst-, metal-, and irradiation-free condition. Moreover, **4** readily undergoes a reversible dearomative coupling reaction with polycyclic aromatic hydrocarbons to afford diboration products. The latter represents the first reversible intermolecular dearomative diboration of arenes.

Organoboranes are ubiquitous in various organic transformations being found as synthetic intermediates, and hence, its simple and convenient synthesis has received significant attention.[1] Among them, direct borylation of non-activated aromatic hydrocarbons has been the subject of a number of landmark studies over the past several decades, as it represents straightforward conversion of inert raw materials into value-added chemical building blocks. To achieve this task, various transition metal catalysts, as well as, other metal-containing molecules, have been dominantly employed for borylation of arenes.[2,3]

On the other hand, metal-free borylation of aromatic hydrocarbons has been described in the literature,[4] that involve (i) C–H bond borylation of arenes **I** under heating and Lewis acidic conditions or irradiation of light (Figure 1a),[5] (ii) photo-induced C–F bond borylation of fluoroarenes **II** (Figure 1b),[6] (iii) intramolecular dearomative borylation of tetracoordinate boron species **III** and **IV** by photochemical reaction or intermolecular trapping of borylene **V** (Figure 1c).[7,8,9] Despite recent progress in this area, facile metal-free borylation of C–F bonds of aromatic hydrocarbons, especially without photolysis, still remains extremely challenging, and to our knowledge, intermolecular and thermally reversible dearomative borylation is hitherto unprecedented. Recently, we have reported that annulated 1,3,2,5-diazadiborinine **VI** featuring a relatively small HOMO–LUMO gap (2.84 eV) cleavages the H–H bond of dihydrogen and an N–H bond of ammonia under mild conditions (Figure 1d).[10] With this approach in hand, we envisaged that reducing the steric congestion around the boron center of 1,3,2,5-diazadiborinine would allow access to the more reactive derivative, which may be applied for metal-free borylation of arenes, even without photo irradiation. Herein, we report the synthesis, single crystal X-ray diffraction analysis and computational studies of a 5-chlorinated 1,3,2,5-diazadiborinine (Figure 1e). We also present its reactivity towards a series of aromatic hydrocarbons and partially fluorinated arenes.

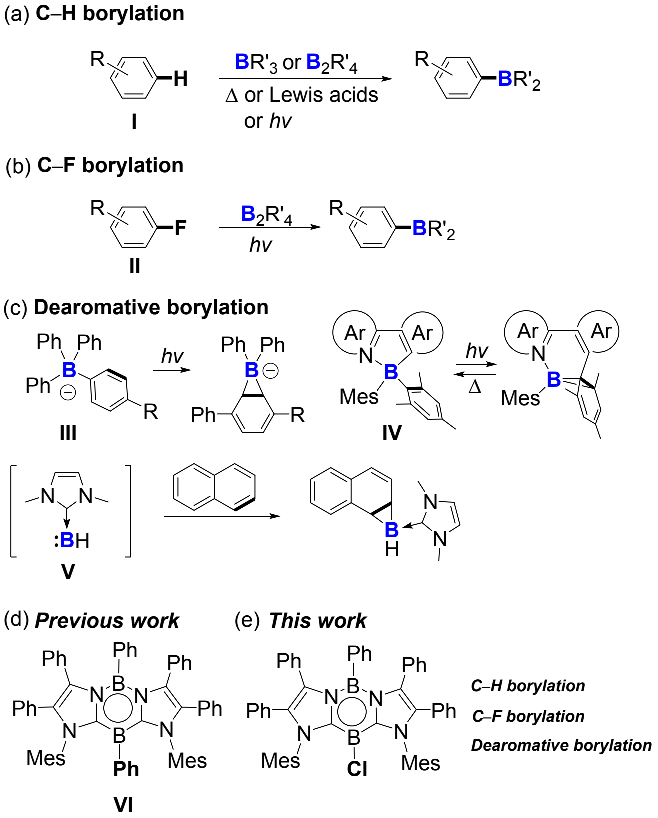
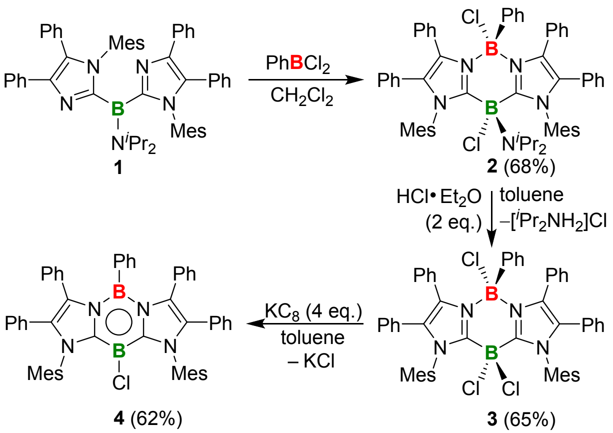


Figure 1. Reported examples of metal-free borylation of arenes via (a) C–H bond activation, (b) C–F bond activation, and (c) photo-induced dearomatization. (d) Our previous work, and (e) present work.

