Palladium(0)-Catalyzed Cross-Coupling Reaction of Alkoxydiboron with Haloarenes: A Direct Procedure for Arylboronic Esters

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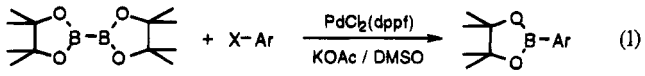
Received July 10, 1995[⊗]

The palladium-catalyzed cross-coupling reaction of the pinacol ester of diboronic acid [$(Me_4C_2O_2)BB(O_2C_2Me_4)$, **1**] with haloarenes gave a direct procedure for arylboronic esters from aryl halides in a range of 60–98%. The reaction was catalyzed by $PdCl_2$(dppf) (3 mol %) at 80 °C in the presence of KOAc (3 equiv) in DMSO and available with various functional groups such as nitro, cyano, ester, and carbonyl groups. The *trans*-ArPd(II)(OAc)$(PPh_3)_2$ intermediate was isolated and characterized to propose the catalytic cycle involving the transmetalation between the phenylpalladium(II) acetate complex and **1**.

Considerable attention has recently been paid to arylboronic acids and esters due to their usefulness in organic synthesis,[1] their biological activity,[2] and their molecular recognition properties.[3] Several syntheses of boronic acids have been reported, but the best methods are based on the reaction of trialkyl borates with Grignard or lithium reagents.[4] The transition-metal-catalyzed cross-coupling reaction of boron nucleophiles with aryl electrophiles is an alternative and convenient route to such boronic acids and esters, but the lack of suitable boron nucleophiles has limited this protocol,[5] whereas the cross-coupling reaction of disilanes[6] or distannanes[7] has been extensively studied. Recently, we found that the addition of tetraalkoxydiboron to alkynes to give *cis*-diborylalkenes is catalyzed by platinum(0) complexes.[8] Since alkoxydiborons are thermally stable and easily handled in air, the reagent should be useful as a boron nucleophile for the cross-coupling reaction with organic halides.

In this paper, we report the palladium-catalyzed coupling reaction of the pinacol ester of diboron (**1**)[9] and aryl halides **2**, which represents the first one-step procedure for preparing arylboronic esters **3** from aryl halides (eq 1).



(1)

1 **2** **3**

The reaction conditions were optimized at 80 °C using bromobenzene as a substrate. We previously reported that the cross-coupling reaction of organoboron reagents with organic halides smoothly proceeds in the presence of base and a palladium catalyst.[1,10] A suitable base is also essential for the cross-coupling reaction of **1**. Although very weak bases such as KOAc generally did not accelerate the cross-coupling reaction of organoboron compounds, it was unexpectedly the best base to achieve high yields and high selectivity. Stronger bases, such as K_3PO_4 and K_2CO_3, promoted the further reaction of **3** (Ar = Ph) with bromobenzene, resulting in contamination by a substantial amount of biphenyl (36–60% yields). The solvent also plays an important role in the rate of the cross-coupling. The reaction is accelerated in polar solvents: e.g., DMSO ≥ DMF > dioxane > toluene.

As for the catalyst, $PdCl_2$(dppf) gave the best results for haloarenes having either an electron-withdrawing or -donating group. The $Pd(PPh_3)_4$-catalyzed reaction of 4-bromoanisole with **1** gave 62% of (4-methoxyphenyl)-boronate together with an 8% yield of phenylboronate. The contamination by this unexpected byproduct, arising from the coupling with a phenyl group on triphenylphosphine,[11] was also observed in the reaction with 4-(dimethylamino)bromobenzene. Other catalysts, such as $Ni(PPh_3)_4$, $Pt(PPh_3)_4$, and $RhCl(PPh_3)_3$, did not catalyze the reaction at all. The results of the $PdCl_2$(dppf)-

