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Solventless and Metal-Free Synthesis of High Molecular Mass Polyaminoboranes from Diisopropylaminoborane and Primary Amines

Carlos Antonio De Albuquerque Pinheiro,^[a] Claire Roiland,^[a] Philippe Jehan^[b] and Gilles Alcaraz^{*[a]}

Abstract: The solventless reaction of diisopropylaminoborane with *n*-butylamine, at room temperature, leads to a mixture of well identified B_(sp²)H, B_(sp³)H₂ and B_(sp³)H₃ boron containing species. At low temperature, the reaction outcome is completely modified leading selectively to the formation of high mass polybutylaminoborane. Extended to a variety of primary amines under solventless conditions and at low temperature, this reaction provides a new, efficient and direct metal-free access to high molecular mass polyaminoboranes in good to high yield, in very mild conditions.

The field of inorganic polymers incorporating main group elements in their backbone is a very promising research area that remains relatively underdeveloped due to the lack of efficient synthetic methods available to connect inorganic repeating unit together successively.^[1] Among them and over the last decade, polyaminoboranes that incorporate a BN unit in their backbone, (RHN–BH₂)_n (I–R), have represented an area of considerable interest for novel BN-containing polymers and materials.^[2] They strongly benefited from the development of new systems involved in dihydrogen release derived from catalyzed dehydrocoupling strategies.^[3] To date, the preparation of linear polyaminoboranes is largely dominated by the catalyzed dehydropolymerization of a restricted number of primary amine-boranes or ammoniaborane^[2a, 4] involving expensive metal catalysts and going hand-in-hand with the production of dihydrogen. The lack of simple and efficient synthetic approaches still hampers their promising development, the only metal catalyst-free syntheses resulting in the deprotonation of sophisticated amine-boronium cations and related polar-covalent analogs,^[5] leading only to low molecular mass polyaminoboranes along with salts.

As a part of our program on the aminoboranes chemistry, we report for the first time the use of diisopropylaminoborane (ⁱPr₂NBH₂, DIAB)^[6] as a convenient "BH₂" transfer reagent in the presence of a variety of primary amines for an original and efficient metal-free and solventless synthesis of very high molecular mass polyaminoboranes (RNH–BH₂)_n (I–R) with neither dihydrogen production nor salt formation, in very mild conditions.

Solventless reaction of *n*-butylamine with diisopropyl-

aminoborane at room temperature, under stoichiometric conditions, results in an exothermic reaction leading to the complete disappearance of the starting borane reagent with formation of diisopropylamine along with a mixture of B_(sp²)H, B_(sp³)H₂ and B_(sp³)H₃ boron containing species in a ca 1:2.5:1.4 integration ratio in the ¹¹B{¹H} NMR, respectively (Figure 1 and Scheme 1).

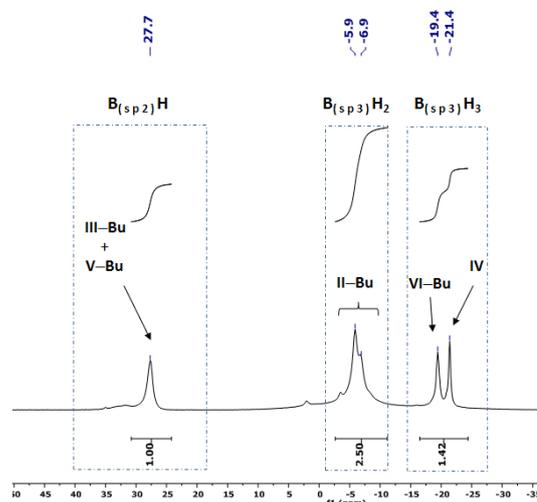
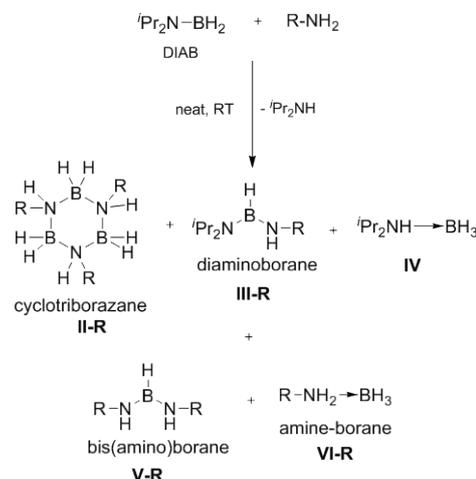


Figure 1. ¹¹B{¹H} NMR spectrum of the crude reaction of *n*-butylamine with diisopropylaminoborane under stoichiometric conditions at room temperature.



