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Reactivity of Lewis Basic Platinum Complexes Towards Fluoroboranes

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Abstract: We herein report detailed investigations into the interaction of Lewis acidic fluoroboranes, for example BF_2Pf (Pf = perfluorophenyl) and BF_2Ar^F (Ar^F = 3,5-bis(trifluoromethyl)phenyl), with Lewis basic platinum complexes such as $[Pt(PEt_3)_3]$ and $[Pt(PCy_3)_2]$ (Cy = cyclohexyl). Two presumed Lewis adducts could be identified in solution and corresponding secondary products of these Lewis adducts were characterized in the solid state. Furthermore, the concept of frustrated Lewis pairs (FLP) was applied to the activation of ethene in the system $[Pt(BPf_3)(CH_2CH_2)(dcpp)]$ (dcpp = 1,3-bis(dicyclohexylphosphino)propane; Pf = perfluorophenyl). Finally, DFT calculations were performed to determine the interaction between the platinum-centered Lewis bases and the boron-centered Lewis acids. Additionally, several possible mechanisms for the oxidative addition of the boranes BF_3, BCl_3, and BF_2Ar^F to the model complex $[Pt(PMe_3)_2]$ are presented.

Keywords: density functional calculations · fluoroboranes · Lewis acids · transition metals

Introduction

In 1963, Shriver reported the reaction of the Lewis basic transition-metal complex $[Cp_2W(H)_2]$ (**1**; Cp = cyclopentadienyl) with BF_3,[1] presenting the first Lewis adduct of a borane with a transition metal, the complex $[Cp_2(H)_2W \rightarrow BF_3]$ (Figure 1; **2**). Until this finding, only Lewis adducts of boranes with main-group Lewis bases, such as amines, were known. After these preliminary results, several other related borane adducts with BCl_3 or B_2H_6 were presented by the same group.[2] These results kick-started investigations aimed at preparing complexes with dative interactions between Lewis basic metal complexes and Lewis acidic substrates, leading to reports of a number of complexes with BF_3 in the coordination sphere of metals such as rhodium or iridium.[3,4] The ability of early-transition-metal complexes to form dative bonds with BH_3 was also investigated.[5,6] Finally, the concept of metal-centered Lewis basicity was applied in the formation of so-called metal-only Lewis pairs (MOLPs).[7,8]

Eventually, the lack of structural data confirming the existence of the dative bond between the boron atom and the Lewis basic metal led to renewed interest in the postulated borane adducts. Thus, we reinvestigated the reactivity of **1** towards BF_3 and several other boranes, which led exclusively to zwitterionic or salt-like compounds such as $[Cp_2W(H)_3][BF_4]$ (Figure 1, **3**).[9–12] While these results experimentally disproved earlier claims of borane adducts of **1**, it should be noted that subsequent theoretical investigations supported the early work of Shriver and suggest that these complexes should be isolable.[13]

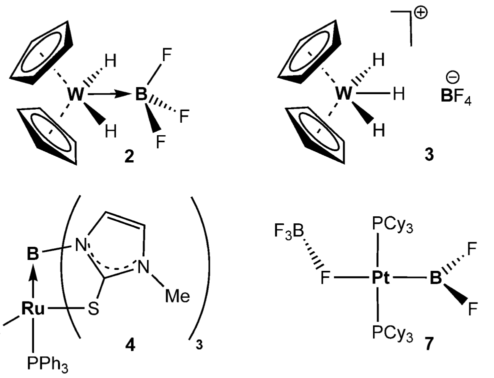

Figure 1. Postulated (**2**) and isolated examples (**4**) of dative bonding between Lewis basic transition metals, and identified byproducts (**3** and **7**).

However, experimental proof for the existence of dative bonds between boranes and Lewis basic transition-metal complexes was disclosed several years later by Hill and coworkers with the synthesis of a supported borane adduct of ruthenium in which the Lewis acidic center is linked to the metal base by a supporting covalent scaffold (Figure 1, **4**),[14] a concept that subsequently has been widely applied to many other borane complexes.[15–30]

Nevertheless, we conducted further experiments in our laboratory aimed at the structural characterization of a complex with an unsupported bond between a borane and a Lewis basic transition metal. To this end, we investigated the well-established complex $[Pt(PCy_3)_2]$ (**5**) in the presence of BF_3. No signs of formation of the adduct *trans*-

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[$(Cy_3P)_2Pt \rightarrow BF_3$] (**6**) could be observed even at low temperatures. Instead, oxidative addition of the very strong B−F bond was detected and the product *trans*-[$(Cy_3P)_2Pt(BF_2)(F \cdots BF_3)$] (**7**) was fully characterized.[31]

Results and Discussion

With these previous investigations and results in mind, we attempted to envisage how the best candidate for an unsupported borane–transition-metal interaction should look. Primarily, the borane should possess high Lewis acidity, which can be realized by σ-electron-withdrawing substituents at the boron center and by minimizing their π-donor ability. Furthermore, all substituents should feature strong or inert bonds that are not easily cleaved by transition metals. In our opinion, fluoroboranes with fluorinated aryl rings fulfill these requirements. One of the most widely used boranes is the borane BPf_3 (Pf = perfluorophenyl, **8**),[32–34] but in the presence of sterically encumbered Lewis bases, activation of the *para*-position of the Pf group is commonplace.[35] Therefore, we synthesized the fluoroborane BF_2Pf (**9**) as it is effectively the smallest Pf-substituted haloborane.

The synthesis of **9** has been previously reported in the literature, usually involving halogen exchange from starting materials such as BCl_2Pf (**10**).[36] We used a commutation reaction between BPf_3 (**8**) and BF_3, providing BF_2Pf (**9**) in a yield of 52 %. Borane **9** was identified by its NMR spectroscopic parameters (Table 1), for example, its $^{11}B\{^1H\}$ ($\delta = 22.2$ ppm) and $^{19}F\{^1H\}$ ($\delta = -73.8$ ppm for the fluorine atoms attached to the boron) resonances. Remarkably, no sign of the formation of $BFPf_2$ (**11**) was detected; therefore the remaining solid after the vacuum transfer was pure **8**, which then was reacted with new BF_3 to yield more **9**.

Table 1. NMR parameters of compounds **9**, **12**, **13**, and **15**.

	9	12	13	15
$^{11}B\{^1H\}$[a]	22.2	–	16.3	2.8
$^{19}F\{^1H\}$[a,b]	−73.8	–	−96.0	−134.8
$^{31}P\{^1H\}$[a,c]	–	41.8	0.3	−0.6
$^{31}P\{^1H\}$[a,d]	–		−2.0	−1.4
$^1J_{P\text{–}Pt}$[c,e]	–	4206	2441	2633
$^1J_{P\text{–}Pt}$[d,e]	–		2021	1984

[a] δ in ppm. [b] Fluorine atoms attached to the boron center. [c] Phosphine ligands in the *trans* position. [d] Phosphine ligands in the *cis* position. [e] Coupling constant in Hz.

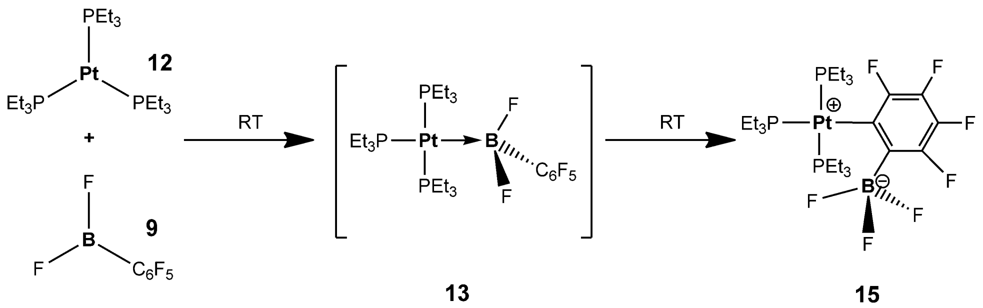
Reaction of the Lewis basic platinum complex [$Pt(PEt_3)_3$] (**12**) with equimolar amounts of **9** resulted in the formation of only one product, as determined by multinuclear NMR spectroscopy (Table 1). In the $^{31}P\{^1H\}$ NMR spectra, the resonance of the starting material ($\delta = 41.8$ ppm, $^1J_{P\text{–}Pt} = 4206$ Hz) could no longer be observed. Instead, two new signals were detected, one at $\delta = 0.3$ ppm with a $^1J_{P\text{–}Pt}$ coupling constant of 2441 Hz, and a less intense resonance at $\delta = -2.0$ ppm ($^1J_{P\text{–}Pt} = 2021$ Hz). The signal at $\delta = 0.3$ ppm appears as a doublet, due to a $^2J_{P\text{–}P}$ coupling constant of 23 Hz, whereas the other signal is detected as a multiplet. In the $^{11}B\{^1H\}$ NMR spectra, a resonance is detected at $\delta = 16.3$ ppm, shifted towards higher field by 6 ppm relative to that of the precursor (**9** = 22.2 ppm). Finally, in the $^{19}F\{^1H\}$ NMR spectra, four resonances are detected, as would be expected for such a Pt→B borane adduct. The signal at $\delta = -96.0$ ppm could be assigned to the two fluorine atoms bound to the boron, and the signals at $\delta = -130.2$, −149.6, and −162.9 ppm belong to the C_6F_5 substituent. These spectroscopic parameters all indicate the formation of the unsupported borane adduct [$(Et_3P)_3Pt \rightarrow BF_2Pf$] (**13**) in solution. However, another possibility would be a type of B−C σ coordination similar to the complex [$(Et_3P)_2Pt$(cyclo-{B(Mes)C(Mes)C(Ph)})] (**14**).[37]

