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# Catalytic Dehydrogenation of (Di)Amine-Boranes with a Geometrically-Constrained Phosphine-Borane Lewis Pair

Maxime Boudjelel,<sup>a</sup> E. Daiann Sosa Carrizo,<sup>b</sup> Sonia Mallet–Ladeira,<sup>c</sup> Stéphane Massou,<sup>c</sup> Karinne Miqueu,<sup>b</sup> Ghenwa Bouhadir<sup>a</sup> and Didier Bourissou<sup>a</sup>\*

<sup>a</sup> CNRS / Université Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA, UMR 5069). 118 Route de Narbonne, 31062 Toulouse Cedex 09 (France)

<sup>b</sup> CNRS / UNIV PAU & PAYS ADOUR, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux (IPREM UMR 5254). Hélioparc, 2 Avenue du Président Angot, 64053 Pau Cedex 09 (France)

<sup>c</sup> Institut de Chimie de Toulouse (FR 2599). 118 Route de Narbonne, 31062 Toulouse Cedex 09 (France)

Supporting Information Placeholder

**ABSTRACT:** The *o*-phenylene bridged phosphine-borane  $iPr_2P(o-C_6H_4)B(Fxyl)_2$  **2** was prepared. Despite ring strain, it adopts a closed form, as substantiated by NMR, XRD and DFT analyses. But the corresponding open form is only slightly higher in energy. The dormant Lewis pair **2** proved to efficiently catalyze the dehydrogenation of a variety of amine- and diamine-boranes under mild conditions. The corresponding phosphonium-borate  $iPr_2PH(o-C_6H_4)BH(Fxyl)_2$  **3** was authenticated as a key intermediate of these dehydrogenation reactions. The propensity of **3** to release H<sub>2</sub> plays a major role in the catalytic turnover.

**KEYWORDS:** Phosphine-borane, Lewis pair, small molecule activation, amine-borane, dehydrogenation, metal-free catalysis.

#### INTRODUCTION

The last 10-15 years have witnessed a spectacular development of catalysis with main-group compounds. In particular, the ability of Frustrated Lewis Pairs (FLP)<sup>1</sup> to activate dihydrogen has opened new avenues in catalytic hydrogenation. Spectacular results have also been obtained in CO<sub>2</sub> reduction.

Although comparatively much less developed, the use of FLP to dehydrogenate amine-boranes has also emerged recently. Catalytic dehydrogenation of amine-boranes is of great synthetic interest.<sup>2</sup> The release of H<sub>2</sub> under mild and controlled conditions makes amine-boranes valuable materials for hydrogen storage. On the other hand, dehydrogenation and dehydrogenative coupling give straightforward access to a variety of BN building blocks useful in synthesis and material science, with H<sub>2</sub> as only byproduct. Transition metal (TM) based catalysts occupy a forefront position in this field. With FLP, stoichiometric studies were first reported in 2010 by Miller<sup>3a</sup> and Manners<sup>3b</sup> (Chart 1a). Soon after, Slootweg and Uhl showed the ability of the geminal phosphinealane FLP A to catalyse the dehydrogenation of dimethylamineborane at 90°C in the melt (Chart 1b).<sup>4</sup> Using xanthene as a rigid linker between phosphine and borane sites, Aldridge further advanced the field in 2016. Ammonia-borane H<sub>3</sub>N→BH<sub>3</sub>, mono and dimethylamine-boranes MeH<sub>2</sub>N→BH<sub>3</sub> (MAB) and Me<sub>2</sub>HN→BH<sub>3</sub> (DMAB) were dehydrogenated in 1-2 days at 55°C using 1 mol% of **B**.<sup>5</sup> These studies point out the potential of FLP,<sup>6</sup> but to make

such main-group catalysts<sup>7</sup> really valuable, their efficiency and generality have to be significantly improved.



Chart 1. FLP applied to B–N dehydrogenation.

