Catalytic C–F Activation

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C–F Activation at Rhodium Boryl Complexes: Formation of 2-Fluoroalkyl-1,3,2-Dioxaborolanes by Catalytic Functionalization of Hexafluoropropene**

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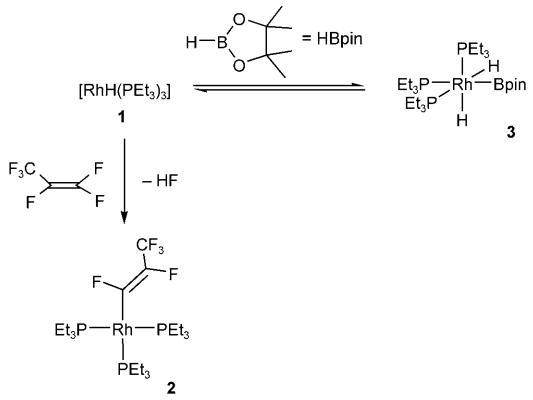
A unique and smart way to access fluorinated building blocks is to derivatize fluoroorganic compounds by C–F activation reactions at transition metal centers.[1–4] Most of the reactions which are known consist of hydrodefluorinations, but examples of C–F bond functionalization, in which the fluorine atom is replaced by a new group to access higher-value fluorinated compounds, are very limited. For fluorinated olefins, such conversions that involve a stoichiometric or even a catalytic cleavage of an olefinic carbon–fluorine bond are very sparse.[5,6] A palladium-catalyzed cross-coupling reaction of 1,1-difluoro-2-naphthylpropene with tolyl zinc chloride to give mono- and ditolyl derivatives has been reported.[6a] We showed recently that hexafluoropropene can be transformed into (3,3,3-trifluoropropyl)silanes by C–F activation.[6b] The reactions are catalyzed by the rhodium complex [Rh{(*Z*)-CF=CF(CF_3)}(PEt_3)$_3$] (**2**; Scheme 1), which can be synthesized by C–F activation of hexafluoropropene at [RhH(PEt_3)$_3$] (**1**) or *cis-fac*-[Rh(H)$_2$($SiPh_3$)(PEt_3)$_3$].[7] Other catalytic olefin derivatizations comprise simple hydrodefluorinations.[1,8] All of the conversions are thermodynamically favorable because of the strength of H–F and Si–F bonds that are formed.[1,9] However, the generation of a boron–fluorine bond would also be a strong driving force for carbon–fluorine bond cleavage, because a B–F bond (ca. 150 kcal mol^{-1}) can be considered to be even stronger than a H–F or a Si–F bond.[10]



Scheme 1. Preparation of the rhodium boryl complex **3**.

A C–F bond borylation has recently been reported by Marder, Perutz et al.[11] They found that fluorinated pyridines can be converted into rhodium(I) pyridyl complexes by carbon–fluorine bond cleavage.[2i,11] Subsequent treatment of fluoropyridyl rhodium derivatives, such as [Rh(2-C_5NF_4)(PMe_3)$_3$] or [Rh(4-C_5NF_4)(PMe_3)$_3$] with B_2cat_2 (Bcat = B(1,2-$O_2C_6H_4$)), gave the pyridyl boronate esters and the complex *fac*-[Rh(Bcat)$_3$(PMe_3)$_3$], but the reactions have so far not been catalytic.

Herein, we present results on the derivatization of hexafluoropropene with HBpin (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, pinacolborane) at rhodium to give fluoroalkyl boronate esters at room temperature. These studies led to the development of a catalytic process that is without precedent in the literature. There is considerable evidence for the involvement of a rhodium(I) boryl complex in the C–F activation step.[12] A rhodium(III) boryl complex was identified as catalytic resting state.

