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configuration as judged by its dihedral angles (0.0–5.6°) with the N1–B1–N2 bond angle of 116.3°, which indicates the boron center has a nearly ideal sp<sup>2</sup> hybridized orbital.<sup>14</sup> In addition to the B(sp<sup>2</sup>) character,<sup>15</sup> effective overlapping between the vacant p-orbital and lone pairs on the adjacent nitrogens results in sufficient diminishment of the B-Lewis acidity: the shorter B1–N2 (1.411 Å vs B1–N1 1.441 Å) bond is suggestive of more contribution of the aniline nitrogen to the diminishment. On the other hand, the presence of the less donative amide nitrogen is responsible for the residual B(aam)-Lewis acidity as compared with (pin)B–B(dan)<sup>16</sup> having more planar sixmembered ring (dihedral angles: 0.1–2.5°) with the B–N bond lengths of 1.420 and 1.425 Å (Fig. 2).<sup>17</sup>



**Fig. 1** Solid-state structure of (pin)B–B(aam) with 50% probability ellipsoids. All of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B1–B2 1.700, B1–N1 1.441, B1–N2 1.411, N1–C3 1.376, N2–C1 1.390, C1–C2 1.407, C2–C3 1.468, N1–B1–N2 116.4, B1–N1–C3 124.4, B1–N2–C1 122.1, N1–C3–C2 116.3, N2–C1–C2 120.1, C1–C2–C3 120.5.



**Fig. 2** Solid-state structure of (pin)B–B(dan) with 50% probability ellipsoids. All of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B1–B2 1.715, B1–N1 1.420, B1–N2 1.425, N1–C2 1.405, N2–C3 1.403, C1–C2 1.432, C1–C3 1.429, N1–B1–N2 116.2, B1–N1–C2 123.8, B1–N2–C3 123.2, N1–C2–C1 117.6, N2–C3–C1 118.1, C2–C1–C3 121.1.

With the new diboron in hand, we carried out the Miyaura-Ishiyama-type reaction with 4-bromotoluene in 1,4-dioxane under palladium catalysis and found that selective B(aam) transfer occurred quantitatively to give 4-MeC<sub>6</sub>H<sub>4</sub>B(aam) (1a) by 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl using (XPhos), as a supporting ligand (Entry 1, Table 2). The borylation proceeded with exclusive chemoselectivity, and thus a product having a B(pin) moiety was not generated at all. Other electronrich monodentate phosphines (PCy<sub>3</sub>, PtBu<sub>3</sub>, and CyJohnPhos) than tBuXPhos could also promote this transformation (Entries 2-5), and moreover the use of dppf only gave a comparable yield of 1a among bidentate ligands surveyed (Entries 6-11). No desired product was formed under ligand-free conditions, verifying the necessity of a phosphine ligand in the B(aam) transfer (Entry 12).

A variety of aryl bromides were found to be directly convertible into the respective Ar–B(aam) under the optimum conditions: the reaction of bromotoluenes or bromoanisoles afforded **1a–1f** in high yield, regardless of the positions of the methyl or methoxy substituent (Table 3). It should be noted



°Conditions: 4-bromotoluene (0.225 mmol), (pin)B–B(aam) (0.150 mmol) Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (3.75  $\mu$ mol), ligand (0.0113 mmol), KOAc (0.450 mmol), 1,4dioxane (0.5 mL), 60 °C, 18 h. <sup>b</sup>GC yield. <sup>c</sup>4-Bromotoluene (1.2 eq), Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (1 mol%), XPhos (3 mol%), 12 h (Li's conditions, ref. 7f).

that even electron-rich aryl chlorides underwent the B(aam) installation to give 1a (53%) and 1d (63%), and high functional group tolerance of the reaction was demonstrated by employing aryl bromides having such a relatively reactive moiety as NH<sub>2</sub>, OH, SiMe<sub>3</sub>, SMe or Ac (1g-1k). The reaction was also applicable to benzodioxole, indole and fused aromatic compounds to furnish 11-1p, and 3-thienylB(aam) (1q) could be prepared in moderate yield. The versatility of the B(aam) transfer was well illustrated by the reaction of 2bromopyridines, which resulted in the smooth formation of diverse 2-pyridylB(aam) (1r-1x) as isolable and bench-stable compounds, being in marked contrast to the unstable properties of the corresponding boronic acids and boronates.18,19 The competitive reaction by using (pin)B-B(aam) and (pin)B-B(dan) was also conducted (Scheme 1): 1a and 4-MeC<sub>6</sub>H<sub>4</sub>B(dan) were formed in 40 and 39% yield, these respectively, indicating similar reactivities of unsymmetrical diborons in the present borylation.