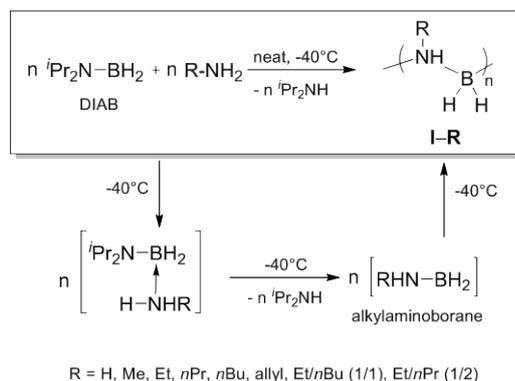
Scheme 1. Reaction of DIAB with primary amines at room temperature.

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Among them, diisopropylamine-borane (**IV**: $\delta(^{11}\text{B})$ -21.4 ppm) and *n*-butylamine-borane (**VI-Bu**: $\delta(^{11}\text{B})$ -19.4 ppm) for the $\text{B}_{(\text{sp}^3)}\text{H}_3$ compounds and *N,N,N'*-tributylcycloborazane as a mixture of two isomers (**II-Bu**: $\delta(^{11}\text{B})$ -5.9, -6.9 ppm)^[7] for the $\text{B}_{(\text{sp}^3)}\text{H}_2$ species could be unambiguously identified. In the presence of a twofold excess of *n*-butylamine, the distribution of the final compounds is modified with a decrease of **II-Bu** and the almost complete disappearance of **IV**, as seen by ^{11}B NMR (see Figure S1 in the Supporting Information).^[8] Careful examination of the data revealed the doublet at $\delta(^{11}\text{B})$ 27.7 (J_{BH} obs = 113 Hz) that collapsed upon proton decoupling results from a mixture of (diisopropylamino)(butylamino)borane (**III-Bu**), and bis(butylamino)borane (**V-Bu**) that were both prepared separately.^[9] Although suspected, *N,N,N'*-tributylborazine could not be unambiguously detected (see Figure S1 and S4 in the Supporting Information). In the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of the reaction mixture, compounds **III-Bu** and **V-Bu** exhibit for the BH group a deshielded doublet at δ 3.92 ($^3J_{\text{BH-NH}} = 8.5$ Hz) and a broad signal at δ 3.76, respectively. The use of a twofold excess of *n*-butylamine results in a signal of greater intensity at δ 3.76 whereas the one at δ 3.92 has almost disappeared, which in agreement with the ^{11}B NMR data recorded both in stoichiometric and super-stoichiometric conditions (see Figure S5 in the Supporting Information).

Surprisingly, performing the same reaction at low temperature led to a different reaction outcome (Scheme 2). With a stoichiometric amount of *n*-butylamine at -40°C , the formation of a white precipitate was initially observed to end up with a gel-like solution. Here again, formation of diisopropylamine was clearly detected along with the expected side products identified as **II-Bu**, **III-Bu**, **IV**, **V-Bu** and **VI-Bu** (See Figure S2-S3 in the supplementary information).^[10] After evaporation of the volatiles under vacuum and workup, a white solid of poor solubility in most common organic solvents was obtained. Solution NMR could however be recorded in deuterated chloroform and the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum exhibits a broad signal at δ -7.6 in agreement with previously reported data^[2a] (see Figure S48-S49 in the Supporting Information). Further analyses of the isolated material revealed its polymeric nature identified as polybutylaminoborane **I-Bu**.



Scheme 2. Reaction of DIAB with primary amines under stoichiometric conditions, at low temperature.

