

# Triarylantimony dicarboxylates as pseudo-halides for palladium-catalyzed cross-coupling reaction with arylboronic acids and triarylbismuthanes without any base

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## Abstract

The reaction of triarylantimony diacetates (**6**) with organoboron reagents (**9**) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> led to the formation of cross-coupling products, biaryls (**10**, **12** and **14–17**), in moderate to excellent yields under mild conditions without any base. Similar reaction of **6** with triarylbismuthanes (**18**) also gave the corresponding cross-coupling products. Single crystal X-ray analysis of tri(*p*-tolyl)antimony diacetate (**6b**) and tris(*p*-trifluoromethylphenyl)antimony diacetate (**6e**) revealed the geometry of both central antimony atoms being intermediate between trigonal bipyramidal and pentagonal bipyramidal arrangement with intramolecular coordination between the antimony and two carbonyl oxygen atoms with *cis* orientation.

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**Keywords:** Base-free; Triarylantimony diacetate; Aryl–aryl bond formation; Pd-catalyzed cross-coupling; Arylboronic acid; Triarylbismuthane

## 1. Introduction

The chemistry of organoantimony compounds has been developed and the potential of such compounds in organic synthesis is currently increasing [1]. With regard to transition metal-catalyzed cross-coupling reaction by use of organoantimony (III and V) compounds, various kinds of carbon–carbon bond forming reactions have been reported during the last decade. For instance, trivalent (Ph<sub>2</sub>SbCl) and pentavalent [Ar<sub>3</sub>Sb(OAc)<sub>2</sub>, Ar<sub>4</sub>SbOAc, Ar<sub>4</sub>SbCl, Ar<sub>3</sub>SbCl<sub>2</sub>] organoantimony compounds have been utilized as pseudo-halides for Heck-type arylation of alkenes [2,3], Stille-type coupling with organostannes [4], Hiyama-type reaction with alkynylsilane [5] and arylation to silyl enol ether [6]. We have also recently reported that

trivalent organoantimony compounds such as aryl- and ethynyl-stibanes were useful transmetallating agents for Pd-catalyzed cross-coupling reaction with organic halides; in particular, Sb-ethynyl- and Sb-aryl-1,5-azastibocines having Sb–N intramolecular coordination could be coupled with acyl, vinyl, and aryl halides to afford ethynyl ketones, diarylacetylenes, 1,3-enynes, diaryl ketones, and biaryls under mild reaction conditions [7].

Aryl–aryl bond formation is one of the most important tools in organic synthesis due to its wide applicability to the synthesis of various biologically active compounds [8]. Among these, transition metal-catalyzed cross-coupling of organometallic compounds (B, In, Si, Ge, Sn, Sb and Bi) with aryl halides and triflates is an attractive reaction for the synthesis of biaryl derivatives [7a,8]. However, most of these reactions require base, oxidant, or inorganic salt as an additive. Therefore, development of new pseudo-halides for aryl–aryl bond formation without additives is

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well worth consideration. Thus, for Suzuki-type reaction with arylboron reagents and Stille-type coupling with arylstannanes, aryl halides were replaced with arendiazonium salts [9],  $\lambda^3$ -organoiodanes [10], and triarylbismuth diacetate [11], which improved the reactions to proceed without these additives.

We present here a novel and efficient Pd-catalyzed cross-coupling reaction of pentavalent organoantimony compounds, triphenylantimony diacetate, with arylboronic acids and triarylbismuthanes to form appropriate biaryls under additive-free conditions [12]. It is worth noting that the reaction did not take place when boronic ester was employed as a transmetallating agent instead of free boronic acid, indicating that the acid moiety of the boron reagent plays an important role to proceed the reaction. Full details of these reactions including preparation of several triarylantimony diacetates as well as single crystal X-ray structures of tri(*p*-tolyl)antimony diacetate (**6b**) and

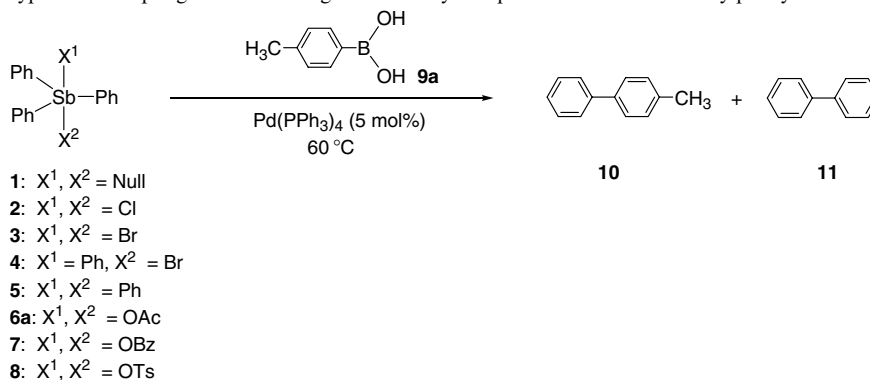
tris(4-trifluoromethylphenyl)antimony diacetate (**6e**) are described here.

