B–F Activation

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Oxidative Addition of Boron Trifluoride to a Transition Metal**

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Dedicated to Professor Gerhard Bringmann on the occasion of his 60th birthday

Organic synthesis, at its most fundamental level, is the study of carbon–carbon and carbon–element bond formation. As these bonds are rather stable and many organic compounds lack accessible coordination sites, the first step of a reaction has to be the cleavage of a bond. In catalysis, this is often carried out by a transition metal by means of an oxidative addition.

The synthesis of pharmaceutical, agricultural, and other fine chemicals is the most crucial and demanding arena for any new homogeneous catalytic process. In this setting, selective and protecting-group-free organic synthesis under mild conditions, and with a minimum of waste, has always been an ideal.[1,2] With convenience and atom-efficiency in mind, mild functionalization of the (particularly unreactive) C–H bond has become a prominent endeavor, albeit one that rests heavily on the non-trivial ability of the transition metal to cleave this bond.[3] Similarly, transition-metal-catalyzed processes involving initial element–element bond oxidative addition steps are also established, including hydrogenation,[4] hydrosilylation,[5] and hydroboration,[6] leading to transfer of (H)(H), (R_3Si)(H), or (R_2B)(H) groups to an unsaturated organic substrate.

The search for strongly reactive and Lewis basic transition-metal complexes by inorganic and organometallic chemists has been in part motivated by the desire to activate ever more recalcitrant element–element bonds. Tools might thereby be developed to create bonds using more abundant (for example alkanes instead of alkenes) or less reactive reagents (such as aryl chlorides instead of aryl iodides), or to functionalize unreactive sites of organic molecules that would be otherwise inaccessible. Much progress in the area of C–C bond activation (bond dissociation energy (BDE): 346 kJ mol^{-1}) has been made by Milstein's group,[7] and even strong C–F bonds (BDE: 485 kJ mol^{-1}) have been activated, both by oxidative addition to transition metals[8] and transition-metal-mediated processes,[9] leading to important applications in the area of pharmaceutical chemistry.

The significantly stronger and highly polar B–F bond (BDE: 651 kJ mol^{-1}) ranks among the most stable σ bonds. Consequently, boronfluorides have hitherto eluded oxidative addition to a metal center, thus precluding direct metal mediated fluoroboration of unsaturated organic molecules. Such a process would be a potentially convenient way to install two functional groups of opposite polarity at adjacent carbon atoms, thereby creating two controllable access points for sequential functionalization. Also of direct relevance to B–F bond activation is the growing interest in organofluoroborates as substrates for the widely-used Suzuki–Miyaura coupling protocol and their attendant possibilities for application in organic and pharmaceutical chemistry.[10]

In the course of our studies on the zerovalent platinum species [($Cy_3P)_2$Pt] (**1**) and related electron-rich late-transition-metal complexes, we have explored the limits of the Lewis basicity of **1** and its pronounced propensity to oxidatively add B–Cl and B–Br bonds.[11,12] By extension, naturally, we became interested in its reactivity towards fluoroboranes. We hereby report the hitherto unknown oxidative addition of a B–F bond, namely that of borontrifluoride (BF_3), to a metal center.

Reaction of [($Cy_3P)_2$Pt] (**1**) with equimolar amounts of gaseous BF_3 instantaneously affords a mixture of remaining starting material and two new products, as determined by $^{31}P\{^1H\}$ NMR spectroscopy. However, use of two equivalents of BF_3 leads to complete conversion of the starting material into the two new products. In the $^{19}F\{^1H\}$ NMR spectra, a platinum-bound difluoroboryl ligand could be identified by its broad resonance at −33.3 ppm, flanked by characteristic ^{195}Pt satellites ($^2J_{F-Pt} = 1230$ Hz). These findings are in good agreement with *cis*-[($Ph_3P)_2$Pt($BF_2)_2$] (**2**; $\delta(^{19}F\{^1H\}) = -17.4$ ppm; $^2J_{F-Pt} = 1040$ Hz).[13]

