

# Cooperative Transition Metal/Lewis Acid Bond-Activation Reactions by a Bidentate (Boryl)iminomethane Complex: A Significant Metal–Borane Interaction Promoted by a Small Bite-Angle LZ Chelate

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**S** Supporting Information

**ABSTRACT:** The synthesis of a three-coordinate Pt–borane complex featuring a bidentate “LZ” (boryl)iminomethane (BIM) ligand is reported. Unlike other LZ-type borane ligands featuring a single-donor buttress, the small bite angle enforced by the BIM ligand is shown to promote a significant metal–borane reverse-dative  $\sigma$ -interaction akin to multiply strapped metalboratranes. The steric accessibility of the reactive Pt  $\rightarrow$  B bond fostered by the BIM ligand allows for a rich reactivity profile toward small molecules that exploit metal–borane cooperative effects. The unligated (boryl)iminomethane BIM is also synthetically accessible and functions as a Frustrated Lewis Pair (FLP). The ability of the free BIM to effect bond activation reactions is contrasted with the behavior seen in the corresponding platinum-bound complexes.

Transition metal–borane complexes ( $L_nM \rightarrow BR_3$ ) featuring so-called reverse-dative  $\sigma$ -interactions have received increasing attention in coordination and small-molecule activation chemistry.<sup>1–7</sup> It is now established that coordination of a Lewis acidic borane (Z-type ligand) can significantly modulate the electronic and geometric structure properties of a transition metal center in a manner distinct from traditional Lewis basic, two-electron donor ligands (L-type ligand).<sup>4,8,9</sup> Increasingly, reactivity profiles of metal–borane complexes with small molecule substrates have been uncovered that significantly diverge from those of either free boranes ( $BR_3$ ) or transition metal fragments featuring only  $\sigma$ -donating, L-type ligands.<sup>5,7</sup> These studies have led to new catalytic processes that exploit the “reverse polarity” of the metal–borane unit<sup>10,11</sup> and have also demonstrated the ability of coordinated boranes to function in a hemilabile fashion to modulate the electronic structure of a metal center during multielectron transformations of small molecules.<sup>12–14</sup>

Ligand design strategies that enable a significant primary interaction between a transition metal and a borane have relied on the presence of two or more L-type ligands to buttress the metal-to-borane  $\sigma$ -interaction (i.e.,  $L_2Z$  or  $L_3Z$ ).<sup>4–7</sup> Traditionally, multiple donor groups have been incorporated within a borane–ligand framework to overcome the inherently low coordinative ability of free borane molecules ( $BR_3$ ). Indeed, transition metal–borane complexes that lack additional donor groups and are also devoid of any secondary coordinative interactions have yet to be fully authenticated.<sup>15</sup> In addition,

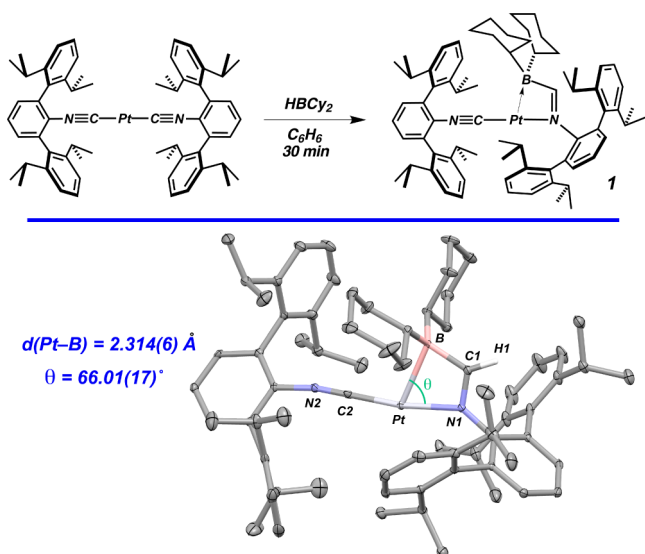
ligand frameworks possessing only a single L-type buttress have thus far shown limited ability to foster a significant metal-to-borane interaction.<sup>16,17</sup> This follows from the fact that borane-containing LZ ligands most closely mimic the coordinative abilities of a free borane. However, such bidentate LZ chelates are of interest for the development of isolable metal–borane complexes that offer increased coordinative unsaturation and flexibility toward incoming ligands and substrates. Accordingly, herein we report platinum complexes featuring a (boryl)iminomethane ( $(R_2B)(H)C=NR$ ; BIM) ligand that enables the formation of significant metal–borane interactions within a bidentate LZ chelate. We also demonstrate a rich and cooperative reaction chemistry of the Pt-to-borane linkage with a host of small-molecule substrates. The ability of the (boryl)iminomethane ligand to provide a significant metal–borane interaction within a bidentate framework arises from a small bite angle between the Z-type borane and L-type N-imino coordinating groups.

