2346 *J. Org. Chem.* **1996,** *61,* 2346−2351

Palladium-Catalyzed Suzuki-Type Self-Coupling of Arylboronic Acids. A Mechanistic Study

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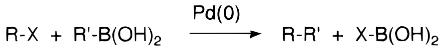
Received August 3, 1995⊗

Symmetrical biaryls are formed from arylboronic acids both under tetrakis(triphenylphosphine)-palladium and under palladium(II) acetate catalysis. The principal mechanistic features of these self-couplings have been determined.

Introduction

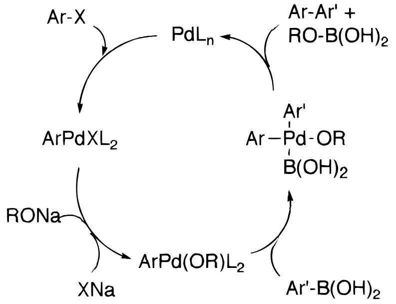
Palladium-catalyzed cross-coupling between a formal electrophile C−X (X mainly Br, I, OTf) and an organometallic species C−M (M mainly Mg, Zn, Sn, and B) is a versatile synthetic method for making C−C bonds.[1] The boron version (Suzuki coupling, Figure 1) has become increasingly popular since (1) it is compatible with the presence of electrophilic functional groups, (2) many boron compounds are stable, (3) several arylboronic acids are commercially available, (4) the inorganic product of the reaction can be easily eliminated in water, and (5) the reaction conditions tolerate aqueous media, which renders elimination of the boron-containing reaction products easier.[2] The Suzuki coupling was initially used for $C(sp^2)-C(sp^2)$ bond forming,[2a] but recently it was extended to accommodate carbon atoms in other hybridizations such as sp^3.[3] A recent improvement of the Suzuki coupling is the introduction of phosphine-free catalytic systems.[4]



$$R\text{-}X + R'\text{-}B(OH)_2 \xrightarrow{Pd(0)} R\text{-}R' + X\text{-}B(OH)_2$$

Figure 1. Palladium(0)-catalyzed Suzuki's cross-coupling.

Scheme 1. Catalytic Cycle for the Suzuki-Type Cross-Coupling



From the mechanistic viewpoint Suzuki proposed a widely accepted catalytic cycle[2b] that we reproduce in Scheme 1 for aryl−aryl coupling. The cycle is initiated by the oxidative addition of the organic halide to the stabilized Pd(0) species. The transmetalation step transfers the Ar' group from the metal boron to the metal palladium to generate an intermediate containing Ar, Ar′, $B(OH)_2$, and RO in the coordination sphere of palladium. Two reductive eliminations from this intermediate produce the coupling Ar−Ar′ product and the final boric acid derivative. In its general trends the cycle is similar to other cycles proposed for cross-couplings induced by other metals such as Mg,[5ab] Zn,[5c] and Sn.[5d,e] The difference is the inclusion of a step in which a base RO− is introduced in the coordination sphere of Pd. The reason is that the presence of a mineral base seems to be fundamental for the success of the Suzuki-type cross-coupling, which makes boron-based couplings different from those based on the other three metals. However, other explanations have been offered for the fundamental role of the base in the Suzuki-type cross-coupling; thus, it has been suggested that the transmetalation step occurs on a $[Ar'B(OH)_3]^-$ species rather than on the arylboronic acid.[2d] In any case, the presence of mineral base seems to be essential. Recently it has been reported that fluoride anion can play the same role.[6]

The general features of the mechanistic cycle have received further support since some of the proposed intermediates have been detected by electrospray ionization mass spectrometry.[7] However, no $RPd(OH)L_n$ intermediate was registered in this study.

In spite of its usefulness, two problems have been pointed out in some Suzuki-type cross couplings:

1. Marcuccio and co-workers have found that coupling of arylboronic acid with the phenyl group from the triphenylphosphine-stabilizing ligand is a side reaction to the desired coupling of the arylboronic acid with an

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⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1996.

