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C−H and C−F Bond Activations at a Rhodium(I) Boryl Complex: Reaction Steps for the Catalytic Borylation of Fluorinated Aromatics

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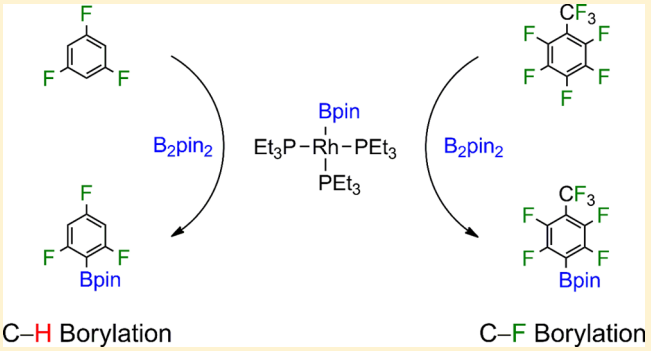
Supporting Information

ABSTRACT: Treatment of the rhodium(I) boryl complex $[Rh(Bpin)(PEt_3)_3]$ (**1**, pin = pinacolato = $O_2C_2Me_4$) with pentafluorobenzene, 1,3,5-trifluorobenzene, 1,3-difluorobenzene, or 3,5-difluoropyridine led to C−H activation reactions to give the aryl complexes $[Rh(C_6F_5)(PEt_3)_3]$ (**4**), $[Rh(2,4,6\text{-}C_6F_3H_2)(PEt_3)_3]$ (**5**), $[Rh(2,6\text{-}C_6F_2H_3)(PEt_3)_3]$ (**6**), and $[Rh\{4\text{-}(3,5\text{-}C_5NF_2H_2)\}(PEt_3)_3]$ (**8**). For **5**, **6**, and **8** consecutive reactions with *in situ* generated HBpin occurred to yield $[Rh(H)(PEt_3)_3]$ (**7**) and boronic esters. The boryl complex **1** gave with hexafluorobenzene or perfluorotoluene the C−F activation products $[Rh(C_6F_5)(PEt_3)_3]$ (**4**) and $[Rh(4\text{-}C_6F_4CF_3)(PEt_3)_3]$ (**9**), respectively. The complexes **5**, **6**, and **9** react with B_2pin_2 to yield **1** and boronic ester derivatives. On the basis of these stoichiometric reactions catalytic C−H and C−F borylation reactions using **1** or **7** were developed to generate 2-Bpin-1,3,5-$C_6F_3H_2$, 2-Bpin-1,3-$C_6F_2H_3$, and 4-Bpin-$C_6F_4CF_3$ from 1,3,5-trifluorobenzene, 1,3-difluorobenzene, or perfluorotoluene and B_2pin_2. On treatment of pentafluoropyridine with B_2pin_2 in the presence of **1** or **7** as catalyst 2-Bpin-C_5NF_4 was synthesized by C−F borylation at the 2-position. Using 2,3,5,6-tetrafluoropyridine, B_2pin_2, and catalytic amounts of **7** led to a C−H borylation reaction at the 4-position. 4-Bpin-C_5NF_4 can also be prepared by the reaction of 2,3,5,6-tetrafluoropyridine with stoichiometric amounts of HBpin or by the reaction of pentafluoropyridine with an excess of HBpin in the presence of **7**, whereas the reaction of pentafluoropyridine with stoichiometric amounts of HBpin and 5 mol % **7** resulted in the formation of 2,3,5,6-tetrafluoropyridine via hydrodefluorination reaction at the 4-position. This regioselectivity contrasts the borylation of pentafluoropyridine at the 2-position with **1** as catalyst. Overall, the obtained fluorinated aryl boronic ester derivatives might serve as versatile building blocks.



INTRODUCTION

Fluorinated organic compounds and building blocks play a key role in many applications because of their exceptional properties. They are employed, for example, in agrochemicals, pharmaceuticals and radiotracers, polymers, optoelectrics, and refrigerants.[1] The transition-metal-mediated activation of a C−F[2] or a C−H bond is a promising strategy to convert commercially available highly fluorinated aromatics into useful starting materials.[2n] Thermodynamically, the breaking of a C−F bond is often hampered by the exceptionally high bond dissociation energy,[3] but C−F activation reactions are often feasible given that a thermodynamically more stable bond is generated, such as H−F, Si−F, or B−F. However, examples of aromatic C−F bond functionalizations, i.e., fluorine atom replacement by a new group to access higher value fluorinated compounds, are limited.[4] In most of these functionalization reactions a hydrodefluorination reaction takes place.[2m,n,5]

The replacement of a C−F bond by a boryl group as a viable entity is particularly beneficial for further conversions. For transition-metal-mediated transformations, intermediate boryl complexes[6] might play a fundamental role. Borylation of a C−F bond was reported by Marder and Perutz et al.[7] The reaction of pentafluoropyridine at $[Rh(SiPh_3)(PMe_3)_3]$ gave the C−F activation products $[Rh(2\text{-}C_5NF_4)(PMe_3)_3]$ and $[Rh(4\text{-}C_5NF_4)(PMe_3)_3]$. Subsequent treatment with B_2cat_2 (cat = catecholato = $O_2C_6H_4$) resulted in the formation of pyridyl boronic ester derivatives. A catalytic C−F borylation using the highly reactive rhodium boryl complex $[Rh(Bpin)(PEt_3)_3]$ (**1**)[8] as catalyst was also reported (Scheme 1). The latter activates selectively the C−F bond at the 2-position of pentafluoropyridine to yield $[Rh(2\text{-}C_5NF_4)(PEt_3)_3]$ (**2**). DFT calculations showed that the C−F bond cleavage step proceeds via a four-centered boryl-assisted transition state in which C−F bond cleavage occurs over the Rh−B bond.[8a] Catalytic reactions of pentafluoropyridine with B_2pin_2 (pin = pinacolato = $O_2C_2Me_4$) and **1** as catalyst give access to the 2,3,4,5-tetrafluoropyridyl boronic ester (Scheme 1). In contrast, in $[Rh(H)(PEt_3)_3]$ (**7**) the C−F bond cleavage at pentafluoropyridine proceeded at the 4-position to give $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**3**).[9] Treatment of pentafluoropyridine with the silyl complex $[Rh\{Si(OEt)_3\}(PEt_3)_3]$[10] or $[Rh(SiPh_3)(PMe_3)_3]$[7] at room temperature

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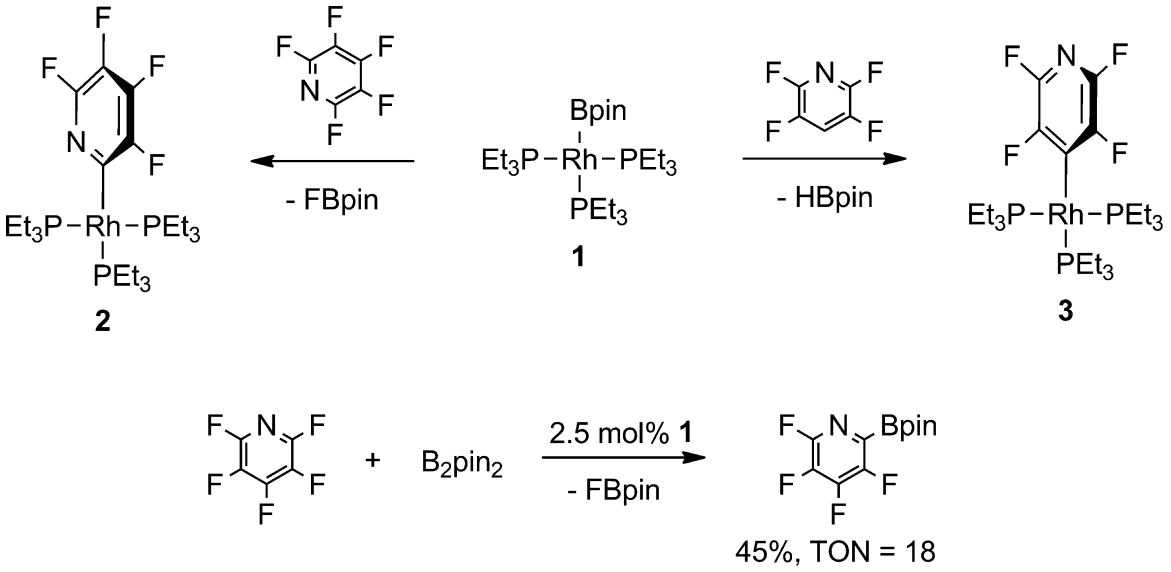
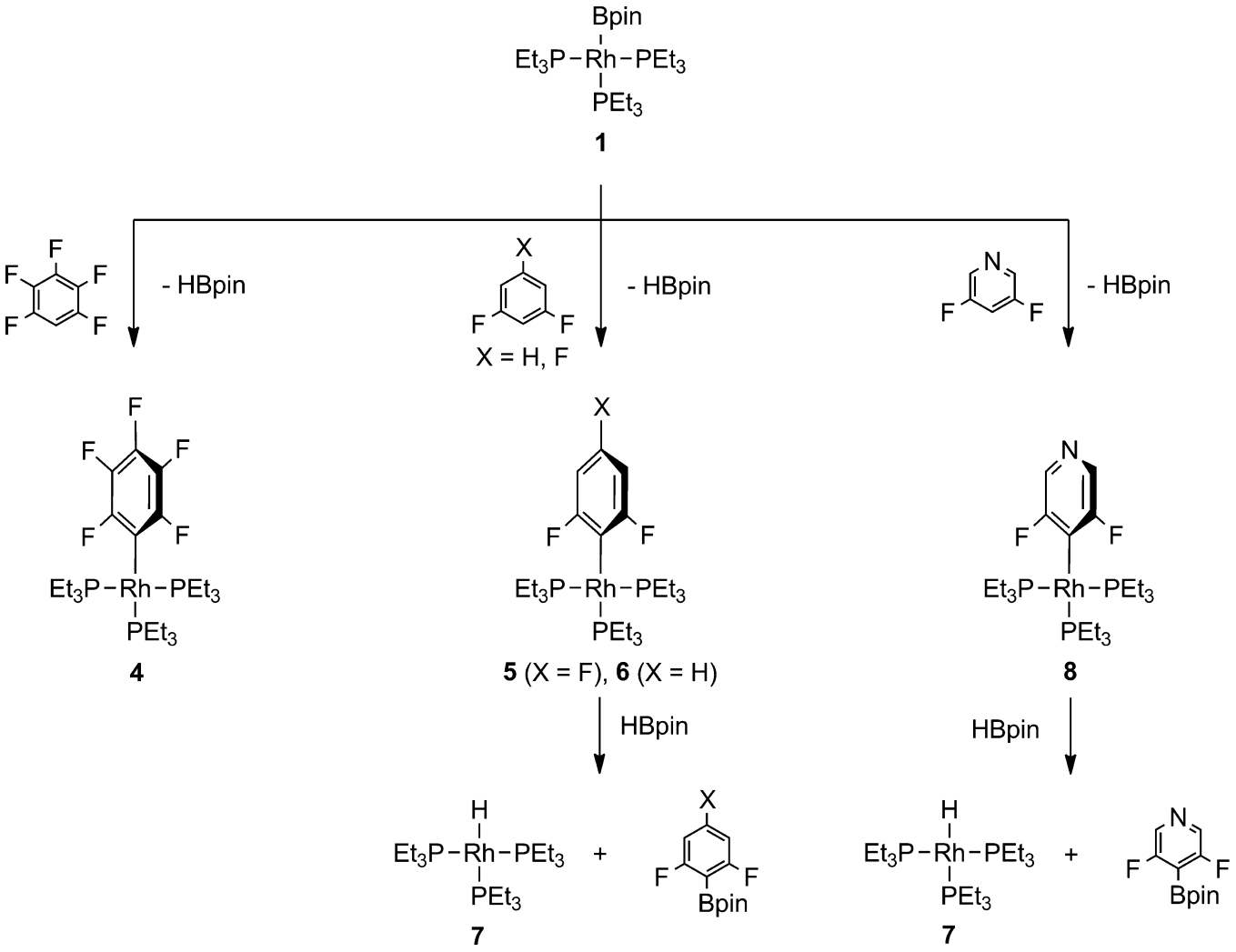
Scheme 1. C−F Activation of Pentafluoropyridine and C−H Activation of 2,3,4,5-Tetrafluoropyridine at 1 as Well as Catalytic C−F Borylation of Pentafluoropyridine[8a]



