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FBpin and its adducts and their role in catalytic borylations†

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We present herein investigations concerning the reactivity of B_2pin_2 and FBpin (pin = pinacolato) with respect to fluoride ions and NHCs (NHC = *N*-Heterocyclic Carbene) in order to understand better the role of added fluoride in our recently reported Ni-catalyzed C–F borylation process, to confirm the nature of the NHC-adducts of FBpin, and to explain the formation of the species detected as side products of the defluoroborylation reaction. We report the calculated gas phase fluoride ion affinities (FIA) of relevant boron species and demonstrate that the presence of one equivalent of added F^- in solution will bind and activate B_2pin_2 (FIA = +247 kJ mol^{-1}), but it will also bind even more effectively to FBpin (FIA = +287 kJ mol^{-1}) formed in the reaction. We prepared the NHC-adducts of FBpin by two different methods and isolated and characterized several examples of the type FBpin·NHC (NHC = $^{i}Pr_2Im$, **1**; Me_2Im, **2**; MeiPrIm, **3**; nPr_2Im, **4**; Mes_2Im **5**). The salts $[pinBF_2][NMe_4]$ **6**, as well as the significantly more soluble analogue $[pinBF_2][NnBu_4]$ **7**, were also isolated and characterized, providing confirmation of the presence of the $pinBF_2$ anion in various stoichiometric and catalytic borylation reactions.

Introduction

The development of methods to introduce fluorinated aromatic building blocks selectively into organic molecules is of interest, as fluorinated organic compounds have exceptional properties that are being exploited in many applications including materials, pharmaceuticals, and agrochemicals.[1] A promising strategy to achieve this goal would be to transform commercially available fluoroaromatics into fluoroaryl boronic acid esters by transition-metal-catalyzed selective C–F borylation, which could then be further used in Suzuki–Miyaura

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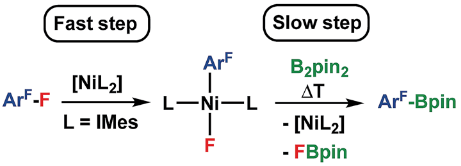
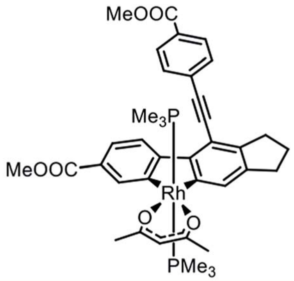
and other cross-coupling reactions and numerous functional group transformations.[2] The challenge of this method is the selective cleavage of a very stable C–F bond,[3] while simultaneously forming an easily transformable C–B bond.

Over the past few years, one of our groups has investigated the use of NHC-stabilized nickel complexes, *e.g.* the dinuclear complex $[Ni_2(^iPr_2Im)_4(\mu\text{-COD})]$ ($^iPr_2Im$ = 1,3-di-iso-propyl-imidazolin-2-ylidene) and related $[Ni(NHC)_2]$ precursors, in stoichiometric and catalytic C–F bond activation reactions.[4] These complexes undergo oxidative addition with a wide range of per- and poly-fluoroaromatics to give products resulting from the insertion of the metal into the C–F bond on a time scale that is relevant for catalysis.[5] Using these complexes, we want to develop convenient methodologies to generate and use suitable poly-fluorinated organic precursors to synthesize new molecules by: (i) the C–F borylation of polyfluoroaromatics; and (ii) the use of the resulting fluoroaryl boronic ester in subsequent transformations, *e.g.* Suzuki–Miyaura coupling reactions. Shortly following the reports of Martin *et al.* and Niwa and Hosoya *et al.* on the borylation of monofluoroarenes using *in situ* generated nickel phosphine complexes,[6] we presented the thermal $[Ni(Mes_2Im)_2]$-catalyzed (Mes_2Im = 1,3-dimesitylimidazolin-2-ylidene) transformation of polyfluoroarenes into fluoroaryl boronic acid pinacol esters *via* C–F bond activation and transmetalation with bis(pinacolato)diboron (B_2pin_2) as the boron source.[7a] Various partially fluorinated arenes with different degrees of fluorination were converted into their corresponding boronate esters. One particularly interesting finding of our study was that activation of the very strong C–F bond by the Ni(0) complex to give the oxidative addition product *trans*-$[Ni(Mes_2Im)_2(F)(Ar^F)]$ (Ar^F = fluoroarene) is fast at ambient temperature,[7a] but the transmetalation step with B_2pin_2 is rate determining and requires elevated temperatures for efficient catalysis (Scheme 1).