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

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Table 1. Cross-Coupling of 1 and Haloarenes (Eq 1)[a]

entry	halide	time (h)	yield (%)[b]
1	BrC_6H_5	2	98
2	$4\text{-}IC_6H_4NMe_2$	6	90
3	$4\text{-}BrC_6H_4NMe_2$	24	23
4	$4\text{-}IC_6H_4OMe$	2	82
5	$4\text{-}BrC_6H_4OMe$	24	69
6	$4\text{-}BrC_6H_4CO_2Me$	1	86
7	$4\text{-}BrC_6H_4COCH_3$	1	(80)
8	$4\text{-}BrC_6H_4C{\equiv}N$	1	(76)
9	$4\text{-}BrC_6H_4NO_2$	2	(86)
10	iodomesitylene	24	(71)
11	3-bromoquinoline	4	(84)
12	3-iodobenzothiophene	4	(60)
13	$4\text{-}IC_6H_4Br$	1	(86)[c]
14	$4\text{-}BrC_6H_4Br$	2	(86)[d]

[a] All reactions were carried out at 80 °C in DMSO using **1** (1.1 equiv), **2** (1.0 equiv), $PdCl_2$(dppf) (3 mol %), and KOAc (3 equiv). [b] GC yields. Isolated yields are shown in parentheses. [c] 1.0 equiv of **1** was used. [d] 2.2 equiv of **1** was used for the coupling.

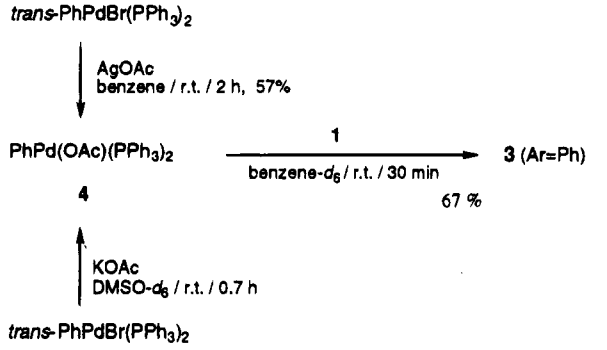
catalyzed cross-coupling of **1** with representative haloarenes are summarized in Table 1.[12]

The cross-coupling reaction of haloarenes having electron-donating groups, such as NMe_2 or OMe, is slow when using the bromides, but the reaction with the iodides completes with a shorter reaction time (entries 2–5). Electron-withdrawing substituents enhance the rate of the coupling, permitting the use of aryl bromides (entries 6–9). Arylboronic acid syntheses using Grignard or lithium reagents require the protection of functional groups sensitive to these reagents, but the present reaction is tolerated by various functional groups, e.g., CO_2Me, COMe, and CN. Sterically hindered halides such as iodomesitylene (entry 10) and heteroaromatic halides (entries 11 and 12) also gave the corresponding arylboronates in high yields. The coupling with the C–I bond is adequately faster than with the C–Br bond that the selective synthesis of (4-bromophenyl)boronate was accomplished (entry 13). The reaction of *p*-dibromobenzene with 2 equiv of **1** directly gave an 86% yield of diboronic ester, which has been used extensively for the synthesis of poly(*p*-phenylene)[13] (entry 14).

This transformation may result from a catalytic cycle[14] that involves the oxidative addition of a haloarene to the palladium(0) complex to give a ArPd(II)X adduct, the transmetalation between **1** and ArPd(II)X to provide a $ArPd(II)B(OR)_2$ intermediate, and the reductive elimination of **3** to regenerate the palladium(0) complex. The mechanism involving a palladium(IV) intermediate generated by the stepwise double-oxidative additions of **1** and **2** to the palladium(0) complex can be excluded because the oxidative addition of **1** to $Pd(PPh_3)_4$ did not proceed under the given reaction conditions.[15]

For the present cross-coupling reaction, the use of KOAc is essential not only to accelerate the reaction but also to prevent the formation of biaryl byproducts. Although oxidative addition and reductive elimination sequences are reasonably well understood and are fundamentally common processes to all cross-coupling reactions of organometallics,[14,16] less is known about the transmetalation step since the process is highly dependent on the organometallics or the conditions used for the couplings. The role of the base is thought to be the acceleration of the transmetalation rate, similar to the related cross-coupling reaction of organoboron compounds.[10] In general, the effect of bases on the cross-coupling reaction of organoboron compounds can be best understood in terms of the following two mechanisms. The first mechanism involves the coordination of a negatively charged base to the boron atom to increase its nucleophilicity for transmetalation to the palladium halide. By the second mechanism, the base first displaces the palladium halide to give an alkoxo-, hydroxo-, or acetoxopalladium(II) species[17] in solution, these being known to transmetalate with organoboron compounds under neutral conditions.[10,18] However, ^{11}B NMR analysis of a mixture of **1** and KOAc in DMSO-d_6 gave no evidence of the coordination of the acetoxy anion to the boron atom, thus suggesting that the latter mechanism, which gives an acetoxopalladium(II) species, is predominant.

