Nickel-catalysed decarbonylative borylation of aroyl fluorides

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Nickel-catalysed decarbonylative borylation of aroyl fluorides

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The first Ni(cod)$_2$/PPh$_3$ catalyst system has been established for decarbonylative borylation of aroyl fluorides with bis(pinacolato)diboron. A wide range of functional groups in the substrates were well tolerated. The ease of access of the starting aroyl fluorides indicates that these results might become an alternative to existing decarbonylation events.

Arylboronic acids and arylboronates are versatile synthetic reagents in synthetic organic chemistry.[1] These compounds are conventionally synthesized by organolithium or magnesium compounds, which are not compatible with functional groups.[2] The further development of transition-metal-catalysed borylation reactions has allowed the synthesis of arylboronates from numerous aryl iodide, bromides, chlorides, or triflates.[3] In recent years, much efforts have been devoted to synthesize arylboronates via C−X (X = H,[4] halogen,[5] SR,[6] OR,[7] CN,[8] or NR$_2$[9]) bond activation.

Taking into account growing concerns on the environmental and sustainable events of our society, carboxylic acid as an aromatic feedstock alternative is in high demand. In particular, facile diversification of carboxylic acids into organoboron compounds shows high value.[10] As such, several attempts have succeeded in transformation of carboxylic acid derivatives such as amides,[11,12] esters,[13-15] thioesters,[16,17] and chloride[18] into the corresponding arylboronates in a decarbonylative manner (Scheme 1a). Very recently, the decarboxylative borylation of aliphatic and aromatic *N*-hydroxyphthalimide esters, derived from the corresponding carboxylic acids, were also disclosed.[19]

On the other hand, aroyl fluorides can easily be prepared from the corresponding carboxylic acids,[20] arguably one of the

simplest and most atom-economical derivatives in the aroyl acid series, have received considerably less attention, presumably due to their low reactivity. In some case, however, aroyl fluorides were
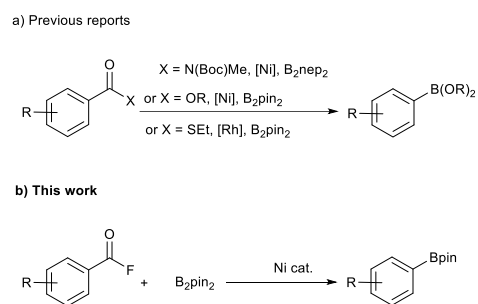
Scheme 1 Decarbonylative borylation of carboxylic acid derivatives.

found to be a cross-coupling partner with organozinc,[21] -silicon,[22] and -boron[23] nucleophiles to generate various ketones without decarbonylation. Recently, Ogiwara and Sakai reported palladium-catalysed reduction of sp^2 and sp^3 acid fluorides in a retentive or decarbonylative manner.[24] This report suggested that the retentive or decarbonylative pathway could be controlled by the ligands employed. Encouraged by the decarbonylative C-C bond formation, namely, trifluoromethylation of acid fluorides under [(cinnamy)PdCl]$_2$/Xantphos catalytic system,[25] we also disclosed decarbonylative alkylation of aroyl fluorides catalysed by Ni(cod)$_2$/DPPE.[26] To the best of our knowledge, however, the decarbonylative borylation of acid fluorides has been virtually unexplored.[27] Herein we report our results on the utilization of aroyl fluorides as the electrophilic component in a nickel-catalysed decarbonylative borylation reaction (Scheme 1b).

Our initial studies involved the evaluation of various ligands and bases in the borylation reaction of benzoyl fluoride (**1a**) with bis(pinacolato)diboron (**2a**, (B$_2$pin$_2$) catalysed by Ni(cod)$_2$ (Table S1-S4). To our delight, 33% of desired product **3a** was

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obtained when a stable and inexpensive ligand PPh₃ was employed. Extensive screening of the reaction conditions (see

Table 1 Optimization of the reaction conditions[a]

Entry	deviation from standard conditions	Yield (%)[b]
1	none	85 (83)[c]
2	NiCl₂ instead of Ni(cod)₂	52
3	Ni(OAc)₂·4H₂O instead of Ni(cod)₂	4
4	Pd(OAc)₂ instead of Ni(cod)₂	16
5	Pd(dba)₂ instead of Ni(cod)₂	23
6	[Rh(OH)(cod)]₂ instead of Ni(cod)₂	50
7	PCy₃ instead of PPh₃	16
8	P(OPh)₃ instead of PPh₃	46
9	PⁿBu₃ instead of PPh₃	71
10	LiCl instead of NaCl	5
11	KCl instead of NaCl	79
12	CsCl instead of NaCl	23
13	TBAC instead of NaCl	25
14	without NaCl	67
15	without Ni(cod)₂	0
16	without PPh₃	0
17	without KF	<1
18	benzoyl chloride instead of **1a**	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)₂ (0.02 mmol), PPh₃ (0.06 mmol), KF (0.5 mmol), NaCl (0.4 mmol), toluene (0.66 mL), octane (0.33 mL), 140 °C, 24 h. [b] Determined by GC analysis. [c] An isolated yield is shown in parentheses.