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Scheme 2. Pd-Catalyzed Self-Coupling of Arylboronic Acids 1

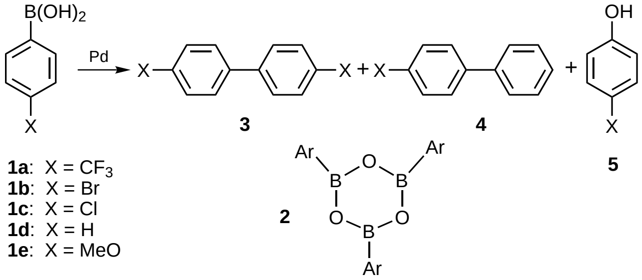

Table 1. Yields of Compounds 3−5 from Arylboronic Acids, 1[a]

run	X	catalyst (%)	time	**3** (%)	**4** (%)	**5** (%)
1	CF_3	$Pd(PPh_3)_4$ (10)	2 days	**3a** (43)	**4a**[b]	**5a** (5)
2	Br	$Pd(PPh_3)_4$ (2)	5 days	**3b** (28)[c]		**5b** (13)
3	Cl	$Pd(OAc)_2$ (3.5)	4 days	**3c** (30)		
4	H	$Pd(PPh_3)_4$ (10)	2.5 h	**3d** (52)	**4d**[d]	**5d** (17)
5	MeO	$Pd(PPh_3)_4$ (10)	2 days	**3e** (18)	**4e** (11)	**5e** (6)

[a] Reactions were performed at rt. Yields are not optimized. [b] Traces. [c] 43% based on reacted **1b**. [d] **4d** is the same as **3d**.

Table 2. Influence of X on Yields of 3 at a Fixed Time (75 min)[a]

$$\underset{\mathbf{1}}{XPhB(OH)_2} \xrightarrow[\text{Pd (2\%)}]{\text{toluene, rt}} \underset{\mathbf{3}}{XPhPhX}$$

run	**3** (X)	yield (%) at 75 min	σ_p (σ_p^+)	yield (%) at longer time
1	**3a** (CF_3)	6	0.53 (0.53)	40 at 73 h
2	**3b** (Br)	17	0.26 (0.15)	50 at 25 h
3	**3c** (Cl)	19	0.24 (0.17)	59 at 21 h
4	**3d** (H)	47	0.00 (0.00)	64 at 5 h
5	**3e** (MeO)	62	−0.28 (−0.78)	62 at 1.3 h

[a] All reactions at [**1**] = 0.035 M.

Table 3. Influence of the Atmosphere on the Yields of 3d

$$\underset{\mathbf{1d}}{PhB(OH)_2} \xrightarrow[\text{Pd(PPh}_3)_4\text{ (2\%)}]{\text{toluene, rt}} \underset{\mathbf{3d}}{PhPh}$$

atmosphere	% of **3d** at the given time
nitrogen	23 at 5 h
air	64 at 5 h
oxygen	66 at 2.6 h

aryl bromide.[8] The same phenomenon has been observed in the closely related Sn-mediated Pd-catalyzed Stille cross-coupling[9] and in the Heck reaction.[10] The aryl−aryl exchange between phosphines and arylpalladium iodides was known, and a mechanistic study has been published.[11]

2. Self-coupling of aryl groups of the arylboronic acids occurs when the cross-coupling is very slow.[12−14] Also, palladium-catalyzed self-coupling of arylstannanes is known.[15]

Sometimes we have experienced the formation of self-coupling products when attempting difficult cross-couplings, and therefore our attention was drawn to the paper by Song and Wong dealing with this matter.[14] These authors turned the self-coupling into a useful synthetic method that they applied for the preparation of furan-3,4-diyl oligomers. However, their mechanistic proposal seems not to follow the conventional beliefs in the field, and they suggested that the success of the self-coupling, in the basic medium they use, depends on the presence of 1,2-bis(bromomethyl) aromatic compounds. At this point, we decided to study the self-coupling from a mechanistic viewpoint.

Results and Discussion

First, we noticed that arylboronic acids **1** could be converted into symmetrical biaryls **3** under Pd(0)-catalysis (Scheme 2 and Table 1). Other products formed were monosubstituted biaryls **4** and phenols **5**. In all cases, neither bases nor bromomethyl compounds were introduced into the reaction, both being therefore unnecessary. Palladium(II) acetate was used as catalyst or precatalyst for the reaction of *p*-chlorophenylboronic acid, **1c** (run 3). It should be mentioned that a mixture of an ester of **1a** and palladium(II) acetate has been reported to yield **3a**.[4b]

Once the basic requirements for self-coupling to occur had been established we turned our attention toward the influence of different factors.