Scheme 1 Thermal borylation of fluoroarenes with B_2pin_2 mediated by $[Ni(Mes_2Im)_2]$ *via* the oxidative addition product *trans*-$[Ni(Mes_2Im)_2(F)(Ar^F)]$.

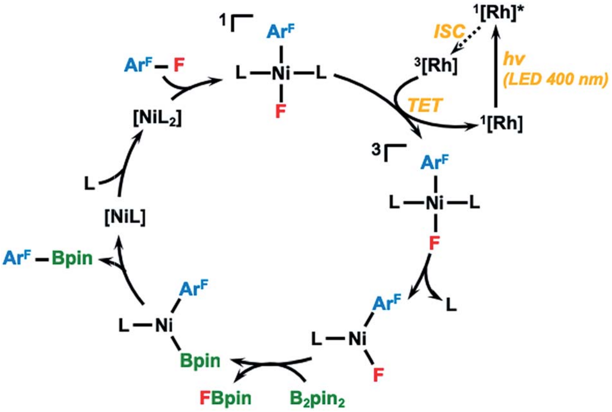
As an alternative to thermally induced C–F bond activation and the subsequent borylation of fluoroarenes by transition metals, we then developed a process that employs visible light photocatalysis,[7b] which has recently emerged as a powerful tool in organic synthesis.[8] This highly selective and general photocatalytic C–F borylation protocol[7b] employs a rhodium biphenyl complex[9] (Fig. 1) as a triplet sensitizer combined with the nickel catalyst $[Ni(Mes_2Im)_2]$ for the C–F bond activation and the defluoroborylation process. This Rh/Ni tandem catalyst system operates with visible (blue, 400 nm) light and achieves the borylation of a wide range of polyfluoroarenes with B_2pin_2 at room temperature in excellent yields and with high selectivity.[7b]



- Broad absorption between 390-440 nm
- Triplet energy of 53 kcal/mol
- Long-lived excited state in solution (338 μs in 2-MeTHF and 181 μs in toluene)

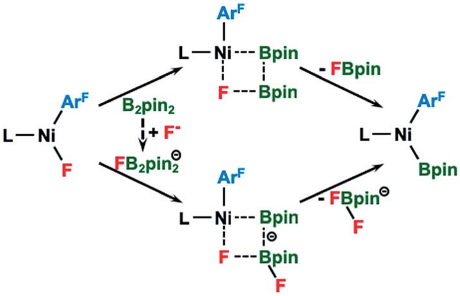
Fig. 1 The Rh biphenyl photocatalyst and its key properties.[7b,9]

The mechanistic studies suggest that the exceptionally long-lived triplet excited state of the Rh biphenyl complex used as the photosensitizer allows for efficient triplet energy transfer (TET) to *trans*-[Ni(Mes$_2$Im)$_2$(F)(Ar^F)], which likely leads to the dissociation of one of the NHC ligands. This contrasts with the majority of current photocatalytic transformations, which employ transition metals as excited state single electron transfer (SET) agents. An investigation of the redox potentials of the participating metal complexes, performed to elucidate a potential SET processes between the rhodium photosensitizer, any of the Ni species, and 1,2,3,5-tetrafluorobenzene as a model substrate, revealed that the ground state oxidation and reduction potentials of the rhodium complex are not sufficient for SET to [Ni(Mes$_2$Im)$_2$] or the intermediate species *trans*-[Ni(Mes$_2$Im)$_2$(F)(Ar^F)]. The triplet excited state reduction potential of the rhodium complex would be sufficient to oxidize [Ni(Mes$_2$Im)$_2$], but this process is not relevant for transmetalation and therefore not relevant to the photocatalytic process (and would likely inhibit the initial C–F bond activation step). The resting state *trans*-[Ni(Mes$_2$Im)$_2$(F)(Ar^F)] itself absorbs very weakly at 400 nm and, although the complex alone is photolytically stable, it decomposes to nickel black in the presence of B$_2$pin$_2$ after irradiation at 400 nm. It has been demonstrated previously that intersystem crossing (ISC) in square-planar nickel(II) complexes can be very slow (timescale of ns).[10] It is thus feasible that the ISC from S$_1$ into a triplet state T_n in *trans*-[Ni(Mes$_2$Im)$_2$(F)(Ar^F)] is also slow and not competitive with the decomposition reaction of its photoexcited S$_1$ state in the presence of B$_2$pin$_2$. However, our TD-DFT computational studies on *trans*-[Ni(Mes$_2$Im)$_2$(F)(Ar^F)] revealed a number of energetically low-lying triplet excited states in the visible region, energetically close to or below the T_1 state of the rhodium complex, which can be sensitized by energy transfer from the exceptionally long-lived triplet state of the rhodium photocatalyst. We have shown experimentally[7b] that the phosphorescence from the Rh triplet state is efficiently quenched by *trans*-[Ni(Mes$_2$Im)$_2$(F)(Ar^F)] and thus that energy transfer occurs from rhodium to the nickel(II) complex in the Rh/Ni system.



