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# Rhodium-Catalyzed Transnitrilation of Aryl Boronic Acids with Dimethylmalononitrile

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**Abstract:** *An efficient transnitrilation of aryl boronic acids with dimethylmalononitrile (DMMN) is described. This rhodium-catalyzed electrophilic cyanation presents a novel approach to prepare aryl nitriles by using a carbon-bound cyanating reagent which undergoes cross-coupling with the aryl boronic acid. The reaction expands the degree of functional-group compatibility exhibited by the transnitrilation of aryl Grignard and aryllithium reagents. A variety of aryl boronic acid derivatives and dialkylmalononitriles were amenable to the transnitrilation.*

Aryl nitriles are key structural motifs found in many pharmaceuticals, natural products, and agrochemicals.[1] In addition, the nitrile may serve as a versatile precursor to diverse functional groups, including amines, carboxylic acids and derivatives, aldehydes, and heterocycles.[2] A notable development in the synthesis of aryl nitriles involves transition metal catalyzed cyanation of aryl halides with toxic cyanide salts.[3] Subsequently less toxic cyanide sources have been developed, such as $K_4[Fe(CN)_6]$,[4] BnCN,[5] and $NH_3$/DMF.[6] Although promising, a major drawback of transition metal catalyzed cyanation is the high affinity of the cyanide anion for the catalyst, and this affinity can result in deactivation of the catalytic system.[7]

A method which circumvents this problem is the electrophilic cyanation of organomagnesium, organolithium, and organozinc reagents.[8] Previously reported electrophilic cyanating agents include cyanogen halides,[9] cyanates,[10] TsCN,[11] and cyanamides.[12] These electrophilic cyanating agents are in some cases either highly toxic or derived from highly toxic cyanide sources, or are noncommercially available, or require low-temperature storage. One remarkable exception is *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS),[13] which can be obtained from the reaction of phenylurea and *p*-toluenesulfonyl chloride.[14] Cyanation of aryl C–H bonds has recently emerged as an alternative approach.[15] However, the need for directing groups or electron-rich arenes presents a considerable challenge for substrate generality and product regioselectivity.

We became interested in developing an electrophilic cyanation of air-stable and readily available organometallic reagents such as organoboron compounds. Organoboron derivatives continue to emerge as essential coupling partners in the construction of carbon–carbon and carbon–heteroatom bonds.[16] The utility of aryl boronic acids in cyanation chemistry has been reported. However, to our knowledge, only one example utilizes an electrophilic cyanation approach.[17,18] Beller and co-workers recently reported a rhodium-catalyzed cyanation of aryl boronic acids using NCTS as the electrophilic cyanating agent.[17] Transition metal catalyzed additions of aryl boronic acids to nitriles have been documented, but exclusively provide aryl ketone products (Figure 1 a).[19,20]

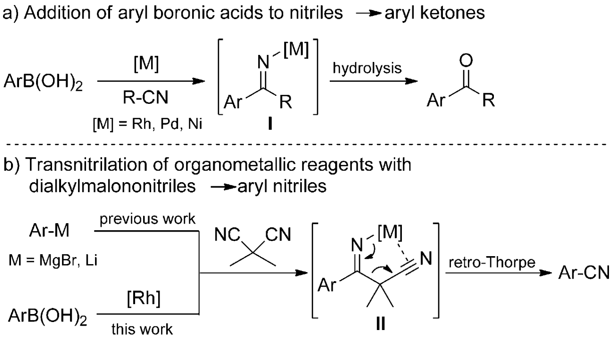

***Figure 1.*** Reactions of organometallic reagents with nitriles.

We recently disclosed the first carbon-bound electrophilic cyanating agent, dimethylmalononitrile (DMMN), for the cyanation of aryl Grignard and lithium reagents via transnitrilation (Figure 1 b).[21] DMMN is a safe, bench-stable, and commercially available reagent which has found use in the synthesis of bis(oxazoline)s.[22] We envisioned that aryl boronic acids, in the presence of a suitable metal catalyst, could add to DMMN to give the metal/ketimine complex **II**. Similar to the reaction with aryl Grignard and lithium reagents, we thought that **II** would undergo a retro-Thorpe fragmentation to release the desired aryl nitrile. Herein we report the transnitrilation of aryl boronic acids utilizing the carbon-bound cyanating agent DMMN.

