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Dedication ((optional))

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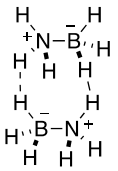
Abstract: Amine-borane dimers and oligomers with varied steric and electronic profiles were prepared via capping agent-controlled AA/BB polycondensations. They were used for transfer hydrogenations to aldehydes, ketones, imines as well as electron-poor alkene/alkyne moieties. The amine-borane Lewis-paired oligomers and the congested bis(amine-borane)s provided the highest yields. This was likely helped by facilitated dissociation (oligomers) or H-bond assistance. In the case of the oligomers, the second equivalent of H_2 present was also engaged in the reaction. Solid-state NMR characterization provides evidence that the Boron-containing materials obtained after transfer dehydrogenation are highly similar to those obtained from thermal dehydrogenation. The oligomers bridge the gap between simple amine-borane molecular reductants and the poly-amine-boranes and provide a full picture of the reactivity changes at the different scales.

Introduction

Hydrogenations are ubiquitous in organic synthesis. However, efforts have been made in the last decades to circumvent the use of gaseous dihydrogen, which requires pressurized containers to enhance concentration. This has led to the development of transfer hydrogenation methodologies,[1] as well as reagents able to serve as dihydrogen source, such as isopropanol or borazane (also called ammonia-borane, $H_3N{\bullet}BH_3$). The latter has elicited considerable interest because of its high 19.6 wt% hydrogen content, more than 13 wt% of which retrievable at a reasonable energetic cost.[2] Ammonia-borane and amine-boranes can dehydrogenate thermally, in the presence of a transition metal catalyst or with a frustrated Lewis pair (FLP).[2-7] The dihydrogen or hydride generated can be transferred to various aldehydes, ketones, imines, pyridines, or olefins.[8,9]

With the highest dihydrogen content, simple borazane is thus especially attractive.[2] However, it is a solid with a tendency to generate unwanted by-products and soiled dihydrogen (traces of borane and ammonia as well as aminoborane primary products usually contaminate the produced H_2).[2-4] The Lewis pair can also fall out during the transfer, leading to the binding of the reduced substrate to the borane moiety, which requires a subsequent hydrolysis step. A lot of studies have examined substituted amine-boranes.[2-7, 10] This addressed part of the limitations. As part of our program devoted to boron polymers[11] we have investigated polyboramines, i. e. polymers containing hydrogen-rich amine-boranes in the repeat units.[11a,b] We observed that polyboramines retained the ability to transfer hydrogen to imines and ketones, without catalyst. In addition, the products were recovered directly without any hydrolysis step.[11a]



DHB

Figure 1. Dihydrogen bonds (DHB) of borazane.

In order for the direct hydrogen transfer from amine-boranes to proceed, the substrate must generate a complex with the amine-borane, which induces the double transfer of the hydrogens. This requires the disruption of the dihydrogen bond (DHB, Figure 1) networks that are specific to amine-boranes, and this has an energetic cost.[2e, 12] The enhanced reactivity of the polymers is likely a consequence of entropy, which hampers strongly ordered chain/chain interactions in polymers, relative to molecular amine-boranes, and facilitates the approach of the small molecule substrates to the polymers in comparison.

