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

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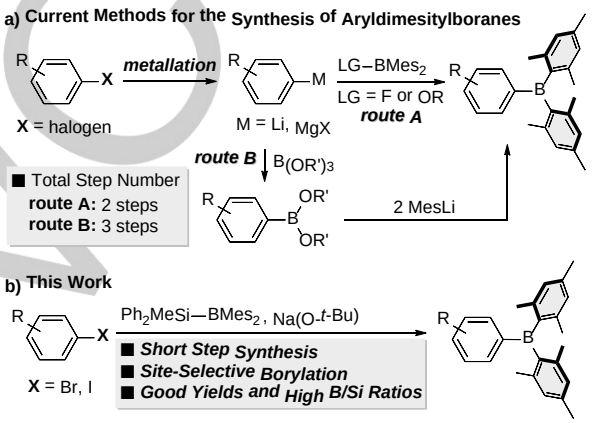
Abstract: The first Dimesitylboryl substitution of aryl halides with a silylborane bearing a dimesitylboryl group in the presence of alkali-metal alkoxides is described. The reactions of aryl bromides or iodides with $Ph_2MeSi–BMes_2$ and Na(O*t*Bu) afforded the desired aryldimesitylboranes in good to 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 dimesitylarylborane 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 pπ-π* conjugation between the vacant p-orbital of the boron atom and the π* orbital of the attached carbon π-conjugated moieties. A dimesitylboryl ($BMes_2$) 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 aryldimesitylboranes involves nucleophilic substitution of dimesitylboryl electrophiles (Mes_2BX, 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 $ArBMes_2$ from ArX. We recently reported a transition-metal-free boryl substitution of organohalides using (phenyldimethylsilyl)pinacolborane [$PhMe_2Si–B(pin)$] and an alkoxy base. This reaction allows the direct boryl substitution of aryl, alkyl, alkenyl and heteroaryl halides without using organometallic reagents.[12] We expected that the use of a silyl borane[13] with a diarylboryl 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 (diphenylmethylsilyl)dimesitylborane ($Ph_2MeSi–BMes_2$)[14] and Na(O*t*Bu), which provides the corresponding aryldimesitylboranes in good to high yield with high borylation:silylation (B:Si) ratios (Scheme 1b). Boryl substitution of the less sterically hindered bromo group of dibromoarene substrates was highly selective and gave monoborylated products. We demonstrate the utility of this method by rapidly constructing a D-π-A dimesitylarylborane containing a non-symmetrical biphenyl spacer.



Scheme 1. a) Current methods for the synthesis of aryldimesitylboranes. b) Direct dimesitylboryl substitution of aryl halide electrophiles with $Ph_2MeSi–BMes_2$/base.

We initially reacted 1-bromo-4-ethylbenzene **2a** with $Ph_2MeSi–BMes_2$ and an alkoxy base (Table 1) using conditions previously optimized for (pinacolato)borylation.[12a] The reaction of **2a** with $Ph_2MeSi–BMes_2$ (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(O*t*Bu) 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 (Table 1, 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(O*t*Bu) and K(O*t*Bu) 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(O*t*Bu) (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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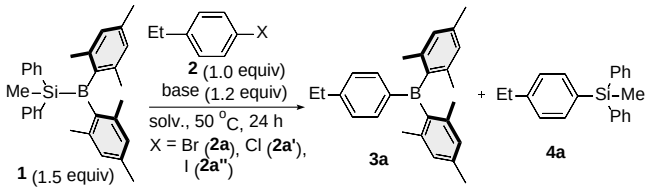
Table 1. Optimization of the reaction conditions.[a]