Treatment of a solution of the rhodium hydride **1** in toluene with HBpin afforded the oxidative addition product *fac*-[Rh(H)$_2$(Bpin)(PEt_3)$_3$] (**3**; Scheme 1).[13] Compound **3** is only stable in solution and in the presence of an excess HBpin. We have no evidence for the production of H_2 from **3**, which is consistent with the observation that for the complex [Cp*Rh(H)$_2$($SiEt_3$)(Bpin)] (Cp* = pentamethylcyclopentadienyl), B–H formation is more rapid than Si–H or H–H formation.[14]

The signals in the NMR spectra of **3** in [D_8]toluene are broadened at room temperature. We attribute this broadening to the presence of free HBpin. At 205 K, the ^{1}H NMR spectrum shows a resonance for the equivalent hydrides of **3** at $\delta = -10.11$ ppm.[13] A large phosphorus–hydrogen coupling of 134 Hz is observed, which is characteristic for a hydride in the *trans* position to a phosphine.[13b] In the low temperature ^{31}P NMR spectrum, complex **3** exhibits a signal at $\delta =$ 17.1 ppm for the phosphines in the *trans* position to the hydrido ligands. The resonances appear in a pattern that indicates doublet couplings to rhodium and to phosphorus of 101 and 21 Hz, which is characteristic for a rhodium(III) compound. A second resonance at $\delta = 7.5$ ppm with a coupling of 78 Hz to rhodium can be assigned to the

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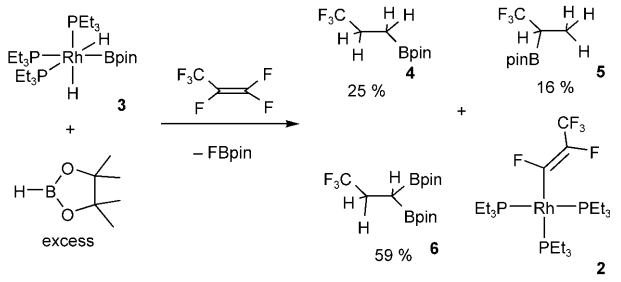
phosphorus in the *trans* position to the Bpin group. We could not resolve any couplings to the ^{11}B nucleus. The ^{11}B NMR spectrum of **3** shows one broad signal at $\delta = 46.3$ ppm ($\Delta\nu_{1/2} = 2400$ Hz, 233 K) at a chemical shift that is typical for a rhodium derivative of a 1,3,2-dioxaborolane.[14–16] Note that for the Bcat ligands in *fac*-[Rh(Bcat)$_3$(PMe$_3$)$_3$] a broad signal appears $\delta = 46.8$ ppm in the ^{11}B NMR spectrum, whereas for [CpRh(H)(Bpin)(PMe$_3$)] a resonance at $\delta = 45.4$ ppm was detected.[16a,b]

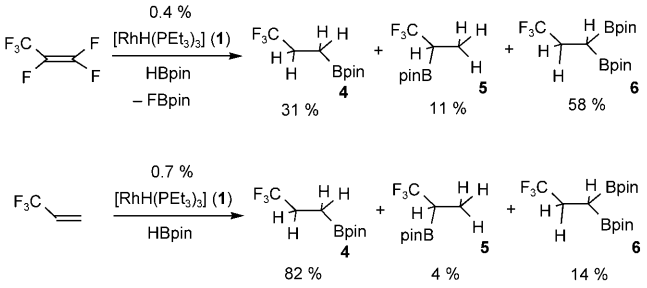
Treatment of a 1:1 mixture of **1** and HBpin in C_6D_6 with excess hexafluoropropene gave very small amounts of the fluoroalkyltrioxaborolanes **4**, **5**, and **6**, but the predominant product was the C–F activation product [Rh{(*Z*)-CF=CF-(CF$_3$)}(PEt$_3$)$_3$] (**2**). However, in the presence of an excess of HBpin, the formation of **4**–**6** in a ratio of 25:16:59 (Scheme 2)



Scheme 2. Borylation of hexafluoropropene by C–F activation.

was observed. The isomers **4** and **5** can be separated from **6** by vacuum distillation. The NMR spectroscopic data of **4**–**6** are depicted in Table 1, and the assignment has been verified by H,H-COSY experiments. The fluorodioxaborolane FBpin could be identified as an additional product (^{19}F NMR: $\delta = -150.9$ ppm). We found no indication for the generation of 3,3,3-trifluoropropene or of its boryl derivatives. Complex **2** along with small amounts of **3** and the trihydrides *mer*-[Rh(H)$_3$(PEt$_3$)$_3$] and *fac*-[Rh(H)$_3$(PEt$_3$)$_3$] could also be identified in the reaction solution.