The reaction results in the transfer of the BH_2 group from DIAB to the primary amine, probably via the transient formation of the amine-DIAB adduct,^[11] followed by the elimination of diisopropylamine and formation of the corresponding alkylaminoborane that further polymerizes to afford polybutylaminoborane **I-Bu** in 78% isolated yield.^[12]

In the infrared spectrum, the presence of characteristic NH ($\nu = 3250\text{ cm}^{-1}$), CH ($\nu = 2960\text{ cm}^{-1}$) and BH ($\nu = 2392, 2297\text{ cm}^{-1}$) stretching vibrations could be clearly observed in agreement with the infrared data reported for polybutylaminoborane obtained by catalytic dehydrocoupling.^[2a] The size-exclusion chromatography (SEC) analysis of the polymer in THF presented a bimodal distribution consisting of a minor narrow peak of low molecular mass oligomers and a major broad peak with a shoulder corresponding to high molecular mass polybutylaminoborane (**I-Bu**: $M_w = 5450000\text{ g}\cdot\text{mol}^{-1}$, PDI = 6.9). **I-Bu** showed a good stability at room temperature as monitored by SEC analysis showing no evidence of polymer degradation after one week stirring in THF (see Figure S23 in the S.I.). Electrospray-ionization mass spectroscopy (ESI-MS) analyses indicated that the material displays a linear polymeric distribution with a *n*-butylaminoborane (*n*-BuNH-BH₂) repeating unit (see Figure S33-S34 in the Supporting Information).

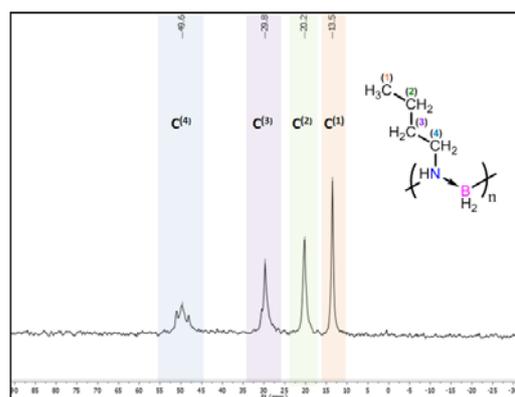


Figure 2. Solid state $^{13}\text{C}\{^1\text{H}\}$ NMR of polybutylaminoborane (**I-Bu**).

The solid state $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy reveals the presence of four characteristic broad carbon signals at δ 13.5, 20.2, 29.8 and 49.6 (Figure 2), ascertaining the presence of the *N*-butyl group of the isolated polybutylaminoborane (**I-Bu**).

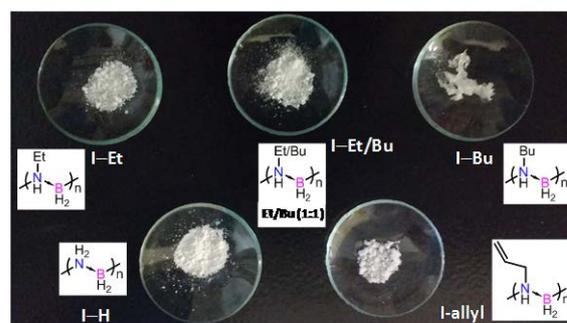


Figure 3. Polyaminoboranes **I-H**, **I-Et**, **I-Bu**, **I-allyl** and random copolymer **I-Et/Bu**.

To go one step further and take advantage of the simplicity of the method involving diisopropylaminoborane as a convenient "BH₂" transfer reagent, a variety of polymers (Figure 3) and random copolymers were prepared, at the gram scale, in good to high yields, from primary amines (table 1, entry 1-6) and mixtures of primary amines (table 1, entry 7-8), respectively.

Table 1. Synthesis and molecular mass data for polyaminoboranes.

Entry	Polymeric material I-R ^[a,b]	(RNH-BH ₂) _n (%) ^[c]	M _w (g.mol ⁻¹) ^[d]	PDI ^[f]
1	R = H ^[a]	74	— ^[f]	— ^[f]
2	R = Me ^[a]	75	201000	10.2
3	R = Et ^[a]	56	251000	2.6
4	R = Pr ^[a]	59	170000	2.1
5	R = Bu ^[a]	78	545000 ^[e]	6.9
6	R = allyl ^[a]	48	580000	1.2
7	R = Et/Bu (1/1) ^[b]	64	1380000	2.5
8	R = Et/2Pr (1/2) ^[b]	61	1800000	2.4

[a] Homopolymer. [b] Copolymer. [c] Isolated yield. [d] Data given from SEC analysis in THF (with 0.1 w/w% nBu₄NBr) and using standard calibration against polystyrene.^[13] [e] Extrapolated data. [f] Not determined; insoluble product.