Scheme 1. Acetoxopalladium(II) Intermediate



The treatment of *trans*-$PhPdBr(PPh_3)_2$ with AgOAc (1.1 equiv) in benzene at room temperature gave a thermally unstable pale yellow solid, $PhPd(OAc)(PPh_3)_2$ (**4**) (Scheme 1).[19] The complex can be *trans*-coordinated,

(12) A typical procedure for **3**: A flask charged with palladium catalyst (0.03 mmol), KOAc (294 mg, 3.0 mmol), and diboron **1** (279 mg, 1.1 mmol) was flushed with nitrogen. DMSO (6 mL) and haloarene **2** (1.0 mmol) were then added. After being stirred at 80 °C for an appropriate period, the product was extracted with benzene, washed with water, and dried over anhydrous magnesium sulfate. Kugelrohr distillation in vacuo gave the arylboronates.

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(15) A mixture of **1** (0.5 mmol) and $Pd(PPh_3)_4$ (0.05 mmol) in toluene (4 mL) was heated at 100 °C for 1 h in an NMR tube. ^{31}P NMR analysis did not give any signal corresponding to the oxidative adducts.

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(19) To a flask were added $PhPdBr(PPh_3)_2$ (0.30 mmol), AgOAc (0.32 mmol), and benzene (4.5 mL). After being stirred at room temperature for 2 h, the precipitate of AgBr was removed by filtration. Evaporation of solvent gave a pale yellow solid which was recrystallized from benzene–ether at lower than room temperature to give 57% of $PhPd(OAc)(PPh_3)_2$ **4**: IR (KBr) 3050, 1600 (s), 1580, 1560, 1480, 1430 (s), 1370 (s), 1320 (s), 1090 (s), 740, 720, 680 cm^{-1}; ^1H NMR (DMSO-d_6) δ 0.77 (br s, 3 H), 6.25 (t, 2 H, J = 6.9 Hz), 6.35–6.55 (m, 3 H), 7.2–7.5 (m, 30 H); ^1H NMR (C_6D_6) δ 1.41 (br s, 3 H), 6.41 (t, 2 H, J = 7.6 Hz), 6.58 (t, 1 H, J = 7.3 Hz), 6.9–7.1 (m, 20 H), 7.70 (br s, 12 H); ^{13}C NMR (C_6D_6) δ 24.18, 122.21, 127.46, 128.56, 129.94, 131.26, 135.11, 138.45, 148.60, 175.50; ^{31}P NMR (C_6D_6) δ 21.39. We wish to thank Professors C. Amatore and A. Jutand for sending us ^1H and ^{31}P NMR spectra of **4**. Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009. Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818–1826. For a related complex, $EtPd(OAc)(PMe_3)_2$, see: Kawataka, F.; Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Organometallics* **1994**, *13*, 3517–3524.

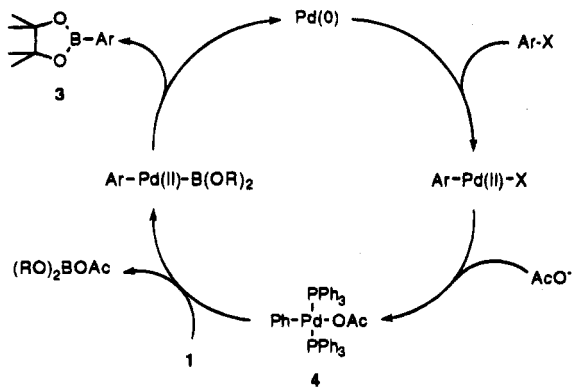

Figure 1.

