Synthetic Methods

DOI: 10.1002/ange.201101461

Mutual Activation: Suzuki–Miyaura Coupling through Direct Cleavage of the sp^2 C–O Bond of Naphtholate**

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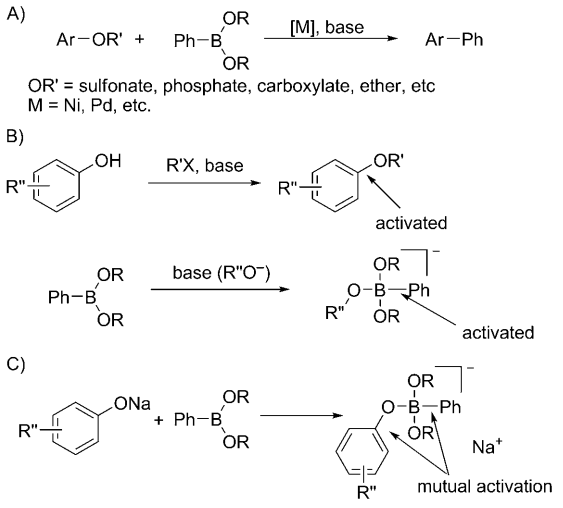
Since the 1970s, the development of various cross-coupling reactions that start from organohalides has provided efficient methods to build up biaryl compounds, which are important structures in bioactive compounds, natural products, and synthetic materials.[1] Cross-coupling reactions were recognized last year with the Nobel Prize, and owing to the mild reaction conditions, high functional-group tolerance, and the wide commercial availability of nontoxic and stable boronic acid derivatives, the Suzuki–Miyaura reaction is particularly attractive among the various cross-coupling reactions.[2] The Suzuki–Miyaura coupling is now successful both under homogeneous and heterogeneous catalysis, and has been widely applied to the synthesis of important drugs, polymers, and materials in both academic and industrial laboratories.[3] Investigations offer excellent chances to use simple arenes in many cross-coupling reactions.[4] However, the lack of accuracy obtained using a directing strategy, indicates that aryl halides are currently not replaceable.[5] Owing to the abundance and availability of phenol derivatives, many methods to activate phenols so that they could take the place of halides in these reactions have been tested.[6] Herein, we report the new concept of mutual activation of the C–O bond in phenols and the C–B bond in aryl boronic acid derivatives to realize the Suzuki–Miyaura coupling of phenols.

Recent advances have made less-reactive aryl ethers, carboxylic esters, and carbamates applicable in Suzuki–Miyaura coupling reactions.[7] Undoubtedly, the use of phenols in the Suzuki–Miyaura coupling would be optimal in terms of meeting the requirements of sustainable chemistry: not only improving step economy and atom economy and starting from naturally available chemicals, but also producing no carbon-containing by-products. Although the recent success in the Kumada–Tamao–Corriu coupling using phenolates with active Grignard reagents provided a potential solution,[8] the challenge to cross-couple phenols and their salts with much less-reactive species, for example, aryl boronic acids, still presents difficulties. Our recent efforts have turned to the development of an efficient method for the application of phenolates in the Suzuki–Miyaura coupling reaction.

In a traditional Suzuki–Miyaura coupling, the hydroxy group of the phenol species is derivatized to form active compounds.[6,7] Meanwhile, the formation of the borate facilitates the transmetalation in the catalytic cycle (Scheme 1 A and B).[9] In our novel design, the phenolate could react with the three-coordinate aryl boronic reagents to generate aryl borates. In these complexes, the borate might activate the aryl C–O bond and the borate anion might play the same role as a derivatized hydroxy group, such as a sulfonate and phosphate. Meanwhile, the formation of the borate activates the C–B bond and promotes the transmetalation later in the reaction cycle (Scheme 1 C). The advantage is that both the coupling partners come from the same in situ generated aryl borate, and the aryl C–O bond and the aryl C–B bond are mutually activated. Notably the two partners activate each other and so avoid the need for preactivation of the phenol species and the addition of extra base (Scheme 1 B).



Scheme 1. Rational design of the new concept of mutual activation by the formation of borate from aryloxylate and boronic acid derivatives.

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[**] We thank Prof. Wen-Xiong Zhang, Dr. Neng-Dong Wang, Prof. Xiang Hao, and Shao-Guang Zhang for the X-ray crystallographic analysis, and Prof. Zhi-Xiang Yu and Qian Li for the use of their glove box. D.-G. Yu thanks Bi-Jie Li, Bing-Tao Guan, Yang Li, and Chang-Liang Sun for constructive discussion, and Xiao-Bo Zhang and Xin Wang for their help in preparation of some of the compounds. Support of this work by NSFC (No. 20925207, 21072010, 20821062) and the "973" Project from the MOST of China (2009CB825300) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201101461.