## 2. Results and discussion

### 2.1. Pd-catalyzed cross-coupling reaction of organoantimony compounds with boron reagents

As a part of our research into transition metal-catalyzed cross-coupling reaction by use of organoantimony compound, we have previously reported that the reaction of triphenylantimony diacetate (**6a**) with arylboronic acids in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> in 1,4-dioxane resulted in cross-coupling reaction to form biaryls [12]. Therefore, we first studied the influence of substituent X on organoantimony reagent (Ph<sub>3</sub>SbX<sub>2</sub>) and the effect of solvents, to search for suitable substrates and reaction conditions for this reaction. The progress of the reaction was monitored

Table 1  
Palladium-catalyzed Suzuki-type cross-coupling reaction of organoantimony compounds **1–8** with 4-methylphenylboronic acid **9a** without a base<sup>a</sup>



Entry	Substrate	Solvent	Time (h)	Yield <sup>b,d</sup>	
				<b>10</b>	<b>11</b>
1	<b>1</b>	1,4-Dioxane	12	2	3
2	<b>2</b>	1,4-Dioxane	12	8	84
3	<b>3</b>	1,4-Dioxane	12	7	25
4	<b>4</b>	1,4-Dioxane	12	2	2
5	<b>5</b>	1,4-Dioxane	12	37	56
6	<b>6a</b>	1,4-Dioxane	6	98 (94) <sup>d</sup>	ND <sup>c</sup>
7	<b>7</b>	1,4-Dioxane	12	74	ND <sup>c</sup>
8	<b>8</b>	1,4-Dioxane	12	27	6
9	<b>6a</b>	THF	6	98	2
10	<b>6a</b>	NMP	6	94	3
11	<b>6a</b>	DME	6	93	2
12	<b>6a</b>	Toluene	6	44	3
13	<b>6a</b>	1,2-DCE	6	40	5
14	<b>6a</b>	CH <sub>3</sub> CN	6	15	1
15	<b>6a</b>	EtOH	6	5	1
16	<b>6a</b>	1,4-Dioxane–H <sub>2</sub> O	6	5	1
17 <sup>e</sup>	<b>6a</b>	1,4-Dioxane	6	91	9

<sup>a</sup> **1–8** (0.5 mmol), **9a** (1.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%).

<sup>b</sup> The yields of **10** and **11** were determined by GLC, and 100% yield corresponds to the involvement of one phenyl group on **6a**.

<sup>c</sup> ND: not detected.

<sup>d</sup> Isolated yield is shown in parenthesis.

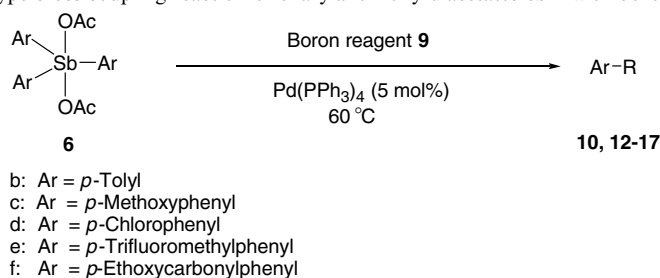
<sup>e</sup> Added base (Na<sub>2</sub>CO<sub>3</sub>: 3.0 mmol).

by gas–liquid chromatography (GLC) and the reaction time was determined when the yields of products **10** and **11** reached maximum values, because it is impossible to detect the disappearance of  $\text{Ph}_3\text{SbX}_2$  and boron reagent by thin-layer chromatography (TLC) or GLC. The results are shown in Table 1. The reaction of **9a** (3 eq.) with a variety of antimony derivatives (**1–8**) was performed under the best condition reported previously {5 mol%  $\text{Pd}(\text{PPh}_3)_4$ , 1,4-dioxane, 60 °C} (entries 1–8). In the preliminary studies, we had noted that triphenylantimony (**1**) and triphenylantimony dichloride (**2**) were inactive in the presence of  $\text{Pd}(\text{OAc})_2$  catalyst in contrast to  $\text{Ph}_3\text{Sb}(\text{OAc})_2$ . Under the conditions shown in Table 1, pentavalent organoantimony compounds (**3** and **4**) having halogen moiety on the antimony were also proved to be inactive, similar to compounds **1** and **2** (entries 1–4). Pentaphenylantimony (**5**) was found to be less reactive toward the cross-coupling reaction, and predominant formation of biphenyl (**11**) resulting from the homo-coupling reaction of phenyl group on **5** was observed (entry 5). In comparison with these results, triphenylantimony dicarboxylates (**6a** and **7**) afforded the expected cross-coupling product (**10**) in excellent yield, and formation of the homo-coupling product **11** was not detected (entries 6 and 7). The ability of the triphenylantimony diacetate (**6a**) was far superior as a pseudo-halide for this type of coupling reaction in terms of the reaction time (6 h) and the yield for **10** (98%). When the reaction of **6a** was carried out by using 1.5 eq. of boron