The zero-valent bis(*m*-terphenyl isocyanide) platinum complex,  $Pt(CNAr^{Dipp2})_2$  ( $Ar^{Dipp2} = 2,6-(2,6-(i-Pr)_2C_6H_3)_2-C_6H_3$ ), is accessed via Mg-metal reduction of the dichloride,  $PtCl_2(CNAr^{Dipp2})_2$  (mixture of *cis*- and *trans*- isomers), in a manner that parallels the synthesis of the palladium congener  $Pd(CNAr^{Dipp2})_2$ .<sup>18</sup> Treatment of  $Pt(CNAr^{Dipp2})_2$  with dicyclohexylborane ( $HBCy_2$ ) results in the clean formation of three-coordinate  $Pt(\kappa^2-N,B-Cy^2BIM)(CNAr^{Dipp2})$  (**1**,  $Cy^2BIM = Cy_2B(H)C=NAr^{Dipp2}$ ), which features a chelating LZ (boryl)iminomethane moiety, via formal 1,1-hydroboration of one  $CNAr^{Dipp2}$  ligand (Figure 1). Despite the bidentate nature of the (boryl)iminomethane ligand in  $Pt(\kappa^2-N,B-Cy^2BIM)(CNAr^{Dipp2})$  (**1**), evidence for a significant Pt  $\rightarrow$  B reverse-dative  $\sigma$ -interaction is provided by both its solid-state structure and solution spectroscopic properties.

In the solid state, complex **1** features a distorted T-shaped geometry with a Pt–B distance of 2.314(6) Å and N1–Pt–B and C2–Pt–B angles of 66.01(17)° and 105.63(17)°, respectively. The N1–Pt–B angle in **1** is of particular note, as this small bite-angle between the rigid  $Cy^2BIM$  ligand and Pt enables a short Pt–borane interaction in the absence of additional donor groups. In comparison, the related platinum *tris*-(*o*-phosphinophenylene)–borane complex,  $Pt[\kappa^4-B,P_3-(o-^{iPr}PC_6H_4)_3B]$ , features an average P–Pt–B bite angle of

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**Figure 1.** Synthesis (top) and molecular structure (bottom) of Pt( $\kappa^2$ -N,B-Cy<sup>2</sup>BIM)(CNAr<sup>Dipp2</sup>) (**1**).

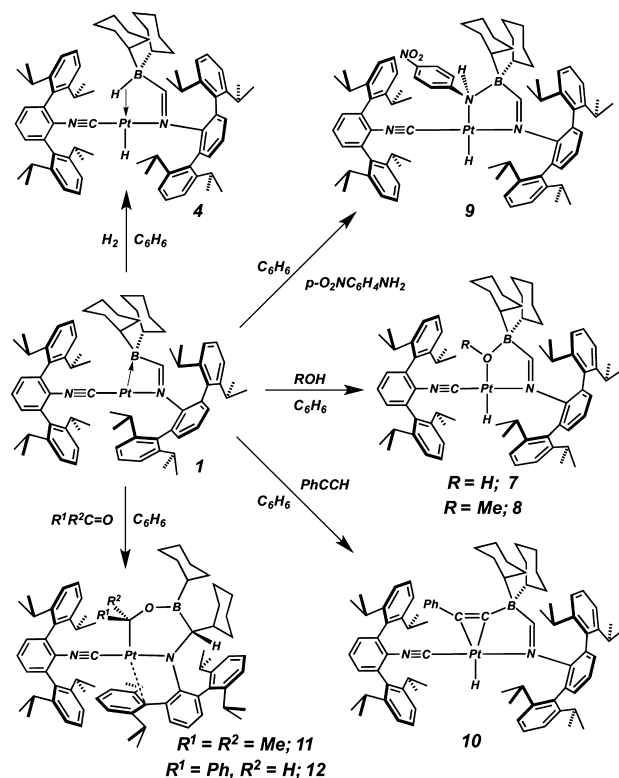
85.7(2)° and accordingly requires a three-donor buttress to stabilize a short Pt–B interaction (2.224(2) Å).<sup>19</sup> Near-90° bite angles are also present in the gold *mono*-(*o*-phosphino-phenylene)–borane LZ chelate complexes ClAu( $\kappa^2$ -B,P-(*o*-iPr<sup>2</sup>PC<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>) and ClAu( $\kappa^2$ -B,P-(*o*-iPr<sup>2</sup>PC<sub>6</sub>H<sub>4</sub>)B(Flu)) (Flu = fluorene),<sup>16</sup> which have been shown by crystallographic and <sup>11</sup>B NMR spectroscopic analyses to possess significantly attenuated Au–B interactions relative to more highly buttressed borane frameworks.<sup>5</sup> In contrast, **1** gives rise to a <sup>11</sup>B NMR signal at +18 ppm that is substantially upfield of the corresponding resonance of the free Cy<sup>2</sup>BIM ligand (+74 ppm; **2**, Scheme 2) and strongly indicates an increase in the coordination number at boron upon ligation to the Pt center.<sup>20</sup> The presence of a significant reverse-dative  $\sigma$ -interaction is also indicated by NBO calculations on the model complex Pt( $\kappa^2$ -N,B-Me<sup>2</sup>BIM)(CNMe), which reveal a fully occupied bonding orbital comprised of 81% Pt character and 19% boron character.<sup>21</sup> Importantly, the boron contribution in this NBO is an admixture of both 2s- and 2p<sub>z</sub>-orbital character, thereby indicating a rehybridization of the boron center from sp<sup>2</sup> to sp<sup>3</sup> upon interaction with Pt. This hybridization change also rationalizes the observed pyramidalization at boron in the solid-state structure of **1** ( $\Sigma(\angle(\text{C}–\text{B}–\text{C})) = 348.4^\circ$ ).