2-Naphtholates **1** with different metal counterions were treated with phenylboroxine (**2a**) in the presence of nickel catalysts to prove our concept. Although the magnesium naphtholate gave no desired product, we found that the lithium, potassium, and zinc salts afforded a trace amount of product **3aa**, and the sodium salt showed the highest reactivity (see Table S1 in the Supporting Information). Notably, the mixed nonpolar solvent system of THF and *o*-xylene is a key requirement to facilitate this transformation. Although the observation of the desired product **3aa** was exciting to us, initially further investigations gave no progress. After numerous trials in which the different parameters were varied, no improvement was seen in the reaction efficiency.

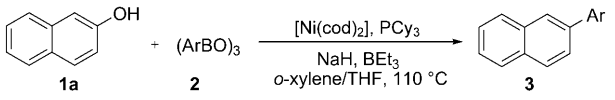
Pleasingly, the addition of the mild Lewis acid BEt_3 (triethylborane) gave a surprising result. Both the conversion and the yield of the isolated product significantly increased in the presence of the appropriate amount of BEt_3, despite being accompanied by a trace amount of reduced and/or ethylated by-products. Trimethoxyborane also promoted the reaction, albeit with a slightly lower efficiency (see Table S1 in the Supporting Information). The combination of $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) and tricyclohexylphosphine (PCy_3) showed the best efficiency, while the prepared $[NiCl_2(PCy_3)_2]$ plus additional PCy_3 gave a lower catalytic activity. Other catalysts completely failed in this transformation (see Table S3 in the Supporting Information). Different phenylboronic reagents were tested and phenylboroxine (**2a**) turned out to be the best (see Table S4 in the Supporting Information).

Further investigations demonstrated the broad substrate scope of this transformation. Various aryl boroxines could be applied in the reaction with good efficiency (Table 1). Electron-donating groups, such as OMe and NMe_2, promoted the reaction (Table 1, entries 4 and 5). In contrast, aryl boroxines that contained electron-withdrawing groups mainly underwent protodeborylation and gave relatively poor conversion into the desired product (Table 1, entry 6). Steric bulk on the aryl group did not hamper the reaction and 2-tolylboroxine also gave the desired product in an excellent yield (Table 1, entry 3). Notably the C–OMe and C–F bonds (Table 1, entries 5 and 7), which can be easily cleaved by nickel catalysis, were tolerated well, and therefore could provide the opportunity for orthogonal cross-coupling reactions with different functionalities.[10,11]

From the aspect of the phenols (Table 2), 1-naphthol gave the desired product (**3bb**), although in a relatively lower yield, under the slightly modified reaction conditions (Table 2, entry 2). Phenanthren-9-ol (**1c**) also showed high reactivity (Table 2, entry 3). Notably the selective cleavage of the C–OH bond over the C–OR bond was observed; for example, the *tert*-butoxy group on the naphthyl ring (**1e**) was tolerated (Table 2, entry 5). Notably, an ester group (**1d**) is also stable under the reaction conditions (Table 2, entry 4). Most importantly, the selective cleavage of simple phenol derivatives could also take place, albeit in a low yield (Table 2, entry 6), thus indicating the potential applicability of this method to the functionalization of simple phenol derivatives.

Mechanistically, the absence of the desired product when the reaction was carried out without a nickel catalyst implied

Table 1: Suzuki–Miyaura coupling of 2-naphthol (**1a**) with different aryl boroxines **2**.[a]



1a 2 3

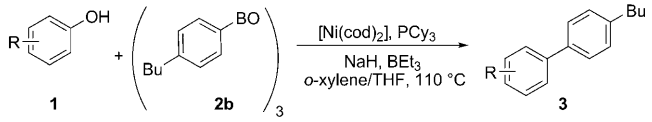
Entry	Ar (**2**)	**3**	Yield [%]
1	**2a**	**3aa**	82
2	*n*Bu **2b**	*n*Bu **3ab**	90
3	Me **2c**	Me **3ac**	80
4	Me_2N **2d**	NMe_2 **3ad**	80
5	MeO **2e**	OMe **3ae**	81
6[b]	F_3C **2f**	CF_3 **3af**	43
7	Me, F **2g**	F **3ag**	65

[a] Reaction conditions: 0.4 mmol of **1a**, 1.0 equiv of aryl boroxine **2**, 10 mol% of $[Ni(cod)_2]$, 40 mol% of PCy_3, 1.0 equiv of NaH, 1.5 equiv of BEt_3 in the mixture of 0.7 mL of *o*-xylene and 0.2 mL of THF at 110 °C for 48 h. [b] 0.2 mmol of **1a** and 3.0 equiv of 5,5-dimethyl-2-(4-trifluoromethylphenyl)-1,3,2-dioxaborinane was used.

