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FULL PAPER

Cyclolinear Oligo- and Poly(iminoborane)s: The Missing Link in Inorganic Main Group Macromolecular Chemistry

Ozan Ayhan, Nicolas A. Riensch, Clemens Glasmacher, and Holger Helten*

Dedicated to Prof. Dr. Jun Okuda on the occasion of his 60th birthday

Abstract: The reaction of *n*-$C_8H_{17}B[N(Me)SiMe_3]_2$ (**1**) with *n*-$C_8H_{17}BCl_2$ (**2a**) yielded, instead of a linear poly(iminoborane), the aminoborane *n*-$C_8H_{17}B(Cl)N(Me)SiMe_3$ (**4**) and after cyclotrimerization the borazine *cyclo*-(*n*-$C_8H_{17}BNMe)_6$ (**6**). Side reactions that result in borazine formation were effectively suppressed when 1,3-bis(trimethylsilyl)-1,3,2-diazaborolidines **7** were employed as the co-monomers in combination with dichloro- or dibromoboranes **2**, **8**. Si/B exchange polycondensation led to oligo(iminoborane)s **11a,b,ac,d**. Alternative synthetic routes to such species involve Sn/B exchange of 1,3-bis(trimethylstannyl)-2-*n*-octyl-1,3,2-diazaborolidine (**16**) and *n*-$C_8H_{17}BBr_2$ (**8a**), and the initiated polycondensation of the dormant monomer **14** in the presence of a Brønsted acid (HCl, HOTf, or $HNTf_2$). While the attempt to obtain an oligo/poly(iminoborane) with phenyl side groups yielded only insoluble material, the incorporation of aryl groups was proven for a derivative having both phenyl and *n*-octyl *B*-substituents (**11ac**) as well as for a derivative with 4-*n*-butylphenyl side groups (**11d**). The highest-molecular-weight sample was obtained of **11ac**. Featuring about 18 catenated BN units on average, this is the closest approach to a poly(iminoborane) to date.

Introduction

Polymers with a backbone composed of inorganic main group elements are of considerable interest as they often exhibit useful properties and functions that complement those of classical organic macromolecular materials.[1] Probably the most prominent examples of such “inorganic polymers” are the well-known polysiloxanes (silicones, **I**, Figure 1), which are noted for their exceptional low-temperature flexibility and thermo-oxidative stability.[2] The particular value of the related polyphosphazenes (**II**) has been recognized as well.[3] Thermal and mechanical properties of these macromolecules are effectively tuned by variation of their side groups. Polysilanes (**III**) have aroused significant research interest owing to the discovery of σ conjugation along the polymer backbone,[4] and they have been used as polymeric precursors to shaped SiC ceramics and as photoresists for microlithographic applications.

The element boron has proved to be a valuable component in π conjugated inorganic–organic hybrid polymers. The boron atom imparts unique characteristics to these materials, thus enabling their use, for example, for (opto)electronic, sensory, and imaging applications.[5,6,7] Surprisingly, well-characterized truly inorganic boron-containing linear polymers became accessible not until 2008 through work by Manners and co-workers with their report of the first poly(aminoborane)s (PABs, **IV**).[8] These species may be regarded as inorganic polyolefin analogues. Since then, poly(aminoborane)s have become a quickly evolving field of research.[9] PABs can be used as polymeric precursors to shaped boron nitride,[8,10] piezoelectric PAB derivatives can possibly be prepared,[11a] and, like boron-rich compounds in general, PABs are of potential interest for the use as boron delivery agents in boron neutron capture therapy (BNCT) of cancer.[11b]

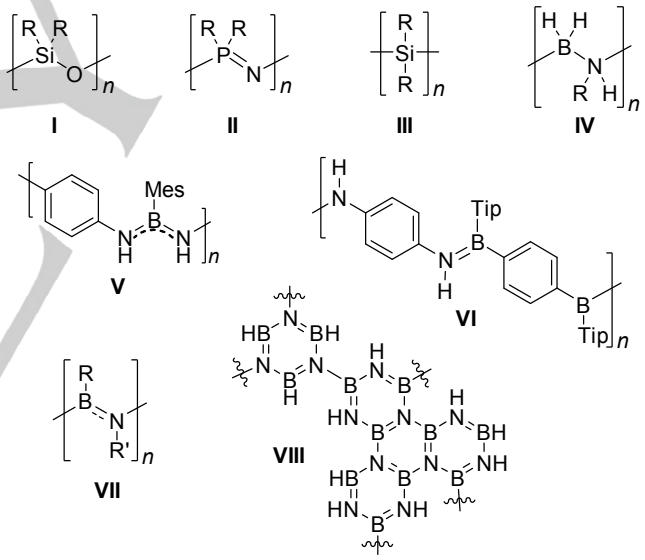

Figure 1. Polysiloxanes (**I**), polyphosphazenes (**II**), polysilanes (**III**), poly(aminoborane)s (**IV**), poly(*p*-phenylene diimidoborane) (**V**; Mes = mesityl), and poly(*p*-phenylene iminoborane) (**VI**; Tip = 2,4,6-triisopropylphenyl), poly(iminoborane)s (**VII**; R, R’ = aryl, alkyl, or H), polyborazylene (**VIII**; approximate structure).

BN and CC units are isoelectronic and isosteric, and the incorporation of BN fragments at specific positions in organic compounds has been successfully exploited for quite some time to produce novel hybrid materials with structural similarities to their all-carbon congeners but in some cases fundamentally altered electronic features.[5j,8,9,12] In terms of unsaturated B=N moieties, the applicability of this concept to polymer chemistry has just been demonstrated.[5j,13-15] We recently reported the B=N-containing inorganic–organic hybrid polymers **V**[14] and **VI**.[15] The latter can be regarded as BN analogue of poly(*p*-phenylene vinylene) (PPV).

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For the synthesis of these materials we developed a novel Si/B exchange polycondensation approach which proceeds via facile spontaneous B–N bond formation with cleavage of volatile Me_3SiCl or Me_3SiBr as the condensation by-product, respectively.

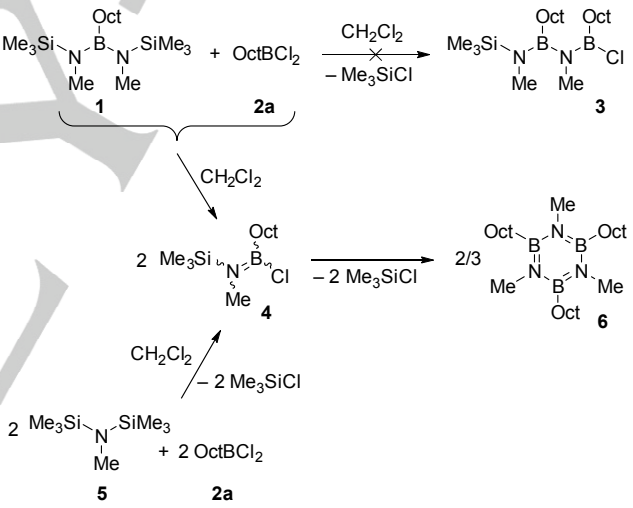
The parent unsaturated B=N polymer, poly(iminoborane) (PIB, **VII**), however, has not been synthesized and characterized by means of current state-of-the-art analysis methods so far, although it has been the subject of several theoretical studies.[16] Formally, **VII** is isoelectronic to polyacetylene, however, theory predicts rather insulating properties for this inorganic polymer.[16b] In several papers, in particular those which discuss the solid-state pyrolysis of ammonia–borane ($NH_3{\cdot}BH_3$, AB), the term "polyiminoborane" or the formula $[BHNH]_n$ appears,[17] though it is not always clear if a linear polymer is meant. During the dehydrogenation process of AB an insoluble solid is formed as an intermediate that has the approximate composition BNH_2. Recent solid-state NMR studies,[18] however, revealed that the constitution of this material should not be described as a linear poly(iminoborane) but rather as a polyborazylene (**VIII**), that is in this case a poorly defined network of partially fused borazine rings.[19,20]

In 1962, Burch, Gerrard, and Mooney reported on the thermolysis of di(alkylamino)phenylboranes, $(RNH)_2BPh$, which gave, depending on the substituent R on nitrogen, either borazine derivatives, $(NRBPh)_3$, a mixture of borazine and non-cyclic products, or the non-cyclic products only.[21] The interpretation of the latter as linear macromolecules was based on IR spectroscopy and viscosimetry. In the 1980s, Paetzold and co-workers reported on the generation of monomeric iminoboranes and subsequent trapping thereof at low temperature.[22,23] In some cases, besides the respective iminoborane trimers (i.e., borazines), insoluble waxy materials were formed and isolated for which the constitution of linear poly(iminoborane)s (**VII**, R = R' = alkyl) was proposed. This assignment was based on elemental analysis and mass spectrometry data and on the observation that one derivative thermally transformed into the corresponding borazine.[22a]

Overall, the intended synthesis of linear poly(iminoborane)s from rational precursors often seems to be hampered by the facile formation of the respective borazines, which are formally inorganic benzene analogues. Recently, we briefly communicated the synthesis and characterization of a well-defined, processable oligo(iminoborane) comprising a linear chain of 12–14 BN units on average.[24] With our synthetic approach, that is, linking the adjacent nitrogen centers of the main chain pairwise via an ethylene bridge, unwanted side reactions that result in the formation of a borazine were effectively prevented. Herein, we report full details of these studies, and we present novel methods for the synthesis of oligo(iminoborane)s, one of which involves previous isolation of a dormant form of the monomer which is activated for polymerization by a Brønsted acid. Furthermore, we prepared a series of new oligo/poly(iminoborane) derivatives, by which it is demonstrated that the physical properties of these materials can be effectively tuned by variation of their side chains. In this study, the highest-molecular-weight derivative to date was isolated, which features about 18 catenated BN units on average.