All the prepared polymers and copolymers have been characterized by SEC when soluble, solution state ¹¹B{¹H} NMR in deuterated chloroform, ¹³C{¹H} solid state NMR, infrared spectroscopy (Figure 4), thermogravimetric and elemental analyses, ESI-MS and solid state ¹¹B{¹H} NMR in the case of I-H and I-Me (Figure S43 and S44) (See the Supporting Information). Except for polyaminoborane I-H that was found insoluble in our conditions, the SEC analysis reveals the obtained polyaminoboranes display higher molecular mass compared to that of analogous polyaminoboranes prepared from their corresponding amine-boranes via metal catalyzed dehydropolymerization^[2a, 4b] or by deprotonation of amine-boronium cations and related compounds.^[5] The relatively high PDI values measured suggest an uncontrolled polymerization process.^[14]

In the case of I-H and I-Me, the infrared spectra (Figure 4) are similar to those reported by Manners, Staubitz et al. under iridium catalysis,^[2a, 4b] by Schneider et al. with ruthenium in the case of I-H,^[15] and by Beweries et al. for the iron hydride catalyzed dehydrocoupling of methylamine-borane for I-Me.^[4f] It is worth noting that this synthesis enables for the first time the preparation of polyaminoboranes incorporating unsaturated substituents at the nitrogen as illustrated with polyallylaminoborane (I-allyl) obtained in 48% isolated yield.

In summary, we have shown that the synthesis of very high molecular mass polyaminoboranes can be performed at the gram scale, in good to high yields, by simply reacting diisopropylaminoborane with a wide range of primary amines or mixture of primary amines under solventless and metal-free conditions, at low temperature, without production of dihydrogen.

The role of diisopropylaminoborane as an efficient "BH₂" transfer reagent has been clearly demonstrated and efforts are currently

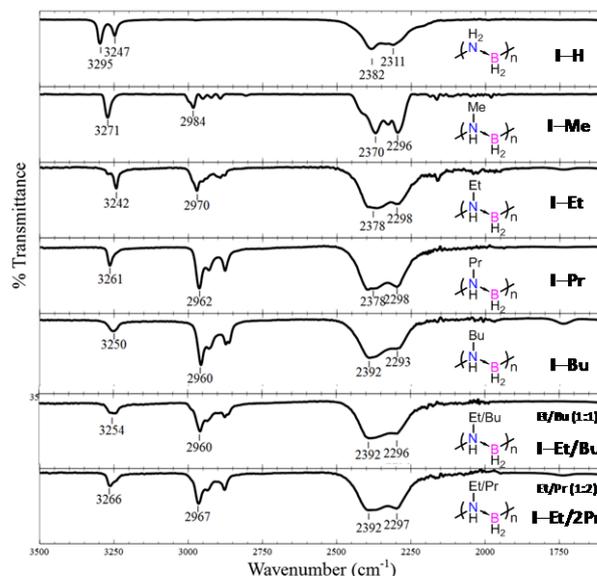


Figure 4. Infrared spectra of polymers I-H, I-Me, I-Et, I-Pr, I-Bu and random copolymers I-Et/Bu and I-Et/2Pr.

underway to rationalize the reaction mechanism and the role of the temperature on the reaction outcome.

With the isolation of polyallylaminoborane (I-allyl), this study provides, for the first time, new insights into the design of side-chain unsaturated amine containing polyaminoboranes. Detailed studies of the synthetic potential of this new family of polyaminoboranes are also in progress.

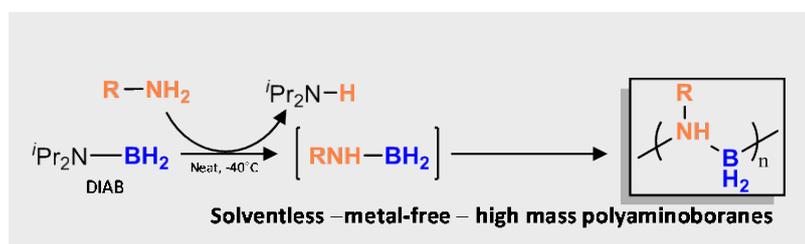
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Keywords: polyaminoboranes • inorganic polymers • aminoboranes • diisopropylaminoborane • BN compounds

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- [14] PDI (M_w/M_n) values range from 1.2 to 10 for polyaminoboranes of M_w ca 200000-5500000 and are within the range of reported PDIs for alike **I-Me** polymer (M_w ca 10000-460000 and PDIs = 1.2-13) reported in reference 4b.
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Diisopropylaminoborane undergoes a BH_2 transfer reaction with primary amines, at low temperature, leading selectively to the formation of high molecular mass polyaminoboranes.