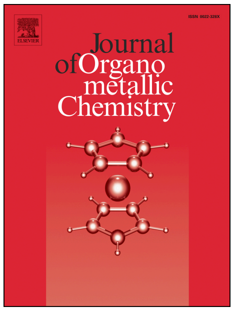

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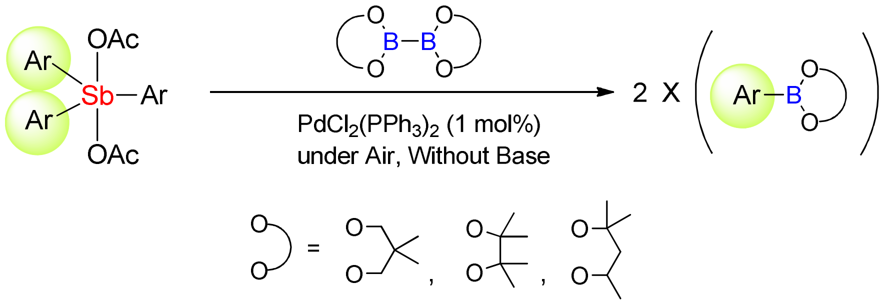
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Simple base-free Miyaura-type borylation of triarylantimony diacetates with tetra(alkoxo)diborons under aerobic conditions

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ABSTRACT

The reaction of triarylantimony diacetates with tetra(alkoxo)diborons in the presence of $PdCl_2(PPh_3)_2$ (1 mol%) catalyst resulted in the Miyaura-type B-arylation to form arylboronates in moderate to good yields under base-free conditions. In the present reaction, two of the three aryl groups of antimony reagent were transferred to the coupling products when the reaction was carried out under aerobic conditions, although only one of the three aryl group of the antimony reagent was involved under an argon atmosphere. The broad scope of the reaction was demonstrated by using a variety of triarylantimony diacetates with sterically hindered aryl groups and highly reactive *p*-bromo-functionalized aryl derivatives.

Keywords

Miyaura-type B-arylation
triarylantimony diacetate
tetra(alkoxo)diboron
base-free
aerobic condition

1. Introduction

Arylboronic acids and their esters are useful reagents in organic synthesis, particularly in Suzuki-Miyaura cross-coupling reaction, which is palladium-catalyzed carbon–carbon bond formation with organic halides [1-5]. Several procedures for the synthesis of arylboron derivatives have been reported. Among these, Pd-catalyzed cross-coupling reactions of tetra(alkoxo)diborons (i.e., Miyaura B-arylation) [6-20] and dialkoxyboranes (i.e., Masuda B-arylation) [21-29] with aryl halides, triflates, mesylates, tosylates and sulfonates have proved to be a powerful method for boron(B) –carbon(C) bond formation. However, in these B-arylation reactions, air sensitive boron reagents [$HB(OR)_2$] and a Pd-phosphine catalyst are employed along with stoichiometric or excess amount of bases. Strongin [30] and Andrus [31] have recently reported that aryldiazonium salts are useful arylating reagents for Pd-catalyzed B–C bond formation with tetra(alkoxo)diborons without any base, although an inert atmosphere is also required to carry out the reaction.

On the other hand, transition metal-catalyzed cross-coupling reaction by using organoantimony compounds as a pseudo-halide or a transmetallation agent has recently been the focus of attention. It has been reported that triarylantimony dicarboxylates $Ar_3Sb(OAc)_2$ are suitable arylating agents in Pd-catalyzed carbon–carbon(Ar) bond formation such as Heck- [32-34], Stille- [35], and Hiyama-type [36] reactions. In the past decade, we have also found that $Ar_3Sb(OAc)_2$ are efficient aryl donors in a base-free Suzuki-type cross-coupling reaction with arylboronic acids and triarylbismuthanes [37, 38]. Moreover, the reaction of $Ar_3Sb(OAc)_2$ with terminal alkynes could be conducted without any copper co-catalyst and base, and led to the Sonogashira-type reaction to form diarylacetylene derivatives [39]. However, transition metal-catalyzed carbon–heteroatom bond formation by using organoantimony compounds as pseudo-halides has only been reported to date for Cu-mediated O- [40, 41] and N-arylation [41, 42]. Herein, we present a novel base-free Pd-catalyzed B-arylation of pentavalent organoantimony compounds $Ar_3Sb(OAc)_2$ with tetra(alkoxo)diborons $[(RO)_2B]_2$. The reaction is simple and easily operated without special care in air and moisture. Furthermore, two of the three aryl groups on $Ar_3Sb(OAc)_2$ could be transferred to the coupling product $ArB(OR)_2$, when the reaction was carried out under aerobic conditions.