Scheme 2. C−H Activation of Partially Fluorinated Aromatics at 1



yielded a product mixture, whereas $[Rh\{Si(OMe)_3\}(PEt_3)_3]$ furnished only **2**.[10]

The catalytic borylation via C−H activation[11] also represents an efficient, convenient, and economical way for the synthesis

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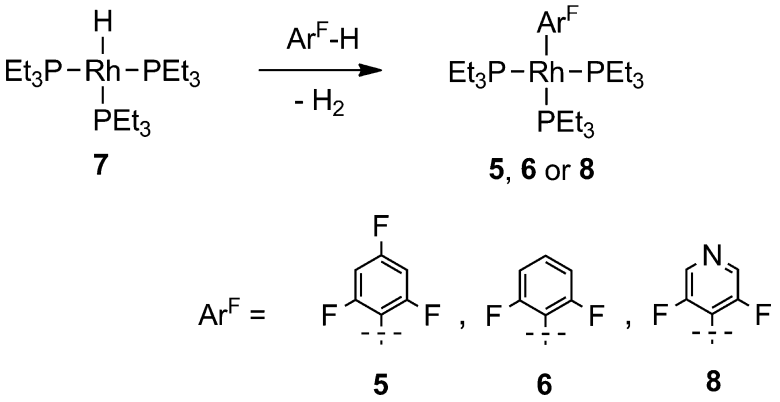
Scheme 3. Reactivity of 7 toward Fluorinated Aromatics



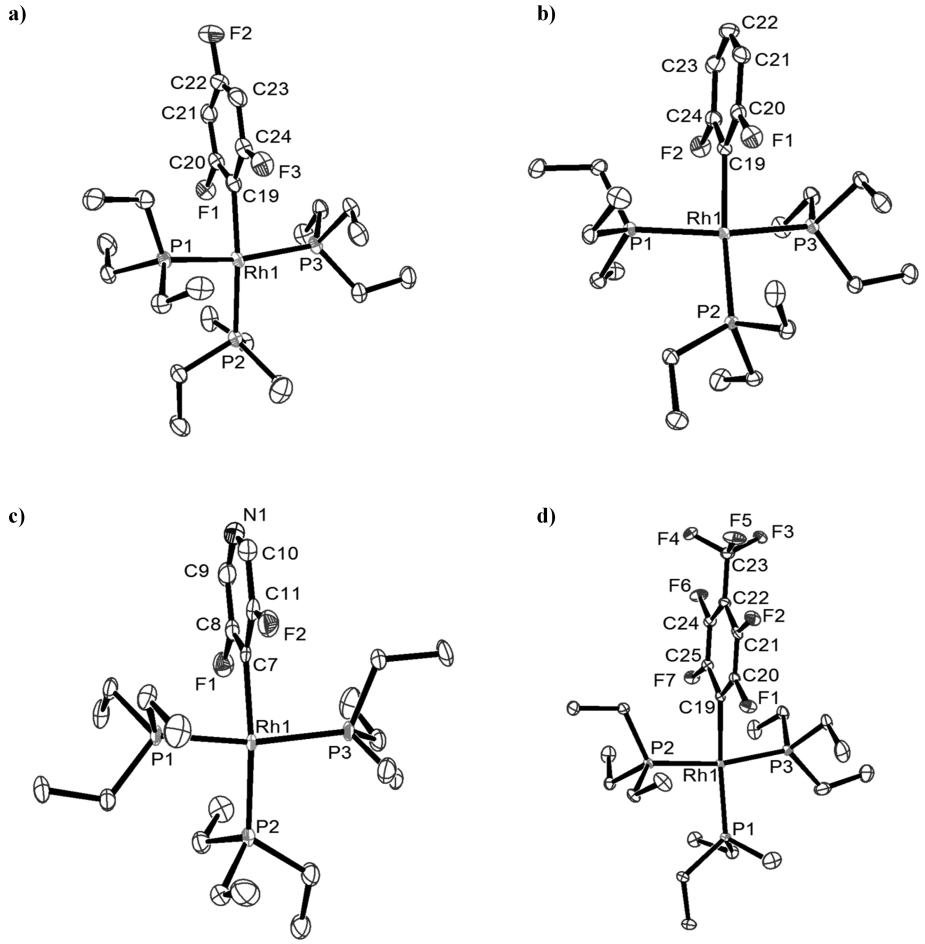


Figure 1. ORTEP diagrams of complexes **5**, **6**, **8**, and **9**. The ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. (a) ORTEP diagram of complex **5**. Selected distances [Å] and angles [deg]: Rh1−C19 = 2.1000(18), Rh1−P2 = 2.2818(5), Rh1−P1 = 2.2971(4), Rh1−P3 = 2.3115(4), P2−Rh1−C19 = 164.96(5), P1−Rh1−P3 = 162.704(17), dihedral angle P1−P2−P3−C19−Rh1 plane versus aryl plane = 86.33(7). (b) ORTEP diagram of complex **6**. Selected distances [Å] and angles [deg]: Rh1−C19 = 2.0904(11), Rh1−P2 = 2.2861(3), Rh1−P1 = 2.2961(3), Rh1−P3 = 2.3096(3), P2−Rh1−C19 = 164.10(3), P1−Rh1−P3 = 161.745(11), dihedral angle P1−P2−P3−C19−Rh1 plane versus aryl plane = 84.39(5). (c) ORTEP diagram of complex **8**. The asymmetric unit cell contains two crystallographically independent molecules, which show only minor differences in the bond lengths and angles, but differ in the conformation of the PEt_3 ligand. Only one of them is shown. Selected distances [Å] and angles [deg]: Rh1−C7 = 2.062(3), Rh1−P2 = 2.2995(8), Rh1−P1 = 2.3161(8), Rh1−P3 = 2.2993(8), P2−Rh1−C7 = 163.32(9), P1−Rh1−P3 = 161.76(3), dihedral angle P1−P2−P3−C7−Rh1 plane versus aryl plane = 88.78(14). (d) ORTEP diagram of complex **9**. Selected distances [Å] and angles [deg]: Rh1−19 = 2.0773(13), Rh1−P1 = 2.2874(3), Rh1−P2 = 2.3045(4), Rh1−P3 = 2.3331(4), P1−Rh1−C19 = 174.67(4), P2−Rh1−P3 = 168.399(13), dihedral angle P1−P2−P3−C19−Rh1 plane versus aryl plane = 89.09(6).

of organoboronic acid derivatives,[12] and the conversion of C−H into C−B bonds is thermodynamically favorable.[13] However, the presence of C−H and C−F bonds in the substrate generates a competition between C−H and C−F activation.[2w,5a,b,7,14] Johnson et al. reported that with $\{Ni(PEt_3)_2\}$ a kinetically controlled C−H activation of aromatic compounds

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can occur reversibly, whereas a subsequent C−F oxidative addition leads to the thermodynamic products.[15] With partially fluorinated pyridines only the C−F oxidative addition products have been found.[14a,15c] For rhodium, there is a preference for C−H activation.[16] For example, the cyclopentadienyl and tris(3,5-dimethylpyrazolyl)borato rhodium complexes give with fluorinated benzenes the C−H activation products.[17] However, for conversions that involve an initial nucleophilic attack of a rhodium center at highly fluorinated substrates C−F bond cleavage reactions were found.[18] The reaction of the hydrido complex $[Rh(H)(PEt_3)_3]$ (**7**) with 2,3,5,6-tetrafluoropyridine resulted in the formation of the C−H activation product **3**. However, with 2,3,4,5-tetrafluoropyridine a product mixture was obtained.[9] The reaction of the boryl complex $[Rh(Bpin)(PEt_3)_3]$ (**1**) with 2,3,5,6-tetrafluoropyridine proceeds with a preference for C−H over C−F bond activation to yield $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**3**, Scheme 1).[8a] Note that the capability of the boryl complex **1** to undergo a C−H bond activation was also demonstrated by a stoichiometric reaction with benzene.[8a,d]

In this contribution we report on C−H and C−F bond activation reactions of fluorinated aromatics at **1** or **7**. Challenging issues concern the chemoselectivity as well as the regioselectivity of the reactions. The development of unprecedented catalytic borylation processes using B_2pin_2 or HBpin as a source of the boryl group is also described.

RESULTS AND DISCUSSION

1. C−H Activation of Partially Fluorinated Aromatics. Treatment of the rhodium(I) boryl complex $[Rh(Bpin)(PEt_3)_3]$ (**1**) with an excess of pentafluorobenzene led after 15 min at room temperature to the quantitative generation of the C−H activation product $[Rh(C_6F_5)(PEt_3)_3]$ (**4**) and HBpin (Scheme 2). The latter can be removed under vacuum to obtain **4** in pure form. The pentafluorophenyl complex **4** was identified by comparison of its NMR data with the literature.[10] In accordance with the above-mentioned reaction of **1** with 2,3,5,6-tetrafluoropyridine, which yields the C−H activation product $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**3**)[8a] and HBpin (Scheme 1), the C−H bond activation is favored over the C−F bond activation at the boryl complex. Note that Milstein et al. found that $[Rh(SiMe_2Ph)(PMe_3)_3]$ reacts in pentafluorobenzene at higher temperature to give 1,2,4,5-tetrafluorobenzene and $[Rh(C_6F_5)(PMe_3)_3]$.[5a,b]

Reaction of $[Rh(Bpin)(PEt_3)_3]$ (**1**) with an excess of 1,3,5-trifluorobenzene or 1,3-difluorobenzene led to the C−H activation products $[Rh(2,4,6\text{-}C_6F_3H_2)(PEt_3)_3]$ (**5**) and $[Rh(2,6\text{-}C_6F_2H_3)(PEt_3)_3]$ (**6**), respectively, as well as HBpin (Scheme 2). Subsequently, the aryl complexes reacted further with HBpin to give the aryl boronate ester 2-Bpin-1,3,5-$C_6F_3H_2$ or 2-Bpin-1,3-$C_6F_2H_3$ and $[Rh(H)(PEt_3)_3]$ (**7**),[19] which can undergo additional reactions (see below and Scheme 3). The formation of HBpin and the aryl boronate esters[20] was confirmed by GC-MS analysis as well as by ^{11}B and ^{19}F NMR spectroscopy. The conversion with 1,3,5-trifluorobenzene seems to be slightly faster: after 7 h 14% of **1** remained in the reaction solution after treatment with 1,3,5-trifluorobenzene, whereas 27% of **1** was left after a reaction with 1,3-difluorobenzene (after 1 d: ratio of **7**:**5** = 2.5:1; ratio of **7**:**6** = 2.2:1). The addition of PEt_3 to a solution of **1** and the arene inhibited the reaction, which indicates that the dissociation of phosphine from the metal center plays a crucial role in the rate-determining step.