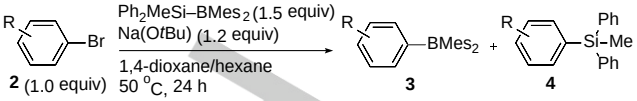


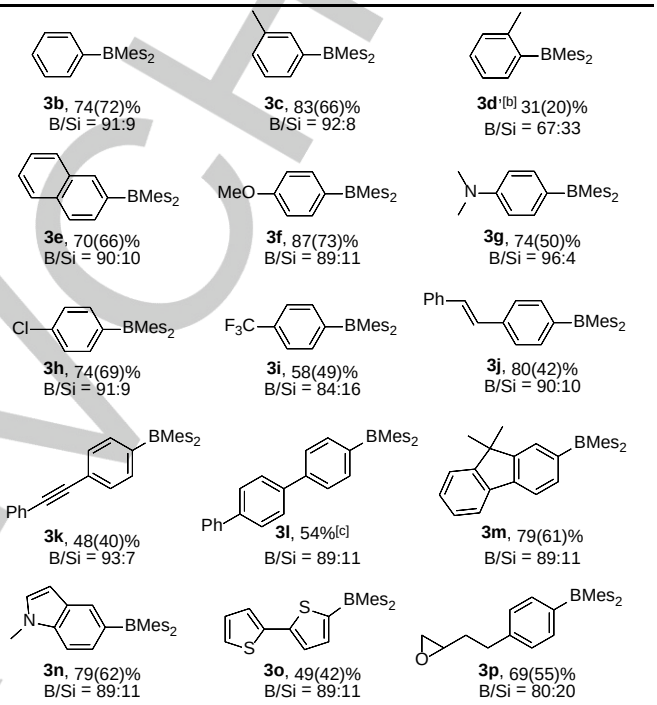
Entry	Solvent	Base	Total Yield (%)[b]	B:Si[c]
1	DME	KOMe	28	39:61
2	1,4-dioxane/hexane[e]	Na(O*t*Bu)	80 (57)[f]	90:10
3	1,4-dioxane	Na(O*t*Bu)	78	87:13
4	hexane	Na(O*t*Bu)	0	
5	DME	Na(O*t*Bu)	24	0:100
6[d]	1,4-dioxane/hexane[e]	Na(O*t*Bu)	33	86:14
7	1,4-dioxane/hexane[e]	Li(O*t*Bu)	0	
8	1,4-dioxane/hexane[e]	K(O*t*Bu)	2	30:70
9	1,4-dioxane/hexane[e]	NaOMe	76	77:23
10[g]	1,4-dioxane/hexane[e]	Na(O*t*Bu)	0	
11[h]	1,4-dioxane/hexane[e]	Na(O*t*Bu)	76	91:9

[a] Conditions: $Ph_2MeSi–BMes_2$ (0.30 mmol), aryl halide (0.20 mmol), base (0.24 mmol) in solvent (2 mL) at 50 °C. [b] GC yield (**3a**+**4a**). [c] B:Si ratio (**3a**:**4a**). [d] Reaction temperature: 30 °C. [e] 1:1 (v/v) Mixture of 1,4-dioxane and hexane solution was used. [f] Isolated yield of **3a** is shown in parentheses. [g] *p*-Chloroethylbenzene was used as a substrate. [h] *p*-Iodoethylbenzene was used as a substrate.

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**: 31(20)%, B:Si = 67:33]. 1-Naphthylbromide provided the borylated product in good yield with good selectivity [**3e**: 70(66)%, B:Si = 90:10]. Substrates containing an electron-donating methoxy or dimethylamino group afforded the expected products in high yields with high selectivity [**3f**: 87(73)%, B:Si = 89:11, **3g**: 74(50)%, B:Si = 96:4]. Reaction of electron-deficient substrates, such as those containing a chloro or trifluoromethyl group, also proceeded to give the products in good yield [**3h**: 74(69)%, B:Si = 91:9, **3i**: 58(49)%, B:Si = 84:16]. The use of substrates bearing an aromatic alkene or alkyne moiety afforded the corresponding products in moderate to high yields [**3j**: 80(42)%, B:Si = 90:10, **3k**: 48(40)%, B:Si = 93:7]. Aryldimesitylboranes containing a terphenyl, 9,9-dimethylfluorenyl or heteroaryl group also proceeded in good yield with high selectivity [**3l**: 54%, B:Si = 89:11, **3m**: 79(61)%, B:Si = 89:11, **3n**: 79(62)%, 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.

