

#### Article

## Reactivity of Tetrahalo- and Difluorodiboranes(4) Towards Lewis-Basic Platinum(0): Bis(boryl), Borylborato and Doubly Boryl-Bridged Platinum Complexes

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## Reactivity of Tetrahalo- and Difluorodiboranes(4) Towards Lewis-Basic Platinum(0): Bis(boryl), Borylborato and Doubly Boryl-Bridged Platinum Complexes

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**ABSTRACT:** The reaction of tetrahalodiboranes(4)  $B_2F_4$ ,  $B_2Cl_4$  and  $B_2Br_4$  with a Lewis basic platinum(0) complex led to isolation of *cis*-bisdifluoroboryl complex *cis*-[(Cy<sub>3</sub>P)<sub>2</sub>Pt(BF<sub>2</sub>)<sub>2</sub>] (1) and novel borylborato complexes *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pt{B(X)-BX<sub>3</sub>}] (2: X = Cl; 3: X = Br), respectively. The *trans*-influence of the borylborato group was found to be one of the strongest ever observed experimentally. Furthermore, the reactivity of little-explored diaryldifluorodiboranes(4) F<sub>2</sub>B–BMes<sub>2</sub> and the new derivative F<sub>2</sub>B–BAn<sub>2</sub> (An = 9-anthryl) towards a range of platinum(0) complexes was investigated. Reactions with relatively non-bulky platinum(0) complexes led to the formation of unsymmetrical *cis*-bis(boryl) complexes *cis*-[(R<sub>3</sub>P)<sub>2</sub>Pt(BF<sub>2</sub>)(BMes<sub>2</sub>)] (6: R = Me; 7: R = Et), as well as the first example of a fourfold unsymmetrical bis(boryl) complexes [{(*i*Pr<sub>3</sub>P)Pt(BF<sub>2</sub>)(BMes<sub>2</sub>)] (12). Use of a more bulky Pt complex provided access to unprecedented dinuclear bis(boryl) complexes [{(*i*Pr<sub>3</sub>P)Pt}<sub>2</sub>(µ-BF<sub>2</sub>)(µ-BAr<sub>2</sub>)] (8: Ar = Mes; 9: Ar = An), which feature two different bridging (µ<sub>2</sub>) boryl ligands.

#### INTRODUCTION

Since the introduction of  $B_2Cl_4$  in 1925 by Stock,<sup>1</sup> diboranes(4) have become an immensely useful class of compounds in organic and inorganic chemistry and have already proven their potential as synthetic precursors in many applications, e.g. functional materials and pharmaceuticals. In particular, the installation of boryl functional groups into organic substrates has been of major interest over the last 20 years, leading to the preparation of a diverse range of substrates for Suzuki-Miyaura coupling reactions and the installation of a wide range of functional groups.<sup>2</sup> Of major importance for this transition-metal (TM)-catalyzed functionalization is research on low-valent transition metal compounds, which are key intermediates in B–C bond formation reactions.<sup>3</sup> Similarly, the formation of a *cis*-bis(boryl) species by oxidative addition of a B-B bond to a metal center is a key step of the catalytic diboration of organic substrates, and insertion of low-valent transition metal fragments into boron-halide bonds is used for the preparation of transition metal boryl species.<sup>4</sup> The known synthetic routes to boryl complexes are oxidative addition of B-H, B-B and B-X bonds, salt elimination from haloboranes or rearrangement of dinuclear boryloxycarbyne complexes.<sup>4</sup> While these reactions have been used to prepare a wide range of transition metal boryl complexes, the homologated variant of boryl complexes – diboran(4)yl complexes (A, Figure 1) of the type  $[L_xM-B(X)-BX_2]$  – are limited to only a few examples derived from diaryl- ( $B_2X_2Ar_2$ ; Ar = Mes, Dur; X = Cl, Br) or diamino ( $B_2X_2(NMe_2)_2$ ; X = Cl, Br, I) diboranes.<sup>5</sup>



Figure 1. Selected transition metal complexes synthesized using diboranes(4).

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Over the last 35 years, a large variety of transition metal complexes with distinct bonding modes have been prepared starting from diborane(4) precursors. In addition to symmetrical and unsymmetrical bis(boryl) complexes (**B**, Figure 1),<sup>6</sup> double oxidative addition of  $B_2(NMe_2)_2I_2$  at platinum,<sup>5c</sup> complexes with bridging boryl groups between two metal centers (**C**, Figure 1)<sup>7</sup> and the coordination of a metal in a H-B-B-H cavity of sp<sup>3</sup>-sp<sup>3</sup> diboranes have been published.<sup>8</sup> *Kleeberg* and coworkers also very recently isolated bis- $\mu$ -boryl-bridged complexes [(*i*Pr<sub>3</sub>P)Cu-BDmab]<sub>2</sub> (Dmab = 1,2-(NMe)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**D**, Figure 1) and [(1,2-C<sub>6</sub>H<sub>4</sub>(Ph<sub>2</sub>P)<sub>2</sub>)Cu-BPin]<sub>2</sub> (Pin = (OC-Me<sub>2</sub>)<sub>2</sub>), starting from unsymmetrical diboranes(4).<sup>9</sup>