Another resonance, assigned to a tetrafluoroborate moiety, was detected at −168 ppm. In the $^{11}B\{^1H\}$ NMR spectra, only the resonance for the latter could be detected at 0.3 ppm, and thus in the typical region for four-coordinate boron. The absence of a detectable resonance for the BF_2 ligand has much precedence in platinum boryl chemistry and is due to unresolved coupling to the platinum and phosphorous nuclei, and in this case additional unresolved coupling to the fluorine.[14] In the $^{31}P\{^1H\}$ NMR spectra, the two new products give rise to resonances at 48.1 (**3**, $^1J_{P-Pt} = 2828$ Hz) and 44.0 ppm (**4**, $^1J_{P-Pt} = 2595$ Hz), respectively. These data confirm the presence of two square-planar platinum(II) complexes in solution.[15] Moreover, and along with the typical resonances for the phosphorous-bound cyclohexyl groups, a significantly upfield-shifted triplet ($^2J_{H-P} = 24$ Hz) at −31.64 ppm flanked by ^{195}Pt satellites ($^1J_{H-Pt} = 1806$ Hz) is detected in the ^{1}H NMR spectra, indicating the presence of a platinum-bound hydrogen.

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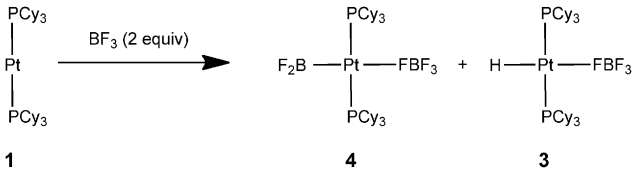
On account of these data, we proposed the formation of two products, *trans*-$[(Cy_3P)_2Pt(H)(FBF_3)]$ (**3**) and *trans*-$[(Cy_3P)_2Pt(BF_2)(FBF_3)]$ (**4**), according to Scheme 1. Monitoring the reaction mixture in benzene by multinuclear NMR spectroscopy disclosed an initial ratio between **3** and **4** of approximately 1:2. The formation of **3** in significant amounts is apparently a nonstoichiometric reaction (with regard to Scheme 1) but could be explained by formation of HF owing to hydrolysis and the unavoidable presence of trace amounts of water (for example on glass surfaces).[16] However, it should be noted that BF_3 is the most stable haloborane with respect to hydrolysis,[17] and under the same reaction conditions (very low temperatures, short reaction time, and rigorous inert conditions; see the Experimental Section) the related complex *trans*-$[(Cy_3P)_2Pt(BBr_2)(Br)]$ (**5**) was easily synthesized in our laboratories from **1** and the far more sensitive borane BBr_3.[12c] Nevertheless, to provide further information regarding a possible hydrolysis of BF_3 to HF and concomitant formation of HBF_4 we repeated the reaction in wet (that is, not dried but degassed) solvents, which led again to the formation of **3** and **4** in approximately the same initial ratio of 1:2 (see the Supporting Information). Therefore, hydrolysis processes seem not to be responsible for the presence of **3**.



Scheme 1. Reaction of **1** with gaseous BF_3 leading to the complexes **3** and **4**.

While mechanistic details for the formation of the latter species are yet elusive, it should be mentioned that the related haloboryl complexes *trans*-$[(Cy_3P)_2Pt(X)(BX_2)]$ convert slowly into the corresponding hydrido species *trans*-$[(Cy_3P)_2Pt(X)(H)]$ (**6**, X = Cl; **7**, X = Br) after elongated storage in solution and under strictly inert conditions. Likewise, in case of the fluoro species **4** and **3**, the initial ratio of 2:1 was found to be reversed after about 1 h at room temperature in solution, and continuously shifted towards full conversion of **4** into **3**. This indicates that the latter hydride complex represents the degradation product of the former boryl species. However, we could not verify the source of the hydrogen in Scheme 1. Of note, the ^1H NMR resonance of the hydric hydrogen in **4** is, compared to **6** or **7**,[15] significantly shifted towards higher field.