reagent (**9a**), a longer reaction time (36 h) was required to finish the reaction, which gave rise to **10** in 91% yield. Triphenylantimony disulfonate (**8**) was less active in the present reaction. A survey of solvents showed that the reaction took place effectively in 1,4-dioxane, tetrahydrofuran (THF), 1-methyl-2-pyrrolidinone (NMP) and 1,2-dimethoxyethane (DME) (entries 6 and 9–11), of which dioxane was proved to be the best solvent giving the highest yield of coupling product (**10**) without any side product (**11**), whereas toluene, 1,2-dichloroethane (DCE), acetonitrile, ethanol, and aqueous solvent (dioxane: $\text{H}_2\text{O}$  = 5:1) gave inferior results (entries 12–16). The total yields of the cross-coupling (**10**) and homo-coupling products (**11**) never exceeded 100% even when the reaction was carried out by use of 3 eq. of boron reagent (**9a**) in the presence of a base ( $\text{Na}_2\text{CO}_3$ ) which has been used to activate boron reagent (entry 17). These results indicate that one of the three phenyl groups on **6a** is involved in the present coupling reaction.

In order to clarify the substituent effect and to prove the generality of the present reaction, we next examined the reaction of triarylantimony diacetates (**6b–f**) with boron reagents (**9b–g**), and the results are summarized in Table 2. Tri(*p*-tolyl)antimony diacetate (**6b**) and a variety of phenylboron reagents (**9b–e**) were reacted under the optimal reaction condition obtained above. Consequently, boronic acid (**9b**) showed the best result to give rise to the cross-coupling product **10** in 96% yield (entry 1). In the

Table 2

Base-free palladium-catalyzed Suzuki-type cross-coupling reaction of triarylantimony diacetates **6b–f** with boron reagents **9**<sup>a</sup>

Entry	Substrate	<b>9</b> : Boron reagent	Time (h)	Yield (%) <sup>b</sup>
1	<b>6b</b>	<b>9b</b> : Phenylboronic acid	6	<b>10</b> : 96
2	<b>6b</b>	<b>9c</b> : 5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane	24	<b>10</b> : 33
3 <sup>c</sup>	<b>6b</b>	<b>9c</b> : 5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane	24	<b>10</b> : 88
4 <sup>d</sup>	<b>6b</b>	<b>9d</b> : Sodium tetraphenylborate	24	<b>10</b> : 81
5	<b>6b</b>	<b>9e</b> : Potassium phenyltrifluoroborate	24	<b>10</b> : 45
6	<b>6b</b>	<b>9f</b> : <i>trans</i> -2-Phenylvinylboronic acid	24	<b>12</b> : 58
7	<b>6b</b>	<b>9g</b> : Cyclohexylboronic acid	24	<b>13</b> : ND
8	<b>6c</b>	<b>9b</b> : Phenylboronic acid	6	<b>14</b> : 84
9	<b>6d</b>	<b>9b</b> : Phenylboronic acid	6	<b>15</b> : 93
10	<b>6e</b>	<b>9b</b> : Phenylboronic acid	6	<b>16</b> : 98
11	<b>6f</b>	<b>9b</b> : Phenylboronic acid	6	<b>17</b> : 69

<sup>a</sup> **6** (0.5 mmol), boron reagent (**9**) (1.5 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%).<sup>b</sup> Isolated yield. **10**: 4-methylbiphenyl, **12**: (E)-4-methylstilbene, **14**: 4-methoxybiphenyl, **15**: 4-chlorobiphenyl, **16**: 4-trifluoromethylbiphenyl, **17**: biphenyl-4-carboxylic acid ethyl ester. 100% yield corresponds to the involvement of one phenyl group on **6**.<sup>c</sup> Added base ( $\text{Na}_2\text{CO}_3$ ; 3.0 mmol).<sup>d</sup> **6b** (0.5 mmol), **9d** (0.5 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%).

