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The platinum complex $[\text{Pt}(\text{I}'\text{Bu}')(\text{I}'\text{Bu})][\text{BAr}^{\text{F}}]$ is a very efficient catalyst in the synthesis of diaminoboranes through dehydrocoupling of amine-boranes and amines. Shimoi-type, $\eta^1\text{-BH}$ 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.¹ 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 η^1 or η^2 coordination modes, undergoing thereafter subsequent reactivities.^{1a,2}

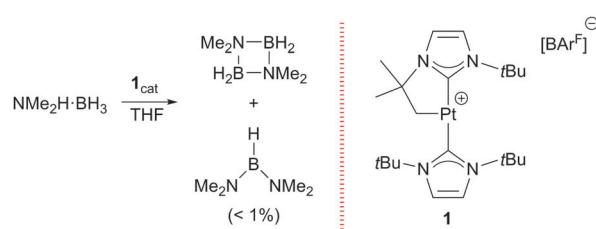
Dehydrogenation of amine-boranes has been mainly focused on the production and release of dihydrogen and on the generation of amino-boranes that can undergo further dimerization, oligomerization or polymerization processes.^{1,2j,3} Less attention has been paid to the production of other boranes, through boron–boron coupling⁴ or the formation of diaminoboranes, $(\text{NR}_2)_2\text{BH}$.⁵ 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 $\eta^1\text{-BH}$ 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 $[\text{Pt}(\text{I}'\text{Bu}')(\text{I}'\text{Bu})][\text{BAr}^{\text{F}}]$ complex (where $\text{I}'\text{Bu}$ stands for 1,3-di-*tert*-butylimidazolylidene and $\text{I}'\text{Bu}'$ its cyclometalated form), **1**,⁶ is able to promote the dehydrocoupling of dimethylamineborane ($\text{NMe}_2\text{H}\text{-BH}_3$) into cyclic $[\text{NMe}_2\text{BH}_2]_2$ (Scheme 1).⁷ During NMR mechanistic studies, we observed that bis(dimethylamino)borane ($\text{NMe}_2)_2\text{BH}$ is also formed in small amounts and its yield increases as the concentration of free NMe_2H 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*-butyl-amineborane (${}^t\text{BuNH}_2\text{-BH}_3$) and **1** equiv. of *tert*-butylamine (${}^t\text{BuNH}_2$) in CD_2Cl_2 , 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_2 (see the ESI†). The ^{11}B NMR spectrum revealed the formation of a single species in nearly quantitative yield after 11.5 min showing a doublet signal at δ 25.8 ppm ($J_{\text{BH}} = 127$ Hz). In addition, the ^1H NMR spectrum exhibits a broad quartet signal centred at 4.12 ppm that sharpens upon ^{11}B decoupling into a triplet ($J_{\text{HH}} = 8.2$ Hz). These values are in agreement with the formation of diaminoborane (${}^t\text{BuNH}_2\text{BH}$, **s1**) (Scheme 2). The calculated TON and TOF values for this process are 400 and 2087 h^{-1} , the highest reported to the best of our knowledge (Table 1).



Scheme 1 Dehydrocoupling of $\text{NMe}_2\text{H}\text{-BH}_3$ catalysed by complex **1**.

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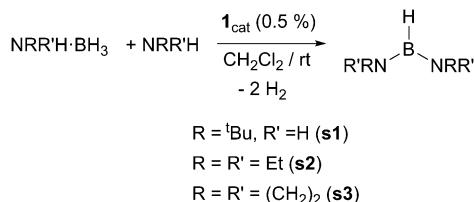
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† Electronic supplementary information (ESI) available: Experimental section, H_2 evolution graphics and X-ray crystallographic data. CCDC 1468913. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc02720b





Scheme 2 Catalytic synthesis of symmetric diaminoboranes.

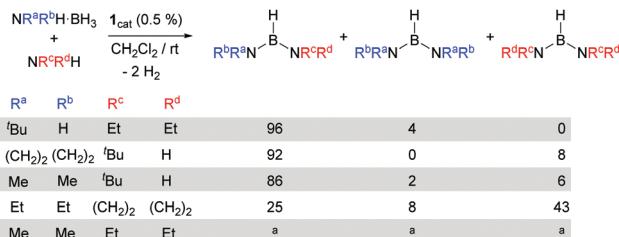
Table 1 Catalytic dehydrocoupling of amine-boranes and amines

