

# Coordination of Phosphinoboranes $R_2PB(C_6F_5)_2$ to Platinum: An Alkene-Type Behavior

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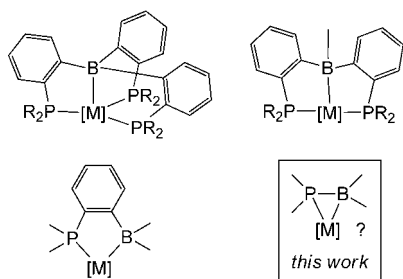
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**S** Supporting Information

**ABSTRACT:** The paucity of boron-containing heteroalkene complexes prompted us to explore the coordination of phosphinoboranes. The complexes  $\{[R_2PB(C_6F_5)_2]Pt(PPh_3)_2\}$  ( $R = Cy, t-Bu$ ) were obtained by ethylene displacement. Spectroscopic and crystallographic data indicated symmetric side-on coordination of the phosphinoborane to Pt. Thorough analysis of the bonding situation by computational means revealed important similarities but also significant differences between the phosphinoborane and ethylene complexes.

The ability of main-group Lewis acids to coordinate to transition metals (TMs) as  $\sigma$ -acceptor ligands (so-called Z-type ligands) has attracted growing interest over the past decade.<sup>1</sup> Thanks to the incorporation of Lewis acid moieties into multidentate, amphiphilic ligands,<sup>2</sup> more understanding has been gained about the nature and influence of TM $\rightarrow$ Z interactions. The scope of Lewis acids capable of behaving as  $\sigma$ -acceptor ligands has also been significantly extended. Typically, we have shown that group 13 or group 14 Lewis acids appended with *o*-(C<sub>6</sub>H<sub>4</sub>)PR<sub>2</sub> donor groups readily engage in TM $\rightarrow$ Z interactions upon coordination (Chart 1).<sup>3</sup> We

**Chart 1. Schematic Representation of Different Ways of Supporting M $\rightarrow$ B Interactions Using Phosphine Buttresses**

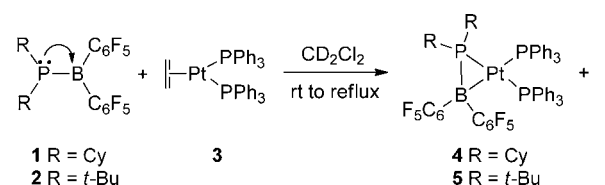


varied the nature of the Lewis acid (B, Al, Ga, In, Si, Sn) and the metal fragment as well as the number of phosphine side arms to gain insight into the factors influencing the magnitude of TM $\rightarrow$ Z interactions. The nature of the linker between the Lewis acid and the donor buttresses was also shown to play an

important role, and the *o*-phenylene moiety proved to be particularly efficient in supporting the coordination of the Lewis acid. At this stage, one may wonder about the actual necessity of a linker. We thus became interested in evaluating the coordination properties of phosphinoboranes (PBs)<sup>4</sup> (Chart 1), and we report here our first results in this area. Side-on coordination of the PBs  $R_2PB(C_6F_5)_2$  ( $R = Cy, t-Bu$ ) to Pt has been crystallographically authenticated, and the original bonding situation has been thoroughly analyzed by computational methods.

Because of their amphiphilic character, PBs tend to form head-to-tail dimers or higher oligomers via intermolecular P $\rightarrow$ B interactions.<sup>4</sup> However, sterically demanding substituents enable the isolation of monomeric species, as first evidenced by Power and co-workers.<sup>5</sup> For this study, we chose PBs **1** and **2**, which were recently shown by Stephan to activate H<sub>2</sub> readily.<sup>6</sup> The *t*-Bu/*Cy* substituents at phosphorus and the C<sub>6</sub>F<sub>5</sub> groups at boron not only prevent aggregation but also amplify the double-bond character as a result of strong  $\pi$  donation from P to B. Accordingly, some parallel may be drawn between the coordination of PBs **1** and **2** and that of alkenes. Coordination of **1** to Pt was readily achieved using the  $[(C_2H_4)Pt(PPh_3)_2]$  precursor **3** (Scheme 1). The ensuing complexes **4** and **5** are extremely air- and moisture-sensitive.