case of arylboronate (**9c**), it was necessary to add a base ( $\text{Na}_2\text{CO}_3$ ) as an activator of boron reagent (entry 3). Sodium tetraphenylborate (**9d**) has been reported to be an atom-economical boron reagent in Suzuki-type cross-coupling with aryl halides, in that all four phenyl groups on **9d** took part in the reaction [13]. However, the reaction of **6b** and **9d** (4:1) gave **10** in low yield (38% based on **6b**). On the other hand, treatment of the borate (**9d**) with **6b** (1:1) brought about **10** in 81% yield (entry 4). (*E*)-Stilbene (**12**) formed by aryl–vinyl bond formation was obtained in moderate yield when vinylboronic acid (**9f**) was employed as a coupling partner (entry 6). However, aliphatic boronic acid (**9g**) was proved to be inactive in this type of coupling reaction (entry 7). Next, a variety of triarylantimony diacetates (**6b–f**) were reacted with phenylboronic acid (**9b**) to disclose the generality of the present reaction. The diacetates (**6b–f**) with an electron-donating and -withdrawing groups on the aromatic ring afforded the corresponding cross-coupling products (**10** and **14–17**) in high yields (entries 1 and 8–11). As the substituent effect could not be understood well from these results, we examined the competitive reaction by using electron-rich **6b** and electron-poor **6e**. The reaction of a 1:1:1 mixture of **6b**, **6e**, and **9b** gave 4-methylbiphenyl and 4-trifluoromethylbiphenyl in 37% and 62% yields, respectively. This result indicates that **6e** having the electron-withdrawing group

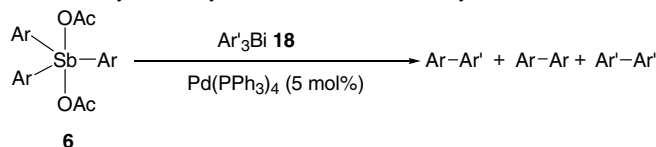
( $\text{CF}_3$ ) shows higher reactivity than **6b** bearing the electron-donating group ( $\text{CH}_3$ ).

## 2.2. Pd-catalyzed cross-coupling reaction of triarylantimony diacetates with triarylbismuthane

Pd-catalyzed cross-coupling for aryl–aryl bond formation by use of organobismuth compounds as a transmetalating agent has recently been the focus of attention [14]. In the reaction with triarylbismuthanes without hypervalent bonds, it is necessary to add a stoichiometric or excess amount of bases for smooth transmetalation [14d]. Taking these reports into consideration, we first examined the base-free coupling reaction of triphenylantimony diacetate (**6a**) with tri(*p*-tolyl)bismuthane (**18b**; 1 eq.) in various solvents at different temperatures in the presence of  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%) (Table 3, entries 1–7). As a result, 1-methyl-2-pyrrolidinone (NMP) was proved to be the superior solvent giving rise to the cross-coupling product (**10**) in highest yield (98%) along with two kinds of symmetric biaryls Ar–Ar (3%) and Ar'–Ar' (5%); the products Ar–Ar and Ar'–Ar' were formed by homo-coupling reactions of **6a** and **18b**, respectively (entry 3). It is also reported that triarylbismuthanes (**18**) were effective transmetalation agents and could couple with 3 eq. of aryl halides [14a,14b,14f]. However, the reaction of 0.35 eq. of **6a** with **18** afforded

Table 3

Palladium-catalyzed cross-coupling reaction of triarylantimony diacetates **6a–d** with triarylbismuth **18** without a base<sup>a</sup>



a: Ar = Phenyl  
b: Ar = *p*-Tolyl  
c: Ar = *p*-Methoxyphenyl  
d: Ar = *p*-Chlorophenyl

Entry	Substrate	Reagent	Solvent	Temperature (°C)	Time (h)	Yield (%) <sup>c</sup>		
						Ar–Ar' <sup>d</sup>	Ar–Ar <sup>e</sup>	Ar'–Ar' <sup>f</sup>
1	<b>6a</b>	<b>18b</b>	Dioxane	60	6	<b>10</b> : 5	1	5
2	<b>6a</b>	<b>18b</b>	Dioxane	100	6	<b>10</b> : 64	35	4
3	<b>6a</b>	<b>18b</b>	NMP	60	3	<b>10</b> : 98	3	5
4 <sup>b</sup>	<b>6a</b>	<b>18b</b>	NMP	60	3	<b>10</b> : 55	6	15
5	<b>6a</b>	<b>18b</b>	NMP	100	3	<b>10</b> : 91	8	12
6	<b>6a</b>	<b>18b</b>	DME	60	6	<b>10</b> : 13	3	4
7	<b>6a</b>	<b>18b</b>	THF	60	6	<b>10</b> : 6	1	7
8	<b>6a</b>	<b>18c</b>	NMP	60	3	<b>14</b> : 99 (97)	6 (5)	8 (6)
9	<b>6a</b>	<b>18d</b>	NMP	60	3	<b>15</b> : 88	5	12
10	<b>6b</b>	<b>18a</b>	NMP	60	3	<b>10</b> : 95	5	8
11	<b>6c</b>	<b>18a</b>	NMP	60	3	<b>14</b> : 87 (85)	7 (6)	5 (5)
12	<b>6d</b>	<b>18a</b>	NMP	60	3	<b>15</b> : 87	13	11

<sup>a</sup> **6** (0.5 mmol), **18** (0.5 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%).

