ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2016, 52, 8389

Received 31st March 2016,
Accepted 3rd June 2016

DOI: 10.1039/c6cc02720b

www.rsc.org/chemcomm

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^{t}Bu′)(I^{t}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.

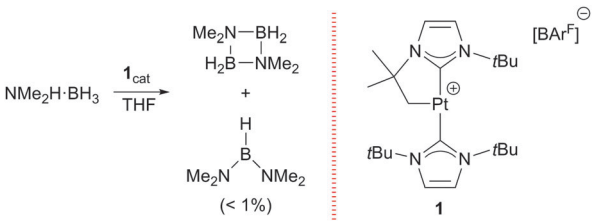
In the last few years amine-boranes and related base-stabilised borane adducts have been shown to produce rich chemistry in which metal catalysed dehydrocoupling processes are involved.[1] During some of these reactions the B–H bonds of the amine borane establish an initial interaction with the metal 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.[1,2j,3] Less attention has been paid to the production of other boranes, through boron–boron coupling[4] or the formation of diaminoboranes, $(NR_2)_2BH$.[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^{t}Bu′)(I^{t}Bu)][BAr^F] complex (where I^{t}Bu stands for 1,3-di-*tert*-butylimidazolylidene and I^{t}Bu′ its cyclometalated form), **1**,[6] is able to promote the dehydrocoupling of dimethylamineborane ($NMe_2H{\cdot}BH_3$) into cyclic $[NMe_2BH_2]_2$ (Scheme 1).[7] During NMR mechanistic studies, we observed that bis(dimethylamino)borane $(NMe_2)_2BH$ 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*-butylamineborane (^{t}BuNH$_2{\cdot}$BH$_3$) and 1 equiv. of *tert*-butylamine (^{t}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 ($^1J_{BH}$ = 127 Hz). In addition, the ^{1}H NMR spectrum exhibits a broad quartet signal centred at 4.12 ppm that sharpens upon ^{11}B decoupling into a triplet (J_{HH} = 8.2 Hz). These values are in agreement with the formation of diaminoborane (^{t}BuNH)$_2$BH,[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).



Scheme 1 Dehydrocoupling of $NMe_2H{\cdot}BH_3$ catalysed by complex **1**.

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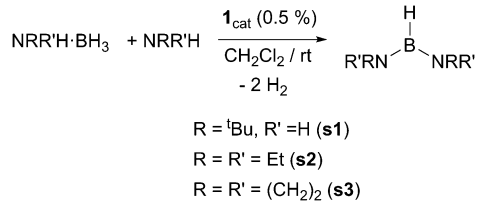
† Electronic supplementary information (ESI) available: Experimental section, H_2 evolution graphics and X-ray crystallographic data. CCDC 1468913. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc02720b



R = ^{t}Bu, R' =H (**s1**)
R = R' = Et (**s2**)
R = R' = $(CH_2)_2$ (**s3**)

Scheme 2 Catalytic synthesis of symmetric diaminoboranes.

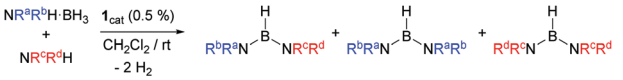
Table 1 Catalytic dehydrocoupling of amine-boranes and amines

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: CH_2Cl_2, rt. [b] Yields determined by ^{11}B NMR spectroscopy with respect to all diaminoboranes formed. [c] Cyclic dimers $[NR_2BH_2]_2$ 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 cyclometalated species **1**, but is slowly hydrogenated into complex $[PtH(I^tBu)_2][BAr^F]$, **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 NEt$_2$H and catalyst **1** (TON = 400, TOF = 2400 h^{-1}). On the other hand, pyrrolidine-borane $(CH_2)_4$NH·BH$_3$ required longer reaction times (2 h) to be converted into $[(CH_2)_4N]_2BH$ (TON = 380, TOF = 193 h^{-1}). In the latter case, 5% of cyclic dimer $[(CH_2)_4NBH_2]_2$ is observed in the ^{11}B NMR spectra. Bulkier amine-boranes, such as ^{i}Pr$_2$NH·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 N^{i}Pr$_2$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}BuNH$_2$·BH$_3$ with NEt$_2$H takes place very fast (6.5 min, TON = 400, TOF = 3692 h^{-1}). According to NMR spectroscopy, borane (^{t}BuNH)(NEt$_2$)BH is formed almost exclusively (*ca.* 4% of (^{t}BuNH)$_2$BH is observed by ^{1}H NMR). If the reaction is carried out in the inverse way, starting from NEt$_2$H·BH$_3$ and ^{t}BuNH$_2$, the process is slower (*ca.* 20 min), but selectivities are comparable. The same behaviour is observed in the catalytic dehydrocoupling of $(CH_2)_4$NH·BH$_3$ and ^{t}BuNH$_2$. In this case, the reaction