Reactions were performed with arylboronic acids **1** under the same conditions including $Pd(PPh_3)_4$ catalysis, and the yields were controlled at the same intervals of time (75 min). The more electron-withdrawing substituent (CF_3) gave the lower yield and the most electron-donating group (OMe) gave the higher yields (Table 2). On the other hand, run 4 of Table 2, performed under normal air atmosphere, was compared with reactions carried out under the same conditions but under different atmospheres (Table 3). The conclusion is that oxygen accelerates the reaction. This looks normal since a self-coupling from a boronic acids requires $(HO)_2B-B(OH)_2$ to be the other reaction product. This diborane derivative seems most improbable from the thermodynamic viewpoint, and some oxidation step is required to release boron as a derivative of boric acid. In this sense, the self-coupling of boronic acids should be considered as an oxidative coupling in sharp contrast with reductive couplings performed on halogen derivatives (ArX) which require a stoichiometric amount of a reducing agent to account for the equivalent of halogen formally liberated.[16] Observations similar to ours were reported by Farina and co-workers who blamed the presence of oxygen as the main cause of the arylstannanes self-coupling.[15] In 1975, Heck reported the reactions of vinylboronic acids with methyl acrylate in the presence of 1 equiv of palladium(II) acetate,[17] which means that boron could finally appear as $(HO)_2B(OAc)$. In contrast, Heck-type reactions of arylboronic acids reported by Uemura require only catalytic palladium(II) acetate;[18] therefore, boron ends up as either $HB(OH)_2$ or an oxidizing agent, and oxygen is probably required.

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Scheme 3. Proposed Catalytic Cycle for the Pd(0)-Catalyzed Self-Coupling of Arylboronic Acids 1