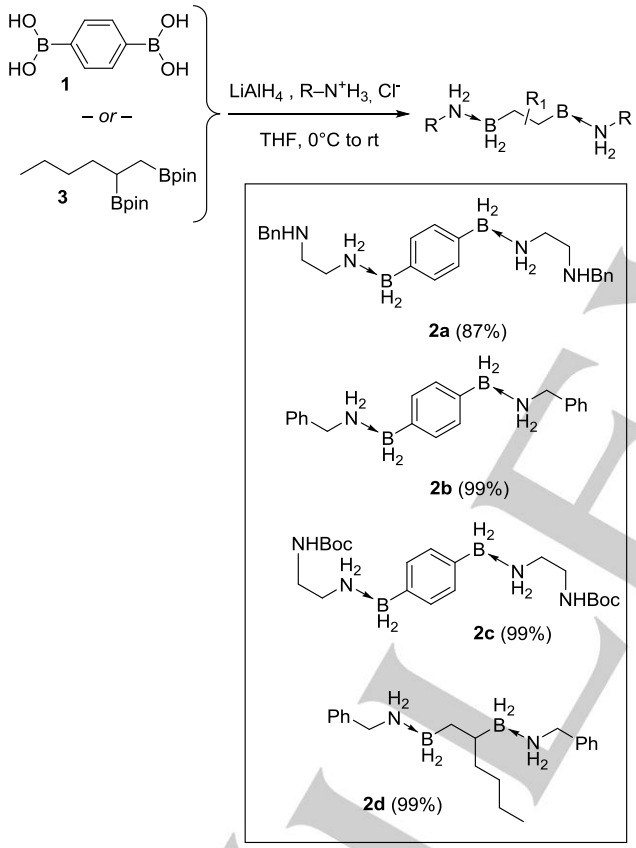
In the present publication, we explore the intermediate structural space between simple molecules and long-chain polymers, that of oligomers of amine-boranes. We introduce two oligomer structures **O1-2** (Schemes 1, 2 and S1) and examine their thermal reactivity, as well as with a variety of transfer hydrogenations substrates (aldehydes, ketones, imines), but

also electron-deficient alkenes and alkynes. Our focus aims at understanding how the chain-lengths influence the reactivities of repetitive amine-boranes. For comparison purposes, we also included dimers **2a-d** in the panel studied.

Results and Discussion

Synthesis

Amine-boranes **2a-c** were synthesized first. They feature two amine-borane Lewis pairs derived from phenyldiboronic acid, with different groups at the amine end of the amine-borane (Scheme 1). **2a** and **2c** are derived from ethylenediamine with two different protecting groups at the ω-amino end. **2b** is derived from benzylamine. **2d** is also derived from benzylamine, but grafted on a more flexible aliphatic 1,2-diboronic core.



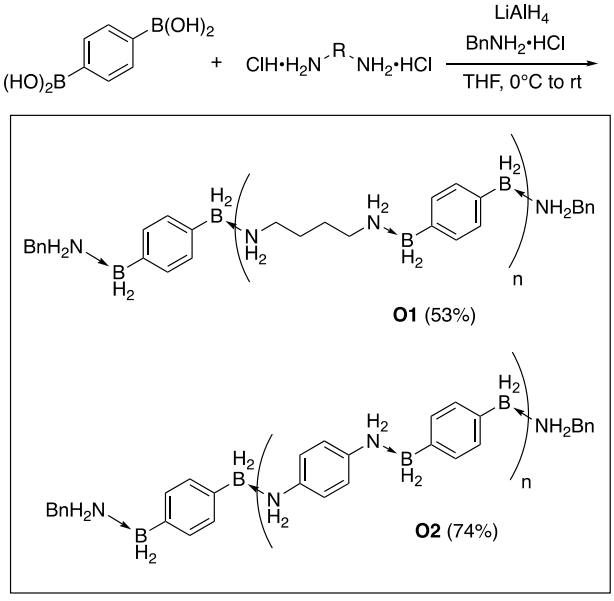
Scheme 1. Synthetic route to the molecular amine-boranes **2a-d** (Bpin = Boron pinacolato, see SI, pp 5-15 for details).

All substrates were prepared from the corresponding ammonium chlorides (Scheme 1, see SI pp 5-15 for their preparations). Lewis pairs **2a-b** were obtained by reducing phenyl-1,4-bisboronic acid **1a** with $LiAlH_4$ in the presence of the ammonium chlorhydrates. The inorganic aluminium and lithium salts were easily filtered off. In the case of **2c**, the lithium borohydride derivative was prepared and isolated first. The direct reaction led to degradation in that case, presumably because $LiAlH_4$ reacted with the Boc group rather than converting the boronic acid to the trihydridoborate intermediate needed to generate the amine-borane. All three bis-amine-boranes were obtained in quasi-quantitative yields and analytically pure. Although minute amounts of residual salts could still be present we did not purify the compounds further.

