Homogeneous Catalysis

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A General Rhodium-Catalyzed Cyanation of Aryl and Alkenyl Boronic Acids**

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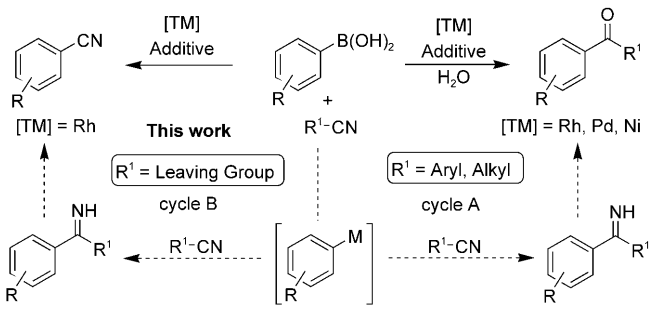
Dedicated to Professor Henri Brunner on the occasion of his 75th birthday

Transition-metal-catalyzed functionalization of organoboron derivatives has emerged as a powerful tool for the selective formation of carbon–carbon and carbon–heteroatom bonds in modern organic synthesis.[1] In addition to palladium-catalyzed coupling reactions, such as the famous Suzuki–Miyaura reaction, rhodium-catalyzed additions of aryl or alkenyl boronic acids to alkynes,[2] alkenes,[3] carbonyl compounds,[4] imines,[5] and nitriles[6,7] are in particular frequently explored nowadays for the straightforward construction of pharmaceutically important scaffolds. Inspired by previous studies (Scheme 1, cycle A), we envisioned a novel catalytic synthesis of (hetero)aryl and alkenyl nitriles from readily available aryl and alkenyl boronic acids in the presence of suitable cyanation reagents (Scheme 1, cycle B).



Scheme 1. Rhodium-catalyzed 1,2-addition of aryl boronic acids to nitriles: A novel strategy for the synthesis of benzonitriles.

The resulting aromatic and vinyl nitriles constitute an integral part of many dyes, herbicides, agrochemicals, pharmaceuticals, and natural products. Furthermore, the nitrile group serves as a valuable intermediate for other diverse functional-group transformations that lead to the generation of benzoic acid derivatives, amines, aldehydes, heterocycles, etc.[8] In the last decade, significant progress has been achieved in the transition-metal-catalyzed synthesis of benzonitriles.[9] Notable examples include palladium-, copper-, and nickel-catalyzed cyanations of aryl halides,[10] direct cyanation of heteroarenes, as well as chelation-assisted reactions.[11] Furthermore, electrophilic cyanation of organolithium, organomagnesium, and organozinc reagents are known.[12] Most recently, we disclosed a general cyanation of Grignard reagents through the use of *N*-cyanobenzimidazole (**4**).[13]

Despite all these studies, the cyanation of more stable and readily available organometallic reagents such as organoboron derivatives has only been rarely studied. So far, only two reports have described this type of reaction. While Zhang and Liebeskind reported the palladium-catalyzed and copper-mediated cyanation of aryl boronic acids with benzylthiocyanate,[14] Hartwig and co-workers demonstrated the combination of iridium-catalyzed borylation and copper-mediated cyanation of arenes.[15] However, stoichiometric amounts of the metal source were used in these reactions, and thus there is great interest in developing the corresponding catalytic variants. Based on our long-standing interest in the synthesis of benzonitriles,[16] we herein disclose the first rhodium-catalyzed cyanation of aryl and alkenyl boronic acids.

The cyanation of phenylboronic acid (**1**) to yield benzonitrile (**2**) was chosen at the start of our investigations as a model reaction. To find an appropriate cyanation reagent, reactions were performed in the presence of 1 mol% of $[\{Rh(OH)(cod)\}_2]$, 1 equivalent of the cyanation reagent, and K_2CO_3 in 1,4-dioxane at 80 °C (Scheme 2).