Further proof for the proposed constitution of **3** and **4** was provided when $[(Cy_3P)_2Pt]$ (**1**) was treated with two equivalents gaseous BF_3 in hexane. Here, immediate precipitation of a colorless solid occurred. Analysis by solid-state MAS-$^{31}P\{^1H\}$ NMR spectroscopy disclosed two resonances, again in a 1:2 ratio at 47.7 (**3**, $^1J_{P-Pt} = 2741$ Hz) and 42.0 ppm (**4**, $^1J_{P-Pt} = 2550$ Hz), which match those derived from NMR spectroscopy in solution. Likewise, elemental analysis supported the formulation of the solid as a mixture of **3** and **4** in a 1:2 ratio. Despite the instability of the difluoroboryl complex **4** in solution, we were able to grow single crystals suitable for X-ray analysis, which finally confirmed the oxidative addition of BF_3 to the zerovalent platinum center with formation of *trans*-$[(Cy_3P)_2Pt(BF_2)(FBF_3)]$ (**4**). It should be mentioned that the constitution of the degradation product *trans*-$[(Cy_3P)_2Pt(H)(FBF_3)]$ (**3**) was further confirmed by its alternative synthesis by reaction of $[(Cy_3P)_2Pt]$ (**1**) with HBF_4/Et_2O and comparison of the spectroscopic data of an authentic sample with those observed for **3** in the reaction mixture.

The fast degradation of *trans*-$[(Cy_3P)_2Pt(BF_2)(FBF_3)]$ (**4**) is somewhat surprising. Although difluoroboryl complexes are scarce, the few species such as *cis*-$[(Ph_3P)_2Pt(BF_2)_2]$ (**2**) or *fac*-$[(Ph_3P)_2Ir(CO)(BF_2)_3]$ (**8**), which were fully characterized in solution and in the solid state,[13] and $[(\eta^5\text{-}C_5Me_5)(Me_3P)Ir(H)(BF_2)]$ (**9**),[18] which was ascertained by multinuclear NMR spectroscopy, display no increased tendency to degrade under ambient conditions. Likewise, fluoroboryl complexes of Fe and Ru, which were characterized in solution, did not reveal an enhanced instability.[19] Thus, we sought to transfer *trans*-$[(Cy_3P)_2Pt(BF_2)(FBF_3)]$ (**4**) into a more stable derivative by replacing the presumably loosely coordinated BF_4^- ligand in *trans* position to the difluoroboryl group. To this end, the synthesis of **4** was carried out in the presence of NBu_4Cl, which indeed furnished the corresponding chloro complex *trans*-$[(Cy_3P)_2Pt(BF_2)(Cl)]$ (**10**) in good yields of 85% as a colorless solid. Compound **10** reveals a markedly increased stability in comparison to **4**, and showed no signs of degradation in benzene, toluene, or dichloromethane solutions over extended periods of time at ambient temperature and could be purified by filtration over a short plug loaded with alumina. The complex *trans*-$[(Cy_3P)_2Pt(BF_2)(Cl)]$ (**10**) was fully characterized in solution by multinuclear NMR spectroscopy, and data thus obtained match those of complexes of the type *trans*-$[(Cy_3P)_2Pt(BX_2)(Br)]$ (X = Br, NMe_2).[12c] However, it should be noted that **10**, in contrast to **4**, gave rise to a detectable, broad ^{11}B NMR resonance at 30 ppm, indicative to the BF_2 ligand (Table 1).

Single crystals of **4** and **10** suitable for X-ray diffraction analyses were obtained as described in the Experimental Section. Both complexes have a square-planar coordination with the two PCy_3 ligands in *trans* position (Figure 1). While the data confirm the constitution of **10**, a significant disorder of the two anionic ligands precludes a detailed discussion of the bond lengths of the fluoroboryl moiety. However, the Pt–B separation of 1.965(3) Å in **4** is comparable to that (1.963(6) Å) found in *trans*-$[(Cy_3P)_2Pt(BBr_2)(Br)]$ (**5**),[11] while the Pt–B distance in *cis*-$[(Ph_3P)_2Pt(BF_2)_2]$ (**2**) (2.052(6) Å) is about 0.09 Å greater, as expected for a mutual *trans* position of the boryl and the phosphine ligand.[20] All other structural parameters of the fluoroboryl ligand in **4** are in very good agreement with previous findings.