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Our interest in the discovery of new bonding modes of diboranes at TM centers led us to consider the little-explored families of diaryldifluorodiboranes(4), which show an unusual 1,1'-substitution pattern,<sup>10</sup> and tetrahalodiboranes ( $B_2X_4$ ; X = F, Cl, Br, I). Tetrahalodiboranes feature historically difficult preparation methods.<sup>11</sup> Our continuing interest in the use of tetrahalodiboranes for the preparation of boron-boron multiple bonds<sup>12</sup> led us to develop simple solution-phase syntheses of  $B_2X_4$  (X = F, Cl, I) starting from  $B_2Br_4$ , making these species more synthetically accessible.<sup>13</sup> In contrast to well-studied diboranes(4), such as bis(pinacolato)-, bis(neopentaneglycolato)- and bis(catecholato)diborane, the only known attempts to react tetrahalodiboranes with TM fragments were made by Norman, Marder and coworkers<sup>14</sup> around the turn of the millennium, and very recently by our group.<sup>15</sup> The former work led to isolation of two products of B-B bond oxidative addition (*cis*-[Pt(BF<sub>2</sub>)<sub>2</sub>L<sub>2</sub>],  $L_2 = 2$  PPh<sub>3</sub>, Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>) as well as an oxidative addition / disproportionation product with Vaska's complex: (fac, trans- $[Ir(BF_2)_3(CO)L_2])$ .<sup>14</sup> Earlier this year we reported the isolation of the diplatinum(II) complex  $[{(Cy_3P)(I_2B)Pt}_2(\mu_2;\eta^3:\eta^3 B_2I_4$ ] (E, Figure 1), supported by the bridging diboranyl dianion ligand  $[B_2I_4]^{2-}$ , which was prepared by addition of  $B_2I_4$  to trans-[PtI(BI<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>].<sup>15</sup>

The work presented herein details our reactivity studies of these two little-studied families of diboranes(4) towards  $Pt^0$  complexes. While in some cases we observed formation of the somewhat expected oxidative addition of the B–B bond, other reactions led to the discovery of a number of novel coordination modes of boron-containing ligands, including neutral and anionic complexes with  $\eta^1$ -borylborato ligands, and dinuclear, doubly-boryl-bridged complexes.

#### **RESULTS AND DISCUSSION**

**Reactivity of** [( $Cy_3P$ )<sub>2</sub>Pt] towards  $B_2X_4$ . As shown by Norman, Marder and coworkers,  $B_2F_4$  reacts with platinum and iridium complexes with activation of the B–B bond.<sup>14</sup> Due to the difficult preparation of  $B_2F_4$ ,<sup>11f</sup> which involves gas-phase syntheses and requires specialized apparatus, the coordination chemistry of this reagent was not explored further. We thus set out to develop a more convenient synthetic protocol for the generation of  $B_2F_4$ . Our simple synthesis of the double dimethylsulfide adduct of  $B_2Br_4$ ,<sup>13</sup> reported recently, led us to attempt its halide exchange with fluoride sources LiF and SbF<sub>3</sub>. Treatment of  $B_2Br_4$ (SMe<sub>2</sub>)<sub>2</sub> with either LiF or SbF<sub>3</sub> led to bromide/fluoride exchange along with dissociation of the dimethyl sulfide donors, providing  $B_2F_4$  (Scheme 1). This synthesis makes the industrially-relevant tetrafluorodibo-

rane(4)<sup>16</sup> easily accessible from commercially available starting materials via solution phase syntheses with standard Schlenk apparatus.





Scheme 1. Top: Formation of cis-[(Cy<sub>3</sub>P)<sub>2</sub>Pt(BF<sub>2</sub>)<sub>2</sub>] (1) and borylborato complexes *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pt{B(X)–BX<sub>3</sub>}] (2: X = Cl; 3: X = Br). Bottom: Crystallographically-determined solid-state structures of 1 and 2. Atomic displacement ellipsoids depicted at the 50% probability level and omitted for the ligand periphery. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for 1: Pt1–P1 2.3902(10), Pt–B1 2.049(4), B1–F1 1.344(4), B1–F2 1.344(4), P1-Pt-P1' 108.82(5), B1-Pt-B1' 71.8(2), P1-Pt-B1 90.00(11), F1-B1-F2 110.3(3). The molecular structure of 2 exhibited disorder of the B(Cl)–BCl<sub>3</sub> unit in a 64:36 ratio. The major orientation is shown; however, detailed discussion of the bond lengths and angles is not possible.

