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Preparing (Multi)Fluoroarenes as Building Blocks for Synthesis: Nickel-Catalyzed Borylation of Polyfluoroarenes via C-F Bond Cleavage

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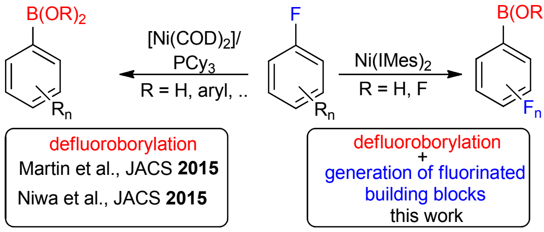
ABSTRACT: The [Ni(IMes)$_2$]-catalyzed transformation of fluoroarenes into arylboronic acid pinacol esters via C-F bond activation and transmetallation with bis(pinacolato)diboron (B$_2$pin$_2$) is reported. Various partially fluorinated arenes with different degrees of fluorination were converted into their corresponding boronate esters.

Arylboronic acid esters are versatile reagents in organic synthesis, especially in the widely employed Suzuki-Miyaura cross-coupling reaction.[1] Transition-metal-catalyzed direct C-H borylation of arenes[2] and borylation of aryl halides[3] has emerged as one of the most important mild and attractive routes for the synthesis of aryl boronates in recent years. Fluoroaromatics play an important role in pharmaceuticals, agrochemicals and materials,[4] and there is currently much research aimed at the development of new ways to introduce fluorine or fluorinated building blocks into organic molecules.[4,5] A smart way to achieve this goal would employ fluoroaromatic boronic acids or boronate esters. The conversion of fluoroaromatics into arylboronic esters via C-F bond activation, however, is relatively unexplored and was restricted to noble metal catalysts until recently. Smith and coworkers observed small amounts of C-F bond borylation products (ca. 5%) in the iridium-catalyzed borylation of pentafluorobenzene and in the rhodium-catalyzed borylation of 1,3,5-trifluorobenzene.[6] C-F bond borylation promoted by [Rh(SiPh$_3$)(PMe$_3$)$_3$] was reported by Marder, Perutz and coworkers[7] in stoichiometric reactions, and Braun *et al.* developed the Rh(I)-catalyzed borylation of pentafluoropyridine, hexafluoropropene and other fluorinated aromatics.[8] Furthermore, Zhang *et al.* reported that commercially available [Rh(cod)$_2$]BF$_4$ catalyzes *ortho*-selective C-F bond borylation of polyfluoroarenes with B$_2$pin$_2$.[9] All of the above protocols employ noble metal catalysts.

Although much work has been done in the field of nickel-mediated C-F bond activation,[5,10] applications of nickel phosphine complexes in catalytic C-F bond borylation appeared just recently. Thus, Martin *et al.*[11] and Niwa and Hosoya *et al.*[12] reported in 2015 the borylation of monofluoroarenes using *in situ* generated nickel phosphine complexes from the reaction of [Ni(COD)$_2$] (COD = 1,5-cyclooctadiene) and PCy$_3$ (> 4 eq.) (Scheme 1). Martin *et al.* chose bis(neopentylglycolato)diboron (B$_2$neop$_2$) as the boron source and NaOPh as a base to promote the reaction in THF at 110 °C, whereas Niwa *et al.* reported borylation using bis(pinacolato)diboron (B$_2$pin$_2$) as the boron source, CsF as an additive and a copper source as a mediator in toluene at 80 °C for 24 h. However, borylation with the [Ni(COD)$_2$]/PCy$_3$ system was only reported for monofluoroarenes and the reactions strongly depend on the conditions employed. Martin *et al.* demonstrated that the use of other nickel sources or co-ligands (e.g. using an NHC precursor or PPhCy$_2$ instead of PCy$_3$) leads to a significant drop in yield and a change of the base (NaO^{t}Bu, HCO$_2$Na, CsF) or the use of B$_2$pin$_2$ as a boron source essentially kills the catalytic process. The results presented by Niwa *et al.* on the [Ni(COD)$_2$]/Cu halide/PCy$_3$-mediated borylation of monofluoroarenes similarly reveal a strong dependence on the copper source (CuI works whereas other copper sources do not) and the base employed (CsF works whereas other additives investigated do not).

