Boryl Complexes

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A Highly Reactive Rhodium(I)–Boryl Complex as a Useful Tool for C–H Bond Activation and Catalytic C–F Bond Borylation**

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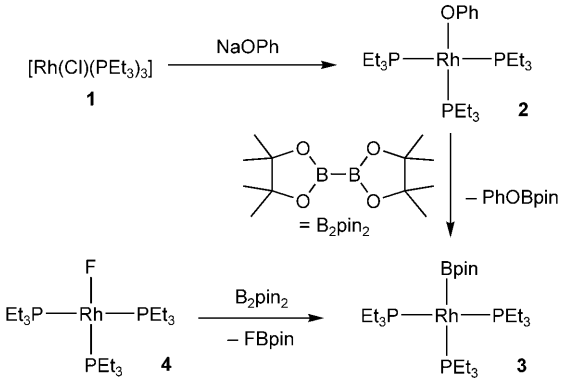
Transition-metal–boryl complexes are key intermediates in catalytic hydroboration and borylation reactions and find applications in boron-based materials.[1] Rhodium complexes can be applied in the rhodium-mediated hydroboration or dehydrogenative borylation reactions of olefins or even in the borylation of alkanes.[2,3] Rhodium and iridium boronates also play a crucial role in the borylation of arenes to give, for instance, Bpin derivatives.[4,5] Thus, it has been reported that rhodium complexes with boryl and phosphine ligands are intermediates in the catalytic borylation reactions of benzene, toluene, *para*-xylene, and mesitylene with HBpin (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, pinacolborane).[4] Although it is conceivable that the C–H activation step occurs at the 14-electron species $\{Rh(Bpin)(P\mathit{i}Pr_3)_2\}$, density functional theory (DFT) calculations indicate that benzylic activation takes place at $\{Rh(H)(P\mathit{i}Pr_3)_2\}$.[4b] In this case, Rh^{I}–Rh^{III} cycles have been suggested, whereas iridium-based catalysts may operate through Ir^{III}–Ir^{V} cycles.[4,5]

Examples of C–F bond functionalization, i.e. where fluorine is replaced by a new group to access higher-value fluorinated compounds, are very limited,[6,7] and most examples involve hydrodefluorination.[6] C–F bond activation is generally thermodynamically favorable, because of the strength of the H–F and Si–F bonds, or even of the M–F bonds that are formed.[6] We have developed a catalytic process for the conversion of hexafluoropropene and HBpin into Bpin derivatives of trifluoropropane using $[Rh(H)(PEt_3)_3]$ as a catalyst.[8] Mechanistic considerations suggest the involvement of a rhodium(I)–boryl species in some of the C–F activation steps, but such a compound could not be detected. The thermodynamic driving force in this case is apparently the generation of B–F bonds.[8] Rhodium(I)–boryl complexes are almost without any precedent in the literature,[1,9] although $[Rh(Bcat)(PMe_3)_4]$ has been synthesized by Marder and co-workers from the treatment of $[Rh(Me)(PMe_3)_4]$ with B_2cat_2 (Bcat = B{1,2-$O_2C_6H_4$}).[10]

Herein, we report the identification of a unique 16-electron rhodium(I) species, $[Rh(Bpin)(PEt_3)_3]$ (**3**). This complex is highly reactive and can effect the C–H activation of benzene, as well as the stoichiometric C–F activation and catalytic C–F borylation of fluorinated substrates.

We reasoned that a phenoxo complex might be an ideal starting compound for the formation of a rhodium(I)–boryl complex, partly because of the high stability of a boron–oxygen bond.[11,12] Treatment of the chloro complex $[Rh(Cl)(PEt_3)_3]$ (**1**) with NaOPh gave the rhodium phenoxide $[Rh(OPh)(PEt_3)_3]$ (**2**; Scheme 1). The ^1H and ^{31}P NMR spectra of



Scheme 1. Synthesis of a rhodium(I)–boryl complex.

complex **2** showed the expected splitting patterns; the phosphorus–rhodium coupling constants in the ^{31}P NMR spectrum of 169 and 142 Hz are characteristic of a rhodium(I) compound.[13] Reaction of **2** in benzene with excess B_2pin_2 (3 equiv) gave $[Rh(Bpin)(PEt_3)_3]$ (**3**) after 16 hours, along with PhOBpin (Scheme 1). Moreover, we found that **3** can be generated in a comparable reaction, starting from the fluoro compound $[Rh(F)(PEt_3)_3]$ (**4**).[14] The fluoroborane FBpin that was also formed can be removed in vacuo. Note that boryl complex **3** does not react with another equivalent of B_2pin_2 to give a Rh^{III} complex that would be comparable to *fac*-$[Rh(Bcat)_3(PMe_3)_3]$.[10]

