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# Catalytic dehydrocoupling of amine-boranes and amines into diaminoboranes: isolation of a Pt(II), Shimoi-type, $\eta^1$ -BH complex†

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**The platinum complex [Pt(I<sup>t</sup>Bu')(I<sup>t</sup>Bu)][BAR<sup>F</sup>] is a very efficient catalyst in the synthesis of diaminoboranes through dehydrocoupling of amine-boranes and amines. Shimoi-type,  $\eta^1$ -BH complexes are key intermediates in the process.**

In the last few years amine-boranes and related base-stabilised borane adducts have been shown to produce rich chemistry in which metal catalysed dehydrocoupling processes are involved.<sup>1</sup> During some of these reactions the B–H bonds of the amine borane establish an initial interaction with the metal centre to form complexes exhibiting  $\eta^1$  or  $\eta^2$  coordination modes, undergoing thereafter subsequent reactivities.<sup>1a,2</sup>

Dehydrogenation of amine-boranes has been mainly focused on the production and release of dihydrogen and on the generation of amino-boranes that can undergo further dimerization, oligomerization or polymerization processes.<sup>1,2,3</sup> Less attention has been paid to the production of other boranes, through boron–boron coupling<sup>4</sup> or the formation of diaminoboranes, (NR<sub>2</sub>)<sub>2</sub>BH.<sup>5</sup> With regard to the latter process, only a couple of catalytic processes have been reported by Alcaraz and Sabo-Etienne, using ruthenium<sup>5a,c</sup> and by Hill,<sup>5b</sup> with calcium and magnesium based catalysts to produce the corresponding diaminoboranes. Catalyst loadings of 2.5% (Ru, Ca, Mg), together with long reaction times (Ru), and even heating (Ca, Mg) were required.

In this communication we wish to report a very efficient platinum(II) complex that promotes diaminoborane formation at a catalyst loading of 0.5% in a few minutes for most of the substrates tested. In addition, we have been able to characterise

by means of X-ray diffraction studies the first Shimoi-type  $\eta^1$ -BH complex of a Lewis base-borane adduct and platinum, which provides structural insights into a key intermediate in the dehydrogenation process of amine-boranes and amines.

Previously, we had reported that the [Pt(I<sup>t</sup>Bu')(I<sup>t</sup>Bu)][BAR<sup>F</sup>] complex (where I<sup>t</sup>Bu stands for 1,3-di-*tert*-butylimidazolylidene and I<sup>t</sup>Bu' its cyclometalated form), **1**,<sup>6</sup> is able to promote the dehydrocoupling of dimethylamineborane (NMe<sub>2</sub>H·BH<sub>3</sub>) into cyclic [NMe<sub>2</sub>BH<sub>2</sub>]<sub>2</sub> (Scheme 1).<sup>7</sup> During NMR mechanistic studies, we observed that bis(dimethylamino)borane (NMe<sub>2</sub>)<sub>2</sub>BH is also formed in small amounts and its yield increases as the concentration of free NMe<sub>2</sub>H in the reaction media increases. Therefore, we analysed the ability of complex **1** to act as a catalyst for the formation of diaminoboranes.

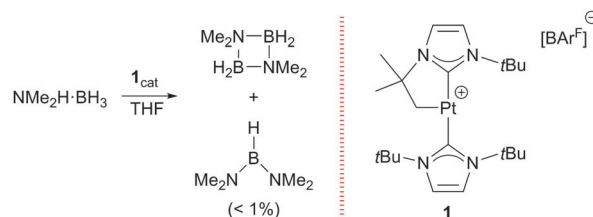
We have first studied the benchmark reaction of *tert*-butylamineborane (<sup>t</sup>BuNH<sub>2</sub>·BH<sub>3</sub>) and 1 equiv. of *tert*-butylamine (<sup>t</sup>BuNH<sub>2</sub>) in CD<sub>2</sub>Cl<sub>2</sub>, using a catalyst loading of 0.5% (Scheme 2). The reaction was monitored both by NMR spectroscopy and by measuring the increase of gas pressure in a closed system due to the generated H<sub>2</sub> (see the ESI†). The <sup>11</sup>B NMR spectrum revealed the formation of a single species in nearly quantitative yield after 11.5 min showing a doublet signal at  $\delta$  25.8 ppm (<sup>1</sup>J<sub>BH</sub> = 127 Hz). In addition, the <sup>1</sup>H NMR spectrum exhibits a broad quartet signal centred at 4.12 ppm that sharpens upon <sup>11</sup>B decoupling into a triplet (*J*<sub>HH</sub> = 8.2 Hz). These values are in agreement with the formation of diaminoborane (<sup>t</sup>BuNH)<sub>2</sub>BH,<sup>8</sup> **s1** (Scheme 2). The calculated TON and TOF values for this process are 400 and 2087 h<sup>-1</sup>, the highest reported to the best of our knowledge (Table 1).