 $B_2F_4$  was subsequently condensed on the transition metal Lewis base [Pt(PCy<sub>3</sub>)<sub>2</sub>] at -78 °C and the reaction was monitored by <sup>31</sup>P{<sup>1</sup>H}, <sup>11</sup>B and <sup>19</sup>F NMR spectroscopy ( $\delta_P = 33.8$  $({}^{1}J_{P-Pt} = 1615 \text{ Hz}) \text{ ppm}; \delta_{B} = 47 \text{ (s) ppm}; \delta_{F} = -12.5 \text{ (br t, } {}^{2}J_{F-Pt}$ = 1044 Hz) ppm). The NMR spectroscopic data of the main product in the reaction mixture was consistent with those of Norman, Marder and coworkers and clearly indicated formation of the bis(boryl) complex  $cis-[(Cy_3P)_2Pt(BF_2)_2]$  (1, Scheme 1).<sup>14</sup> The complex decomposes upon crystallization, precluding its full spectroscopic characterization. However, the structure of 1 was confirmed by multinuclear NMR techniques and X-ray diffraction analysis. Single crystals of 1 suitable for X-ray diffraction were grown by crystallization from dichloromethane. The platinum center is coordinated in a square-planar fashion and the Pt-B bond distances (2.049(4) Å) are nearly identical to those of the *cis*-bis(boryl)platinum complexes synthesized by Norman, Marder and coworkers

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 $(cis-[Pt(BF_2)_2L_2], L_2 = 2PPh_3 (Pt-B: 2.058(6) Å), Ph_2P(CH_2)_4PPh_2 (Pt-B: 2.044(6) Å).^{14}$ 

Having both  $B_2Cl_4$  and  $B_2Br_4$  in hand,<sup>13</sup> we were also eager to test their reactions with  $[Pt(PCy_3)_2]$ . Due to the increasing lability of B-X bonds upon going from B-F to B-Cl and B-Br, we expected that oxidative addition of the B-X bond might be favored over that of the B-B bond. Mixing hexane solutions of  $[Pt(PCy_3)_2]$  and  $B_2X_4$  (X = Cl, Br) at -78 °C led to precipitation of yellow solids 2 and 3 (Scheme 1). Complexes 2 and 3 were found to decompose at ambient temperatures in solution; therefore, NMR spectra were obtained at approximately -40 °C. These compounds showed single resonances in their <sup>31</sup>P NMR spectra (**2**:  $\delta_{\rm P} = 44.8 \ (^{1}J_{\rm P-Pt} = 3175 \text{ Hz});$  **3**:  $\delta_{\rm P} =$ 42.0 ( ${}^{1}J_{P-Pt} = 3160 \text{ Hz}$ )) reminiscent of the signals of cationic T-shaped boryl-diphosphine Pt complexes (e.g.  $[(Cy_3P)_2Pt(BBrFc)][BAr_4]^{17}$  (Fc = ferrocenyl; Ar<sup>F</sup> = 3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>);  $\delta_P$  = 41.7 (<sup>1</sup>J<sub>P-Pt</sub> = 2914 Hz)). Furthermore, the <sup>11</sup>B NMR spectrum of each complex showed two strongly separated resonances (2:  $\delta_B = 67$  (s), 5.4 (s); 3:  $\delta_B = 66$  (s), -5.0 (s)) indicating the presence of both three- and fourcoordinate boron atoms. Solid-state <sup>31</sup>P VACP/MAS NMR (VACP = variable amplitude cross polarization; MAS = magic angle spinning) ( $\delta = 48$  ( ${}^{1}J_{P-Pt} = 3160$  Hz)) and  ${}^{11}B$ VACP/MAS NMR ( $\delta = 67, 3$ ) were performed on solid 2, indicating that the solution structure of 2 is preserved in the solid state.

Single crystals of **2** suitable for X-ray diffraction were grown from toluene, allowing us to describe the structures of **2** and **3** as those shown in Scheme 1, namely as zwitterionic Pt complexes bearing highly unusual borylborato ligands (-B(X)BX<sub>3</sub>; X = Cl, Br) with a trigonal-planar boron atom bound to both the platinum center and a second, tetrahedral boron atom. The molecular structure of **2** was found to have a disorder of the B<sub>2</sub>Cl<sub>4</sub> unit in a 64:36 ratio and the major orientation is shown in Scheme 1.

Compound **2** can also be prepared using  $B_2Cl_4(SMe_2)_2$ ; however, the reactions of  $B_2Br_4(SMe_2)_2$  or  $B_2I_4(SMe_2)_2$  with [Pt(PCy<sub>3</sub>)<sub>2</sub>] did not lead to the analogous borylborato complexes. Tetrachlorodiborane(4) bis-adducts with stronger main group Lewis bases (*e.g.* PMe<sub>3</sub>) were found to be inert towards the platinum complex (see Supporting Information for the synthesis of  $B_2Cl_4(PMe_3)_2$ ).