Entry ^a	Amineborane	Amine	% Yield ^b (isolated)	TON	TOF (h ⁻¹)
1	$^t\text{BuNH}_2\cdot\text{BH}_3$	$^t\text{BuNH}_2$	>99 (99)	400	2087
2	$\text{NET}_2\text{H}\cdot\text{BH}_3$	NET_2H	>99 (88)	400	2400
3	$(\text{CH}_2)_4\text{NH}\cdot\text{BH}_3$	$(\text{CH}_2)_4\text{NH}$	95 ^c (81)	380	193
4	$^t\text{BuNH}_2\cdot\text{BH}_3$	NET_2H	>99 (99)	400	3692
5	$^t\text{BuNH}_2\cdot\text{BH}_3$	$(\text{CH}_2)_4\text{NH}$	94 (68)	376	376
6	$\text{NET}_2\text{H}\cdot\text{BH}_3$	$(\text{CH}_2)_4\text{NH}$	93	372	248
7	$\text{NMe}_2\text{H}\cdot\text{BH}_3$	$^t\text{BuNH}_2$	78 ^c (71) ^d	312	2023
8	$\text{NMe}_2\text{H}\cdot\text{BH}_3$	NET_2H	76 ^c	316	2257

^a Reaction conditions: CH_2Cl_2 , rt. ^b Yields determined by ^{11}B NMR spectroscopy with respect to all diaminoboranes formed. ^c Cyclic dimers $[\text{NR}_2\text{BH}_2]_2$ and other unidentified species constitute the remaining reaction products (see the ESI). ^d Isolated yield corresponds to all the possible products formed.

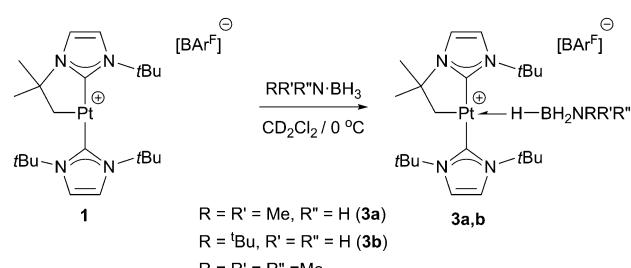
At the very end of the reaction, the catalyst remained the cyclo-metallated species **1**, but is slowly hydrogenated into complex $[\text{PtH}({^t}\text{Bu})_2][\text{BAr}^F]$, **2**. Other amine-boranes were tested under identical reaction conditions to form symmetrical diaminoboranes. Diethylamine-borane was also shown to be efficiently dehydrogenated in *ca.* 10 min in the presence of 1 equiv. of NET_2H and catalyst **1** ($\text{TON} = 400$, $\text{TOF} = 2400 \text{ h}^{-1}$). On the other hand, pyrrolidine-borane $(\text{CH}_2)_4\text{NH}\cdot\text{BH}_3$ required longer reaction times (2 h) to be converted into $[(\text{CH}_2)_4\text{N}]_2\text{BH}$ ($\text{TON} = 380$, $\text{TOF} = 193 \text{ h}^{-1}$). In the latter case, 5% of cyclic dimer $[(\text{CH}_2)_4\text{NBH}_2]_2$ is observed in the ^{11}B NMR spectra. Bulkier amine-boranes, such as $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$, do not undergo dehydrocoupling under similar reaction conditions, while heating at 60°C for 12 h results in the formation of amino-borane $\text{N}^i\text{Pr}_2\text{BH}_2$, 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 $^t\text{BuNH}_2\cdot\text{BH}_3$ with NET_2H takes place very fast (6.5 min, $\text{TON} = 400$, $\text{TOF} = 3692 \text{ h}^{-1}$). According to NMR spectroscopy, borane $(^t\text{BuNH})(\text{NET}_2)\text{BH}$ is formed almost exclusively (*ca.* 4% of $(^t\text{BuNH})_2\text{BH}$ is observed by ^1H NMR). If the reaction is carried out in the inverse way, starting from $\text{NET}_2\text{H}\cdot\text{BH}_3$ and $^t\text{BuNH}_2$, the process is slower (*ca.* 20 min), but selectivities are comparable. The same behaviour is observed in the catalytic dehydrocoupling of $(\text{CH}_2)_4\text{NH}\cdot\text{BH}_3$ and $^t\text{BuNH}_2$. In this case, the reaction