Table 1: NMR parameters of compounds **3**, **4** and **10**.[a]

	$\delta(^{31}P)$ [ppm]	$^1J_{P-Pt}$ [Hz]	$\delta(^{19}F)$ [ppm]	$^2J_{F-Pt}$ [Hz]	$\delta(^{11}B)$ [ppm]
4	44.0	2595	−33.3, *−167*	1230	–, *0.4*
3	48.1	2828	*−169*	–	*0.2*
10	30.7	2604	−24.8	958	30

[a] Values in *italics* are assigned to the BF_4 ligand.

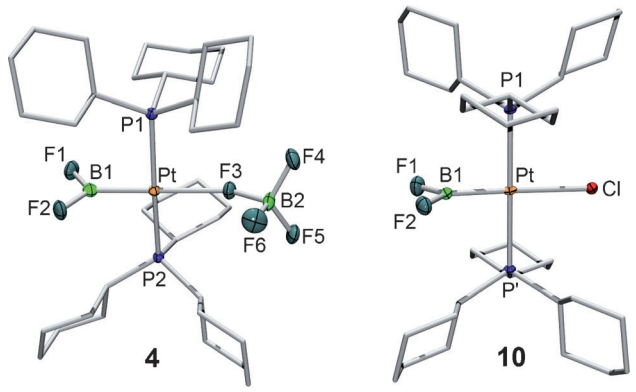


Figure 1. Molecular structures of **4** and **10**. Relevant bond lengths [Å] and angles [°]: **4**: Pt–P1 2.325(1), Pt–P2 2.327(1), Pt–B1 1.965(3), Pt–F3 2.272(2), B1–F1 1.327(4), B1–F2 1.336(3), B2–F3 1.441(3), B2–F4 1.379(4), B2–F5 1.369(4), B2–F6 1.375(4); P1-Pt-P2 170.1(1), P1-Pt-B1 90.6(1), P1-Pt-F3 90.0(1), F1-B1-F2 112.0(2), F3-B2-F4 107.0(2), F3-B2-F5 107.0(4), F3-B2-F6 107.0(2), F4-B2-F5 111.8(2), F4-B2-F6 111.4(2), F5-B2-F6 111.8(3). **10**: Pt–P2.3187(6)); symmetry-related positions ($-x$, $-y$, $-z$) are labeled with ′. Ellipsoids set at 50% probability; ellipsoids of the ligands, solvent molecules, and hydrogen atoms omitted for clarity.

For example, the B1–F separations (1.327(4)/1.336(3) Å) and F1-B1-F2 angle (112.0(2)°) correspond with those (1.327(6)/1.33(7) Å; 110.8(5)°) reported for **2**. The tetrafluoroborate ligand reveals distortion from ideal tetrahedral geometry owing to coordination to the Pt center. Thus, the B2–F3 separation of the bridging fluorine is increased (1.441(3) Å) compared to the mean separation of the terminal fluorine substituents (1.374 Å). Likewise, the F3-B2-F angles amount to about 107°, whereas the other F-B2-F angles are about 112°. Overall, the BF_4 ligand displays the typical structure for η^1-coordinated fluoroborates, as for example reported for $[(I\mathit{t}Bu)(\eta^3\text{-}C_3H_3)Pd(BF_4)]$ (**11**).[21]

Recent work has shown that the length of the Pt–Cl or the Pt–Br bond can be correlated with the degree of *trans* influence exerted by boryl ligands in square-planar platinum(II) complexes, but owing to disorder in the structure of **10**, this approach cannot be applied here.[12c,22] Therefore, density functional calculations were carried out to compare the title compounds with related complexes bearing different boryl ligands. The optimized structures of the complexes $[(Cy_3P)_2Pt(X)(Br)]$ (X = B*t*BuBr (**12**), BCl_2 (**13**), BBr_2 (**5**), BF_2 (**14**), and Bcat (**15**)) were used to assess the relative *trans* influence of the different boryl ligands (Table 2). According to the calculated bond lengths, the fluoroboryl ligand reveals a very weak *trans* influence, which is even smaller than that of the bromoboryl ligand and only slightly larger than that of the BCat ligand (Cat = catecholato). These results are in good agreement with previous findings, which indicated a decrease of the *trans* influence with increase of the electronegativity of the boron-bound substituents.[22]