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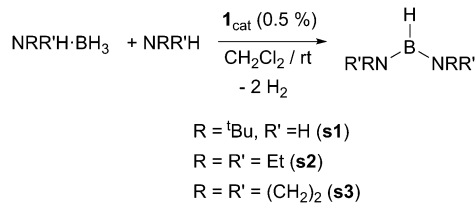
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† Electronic supplementary information (ESI) available: Experimental section, H<sub>2</sub> evolution graphics and X-ray crystallographic data. CCDC 1468913. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc02720b



Scheme 1 Dehydrocoupling of NMe<sub>2</sub>H·BH<sub>3</sub> catalysed by complex **1**.





Scheme 2 Catalytic synthesis of symmetric diaminoboranes.

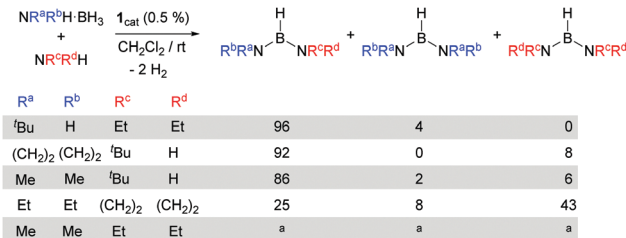
Table 1 Catalytic dehydrocoupling of amine-boranes and amines

| Entry <sup>a</sup> | Amineborane  | Amine                              | % Yield <sup>b</sup><br>(isolated) | TON | TOF<br>(h <sup>-1</sup> ) |
|--------------------|--|------------------------------------|------------------------------------|-----|---------------------------|
| 1                  | <sup>t</sup> BuNH <sub>2</sub> ·BH <sub>3</sub>    | <sup>t</sup> BuNH <sub>2</sub>     | > 99 (99)                          | 400 | 2087                      |
| 2                  | NET <sub>2</sub> H·BH <sub>3</sub>                 | NET <sub>2</sub> H                 | > 99 (88)                          | 400 | 2400                      |
| 3                  | (CH <sub>2</sub> ) <sub>4</sub> NH·BH <sub>3</sub> | (CH <sub>2</sub> ) <sub>4</sub> NH | 95 <sup>c</sup> (81)               | 380 | 193                       |
| 4                  | <sup>t</sup> BuNH <sub>2</sub> ·BH <sub>3</sub>    | NET <sub>2</sub> H                 | > 99 (99)                          | 400 | 3692                      |
| 5                  | <sup>t</sup> BuNH <sub>2</sub> ·BH <sub>3</sub>    | (CH <sub>2</sub> ) <sub>4</sub> NH | 94 (68)                            | 376 | 376                       |
| 6                  | NET <sub>2</sub> H·BH <sub>3</sub>                 | (CH <sub>2</sub> ) <sub>4</sub> NH | 93                                 | 372 | 248                       |
| 7                  | NMe <sub>2</sub> H·BH <sub>3</sub>                 | <sup>t</sup> BuNH <sub>2</sub>     | 78 <sup>c</sup> (71) <sup>d</sup>  | 312 | 2023                      |
| 8                  | NMe <sub>2</sub> H·BH <sub>3</sub>                 | NET <sub>2</sub> H                 | 76 <sup>c</sup>                    | 316 | 2257                      |

<sup>a</sup> Reaction conditions: CH<sub>2</sub>Cl<sub>2</sub>, rt. <sup>b</sup> Yields determined by <sup>11</sup>B NMR spectroscopy with respect to all diaminoboranes formed. <sup>c</sup> Cyclic dimers [NR<sub>2</sub>BH<sub>2</sub>]<sub>2</sub> and other unidentified species constitute the remaining reaction products (see the ESI). <sup>d</sup> Isolated yield corresponds to all the possible products formed.