Cyanation with *p*-toluenesulfonyl cyanide (**3**), a commercially available cyanation reagent, gave only trace amounts (<1%) of the desired product **2**. Similar results were observed with *N*-cyanobenzimidazole (**4**) and *N*-cyanophthalimide (**6**). No product was observed in the reaction with *N*-cyano-4-(*N*,*N*-dimethylamino)pyridinium tetrafluoroborate (**5**). However, to our delight, an excellent yield of benzonitrile (**2**) was obtained by using *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide (**7**). Notably, **7** is readily synthesized in an environmentally friendly manner from inexpensive phenylurea by dehydrative tosylation with *p*-toluenesulfonyl chloride.[17]

Next, we examined various rhodium precursors to understand the effect of the metal precursor on the reaction (Table 1). No reaction was found in the absence of rhodium, thus proving that the model reaction is catalyzed by rhodium (Table 1, entry 2). Changing the hydroxide ligand to either methoxide or chloride resulted in a comparable yield (Table 1, entries 3 and 4), while $[\{Rh(acac)(cod)\}_2]$ afforded

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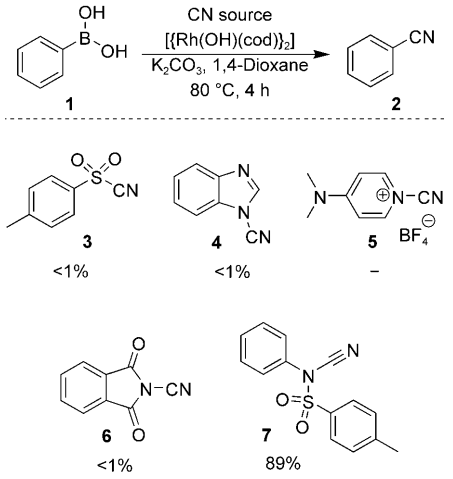
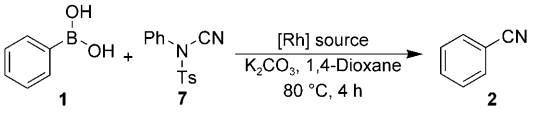


Scheme 2. Rhodium-catalyzed cyanation of phenylboronic acid using different N–CN reagents. Reaction conditions: CN source (0.5 mmol), phenylboronic acid (0.6 mmol), [{Rh(OH)(cod)}$_2$] (1 mol%), K_2CO_3 (0.5 mmol), 1,4-dioxane (1 mL), 80°C, 4 h. Yields given were determined by GC analysis with hexadecane as the internal standard. cod = cycloocta-1,5-diene.

Table 1: Rhodium-catalyzed cyanation of phenylboronic acid: Variation of rhodium precursors.[a]



Entry	[Rh]	Yield [%][b]
1	[{Rh(OH)(cod)}$_2$]	89
2	–	0
3	[{Rh(OMe)(cod)}$_2$]	78
4	[{RhCl(cod)}$_2$]	76
5	[{Rh(acac)(cod)}$_2$]	47
6	[RhCl(PPh$_3$)$_3$]	0
7	$RhCl_3 \cdot 3H_2O$	0
8	5% Rh/C	0
9	5% Rh nanoparticle/alumina	0

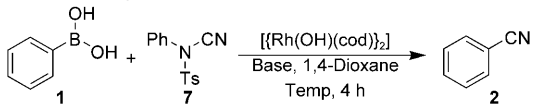
[a] **7** (0.5 mmol), phenylboronic acid (0.6 mmol), [Rh] source (2 mol% with respect to [Rh]), K_2CO_3 (0.5 mmol), 1,4-dioxane (1 mL), 80°C, 4 h. [b] Yields were determined by GC analysis with hexadecane as the internal standard. acac = acetylacetonate.

benzonitrile (**2**) in only 47% yield (Table 1, entry 5). No product was observed on using [RhCl(PPh$_3$)$_3$], $RhCl_3$, Rh/C, or Rh nanoparticles (Table 1, entries 6–9).

After identifying a suitable cyanation reagent and rhodium precursor, we optimized other critical parameters such as additive, solvent, and temperature. As shown in Table 2, catalytic cyanation in the absence of potassium carbonate was sluggish and afforded **2** in only 44% yield after 24 h (Table 2, entries 1 and 2). The use of other basic additives such as KF and K_3PO_4 afforded **2** in 79% and 64% yield, respectively (Table 2, entries 4 and 5).

Surprisingly, the use of boric acid (H_3BO_3) as an additive afforded **2** in an excellent yield (Table 2, entry 6).[6c] Notably, this novel cyanation also proceeded at 50°C and even at room temperature to give 71% (8 h) and 57% (16 h) of benzonitrile, respectively (Table 2, entries 7 and 9).