Complex **3** was only characterized in solution; the ^{31}P NMR spectrum at room temperature revealed only one broad signal at $\delta = 15.1$ ppm. This indicates a dynamic behavior, which involves the exchange of the phosphine

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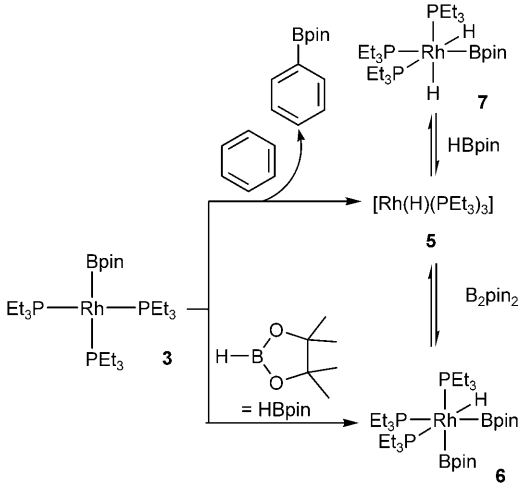
ligands, similar to the fluxionality which has been observed for $[Rh(H)(PEt_3)_3]$ (**5**).[15] Variable-temperature ^{31}P NMR analysis shows that the free phosphine has no influence on the dynamic behavior, which suggests that the process is intramolecular. The ^{31}P NMR spectrum at 203 K exhibits a signal at $\delta = 20.5$ ppm for the phosphine atoms that are in a mutually *trans* position. The resonance features characteristic couplings for a rhodium(I) compound, with doublet couplings to rhodium and to phosphorus of 166 Hz and 30 Hz, respectively.[12,13] A second resonance at $\delta = 9.1$ ppm, with a coupling to rhodium of 110 Hz, can be assigned to the phosphorus ligand that is in the position *trans* 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 $\delta =$ 46.5 ppm ($\Delta\nu_{1/2} = 338$ Hz); this chemical shift is typical for a rhodium derivative of a 1,3,2-dioxaborolane.[16]

NMR spectroscopic investigations revealed that **3** is not very stable in benzene and converts slowly into the hydride $[Rh(H)(PEt_3)_3]$ (**5**) at room temperature, with concomitant formation of PhBpin (Scheme 2). In the presence of B_2pin_2, complex **5** reacts further to give the Rh^{III} complex *cis-fac*-$[Rh(H)(Bpin)_2(PEt_3)_3]$ (**6**).



Scheme 2. Formation and reactivity of rhodium–boryl complexes.

These observations indicate that C–H activation of benzene may occur at $[Rh(Bpin)(PEt_3)_3]$ (**3**), possibly via a Rh^{III} intermediate, $[Rh(H)(Ph)(Bpin)(PEt_3)_3]$, although this could not be detected.[4] Reaction of **3** in C_6D_6 furnished (D_5C_6)Bpin and $[Rh(H)(PEt_3)_3]$ (**5**). ^1H NMR EXSY spectra (400 MHz; EXSY = exchange spectroscopy) of **5** confirmed exchange between the hydrogen atom that is bound to the metal and the CH_2 and CH_3 hydrogen atoms of the *cis* phosphine ligands. It appears that intramolecular cyclometalation processes are occurring, which result in the transfer of deuterium atoms from being bound to the metal onto the phosphine alkyl groups.[17]

We have no indication for the generation of HBpin. It seems that reductive elimination from **6** to afford rhodium(I)–boryl complex **3** does not occur under the reaction conditions. This observation might explain why it was not possible to develop a catalytic process for the generation of PhBpin from benzene and B_2pin_2. Complex **6** can also be synthesized independently, starting from $[Rh(Bpin)(PEt_3)_3]$ (**3**; Scheme 2). A solution of **3** was treated with HBpin to give **6** plus considerable amounts of *cis-fac*-$[Rh(H)_2(Bpin)(PEt_3)_3]$ (**7**). The formation of **7** can be explained by the reductive elimination of B_2pin_2 from **6** to furnish the hydrido complex $[Rh(H)(PEt_3)_3]$ (**5**). It has been previously reported that treatment of **5** with HBpin affords **7**.[8]