Our group has a long standing interest in *o*-phenylene bridged phosphine-boranes.<sup>8</sup> The proximity of the two Lewis pairs imparts unique properties and favours cooperativity.<sup>9</sup> Here, we report that compound **C** (Chart 1) featuring a highly Lewis acidic boron center is an efficient catalyst for the dehydrogenation of a variety of amine- and diamine-boranes. It adopts a dormant closed form, but the corresponding open form is readily accessible in energy.<sup>10</sup>

#### **RESULTS AND DISCUSSION**

The design and preparation of the target compound **C** face several challenges. Introduction of the  $B(C_6F_5)_2$  moiety by ionic coupling, the general route to prepare *o*-phenylene bridged phosphine-boranes,<sup>8</sup> suffers from competitive aromatic nucleophilic substitution of fluoride.<sup>11</sup> So far, it has only been possible by indirect means, namely electrocyclic ring closure of P,Bsubstituted hexatrienes.<sup>12</sup> Inspired by the recent work of Wagner on P(CH<sub>2</sub>)<sub>n</sub>B FLP (n = 1,2),<sup>13</sup> we turned our attention to the B(Fxyl)<sub>2</sub> moiety (Fxyl = 3,5-(F<sub>3</sub>C)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) whose boron center is both highly electro-deficient and relatively unhindered sterically. Lithiation of the *o*-bromo phenylphosphine **1** followed by electrophilic trapping with FB(Fxyl)<sub>2</sub><sup>14</sup> cleanly afforded the desired phosphine-borane **2** (Scheme 1). After work-up, **2** was isolated in 60% yield as a white solid (mp 92°C).<sup>15</sup> The <sup>31</sup>P and <sup>11</sup>B NMR data indicate the presence of a strong P→B interaction in solution. The <sup>31</sup>P NMR signal of **2** appears at 29.8 ppm, while the <sup>11</sup>B spectrum shows a sharp signal at 2.8 ppm. According to X-ray diffraction analysis, **2** also adopts a monomeric closed form in the solid state. The boron center is in tetrahedral environment ( $\Sigma$ (CBC) = 345.8(5)°) and the P–B distance is short (2.072(2) Å), despite the ring strain associated with the four-membered ring.<sup>16</sup>

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Scheme 1. Synthesis and molecular structure of 2 as determined by X-ray diffraction analysis; *i*Pr and Fxyl simplified, and H atoms omitted for clarity.



**Figure 1.** Reaction profile computed for the heterolytic splitting of  $H_2$  by the phosphine-borane **2** at B97D/6-31G\*\* level of theory. Distances in Å.

No sign of a reaction between 2 and H<sub>2</sub> was detected even after days at 50°C and 2 atm pressure. The phosphine-borane also remained unchanged when treated with a 1:1 mixture of H<sub>2</sub> and D<sub>2</sub> under the same conditions, but according to <sup>1</sup>H NMR spectroscopy, some H/D scrambling occurred (HD detected among the dissolved gas, 15% conversion).<sup>15</sup> These experiments suggest that the fixation and splitting of  $H_2$  by 2 is thermodynamically unfavourable and slow but accessible kinetically. To gain more insight into the energy balance and activation barrier of the reaction, DFT calculations were performed at B97D/6-31G\*\* level of theory (Figure 1). The optimized geometry of the closed form 2 nicely matches that determined crystallographically (P-B distance 2.094 Å).<sup>15</sup> In the corresponding open form 2', the ring strain is relieved, the boron center is trigonal planar and the P•••B distance is long (2.890 Å). 2' is located only 1.6 kcal/mol above the closed structure 2, which can thus be viewed as a dormant form. Consistent with experimental observations, the activation of H<sub>2</sub> is endergonic ( $\Delta G$  12.7 kcal/mol)<sup>17</sup> and requires a fairly large activation barrier ( $\Delta G^{\neq}$  26.2 kcal/mol). Conversely, the phosphoniumborate 3 should be prone to release H<sub>2</sub>: the reaction is downhill in energy and its activation barrier is only 13.5 kcal/mol. These

features make the phosphine-borane 2 a promising candidate for the catalytic dehydrogenation of amine-boranes.

To start with, the reaction of **2** with methylamine-borane (MAB) was investigated.<sup>18</sup> Addition of one equivalent of MeH<sub>2</sub>N $\rightarrow$ BH<sub>3</sub> to the phosphine-borane at 25°C leads to H<sub>2</sub> release and <sup>11</sup>B NMR spectroscopy indicates complete conversion of MAB within 1 h. According to <sup>31</sup>P NMR, **2** is recovered at the end of the reaction, which prompted us to react MAB with a catalytic amount of phosphine-borane (5 mol%). After 12 h at 55°C, MAB is completely consumed and a mixture of borazane (HMeNBH<sub>2</sub>)<sub>3</sub> and borazine (MeNBH)<sub>3</sub> (40 and 60% yield, respectively) is obtained. The activity of **2** towards MAB is relatively modest but this result shows the ability of the phosphine-borane to act as a dehydrogenation catalyst. We then explored its behaviour towards various amine- and diamine-boranes.