Results and Discussion

Attempted synthesis of a fully linear poly(iminoborane). In an attempt to prepare an essentially linear poly(iminoborane) we performed the reaction of diaminoborane **1** with dichloro-*n*-octylborane (**2a**) (Scheme 1). Based on our previous experience with *N*-silylamines combined with chloro- or bromoboranes,[5j,13e,14,15] we anticipated that **1** and **2a** should undergo spontaneous Si/B exchange in solution with elimination of Me_3SiCl and formation of a new B–N bond to give the linear diborazene **3** in the first step. As this species comprises a linear chain of four alternating B and N atoms, unwanted follow-up reactions to yield small cyclic species should be less likely. In particular, the formation of the six-membered ring compound borazine **6** should be impossible – as long as redistribution processes are absent.[25] We anticipated that **3** should then further oligomerize in a linear fashion to afford the desired poly(iminoborane). The *n*-octyl groups (herein denoted as Oct) at boron were chosen in order to impart good solubility to the product in organic solvents. However, when we mixed **1** with **2a** in CH_2Cl_2, instead of the expected condensation, a ligand exchange reaction occurred.[26]



Scheme 1. Reaction between diaminoborane **1** and dichloro-*n*-octylborane (**2a**) with formation of **4** and subsequent cyclotrimerization of the latter to give **6** (Oct = *n*-C_8H_{17}), and independent synthesis of **4**.

The formation of the aminoborane[27] **4** as a mixture of two diastereomers that differ from one another by the relative configuration at the partial B=N double bond (i.e., *E/Z* isomers) was evidenced by ^1H and ^{11}B NMR spectroscopy from the reaction solution. The $^{11}B\{^1H\}$ NMR spectrum showed a signal at δ_B = 43.8 ppm which is reasonably assigned to **4**. For comparison, the related aminoborane derivative Cl(*t*Bu)B=N(*i*Pr)$SiMe_3$ resonates at δ_B = 44.7 ppm.[28] The ^1H NMR spectrum displayed two sets of resonances for the *N*–CH_3 and the *N*–$Si(CH_3)_3$ protons corresponding to the *E/Z* isomers of **4**. To further unequivocally confirm the formation of **4** in this reaction, we prepared it by an independent synthesis via the condensation of **2a** with heptamethyldisilazane (**5**)

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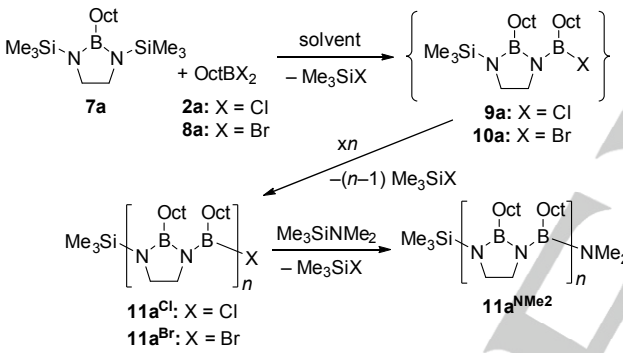
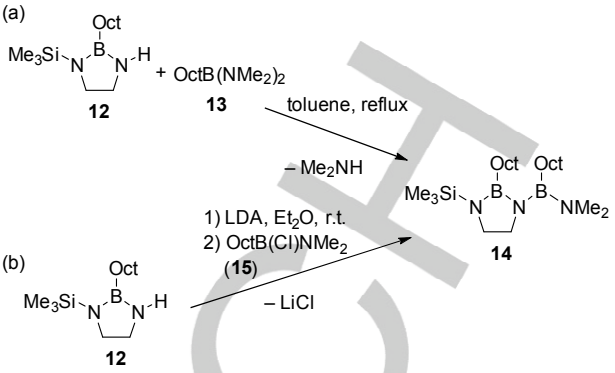
(Scheme 1). This gave identical NMR data. Subsequently, **4** underwent further spontaneous condensation with cyclotrimerization to quantitatively yield the borazine **6**[29] within 16 h at room temperature.

Polycondensation of cyclolinear building blocks via Si/B exchange. As the approach described above was not effective in preventing the formation of the borazine **6**, we chose a different strategy to achieve linear BN catenation: We introduced a short hydrocarbon bridge, that is, an ethylene group, between the nitrogen atoms of the monomer, i.e. **7a** (Scheme 2). Upon polycondensation with **2a** or **8a**, the ethylene bridges would pairwise link the adjacent N centers of the chain in the targeted cyclolinear product **11a**. This should preclude the formation of a borazine, or small BRNR cycles in general, for steric reasons. At the same time, redistribution processes that might occur in the first step of the synthesis should be unfavored as a result of the chelate effect. Related approaches have been followed previously by Neilson et al., but, to the best of our knowledge, the identification of a poly- or an extended oligo(iminoborane) has not been achieved in their studies.[30]



Scheme 2. Polycondensation of 1,3-bis(trimethylsilyl)-2-*n*-octyl-1,3,2-diazaborolidine (**7a**) and dichloro- (**2a**) or dibromo-*n*-octylborane (**8a**) by Si/B exchange and subsequent end-capping (Oct = *n*-C_8H_{17}).

We successfully synthesized the oligo(iminoborane) **11a** using our Si/B exchange polycondensation approach (Scheme 2).[24] Additionally, we prepared compound **14** as a molecular model system for **11a** (i. e., **14** is equivalent to **11a^{NMe2}** with n = 1). In our previous communication we presented the synthesis of **14** by transamination between **12** and **13** (Scheme 3a).[24] We now found that **14** can be obtained more conveniently by deprotonation of **12** with LDA, followed by salt elimination with chlorodimethylamino-*n*-octylborane (**15**) (Scheme 3b). The latter is easily accessed via ligand redistribution between **2a** and **13**.



Scheme 3. Synthesis of model compound **14**.

The reaction of 1,3-bis(trimethylsilyl)-1,3,2-diazaborolidine[31] **7a** with either dichloro- (**2a**) or dibromo-*n*-octylborane (**8a**) was performed in different chlorinated non-donor solvents (CH_2Cl_2, CD_2Cl_2, and $CDCl_3$) and at various temperatures (Scheme 2 and Table 1). In a typical experiment (e. g., entry 2 in Table 1), **7a** and **2a** were mixed in dichloromethane at ambient temperature to give a 1 M starting concentration of the reactants. Monitoring of the reaction in CD_2Cl_2 by $^{11}B\{^1H\}$ and ^1H NMR spectroscopy revealed that both **7a** and **2a** were immediately consumed with initial formation of **9a**[24] (see Figure S42 in the Supporting Information). Even after short reaction times, the spectra showed that further oligomerization had occurred. The ^{11}B resonance for the B–Cl end groups of the growing chain (at around 44.5 ppm) continuously decreased in intensity. One broad signal remained in the $^{11}B\{^1H\}$ NMR spectrum for the bulk boron atoms of the oligomer **11a^{Cl}**, which in the course of the reaction was shifted slightly upfield to δ = 31 ppm. In the ^1H NMR spectrum, a common signal appeared for the protons of the ethylene bridge, centered at δ = 3.32 ppm. Small peaks at δ = 3.00–3.25 and 3.45–3.65 ppm remained which we assign to the ethylene protons of the rings at the chain ends. The proton resonance for the $SiMe_3$ end group was detected at δ = 0.15 ppm, that is, at identical chemical shift as that of the $SiMe_3$ group of **14**. Concomitant formation of the volatile condensation by-product Me_3SiCl was evidenced by its ^1H resonance at δ = 0.45 ppm. Quantitative evaluation of the signals over time revealed that conversion of the reactive groups leveled off at about 85 %. This may be associated with a rate reduction due to a marked increase in the viscosity of the solution. Estimation of the degree of polymerization after 14 days by using Carothers' equation yielded $DP_n \approx 7$. Then, Me_3SiNMe_2 (6 mol%) was added to deactivate the B–Cl end groups of **11a^{Cl}**. The end-capped product **11a^{NMe2}** was purified by adding the mixture to an excess amount of anhydrous acetonitrile, which resulted in separation of **11a^{NMe2}** from solution. This afforded oligo(iminoborane) **11a^{NMe2}** as a highly viscous amber fluid in 83 % yield.[24]

Similarly, reactions of **7a** with the dibromoborane **8a** gave **11a^{Br}** via **10a**, besides Me_3SiBr as the condensation by-product, as evidenced by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy. Subsequent end-capping with Me_3SiNMe_2 furnished **11a^{NMe2}** as well. Irrespective of the reaction time (cf. entries 1 and 2 in Table 1), temperature, solvent, and the use of **2a** vs. **8a**, gel permeation chromatography

(GPC) analysis of the products revealed comparable molecular weight distributions with M_n = 1.51 – 1.81 kDa and M_W = 1.56 – 2.05 kDa (Figure 2a). This corresponds to chain lengths of about DP_n = 5 – 6 repeat units on average.