At the outset of this work, we recognized two major challenges. First, the general reactivity of DMMN with aryl boronic acids for the initial 1,2-addition was unknown. Second, was the challenge in product selectivity towards transnitrilation over the formation of aryl ketones. The investigation began by reacting phenyl boronic acid with

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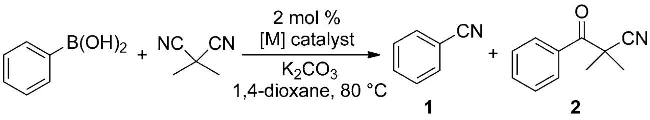
***Table 1:*** Screening of transition-metal catalysts.



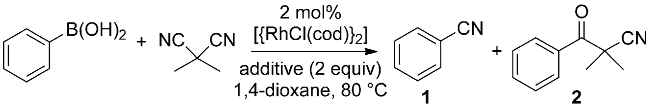
| Entry | Catalyst | Yield [%][b] | |
|---|---|---|---|
| | | **1** | **2** |
| 1 | none | 0 | 0 |
| 2 | [{Rh(OH)(cod)}$_2$] | 35 | 51 |
| 3 | [{RhCl(cod)}$_2$] | 52 | 43 |
| 4 | [RhCl(PPh$_3$)$_3$] | 3 | 17 |
| 5 | [Rh(nor)$_2$BF$_4$] | 5 | 45 |
| 6 | [Rh(cod)$_2$OTf] | 12 | 70 |
| 7 | [{IrCl(cod)}$_2$] | $<2$ | $<2$ |
| 8 | [RuCl$_2$(cod)] | 0 | 0 |
| 9 | [PdCl$_2$(cod)] | 0 | 0 |
| 10 | [Ni(cod)$_2$]/5 mol % PCy$_3$ | 4 | $<2$ |

[a] Reaction conditions: 0.75 mmol PhB(OH)$_2$, 0.50 mmol DMMN, 2 mol% catalyst, and 1 mmol K$_2$CO$_3$ in 1 mL 1,4-dioxane, 80 °C, 24 h; for entries 4–6 and 8,9, 4 mol% catalyst was used. [b] HPLC assay yields. cod = 1,5-cyclooctadiene, nor = norbornene.

DMMN using several transition metal catalysts in the presence of potassium carbonate as an additive (Table 1). Rhodium catalysts showed superior reactivity over other transition metal catalysts screened. In particular, rhodium dimers, [{RhCl(cod)}$_2$] and [{Rh(OH)(cod)}$_2$],[23] provided high conversions with modest selectivities towards the desired transnitrilation product benzonitrile (**1**) over the ketone **2** (entries 2 and 3). Throughout this work, it was found that optimal yields of the **1** were obtained when DMMN was used as the limiting reagent and the arylboronic acid was used in 1.5-fold excess, because of competitive proto-deborylation. The use of 1:1 stoichiometry or of excess DMMN resulted in reduced yields.