2. Results and discussion

We have recently studied the reaction of $Ar_3Sb(OAc)_2$ with terminal alkynes in the presence of $PdCl_2(PPh_3)_2$ under aerobic conditions in 1,4-dioxane to form diarylacetylenes, in which two of the three aryl groups on the antimony reagent are involved in the formation of the coupling products [39]. To search for suitable antimony reagents for the anticipated B-arylation, we first examined the reaction of **11a** with antimony(V) reagents (Ph_3SbX_2) having a variety of functional groups X. It was difficult to detect the disappearance of Ph_3SbX_2 and boron reagent by thin-layer chromatography (TLC) as well as gas chromatography (GC) methods. Therefore, the progress of the reaction was followed by monitoring the concentration of the cross-coupling (**12**) and homo-coupling product (**13**) products using GC-MS analysis with octadecane as an internal standard. The results are listed in Table 1. The reaction times were determined at the maximum yield of the products (**12**) and (**13**). The reaction of a variety of antimony compounds (**1–7**) with bis(neopentylglycolate)diboron (**11a**) (3 eq) was performed in the presence of $PdCl_2(PPh_3)_2$ catalyst (5 mol%) without any base under air atmosphere in 1,4-dioxane at 60 ºC (entries 1-7). Triphenylantimony dicarboxylates (**1a** and **2**) and dichloride (**4**) afforded the expected 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**12**) in good yields. It should be emphasized that in the present B-arylation, two of the three aryl groups were transferred from the antimony reagents to the coupling product (**12**), although one of the three aryl groups on the reagents was involved if the reaction was carried out under an argon atmosphere (see below). Among these, triphenylantimony diacetate (**1a**) was superior to the other antimony reagents (**2-7**) in terms of the reaction time and the yield of **12**. In the reactions with bismuth reagents (**8-10**), homo-coupling reaction of phenyl groups of the bismuth reagents took precedence over the expected cross-coupling reaction (entries 8-10). These results show that the nature of the central metal atom influences the outcome in the B-arylation. Compound **12** was obtained in satisfactory yields in all solvents examined in this work (entries 11-18). Dimethoxyethane (DME) was the best solvent for this reaction in terms of the yield of the cross-coupling product (**12**) (99%) and reaction time (3 h). As can be seen, decreaseing the catalyst loading from 5 mol% to 1 mol% did not affect the results, and the coupling product **12** was formed in 98% yield albeit after a longer reaction time (entry 12). We have also examined the same reaction using a variety of Pd-catalysts, such as $PdCl_2$, $Pd(OAc)_2$ $Pd(OAc)_2$-dppf, $Pd(PPh_3)_4$, and $Pd(dba)_2$-dppf. However, these catalysts did not provide better results. The addition of a base such as KOAc was ineffective in the present reaction and the yield of **12** was considerably decreased (42%). Consequently, the best results were obtained for the reaction of antimony reagent **1a** with the tetra(alkoxo)diboron compound **11a** (3 eq) in the presence of $PdCl_2(PPh_3)_2$ (1 mol%) catalyst under aerobic conditions in DME at 60 ºC (entry 12).

Table 1

In general, the electronic nature and steric bulk of the aryl halides and sulfonates have an impact on the Pd-catalyzed Miyaura B-arylation and Masuda B-arylation. For example, in the Miyaura-B-arylation, aryl donors with electron-donating group, such as *p*-NMe_2 and *p*-OMe, reduce the rate of the coupling reaction [6, 9, 10]. Moreover, the syntheses of 2-pyridyl, 2-thienyl, and 2-fulylboroates according to this protocol were unsuccessful, because such carbon–boron bond adjacent to a heteroatom is highly prone to protodeboronation in the presence of added bases [6]. On the other hand, Masuda B-arylation exhibits the opposite electronic effect: the aryl donors with electron-donating group enhance the rate of the B-arylation reaction [21-24]. Overcoming the drawbacks related to the electronic nature and steric demands of the aryl donors still remains a challenge in the transition metal-catalyzed B-arylation of boron compounds with appropriate aryl donors. Synthesis of the sterically hindered arylboronates by Masuda B-arylation was accomplished by using a $PdCl_2(CH_3CN)_2$-monophosphorous ligand catalytic system [26]. Very recently, efficient Miyaura B-arylation has also been achieved with sterically hindered aryl bromides and chlorides by using biaryl monophosphane having anthracenyl moiety, silica-supported phosphane and indolylphosphane as ligand for palladium. [17, 19, 20].