Unfortunately, after several hours these resonances gradually diminished and a colorless microcrystalline solid formed in the NMR tube. Dissolving the solid in a more polar solvent and subjecting this to NMR spectroscopy indicated the formation of a new product (Table 1). The resonances in the $^{31}P\{^1H\}$ NMR spectra were located at $\delta = -0.6$ ($^1J_{P\text{–}Pt} = 2633$ Hz) and −1.4 ppm ($^1J_{P\text{–}Pt} = 1984$ Hz), whereas the coupling pattern of the more intense signal was still a doublet ($^2J_{P\text{–}P} = 24$ Hz). However, the resonance at $\delta = -1.4$ ppm now consisted of a triplet ($^2J_{P\text{–}P} = 24$ Hz) of doublets ($J = 10$ Hz) of doublets ($J = 4$ Hz). In the $^{19}F\{^1H\}$ NMR spectra, five signals were detected, whereby the resonance at $\delta = -134.8$ ppm revealed an approximate threefold higher intensity than the signals at $\delta = -112.9$, −134.1, −162.8, and −164.9 ppm. Surprisingly, the resonance at $\delta = -112.9$ ppm shows a characteristic platinum–fluorine coupling with a coupling constant of 386 Hz. The coupling patterns could be confirmed by the parameters derived from the $^{195}Pt\{^1H\}$ NMR spectra; the resonance at $\delta = -4757$ ppm appeared as a triplet ($^1J_{Pt\text{–}P} = 2633$ Hz) of doublets ($^1J_{Pt\text{–}P} = 1984$ Hz) of doublets ($^3J_{Pt\text{–}F} = 386$ Hz). Based on the resonance at $\delta = 2.8$ ppm in the $^{11}B\{^1H\}$ NMR spectra, the activation of an aromatic C−F bond leading to the zwitterionic compound [$(Et_3P)_3Pt(C_6F_4\text{-}2\text{-}BF_3)$] (**15**) was postulated (Scheme 1).

In order to confirm the postulated constitution, X-ray diffraction analysis of single crystals of **15** was performed (Figure 2). The molecular structure exhibits a square-planar arrangement at the platinum center with P−Pt distances of 233.2(2) to 236.8(2) pm and a C−Pt distance of 208.7(6) pm. The boron atom is coordinated in an almost ideal tetrahedral geometry with angles between 107.7(6) and 108.6(5)°.

Given that the borane BF_2Pf (**9**) appears to possess an aromatic C−F bond too reactive to allow isolation of the intermediate, the related fluoroborane BF_2Ar^F (**16**; Ar^F = 3,5-bis(trifluoromethyl)phenyl) was synthesized. Borane **16** can be obtained by the reaction of Me_3SnAr^F (**17**)[38] with BF_3 in a range of non-coordinating solvents like hexanes or toluene.

The reaction of **16** with [$Pt(PEt_3)_3$] (**12**) did not yield definite products, therefore the complex [$Pt(PCy_3)_2$] (**5**) was used. In an NMR tube charged with equimolar amounts of **5** and **16**, immediate formation of a new compound could be observed by the broad resonance at $\delta = 58$ ppm in the



Scheme 1. Reaction of the complex [Pt(PEt$_3$)$_3$] (**12**) and the borane BF$_2$Pf (**9**) to form the Lewis adduct [(Et$_3$P)$_3$Pt→BF$_2$Pf] (**13**) and subsequent formation of the zwitterionic complex [(Et$_3$P)$_3$Pt(C$_6$F$_4$-2-BF$_3$)] (**15**).

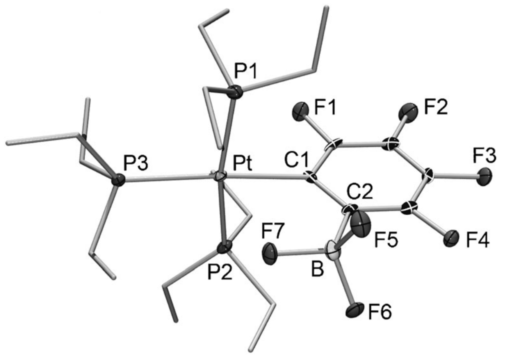
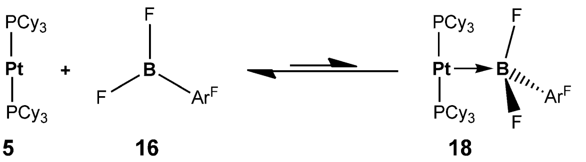


Figure 2. Molecular structure of [(Et$_3$P)$_3$Pt(C$_6$F$_4$-2-BF$_3$)] (**15**). Ellipsoids drawn at the 50% probability level; ellipsoids of the ligands and hydrogen atoms omitted for clarity. Relevant bond lengths [pm] and angles [°]: Pt–P1 233.8(2), Pt–P2 236.8(2), Pt–P3 233.2(2), Pt–C1 208.7(6), B–C2 162.7(9), B–F5 142.9(8), B–F6 140.8(8), B–F7 140.1(8); P1-Pt-P2 166.8(1), P1-Pt-P3 96.6(1), P2-Pt-P3 94.8(1), P1-Pt-C1 86.1(1), P2-Pt-C1 82.8(2), P3-Pt-C1 176.7(1), C2-B-F5 108.6(5), F5-B-F6 107.7(6), F5-B-F7 108.1(5), F6-B-F7 107.8(5).

^{31}P{^{1}H} NMR spectrum with a $^1J_{\text{Pt-P}}$ coupling constant of 4080 Hz (**5**; $\delta = 62.3$ ppm, 4164 Hz) and a resonance at $\delta = 12$ ppm in the ^{11}B{^{1}H} NMR spectrum (**16**: $\delta = 23.5$ ppm). In addition, no signs of decomposition of the either the borane or the complex **5** could be detected in the ^{19}F{^{1}H} and ^{1}H NMR spectra. Therefore, we propose that this complex is a Lewis adduct of the platinum-centered Lewis base **5** with the borane **16**, with the formula *trans*-[(Cy$_3$P)$_2$Pt→BF$_2$Ar^F] (**18**; Scheme 2).

However, the information gained from the ^{31}P{^{1}H} NMR spectrum indicates an equilibrium between complex **5** and the formed **18**, due to the fact that NMR spectroscopic parameters of **18** are quite similar to those of **5**. Additionally, the resonances in the ^{11}B{^{1}H}, ^{19}F{^{1}H} (for the fluorine atoms attached to the boron), and ^{31}P{^{1}H} NMR spectra are remarkably broadened. In order to favor **18** instead of **5** and **16**, we performed NMR spectroscopic experiments at variable temperatures. As a result, we were able to characterize **18** at −80 °C by the recorded ^{31}P{^{1}H} NMR spectrum in which a resonance of **18** was found at $\delta = 49.7$ ppm ($^1J_{\text{P-Pt}} = 3760$ Hz). Interestingly, the resonance appeared as a triplet due to the $^3J_{\text{P-F}}$ coupling of 18 Hz due to the two fluorine atoms attached to the Lewis acidic boron center (Table 2).



Scheme 2. Postulated equilibrium between the Lewis basic complex [Pt(PCy$_3$)$_2$] (**5**), the borane BF$_2$Ar^F (**16**), and the Lewis adduct *trans*-[(Cy$_3$P)$_2$Pt→BF$_2$Ar^F] (**18**).

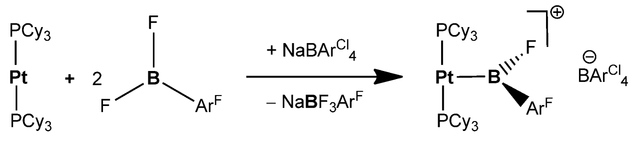
Table 2. NMR parameters of compounds **16**, **5**, **18**, and **19**.