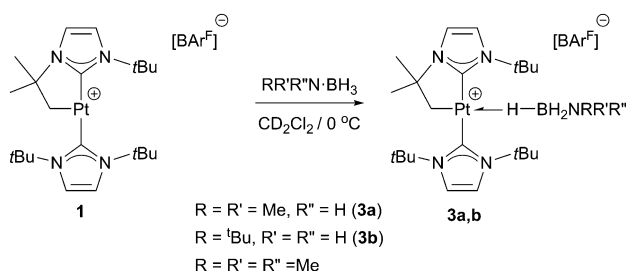
At the very end of the reaction, the catalyst remained the cyclo-metallated species **1**, but is slowly hydrogenated into complex [PtH(<sup>t</sup>Bu)<sub>2</sub>][BAR<sup>f</sup>], **2**. Other amine-boranes were tested under identical reaction conditions to form symmetrical diaminoboranes. Diethylamine-borane was also shown to be efficiently dehydrogenated in *ca.* 10 min in the presence of 1 equiv. of NET<sub>2</sub>H and catalyst **1** (TON = 400, TOF = 2400 h<sup>-1</sup>). On the other hand, pyrrolidine-borane (CH<sub>2</sub>)<sub>4</sub>NH·BH<sub>3</sub> required longer reaction times (2 h) to be converted into [(CH<sub>2</sub>)<sub>4</sub>N]<sub>2</sub>BH (TON = 380, TOF = 193 h<sup>-1</sup>). In the latter case, 5% of cyclic dimer [(CH<sub>2</sub>)<sub>4</sub>NBH<sub>2</sub>]<sub>2</sub> is observed in the <sup>11</sup>B NMR spectra. Bulkier amine-boranes, such as <sup>i</sup>Pr<sub>2</sub>NH·BH<sub>3</sub>, do not undergo dehydrocoupling under similar reaction conditions, while heating at 60 °C for 12 h results in the formation of amino-borane N<sup>i</sup>Pr<sub>2</sub>BH<sub>2</sub>, with no evidence of the corresponding diaminoborane.

Asymmetrical diaminoboranes are challenging substrates to be produced catalytically in a selective manner. Hill *et al.* have recently reported a method for the preparation of this type of substance using group 2 metal catalysts.<sup>5b</sup> Although in most of the cases the reaction proceeds with excellent selectivities, long reaction times (24–92 h) and mild heating are usually necessary. Complex **1** has shown very good catalytic behaviour in the formation of unsymmetrical diaminoboranes (Scheme 3). The reaction of <sup>t</sup>BuNH<sub>2</sub>·BH<sub>3</sub> with NET<sub>2</sub>H takes place very fast (6.5 min, TON = 400, TOF = 3692 h<sup>-1</sup>). According to NMR spectroscopy, borane (<sup>t</sup>BuNH)(NET<sub>2</sub>)BH is formed almost exclusively (*ca.* 4% of (<sup>t</sup>BuNH)<sub>2</sub>BH is observed by <sup>1</sup>H NMR). If the reaction is carried out in the inverse way, starting from NET<sub>2</sub>H·BH<sub>3</sub> and <sup>t</sup>BuNH<sub>2</sub>, the process is slower (*ca.* 20 min), but selectivities are comparable. The same behaviour is observed in the catalytic dehydrocoupling of (CH<sub>2</sub>)<sub>4</sub>NH·BH<sub>3</sub> and <sup>t</sup>BuNH<sub>2</sub>. In this case, the reaction

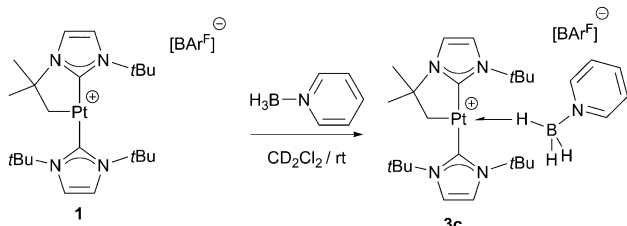
Scheme 3 Catalytic synthesis of asymmetric diaminoboranes. <sup>a</sup> Signal overlapping in the <sup>1</sup>H and <sup>11</sup>B(<sup>1</sup>H) NMR spectra precluded establishing the exact amount of each diaminoborane (see the ESI<sup>†</sup>).

