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

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The platinum complex [Pt(I'Bu')(I'Bu)][BAR^F] is a very efficient catalyst in the synthesis of diaminoboranes through dehydrocoupling of amine-boranes and amines. Shimoi-type, η^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.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.^{1,2,3} Less attention has been paid to the production of other boranes, through boron–boron coupling⁴ or the formation of diaminoboranes, (NR₂)₂BH.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 η^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'Bu')(I'Bu)][BAR^F] complex (where I'Bu stands for 1,3-di-*tert*-butylimidazolyldiene and I'Bu' its cyclometalated form), **1**,⁶ is able to promote the dehydrocoupling of dimethylamineborane (NMe₂H·BH₃) into cyclic [NMe₂BH₂]₂ (Scheme 1).⁷ 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 NMe₂H in the reaction media increases. Therefore, we analysed the ability of complex **1** to act as a catalyst for the formation of diaminoboranes.

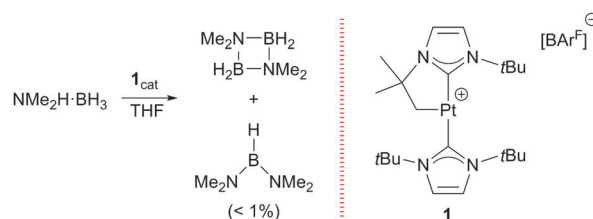
We have first studied the benchmark reaction of *tert*-butylamineborane (tBuNH₂·BH₃) and 1 equiv. of *tert*-butylamine (tBuNH₂) in CD₂Cl₂, using a catalyst loading of 0.5% (Scheme 2). The reaction was monitored both by NMR spectroscopy and by measuring the increase of gas pressure in a closed system due to the generated H₂ (see the ESI†). The ¹¹B 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 (¹J_{BH} = 127 Hz). In addition, the ¹H NMR spectrum exhibits a broad quartet signal centred at 4.12 ppm that sharpens upon ¹¹B decoupling into a triplet (*J*_{HH} = 8.2 Hz). These values are in agreement with the formation of diaminoborane (tBuNH)₂BH,⁸ **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).

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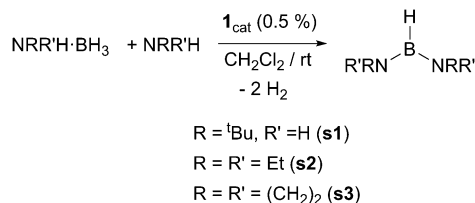
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† Electronic supplementary information (ESI) available: Experimental section, H₂ evolution graphics and X-ray crystallographic data. CCDC 1468913. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc02720b



Scheme 1 Dehydrocoupling of NMe₂H·BH₃ catalysed by complex **1**.





Scheme 2 Catalytic synthesis of symmetric diaminoboranes.

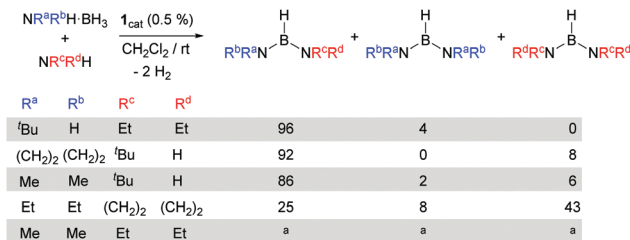
Table 1 Catalytic dehydrocoupling of amine-boranes and amines

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

^a Reaction conditions: CH₂Cl₂, rt. ^b Yields determined by ¹¹B NMR spectroscopy with respect to all diaminoboranes formed. ^c Cyclic dimers [NR₂BH₂]₂ and other unidentified species constitute the remaining reaction products (see the ESI). ^d Isolated yield corresponds to all the possible products formed.