Table 1. Catalytic dehydrogenation of DMAB.

$$\begin{array}{c} \mathsf{Me}_{2}\mathsf{HN} \longrightarrow \mathsf{BH}_{3} & \underbrace{\begin{array}{c} 2 (x \text{ mol}\%) \\ additive: \end{array}}_{additive:} & \underbrace{\begin{array}{c} \mathsf{Me}_{2}\mathsf{N} \longrightarrow \mathsf{BH}_{2} \\ \mathsf{H}_{2}\mathsf{B} \longrightarrow \mathsf{NMe}_{2} \end{array}}_{PhCH=\mathsf{N}t\mathsf{Bu} \ \mathbf{5} \qquad \mathbf{4} \end{array}$$

entry	2 (mol%)	$T(^{\circ}C)$	additive	time (h)	yield (%) <sup>a</sup>
1	5	25	/	96	99
2	5	55	/	1.5	99
3	5	70	/	0.5	99
4	1	55	/	6	99
5	0.2	70	/	44	99
6	0	70	/	144	0
7	5	25	1 eq <b>5</b>	6	99
8	0	25	1 eq <b>5</b>	48	0

 $^{\rm a}$  Reactions performed in benzene at 0.83 M. Yields determined by  $^{\rm l}{\rm H}$  NMR using hexamethylbenzene as internal standard.

Using 5 mol% of 2, dimethylamine-borane (DMAB), the benchmark substrate in FLP chemistry,<sup>4,5</sup> is slowly dehydrogenated at 25°C (Table 1). The reaction is complete in 4 days and quantitatively leads to the cyclic dimer 4 (entry 1). Among common solvents, the best results were obtained in benzene and toluene. Lower rates and yields were observed in ethereal solvents (Table S3).<sup>15</sup> Complete dehydrogenation of DMAB requires only 1.5 h at 55°C and 0.5 h at 70°C (entries 2 and 3). It is possible to decrease the catalytic loading of 2. The reaction takes only 6 h at 1 mol% and 55°C (entry 4). For comparison, the xanthene-derived FLP B requires 48 h of reaction under similar conditions.<sup>5b</sup> Importantly, a control experiment without 2 (entry 6) showed no sign of a reaction even after prolonged heating, substantiating the catalytic role of the phosphine-borane.<sup>19</sup> The ability of H<sub>2</sub> acceptors to significantly improve the efficiency of dehydrogenation and dehydrocoupling reactions,20 prompted us to envision the use of an additive. Gratifyingly, the addition of 1 equiv. of the aldimine PhHC=NtBu 5 proved very beneficial.<sup>21-23</sup> The reaction is considerably speeded up and now proceeds within only 6 h even at 25°C (entry 7). According to the control experiment performed without 2 (entry 8), the combination of the phosphine-borane and aldimine is really critical for the reaction to proceed so efficiently.

The phosphine-borane proved also an efficient catalyst for the dehydrogenation of  $iPr_2HN \rightarrow BH_3$ . The steric demand of the substrate slows down the reaction but the monomeric aminoborane  $iPr_2N=BH_2$  was quantitatively obtained within 12 h at 70°C using 5 mol% of **2**.<sup>15</sup> We then turned to cyclic amineboranes which have recently attracted interest as hydrogen storage

materials.<sup>24</sup> As reported by Liu *et al*, the five and six-membered rings **6a** and **6b** (Scheme 2) can release two equivalents of H<sub>2</sub> per substrate molecule to give trimeric products (borazines **7a,b**). Thermal activation requires harsh conditions (150°C, 1-2 h), but with transition metal halides as catalysts, **6b** can be dehydrogenated at 80°C (complete conversion within ~0.5 h using 5 mol% of FeCl<sub>2</sub> for example).<sup>24b</sup> Pleasingly, we found that the phosphineborane **2** is able to dehydrogenate both **6a** and **6b** under mild conditions. For the five-membered ring substrate, complete conversion is achieved within 3.5 h at 80°C using 5 mol% of **2** and the borazine is obtained in 97% yield.<sup>15</sup>



Scheme 2. Dehydrogenation of cyclic amine-boranes **6a,b** catalysed by 2.