As depicted in Scheme 2, 2-pyridylB(aam) (**1r**) could not be synthesized by the conventional dehydrative condensation of 2pyridylB(OH)<sub>2</sub> and aam,<sup>9</sup> probably owing to a considerable tendency to be protodeborylated,<sup>18</sup> which demonstrates the superiority of the present reaction. The synthetic utility of 2pyridylB(aam) (**1t**) has preliminarily been illustrated by deprotection-free cross-coupling with 4-bromotoluene under aqueous conditions (Scheme 3).<sup>20</sup>

The present reaction would be commenced by oxidative addition of an aryl halide to a palladium(0) catalyst, that gives an Ar–Pd–X (**2a**) complex, as is the case of the conventional Miyaura–Ishiyama borylation (Scheme 4).<sup>2,7f</sup> Subsequent counter anion exchange between **2a** and potassium acetate

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#### Table 3 Substrate scope on aryl halides<sup>a</sup>



<sup>α</sup>Isolated yield. Conditions: aryl halide (0.225 mmol), (pin)B–B(aam) (0.150 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (3.75 μmol), XPhos (0.0113 mmol), KOAc (0.450 mmol), 1,4dioxane (0.5 mL), 60 °C, 18 h. <sup>b</sup>from aryl chloride. <sup>c</sup>100 °C. <sup>d</sup>dppf was used instead of XPhos.



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Scheme 3 Deprotection-free cross-coupling with 2-pyridylB(aam)

provides Ar–Pd–OAc (**2b**), which is then exclusively converted into an Ar–Pd–B(aam) (**2c**) through  $\sigma$ -bond metathesis with (pin)B–B(aam). The sole formation of **2c** can be rationally explained by selective interaction of the acetoxy moiety with the Lewis acidic B(pin) moiety in a similar manner to the cheomselective  $\sigma$ -bond metathesis between a copper alkoxide complex and (pin)B–B(dan), operative in the Cu-catalyzed B(dan)-installing reactions.<sup>7b,c,g-i</sup> Finally, an Ar–B(aam) is produced through reductive elimination with regeneration of a palladium(0) complex. Although an alternative pathway that involves initial formation of Ar–B(pin)<sup>21</sup> followed by pin–aam exchange might be possible, this possibility could be excluded by the reaction of 4-(pin)BC<sub>6</sub>H<sub>4</sub>Br with (pin)B–B(aam), where 4-(pin)BC<sub>6</sub>H<sub>4</sub>B(aam) (**1y**) was solely produced with the B(pin) moiety remained intact (Scheme 5).



Scheme 4 Catalytic cycle for B(aam)-installing borylation



In conclusion, we have developed the new unsymmetrical diboron having contrasting boron-Lewis acidities, (pin)B–B(aam), that can be utilized for the palladium-catalyzed B(aam) installation via the chemoselective Miyaura–Ishiyama-type coupling with aryl halides, leading to the direct and convenient access to diverse Ar–B(aam). Further studies on catalytic

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borylation reactions with (pin)B–B(aam) via chemoselective B(aam) transfer are in progress.

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## **Conflicts of interest**

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There are no conflicts to declare.

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- 13 An insoluble and unidentified product was also formed in the diboron synthesis, which resulted in the moderate yield of (pin)B-B(aam).
- 14 The diboron was found to exist as two molecular structures having different N1–B1–B2–O1 torsion angles in solid state, and Fig. 1 shows one of them for simplification. See Supplementary information for details.
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- 19 2-PyridylB(aam) (1r-1x) can stably be isolated by Florisil column chromatography in an open atmosphere.
- 20 This result is contrary to the previous cross-coupling with Ar– B(aam), which requires prior acidic deprotection (see ref. 9). Details of the deprotection-free cross-coupling will be reported in due course.
- 21 We could not detect Ar–B(pin) even in the early stage of the reaction described in Table 3.

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