Scheme 2 Proposed mechanism for the photocatalytic borylation of fluoroarenes by the Rh/Ni-system using triplet energy transfer (TET). L = Mes$_2$Im; Ar^F = fluoroarene; ISC = intersystem-crossing.

Thus, [Ni(Mes$_2$Im)$_2$] undergoes very fast oxidative addition of the C(Ar^F)–F bond to give the oxidative addition product *trans*-[Ni(Mes$_2$Im)$_2$(F)(Ar^F)], which is the resting state of the catalytic cycle (Scheme 2). The rhodium biphenyl complex employed as the photocatalyst is excited to the S$_1$ state by irradiation with the 400 nm LED and, following ISC, energy transfer from its triplet excited state T_1 to *trans*-[Ni(Mes$_2$Im)$_2$(F)(Ar^F)] occurs. The triplet sensitization of *trans*-[Ni(Mes$_2$Im)$_2$(F)(Ar^F)], which bypasses the S$_1$ state of the [Ni^{II}] complex and thus its decomposition reaction with B$_2$pin$_2$, leads to the population of the M–L σ-antibonding d$_{x^2-y^2}$ orbital. The TD-DFT-optimized geometries of these excited states exhibit a significant elongation of the Ni–C(NHC) bonds, implying that NHC ligand dissociation can be facilitated by the triplet sensitization. Thus, TET leads to NHC ligand dissociation, and the resulting trigonal complex [Ni(Mes$_2$Im)(F)(Ar^F)] is sterically much less encumbered and then reacts with B$_2$pin$_2$. After transmetalation, the reductive elimination of Ar^F-Bpin is fast[11] and the resulting Ni(0) species is then stabilized by the re-coordination of Mes$_2$Im, giving [Ni(Mes$_2$Im)$_2$], and the catalytic cycle starts again.



Scheme 3 Possible transmetalation route with or without CsF.

A question that remained unresolved is the role of added fluoride present in solution (Scheme 3). While the addition of a fluoride source, such as CsF, enhances the yield, it is not absolutely required for the reaction to take place. There are two reasonable explanations for the effect of added CsF, based on our previous studies of the anionic adducts of B_2pin_2 and their reactivity with electrophiles.[12] Thus, the formation of the known ionic adduct[12a] $[FB_2pin_2]^-$ from B_2pin_2 and F^- would create a much more nucleophilic $\{Bpin^-\}$ fragment,[12] which would be expected to enhance the rate constant for the transmetalation step of the reaction (Scheme 3). Another explanation for this yield-enhancing effect would be the partial trapping of the side product FBpin (pinacolatofluoroborane) by the formation of $Cs[F_2Bpin]$, which would also avoid the formation of a significant amount of Lewis base–Lewis acid adduct FBpin·NHC, if its formation is feasible, and consequently the decomposition of $[Ni(NHC)_2]$ in the reaction mixture. We present herein investigations concerning the reactivity of B_2pin_2 and FBpin with respect to fluoride ions and NHCs to shed some light to the role of added fluoride in the defluoroborylation process, to prove the existence of NHC-adducts of FBpin, and to explain the formation and the existence of species detected as side products of the defluoroborylation reaction. We reported on the reactivity of B_2pin_2 with fluoride[12] and of NHCs with B–B, B–H and B–C bonded systems,[13] and on the reactions of amines, pyridines, and phosphines[14] with diboron reagents and catBCl[15] (cat = catecholato) in detail earlier.