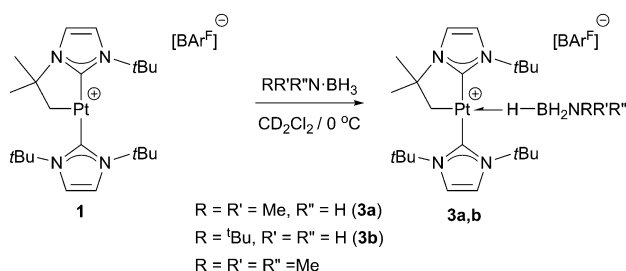
At the very end of the reaction, the catalyst remained the cyclo-metallated species **1**, but is slowly hydrogenated into complex [PtH(^tBu)₂][BAR^F], **2**. Other amine-boranes were tested under identical reaction conditions to form symmetrical diaminoboranes. Diethylamine-borane was also shown to be efficiently dehydrogenated in *ca.* 10 min in the presence of 1 equiv. of NEt₂H and catalyst **1** (TON = 400, TOF = 2400 h⁻¹). On the other hand, pyrrolidine-borane (CH₂)₄NH·BH₃ required longer reaction times (2 h) to be converted into [(CH₂)₄N]₂BH (TON = 380, TOF = 193 h⁻¹). In the latter case, 5% of cyclic dimer [(CH₂)₄NBH₂]₂ is observed in the ¹¹B NMR spectra. Bulkier amine-boranes, such as ⁱPr₂NH·BH₃, do not undergo dehydrocoupling under similar reaction conditions, while heating at 60 °C for 12 h results in the formation of amino-borane NⁱPr₂BH₂, 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 ^tBuNH₂·BH₃ with NEt₂H takes place very fast (6.5 min, TON = 400, TOF = 3692 h⁻¹). According to NMR spectroscopy, borane (^tBuNH)(NEt₂)BH is formed almost exclusively (*ca.* 4% of (^tBuNH)₂BH is observed by ¹H NMR). If the reaction is carried out in the inverse way, starting from NEt₂H·BH₃ and ^tBuNH₂, the process is slower (*ca.* 20 min), but selectivities are comparable. The same behaviour is observed in the catalytic dehydrocoupling of (CH₂)₄NH·BH₃ and ^tBuNH₂. In this case, the reaction

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

exhibits good selectivities towards the asymmetric diaminoborane (^tBuNH)[(CH₂)₄N]BH (92%), whereas the only symmetric borane detected is [(CH₂)₄N]₂BH (8%), with complete conversion after 2 h at rt. When the reaction is carried out the other way around, that is, starting from ^tBuNH₂·BH₃ and (CH₂)₄NH, the selectivities are only slightly different (85% of (^tBuNH)[(CH₂)₄N]BH, 15% of [(CH₂)₄N]₂BH), 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 (NEt₂)₂BH, [(CH₂)₄N]₂BH and (NEt₂)[(CH₂)₄N]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 ¹H NMR (see the ESI†). Nevertheless, good selectivities are produced in the reaction of NMe₂H·BH₃ and ^tBuNH₂ (Scheme 3). Very interestingly, the reaction of ^tBuNH₂·BH₃ with ⁱPr₂NH generates diaminoborane (^tBuNH)₂BH (**s1**) and amino-borane ⁱPr₂N-BH₂ in *ca.* 5 min at rt. Since **1** does not catalyse the dehydrocoupling of ⁱPr₂NH·BH₃ at rt, ⁱPr₂N-BH₂ is probably formed through the reorganization of amino-borane ^tBuNH-BH₂ and ⁱPr₂NH.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 NR₂BH₂ is a key step.⁵ Previously, we have reported that complex **1** is able to dehydrogenate NMe₂H·BH₃ into NMe₂BH₂ (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 BH₃ moiety is η¹-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 CD₂Cl₂. ^tBuNH₂·BH₃ reacts with **1** leading to a new species that has been postulated as the η¹-BH derivative **3b** (Scheme 4). The BH₃ group resonates as a broad signal centred at 0.12 ppm that sharpens upon ¹¹B broadband decoupling. This signal is shifted upfield from the free ^tBuNH₂·BH₃ (δ 1.36). In addition, *J*_{PtH} of the CH₂-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 ¹¹B 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 constraints, thus allowing the establishment of a correlation between the bulkiness of the amine-borane and its interaction with **1** (stronger interaction: ^tBuNH₂·BH₃ > NMe₂H·BH₃ > NMe₃·BH₃). Consequently, the less hindered Lewis base stabilised borane C₆H₅N·BH₃ 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 BH₃ protons (2.55 ppm in free C₆H₅N·BH₃). The ¹¹B{¹H} spectrum exhibits a signal at −8.9 ppm, nearly 3 ppm down-field shifted with respect to C₆H₅N·BH₃. The apparent coupling constant ¹*J*_{B,H} is *ca.* 85 Hz, that is, 12 Hz smaller than in free C₆H₅N·BH₃, and compares well with previously described Shimoi-type complexes.^{11,12} The coupling constant of the CH₂-Pt protons with ¹⁹⁵Pt 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 CH₂Cl₂ 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 C₆H₅N·BH₃ ligand in which one of the hydride atoms of the BH₃ 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.

