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Palladium-Catalyzed Borylation of Aryl Halides or Triflates with Dialkoxyborane: A Novel and Facile Synthetic Route to Arylboronates

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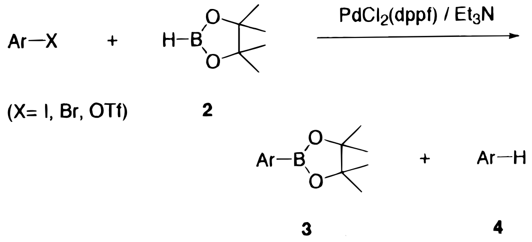
A direct borylation of aryl halides or triflates with dialkoxyborane was investigated. The coupling reaction of pinacolborane with aryl halides or triflates in the presence of a catalytic amount of PdCl$_2$(dppf) together with a base provided arylboronates in high yields. The product distributions were strongly dependent on the base employed, and the tertiary amine, especially Et$_3$N, was effective for the selective formation of the boron−carbon bond. The reaction conditions were so mild that arylboronates having a variety of functional groups such as carbonyl, cyano, and nitro groups were readily prepared.

Introduction

Arylboronic acids and their esters are valuable reagents in organic synthesis,[1−3] and much attention has been paid to them in biology[4] and in the study of molecular recognition.[5,6] Ordinarily, arylboron compounds can be prepared by the transmetalation between arylmagnesium or -lithium reagents and boron compounds that have good leaving groups such as the halogen or alkoxy group.[7] In a few cases, this synthesis has been conducted by the use of boron compounds containing a boron−hydrogen bond.[8,9] On one hand, the direct borylation of aryl halides or pseudo-halides has been expected to be a more convenient procedure for preparing arylboronates. Thus, Miyaura and co-workers reported on a palladium-catalyzed cross-coupling reaction of tetraalkoxydiboron, which provided a one-step procedure for deriving organoboronates from organic electrophiles.[10]

Recently, Kunai and his colleague have found that the PdCl$_2$-catalyzed reaction of alkyl iodides with Et$_2$SiH$_2$ afforded Et$_2$ISi−R to some extent,[11] indicating the potential use of metal hydride as a metalating reagent in the presence of a palladium catalyst. More recently, we have developed each palladium-catalyzed selective metalations of aryl halides utilizing trialkoxysilanes[12] and dialkoxyboranes[13] as metalating reagents. Thus, the latter novel palladium-catalyzed coupling reaction of dialkoxyhydroborane **2** with aryl halides **1** afforded the corresponding arylboronates **3** in high yield (eq 1).[13,14] In this paper, we describe in detail the scope and limitation



(1)

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Table 1. Reaction of 1-Iodonaphthalene under Various Conditions[a]

entry	catalyst	base	solvent	yield (%)[b] 3	yield (%)[b] 4
1	$PdCl_2(dppf)$[c]	none	dioxane	0	3
2	$PdCl_2(dppf)$	Et_3N	dioxane	89	6
3	$PdCl_2(dppf)$	$i\text{-}Pr_2NEt$	dioxane	64	29
4	$PdCl_2(dppf)$	pyridine	dioxane	12	47
5	$PdCl_2(dppf)$	DBU	dioxane	3	36
6	$PdCl_2(dppf)$	KOAc	dioxane	6	82
7	$PdCl_2(PPh_3)_2$	Et_3N	dioxane	75	13
8	$PdCl_2(PPh_3)_2/PPh_3$	Et_3N	dioxane	0	0
9	$Pd(PPh_3)_4$	Et_3N	dioxane	10	1
10	$PdCl_2(dppf)$	Et_3N	toluene	79	7
11	$PdCl_2(dppf)$	Et_3N	CH_2ClCH_2Cl	81	7
12	$PdCl_2(dppf)$	Et_3N	CH_3CN	83	8
13	$PdCl_2(dppf)$	Et_3N	DMF	27	23