since the ^{31}P NMR spectrum exhibited one singlet at 21.39 ppm and the ^{13}C NMR signal due to the phenyl C(1) carbon occurred at 148.60 ppm. Strong absorptions at 1600 and 1430 cm^{-1} are characteristic for the η^1-coordination of an acetoxy ligand. The quantitative formation of the same complex under the conditions used for the cross-coupling was immediately observed by ^1H NMR analysis of a *trans*-$PhPdBr(PPh_3)_2$ and KOAc (10 equiv) mixture in DMSO-d_6.[20] The isolated complex **4** exhibited high reactivity toward **1** giving a 67% yield of **3** (Ar = Ph) at room temperature.[21] Although the cross-coupling reaction proceeded at 80 °C, the above two reactions (which involve three steps: the ligand exchange with acetoxy anion, the transmetalation with **1**, and the reductive elimination of **3**) easily occurred at room temperature. On the basis of these results, the mechanism must be comprised of a catalytic cycle entailing the transmetalation between **1** and the acetoxopalladium(II) intermediate, as outlined in Figure 1.

The high reactivity of oxopalladium complexes toward transmetalation with organoboron compounds can be attributed to both the high reactivity of the Pd–O bond, which consists of a soft acid and a hard base combination, and the high oxophilicity of the boron center. The kinetic study reflects the transmetalation process taking place, first the coordination of the alkoxy ligand to the boron atom followed by the transfer of the organic group on boron to the palladium atom.[18] A similar high reactivity of RO-Pd complexes toward transmetalation with organosilicon compounds has recently been reported by Hiyama.[22] Thus, it is reasonable to anticipate a similar effect of base on the other cross-coupling reactions of less reactive organometallics.

The cross-coupling reaction of alkoxydiboron provides new access to various boronic esters directly from organic halides. The cross-coupling with other organic halides is being actively investigated.

Experimental Section

Spectral Data for Arylboronates 3. $C_6H_5B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.35 (s, 12 H), 7.36 (t, 2 H, J = 7.3 Hz), 7.46 (t, 1 H, J = 7.3 Hz), 7.81 (d, 2 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 24.89, 83.78, 127.72, 131.25, 134.77; ^{11}B NMR ($CDCl_3$) δ 26.67; exact mass calcd for $C_{12}H_{17}O_2B$ 204.1321, found 204.1320.

4-$Me_2NC_6H_4B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.32 (s, 12 H), 2.98 (s, 6 H), 6.69 (d, 2 H, J = 8.8 Hz), 7.69 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 24.85, 40.14, 83.18, 111.28, 136.16, 152.56; ^{11}B NMR ($CDCl_3$) δ 30.92; exact mass calcd for $C_{14}H_{22}O_2NB$ 247.1744, found 247.1737.

4-$MeOC_6H_4B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.33 (s, 12 H), 3.82 (s, 3 H), 6.89 (d, 2 H, J = 8.3 Hz), 7.75 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 24.87, 55.10, 83.56, 113.33, 136.52, 162.18; ^{11}B NMR ($CDCl_3$) δ 30.75; exact mass calcd for $C_{13}H_{19}O_3B$ 234.1427, found 234.1438.

4-$MeO_2CC_6H_4B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.36 (s, 12 H), 3.92 (s, 3 H), 7.87 (d, 2 H, J = 8.3 Hz), 8.02 (d, 2 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 24.91, 52.18, 84.22, 128.62, 132.35, 134.69, 167.17; ^{11}B NMR ($CDCl_3$) δ 30.60; exact mass calcd for $C_{14}H_{19}O_4B$ 262.1376, found 262.1385.

4-$MeC(O)C_6H_4B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.36 (s, 12 H), 2.62 (s, 3 H), 7.89 (d, 2 H, J = 8.3 Hz), 7.93 (d, 2 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 24.89, 26.78, 84.22, 127.30, 134.93, 139.03, 198.46; ^{11}B NMR ($CDCl_3$) δ 30.66; exact mass calcd for $C_{14}H_{19}O_3B$ 246.1427, found 246.1406.