We therefore turned our attention to catalytic experiments using **1** as catalytic precursor. In the presence of 0.4 mol% catalyst (based on the amounts of HBpin) and with an excess of hexafluoropropene, the fluoroalkyldioxaborolanes **4**–**6** were generated at room temperature in C_6D_6 in a ratio of 31:11:58 (Scheme 3).[17] Another experiment with



Scheme 3. Catalytic borylation of hexafluoropropene and 3,3,3-trifluoropropene.

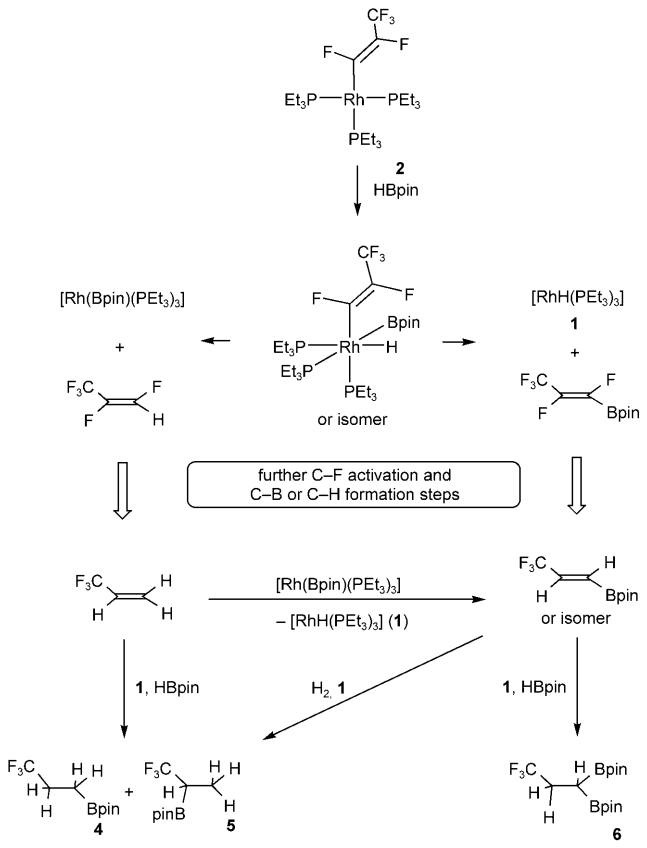
only four equivalents of hexafluoropropene (based on the amount of **1**) and an excess of HBpin (250 equiv) gave a comparable ratio of 22:14:64. Similar experiments with only a slight excess of nine and six equivalents of HBpin led to ratios of **4**/**5**/**6** of 50:5:45 and 50:20:30, respectively. Thus, if a low ratio of HBpin to hexafluoropropene is used, the amount of the doubly borylated product **6** is less. There is no reaction of HBpin with hexafluoropropene at room temperature in the absence of the catalyst. Note that Marder et al. found that the C–H functionalization of benzene or toluene with HBpin to yield aryl or benzyl boronate esters is catalyzed by [Rh(Cl)-(P*i*Pr$_3$)$_2$(N$_2$)] at elevated temperatures.[18] DFT calculations suggest that the C–H activation step occurs at a 14-electron rhodium hydride. We have found no evidence for the formation of pinBC$_6$D$_5$.

