

## Accepted Article

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# Transition Metal $\pi$ -Ligation of a Tetrahalodiborane

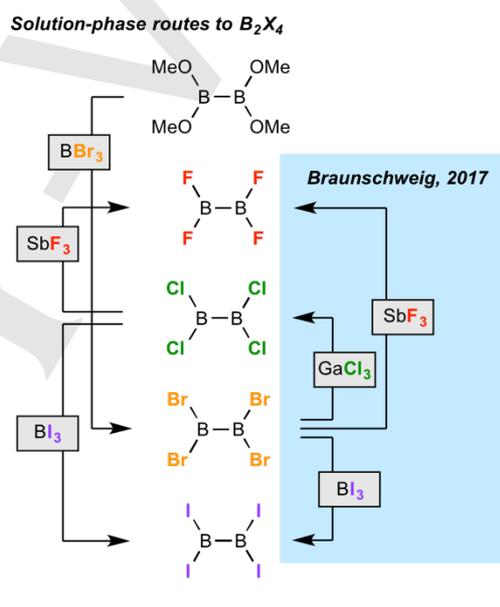
Holger Braunschweig,\* Rian D. Dewhurst, J. Oscar C. Jiménez-Halla, Eduard Matito, Jonas H. Muessig

**Abstract:** The reaction of tetraiododiborane ( $B_2I_4$ ) with *trans*-[Pt( $BI_2$ )(PCy<sub>3</sub>)<sub>2</sub>] led to isolation of the diplatinum(II) complex [(Cy<sub>3</sub>P)(I<sub>2</sub>B)Pt]<sub>2</sub>( $\mu_2$ : $\eta^3$ : $\eta^3$ -B<sub>2</sub>I<sub>4</sub>), supported by the bridging diboranyl dianion ligand [B<sub>2</sub>I<sub>4</sub>]<sup>2-</sup>. The complex is the first transition metal complex of a diboranyl dianion, as well as the first example of intact coordination of a B<sub>2</sub>X<sub>4</sub> (X = halide) unit of any type to a metal center.

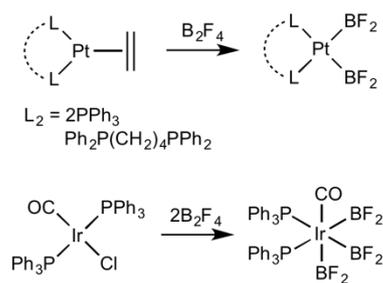
Tetrahalodiboranes (B<sub>2</sub>X<sub>4</sub>; X = F, Cl, Br, I) are enigmatic compounds that are both steeped in history<sup>[1,2]</sup> and yet have massively underexplored synthetic chemistry. Unlike their synthetically useful tetrasubstituted cousins bis(pinacolato)- and bis(catecholato)diboron,<sup>[3]</sup> synthetic interest in tetrahalodiboranes ebbed after an initial spike in their use in the mid-20th century. In fact, as we pointed out recently,<sup>[4]</sup> over the past five years, the filing of patents involving tetrahalodiboranes(4) has outpaced their appearance in journal articles at a rate of two to one, mostly thanks to the current interest in B<sub>2</sub>F<sub>4</sub> in the implantation of B<sup>+</sup> ions into silicon for semiconductor device fabrication.<sup>[5]</sup> Given their lability and immense potential reactivity, the relative absence of literature on tetrahalodiboranes is almost certainly due to their historically difficult preparation, which in many cases involved gas-phase synthesis.<sup>[6]</sup> Very recently, however, we presented simple solution-phase syntheses of B<sub>2</sub>X<sub>4</sub> (X = F, Cl, I) from B<sub>2</sub>Br<sub>4</sub>, making all four tetrahalodiboranes considerably more accessible in practical amounts (Figure 1, top).<sup>[4]</sup>