Marder, Lin and Braunschweig have demonstrated that the *trans*-influence of boryl ligands can be gauged by comparison of the X-Pt bond length *trans* to the boryl group in complexes of the type  $trans-[(Cy_3P)_2PtX\{BX(R)\}]$ .<sup>4c,19</sup> To gain information about the trans-influence of the -B(X)BX3 ligand, compound 2 was reacted with  $[N(nBu)_4]X$  (X = Cl, Br) to transfer a halide to the platinum center (Scheme 2). The <sup>11</sup>B NMR spectra of the isolated compounds (4: X = Cl; 5: X = Br)showed two broad singlets slightly shifted to low field compared to the resonances of 2 (4:  $\delta_B = 78$ , 10; 5:  $\delta_B = 69$ , 6) while their <sup>31</sup>P{<sup>1</sup>H} NMR spectra show similar signals (4:  $\delta_P$  = 42.7 ( ${}^{1}J_{\text{P-Pt}} = 3215 \text{ Hz}$ ; **5**:  $\delta_{\text{P}} = 43.5 ({}^{1}J_{\text{P-Pt}} = 3216 \text{ Hz})$ ) with slightly larger  ${}^{1}J_{P-Pt}$  coupling constants, consistent with a small increase in electron density at the Pt center. Complexes 4 and 5 are temperature sensitive and decompose in solution at ambient temperature. Likely due to the higher lability of its B-Br bonds, we were unable to isolate corresponding halideaddition complexes derived from 3. Nevertheless, <sup>11</sup>B and

<sup>31</sup>P{<sup>1</sup>H} NMR spectra indicated the formation of these complexes.



Scheme 2. Top: Formation of 4 and 5. Bottom: Crystallographically-determined solid-state structure of 4. Atomic displacement ellipsoids depicted at the 50% probability level and omitted for the ligand periphery. Hydrogen atoms and the  $[N(nBu)_4]$  cation are omitted for clarity. Selected bond lengths (Å) and angles (°) for 4: Pt1–P1 2.3310(14), Pt–B1 1.984(7), Pt–Cl5 2.5415(14), B1–B2 1.768(10), B1–Cl1 1.850(7), B2–Cl 1.884(7)-1.903(6), Cl5-Pt-B1 178.6(2), P1-Pt-P2 175.18(5).

Single crystals of 4 suitable for X-ray diffraction were grown by crystallization from diffusion of hexane into a saturated dichloromethane solution at -30 °C. Upon halide addition, the geometry around the platinum center changes from distorted T-shaped (2) to square-planar (4) (P1-Pt-P2 175.18(5)°). The B–B distances of **4** (1.768(10) Å) and  $B_2Cl_4^{20}$ (1.75(5) Å) are identical within experimental uncertainty; however, this is likely just a reflection of the high uncertainty in the latter distance. The Pt-B bond length of 4 is in the expected range (4: 1.984(7) Å).<sup>19,21-23</sup> As judged by comparison of the Pt-Cl distance, the trans influence of the -B(Cl)BCl<sub>3</sub> ligand (4: Pt-Cl 2.5415(14) Å) is significantly stronger than that of both mono- and diboryl ligands, e.g. those of trans-Å),<sup>21</sup>  $[(Cy_3P)_2PtCl(BCl_2)]$ (Pt-Cl: 2.441(2)trans- $[(Cy_3P)_2PtCl(BClMes)]$  (Pt-Cl: 2.5019(4) Å)<sup>22</sup> trans- $[(Cy_3P)_2PtCl{B(Mes)BXMes)}]$  (Pt-Cl: 2.5016(5) Å),<sup>5</sup> and to our knowledge represents the longest Pt-Cl bond ever observed in *trans*-boryl complexes. Comparison with other boryl ligands is difficult as their *trans*-influence was evaluated by measurement of a Pt-Br distance, and chloro-substituted diboranes(4) do not always react in the same manner as the bromo derivatives. In other cases, there is no solid-state structure available for the chloro derivatives. According to these results, the borylborato group has one of the strongest trans-influences determined at square planar Pt(II) centers and therefore is likely one of the strongest  $\sigma$ -donor boryl ligands reported to date. The formation of complexes 2 and 3 is likely driven by a combination of the strong trans-influence of the diboryl (-B(Cl)BCl<sub>2</sub>) moiety, which labilizes the Cl ligand *trans* to it in the initially formed BCl oxidative addition product, combined with the strong Lewis acidity of the B–BCl<sub>2</sub> unit which accepts the chloride anion. It should be noted that an analogous main-group example of a chloride migration at a B<sub>2</sub>Cl<sub>4</sub> fragment was observed by Siebert upon reacting B<sub>2</sub>Cl<sub>4</sub> with decamethylsilicocene, which led to the mixed-valent B<sup>1/111</sup> species (Me<sub>5</sub>C<sub>5</sub>)B–BCl<sub>3</sub>.<sup>18</sup> Due to the fact that the initially formed BCl oxidative addition product could not be detected by NMR spectroscopy even in the solid state, a direct halide migration from boron to boron cannot be completely ruled out.