After identifying the effective catalyst, several parameters were investigated to improve the selectivity towards transnitrilation (Table 2). The choice of additive was found to be important for the selectivity. For example, when either K$_3$PO$_4$ or KOH was used instead of K$_2$CO$_3$, high conversion was obtained, but with low selectivity (entries 1 and 2). Gratifyingly, the use of either Cs$_2$CO$_3$ or CsF provided significant improvement in product selectivity (**1**/**2** = 60: < 2–5) but with moderate yields (entries 3 and 4). Additives such as ZnCl$_2$ or CuI resulted in low yields and selectivities. To our delight, when the temperature was increased to 100 °C using Cs$_2$CO$_3$, **1** was obtained in 94 % yield after 4 hours with excellent selectivity (entry 8). Under these reaction conditions, the catalyst loading could be lowered to 1 mol % [{RhCl(cod)}$_2$] with similar yield and selectivity. When the reaction was carried out with lower amounts of Cs$_2$CO$_3$, poor conversions and selectivities were obtained (entries 9 and 10).

***Table 2:*** Screening of additives and effect of temperature.

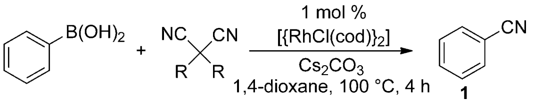


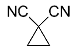
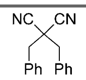
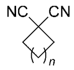
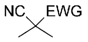
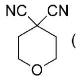
| Entry | Additive | Yield [%][b] | |
|---|---|---|---|
| | | **1** | **2** |
| 1 | K$_3$PO$_4$ | 20 | 61 |
| 2 | KOH | 55 | 35 |
| 3 | Cs$_2$CO$_3$ | 61 | $<2$ |
| 4 | CsF | 62 | 5 |
| 5 | ZnCl$_2$ | 6 | 31 |
| 6 | CuI | $<2$ | 29 |
| 7 | Cs$_2$CO$_3$; THF, 60 °C | 6 | 59 |
| 8 | Cs$_2$CO$_3$; 100 °C, 4 h | 94 (93)[c] | 4 (5)[c] |
| 9 | 1 equiv Cs$_2$CO$_3$; 100 °C | 12 | 56 |
| 10 | no additive, 100 °C | 0 | 6 |

[a] Reaction conditions: 0.75 mmol PhB(OH)$_2$, 0.50 mmol DMMN, 2 mol% [{RhCl(cod)}$_2$], and 1 mmol additive in 1 mL 1,4-dioxane at 80 °C, 24 h. [b] HPLC assay yields. [c] 1 mol% [{RhCl(cod)}$_2$], 4 h. THF = tetrahydrofuran.

After identifying the optimized reaction conditions, we explored the potential of several dialkylmalononitriles as transnitrilation reagents with phenyl boronic acid (Table 3).[24] Dialkylmalononitriles (entries 2–6) underwent transnitrilation, thus providing **1** in good to excellent yields. The dicyanocyclopropane (entry 1) gave complete conversion, but very low product formation was detected. This low yield could be due to the potential oxidative addition of rhodium(I) to the strained and electron-deficient cyclopropane moiety and subsequent side reactions.[25] Ester and amide derivatives of DMMN (entries 7 and 8) did not show any reactivity toward either 1,2-addition or nucleophilic acyl substitution.

***Table 3:*** Survey of several transnitrilation reagents.

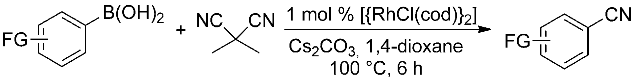


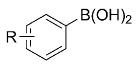
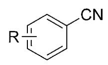
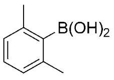
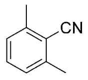
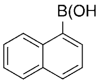
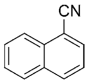
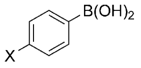
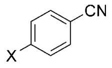
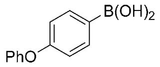
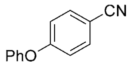
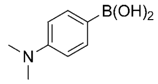
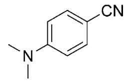
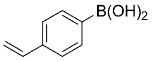
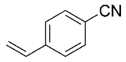
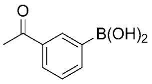
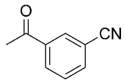
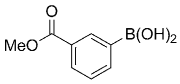
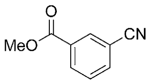
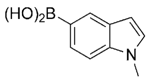
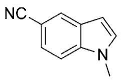
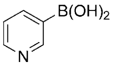
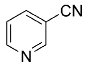
| Entry | Dinitrile | Yield [%][b] | Entry | Dinitrile | Yield [%][b] |
|---|---|---|---|---|---|
| 1 |  | $<5$ | 6 |  | 70[c] |
| |  | | |  | |
| 2 | $n = 1$ | 78 | 7 | EWG = CO$_2$Et | 0[d] |
| 3 | $n = 2$ (**3**) | 93 | 8 | EWG = CONEt$_2$ | 0[d] |
| 4 | $n = 3$ | 86 | | | |
| 5 |  (**4**) | 88 | | | |