Although the generation of **7** occurred before the boryl complex **1** was completely converted, complexes **5** and **6** were isolated successfully by crystallization at low temperature from the reaction mixtures in *n*-hexane. Both compounds were characterized by NMR spectroscopy and elemental analysis. The molecular structures of **5** and **6** were confirmed by single-crystal X-ray analysis (Figure 1a and b, Table S1) as well. The $^{31}P\{^1H\}$ spectra show a resonance for the phosphorus atom in the *trans* position to the fluorinated ligand at δ 19.6 ppm with a rhodium−phosphorus coupling of 132 Hz for **5** and at δ 18.9 ppm with a coupling of 129 Hz for **6**. The fluorine−phosphorus couplings of $^4J_{FP}$ = 13 Hz for both compounds are in the expected range.[9] The phosphine ligands in a mutually *trans* arrangement give a doublet of doublets at δ 15.0 ppm for **5** and at δ 14.6 ppm for **6** with similar coupling constants of 145 Hz to the rhodium atom and of 39 Hz to the other phosphorus atom. The magnitude of the rhodium−phosphorus and phosphorus−phosphorus coupling constants is comparable to those for other square planar fluorinated (hetero)aryl rhodium(I) phosphine complexes.[8a,9,10,21] The ^{19}F NMR spectrum of **5** displays two multiplets at δ −77.2 and −121.1 ppm, which integrate to the ratio of 2:1. For the fluorine atoms of complex **6**, a resonance at δ −79.3 ppm was detected in the ^{19}F NMR spectrum, which exhibits two phosphorus−fluorine and a rhodium−fluorine coupling. The chemical shifts are in agreement with other complexes bearing a 2,4,6-trifluoro- or 2,6-difluorophenyl ligand.[17a]

In accordance with the results described above, treatment of **1** with stoichiometric amounts of 3,5-difluoropyridine led to C−H activation at the 4-position, and $[Rh\{4\text{-}(3,5\text{-}C_5NF_2H_2)\}(PEt_3)_3]$ (**8**) and $[Rh(H)(PEt_3)_3]$ (**7**) were formed in a ratio of 1:0.16 as main products (Scheme 2). In addition, minor amounts of 3% and 4% *mer*-$[Rh(H)_3(PEt_3)_3]$ and *cis-fac*-$[Rh(H)_2(Bpin)(PEt_3)_3]$ were observed by $^{31}P\{^1H\}$ NMR spectroscopy (see below). Furthermore, HBpin and 4-Bpin-3,5-$C_5NF_2H_2$ were detected by GC-MS analysis. The reaction of **1** with 3,5-difluoropyridine is significantly faster than those with the fluorinated benzene derivatives despite the use of stoichiometric amounts of pyridine, which results in complete conversion within 3 h.

Complex **8** was isolated after crystallization in *n*-hexane at −30 °C and was characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray analysis (Figure 1c). The $^{31}P\{^1H\}$ spectrum of **8** displays two signals at δ 17.1 and 11.8 ppm in a ratio of 1:2. The resonance for the phosphorus atom in the position *trans* to the fluorinated ligand at δ 17.1 ppm exhibits coupling to rhodium, two phosphorus atoms, and two *ortho* fluorine atoms. The signal at δ 11.8 ppm, which can be assigned to the phosphorus atoms that are in a mutually *trans* position, shows a doublet of doublets splitting pattern. The chemical shifts and the coupling constants are in agreement with those found for the aryl complexes **3**−**6** and confirm the oxidation state of Rh(I). A resonance at δ −94.1 ppm in the ^{19}F NMR spectrum as well as the signals in the aromatic region in the ^1H and ^{13}C NMR spectra indicate the presence of the heteroaryl ligand.

All the reactions described above show that at **1** C−H bond activation is preferred over C−F bond activation. Note that the products of the C−H activation reactions of the fluorinated substrates are aryl complexes, whereas, as reported in the literature, the reaction of **1** with benzene or SCF_3 arenes resulted in the formation of the hydrido complex $[Rh(H)(PEt_3)_3]$ (**7**) as well as of borylated aromatics. One reason

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might be the stabilizing effect of the fluorinated ligand.[22] In addition, the results demonstrate that the C−H activation occurs regioselectively at the carbon atom adjacent to two fluorine atoms in each case. In combined experimental and computational studies it was demonstrated that for C−H activation reactions of fluorinated substrates at rhodium the products with the fluorine atoms at the *ortho* position to the metal center are favored.[2n,17a,d,e,23]

The hypothesis that the aryl complexes [Rh(2,4,6-$C_6F_3H_2$)-(PEt_3)$_3$] (**5**), [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (**6**), and [Rh{4-(3,5-$C_5NF_2H_2$)}(PEt_3)$_3$] (**8**) react with HBpin in a consecutive reaction to give [Rh(H)(PEt_3)$_3$] (**7**) and borylated fluoroaromatics is supported by independent reactions (Scheme 2). Treatment of **5**, **6**, or also **8** with one equivalent of HBpin in cyclohexane for 1 d generated **7** as the main product in varying amounts. Mechanistically, the reactions of the aryl complex **5**, **6**, or **8** with HBpin might involve the generation of a rhodium(III) intermediate, which eliminates the aryl boronic ester due to the favored formation of a C−B bond. Reductive elimination of a tolyl boronate ester after oxidative addition of B_2cat_2 or HBcat was observed at *cis*-[Os(Bcat)(*o*-tolyl)-(CO)$_2$(PPh_3)$_2$].[24] However, a concerted reaction pathway[25] for the generation of **7** and the borylated product would also be conceivable.

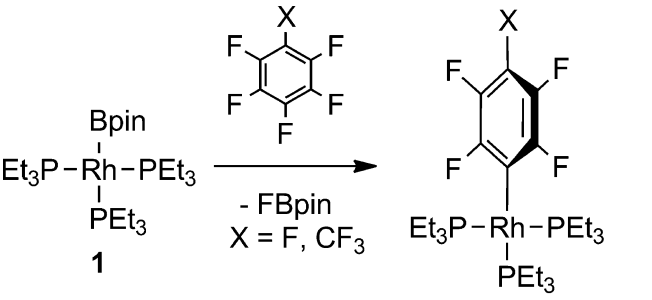
With regard to the generation of **7** and the formation of borylated aromatics that are shown in Scheme 2, the reactivity of the hydrido complex **7** toward partially fluorinated aromatics was studied. Note that DFT calculations for the rhodium-catalyzed benzylic borylation of toluenes on using [Rh(Cl)-(P^iPr_3)$_2$(N_2)] as catalyst suggest that the C−H activation reaction step also occurs at a hydrido species, {Rh(H)-(P^iPr_3)$_2$}.[26]

Remarkably, on treatment of **7** with 1,3,5-trifluorobenzene, 1,3-difluorobenzene, or 3,5-difluoropyridine, the formation of the aryl complex **5**, **6**, or **8** was observed, which demonstrates that **7** is also capable of undergoing aromatic C−H bond activation reactions (Scheme 3). With 3,5-difluoropyridine the C−H activation reaction at **7** appears to be significantly faster than with the fluorinated benzene derivatives and resulted in a mixture of **7**, [Rh{4-(3,5-$C_5NF_2H_2$)}(PEt_3)$_3$] (**8**), and small amounts of *mer*-[Rh(H)$_3$(PEt_3)$_3$] and *fac*-[Rh(H)$_3$(PEt_3)$_3$] in a ratio of 1:1:0.06:0.01 after 2 h at room temperature. Treatment of **7** with an excess of 1,3,5-trifluorobenzene gave a mixture of **7**, [Rh(2,4,6-$C_6F_3H_2$)(PEt_3)$_3$] (**5**), and small amounts of *mer*-[Rh(H)$_3$(PEt_3)$_3$] and *fac*-[Rh(H)$_3$(PEt_3)$_3$] in a ratio of 3.4:1:0.3:0.05 after 1 d at room temperature, and with an excess of 1,3-difluorobenzene the reaction mixture contained **7** and [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (**6**) in a ratio of 10:1 after 4 d at 50 °C. The results suggest that the reaction of **7** with 1,3-difluorobenzene is much slower than with 1,3,5-trifluorobenzene, and such considerable difference in the reaction rates was not found using **1**.

The reactivity observed for **7** also explains the subsequent reactions in the conversions of **5**, **6**, and **8** into **7** and borylated aromatics, which are described above (Scheme 2). The presence of the additional product *cis-fac*-[Rh(H)$_2$(Bpin)-(PEt_3)$_3$] as well as of *mer*-[Rh(H)$_3$(PEt_3)$_3$] and *fac*-[Rh-(H)$_3$(PEt_3)$_3$] can be explained by reactions of **7** with HBpin or H_2 as reported before.[5c,21] After completion of the reactions and bringing the solution to dryness, the solids contained 4% *mer*-[Rh(H)$_3$(PEt_3)$_3$] as well as 1% *fac*-[Rh(H)$_3$(PEt_3)$_3$] after reaction with 1,3,5-trifluorobenzene, 6% *cis-fac*-[Rh(H)$_2$(Bpin)-(PEt_3)$_3$] as well as 1% *mer*-[Rh(H)$_3$(PEt_3)$_3$] after reaction with 1,3-difluorobenzene, and 4% *cis-fac*-[Rh(H)$_2$(Bpin)(PEt_3)$_3$] as well as 3% *mer*-[Rh(H)$_3$(PEt_3)$_3$] after reaction with 3,5-difluoropyridine.

2. C−F Activation of Perfluorinated Aromatics. The reported C−F activation capability of [Rh(Bpin)(PEt_3)$_3$] (**1**) with pentafluoropyridine (Scheme 1) and perfluoropropene[8a] encouraged us to probe its reactivity toward other perfluorinated aromatics. Treatment of the rhodium boryl complex **1** with an excess of hexafluorobenzene gave the complex [Rh(C_6F_5)(PEt_3)$_3$] (**4**) and the fluoroborane FBpin via C−F bond cleavage (Scheme 4). As described above, **4** is also

Scheme 4. C−F Activation of Perfluorinated Aromatics at 1



accessible from pentafluorobenzene. Note that Milstein et al. reported the C−F activation of hexafluorobenzene at [Rh(H)-(PMe_3)$_3$].[5b] Furthermore, rhodium silyl complexes undergo C−F activation with hexafluorobenzene.[5a,b,10]

Treatment of **1** with stoichiometric amounts of perfluorotoluene yielded [Rh(4-$C_6F_4CF_3$)(PEt_3)$_3$] (**9**) as well as FBpin by C−F activation at the position *para* to the CF_3 group (Scheme 4). The same regioselectivity in the activation reaction of perfluorotoluene was obtained at [Rh{Si(OR)$_3$}(PEt_3)$_3$] (R = Me, Et).[10] Note that the activation of the C−F bond at the *para* position of perfluorotoluene was also achieved at Ni or other metals.[4d,14c,27] Complex **9** was identified by comparison of its NMR data with the literature data.[10] In addition its molecular structure in the solid state was determined by X-ray diffraction analysis (Figure 1d).

Several mechanistic possibilities for C−F activation reactions are discussed in the literature.[2b,j,n] For instance, the formation of a rhodium(III) fluoro intermediate by oxidative addition of perfluorinated substrates at **1** and subsequent reductive elimination of FBpin is conceivable. However, concerted reaction pathways that involve a C−F bond cleavage step that is assisted by a boryl[8a] or phosphine ligand[28] are also possible.[2n] The regioselectivity of the activation of perfluorotoluene at the 4-position would in addition be in accordance with other reaction mechanisms such as a nucleophilic reaction pathway or an electron transfer step.[2d,f,g,p]

3. Development of Catalytic C−F and C−H Bond Borylation Reactions. To develop a catalytic borylation process, the aryl complexes [Rh(4-C_5NF_4)(PEt_3)$_3$] (**3**), [Rh(2,4,6-$C_6F_3H_2$)(PEt_3)$_3$] (**5**), [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (**6**), [Rh{4-(3,5-$C_5NF_2H_2$)}(PEt_3)$_3$] (**8**), and [Rh(4-$C_6F_4CF_3$)-(PEt_3)$_3$] (**9**) were treated stoichiometrically with B_2pin_2 (Scheme 5). The phenyl complexes, **5**, **6**, and **9** were converted to the boryl complex **1** and the borylated aromatics 2-Bpin-1,3,5-$C_6F_3H_2$, 2-Bpin-1,3-$C_6F_2H_3$, and 4-Bpin-$C_6F_4CF_3$, but the reactions appear to be very slow at room temperature. For **5** and **6** a complete conversion was observed after 10 or 5 d,