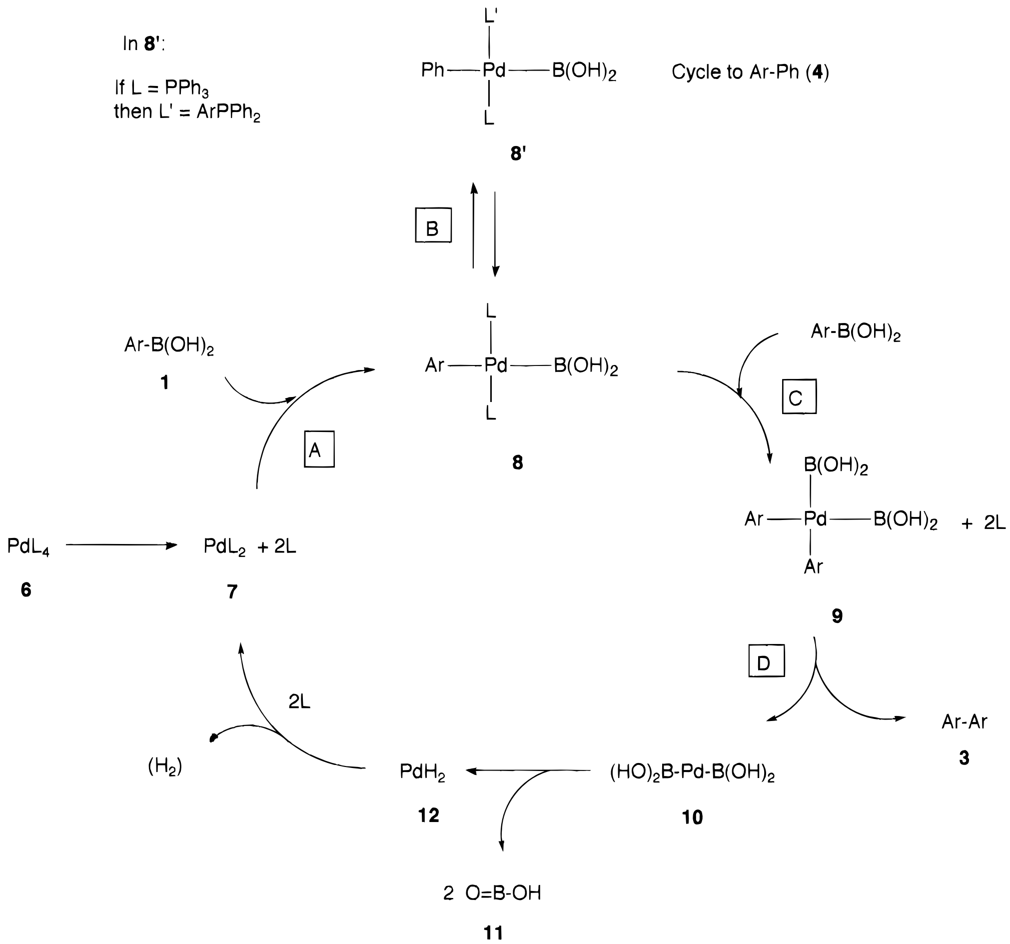

Table 4. Catalytic Effect of Several Pd(0) Species in the Formation of 3

$$\mathrm{XPhB(OH)_2} \xrightarrow[\mathrm{Pd(0)}]{\text{toluene}} \underset{\mathbf{3}}{\mathrm{XPhPhX}}$$

run	**1** (concn, M)	catalyst	condns	**3** (%)
1	**1a** (0.035)	$Pd(dba)_2$ (2%), Fu_3P (8%)	rt, 50 h	**3a** (72)
2	**1a** (0.035)	$Pd(dba)_2$ (10%), Fu_3P (40%)	rt, 15 h	**3a** (93)
3	**1d** (0.109)	$Pd(dba)_2$ (10%)	N_2, reflux, 48 h	
4	**1d** (0.109)	$Pd(dba)_2$ (10%), PPh_3 (40%)	N_2, reflux, 24 h	**3d** (55)
5	**1d** (0.066)	Pd(10%)−C	rt, 41 h	**3d** (10)

Other forms of Pd(0) were also tested as catalysts in our oxidative couplings, and the results are collected in Table 4; thus, $Pd(dba)_2$ (10% molar) was completely inert toward **1d** after refluxing in toluene for 48 h under a nitrogen atmosphere (Table 4, run 3). However, the addition of triphenylphosphine (40% molar) led to **3d** in 55% in 24 h (Table 4, run 4). Probably, the catalytic species formed between $Pd(dba)_2$ and PPh_3 in a molar ratio 1:4 is similar to the catalytic species emerging from $Pd(PPh_3)_4$. The heterogeneous palladium (10%) on charcoal showed some activity; thus, a 0.066 M solution of **1d** in toluene at room temperature afforded 10% of **3d** in 41 h (Table 4, run 5). Finally, it should be mentioned that an important improvement in the yield of **3a** was observed when the sluggish **1a** was treated with $Pd(dba)_2$ and tri(2-furyl)phosphine (Table 4, runs 1 and 2).

With all this information, we propose the mechanistic cycle of Scheme 3. First, it should be mentioned that the concepts of oxidative addition and transmetalation merge in Scheme 3. Indeed, would step A of Scheme 3 have had an aryl bromide or iodide as protagonist, it would be classified in the category of oxidative addition. Although this still holds in our case, it is also true that it gives rise to a transfer of aryl from the metal boron to the metal palladium. Of course, this semantic difference depends on the consideration of boron (and not of bromine or iodine) as a metal. The same applies to step C. Step B is an isomerization between an arylpalladium(II) species and a ligand (e.g., L = triphenylphosphine). The resulting **8′** would afford the mixed biphenyls **4** by a cycle analogous to the main one leading to **3**. Whatever the isomerization mechanism is, step B is required to account for the formation of **4**. At least two completely different mechanisms have been proposed for this type of ligand scrambling.[9,11] Intermediate **8** formed in step A reacts with a second equivalent of arylboronic acid to afford intermediate **9**. If step C is slow enough, then isomerization to **8′** has a chance to occur in the presence of stabilizing ligands. One reductive elimination is required to form the final biaryls **3** and species **10** featuring Pd−B bonds. As previously commented, the elimination of tetrahydroxydiborane ($(HO)_2B{-}B(OH)_2$) is highly improbable, and it is much more reasonable to accept that boron ends up in the form of a boric acid derivative such as metaboric acid **11** (in the usual alkaline water medium used in the Suzuki couplings, **11** will be converted into