2d was obtained directly from bis-boronate ester **1b**. It exhibits a ^{11}B signal at –9 ppm, as expected for the amine-borane. However, in this case the reduction generates pinacol salts which proved very soluble in THF. This made their elimination extremely difficult. As a result, **2d** is contaminated by much more salts. We nonetheless kept it to get a general idea of its reactivity, but decided not to use **1b** to generate oligomers as the presence of salts would perturb too much the stoichiometry required for the AA/BB type polycondensation (see below).

With the synthesis of the bis-amine-boranes in hands, we selected an AA/BB polycondensation strategy. An end-capping agent was added to stop the polymerization at the oligomer level. We prepared two oligomers derived from bis-boronic acid **1a**. The flexibility of the oligomers was controlled via the diamine partner (Scheme 2). 1,4-dianiline is a rigid diamine and butyl-1,4-diamine is flexible. Benzylamine was used as capping agent in both cases. In a typical experiment, a mixture of the bisboronic acid and the bis-ammonium hydrochloride in THF was reacted with $LiAlH_4$ in the presence of benzylamine hydrochloride, in a procedure similar to that used for preparing **2a-b**.

A degree of polymerization (DP) between 3 and 4 was targeted using a non-stoechiometric amount of bisboronic acid and diamine monomers. Oligomer **O1** (resp. **O2**) was obtained in 53% (resp. 74%) yield. Using ^1H NMR we determined the numbers of repetition units as being 1-2 for **O1** and 2-4 for **O2** (see SI, pp 13 & 45). The theoretical values were not reached likely because of chain discrimination during filtration. The longer chains of **O1** may have precipitated in THF and therefore been lost in the salt filtration step. This is also in line with the observed yields. Nonetheless, the formation of the amine-boranes was evidenced by ^{11}B NMR (broad singlet from in the –9 to –11 ppm), and by ^1H NMR (broad singlet in the 2.3-2.5 ppm region), as well as by IR (ν_{B-H} ~ 2300 cm^{-1}, see the SI, pp 60-64 for the complete analyses).



Scheme 2. Preparation of the amine-borane oligomers (with benzylamine as end-capping agent).

Thermal dehydrogenation

We first focused on the thermal dehydrogenation profiles of the materials obtained in order to assess their inherent ability to release molecular dihydrogen, i. e. without catalysis. Differential scanning calorimetry (DSC) indicated that neat amine-boranes **2a-c** liberate a first equivalent of H_2 at respectively 84, 111, and 112 °C. In all cases the processes initially generating aminoboranes were exothermal (see SI, pp 55-60).[11a,b] **O1** and **O2** liberated their first equivalent of H_2 at 120 °C and 102 °C respectively, also as an exothermal process. However, in the case of **O2** the exotherm was immediately preceded by an endothermal event (see SI, page 57). This might be attributed to a transition to higher chain mobility and/or the formation of the intermolecular dihydrogen-bonding network necessary for the thermal dehydrogenation, which is more pronounced in the oligomers relative to the small molecules.

The (exothermal) DSC profiles of the first dehydrogenation show that oligomers **O1-2** behave like their molecular counterparts. An endothermic dehydrogenation profile was observed for the corresponding polyamine-boranes.[11a] In the polymer, the architecture reorganization needed to establish the interactions required for the dehydrogenation is likely both more pronounced than in the oligomers. It is therefore shifted at slightly higher temperatures, and finally overlaps with (and offsets) the exothermic dehydrogenation. The overall process is therefore endothermic. Therefore, the thermal dehydrogenation profile of oligomers **O1** and **O2** bridges the gap between pure molecules and polymers.

The second dehydrogenation to the fully dehydrogenated iminoboranes was more difficult to observe because it is spread over a wider temperature range. The baseline is not very stable and the DSC chromatograms are thus more difficult to integrate. Nonetheless, for **2a-c** exothermal dehydrogenations were observed at respectively 137, 179 and 154 °C, and endothermal ones were detected for **O1** and **O2** at respectively 164 and 142 °C, that once again could result from two concomitant processes, like in the polymers.

Transfer hydrogenation

We next investigated the transfer hydrogenation of the amine-boranes to various substrates: aldehydes, ketones, imines, alkenes, and alkynes (Table 1). All yields and conversions were determined by ^{1}H and ^{11}B NMR spectroscopy, using tetrachloroethane as internal standard.