exhibits good selectivities towards the asymmetric diaminoborane (<sup>t</sup>BuNH)[(CH<sub>2</sub>)<sub>4</sub>N]BH (92%), whereas the only symmetric borane detected is [(CH<sub>2</sub>)<sub>4</sub>N]<sub>2</sub>BH (8%), with complete conversion after 2 h at rt. When the reaction is carried out the other way around, that is, starting from <sup>t</sup>BuNH<sub>2</sub>·BH<sub>3</sub> and (CH<sub>2</sub>)<sub>4</sub>NH, the selectivities are only slightly different (85% of (<sup>t</sup>BuNH)[(CH<sub>2</sub>)<sub>4</sub>N]BH, 15% of [(CH<sub>2</sub>)<sub>4</sub>N]<sub>2</sub>BH), although the reaction proceeds in 1 h. The combination of pyrrolidine and diethylamine substrates indicates that the reaction is not selective yielding all possible reaction products (NET<sub>2</sub>)<sub>2</sub>BH, [(CH<sub>2</sub>)<sub>4</sub>N]<sub>2</sub>BH and (NET<sub>2</sub>)[(CH<sub>2</sub>)<sub>4</sub>N]BH in a 1 : 5.4 : 3.1 ratio, respectively, independent of the two possible combinations utilised. A similar behaviour was observed in the reaction of NMe<sub>2</sub>H·BH<sub>3</sub> with NET<sub>2</sub>H, although we could not establish the exact ratio due to signal overlapping in the <sup>1</sup>H NMR (see the ESI<sup>†</sup>). Nevertheless, good selectivities are produced in the reaction of NMe<sub>2</sub>H·BH<sub>3</sub> and <sup>t</sup>BuNH<sub>2</sub> (Scheme 3). Very interestingly, the reaction of <sup>t</sup>BuNH<sub>2</sub>·BH<sub>3</sub> with <sup>i</sup>Pr<sub>2</sub>NH generates diaminoborane (<sup>t</sup>BuNH)<sub>2</sub>BH (**s1**) and amino-borane <sup>i</sup>Pr<sub>2</sub>N-BH<sub>2</sub> in *ca.* 5 min at rt. Since **1** does not catalyse the dehydrocoupling of <sup>i</sup>Pr<sub>2</sub>NH·BH<sub>3</sub> at rt, <sup>i</sup>Pr<sub>2</sub>N-BH<sub>2</sub> is probably formed through the reorganization of amino-borane <sup>t</sup>BuNH-BH<sub>2</sub> and <sup>i</sup>Pr<sub>2</sub>NH.<sup>9</sup>

With regard to the mechanism by which these transformations occur, it has been previously shown that dehydrogenation of amine-boranes NR<sub>2</sub>H·BH<sub>3</sub> leading to the corresponding aminoboranes NR<sub>2</sub>BH<sub>2</sub> is a key step.<sup>5</sup> Previously, we have reported that complex **1** is able to dehydrogenate NMe<sub>2</sub>H·BH<sub>3</sub> into NMe<sub>2</sub>BH<sub>2</sub> (that then dimerises) through a distinct mechanism that involves a first step in which the amine-borane interacts with the platinum atom through the BH<sub>3</sub> protons (complex **3a** in Scheme 4) followed by nucleophilic addition of free amine present in solution to the activated boron atom.<sup>7</sup> According to DFT calculations the most stable coordination mode of the BH<sub>3</sub> moiety is η<sup>1</sup>-BH (Shimoi type complex) but, unfortunately, no experimental evidence for this

Scheme 4 Formation of complexes **3a,b**.