We are currently developing convenient methodologies to generate and use suitable, partially fluorinated organic precursors. One strategy we follow employs (i) C-F borylation of polyfluoroaromatics and (ii) use of the resulting fluoroaryl boronic ester in subsequent Suzuki-Miyaura coupling reactions. The reports by Martin *et al.*[11] and Niwa and Hosoya *et al.*[12] prompted us to disclose our results on the NHC nickel-catalyzed borylation of polyfluorinated aromatics (Scheme 1).

Scheme 1. Nickel-Catalyzed Borylation of Fluoroaromatics.



We have demonstrated earlier that $[Ni_2(^iPr_2Im)_4(COD)]$ ($^iPr_2Im$ = 1,3-di*iso*propyl-imidazolin-2-ylidene),[10a] reacts with fluorinated arenes with high chemo- and regioselectivity and catalyzes C-F bond transformations.[10] Thus, we envisioned this complex as a precatalyst for C-F bond borylation, but our initial experiments revealed that the nickel compound decomposes in the presence of B_2pin_2 or B_2cat_2. As an alternative, the complex $[Ni(IMes)_2]$ with the sterically more demanding NHC IMes (IMes = 1,3-dimesitylimidazolin-2-ylidene), which is sufficiently stable in the presence of diboron esters,[13] was used in the current study.

Table 1. Optimization of the Borylation of 1,2,3-$C_6F_3H_3$

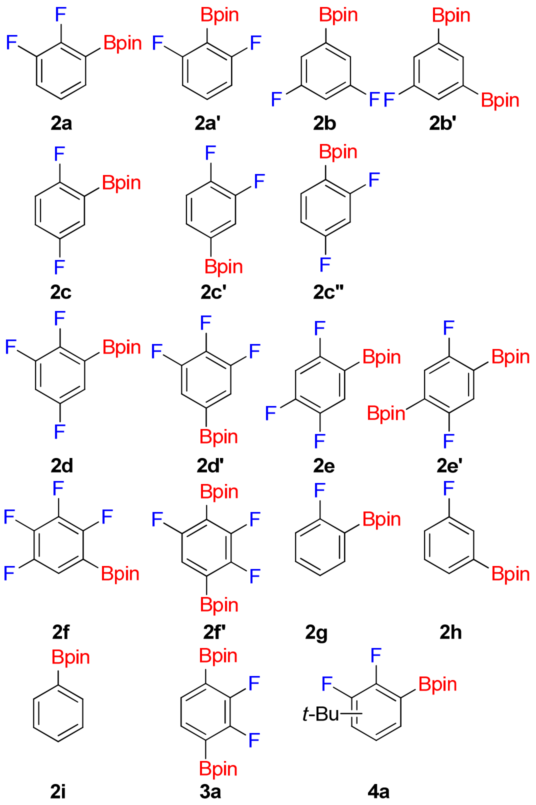
	1a/B_2pin_2	Base	Solvent	Yield(%)[a,b]
1	1.1:1	CsF (1 eq.)	THF	39
2	1.1:1	CsF (1 eq.)	C_9H_{12}	50
3	1.1:1	CsF (1 eq.)	C_6H_{12}	50
4	3:1	CsF (1 eq.)	C_9H_{12}	75
5	1.1:1	NMe_4F (1 eq.)	C_9H_{12}	62
6	1.1:1	NMe_4F (0.5 eq.)	C_9H_{12}	76
7	1.1:1	NMe_4F (0.5 eq.)	C_6H_{12}	79

[a] Reaction conditions: 29.0 mg (0.22 mmol) 1,2,3-$C_6F_3H_3$ **1a**; $[Ni(IMes)_2]$ (10 mol%), solvent (1 mL), 80 °C, 15 h. The yields were determined by *in situ* ^{19}F NMR spectroscopy.[b] Trace amounts of isomeric C-F and C-H borylation products were detected by GC-MS. C_9H_{12} = mesitylene; C_6H_{12} = methylcyclopentane. For more details see the SI.