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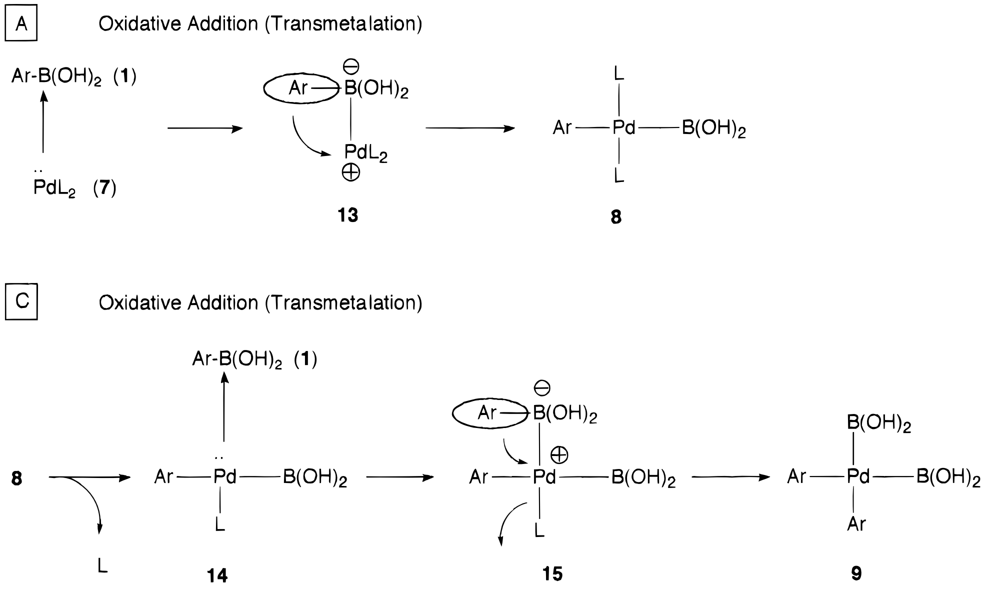
Scheme 4. Proposed Mechanism for the Oxidative Addition Steps of Scheme 3



borate). The intermediate palladium hydride, **12**, can release hydrogen or reduce oxidants present in the reaction media (oxygen in normal atmospheres).

Another important point is the observed outstanding tendency of the higher reaction rates for electron-donating substituents X in the arylboronic acid, **1**. A closer examination of steps A and C as indicated in Scheme 4 will help to substantiate this phenomenon.

Step A probably consists of two different processes. Arylboronic acids, **1**, (and the cyclic trimeric anhydrides, **2**, which accompany them) should be considered as strong Lewis acids at the boron atom. On the other hand, palladium species PdL$_n$ (n < 4) function at the same time both as Lewis bases and as Lewis acids. We represent in Scheme 4 a pair of electrons of the coordinatively unsaturated (14 electrons) species PdL$_2$, **7**. An acid–base reaction between **1** and **7** looks reasonable, and it should be fast (*vide infra*) to afford intermediate **13**. A 1,2 migration of the aryl group to the electronically deficient positive palladium atom is reminiscent of the Wagner–Meerwein and related rearrangements, and it should be favored by the electron-donating ability of the group X. The same arguments could be repeated for the second oxidative addition or transmetalation, namely, the conversion of **8** + **1** into **9**. Of course, the slow step or rate-determining step of the cycle could depend on the group X, and the effect of the atmosphere in the conversion of **1d** into **3d** (Table 3) points out that regeneration of PdL$_n$ from **10** could embrace the slow step when X = H. However, for reactions in which the aryl group has a low migrating ability (X = CF$_3$) A or C (or more exactly the rearrangement part of one of them) could be the rate-determining step. The observed rate increase in the formation of **3a** by using tri-2-furylphosphine instead of triphenylphosphine is more difficult to understand (Table 4).

To obtain more information on the relative rates of the steps in the cycle of Schemes 3 and 4, we performed the reaction between **1a** and 1 equiv of tetrakis(triphenylphosphine)palladium in toluene-d_8 in the ^{19}F NMR probe at an initial temperature of 300 K, registering spectra at different periods of time. Figure 2 contains a superimposition of spectra. The following facts are remarkable:

1. The spectra of **1a** and **2a** (δ 0.7 and −0.4) were not observed. Thus, **1a** and **2a** disappear almost immediately through fast reactions (less than 2 min).