 Table 2. Catalytic dehydrogenation of the diamine-boranes
 8a-c.



	substrate	2 (mol%)	T (°C)	additive	time (h)	yield (%) <sup>a</sup>
	<b>8a</b> R = Me	5	70	/	1	90
		2.5	70	/	6	90
		1	70	/	8	90
		0	70	/	8	0
		5	25	2 eq <b>5</b>	6	91
		2.5	25	2 eq <b>5</b>	24	90
		0	25	2 eq <b>5</b>	24	0
	<b>8b</b> R = <i>t</i> Bu	5	25	/	72	90
		5	70	/	1.5	90
		2.5	70	/	2.5	90
		1	70	/	5	90
		0	70	/	5	0
		5	25	2 eq <b>5</b>	4.5	90
		2.5	25	2 eq <b>5</b>	24	99
		0	25	2 eq <b>5</b>	180	0
-	<b>8c</b> R = Bn	5	70	/	2.5	95
		2.5	70	/	3.5	95
		1	70	/	4	95
		0	70	/	4	0
		5	25	2 eq <b>5</b>	36	80
		0	25	2 eq <b>5</b>	72	0

 $^aReactions$  performed in benzene at 0.77 M. Yields determined by  $^1H$  NMR using hexamethylbenzene as internal standard.

Recent studies have also pointed out the ability of diamineboranes  $\mathbf{8}$  to release two molecules of H<sub>2</sub> affording 1,3,2-

diazaborolidines by a sequence of dehydrogenation and dehydrogenative coupling (Table 2).<sup>25</sup> To date, only two catalysts have been disclosed for this reaction. The first one, namely  $[RuH_2(\eta^2 -$ H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>], was reported by Alcaraz and Sabo-Etienne in 2012.25a,b Working at 25°C with 2.5 mol% Ru catalyst, the reaction takes from 3 h to 3 d. The other catalyst, reported by Robertson and Mulvey, is a group 1 complex, namely a lithiodihydropyridine.<sup>25c</sup> In this case, the reaction is carried out at 70°C with 5 mol% catalyst and takes from 6 h to 2 d. With the phosphine-borane 2 (Table 2), the diamine-borane 8a is rapidly converted into the corresponding 1,3,2-diazaborolidine 9a at 70°C (the reaction is complete within 1 h at 5 mol%). The catalytic loading can be reduced (at 1 mol%, the reaction is complete within 12 h) and using the aldimine 5 as additive (2 equiv.), the reaction works as well at 25°C. Good results were also obtained with substrates **8b,c** featuring more sterically demanding substituents at the nitrogen atoms. For example, complete reaction of the tBu substrate 8b is achieved within only 5 h at 70°C using 1 mol% of 2, and within 4.5 h at 25°C using 5 mol% of 2 and 2 equiv. of 5. The dehydrogenation of **8b** was scaled up at 6.4 mmol and 1,3,2diazaborolidine 9b was isolated in 83% yield by simple distillation.<sup>15</sup> Again, no sign of a reaction is observed in the absence of phosphine-borane (with or without the aldimine additive). These results further substantiate the ability and efficiency of the phosphine-borane 2 to catalyze dehydrogenation and dehydrogenative coupling of amine-boranes. It works well with a variety of substrates and reactions proceed under mild conditions.

Finally, we tried to identify the features that make **2** a good catalyst for such dehydrogenation reactions. To substantiate the cooperativity of the P and B sites, and the key role of the geometric constraints induced by the *o*-phenylene linker, the catalytic activity of **2** was compared with that of a related bimolecular Lewis pair. Using the *i*Pr<sub>2</sub>PhP $\rightarrow$ B(Fxyl)<sub>3</sub> adduct as catalyst,<sup>15</sup> dehydrogenation of DMAB is very slow: only 35% conversion after 18 h at 70°C and 5 mol% cat. loading, while the reaction is complete within 0.5 h with **2**.

