## ChemComm



**View Article Online** 

COMMUNICATION



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( $\mu$ ), Shimoi-type,  $\eta^1$ -BH complex<sup>+</sup>

Marta Roselló-Merino,<sup>a</sup> Raquel J. Rama,<sup>a</sup> Josefina Díez<sup>b</sup> and Salvador Conejero\*<sup>a</sup>

The platinum complex [Pt(l<sup>t</sup>Bu')(l<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,  $(NR_2)_2BH$ .<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>5*a*,*c*</sup> and by Hill,<sup>5*b*</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(u) 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  $[Pt(I^tBu')(I^tBu)][BAr^F]$ complex (where I<sup>t</sup>Bu stands for 1,3-di-*tert*-butylimidazolylidene and I<sup>t</sup>Bu' its cyclometalated form), **1**,<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<sup>†</sup>). 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).



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

<sup>&</sup>lt;sup>a</sup> Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica, Centro de Innovación en Química Avanzada (ORFEO-CINCA), CSIC and Universidad de Sevilla, Avda. Américo Vespucio 49, 41092 Sevilla, Spain. E-mail: sconejero@iiq.csic.es; Tel: +34 954489563

<sup>&</sup>lt;sup>b</sup> Laboratorio de Compuestos Organometálicos y Catálisis

<sup>(</sup>Unidad asociada al CSIC), Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, C/Julián Clavería 8, 33006, Oviedo, Spain

 $<sup>\</sup>dagger$  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 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	$\begin{array}{c} \text{TOF} \\ (h^{-1}) \end{array}$	
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 <sub>2</sub> ) <sub>4</sub> NH·BH <sub>3</sub>	$(CH_2)_4NH$	$95^{c}(81)$	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>	$(CH_2)_4NH$	94 (68)	376	376	
6	$NEt_2H \cdot BH_3$	$(CH_2)_4NH$	93	372	248	
7	NMe <sub>2</sub> H·BH <sub>3</sub>	<sup>t</sup> BuNH <sub>2</sub>	$78^c (71)^d$	312	2023	
8	NMe <sub>2</sub> H·BH <sub>3</sub>	$NEt_2H$	76 <sup>c</sup>	316	2257	

 $^a$  Reaction conditions: CH\_2Cl\_2, rt.  $^b$  Yields determined by  $^{11}{\rm B}$  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).<sup>d</sup> 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 <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  $h^{-1}$ ). 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

NR <sup>a</sup> F NR	¢H∙BH + ¢R <sup>d</sup> H	H <sub>3</sub> 1 <sub>cat</sub> (0 CH <sub>2</sub> 0 - 2	0.5 %) Cl <sub>2</sub> / rt H <sub>2</sub>	H   R <sup>b</sup> R <sup>a</sup> N <sup>-B</sup> NR <sup>c</sup> R <sup>d</sup> <sup>†</sup>	H R <sup>b</sup> R <sup>a</sup> N <sup>-B</sup> NR <sup>a</sup> R <sup>b</sup>	H     R <sup>d</sup> R <sup>c</sup> N <sup>-</sup> <sup>B</sup> NR <sup>c</sup> R <sup>d</sup>
R <sup>a</sup>	R <sup>b</sup>	Rc	R <sup>d</sup>			
<sup>t</sup> Bu	н	Et	Et	96	4	0
(CH <sub>2</sub> ) <sub>2</sub>	(CH <sub>2</sub> )	<sub>2</sub> <sup>t</sup> Bu	н	92	0	8
Me	Me	<sup>t</sup> Bu	н	86	2	6
Et	Et	(CH <sub>2</sub> ) <sub>2</sub>	(CH <sub>2</sub> ) <sub>2</sub>	25	8	43
Me	Me	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<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  ${}^{t}$ 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  $[(CH_2)_4N]_2BH$ , 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<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  ${}^{1}Pr_{2}NH \cdot BH_{3}$  at rt,  ${}^{1}Pr_{2}N - BH_{2}$  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 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  $\eta^{1}$ -BH (Shimoi type complex) but, unfortunately, no experimental evidence for this



Scheme 4 Formation of complexes 3a,b

## ChemComm

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  $\eta^1$ -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> ( $\delta$  1.36). In addition,  $J_{PtH}$  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 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 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 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 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  ${}^{1}J_{B,H}$ 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.<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 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.