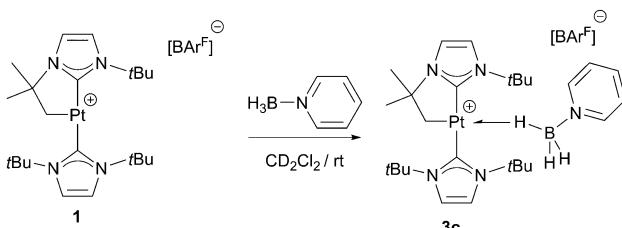
Scheme 3 Catalytic synthesis of asymmetric diaminoboranes. ^a Signal overlapping in the ^1H and ^{11}B (^1H) NMR spectra precluded establishing the exact amount of each diaminoborane (see the ESI†).

exhibits good selectivities towards the asymmetric diaminoborane $(^t\text{BuNH})([\text{CH}_2)_4\text{N}]_2\text{BH}$ (92%), whereas the only symmetric borane detected is $[(\text{CH}_2)_4\text{N}]_2\text{BH}$ (8%), with complete conversion after 2 h at rt. When the reaction is carried out the other way around, that is, starting from $^t\text{BuNH}_2\cdot\text{BH}_3$ and $(\text{CH}_2)_4\text{NH}$, the selectivities are only slightly different (85% of $(^t\text{BuNH})([\text{CH}_2)_4\text{N}]_2\text{BH}$, 15% of $[(\text{CH}_2)_4\text{N}]_2\text{BH}$), 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_2BH , $[(\text{CH}_2)_4\text{N}]_2\text{BH}$ and $(\text{NET}_2)_2\text{BH}$ 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 $\text{NMe}_2\text{H}\cdot\text{BH}_3$ with NET_2H , although we could not establish the exact ratio due to signal overlapping in the ^1H NMR (see the ESI†). Nevertheless, good selectivities are produced in the reaction of $\text{NMe}_2\text{H}\cdot\text{BH}_3$ and $^t\text{BuNH}_2$ (Scheme 3). Very interestingly, the reaction of $^t\text{BuNH}_2\cdot\text{BH}_3$ with $^i\text{Pr}_2\text{NH}$ generates diaminoborane $(^t\text{BuNH})_2\text{BH}$ (**s1**) and amino-borane $^i\text{Pr}_2\text{N}-\text{BH}_2$ in *ca.* 5 min at rt. Since **1** does not catalyse the dehydrocoupling of $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ at rt, $^i\text{Pr}_2\text{N}-\text{BH}_2$ is probably formed through the reorganization of amino-borane $^t\text{BuNH}-\text{BH}_2$ and $^i\text{Pr}_2\text{NH}$.⁹

With regard to the mechanism by which these transformations occur, it has been previously shown that dehydrogenation of amine-boranes $\text{NR}_2\text{H}\cdot\text{BH}_3$ leading to the corresponding aminoboranes NR_2BH_2 is a key step.⁵ Previously, we have reported that complex **1** is able to dehydrogenate $\text{NMe}_2\text{H}\cdot\text{BH}_3$ into NMe_2BH_2 (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.⁷ According to DFT calculations the most stable coordination mode of the BH_3 moiety is $\eta^1\text{-BH}$ (Shimoji 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_2Cl_2 . $^t\text{BuNH}_2\cdot\text{BH}_3$ reacts with **1** leading to a new species that has been postulated as the $\eta^1\text{-BH}$ derivative **3b** (Scheme 4). The BH_3 group resonates as a broad signal centred at 0.12 ppm that sharpens upon ^{11}B broadband decoupling. This signal is shifted upfield from the free $^t\text{BuNH}_2\cdot\text{BH}_3$ (δ 1.36). In addition, J_{PtH} of the $\text{CH}_2\text{-Pt}$ 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_2 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 ^{11}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 $\text{NMe}_3\cdot\text{BH}_3$ 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: $^t\text{BuNH}_2\cdot\text{BH}_3 > \text{NMe}_2\text{H}\cdot\text{BH}_3 > \text{NMe}_3\cdot\text{BH}_3$). Consequently, the less hindered Lewis base stabilised borane $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$ 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_3 protons (2.55 ppm in free $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$). The $^{11}\text{B}\{^1\text{H}\}$ spectrum exhibits a signal at -8.9 ppm, nearly 3 ppm down-field shifted with respect to $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$. The apparent coupling constant $J_{\text{B},\text{H}}$ is *ca.* 85 Hz, that is, 12 Hz smaller than in free $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$, and compares well with previously described Shimoi-type complexes.^{11,12} The coupling constant of the $\text{CH}_2\text{-Pt}$ protons with ^{195}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_2Cl_2 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 ($\text{C}(1)\text{-Pt}(1)\text{-C}(12)$: 168.38(19)°) one of which is cyclometalated. The fourth coordination site is occupied by the $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$ ligand in which one of the hydride atoms of the BH_3 unit bridges the platinum nucleus. The $\text{Pt}(1)\text{-H}(1\text{B})$ and $\text{H}(1\text{B})\text{-B}(1)$ bond distances are 1.96(5) and 1.03(2) Å, respectively.