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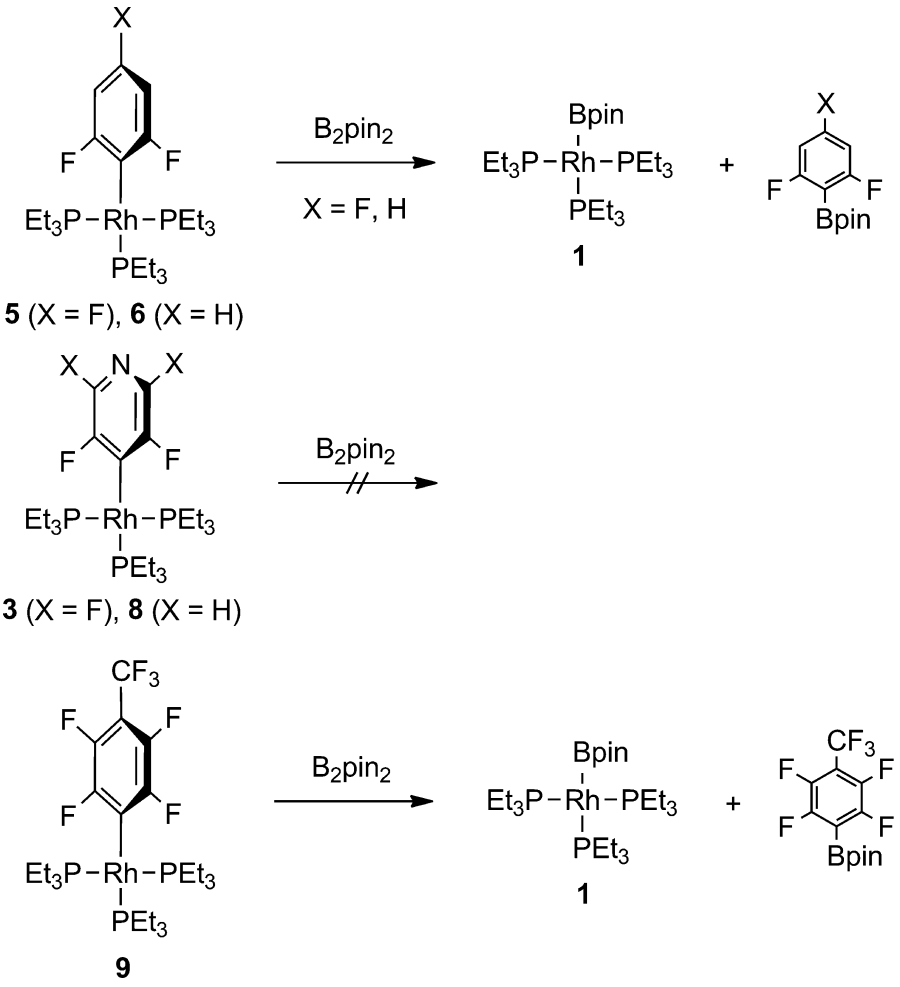
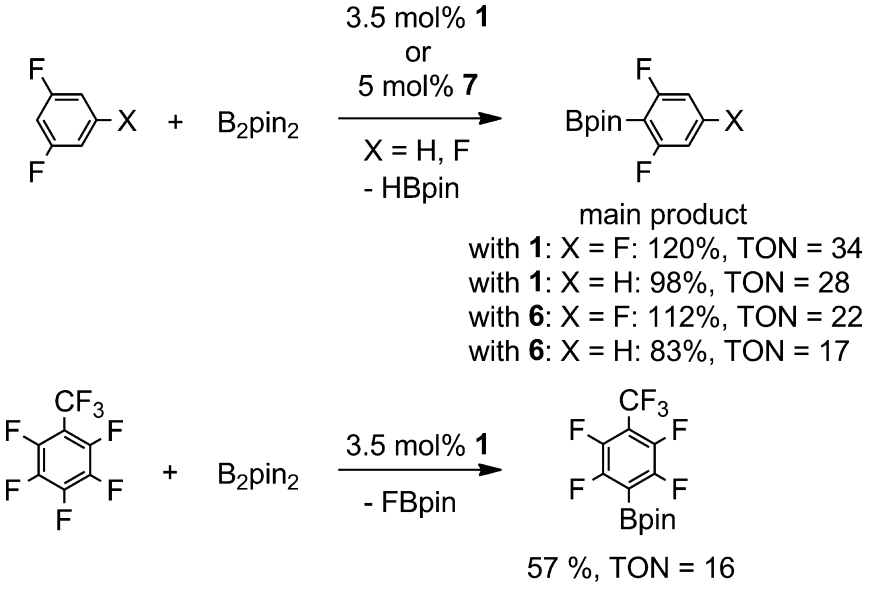
Scheme 5. Treatment of the Aryl Complexes 3, 5, 6, 8, and 9 with B_2pin_2



Scheme 6. Catalytic Borylation of Fluorinated Benzenes via C–H and C–F Bond Activation with B_2pin_2 on Using 1 or 7[a]



[a]TON based on borylation steps/mol catalyst.

respectively. For **9** a conversion of 50% was observed after 5 d. Treatment of the pyridyl complexes **3** and **8** with B_2pin_2 led to no reaction, not even at 50 °C. The stability and sometimes weak reactivity of the pyridyl complexes in comparison to phenyl counterparts are mainly caused by the strength of the metal–carbon bond to the perfluorinated ligand.[9,29] As

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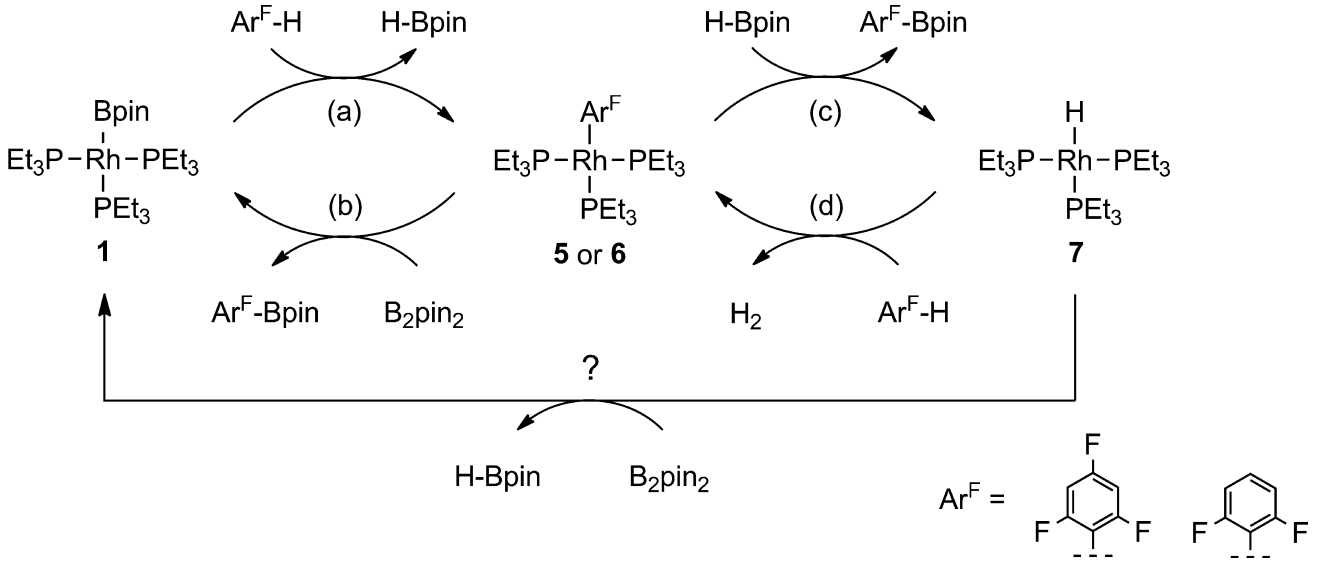
Scheme 7. Possible Pathways for the Catalytic Formation of Aryl Boronic Esters via C−H Borylation at 1 or 7



mentioned above, Marder and Perutz et al.[7] achieved a borylation of the heteroaryl complexes at $[Rh(Ar)(PMe_3)_3]$ (Ar = 2-C_5NF_4, 4-C_5NF_4, 2-(4-Me-C_5NF_3), 6-(2,3,5-C_5NF_3H)) with B_2cat_2 yielding borylated pyridines as well as the trisboryl complex *fac*-$[Rh(Bpin)_3(PMe_3)_3]$, which is presumably a thermodynamic sink.

On the basis of the stoichiometric reactions, we investigated the catalytic borylation of partially fluorinated benzene derivatives. In the presence of 3.5 mol % $[Rh(Bpin)(PEt_3)_3]$ (**1**), B_2pin_2 and 1,3,5-trifluorobenzene or 1,3-difluorobenzene can be converted into the aryl boronate esters by C−H activation (Scheme 6). The reactions were carried out at 50 °C in cyclohexane with a 6-fold excess of the arene to give the monoborylated benzene derivatives as main products in a yield of formally 120% (2-Bpin-1,3,5-$C_6F_3H_2$) or 98% (2-Bpin-1,3-$C_6F_2H_3$) after 24 h. The yields, which are based on the amount of B_2pin_2, larger than 100% indicate that the generated HBpin also acts as a borylation agent in the catalytic processes. However, the formation of HBpin was detected by GC-MS analysis and ^{1}H NMR spectroscopy. We were not able to observe the formation of H_2. On using 1,3,5-trifluorobenzene, the diborylated compound 2,4-$(Bpin)_2$-1,3,5-C_6F_3H was found in small amounts (8%), whereas the use of 1,3-difluorobenzene also led to a variety of additional products. GC-MS data indicate the presence of mono- and diborylated difluorobenzenes (approximately overall 37%, based on the amount of B_2pin_2, according to a ^{19}F NMR spectrum), which were not further characterized. C−H bond borylation reactions to access fluorinated aryl boronic are documented in the literature.[12b,30] Note that 2-Bpin-1,3,5-$C_6F_3H_2$[31] can also be synthesized by iridium- or rhodium-catalyzed C−H borylations of 1,3,5-trifluorobenzene with HBpin at 150 °C.[30a,32] With 2 mol % $[(Cp^*)Rh(\eta^4\text{-}C_6Me_6)]$ and a 2-fold excess of arene a mixture of $C_6F_3H_2$(Bpin) (46%), $C_6F_3H(Bpin)_2$ (7%), and $C_6F_2H_3$(Bpin) (6%) was obtained.[30a] The compound 2-Bpin-1,3-$C_6F_2H_3$ was generated as a minor product in the iridium-catalyzed borylation of 1,3-difluorobenzene.[20b,33] The major product is the isomer 5-Bpin-1,3-$C_6F_2H_3$, which suggests that the regioselectivity for iridium-mediated C−H borylation reactions is predominantly determined by steric factors.[11,34]

With regard to the C−H activation reactions at $[Rh(H)(PEt_3)_3]$ (**7**) with di- and trifluorinated benzenes that are described above, complex **7** was also tested as catalytic precursor. Indeed, treatment of 1,3,5-trifluorobenzene or 1,3-difluorobenzene with B_2pin_2 in the presence of 5 mol % **7** at 50 °C led to the formation of the aryl boronate esters 2-Bpin-1,3,5-$C_6F_3H_2$ and 2-Bpin-1,3-$C_6F_2H_3$ in good, but slightly lower, yields when compared to the reactions with **1** as catalyst (Scheme 6).

Mechanistically, we suggest that an active species in the catalytic process on using **7**, which is probably the boryl complex **1**, can be generated from *fac*-$[Rh(H)(Bpin)_2(PEt_3)_3]$ (**10**). The latter compound might be furnished from **7** and B_2pin_2. Alternatively, the catalysis can be started by the generation of the aryl complex **5** or **6** from **7** by C−H activation (Scheme 7, (d)). The aryl complex reacts with diborane under release of the aryl boronic ester and the formation of **1** (b), which undergoes C−H activation with another substrate molecule to yield HBpin and the aryl complex **5** or **6** (a). However, this species is capable of reacting with B_2pin_2 (b) or with the generated HBpin (on a slower time scale) to give **7** (c). For both reactions of **5** or **6** with B_2pin_2 or HBpin the borylated arene would be generated.