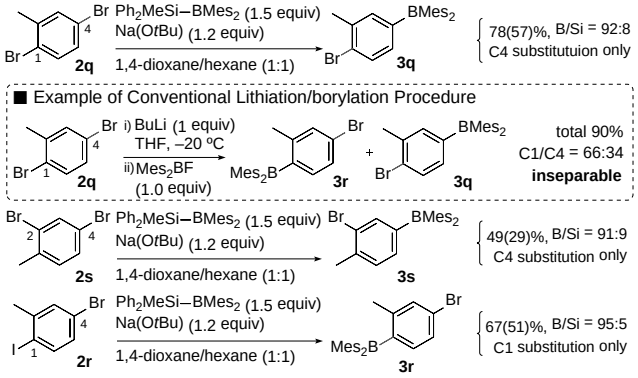
Table 2. Substrate scope: dimesitylborylation of aryl bromides with $Ph_2MeSi–BMes_2$ and Na(O*t*Bu).[a]





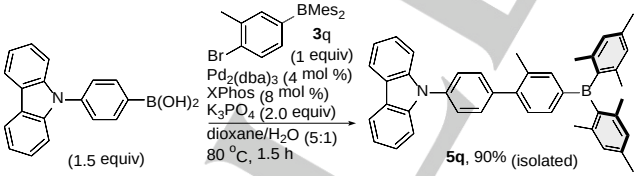
[a] Conditions: $Ph_2MeSi–BMes_2$ (0.30 mmol), aryl halide (0.20 mmol), Na(O*t*Bu) (0.24 mmol) in 1:1 (v/v) mixture of 1,4-dioxane and hexane (total 2 mL) at 50 °C for 24 h. Yield (**3**) and borylation:silylation ratios (**3**:**4**) are based on ^{1}H NMR analysis with isolated yields of **3** shown in parentheses. [b] Reaction time: 36 h. [c] Isolated yield of **3**.

We proceeded to examine the selective dimesitylborylation 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.[15] 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 iodo group of 4-bromo-1-iodo-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].



Scheme 2. Diarylborylation of dihaloarenes with $Ph_2MeSi–BMes_2$ and Na(O*t*Bu). Reactions were carried out at 50 °C for 24 h. Yield is based on ^{1}H NMR analysis of the crude products. Isolated yield of the borylated product is shown in parentheses. B:Si ratio and ratios of regioisomers were determined based on ^{1}H NMR analysis.

The utility of this selective dimesitylborylation was demonstrated by the rapid construction of a donor-(π-spacer)-acceptor (D-π-A) system[2d] 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_2B group is known to serve as an effective coupling partner under typical Suzuki–Miyaura coupling conditions,[16] and unsatisfactory yields of desired coupling products using $Pd(PPh_3)_4$ have been reported in the literature,[17] probably because of a competing undesired coupling process. We confirmed that the compound **5q** shows strong luminescence in CH_2Cl_2 (emission quantum yield Φ_{em} is 36%, Figure S2) and in the solid state ($\lambda_{em,max}$ = 431 nm, Φ_{em} = 65%; Figure 1). It is noted that **5t** also displays strong luminescence with higher Φ_{em} in the solid state ($\lambda_{em,max}$ = 421 nm, Φ_{em} = 95%; Figure 1).



Scheme 3. Rapid construction of a D-π-A dimesitylarylborane with a non-symmetrical biphenyl spacer.

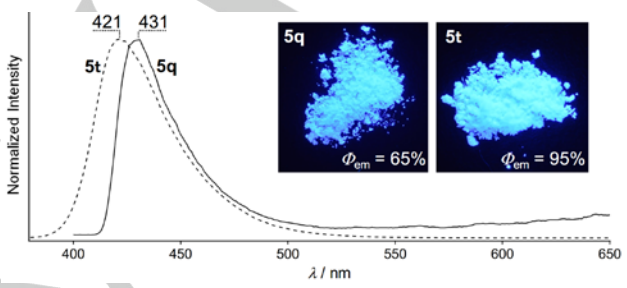


Figure 1. Emission spectra of **5q** and **5t** (λ_{ex} = 365 nm). Inset shows photographs of **5q** and **5t** taken under UV light.