We began our investigation with the preparation of 1,3,2,5-diazadiborinine featuring a small Cl substituent on the boron atom between two carbon atoms (Scheme 1). Treatment of compound **1** with one equivalent of dichlorophenylborane gave compound **2** in 68% yield, which was further reacted with two equivalents of hydrogen chloride, affording a 2,5,5-trichloro-1,3,2,5-diazadiborinine derivative **3** as a white powder in 65% yield. Reduction of **3** with four equivalents of potassium graphite in toluene under ambient condition afforded, after work up, 5-chlorinated 1,3,2,5-diazadiborinine derivative **4** as an orange powder in 62% yield. Spectroscopically, the ^{11}B NMR spectrum of **4** displays a singlet for the boron atom between two carbon atoms at δ = 10.5 ppm and a broad peak for the boron between two nitrogen atoms at δ = 25.8 ppm, both of which are shifted downfield relative to those of the precursor **3** (δ = –6.2 and 4.0 ppm), and comparable to those of **VI** (δ = 9.8 and 25.4 ppm).[10] Structurally, **4** features a geometry (Figure 2), which is nearly identical to that of **VI**. Nevertheless, the space-filling model of **4** clearly shows the steric congestion around the boron atom between two carbon atoms is significantly less than that of **VI**, owing to the replacement of the phenyl group in **VI** by the smaller chloride in **4**. Theoretically, the energy gap between the HOMO and the LUMO (Figure S98) of **4** is estimated to be 2.85 eV, which is comparable to that (2.84 eV) of **VI**. [10]



Scheme 1. Synthesis of 5-chlorinated 1,3,2,5-diazadiborinine **4** (Mes = 2,4,6-trimethylphenyl).

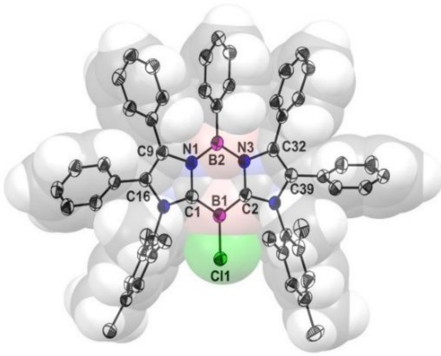
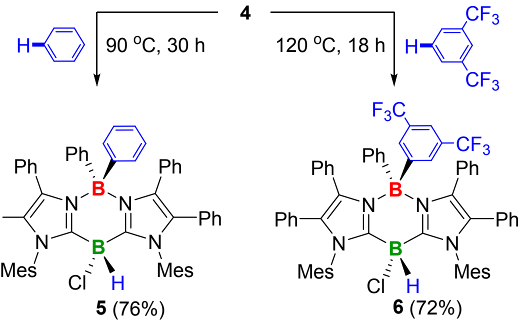


Figure 2. Solid-state structure of **4** (Hydrogen atoms are omitted for clarity), overlaid with the Space-filling model.

Next, we examined the reactivity of **4** towards benzene and its derivative (Scheme 2). Heating a benzene solution of **4** at 90 °C for 30 h led to a colorless solution. After workup, compound **5** was isolated as a white solid in 76% yield. Analogously, treatment of **4** with 1,3-di(trifluoromethyl)benzene at 120 °C afforded compound **6** as a white powder in 72% yield. Compounds **5** and **6** have been characterized by standard spectroscopic, analytical and crystallographic methods, confirming that the aryl group is attached on the boron between two nitrogen atoms and the H atom forms a bond with the boron atom between two carbon atoms. Both the aryl group and the H atom on the boron atoms are on the same side with respect to the $B_2C_2N_2$ six-membered ring, indicating that the C–H activation proceeds regio-and stereoselectively. Note that formation of **5** and **6** represents the first examples of C–H activation of arenes by diazadiborinine.[11] DFT calculations at the M06-2X/Def2-SVP level shows that C–H activation of benzene by **4** may proceed in a concerted manner with the activation barrier of 24.4 kcal·mol^{-1} (Figure 3). NBO analysis indicates that the Mulliken charge of the boron between two nitrogen atoms is more positive than that of the boron between two carbon atoms (Figure S99 and Table S3), supporting the regioselectivity of the reaction.



Scheme 2. Reactions of **4** with benzene and 1,3-di(trifluoromethyl)benzene.