	16	**5**	**18**	**19**
^{19}F{^{1}H}[a,b]	−87.8	–	−167	−20.5
^{31}P{^{1}H}[a]	–	62.3	49.7[c]	48.5
$^1J_{\text{P-Pt}}$[d]	–	4164	3760[c]	2631

[a] δ in ppm. [b] Fluorine atoms attached to the boron center. [c] Recorded at −80 °C. [d] Coupling constant in Hz.

In further experiments, we tried to shift the equilibrium towards **18** by adding additional equivalents of **16** to an equimolar solution of **5** and **16**. At a **5**/**16** ratio of 1:2, the resonance detected in the ^{31}P{^{1}H} NMR spectrum was located at about $\delta = 53$ ppm ($^1J_{\text{P-Pt}} = 3770$ Hz). At a ratio of 1:10, the detected resonance was located at $\delta = 46$ ppm ($^1J_{\text{P-Pt}} = 3230$ Hz). In addition, in the ^{19}F{^{1}H} NMR spectrum an unexpected resonance at $\delta = -46$ ppm was observed, together with the expected resonances at $\delta = -63.7$ (CF$_3$ groups) and −102 ppm (BF$_2$ moiety). Comparison of these ^{19}F{^{1}H} NMR resonances with those of the complex *trans*-[(Cy$_3$P)$_2$Pt(BF$_2$)(FBF$_3$)] (**6**, $\delta = -33.3$ ppm for the BF$_2$ ligand)[31] led us to the assumption that, in the reaction between **5** and **16**, an oxidative addition also takes place, however, in this case it seems to be reversible.

Using this Lewis base–Lewis acid system, we also observed an irreversible reaction analogous to the synthesis of T-shaped, cationic platinum–boryl complexes.[39,40] For this purpose, one equivalent of a halide abstraction reagent, Na[BAr$^{Cl}_4$] (Ar^{Cl} = 3,5-bis(trichloromethyl)phenyl), was added to a mixture of one equivalent of **5** and two equivalents of **16**, yielding the complex *trans*-[(Cy$_3$P)$_2$Pt(BFAr^F)][BAr$^{Cl}_4$] (**19**, Table 2, Scheme 3). In the ^{31}P{^{1}H} NMR spectrum the

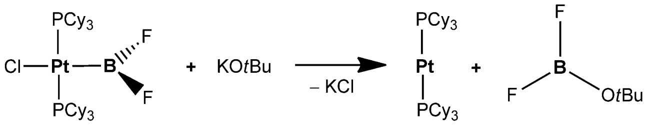


5 **16** **19**

Scheme 3. Reaction of [Pt(PCy$_3$)$_2$] (**5**) with two equivalents of BF$_2$Ar^F (**16**) and one equivalent of Na[BAr$^{Cl}_4$], yielding the complex *trans*-[(Cy$_3$P)$_2$Pt(BFAr^F)][BAr$^{Cl}_4$] (**19**).

resonance of **19** was located at $\delta = 48.5$ ppm ($^1J_{P-Pt} = 2631$ Hz), whereas the resonance appears as a doublet due to the $^3J_{P-F}$ coupling of 9 Hz with the boron-bound fluorine nucleus. In addition, the $^{19}F\{^1H\}$ NMR spectrum reveals a resonance at $\delta = -20.5$ ppm with a $^2J_{F-Pt}$ coupling constant of 637 Hz together with the resonance of the CF$_3$ groups at $\delta = -63.3$ ppm.

An alternative strategy for the synthesis of an unsupported metal-borane complex is the construction of the borane ligand directly in the coordination sphere of a suitable platinum complex. To this end, we treated the compound *trans*-[(Cy$_3$P)$_2$Pt(BF$_2$)Cl] (**20**)[31] with an equimolar amount of KO*t*Bu in a sealable NMR tube (Scheme 4).



20 **5** **21**

Scheme 4. Reaction of *trans*-[(Cy$_3$P)$_2$Pt(BF$_2$)Cl] (**20**) with one equivalent KO*t*Bu, yielding the free Lewis base [Pt(PCy$_3$)$_2$] (**5**) and the borane BF$_2$O*t*Bu (**21**).

Directly after addition of the KO*t*Bu, a new resonance was detected in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 62.3$ ppm ($^1J_{P-Pt} = 4164$ Hz), which was identified as the platinum(0) complex [Pt(PCy$_3$)$_2$] (**5**). In addition, the resonance of **20** ($\delta = 30.7$ ppm, $^1J_{P-Pt} = 2604$ Hz) remained for about five days at room temperature. Thus the reaction takes place very slowly and the other reaction product, borane BF$_2$O*t*Bu (**21**), could be identified by its $^{19}F\{^1H\}$ ($\delta = -139.4$ ppm) and $^{11}B\{^1H\}$ ($\delta = 16.1$ ppm) NMR spectra (Table 3). Interestingly, neither the platinum complex **5** nor the borane **21** show any sign of interaction or formation of the Lewis pair *trans*-[(Cy$_3$P)$_2$Pt→BF$_2$O*t*Bu] (**22**) and therefore can be regarded as a frustrated Lewis pair (FLP).[41]

To summarize, we were able to detect what appeared to be platinum–borane Lewis adducts [(Et$_3$P)$_3$Pt→BF$_2$Pf] (**13**) and *trans*-[(Cy$_3$P)$_2$Pt→BF$_2$Ar^F] (**18**), but were unable to isolate them. However, the formation of a FLP between [Pt(PCy$_2$)$_3$] (**5**) and BF$_2$O*t*Bu (**21**) could be an interesting approach to further investigate the properties of the herein presented complexes. The activation of small, unreactive molecules such as H$_2$, CO$_2$ or alkenes by FLPs[42] interested us due to the fact that in our systems the Lewis base is a transition-metal complex. We chose ethene for initial activation tests as it is not only a widely-used resource for industrial processes, but also a well-established ligand in transition metal chemistry.

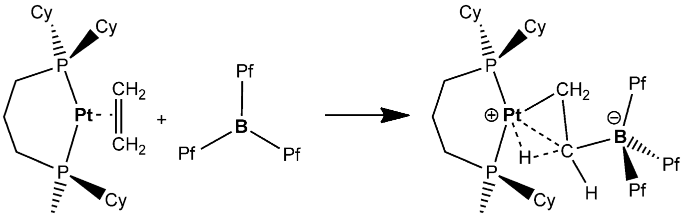
Table 3. NMR parameters of compounds **20**, **5**, and **21**.

	20	**5**	**21**
$^{11}B\{^1H\}$[a]	30	–	16.1
$^{19}F\{^1H\}$[a,b]	–24.8	–	–139.4
$^{31}P\{^1H\}$[a]	30.7	62.3	–
$^1J_{P-Pt}$[c]	2604	4164	–

[a] δ in ppm. [b] Fluorine atoms attached to the boron center. [c] Coupling constant in Hz.

After exchange of the argon atmosphere to an ethene atmosphere in a sealable NMR tube charged with a benzene solution of equimolar amounts of **5** and **16**, the complex *trans*-[(Cy$_3$P)$_2$Pt(C$_2$H$_4$)] (**23**)[43] is exclusively formed, identified by $^{31}P\{^1H\}$ NMR spectroscopy (**23**; $\delta = 41.3$ ppm, $^1J_{P-Pt} = 3604$ Hz). No signs of an activation process could be detected by NMR spectroscopy.