<sup>b</sup> **18b** (0.175 mmol, 0.35 eq.).

<sup>c</sup> GLC yield. 100% yield corresponds to the involvement of one phenyl group on **6**. Isolated yield is shown in parenthesis.

<sup>d</sup> Ar–Ar': cross-coupling product (asymmetric biaryl compound) from **6** and **18**. **10**: 4-methylbiphenyl, **14**: 4-methoxybiphenyl, **15**: 4-chlorobiphenyl.

<sup>e</sup> Ar–Ar: homo-coupling product from triarylantimony diacetate **6**.

<sup>f</sup> Ar'–Ar': homo-coupling product from bismuth reagent **18**.

the cross-coupling product (**10**) in 55% yield (entry 4). It also became apparent that the reaction at higher temperature stimulated the formation of the homo-coupling products Ar–Ar and Ar'–Ar' rather than that of cross-coupling product (**10**) (entry 5). Consequently, the best result was obtained when the reaction was carried out by using triphenylantimony diacetate (**6a**), 1 eq. of bismuth reagent (**18b**), and 0.05 eq. of Pd(PPh<sub>3</sub>)<sub>4</sub> in NMP at 60 °C.

Taking the above results into account, we next examined the reaction of several un- and *p*-substituted triarylantimony diacetates (**6b–d**) with triaryl bismuthanes (**18a–d**). The reaction of **6a** with the *p*-substituted triaryl bismuthanes (**18b–d**) proceeded effectively to give the corresponding coupling products (**10**, **14** and **15**) in good yield. Similarly, *p*-functionalized triarylantimony diacetate (**6b–d**) also afforded the same coupling products (**10**, **14** and **15**) on treatment with

**18a**. The above reactions between various **6** and **18** having *p*-substituted phenyl groups showed that the intrinsic electronic factor of triarylantimony diacetates and triaryl bismuthanes did not affect the outcome of the present cross-coupling reaction. These results also indicated that, in terms of the reaction time, the triaryl bismuthane was superior to arylboronic acids as a transmetallating agent.

Fig. 1 shows a plausible reaction mechanism of the present cross-coupling reaction with **18**. The reaction should proceed similarly to that of triarylantimony diacetates with arylboronic acids reported in our previous paper [12]. After initial oxidative addition of **6** to Pd(0) species giving rise to intermediate **A**, transmetalation between **A** and **18** gave diorganopalladium complex **E** via intermediate **B**. In the intermediate **B**, coordination between the bismuth and oxygen on acetoxy moiety should assist the transmetalation. It is known that bismuth shows affinity for oxygen [15], and several novel reactions based on the affinity of bismuth for oxygen have been developed to date [16].

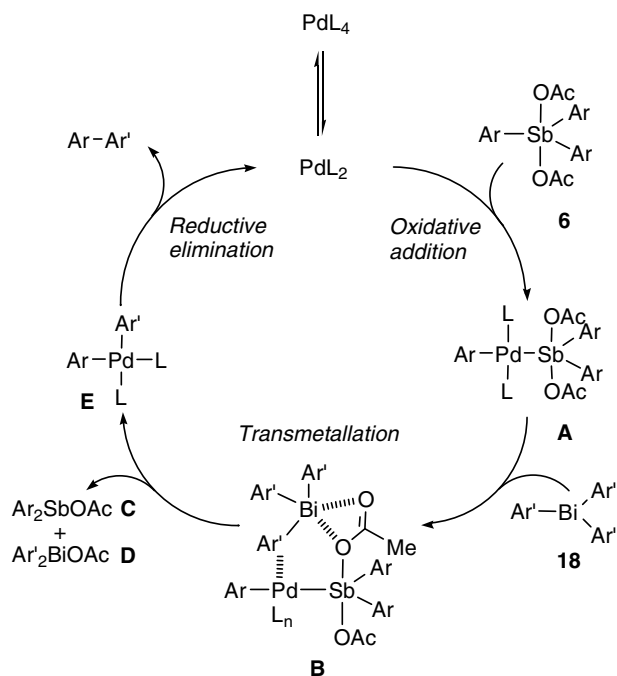


Fig. 1. Plausible reaction mechanism.