To study the scope and limitations of B-arylation under the optimal reaction conditions, we performed the reactions of alternative boron reagents, diborons (**11b, c**) and dialkoxyborane (**11d**), with various triarylantimony diacetates (**1a-i**) substituted with electron-donating and electron-withdrawing aryl groups as well as with sterically hindered aryl groups (Table 1, entry 12). The reaction time was fixed at 12 h, and the results are summarized in Table 2. The reaction of **1a** with diborons (**11b**, **c**) afforded the corresponding coupling products **14** and **15** in 72% and 83% yields, respectively (entries 1, 2). However, the reaction of **1a** with dialkoxyborane (**11d**) resulted in the reduction of **1a** to give triphenylstibane in 74% yield (entry 3) and did not form the coupling products (**12** and/or **13**). These results indicate that the tetra(alkoxo)diborons are useful coupling partners of **1a** for the preparation of arylboronate compounds. Various triarylantimony diacetates (**1b-i**) were reacted with **11a** under the same reaction conditions. All triaryldiacetates (**1b-i**) with electron-donating and electron-withdrawing groups attached to the aromatic ring afforded the corresponding cross-coupling products (entries 4-11). It has been reported that the electron-rich aryl bromides (e.g., 4-bromoanisole) are less reactive than electron-poor aryl bromides (e.g., 4-bromoacetophenone), in the Miyaura B-arylation [9]. Therefore, we have examined a competitive reaction using a mixture of electron-rich **1b** [$(4\text{-MeOC}_6\text{H}_4)_3\text{Sb(OAc)}_2$], electron-poor **1h** [$(4\text{-CF}_3\text{C}_6\text{H}_4)_3\text{Sb(OAc)}_2$], and **11a** [1 : 1 : 2 (1 : 1: 4)]. The reaction gave the B-arylated products **16** and **22** in 41% (73%) and 53% (79%) yields, respectively. These results indicate that, in the present reaction, the electron-poor **1h** is merely reactive compared to the electronic-rich **1b**.

Generally, B-arylation of sterically hindered aryl bromides or sulfonates with bis(pinacolato)diboron was difficult as noted above. In the present B-arylation with antimony reagent, tris(2-methylphenyl) and trimesityl antimony compounds (**1d** and **1e**) successfully produced the corresponding coupling products (**18**) and (**19**) in moderate yields after 12 h (entries 6, 7). This procedure was also applicable to the synthesis of 4-bromophenylneopentylglycolate boronate (**20**) with a highly reactive bromine moiety; treatment of **11a** with tris(4-bromophenyl)antimony diacetate (**1f**) gave the boronate (**20**) in 60% yield with the bromine moiety of **1f** remaining intact (entry 8). This result shows that the antimony–carbon(Ar) bond of **1f** is more reactive than the bromine–carbon(Ar) bond in this B-arylation reaction.

Table 2

As noted above, two of the three aryl groups on triphenylantimony diacetate (**1a**) transferred to the coupling products, when the B-arylation reaction was carried out under aerobic conditions. However, one aryl group of **1a** participated in the reaction under an argon atmosphere. To understand the mechanisms of the B-arylation in detail, we studied the influence of the reaction atmosphere on the yield of the coupling products. The reaction was performed using **1a**, **11a** (3 eq), and $PdCl_2(PPh_3)_2$ (5 mol%) in DME at 60 ºC. The reaction gave **12** in 99% yield after 5 h under an argon atmosphere. The 100% yield corresponds to the involvement of one phenyl group of **1a**. Introduction of air to the reaction mixture facilitated further reaction, and the yield of **12** reached to 182% yield after additional 10 h (Fig. 1). Similar results were obtained when the reaction was carried out under pure oxygen atmosphere. These results show that only one of the three phenyl groups on **1a** could contribute to the reaction under an inert atmosphere, whereas two of them could participate in the formation of **12** in the presence of oxygen. However, in the present B-arylation, the third phenyl group of **1a** could not be coupled with the boron atom even after a prolonged reaction time of 48 h.