**Scheme 1. Coordination of the Phosphinoboranes **1** and **2** to Pt**



According to in situ NMR monitoring, the formation of complex **4** was complete within 30 min at room temperature. The release of ethylene was clearly apparent by <sup>1</sup>H NMR analysis (4.2 ppm), and the <sup>31</sup>P and <sup>11</sup>B NMR data argue in favor of the coordination of both the phosphorus and boron

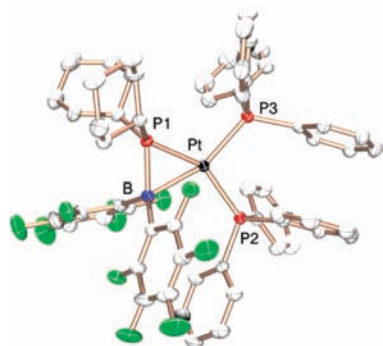
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atoms of the PB. The  $^{31}\text{P}$  NMR resonance signal in complex **4** appears at 31 ppm (vs 121 ppm in **1**) as a doublet of doublets ( $J_{\text{P-P}} = 230$  and 13 Hz involving the two inequivalent  $\text{PPh}_3$  coligands) with  $^{195}\text{Pt}$  satellites ( $J_{\text{P-Pt}} = 3750$  Hz). The  $^{11}\text{B}$  NMR signal is shifted upfield by  $\sim 60$  ppm upon coordination and resonates in **4** at  $-19$  ppm, in the typical range for tetracoordinate boron centers enclosed in three-membered rings.<sup>7</sup> The change in the boron environment from tri- to tetracoordinate is further supported by the chemical shift difference between the para and meta fluorine atoms of the  $\text{C}_6\text{F}_5$  fragments [ $\Delta\delta(^{19}\text{F}_{\text{p,m}}) = 4$  ppm in complex **4** vs 8 ppm in ligand **1**].<sup>8</sup> Also noteworthy is the presence of a significant  $J_{\text{P-B}}$  coupling constant in complex **4** (42 Hz). This suggests that the PB framework is retained but probably weakened upon coordination to Pt (**1** displays a much larger  $J_{\text{P-B}}$  coupling of 150 Hz).

PB **2** featuring *t*-Bu groups at phosphorus was also reacted with **3**. The higher steric demand of the ligand was found to markedly disfavor the coordination (only 75% conversion could be achieved even after 5 days at 35 °C), but according to  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR spectroscopy,<sup>9</sup> the ensuing complex **5** adopts a structure very similar to that of **4**.

The coordination modes of complexes **4** and **5** were then analyzed by X-ray diffraction studies (single crystals were grown from dichloromethane or pentane/ether solutions at room temperature).<sup>9</sup> The two compounds adopt very similar structures, and for sake of clarity, only that of **4** (Figure 1)



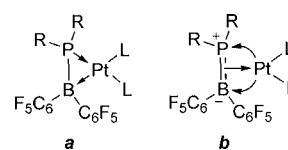
**Figure 1.** X-ray crystal structure of **4**. Thermal ellipsoids have been drawn at 50% probability, and H atoms and solvate molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1–B, 1.917(3); P1–Pt, 2.2984(6); Pt–B, 2.234(3); P3–Pt, 2.3377(6); P2–Pt, 2.2961(6); P1–Pt–B, 50.02(7); P2–Pt–P3, 100.97(2).