In addition to our continuing interest in tetrahalodiboranes as precursors to species with boron-boron multiple bonds,<sup>[3c-e,6]</sup> we were also interested in the reactivity of these fundamental boron species with transition metal (TM) fragments, about which very little is known. The coordination chemistry of diboron units with transition metals is quite well-developed and diverse, including their metal-catalyzed boration and diboration chemistry,<sup>[3]</sup> as well as complexes where a metal binds inside a H-B-B-H cavity of sp<sup>3</sup>-sp<sup>3</sup> diboranes,<sup>[7]</sup> complexes based on covalently-bound  $\eta^1$ - and  $\eta^2$ -diboran(4)yl ligands,<sup>[8]</sup> complexes of base-free<sup>[9]</sup> and

base-stabilized  $\eta^2$ -diborenes,<sup>[10]</sup> and  $\eta^2$ -diborynes.<sup>[11]</sup> In contrast, the only known attempts to combine tetrahalodiboranes with transition metal fragments were made by Norman and coworkers with B<sub>2</sub>F<sub>4</sub> (Figure 1, bottom), who isolated two products of B-B bond oxidative addition (*cis*-[Pt(BF<sub>3</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>), as well as an oxidative addition / disproportionation product with Vaska's complex (*fac,trans*-[Ir(BF<sub>3</sub>)<sub>3</sub>(CO)L<sub>2</sub>]).<sup>[12]</sup>



**Reactivity of B<sub>2</sub>X<sub>4</sub> with metal complexes**  
Norman et al. 1998-2000



**Figure 1.** Top: Solution-phase routes to tetrahalodiboranes, with our recently-published routes highlighted in blue.<sup>[4]</sup> Bottom: Reactions of B<sub>2</sub>F<sub>4</sub> with Pt<sup>0</sup> and Ir<sup>I</sup> complexes from the group of Norman et al.

In Norman's work, the exclusive reactivity of B<sub>2</sub>F<sub>4</sub> through its B-B bond is intuitive, given its substantially more inert boron-halide bonds than those of its heavier tetrahalodiborane congeners (B<sub>2</sub>X<sub>4</sub>; X = Cl, Br, I). In contrast, we envisaged more interesting reactivity of electron-rich transition metal fragments with the heavier tetrahalodiboranes, and thus initially sought to probe the reactivity of B<sub>2</sub>I<sub>4</sub> with the low-valent transition metal species [Pt(PCy<sub>3</sub>)<sub>2</sub>]. The results of these studies, presented herein, are indeed underpinned by the greater lability of the B-I

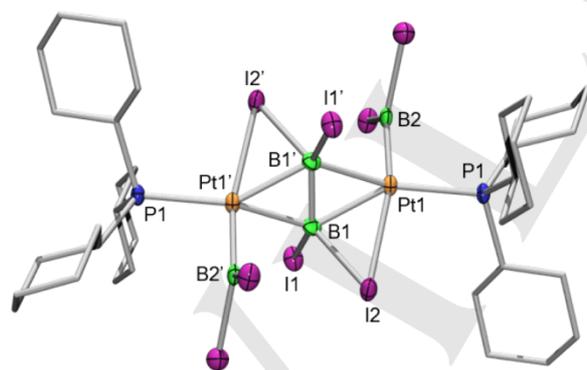
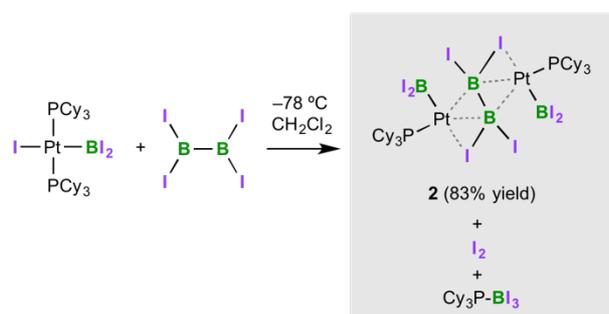
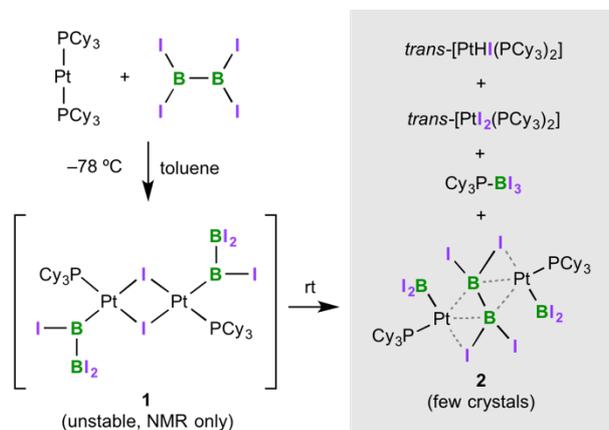
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bonds, and led to the isolation of a highly unusual diplatinum complex containing two boryl ligands and a bridging  $[B_2I_4]$  ligand best described as a diboranyl dianion. The complex is the first transition metal complex of an intact  $B_2X_4$  ( $X = \text{halide}$ ) species of any sort, and the first example of transition metal coordination to a reduced diborane species, compounds known since the pioneering work of Berndt, Nöth and Power in the 1980s and 1990s.<sup>[13,14]</sup>