On the basis of the stoichiometric C−F activation reactions, the catalytic C−F borylation of perfluorotoluene was developed. Treatment with B_2pin_2 in benzene at 55 °C for 2 d in the presence of 3.5 mol % $[Rh(Bpin)(PEt_3)_3]$ (**1**) led to the formation of 4-Bpin-$C_6F_4CF_3$ in a yield of 57% (Scheme 6). Only the monoborylated product was observed, and a consecutive second borylation did not take place. The borylation of pentafluoropyridine, which was reported before,[8a] and the conversion of perfluorotoluene represent unique examples for catalytic borylation of perfluorinated benzene derivatives via C−F bond cleavage. The compound 4-Bpin-$C_6F_4CF_3$ was characterized by NMR spectroscopy and GC-MS analysis. The ^{19}F NMR spectrum exhibits three multiplets at δ −57.3, −129.2, and −142.1 ppm, which integrate in a ratio of 3:2:2. For the boryl group, the ^{11}B NMR spectrum shows a resonance at δ 29 ppm, which is in a typical range for aryl boronic esters.[8a,20,35] Whereas the C−F borylation reaction of perfluorotoluene with B_2pin_2 is selective, the conversion of

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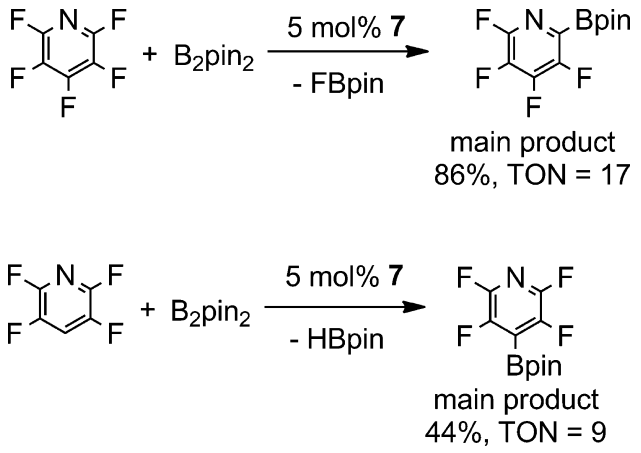
hexafluorobenzene and B_2pin_2 in the presence of **1** gives only a product mixture, which was not analyzed further.

The catalytic C−F borylation of pentafluoropyridine at the boryl complex **1** results selectively in the formation of 2-boryltetrafluoropyridine as mentioned above (Scheme 1). Since **1** undergoes C−F activation at the 2-position and **7** activates stoichiometrically the C−F bond at the 4-position,[8a,9] we were surprised to find that **7** can also be used as catalytic precursor to achieve mainly a borylation at the 2-position (Scheme 8). With

Scheme 8. Catalytic Borylation of Fluorinated Pyridines via C−F or C−H Bond Activation with B_2pin_2 on Using 7

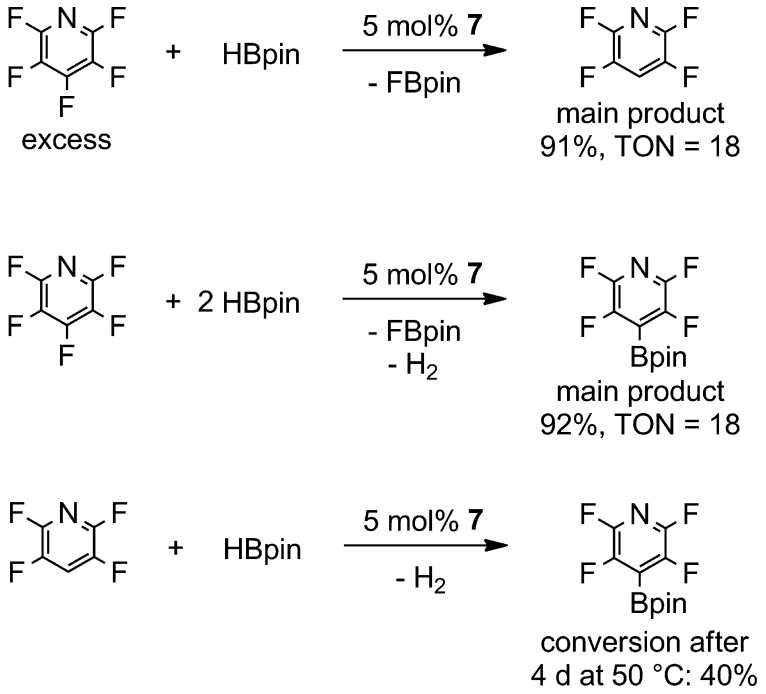


5 mol % of the hydrido complex **7**, pentafluoropyridine and B_2pin_2 were converted into 2-Bpin-C_5NF_4 in a yield of 86% after 1 d at 50 °C. Only minor amounts (3%) of 4-Bpin-C_5NF_4 were observed. We assume that in the first step of the catalytic process **7** reacts with pentafluoropyridine to give **3** via C−F activation reaction at the 4-position, followed by reaction of **3** with B_2pin_2 to furnish the boryl complex **1**. Subsequent reactions lead to a borylation of pentafluoropyridine at the 2-position. Alternatively, there are indications that the initial formation of *fac*-[Rh(H)(Bpin)$_2$(PEt$_3$)$_3$] (**10**) from **7** and B_2pin_2 is possible. The diborylhydrido complex **10** activates the C−F bond at the 2-position of pentafluoropyridine to give [Rh(2-C_5NF_4)(PEt$_3$)$_3$] (**2**), shown in an independent reaction. This observation suggests that **10** can be converted into **1**.[8d]

Although [Rh(4-C_5NF_4)(PEt$_3$)$_3$] (**3**) does not react with B_2pin_2 in a stoichiometric reaction, we considered the catalytic C−H borylation of 2,3,5,6-tetrafluoropyridine with B_2pin_2 catalyzed by **1** or **7** in order to synthesize 4-Bpin-C_5NF_4. On using **1** the reaction yielded a product mixture of mono- and diborylated pyridine derivatives, which could not be identified further. A GC-MS analysis of the reaction solution indicated that C−H and C−F borylation as well as hydrodefluorination steps occur. Surprisingly, with **7** as catalyst 4-Bpin-C_5NF_4 was obtained as the main product under release of HBpin (Scheme 8). After 1 week at 50 °C 2,3,5,6-tetrafluoropyridine was converted into 4-Bpin-C_5NF_4 in a yield of 44%. The compound 4-Bpin-C_5NF_4 was identified by NMR spectroscopy and GC-MS analysis. In the ^{19}F NMR spectrum two signals at δ −92.8 and −132.6 ppm in a ratio of 1:1 were detected. The chemical shifts are in agreement with those found for the corresponding boronic acid and 4-Bcat-C_5NF_4.[7,36] A signal at δ 29 ppm in the ^{11}B NMR spectrum as well as the resonance at δ 1.09 ppm in the ^{1}H NMR spectrum indicates the presence of the boryl group.

We also employed HBpin as reagent in C−F activation reactions at pentafluoropyridine. With 5 mol % **7**, HBpin, and an excess of pentafluoropyridine, the hydrodefluorination[2m,o,5,14d,37] product 2,3,5,6-tetrafluoropyridine was obtained as the main product in a yield of 91% (Scheme 9). Furthermore, small amounts of 4-Bpin-C_5NF_4 were generated. At room temperature the reaction was completed within 1 day.

Scheme 9. Catalytic Borylation and Hydrodefluorination of Fluorinated Pyridines via C−H and C−F Bond Activation with HBpin on Using 7



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On the basis of C−F bond cleavage steps at the 4-position a turnover number of 19 was determined. We assume that dihydrogen, which can be generated from HBpin and HF, serves mainly as hydrogen source for the hydrodefluorination. Note that the activation of pentafluoropyridine at **7** at the 4-position as well as a catalytic hydrodefluorination of pentafluoropyridine with dihydrogen to give 2,3,5,6-tetrafluoropyridine was reported before.[5c,9]

However, 4-Bpin-C_5NF_4 was prepared in high yield from the reaction of a 2:1 mixture of HBpin and pentafluoropyridine in the presence of 5 mol % **7** in benzene (Scheme 9). The reaction time at room temperature had to be extended to 3 weeks, until pentafluoropyridine was completely converted. We suggest that intermediately formed 2,3,5,6-tetrafluoropyridine reacts with a second equivalent of HBpin to the boronic ester derivative under release of H_2. Remaining 2,3,5,6-tetrafluoropyridine was detected in a yield of 5%. An independent reaction supports this hypothesis. Treatment of 2,3,5,6-tetrafluoropyridine with HBpin in the presence of 5 mol % **7** led to the formation of 4-Bpin-C_5NF_4. A conversion of 40% was observed after 3 d at 50 °C.

Overall, the treatment of pentafluoropyridine with B_2pin_2 results in the C−F borylation at the 2-position. For 2,3,5,6-tetrafluoropyridine with **7** as catalyst a C−H borylation reaction takes place. In contrast, with HBpin as reagent the bond at the 4-position of 2,3,5,6-tetrafluoropyridine or pentafluoropyridine is activated. Therefore, the regioselectivity of the C−F borylation of pentafluoropyridine can be controlled by the choice of the borylation agent.

CONCLUSION

Reactions of the boryl complex $[Rh(Bpin)(PEt_3)_3]$ (**1**) with partially fluorinated benzene and pyridine derivatives resulted in C−H activation products, which reveals a preference for C−H over C−F activation. Treatment of **1** with the perfluorinated substrate hexafluorobenzene or perfluorotoluene led to the C−F activation products. The regiochemistry of the C−H activation reactions seems to be dominated by the strength of metal−carbon bond interaction which is linked with a maximum number of fluorine atoms *ortho* to the metal center. Initial formation of fluoroaryl complexes in stoichiometric reactions instead of a borylation of the fluoroaryl moiety might in part be attributed to the stabilizing effect of fluorinated organyl ligands. In contrast to the pyridyl complexes, the fluorophenyl complexes are prone to a stoichiometric borylation with B_2pin_2. The hydrido complex $[Rh(H)(PEt_3)_3]$ (**7**) is also capable of C−H activation reactions of partially fluorinated benzenes and 2,3,5,6-tetrafluoropyridines. Based on the stoichiometric transformations, catalytic C−H and C−F borylation reactions using **1** or **7** as catalyst were developed. These reactions show a good selectivity and proceed under mild conditions when compared to other rhodium-catalyzed borylation processes. Although rhodium-catalyzed arene borylation reactions are known,[13,30a,b] they usually require fairly harsh reaction conditions and are regarded to be less selective, in contrast to the iridium-catalyzed processes.[30a−d,32,38] The synthesized boronic esters can be valuable starting compounds for further transformations. The regioselectivity of the rhodium-catalyzed C−F borylation reaction of pentafluoropyridine can be controlled by the choice of the borylating reagent; that is, using 5 mol % **7**, B_2pin_2 leads to a borylation at the 2-position, whereas HBpin yields the 4-borylpyridine derivative. However, in the latter case 2,3,5,6-tetrafluoropyridine was generated by catalytic hydrodefluorination with a substoichiometric amount of HBpin.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out in an argon atmosphere. $[D_6]$Benzene, $[D_8]$toluene, $[D_{12}]$cyclohexane, cyclohexane, hexane, and hexamethyldisilane were dried by stirring over Na/K and then distilled. PFA NMR tubes were used for highly sensitive compounds to inhibit reactions at glass surfaces. Complex $[Rh(Bpin)(PEt_3)_3]$ (**1**) was prepared according to the literature.[8a,b] The NMR spectra were recorded at 300 K (if not stated otherwise) on a Bruker Avance 400, a Bruker DPX 300, or a Bruker Avance III 300 NMR spectrometer. The ^{1}H NMR chemical shifts were referenced to residual C_6D_5H at δ 7.16 ppm, $[D_7]$toluene at δ 2.09 ppm, or $[D_{11}]$cyclohexane at δ 1.43 ppm. The $^{11}B\{^1H\}$ NMR spectra were referenced to external $BF_3{\cdot}OEt_2$ at δ 0.0 ppm, the ^{19}F NMR spectra to external $CFCl_3$ at δ 0.0 ppm, and the $^{31}P\{^1H\}$ NMR spectra to external H_3PO_4 at δ 0.0 ppm. In order to get a ^{2}H lock signal, C_6D_6 was introduced in the space between the glass NMR tubes and the PFA inliners, which contained the reaction mixture with hexamethyldisilane or cyclohexane as a solvent. GC-MS spectra were measured at an Agilent 6890N gas-phase chromatograph (Agilent 19091S-433 Hewlett-Packard), which was equipped with an Agilent 5973 Network mass selective detector at 70 eV. The microanalyses were obtained with a Euro EA HEKAtech elemental analyzer.