With respect to the formation of **1**, it is important to note that the reaction between Pt(CNAr<sup>Dipp2</sup>)<sub>2</sub> and HBCy<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> solution is complete in ca. 30 min and no intermediates are observed by <sup>1</sup>H NMR spectroscopy during the course of the reaction. Furthermore, the free Cy<sup>2</sup>BIM ligand **2** is easily prepared and isolated by 1,1-hydroboration of CNAr<sup>Dipp2</sup> upon the addition of HBCy<sub>2</sub>. Free Cy<sup>2</sup>BIM (**2**) reacts readily with BCl<sub>3</sub> to form an imino-borane/bridging-chloride double Lewis acid/base adduct that has been structurally characterized (**3**, Scheme 2), thus demonstrating the generality of the framework to serve as an ambiphilic donor–acceptor species.<sup>22</sup> However, free Cy<sup>2</sup>BIM (**2**) does not react with Pt(CNAr<sup>Dipp2</sup>)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> solution over the course of several days, which is an observation we attribute to a slow rate of isocyanide dissociation from two-coordinate Pt(CNAr<sup>Dipp2</sup>)<sub>2</sub>. FTIR and 2D EXSY <sup>1</sup>H NMR spectroscopic studies are consistent with this proposal and do not indicate a fast isocyanide dissociation process from

Pt(CNAr<sup>Dipp2</sup>)<sub>2</sub> that would lead to 1,1-hydroboration of free CNAr<sup>Dipp2</sup> by HBCy<sub>2</sub>, followed by combination of the newly formed Cy<sup>2</sup>BIM ligand with the zero-valent [Pt(CNAr<sup>Dipp2</sup>)] fragment. Instead, we presently favor a tandem sequence involving H–B bond oxidative addition to the Pt center in Pt(CNAr<sup>Dipp2</sup>)<sub>2</sub>, followed by  $\alpha$ -H migration and B–C bond reductive elimination from the putative boryl-hydride intermediate [HPt(BCy<sub>2</sub>)(CNAr<sup>Dipp2</sup>)<sub>2</sub>] to furnish complex **1**.<sup>23,24</sup>

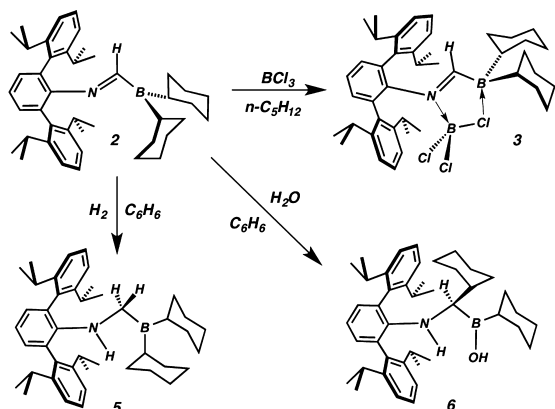
The absence of a multiple-donor buttress in **1** allows it to react readily with a variety of substrates in a manner that demonstrates cooperation between the Pt and borane units in bond activation processes. For example, exposure of **1** to H<sub>2</sub> (1 atm) in C<sub>6</sub>H<sub>6</sub> leads to the eradication of the Pt→B  $\sigma$ -interaction and irreversible formation of the hydride–borohydride complex, PtH( $\eta^2$ -H,B- $\kappa^1$ -N-H<sup>Cy2</sup>BIM)(CNAr<sup>Dipp2</sup>) (**4**, Scheme 1), as determined by X-ray diffraction.<sup>25</sup> The