We started our investigation using 1,2,3-trifluorobenzene **1a** (1 eq.) as the model substrate, B_2pin_2 (1 eq.) as the boron source, CsF (1 eq.) as an additive, $[Ni(IMes)_2]$ (10 mol %) as the catalyst and THF as the solvent of choice. A C-F borylation product was obtained from this reaction in 39 % yield (judged by ^{19}F NMR spectroscopy; Table 1, entry 1), which was identified as compound **2a** (Scheme 2), i.e. the product from a defluoroborylation at the 1-position. In addition to **2a**, the regioisomer **2a'** (borylation at the 2-position), traces of the hydrodefluorination/borylation products **2g** and **2h** and a C-H borylation product were detected by GC-MS analysis. Interestingly, trace amounts of the diborylation compound **3a**, presumably formed by subsequent C-H- and C-F-borylation, were detected as well. Note that the preference of NHC nickel insertion into the C-F bond at the 1-position of 1,2,3-$C_6F_3H_3$ was observed before.[10d] With this promising first result, different solvents, bases, and different stoichiometric ratios of fluorobenzenes and B_2pin_2 were screened using standardized conditions (80°C, 15 h) to assess the scope and limitations of this reaction (Table 1, Tables S1 – S4 in the SI). First of all, our studies clearly reveal that the nature of the solvent used is very important. For hexane, mesitylene or methylcyclopentane instead of THF the yields of **2a** increase to 45 % (hexane) and 50 % (mesitylene or methylcyclopentane), respectively (Table S1; Table 1, entries 2, 3), whereas acetonitrile shuts the reaction down completely (Table S1). Methyl *t*-butyl ether works similarly well compared to THF; in this case, however, the C-F/C-H diborylation product **3a** and the alkylation product **4a** (Scheme 2) were detected in trace amounts (Table S1). The latter compound implies C-O bond cleavage of MTBE under catalytic conditions.[14] In general, yields and turnover rates are low, but some improvement with respect to the consumption of B_2pin_2 was achieved if the amount of fluoroarene was increased to 3 equivalents (75 % **2a**; Table S2, Table 1, entry 4). An increase of the amount of B_2pin_2 (and CsF) to 2 equivalents leads to the formation of a mixture of monoborylated **2a** and bisborylated **3a**. A screening of different additives further reveals that the choice of the base also dramatically affects the reaction and that the presence of fluoride is crucial and beneficial (Table S3). Interestingly, the addition of 0.5 equivalents of water-free NMe_4F instead of CsF provided a superior yield, especially, if methylcyclopentane was used as the solvent (Table S4, Table 1, entries 5-7). However, considering the fact that water-free NMe_4F is relatively expensive,[15] we also provide the conditions and results for reactions using much cheaper and commercially available fluoride sources such as CsF, KF, or NBu_4F (Tables S1-S4). CsF and KF were moderately effective and provide the product in 50 % yield, while the use of water-containing TBAF shuts the reaction down completely. With water-free NMe_4F in hand, the conditions as given in Table 1, entry 7 are the best for the formation of **2a** (1.1 eq. $C_6F_3H_3$, 1 eq. B_2pin_2, 10 mol% $[Ni(IMes)_2]$, 0.5 eq. NMe_4F, methylcyclopentane, 80 °C, 15 h).