Results and discussion

We began our study with the calculation of the gas phase fluoride ion affinities (FIA) of the relevant boron compounds using a procedure introduced by Krossing *et al.*[16] It is based on the FIA of the trimethylsilyl cation ($Me_3Si^+ + F^- \rightarrow Me_3SiF$) calculated at a high level of theory, whereas the present calculations of molecules under investigation were assessed based on subsequent isodesmic reactions calculated at a much less expensive level (here: BP86/SV(P)). The values obtained for different diboron(4) esters and other species in solution relevant to the defluoroborylation process are given in Table 1. The FIA values calculated for the different diboron(4) compounds clearly reveal a decrease of the Lewis-acidity along the row B_2cat_2 (+341 kJ mol^{-1}) ≫ B_2pin_2 (+247 kJ mol^{-1})/B_2eg_2 (+241 kJ mol^{-1})/B_2neop_2 (+238 kJ mol^{-1}) (eg = ethylene glycolato; neop = neopentane gycolato). However, in our system, we note that F^- in solution will bind and activate B_2pin_2 (FIA = +247 kJ mol^{-1}), but it will also bind even more

Table 1 FIA values [in kJ mol^{-1}] of different diboron(4) esters and other relevant molecules calculated at the BP86/SV(P) level

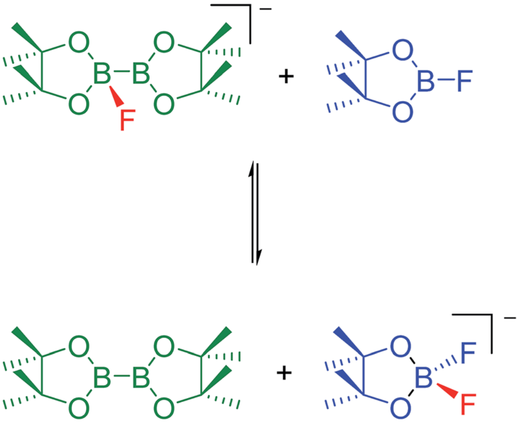
Ion pair	FIA
BF_3/BF_4^-	+342
$B_2cat_2/FB_2cat_2^-$	+341
$FBpin/F_2Bpin^-$	+287
$B_2pin_2/FB_2pin_2^-$	+247
$B_2eg_2/FB_2eg_2^-$	+241
$B_2neop_2/FB_2neop_2^-$	+238

effectively to FBpin (FIA = +287 kJ mol^{-1}) formed in the reaction. In the presence of B_2pin_2 and FBpin, the latter preferentially reacts with fluoride in solution. So, one equivalent of added F^- will bind, at the beginning of the reaction, to B_2pin_2 but, as the reaction proceeds, it will preferentially trap the side product FBpin as F_2Bpin^-.

Accordingly, we typically do not observe FBpin as the major by-product for the "second" Bpin moiety resulting from the transmetalation step of the defluoroborylation. Instead, the corresponding signals in the ^1H, $^{11}B\{^1H\}$ and in the ^{19}F-NMR data are consistent with the formation of F_2Bpin^-, a set of resonances that was tentatively assigned to an NHC adduct of FBpin, and to a BF_4^- salt. The F_2Bpin^- anion was observed earlier in the reaction of isolated $FB_2pin_2^-$ with aryl diazonium salts, which led to the borylation of the arene.[12a] For these reactions we demonstrated that, for complete conversion of the starting material to product, an excess of the anionic adduct was required, which we speculated to result from the preferential trapping of FBpin giving F_2Bpin^-, thus diminishing the amount of the reactive $FB_2pin_2^-$ in solution as FBpin is produced (Scheme 4).

The FIAs of the Lewis acidic boron-containing molecules involved suggest that this equilibrium, at least as calculated in the gas phase, is thermodynamically feasible, but it is also strongly favoured in THF solution, and we calculated a ΔG^{298}(THF) of 54.5 kJ mol^{-1} in favour of the formation of B_2pin_2 and F_2Bpin^-. The formation of F_2Bpin^- may also account for the presence of some free B_2pin_2 even if one equivalent of fluoride is added to the reaction. According to the FIAs, FBpin is a better fluoride acceptor than B_2pin_2 and depletes $FB_2pin_2^-$ competitively with its reaction with the trigonal complex [Ni(Mes$_2$Im)(F)(Ar^F)], thus inhibiting the transmetalation process as the concentration of FBpin increases.