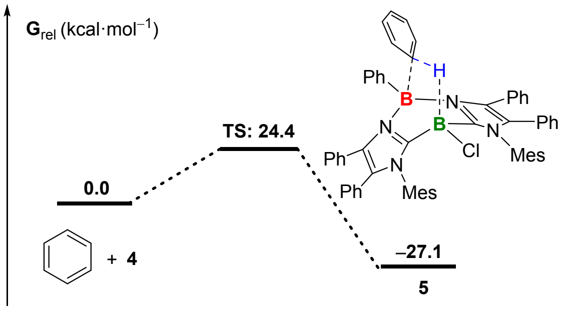
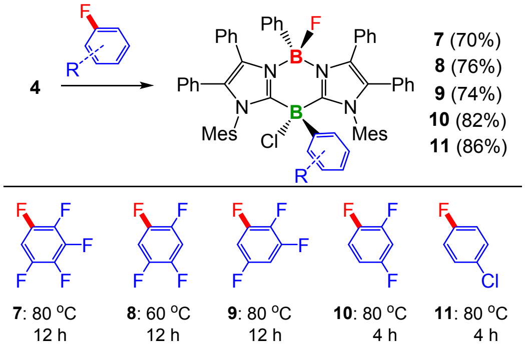


Figure 3. Plausible reaction pathway for the formation of **5**.

Interestingly, when partially fluorinated arene derivatives were employed as the reactants, chemoselective C-F bond activation was observed (Scheme 3).[3, 12] Thus, treatment of **4** with pentafluorobenzene at 80 °C for 12 h afforded **7** in 70% yield. In the ^{11}B NMR spectrum of **7**, two broad resonances were detected at –11.0 and 4.8 ppm. The ^{19}F NMR spectrum of **7** displays four multiplets at –129.3 ppm, –143.2 ppm, –160.4 ppm and –161.6 ppm for the fluorine atoms substituted on the arene ring and one broad singlet at –153.8 ppm for the boron-bound fluorine atom. The *C*H in the fluorinated aryl group is signaled at 115.1 ppm in the ^{13}C (DEPT135) NMR spectrum and 6.14 ppm in the ^{1}H NMR spectrum, respectively. An X-ray diffraction analysis revealed that **7** is formed via the cleavage of a C–F bond of pentafluorobenzene (Figure S74). The fluorinated aryl group is bound to the boron atom between two carbon atoms and the fluorine atom is attached on the boron atom between two nitrogen atoms with the B–F bond distance of 1.406(4) Å, which are on the same side with respect to the B2C2N2 six-membered ring. Previous experimental and computational studies have indicated that activation of the C–F bond in pentafluorobenzene typically becomes more favorable in the order *para* > *meta* > *ortho* fluorine atom with respect to C–H bond.[3, 12] In marked contrast, the C–F bond cleavage of pentafluorobenzene by **4** regioselectively occurred at *ortho* position with respect to the C–H bond, the least plausible position. Similarly, the C–F bond activation over the C-H bond cleavage was observed in the reaction of **4** with 1,2,4,5-tetrafluorobenzene, and **8** was obtained in 76% yield. Treatment of **4** with less fluorinated arenes, such as 1,2,3,5-tetrafluorobenzene and 1,2,4-trifluorobenzene, afforded **9** (74% yield) and **10** (82% yield), respectively, the regioselectivity of which are also in contrast to the previous reports (Scheme 3). Moreover, when 1-chloro-4-fluorobenzene was employed, **4** cleaved the C–F bond, rather than the weaker C–Cl bond, to furnish **11** in 86% yield.



Scheme 3. Reactions of **4** with partially fluorinated arenes.

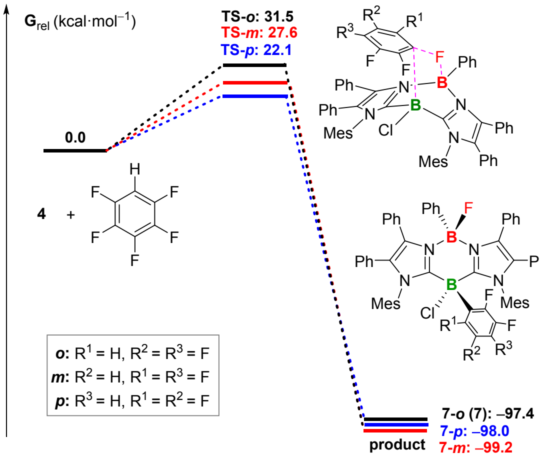
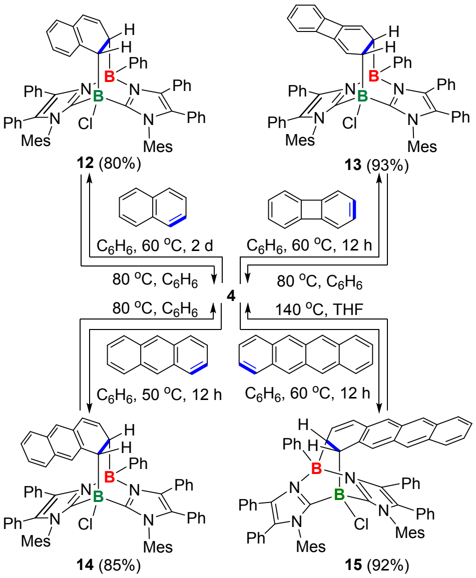