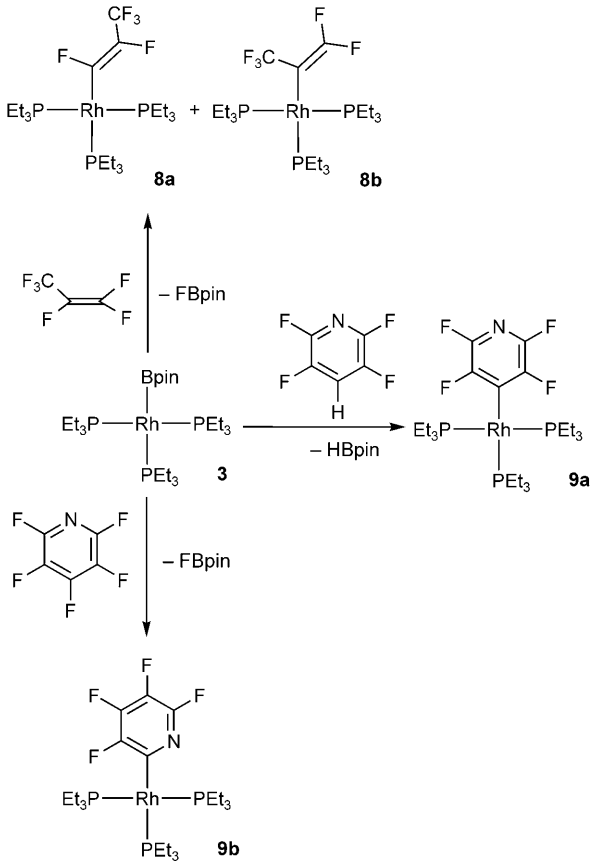
A signal at $\delta = -10.18$ ppm in the ^1H NMR spectrum of **6** confirms the presence of the hydrido ligand. The ^{31}P NMR spectrum shows rhodium–phosphorus coupling constants of 98 Hz and 75 Hz for the doublet of triplets at $\delta = 8.1$ ppm and the doublet of doublets at $\delta = 2.3$ ppm, respectively, reveal the presence of a Rh^{III} compound.[12] The relatively small coupling constant of 75 Hz suggests that the two equivalent phosphine ligands are located *trans* to the boryl ligands. This arrangement is compatible with a *fac* configuration for **6**; for complex **7**, $^1J(Rh,P) = 78$ Hz for the phosphorus atom in the position *trans* to the boryl ligand has been observed.[8] The ^{11}B NMR spectrum of **6** shows one broad signal at $\delta =$ 47.1 ppm ($\Delta\nu_{1/2} = 633$ Hz), which confirms the presence of the boryl ligands.[8]

To avoid activation of the aromatic C–H bonds on **3**, the phenoxo complex $[Rh(OPh)(PEt_3)_3]$ (**2**) and the fluoro compound $[Rh(F)(PEt_3)_3]$ (**4**) were treated stoichiometrically with B_2pin_2 in $Me_3SiSiMe_3$ as a solvent. Under these reaction conditions, boryl complex **3** was observed as the sole product (Scheme 1). The stability of **3** in $Me_3SiSiMe_3$ enabled us to perform further studies on the reactivity of **3** towards the activation of carbon–fluorine bonds.[6]

Treatment of **3** with perfluoropropene in $Me_3SiSiMe_3$ gave the propenyl compound $[Rh\{(Z)CF{=}CF(CF_3)\}(PEt_3)_3]$ (**8a**) and the isomeric complex $[Rh\{C(CF_3){=}CF_2\}(PEt_3)_3]$ (**8b**) in a ratio of 2:7 (Scheme 3). Therefore, compound **3** might indeed be an intermediate in the conversion of hexafluoropropene and HBpin into Bpin derivatives of trifluoropropane, as has been previously proposed.[8] The formation of complex **8a** has been previously reported from the treatment of $[Rh(H)(PEt_3)_3]$ (**5**) with perfluoropropene.[14c] The NMR spectra of **8b** show the expected splitting pattern with a geminal fluorine–fluorine coupling constant of 61 Hz in the ^{19}F NMR spectrum.[18]