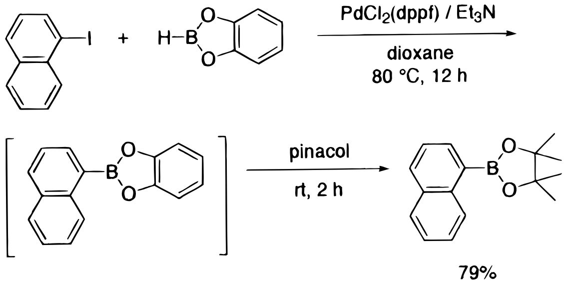
[a] Reactions of 1-iodonaphthalene **1** (1.0 mmol) with **2** (1.5 mmol) were carried out at 80 °C for 2 h in 4 mL of solvent by using 3 mol % of catalyst and base (3 mmol). [b]GLC yields are based on **1** used. [c]DPPF is 1,1′-bis(diphenylphosphino)ferrocene.

of the borylation of aryl halides and the successful application of facile aryl sulfonates to this reaction. Dialkoxyboranes are more readily available than the diboron reagents, and the borylation using dialkoxyboranes is an atom economical manner. In addition, pinacolborane **2** tolerates various functional groups, and pinacolboronates **3** are insensitive to air, moisture, and chromatography.[15] Thus, the present borylation methodology possesses several great advantages to allow for a wide range of **3**.

Results and Discussion

To disclose the aptitude of the borylation, the reaction of 1-iodonaphthalene (**1**) with **2** was carried out under various conditions (Table 1). This coupling work was achieved with the aid of palladium catalysts and bases in analogy with the Suzuki−Miyaura cross-coupling reaction (entries 1 and 2).[1] The desired products tended to be contaminated with naphthalene **4**, the normal cross-coupling-like product, in each case as a result of the behavior of pinacolborane as a hydride source. However, this situation was greatly improved by the choice of a suitable base. Thus, the tertiary amine, especially Et_3N, which was generally known not to contribute to the coupling reaction of boron compounds, was recognized to be most effective for the selective formation of **3** (entries 2 and 3).[16] In the presence of other weak bases, the formation of undesirable **4** unexpectedly predominated (entries 4−6). Then, the reaction was efficiently catalyzed by the palladium(II) complexes having 2 equiv of phosphine ligands, such as $PdCl_2(dppf)$ and $PdCl_2(PPh_3)_2$ (entries 2 and 7). However, an additional phosphine ligand tended to retard the reaction (entries 8 and 9). In testing the four solvents, dioxane, toluene, MeCN, and CH_2ClCH_2Cl, it was found that these did not play a distinguished role in the present reaction (entries 2 and 10−12). However, the use of the polar solvent DMF caused both a low yield and selectivity due to a decomposition of dialkoxyborane to diborane B_2H_6 (entry 13).[17]

Also, the procedure could be applied for catecholborane (eq 2). Although the resulting catechol esters are sensitive to moisture and chromatography unlike inert pinacol esters **3**, they moderately favor the transesterification with other diols.[18] Thus, the borylation of 1-iodonaphthalene with 1.5 equiv of catecholborane at 80 °C for 12 h, followed by transesterifying with pinacol, gave a 79% yield of **3** along with naphthalene **4** (18%).



(2)

On the basis of the typical result obtained above, subsequent experiments with a considerable number of representative aryl halides or sulfonates **1** were carried out to give the corresponding products **3**. They are summarized in Table 2. Generally, aryl iodides exhibited higher reactivity than aryl bromides or fluoroalkanesulfonates in the present reaction. However, from the synthetic point of view, the use of aryl fluoroalkanesulfonates, such as aryl triflates ($X = OSO_2CF_3$) and nonaflates ($X = OSO_2(CF_2)_3CF_3$, entry 4), has some advantages, in part due to the easy access from phenols.[19] Also, in the case of aryl iodides or triflates having an electron-donating group such as OMe and Me, the reaction proceeded smoothly at 80 °C similarly to that above (entries 1 and 5). The presence of powerful electron-withdrawing substituents such as NO_2 is known to induce the reductive dehalogenation of **1**;[20c] nevertheless, the differences in the yields and on the selectivity among aryl iodides having electron-donating or -withdrawing groups were not particularly large (entries 1, 7, 15, 18, and 19). As in the case of aryl iodides, the product yields of the borylation of aryl triflates also were not substantially affected by their substituent moieties of **1**, but the reaction of those having electron-withdrawing groups was sluggish at 80 °C, requiring a more elevated temperature (100 °C) (entries 3, 9, 17, and 25). On the whole, the reactivity of aryl bromides was not favorable when compared with that of aryl iodides or triflates. In addition, the borylation of aryl bromides having electron-donating groups proceeded smoothly at 100 °C (entries 2 and 22); however, the presence of electron-withdrawing substituents remarkably decreased the yield of **3** (entries 14 and 16).