[a] Reaction conditions: 0.75 mmol PhB(OH)$_2$, 0.5 mmol nitrile, 1 mol% [{Rh(cod)Cl}$_2$] and 1 mmol Cs$_2$CO$_3$ in 1 mL 1,4-dioxane, 100 °C, 4 h. [b] HPLC assay yields. [c] Reaction was done in 24 h. [d] No reaction was observed.

By using the optimized reaction conditions, we sought to explore the scope of the transnitrilation of different arylboronic acids with DMMN (Table 4). Several electron-rich and electron-neutral arylboronic acids underwent transnitrilation in good to excellent yields. Hindered *ortho*-substituted arylboronic acids provided aryl nitriles in good yields (entries 5–7). Aryl boronic acids having electron-deficient

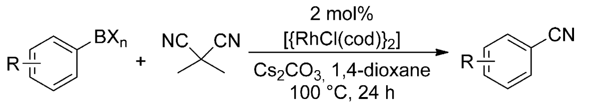
**Table 4:** Scope of the rhodium-catalyzed transnitrilation of arylboronic acids.

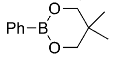
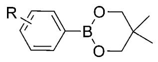
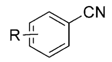
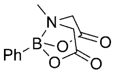
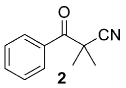


| Entry | Aryl boronic acid | Product | Yield [%][b] |
|---|---|---|---|
| 1 |  |  | R = H: 89 |
| 2 | | | 4-Me: 94 |
| 2 | | | 4-OMe: 97 |
| 4 | | | 3-OMe: 80 |
| 5[c] | | | 2-OMe: 68 |
| 6 |  |  | 90 |
| 7 |  |  | 75 |
| 8 |  |  | X = Cl: 80 |
| 9 | | | Br: 77 |
| 10 |  |  | 86 |
| 11 |  |  | 84 |
| 12[d] | | | 87 |
| 13[e] | | | 75 |
| 14[f] |  |  | 71 |
| 15[f] |  |  | 68 |
| 16[f] |  |  | 65 |
| 17 |  |  | 78 |
| 18[c] |  |  | 52 |

[a] Reaction conditions: 3.0 mmol arylboronic acid, 2.0 mmol DMMN, 1 mol% [{RhCl(cod)}$_2$] and 4.0 mmol $Cs_2CO_3$ in 4 mL 1,4-dioxane, 100°C, 6 h. [b] Yields of isolated products. [c] 2.0 mol% [{RhCl(cod)}$_2$]. [d] 2.0 mmol nitrile **3** was used. [e] 2.0 mmol nitrile **4** was used. [f] 2 mol% [{RhCl(cod)}$_2$] at 110°C, 20 h.

