Direct Introduction of a Dimesitylboryl Group Using Base-Mediated Substitution of Aryl Halides with Silyldimesitylborane

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Abstract: The first Dimesitylboryl substitution of aryl halides with a silylborane bearing a dimesitylboronyl group in the presence of alkali-metal alkoxides is described. The reactions of aryl bromides or iodides with Ph2MeSi–BMes2 and Na(OtBu) afforded the desired arylidimesitylboranes in good to high yields and with high borylation:silylation ratios. Selective reaction of the sterically less-hindered C–Br bond of dibromoarenes provided monoborylated products. This reaction was used to rapidly construct a D–π–A dimesitylborylarene with a non-symmetrical biphenyl spacer.

Boron-containing π-conjugated compounds have received considerable attention as an important class of organic materials[1] with uses such as emissive materials,[2] two-photon absorption materials,[3] ion sensors,[4] electron-transporting materials,[5] and nonlinear optical materials.[6] The unique optical properties of these compounds arise from the π–π* conjugation between the vacant p-orbital of the boron atom and the π* orbital of the attached carbon π-conjugated moieties. A dimesitylboryl (BMes2) group has been employed in most of these compounds because of its strong π-electron accepting ability and air stability. The routes to access aryldimesitylborane are highly limited despite considerable efforts to develop methods to synthesis organoboron compounds.[7-10] The most popular synthesis of arylidimesitylboranes involves nucleophilic substitution of dimesitylboryl electrophiles (Mes2BX, X = halogen or OR) with organometallic compounds (ArM, M = Li, Mg). Aryldimesitylboranes are also synthesized by reaction of aryl boronic acid esters and MesLi.[11] These reactions are laborious and must be individualized for each aryldimesitylborane prepared. The use of organometallic reagents limits reaction scope and these reagents require multi-step syntheses, with low total yields (Scheme 1a). There are no direct methods to synthesize ArBMes2 from ArX. We recently reported a transition-metal-free boryl substitution of organohalides using (phenyldimethylsilyl)pinacolborane [Ph2MeSi–B(pin)] and an alkoxy base. This reaction allows the direct boryl substitution of aryl, alkyll, alkenyl and heteroaryl halides without using organometallic reagents.[12] We expected that the use of a silyl borane[13] with a diarylboronyl group instead of B(pin) could provide a potent complementary method for the synthesis of triarylboranes. Herein, we report the first direct dimesitylboryl substitution of aryl halides using (diphenyldimethylsilyl)dimesitylboryl (Ph2MeSi–BMes2)[14] and Na(OtBu), which provides the corresponding arylidimesitylboranes in good to high yield with high borylation:silylation (B:Si) ratios (Scheme 1b).


We initially reacted 1-bromo-4-ethylbenzene 2a with Ph2MeSi–BMes2 and an alkoxy base (Table 1) using conditions previously optimized for (pinacolato)borylation.[12b] The reaction of 2a with Ph2MeSi–BMes2 (1.5 equiv) and KOMe (1.2 equiv) in DME at 30 °C provided the corresponding borylated and silylated products 3a and 4a, respectively, in 28% total yield with a 4a:3a ratio of 39:61 (entry 1). The yields and B:Si selectivity were largely dependent on the solvents and bases used for the reaction. The use of 1,4-dioxane:hexane (1:1) and Na(OtBu) provided the substituted products in high yield with high B:Si selectivity (entry 2, total 80% yield, B:Si = 90:10, isolated yield of 3a: 57%). It is worthy of note that a high stirring speed (800 rpm) is important to assure the product yield. When neat 1,4-dioxane was used, the yield and selectivity were slightly lower (entry 3, 78%, B:Si = 87:13). The use of hexane resulted in no reaction (entry 4). Performing the reaction in DME resulted in exclusive silyl substitution (entry 5, 24%, B:Si = 0:100). Performing the reaction at 30 °C reduced the yield and selectivity (entry 6, 33%, B:Si = 86:14). The use of the alternative bases Li(OtBu) and K(OtBu) afforded very little substituted products (Table 1, entries 7 and 8). Using a less bulky base (NaOMe) promoted the reaction, albeit with lower yield and B:Si selectivity compared with those achieved using Na(OtBu) (entry 9, 76%, B:Si = 77:23). Attempting the reaction with 1-chloro-4-ethylbenzene gave no expected products, while 1-ethyl-4-iodobenzene afforded the products in comparable yield and B:Si ratio to those achieved with 2a (entry 10 and 11, respectively).

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**[2]** Supporting information for this article is given via a link at the end of the document.
With the optimized conditions in hand, we proceeded to examine the substrate scope of this borylation (Table 2). Phenylbromide (2b) and 3-tolylbromide (2c) reacted to give the corresponding borylated products 3b and 3c, respectively, in good yields with good B:Si selectivities [3b: 74(72)%, B:Si = 91:9, 3c: 83(66)%, B:Si = 92:8]. 2-Tolylbromide (2d) reacted with lower yield and selectivity [3d: 54%, B:Si = 89:11]. Naphthylbromide provided the borylated product in good yield with good selectivity [3e: 70(66)%, B:Si = 96:4]. Substrates containing an electron-donating methoxy or dimethylamino group afforded the expected products in high yields with high selectivity [3f: 87(73)%, B:Si = 90:10]. Substrates containing a chloro or trifluoromethyl group, also proceeded to give the products in good yield [3g: 74(50)%, B:Si = 94:6]. Reaction of electron-deficient substrates, such as those containing a chloro or trifluoromethyl group, also provided the corresponding products in moderate to high yields [3h: 80(42)%, B:Si = 90:10, 3i: 58(49)%, B:Si = 84:16]. The use of substrates bearing an aromatic alkene or alkyn moiety afforded the corresponding products in moderate to high yields [3j: 79(61)%, B:Si = 89:11, 3k: 80(42)%, B:Si = 90:10, 3l: 54%, B:Si = 93:7]. Aryldimethylyboranes containing a terphenyl, 9,9-dimethylflourene or heteroaryl group also proceeded in good yield with high selectivity [3m: 54%, B:Si = 89:11, 3n: 79(61)%, B:Si = 89:11, 3o: 49(42)%, B:Si = 89:11]. Furthermore, substrate having a terminal epoxide 2p also underwent the reaction to provide the desired product in 69(55)% yield with a B:Si ratio of 80:20.