4-$NCC_6H_4B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.35 (s, 12 H), 7.64 (d, 2 H, J = 8.3 Hz), 7.88 (d, 2 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 24.87, 84.51, 114.58, 118.89, 131.14, 135.11; ^{11}B NMR ($CDCl_3$) δ 30.46; exact mass calcd for $C_{13}H_{16}O_2BN$ 229.1274, found 229.1288.

4-$O_2NC_6H_4B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.37 (s, 12 H), 7.96 (d, 2 H, J = 8.8 Hz), 8.19 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 24.89, 84.64, 122.42, 135.68, 149.87; ^{11}B NMR ($CDCl_3$) δ 30.33; exact mass calcd for $C_{12}H_{16}O_4BN$ 249.1172, found 249.1185.

2,4,6-$Me_3C_6H_2B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.37 (s, 12 H), 2.24 (s, 3 H), 2.36 (s, 6 H), 6.77 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.25, 22.20, 24.96, 83.47, 127.45, 138.94, 142.15; ^{11}B NMR ($CDCl_3$) δ 32.18; exact mass calcd for $C_{15}H_{23}O_2B$ 246.1791, found 246.1810.

3-[($Me_4C_2O_2$)B]quinoline: ^1H NMR ($CDCl_3$) δ 1.40 (s, 12 H), 7.54 (t, 1 H, J = 8.1 Hz), 7.75 (t, 1 H, J = 8.3 Hz), 7.84 (d, 1 H, J = 8.3 Hz), 8.12 (d, 1H, J = 8.3 Hz), 8.63 (s, 1 H), 9.20 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.93, 84.35, 126.48, 127.58, 128.42, 129.37, 130.54, 144.28, 149.45, 154.81; ^{11}B NMR ($CDCl_3$) δ 30.77; exact mass calcd for $C_{15}H_{18}O_2BN$ 255.1431, found 255.1459.

3-[($Me_4C_2O_2$)B]benzothiophene: ^1H NMR ($CDCl_3$) δ 1.38 (s, 12 H), 7.33 (t, 1 H, J = 6.8 Hz), 7.40 (t, 1 H, J = 6.8 Hz), 7.88 (d, 1 H, J = 8.3 Hz), 8.07 (s, 1 H), 8.37 (d, 1 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 24.95, 83.58, 122.15, 124.12, 124.30, 125.42, 139.03, 140.75, 142.81; ^{11}B NMR ($CDCl_3$) δ 24.87; exact mass calcd for $C_{14}H_{17}O_2BS$ 260.1043, found 260.1031.

4-$BrC_6H_4B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.34 (s, 12 H), 7.50 (d, 2 H, J = 7.8 Hz), 7.66 (d, 2 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 24.87, 84.05, 126.24, 130.96, 136.32; ^{11}B NMR ($CDCl_3$) δ 30.81; exact mass calcd for $C_{12}H_{16}O_2BBr$ 284.0406, found 284.0392.

4-($Me_4C_2O_2$)$BC_6H_4B(O_2C_2Me_4)$: ^1H NMR ($CDCl_3$) δ 1.35 (s, 24 H), 7.80 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 24.89, 83.85, 133.91; ^{11}B NMR ($CDCl_3$) δ 31.16; exact mass calcd for $C_{18}H_{28}O_4B_2$ 330.2174, found 330.2148.

Supporting Information Available: Copies of NMR spectra of **3** and $PhPd(OAc)(PPh_3)_2$ (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(20) The ^1H NMR analysis of a mixture of $PhPdBr(PPh_3)_2$ and KOAc (10 equiv) in DMSO-d_6 gave the same spectrum with **4**, except there was a large signal corresponding to KOAc at 1.57 ppm.

(21) A mixture of **4** (0.039 mmol) and **1** (0.035 mmol) in C_6D_6 (0.5 mL) was stirred at room temperature for 30 min. The ^1H NMR analysis indicated the formation of phenylboronate **3** (Ar = Ph) in a 67% yield.

(22) Matsuhashi, H.; Hatanaka, Y.; Kuroboshi, M.; Hiyama, T. *Tetrahedron Lett.* **1995**, *36*, 1539–1540.