The amine-boranes were first reacted with aldehydes at room temperature in THF-d[8] (Table 1, Entries 1-2). This led to almost quantitative conversions, except for **2a-b,** and good yields of the desired alcohols. The putative aminoborane by-products were insoluble and could be easily filtered off. However, imines obtained from the reaction between benzaldehyde and the benzylamine from amine-boranes **2b** and **O2** were isolated in 46% and 23% yield, respectively. We suppose that unwanted side-products form when the transfer hydrogenation is slow, and the imine is easily formed and stable.

The amine-boranes were then mixed with acetophenone and benzophenone (Entries 3-4). The conversions were lower than for the aldehydes, except for dimer **2c** and oligomer **O1** that led to good yields of the reduced products (~80%). The selectivity was 100% in all cases, with exclusively the alcohol formed, thus suggesting that no decomposition occurred.

Table 1. Transfer hydrogenation from amine-borane dimers and oligomers to various substrates.

Entry	Substrate	Yield (conversion) (%) for the reduction by the amine-borane indicated[a]					
		2a	**2b**	**2c**	**2d**	**O1**	**O2**
1	Benzaldehyde	27 (70)	32 (90)	99 (99)	39 (99)	99 (99)	78 (99)
2	Hexanal	97 (99)	29 (99)	90 (99)	39 (99)	99 (99)	97 (99)
3	Acetophenone	22 (22)	32 (35)	82 (82)	31 (49)	85 (85)	37 (37)
4	Benzophenone	8 (8)	27 (36)	73 (73)	36 (37)	83 (83)	34 (34)
5	Diphenylimine	34 (88)	14 (87)	59 (96)	39 (92)	62 (87)	20 (59)
6	Sulfonylimine	78 (99)	23 (99)	73 (99)	42 (99)	88 (99)	28 (99)
7	MeO_2C—≡—CO_2Me	0 (81)	12[b] (74) [*E*]	25[b] (94) [*E*]	16[c] (99) [*E*]	28[d] (99) [*E*]	5[e] (99) [*E*]
8	EtO_2C—≡—CO_2Et	13[f] (84) [*E*/*Z* = 2.2:1]	5[g] (47) [*E*/*Z* = 1.5:1]	45[h] (99) [*E*/*Z* = 1:1]	11[b] (81) [*E*/*Z* = 2.7:1]	32[h] (99) [*E*/*Z* = 1.9:1]	9[d] (81) [*E*/*Z* = 2:1]
9	MeO_2C, CO_2Me	12 (45)	0 (32)	23 (54)	1 (42)	28 (53)	5 (31)
10	CO_2Me, CO_2Me	14[i] (68)	3[j] (96)	23[j] (99)	0[k] (93)	41[l] (99)	5[m] (72)

[a] Conditions: Substrate (0.08 mmol), amine-borane (0.08 mmol of Lewis pairs), THF-d[8], r. t., 18 h; [b] ~60% of aminated adducts were isolated; [c] ~70% of aminated adducts were isolated; [d] ~50% of aminated adducts were isolated; [e] ~15% of aminated adducts were isolated; [f] ~20% of aminated adducts were isolated; [g] ~25% of aminated adducts were isolated; [h] ~35% of aminated adducts were isolated; [i] ~50% of fumarate (*E* compound) was formed; [j] ~80% of

fumarate (*E* compound) was formed; [k] [i] ~70% of fumarate (*E* compound) was formed; [l] ~30% of fumarate (*E* compound) was formed; [m] ~60% of fumarate (*E* compound) was formed.