Figure 4. Concerted C–F bond activation of pentafluorobenzene by **4**.

To gain insight into the reaction mechanism, the pathways for the reaction of **4** with pentafluorobenzene were explored theoretically using M06-2X/Def2-SVP functional (Figure 4). The activation barriers for the direct C-F bond cleavage are found to be 31.5 kcal·mol⁻¹ (**TS-*o***), 27.6 kcal·mol⁻¹ (**TS-*m***) and 22.1 kcal·mol⁻¹ (**TS-*p***), respectively, which is inconsistent with the experimentally observed *ortho*-C–F bond activation, and thus unlikely to occur. In addition, **7-o** is also predicted to be the thermodynamically least stable isomer, thus, **7-o** may be formed through a kinetically controlled pathway (Figure S102). While the detail of the selectivity of the reaction is still unclear, the symmetry of the frontier molecular orbitals, charge distribution in the substrates, as well as, the steric factor, would affect the activation barrier of the rate-determining step (for Mulliken charges and MOs of 1,2,4,5-$C_6F_4H_2$, 1,2,3,5-$C_6F_4H_2$, 1,2,4-$C_6F_3H_3$, *p*-C_6ClFH_4, see Table S3).

While no intermediates were experimentally detected during the formation of compounds **5–11**, dearomative diboration products were obtained from the reactions of **4** with polycyclic aromatic hydrocarbons (Scheme 4). Thus, treatment of **4** with excess amount of naphthalene exclusively afforded **12** in 89% yield, which was fully characterized by standard spectroscopic and analytical techniques, and its structure in the solid state was determined by single-crystal X-ray diffraction (Figure S79). The carbon atoms at the 1- and 2-position of naphthalene regioselectively bind to the boron between two carbon atoms and the boron between two nitrogen atoms in **4**, respectively. Remarkably, upon heating a C_6D_6 solution at 80 °C for 3.5 h, **12** undergoes a retro[4+2] cycloaddition to reproduce **4** and naphthalene in a equilibrium. Van't Hoff Analysis revealed the free energy of **12** (ΔG = -11.6 kcal·mol⁻¹, ΔH = -26.5 kcal·mol⁻¹, ΔS = -50.1 cal·mol⁻¹·K⁻¹) is lower than that of **4** and naphthalene (Figures S67 and S68). Analogously, reactions of **4** with biphenylene, anthracene, and tetracene readily afforded the dearomatic product **13** (93% yield), **14** (85% yield), and **15** (92% yield), respectively, and all products **13–15** were thoroughly characterized (Figure S80-82). Two boron atoms in **4** regioselectively bind to the carbons at the 2- and 3-position of biphenylene to afford **13**, and at the 1- and 2-position of anthracene and tetracene to form **14** and **15**, respectively, all of which are formed by binding at the thermodynamically favored positions of the substrates.[13] Analogous to **12**, compounds **13–15** undergo retro [4+2] cycloaddition reactions at 80–140 °C to regenerate **4** and the corresponding arene in an equilibrium process. Note that the formation of **12–15** represents the first examples of intermolecular and thermally reversible dearomative diboration of arenes.[8,14,15]



Scheme 4. Reactions of **4** with polycyclic aromatic hydrocarbons.

In summary, we have demonstrated that an annulated, 5-chlorinated 1,3,2,5-diazadiborinine **4** selectively cleaves the C–H bond in arenes and C–F bond in partially fluorinated arenes, as well as, undergoes reversible dearomative coupling reaction with polycyclic aromatic hydrocarbons. The former represents a rare example of metal-free borylation of arenic C–F bonds whereas the latter can be viewed as dearomative diboration.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Complete experimental data and computational details including Cartesian coordinates for stationary points (PDF) Crystallographic data (CIF) of **1-15** (ZIP) [CCDC: 1916645-1916659].

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Notes

The authors declare no competing financial interests.

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(15) For the influence of the Cl-substituent on the B atom in **4**, see the Supporting Information.

SYNOPSIS TOC