Table 2: Selected bond lengths [Å] of DFT-optimized complexes.[a]

	12	13	5	14	15
Pt–Br	2.739	2.698	2.695	2.692	2.689
Pt–B	2.013	1.987	1.980	2.002	2.013

[a] DFT methods using the 6-31G(d,p) basis set for H, B, C, Cl, F, O, P, 6-311G(d,p) for Br, and "Stuttgart Relativistic Small Core" ECP Basis Set for Pt.

In summary, we have presented the first oxidative addition of one boron–fluorine bond of BF_3 to a transition metal. As the product of the oxidative addition (**4**) is not stable in solution, the fluoroboryl ligand could be preserved in a subsequent reaction rendering the complex to the more stable *trans*-chloro derivative **10**; single-crystal X-ray diffraction was applied to both complexes. Furthermore, the degradation product **3** could be obtained by an alternate reaction pathway. All of the complexes were examined by multinuclear NMR spectroscopy, both in the solid state and in solution, and by IR spectroscopy, elemental analysis, and DFT calculations.

Experimental Section

General considerations regarding the experimental procedures, X-ray diffraction, and computational studies are provided in the Supporting Information.

4: In a Schlenk flask equipped with a Teflon valve, **1** (100 mg, 0.13 mmol) was dissolved in hexane (5 mL), cooled to −196 °C, and the flask was evacuated. At the same time, a gas trap with two Teflon valves was filled with gaseous BF_3 (18 mg, 0.26 mmol). After melting of the reaction mixture, the BF_3 was immediately added by connection of the gas trap to the Schlenk flask (by opening the first Teflon valve) and finally the vacuum was equalized with argon (by opening the second valve of the gas trap). Under warming to room temperature, the mixture was stirred for 15 min; meanwhile a colorless precipitate was formed. After decanting off the solvent the precipitate was washed two times with hexane, all volatiles were removed in vacuo, yielding 102 mg of a colorless powder. The constitution of the product was determined by solid-state NMR spectroscopy as a 2:1 mixture of the product **4** and the degradation product **3**. Despite the instability in solution, a small amount of crystals suitable for X-ray diffraction could be obtained instantaneously after addition of BF_3 to a benzene solution of **1** in a Young NMR tube. The crystals were found after 1 h at room temperature.

^{1}H NMR (400.1 MHz, C_6D_6): $\delta = 2.53–2.41$ (m, 6H, *Cy*), 2.14–1.08 (m, 60H, *Cy*); ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): $\delta =$ 0.3 ppm; ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta = 35.4$ (vt, N = $|{}^1J_{P\text{-}C} + {}^3J_{P\text{-}C}| = 27$ Hz, C_1 *Cy*), 30.6 (s, $C_{3,5}$ *Cy*), 27.5 (vt, N = $|{}^2J_{P\text{-}C} + {}^4J_{P\text{-}C}| =$ 11 Hz, $C_{2,6}$ *Cy*), 26.8 ppm (s, C_4 *Cy*); ^{19}F{^{1}H} NMR (376.5 MHz, C_6D_6): $\delta = -33.3$ (vbr s, $^2J_{Pt\text{-}F} = 1230$ Hz), −167.0 ppm (vbr s); ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6): $\delta = 44.0$ ppm (s, $^1J_{Pt\text{-}P} = 2595$ Hz); ^{31}P HPDec/MAS NMR (162.0 MHz): $\delta = 42.0$ ppm (s, $^1J_{Pt\text{-}P} = 2550$ Hz). IR: 1147, 1215 cm^{-1} (BF_2), 1115, 1174 cm^{-1} (BF_4). C,H analysis calcd. [%] for a 2:1 mixture of $C_{36}H_{66}B_2F_6P_2Pt$ and $C_{36}H_{67}BF_4P_2Pt$: C 49.38, H 7.64; found: C 49.71, H 7.77.