 $\begin{array}{c}
\overbrace{\begin{subarray}{c}N\\Pt\\fBu-N\\1\end{array}}^{N} \overbrace{\begin{subarray}{c}N\\FBu}{\begin{subarray}{c}N\\FBu\\I\end{array}\end{array}}^{(BAr^{F})} \\
\overbrace{\begin{subarray}{c}H_{3}B-N\\FBu\\CD_{2}Cl_{2}/rt\end{array}}^{H_{3}B-N} \overbrace{\begin{subarray}{c}N\\FBu\\I\end{array}}^{N} \overbrace{\begin{subarray}{c}H_{3}B-N\\FBu\\I\end{array}}^{N} \overbrace{\begin{subarray}{c}H_{3}B-N\\FBu}I$ 

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  $\eta^1$ -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<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  $\delta$  –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<sup>t</sup>Bu)<sub>2</sub>][BAr<sup>F</sup>], 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  $\delta$  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).<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  $^{195}$ 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 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  $C_6H_5N\cdot BH_3$ .

with  $C_6H_5N$ ·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 ( $NHR_2$ )<sub>2</sub> $BH_2^+$  and the neutral platinum hydride [PtH(I<sup>f</sup>Bu')(I<sup>f</sup>Bu)], 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 [ $NMe_2BH_2$ ]<sub>2</sub> as a precursor<sup>17</sup> or during monitoring the dehydrogenation reaction of 1 and  $NMe_2H \cdot BH_3$  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 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  $BH_3$  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.

## Notes and references

- (a) H. C. Johnson, T. N. Hooper and A. S. Weller, *Top. Organomet. Chem.*, 2015, **49**, 153; (b) E. M. Leitao, T. Jurka and I. Manners, *Nat. Chem.*, 2013, **5**, 817; (c) N. E. Stubbs, A. P. M. Robertson, E. M. Leitao and I. Manners, *J. Organomet. Chem.*, 2013, **730**, 84; (d) A. S. John, K. I. Goldberg and D. M. Heinekey, *Top. Organomet. Chem.*, 2013, **40**, 271.
- (a) H. C. Johnson and A. S. Weller, Angew. Chem., Int. Ed., 2015, 54, 10173; (b) M. A. Esteruelas, A. M. López, M. Mora and E. Oñate, ACS Catal., 2015, 5, 187; (c) A. G. Algarra, L. J. Sewell, H. C. Johnson, S. A. Macgregor and A. S. Weller, Dalton Trans., 2014, 43, 11118;

(d) S. Muhammad, S. Moncho, E. N. Brothers and A. A. Bengali, *Chem. Commun.*, 2014, **50**, 5874; (e) L. J. Sewell, G. C. Lloyd-Jones and A. S. Weller, *J. Am. Chem. Soc.*, 2012, **134**, 3598; (f) C. Y. Tang, N. Phillips, M. J. Kelly and S. Aldridge, *Chem. Commun.*, 2012, **48**, 11999; (g) R. Kumar and B. R. Jagirdar, *Inorg. Chem.*, 2013, **22**, 28; (h) H. C. Johnson, A. P. M. Robertson, A. B. Chaplin, L. J. Sewell, A. L. Thompson, M. F. Haddow, I. Manners and A. S. Weller, *J. Am. Chem. Soc.*, 2011, **133**, 11076; (i) R. Dallanegra, A. P. M. Robertson, A. B. Chaplin, I. Manners and A. S. Weller, *Chem. Commun.*, 2011, **47**, 3763; (j) G. Alcaraz and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2010, **49**, 7170; (k) C. Y. Tang, A. L. Thompson and S. Aldridge, *J. Am. Chem. Soc.*, 2010, **132**, 10578; (l) T. M. Douglas, A. B. Chaplin, A. S. Weller, X. Yang and M. B. Hall, *J. Am. Chem. Soc.*, 2009, **131**, 15440.