The presence of functional groups, such as CO_2Et (entries 15−17), COMe (entries 18 and 25), CN (entries

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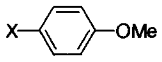
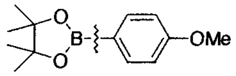
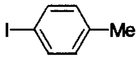
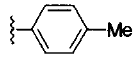
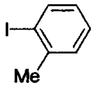
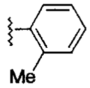
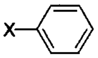
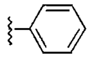
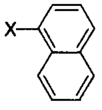
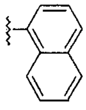
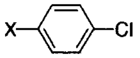
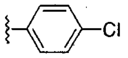
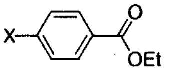
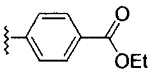
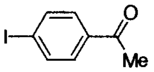
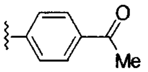
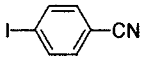
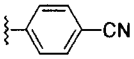
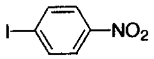
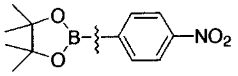
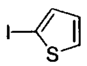
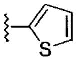
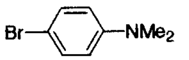
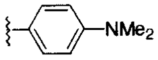
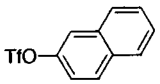
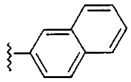
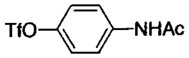
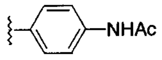
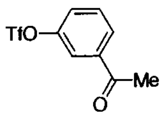
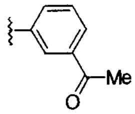
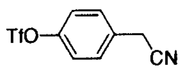
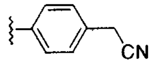
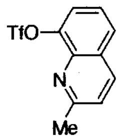
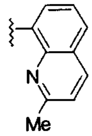
Table 2. Reaction of Representative 1 with 2^{a}

entry	aryl halide or triflate **1**		time (h)	product **3**	yield (%)^{b}	
					3	**4**
1		X= I	1		77	16
2		Br	$3^{c,d}$		77	11
3		OTf^{e}	4		81	12
4		ONf^{f}	4		74	18
5			1		(79)	
6			5		(78)	
7		X= I	2		84	
8		Br	6^{c}		67	
9		OTf	4		93	
10		X= I	2		89	6
11		Br	6^{c}		75	18
12		OTf	4^{c}		82	18
13		X= I	3		(83)	
14		Br	$4^{c,d}$		(49)	
15		X= I	2		79	17
16		Br	$18^{c,d}$		43	20
17		OTf	2^{c}		77	21
18			4		(74)	
19			4		(73)	
20			4		(84)	
21			4		(80)	
22			$2^{c,d}$		(79)	
23			4		(73)	
24			4		(77)	
25			$4^{c,g}$		(55)	
26			6^{c}		(73)	
27			4		(63)	

[a] Reactions of **1** (1.0 mmol) with **2** (1.5 mmol) were carried out at 80 °C by using $PdCl_2$(dppf) (3 mol %), Et_3N (3 mmol), and dioxane (4 mL). [b] GLC yields are based on **1**. Yields in parentheses are isolated yields. [c] Reactions were carried out at 100 °C. [d] $PdCl_2(PPh_3)_2$ was used as catalyst. [e] OTf = OSO_2CF_3. [f] ONf = $OSO_2(CF_2)_3CF_3$. [g] 3 mmol of **2** was used.

19 and 26), and NHAc (entry 24), in the starting **1** did not interfere with the outcome of the present reaction at 80−100 °C. Similarly, the present procedure tolerates various functional groups owing to the inertness of **2** to these.[15] In contrast, the previous methods via Grignard reagents or organolithiums[7] frequently require the protection of functional groups. Then, both of yield and the selectivity are almost independent of the steric requirement (entries 6, and 10−12). A heteroaromatic iodide was also coupled with **2** without any difficulty (entry 21). As a whole, the desired products **3** were contaminated with small amounts of the reduced byproducts **4**, but their isolation was very easy (see Experimental Section). Accordingly, the present reaction provides a simple and available procedure for synthesizing arylboronates **3**.