type of coordination could be provided. Here we further investigate these adducts by carrying out stoichiometric reactions between complex **1** and amine-boranes at 0 °C in CD<sub>2</sub>Cl<sub>2</sub>. <sup>t</sup>BuNH<sub>2</sub>·BH<sub>3</sub> reacts with **1** leading to a new species that has been postulated as the η<sup>1</sup>-BH derivative **3b** (Scheme 4). The BH<sub>3</sub> group resonates as a broad signal centred at 0.12 ppm that sharpens upon <sup>11</sup>B broadband decoupling. This signal is shifted upfield from the free <sup>t</sup>BuNH<sub>2</sub>·BH<sub>3</sub> (δ 1.36). In addition, *J*<sub>PtH</sub> of the CH<sub>2</sub>-Pt fragment has a value of 90 Hz, that is, 30 Hz smaller than in complex **1** (120 Hz), consistent with the coordination of a ligand *trans* to the CH<sub>2</sub> moiety.<sup>10</sup> This value is smaller than that observed in dimethylamine-borane **3a** (103 Hz) suggesting that the interaction with the platinum atom is stronger. The <sup>11</sup>B NMR spectrum shows a signal at -18.2 ppm that is shifted with respect to free amine-borane (-21.1 ppm). All these data agree well with the formulation of **3b** as depicted in Scheme 4.<sup>11</sup> Unfortunately, the instability of **3a** and **3b** due to their propensity to undergo dehydrocoupling precluded their isolation as pure compounds and further characterization. To avoid this problem, tertiary amine-borane NMe<sub>3</sub>·BH<sub>3</sub> was used. However, no interaction with **1** was observed, probably due to steric constraints, thus allowing the establishment of a correlation between the bulkiness of the amine-borane and its interaction with **1** (stronger interaction: <sup>t</sup>BuNH<sub>2</sub>·BH<sub>3</sub> > NMe<sub>2</sub>H·BH<sub>3</sub> > NMe<sub>3</sub>·BH<sub>3</sub>). Consequently, the less hindered Lewis base stabilised borane C<sub>6</sub>H<sub>5</sub>N·BH<sub>3</sub> was a judicious choice. This borane reacts with **1** to yield **3c** (Scheme 5) quantitatively by NMR spectroscopy. The main feature of **3c** is the broad NMR signal centred at 1.25 ppm attributed to the BH<sub>3</sub> protons (2.55 ppm in free C<sub>6</sub>H<sub>5</sub>N·BH<sub>3</sub>). The <sup>11</sup>B{<sup>1</sup>H} spectrum exhibits a signal at -8.9 ppm, nearly 3 ppm down-field shifted with respect to C<sub>6</sub>H<sub>5</sub>N·BH<sub>3</sub>. The apparent coupling constant <sup>1</sup>*J*<sub>B,H</sub> is *ca.* 85 Hz, that is, 12 Hz smaller than in free C<sub>6</sub>H<sub>5</sub>N·BH<sub>3</sub>, and compares well with previously described Shimoi-type complexes.<sup>11,12</sup> The coupling constant of the CH<sub>2</sub>-Pt protons with <sup>195</sup>Pt of 93 Hz is similar to that of complex **3b**. A definite proof of the nature of this compound came from the solid-state structure obtained by X-ray diffraction studies. Colourless crystals suitable for this analysis were obtained by slow diffusion of a concentrated solution of **3c** in CH<sub>2</sub>Cl<sub>2</sub> into pentane at 0 °C. Fig. 1 depicts an ORTEP-type view of the cation of complex **3c**. The complex is four-coordinated, with two N-heterocyclic carbene units in the expected *trans* arrangement (C(1)-Pt(1)-C(12): 168.38(19)°) one of which is cyclometalated. The fourth coordination site is occupied by the C<sub>6</sub>H<sub>5</sub>N·BH<sub>3</sub> ligand in which one of the hydride atoms of the BH<sub>3</sub> unit bridges the platinum nucleus. The Pt(1)-H(1B) and H(1B)-B(1) bond distances are 1.96(5) and 1.03(2) Å, respectively.



Scheme 5 Synthesis of complex **3c**.

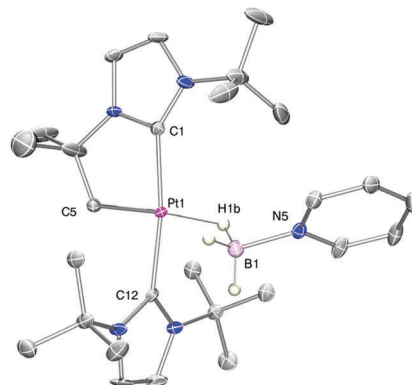


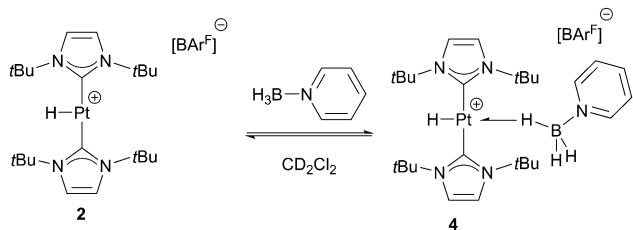
Fig. 1 ORTEP-type view of the cation of complex **3c**. Hydrogen atoms, except those of the BH<sub>3</sub> unit, have been omitted for clarity (ellipsoids are drawn at 30% probability). Selected bonds (Å) and angles (°): Pt1-H1b 1.96(5), Pt1-C5 2.045(5), B1-H1b 1.03(2); Pt1-H1b-B1 147.48(485), C1-Pt1-C12 168.38(19).