Taking these results into consideration, we proposed that the mechanism of the present B-arylation reaction is similar to the mechanism of Sonogashira-type reaction between terminal alkynes and **1** reported in our previous paper [39]. As was reported by Gushchin and co-workers [32-34], the initial step would be oxidative addition of **1a** to the Pd(0) species (**A**) to form Pd-Sb complex (**B**) and followed by the transformation of **B** to $ArPdOAcL_2$ complex (**C**) accompanied by elimination of Ar_2SbOAc (**D**). The complex (**C**) is a key intermediate in Miyaura B-arylation [9]. Transmetallation between **C** and tetra(alkoxo)diboron (**11**) gives rise to the $ArPdB(OR)_2L_2$ intermediate (**E**) that undergoes reductive elimination to give the coupling product $ArB(OR)_2$ and regenerates the Pd(0) species **A** (Fig. 2). Recently, the generation of palladium peroxo complexes from Pd(0) species and molecular oxygen and its application to a variety of Pd-catalyzed oxidative reactions has been reported [43, 44]. Involvement of the second aryl group in the present reaction can be explained by the generation of Pd-peroxo complex (**F**) from **A** and molecular oxygen. The complex **F** formed in this way oxidizes **D** to pentavalent $Ar_2Sb(O)OAc$ (**G**), which would generates $ArPdOAcL_2$ complex (**C**) via the intermediate (**H**). Finally, **C** gives the product $ArB(OR)_2$, which is similar to the first catalytic cycle (Fig. 3).

Fig. 1, 2, and 3

3. Conclusion

In conclusion, we found that triarylantimony diacetates can be used as new effective B-arylating agents under simple and mild reaction conditions and without special requirement related to exogenous oxygen and moisture. It was shown that triarylantimony diacetates in the presence of transition metal-catalyst play as a versatile pseudo-halides not only in carbon–carbon(Ar) bond formation such as Suzuki- and Sonogashira-type cross-coupling but also in carbon–heteroatom (boron) bond formation. Further applications of the triarylantimony dicarboxylates and analogous pentavalent organoantimony compounds to other cross-coupling reactions such as Hirao-type P-arylation are currently under investigation, and these will be reported in the near future.

4. Experimental

4.1. General

Melting points were taken on a Yanagimoto micro melting point hot-stage apparatus (MP–S3) and are not corrected. ^{1}H-NMR (TMS: δ: 0.00 as an internal standard) and ^{13}C-NMR ($CDCl_3$: δ: 77.00 as an internal standard) spectra were recorded on a JEOL JNM–ECA400 (400 MHz and 100 MHz) spectrometers in $CDCl_3$. Mass spectra (MS) were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 μA). All chromatographic separations were accomplished with Silica Gel 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey-Nagel Pre-coated TLC plates Sil G25 UV_{254}. Triphenylantimony diacetate (**1a**) was purchased from TCI Fine Chemicals, Japan, and other triarylantimony diacetates such as **1b-e** [33], **1g** [38]**, 1h** [38], **1i** [45] were prepared according to the reported procedures.

4.2. Synthesis of tris(4-bromophenyl)antimony diacetate (*1f*)

A mixture of tris(4-bromophenyl)stibane (3.2 g, 5.4 mmol) and (diacetoxyiodo)benzene (1.92 g, 6 mmol, 1.1 eq) in dichloromethane (25 mL) was stirred for 24 h at room temperature. The solvent was concentrated under reduced pressure to small volume. Hexane (30 mL) was added and the solution was stirred in an ice bath. The solid was filtered and recrystallized from a mixture of benzene-dichloromethane (3 : 1) to give **1f** as colorless prisms (2.29 g, 60%). mp 131 ºC (decomp.). ^{1}H-NMR ($CDCl_3$) δ: 1.83 (6H, s, 2 x OAc), 7.61 (6H, d, J = 8.5 Hz, Ar-H), 7.80 (6H, d, J = 8.5 Hz, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 21.6 (q), 126.2 (s), 132.3 (d), 135.2 (d), 138.3 (s), 176.9 (s). IR (KBr) cm^{-1}: 1628 (C=O). LS-MS *m/z*: 648 (M-OAc$^+$). *Anal* Calcd for $C_{22}H_{18}Br_3O_4Sb$: C37.33; H, 2.56; Found: C37.24, H2.71.

4.3. Reaction of triarylantimony diacetates with tetra(alkoxo)diborons

A solution of triarylantimony diacetate (**1**: 0.5 mmol), tetra(alkoxo)diboron (**11**: 1.5 mmol), and dichlorobis(triphenylphosphine)palladium (II) (0.005 mmol) in DME (5 mL) was stirred at 60 ˚C for 12 h under air atmosphere. After dilution with CH_2Cl_2 (30 mL) and water (20 mL), the reaction mixture was separated and the aqueous layer was extracted with CH_2Cl_2 (30 mL x 2). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatograph on silica gel to give arylboronates (**12**, **14-23**). The products were confirmed by comparison of NMR data and MS spectra with that in the literature.