**Figure 2.** Unselective (top) and selective (middle) syntheses of complex **2**. Crystallographically derived structures of **2** (bottom). Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms and solvent molecules (two molecules of  $CH_2Cl_2$ ) have been removed for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ):  $B1-B1'$  1.744(6),  $Pt1-B1$  2.202(4),  $Pt1-B1'$  2.220(5),  $Pt1-B2$  1.972(5),  $Pt1-I2$  2.7834(5),  $B1-I1$  2.194(4),  $B1-I2$  2.287(5);  $B2-Pt1-I2$  165.33(14); torsion  $Pt1-B1-B1'-Pt1'$

Treating  $[Pt(PCy_3)_2]$  with one equivalent of  $B_2I_4$  at  $-78\text{ }^\circ\text{C}$  led to the observation of one predominant species with a single  $^{31}P\{^1H\}$  NMR signal ( $\delta$  47.1;  $^1J_{P-Pt} = 4320\text{ Hz}$ ) and two  $^{11}B$  NMR signals ( $\delta$  70, 40). These data were initially thought to correspond to the

twofold iodide-bridged dinuclear complex  $[Pt\{B(I)BI_2\}(\mu-I)(PCy_3)_2]_2$  (**1**), a product of oxidative addition of one B-I bond of  $B_2I_4$  to the platinum center (Figure 2, top). However, the previously reported complexes  $[Pt\{BBrFc\}(\mu-Br)(PCy_3)_2]_2$  ( $\delta_P$  23.6;  $^1J_{P-Pt} = 4739\text{ Hz}$ )<sup>[15]</sup> and  $[Pt\{BI_2\}(\mu-I)(PCy_3)_2]_2$  ( $\delta_P$  15.8;  $^1J_{P-Pt} = 4460\text{ Hz}$ )<sup>[16]</sup> which have similar structures and the same phosphine ligand as **1**, show  $^{31}P$  NMR signals significantly upfield of those observed herein, albeit with roughly similar  $^{31}P$ - $^{195}Pt$  coupling constants. Therefore, our assignment of the structure of **1** remains tentative.

Compound **1** decomposes within minutes at  $-78\text{ }^\circ\text{C}$  to a complex mixture of products including  $trans-[PtI(PCy_3)_2]$ ,  $trans-[PtI_2(PCy_3)_2]$ ,  $Cy_3P-BI_3$  and other minor byproducts. Attempts to crystallize a pure product from this mixture provided a few yellow crystals, which were subjected to single-crystal X-Ray diffraction. This study revealed a highly unusual structure based on two  $[Pt(BI_2)(PCy_3)]$  fragments bridged by a single  $B_2I_4$  unit through a network of interactions of the Pt centers with B-I and B-B  $\sigma$  bonds ( $[Pt(BI_2)(PCy_3)]_2(\mu_2-\eta^3:\eta^3-B_2I_4)$  (**2**), structure discussed below; Figure 2, bottom).