We extended this study to the use of borane BPf$_3$ (**8**), a common Lewis acid in FLP chemistry.[44] In addition, we used the compound [(dcpp)Pt(C$_2$H$_4$)] (**24**, dcpp = 1,3-bis(dicyclohexylphosphino)propane) that could be synthesized by reduction of *cis*-[PtCl$_2$(dcpp)] (**25**) under an atmosphere of ethene, as a Lewis base with a pre-coordinated small molecule, the ethene ligand. After addition of **8** to a suspension of **24** in benzene, immediate formation of a pale yellow solution was observed (Scheme 5). Analysis of the $^{31}P\{^1H\}$ NMR spectra revealed two resonances, one at $\delta = 26.5$ ppm and the other at $\delta = 16.8$ ppm (**24**; $\delta = 25.7$ ppm, $^1J_{P-Pt} = 3270$ Hz). The resonance at $\delta = 26.5$ ppm is a quartet of doublets due to $^2J_{P-P}$ and J_{P-B} coupling (both 7 Hz). Furthermore, the resonance is accompanied by ^{195}Pt satellites with a $^1J_{P-Pt}$ coupling of 4755 Hz. The second resonance at $\delta = 16.8$ ppm is split into a doublet ($^2J_{P-P} = 7$ Hz) in addition to a $^1J_{P-Pt}$ coupling constant of 2738 Hz. The $^{11}B\{^1H\}$ NMR spectra shows only one resonance located at $\delta = -13.5$ ppm, which lies in the established region for Lewis adducts of **5**. Further proof for the tetra-coordination at the boron atom is given by the $^{19}F\{^1H\}$ NMR spectra. Herein, three resonances are detected at $\delta = -131.0$, -162.0, and -166.3 ppm. All resonances indicate $^1J_{F-F}$ coupling whereas the resonance at $\delta = -131.0$ ppm could be assigned to the *ortho* fluorine atoms and the resonance at $\delta = -166.3$ ppm was assigned to the *meta* fluorine atoms. Therefore, the resonance at $\delta = -162.0$ ppm repre-



24 **8** **26**

Scheme 5. Reaction of [(dcpp)Pt(C$_2$H$_4$)] (**24**) with BPf$_3$ (**8**), resulting in the formation of the complex [(dcpp)Pt(BPf$_3$)(CH$_2$CH$_2$)] (**26**).

sents the fluorine atoms in *para* position. This pronounced shift with respect to the starting material **8** (resonance of the fluorine atoms in *para* postion: $\delta = -143.0$ ppm) provides further evidence for tetra-coordination of **8** (Table 4).

Table 4. NMR parameters of compounds **8**, **24**, and **26**.

	8	**24**	**26**
$^{11}B\{^{1}H\}$[a]	59.4	–	−13.5
$^{19}F\{^{1}H\}$[a,b]	−130.1, −143.0, −164.4	–	−131.0, −162.0, −166.3
$^{31}P\{^{1}H\}$[a]	–	25.7	26.5, 16.8
$^{1}J_{P\text{–}Pt}$[c]	–	3270	4755, 2738

[a] δ in ppm. [b] Fluorine atoms in *ortho*, *para* and *meta* positions. [c] Coupling constant in Hz.

Finally, the ^{1}H NMR spectra reveals, in addition to the resonances of the dcpp ligand, a doublet at $\delta = -0.05$ ppm with a coupling constant of 33 Hz in addition to a characteristic $^{1}J_{H\text{–}Pt}$ coupling of 66 Hz. The origin of the smaller coupling was determined by $^{1}H\{^{31}P\}$ NMR, wherein the resonance at $\delta = -0.05$ ppm appeared as a singlet.

These spectroscopic data suggest an agostic interaction between the ethene ligand and the platinum center. However, in order to determine the chemical structure of the newly formed complex, X-ray diffraction analysis of a suitable single crystal was performed. On the basis of these results, the formula [(dcpp)Pt(BPf_3)(CH_2CH_2)] (**26**) could be assigned (Figure 3).

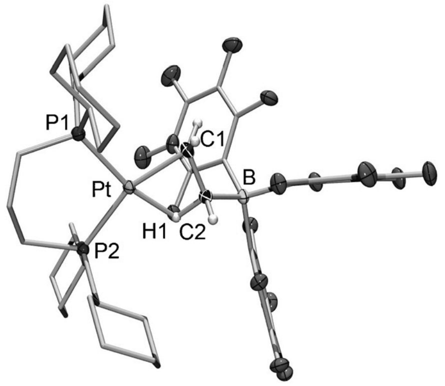


Figure 3. Molecular structure of [(dcpp)PtBPf_3(CH_2CH_2)] (**26**). Ellipsoids drawn at the 50 % probability level; the hydrogen atoms of the ethylene bridge are refined without constraints, and the ellipsoids of the ligands, solvent molecules and all other hydrogen atoms are omitted for clarity. Relevant bond lengths [pm] and angles [°]: Pt–P1 222.5(1), Pt–P2 230.7(1), Pt–C1 207.3(4), Pt–H1 175(3), Pt–C2 232.2(4), C1–C2 152.2(5), B–C2 167.4(5), B–C3 165.6(5), B–C4 166.2(5), B–C5 165.5(5); P1-Pt-P2 99.2(1), P1-Pt-C1 99.7(1), P2-Pt-C1 160.1(1), P1-Pt-C2 138.5(1), P2-Pt-C2 121.6(1), C1-Pt-C2 39.0(2), Pt-C2-B 136.1(2), C1-C2-B 119.4(3), C2-B-C3 104.2(3), C2-B-C4 110.2(3), C2-B-C5 112.5(3), C3-B-C4 114.4(3), C3-B-C5 113.2(3), C4-B-C5 102.4(3).

Due to the aforementioned agostic interaction in the *trans* position to the P1 atom, the Pt–P1 bonding distance (222.5(1) pm) is about 8 pm shorter than the Pt–P2 distance (230.7(1) pm). This pronounced difference in the bonding distances is also reflected in the smaller coupling constants between platinum and P2 ($^{1}J_{P2\text{–}Pt} = 2738$ Hz) and in contrast to the large $^{1}J_{P1\text{–}Pt}$ coupling (4755 Hz). However, the overall coordination at the platinum center is square-planar with an angular sum of 395.5(5)°. Hereby, the P2-Pt-C2 (121.6(1)°) and the C1-Pt-C2 (39.0(2)°) angles reveal the most pronounced deviance from ideal square-planarity (90°). The boron is coordinated in a tetrahedral geometry with C-B-C angles between 102.4(3) and 114.3(3)°.

In order to further examine the interactions between platinum complexes and fluoroboranes, theoretical calculations were performed using the functionals B3LYP and M05-2X. The first functional was chosen due to its frequent application in the calculation of bond dissociation enthalpies (BDE) in Lewis pairs with transition metals,[45–48] the second was chosen due to its ability to reproduce weak interactions in Lewis pairs, as demonstrated for example in the calculation of the FLP [(I*t*Bu)(BPf_3)] (I*t*Bu = *N*,*N*′-bis(*tert*-butyl)-imidazol-2-ylidene, $\mathbf{27}_{opt}$).[49] The free formation energies ($\Delta\Delta G$) of the complexes [$(Et_3P)_3Pt \rightarrow BF_2Pf$] ($\mathbf{13}_{opt}$), *trans*-[$(Cy_3P)_2Pt \rightarrow BF_2Ar^F$] ($\mathbf{18}_{opt}$) and *trans*-[$(Cy_3P)_2Pt \rightarrow BF_2OtBu$] ($\mathbf{22}_{opt}$) were determined by comparing the Gibbs free energies (at 298.15 K) of the free Lewis acids and bases with the associated Lewis pairs (Figure 4 and Table 5).

Interestingly, the $\Delta\Delta G_{B3LYP}$ values are all positive, in a range from $+21$ kJ mol^{-1} for $\mathbf{13}_{opt}$ and $+33$ kJ mol^{-1} for $\mathbf{18}_{opt}$ up to $+57$ kJ mol^{-1} for $\mathbf{22}_{opt}$, therefore indicating endergonic reactions for all investigated systems. This is in stark contrast to the $\Delta\Delta G_{M05\text{-}2X}$ values. Here, the complexes $\mathbf{13}_{opt}$ and $\mathbf{18}_{opt}$ indicate, with values for the $\Delta\Delta G_{M05\text{-}2X}$ of -32 kJ mol^{-1} and -40 kJ mol^{-1}, respectively, an exergonic reaction. However, the $\Delta\Delta G_{M05\text{-}2X}$ value for the compound $\mathbf{22}_{opt}$ amounts only to -3 kJ mol^{-1}, being almost neutral. This is in good agreement with the experimental results in which the Lewis adducts **13** and **18** could be detected, whereas no evidence for the Lewis adduct **22** could be observed. These overall lower values for $\Delta\Delta G_{M05\text{-}2X}$ can be explained by the difference between the two functionals. Hereby, the functional M05-2X takes weak interactions into account and therefore predicts stronger bonds in Lewis pairs on the whole. This functional seems, in this case, to be more adequate in representing the experimental results.