Table 1. GPC results for **11a/11a'** prepared under various reaction conditions and GPC results for **11ac** and **11d**.

Entry	Co-monomers	Solvent	*T*/ °C	Reac-tion time	M_n/ kDa	M_W/ kDa	DP_n
1	**7a, 2a**	CH_2Cl_2	20	14 d	1.72	2.03	6
2	**7a, 2a**	CH_2Cl_2	20	24 h	1.78	1.94	6
3	**7a, 8a**	CH_2Cl_2	20	24 h	1.54	1.62	5
4	**7a, 2a**	CH_2Cl_2	40	24 h	1.51	1.56	5
5	**7a, 8a**	CH_2Cl_2	40	24 h	1.57	1.61	5
6	**7a, 2a**	$CDCl_3$	61	24 h	1.51	1.78	5
7	**7a, 8a**	$CDCl_3$	61	24 h	1.81	2.05	6
8	**16, 8a**	CH_2Cl_2	20	24 h	1.77	2.00	6
9	**14**, HCl	CH_2Cl_2/ Et_2O	20	24 h	1.75	2.10	6
10	**14**, HOTf	$CDCl_3$	20	96 h	2.24	2.86	7
11[a]	**14**, $HNTf_2$	CD_2Cl_2	20	24 h	1.91	2.33	6
12[b]	**7b, 2b**	CH_2Cl_2	20	96 h	2.43	2.48	13
13	**7a, 2c**	CH_2Cl_2	20	24 h	2.50	3.77	9
14[a]	**7d, 2d**	CH_2Cl_2	20	24 h	2.16	2.81	6

[a] In this case, the GPC results from the product **11d^{Cl}** before end-capping are given because some degradation had occurred during the end-capping process (see the Supporting Information). [b] The GPC revealed a multimodal distribution; the data given corresponds to the higher molecular-weight fraction.

The oligo(iminoborane) **11a^{NMe2}** was further analyzed by multinuclear NMR spectroscopy (including ^{1}H DOSY), UV–vis spectroscopy, elemental analysis, dynamic light scattering (DLS, Figure 3a), small-angle X-ray scattering (SAXS), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The NMR data of **11a^{NMe2}** are consistent with those of its precursor **11a^{Cl}** described beforehand. The ^{1}H resonance of the NMe_2 end group of **11a^{NMe2}** was detected at δ = 2.68 ppm, i. e., the chemical shift being virtually identical to that of the NMe_2 group in the model compound **14**. A detailed discussion of the analytical data for **11a^{NMe2}** has been provided in our previous communication.[24] It is noteworthy that **11a^{NMe2}** exhibits a very low glass transition temperature, T_g = −71 °C. The results from the TGA confirm the stabilizing effect of the ethylene bridge in **11a^{NMe2}** (Figure 3c). Mass loss occurred in basically two steps. In a narrow temperature range at about 350 °C, 72.9 % of the initial mass was lost, which matches well with the fraction of the *n*-octyl groups. In the second, broader step starting from 450 °C, the sample lost further 9.0 % of its mass, corresponding to an expulsion of the ethylene bridges. The overall mass loss at 1000 °C amounts to 81.9 %. The remaining 18.1 % correspond well to the fraction of BN in **11a^{NMe2}** being 16.3 %.

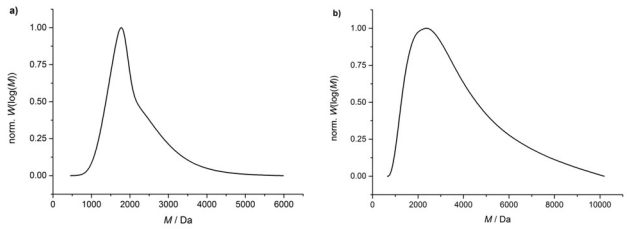
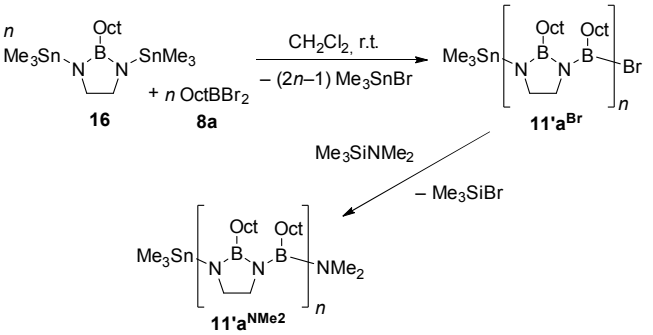


Figure 2. GPC trace of **11a^{NMe2}** (in THF, versus polystyrene standards) obtained by (a) Si/B exchange polycondensation of **7a** and **2a** in CH_2Cl_2 at 20 °C and (b) by activation of **14** with 2 equiv. of HOTf.

Polycondensation by Sn/B exchange. We also explored tin/boron exchange as an alternative polymerization strategy. For the synthesis of organoborane polymers featuring B–C linkages along the backbone, Sn/B exchange polycondensation, which in that case proceeds via B–C coupling, is a well-established method.[6b] Different from polymerization by Si/B exchange at carbon,[6s] this type of reaction usually does not require a catalyst to proceed. In our reaction, 1,3-bis(trimethylstannyl)-1,3,2-diazaborolidine **16** and dibromoborane **8a**, as expected, underwent smooth polycondensation at ambient temperature to give **11'a^{Br}** with concomitant release of Me_3SnBr (Scheme 4). The proton resonance of the Me_3Sn end group was detected at δ = 0.29 ppm. The reactive *B*–Br end group was deactivated by subsequent reaction with Me_3SiNMe_2 to give **11'a^{NMe2}**. The GPC analysis revealed a molecular weight distribution for **11'a^{NMe2}** (Table 1, entry 8) comparable to that of **11a^{NMe2}** obtained by the Si/B exchange reactions described in the previous section.



Scheme 4. Polycondensation of **16** with **8a** by Sn/B exchange.

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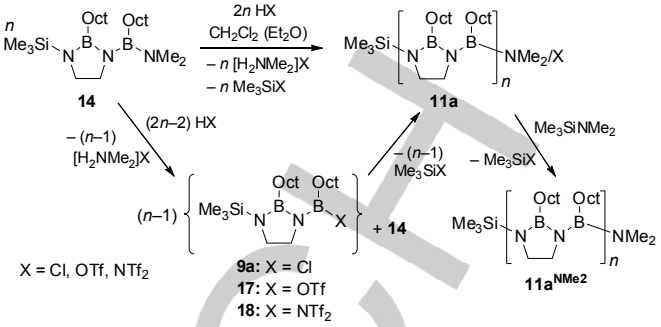
Polycondensation of 14 through initiation with a Brønsted acid. In the polymerizations described so far the true monomer (e.g., **9a**, **10a**) generally had remained elusive. Although **9a** was observed by NMR spectroscopy in the reaction of **7a** with **2a**, some follow-up condensation was already visible at an early stage. Therefore, in our next approach we decided to employ a dormant form of the monomer which is isolable but might be activated under certain conditions to undergo polymerization. We anticipated that compound **14** could serve this purpose. Previous examples have shown that in some cases the amino group of an aminoborane can be substituted by Cl upon reaction with anhydrous HCl.[32] For this, an excess of the acid (ca. 2 equiv.) is usually needed to suppress the reverse reaction by irreversible formation of the corresponding ammonium salt.

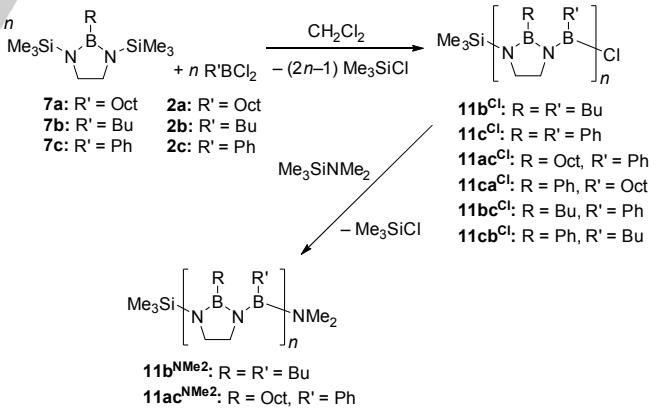
Indeed, when a solution of **14** in CH_2Cl_2 was treated with HCl in Et_2O (2 equiv.), polycondensation occurred to give the oligo(iminoborane) **11a** (Scheme 5). Monitoring of the reaction by $^{11}B\{^1H\}$ NMR spectroscopy clearly showed the formation of B–Cl species. At about δ = 44 ppm a broad signal appeared (see Figure S61 in the Supporting Information) which we assign to the B–Cl group of initially formed **9a**, and in the further course of the reaction, to the end group of **11a^{Cl}**. This signal decreased over time, consistent with elongation of the chains through condensation. Consequently, the formation of **11a** is initiated by replacement of NMe_2 with Cl, thus, generating the reactive monomer **9a**, which undergoes facile subsequent polycondensation. Volatile Me_3SiCl is released, and the salt $[H_2NMe_2]Cl$ formed as the second by-product is easily removed by filtration in the work-up procedure. According to the formal stoichiometry of the reaction (cf. Scheme 5), exactly $2n - 2$ equivalents of HCl are required to afford the NMe_2-end-capped form of **11a**, i.e., **11a^{NMe2}**. However, the result of a ^1H NMR end group analysis did not fully match that of the GPC analysis. It is plausible that some B–Cl end groups had remained (see Figure S63 in the Supporting Information). In order to fully transform these into B–NMe_2 groups, Me_3SiNMe_2 was subsequently added which afforded **11a^{NMe2}**. The integral of the ^1H NMR signal for the $SiMe_3$ end group, on the other hand, was somewhat too low. Hence, we assume that partial desilylation of the substrate had occurred during polymerization in the presence of the acid. Overall, our investigations revealed that the best results are obtained with approximately 2 equiv. of HCl. The use of a greater excess turned out to be unfavorable, probably due to protonation of nitrogen atoms in the chain and chain scission and/or salt formation.