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

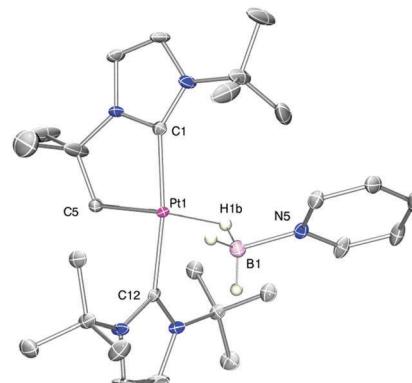
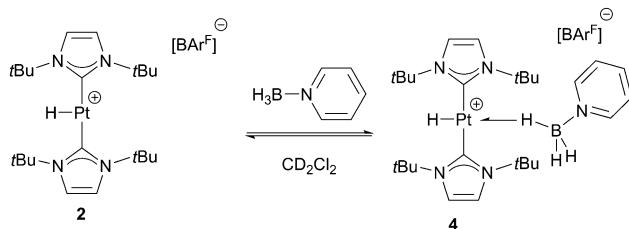


Fig. 1 ORTEP-type view of the cation of complex **3c**. Hydrogen atoms, except those of the BH_3 unit, have been omitted for clarity (ellipsoids are drawn at 30% probability). Selected bonds (Å) and angles (°): Pt1-H1b 1.96(5), Pt1-C5 2.045(5), B1-H1b 1.03(2); Pt1-H1b-B1 147.48(485), C1-Pt1-C12 168.38(19).

The $\text{Pt}(1)\text{-H}(1\text{B})\text{-B}(1)$ angle of 147.48(485)° together with the long $\text{Pt}(1)\cdots\text{B}(1)$ bond distance (2.8436(5) Å) indicates a negligible interaction between platinum and boron, and therefore this complex is best described as a $\eta^1\text{-BH}$ or Shimoi-type complex.^{12,13}

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_3 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 ^{11}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 $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$ with the hydrogenated form of complex **1**, the hydride derivative $[\text{PtH}(\text{I}^t\text{Bu})_2][\text{BArF}]$, **2**.¹⁵ No evidence of interaction between **2** and $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$ is observed at 298 K. At this temperature, the BH_3 protons resonate at δ 2.49, whereas the platinum-hydride signal appears at δ -25.47 exhibiting a J_{PtH} of 2550 Hz, only marginally different from that of complex **2** in the absence of $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$ ($J_{\text{PtH}} = 2564$ Hz).¹⁵ However, the ^1H 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 ($J_{\text{PtH}} = 1920$ Hz) and another broad signal at 0.28 ppm (3H relative integral) that sharpens upon ^{11}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 $^{11}\text{B}\{^1\text{H}\}$ NMR spectra at all temperatures exhibit a single very broad signal at -12.3 ppm that does not show splitting upon coupling to ^1H below 208 K. Interestingly, even at 188 K the BH_3 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 $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$.

with $\text{C}_6\text{H}_5\text{N}\cdot\text{BH}_3$ can be easily rationalised in terms of the different steric protection that the cyclometalated $\text{t}^{\prime}\text{Bu}$ ligand exerts on the platinum atom compared to its non-cyclometalated form. When the $\text{t}^{\prime}\text{Bu}$ ligand is cyclometalated the $\text{t}^{\prime}\text{Bu}$ group is tilted¹⁶ 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_2BH_2 , takes place through a mechanism that involves the intermediacy of boronium cations $(\text{NHR}_2)_2\text{BH}_2^+$ and the neutral platinum hydride $[\text{PtH}(\text{t}^{\prime}\text{Bu})(\text{t}^{\prime}\text{Bu})]$.^{5,7} It must be noted that we have not observed an interaction between complex **1** and amino-borane NMe_2BH_2 (either using cyclic dimer $[\text{NMe}_2\text{BH}_2]_2$ as a precursor¹⁷ or during monitoring the dehydrogenation reaction of **1** and $\text{NMe}_2\text{H}\cdot\text{BH}_3$ at 0 °C).⁷ 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⁻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 (Shimoi type) that was demonstrated crystallographically in the pyridine·BH₃ adduct **3c**. Ongoing efforts are geared towards unveiling the mechanism by which amino-boranes are transformed into diaminoboranes.

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