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## Catalytic dehydrocoupling of amine-boranes and amines into diaminoboranes: isolation of a Pt(11), Shimoi-type, η<sup>1</sup>-BH complex†

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The platinum complex [Pt(I<sup>t</sup>Bu<sup>'</sup>)(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, n<sup>1</sup>-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. 1a,2

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. 1,2j,3 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  $^{5a,c}$  and by Hill,  $^{5b}$ 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.

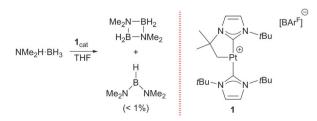
In this communication we wish to report a very efficient platinum(II) complex that promotes diaminoborane formation at a catalyst loading of 0.5% in a few minutes for most of the substrates tested. In addition, we have been able to characterise

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  $[Pt(I^tBu')(I^tBu)][BAr^F]$ complex (where I<sup>t</sup>Bu stands for 1,3-di-tert-butylimidazolylidene and I<sup>t</sup>Bu' its cyclometalated form), 1,6 is able to promote the dehydrocoupling of dimethylamineborane (NMe2H·BH3) 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 (NMe2)2BH 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 ( ${}^{1}J_{BH}$  = 127 Hz). In addition, the <sup>1</sup>H NMR spectrum exhibits a broad quartet signal centred at 4.12 ppm that sharpens upon 11B decoupling into a triplet ( $I_{HH}$  = 8.2 Hz). These values are in agreement with the formation of diaminoborane (\*BuNH)<sub>2</sub>BH, \* 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).

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental section, H2 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.

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NRR'H·BH<sub>3</sub> + NRR'H 
$$\frac{\mathbf{1}_{cat} (0.5 \%)}{CH_2Cl_2 / rt} + \frac{\mathbf{1}_{cat} (0.5 \%)}{R'RN} = \frac{\mathbf{1}_{cat} (0.5 \%)}{R'RN} + \frac{\mathbf{1}_{cat} (0.5 \%)}{R'RN} = \frac{\mathbf{1}_{cat} (0.5 \%)}{R'RN} + \frac{\mathbf{1$$

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> (isolated)	TON	$_{\left( h^{-1}\right) }^{TOF}$
1	<sup>t</sup> BuNH <sub>2</sub> ⋅BH <sub>3</sub>	<sup>t</sup> BuNH <sub>2</sub>	>99 (99)	400	2087
2	$NEt_2H \cdot BH_3$	$NEt_2H$	>99 (88)	400	2400
3	$(CH_2)_4NH \cdot BH_3$	(CH <sub>2</sub> ) <sub>4</sub> NH	$95^{c}(81)$	380	193
4	$^{t}$ BuNH $_{2}$ ·BH $_{3}$	$NEt_2H$	>99 (99)	400	3692
5	<sup>t</sup> BuNH₂⋅BH₃	(CH <sub>2</sub> ) <sub>4</sub> NH	94 (68)	376	376
6	$NEt_2H \cdot BH_3$	$(CH_2)_4NH$	93	372	248
7	$NMe_2H \cdot BH_3$	<sup>t</sup> BuNH <sub>2</sub>	$78^{c} (71)^{d}$	312	2023
8	$NMe_2H \cdot BH_3$	$NEt_2H$	76 <sup>c</sup>	316	2257

 $<sup>^</sup>a$  Reaction conditions: CH $_2$ Cl $_2,\,$ rt.  $^b$  Yields determined by  $^{11}B$  NMR spectroscopy with respect to all diaminoboranes formed.  $^c$  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). d Isolated yield corresponds to all the possible products formed.

At the very end of the reaction, the catalyst remained the cyclometalated species 1, but is slowly hydrogenated into complex [PtH(I<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  $h^{-1}$ ). 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  $[(CH_2)_4N]_2BH$  (TON = 380, TOF = 193 h<sup>-1</sup>). In the latter case, 5% of cyclic dimer  $[(CH_2)_4NBH_2]_2$  is observed in the 11B 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. 5b 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  $^{t}$ BuNH<sub>2</sub>·BH<sub>3</sub> with NEt<sub>2</sub>H takes place very fast (6.5 min, TON = 400, TOF =  $3692 \text{ h}^{-1}$ ). 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

NRªR <sup>b</sup> l + NR <sup>c</sup> F		1 <sub>cat</sub> (0.5 CH <sub>2</sub> Cl <sub>2</sub> - 2 H <sub>2</sub>	/rt F	<sup>₹</sup> PaN	H    B  NR <sup>c</sup> R <sup>d</sup> +	R <sup>b</sup> R <sup>a</sup> N E	NR <sup>a</sup> R <sup>b</sup> +	R <sup>d</sup> R <sup>c</sup> N	`NR <sup>c</sup> R <sup>d</sup>
R <sup>a</sup> I	R <sup>b</sup>	R <sup>c</sup>	$R^d$						
<sup>t</sup> Bu	Н	Et	Et		96	4		0	
(CH <sub>2</sub> ) <sub>2</sub> (0	CH <sub>2</sub> ) <sub>2</sub>	<sup>t</sup> Bu	Н		92	C		8	
Me	Me <sup>1</sup>	Bu	Н		86	2		6	
Et I	Et (C	(H <sub>2</sub> ) <sub>2</sub> (0	$CH_2)_2$		25	8	1	4:	3
Me I	Иe	Et	Et		а	а		а	