The reduction of diphenylimine and sulfonylimine proceeded in high conversions (Entries 5-6), especially with the more electrophilic one, the sulfonylimine, albeit the more rigid **O2** was slightly less reactive toward diphenylimine. Some side-products were still observed. The alcohols coming from the reduction of the aldehyde part of the starting imines (benzaldehyde) were observed when **2a** (7% for entry 5; 11% for entry 6), **2c** (15% for entry 5; traces for entry 6) or **2d** (4% for entry 5 only) were used. Similarly, as in entries 1-2 the imines derived from the decomplexation of the corresponding amine from the borane and subsequent condensation were also observed (see SI, pp 16-25 for details). In some cases, these by-products were actually the major ones, as for the reduction of diphenylimine with **2d** (41%), or that of the sulfonylimine with **2b** (77%) or **2d** (58%). Also, the reaction of the sulfonylimine with **O2** delivered 65% of 4-(benzylideneamino)aniline. In this case it is the diamine (1,4-dianiline) at the core of the oligomer which is transferred, rather than one positioned at the end of a chain. Despite these shortcomings, the isolated amine yields and selectivities are the highest for amine-boranes **2c** and particularly **O1** – which are consistently more reactive all throughout entries 1-6.

Overall, given that **2b** and **2d** roughly behaves similarly, it shows that the transfer hydrogenation is not highly sensitive to the presence of the salt residues.To summarize the results in entries 1-6, the amine-borane dimers and oligomers proved quite efficient as high yields could be accessed in most cases using only one equivalent of amine-borane relative to the substrate. This is to be compared with $H_3N{\bullet}BH_3$ which often requires excesses of amine-borane and/or a metal catalyst to assist the hydrogen transfer, and as a fluffy solid is practically difficult to deal with. This is in line with the existing literature body on hydrogenations with small-molecules substituted amine-boranes. To better understand the role of the oligomer/polymer environment we wished to get a deeper insight into the reactivity. Two distinct pathways have been proposed to account for the direct transfer of dihydrogen from the amine-boranes to different substrates (Figure 2).[8h] A first path proceeds via a concerted double H transfer with a six-center transition state (Figure 2a). It is generally followed in the hydrogenations of imines and ketones/aldehydes.[8d,e,f] A second pathway, which is often followed for olefins and less reactive carbonyls, involves a sequential transfer with an initial hydroboration step (hydride from the boron end), followed by a protodeboronation (proton from the amine end) one (Figure 2b).[13]

The mechanism for these polarized substrates is likely a concerted double-hydrogen-transfer reaction with a six-membered transition state (Figure 2a).[8d,e,f] Oligomer **O1** (and to a lesser extent **O2**) as well as diamine-borane **2c** (and to a lesser extent **2a**) perform better than the other reagents. In the case of **2c** we believe this is due to the likely formation of a chelate via an additional H-bond (Figure 2c) that enhances the polarization of the reagent. This additional H-bond can also be established in the case of **2a**, but with less effect as it is now an amine, not a carbamate. The reactivity enhancement in the oligomers likely arises from similar synergistic effects favouring necessary six-membered intermediates. **O2** is less reactive than **O1** because it is less flexible (and different Lewis pairs), which would be consistent with **O1** readily able to develop favorable transfer hydrogenation intermediates.

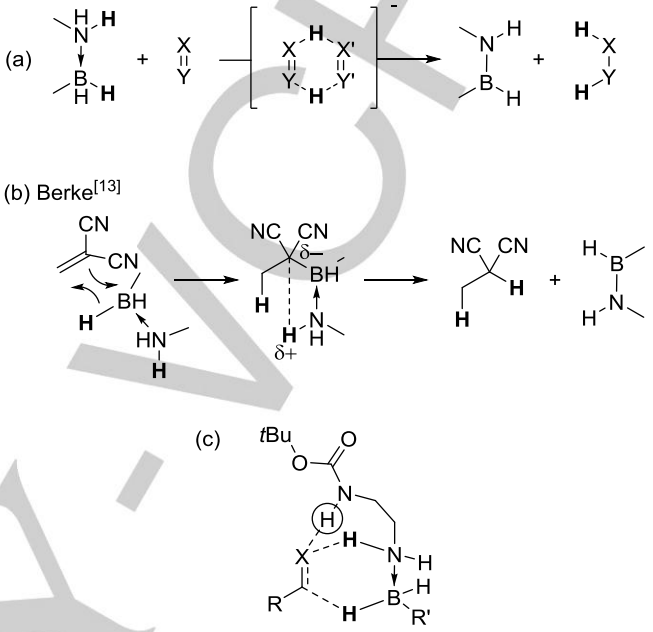


Figure 2. Main mechanistic pathways for the amine-borane transfer hydrogenation: a) synchronous transfer; b) stepwise hydroboration/protodeboration; c) additional activation via intramolecular H-bond.