- 3 (a) A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.*, 2010, 110, 4079; (b) N. C. Smythe and J. C. Gordon, *Eur. J. Inorg. Chem.*, 2010, 509; (c) C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, 38, 279.
- 4 H. C. Johnson, C. L. McMullin, S. D. Pike, S. A. Macgregor and A. S. Weller, Angew. Chem., Int. Ed., 2013, 52, 9776.
- 5 (a) C. J. Wallis, G. Alcaraz, A. S. Petit, A. I. Poblador-Bahamonde, E. Clot, C. Bijani, L. Vendier and S. Sabo-Etienne, *Chem. – Eur. J.*, 2015, **21**, 13080; (b) P. Bellham, M. S. Hill, G. Kociok-Köhn and D. J. Liptrot, *Chem. Commun.*, 2013, **49**, 1960; (c) C. J. Wallis, H. Dyer, L. Vendier, G. Alcaraz and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2012, **51**, 3646; (d) It has been reported that aromatic amine-boranes can produce diaminoboranes without a catalyst: H. Helten, A. P. M. Robertson, A. Staubitz, J. R. Vance, M. F. Haddow and I. Manners, *Chem. – Eur. J.*, 2012, **18**, 4665.
- 6 O. Rivada-Wheelaghan, B. Donnadieu, C. Maya and S. Conejero, Chem. Eur. J., 2010, 16, 10323.
- 7 M. Roselló-Merino, J. López-Serrano and S. Conejero, J. Am. Chem. Soc., 2013, 135, 10910.
- 8 (a) P. Bellham, M. S. Hill and G. Kociok-Köhn, Organometallics, 2014, 33, 5716; (b) Y. Kawano, M. Uruichi, M. Shimoi, S. Taki, T. Kawaguchi, T. Kakizawa and H. Ogino, J. Am. Chem. Soc., 2009, 131, 14946.
- 9 A. P. M. Robertson, E. M. Leitao and I. Manners, J. Am. Chem. Soc., 2011, 133, 19322.
- 10 M. A. Ortuño, S. Conejero and A. Lledós, *Beilstein J. Org. Chem.*, 2013, 9, 1352.
- 11 G. Alcaraz and S. Sabo-Etienne, Coord. Chem. Rev., 2008, 252, 2395.
- (a) R. Dallanegra, A. B. Chaplin, J. Tsim and A. S. Weller, *Chem. Commun.*, 2010, 46, 3092; (b) M. Shimoi, S. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi and H. Ogino, *J. Am. Chem. Soc.*, 1999, 121, 11704.
- 13 (a) A. E. W. Ledger, C. E. Ellul, M. F. Mahon, J. M. J. Williams and M. K. Whittlesey, *Chem. – Eur. J.*, 2011, **17**, 8704; (b) R. Dallanegra, A. B. Chaplin and A. S. Weller, *Angew. Chem., Int. Ed.*, 2009, **48**, 6875; (c) Y. Kawano, K. Yamaguchi, S. Miyake, T. Kakizawa and M. Shimoi, *Chem. – Eur. J.*, 2007, **13**, 6920; (d) Y. Kawano, M. Hashiva and M. Shimoi, *Organometallics*, 2006, **25**, 4420; (e) N. Merle, G. Koicok-Köhn, M. F. Mahon, C. G. Frost, G. D. Ruggerio, A. S. Weller and M. C. Willis, *Dalton Trans.*, 2004, 3883; (f) T. Yasue, Y. Kawano and M. Shimoi, *Angew. Chem., Int. Ed.*, 2003, **42**, 1727.
- 14 A similar behavior has been observed in a ruthenium complex. See ref. 13*a*.
- 15 (a) M. A. Ortuño, P. Vidossich, S. Conejero and A. Lledós, Angew. Chem., Int. Ed., 2014, 53, 14158; (b) O. Rivada-Wheelaghan, M. Roselló-Merino, M. A. Ortuño, P. Vidossich, E. Gutiérrez-Puebla, A. Lledós and S. Conejero, Inorg. Chem., 2014, 53, 4257.
- 16 J.-N. Luy, S. A. Hauser, A. B. Chaplin and R. Tonner, *Organometallics*, 2015, 34, 5099.
- 17 G. Bénac-Lestrille, U. Helmstedt, L. Vendier, G. Alcaraz, E. Clot and S. Sabo-Etienne, *Inorg. Chem.*, 2011, 50, 11039.