Furthermore, a possible mechanistic pathway for the oxidative addition of BF_2Ar^F ($\mathbf{16}_{opt}$) to the model complex [Pt(PMe_3)$_2$] ($\mathbf{5}_{mod}$) was investigated (Scheme 6). For comparison, mechanisms for the oxidative addition of BF_3 and BCl_3 to $\mathbf{5}_{mod}$ were determined. These calculations were exclusively performed with the functional M05-2X, due to the aforementioned results. Initially, the pathway found for the oxidative addition of BF_3 at $\mathbf{5}_{mod}$ reveals formation of the Lewis adduct *trans*-[$(Me_3P)_2Pt \rightarrow BF_3$] ($\mathbf{6}_{mod}$), which has a free energy about -54 kJ mol^{-1} below the starting materials. The actual transition state of the oxidative addition ($\mathbf{6}_{TS}$) is $+225$ kJ mol^{-1} higher in energy than the starting materials and can be described as a BF_3 moiety coordinated side-on by one B–F bond with the two phosphine ligands still in *trans* position to each other. However, the product of the oxidative addition, the complex *trans*-[$(Me_3P)_2Pt(BF_2)F$] ($\mathbf{28}_{mod}$) is still about $+42$ kJ mol^{-1} higher in energy than the

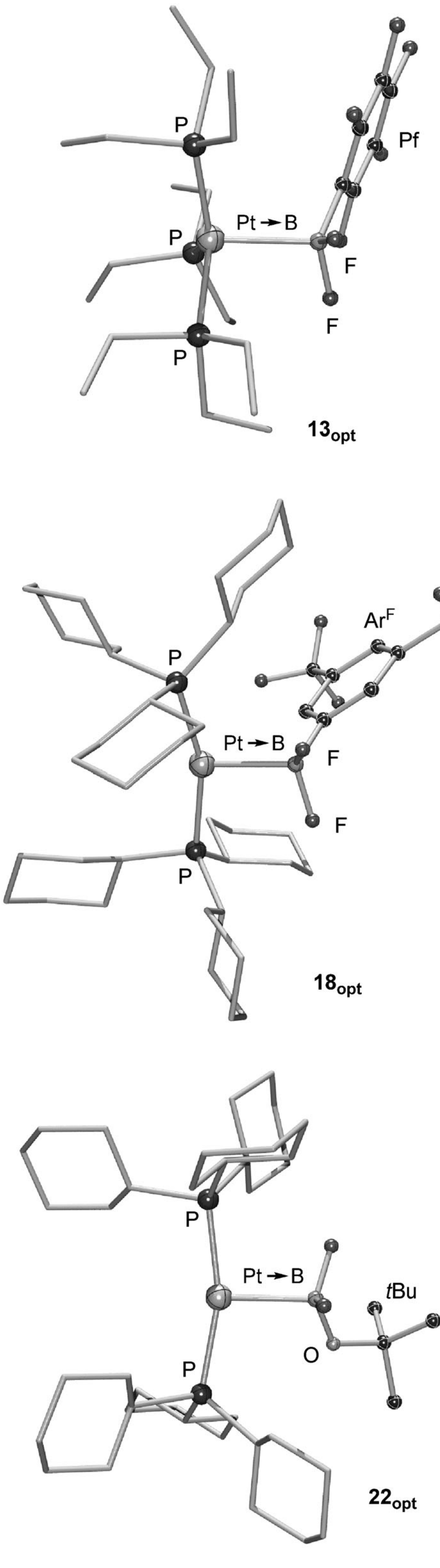


Figure 4. Optimized gas-phase structures of the Lewis adducts $[(Et_3P)_3Pt{\rightarrow}BF_2Pf]$ ($\mathbf{13_{opt}}$), *trans*-$[(Cy_3P)_2Pt{\rightarrow}BF_2Ar^F]$ ($\mathbf{18_{opt}}$), and *trans*-$[(Cy_3P)_2Pt{\rightarrow}BF_2O\mathit{t}Bu]$ ($\mathbf{22_{opt}}$).

starting materials. Addition of another equivalent of BF_3 furnishes the complex *trans*-$[(Me_3P)_2Pt(BF_2)(FBF_3)]$ ($\mathbf{7_{mod}}$), now having a free energy of $-96\ kJ\,mol^{-1}$ below the starting materials and making the overall reaction exergonic. This is in agreement with experiment, in which case only the complex *trans*-$[(Cy_3P)_2Pt(BF_2)(FBF_3)]$ (**7**) was observed.

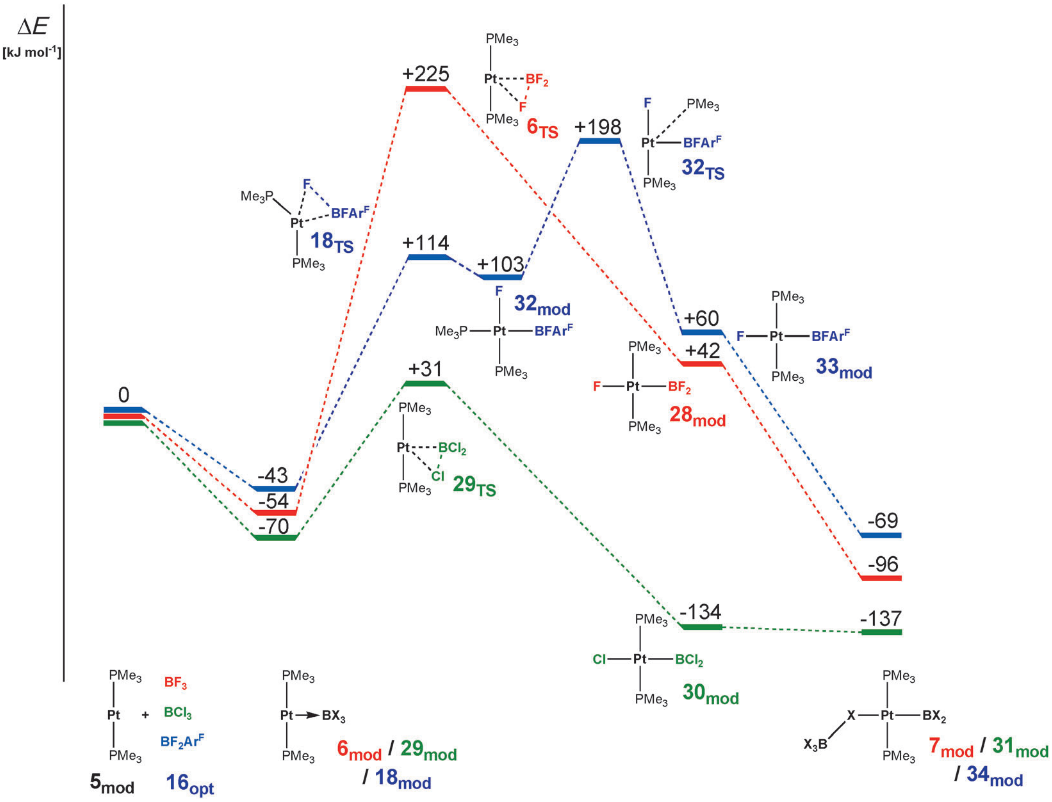
Table 5. Selected calculated parameters for complexes $\mathbf{13_{opt}}$, $\mathbf{18_{opt}}$, and $\mathbf{22_{opt}}$.

	$\mathbf{13_{opt}}$	$\mathbf{18_{opt}}$	$\mathbf{22_{opt}}$
$\Delta\Delta H_{B3LYP}$[a]	−44	−33	0
$\Delta\Delta H_{M05\text{-}2X}$[a]	−104	−99	−54
$\Delta\Delta G_{B3LYP}$[a]	+21	+33	+57
$\Delta\Delta G_{M05\text{-}2X}$[a]	−32	−40	−3

[a] Enthalpies and Gibbs free energies (at 298.15 K) in $kJ\,mol^{-1}$.

For comparison, calculation of the mechanistic pathway of the oxidative addition of BCl_3 to $\mathbf{5_{mod}}$ revealed similar steps. At first, the Lewis adduct *trans*-$[(Me_3P)_2Pt{\rightarrow}BCl_3]$ ($\mathbf{29_{mod}}$) was determined to have a free energy of $-70\ kJ\,mol^{-1}$ below the starting materials, whereas the side-on coordinated transition state ($\mathbf{29_{TS}}$) is $+31\ kJ\,mol^{-1}$ higher in energy than the starting materials. In contrast to the oxidative addition of BF_3, the product *trans*-$[(Me_3P)_2Pt(BCl_2)Cl]$ ($\mathbf{30_{mod}}$) is exergonic by a free energy of $-134\ kJ\,mol^{-1}$ below the starting materials. Additionally, the calculated geometry of a product of the addition of two equivalents of BCl_3, the complex *trans*-$[(Me_3P)_2Pt(BCl_2)(ClBCl_3)]$ ($\mathbf{31_{mod}}$), has a free energy only about $-3\ kJ\,mol^{-1}$ lower than $\mathbf{30_{mod}}$. This again is in agreement with the experimental investigations, wherein no signs of addition of BCl_3 to the complex *trans*-$[Pt(BCl_2)Cl(PCy_3)_2]$ (**30**) were observed.