In light of these results, we were interested in the behaviour of B_2pin_2 in the presence of a fluoride ion source and a free NHC. To obtain a good solubility of the fluoride ion in THF, we chose NMe_4F as the fluoride source and, initially, to avoid too much steric hindrance, we employed sterically less demanding alkyl-substituted NHCs. The conditions used were the same in all reactions; in particular, the ratio of the starting materials was 1 : 1 : 1, THF was the solvent, and higher temperatures (up to 70 °C) were employed (NMe_4F is quite soluble in

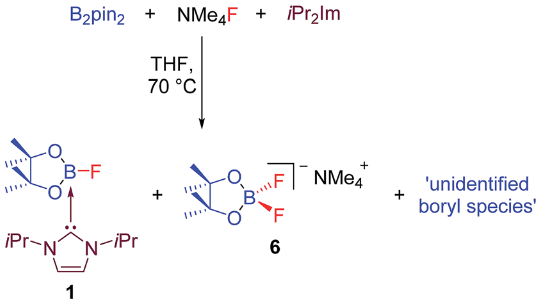


Scheme 4 Equilibrium involved in the reaction between $FB_2pin_2^-$ and FBpin.

refluxing THF). We reported earlier the isolation and detailed structural characterization of the neutral mono- and bis-NHC adducts of several diboron(4) esters.[13] The bis-NHC adducts, in particular, can undergo thermally induced rearrangement, forming a 6-membered –B–C=N–C=C–N-heterocyclic ring *via* C–N bond cleavage and ring expansion of the NHC, whereas the mono-NHC adducts are often stable. We pointed out that the reactivity strongly depends on the steric effects of the NHCs and the diboron(4) compounds, as well as on their corresponding Lewis basicity and Lewis acidity. From that work, we realized that B_2pin_2 reacts with the NHC $^iPr_2Im$ with the formation of the mono-NHC adduct iPr_2Im-B_2pin_2. This compound is thermally stable and does not rearrange to a ring-expanded product up to the temperatures of refluxing THF. Thus, we started our investigation with the NHC iPr_2Im, which was reacted with B_2pin_2 and NMe_4F in equimolar amounts in refluxing THF (Scheme 5).

Two compounds were isolated from the reaction mixture. The first compound was an insoluble solid, which precipitated and was identified as $[pinBF_2][NMe_4]$ **6** as the main-product (42%). Compound **6** was characterized *via* ^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$ and ^{19}F NMR spectroscopy, HRMS, as well as elemental analysis. The ^1H NMR spectrum revealed a singlet with a chemical shift of 1.60 ppm for the methyl-groups of the ammonium cation and another singlet for the pinacol groups of the Bpin moiety at 1.00 ppm. The $^{11}B\{^1H\}$ NMR spectrum shows one sharp triplet at 5.02 ppm and the fluorine atoms are detected as a quartet at −141.5 ppm in the $^{19}F\{^1H\}$ NMR spectrum, revealing a B–F coupling constant of 21 Hz. To improve solubility, we reacted tetrabutylammonium fluoride (TBAF) with B_2pin_2 under the same conditions generating the analogous salt $[pinBF_2][N\textit{n}Bu_4]$ **7**. Whilst compound **6** is moderately soluble in acetonitrile, the *n*-butyl groups of the cation of **7** increase its solubility significantly. Compound **7** was characterized *via* ^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$ and ^{19}F NMR spectroscopy, HRMS, as well as elemental analysis, and its connectivity was confirmed by single-crystal X-ray diffraction (see ESI†).

From the mother liquor, the compound $FBpin\cdot iPr_2Im$ **1** was isolated in very low yield (11%) by crystallization at −30 °C. Compound **1** was characterized *via* ^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$ and ^{19}F NMR spectroscopy, as well as elemental analysis. The ^1H NMR spectrum shows one set of signals for iPr_2Im; the protons of the backbone are observed at 6.39 ppm and the methine iPr-CH proton at 6.02 ppm as a septet. The doublet resonance of the methyl groups of the iPr_2Im is detected at 1.06 ppm. The pinacol groups of the Bpin moiety are detected at 1.20 and



Scheme 5 Reaction of B_2pin_2 with NMe_4F and iPr_2Im yielding $FBpin\cdot iPr_2Im$ **1**, $[pinBF_2][NMe_4]$ **6** and unidentified boryl species.