In the catalytic borylation reaction of 1,3,5-trifluorobenzene and 1,3-difluorobenzene the yields or the sum of the yields of borylated products is larger than 100% (based on the amount of B_2pin_2 as a source of one boryl group). This is caused by the fact that the generated HBpin can act as a borylation agent. TONs are defined as number of borylation steps or C−F bond cleavage steps/mol of Rh complex.

Treatment of $[Rh(Bpin)(PEt_3)_3]$ (1) with Pentafluorobenzene: Synthesis of $[Rh(C_6F_5)(PEt_3)_3]$ (4). A solution of $[Rh(Bpin)(PEt_3)_3]$ (**1**) (9.9 mg, 17 μmol) in Me_6Si_2 (0.5 mL) in a PFA tube was treated with pentafluorobenzene (50 μL, 0.45 mmol). After 15 min the NMR spectroscopic data of the reaction solution revealed the complete conversion of **1** and the formation of $[Rh(C_6F_5)(PEt_3)_3]$ (**4**) and HBpin. The latter was detected by GC-MS analysis and can be removed under vacuum. Complex **4** was identified by comparison of the NMR data with those in the literature.[10] Additional analytical data: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ 18.6 (dttt, ^1J(Rh,P) = 133 Hz, ^2J(P,P) = 40 Hz, ^4J(F,P) = 15 Hz, ^5J(F,P) = 8 Hz, 1P), 14.1 (dd, ^1J(Rh,P) = 140 Hz, ^2J(P,P) = 40 Hz, 2P).

Treatment of $[Rh(Bpin)(PEt_3)_3]$ (1) with 1,3,5-Trifluorobenzene: Synthesis of $[Rh(2,4,6\text{-}C_6F_3H_2)(PEt_3)_2]$ (5). A solution of $[Rh(Bpin)(PEt_3)_3]$ (**1**) (34.6 mg, 59 μmol) in cyclohexane (0.2 mL) in a PFA tube was treated with 1,3,5-trifluorobenzene (122 μL, 1.18 mmol). After 1 d the NMR spectroscopic data of the reaction solution revealed the complete conversion of **1** and the formation of $[Rh(H)(PEt_3)_3]$ (**7**) and $[Rh(2,4,6\text{-}C_6F_3H_2)(PEt_3)_3]$ (**5**) in a ratio of 2.5:1 (according to the $^{31}P\{^1H\}$ NMR spectrum). HBpin and 2-Bpin-1,3,5-$C_6F_3H_2$ were detected by GC-MS analysis. 2-Bpin-1,3,5-$C_6F_3H_2$ and **5** were formed in a ratio of 2:1 (according to the ^{19}F NMR spectrum). The volatiles were removed and the residue was dissolved in toluene-d_8. The complexes *mer*-$[Rh(H)_3(PEt_3)_3]$ and *fac*-$[Rh(H)_3(PEt_3)_3]$ were found in traces (4% and 1% based on the amounts of **1** as starting compound) by NMR spectroscopy at 203 K. 2-Bpin-1,3,5-$C_6F_3H_2$ was identified by comparison of the NMR data with those in the literature.[30a,31,32] Orange crystals of $[Rh(2,4,6\text{-}C_6F_3H_2)(PEt_3)_3]$ (**5**) were obtained at −30 °C by crystallization from a solution of the reaction products in *n*-hexane. Analytical data for $[Rh(2,4,6\text{-}C_6F_3H_2)(PEt_3)_3]$ (**5**): ^{1}H NMR (300.1 MHz, C_6D_6) δ 6.60 (m, br s in the $^1H\{^{19}F\}$ NMR spectrum, 2H, CH_{ar}), 1.46 (m, q in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 8 Hz, 6H, CH_2), 1.36 (m, q in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 8 Hz, 12H, CH_2), 1.06 (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 8 Hz, 9H, CH_3), 1.03 (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7 Hz, 18H, CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 167.8 (ddd, ^1J(F,C) = 234 Hz, J = 31 Hz,

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^3J(F,C) = 14 Hz, CF), 161.3 (dt, ^1J(F,C) = 237 Hz, ^3J(F,C) = 14 Hz, CF), 98.0 (dd, ^2J(F,C) = 38 Hz, ^2J(F,C) = 22 Hz, CH_{ar}), 20.1 (dt, ^1J(P,C) = 18 Hz, J = 3 Hz, CH_2), 18.3 (t, J = 10 Hz, CH_2), 8.8 (s, CH_3), 8.6 (s, CH_3), the signal for the Rh−C atom was not observed; $^{19}F\{^1H\}$NMR (282.4 MHz, C_6D_6) δ −77.2 (ddm, J = 16 Hz, J = 10 Hz, 2F), −121.1 (m, 1F); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ 19.6 (dtt, ^1J(Rh,P) = 132 Hz, ^2J(P,P) = 39 Hz, ^4J(F,P) = 13 Hz, 1P), 15.0 (dd, ^1J(Rh,P) = 145 Hz, ^2J(P,P) = 39 Hz, 2P). Anal. Calcd (%) for $C_{24}H_{47}F_3P_3Rh$: C, 48.99; H, 8.05. Found: C, 49.08; H, 8.25.

Treatment of [Rh(Bpin)(PEt_3)$_3$] (1) with 1,3-Difluorobenzene: Synthesis of [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (6). A solution of [Rh(Bpin)(PEt_3)$_3$] (**1**) (43.3 mg, 74 μmol) in cyclohexane (0.2 mL) in a PFA tube was treated with 1,3-difluorobenzene (145 μL, 1.48 mmol). After 1 d the NMR spectroscopic data of the reaction solution revealed the complete conversion of **1** and the formation of [Rh(H)(PEt_3)$_3$] (**7**) and [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (**6**) in a ratio of 2.2:1 (according to the $^{31}P\{^1H\}$ NMR spectrum). HBpin and 2-Bpin-1,3-$C_6F_2H_3$ were detected by GC-MS analysis. 2-Bpin-1,3-$C_6F_2H_3$ and **6** were formed in a ratio of 2:1 (according to the ^{19}F NMR spectrum). Furthermore, after removing the volatiles and dissolving the residue in toluene-d_8 *mer*-[Rh(H)$_3$(PEt_3)$_3$] and *cis-fac*-[Rh(H)$_2$(Bpin)(PEt_3)$_3$] were found in traces (2% and 6% based on the amounts of **1** as starting compound) by NMR spectroscopy at 203 K. 2-Bpin-1,3-$C_6F_2H_3$ was identified by comparison of the NMR data with those in the literature.[20b,33] Orange crystals of [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (**6**) were obtained at −30 °C by crystallization from a solution of the reaction products in *n*-hexane. Analytical data for [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (**6**): ^1H NMR (300.1 MHz, C_6D_6) δ 6.87 (m, 1H, CH_{ar}), 6.77 (dm, ^3J(H,H) = 6 Hz, 2H, CH_{ar}), 1.60 (m, q in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7 Hz, 6H, CH_2), 1.51 (m, q in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7 Hz, 12H, CH_2), 1.20 (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7 Hz, 9H, CH_3), 1.17 (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7 Hz, 18H, CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 169.1 (dd, ^1J(F,C) = 223 Hz, J = 25 Hz, CF), 124.1 (t, ^3J(F,C) = 8 Hz, CH_{ar}), 109.3 (d, ^2J(F,C) = 34 Hz, CH_{ar}), 20.2 (d, ^1J(P,C) = 17 Hz, CH_2), 18.4 (t, J = 11 Hz, CH_2), 8.9 (s, CH_3), 8.6 (s, CH_3), the signal for the Rh−C atom was not observed; $^{19}F\{^1H\}$ NMR (282.4 MHz, Me_6Si_2) δ −79.3 (ddt, ^3J(Rh,F) ≈ ^4J(P,F) ≈ 13 Hz, ^4J(P,F) = 5 Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ 18.9 (dtt, ^1J(Rh,P) = 129 Hz, ^2J(P,P) = 39 Hz, ^4J(F,P) = 13 Hz, 1P), 14.6 (bdd, ^1J(Rh,P) = 145 Hz, ^2J(P,P) = 39 Hz, 2P). Anal. Calcd (%) for $C_{24}H_{48}F_2P_3Rh$: C, 50.53; H, 8.48. Found: C, 50.96; H, 8.61.

Comparison of Conversion in the C−H Activation Reaction of 1,3,5-Trifluorobenzene and 1,3-Difluorobenzene. A solution of [Rh(Bpin)(PEt_3)$_3$] (**1**) (29.8 mg, 51 μmol) in cyclohexane (0.2 mL) in a PFA tube was treated with 1,3,5-trifluorobenzene (105 μL, 1.02 mmol) or 1,3-difluorobenzene (100 μL, 1.02 mmol). After 7 h the NMR spectroscopic data of the reaction solution revealed that 86% of **1** was converted into **5** and **7** from 1,3,5-trifluorobenzene vs 73% conversion into **6** and **7** from 1,3-difluorobenzene according to the $^{31}P\{^1H\}$ NMR spectra.

Treatment of [Rh(Bpin)(PEt_3)$_3$] (1) with 3,5-Difluoropyridine: Synthesis of [Rh{4-(3,5-$C_5NF_2H_2$)}(PEt_3)$_3$] (8). A solution of [Rh(Bpin)(PEt_3)$_3$] (**1**) (36.4 mg, 62 μmol) in cyclohexane (0.2 mL) in a PFA tube was treated with 3,5-difluoropyridine (6 μL, 62 μmol). After 3 h the NMR spectroscopic data of the reaction solution revealed the complete conversion of **1** and the formation of [Rh{4-(3,5-$C_5NF_2H_2$)}(PEt_3)$_3$] (**8**) and [Rh(H)(PEt_3)$_3$] (**7**) in a ratio of 1:0.16 (according to the $^{31}P\{^1H\}$ NMR spectrum). HBpin and 4-Bpin-3,5-$C_5NF_2H_2$ were detected by GC-MS analysis. 4-Bpin-3,5-$C_5NF_2H_2$ and **7** were formed in a ratio of 0.1:1 (according to the ^{19}F NMR spectrum). Furthermore, after removing the volatiles and dissolving the residue in toluene-d_8 *mer*-[Rh(H)$_3$(PEt_3)$_3$] and *cis-fac*-[Rh(H)$_2$(Bpin)(PEt_3)$_3$] were determined in traces (3% and 4% based on the amounts of **1** as starting compound) by NMR spectroscopy at 203 K. Orange crystals of [Rh{4-(3,5-$C_5NF_2H_2$)}(PEt_3)$_2$] (**8**) were obtained at −30 °C by crystallization from a solution of the reaction products in *n*-hexane. Analytical data for [Rh{4-(3,5-$C_5NF_2H_2$)}(PEt_3)$_3$] (**8**): ^1H NMR (300.1 MHz, C_6D_6) δ 8.20 (s, 2H, CH_{ar}), 1.43 (m, q in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 8 Hz, 6H, CH_2), 1.29 (m, q in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 8 Hz, 12H, CH_2), 1.03 (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7 Hz, 9H, CH_3), 0.95 (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 8 Hz, 18H, CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, Me_6Si_2) δ 167.3 (ddm, ^1J(F,C) = 235 Hz, J = 20 Hz, CF), 130.3 (d, ^2J(F,C) = 36 Hz, CH_{ar}), 19.9 (dt, ^2J(P,C) = 18 Hz, J = 3 Hz, CH_2), 18.3 (tt, J = 11 Hz, J = 4 Hz, CH_2), 8.8 (s, CH_3), 8.5 (s, CH_3) (the signal for the Rh−C atom was not observed); $^{19}F\{^1H\}$ NMR (282.4 MHz, Me_6Si_2) δ −94.1 (dd, ^3J(Rh,F) ≈ ^4J(P,F) ≈ 12 Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, Me_6Si_2) δ 17.1 (dtt, ^1J(Rh,P) = 126 Hz, ^2J(P,P) = 41 Hz, ^4J(F,P) = 13 Hz, 1P), 11.8 (dd, ^1J(Rh,P) = 142 Hz, ^2J(P,P) = 41 Hz, 2P). Anal. Calcd (%) for $C_{23}H_{47}F_2NP_3Rh$: C, 48.34; H, 8.29; N, 2.45. Found: C, 48.31; H, 8.28; N, 2.10. Analytical data for 4-Bpin-3,5-$C_5NF_2H_2$: ^1H NMR (300.1 MHz, cyclohexane) δ 8.39 (s, 2H, CH_{ar}), 1.39 (s, 12H, CH_3); ^{11}B NMR (96.3 MHz, cyclohexane) δ 30 (s); $^{13}C\{^1H\}$ NMR (75.5 MHz, cyclohexane) δ 162.3 (d, ^1J(F,C) = 262 Hz, CF), 133.9 (d, ^2J(F,C) = 25 Hz, CH_{ar}), ∼113.5 (br s, CB), 84.8 (s, $C(CH_3)_2$), 24.8 (s, $C(CH_3)_2$); $^{19}F\{^1H\}$ NMR (282.4 MHz, cyclohexane) δ −116.8 (s).