Fluorinated pyridines are also interesting substrates for investigating C–F activation reactions with boryl complex **3**.[19–21] For instance, the reaction of C_5NF_5 with $[Rh(H)(PEt_3)_3]$ (**5**) gives $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**9a**) and HF,[20] whilst reaction with $[Rh(SiPh_3)(PMe_3)_3]$ revealed the isomeric compounds $[Rh(2\text{-}C_5NF_4)(PMe_3)_3]$ and $[Rh(4\text{-}C_5NF_4)(PMe_3)_3]$ in a 3:1 ratio, along with $FSiPh_3$.[19,22] When 2,3,5,6-tetrafluoropyridine was used as the substrate, a delicate balance between C–H and C–F activation was observed.[6,21e,23] Thus, reaction with $[Rh(H)(PEt_3)_3]$ (**5**) furnished **9a** by C–H activation,[7] whereas reaction with $[Rh(SiPh_3)(PMe_3)_3]$ gave a mixture of products that were derived from activation at the 2-(C–F) and 4-(C–H) positions.[19]

Reaction of **3** with 2,3,5,6-tetrafluoropyridine gave the C–H activation product $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**9a**) and HBpin, with no observed C–F bond cleavage (Scheme 3).



Scheme 3. C–F Activation at the rhodium–boryl complex **3**.

However, treatment of in situ generated **3** with pentafluoropyridine selectively gave the C–F activation product [Rh(2-C_5NF_4)(PEt_3)$_3$] (**9b**), with FBpin by-product at room temperature. Thus, C–F activation at the boryl species **3** occurs exclusively at the 2-position of the fluorinated substrate. The ^{31}P NMR spectrum of **9b** showed a doublet of doublets at $\delta =$ 16.0 ppm and a resonance at $\delta = 19.7$ ppm, with a complex splitting pattern arising from coupling with phosphorus, rhodium, and fluorine atoms. The four signals at $\delta = -87.7$, -125.0, -155.4, and -175.9 ppm in the ^{19}F NMR spectrum indicate the presence of the pyridyl ligand, with the metal at the 2-position.[19,21]

C–F bond activation of pentafluoropyridine most frequently involves reaction at the 4-position, *para* to the nitrogen, and such selectivity is often associated with radical pathways or those involving initial nucleophilic attack. Activation at the 2-position is less common, although it has been suggested that it may occur by a concerted oxidative addition process.[6,21,24] Therefore, we wanted to investigate this unusual selectivity in the reaction of **3** with pentafluoropyridine.

Recently, a novel mechanism for aromatic C–F bond activation has been characterized at electron-rich iridium and platinum metal centers.[25] This process involves the addition of a C–F bond across a {M–PR_3} moiety via a four-centered transition state, which can account for the selective activation at the 2-position of pentafluoropyridine and {Ni(PEt_3)$_2$} fragments.[25,26] Key to such phosphine-assisted processes is the Lewis acidity of the accepting phosphine ligand. By analogy, we reasoned that an equivalent boryl-assisted process may be possible for complex **3**, wherein the formally sp^2-hybridized boron atom may be a particularly effective Lewis acid.

The mechanism and selectivity of the reaction of pentafluoropyridine with **3** were investigated using DFT calculations on model complex [Rh(Bpin)(PMe_3)$_3$] (**3′**).[27] Both concerted oxidative addition and boryl-assisted processes were considered, and the lowest energy C–F activation transition states for reaction at the 2- and 4-positions are shown schematically in Figure 1.

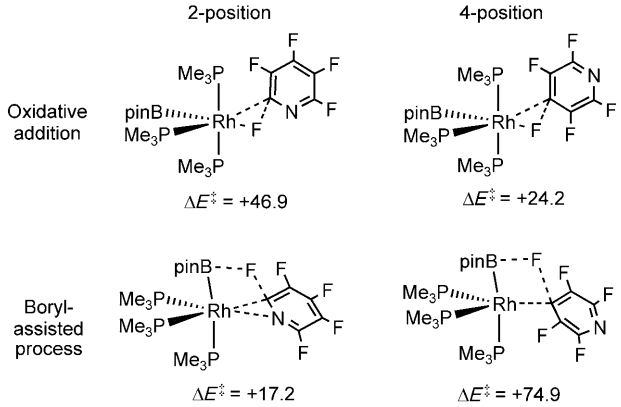


Figure 1. Computed transition states and energies [kJ mol^{-1}] for C–F activation of pentafluoropyridine at [Rh(Bpin)(PMe_3)$_3$] (**3′**).