5,5-Dimethy-2-phenyl-1,3,2-dioxaborinane (**12**) [46]: Colorless plates. mp 62-64.5 ˚C (from MeOH). ^{1}H NMR ($CDCl_3$) δ: 1.04 (6H, s, Me), 3.78 (4H, s, CH_2), 7.27-7.44 (3H, m, Ar-H), 7.81 (2H, d, J = 6.9 Hz, Ar-H). LR-MS m/z: 204 (M^+).

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (**14**) [47]**:** Colorless oil. ^{1}H NMR ($CDCl_3$) δ: 1.35 (12H, s, Me), 7.36 (2H, t, J = 7.3 Hz, Ar-H), 7.46 (1H, t, J = 7.3 Hz, Ar-H), 7.81 (2H, d, J = 7.3 Hz, Ar-H). LR-MS *m/z*: 204 (M^+).

4,4,6-Trimethyl-2-phenyl-1,3,2-dioxaborinane (**15**) [20]: Colorless oil. ^{1}H NMR ($CDCl_3$) δ: 1.34 (3H, d, J = 6.4 Hz, Me), 1.36 (3H, s, Me), 1.37 (3H, s, Me), 1.58 (1H, t, J = 13.0 Hz, CH_2), 1.86 (1H, dd, J = 13.0 Hz, 3.0 Hz, CH_2), 4.33 (1H, m, CH), 7.30-7.41 (3H, m, Ar-H), 7.81 (2H, d, J = 6.9 Hz, Ar-H). LR-MS m/z: 205 (M^+).

5,5-Dimethy-2-(4-methoxyphenyl)-1,3,2-dioxaborinane (**16**) [46]**:** Colorless prisms. mp 54-56 ˚C (from MeOH). ^{1}H NMR ($CDCl_3$) δ: 1.01 (6H, s, Me), 3.75 (4H, s, CH_2), 3.82 (3H, s, OMe), 6.88 (2H, d, J = 8.7 Hz, Ar-H), 7.74 (2H, d, J = 8.7 Hz, Ar-H). LR-MS m/z: 220 (M^+).

5,5-Dimethy-2-(4-methylphenyl)-1,3,2-dioxaborinane (**17**) [46]: Colorless prisms. mp 93-95 ˚C (from MeOH). ^{1}H NMR ($CDCl_3$) δ: 1.02 (6H, s, Me), 2.36 (3H, s, Me), 3.76 (4H, s, CH_2), 7.17 (2H, d, J = 7.8 Hz, Ar-H), 7.69 (2H, d, J = 7.8 Hz, Ar-H). LR-MS m/z: 204 (M^+).

5,5-Dimethy-2-(2-methylphenyl)-1,3,2-dioxaborinane (**18**) [46]: Colorless oil. ^{1}H NMR ($CDCl_3$) δ: 1.03 (6H, s, Me), 2.51 (3H, s, Me), 3.77 (4H, s, CH_2), 7.13 (1H, d, J = 7.3 Hz, Ar-H), 7.14 (1H, t, J = 7.3 Hz, Ar-H), 7.27 (1H, t, J = 7.3 Hz, Ar-H), 7.72 (1H, d, J = 7.3 Hz, Ar-H). LR-MS m/z: 204 (M^+).

5,5-Dimethy-2-(2,4,6-trimethylphenyl)-1,3,2-dioxaborinane (**19**) [48]**:** Colorless oil. ^{1}H NMR ($CDCl_3$) δ: 1.08 (6H, s, Me), 2.23 (3H, s, Me), 2.35 (6H, s, Me), 3.77 (4H, s, CH_2), 6.77 (2H, s, Ar-H). LR-MS m/z: 220 (M^+).

2-(4-Bromophenyl)-5,5-dimethy-1,3,2-dioxaborinane (**20**) [49]: Colorless prisms. mp 110-112 ˚C (from MeOH). ^{1}H NMR ($CDCl_3$) δ: 1.02 (6H, s, Me), 3.76 (4H, s, CH_2), 7.48 (2H, d, J = 8.2 Hz, Ar-H), 7.65 (2H, d, J = 8.2 Hz, Ar-H). LR-MS m/z: 268 (M^+).