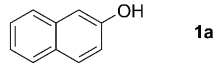
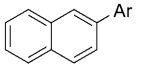
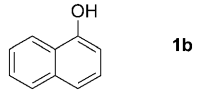
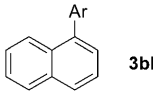
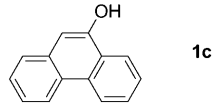
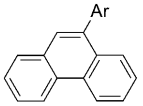
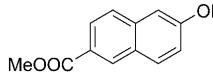
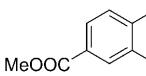
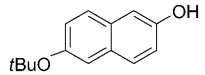
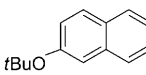
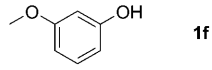
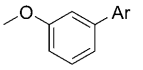
that the nickel species played a vital role in the activation and cleavage of the C–O bond of the phenolates. Importantly the significant effect of the BEt_3 is due to its Lewis acidity. Several different hypotheses were proposed, as illustrated in Scheme 2. As a Lewis acid, BEt_3 might directly react with the phenolate to form a borate and thus activate the C–O bond (Scheme 2A). Another possibility is a second Lewis acid/Lewis base interaction between the in situ generated borate and BEt_3, which can be defined as a Lewis acid assisted Lewis acid effect (LA/LA) to promote the reactivities of both C–O and C–B bonds (Scheme 2B).[12]

Experimentally, both BEt_3 and the phenylboronic reagent could indeed react with sodium naphtholate to form borate, as shown by ^{11}B NMR spectroscopy (Scheme 3, spectra (1)–(4)). However, the ^{11}B NMR signal of BEt_3 in the presence of the phenyl boronate ester and sodium naphtholate moved only slightly upfield, thus implying that the formation of the borate from BEt_3 and naphtholate (Scheme 2A) did not occur in the presence of the phenyl boronate ester (Scheme 3, spectrum (5)). The observed reactivity in the absence of BEt_3 also

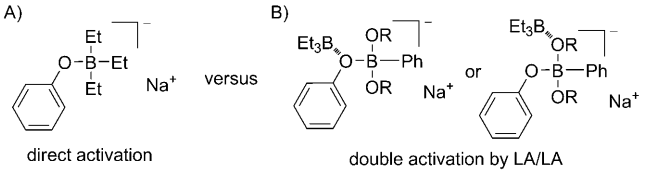
Table 2: Suzuki–Miyaura coupling of **2b** with different phenols **1**.[a]



1 **2b** **3**

Entry	**1**	**3** (Ar = 4-*n*BuC$_6$H$_4$)	Yield [%]
1	 **1a**	 **3ab**	88
2	 **1b**	 **3bb**	68
3	 **1c**	 **3cb**	82
4	 **1d**	 **3db**	62
5	 **1e**	 **3eb**	63
6[b]	 **1f**	 **3fb**	18

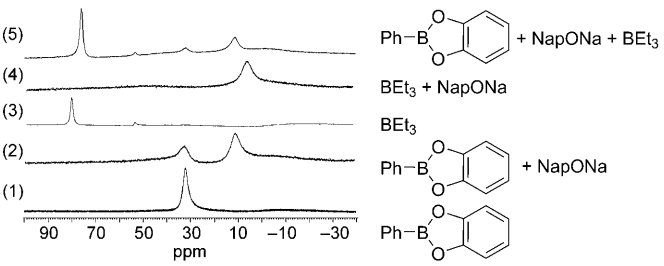
[a] Reaction conditions: 0.2 mmol of **1**, 1.0 equiv of **2b**, 10 mol% of [Ni(cod)$_2$], 40 mol% of PCy$_3$, 1.0 equiv of NaH, 3.0 equiv of BEt$_3$ in the mixture of 0.35 mL of *o*-xylene and 0.1 mL of THF at 110°C for 48 h. [b] 1.5 equiv of BEt$_3$ was added.



Scheme 2. The possible role of BEt$_3$ in the catalytic cycle. **A** direct activation of phenolate; **B** double activation through a Lewis acid assisted Lewis acid (LA/LA) pathway.

supports the pathway involving the Lewis acid assisted Lewis acid effect (Scheme 2B). Also, the slight upfield shift of the ^{11}B NMR signal of BEt$_3$ in the presence of the phenyl boronate ester and sodium naphtholate (Scheme 3, spectra (3) and (5)) indicated a weak interaction between the formed borate and the additional Et$_3$B by the above-mentioned LA/LA interaction (Scheme 2B). These studies provide strong evidence in support of the hypothesis of double activation. Notably, the possibility that the BEt$_3$ plays the role of a radial initiator at the initial stage of the oxidative addition, as previously reported, could not be ruled out.[13] Mass spectrmeric analysis of the reaction mixture also provided strong evidence to support the formation of borate complexes (see the Supporting Information).