**Scheme 1.** Reaction Pinwheel for Complex **1**



structural parameters of the Pt–(HB) contact in complex **4** are consistent with its formulation as an  $\eta^2$ -H,B-borohydride  $\sigma$ -complex and are corroborated by a <sup>11</sup>B NMR chemical shift of –7 ppm, which is slightly downfield of those found for four-coordinate, sp<sup>3</sup>-hybridized hydridoborates.<sup>20</sup> Importantly, free Cy<sup>2</sup>BIM also reacts with H<sub>2</sub>, but in a fashion distinct from Pt-ligated **1**. Thus, treatment of Cy<sup>2</sup>BIM with H<sub>2</sub> affords the methylene-bridged aminoborane, Cy<sub>2</sub>BCH<sub>2</sub>N(H)Ar<sup>Dipp2</sup> (**5**, Scheme 2), in an apparent H<sub>2</sub>-activation/intramolecular imine hydrogenation sequence reminiscent of untethered imine-borane Frustrated Lewis Pairs (FLPs).<sup>26</sup> Accordingly, ligation to the low-valent Pt center modulates the H<sub>2</sub>-reactivity of Cy<sup>2</sup>BIM in favor of 1,2-addition across the Pt–B interaction rather than internal hydrogenation.

Free Cy<sup>2</sup>BIM and **1** show similarly divergent reactivity toward H<sub>2</sub>O. Whereas Cy<sup>2</sup>BIM reacts with H<sub>2</sub>O to yield boronate-amine **6** via H–O bond cleavage and a 1,2-cyclohexyl shift

Scheme 2. Reactivity of Free  $\text{C}^{\text{y}2}\text{BIM}$  (2)

(Scheme 2), addition of  $\text{H}_2\text{O}$  to **1** results in a formal Pt-centered H–O bond oxidative addition to afford  $\text{PtH}(\mu\text{-OH})(\text{C}^{\text{y}2}\text{BIM})(\text{CNAr}^{\text{Dipp}2})$  (**7**, Scheme 1), in which a hydroxide group bridges the  $\text{C}^{\text{y}2}\text{BIM}$ -borane and newly formed Pt–H units. Crystallographic characterization of complex **7** (Figure 2) revealed a B–O bond distance of 1.541(3) Å, which is considerably longer than the average B–O distance of four-coordinate, O-coordinated borates (i.e.,  $\text{ROBR}_3$ ;  $d(\text{B}-\text{O})_{\text{av}} = 1.481(\pm 0.041)$  Å) contained within the Cambridge Structural Database.<sup>27</sup> This long B–O bond in **7**, which undoubtedly results from coordination of the hydroxide ligand to the Lewis acidic Pt(II) center, likely lessens a buildup of charge on the boron atom and obviates the need for cyclohexyl-group migration within the  $\text{C}^{\text{y}2}\text{BIM}$  fragment. It is also noteworthy that well-defined H–O bond oxidative addition of  $\text{H}_2\text{O}$  to low-valent transition metal centers is still limited to only a few examples.<sup>28–31</sup> However, it has been shown that pendant hydrogen-bond donor groups in the ligand periphery can promote  $\text{H}_2\text{O}$  oxidative addition to zerovalent Group 10 metals.<sup>28</sup> Accordingly, the reaction between **1** and  $\text{H}_2\text{O}$  offers a complement to this approach, wherein O–H bond activation is facilitated by direct coordination of a Lewis acidic group to a transition metal center.

The activation of H–X bonds by the Pt→B unit in **1** can also be extended to other substrates. Addition of methanol or *p*-nitroaniline to  $\text{Pt}(\kappa^2\text{-N},\text{B}-\text{C}^{\text{y}2}\text{BIM})(\text{CNAr}^{\text{Dipp}2})$  (**1**) results in formal H–X oxidative addition and formation of the platinum–hydride complexes  $\text{PtH}(\mu\text{-OMe})(\text{C}^{\text{y}2}\text{BIM})(\text{CNAr}^{\text{Dipp}2})$  (**8**) and  $\text{PtH}(\mu\text{-N}(\text{H})\text{C}_6\text{H}_4\text{NO}_2)(\text{C}^{\text{y}2}\text{BIM})(\text{CNAr}^{\text{Dipp}2})$  (**9**), respectively (Scheme 1). Structural characterization of **8** and **9** revealed that