Treatment of [Rh(2,4,6-$C_6F_3H_2$)(PEt_3)$_3$] (5) with HBpin. A solution of [Rh(2,4,6-$C_6F_3H_2$)(PEt_3)$_3$] (**5**) (4.4 mg, 7 μmol) in cyclohexane (0.1 mL) was treated with HBpin (1.1 μL, 7 μmol) in a NMR tube. After 1 d the volatiles were removed under vacuum, and the residue was dissolved in toluene-d_8. The NMR spectroscopic data of the reaction solution at 203 K revealed the presence of a mixture containing **5** and [Rh(H)(PEt_3)$_3$] (**7**) as well as small amounts of *mer*-[Rh(H)$_3$(PEt_3)$_3$] and *fac*-[Rh(H)$_3$(PEt_3)$_3$] in a ratio of 1:1.5:0.2:0.03 (according to the $^{31}P\{^1H\}$ NMR spectrum). Furthermore, the formation of 2-Bpin-1,3,5-$C_6F_3H_2$ and 1,3,5-trifluorobenzene was detected by ^{19}F NMR spectroscopy and GC-MS analysis. 2-Bpin-1,3,5-$C_6F_3H_2$ was identified by comparison of the NMR data with those in the literature.[30a,31,32]

Treatment of [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (6) with HBpin. A solution of [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (**6**) (2.2 mg, 4 μmol) in cyclohexane (0.1 mL) was treated with HBpin (0.6 μL, 4 μmol) in a NMR tube. After 1 d the volatiles were removed under vacuum and the residue was dissolved in toluene-d_8. The NMR spectroscopic data of the reaction solution at 203 K revealed the presence of a mixture containing **6** and [Rh(H)(PEt_3)$_3$] (**7**) as well as small amounts of *mer*-[Rh(H)$_3$(PEt_3)$_3$] in a ratio of 1:1.1:0.15 (according to the $^{31}P\{^1H\}$ NMR spectrum). Furthermore, the formation of 2-Bpin-1,3-$C_6F_2H_3$ and 1,3-difluorobenzene was detected by ^{19}F NMR spectroscopy and GC-MS analysis. 2-Bpin-1,3-$C_6F_2H_3$ was identified by comparison of the NMR data with those in the literature.[20b,33]

Treatment of [Rh{4-(3,5-$C_5NF_2H_2$)}(PEt_3)$_3$] (8) with HBpin. A solution of [Rh{4-(3,5-$C_5NF_2H_2$)}(PEt_3)$_3$] (**8**) (3.0 mg, 5 μmol) in cyclohexane (0.1 mL) in a NMR tube was treated with HBpin (0.8 μL, 5 μmol). After 1 d the volatiles were removed under vacuum, and the residue was dissolved in toluene-d_8.The NMR spectroscopic data of the reaction solution at 203 K revealed the presence of a mixture containing **8** and [Rh(H)(PEt_3)$_3$] (**7**) in a ratio of 1:3 (according to the $^{31}P\{^1H\}$ NMR spectrum).

Treatment of [Rh(H)(PEt_3)$_3$] (7) with 1,3,5-Trifluorobenzene. A solution of [Rh(H)(PEt_3)$_3$] (**7**) (22.4 mg, 49 μmol) in cyclohexane (0.15 mL) in a PFA tube was treated with 1,3,5-trifluorobenzene (101 μL, 0.98 mmol). After 1 d the volatiles were removed under vacuum and the residue was dissolved in toluene-d_8. The NMR spectroscopic data of the reaction solution at 203 K revealed the presence of a mixture containing **7**, [Rh(2,4,6-$C_6F_3H_2$)(PEt_3)$_3$] (**5**), and small amounts of *mer*-[Rh(H)$_3$(PEt_3)$_3$] and *fac*-[Rh(H)$_3$(PEt_3)$_3$] in a ratio of 3.4:1:0.3:0.05 (according to the $^{31}P\{^1H\}$ NMR spectrum).

Treatment of [Rh(H)(PEt_3)$_3$] (7) with 1,3-Difluorobenzene. A solution of [Rh(H)(PEt_3)$_3$] (**7**) (18.0 mg, 39 μmol) in cyclohexane (0.2 mL) in a PFA tube was treated with 1,3-difluorobenzene (77 μL, 0.79 mmol). After 4 d at 50 °C the volatiles were removed under vacuum and the residue was dissolved in toluene-d_8. The NMR spectroscopic data of the reaction solution at 203 K revealed the presence of a mixture containing **7** and [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (**6**) in a ratio of 10:1 (according to the $^{31}P\{^1H\}$ NMR spectrum).

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Treatment of [Rh(H)(PEt_3)$_3$] (7) with 3,5-Difluoropyridine. A solution of [Rh(H)(PEt_3)$_3$] (**7**) (22.6 mg, 49 μmol) in cyclohexane (0.15 mL) in a PFA tube was treated with 3,5-difluoropyridine (4.5 μL, 49 μmol). After 2 h the volatiles were removed under vacuum and the residue was dissolved in toluene-d_8. The NMR spectroscopic data of the reaction solution at 203 K revealed the presence of a mixture containing **7**, [Rh(4-{3,5-$C_5NF_2H_2$})(PEt_3)$_3$] (**8**), and small amounts of *mer*-[Rh(H)$_3$(PEt_3)$_3$] and *fac*-[Rh(H)$_3$(PEt_3)$_3$] in a ratio of 1:1:0.06:0.01 (according to the $^{31}P\{^1H\}$ NMR spectrum).

Treatment of [Rh(Bpin)(PEt_3)$_3$] (1) with Hexafluorobenzene: Synthesis of [Rh(C_6F_5)(PEt_3)$_3$] (4). A solution of [Rh(Bpin)(PEt_3)$_3$] (**1**) (9.9 mg, 17 μmol) in Me_6Si_2 (0.5 mL) in a PFA tube was treated with hexafluorobenzene (100 μL, 0.45 mmol). After 2 h the NMR spectroscopic data of the reaction solution revealed the complete conversion of **1**. The volatiles were removed under vacuum, and the residue was extracted with *n*-hexane. Removing the solvent from the extract led to a solid, which was [Rh(C_6F_5)(PEt_3)$_3$] (**4**) according to its NMR spectra.

Treatment of [Rh(Bpin)(PEt_3)$_3$] (1) with Perfluorotoluene: Synthesis of [Rh(4-$C_6F_4CF_3$)(PEt_3)$_3$] (9). A solution of [Rh(Bpin)(PEt_3)$_3$] (**1**) (18.1 mg, 31 μmol) in Me_6Si_2 (0.5 mL) in a PFA tube was treated with perfluorotoluene (10 μL, 71 μmol). After 4 h the NMR spectroscopic data of the reaction solution revealed the complete conversion of **1**. The volatiles were removed under vacuum, and the residue was extracted with *n*-hexane. After removal of the solvent from the extract [Rh(4-$C_6F_4CF_3$)(PEt_3)$_3$] (**9**) was obtained as a yellow solid (yield: 19 mg, 90%). Yellow crystals of **9** were obtained by crystallization from a solution in *n*-hexane. Complex **9** was identified by comparison of the NMR data with those in the literature.[10] Additional analytical data: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ 17.7 (dttt, ^1J(Rh,P) = 130 Hz, ^2J(P,P) = 40 Hz, ^4J(F,P) = 14, ^5J(F,P) = 18 Hz, 1P), 13.4 (dd, ^1J(Rh,P) = 140 Hz, ^2J(P,P) = 40 Hz, 2P); coupling constants were determined by simulation with gNMR.[39] Anal. Calcd (%) for $C_{25}H_{45}F_7P_3Rh$: C, 44.52; H 6.73. Found: C, 44.17; H, 6.85.

Treatment of [Rh(2,4,6-$C_6F_3H_2$)(PEt_3)$_3$] (5) with B_2pin_2. A solution of [Rh(2,4,6-$C_6F_3H_2$)(PEt_3)$_3$] (**5**) (7.5 mg, 13 μmol) in cyclohexane (0.2 mL) in a NMR tube was treated with B_2pin_2 (9.9 mg, 39 μmol). After 10 d the NMR spectroscopic data of the reaction solution revealed the complete conversion of **5** and the formation of [Rh(Bpin)(PEt_3)$_3$] (**1**). The formation of 2-Bpin-1,3,5-$C_6F_3H_2$ was confirmed by ^{19}F NMR spectroscopy and GC-MS analysis. 2-Bpin-1,3,5-$C_6F_3H_2$ was identified by comparison of the NMR data with those in the literature.[30a,31,32]

Treatment of [Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (6) with B_2pin_2. A solution of Rh(2,6-$C_6F_2H_3$)(PEt_3)$_3$] (**6**) (12.1 mg, 21 μmol) in Me_6Si_2 (0.15 mL) in a PFA tube was treated with B_2pin_2 (10.7 mg, 42 μmol). After 5 d the NMR spectroscopic data of the reaction solution revealed the complete conversion of **6** and the formation of [Rh(Bpin)(PEt_3)$_3$] (**1**). The formation of 2-Bpin-1,3-$C_6F_2H_3$ was confirmed by ^{19}F NMR spectroscopy and GC-MS analysis. 2-Bpin-1,3-$C_6F_2H_3$ was identified by comparison of the NMR data with those in the literature.[20b,33]

Treatment of [Rh(4-$C_6F_4CF_3$)(PEt_3)$_3$] (9) with B_2pin_2. A solution of [Rh(4-$C_6F_4CF_3$)(PEt_3)$_3$] (**9**) (19.5 mg, 29 μmol) in cyclohexane (0.15 mL) in a PFA tube was treated with B_2pin_2 (14.7 mg, 58 μmol). After 5 d the NMR spectroscopic data of the reaction solution revealed that 50% of **9** was converted into [Rh(Bpin)(PEt_3)$_3$] (**1**). The formation of 4-Bpin-$C_6F_4CF_3$ was confirmed by ^{19}F NMR spectroscopy and GC-MS analysis. Analytical data for 4-Bpin-$C_6F_4CF_3$: ^1H NMR (300.1 MHz, C_6D_6) δ 1.18 (s, CH_3); ^{11}B NMR (96.3 MHz, C_6D_6) δ 29 (s); ^{19}F NMR (282.4 MHz, C_6D_6) δ −57.3 (t, ^4J(F,F) = 21 Hz, 3F, CF_3), −129.2 (m, 2F, 3/5-CF), −142.1 (m, 2F, 2/6-CF).