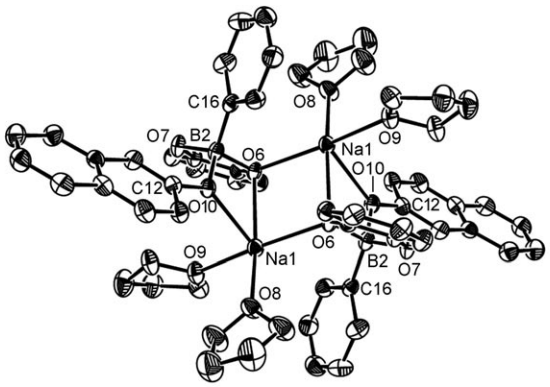
To further prove our concept, many attempts have been made to isolate the key

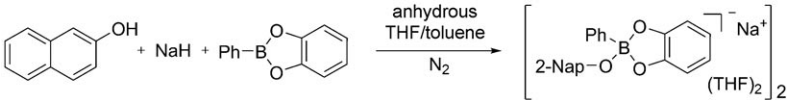


Scheme 3. ^{11}B NMR spectra: (1) 2-phenylbenzo[*d*]1,3,2-dioxaborole, $\delta = 32.1$ ppm; (2) NapONa + 2-phenylbenzo[*d*]1,3,2-dioxaborole, $\delta = 32.1$ and 10.9 ppm; (3) BEt$_3$, $\delta = 80.8$ ppm; (4) BEt$_3$ + NapONa, $\delta = 5.5$ ppm; (5) NapONa + 2-phenylbenzo[*d*]1,3,2-dioxaborole + BEt$_3$, $\delta = 76.4$, 32.0 and 11.4 ppm. Nap = naphthyl.

intermediate. Pleasingly, the isolation of the key intermediate was achieved and its structure, which was determined by X-ray crystallographic analysis, gave support to our hypothesis (Scheme 4). This compound was isolated from the reaction performed under similar reaction conditions as shown in Scheme 4 in the absence of the catalysts, thus THF played the role of a ligand in the isolated dimer. From the X-ray crystallographic data we found that both the C–O bond (1.370 Å) and C–B bond (1.606 Å) were slightly longer than the corresponding bonds in **1a** (1.336 Å) and phenyl boronic ester (1.537 Å).[8a,14] This information gave strong support for our concept of mutual activation. Notably, the bridged sodium ions might play a role similar to that of the additional Et$_3$B to further facilitate the double activation. Direct application of this borate to the optimized reaction conditions also afforded the desired product in 60% yield (see the Supporting Information).

In summary, starting from in situ generated sodium phenolates, the first direct cross-coupling with aryl boroxines to produce biaryl compounds was carried out using nickel catalysis. The key point is the formation of the borate, which offered the mutual activation of the two coupling partners. Additional preactivation of phenols and the addition of





Scheme 4. X-ray crystal structure of borate to support the mutual activation concept. For clarity, the hydrogen atoms are omitted. Thermal ellipsoids are shown at 30% probability.[15]

strong bases was not required and thus made such a cross-coupling both step and carbon atom economical. The promotion of efficiency of the reaction by the addition of BEt_3 implies a new pathway to activate the "inert" C–O bond by the double activation through the LA/LA interaction. Not only is this an efficient method to produce biaryl compounds from easily available phenols, but it also demonstrates the novel concept of mutual activation, which could be used for the design of further sustainable transformations.

Experimental Section

An oven-dried Schlenk tube containing a stir bar was charged with 2-naphthol (57.6 mg, 0.4 mmol), phenylboroxine (124.8 mg, 0.4 mmol), and NaH (12.0 mg, 0.4 mmol) in a glovebox. After being taken out of the glove box, the tube was degassed and refilled with N_2 3 times. Then, THF (1.0 mL) was injected in by using a syringe under N_2 and the reaction mixture was stirred at room temperature for 5 min. The solvent was removed under reduced pressure at room temperature (30 °C). Then THF (0.2 mL) and BEt_3 (1 M in hexane; 0.6 mL) were injected in and the solution was stirred at room temperature for 5 min. After the solution of $[Ni(cod)_2]$ (11 mg, 0.04 mmol) and PCy_3 (44.8 mg, 0.16 mmol) in *o*-xylene (0.7 mL) was injected into the tube under N_2, the reaction mixture was stirred at 110 °C in the sealed tube for 48 h. The reaction mixture was then cooled to room temperature, quenched with EtOAc, and filtered through a short pad of silica gel. The solvent was removed and the product was purified by flash column chromatography on silica gel (eluent: petroleum ether).

Received: February 28, 2011
Published online: June 24, 2011

Keywords: C–O activation · cross-coupling · homogeneous catalysis · Lewis acids · nickel

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[15] CCDC 825905 contains 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.