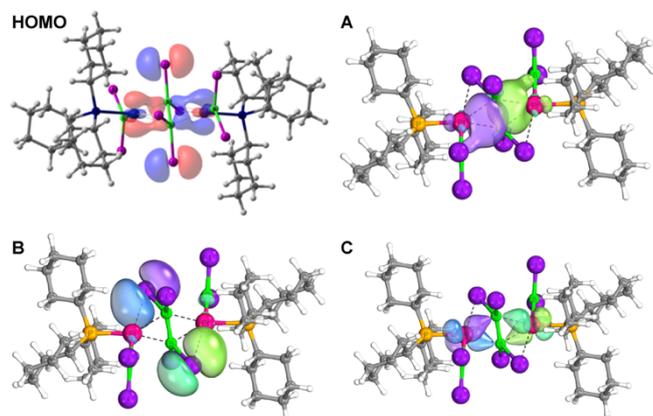
Given the confirmed – but very low-yielding – synthesis of complex **2**, we were naturally eager to develop a selective preparation of this complex. During a number of attempts, we found that traces of  $BI_3$  in the reaction mixture (from the spontaneous disproportionation of the thermally unstable  $B_2I_4$ ) increased the amount of **2** in the product mixture, and that using a 50:50 mixture of  $BI_3$  and  $B_2I_4$  provided almost exclusively complex **2**, along with elemental iodine (as determined by a positive starch test from the mixture but a negative test with pure **2**) and one equivalent of  $Cy_3P-BI_3$ . To further improve the protocol, we reacted  $trans-[Pt(BI_2)I(PCy_3)_2]$  with an equimolar amount of  $B_2I_4$ , providing **2** in 83% yield. The  $^{31}P\{^1H\}$  NMR spectrum of **2** showed a singlet at  $\delta = 30.5\text{ ppm}$  with a  $^{31}P$ - $^{195}Pt$  coupling constant of 2835 Hz, while the  $^{11}B$  NMR spectrum showed two signals ( $\delta$  40, 7). The former  $^{11}B$  NMR signal is identical to that found in **1**, presumably being that of the boron atoms of the terminal boryl ligands. Complex **2** is stable enough in solution to perform NMR experiments, but has to be stored at  $-30\text{ }^\circ\text{C}$  and under exclusion of light to prevent decomposition.

An X-ray diffraction study of single crystals of **2** from this reaction further confirmed the successful synthesis of the minor product detected in the first reaction (Figure 2). The structure shows a planar  $Pt_2B_2$  unit, with each Pt center binding in a  $\sigma$  fashion to one B-B bond ( $Pt-B1$ : 2.202(4) Å;  $Pt-B1'$ : 2.220(5) Å) and one B-I bond ( $Pt1-I2$ : 2.7834(5) Å). It should be noted that the distance of the diborane unit to the platinum centers in **2** is about 11% longer than the  $Pt-B^{boryl}$  distance (1.972(5) Å), as the  $B_2I_4$  ligand is bound through weaker 2e-3c bonds (see computational results below). The Pt-bound B-I bonds (2.287(5) Å) are significantly longer than the adjacent non-Pt-bound B-I bonds (2.194(4) Å), which in turn are longer than the B-I bonds of the terminal boryl ligand (2.150(5), 2.167(5) Å). Similarly, the  $Pt1-I2$  distance (2.7834(5) Å) is significantly longer than regular  $Pt^I-I$  bonds.

The B-B bond length of complex **2** (1.744(9) Å) is identical to that of isolated  $B_2Cl_4$  (1.75(5) Å)<sup>[17]</sup> within experimental uncertainty. However, this distance is much larger than the corresponding bonds of TM-bound neutral, base-stabilized diborenes of the form  $[MX_n(\eta^2-ArLB=BLAr)]^{[10]}$  ( $d_{BB} = 1.61\text{--}1.65\text{ Å}$ ;  $MX_n = CuCl, AgCl, CdCl_2, ZnCl_2, ZnBr_2$ ;  $L = NHC, \text{phosphine}$ ;  $Ar = \text{duryl, anthryl}$ ), despite their isoelectronic relationship and