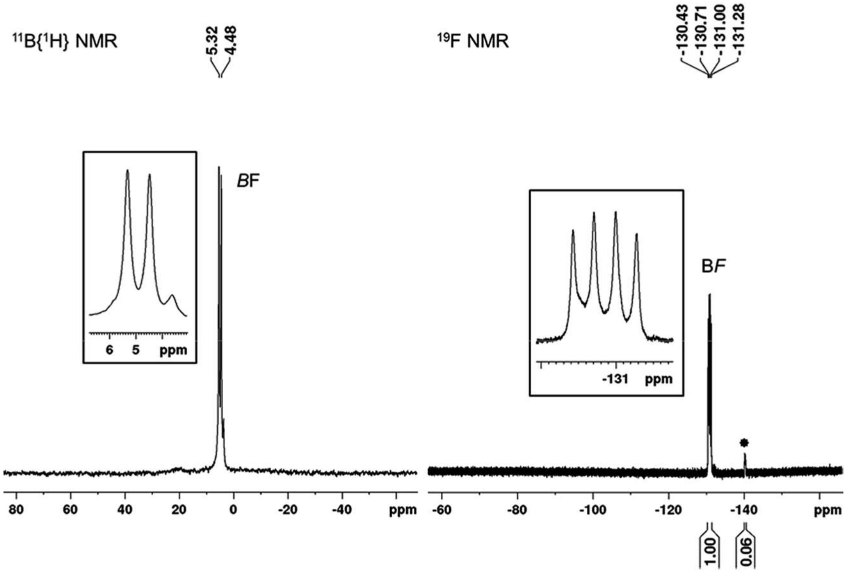


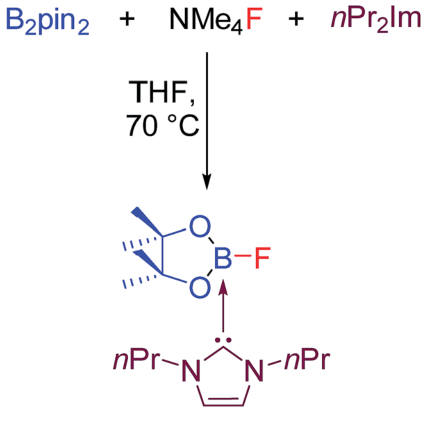
Fig. 2 $^{11}B\{^1H\}$ (left) and ^{19}F (right) NMR spectra of FBpin·iPr$_2$Im **1** recorded in C_6D_6 (* = [pinBF$_2$][NMe$_4$] **6**).

1.57 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance of the carbene carbon atom is observed at 162.3 ppm, significantly upfield shifted compared to the uncoordinated NHC (211.9 ppm).[17] The $^{11}B\{^1H\}$ NMR spectrum reveals one sharp doublet at 4.90 ppm and the fluorine atom gives rise to a quartet at −130.9 ppm in the $^{19}F\{^1H\}$ NMR spectrum, with a B–F coupling constant of 54 Hz (Fig. 2).

Similar results were obtained using Me$_2$Im (Me$_2$Im = 1,3-di-methyl-imidazolin-2-ylidene), MeiPrIm (MeiPrIm = 1-iso-propyl-3-methylimidazolin-2-ylidene) and *n*Pr$_2$Im (*n*Pr$_2$Im = 1,3-di-*n*-propyl-imidazolin-2-ylidene) as the NHC. The main product of the reactions was the salt [pinBF$_2$][NMe$_4$] **6**, but the adducts FBpin·Me$_2$Im **2**, FBpin·MeiPrIm **3**, and FBpin·*n*Pr$_2$Im **4** were isolated and characterized *via* ^1H, $^{11}B\{^1H\}$ and ^{19}F NMR spectroscopy. The NMR data obtained are summarized in Table 2. Whereas **1–3** were obtained in low yield, the

Table 2 Selected ^1H, $^{11}B\{^1H\}$ ^{19}F and $^{13}C\{^1H\}$ NMR data [ppm] as well as the isolated yield (%) of the mono-NHC adducts FBpin·iPr$_2$Im **1**, FBpin·Me$_2$Im **2**, FBpin·MeiPrIm **3**, FBpin·*n*Pr$_2$Im **4** and FBpin·Mes$_2$Im **5**

	FBpin·iPr$_2$Im 1	FBpin·Me$_2$Im 2	FBpin·MeiPrIm 3	FBpin·*n*Pr$_2$Im 4	FBpin·Mes$_2$Im 5
^1H	1.60, 1.20, 1.57, 6.02, 6.40	0.94, 1.23, 3.90, 6.98	1.00, 1.20, 1.60, 3.55, 5.74, 5.91, 6.01	0.88, 0.92, 1.11, 1.78, 4.32, 7.03	0.91, 1.25, 2.08, 2.18, 5.88, 6.75
$^{11}B\{^1H\}$	4.90	4.25	4.85	3.35	4.34
$^{13}C\{^1H\}$	N*C*N:162.3	n/a	n/a	N*C*N:162.2	N*C*N: 167.5
^{19}F	−130.9	−133.6	−132.1	−131.0	−131.4
Yield	11	8	9	91	55



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Scheme 6 Reaction of B_2pin_2 with NMe_4F and $n$$Pr_2Im$ yielding FBpin·$n$$Pr_2Im$ **4**.