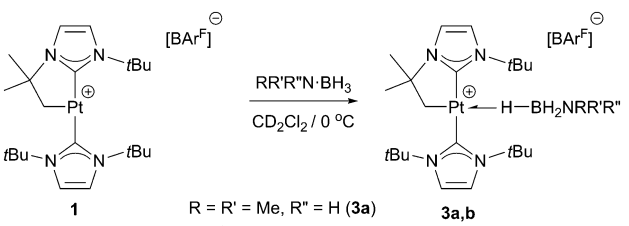


R^a	R^b	R^c	R^d			
^{t}Bu	H	Et	Et	96	4	0
$(CH_2)_2$	$(CH_2)_2$	^{t}Bu	H	92	0	8
Me	Me	^{t}Bu	H	86	2	6
Et	Et	$(CH_2)_2$	$(CH_2)_2$	25	8	43
Me	Me	Et	Et	[a]	[a]	[a]

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

exhibits good selectivities towards the asymmetric diaminoborane (^{t}BuNH)[$(CH_2)_4$N]BH (92%), whereas the only symmetric borane detected is $[(CH_2)_4N]_2BH$ (8%), with complete conversion after 2 h at rt. When the reaction is carried out the other way around, that is, starting from ^{t}BuNH$_2$·BH$_3$ and $(CH_2)_4$NH, the selectivities are only slightly different (85% of (^{t}BuNH)[$(CH_2)_4$N]BH, 15% of $[(CH_2)_4N]_2BH$), 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 $(NEt_2)_2BH$, $[(CH_2)_4N]_2BH$ and (NEt_2)[$(CH_2)_4$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$_2$H·BH$_3$ with NEt$_2$H, although we could not establish the exact ratio due to signal overlapping in the ^{1}H NMR (see the ESI†). Nevertheless, good selectivities are produced in the reaction of NMe$_2$H·BH$_3$ and ^{t}BuNH$_2$ (Scheme 3). Very interestingly, the reaction of ^{t}BuNH$_2$·BH$_3$ with ^{i}Pr$_2$NH generates diaminoborane (^{t}BuNH)$_2$BH (**s1**) and amino-borane ^{i}Pr$_2$N–BH$_2$ in *ca.* 5 min at rt. Since **1** does not catalyse the dehydrocoupling of ^{i}Pr$_2$NH·BH$_3$ at rt, ^{i}Pr$_2$N–BH$_2$ is probably formed through the reorganization of amino-borane ^{t}BuNH–BH$_2$ and ^{i}Pr$_2$NH.[9]

With regard to the mechanism by which these transformations occur, it has been previously shown that dehydrogenation of amine-boranes NR$_2$H·BH$_3$ leading to the corresponding aminoboranes NR$_2$BH$_2$ is a key step.[5] Previously, we have reported that complex **1** is able to dehydrogenate NMe$_2$H·BH$_3$ into NMe$_2$BH$_2$ (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 η^1-BH (Shimoi type complex) but, unfortunately, no experimental evidence for this