We also performed analogous reactions of **14** with the stronger Brønsted acids HOTf and $HNTf_2$. Here, similar observations were made. The salt by-product, $[H_2NMe_2]OTf$, obtained from the reaction to **17** was unambiguously identified by ^1H and $^{19}F\{^1H\}$ NMR spectroscopy. During the reaction with $HNTf_2$,[33] $^{11}B\{^1H\}$ NMR spectroscopic monitoring evidenced the formation of B–NTf_2 species (i.e., **18** and the respective growing chain) by a signal at about δ = 39–40 ppm (see Figure S82 in the Supporting Information). From each of these reactions the oligo(iminoborane) **11a** was isolated and subjected to GPC analysis (Table 1, entries 9–11). The best result was obtained with 2 equiv. of HOTf in $CDCl_3$. This yielded the highest molecular weight for **11a** of all reactions described so far, i.e., M_n = 2.24 kDa and M_W = 2.86 kDa, corresponding to a number average degree of polymerization of DP_n = 7.



Scheme 5. Polymerization of the dormant monomer **14** initiated by Brønsted acids.

Variation of the side groups. We then aimed at tailoring the properties of oligo/poly(iminoborane)s through variation of the side groups. For the synthesis of the new derivatives we chose the Si/B exchange polycondensation approach using appropriate combinations of a 1,3-bis(trimethylsilyl)-1,3,2-diazaborolidine and a dichloroborane (Scheme 6). Our first target was the derivative **11b** having *n*-butyl side chains attached to the boron centers. The formation of **11b^{Cl}** proceeded just as smoothly as that of **11a^{Cl}**. Subsequently, it was end-capped to give **11b^{NMe2}**. Its identity was unambiguously ascertained by multinuclear NMR spectroscopy. Analysis of **11b^{NMe2}** by GPC yielded a multimodal distribution, which is presumably due to some decomposition during the measurement. The higher molecular-weight fraction showed weight averages of M_n = 2.43 kDa and M_W = 2.48 kDa, suggesting a degree of polymerization of DP_n = 13. Analysis of **11b^{NMe2}** by DLS yielded a hydrodynamic radius of R_h = 2.0 nm for **11b** in *n*-pentane (Figure 3b), which is well comparable to that of **11a** (R_h = 2.2 nm, Figure 3a).



Scheme 6. Polycondensation of 1,3-bis(trimethylsilyl)borolidines (**7**) and dichloroboranes (**2**) by Si/B exchange and subsequent end-capping of the soluble derivatives.

The appearance of **11b** was that of a sticky fluid with a markedly higher viscosity compared to **11a**. Despite the shorter side chains,

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11b was readily soluble in THF, CH_2Cl_2, chloroform, and *n*-pentane. Its DSC trace showed a glass transition at T_g = −20.1 °C. The shape of the TGA trace of **11b** (Figure 3d) was similar to that of **11a** (Figure 3c). Likewise, it showed one sharp and one broad step, corresponding to expulsion of the alkyl side groups and the ethylene bridges, respectively. Although the percentages of mass loss for the individual steps, 67.7 and 7.9 %, do not fit as well as in the case of **11a** with the ratio of the two fragments expulsed, the overall mass loss of 75.6 %, leaving 24.4 %, corresponds well to the BN fraction of **11b** being 23.6 %.

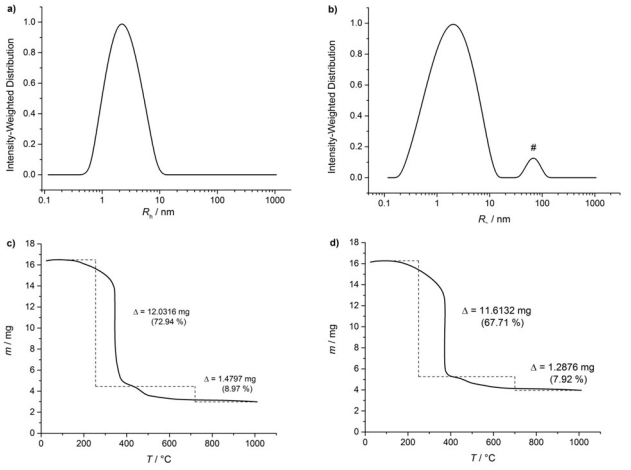

Figure 3. Intensity-weighted size distribution of (a) **11a^{NMe2}** and (b) **11b^{NMe2}** in *n*-pentane by DLS (additional peak # assigned to aggregates of **11b^{NMe2}**), TGA trace of (c) **11a^{NMe2}**, and (d) **11b^{NMe2}**.

Our next target was to incorporate aromatic side groups, which was expected to significantly alter the mechanical and thermal properties of the new materials. We first performed the reaction of the *B*-phenyl substituted co-monomers **7c** and **2c** under Si/B polycondensation conditions. This, however, yielded only insoluble material. Shortly after **7c** and **2c** were mixed in dichloromethane at room temperature, the formation of a precipitate was observed. An ^{1}H NMR spectrum from the overlaying solution showed the formation of Me_3SiCl, thus, confirming that some condensation had occurred. However, nearly the entire boron content of the sample had precipitated, and the colorless solid obtained after filtration did not dissolve in any of the common organic solvents tested. Therefore, we decided in the next step to attempt the synthesis of poly(iminoborane) derivatives with mixed substituents, one of which being phenyl and the other an alkyl chain.

Combinations of a phenyl and an *n*-butyl substituent at the two boron centers, i.e., reactions of **7b** with **2c** and **7c** with **2b** yielded insoluble products, **11bc^{Cl}** and **11cb^{Cl}**, as well. It should be noted though, that precipitation only occurred at a later stage of the polymerization process. From the reaction of dichloro-*n*-octylborane (**2a**) with the *B*-phenyl derivative **7c**, a partially soluble product was obtained. GPC analysis of the dissolved parts showed a rather weak signal corresponding to a mass of approximately 1 kDa while most of the product **11ca** did not dissolve. Finally, interchanging the substituents by performing the reaction between **7a** and **2c**, after end-capping and work-up, yielded the amber colored solid product **11ac^{NMe2}** which was readily soluble in THF, CH_2Cl_2, chloroform, and *n*-pentane. The results from GPC analysis suggested mass averages of M_n = 2.50 kDa and M_W = 3.77 kDa for **11ac^{NMe2}** (Table 1, entry 13, and Figure 4a). This corresponds to chains of on average 9 repeat units or 18 BN units, respectively, which is the longest-chain iminoborane oligomer and the closest approach to a poly(iminoborane) unambiguously characterized by GPC so far.

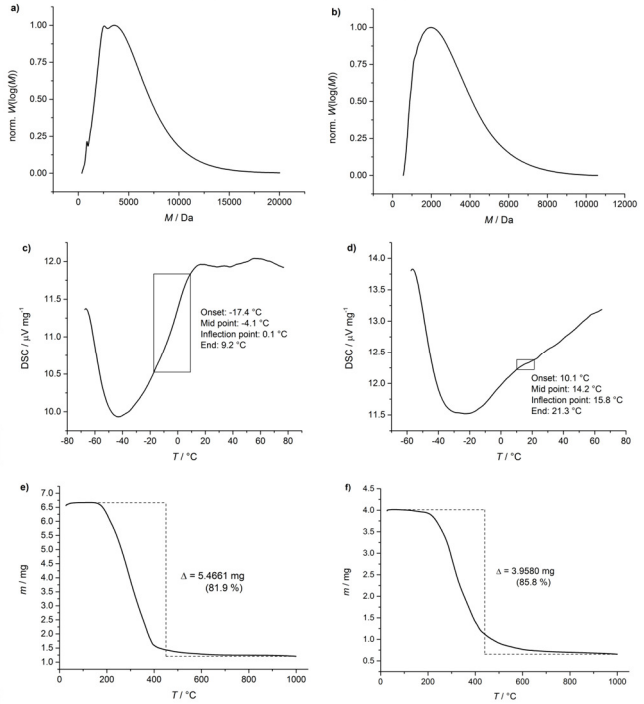

Figure 4. GPC trace of (a) **11ac^{NMe2}** and (b) **11d^{NMe2}** (in THF, versus polystyrene standards), DSC trace of (c) **11ac^{NMe2}** and (d) **11d^{NMe2}**, and TGA trace of (e) **11ac^{NMe2}** and (f) **11d^{NMe2}**.