The most accessible oxidative addition process corresponds to activation at the 4-position ($\Delta E^{\ddagger} = +24.2$ kJ mol^{-1} cf. $+46.9$ kJ mol^{-1} at the 2-position). These processes give stable *mer*-[Rh(Bpin)(F)(4-C_5NF_4)(PMe_3)$_3$] and *mer*-[Rh(Bpin)(F)(2-C_5NF_4)(PMe_3)$_3$] complexes, in which the fluoride ligand is *trans* to the Bpin group. However, subsequent isomerization and reductive elimination of FBpin to give [Rh(4- or 2-C_5NF_4)(PMe_3)$_3$] (**9′a** or **9′b**) is facile (see the Supporting Information). Therefore, oxidative addition of the C–F bond is the overall rate-determining step and, most importantly, indicates a kinetic preference for reaction at the 4-position, which is at odds with experimental observations.

In contrast, boryl-assisted C–F activation clearly favors the 2-position ($\Delta E^{\ddagger} = +17.2$ kJ mol^{-1} cf. $+74.9$ kJ mol^{-1} at the 4-position). Both processes lead directly to **9′a/b** and FBpin. Moreover, boryl-assisted C–F activation at the 2-position is now more accessible than oxidative addition at the 4-position, and so this pathway accounts for the experimentally observed selectivity. One factor that might contribute to the greater accessibility of the boryl-assisted process at the 2-position is the short Rh···N contact in the transition state (2.22 Å); donation of electron density from the nitrogen atom lone pair serves to stabilize the rhodium center (Figure 2).[25c]

We also experimentally investigated the reactivity of **3** in catalytic borylation reactions of pentafluoropyridine. In $Me_3SiSiMe_3$ solvent, we anticipated a selective borylation reaction at the 2-position of pentafluoropyridine, because the formation of [Rh(H)(PEt_3)$_3$] (**5**) would not occur. As

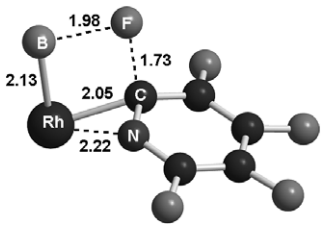
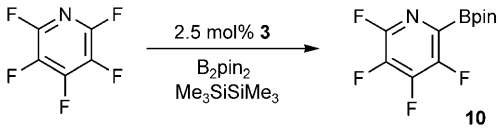


Figure 2. Key computed distances [Å] in the boryl-assisted transition state for activation at the 2-position of pentafluoropyridine at **3′**.

mentioned above, the latter led to C–F bond cleavage at the 4-position.[20] Indeed, pentafluorpyridine was catalytically converted into its 2-boryl derivative **10** (45% yield) in the presence of 2.5 mol% **3** as the catalyst (based on equimolar amounts of C_5NF_5 and B_2pin_2; Scheme 4). Borylation of the



Scheme 4. Catalytic formation of a pyridyl boronate ester.

C–F bond has also been reported by Marder, Perutz, and co-workers[19] The treatment of C–F activation products, such as $[Rh(2\text{-}C_5NF_4)(PMe_3)_3]$ or $[Rh(4\text{-}C_5NF_4)(PMe_3)_3]$, with B_2cat_2 gave the pyridyl boronate esters and the Rh^{III} complex *fac*-$[Rh(Bcat)_3(PMe_3)_3]$. However, in these examples the reactions were not catalytic.

In conclusion, a 16-electron rhodium(I)–boryl complex (**3**) has been synthesized which undergoes C–H activation at room temperature with benzene to give PhBpin. Reaction with fluorinated substrates, such as pentafluoropyridine and perfluoropropene, results in C–F activation products. DFT calculations suggest that C–F activation proceeds along a boryl-assisted pathway that involves direct transfer of fluorine onto the boron center via a four-membered transition state. This mechanism also shows that the selective activation at the 2-position arises because of a stabilizing Rh···N interaction in the transition state. Investigation of the catalytic borylation reaction led to the formation of tetrafluoropyridyl boronate esters, which can provide new fluorinated building blocks.[28] Note that it is extremely difficult to access tetrafluoropyridines that are further functionalized at the 2-position.[6,21]

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