For the catalytic formation of **4**–**6**, we propose that in an initial step the intermediate rhodium(I) species [Rh(H)-(PEt$_3$)$_3$] **1** is generated from *fac*-[Rh(H)$_2$(Bpin)(PEt$_3$)$_3$] **3** prior to the C–F activation reaction (Scheme 1). The subsequent C–F activation step initiated by **1** yields [Rh{(*Z*)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] (**2**).[7] It is reasonable that [Rh{(*Z*)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] reacts with HBpin, yielding initially an isomer of the oxidative addition product [Rh(H)(Bpin){(*Z*)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] and then by reductive elimination either pentafluoropropene and [Rh(Bpin)(PEt$_3$)$_3$], or a Bpin derivative of the fluorinated olefin and **1** (Scheme 4). Further C–F activation and C–H or C–B coupling steps eventually give 3,3,3-trifluoropropene or a Bpin derivative of 3,3,3-trifluoropropene. Additional products are HF or FBpin. The former together with HBpin generate FBpin and H$_2$, which can in turn lead to the generation of *mer*-[Rh(H)$_3$(PEt$_3$)$_3$] and *fac*-[Rh(H)$_3$(PEt$_3$)$_3$] by oxidative addition at **1**.[13b] We could show in an independent experiment that HBpin reacts with Et$_3$N·3HF to give FBpin. The products **4** and **5** are finally furnished by hydroboration of 3,3,3-trifluoropropene or hydrogenation of a borylated derivative. The hydroboration of a Bpin derivative of 3,3,3-trifluoropropene yields **6**.[12,18] Moreover, dehydrogenative borylations of an olefin, as an additional possibility to introduce a Bpin group, are conceivable (see below).[19]

Table 1: EI mass spectrometric and NMR spectroscopic data for **4**–**6**.

Compound	^1H NMR[a] [ppm]	^{19}F NMR[b] [ppm]	$^{11}B\{^1H\}$ NMR [ppm]	MH$^+$ [*m*/*z*]
4	2.02 (qt, 2H, ^3J(F,H) = 11 Hz, ^3J(H,H) = 8 Hz, CF_3CH_2), 0.98 (s, 12H, CH_3), 0.94 (t, br, 2H, ^3J(H,H) = 8 Hz, CH_2B).	−67.6 (t, CF_3, J(F,H) = 11 Hz)	33.5 (s, br)	225
5	1.84 (m, 1H, CF_3CH), 1.07 (d, br, 3H, ^3J(H,H) = 8 Hz, CH_3CH), 0.98 (s, 12H, CH_3).	−64.4 (d, CF_3, J(F,H) = 11 Hz)	32.0 (s, br)	225
6	2.58 (qd, 2H, ^3J(F,H) = 11 Hz, ^3J(H,H) = 8 Hz, CF_3CH_2), 1.32 (t, br, 1H, ^3J(H,H) = 8 Hz, CH(Bpin)$_2$), 0.98 (s, 12H, CH_3).	−66.7 (t, CF_3, J(F,H) = 11 Hz)	33.5 (s, br)	351

[a] The F,H couplings were determined by ^{19}F decoupling experiments, and the assignment was verified by H,H-COSY experiments. [b] Singlets were observed with ^1H decoupling.



Scheme 4. Possible mechanism for the catalytic formation of **4**–**6**.

Generation of the intermediate rhodium(I) boryl species $[Rh(Bpin)(PEt_3)_3]$ would, therefore, be coupled to the formation of C–H bonds (Scheme 4).[12] Because in our experiments hydrodefluorination steps are predominant over the formation of C–B bonds, it is likely that $[Rh(Bpin)(PEt_3)_3]$ plays a crucial role in the C–F activation of intermediate fluorinated propenes. There is no evidence for the production of H_2 and pinBBpin from two equivalents of HBpin by a dehydrodimerization pathway, which is endothermic.[18b] This suggests that $[Rh(Bpin)(PEt_3)_3]$ can not be converted into the hydride **1** and pinBBpin by such a pathway.