2. The phenol **5a** is formed very rapidly at the initial stages of the process (7 min), and its concentration remains constant for the rest of the time. Palladium is required for phenol formation since mixtures of **1a** and triphenylphosphine, and of **1d** and triphenylphosphine in toluene, at room temperature did not show the presence of phenols after 24 h.

3. An intermediate (A, δ ca. 1.0) is formed and accumulates before the presence of biphenyls **3a** and **4a** is observed.

4. The first intermediate A converts into a second intermediate B (δ ca. 0.45). This intermediate B disappears slowly while symmetrical biphenyl **3a** (first) and the unsymmetrical **4a** (later) appear. Intermediate B was forced to convert into **3a** and **4a** by heating at 343 K after 16 h of reaction. Unfortunately, attempts to isolate the accumulated intermediates failed, and therefore, their structures remain speculative.

Since both **3a** and **4a** are formed when A is already absent and at the same time as B disappears, B should be attributed structure **8**, and this leaves structure **13** for the first-formed intermediate A. Another possibility requires reversibility of the acid–base reactions affording **13** and **15**; if formation of **15** from **8** is reversible, intermediate A could be **13** and intermediate B could be **15**, the slow steps for X = CF$_3$ being the unfavorable 1,2-rearrangements. In any case, for X = CF$_3$ the slow steps are at the level of oxidative additions (transmetalations).

Next, we performed studies using palladium(II) acetate as catalyst or catalyst precursor. All reactions were slower than with Pd(PPh$_3$)$_4$ catalysis with one exception: **1a**. Thus, in sharp contrast with the Pd(0)-catalyzed reactions, boronic acid **1a** (X = CF$_3$), exhibited the highest rate not only in comparison with other boronic acids but also in comparison with the rate exhibited by the same **1a** with Pd(0). The reactions under Pd(OAc)$_2$ catalysis showed no clearly defined tendency (CF$_3$ > H > OMe > Cl >> Br), compound **1b** (X = Br) being inactive. The results are depicted in Table 5. Also, no clear tendencies were evident when the effects