the presence of a  $\pi_{BB}$  bond in both. The B–B distance of **2** is even further removed from that of the base-free diborene complex  $[(Et_3P)_2Pt(B_2Dur_2)]$  ( $d_{BB} = 1.51(1)$  Å), which features B–B-bond-strengthening  $\pi$  backdonation from the metal.<sup>[9a]</sup> These data point to the diboranyl dianion complex **2** having much stronger covalent bonding with the Pt center than in TM complexes of neutral diborenes, where electrostatic contributions predominate.

Attempts to prepare analogous complexes by the reactions of (a) *trans*-[Pt(BX<sub>2</sub>)X(PCy<sub>3</sub>)<sub>2</sub>] (X = Cl, Br, I) with B<sub>2</sub>Cl<sub>4</sub>, (b) *trans*-[Pt(BBr<sub>2</sub>)Br(PCy<sub>3</sub>)<sub>2</sub>] with B<sub>2</sub>Br<sub>4</sub>, and (c) *trans*-[Pt(BI<sub>2</sub>)I(PCy<sub>3</sub>)<sub>2</sub>] with B<sub>2</sub>I<sub>4</sub>, were all unsuccessful. It should also be noted that based on these results, and the diverse coordination modes of diboranes proposed theoretically with the [Cr(CO)<sub>4</sub>] fragment by Jemmis et al.,<sup>[18]</sup> we also attempted to coordinate a range of tetrahalodiboranes to zerovalent chromium. However, treatment of B<sub>2</sub>X<sub>4</sub> (X = Cl, Br, I) with [Cr(CO)<sub>6</sub>] failed to provide tractable products either under thermal or photolytic conditions.

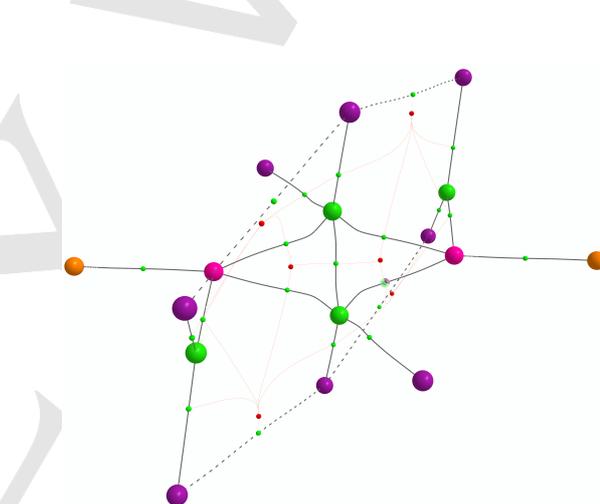


**Figure 3.** Calculated HOMO (top left) and the three intrinsic bond orbitals of most relevance to the Pt-B<sub>2</sub>I<sub>4</sub> interaction of **2** (A–C).

The connectivity of **2** naturally raises questions about the identity of the diborane bridging ligand and the nature of the Pt–B bonding, prompting us to undertake theoretical calculations at the  $lc-\omega$ PBE/SBKJC level. The solid-state structure of **2** shows that both the B–I and Pt–I bonds of the B–Pt–I triangle are very long (vide supra), and this is reflected in the low atoms-in-molecules (AIM)<sup>[19]</sup> bond orders<sup>[20]</sup> calculated for these bonds (B–I<sup>bridging</sup>: 0.72, c.f. B–I<sup>terminal</sup>: 0.91; Pt–I: 0.60). These data suggest a relatively even sharing of the bridging iodides between the boron and platinum atoms. This unit is bound to the Pt centers through three-center-two-electron (3c2e) PtB<sub>2</sub> bonds as confirmed by multicenter bond indices<sup>[21]</sup> that are larger than those present in diborane, and the presence of ring critical points (RCPs) of electron density in the center of each B–Pt–B triangle.<sup>[19]</sup> The shape of the HOMO of **2** (Figure 3, top left), reveals an interaction between the [B<sub>2</sub>I<sub>4</sub>] unit and the two Pt atoms. Analysis of the intrinsic bond orbitals (IBOs)<sup>[22]</sup> related to the Pt–[B<sub>2</sub>I<sub>4</sub>] interaction shows that the most relevant interactions are: (A, Figure 3) twofold  $\pi_{BB} \rightarrow d_{Pt}$  donation, (B) iodide lone-pair-to-platinum ( $LP_{I} \rightarrow d_{Pt}$ ) donation, and (C) twofold  $d_{Pt} \rightarrow \pi_{BB}^*$  backdonation. Interaction A is characterized by a two-fold interaction of the B–B bond with the Pt centers, thus confirming the multicenter character of this bond.