will be discussed here. The Pt center is tetracoordinated and adopts a distorted square-planar arrangement. The PB coordinates in a side-on fashion and lies almost in the same plane as the two  $\text{PPh}_3$  coligands (the P1–Pt–B plane deviates by only 6.3° from the P2–Pt–P3 plane). The Pt–B distance is short [2.234(3) Å] and falls in the same range as those observed for supported Pt→borane interactions (2.12–2.43 Å).<sup>10</sup> In fact, the Pt–B and Pt–P1 [2.298(6) Å] distances are very close to the sum of their respective covalent radii,<sup>11</sup> indicating the symmetric coordination of the PB ligand. Upon coordination, the PB is slightly pyramidalized [ $\sum_{\alpha}\text{B} = 349.6(6)^\circ$  and  $\sum_{\alpha}\text{P1} = 351.2(3)^\circ$ ] and the P1–B bond length is noticeably elongated [from 1.762(4) Å in the free ligand **1**<sup>6b</sup> to 1.917(3) Å in complex **4**]. Replacement of ethylene with the PB at Pt also affects the geometry of the  $[\text{Pt}(\text{PPh}_3)_2]$  fragment. In particular, steric repulsion between the large substituents at

P and B and the  $\text{PPh}_3$  coligands induces a substantial shrinking of the P2–Pt–P3 bond angle [from 111.6(1)° in **3**<sup>12</sup> to 101.0(2)° in **4**]. Notably, because of the unsymmetrical nature of the PB ligand, the two  $\text{PPh}_3$  coligands are not equivalent in complex **4**, and the two Pt– $\text{PPh}_3$  distances are slightly different. The longer Pt–P distance is that to P3, which is trans to boron [Pt–P3 = 2.3377(6) Å, Pt–P2 = 2.2961(6) Å], which may be attributed to the stronger trans effect of the borane relative to the phosphine.<sup>1</sup>

The X-ray structures of complexes **4** and **5** revealed symmetric side-on coordination of the PB to Pt. From the ensuing geometrical data, the bonding situation can be formally described as a Pt→borane interaction supported by adjacent phosphine coordination (Chart 2, structure **a**). If the double-

**Chart 2. Schematic Descriptions of the Coordination of 1 and 2 to Pt**



bond character of the PBs is taken into account, complexes **4** and **5** can also be considered as olefin-type complexes, with participation of  $\pi(\text{PB})\rightarrow\text{Pt}$  donation and  $\text{Pt}\rightarrow\pi^*(\text{PB})$  back-donation (structure **b**). A thorough density functional theory (DFT) study was carried out to gain more insight into the coordination mode of the PB ligand and to draw an in depth comparison with the corresponding ethylene complex.<sup>13</sup>

Calculations were carried out on complexes **3** and **4** (with  $\text{PPh}_3$  coligands) and **3\*** and **4\*** (with  $\text{PMe}_3$  coligands). The optimized geometries reproduced well the key features of the structures determined crystallographically (Table S2).<sup>9</sup> Replacement of  $\text{PPh}_3$  by  $\text{PMe}_3$  had only a small influence, and thus, further analysis was focused on the model systems **3\*** and **4\***. Displacement of ethylene by the PB on  $[\text{Pt}(\text{PMe}_3)_2]$  is slightly favored energetically ( $\Delta E = -8.2$  kcal/mol,  $\Delta G = -1.6$  kcal/mol at 25 °C for the reaction outlined in Scheme 1), in agreement with the experimental observations.

The nature of the bonding interaction was then thoroughly investigated starting with energy decomposition analysis (EDA), as introduced by Morokuma and Ziegler<sup>14</sup> (Table 1). The bond dissociation energy predicted for **4\*** exceeds that for **3\*** by  $\sim 5$  kcal/mol ( $D_e = 24.3$  vs 19.1 kcal/mol). Interestingly, the interaction energy between the two fragments is much higher for the PB than for ethylene ( $\Delta E_{\text{int}} = -82.1$  vs  $-63.1$  kcal/mol), but the respective preparation energies required to

**Table 1. EDA of Complexes  $[(\text{C}_2\text{H}_4)\text{Pt}(\text{PMe}_3)_2]$  (**3\***) and  $\{[\text{Cy}_2\text{PB}(\text{C}_6\text{F}_5)_2]\text{Pt}(\text{PMe}_3)_2\}$  (**4\***) (Energies Reported in kcal/mol)**