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# Reactivity of Pt<sup>0</sup> complexes towards unsymmetrical difluorodiboranes(4)

We have recently 1.1'demonstrated that difluorodiboranes(4) of the type  $F_2B-BAr_2$  (Ar = Mes, Dur), first synthesized by Berndt and coworkers,<sup>10</sup> show interesting reactivity and can be used to access species that are not available with symmetrical 1,2-diaryldihalodiboranes(4). While symmetric diboranes(4) react with Lewis bases to form either halide-bridged adducts or rearranged sp<sup>2</sup>-sp<sup>3</sup> diboranes,<sup>36</sup> difluorodiboranes(4) react with small Lewis bases to either form bis-adducts or monoadducts wherein the BAr2 unit bears the Lewis base donor.<sup>24</sup> With this in mind, we sought to determine if the reactivity of unsymmetrical diboranes F<sub>2</sub>B–BAr<sub>2</sub> with transition metals would yield similarly unusual structures.

To extend the structural variety of the family of difluorodiboranes(4) we synthesized the corresponding bis(9-anthryl) derivative (for details see Supporting Information).

The reaction of F<sub>2</sub>B-BMes<sub>2</sub> with equimolar amounts of sterically undemanding, bisphosphine platinum(0) complexes [Pt(PMe<sub>3</sub>)<sub>2</sub>] (generated in situ from [Pt(nbe)<sub>3</sub>] and two equivalents of PMe<sub>3</sub>)<sup>25</sup> and [Pt(PEt<sub>3</sub>)<sub>3</sub>] (generated from [Pt(PEt<sub>3</sub>)<sub>4</sub>])<sup>26</sup> results in oxidative addition of the B-B bond to afford unsymmetrical bis(boryl) complexes  $cis-[(R_3P)_2Pt(BF_2)(BMes_2)]$ (6: R = Me; 7: R = Et) (Scheme 3). After workup, 6 and 7 were isolated as yellow crystals in low yields of 28% and 23%, due predominantly to the extreme solubility of the compounds even in nonpolar solvents. Each <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows one multiplet signal (6:  $\delta_{\rm P} = -19.4$ ,  ${}^{1}J_{\rm P-}$  $P_{t} = 1648$  Hz; 7:  $\delta_{P} = 11.2$ ,  ${}^{1}J_{P-Pt} = 1672$  Hz) as well as one doublet signal (6:  $\delta_{P} = -20.8$ ,  ${}^{1}J_{P-Pt} = 812$  Hz,  ${}^{2}J_{P-P} = 29$  Hz; 7:  $\delta_{P} = 12.2$ ,  ${}^{1}J_{P-Pt} = 841$  Hz,  ${}^{2}J_{P-P} = 27$  Hz), all with Pt satellites. The detected  ${}^{1}J_{P-Pt}$  coupling constants are, to the best of our knowledge, the smallest ever observed in platinum cis-(bisboryl) complexes. As expected, two signals were observed in the <sup>11</sup>B NMR spectrum of both complexes (6:  $\delta_{\rm P} = 105.5$ and 43.4; 7:  $\delta_{\rm P} = 104.9$  and 42.4), which are both low-field shifted with respect to the corresponding resonances of F<sub>2</sub>B-84).10 (δ BMes<sub>2</sub> = 28,



Scheme 3. Top: Formation of *cis*-bis(boryl) complexes 6 and 7 and bis-µ-boryl-bridged complexes 8, 9, 10 and 11. Bottom: Crystallographically-determined solid-state structures of 6, 7 and 9. Atomic displacement ellipsoids depicted at the 50% probability level and omitted for the ligand periphery. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for 6: Pt-P1 2.3476(8), Pt-P2 2.3394(11), Pt-B1 2.036(4), B1-B2 2.621(4), Pt-B2 2.098(3), B1-F1 1.343(4), B1-F2 1.348(3), P1-Pt-P2 97.62(3), P1-Pt-B1 86.47(9), B1-Pt-B2 78.66(13), B2-Pt-P2 97.51(8), P2-Pt-B1 175.57(9), P1-Pt-B2 163.07(8) F1-B1-F2 110.1(3); for 7: Pt1-B1 2.041(3), Pt1-B2 2.096(3), Pt1- B1-B2 2.519(3), P1 2.3494(7), Pt1-P2 2.3591(7), B1-F1 1.341(3), B1-F2 1.350(3), B1-Pt1-B2 75.03(10), P1-Pt1-P2 97.28(2), B1-Pt1-P1 89.53(8), B2-Pt1-P2 98.96(7), B1-Pt1-P2 169.94(8), B2-Pt1-P1 163.07(6), F1-B1-F2 110.5(2); for 9: Pt1-Pt2 2.6630(7), Pt1-P1 2.2741(12), Pt2-P2 2.2778(12), B1-Pt1 2.113(5), B1-Pt2 2.111(5), B2-Pt1 2.122(4), B2-Pt2 2.140(5), B1-Pt1-B2 50.87(13), 102.35(18), B1-Pt2-B2 101.81(18), Pt1-B2-Pt2 77.33(15), B1-Pt1-Pt2 B2-Pt1-Pt2 51.64(12)