To conclude the mechanistic studies herein, we determined a possible mechanism for the oxidative addition of BF_2Ar^F ($\mathbf{16_{opt}}$) to $[Pt(PMe_3)_2]$ ($\mathbf{5_{mod}}$). The first step, the formation of the Lewis adduct *trans*-$[(Me_3P)_2Pt{\rightarrow}BF_2Ar^F]$ ($\mathbf{18_{mod}}$) again is similar to the reaction of BF_3 and BCl_3. The complex $\mathbf{18_{mod}}$ has a free energy of about $-43\ kJ\,mol^{-1}$ with respect to its starting materials. The geometry in the transition state ($\mathbf{18_{TS}}$) again reveals a side-on coordination of one B−F bond, with a free energy of approximately $+114\ kJ\,mol^{-1}$ with respect to the starting materials. However, the two phosphine ligands are now mutually *cis*. This stands in contrast to the transition states found for the other two calculated pathways. Another difference is the complex *cis*-$[(Me_3P)_2Pt(BFAr^F)F]$ ($\mathbf{32_{mod}}$) that is found as an intermediate on the reaction path lying about $+103\ kJ\,mol^{-1}$ above the starting materials. As the next step, a *cis–trans* isomerization could be identified, resulting in the complex *trans*-$[(Me_3P)_2Pt(BFAr^F)F]$ ($\mathbf{33_{mod}}$). Complex $\mathbf{33_{mod}}$ has a free energy of $+60\ kJ\,mol^{-1}$ above the starting materials. Interestingly, the geometry in the transition state ($\mathbf{32_{TS}}$) reveals a mutually-*cis* arrangement of the fluorine and boryl ligands with one phosphine ligand dissociated, overall with a free energy $+95\ kJ\,mol^{-1}$ higher than the complex $\mathbf{32_{mod}}$. This is in contrast to the findings for the oxidative addition of B−H bonds to platinum complexes, in which hexacoordinate transition states were identified.[50] However, as in the oxidative addition of BF_3, further addition of a second equivalent of the borane $\mathbf{16_{opt}}$ furnishes the complex *trans*-$[Pt(BFAr^F)(FBF_2Ar^F)(PMe_3)_2]$ ($\mathbf{34_{mod}}$), which has a free energy of



Scheme 6. Possible mechanistic pathways for the oxidative addition of BF_3, BCl_3, and BF_2Ar^F (**16**$_{\mathbf{opt}}$) to the model complex $[Pt(PMe_3)_2]$ (**5**$_{\mathbf{mod}}$).

$-69\,kJ\,mol^{-1}$ with respect to the starting materials. This mechanism is in good agreement with the experimental results, in which a reversible oxidative addition of **16** to the complex **5** was found. Thus the overall more shallow energy barriers for the reaction of BF_2Ar^F (**16**$_{\mathbf{opt}}$), in contrast to the reaction of BF_3, could be an explanation for the reversibility. In addition, the *cis* configuration in the intermediate *cis*-$[(Me_3P)_2Pt(BFAr^F)F]$ (**32**$_{\mathbf{mod}}$) enables an easy reductive elimination and therefore facilitates the reverse reaction of the oxidative addition.

Conclusion

We report herein detailed investigations into the interaction of Lewis acidic fluoroboranes with Lewis basic platinum complexes. Two presumed Lewis adducts were identified in solution, but these were not able to be characterized in the solid state. However, secondary products of these Lewis adducts were fully characterized.

Additionally, the concept of frustrated Lewis pairs (FLP) was applied by the activation of ethene in the system $[(dcpp)Pt(CH_2CH_2)BPf_3]$ (**26**). Furthermore, DFT calculations were performed to determine the interaction between the platinum-centered Lewis bases and the boron-centered Lewis acids. Finally, possible mechanisms for the oxidative addition of BF_3, BCl_3 and BF_2Ar^F (**16**$_{\mathbf{opt}}$) to $[Pt(PMe_3)_2]$ (**5**$_{\mathbf{mod}}$) are presented.

Experimental Section

Theoretical calculations: The computations were performed using DFT methods, applying the functionals B3LYP and M05-2X, using the 6-31G-(d,p) basis set for H, B, C, F, Cl, O, P, and the Stuttgart RSC ECP basis set for Pt. More detailed information concerning the calculations, including Cartesian coordinates of the optimized geometries, can be found in the Supporting Information.

General considerations: All manipulations were performed either under dry argon or in vacuo using standard Schlenk line and glovebox techniques.[51] Solvents were purified by standard procedures and stored under Argon over molecular sieves. BPf_3 (**8**),[34] $[Pt(PEt_3)_4]$,[52] Me_3SnAr^F (**17**),[38] $[Pt(PCy_3)_2]$ (**5**),[53] and *trans*-$[(Cy_3P)_2Pt(BF_2)Cl]$ (**20**)[31] were prepared according to previously published procedures. NMR spectra in solution were acquired on a BrukerAvance 400 (^1H: 400.1 MHz, $^{11}B\{^1H\}$: 128.4 MHz, $^{13}C\{^1H\}$: 100.6 MHz, $^{19}F\{^1H\}$: 376.5 MHz, $^{31}P\{^1H\}$: 162.0 MHz, $^{195}Pt\{^1H\}$: 86.0 MHz) NMR spectrometer. NMR spectra were referenced to external $SiMe_4$ (^1H, ^{13}C), $[BF_3{\cdot}Et_2O]$ (^{11}B), $CFCl_3$ (^{19}F), 85% H_3PO_4 (^{31}P), and $Na_2[PtCl_6]$ in D_2O (^{195}Pt). Microanalyses were performed on an EuroEA3000 elemental analyzer.

Synthesis of BF_2Pf (9): BPf_3 (**8**, 0.300 g, 586 μmol) was dissolved in toluene (10 mL) in a Schlenk flask equipped with a Teflon valve and the Argon atmosphere was exchanged by an atmosphere of BF_3. After stirring at 80 °C for three days all volatiles were transferred from the remaining **8** and the excess BF_3 was removed by degassing of the colorless solution. The yield of **9** was determined by $^{19}F\{^1H\}$ NMR spectroscopy, by adding **8** (5.1 mg, 10 μmol) to 0.1 mL of the yielded solution of **9**. The ratio hereby was 0.9 (**9**) to 1 (**8**), resulting in an overall yield of 52% (0.198 g, 917 μmol). $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): $\delta = 22.2$ ppm (br s, FWHM ≈ 130 Hz); $^{19}F\{^1H\}$ NMR (376.5 MHz, C_6D_6): $\delta = -73.8$ (br s, FWHM ≈ 350 Hz, B*F*$_2$), −128.2 (m, *o-F*), −144.5 (m, *p-F*), −161.5 ppm (m, *m-F*).

Synthesis of [(Et$_3$P)$_3$Pt→BF$_2$Pf] (13): In a J. Young NMR tube, one equivalent of PEt$_3$ was removed in vacuo at 60 °C from the complex [Pt(PEt$_3$)$_4$] (30.0 mg, 45 μmol). The resulting complex [Pt(PEt$_3$)$_3$] (**12**, 24.7 mg, 45 μmol) was then dissolved in C$_6$D$_6$ (0.1 mL) and a solution of BF$_2$Pf (**9**, 0.50 mL, 0.09 M in toluene, 45 μmol) was added. ^{11}B{^{1}H} NMR (128.4 MHz, C$_6$D$_6$): $\delta = 16.3$ ppm (br s, FWHM ≈ 150 Hz); ^{19}F{^{1}H} NMR (376.5 MHz, C$_6$D$_6$): $\delta = -96.0$ (vbr s, FWHM ≈ 380 Hz, B*F*$_2$), −130.2 (m, *o-F*), −149.6 (m, *p-F*), −162.9 ppm (m, *m-F*); ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$): $\delta = 0.3$ (d, $^2J_{P-P} = 23$ Hz, $^1J_{P-Pt} = 2441$ Hz), −2.0 ppm (br m, $^1J_{P-Pt} = 2021$ Hz).