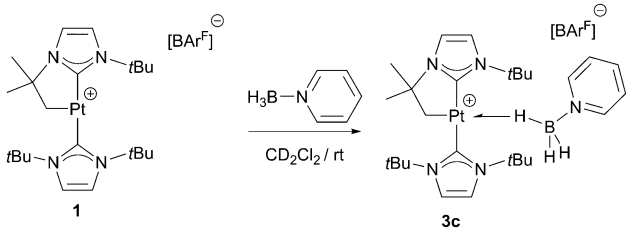


1 **3a,b**

R = R' = Me, R" = H (**3a**)
R = ^{t}Bu, R' = R" = H (**3b**)
R = R' = R" =Me

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. $^tBuNH_2{\cdot}BH_3$ reacts with **1** leading to a new species that has been postulated as the η^1-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 $^tBuNH_2{\cdot}BH_3$ (δ 1.36). In addition, J_{PtH} of the CH_2–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 $NMe_3{\cdot}BH_3$ 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: $^tBuNH_2{\cdot}BH_3 > NMe_2H{\cdot}BH_3 > NMe_3{\cdot}BH_3$). Consequently, the less hindered Lewis base stabilised borane $C_6H_5N{\cdot}BH_3$ 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 $C_6H_5N{\cdot}BH_3$). The $^{11}B\{^1H\}$ 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 $C_6H_5N{\cdot}BH_3$, and compares well with previously described Shimoi-type complexes.[11,12] The coupling constant of the CH_2–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 (C(1)–Pt(1)–C(12): 168.38(19)°) one of which is cyclometalated. The fourth coordination site is occupied by the $C_6H_5N{\cdot}BH_3$ ligand in which one of the hydride atoms of the BH_3 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**.

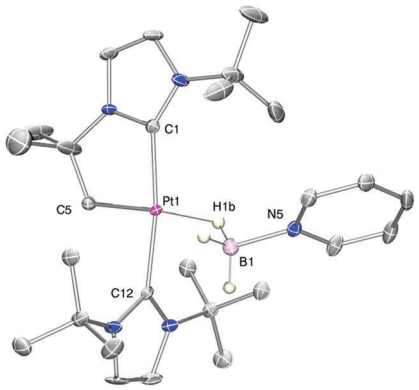
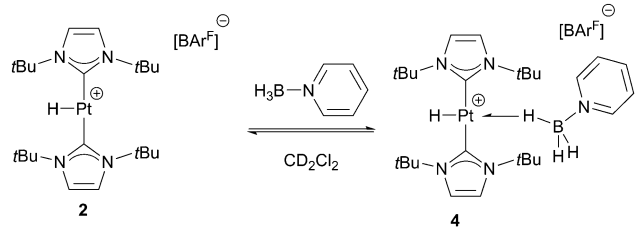


Fig. 1 ORTEP-type view of the cation of complex **3c**. Hydrogen atoms, except those of the BH_3 unit, have been omitted for clarity (ellipsoids are drawn at 30% probability). Selected bonds (Å) and angles (°): Pt1–H1b 1.96(5), Pt1–C5 2.045(5), B1–H1b 1.03(2); Pt1–H1b–B1 147.48(485), C1–Pt1–C12 168.38(19).

The 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^1-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 $C_6H_5N{\cdot}BH_3$ 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 $C_6H_5N{\cdot}BH_3$ 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 $J_{Pt,H}$ 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).[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 ($J_{Pt,H}$ = 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 $^{11}B\{^1H\}$ 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 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 $C_6H_5N{\cdot}BH_3$.

with $C_6H_5N{\cdot}BH_3$ can be easily rationalised in terms of the different steric protection that the cyclometalated I^{t}Bu ligand exerts on the platinum atom compared to its non-cyclometalated form. When the I^{t}Bu ligand is cyclometalated the ^{t}Bu group is tilted[16] 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^{t}Bu′)(I^{t}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 $[NMe_2BH_2]_2$ as a precursor[17] or during monitoring the dehydrogenation reaction of **1** and $NMe_2H{\cdot}BH_3$ 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·BH_3 adduct **3c**. Ongoing efforts are geared towards unveiling the mechanism by which amino-boranes are transformed into diaminoboranes.

Financial support (FEDER contribution) from the MINECO (Projects CTQ2013-45011-P and CTQ2014-51912-REDC) and the Junta de Andalucía (Project FQM-2126) is gratefully acknowledged.

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