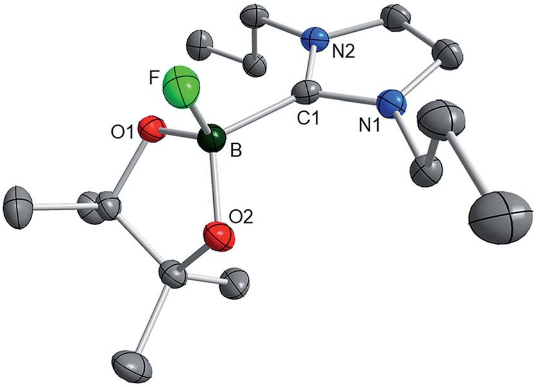
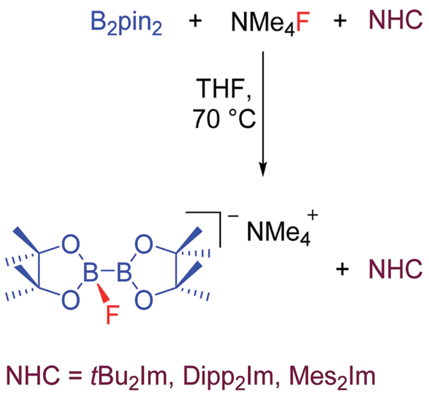


Fig. 3 Molecular structure of FBpin·iPr_2Im **1**. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms and the counter ion are omitted for clarity. Selected bond distances (Å) and angles (°): B–C1 1.664(3), B–F 1.436(2), B–O1 1.447(3), B–O2 1.450(3); F–B–C1 104.5(2), F–B–O1 113.0(2), F–B–O2 108.6(2).

reaction of B_2pin_2 and NMe_4F with the NHC $n$$Pr_2Im$ afforded FBpin·$n$$Pr_2Im$ **4** as the main-product in a very good yield of 91% (Scheme 6).

Single crystals suitable for X-ray diffraction were grown from a saturated hexane solution at −30 °C. The crystal structure of FBpin·$n$$Pr_2Im$ **4** (Fig. 3) confirmed the structure deduced from the NMR data.

The boron atom is tetrahedral, coordinated with two oxygen atoms, one fluorine atom, and the carbene–carbon atom. The NHC binds to the boron atom and the B1–C1 bond distance of 1.667(2) Å is comparable to the bond length reported for the neutral sp^2–sp^3 diboron adduct B_2pin_2·Cy_2Im (1.673(2) Å).[13b] Furthermore, the B–F (1.436(2) Å) distance is slightly shorter than that in the fluorine adduct $[B_2pin_2F][NMe_4]^-$ (1.478(2) Å).[12a] The B–O distances are comparable to those discussed previously for alkoxy adducts of B_2pin_2.[12a]



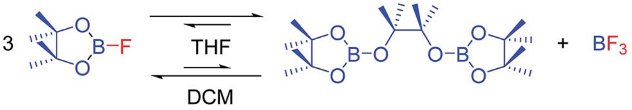
Scheme 7 Reaction of B_2pin_2, NMe_4F and different sterically more demanding NHCs.

The reactions of B_2pin_2, and NMe_4F with sterically more demanding NHCs, such as *t*Bu_2Im, Mes_2Im and $Dipp_2$Im, were also examined under the same conditions (refluxing THF as the solvent). From all of these reactions only the anionic adduct $[B_2pin_2F][NMe_4]$ and the "free" NHC were identified and isolated (Scheme 7).

Another more direct approach to synthesize adducts of the type FBpin·NHC was to start from FBpin. We thus prepared FBpin according to a procedure reported by Davies and co-workers.[18] Freshly prepared 2,3-bis(trimethylsilyloxy)-2,3-dimethylbutane[18] was reacted with a slight excess of $BF_3 \cdot OEt_3$ in dichloromethane at 0 °C. While attempting to synthesize and isolate FBpin, we observed an equilibrium between FBpin, B_2pin_3 and BF_3. Upon concentrating the solution, an increasing amount of BF_3 was detected and B_2pin_3 precipitated.

The balance of this equilibrium strongly depends on the solvent, as the poor solubility of B_2pin_3 in many solvents shifts the equilibrium towards B_2pin_3 and BF_3 (Scheme 8). In THF, the solubility is extremely low. Thus, even without concentrating the solution, B_2pin_3 started to precipitate and no FBpin remained. When the reaction was carried out in dichloromethane (DCM) at room temperature, we were able to trap the generated FBpin *in situ* by adding the free NHC Mes_2Im. The corresponding adduct FBpin·Mes_2Im **5** was thus isolated in 55% yield (Table 2). Interestingly, although free NHCs are usually unstable in protic and chlorinated solvents, the strong Lewis acidity of FBpin leads to the immediate formation of the NHC-adduct, which is stable in DCM for some time.