Using these optimized conditions, we then explored the scope of the nickel-catalyzed C-F bond borylation using different fluoroarenes. As shown in Table 2, the borylation of fluoroarenes containing different degrees of fluorination was achieved in moderate to good yields. For example, using 1,3,5-$C_6F_3H_3$ (**1b**), mono-borylated **2b** was obtained in 93 % yield (Table 2, entry 2;). Borylations of 1,2,3-trifluorobenzene (**1a**) and 1,2,3,5-$C_6F_4H_2$ (**1d**) were also accomplished with good selectivity and yield (Table 2, entries 1, 4). For other substrates such as 1,2,4-$C_6F_3H_3$ (**1c**), 1,2,4,5-$C_6F_4H_2$ (**1e**) and C_6F_5H (**1f**), the temperature had to be raised to 100°C for successful borylation (Table 2, entries 3, 5, 6). For 1,2,4-$C_6F_3H_3$ (**1c**), borylation of the 2-position (**2c**) prevails and only minor amounts of the isomers from borylation of the 1-(**2c''**) or of the 4-positions (**2c'**) (ratio approximately 10:1:1, judged from ^{19}F NMR spectroscopy) were formed. For 1,2,4,5-$C_6F_4H_2$ (**1e**), diborylation to give **2e'** was observed when using the standard reaction conditions. However, the formation of mono-borylation product (**2e**) and diborylation product (**2e'**) as the main product can be controlled by the ratio of fluoroaromatic and diboron reagent used. One equivalent of 1,2,4,5-$C_6F_4H_2$, 2 equivalents B_2pin_2 and CsF leads to diborylation product **2e'** in 73 % yield. If the amount of 1,2,4,5-$C_6F_4H_2$ is increased to 4 equivalents, the monoborylation product **2e** was obtained in good yield with only small amounts of **2e'**. Compounds **2e** and **2e'** can be separated easily by column chromatography (see SI). The borylation of C_6F_5H occurs not at the most nucleophilic 3-position, as probably expected, but at the position *ortho* to the hydrogen substituent. However, selective *ortho*-C-F bond activation of C_6F_5H at nickel was observed before.[16] We were unsuccessful in improving the reaction with $[Ni(IMes)_2]$ from being essentially stoichiometric in nickel (12 % yield at 100 °C). However, we found that the use of [Ni(IPr)2], bearing the sterically more demanding NHC 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene IPr, as a precatalyst is beneficial to this reaction, and formation of the borylation product was observed in more than 80 % yield. For 1,2-$C_6F_2H_4$ (**1g**) and 1,3- $C_6F_2H_4$ (**1h**), C-F borylation products were formed in somewhat lower yields, with trace amounts of C-H bond borylation observed by GC-MS (Table 2, entries 7, 8). Borylation of monofluorobenzene leads to PhBpin **2i** in only 20 % yield (Table 2, entry 9). Moreover, we observe no reaction or only traces of products for the borylation of perfluorinated substrates such as hexafluorobenzene or octafluorotoluene. We also provide yields of the isolated product using CsF as a base in Table 2. All products have been characterized by multinuclear NMR spectroscopy and high resolution mass spectroscopy and, for **3a**, **2e'** and **2f'**, by X-ray diffraction (see SI).

Scheme 2. Borylation Products and Side-Products



In previous work we have shown that NHC nickel complexes readily insert into C-F bonds of polyfluorinated aromatics.[10] Using [Ni(IMes)$_2$], C-F bond activation also occurs cleanly. The reaction of 1,2,3,5-$C_6F_4H_2$ (**1d**) with [Ni(IMes)$_2$] affords the nickel fluoride complex *trans*-[Ni(IMes)$_2$(F)(2,3,5-$C_6F_3H_2$)] **5** in good isolated yield (see SI). This reaction is quantitative according to ^{1}H and ^{19}F NMR spectroscopy. Complex **5** has been characterized by proton and fluorine NMR spectroscopy, mass spectrometry, elemental analysis and X-ray diffraction. Most significantly, the Ni-F ligand of **5** gives rise to a resonance at –344.5 ppm in the ^{19}F NMR spectrum.