Crystallographic analyses indicate that introduction of methyl group into a biphenyl bridge unit alter conformation of the resulting D-π-A compounds. X-ray diffraction analyses indicate that **5q** and **5t** crystallize into *I*2/*a* (monoclinic) and *P*-1 (triclinic) respectively (Figure 2, and see the SI for details), indicating that the methyl-substituted **5q** is in less symmetric crystalline lattice. **5q** exhibits rotational disorder at the methyl-substituted benzene ring (Figure 2). Conformations of molecules in two crystals **5q** and **5t** are different: dihedral angle of two benzene rings of biphenyl moiety of **5q**, which does not have methyl group, is 27.29°, while the corresponding dihedral angle of methyl-substituted **5t** is 70.49°. This would be the origin of the aforementioned lower Φ_{em} of **5q** (Figure 1) as well as lower melting temperature of **5q** (236 °C for **5q**; 262 °C for **5t**). This synthetic procedure can contribute the modified conformation of the "π" segment of D-π-A fluorophores and this may further result in the tuning of their solid structure and the photophysical properties.

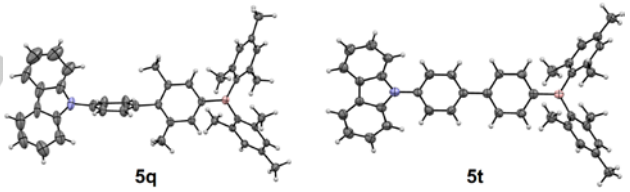
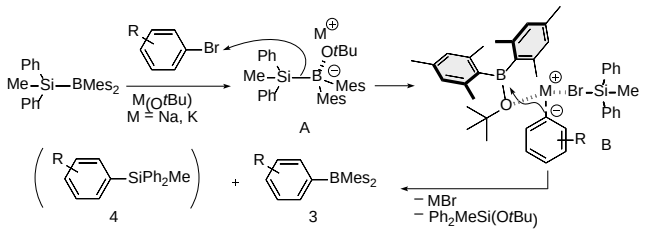


Figure 2. Single crystal structures of **5q** and **5t**. In **5q**, two methyl groups were observed because of the rotational disorder.

A possible mechanism for our dimesitylboryl substitution is depicted in Scheme 4.[12,18] $Ph_2MeSi–BMes_2$ initially reacts with Na(O*t*Bu) to give the corresponding ate complex **A**. The nucleophilic Ph_2MeSi group of **A** attacks the bromine atom in the arylbromide to give the aryl anion intermediate **B**. Subsequent nucleophilic attack of the carbanion species to the boron atom in the Mes_2B(O*t*Bu) affords triarylborane **3**. This proposed mechanism follows the same process as the mechanism for boryl substitution with $PhMe_2Si–B(pin)$ and an alkoxy base.[12] However, the optimized conditions for dimesityl borylation are slightly different from those for the previously reported borylation [$PhMe_2Si–B(pin)$ (1.5 equiv) and KOMe (1.2 equiv) in DME at 30 °C].[12a] 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 alkoxide to the boron centre may affect the reactivity and selectivity because the dimesitylboryl group has stronger Lewis acidity than a pinacol boryl group.



Scheme 4. A proposed mechanism.

In conclusion, we developed a method to synthesize aryldimesityl boranes using $Ph_2MeSi–BMes_2$ and Na(O*t*Bu) 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 dibromoarenes was achieved, which can provide rapid access to various aryl dimesitylboranes. The utility of this method was demonstrated by the synthesis of a D-π-A dimesitylarylborane with a non-symmetrical biphenyl spacer.

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Keywords: silylborane • triarylborane • boryl substitution • dimesitylborylation • base-mediated borylation

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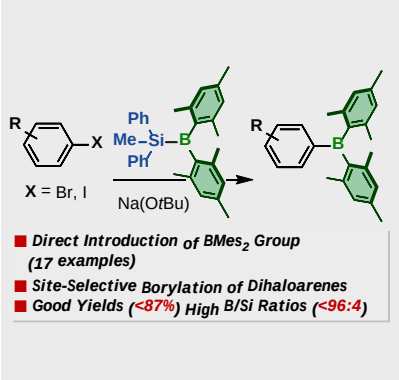
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Dimesitylboryl substitution of aryl halides using $Ph_2MeSi–BMes_2$ and Na(O*t*Bu) was developed as a novel direct method to synthesize aryldimesityl 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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Title: Direct Introduction of a Dimesitylboryl Group Using Base-Mediated Substitution of Aryl Halides with Silyldimesitylborane