**Table 5:** Scope of the rhodium-catalyzed transnitrilation of arylboronic acid derivatives.



| | Aryl boronates | Nitrile product | Yield [%][b] |
|---|---|---|---|
| 1[c] | $Ph{-}BF_3K$ | **1** | 64 |
| 2 |  | **1** | 72 (65) |
| 3 |  | <br>R = 2,4,6-trimethoxy | (45) |
| 4[c] | Ph–Bpin | **1** | 9 |
| 5[c] |  | <br>**2** | **1**: 0<br>**2**: (40) |

[a] Reaction conditions: 1.5 mmol arylboronate, 1.0 mmol DMMN, 2 mol% [{RhCl(cod)}$_2$] and 2 mmol base in 2 mL 1,4-dioxane, 100°C, 24 h. [b] HPLC assay yield. Values within parentheses are yields of the isolated products. [c] The use CsF or $K_2CO_3$ as additives provided similar outcomes or slightly lower yields. pin = pinacol.

substituents were transformed into the corresponding nitriles in good yields (entries 15 and 16). Likewise, heteroaryl boronic acids underwent transnitrilation with DMMM in moderate yields (entries 17 and 18). The use of the cyanating agents **3** and **4** furnished 4-(dimethylamino)benzonitrile in comparable yields to that obtained with DMMN (entries 11–13).

The observed functional-group tolerance of this transnitrilation method is remarkable. For example, benzonitriles having vinyl, ketone, and ester substituents (Table 4, entries 14–16) were obtained in good yields. Such functional groups cannot be tolerated in the transnitrilation of aryl Grignard or lithium reagents with DMMN.[21] Moreover, in this rhodium-catalyzed transnitrilation method, *p*-fluorobenzonitrile was obtained in 77% yield (entry 9). This product was found to undergo $S_NAr$ reaction with the byproduct isobutyronitrile anion during the transnitrilation of *p*-fluorophenylmagnesium bromide with DMMN.[21]

To further explore the potential of this novel rhodium-catalyzed transnitrilation method, several aryl boronic acid derivatives were examined (Table 5). Phenyl potassium trifluoroborate underwent transnitrilation in moderate yield (entry 1). Transnitrilation of neopentylglycol aryl boronic acid esters with DMMN also provided aryl nitriles in acceptable yields (entries 2 and 3). The sterically hindered phenyl pinacolboronate ester gave very low conversion, while phenyl boronic acid MIDA ester exclusively gave the adduct **2** in 40% yield. It is worth noting that the aryl boronates in entries 1–4 did not give detectable amounts of ketone adducts. The observed lower yields are mainly a result of their lower reactivity under the reaction conditions used.