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†).

exhibits good selectivities towards the asymmetric diaminoborane (\*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 (\*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 NMe2H·BH3 with NEt2H, although we could not establish the exact ratio due to signal overlapping in the <sup>1</sup>H NMR (see the ESI†). Nevertheless, good selectivities are produced in the reaction of  $NMe_2H \cdot BH_3$  and  $^tBuNH_2$  (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 (\*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 Pr<sub>2</sub>NH·BH<sub>3</sub> at rt, Pr<sub>2</sub>N-BH<sub>2</sub> is probably formed through the reorganization of amino-borane  $^t$ BuNH–BH $_2$  and  $^1$ Pr $_2$ NH. $^9$ 

With regard to the mechanism by which these transformations occur, it has been previously shown that dehydrogenation of amine-boranes NR2H·BH3 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 protons (complex 3a in Scheme 4) followed by nucleophilic addition of free amine present in solution to the activated boron atom. 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

$$[BAr^{F}] \\ \bigcirc \\ Pt \\ (Bu-N) \\ IBu \\ N \\ IBu$$

Scheme 4 Formation of complexes 3a,b

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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  ${}^{t}BuNH_{2}\cdot BH_{3}$  ( $\delta$  1.36). In addition,  $I_{PtH}$  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 CH2 moiety. 10 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 4.11 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 NMe3·BH3 was used. However, no interaction with 1 was observed, probably due to steric constrains, thus allowing the establishment of a correlation between the bulkiness of the amine-borane and its interaction with 1 (stronger interaction:  ${}^{t}BuNH_{2} \cdot BH_{3} > NMe_{2}H \cdot BH_{3} > NMe_{3} \cdot BH_{3}$ ). 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  $C_6H_5N\cdot BH_3$ . The apparent coupling constant  ${}^1J_{B,H}$ 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. 11,12 The coupling constant of the CH2-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 fourcoordinated, with two N-heterocyclic carbene units in the expected trans arrangement (C(1)-Pt(1)-C(12):  $168.38(19)^{\circ}$ ) 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.

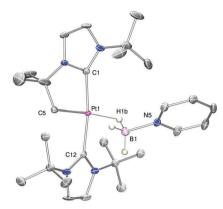


Fig. 1 ORTEP-type view of the cation of complex 3c. Hydrogen atoms, except those of the BH3 unit, have been omitted for clarity (ellipsoids are drawn at 30% probability). Selected bonds (Å) and angles (°): Pt1-H1b 1.96(5), Pt1-C5 2.045(5), B1-H1b 1.03(2); Pt1-H1b-B1 147.48(485), C1-Pt1-C12 168.38(19)

The Pt(1)-H(1B)-B(1) angle of  $147.48(485)^{\circ}$  together with the long  $Pt(1) \cdot \cdot \cdot B(1)$  bond distance (2.8436(5) Å) indicates a negligible interaction between platinum and boron, and therefore this complex is best described as a  $\eta^{1}$ -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 BH3 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. 14 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 11B NMR spectra, a very broad signal centred at  $\delta$  -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(I'Bu)2][BArF], 2.15 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  $\delta$  2.49, whereas the platinum-hydride signal appears at  $\delta$  –25.47 exhibiting a  $J_{Pt,H}$ of 2550 Hz, only marginally different from that of complex 2 in the absence of  $C_6H_5N\cdot BH_3$  ( $J_{Pt,H} = 2564$  Hz). 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  $^{195}$ Pt ( $J_{Pt,H}$  = 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  ${}^{11}B{}^{1}H{}$  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 BH3 group still shows fast exchange between terminal and bridging hydrogens. The different behaviour of compounds 1 and 2 toward the interaction

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$$(Bu - N - fBu)$$

$$(Bu -$$

Scheme 6 Equilibrium between complexes  $\bf 2$  and  $\bf 4$  in the presence of  $C_6H_5N\cdot BH_3$ .

with C<sub>6</sub>H<sub>5</sub>N·BH<sub>3</sub> can be easily rationalised in terms of the different steric protection that the cyclometalated I<sup>t</sup>Bu ligand exerts on the platinum atom compared to its non-cyclometalated form. When the I<sup>t</sup>Bu ligand is cyclometalated the <sup>t</sup>Bu 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 Shimoi-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  $[PtH(I^tBu')(I^tBu)]$ , 5. 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 or during monitoring the dehydrogenation reaction of 1 and  $NMe_2H \cdot BH_3$  at 0 °C). At this point, we do not have further information on the mechanism by which the amino-borane is converted into diaminoboranes 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 diaminoboranes achieving TON and TOF values of 400 and 3692 h<sup>-1</sup>, 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 (Shimoi type) that was demonstrated crystallographically in the pyridine BH<sub>3</sub> adduct 3c. Ongoing efforts are geared towards unveiling the mechanism by which amino-boranes are transformed into diaminoboranes.

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