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The <sup>19</sup>F NMR spectra of compounds **6** and **7** show typical signals for BF<sub>2</sub> ligands bound to Pt(II) centers (**6**:  $\delta_{\rm F} = -28.2$  (t, <sup>2</sup> $J_{\rm F-Pt} = 975$  Hz); **7**:  $\delta_{\rm F} = -28.7$  (t, <sup>2</sup> $J_{\rm F-Pt} = 966$  Hz)) and are consistent with the <sup>19</sup>F NMR data of *cis*-[Pt(BF<sub>2</sub>)<sub>2</sub>L<sub>2</sub>] (L<sub>2</sub> = 2PPh<sub>3</sub>, Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>).<sup>14</sup>

Single crystals of 6 and 7 suitable for X-ray diffraction were grown from pentane at -35 °C. The X-ray structures of 6 and 7 confirmed the selective *cis* oxidative addition of the B-B bond and the nearly square-planar platinum(II) centres (6:  $\Sigma_{Pt}$ = 360.3°; 7:  $\Sigma_{Pt}$  = 360.8°) (Scheme 3). The Pt–B1 bond lengths are slightly shorter (6: 2.036(4) Å; 7: 2.041(3) Å) than the Pt-B2 bond lengths (6: 2.098(3) Å; 7: 2.096(3) Å). The P1-Pt-P2 angles (6: 97.62(3)°; 7: 97.82(2)°) are significantly larger than the B1-Pt-B2 angles (6: 78.66(13)°; 7: 75.03(10)°). Nevertheless, the B1–B2 distance (6: 2.621(4) Å, 7: 2.519(3) Å) does not indicate a B...B interaction as observed in [(Me<sub>3</sub>P)<sub>3</sub>Co(Bcat)<sub>2</sub>] (2.185 Å).<sup>27</sup> All other structural parameters of complexes 6 and 7 are in good agreement with previous findings; for example, the B1–F bond lengths (6: 1.342(4), 1.348(4) Å; 7: 1.341(3), 1.350(3) Å) and F1-B1-F2 angles (6: 110.1(3)°; 7: 110.5(2)°) correspond to those reported for  $cis-[(Ph_3P)_2Pt(BF_2)_2]^{14}$  (1.327(6), 1.33(7) Å; 110.8(5)°).

Upon reacting F<sub>2</sub>B–BMes<sub>2</sub> or F<sub>2</sub>B–BAn<sub>2</sub> (An = 9-anthryl) with bis-phosphine platinum(0) complexes bearing bulkier and stronger  $\sigma$ -donor phosphine ligands (*PiPr*<sub>3</sub> or PCy<sub>3</sub>), we observed color changes to dark red solutions and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of higher order ( $\delta_P$  = 77.7 (8), 78.2 (9) and 64.9 (10)), indicating formation of dinuclear complexes (Scheme 3). The <sup>11</sup>B NMR spectra of 8-10 showed broad singlets in the range of 85-90 ppm for the BAr<sub>2</sub> ligand and broad multiplets between

8-21 ppm for the BF<sub>2</sub> ligand. The <sup>19</sup>F NMR spectra of **8-10** showed multiplets from -40.0 to -45.8 ppm.

Single crystals of 9 suitable for X-ray diffraction were grown by crystallization from benzene. The core of the dinuclear bis(boryl) complex 9 resembles a planar rhombus with four sides of nearly identical lengths. The Pt-B distances (Pt1-B1 2.112(4) Å, Pt1–B2 2.122(4) Å, Pt2–B1 2.111(5) Å, Pt2– B2 2.140(5) Å) of complex 9 are longer than those of bis(boryl) complexes 1, 6, and 7 (avg. Pt–B distance: 2.072 Å) previously reported borylene-bridged complex and the  $[(OC)_2(Me_3P)Fe(\mu-CO)(\mu-BDur)Pt(PCy_3)]^{28}$  (Pt-B 1.976(4) Å, Fe-B 1.970(4) Å, Fe-B-Pt 81.32(14)°). While the B1-F distances (1.365(5), 1.373(6) Å) are also slightly longer than those of 6 and 7, the F1-B1-F2 angle of 9  $(110.2(4)^{\circ})$  lies in the expected range. Both Pt–P distances (2.274(1), 2.278(1) Å) are shorter than those of complexes 6 and 7, while the P-Pt-B angles (B1-Pt1-P1 104.7(1)°, B2-Pt1-P1 151.7(1)°) indicate a dramatic bending of the phosphine ligands towards the less bulky difluoroboryl ligand. The Pt-Pt bond (2.6630(7) Å) is comparable to that in  $[Pt_2Cl_2(dppm)_2]$  (Pt–Pt 2.651(2)<sup>29</sup> and shorter than in the A-frame complex  $[Pt_2(\mu-HgCl_2)Cl_2(dppm)_2]$ (Pt-Pt 2.7119(8) Å).<sup>30</sup>