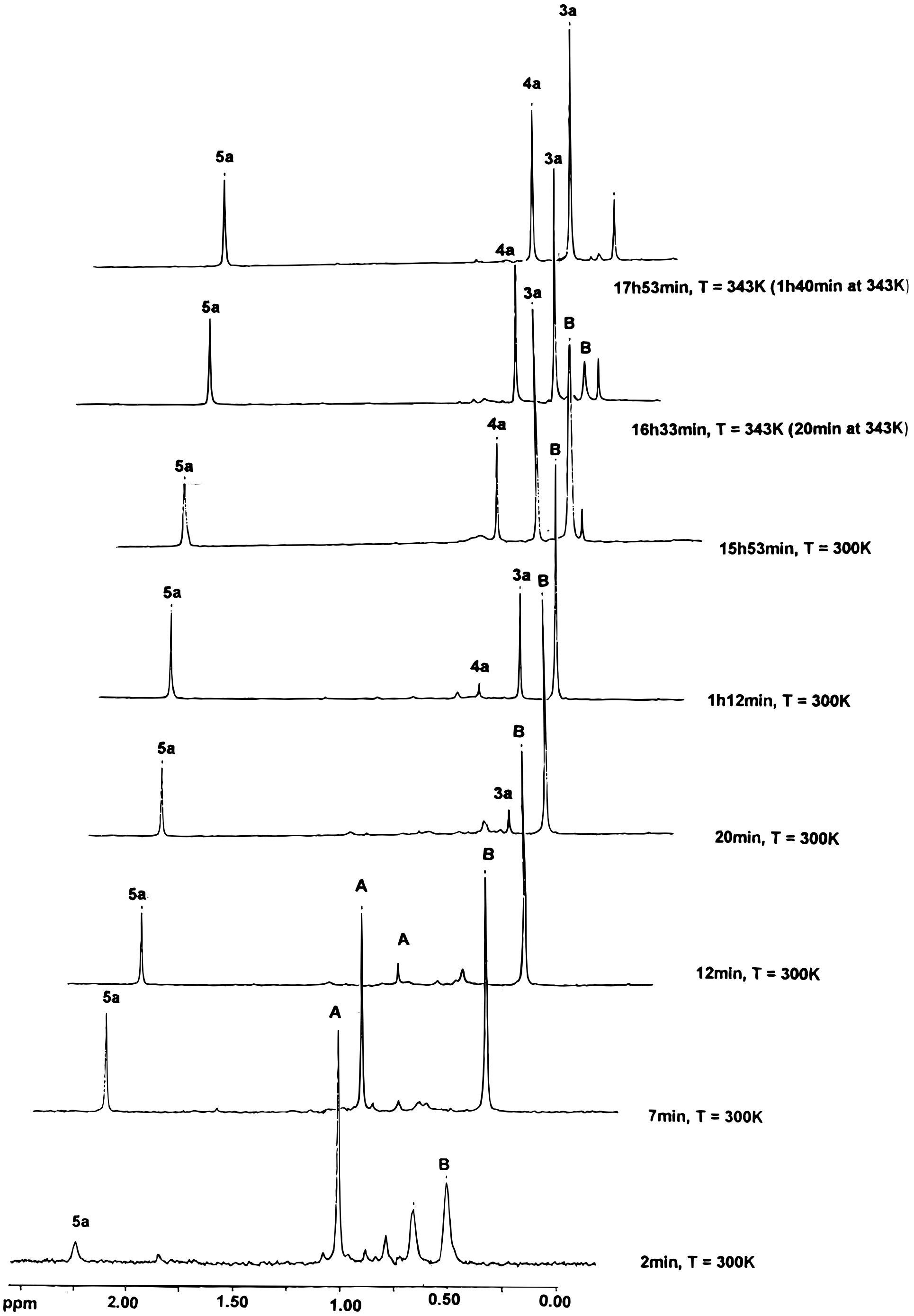


Figure 2. ^{19}F NMR spectra at different times of the reaction of **1a** with tetrakis(triphenylphosphine)palladium in toluene-d_8.

of the type of atmosphere and of the presence of triphenylphosphine in reactions of **1d** mediated by palladium acetate were studied.

As previously noted, the conversion of an ester of **1a** into **3a** under Pd(OAc)$_2$ catalysis has been reported.[4b] An initial stoichiometry as indicated in Scheme 5 (eq 1) seems reasonable, but the reactions shown in Table 5 occur with catalytic amounts of the initial palladium acetate. However, Pd(II) is consumed and reduced to Pd(0) according to eq 1. The possible explanation is that the continuation of the reaction occurs under Pd(0) catalysis.

Table 5. Influence of X in the Yields of 3 under Pd(OAc)$_2$ Catalysis[a]

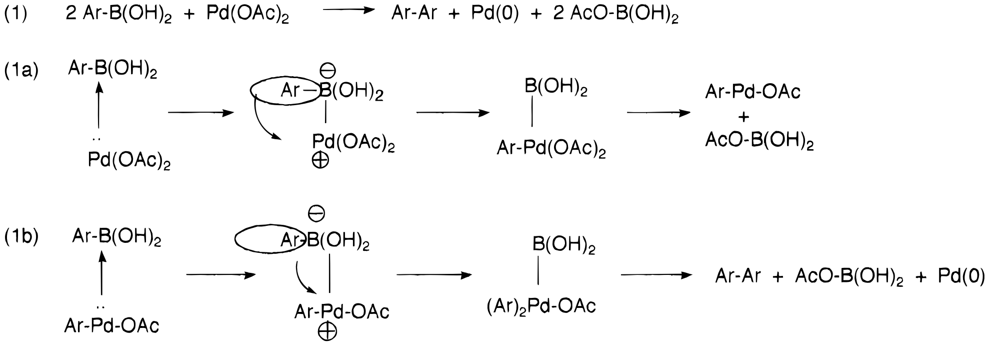
$$\underset{\mathbf{1}}{\mathrm{XPhB(OH)_2}} \xrightarrow[\mathrm{Pd(OAc)_2\ (2\%)}]{\mathrm{toluene,\ rt}} \underset{\mathbf{3}}{\mathrm{XPhPhX}}$$

run	X	time (h)	**3** (%)
1	CF_3	3.1	**3a** (64)
2	Br	3.2	**3b** (1)
3	Cl	44.5	**3c** (19)
4	H	10.1	**3d** (51)
5	OMe	4.2	**3e** (32)

[a] [**1**] = 0.035 M.