Synthesis of [(Et$_3$P)$_3$Pt(C$_6$F$_4$-2-BF$_3$)] (15): In a J. Young NMR tube, one equivalent PEt$_3$ was removed in vacuo at 60 °C from the complex [Pt(PEt$_3$)$_4$] (30.0 mg, 45 μmol). The resulting complex [Pt(PEt$_3$)$_3$] (**12**, 24.7 mg, 45 μmol) was then dissolved in C$_6$D$_6$ (0.1 mL) and a solution of BF$_2$Pf (**9**, 0.50 mL, 0.09 M in toluene, 45 μmol) was added. After 6 h at RT colorless crystals started to grow in the NMR tube. After 18 h at RT the solvent was decanted off and the residue was washed with hexanes (1 mL) to yield **15** as a colorless, microcrystalline solid (13.0 mg, 17 μmol, 37 %). Crystals suitable for X-ray diffraction were obtained by layering a solution of **15** in dichloromethane with hexanes at RT. ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$): $\delta = 2.02$–1.90 (m, 6H, P(C*H*$_2$CH$_3$)$_3$), 1.80–1.52 (m, 12H, P(C*H*$_2$CH$_3$)$_3$), 1.27–1.16 (m, 9H, P(CH$_2$C*H*$_3$)$_3$), 1.11–0.99 ppm (m, 18H, P(CH$_2$C*H*$_3$)$_3$); ^{11}B{^{1}H} NMR (128.4 MHz, CD$_2$Cl$_2$): $\delta = 2.8$ ppm (br s, FWHM ≈ 130 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 17.4$ (dt, $^1J_{C-P} = 28$ Hz, $^3J_{C-P} = 4$ Hz, P(*C*H$_2$CH$_3$)$_3$), 16.9 (vtd, $N = {}^1J_{C-P} + {}^3J_{C-P} = 34$ Hz, $^3J_{C-P} = 2$ Hz, P(*C*H$_2$CH$_3$)$_3$), 8.2 (d, $^2J_{C-P} = 2$ Hz, P(CH$_2$*C*H$_3$)$_3$), 8.1 ppm (bs, P(CH$_2$*C*H$_3$)$_3$); ^{19}F{^{1}H} NMR (376.5 MHz, CD$_2$Cl$_2$): $\delta = -112.9$ (m, $^3J_{F-Pt} = 386$ Hz, *o-F*), −134.1 (m, *p-F*), −134.8 (br s, FWHM ≈ 140 Hz, B*F*$_3$), −162.8 (m, *m-F*); −164.9 ppm (dd, $^1J_{F-F} = 24$ Hz, $^1J_{F-F} = 24$ Hz, *m-F*); ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$): $\delta = -0.6$ (d, $^2J_{P-P} = 24$ Hz, $^1J_{P-Pt} = 2633$ Hz,), −1.4 ppm (tdd, $^2J_{P-P} = 24$ Hz, $^3J_{P-F} = 10$ Hz, $^4J_{P-F} = 4$ Hz, $^1J_{P-Pt} = 1984$ Hz,); ^{195}Pt{^{1}H} NMR (106.9 MHz, CD$_2$Cl$_2$): $\delta = -4757$ ppm (tdd, $^1J_{Pt-P} = 2633$ Hz, $^1J_{Pt-P} = 1984$ Hz, $^3J_{Pt-F} = 386$ Hz); elemental analysis calcd (%) for C$_{24}$H$_{45}$BF$_7$P$_3$Pt (M_w = 765.430): C 37.66, H 5.93; found: C 38.08, H 6.02.

Synthesis of BF$_2$Ar^F (16): Me$_3$SnAr^F (**17**, 500 mg, 1.33 mmol) was dissolved in hexanes (5 mL) in a Schlenk flask equipped with a Teflon valve and the Argon atmosphere was exchanged for an atmosphere of BF$_3$. After stirring at 60 °C for 18 h all volatiles were transferred and the spare BF$_3$ was removed by degassing of the yielded colorless solution. The yield of **16** was determined by ^{1}H and ^{19}F{^{1}H} NMR spectroscopy by adding norbornene (4.7 mg, 50 μmol) and BPf$_3$ (**8**, 5.1 mg, 10 μmol), respectively, to a portion of the obtained solution of **16** (0.1 mL). The ratio hereby was 1 (**16**) to 2.2 (norbornene) in the ^{1}H NMR spectrum, or 2.3 (**16**) to 1 (**8**) in the ^{19}F{^{1}H} NMR spectrum, resulting in an overall yield of 86 % (0.299 g, 1.14 mmol). ^{1}H NMR (400.1 MHz, C$_6$D$_6$): $\delta = 7.76$ (s, 1H, *p-H*), 7.73 ppm (s, 2H, *o-H*); ^{11}B{^{1}H} NMR (128.4 MHz, C$_6$D$_6$): $\delta = 23.5$ ppm (br s, FWHM ≈ 190 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$): $\delta = 135.7$ (m), 131.7 (q, $^2J_{C-F} = 34$ Hz), 127.0 (sept, $^3J_{C-F} = 4$ Hz), 123.5 ppm (q, $^1J_{C-F} = 272$ Hz, *C*F$_3$); ^{19}F{^{1}H} NMR (376.5 MHz, C$_6$D$_6$): $\delta = -63.0$ (s, C*F*$_3$), −87.8 ppm (br s, FWHM ≈ 110 Hz, B*F*$_2$).

Synthesis of *trans*-[(Cy$_3$P)$_2$Pt→BF$_2$Ar^F] (18): In a J. Young NMR tube, [Pt(PCy$_3$)$_2$] (**5**, 34.7 mg, 46 μmol) was dissolved in C$_6$D$_6$ (0.4 mL) and a solution of BF$_2$Ar^F (**16**, 0.20 mL, 0.23 M in hexanes, 46 μmol) was added. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 300 K): $\delta = 8.54$ (s, 2H, *o-H*), 7.85 (s, 1H, *p-H*), 2.27–1.29 ppm (m, 66H, Cy); ^{11}B{^{1}H} NMR (160.5 MHz, C$_7$D$_8$, 300 K): $\delta = 11.5$ ppm (vbr s, FWHM ≈ 260 Hz); ^{19}F{^{1}H} NMR (376.5 MHz, C$_6$D$_6$, 300 K): $\delta = -62.7$ (s, C*F*$_3$), −167.0 ppm (vbr s, FWHM ≈ 300 Hz, B*F*$_2$Ar^F); ^{31}P{^{1}H} NMR (202.5 MHz, C$_7$D$_8$, 300 K): $\delta = 58$ (br s, FWHM ≈ 60 Hz, $^1J_{P-Pt} = 4080$ Hz); ^{31}P{^{1}H} NMR (202.5 MHz, C$_7$D$_8$, 193 K): $\delta = 49.7$ ppm (t, $^3J_{P-F} = 19$ Hz, $^1J_{P-Pt} = 3790$ Hz).

Ratio of **5**/**16** of 1:2: ^{11}B{^{1}H} NMR (128.4 MHz, C$_6$D$_6$): $\delta = 16$ ppm (vbr s, FWHM ≈ 490 Hz); ^{19}F{^{1}H} NMR (376.5 MHz, C$_6$D$_6$): $\delta = -62.6$ (s, C*F*$_3$), −101 ppm (vbr s, FWHM ≈ 1600 Hz, B*F*$_2$Ar^F); ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$): $\delta = 53$ ppm (vbr s, $^1J_{P-Pt} = 3770$ Hz).

Ratio of **5**/**16** of 1:10: ^{11}B{^{1}H} NMR (128.4 MHz, C$_6$D$_6$): $\delta = 18$ ppm (vbr s, FWHM ≈ 680 Hz); ^{19}F{^{1}H} NMR (376.5 MHz, C$_6$D$_6$): $\delta = -46$ (vbr s, B*F*Ar^F), −63.7 (s, C*F*$_3$), −102 ppm (vbr s, FWHM ≈ 1100 Hz, B*F*$_2$Ar^F); ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$): $\delta = 46$ ppm (vbr s, $^1J_{P-Pt} = 3230$ Hz).

Synthesis of *trans*-[Pt(BFAr^F)(PCy$_3$)$_2$][BAr$^{Cl}{}_4$] (19): [Pt(PCy$_3$)$_2$] (**5**, 69.5 mg, 92 μmol) was dissolved in fluorobenzene (3 mL) and a solution of BF$_2$Ar^F (**16**, 0.80 mL, 0.23 M in hexanes, 0.18 mmol) was added at RT. Then, Na[BAr$^{Cl}{}_4$] (48.8 mg, 92 μmol) was added and the reaction mixture was stirred for 15 min at RT. After filtering and removing of all volatiles in vacuo the crude product was washed with toluene (5 mL) and hexanes (5 mL) to yield **19** as a yellow solid (55.9 mg, 35 μmol, 38 %). ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$): $\delta = 8.46$ (s, 2H, *o-H*), 8.19 (s, 1H, *p-H*), 7.06–7.00 (m, 12H, BAr$^{Cl}{}_4$), 2.24–1.15 ppm (m, 66H, Cy); ^{11}B{^{1}H} NMR (128.4 MHz, CD$_2$Cl$_2$): $\delta = -7.0$ ppm (s, $^1J_{B-C} = 49$ Hz); ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 165.1$ (q, $^1J_{C-B} = 49$ Hz, BAr$^{Cl}{}_4$), 135.9 (m, BAr^F), 133.5 (q, $^2J_{C-B} = 2$ Hz, BAr$^{Cl}{}_4$), 133.3 (q, $^3J_{C-B} = 4$ Hz, BAr$^{Cl}{}_4$), 132.4 (q, $^2J_{C-F} = 34$ Hz, BAr^F), 127.4 (m, BAr^F), 123.4 (s), 123.3 (q, $^1J_{C-F} = 273$ Hz, *C*F$_3$), 35.4 (vt, $N = {}^1J_{C-P} + {}^3J_{C-P} = 27$ Hz, C$_1$ *Cy*), 30.6 (s, C$_{3,5}$ *Cy*), 27.4 (vt, $N = {}^2J_{C-P} + {}^4J_{C-P} = 12$ Hz, C$_{2,6}$ *Cy*), 26.1 ppm (s, C$_4$ *Cy*); ^{19}F{^{1}H} NMR (376.5 MHz, CD$_2$Cl$_2$): $\delta = -20.5$ (br s, FWHM ≈ 70 Hz, $^2J_{F-Pt} = 637$ Hz, B*F*Ar^F), −63.3 ppm (s, C*F*$_3$); ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$): $\delta = 48.5$ (d, $^2J_{P-F} = 9$ Hz, $^1J_{P-Pt} = 2631$ Hz); elemental analysis calcd (%) for C$_{68}$H$_{81}$B$_2$Cl$_8$F$_7$P$_2$Pt·C$_6$H$_6$ (M_w = 1671.772): C 53.17, H 5.25; found: C 52.76, H 5.21.