As the strategy to incorporate both alkyl and phenyl side chains was generally working, we next attempted to combine both features in one substituent. For this, we devised 4-*n*-butylphenyl as the *B*-substituent, with which an aryl group can be attached to each boron center while butyl groups are present to impart solubility, though having minor influence on the steric and electronic situation at the boron centers (Scheme 7). Indeed, the reaction between **7d** and **2d** afforded **11d^{Cl}** as a solid yet readily soluble product. GPC suggested mass averages of M_n = 2.16 kDa and M_W = 2.81 kDa, corresponding to DP_n = 6 (Table 1, entry 14, and Figure 4b). After deactivation of the end groups with Me_3SiNMe_2, the molecular weight of the resulting **11d^{NMe2}** was somewhat decreased (M_n = 1.73 kDa and M_W = 2.29 kDa), presumably due to slight degradation during the end-capping process.

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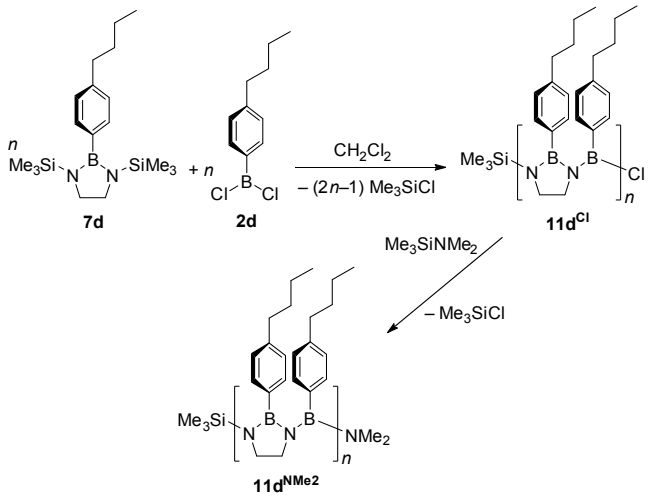

Scheme 7. Polycondensation of 1,3-bis(trimethylsilyl)borolidine **7d** and dichloroborane **2d** by Si/B exchange and subsequent end-capping.

bonded phenyl groups in **11c^{NMe2}** are twisted with respect to the respective BR_3 planes by 39.2° on average (in the tetramer). The adjacent phenyl rings along the chain are close to parallel oriented with interplanar angles of on average 35.7°. The mean distance between the *ipso*-carbon atoms is 3.146 Å.

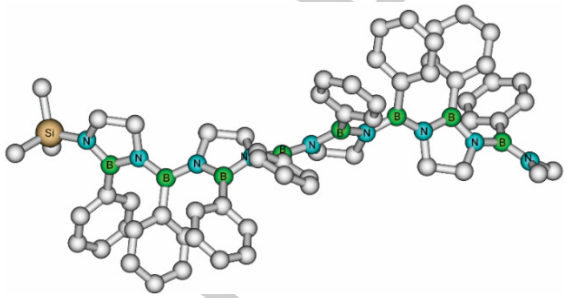

Figure 5. Optimized structure of **11c^{NMe2}** (n = 4, H-atoms omitted for clarity; B3LYP-D3(BJ)/def2-SV(P)).

The new oligo(iminoborane) derivatives **11ac^{NMe2}** and **11d^{NMe2}** were further characterized by multinuclear NMR spectroscopy (including ^{1}H DOSY), UV–vis spectroscopy, DLS, DSC, and TGA. Dynamic light scattering revealed hydrodynamic radii of R_h = 2.2 (**11ac^{NMe2}**) and 1.5 nm (**11d^{NMe2}**) in CH_2Cl_2, respectively. Differential scanning calorimetry revealed glass transitions at 0.1 °C (**11ac^{NMe2}**) and 15.8 °C (**11d^{NMe2}**) (Figure 3c,d). This trend confirms the expected increase in the crystallinity of the product with increasing ratio of phenyl groups attached to boron. Both derivatives **11ac^{NMe2}** and **11d^{NMe2}** readily dissolve in most of the common organic solvents. However, it is noteworthy that for **11d^{NMe2}** *n*-pentane is a notably poorer solvent. In the TGA traces of **11ac^{NMe2}** and **11d^{NMe2}** the two stages of mass loss are not resolved (Figure 3e,f). Both compounds show major mass loss in a broad temperature range starting at about 150 °C. Up to 1000 °C, **11ac^{NMe2}** lost 81.9 % of its weight. The residual mass amounts to 18.1 %, which fits to the theoretical fraction of boron and nitrogen being 17.9 %. The residual 14.2 % of **11d^{NMe2}** at 1000 °C fit likewise well to the theoretical fraction of BN in **11d^{NMe2}** being 14.0 %.

Computational studies. In order to gain insight into structural features of the new compounds, we carried out geometry optimizations on DFT niveau including dispersion correction (B3LYP-D3(BJ)/def2-SV(P)).[34-38] In our preliminary communication[24] we reported calculations on oligomers of the *B*-methyl substituted derivative **11e^{NMe2}**, which serves as a truncated model system for **11a,b^{NMe2}** and **11a,b^{NMe2}**. We now additionally calculated the *B*-phenyl derivative **11c^{NMe2}** with chain lengths of *n* = 1 to 4 repeat units (Figure 5). The backbone structure of **11c^{NMe2}** is very similar to that of **11e^{NMe2}**. The boron and the nitrogen centers are trigonal-planar coordinated, and in **11c^{NMe2}** the mean angle sums amount to 360.0° (at B) and 359.8° (at N), respectively. The N-B-N and the B-N-B planes are not fully coplanar but have an average torsion angle of 20.2° (in the tetramer; in **11e^{NMe2}**, 19.5°). For both derivatives this causes a helical structure with a periodicity of about 5 structural units as the most stable conformation. The *B*-

Conclusions

This study has demonstrated that skeletal backbone stabilization is an effective approach to prevent the unwanted formation of small cyclic (by)products such as borazines in the targeted synthesis of poly(iminoborane)s. While an attempt to use acyclic comonomers **1** and **2a** in a Si/B exchange reaction did not afford linear BN catenation, but exclusive formation of borazine **6** instead, the use of 1,3-bis(trimethylsilyl)-1,3,2-diazaborolidines **7** together with **2** or **8** cleanly yielded the oligo(iminoborane)s **11a,b,ac,d**. Furthermore, two alternative synthetic routes to such species were disclosed in this study: Sn/B exchange of **13** and **8a**, and initiated polycondensation of the dormant monomer **14** in the presence of a Brønsted acid (HCl, HOTf, or $HNTf_2$). The latter method utilizes *in situ* transformation of dormant B–NMe_2 groups into active B–X groups (X = Cl, OTf, or NTf_2), which are then prone to undergo facile condensation with the N–$SiMe_3$ termini.

Effective stabilization of the backbone in the obtained oligo(iminoborane)s through the ethylene bridges was further supported by our TGA studies. With the synthesis of **11ac** and **11d** we achieved the incorporation of aromatic side groups, and DSC measurements showed that the glass transition temperatures systematically increase with the aryl group content (in the order, **11a** < **11b** < **11ac** < **11d**). Derivative **11ac**, with about 18 catenated BN units on average, is the closest approach to a poly(iminoborane) to date. Currently, we are exploring further synthetic routes that eventually should lead to high-molecular-weight poly(iminoborane)s, and we are probing the potential of these new materials for applications in materials science.

Experimental Section

General procedures. All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glovebox. Solvents (dichloromethane, *n*-pentane, and diethylether) were

dried and degassed by means of an MBraun SPS-800 solvent purification system. $CDCl_3$ and CD_2Cl_2 for NMR spectroscopy were dried and degassed at reflux over CaH_2 and freshly distilled prior to use. Boron trichloride solution (1 M in hexanes), *n*-butyllithium solution (2.5 M in hexanes), boron trichloride, 1-butene, bromobenzene, 1-bromo-4-iodobenzene, 1-bromobutane, chlorotrimethylstannane, HCl solution (2 M in diethyl ether), heptamethyldisilazane (**5**), and trifluoromethanesulfonic acid were commercially purchased and used as received. Dimethylammonium chloride, methylammonium chloride, and potassium hydroxide were dried *in vacuo* prior to use. Dimethylamine and methylamine were generated from their ammonium chlorides with potassium hydroxide and recondensed prior to use. 1-Octene, triethylamine and ethylenediamine were dried and degassed at reflux over Na and freshly distilled prior to use. Pentamethylsilazane was dried and degassed by inert-gas distillation from CaH_2. Trimethylsilyl chloride, trimethylsilane, and triethylsilane were purified by inert-gas distillation. Dichloro-*n*-octylborane (**2a**),[39] *n*-butyldichloroborane (**2b**)[40] and dibromo-*n*-octylborane (**8a**)[41] were prepared according to methods described in the literature for boranes with other alkyl substituents.[42] 1-bromo-4-trimethylsilylbenzene,[43] dichlorophenylborane (**2c**),[44] lithium diisopropylamide,[45] bistriflamidic acid,[46] and trimethylsilylbenzene[47] were prepared according to procedures described in the literature. NMR spectra were recorded at 25 °C on a Bruker Avance II-400 spectrometer or on a Bruker Avance III HD spectrometer operating at 400 MHz. Chemical shifts were referenced to residual protic impurities in the solvent (^{1}H) or the deuterio solvent itself (^{13}C) and reported relative to external $SiMe_4$ (^{1}H, ^{13}C, ^{29}Si), $BF_3{\cdot}OEt_2$ (^{11}B), or $CFCl_3$ (^{19}F) standards. Mass spectra were obtained with the use of a Finnigan MAT95 spectrometer employing electron ionization (EI) using a 70 eV electron impact ionization source. UV/vis-spectra were obtained using a Jasco V-630 spectrophotometer. DSC measurements were performed on a Netzsch DSC 204 F1 phoenix device with a heating/cooling rate of 10 K min^{-1}. TGA measurements were performed on a Mettler-Toledo TGA/SDTA 851e device at a heating rate of 5 K min^{-1} under N_2. GPC chromatograms were recorded on an Agilent 1100 Series, using a flow rate of 1 mL min^{-1} in THF at 25 °C, calibrated against polystyrene standards. Dynamic light scattering (DLS) measurements were performed in CH_2Cl_2 (c = 2.5 g L^{-1}) at 20 °C with an ALV 5000 E autocorrelator equipped with a red laser (λ = 633 nm). The time-resolved signal of two Single Photon Counting Modules (SPCM-CD 2969; Perkin Elmer) was cross-correlated. Hereby, the CONTIN analysis was performed in an angular dependent way. For each measurement (sampling time 90 s), the intensity-weighted decay-time τ distributions (as obtained from the field autocorrelation function obtained by use of the Siegert relation)[48] were analyzed in respect to multimodality, where for each diffusive mode its (intensity-) average decay rate Γ ($1/\tau$) was extracted (if necessary, the probability factor of the CONTIN algorithm was adjusted in order to increase resolution). Then, the decay rates were plotted against the squared length of the scattering vector q^2. The slope gave the diffusion coefficient D and its value was transformed to the hydrodynamic radius R_h by the Stokes-Einstein equation.