2-(4-Ethoxycarbonylphenyl)-5,5-dimethy-1,3,2-dioxaborinane (**21**) [50]: Colorless prisms. mp 97-100 ˚C (from MeOH). ^{1}H NMR ($CDCl_3$) δ: 1.03 (6H, s, Me), 1.40 (3H, t, J = 7.1 Hz, Me), 3.78 (4H, s, CH_2), 4.38 (2H, q, J = 7.1 Hz, CH_2), 7.86 (2H, d, J = 8.3 Hz, Ar-H), 8.01 (2H, d, J = 8.3 Hz, Ar-H). LR-MS m/z: 262 (M^+).

5,5-Dimethy-2-(4-trifluoromethylphenyl)-1,3,2-dioxaborinane (**22**) [51]**:** Colorless prisms. mp 97-100 ˚C (from MeOH). ^{1}H NMR ($CDCl_3$) δ: 1.03 (6H, s, Me), 3.79 (4H, s, CH_2), 7.59 (2H, d, J = 7.8 Hz, Ar-H), 7.90 (2H, d, J = 7.8 Hz, Ar-H). LR-MS m/z: 258 (M^+).

5,5-Dimethy-2-(2-thienyl)-1,3,2-dioxaborinane (**23**) [50]: Colorless prisms. mp 95-96˚C (from MeOH). ^{1}H NMR ($CDCl_3$) δ: 1.05 (6H, s, Me), 3.78 (4H, s, CH_2), 7.18 (1H, t, J = 4.1 Hz, Ar-H), 7.58-7.60 (2H, m, Ar-H). LR-MS m/z: 196 (M^+).

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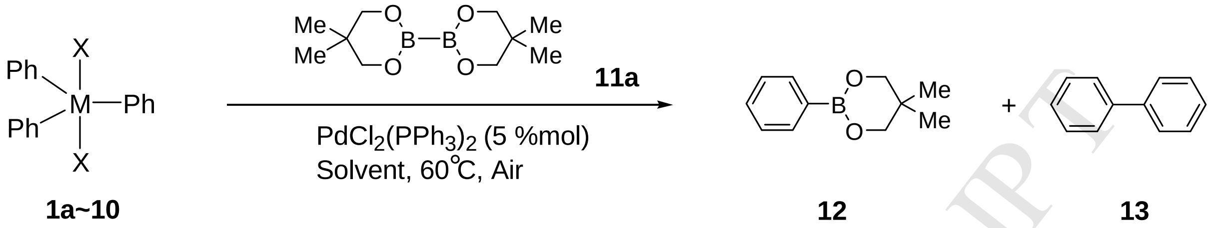
Table 1. Pd-catalyzed B-arylation of organoantimony and bismuth reagents **1a~10** with bis(neopentylglycolate)diboron **11a** [a]



Entry	Substrate	M	X	Solvent	Time (h)	**12** (%)[b]	**13** (%)[b]
1	**1a**	Sb	OAc	1,4-Dioxane	6	98	<1
2	**2**		OBz		6	86	1
3	**3**		OTs		6	48	2
4	**4**		Cl		24	95	2
5	**5**		Br		24	48	1
6	**6**		Ph		6	13	48
7	**7**		Null		24	3	6
8	**8**	Bi	OAc		6	49	66
9	**9**		Cl		6	39	43
10	**10**		Null		24	13	25
11	**1a**	Sb	OAc	DME	3	99 (95)[c]	<1
12 [d]				DME	12	98	< 1
13				THF	6	97	3
14				Toluene	6	98	<1
15				1,2-DCE	6	91	<1
16				CH_3CN	6	78	1
17				NMP	6	98	<1
18				EtOH	6	93	<1

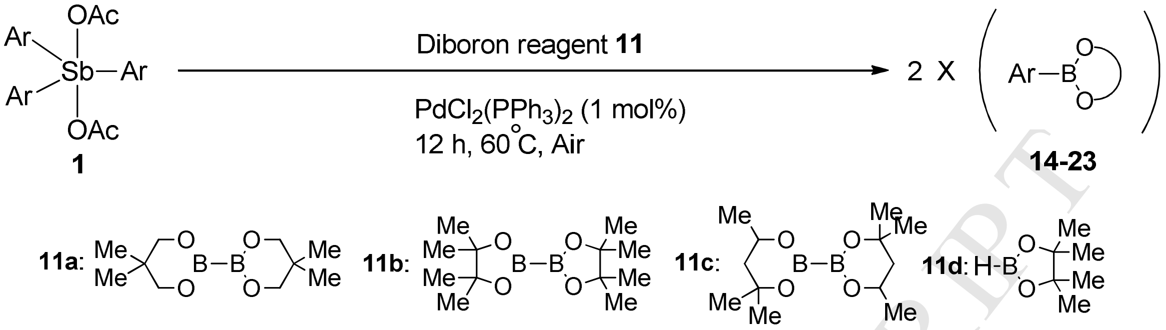
[a] Conditions: **1a-10** (0.5 mmol), **11a** (1.5 mmol).