Table 4

Selected bond lengths (Å) and bond angles (°) for Ar<sub>3</sub>Sb(OAc)<sub>2</sub> **6b** and **6e**

	<b>6b</b>	<b>6e</b>
<i>Bond lengths (Å)</i>		
Sb–C(1)	2.112(2)	2.117(3)
Sb–C(1)'	2.111(2)	2.118(3)
Sb–C(1)''	2.116(2)	2.134(3)
Sb–O(1)	2.1471(14)	2.157(2)
Sb–O(1)'	2.1337(15)	2.127(2)
Sb–O(2)	2.7118(17)	2.5814(24)
Sb–O(2)'	2.8211(16)	2.6406(24)
<i>Bond angles (°)</i>		
O(1)–Sb–O(1)'	175.46(5)	174.48(8)
C(1)–Sb–C(1)'	146.36(8)	152.99(12)
C(1)–Sb–C(1)''	104.65(8)	103.44(12)
C(1)'–Sb–C(1)''	109.00(8)	103.56(12)
O(1)–Sb–C(1)	89.86(7)	89.34(10)
O(1)–Sb–C(1)'	90.90(7)	91.02(10)
O(1)–Sb–C(1)''	88.10(7)	87.66(10)
O(1)'–Sb–C(1)	92.45(7)	92.75(10)
O(1)'–Sb–C(1)'	89.33(7)	89.43(10)
O(1)'–Sb–C(1)''	87.53(7)	86.88(10)



Fig. 2. Molecular structure of **6b** and **6e**. All hydrogen atoms were omitted for clarity.

Pentavalent organoantimony (V) compounds are also known to be reduced to Sb(III) compounds with ease [16a,17]. The easy transformation of valence deviation of the antimony from V to III would also be another driving force for the present reaction. As a result, complex **E** thus formed undergoes reductive elimination to afford the cross-coupling product **10** and regenerates the Pd(0) species.

### 2.3. X-ray crystal structures of triarylantimony diacetates

The molecular structure of triarylantimony diacetates (**6b**, **e**) is depicted in Fig. 2, and selected geometrical parameters are shown in Table 4. Both central antimony atoms of **6b** and **6e** exhibit intermediate between trigonal bipyramidal (TBP) and pentagonal bipyramidal (PBP) arrangement accompanied by two Sb–O(carbonyl) intramolecular non-bonding interactions. The three carbon atoms [C(1), C(1)', and C(1)''] on the aryl ligands lie the equatorial plane, and O(1) and O(1)' of the carboxylate moiety occupy the axial position in the TBP structure. The sums of angles in the equatorial plane [C(1)–Sb–C(1)', C(1)–Sb–C(1)'', C(1)'–Sb–C(1)''] are 360° for **6b** and **6e**, and axial angles [O(1)–Sb–O(1)'] are 175.46° for **6b** and 174.48° for **6e**. Moreover, the angles of O(1)–Sb–C and O(1)'–Sb–C are approximately 90°: 87.53–92.45° for **6b** and 86.88–92.75° for **6e**. The Sb–C bond distances of **6e** (2.117–2.134 Å) are longer than those of **6b** (2.111–2.116 Å). The results also revealed the presence of intramolecular interaction between the antimony and the carbonyl oxygen atoms [O(2), O(2)'], and the distances for **6e** (2.5814 Å and 2.6406 Å) are noticeably shorter than those for **6b** (2.8211 Å and 2.7188 Å), which correspond to 72–78% of the sum of the van der Waals radii of both elements (3.60 Å) [18]. These results can be explained by the presence of the electron-withdrawing CF<sub>3</sub> group at the *p*-position on the phenyl ring of **6e**, in that the CF<sub>3</sub> group brings about electron-poor antimony center for stronger Sb–O(2, 2') interaction. Since the carbonyl oxygen atoms are *cis*-orientation to antimony, the angles of C(1)–Sb–C(1)' are remarkably extended to 146.36(8)° for **6b** and 152.99(12)° for **6e** and those of C(1)–Sb–C(1)'' and C(1)'–Sb–C(1)'' get narrow. Similar relations between Sb–O(carbonyl) distances and C(1)–Sb–C(1)' angles have been widely recognized in a variety of triarylantimony dicarboxylates, in that the C(1)–Sb–C(1)' angle increases with decreasing the Sb–O(carbonyl) distance and the conformation of the central antimony atom changes gradually from TBP to PBP arrangement [19,20]. It should be noted that the Sb–O(carbonyl) distance of **6e** is shortest in this type of compound reported at present. The results imply that **6e** has strong Sb–O(carbonyl) coordination. In this point of view, the conformation of **6b** and **6e** is also considered to exhibit distorted PBP structure; the aryl carbon C(1)'' and four oxygen atoms [O(1), O(2), O(1)', and O(2)'] lie equatorial plane and the aryl carbons C(1) and C(1)' occupy apical position with the C(1)–Sb–C(1)' angles to be 146.36° and 152.99°, respectively.