3: In a Schlenk flask, **1** (100 mg, 0.13 mmol) was dissolved in 5 mL (Et_2O), and an excess of HBF_4 (1 mL, 50% in Et_2O) was added. After stirring for 30 min, all volatiles were removed in vacuo, the residue was extracted with toluene and again all volatiles were removed in vacuo yielding **3** (93.4 mg, 0.11 mmol, 85%) as a colorless powder.

^{1}H NMR (400.1 MHz, C_6D_6): $\delta = 2.29–2.20$ (m, 6H, *Cy*), 2.14–1.08 (m, 60H, *Cy*), −31.64 ppm (t, $^2J_{P\text{-}H} = 24$ Hz, $^1J_{Pt\text{-}H} =$ 1806 Hz); ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): $\delta = 0.2$ ppm; ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta = 34.8$ (vt, N = $|{}^1J_{P\text{-}C} + {}^3J_{P\text{-}C}| =$ 27 Hz, C_1 *Cy*), 30.9 (s, $C_{3,5}$ *Cy*), 27.5 (vt, N = $|{}^2J_{P\text{-}C} + {}^4J_{P\text{-}C}| = 11$ Hz, $C_{2,6}$ *Cy*), 26.8 ppm (s, C_4 *Cy*); ^{19}F{^{1}H} NMR (376.5 MHz, C_6D_6): $\delta =$ −169.0 ppm (vbr s); ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6): $\delta = 48.1$ ppm (s, $^1J_{Pt\text{-}P} = 2828$ Hz); ^{31}P HPDec/MAS NMR (162.0 MHz): $\delta =$

47.7 ppm (s, $^{1}J_{Pt-P} = 2741$ Hz). IR: 1113, 1169 cm^{-1} (BF_4). C,H analysis calcd. [%] for $C_{36}H_{67}BF_4P_2Pt$: C 51.25, H 8.00; found: C 50.90, H 8.04.

10: Using the same apparatus as in synthesis of **4**, complex **1** (100 mg, 0.13 mmol) and NBu_4Cl (36.7 mg, 0.13 mmol) were reacted with BF_3 (18 mg, 0.26 mmol) in toluene (5 mL). The mixture was stirred with warming to room temperature for 60 min. The reaction mixture was then filtered over a short plug with alumina (activity grade 1) and all volatiles were removed in vacuo. The colorless precipitate was washed twice with hexane, and again all volatiles were removed in vacuo, yielding **10** (88.4 mg, 0.11 mmol, 85%) as a colorless powder. Crystals suitable for X-ray diffraction were grown from a benzene solution at room temperature.

^{1}H NMR (400.1 MHz, C_6D_6): $\delta = 2.71-2.60$ (m, 6H, *Cy*), 2.23–2.15 (m, 12H, *Cy*), 1.81–1.20 (m, 48H, *Cy*); $^{11}B\{^{1}H\}$ NMR (128.4 MHz, C_6D_6): $\delta = 30$ ppm; $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6): $\delta = 35.8$ (vt, $N = |{}^{1}J_{P-C} + {}^{3}J_{P-C}| = 28$ Hz, C_1 *Cy*), 30.5 (s, $C_{3,5}$ *Cy*), 28.0 (vt, $N = |{}^{2}J_{P-C} + {}^{4}J_{P-C}| = 11$ Hz, $C_{2,6}$ *Cy*), 27.0 ppm (s, C_4*Cy*); $^{19}F\{^{1}H\}$ NMR (376.5 MHz, C_6D_6): $\delta = -24.8$ ppm (vbr s, $^{2}J_{Pt-F} = 958$ Hz); $^{31}P\{^{1}H\}$ NMR (162.0 MHz, C_6D_6): $\delta = 30.7$ ppm (s, $^{1}J_{Pt-P} = 2604$ Hz). IR: 1136, 1171 cm^{-1} (BF_2). C,H analysis calcd. [%] for $C_{36}H_{66}BClF_2P_2Pt$: C 51.46, H 7.92; found: C 52.12, H 8.11.

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