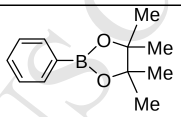
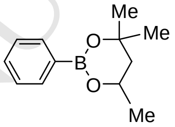
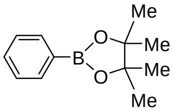
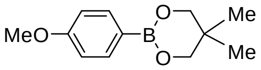
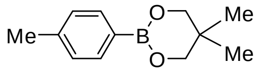
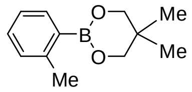
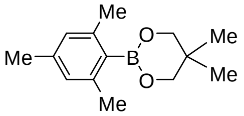
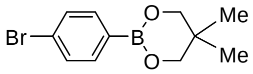
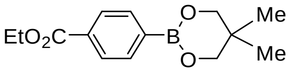
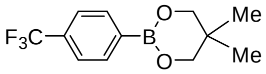
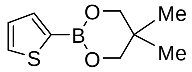
[b] GC yield using octadecane as internal standard. The yield 100% corresponds to the formation of 1 mmol of **12** and 0.75 mmol of **13**.

[c] Isolated yield.

[d] Pd catalyst (1 mol%).

Table 2. Pd-catalyzed Miyaura-type coupling reaction of triarylantimony diacetates **1** with diboron reagents **11**[a]



Entry	Sb reagent	Ar	Boron reagent	Product		Yield (%)[b]
1	**1a**	Phenyl	**11b**		**14**	72
2	**1a**	Phenyl	**11c**		**15**	83
3	**1a**	Phenyl	**11d**		**14**	0[c]
4	**1b**	4-Methoxyphenyl	**11a**		**16**	89
5	**1c**	4-Methylphenyl	**11a**		**17**	79
6	**1d**	2-Methylphenyl	**11a**		**18**	55
7	**1e**	2,4,6-Trimethylphenyl	**11a**		**19**	47
8	**1f**	4-Bromophenyl	**11a**		**20**	60
9	**1g**	4-Ethoxycarbonylphenyl	**11a**		**21**	80
10	**1h**	4-Trifluoromethylphenyl	**11a**		**22**	75
11	**1i**	2-Thienyl	**11a**		**23**	61

[a] **1** (0.5 mmol), **11** (1.5 mmol), $PdCl_2(PPh_3)_2$ (0.005 mmol).

[b] Isolated yield. The yield 100% corresponds to the involvement of two aryl groups on **1**.

[c] Triphenylstibane (Ph_3Sb) was isolated in 74% yield.