While the reactions with  $[Pt(PiPr_3)_2]$  were performed at ambient temperatures and showed full conversion to the corresponding product within 15 h, reaction of  $F_2B$ -BMes<sub>2</sub> with more sterically demanding  $[Pt(PCy_3)_2]$  did not lead to full conversion to **10** even at higher temperatures (80 °C), presumably due to steric hindrance. The persistence of starting material and the large amount of decomposition products in the reaction mixture made isolation of **10** impossible. It should be

noted that the difluorodiboranes used are not thermally stable, which partly explains the substantial amount of decomposition products observed. This is particularly problematic when the reaction is performed at 80 °C, which is required in order to induce reaction of  $[Pt(PCy_3)_2]$  with diboranes. However, the similarity of the multinuclear NMR data obtained from 10 to those of 8 and 9 provide confidence about the constitution of the former. Reaction of  $F_2B$ –BAn<sub>2</sub>, which is presumed to have a stronger  $\pi$ -accepting BAr<sub>2</sub> group than F<sub>2</sub>B–BMes<sub>2</sub>, with  $[Pt(PCy_3)_2]$  showed no reaction even at higher temperatures (up to 80 °C). These results led us to propose the synthesis of doubly-boryl-bridged complexes like 10 by employing  $Pt^0$ complexes bearing one phosphine and labile co-ligands. Thus, upon treating  $[(Cy_3P)Pt(nbe)_2]$  (nbe = norbornene)<sup>31</sup> with F<sub>2</sub>B–BMes<sub>2</sub>, NMR spectroscopy of the reaction mixture indicated formation of compound 10 after heating (60 °C). However, the isolation problems observed earlier, due to incomplete conversion and decomposition, remained. In an attempt to use a more activated diborane precursor to promote this reaction,  $[Pt(PCy_3)_2]$  was combined with the sp<sup>2</sup>-sp<sup>3</sup> diborane  $F_2B-BMes_2(PMe_3)^{24a}$  at room temperature; however, this reaction did not result in formation of 10. Instead, a yellow solid was isolated (12, Scheme 4) that showed two multiplets in its  ${}^{31}P{}^{1}H$  NMR spectrum ( $\delta_{P} = 37.7 \ ({}^{1}J_{P-Pt} = 971 \ Hz,$  ${}^{2}J_{P-F} = 28.5 \text{ Hz}$ ,  $-22.0 \quad ({}^{1}J_{P-Pt} = 1545 \text{ Hz}, {}^{2}J_{P-F} = 127 \text{ Hz})$ which, together with its <sup>11</sup>B NMR ( $\delta_{\rm B} = 106.2$  (s, BMes<sub>2</sub>), 42.4 (s,  $BF_2$ )) and the <sup>19</sup>F NMR data ( $\delta_F = -28.3$  (br s)), indicated formation of the heteroleptic bis(boryl) complex  $[(Me_3P)(Cy_3P)Pt(BF_2)(BMes_2)]$  12 (Scheme 4).



**Scheme 4.** Formation of unsymmetrical bis(boryl) complex [(Me<sub>3</sub>P)(Cy<sub>3</sub>P)Pt(BF<sub>2</sub>)(BMes<sub>2</sub>)] **12**.

To gain more information about the constitution of **12**, 2D NMR experiments were performed. <sup>31</sup>P-<sup>1</sup>H HMQC measurements show correlation of the <sup>31</sup>P NMR resonance at  $\delta_P = -22.0$  ppm with only one signal in the <sup>1</sup>H NMR spectrum at 0.98 ppm (d, 9H, <sup>2</sup>J<sub>P-H</sub> = 7.1 Hz), indicating that this <sup>31</sup>P NMR resonance corresponds to the PMe<sub>3</sub> ligand. Furthermore, both phosphine resonances sharpen significantly upon <sup>19</sup>F decoupling, indicating a strong phosphorus-fluorine interaction. Analysis of the <sup>2</sup>J<sub>P-F</sub> coupling constants led us to determine that the PMe<sub>3</sub> ligand (<sup>2</sup>J<sub>P-F</sub> = 127 Hz) is mutually *trans* to the BF<sub>2</sub> ligand, while the PCy<sub>3</sub> ligand (<sup>2</sup>J<sub>P-F</sub> = 28.5 Hz) is *cis* to the BF<sub>2</sub> ligand. This was also found to be the case in the solid state, as determined by crystallographic analysis of **12** (see

Supporting Information for details). This allowed us to assign the <sup>31</sup>P NMR spectra of **6** and **7** with confidence. The very small <sup>1</sup> $J_{P-Pt}$  coupling constants of 812 and 841 Hz, respectively, can be assigned to PR<sub>3</sub> ligands *trans* to the BMes<sub>2</sub> group, consistent with the much larger *trans*-influence of the latter than the BF<sub>2</sub> group. It should also be noted that **12** can also be prepared by combination of F<sub>2</sub>B–BMes<sub>2</sub>, PMe<sub>3</sub> and [Pt(PCy<sub>3</sub>)<sub>2</sub>] at -55 °C.