Supporting Information) revealed that 10 mol % of Ni(cod)₂, 30 mol % of PPh₃, 2.5 equiv of KF, and 2.0 equiv of NaCl as the additive at 140 °C for 24 h in a mixed solvent system, toluene and octane (v/v = 2/1) provided the best result, affording **3a** in 83% yield (Table1, entry 1). Other air-stable Ni(II) salts other than Ni(cod)₂ resulted in lower yield of **3a** (entries 2-3). Palladium catalysts such as Pd(OAc)₂ and Pd(dba)₂ were inefficient (entries 4-5). Although [Rh(OH)(cod)]₂ was reported to be efficient in decarbonylative borylation of aromatic thioesters,[16] it showed moderated reactivity (entry 6). Replacement of PPh₃ with other monodentate phosphine ligands under identical reaction conditions decreased the yield (entries 7-9). Interestingly, the yield of **3a** was increased in the order of CsF < NaF < KF (Table S4), suggesting that a counteraction is important to some extents.[28] The similar tendency was observed in the additives; NaCl and KCl afforded good yields, while LiCl, CsCl and TBAC (tetrabutylammonium chloride) gave poor results (entries 10-13). It revealed that the suitable countercations may play a vital role in this transformation. These results associate with recent publications that demonstrate the important role of countercations for C-O bond activation in reactions of aryl ethers.[29] When no NaCl was added, the yield was slightly decreased to 67% (entry 14). No desired product was detected

in the absence of Ni(cod)₂ or PPh₃ in decarbonylative borylation process (entries 15-16). The additive KF was found to be essential to proceed the reaction (entry 17), suggesting an external activator of B₂pin₂ is required. When we applied the

Table 2 Decarbonylative borylation of aroyl fluorides[a,b]

R = H (**3a**): 83%
p-Me (**3b**): 65%
p-ⁿBu (**3c**): 82%
p-OMe (**3d**): 60%
p-OⁿBu (**3e**): 68%
p-OBn (**3f**): 50%
p-Ph (**3g**): 87%
p-NMe₂ (**3h**): 60%
p-CO₂Me (**3i**): 64%
p-COPh (**3j**): 71%
p-CN (**3k**): 45%
p-CF₃ (**3l**): 56%
m-Ph (**3m**): 60%
o-Me (**3n**): 38% (55%)[b]
o-Ph (**3o**): 78%
o-CF₃ (**3p**): 49% (62%)[b]

3q: 82%   **3r**: 68%   **3s**: 55%   **3t**: 71%   **3u**: 50%   **3v**: 75%

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)₂ (0.02 mmol), PPh₃ (0.06 mmol), KF (0.5 mmol), NaCl (0.4 mmol), toluene (0.66 mL), octane (0.33 mL), 140 °C, 24 h. [b] Ni(cod)₂ (0.06 mmol), PPh₃ (0.18 mmol).

certain conditions to the analogous benzoyl chloride at 140 °C (entry 18) and even at room temperature, 50 °C, or 80 °C, no decarbonylative borylation product was detected.   It is indicated that a fluoride moiety plays a crucial role and conversion of benzoyl fluoride in situ into benzoyl chloride in the presence of NaCl can be ruled out during this transformation.

With the optimized conditions in hand, the generality of the reaction was subsequently investigated (Table 2). A wide range of electronically and sterically diverse aroyl fluorides with bis(pinacolato)diboron (**2a**) were smoothly converted into the corresponding arylboronates. Aroyl fluorides bearing electron-donating alkyl and alkoxy groups in the *para*-position, afforded arylboronates **3b**-**3f** in 50-82% yields. High chemoselectivity of this decarbonylative borylation was demonstrated by the synthesis of **3i** bearing the ester functionality unreacted. This result suggests that this methodology is complementary to the decarbonylative borylation of aromatic esters.[13-15] Moreover, the introduction of electron-withdrawing groups onto benzoyl fluoride led to a slight decrease in the yields of the products **3k** and **3l**. Benzoyl fluoride with *ortho*-substituents under the identical reaction conditions proceed smoothly to yield **3n-3p**. Naphthyl (**3q** and **3r**), anthracenyl (**3s**), and biphenyl (**3g**, **3m**, and **3t**)-containing arylboronates were successfully obtained in good to high yields.   On the other hand, although the

decarbonylative borylation using vinyl and benzyl precursors have been elucidated, no traces of the desired products **3** were detected.

To evaluate the utility of this decarbonylative borylation reaction, reactions of a series of diborons have been carried out (Table 3). Using bis(hexylene glycolato)diboron (**2b**) and bis(neopentyl glycolato)diboron (**2c**, B$_2$nep$_2$) instead of **2a** with benzoyl fluoride (**1a**) gave the corresponding arylboronates **4b** and **4c** in 54% and 55% yields, respectively. The reaction of 2-naphthoyl fluoride (**1r**) with bis(catecholato)diboron (**2d**, B$_2$cat$_2$), followed by the replacement with pinacol also yielded **3r** in 55% yield.