Formation of 2-Bpin-1,3,5-$C_6F_3H_2$ from 1,3,5-Trifluorobenzene and B_2pin_2 with 3.5 mol % [Rh(Bpin)(PEt_3)$_3$] (1). A solution of [Rh(Bpin)(PEt_3)$_3$] (**1**) (5.8 mg, 10 μmol) in cyclohexane (0.15 mL) in a PFA tube was treated with B_2pin_2 (72.6 mg, 286 μmol) and 1,3,5-trifluorobenzene (177 μL, 1.72 mmol) and heated to 50 °C. After 24 h the NMR spectroscopic data of the reaction solution revealed the formation of 2-Bpin-1,3,5-$C_6F_3H_2$ in a yield of 120% (based on the amount of B_2pin_2), which was determined by integration of the signals in the ^{19}F NMR spectrum (TON = 34, based on borylation steps). Small amounts (8% based on the amount of B_2pin_2) of 2,4-(Bpin)$_2$-1,3,5-C_6F_3H were determined by ^{19}F NMR spectroscopy and GC-MS analysis. Furthermore, HBpin was detected by ^1H NMR spectroscopy and GC-MS analysis. Analytical data for 2,4-(Bpin)$_2$-1,3,5-C_6F_3H: ^{19}F NMR (282.4 MHz, cyclohexane) δ −84.4 (t, ^4J(F,F) = 7 Hz, 1F), −93.6 (dd, ^3J(H,F) = 9 Hz, ^4J(F,F) = 7 Hz, 2F).

Formation of 2-Bpin-1,3-$C_6F_2H_3$ from 1,3-Difluorobenzene and B_2pin_2 with 3.5 mol % [Rh(Bpin)(PEt_3)$_3$] (1). A solution of [Rh(Bpin)(PEt_3)$_3$] (**1**) (6.4 mg, 11 μmol) in cyclohexane (0.15 mL) in a PFA tube was treated with B_2pin_2 (79.8 mg, 314 μmol) and 1,3-difluorobenzene (185 μL, 1.88 mmol) and heated to 50 °C. After 24 h the NMR spectroscopic data of the reaction solution revealed the formation of 2-Bpin-1,3-$C_6F_2H_3$ in a yield of 98% (based on the amount of B_2pin_2), which was determined by integration of the signals in the ^{19}F NMR spectrum (TON = 28, based on borylation steps). In addition, mono- and diborylated difluorobenzene derivatives in a yield of 37% (based on the amount of B_2pin_2) were determined by integration of the signals in the ^{19}F NMR spectrum (based on the assumption that no C−F bond cleavage steps occur, FBpin or HF could not be observed) and identified by GC-MS analysis. Furthermore, HBpin was detected by ^1H NMR spectroscopy and GC-MS analysis.

Formation of 2-Bpin-1,3,5-$C_6F_3H_2$ from 1,3,5-Trifluorobenzene and B_2pin_2 with 5 mol % [Rh(H)(PEt_3)$_3$] (7). A solution of [Rh(H)(PEt_3)$_3$] (**7**) (6.9 mg, 15 μmol) in cyclohexane (0.1 mL) in a PFA tube was treated with B_2pin_2 (76.5 mg, 301 μmol) and 1,3,5-trifluorobenzene (187 μL, 1.80 mmol) and heated to 50 °C. After 24 h the NMR spectroscopic data of the reaction solution revealed the formation of 2-Bpin-1,3,5-$C_6F_3H_2$ in a yield of 112% (based on the amount of B_2pin_2), which was determined by integration of the signals in the ^{19}F NMR spectrum (TON = 22, based on borylation steps). Small amounts (7% based on the amount of B_2pin_2) of 2,4-(Bpin)$_2$-1,3,5-C_6F_3H were determined by ^{19}F NMR spectroscopy and GC-MS analysis. Furthermore, HBpin was detected by ^1H NMR spectroscopy and GC-MS analysis.

Formation of 2-Bpin-1,3-$C_6F_2H_3$ from 1,3-Difluorobenzene and B_2pin_2 with 5 mol % [Rh(H)(PEt_3)$_3$] (7). A solution of [Rh(H)(PEt_3)$_3$] (**7**) (4.4 mg, 12 μmol) in cyclohexane (0.1 mL) in a PFA tube was treated with B_2pin_2 (48.8 mg, 192 μmol) and 1,3-difluorobenzene (113 μL, 1.15 mmol) and heated to 50 °C. After 24 h the NMR spectroscopic data of the reaction solution revealed the formation of 2-Bpin-1,3-$C_6F_2H_3$ in a yield of 83% (based on the amount of B_2pin_2), which was determined by integration of the signals in the ^{19}F NMR spectrum (TON = 17, based on borylation steps). In addition, mono- and diborylated difluorobenzene derivatives in a yield of 34% (based on the amount of B_2pin_2) were determined by integration of the signals in the ^{19}F NMR spectrum (based on the assumption that no C−F bond cleavage steps occur, FBpin or HF could not be observed) and identified by GC-MS analysis. Furthermore, HBpin was detected by ^1H NMR spectroscopy and GC-MS analysis.

Formation of 4-Bpin-$C_6F_4CF_3$ from Perfluorotoluene and B_2pin_2 with 3.5 mol % [Rh(Bpin)(PEt_3)$_3$] (1). A solution of [Rh(Bpin)(PEt_3)$_3$] (**1**) (5.3 mg, 9 μmol) in C_6D_6 (0.5 mL) in a PFA tube was treated with B_2pin_2 (65.8 mg, 259 μmol) and perfluorotoluene (36 μL, 433 μmol). After 2 d at 55 °C the NMR spectroscopic data of the reaction solution revealed the formation of 4-Bpin-$C_6F_4CF_3$ in a yield of 57% (based on the amount of B_2pin_2), which was determined by integration of the signals in the ^{19}F NMR spectrum (TON = 16, based on borylation steps).

Formation of 2-Bpin-C_5NF_4 from Pentafluoropyridine and B_2pin_2 with 5 mol % [Rh(H)(PEt_3)$_3$] (7). A solution of [Rh(H)(PEt_3)$_3$] (**7**) (5.3 mg, 12 μmol) in cyclohexane (0.2 mL) in a NMR tube was treated with B_2pin_2 (58.9 mg, 232 μmol) and pentafluoropyridine (25 μL, 232 μmol). After 1 d at 50 °C the NMR spectroscopic data of the reaction solution revealed the formation of 2-Bpin-C_5NF_4 in a yield of 86% and 4-Bpin-C_5NF_4 in a yield of 3% (based on the amount of B_2pin_2, determined by

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integration of the signals in the ^{19}F NMR spectrum, TON = 18, based on borylation steps). Furthermore, FBpin was detected by ^{19}F NMR spectroscopy.

Treatment of *fac*-[Rh(Bpin)$_2$(H)(PEt$_3$)$_3$] (10) with Pentafluoropyridine: Formation of [Rh(2-C$_5$NF$_4$)(PEt$_3$)$_3$] (2). A solution of *fac*-[Rh(Bpin)$_2$(H)(PEt$_3$)$_3$] (**10**) (4.2 mg, 6 μmol) in C_6D_6 (0.2 mL) in a NMR tube was treated with pentafluoropyridine (0.8 μL, 7 μmol). After 5 min the NMR spectroscopic data of the reaction solution revealed the quantitative formation of [Rh(2-C_5NF_4)(PEt$_3$)$_3$] (**2**) and FBpin.

Catalytic Reaction of 2,3,5,6-Tetrafluoropyridine with B_2pin_2 on Using 3.5 mol % [Rh(Bpin)(PEt$_3$)$_3$] (1). A solution of [Rh(Bpin)(PEt$_3$)$_3$] (**1**) (6.4 mg, 11 μmol) in cyclohexane (0.2 mL) in a PFA tube was treated with B_2pin_2 (79.8 mg, 314 μmol) and 2,3,5,6-tetrafluoropyridine (32 μL, 314 μmol). After 2 d at 50 °C the ^{19}F NMR spectroscopic data of the reaction solution revealed the formation of a product mixture. A GC-MS analysis of the reaction solution confirms the presence of mono- and diborylated pyridine derivatives and indicates that C−H and C−F borylation as well as hydrodefluorination steps occurred.

Formation of 4-Bpin-C_5NF_4 from 2,3,5,6-Tetrafluoropyridine and B_2pin_2 with 5 mol % [Rh(H)(PEt$_3$)$_3$] (7). A solution of [Rh(H)(PEt$_3$)$_3$] (**7**) (5.5 mg, 12 μmol) in cyclohexane (0.2 mL) in a PFA tube was treated with B_2pin_2 (61.0 mg, 240 μmol) and 2,3,5,6-tetrafluoropyridine (22 μL, 240 μmol). After 7 d at 50 °C the ^{19}F NMR spectroscopic data of the reaction solution revealed the formation of 4-Bpin-C_5NF_4 in a yield of 44% (based on the amount of B_2pin_2, determined by integration of the signals in the ^{19}F NMR spectrum, TON = 9, based on C−H borylation steps). Small amounts (6% based on the amount of B_2pin_2, determined by integration of the signals in the ^{19}F NMR spectrum) of additional products such as **3** were detected, but were not identified further. Furthermore, HBpin was detected by ^1H NMR spectroscopy and GC-MS analysis. Analytical data for 4-Bpin-C_5NF_4: ^1H NMR (300.1 MHz, C_6D_6) δ 1.09 (s, CH_3); ^{11}B NMR (96.3 MHz, C_6D_6) δ 29 (s); ^{19}F NMR (282.4 MHz, C_6D_6) δ −92.8 (m, J(F,F) = 31 Hz, J(F,F) = 20 Hz, 2F, 2/6-CF), −132.6 (m, J(F,F) = 31 Hz, J(F,F) = 20 Hz, J(F,F) = 13 Hz, 2F, 3/5-CF) (coupling constants were confirmed by simulation with gNMR[39,40]).

Formation of 2,3,5,6-Tetrafluoropyridine from Pentafluoropyridine and HBpin with 5 mol % [Rh(H)(PEt$_3$)$_3$] (7). A solution of [Rh(H)(PEt$_3$)$_3$] (**7**) (6.6 mg, 14 μmol) in C_6D_6 (0.5 mL) in a NMR tube was treated with HBpin (42 μL, 289 μmol). After 5 min pentafluoropyridine (190 μL, 1.73 mmol) was added. After 1 d the NMR spectroscopic data of the reaction solution revealed the quantitative conversion of HBpin and the formation of 2,3,5,6-tetrafluoropyridine[40,41] in a yield of 91% and 4-Bpin-C_5NF_4 in a yield of 5% (based on the amount of HBpin, determined by integration of the signals in the ^{19}F NMR spectrum, TON = 19, based on C−F cleavage steps).

Formation of 4-Bpin-C_5NF_4 from Pentafluoropyridine and HBpin with 5 mol % [Rh(H)(PEt$_3$)$_3$] (7). A solution of [Rh(H)(PEt$_3$)$_3$] (**7**) (12.4 mg, 27 μmol) in C_6D_6 (0.5 mL) in a NMR tube was treated with HBpin (160 μL, 1.10 mmol). After 5 min pentafluoropyridine (60 μL, 0.55 mmol) was added. After 21 d the NMR spectroscopic data of the reaction solution revealed quantitative conversion of pentafluoropyridine and the formation of 2,3,5,6-tetrafluoropyridine in a yield of 5% and 4-Bpin-C_5NF_4 in a yield of 92% (based on the amount of pentafluoropyridine, determined by integration of the signals in the ^{19}F NMR spectrum, TON = 19, based on C−F cleavage steps). The formation of both compounds was confirmed by GC-MS analysis.

Formation of 4-Bpin-C_5NF_4 from 2,3,5,6-Tetrafluoropyridine and HBpin with 5 mol % [Rh(H)(PEt$_3$)$_3$] (7). A solution of [Rh(H)(PEt$_3$)$_3$] (**7**) (5.7 mg, 12 μmol) in cyclohexane (0.2 mL) in a NMR tube was treated with HBpin (36 μL, 0.25 mmol). After 1 min 2,3,5,6-tetrafluoropyridine (23 μL, 0.25 mmol) was added. After 3 d at 50 °C the NMR spectroscopic data of the reaction solution revealed the formation of 4-Bpin-C_5NF_4 in a yield of 40% (based on the amount of HBpin, determined by integration of the signals in the ^{19}F NMR spectrum, TON = 8, based on C−H cleavage steps) as the only product, which was detectable in a significant amount.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information contains the crystallographic data of compounds **5**, **6**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data are also available from the Cambridge Crystallographic Database as file numbers CCDC 1023372−1023375.

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Notes

The authors declare no competing financial interest.

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