### 3. Conclusion

In conclusion, the Pd-catalyzed cross-coupling reaction of the triarylantimony diacetates with organoboronic acids under mild conditions was achieved without any base, in that one of the three phenyl groups on the antimony diacetates could participate to form biaryl derivatives. Various antimony reagents having electron-donating and -withdrawing functional groups afforded the corresponding cross-coupling product. Also apparent was that triarylbismuthanes were a good coupling partner in the present cross-coupling reaction. No perceptible differences in the yield of the cross-coupling products were observed even when electron-donating and -withdrawing groups on the antimony reagents were used. The present reaction will be broadly utilized for the syntheses of biaryl derivatives. Further reactions of triarylantimony diacetates with less reactive coupling partners are now in progress and will be reported by us in due course.

### 4. Experimental

#### 4.1. General

All reactions were carried out in pre-dried glassware under an argon atmosphere. Ether was distilled from its LiAlH<sub>4</sub> suspension and dried over sodium wire. Melting points were taken on a Yanagimoto micro melting point hot-stage apparatus and are not corrected. <sup>1</sup>H NMR (TMS: δ: 0.00 as an internal standard) and <sup>13</sup>C NMR (CDCl<sub>3</sub>: δ: 77.00 as an internal standard) spectra were recorded on JEOL JNM-ECA400 (400 MHz and 100 MHz) spectrometers in CDCl<sub>3</sub> unless otherwise stated. Mass spectra (MS) were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 μA) and IR spectra were recorded on a HORIBA FT-720 instrument. GLC analyses of the products were made using Shimadzu GC-16A. 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<sub>254</sub>. The group 15 metal reagents, triphenylantimony dibromide (**3**) [21], triarylantimony diacetates such as **6a** [5], **6b** [5], **6c** [2c], **6d** [12], triphenylantimony dibenzoate (**7**) [2c], triphenylantimony ditylosylate (**8**) [22] and triarylbismuthanes such as **18b** [23], **18c** [23], **18d** [23] were prepared according to the reported procedures, and others were purchased from Tokyo Kasei Kogyo Co., Ltd., Japan.

#### 4.2. Preparation of triarylantimony diacetates (**6e**, **f**)

*General procedure.* A mixture of tris(*p*-trifluoromethylphenyl)stibane or tris(*p*-ethoxycarbonylphenyl)stibane (2 mmol) and (diacetoxyiodo)benzene (2.2 mmol) in dichloromethane (10 ml) was stirred for 24 h at rt. The solvent was concentrated under reduced pressure to a small volume. Hexane (10 ml) was added and the solution was

stirred in an ice bath. The solid was filtered and recrystallized from a mixture of dichloromethane–hexane to give **6e**, **f**.

#### 4.2.1. Tris(*p*-trifluoromethylphenyl)antimony diacetate (**6e**)

Colorless prisms (918 mg, 68%), m.p. 138–143 °C. <sup>1</sup>H NMR (400 MHz)  $\delta$ : 1.87 (6H, s), 7.75 (6H, d,  $J = 8.2$  Hz), 8.08 (6H, d,  $J = 8.2$  Hz). <sup>13</sup>C NMR (100 MHz)  $\delta$ : 21.23 (q), 123.55 (q,  $J_{C,F} = 272$  Hz), 125.97 (d), 133.06 (q,  $J_{C,F} = 33$  Hz), 134.16 (d), 144.22 (s), 177.77 (s). IR (KBr, cm<sup>-1</sup>): 1600 (C=O). EIMS (relative intensity)  $m/z$ : 615 (M–OAc<sup>+</sup>, 100), 573 (34), 487 (6), 411 (7), 271 (66). Anal. Calc. for C<sub>25</sub>H<sub>18</sub>F<sub>9</sub>O<sub>4</sub>Sb: C, 44.47; H, 2.69. Found: C, 44.50; H, 2.80%.

#### 4.2.2. Tris(*p*-ethoxycarbonylphenyl)antimony diacetate (**6f**)

Colorless prisms (852 mg, 62%), m.p. 116–120 °C. <sup>1</sup>H NMR (400 MHz)  $\delta$ : 1.40 (9H, t,  $J = 7.3$  Hz), 1.84 (6H, s), 4.41 (6H, q,  $J = 7.33$  Hz), 8.04 (6H, d,  $J = 8.2$  Hz), 8.14 (6H, d,  $J = 8.2$  Hz). <sup>13</sup>C NMR (100 MHz)  $\delta$ : 14.26 (q), 21.55 (q), 61.34 (t), 129.98 (d), 132.78 (s), 133.66 (d), 144.58 (s), 165.81 (s), 176.97 (s). IR (KBr, cm<sup>-1</sup>): 1720, 1645 (C=O). EIMS (relative intensity)  $m/z$ : 627 (M–OAc<sup>+</sup>, 37), 568 (5), 537 (15), 478 (6), 390 (2), 329 (17), 253 (100). Anal. Calc. for C<sub>31</sub>H<sub>33</sub>O<sub>10</sub>Sb: C, 54.17; H, 4.84. Found: C, 53.73; H, 4.79%.