In situ NMR studies were also performed. In most cases, complex spectra with multiple broad signals were obtained, suggesting the coexistence of different species. Varying the conditions, we could eventually characterize a key intermediate upon reacting 2 with 3 equivalents of DMAB in dichloromethane. Under these conditions, dehydrogenation is complete after 2 h, but freezing the reaction mixture at -80°C just after mixing provided valuable information. <sup>31</sup>P NMR spectroscopy revealed the presence of two species resonating at  $\delta$  57.1 and 21.7 ppm in approximately 70:30 ratio.<sup>15</sup> Multi-nuclear NMR analyses including <sup>31</sup>P{<sup>11</sup>B}, <sup>11</sup>B{<sup>31</sup>P}, <sup>1</sup>H/<sup>11</sup>B TOCSY experiments enabled us to authenticate the two formed products as rotamers of the phosphonium-borate **3**.<sup>15</sup> Most diagnostic are the  ${}^{1}J_{P-H}$  and  ${}^{1}J_{B-H}$  coupling constants: 476 / 81 Hz for the major species 3a and 402 / 75 Hz for the minor one 3b. Slow exchange between 3a and 3b at the NMR timescale is apparent from <sup>31</sup>P/<sup>31</sup>P and <sup>11</sup>B/<sup>11</sup>B EXSY experiments. The coexistence of two rotamers of 3 is somewhat surprising, but consistent with the presence of four local minima close in energy according to DFT calculations (Figure 2). It is hardly possible at this stage to identify precisely the structures of two rotamers observed experimentally. But the computed NMR data reveal large variations in the NMR chemical shifts of the P and H atoms as well as of the  ${}^{1}J_{PH}$  coupling constant, consistent with the values determined experimentally. To confirm our interpretation, the phosphonium-borate 3 was independently synthesized by reacting 2 consecutively with triflic acid and triethylsilane (Scheme 3).<sup>26</sup> The NMR data show two species matching exactly those characterized *in situ*. In addition, crystals of **3** were grown at -25°C and its molecular structure was confirmed by X-ray diffraction analysis. The solid-state structure of 3 determined by X-

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ray diffraction resembles most rotamer **3**. Compared to **2**, the P...B distance is now 3.195(3) Å and the PCC and CCB bond angles open to 119.7(2) and  $123.2(2)^\circ$ , respectively [*vs* 105.0(2) and 97.5(1)° in **2**]. The proton at phosphorus and the hydride at boron could be located in the difference Fourier map without position constraints. The long H•••H distance (2.38 Å) suggests the absence of hydrogen bonding. Upon warm up, solutions of **3** spontaneously and rapidly release H<sub>2</sub> with recovery of the phosphine-borane **2** (50% conversion after 10 min at 25°C according to <sup>31</sup>P NMR).



**Scheme 3.** Synthesis and molecular structure of **3** as determined by X-ray diffraction analysis; *i*Pr and Fxyl simplified, and H atoms, except the ones at P and B, omitted for clarity.



**Figure 2.** Structures and relative energies of the different rotamers found for compound **3** at the B97D/6-31G\*\* level of theory.  $\Delta G$  (and  $\Delta E$ ) values in kcal/mol.

Of note, when Lewis pairs such as **2** are reacted with a large excess of amine-boranes, BH<sub>3</sub> transfer (from N to P) may occur, a potential side-reaction.<sup>27</sup> Such a process is not observed with **2**. The corresponding BH<sub>3</sub> adduct does not form easily<sup>15</sup> and it was actually not detected in the catalytic runs.

#### CONCLUSION

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In conclusion, the phosphine-borane 2 proved to be an efficient catalyst for the dehydrogenation of amine-boranes, surpassing known metal-free systems in activity and generality. Two key features of this Lewis pair have been highlighted: (i) the presence of a strong but geometrically-constrained  $P \rightarrow B$  interaction, and (ii) the propensity of the corresponding phosphonium-borate **3** to release dihydrogen. The mechanism of amine-borane dehydrogenation by 2 remains unclear at this stage. The non-observation of the linear condensation product Me2NBH2NMe2BH3 is not in favor of a chain-growth mechanism, as proposed for the xanthenederived phosphine-borane **B**.<sup>5b</sup> We hypothesize that the reaction proceeds by hydrogen transfer from the amine-borane to 2 (concerted proton transfer from N to P and hydride transfer from B to B),  $^{28,29}$  and that the imine additive facilitates the H<sub>2</sub> release from the phosphonium-borate 3. Future work from our group will seek to explore further the behaviour of phosphine-borane 2 towards small molecule activation and as ambiphilic ligand for transition metals.30

#### AUTHOR INFORMATION

#### **Corresponding Author**

#### dbouriss@chimie.ups-tlse.fr

#### Notes

The authors declare no competing financial interests.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge via the Internet at <u>http://pubs.acs.org</u>. Experimental procedures, characterization of the catalyst and intermediates (PDF). Crystallographic data for **2**, **2.BH**<sub>3</sub> and **3** (CIF).

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