Synthesis of lithium trimethylsilyl(methyl)amide. $MeNH_2$ (26.2 g, 0.844 mol) was recondensed onto a frozen ($N_{2(l)}$ cooled) solution of chlorotrimethylsilane (36.67 g, 0.3376 mol) in diethyl ether (340 mL). Subsequently the mixture was allowed to warm to ambient temperature and was stirred overnight. A colorless precipitate formed which was filtered off and washed with *n*-pentane. The volatiles were removed from the filtrate and the residue was distilled (41.47 mmol, 4.28 g, 12 %). The product was dissolved in diethyl ether (40 mL) and a solution of *n*-BuLi (2.5 M, 16.2 mL, 40.5 mmol) in hexanes was added dropwise at −78 °C. After 1 h, the solution was warmed to ambient temperature and it was stirred for 2 h. The volatiles were removed *in vacuo*. The product was received quantitatively as a colorless solid and was used without further purification for the next step.

Synthesis of bis(trimethylsilyl(methyl)amino)-*n*-octylborane (1). To a solution of lithium trimethylsilyl(methyl)amide (2.17 g, 19.9 mmol) in diethyl ether (10 mL) dichloro-*n*-octylborane (1.94 g, 9.96 mmol) was added dropwise at −78 °C. It was stirred for 1.5 h, warmed to ambient temperature, and stirred for another 2 h. The volatiles were removed *in vacuo* and *n*-pentane (30 mL) was added to the residue. It was filtered off and washed with *n*-pentane. Distillation at 15 mbar and 112 °C yielded a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.57 (s, 6 H, NCH_3), 1.28 (m, 12 H), 0.90 (t, 3 H), 0.79 (t, 2 H, BCH_2), 0.13 (s, 18 H, $Si(CH_3)_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 42.2 (s) ppm.

Attempted synthesis of the diborazene 3 and successive formation of chloro(trimethylsilyl(methyl)amino)-*n*-octylborane (4) and *N,N',N''*-trimethyl-*B,B',B''*-tri-*n*-octylborazine (6).[49] To a solution of bis(trimethylsilyl(methyl)amino)-*n*-octylborane (0.3409 g, 1.0378 mmol) in $CDCl_3$ (1 mL) dichloro-*n*-octylborane (0.2007 g, 1.0295 mmol) was added. After 45 min it was evidenced by ^{1}H NMR that the aminoborane **4** had formed quantitatively as two isomers. Isomer 1: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84 (s, 3 H, NCH_3), 1.46 (br, 2 H, BCH_2), 1.28 (m, 12 H), 0.89 (t, 3 H), 0.26 (s, 9 H, $Si(CH_3)_3$) ppm; Isomer 2: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.75 (s, 3 H, NCH_3), 1.46 (br, 2 H, BCH_2), 1.28 (m, 12 H), 0.89 (t, 3 H), 0.28 (s, 9 H, $Si(CH_3)_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 43.8 (s) ppm. Additionally, the formation of some borazine **6** was evidenced.

After 16 h it was confirmed that the borazine **6**[49] had formed quantitatively: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.94 (s, 3 H, NCH_3), 1.46–1.20 (m, 12 H), 1.03 (br, 2 H, BCH_2), 0.89 (t, 3 H) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 36.8 (s) ppm.

Alternative synthesis of 4 and formation of 6. To a solution of dichloro-*n*-octylborane (0.551 g, 2.83 mmol) in CH_2Cl_2 (2 mL) was added slowly and dropwise heptamethyldisilazane (**5**) (0.489 g, 2.78 mmol) at −78 °C. After 10 min, the cooling bath was removed. ^{1}H and ^{11}B {^{1}H} NMR of the solution immediately after the start of the reaction confirmed the formation of aminoborane **4**. After 1 d, the NMR spectra revealed the formation of the borazine **6**.

Synthesis of chlorodimethylamino-*n*-octylborane (15). To dichloro-*n*-octylborane (5.848 g, 30.00 mmol) bis(dimethylamino)-*n*-octylborane (6.366 g, 30.00 mmol) was added and the mixture was stirred for 30 min. Distillation at 25 mbar and 115 °C afforded the product quantitatively. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 3 H, N–CH_3), 2.82 (s, 3 H, N–CH_3), 1.44 (t, 2 H, CH_2), 1.29 (m, 10 H, alkyl), 1.04 (t, 2 H, CH_2), 0.89 (t, 3 H, CH_3); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 39.1 (s) ppm.

Synthesis of 3-(dimethylamino-*n*-octylboryl)-2-*n*-octyl-1-trimethylsilyl-1,3,2-diazaborolidine (14).[24] To a solution of 2-*n*-octyl-1-trimethylsilyl-1,3,2-diazaborolidine (**12**)[24] (0.1429 g, 0.5619 mmol) in toluene (0.7 mL) was added bis(dimethylamino)-*n*-octylborane (0.1509 g, 0.7112 mmol). The mixture was heated at reflux for 5 d. The volatile compounds were removed *in vacuo* yielding crude **14** as a yellowish viscous liquid which was evaporated at 160 °C and $4 \cdot 10^{-2}$ mbar and recondensed at −196 °C to give **14** as a colorless liquid (yield 15 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26–3.13 (m, 4 H, N–C_2H_4–N), 2.68 (br, 6 H, $N(CH_3)_2$), 1.28 (m, 24 H, CH_2), 0.89 (t, 6 H, CH_3), 0.82 (t, 2 H, B–CH_2), 0.72 (t, 2 H, B–CH_2), 0.15 (s, 9 H, $Si(CH_3)_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 37.1 (s) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 49.3 (s, B–N–CH_2–CH_2–N–Si), 47.7 (s, B–N–CH_2–CH_2–N–Si), 39.3 (br, $N(CH_3)_2$), 33.4 (s, CH_2), 33.2 (s, CH_2), 32.0 (s, CH_2), 29.7 (s, CH_2), 29.6 (s, CH_2), 29.4 (s, CH_2), 29.4 (s, CH_2), 26.6 (s, CH_2), 25.6 (s, CH_2), 22.7 (s, CH_2), 16.2 (br, B–CH_2), 14.9 (br, B–CH_2), 14.1 (s, CH_3), 0.8 (s, $Si(CH_3)_3$) ppm; ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$): δ = 3.3 (s) ppm; MS (EI, 70 eV): *m/z* (%) = 421.5 ([M^+], 9), 308.4 ([$M^+-C_8H_{17}$], 100), 239.4 ([$M^+-C_{11}H_{25}BN$], 53), 73.2 ([$C_3H_9Si^+$], 16);

HRMS: found *m/z* = 421.4195, theo. mass for $^{12}C_{23}{}^{1}H_{53}{}^{14}N_3{}^{11}B_2{}^{28}Si$ = 421.4189; UV/vis (THF): λ_{max} = 248 nm ($\varepsilon = 1.3 \cdot 10^3$ L cm^{-1} mol^{-1}).

Alternative synthesis of 14. To a solution of 2-*n*-octyl-1-trimethylsilyl-1,3,2-diazaborolidine (0,5086 g, 2.000 mmol) in diethyl ether (2 mL) was added a solution of lithium diisopropylamide (0.2678 g, 2.500 mmol) in diethyl ether (2 mL). The mixture was stirred for 30 min and chlorodimethylamino-*n*-octylborane (0.5293 g, 2.600 mmol) was added. After 30 min, the volatiles were removed *in vacuo* and *n*-pentane (4 mL) was added to the residue. It was filtered off and the volatiles and by-products were removed at $5 \cdot 10^{-2}$ mbar and 70 °C yielding the product **14** as a yellowish liquid quantitatively.