We proceeded to examine the selective dimetalsylationborylation of dihaloarenes. A directing group with a lone pair is necessary for selective mono-metallation of multi-halogenated arenes when using organometallic reagents. Mono-metallation is useful for short-step syntheses of various functionalized arenes. However, the necessity of the directing group strongly limits the reaction scope. When 1,4-dibromo-2-methylbenzene (2q) was subjected to our standard borylation conditions C4 was selective borylated in high yield with high B:Si selectivity [Scheme 2, 78(57)%, B:Si = 92:8, C4-substitution only]. Conventional lithiation-borylation procedures provided the borylated products with low site selectivity (90%, C1: C4 = 66:34, inseparable). Borylation of 2,4-dibromo-1-methylbenzene (2s) afforded the C4-substituted product 3s selectively, albeit in low yield. The sterically hindered iodide group of 4-bromo-1-ido-2-methylbenzene (2r) underwent exclusive boryl substitution to give product 3r in good yield with a high B:Si ratio [67(51)%, B:Si = 95:5].
The utility of this selective dimesitylborylation was demonstrated by the rapid construction of a donor-(π-spacer)-acceptor (D-π-A) system\textsuperscript{19} with a non-symmetrical biphenyl spacer (Scheme 3). Aryl bromide 3q was prepared in one step from dihaloarene 2q and successfully underwent Suzuki–Miyaura coupling using XPhos ligand to afford the corresponding new compound 5q in 90% yield. This good yield can be achieved only with the present synthetic procedure. The Mes$_2$B group is known to serve as an effective coupling partner under typical Suzuki–Miyaura coupling conditions,\textsuperscript{16} and unsatisfactory yields of desired coupling products using Pd(PPh$_3$)$_4$ have been reported in the literature,\textsuperscript{17} probably because of a competing undesired coupling process. We confirmed that the compound 5q shows strong luminescence in CH$_2$Cl$_2$ (emission quantum yield $\Phi_{em}$ is 36%, Figure S2) and in the solid state ($\lambda_{em,max}$ = 431 nm, $\Phi_{em}$ = 65%; Figure 1). It is noted that 5t also displays strong luminescence with higher $\Phi_{em}$ in the solid state ($\lambda_{em,max}$ = 421 nm, $\Phi_{em}$ = 95%; Figure 1).

A possible mechanism for our dimesitylboryl substitution is depicted in Scheme 4.\textsuperscript{12,18} Ph$_2$MeSi–BMes$_2$ initially reacts with Na(OtBu) to give the corresponding ate complex A. The nucleophilic Ph$_2$MeSi group of A attacks the bromine atom in the arylobromide to give the aryl anion intermediate B. Subsequent nucleophilic attack of the carbanion species to the boron atom in the Mes$_2$B(OtBu) affords triarylborane 3. This proposed mechanism follows the same process as the mechanism for boryl substitution with PhMe$_2$Si–B(pin) and an alkoxy base.\textsuperscript{12} However, the optimized conditions for dimesityl borylation are slightly different from those for the previously reported borylation [PhMe$_2$Si–B(pin) (1.5 equiv) and KOMe (1.2 equiv) in DME at 30 °C].\textsuperscript{12d} An important difference is that our reaction requires the sterically hindered tert-butoxide base to ensure high B:Si ratio, while the use of a small methoxide base is important for high B:Si ratio in the previously reported borylation. We speculated that the coordination of the solvent or additional alkoxy to the boron centre may affect the reactivity and selectivity because the dimesitylboryl group has stronger Lewis acidity than a pinacol boryl group.
In conclusion, we developed a method to synthesize aryl dimesitylboranes using Ph$_2$MeSi–BMes$_2$ and Na(OBu)$_2$ for the first time. This reaction afforded aryl dimesitylboranes in good to high yields with high B:Si ratios. In addition, the site-selective dimesitylborylation of dibromoaranes was achieved, which can provide rapid access to various aryl dimesitylboranes. The utility of this method was demonstrated by the synthesis of a D-n-A dimesitylborylamine with a non-symmetrical biphenyl spacer.

Acknowledgements

We thank Prof. Todd B. Marder for a fruitful discussion. This work was financially supported by the MEXT (Japan) program “Strategic Molecular and Materials Chemistry through Innovative Coupling Reactions” of Hokkaido University. This work was also supported by JSPS KAKENHI (grant numbers 15H03804, 15K13633 and 26-2447). E. Y. was supported by a Grant-in-Aid for JSPS Fellows.

Keywords: silylborane • triarylboration • boryl substitution • dimesitylboration • base-mediated boration


Scheme 4. A proposed mechanism.


Dimesitylboryl substitution of aryl halides using Ph$_2$MeSi–BMes$_2$ and Na(OtBu) was developed as a novel direct method to synthesize aryl dimesityl boranes. This reaction afforded aryl dimesityl boranes in good to high yields with high B:Si ratios. In addition, the site-selective dimesityl borylation of dibromoarenes was achieved, which can provide rapid access to various aryl dimesitylboranes.

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