Table 2: Rhodium-catalyzed cyanation of phenylboronic acid: Variation of additive and temperature.[a]



Entry	[{Rh(OH)(cod)}$_2$] [mol%]	Additive	T [°C]	Yield [%][b]
1	1	K_2CO_3	80	89
2	1	–	80	27 (44)[c]
3	2.5	K_2CO_3	80	94
4	1	KF	80	79
5	1	K_3PO_4	80	64
6	1	H_3BO_3	80	92
7	1	K_2CO_3	50	71[d]
8	1	K_2CO_3	50	64[e]
9	1	K_2CO_3	RT	57[f]
10	2.5	K_2CO_3	RT	78[f]

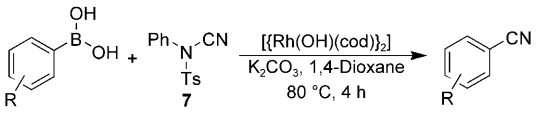
[a] **7** (0.5 mmol), phenylboronic acid (0.6 mmol), [{Rh(OH)(cod)}$_2$] (x mol%), additive (0.5 mmol), 1,4-dioxane (1 mL), 80°C, 4 h. [b] Yields were determined by GC analysis with hexadecane as the internal standard. [c] 24 h. [d] 8 h. [e] THF, 12 h. [f] 16 h.

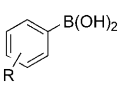
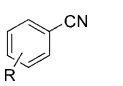
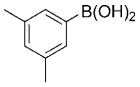
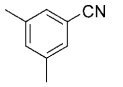
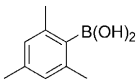
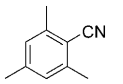
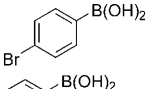
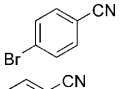
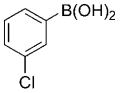
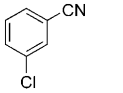
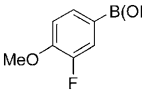
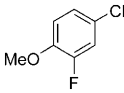
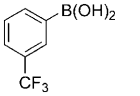
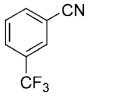
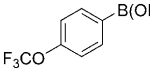
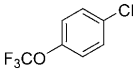
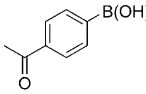
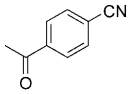
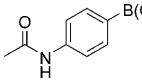
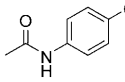
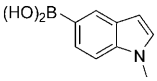
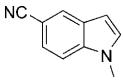
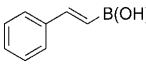
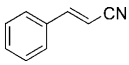
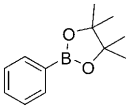
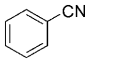
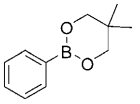
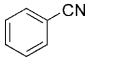
Based on these results we chose the following conditions for further exploration of substrates: 1 mol% of [{Rh(OH)(cod)}$_2$], one equivalent of K_2CO_3,[18] 1,4-dioxane, 80°C, 4 h. As shown in Table 3, the rhodium-catalyzed cyanation of simple aryl boronic acids such as *o*-tolyl- and *p*-methoxyphenylboronic acids gave the corresponding benzonitriles in excellent yield (Table 3, entries 1 and 2). Sterically demanding (Table 3, entries 3 and 6) as well as nonhindered aryl boronic acids (Table 3, entries 2, 4, and 5) were also cyanated effectively under these conditions. Halogenated benzonitriles, which are useful substrates in organic synthesis and have appropriate functional groups, were readily synthesized from the corresponding boronic acids in good to excellent yields (Table 3, entries 7–9). Pharmaceutically interesting fluorinated and trifluoromethylated benzonitriles were synthesized in reasonable yields (70% and 58%; Table 3, entries 9 and 10). Furthermore, electronically different aryl boronic acids reacted smoothly and afforded the corresponding nitriles in good yield (Table 3, entries 2–4 and 9–11). Moreover, more challenging functionalized aryl boronic acids are also compatible with the present cyanation conditions (Table 3, entries 11–14). For example, 5-cyano-*N*-methylindole was formed in 76% yield from the commercially available indolylboronic acid. It is interesting to note that an alkenyl boronic acid was also converted effectively into cinnamylnitrile in 69% yield (Table 3, entry 15).

Having found suitable conditions for the cyanation of a variety of aryl(alkenyl) boronic acids, we next investigated readily accessible boronates. While the respective pinacolate did not undergo cyanation, the neopentylglycol ester was transformed effectively into benzonitrile in 69% yield (Table 3, entries 16 and 17).