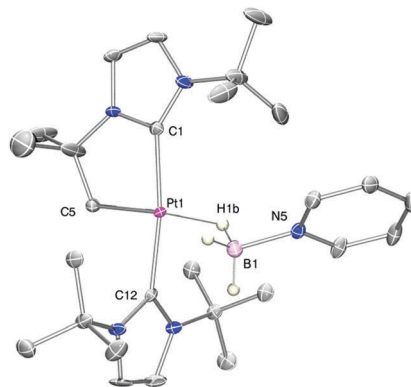
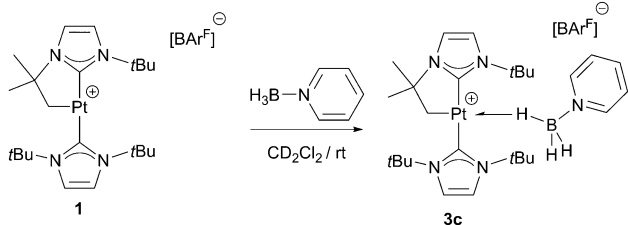


Fig. 1 ORTEP-type view of the cation of complex **3c**. Hydrogen atoms, except those of the BH₃ unit, have been omitted for clarity (ellipsoids are drawn at 30% probability). Selected bonds (Å) and angles (°): Pt1–H1b 1.96(5), Pt1–C5 2.045(5), B1–H1b 1.03(2); Pt1–H1b–B1 147.48(485), C1–Pt1–C12 168.38(19).

The Pt(1)–H(1b)–B(1) angle of 147.48(485)° 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 η¹-BH or Shimoi-type complex.^{12,13}

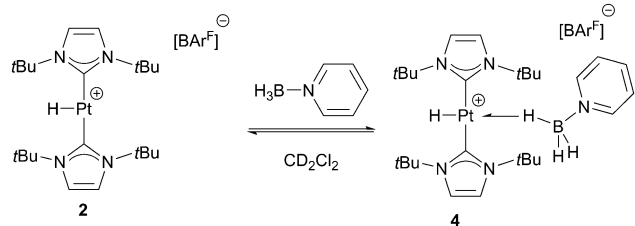
Variable temperature NMR spectroscopy was used to study the dynamic behaviour due to exchange between bridging and terminal BH protons. The resonance for the BH₃ protons collapses into the baseline at *ca.* 223 K. Upon cooling to 203 K, a new signal of relative integral 2 appears at 2.47 ppm, in the 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 δ −12.2 is detected at this temperature.

For comparison purposes, we have analysed the interaction of C₆H₅N·BH₃ with the hydrogenated form of complex **1**, the hydride derivative [PtH(I^tBu)₂][BAR^F], **2**.¹⁵ No evidence of interaction between **2** and C₆H₅N·BH₃ is observed at 298 K. At this temperature, the BH₃ protons resonate at δ 2.49, whereas the platinum-hydride signal appears at δ −25.47 exhibiting a *J*_{Pt,H} of 2550 Hz, only marginally different from that of complex **2** in the absence of C₆H₅N·BH₃ (*J*_{Pt,H} = 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 ¹⁹⁵Pt (*J*_{Pt,H} = 1920 Hz) and another broad signal at 0.28 ppm (3H relative integral) that sharpens upon ¹¹B 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 ¹¹B{¹H} 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 BH₃ group still shows fast exchange between terminal and bridging hydrogens. The different behaviour of compounds **1** and **2** toward the interaction



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





Scheme 6 Equilibrium between complexes **2** and **4** in the presence of $\text{C}_6\text{H}_5\text{N-BH}_3$.

with $\text{C}_6\text{H}_5\text{N-BH}_3$ 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 tilted¹⁶ 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, $\text{NR}_2\text{-BH}_2$, takes place through a mechanism that involves the intermediacy of boronium cations $(\text{NHR}_2)_2\text{BH}_2^+$ and the neutral platinum hydride $[\text{PtH}(\text{tBu})(\text{tBu})]$, **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 $\text{NMe}_2\text{H-BH}_3$ 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 (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 diaminoboranes.

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