The reaction of [Ni(IMes)$_2$] with 1,2,3,5-$C_6F_4H_2$ (**1d**) in the presence of B$_2$pin$_2$ and NMe$_4$F leads to the initial formation of the C-F bond activation product **5** (see SI). The boryl transfer reagent should be either B$_2$pin$_2$ or its fluoride adduct, i.e. [NMe$_4$][B$_2$pin$_2$F] **7**.[17] The reaction of **5** with an excess of B$_2$pin$_2$ and NMe$_4$F using catalytic conditions leads to borylated fluoroarene, complex **5** and [NMe$_4$][F$_2$Bpin]. We favor at present a mechanism as outlined in Scheme 3. The reaction of [Ni(IMes)$_2$] **I** with the fluoroarene leads in a first step to oxidative addition of the C-F bond with formation of *trans*-[Ni(IMes)$_2$(F)(Ar_F)] **II**. Although an initial "kinetic" C-H bond activation step[5d,e] would explain the regioselectivity of the borylation reaction (borylation occurs at a site adjacent to an hydrogen substituent), we can not observe such an species even at low temperatures (see Figure S 68 – S70). The complex *trans*-[Ni(IMes)$_2$(F)(Ar_F)] **II** reacts then with [NMe$_4$][B$_2$pin$_2$F] by boryl transfer to give *trans*-[Ni(IMes)$_2$(Bpin)(Ar_F)] **III** and [NMe$_4$][F$_2$Bpin]. A final reductive elimination step (e.g. after ligand elimination from a three coordinate species as indicated in Scheme 3 or after *cis*/*trans* isomerization of the boryl complex) delivers the borylated fluoroaromatic Ar_F-Bpin and regenerates [Ni(IMes)$_2$] **I**. The borylation of the nickel fluoride complex seems to be the rate limiting process in the sequence, as we (i) observe larger quantities of the nickel fluoride as the resting state in the reaction mixtures under catalytic conditions (see SI) and (ii) failed to isolate complexes *trans*-[Ni(IMes)$_2$(Bpin)(Ar_F)] so far from the stoichiometric reaction of *trans*-[Ni(IMes)$_2$(F)(ArF)] with B$_2$pin$_2$/NMe$_4$F.

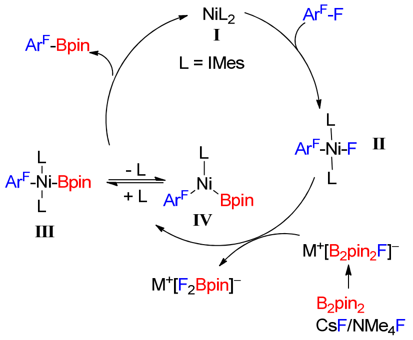
Table 2. Scope of the Ni-catalyzed C-F borylation

$$\mathrm{Ar^F\text{-}F} \xrightarrow[\substack{\mathrm{B_2pin_2}\ (1\ \mathrm{eq.}),\ \mathrm{solvent} \\ \mathrm{NMe_4F}\ (0.5\ \mathrm{eq.})/\mathrm{CsF}\ (1\ \mathrm{eq.})}]{[\mathrm{Ni(IMes)_2}](10\ \mathrm{mol}\ \%)} \mathrm{Ar^F\text{-}Bpin}$$