Considering the previous results, we chose to study the more challenging alkenes and alkynes, whose hydrogenation likely proceed via a stepwise transfer when the alkenes are highly polarized (Figure 2b).[8g, 14-16] To gauge the reactivity of our amine-borane oligomers, we selected two electron-poor yet symmetrical alkynes, so as not to facilitate the hydrogenation by tweaking the electronic configuration of the unsaturations. We also picked dimethyl fumarate and dimethyl maleate – the corresponding electron-poor alkenes.

Both alkynes led to high conversions (Entries 7-8) with all amine-boranes. Yet, only average hydrogenation yields were observed. The maximum yields were again observed with amine-borane **2c** (25% and 45%, respectively) and oligomer **O1** (28% and 32%, respectively). The major isomer for the diethyl diester was the alkene *E* (fumarate) although the stereoselectivities remain poor. Oddly, the dimethyl diester led to only dimethyl fumarate. Given that the yields from the dimethyl diester (Entry 7) are somewhat lower than those of entry 8, it is possible that this enhanced selectivity is due to selective degradation. The main by-product (which actually is the main product in most cases) is the result of the hydro-amination: the amine part of the amine-borane reacts with the substrate. In the case of **2c**, the nucleophilic attack of the chain-end amine (H_2N-CH_2-CH_2-NH-Boc) led first to the *E* isomer. After 4-6 hours, the kinetic product was gradually converted into the *Z* isomer, which seems to be thermodynamically favoured, although the final ratio

between both isomers depends on the amine-borane used (see SI, pp 16-25).

The reduction of dimethyl fumarate (*E* isomer) (entry 9) and dimethyl maleate (*Z* isomer) (entry 10) were also attempted. In the case of the former, a similar trend as for entries 7-8 was observed, albeit with much reduced conversions. Again, **2c** and **O1** led to the best yields. In the case of the latter substrate, the conversions were much higher in all cases. This is likely due to the equilibrated isomerization of the maleate into the fumarate during reaction.

This equilibration (reminiscent of the presence of the *trans* hydrogenation product in entry 8) coupled to the observation of hydroamination products when starting from the alkynes suggest that this inversion may be due to a reversible amine transfer, with a concerted attack of nucleophilic amine (Michael addition). Nonetheless, in the case of the alkynes, a stepwise mechanism, leading to a stereochemical loss either at the initial hydroboration step, or at the protodeboronation one, cannot be excluded.

As before, we believe oligomer **O1** and amine-borane **2c** perform better because of the possible cooperative interactions they can develop, either because they are multivalent oligomers, or because of the additional H-bond.

Comparison between thermal dehydrogenation and transfer hydrogenation

Amine-boranes **2c** and **O1** were heated in a Schlenk tube for 5h at about 160 °C and the spent material was analyzed in DSC. The initial heating treatment was designed to extract the first equivalent of dihydrogen and generate the aminoborane, prior to the DSC analysis. This results in "isolating" the second dehydrogenation (see SI, pp 55-60). The spent material exhibits an endothermic process at about 150 °C. This corresponds to the second dehydrogenation in the previous DSC analysis.

We used ^{11}B CP-MAS and direct-detection very high-field solid-state NMR spectroscopy to compare the products from the first thermal dehydrogenation and those isolated post-transfer hydrogenation (see SI p.54 for description of experiment). Both materials display very similar spectroscopic signatures (see Figure 3). Because these spectra were acquired on a 1 GHz spectrometer, and very high rotational speeds were used, the isotropic shift can almost be derived from these relatively narrow spectra. The chemical shifts are consistent with a mixture of aminoboranes (massif between 0-5ppm for unimeric form and ~25 ppm for di-hydrogen-bonded dimeric structures) and iminoboranes (massif between 15-20 ppm).[2-4, 11, 17] We based our assignment of the signals on that of the native amine-boranes (see SI, page 54). We observed the signal corresponding to the amine-boranes **2c** and **O1** centered ~ –1 ppm, along with exactly two signals i) between 0-5 ppm corresponding to unimeric aminoboranes and ii) at ~25 ppm, corresponding to dimeric structures. Both signals arise from the first dehydrogenation. These signals grow simultaneously during the acquisition (see Figure 50 in the SI). The dehydrogenation observed during NMR acquisition is due to the 33.33 kHz spinning rate of the NMR rotor, which produces enough heat to promote partial release of the first H_2 equivalent.