Evidence for dehydrogenative borylation steps is given by independent catalytic experiments on the hydroboration of 3,3,3-trifluoropropene with HBpin using **1** as catalyst (0.7% based on the amount of HBpin; Scheme 3). In addition to the 2-trifluoro-1,3,2-dioxaborolanes **4** and **5**, the generation of the doubly borylated product **6** was observed (ratio 82:4:14). This shows that hydroboration of 3,3,3-trifluoropropene with **1** as catalyst is possible, and it also substantiates that dehydrogenative borylations are possible. Note that a rhodium-catalyzed conversion of pentafluorostyrene with HBpin yields products of hydroboration and dehydrogenative borylation reactions.[19d] A selective catalytic synthesis of vinylboronate esters by dehydrogenative borylation using *trans*-$[RhCl(CO)(PPh_3)_2]$ as catalyst has recently been reported.[19b,e]

In conclusion, we have developed a unique catalytic process for the conversion of hexafluoropropene and 1,3,2-dioxaborolane into Bpin derivatives of trifluoropropane. The reactions proceed at room temperature in quantitative yields, as shown by the NMR spectra. To the best of our knowledge, C–F bond borylation of fluorinated olefins are without precedent. Furthermore, the conversions represent some extremely rare examples for catalytic C–F activation reactions of a highly fluorinated alkene that do not result in simple hydrodefluorination products.[2,6] Instead, higher value fluorinated boryl compounds are formed.[20] The catalytic cycles involve defluorination reactions of hexafluoropropene, which are coupled consecutively with catalytic hydroborylation, hydrogenation, and/or dehydrogenative borylation steps. The mechanistic considerations also suggest the involvement of a rhodium(I) boryl species in most of the C–F activation steps. The rhodium(III) complex *fac*-$[Rh(H)_2(Bpin)(PEt_3)_3]$ **3** can serve as catalytic resting state by reductive elimination of HBpin.

Experimental Section

Catalytic formation of **4**–**6** from hexafluoropropene: A solution of **1** (26 mg, 0.05 mmol) in C_6D_6 (2 mL) was treated with HBpin (2 mL, 12.5 mmol). After 5 min, hexafluoropropene was bubbled through the solution for 5 min. After 20 min the mixture was analyzed by ^{19}F NMR spectroscopy to determine the ratio of **4**–**6** (31:11:58). The conversion of HBpin was quantitative; no signal for the HBpin was detected in the ^{11}B NMR spectrum or by GC-MS. The solvent was then removed from the filtrate in vacuo. A mixture of **4** and **5** can be obtained by distillation at 70 °C (0.1 Torr). Experiments with a 0.06 M solution of **1** as catalyst (0.5 mL C_6D_6), four equivalents of hexafluoropropene and 6, 9, or 250 equivalents of HBpin were also performed. The olefin was consumed completely in these cases. For product ratios see text. Elemental analysis (%) calcd for $C_9H_{16}BF_3O_2$: C 48.23, H 7.20; found: C 48.18, H 7.32.

Catalytic formation of **4**–**6** from 3,3,3-trifluoropropene: A solution of **1** (35 mg, 0.06 mmol) in C_6D_6 (2 mL) was treated with HBpin (1.25 mL, 9.06 mmol). After 5 min, 3,3,3-trifluoropropene was bubbled through the solution for 5 min. After 20 min the mixture was analyzed by ^{19}F NMR spectroscopy to determine the ratio of **4**–**6** (82:4:14). No signal for the HBpin was detected in the ^{11}B NMR spectrum or by GC-MS.

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[13] a) Traces of water can react with HBpin to give H_2 and pinBOBpin. The former reacts with **1** to give the trihydrido complexes *cis-mer*-$[Rh(H)_3(PEt_3)_3]$ and *cis-fac*-$[Rh(H)_3(PEt_3)_3]$. The signal for the hydride in **3** in the ^{1}H NMR spectrum can then be obscured by the signal for *cis-fac*-$[Rh(H)_3(PEt_3)_3]$ at $\delta = -10.26$ ppm. b) T. Braun, D. Noveski, M. Ahijado, F. Wehmeier, *Dalton Trans.* **2007**, 3820 – 3825.

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