	<b>3*</b>	<b>4*</b>
$\Delta E(-D_e)$	-19.1	-24.3
$\Delta E_{\text{int}}$	-63.1	-82.1
$\Delta E_{\text{prep}}$	44.0	57.9
$\Delta E_{\text{Pauli}}$	207.6	262.0
$\Delta E_{\text{elstat}}$	-172.3 (63.7%) <sup>a</sup>	-218.2 (63.5%) <sup>a</sup>
$\Delta E_{\text{orb}}$	-98.4 (36.3%) <sup>a</sup>	-125.4 (36.5%) <sup>a</sup>

<sup>a</sup>Percentage contributions to the total attractive interaction energies are given in parentheses.

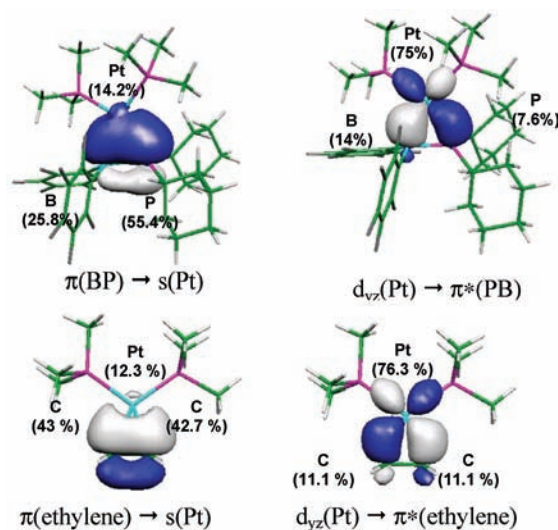
distort the two fragments to reach their actual geometries in the complexes ( $\Delta E_{\text{prep}} = 57.9$  vs  $44.0$  kcal/mol) compensates for this difference. The three components of  $\Delta E_{\text{int}}$  ( $\Delta E_{\text{Pauli}}$ ,  $\Delta E_{\text{elstat}}$  and  $\Delta E_{\text{orb}}$ ) are all larger in magnitude in the PB complex **4\*** than in the ethylene complex **3\***, but their relative contributions are about the same, with the electrostatic term  $\Delta E_{\text{elstat}}$  representing  $\sim 63\%$  of the attractive interactions in both complexes.

The nature of the covalent bonding was further assessed using the charge decomposition analysis (CDA) method developed by Frenking.<sup>14d,e,15</sup> Donation and back-donation contribute equally in the PB complex **4\*** ( $d = 0.623$ ,  $b = 0.624$ ), whereas donation predominates over back-donation in the ethylene complex **3\*** ( $d = 0.566$ ,  $b = 0.430$ ). Basically, the bonding can be described within the Dewar–Chatt–Duncanson (DCD) model,<sup>16</sup> but the presence of a non-negligible residual term in **4\*** ( $\Delta = -0.15$ ) suggests some covalent bonding (associated with a metallacyclic structure) in addition to the donor–acceptor interactions.