Synthesis of 1,3-bis(trimethylstannyl)-2-*n*-octyl-1,3,2-diazaborolidine (16). To a solution of 2-*n*-octyl-1,3,2-diazaborolidine (0.9275 g, 5.093 mmol) in diethyl ether (15 mL) at −78 °C a solution of lithium diisopropylamide (1.1875 g, 11.098 mmol) in diethyl ether (8 mL) was added. After 1.5 h, the clear solution was warmed to ambient temperature. A solution of chlorotrimethylstannane (2.31 g, 11.6 mmol) in diethyl ether (9 mL) was added and the mixture was stirred overnight. The volatiles were removed *in vacuo* and *n*-pentane (30 mL) was subsequently added. It was filtered off and washed with *n*-pentane (2 x 10 mL). The volatiles of the filtrate were removed *in vacuo* and the product used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.32 (s, 4 H, N–C_2H_4–N), 1.27 (m, 12 H), 0.89 (t, 3 H), 0.57 (t, 2 H, BCH_2), 0.26 (s, 18 H, $Sn(CH_3)_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 38.4 (s) ppm.

Synthesis of *n*-butylbis(dimethylamino)borane.[50] Trichloroborane (10.76 g, 91.84 mmol) and 1-butene (5.72 g, 102.1 mmol) were condensed into a flask and dissolved in *n*-pentane (100 mL) at −78 °C. Triethylsilane (14.4 mL, 90.2 mmol) was added slowly dropwise. After 1 h, *n*-pentane (100 mL) was added and dimethylamine (24 g, 0.54 mol) was condensed into the solution. The mixture was allowed to reach ambient temperature while stirring overnight. The mixture was filtered off and the precipitate was washed with *n*-pentane (2 x 40 mL). Removal of the volatiles and distillation at 15 mbar and 63 °C yielded the product as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (s, 12 H, $N(CH_3)_2$), 1.37–1.21 (m, 4 H), 0.91 (t, 3 H), 0.75 (t, 2 H, BCH_2) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 34.1 (s) ppm.

Synthesis of 2-*n*-butyl-1,3,2-diazaborolidine.[51] To a solution of *n*-butylbis(dimethylamino)borane (9.24 g, 60.2 mmol) in toluene (60 mL) at 0 °C ethylenediamine (4.4 mL, 66 mmol) was added slowly and dropwise. The mixture was allowed to reach ambient temperature while stirring overnight. Removal of the volatiles *in vacuo* yielded a colorless oil in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.30 (s, 4 H, N–C_2H_4–N), 2.60 (br, 2 H), 1.24–1.35 (m, 4 H), 0.87 (t, 3 H), 0.70 (s, 2 H) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ = 35.7 (s) ppm.

Synthesis of 2-*n*-butyl-1,3-bis(trimethylsilyl)-1,3,2-diazaborolidine (7b). To a solution of 2-*n*-butyl-1,3,2-diazaborolidine (7.53 g, 60.0 mmol) in *n*-pentane (110 mL) and diethyl ether (55 mL) at −78 °C *n*-BuLi in hexanes (2.5 M, 55.2 mL, 138 mmol) was added dropwise. The mixture was stirred for 2 h at −78 °C and another 1 h at ambient temperature. It was cooled to −78 °C again and chlorotrimethylsilane (18.1 mL, 138 mmol) was added. The mixture was allowed to reach ambient temperature while stirring overnight. The volatiles were removed *in vacuo* and *n*-pentane (50 mL) was added to the residue. It was filtered off and the volatiles removed *in vacuo*. Distillation at 0.1 mbar and 60 °C yielded **7b** as a colorless oil (12.97 g, 48.0 mmol, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.21 (s, 4 H, N–C_2H_4–N), 1.24–1.38 (m, 4 H), 0.90 (t, 3 H), 0.70–0.77 (m, 2 H), 0.13 (s, 18 H) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ = 37.7 ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 47.8 (s, N–C_2H_4–N), 28.8 (s, butyl-C2), 26.4 (s, butyl-C3), 13.9 (s, butyl-C4), 13.8 (br, butyl-C1), 0.6 (s, $Si(CH_3)_3$) ppm; ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$): δ = 3.3 (s) ppm; MS (EI, 70 eV): m/z (%) = 270.4 ([M^+], 27), 255.4 ([$M^+ - CH_3$], 57), 213.3 ([$M^+ - C_4H_9$], 100), 199.3 ([$M^+ - C_5H_{10}$], 26), 155.3 ([$M^+ - C_6H_{15}Si$], 16), 73.3 ([$C_3H_9Si^+$], 92).

Synthesis of bis(dimethylamino)phenylborane.[52] Dimethylamine (ca. 175 mmol) was slowly recondensed into a solution of dichloro(phenyl)borane (4.6 g, 29 mmol) in *n*-pentane (60 mL) at −78 °C. The mixture was allowed to reach ambient temperature while stirring overnight. The precipitate was filtered off and washed with *n*-pentane (3 x 10 mL). Removal of the volatiles *in vacuo* yielded the product quantitatively as a colorless oil which was used without further purification for the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.28 (m, 5 H), 2.71 (s, 12 H, $N(CH_3)_2$) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 32.6 (s) ppm.

Synthesis of 2-phenyl-1,3,2-diazaborolidine.[53] To a solution of bis(dimethylamino)phenylborane (5.1 g, 29 mmol) in toluene (15 mL) at −78 °C ethylenediamine (2.3 mL, 35 mmol) was added slowly and dropwise. The mixture was allowed to reach ambient temperature while stirring overnight. Removal of the volatiles *in vacuo* yielded a colorless solid. It was stirred in *n*-pentane for 30 min and filtered off. The solid was dried *in vacuo*. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.53–7.47 (m, 2 H), 7.29–7.24 (d, 3 H), 3.15 (s, 4 H, N–C_2H_4–N), 2.55 (br, 2 H, NH) ppm; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ = 32.8 (s) ppm.

Synthesis of 1,3-bis(trimethylsilyl)-2-phenyl-1,3,2-diazaborolidine (7c). To a suspension of 2-phenyl-1,3,2-diazaborolidine (1.46 g, 10.0 mmol) in THF (100 mL) at 0 °C *n*-BuLi in hexanes (8.2 mL, 2.5 M, 20.5 mmol) was added. After 2 h the mixture had reached ambient temperature and chlorotrimethylsilane (2.7 mL, 21 mmol) was added while the mixture became clear. The solution was stirred overnight and the volatiles were removed *in vacuo*. *n*-Pentane (20 mL) was added to the residue and the mixture was filtered off and washed with *n*-pentane (2 x 10 mL). Removal of the volatiles and distillation at $5 \cdot 10^{-2}$ mbar and 90 °C yielded the product as a colorless oil (1.5 g, 5.1 mmol, 51 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.22 (m, 5 H), 3.41 (s, 4 H, N–C_2H_4–N), −0.15 (s, 18 H, $Si(CH_3)_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 36.4 (s) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 132.2 (s, *ortho*-C), 127.2 (s, *para*-C), 127.0 (s, *meta*-C), 48.2 (s, N–C_2H_4–N), 0.3 (s, $Si(CH_3)_3$) ppm; ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$): δ = 4.6 (s) ppm.

Synthesis of 4-*n*-butyl-1-trimethylsilylbenzene.[54] To a solution of 1-bromo-4-trimethylsilylbenzene (11.59 g, 50.61 mmol) in THF (100 mL) held at ambient temperature with a water bath *n*-BuLi in hexanes (24 mL, 2.5 M, 60 mmol) was added dropwise. After 30 min, 1-bromobutane (5.3 mL, 50 mmol) was added and the mixture was stirred overnight. Water (50 mL) and diethylether (100 mL) were added and the phases were separated. The aqueous phase was extracted with diethylether (3 x 20 mL) and the combined organic phases were washed with brine. After drying with $MgSO_4$ and filtration, the solvent was removed with a rotary evaporator. Further drying *in vacuo* yielded the product as a colorless oil (10.12 g, 49.13 mmol, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, 2 H, aryl), 7.19 (d, 2 H, aryl), 2.61 (t, 2 H, butyl-C1), 2.27 (m_c, 2 H, butyl-C2), 1.38 (m_c, 2 H, butyl-C3), 0.94 (t, 3 H, butyl-C4), 0.27 (s, 9 H, $Si(CH_3)_3$) ppm.

Synthesis of 4-*n*-butylphenyldichloroborane (2d). To a solution of BCl_3 (18.24 g, 155.7 mmol) in CH_2Cl_2 (120 mL) at −78 °C 4-*n*-butyl-1-trimethylsilylbenzene (21.593 g, 104.62 mmol) was added dropwise. The solution changed over yellow to a dark orange over time. The mixture was allowed to reach ambient temperature while stirring overnight. Removal of the volatiles and distillation at $7 \cdot 10^{-2}$ mbar and 55 °C yielded the product as a colorless oil in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, 2 H, aryl), 7.30 (d, 2 H, aryl), 2.70 (t, 2 H, butyl-C1), 1.64 (m_c, 2 H, butyl-C2), 1.38 (m_c, 2 H, butyl-C3), 0.95 (t, 3 H, butyl-C4) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 54.9 (s) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ =

151.3 (s, *para*-C), 137.1 (s, *ortho*-C), 131.4 (br, *ipso*-C), 128.4 (s, *meta*-C), 36.0 (s, butyl-C1), 33.1 (s, butyl-C2), 22.3 (s, butyl-C3), 13.9 (s, butyl-C4) ppm.