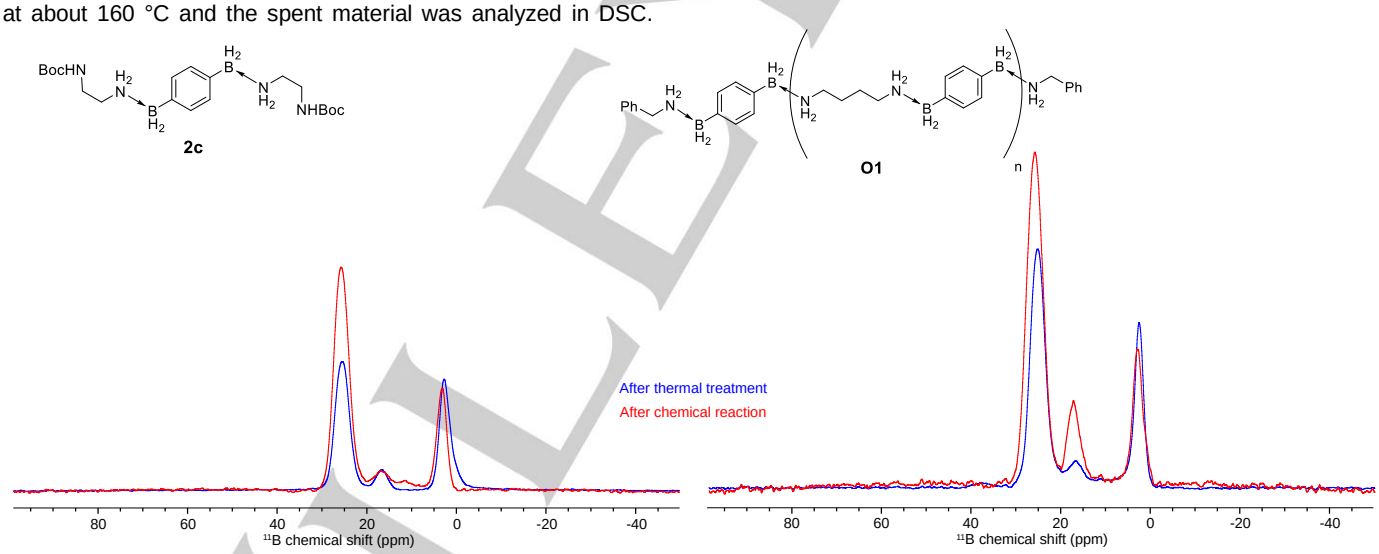
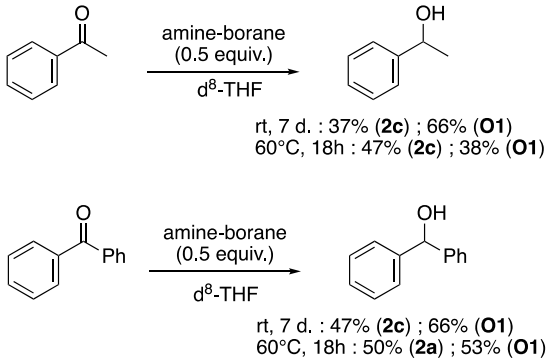


Figure 3. ^{11}B solid-state NMR spectra of **2c** and **O1** after thermal treatment (blue) and transfer dehydrogenation (red).

Both analyses indicate the formation of polyaminoboranes, but also of a small proportion of iminoboranes – *i.e.* coming from a second dihydrogen transfer. We conclude that the boron by-products issued from the thermal and chemical dehydrogenation of the dimeric and oligomeric amine-boranes are similar. Solid-state NMR additionally suggests that more than one equivalent of H_2 is utilized during transfer dehydrogenation with **O1**. The amount of iminoboranes obtained after the chemical reaction is significantly higher than in the case of the controlled thermal treatment.