Compound **5** was characterized *via* ^{1}H, ^{11}B{^{1}H}, ^{13}C{^{1}H} and ^{19}F NMR spectroscopy, HRMS, as well as elemental analysis. The ^{1}H NMR spectrum shows one signal at 6.75 ppm for the aromatic protons of the mesityl moiety. The protons of



Scheme 8 Observed equilibrium between FBpin and B_2pin_3 and BF_3 in THF *versus* dichloromethane (DCM).

the backbone are observed at 5.89 ppm and the methyl groups of the mesityl moiety are detected at 2.08 and 2.18 ppm. The pinacol groups of the Bpin moiety give rise to two singlets at 0.90 and 1.24 ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance of the carbene carbon atom is observed at 167.5 ppm, significantly upfield shifted compared to the uncoordinated NHC (219.5 ppm).[17] The $^{11}B\{^1H\}$ NMR spectrum gives rise to one sharp doublet at 4.34 ppm and the fluorine atom reveals a quartet at −131.4 ppm in the ^{19}F NMR spectrum, also with a B–F coupling constant of 54 Hz. The data obtained are in accordance with those shown for the other FBpin-adducts **1–4** (Table 2).

The isolation and characterization of **5** now provides confirmation of its formation in the reactions of the Ni(II) complex with B_2pin_2 as proposed previously[7b] on the basis of the *in situ* ^{11}B and ^{19}F NMR spectra. We demonstrate that this process can be inhibited by the addition of a fluoride source that removes Lewis acidic FBpin as the F_2Bpin anion. During our previous studies of thermal $[Ni(Mes_2Im)_2]$-catalyzed aryl C–F borylation[7a] we observed the formation of a precipitate during the course of the reactions, which we proposed to be $[pinBF_2][NMe_4]$ **6**. With the isolation and characterization of **6** reported herein, we can now confirm that our proposed structure was correct.

Conclusion

We investigated the reactivity of B_2pin_2 and FBpin with fluoride ions and NHCs in order to improve our understanding of the role of added fluoride in our recently reported Ni-catalyzed defluoroborylation process.[7] Starting with the calculations of the gas phase fluoride ion affinities (FIA) of relevant boron species, we showed that the presence of one equivalent of added F^- will, at the beginning of the reaction, bind and activate B_2pin_2 (FIA = +247 kJ mol^{-1}) giving $FB_2pin_2^-$ and, as the reaction proceeds, it will trap the arising side product FBpin (FIA = +287 kJ mol^{-1}) as F_2Bpin^-. As FBpin is a better fluoride acceptor than B_2pin_2, it depletes the reactive $FB_2pin_2^-$ competitively with its reaction with the trigonal complex $[Ni(Mes_2Im)(F)(Ar^F)]$. Consequently, in the absence of sufficient added fluoride, the transmetalation step is inhibited as the borylation reactions proceed and the concentration of FBpin increases. Furthermore, we prove the existence of NHC-adducts of FBpin by reacting B_2pin_2 with different NHCs and a fluoride source in equimolar amounts in refluxing THF. We isolated and characterized several adducts of the type FBpin·NHC (NHC = $^iPr_2Im$, **1**; Me_2Im, **2**; MeiPrIm, **3**; nPr_2Im, **4**). In the course of those reactions we also isolated and characterized $[pinBF_2][NMe_4]$ **6**, as well as its significantly more soluble analogue $[pinBF_2][NnBu_4]$ **7** confirming the presence of this anion in borylation reaction mixtures. The use of sterically more demanding NHCs under the same conditions did not lead to analogous NHC adduct formation, as only the anionic adduct $[B_2pin_2F][NMe_4]$ and the "free" NHC were detected. A more direct route for the synthesis of adducts of the type FBpin·NHC, starting from *in situ* prepared FBpin, yielded the adduct FBpin·Mes_2Im **5**, a previously proposed source of catalyst decomposition when $[Ni(Mes_2Im)_2]$ was employed. This process can be inhibited by added fluoride, which removes Lewis acidic FBpin as the F_2Bpin anion. Thus, added fluoride can play several roles in borylation reactions and one must also be aware of the non-innocence of reaction byproducts such as FBpin.

Conflicts of interest

There are no conflicts to declare.

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