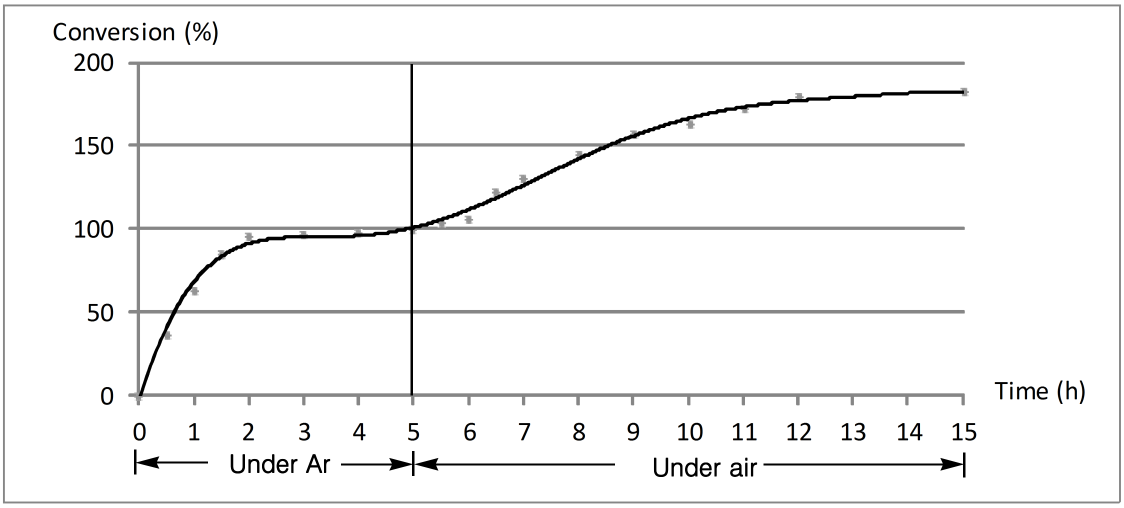


Fig. 1. Influence of atmosphere upon B-arylation of **11a** with **1a**

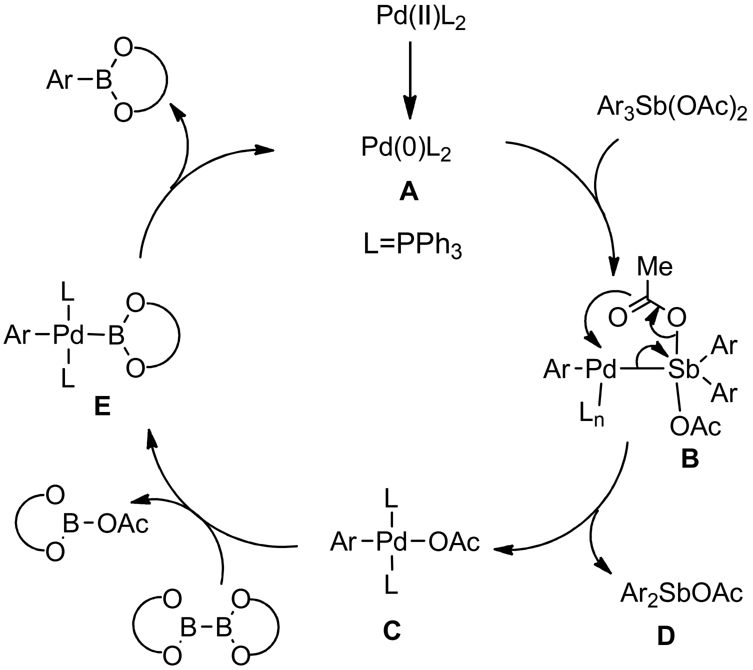


Fig. 2. Possible Mechanism (1st cycle)

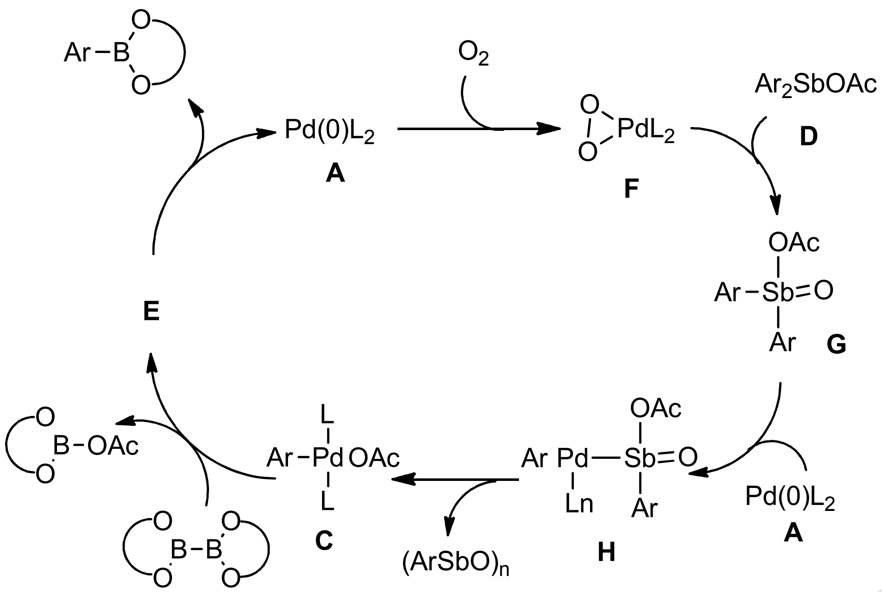


Fig. 3. Possible Mechanism (2nd cycle)

Highlights

Miyaura-type borylation under aerobic conditions without any base was developed.

Triarylantimony diacetates can be used as new effective B-arylating agents.

A wide range of triarylantimony diacetates gave arylboronates with good to excellent yields.