	Substrate	Product and Yield
1	1,2,3-$C_6F_3H_3$	1-Bpin-2,3-$C_6F_2H_3$(**2a**) 79 % (38 %)[b]
2	1,3,5-$C_6F_3H_3$	1-Bpin-3,5-$C_6F_2H_3$(**2b**) 93 % (75 %)[b]
3	1,2,4-$C_6F_3H_3$	1-Bpin-2,4-$C_6F_2H_3$(**2c**) 77 % (60 %)[c] **2c**:**2c'**:**2c''**=10:1:1 [c]
4	1,2,3,5-$C_6F_4H_2$	1-Bpin-2,3,5-$C_6F_3H_2$(**2d**) 99 % (71 %)[b] **2d**:**2d'**=10:1
5	1,2,4,5-$C_6F_4H_2$	1-Bpin-2,4,5-$C_6F_3H_2$(**2e**) 70 % (65 %)[d] 1,4-bisBpin-2,5-$C_6F_2H_2$(**2e'**) 85 %[e,f] (73 %)[e]
6	C_6F_5H	1-Bpin-2,3,4,5-C_6F_4H (**2f**) 85 %[f] (80 %)[b,f]
7	1,2-$C_6F_2H_4$	1-Bpin-2-C_6FH_4 (**2g**) 48 %[g] (30 %)[g]
8	1,3-$C_6F_2H_4$	1-Bpin-3-C_6FH_4 (**2h**) 50 %[g] (35 %)[g]
9	C_6FH_5	C_6H_5Bpin (**2i**) 20 %[g, h]

[a] Reaction conditions (unless specified otherwise): B$_2$pin$_2$ (0.2 mmol), fluoroarene (0.22 mmol), [Ni(IMes)$_2$] (10 mol %), NMe$_4$F (0.1 mmol), methylcyclopentane (1 mL), 80 °C, 15 h. Yields determined by ^{19}F NMR spectroscopy based on B$_2$pin$_2$. [b] Reaction conditions: B$_2$pin$_2$ (2 mmol), fluoroarene (2.2 mmol), [Ni(IMes)$_2$] (10 mol %), CsF (2 mmol), methylcyclopentane (10 mL), 80 °C, 15 h. Isolated yields. [c] methylcyclohexane, 100 °C. [d] **2e** (4 eq.), methylcyclohexane, 100 °C. [e] B$_2$pin$_2$ (2 eq.), fluoroarene (1 eq.), CsF (2 eq.), methylcyclohexane (20 mL), 100 °C, 15 h. [f] [Ni(IPr)$_2$] (10 mol %) instead of [Ni(IMes)$_2$]. [g] Fluoroarene (2 eq., 0.4 mmol). [h] Yield was determined by GC-MS using $C_{12}H_{26}$ as the internal standard. For more details see the SI.

Scheme 3. Proposed Mechanism for the NHC-Nickel-Catalyzed Borylation of Fluoroarenes.



In summary, we have developed an efficient procedure for the C-F borylation of fluoroaromatic compounds using [Ni(IMes)$_2$] ([Ni(IPr)$_2$] for pentafluorobenzene) as a catalyst, NMe$_4$F or CsF as a fluoride source, and B$_2$pin$_2$ as the boron source. In combination with the wide versatility of borylarene transformations, this method will enable the variation of C-F-bonds in polyfluoroarenes in the future, e.g. replacing selected fluorine substituents with other groups such as other halides, amides, carboxylate or ether functionalities. On the other hand, typical C-C bond formation steps will allow the introduction of partially fluorinated arenes into larger organic molecules. Detailed investigations concerning the applications and mechanistic details of this reaction are in progress.

ASSOCIATED CONTENT

Supporting Information

Experimental details, spectroscopic data, copies of ^{1}H, ^{13}C{^{1}H}, ^{11}B, ^{19}F{^{1}H} and ^{19}F NMR spectra and HRMS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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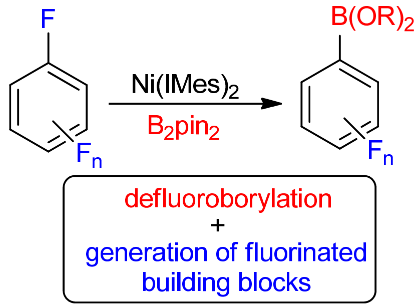
F
F_n
$Ni(IMes)_2$
B_2pin_2
$B(OR)_2$
F_n
defluoroborylation
+
generation of fluorinated building blocks