Synthesis of BF$_2$O*t*Bu (21): *trans*-[(Cy$_3$P)$_2$Pt(BF$_2$)Cl] (**20**, 10.0 mg, 12 μmol) and KO*t*Bu (1.3 mg, 12 μmol) were dissolved in C$_6$D$_6$ (0.6 mL) in a J. Young NMR tube. After 5 days at RT the conversion to [Pt(PCy$_3$)$_2$] (**5**), KCl and **21** was complete as determined by the absent resonances of the starting materials. ^{1}H NMR (400.1 MHz, C$_6$D$_6$): $\delta = 1.39$ ppm (s); ^{11}B{^{1}H} NMR (128.4 MHz, C$_6$D$_6$): $\delta = 16.1$ ppm (br s, FWHM ≈ 180 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$): $\delta = 72.4$ (s, *C*-(CH$_3$)$_3$), 30.4 ppm (s, C(*C*H$_3$)$_3$); ^{19}F{^{1}H} NMR (376.5 MHz, C$_6$D$_6$): $\delta = -139.4$ ppm (br s, FWHM ≈ 200 Hz).

Synthesis of [PtCl$_2$(dcpp)] (25): [Pt(cod)Cl$_2$] (0.187 g, 500 μmol) was suspended in toluene (10 mL) and dcpp (1.0 mL of a 0.5 M solution in benzene, 500 μmol) was added. After stirring for 30 min at RT all volatiles were removed in vacuo and the brownish residue was washed with pentane (2×10 mL) to yield **25** as a colorless solid (0.334 g, 475 μmol, 95 %). ^{1}H NMR (400.1 MHz, CDCl$_3$): $\delta = 2.48$–1.04 ppm (m, 50H); ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): $\delta = 8.1$ ppm (s, $^1J_{P-Pt} = 3458$ Hz).

Synthesis of [(dcpp)Pt(C$_2$H$_4$)] (24): [(dcpp)PtCl$_2$] (**25**, 0.120 g, 171 μmol) was suspended in THF (5 mL) and the argon atmosphere was exchanged with an ethene atmosphere followed by slow addition of a sodium naphthalide solution (0.33 M in THF, 1.04 mL, 0.34 mmol). After stirring for 10 min at RT all volatiles were removed in vacuo, the off-white residue was extracted with dichloromethane (10 mL) and filtered. After again removing all volatiles in vacuo the residue was washed with pentane (2×5 mL) to yield **24** as a colorless solid (98.3 mg, 149 μmol, 87 %). ^{1}H NMR (400.1 MHz, C$_6$D$_6$): $\delta = 2.33$–0.91 (m, 50H), 2.25 ppm (d, $^3J_{H-P} = 3$ Hz, $^2J_{H-Pt} = 57$ Hz, 4H); ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$): $\delta = 25.7$ ppm (s, $^1J_{P-Pt} = 3270$ Hz).

Synthesis of [(dcpp)Pt(CH$_2$CH$_2$BPf$_3$)] (26): In a J. Young NMR tube [(dcpp)Pt(C$_2$H$_4$)] (**24**, 19.8 mg, 30 μmol) was suspended in C$_6$D$_6$ (0.6 mL) and BPf$_3$ (**8**, 15.4 mg, 30 μmol) was added, thus providing a pale yellow solution. After removing all volatiles in vacuo and washing the residue with hexanes (1 mL), **26** was obtained as a colorless solid (28.6 mg, 25 μmol, 83 %). Crystals suitable for X-ray diffraction could be gained by layering a solution of **26** in benzene with hexanes at RT. ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$): $\delta = 2.08$–1.58 (m, 30H), 1.40–1.00 (m, 20H), −0.05 ppm (vbr d, FWHM ≈ 20 Hz, 2H, $^2J_{H-P} = 31$ Hz, $^1J_{H-Pt} = 66$ Hz), ^{11}B{^{1}H} NMR (128.4 MHz, CD$_2$Cl$_2$): $\delta = -13.5$ ppm (s, FWHM ≈ 20 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 148.7$ (dm, $^1J_{C-F} = 246$ Hz), 138.9 (dm, $^1J_{C-F} = 248$ Hz), 137.1 (dm, $^1J_{C-F} = 251$ Hz), 37.8–18.7 ppm (dcpp and C$_2$H$_4$); ^{19}F{^{1}H} NMR (376.5 MHz, CD$_2$Cl$_2$): $\delta = -131.0$ (d, $^1J_{F-F} = 23$ Hz, *o-F*), −162.0 (t, $^1J_{F-F} = 20$ Hz, $^1J_{F-F} = 23$ Hz, *p-F*), −166.3 ppm (dd, $^1J_{F-F} = 23$ Hz, $^1J_{F-F} = 20$ Hz, *m-F*); ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$): $\delta = 26.5$ (dq, $^2J_{P-P} = 7$ Hz, $^3J_{P-B} = 7$ Hz, $^1J_{P-Pt} = 4755$ Hz), 16.8 ppm (d, $^2J_{P-P} = 7$ Hz, $^1J_{P-Pt} = 2738$ Hz); elemental analysis calcd (%) for C$_{47}$H$_{54}$BF$_{15}$P$_2$Pt·$\frac{1}{2}$ C$_6$H$_6$ (M_w = 1210.824): C 49.60, H 4.74; found: C 49.92, H 4.85.

Crystal structure determination: The crystal data of **15** and **26** were collected on a Bruker X8APEX diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package[51] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealized geometric positions, except the hydrogen atoms of the ethene ligand in **26**, which also were refined.

Crystal data for 15: $C_{24}H_{45}BF_7P_3Pt$, $M_r = 765.41$, colorless block, $0.610 \times 0.427 \times 0.172\ mm^3$, orthorhombic space group $P2_12_12_1$, $a = 9.8891(4)$, $b = 16.4502(6)$, $c = 18.3510(6)$ Å, $V = 2985.30(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.703\ g\,cm^{-3}$, $\mu = 4.918\ mm^{-1}$, $F(000) = 1520$, $T = 102(2)$ K, $R_1 = 0.0391$, $wR^2 = 0.0661$, 5938 independent reflections [$2\theta \leq 52.74°$] and 325 parameters.

Crystal data for 26: $C_{109}H_{123}B_2F_{30}P_4Pt_2$, $M_r = 2538.75$, colorless block, $0.34 \times 0.32 \times 0.24\ mm^3$, tetragonal space group $I\bar{4}$, $a = 30.581(8)$, $b = 30.581(8)$, $c = 11.352(3)$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 90.00°$, $V = 10617(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.588\ g\,cm^{-3}$, $\mu = 2.793\ mm^{-1}$, $F(000) = 5092$, $T = 100(2)$ K, $R_1 = 0.0267$, $wR^2 = 0.0496$, 10792 independent reflections [$2\theta \leq 52.68°$] and 679 parameters.

CCDC929469 (**15**) and 929470 (**26**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Acid–Base Interactions

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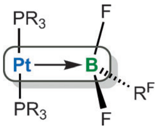
Reactivity of Lewis Basic Platinum Complexes Towards Fluoroboranes



Still elusive: Several attempts to yield the elusive, unsupported Lewis adduct between a Lewis basic transition-metal complex and a Lewis acidic borane are presented, including NMR spectroscopic characterization at low temperatures, isolation of secondary products and detailed DFT calculations (see figure).