The above results differ widely from those of the well-known palladium-catalyzed coupling reactions between organometallic reagents and halides. Generally, in the presence of a palladium catalyst, such metal hydrides as Bu_3SnH,[20] Et_3SiH,[21] and $NaBH_4$[22] greatly facilitate the hydrogenolysis of organic electrophiles. Thus, it is recognized that this common process involves a sequence of oxidative addition of the electrophiles to Pd^0 giving an $R-Pd^{II}-X$ species, transmetalation with the hydride forming an $R-Pd^{II}-H$, and reductive elimination of the R−H. It now can be seen that, under the present conditions, the slow transmetalation with **2** due to the low nucleophilicity of the hydride suppresses the hydrogenolysis, which appears to produce a small amount of the byproduct **4**.

Also, the organometallic reagents such as arylmercury compounds are known to react with borane to give the arylboronic acids.[8] Very recently, Iverson and Smith have reported that a phenyliridium complex reacted with **2** to yield the corresponding phenylboronate.[23] In analogy with this, the $Ar-Pd^{II}-X$ species generated by the oxidative addition of **1** to Pd^0 may react with **2** to form the B−C bond in the present process. Actually, the treatment of the authentically isolated $(4\text{-MeO}-C_6H_4)PdI(PPh_3)_2$ with **2** at 80 °C in the presence of Et_3N[24] gave the corresponding arylboronate **3** (yield, 14%) and phenylboronate (6%),[25] together with **4** (5%), although the reaction conditions were not optimized. On one hand, a similar treatment without a base decreased the yield of borylation product (**3**, 10%) and increased the reduced one (**4**, 22%). Thus, for the present reaction, Et_3N appeared to play an important role in not only preventing the production of **4** but also facilitating the B−C bond formation. In related Et_3N−metal hydride systems, Benkeser postulated that a silyl anion species was generated by the Et_3N−hydrosilane combination.[26] With the above effect of Et_3N in mind, we propose a mechanism involving a boryl anion analogue generated by the Et_3N−dialkoxyborane combination and then a reasonable catalytic cycle for the borylation with dialkoxyborane **2**, as following Figure 1. Initially, the aryl electrophile **1** would add oxidatively to the palladium catalyst to give arylpalladium(II) species $Ar-Pd^{II}-X$. Then, the ligand exchange between X of $Ar-Pd^{II}-X$ and the boryl anion analogue would produce the $Ar-Pd^{II}-B(OR)_2$ intermediate and $Et_3NH{\cdot}X$, and the subsequent reductive elimination would furnish the arylboronate **3** along with the regeneration of the catalyst.

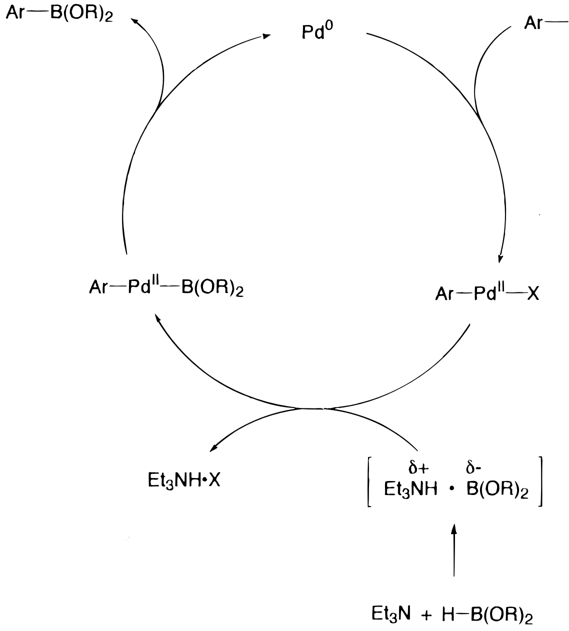


Figure 1. A plausible catalytic cycle for borylation.