Table 3 Elucidation of other diborons[a,b]
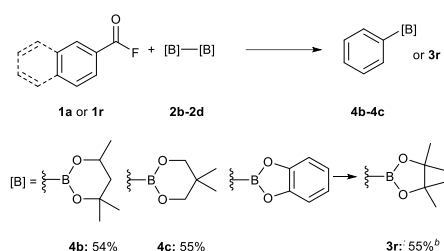
[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), PPh$_3$ (0.06 mmol), KF (0.5 mmol), NaCl (0.4 mmol), toluene (0.66 mL), octane (0.33 mL), 140 °C, 24 h. [b] **1r** (0.2 mmol), **2d** (0.4 mmol), then pinacol (4 equiv) and NEt$_3$ (0.5 mL) at room temperature for 1 h.

This nickel-catalysed decarbonylative borylation was also viable with complex molecular precursors bearing functional groups. For example, a carboxylic acid-containing drug, probenecid,[30] primarily used to treat gout and hyperuricemia, could be subjected to the two-step fluorination/decarbonylative borylation sequences. After fluorination of probenecid by conventional method,[20c] aroyl fluoride **1w** was smoothly converted into the target arylboronate **3w** in 74% yield (Scheme 2). Whereas the attempt to elucidate the one-pot synthesis of arylboronates without isolation of aroyl fluorides were found to be unsuccessful. To our delight, this decarbonylative borylation is applicable to a large-scale synthesis. The 10-mmol scale experiment provided the 1.19 g of **3a** in 58% yield.
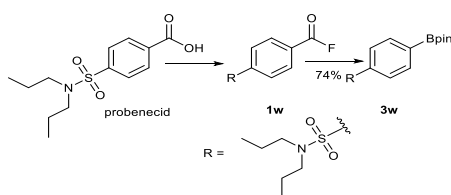

[a] Reaction conditions: **1w** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), PPh$_3$ (0.06 mmol), KF (0.5 mmol), NaCl (0.4 mmol), toluene (0.66 mL), octane (0.33 mL), 140 °C, 24 h.

Scheme 2 Two-step borylation of probenecid.[a]

Proposed mechanism of decarbonylative borylation of aroyl fluorides is shown in Scheme 3. Initially, oxidative addition of aroyl fluoride to Ni(0) generates the acyl-nickel (II) intermediate **A**.[31-33] Although our attempt to isolate **A** was unsuccessful, we found some

clues for arylnickel species **B**. The reaction of Ni(cod)$_2$/2 PPh$_3$ with benzoyl fluoride in THF-d_8 at rt provided a characteristic broad singlet at -409.9 ppm in the ^{19}F{^{1}H} NMR and a doublet at 15.1 ppm with a J_{P-F} of 44 Hz in the ^{31}P{^{1}H} NMR even after 1 h. Considering the results obtained by Sanford;[33] the formed oxidative adduct Ni(COPh)F(PCy$_3$)$_2$ caused decarbonylation to form Ni(Ph)F(PCy$_3$)$_2$ at room temperature within 10 min, in our case, the *in-situ* generated Ni(COPh)F(PPh$_3$)$_2$ must be more unstable due to the weak coordination ability of PPh$_3$ than PCy$_3$. We thus concluded that the subsequent extrusion of carbon monoxide forming **B** could take place prior to transmetalation. Transmetalation between complex **B** and B$_2$pin$_2$ assisted by the external KF (and NaCl) affords borylnickel(II) intermediate **C**. Finally, reductive elimination delivers the targeted arylboronates **3**, regenerates the Ni (0) species to complete a catalytic cycle.
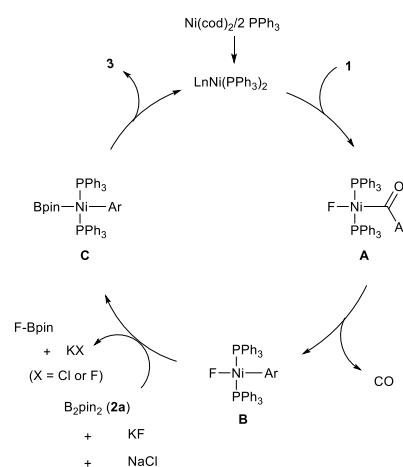
Scheme 3 Proposed mechanism.

In summary, we have developed the first decarbonylative borylation of aroyl fluorides with the assistance of an abundant and inexpensive metal Ni/PPh$_3$ catalytic system with B$_2$pin$_2$ as coupling nucleophile, which is capable of producing various aromatic boronates. Importantly, this method realized that carboxylic acids can be converted into a wide array of arylboronates via aroyl fluorides. Currently, we are investigating the theoretical calculations to determine the reaction mechanism including a decarbonylation step, and other transition-metal-catalysed transformations of aroyl fluorides.

Conflicts of interest

There are no conflicts to declare.

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