The Pt(1)-H(1B)-B(1) angle of 147.48(485)° together with the long Pt(1)··B(1) bond distance (2.8436(5) Å) indicates a negligible interaction between platinum and boron, and therefore this complex is best described as a η<sup>1</sup>-BH or Shimoi-type complex.<sup>12,13</sup>

Variable temperature NMR spectroscopy was used to study the dynamic behaviour due to exchange between bridging and terminal BH protons. The resonance for the BH<sub>3</sub> protons collapses into the baseline at *ca.* 223 K. Upon cooling to 203 K, a new signal of relative integral 2 appears at 2.47 ppm, in the expected region for terminal BH protons. Nevertheless, at this temperature, the signal corresponding to the Pt-H-B proton is not discernible.<sup>14</sup> Further cooling to 183 K provided evidence for a very broad resonance at *ca.* -4 ppm (approx. integral value of 1), with the terminal BH protons resonating at 2.44 ppm. With respect to the <sup>11</sup>B NMR spectra, a very broad signal centred at δ -12.2 is detected at this temperature.

For comparison purposes, we have analysed the interaction of C<sub>6</sub>H<sub>5</sub>N·BH<sub>3</sub> with the hydrogenated form of complex **1**, the hydride derivative [PtH(<sup>t</sup>Bu)<sub>2</sub>][BARF], **2**.<sup>15</sup> No evidence of interaction between **2** and C<sub>6</sub>H<sub>5</sub>N·BH<sub>3</sub> is observed at 298 K. At this temperature, the BH<sub>3</sub> protons resonate at δ 2.49, whereas the platinum-hydride signal appears at δ -25.47 exhibiting a *J*<sub>Pt,H</sub> of 2550 Hz, only marginally different from that of complex **2** in the absence of C<sub>6</sub>H<sub>5</sub>N·BH<sub>3</sub> (*J*<sub>Pt,H</sub> = 2564 Hz).<sup>15</sup> However, the <sup>1</sup>H NMR spectra at temperatures below 233 K indicate the presence of a new species, **4** (Scheme 6), coexisting with complex **2**, in a 0.3 to 1 ratio (**4**:**2**). This compound is characterised by a signal in the hydride region at -21.85 ppm showing a reduced coupling constant with <sup>195</sup>Pt (*J*<sub>Pt,H</sub> = 1920 Hz) and another broad signal at 0.28 ppm (3H relative integral) that sharpens upon <sup>11</sup>B decoupling. As the temperature decreases, the concentration of **4** increases at the expense of **2**, reaching a maximum at 188 K (**4**:**2** ratio, *ca.* 4:1). The <sup>11</sup>B{<sup>1</sup>H} NMR spectra at all temperatures exhibit a single very broad signal at -12.3 ppm that does not show splitting upon coupling to <sup>1</sup>H below 208 K. Interestingly, even at 188 K the BH<sub>3</sub> group still shows fast exchange between terminal and bridging hydrogens. The different behaviour of compounds **1** and **2** toward the interaction





Scheme 6 Equilibrium between complexes **2** and **4** in the presence of  $C_6H_5N-BH_3$ .

with  $C_6H_5N-BH_3$  can be easily rationalised in terms of the different steric protection that the cyclometalated  $tBu$  ligand exerts on the platinum atom compared to its non-cyclometalated form. When the  $tBu$  ligand is cyclometalated the  $tBu$  group is tilted<sup>16</sup> away from the metal centre favouring the interaction with amine-boranes.

Once the amine-borane binds the metal in a Shimoï-type fashion, dehydrogenation leading to amino-boranes,  $NR_2-BH_2$ , takes place through a mechanism that involves the intermediacy of boronium cations  $(NHR_2)_2BH_2^+$  and the neutral platinum hydride  $[PtH(tBu)(tBu)]$ , **5**.<sup>7</sup> It must be noted that we have not observed an interaction between complex **1** and amino-borane  $NMe_2BH_2$  (either using cyclic dimer  $[NMe_2BH_2]_2$  as a precursor<sup>17</sup> or during monitoring the dehydrogenation reaction of **1** and  $NMe_2H-BH_3$  at 0 °C).<sup>7</sup> At this point, we do not have further information on the mechanism by which the amino-borane is converted into diamminoboranes and the role of complex **1** in the process.

In summary, the coordinatively unsaturated Pt(II) complex **1** is a very efficient catalyst for the synthesis of diamminoboranes achieving TON and TOF values of 400 and  $3692 h^{-1}$ , respectively, the highest reported to date. The process takes place through the initial coordination of the BH protons of amine-boranes to the platinum centre in an end-on mode (Shimoï type) that was demonstrated crystallographically in the pyridine- $BH_3$  adduct **3c**. Ongoing efforts are geared towards unveiling the mechanism by which amino-boranes are transformed into diamminoboranes.

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