Equations 1a and 1b of Scheme 5 represent the mechanistic explanation of eq 1, involving acid−base reactions between Pd(II) species and arylboronic acids (for the sake of simplicity Pd(OAc)$_2$ has been written as monomeric) followed by 1,2-rearrangements of aryl groups to the electron-deficient positive palladium species.

Scheme 5. Proposed Mechanism for the Oxidative Self-Coupling of Arylboronic Acids, 1, Induced by Pd(II)



^{19}F NMR studies were performed on a reaction of **1a** with 10% of Pd(OAc)$_2$ in toluene-d_8 at 300 K. The starting materials **1a** (and **2a**) showed peaks at δ ca. 0.7 and −0.4 which disappear steadily while the peak of **3a** at δ ca. 0.5 increases. Intermediates could not be detected with the same clarity as for the Pd(0)-catalyzed reaction.

Experimental Section

^{19}F NMR spectra were recorded at 376.3 MHz with CF$_3$Ph as external reference. ^{13}C NMR spectra were recorded at 62.5 MHz. Mass spectra were recorded under electron impact at 70 eV. The yields given in the nonpreparative experiments of Tables 2−5 were determined by GC taking off aliquot samples from the reaction mixtures and adding 4-nitroveratrole as internal standard. Therefore, these yields do not account for mechanical losses during isolation.

4,4′-Dibromobiphenyl (3b) (General Procedure). A mixture of 4-bromophenylboronic acid, **1b** (0.400 g, 1.99 mmol), tetrakis(triphenylphosphine)palladium(0) (46 mg, 0.04 mmol), and toluene (40 mL) was stirred at rt for 5 days (GLC monitoring). The mixture was evaporated and the residue chromatographed through a column of silica gel. With hexane as eluent product **3b** was obtained (86 mg, 28% isolated yield, 43% yield based on consumed **1b**), mp 165−168 °C.[19] 4-Bromophenol, **5b**, was eluted later (46 mg, 13%), and it was compared with an authentic sample (GC).

All other known symmetrical biphenyls gave mp's as reported.[19] 4,4′-Bis(trifluoromethyl)biphenyl, **3a**: mp 78−81 °C; IR (KBr) 1324, 1166, 1133, 1114, 1070, 829 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 124.8 (q, J = 272 Hz), 126.7 (q, J = 4 Hz), 127.5, 131.3 (q, J = 32 Hz), 143.8; ^{19}F NMR (toluene-d_8) δ 0.54; MS (m/z) 290 (M$^+$, 100). Anal. Calcd for C$_{14}$H$_8$F$_6$: C, 57.94; H, 2.78. Found: C, 58.35; H, 3.06.

4-(Trifluoromethyl)biphenyl, **4a**, was characterized by GC−MS: (m/z) 222 (M$^+$, 37), 154 (100). 4-Methoxybiphenyl, **4e**, was characterized by GC−MS: (m/z) 184 (M$^+$, 100), 169 (48), as well as compared with an authentic sample (GC).

4-(Trifluoromethyl)phenol **5a** was characterized by GC−MS: 162 (M$^+$, 76), 143 (100), 112 (85). All other phenols were compared with authentic samples (GC).

Acknowledgment. Financial support from DGICYT (Ministry of Education and Science of Spain) (Project PB93-0896 and a predoctoral scholarship (to M.P.)) and CIRIT (Generalitat de Catalunya) (Project GRQ93-2011) is gratefully acknowledged.

Supporting Information Available: ^{13}C NMR spectrum of compound **3a** and ^{19}F NMR spectra of the reaction of 4-(trifluoromethyl)phenylboronic acid, **1a**, with tetrakis(triphenylphosphine)palladium(0) in toluene-d_8 at different reaction times (12 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.

JO9514329

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[19] Biphenyls **3b**−**e** showed mp's coincident to those reported in Aldrich or Lancaster catalogs.