the methoxide and *p*-nitroaniline ligands bridge the Pt and B centers in a manner analogous to the hydroxide ligand in **7**. In contrast, the addition of phenylacetylene (HCCPh) to **1** provides the hydride complex,  $\text{PtH}(\eta^2\text{-C},\text{C}-\kappa^1\text{-N-PhCC-C}^{\text{y}2}\text{BIM})(\text{CNAr}^{\text{Dipp}2})$  (**10**, Scheme 1), which possesses an acetylide group  $\sigma$ -bound to the  $\text{C}^{\text{y}2}\text{BIM}$  boron center and  $\eta^2\text{-C},\text{C}$  ligated to platinum (Figure 2). Most notably, the  $\eta^2\text{-C},\text{C}$ -acetylide coordination mode found in **10** is in direct contrast to the large number of  $\sigma$ -bound Pt(II) acetylides reported in the literature<sup>32,33</sup> and demonstrates how borane ligation to a transition metal not only facilitates substrate activation but also significantly influences the structural properties of resultant products.

Finally, cooperative bond activation by the Pt and B centers in **1** is also apparent in its reactivity toward organic carbonyl compounds. Treatment of **1** with acetone or benzaldehyde results in C=O bond reduction and formation of complexes **11** and **12**, respectively, featuring oxymethyl groups that are C-bound to a formally Pt(II) center and O-bound to boron ( $d(\text{C}-\text{O}) = 1.429(3)$  Å for **11**, Figure 2;  $d(\text{C}-\text{O}) = 1.419(2)$  Å for **12**). The C=O bond reductions leading to complexes **11** and **12** are accompanied by a 1,2-cyclohexyl shift, which transforms the  $\text{C}^{\text{y}2}\text{BIM}$  ligand into a dianionic amidoborionate. This cyclohexyl migration mirrors the reactivity of free  $\text{C}^{\text{y}2}\text{BIM}$  with  $\text{H}_2\text{O}$  and, likewise, reasonably occurs to compensate for an increase of charge on the borane center. In this respect, cooperative carbonyl reduction by the Pt–borane unit in **1** is reminiscent of the C=O bond insertion chemistry available to some late transition metal  $\sigma$ -boryl complexes.<sup>34,35</sup> Accordingly, the  $\text{C}^{\text{y}2}\text{BIM}$  system provides a platform to directly probe the principles differentiating the reactivity of M→B reverse-dative interactions and  $\sigma$ -bound boryls.<sup>36</sup> These investigations, as well as others aimed at further exploiting accessible M→B reverse-dative interactions fostered by the small bite-angle (boryl)-iminomethane framework, are in progress.

## ■ ASSOCIATED CONTENT

### Supporting Information

Synthetic, computational and crystallographic details (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

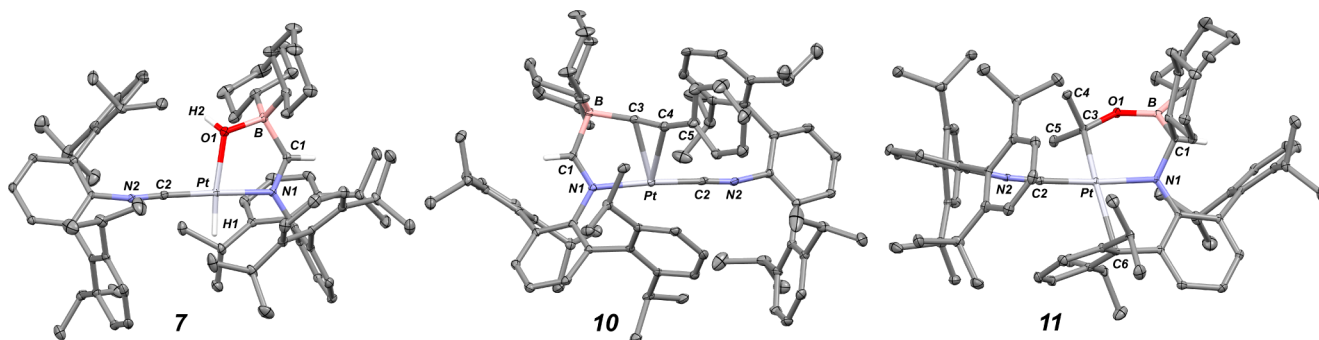
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### Notes

The authors declare no competing financial interest.



**Figure 2.** Molecular structures of complexes **7**, **10**, and **11**. The hydride ligand in **10** was not found in the electron-density difference map. Complex **11** possesses an  $\eta^1$ -ipso interaction between Pt and one flanking Dipp ring in the solid state.



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