More insight into the relative contributions of P and B in the PB complex **4\*** was then obtained from molecular orbital (MO) analysis (Figure S2).<sup>9</sup> The frontier MOs (FMOs) of the PB **1** are essentially  $\pi(\text{PB})$  and  $\pi^*(\text{PB})$  MOs, in line with the strong  $\pi$  donation from P to B. The coordination of the PB ligand to the  $[\text{Pt}(\text{PMe}_3)_2]$  fragment involves the same type of orbital interactions as for ethylene:  $\pi(\text{PB}) \rightarrow \text{Pt}$  donation and  $\text{Pt} \rightarrow \pi^*(\text{PB})$  back-donation. However, noticeable differences between the PB complex **4\*** and the ethylene complex **3\*** were found. Indeed, the electronic dissymmetry of the PB imparts substantial polarization to the FMOs of the PB fragment [ $\pi(\text{PB})$  is centered on P while  $\pi^*(\text{PB})$  is centered on B], and the ensuing MOs in **4\*** are similarly polarized. In addition,  $\pi(\text{PB})$  is higher in energy than  $\pi(\text{ethylene})$  and  $\pi^*(\text{PB})$  is lower in energy than  $\pi^*(\text{ethylene})$ , and thus, the energy gap between the FMOs is significantly lower for **1** than for ethylene (3.3 vs 6.2 eV; Figures S2 and S3).<sup>9</sup> As a result, the orbital interactions are stronger in the PB complex **4\***, in agreement with the higher  $\Delta E_{\text{orb}}$  value found in the EDA. Overall, the bonding situation in **4\*** can thus be described by the DCD model, taking into account the fact that the donation and back-donation interactions are polarized toward P and B, respectively. Natural localized MO (NLMO) analyses further corroborated these conclusions (Figure 2). The NLMO associated with  $\text{PB} \rightarrow \text{Pt}$  donation is mainly localized on the ligand and strongly polarized toward P (55.4% contribution from P but only 25.8% from B). As for the related ethylene complex, slight delocalization tails are observed over Pt (14%). Reciprocally, the NLMO associated with  $\text{Pt} \rightarrow \text{PB}$  back-donation is centered on Pt (75%), with the contribution from B predominant over that from P (14.0 vs 7.6%).

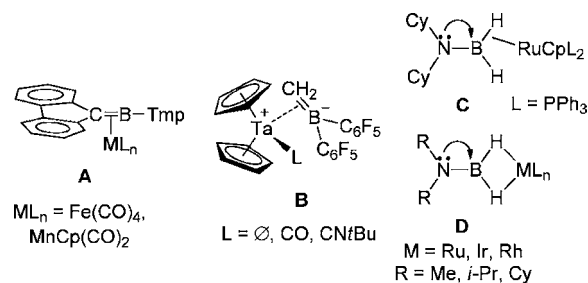
In conclusion, this detailed bonding analysis has revealed important similarities but also significant differences between the coordination of PB **1** and ethylene to  $\text{Pt}(0)$ . Side-on coordination of the PB ligand is geometrically symmetric but electronically dissymmetric, and the bonding situation in complex **4** is best represented as a superposition of forms **a** and **b** in Chart 2.

To date, the coordination chemistry of acyclic boron-containing  $\pi$  ligands has been explored only scarcely.<sup>17</sup> Typically, boron-containing alkene-type complexes are limited to the *B*-amino-9-fluorenylideneborane Fe and Mn complexes **A** reported by Nöth<sup>18</sup> on one hand and the Ta borataalkene complexes **B** reported by Piers<sup>19</sup> on the other (Chart 3).



**Figure 2.** Molekel plots (cutoff: 0.04) of the NLMOs accounting for the  $\pi \rightarrow \text{Pt}$  and  $\text{Pt} \rightarrow \pi^*$  interactions in the model complexes **3\*** (bottom) and **4\*** (top). Atomic contributions (%) are reported in parentheses.

### Chart 3. Known Complexes of Boron-Containing Heteroalkenes



Among  $E_{15}=\text{E}_{13}$  heteroalkenes ( $E_{15}$  = group 15 element,  $E_{13}$  = group 13 element), only aminoboranes have been coordinated to TMs. The mono and bis  $\sigma$ -(B–H) complexes **C** and **D**, respectively, have recently been characterized,<sup>20</sup> but side-on coordination has not been authenticated experimentally to date, although a few DFT studies have supported its possible existence.<sup>20a,b,21</sup> The PB complexes **4** and **5** reported here provide unambiguous evidence for alkene-type coordination with  $E_{15}=\text{E}_{13}$  heteroalkenes.<sup>22–24</sup> Future work will seek to explore the generality of such side-on coordination and determine the influence of the metal fragment and the substitution patterns at P and B.

### ■ ASSOCIATED CONTENT

#### Supporting Information

Detailed experimental conditions and procedures and computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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#### Notes

The authors declare no competing financial interest.

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