#### 4.3. Reaction of triarylantimony diacetates with boron reagents

A solution of triarylantimony diacetates (**6**: 0.5 mmol), boronic acids (**9**: 1.5 mmol), and tetrakis(triphenylphosphine)palladium (0) (0.025 mmol) in 1,4-dioxane (3 ml) was heated at 60 °C for 6–18 h, as shown in Tables 1 and 2 under an argon atmosphere. After dilution with ether (20 ml) and water (20 ml), the reaction mixture was separated and the aqueous layer was extracted with ether (20 ml). The combined organic layer was washed with water, dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by short silica gel column chromatograph using hexane (for **10**, **12**, **15** and **16**) or hexane–CH<sub>2</sub>Cl<sub>2</sub> (for **14** and **17**) as eluents to give biaryl derivatives **10**, **12**, **14**–**17**. The yields are listed in Tables 1 and 2. The products were confirmed by comparison of the melting point, NMR data and MS spectra with those in the literature.

**4-Methylbiphenyl (10)** [24]: Colorless plates, m.p. 49–50 °C (lit. 49–50 °C).

**(E)-4-Methylstilbene (12)** [25]: Colorless plates, m.p. 119–120 °C (lit. 119–122 °C).

**4-Methoxybiphenyl (14)** [26]: Colorless prisms, m.p. 86–88 °C (lit. 87.5–89 °C).

**4-Chlorobiphenyl (15)** [26]: Colorless plates, m.p. 76–77 °C (lit. 77–78.5 °C).

**4-Trifluoromethylbiphenyl (16)** [25]: Colorless plates, m.p. 67–69 °C (lit. 70–70.5 °C).

**Ethyl biphenyl-4-carboxylate (17)** [25]: Colorless prisms, m.p. 48–50 °C (lit. 48–49 °C).

#### 4.4. Reaction of triarylantimony diacetates with triarylbismuthanes

The reactions were carried out according to the procedure described above; A solution of triarylantimony diacetates (**6**: 0.5 mmol), triarylbismuthanes (**18**: 0.5 mmol), and tetrakis(triphenylphosphine)palladium (0) (0.025 mmol) in NMP (3 ml) was heated at 60 °C for 3 h under argon atmosphere. Yields of the cross-coupling (**10**, **14** and **15**) and homo-coupling products were calculated by GLC analysis (5% SE-30, 1.5 m, column temperature 120–240 °C) using octadecane as an internal standard. Results are listed in Table 3.

#### 4.5. Crystallography

##### 4.5.1. X-ray crystallography

Data collections were performed using a Bruker SMART 1000 CCD area detector diffractometer with Mo K $\alpha$  radiation with an  $\omega$ -scan mode ( $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined by full-matrix least-squares refinements based on  $F^2$ . Empirical absorption corrections were carried out utilizing SADABS routine. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were added geometrically and refined with a riding model. Structure solutions and refinement were performed with the SHELXS-97 and SHELXL-97 [27].

##### 4.5.2. Crystal data

**6b**: Crystal dimensions 0.30 × 0.20 × 0.13 mm<sup>3</sup>; C<sub>25</sub>H<sub>27</sub>O<sub>4</sub>Sb,  $M_r = 513.22$ ; monoclinic space group  $P2_1/n$ ,  $a = 8.1217(9)$  Å,  $b = 20.302(2)$  Å,  $c = 14.3458(16)$  Å,  $\beta = 104.326(2)^\circ$ ,  $V = 2291.9(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.487$  g cm<sup>-3</sup>,  $T = 150$  K, 5442 unique and 4688 observed [ $I > 2\sigma(I)$ ] reflections, 276 parameters, final [ $I > 2\sigma(I)$ ]  $R_1 = 0.0270$ ,  $wR_2 = 0.0685$ .  $S = 1.085$ .

**6e**: Crystal dimensions 0.37 × 0.30 × 0.20 mm<sup>3</sup>; C<sub>25</sub>H<sub>18</sub>F<sub>9</sub>O<sub>4</sub>,  $M_r = 675.14$ ; triclinic space group  $P\bar{1}$ ,  $a = 10.6111(11)$  Å,  $b = 11.4548(12)$  Å,  $c = 12.7332(14)$  Å,  $\alpha = 95.366(1)^\circ$ ,  $\beta = 108.273(1)^\circ$ ,  $\gamma = 112.237^\circ$ ,  $V = 1320.1(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.698$  g cm<sup>-3</sup>,  $T = 150$  K, 6208 unique and 5550 observed [ $I > 2\sigma(I)$ ] reflections, 354 parameters, final [ $I > 2\sigma(I)$ ]  $R_1 = 0.0373$ ,  $wR_2 = 0.0983$ .  $S = 1.069$ .

#### 5. Supplementary material

CCDC 661306 and 661307 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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