The presence of signals arising from the transfer of the second equivalent of dihydrogen in our materials, led us to investigate whether this second equivalent of dihydrogen might be harnessed for the transfer hydrogenation without help from any external catalyst (Scheme 3). Borazane is able to accommodate this second transfer presumably via a solvent-stabilized form (S–$H_2B{=}NH_2$),[13] or cyclic structures such as cyclotriborazane or B-(cyclodiborazanyl)amino-borohydride.[8e] So we wished to learn whether our oligomers could also produce their H_2 second equivalent in a synthetically productive way.

Acetophenone was reacted with **2c** (resp. **O1**, 0.5 equivalent of Lewis pair) in THF-d^8 in J-young tubes. Tetrachloroethane was used as internal standard. After 18 hours at room temperature, the conversion was 31% (resp. 59%). The reaction was left for one week. With amine-borane **2c**, the conversion peaked at 36%, while it increased to 66% with oligomer **O1**. The selectivity was good, as no degradation or side-products were identified. The isolated yields were identical to the conversions. The same conversions were obtained after only 18 h at 60 °C, albeit the isolated yields dropped when **O1** was used. Benzophenone behaved identically, except that less degradation was observed at 60 °C.



Scheme 3. Reduction of (a) acetophenone and (b) benzophenone with a half-equivalent of amine-boranes **2c** and **O1**.

Gratifyingly, in the case of **O1** both alcohols were obtained in more than 50% yield. This shows that **O1** is able to engage the second equivalent of H_2 in the transfer hydrogenation, but not **2c**. This confirms the NMR spectroscopic of Figure 4. There is a clear improvement with the oligomers, further highlighting the potential of the oligomer and polymer structural space for hydrogen-rich amine-boranes. Interestingly this can be achieved in the absence of catalyst, but could also be advantageous for more challenging substrates and in the presence of a catalyst.[18]

Conclusion

In the present work we showed that amine-borane dimers and oligomers promote transfer hydrogenations with enhanced efficiency. We evidenced that this happened via cooperative dihydrogen-bond networks and likely favourable substrate-reducing agent dipolar interactions. Therefore, the flexible **O1** oligomer is a better dihydrogen donor. A similar reactivity improvement was observed on shorter amine-boranes when an H-bond was adequately positioned to generate a cooperative effect, such as in **2c**. Very interestingly, the oligomer is able to transfer more than one equivalent of dihydrogen. Furthermore it was shown that the oligomers bridge the gap between the DSC profiles of the thermal dehydrogenation of small molecules and poly(amine-borane)s. The differences likely arise from the increasing cost required to preorganize the materials for dehydrogenation. This illustrates the interest there is in exploring the poly(amine-borane) structural field to tune or change established reactivities. Further work will focus on the rehydrogenation/recycling of the identified corresponding polyaminoboranes and/or polyiminoboranes, ideally without catalyst assistance.

Acknowledgements

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Keywords: boron, dehydrogenation, hydrogen transfer, amine-boranes, oligomers

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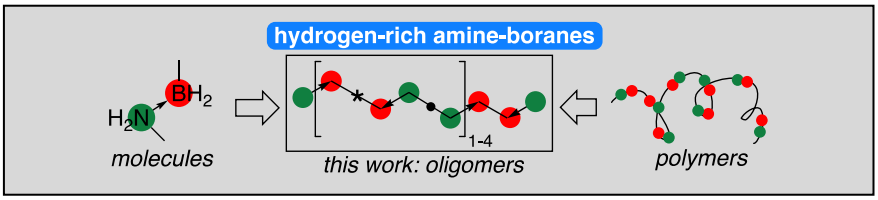
Entry for the Table of Contents



Small hydrogen-rich amine-borane oligomers were prepared via capping agent-controlled AA/BB polycondensation. Solid-state NMR spectroscopy, Differential Scanning Calorimetry and reactivity in catalyst-free transfer hydrogenations – to aldehydes, imines, electron-poor alkenes and alkynes – were used to assess how the oligomers bridge the gap between molecular amine-boranes and poly(amine-borane)s.