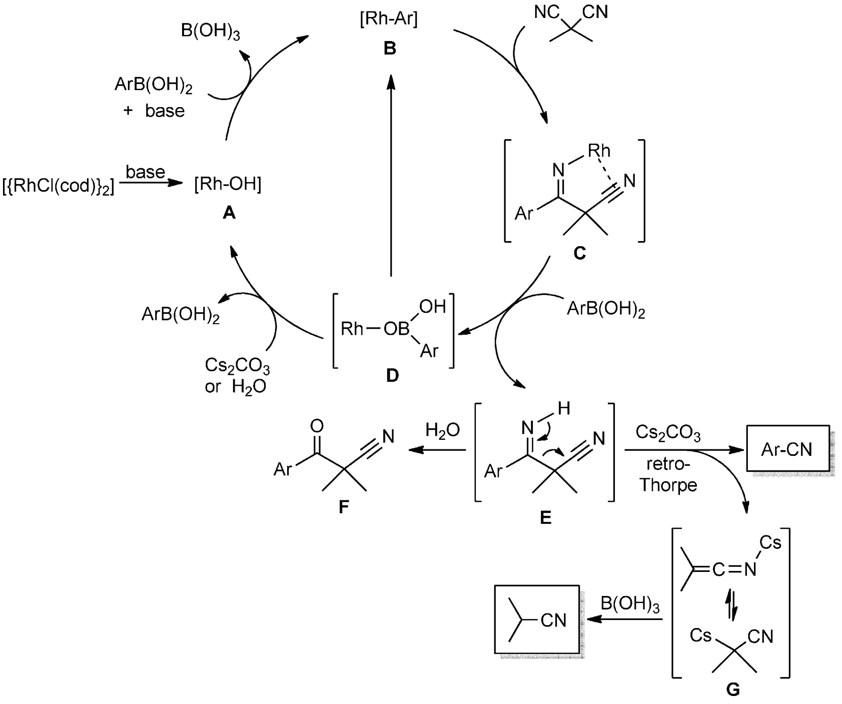
Based on mechanistic results we obtained for the transnitrilation of aryl Grignard reagents[21] with DMMN and previous reports on rhodium-catalyzed addition of arylboronic acids to nitriles,[19] we propose the following mechanism (Scheme 1). First, transmetallation of the $Rh^I$ species **A** with the arylboronic acid would generate the aryl rhodium **B**. Aryl transfer to DMMN would result in formation of a rhodium ketimine intermediate (**C**). This rhodium complex is analogous to the magnesium ketimine intermediate observed in our previous work.[21] Protonation of the ketimine with arylboronic acid would give the rhodium borate **D** and ketimine **E**. The rhodium borate **D** could directly form **B**, or alternatively, it could undergo hydrolysis to **A** with regeneration of the arylboronic acid. Hydrolysis of **E** would give the undesired β-ketonitrile byproduct **F**.[26] Deprotonation of **E** with $Cs_2CO_3$ results in retro-Thorpe fragmentation to give the product aryl nitrile and the isobutyronitrile anion **G**. The anion **G** may be protonated by boric acid (or arylboronic acid) to give isobutyronitrile. As with the transnitrilation of aryl Grignard and lithium reagents, we have confirmed that isobutyronitrile is the byproduct of the reaction by GC-MS and $^1$H and $^{13}$C NMR analysis.

The significant effect of the base on the selectivity towards transnitrilation versus β-ketonitrile formation deserves further comment. We believe that a strong base is necessary to efficiently promote the retro-Thorpe fragmentation of **E** by deprotonation of the N−H. In addition, we suspect that the dessicant ability of the base could also affect the selectivity by scrubbing any trace water from the reaction mixture, thus minimizing hydrolysis of **E** to **F**. Finally, the solubility of the base is likely important, as low solubility might reduce the availability of the base to promote the retro-Thorpe reaction and thus enable hydrolysis of the ketimine adduct to give β-ketonitrile byproduct **F**.

In summary, we have developed the first transnitrilation of arylboronic acids with dimethylmalononitrile in an electrophilic cyanation approach. Aryl boronic acid derivatives, (potassium trifluoroborate and neopentylglycol ester) and several dialkylmalononitriles could also undergo transnitrilation. Complementary to the cyanation of aryl Grignard and lithium reagents, this rhodium-catalyzed transnitrilation is amenable to arylboronic acids having reactive functional groups (such as ketone, ester, styryl, and fluoride), thus providing aryl nitriles with valuable synthetic handles.

## Experimental Section

Typical procedure: Under a nitrogen atmosphere, a mixture of *p*-tolylboronic acid (405 mg, 3.0 mmol), DMMN (188 mg, 2.0 mmol), [{RhCl(cod)}$_2$] (9.8 mg, 0.02 mmol), and $Cs_2CO_3$ (1.30 g, 4.0 mmol) in 1,4-dioxane (4 mL) was stirred at 100 °C for 6 h. After cooling, the reaction mixture was quenched with aqueous saturated $NH_4Cl$ and extracted with MTBE (10 mL × 3). The combined organic phases were dried with anhydrous $Na_2SO_4$, filtered, and then concentrated in vacuo. Purification of the crude residue by silica column chromatography using MTBE/hexanes as the eluent afforded 4-methylbenzonitrile (220 mg, 94 % yield) as a white solid.



*Scheme 1.* Proposed mechanism for the rhodium-catalyzed transnitrilation of arylboronic acids with DMMN. Ligands on rhodium omitted for simplicity.

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