Figure 2. Left: HOMO; middle: LUMO; right: IBO of compound 9.

Finally, we computed the structure of complex 9 (see Supporting Information for further details) in order to visualize the frontier molecular orbitals (Fig. 2). The HOMO is mainly located at the two platinum centers and the BAn<sub>2</sub> boron atom, which describes the nucleophilic part of the compound. In contrast, the LUMO is the antibonding orbital of the same Pt-Pt-B ring, which comprises the electrophilic portion of 9. These findings are in contrast with Kleeberg's bis-µ-borylbridged complex  $[(iPr_3P)Cu-BDmab]_2$  (E, Fig. 1), which was found to have multicenter bonding character within the B<sub>2</sub>Cu<sub>2</sub> core involving the HOMO, HOMO-5, HOMO-11 and HOMO-16 orbitals. All these molecular orbitals showing substantial boron and copper contributions are symmetrical and involve both bridging boryl groups.<sup>9</sup> However, by visualizing intrinsic bond orbitals (IBOs), we found one showing multicenter contributions over the Pt<sub>2</sub>B<sub>2</sub> core (for a complete analysis, see SI). Because of an asymmetry between BAn<sub>2</sub> and BF<sub>2</sub>, this MO gets more contribution from the BAn<sub>2</sub> boron atom (52%) than the  $BF_2$  boron (25%), so the multicenter bonding character is slipped from the four-membered ring center, in contrast to symmetrical complexes like that of Kleeberg. The dramatic bending of the phosphine ligands towards the less bulky difluoroboryl ligand in 9 itself indicates a different bonding situation than in  $[(iPr_3P)Cu-BDmab]_2$  (see solid-state structure in Scheme 3).

Moreover, calculated Wiberg bond indices reveal the bis- $\mu$ -boryl-bridged bonding mode of **9** (mean value of 0.65 among the Pt–B interactions), whereas the Pt–Pt interaction shows a very low value of 0.29. Both platinum centers hold an atomic charge of -0.248, but the boron atoms exhibit different charges: -0.072 (for the BAn<sub>2</sub> fragment) and +0.958 (for the BF<sub>2</sub> moeity). Thus, this analysis shows there is some delocalized charge in the Pt–B–Pt–B ring, and that **9** is effectively a bis(boryl)-bridged compound.

#### **SUMMARY & CONCLUSIONS**

This work presents a number of novel classes of platinum boryl complexes and demonstrates the diverse bonding modes accessible when diboranes(4) react with TM centers. A new protocol was also developed for the preparation of  $B_2F_4$ , which

makes it easily accessible via solution phase synthesis. While with  $B_2F_4$  and  $Pt^0$  a *cis*-bis(boryl) complex is formed,  $B_2Cl_4$ and B<sub>2</sub>Br<sub>4</sub> led to the synthesis of zwitterionic platinum complexes bearing novel borylborato  $(-B(X)BX_3)$  ligands, which were found to be exceedingly strong  $\sigma$ -donor ligands. A new unsymmetrical 1,1-diaryl-2,2-difluorodiborane(4) compound was prepared bearing 9-anthryl substituents, and the reactivity of this family of diboranes was studied with Pt<sup>0</sup> precursors. F<sub>2</sub>B-BMes<sub>2</sub> forms oxidative addition products when treated with Pt<sup>0</sup> complexes bearing small phosphines, including the first example of a fourfold unsymmetrical cis-bis(boryl) complex, whereas increasing the size and the donor strength of the phosphine ligands leads to unprecedented doubly borylbridged diplatinum complexes. The presented results highlight the sensitivity of these reactions to steric hindrance and donor strength at the TM center.

#### ASSOCIATED CONTENT

Supporting Information including full experimental details, spectra, crystallographic files (CIF) and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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TOC graphic:					
	$R = R = P^{0}$	bisbory/ R <sub>3</sub> P, BR <sub>2</sub> Pt R <sub>3</sub> P BR <sub>2</sub>	bory/borato ⊕ PCy <sub>3</sub> × Pt-B Pt-B Pt-B BX <sub>3</sub>	doubly bory/ bridged F, F R <sub>3</sub> P-Pt—Pt B, Pt—PR <sub>3</sub>	
			POy <sub>3</sub> (5)	Ar <sup>a</sup> r	
	ACS	Paragon Plus	Environment		