Formal considerations dictate either a Pt(II) / [B<sub>2</sub>I<sub>4</sub>]<sup>2-</sup> or a Pt(I) / [B<sub>2</sub>I<sub>4</sub>]<sup>0</sup> description for **2**. However, the latter case invokes rare monovalent Pt and implies the presence of a platinum-based diradical, which we do not observe. Thus, from an experimental standpoint the former situation appears to be a far better description. AIM analysis suggests the presence of two multicenter PtB<sub>2</sub> 3c2e bonds, similar to the two B<sub>3</sub> 3c2e bonds seen in Himmel's rhomboidal B<sub>4</sub> compound.<sup>[23]</sup> The observation of PtB<sub>2</sub> RCPs in **2** (Figure 4) is furthermore in line with the calculation of a similar NiC<sub>2</sub> RCP for the  $\pi$ -olefin complex [Ni(C<sub>2</sub>H<sub>4</sub>)(tBu<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PtBu<sub>2</sub>)],<sup>[24]</sup> to which the Dewar-Chatt-Duncanson ( $\sigma$ -donation /  $\pi$ -backbonding) model applies. Thus, the B<sub>2</sub>I<sub>4</sub> unit can be seen as an analogue of an olefin.

However, regardless of the true nature of the bonding in **2**, the complex is the surprising first example of the intact coordination of a reactive tetrahalodiborane unit to a metal. The results reported herein provide a glimpse of the potentially exciting coordination chemistry of tetrahalodiboranes, about which very little is currently known.



**Figure 4.** Topological analysis of the electron density<sup>[19]</sup> of **2**. Only the core of the complex is shown; Pt: pink, B: green, I: purple, P: orange. The analysis reveals bond critical points (small dots in green) for B–B, Pt–B and several B–I bonds, as well as two ring critical points (small dots in red) in the two B–Pt–B triangular structures. The bond paths (grey lines) are slightly curved for the four B–Pt bonds that form the rhomboid structures. All these features suggest two 2e3c bonds for each B–Pt–B structure.

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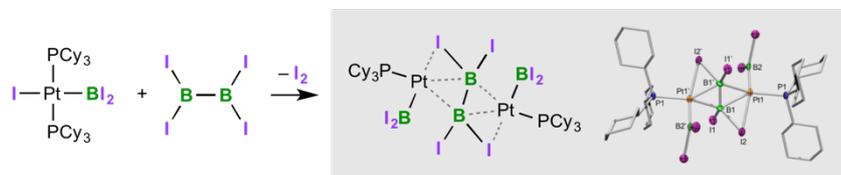
**Keywords:** boron • platinum •  $\sigma$ -bond complexes • diboranes • haloboranes

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## Entry for the Table of Contents

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The reaction of tetraiododiborane with *trans*-[Pt(BI<sub>2</sub>)I(PCy<sub>3</sub>)<sub>2</sub>] led to isolation of a diplatinum(II) complex supported by a bridging [B<sub>2</sub>I<sub>4</sub>] unit. The complex is the first transition metal complex of a diboranyl dianion, as well as the first example of intact coordination of a B<sub>2</sub>X<sub>4</sub> (X = halide) unit of any type to a metal center.

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Transition Metal  $\pi$ -Ligation of a Tetrahalodiborane