However, bearing in mind the previously described result,[27] it seems also possible that dialkoxyborane **2** first added oxidatively to the palladium(0) complexes. This is because in the $PdCl_2$-catalyzed silylation of alkyl iodides such a mechanism that involved the first oxidative addition of hydrosilane to a Pd catalyst followed by a σ-bond metathesis between an Si−Pd bond and a C−I bond has been postulated.[11] Accordingly, at present, the mechanism involving the oxidative addition of dialkoxyborane **2** cannot necessarily be ruled out.[28]

In conclusion, dialkoxyhydroborane **2** was one of the most accessible alternative borylation reagents of aryl halides or triflates **1** in the presence of the palladium catalyst and the tertiary amine. The present coupling reaction provides a new and available synthetic route to a wide range of **3** from **1**.

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(24) A mixture of $(4\text{-MeO}-C_6H_4)PdI(PPh_3)_2$ (0.050 mmol), **2** (0.098 mmol), and Et_3N (0.30 mmol) in dioxane (1 mL) was stirred at 80 °C for 6 h. A GLC analysis of the reaction mixtures indicated formations of phenylboronate (yield, 6%), the corresponding **3** (14%), and **4** (5%).

(25) For an aryl−phenyl exchange reaction of $ArPdX(PPh_3)_2$, see: (a) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6313. (b) Herrmann, W. A.; Brossmer, C.; Priermeier, T.; Öfele, K. *J. Organomet. Chem.* **1994**, *481*, 97. (c) Segelstein, B. E.; Butler, T. W.; Chenard, B. L. *J. Org. Chem.* **1995**, *60*, 12. (d) Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1995**, 1101.

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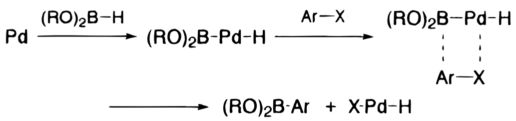
(28) As shown by eq i, it may be possible that the borane first adds to the palladium(0) and then the metathesis of the boryl−palladium complex with aryl halides takes place. However, NMR analysis of a mixture of **2** (0.2 mmol) and $Pd(PPh_3)_4$ (0.02 mmol) in C_6D_6 (0.5 mL) did not exhibit any signal corresponding to $H-Pd^{II}-B(OR)_2$ species.



(i)

Experimental Section

All the experiments were carried out under an argon atmosphere. Solvents were distilled before use from either sodium benzophenone ketyl (toluene, dioxane) or CaH_2 (DMF). $PdCl_2(dppf)$,[29] $PdCl_2(PPh_3)_2$,[30] and $Pd(PPh_3)_4$[31] were prepared by the established methods. $(4\text{-MeO}-C_6H_4)PdI(PPh_3)_2$ was obtained from 4-iodoanisole and $Pd(PPh_3)_4$.[32] Pinacolborane[15a] and catecholborane[33] were synthesized as reported previously. All aryl iodides and bromides were commercial products except for 4-iodobenzonitrile and 4-iodoacetophenone, which were prepared from the corresponding bromides by the known method.[34] Aryl triflates were obtained from the corresponding phenols and trifluoromethanesulfonic anhydride.[35]

Synthesis of Arylboronates. Typical Procedure. The general procedure for the synthesis of arylboronates is illustrated by the synthesis of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)naphthalene. To a solution of $PdCl_2(dppf)$ (22 mg, 0.03 mmol) in dioxane (4 mL) was added 1-iodonaphthalene (250 mg, 0.98 mmol), Et_3N (0.42 mL, 3.0 mmol), and pinacolborane (0.22 mL, 1.5 mmol). After being stirred for 2 h at 80 °C, the mixture was extracted with benzene. The extract was washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by Kugelrohr distillation to give 212 mg (85% yield) of the corresponding arylboronate: ^1H NMR ($CDCl_3$) δ 1.43 (s, 12 H), 7.4−7.6 (m, 3 H), 7.82 (d, $J = 9.3$ Hz, 1 H), 7.92 (d, $J = 8.2$ Hz, 1 H), 8.07 (d, $J = 7.0$ Hz, 1 H), 8.76 (d, $J = 8.2$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.96, 83.72, 124.93, 125.46, 126.27, 128.31, 128.47, 131.57, 133.28, 135.64, 136.98; HRMS for $C_{16}H_{19}O_2B$ calcd 254.1426, found 254.1452.

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Supporting Information Available: Spectral data (^1H and ^{13}C NMR, IR, MS, and HRMS) of **3** and copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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