Next, we thought that our rhodium-catalyzed cyanation might easily be combined with the straightforward preparation of organoboron substrates to provide new efficient reaction sequences towards aromatic and vinyl nitriles. Thus, an iridium-catalyzed borylation of 1,3-dimethoxybenzene with bis(pinacolato)diboron (B_2pin_2) followed by hydrolysis

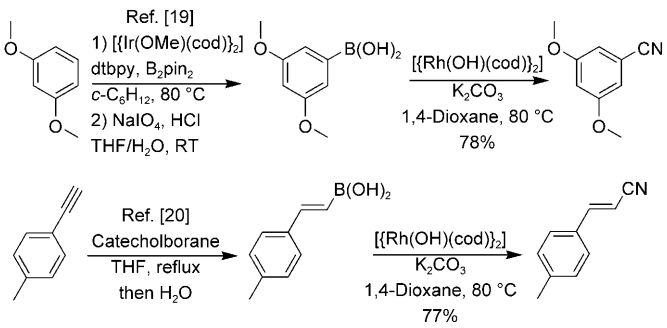
Table 3: Rhodium-catalyzed cyanation of aryl boronic acids: Scope and limitations.[a]



Entry	Aryl boronic acid	Aryl nitriles		Yield [%][b]
1			R = 2-Me	84
2			R = 4-OMe	90
3			R = 2-OMe	64[c]
4			R = 3-OEt	71
5				83
6				86
7				74
8				76[c]
9				70
10				58[c]
11				65[c]
12				72[c]
13				81[c]
14				76
15				69
16				0[d]
17				69[d]

[a] **7** (1 mmol), aryl boronic acid (1.1 mmol), [{Rh(OH)(cod)}$_2$] (1 mol%), K_2CO_3 (1 mmol), 1,4-dioxane (2 mL), 80°C, 4 h. [b] Yield of isolated product. [c] 2.5 mol% of [{Rh(OH)(cod)}$_2$]. [d] Yields were determined by GC analysis with hexadecane as the internal standard.

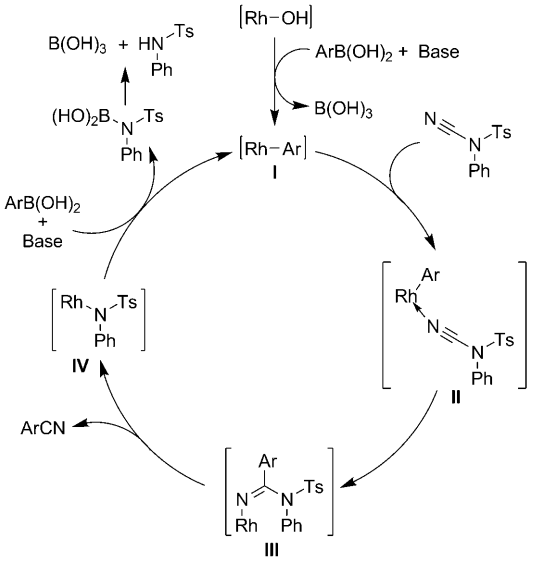
of the boronate was carried out according to the recent report by Hartwig and co-workers.[19] Subsequent reaction of the resultant 3,5-dimethoxyphenylboronic acid under rhodium-catalyzed cyanation conditions produced the 3,5-dimethoxybenzonitrile in 78% yield (Scheme 3). Similarly, 2-(4-methylphenyl)vinylnitrile was obtained from the corresponding



Scheme 3. Functionalization of arene(alkyne) to aryl(alkenyl) nitirles. dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine.

alkyne through hydroboration with catecholborane, hydrolysis,[20] and rhodium-catalyzed cyanation.

On the basis of previous reports on rhodium-catalyzed additions of aryl boronic acids to an unsaturated system,[2–7] we postulate the following mechanism for our reaction (Scheme 4). Transmetalation of the aryl boronic acid with



Scheme 4. Proposed mechanism for the rhodium-catalyzed cyanation of aryl boronic acids. Ts = 4-toluene sulfonyl.

an active rhodium(I) species would generate the aryl–rhodium species **I**, which on coordination with the N–CN reagent would form intermediate **II**. The formation of rhodium species **III** can be envisaged by transfer of the aryl motif to the nitrile carbon atom. Rearrangement of **III** produces the benzonitrile along with the reactive rhodium species **IV**. Finally, transmetalation affords the aryl–rhodium **I** to complete the catalytic cycle.

In conclusion, we have demonstrated the first rhodium-catalyzed cyanation of aryl and alkenyl boronic acids. The use of *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide as a cyanation reagent enables a variety of aromatic and vinyl nitriles to be obtained in good yields under mild conditions. The developed procedure can easily be combined with direct

borylations of arenes and hydroborations of alkynes to give various nitriles in a straightforward manner.

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