Synthesis of 4-*n*-butylphenylbis(dimethylamino)borane. Dimethylamine (ca. 360 mmol) was slowly recondensed into a solution of (4-*n*-butylphenyl)dichloroborane (13.0850 g, 62.103 mmol) in *n*-pentane (120 mL) at −78 °C. The mixture was allowed to reach ambient temperature while stirring overnight. The precipitate was filtered off and washed with *n*-pentane (3 x 20 mL). Removal of the volatiles *in vacuo* yielded the product as a colorless oil (13.55 g, 58.37 mmol, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, 2 H, aryl), 7.12 (d, 2 H, aryl), 2.66 (s, 12 H, $N(CH_3)_2$), 2.60 (t, 2 H, butyl-C1), 2.30 (m_c, 2 H, butyl-C2), 1.38 (m_c, 2 H, butyl-C3), 0.94 (t, 3 H, butyl-C4) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 32.8 (s) ppm.

Synthesis of 2-(4-*n*-butylphenyl)-1,3,2-diazaborolidine. To a solution of (4-*n*-butylphenyl)-bis(dimethylamino)borane (13.30 g, 58.37 mmol) in toluene (60 mL) at −78 °C ethylenediamine (4.1 mL, 61 mmol) was added slowly and dropwise. The mixture was allowed to reach ambient temperature while stirring overnight. Removal of the volatiles *in vacuo* yielded a highly viscous liquid. The product was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, 2 H, aryl), 7.19 (d, 2 H, aryl), 3.51 (s, 4 H, N–C_2H_4–N), 3.07 (br, 2 H, NH), 2.64 (t, 2 H, butyl-C1), 1.63 (m_c, 2 H, butyl-C2), 1.39 (m_c, 2 H, butyl-C3), 0.95 (t, 3 H, butyl-C4) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 33.1 (s) ppm.

Synthesis of 2-(4-*n*-butylphenyl)-1,3-bis(trimethylsilyl)-1,3,2-diazaborolidine (7d). To a solution of 2-(4-*n*-butylphenyl)-1,3,2-diazaborolidine (ca. 58 mmol) in CH_2Cl_2 (180 mL) triethylamine (34 mL, 248 mmol) was added. After 20 min chlorotrimethylsilane (17.3 mL, 136 mmol) was added while a large amount of precipitate formed. After 60 h the most part of the precipitate had dissolved. The volatiles were removed *in vacuo* and *n*-pentane (60 mL) was added to the residue. The mixture was filtered off and washed with *n*-pentane (2 x 60 mL). Removal of the volatiles and distillation at 5 · 10^{-2} mbar and 110 °C yielded **7d** in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, 2 H, aryl), 7.06 (d, 2 H, aryl), 4.19 (s, 4 H, N–C_2H_4–N), 2.59 (t, 2 H, butyl-C1), 1.60 (m_c, 2 H, butyl-C2), 1.33 (m_c, 2 H, butyl-C3), 0.92 (t, 3 H, butyl-C4), −0.14 (s, 18 H, $Si(CH_3)_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 36.6 (s) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 144.7 (s, *para*-C), 136.0 (br, *ipso*-C), 132.1 (s, *ortho*-C), 127.1 (s, *meta*-C), 48.1 (s, N–C_2H_4–N), 35.6 (s, butyl-C1), 33.7 (s, butyl-C2), 22.2 (s, butyl-C3), 14.0 (s, butyl-C4), 0.4 (s, $Si(CH_3)_3$) ppm; ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$): δ = 4.5 (s) ppm; MS (EI, 70 eV): m/z (%) = 346.4 ([M^+], 32), 331.4 ([$M^+ - CH_3$], 100), 147.2 ([$M^+ - C_8H_{22}BNSi_2$], 35), 73.3 ([$C_3H_9Si^+$], 24).

Synthesis of 11a^{NMe2}.[24] To a solution of **7a** (326.5 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) a solution of **2a** (194.9 mg, 1.000 mmol) or **8a** (283.8 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) was added at ambient temperature. After 24 h, pentamethylsilazane (ca. 0.2 mmol) was added to deactivate the reactive end groups. After another 30 min, the volatiles were removed *in vacuo*. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66–2.87 (m, 4 H, N–C_2H_4–N), 2.80–2.55 (m, 0.09 H, $N(CH_3)_2$ end group), 1.80–0.60 (m, 34 H, alkyl), 0.19–0.13 (m, 0.10 H, $Si(CH_3)_3$ end group) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 31.1 (br) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 48.8 (s, N–C_2H_4–N), 35.5 (s, $N(CH_3)_2$ end group, from ^{1}H,^{13}C HSQC NMR measurement), 33.7 (s, CH_2), 33.5 (s, CH_2), 32.1 (s, CH_2), 32.0 (s, CH_2), 29.9 (s, CH_2), 29.7 (s, CH_2), 29.6 (s, CH_2), 29.5 (s, CH_2), 27.4 (s, CH_2), 25.9 (s, CH_2), 22.8 (s, CH_2), 22.7 (s, CH_2), 18.7 (br, B–CH_2), 15.9 (br, B–CH_2), 14.1 (s, CH_3), 0.8 (s, $Si(CH_3)_3$ end group) ppm; UV/vis (THF): λ_{max} = 269 nm (ε = 0.86 · 10^5 L cm^{-1} mol^{-1}); DLS (*n*-pentane): R_h = 2.2 nm, D = 4.1 · 10^{-10} m^2 s^{-1}; DOSY NMR ($CDCl_3$): D = 4.4 · 10^{-10} m^2 s^{-1}; GPC (THF): M_n = 1.78 kDa, M_W = 1.94 kDa; DSC: T_g = −71 °C.

NMR data for **11a^{Cl}**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.00–2.80 (m, 4 H; N-C_2H_4-N), 1.80–0.60 (m, 34 H; alkyl), 0.19–0.13 (m, 0.16 H; Si-$(CH_3)_3$ end group) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 31.1 (br) ppm.

For the temperature-dependent experiments the reaction mixtures were heated to 40 °C or 61 °C, respectively, over the duration of the reaction. The experiment at 61 °C was conducted in $CDCl_3$.

Synthesis of 11'a^{NMe2}. To a solution of **16** (507.7 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) a solution of **8a** (283.8 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) was added at ambient temperature. After 24h, all volatiles were removed *in vacuo*, yielding the intermediate product **11'a^{Br}**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66–2.87 (m, 4 H, N–C_2H_4–N), 1.80–0.79 (m, 34 H, alkyl), 0.29 (s, 0.77 H, $Sn(CH_3)_3$ end group) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 37.3 (s) ppm; GPC (THF): M_n = 1.73 kDa, M_W = 2.00 kDa.

11'a^{Br} was dissolved in CH_2Cl_2 (1mL) and treated with pentamethylsilazane (ca. 0.2 mmol) at ambient temperature to deactivate the end groups. After 30 min, all volatiles were removed *in vacuo* yielding **11'a^{NMe2}**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92–2.82 (m, 4 H, N–C_2H_4–N), 2.82–2.54 (br, 0.09 H, $N(CH_3)_2$ end group), 1.75–0.60 (m, 34 H, alkyl), 0.28 (s, 1.16 H, $Sn(CH_3)_3$ end group) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 36.7 (br) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 48.9 (br, N–C_2H_4–N), 33.7 (s, CH_2), 33.5 (s, CH_2), 32.0 (s, CH_2), 29.7 (s, CH_2), 29.5 (s, CH_2), 27.4 (br, CH_2), 27.1 (br, CH_2), 25.9 (br, CH_2), 25.6 (br, CH_2), 22.7 (s, CH_2), 18.7 (br, B–CH_2), 15.9 (br, B–CH_2), 14.1 (s, CH_3), -6.1 (s, $Sn(CH_3)_3$ end group) ppm; GPC (THF): M_n = 1.77 kDa, M_W = 1.98 kDa.

Synthesis of 11a^{NMe2} by activation of 14 with HCl. To a solution of **14** (0.1870 g, 0.4437 mmol) in CH_2Cl_2 (0.35 mL) a solution of HCl in diethyl ether (0.44 mL, 2 M, 0.88 mmol) was added at ambient temperature. It was stirred for 1 d and the volatiles were removed *in vacuo*. *n*-Pentane (1 mL) was added to the residue and it was filtered off and washed with *n*-pentane (2 x 0.5 mL). The volatiles were removed *in vacuo*, yielding the amber colored product. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87–2.90 (m, 4 H, N–C_2H_4–N), 2.70 (br, 0.50 H, $N(CH_3)_2$ end groups), 1.78–0.56 (m, 34 H, alkyl), 0.17 (s, 0.11 H, $Si(CH_3)_3$ end groups) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 38.9 (br), 34.1 (sh) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 49.1 (s, N–C_2H_4–N), 33.7–32.5 (m, CH_2), 32.0 (s, CH_2), 30.2–29.2 (m, CH_2), 26.6–23.8 (m, CH_2), 22.7 (s, CH_2), 16.7 (br, B–CH_2), 16.1 (br, B–CH_2), 14.1 (s, CH_3), 1.0 (s, $Si(CH_3)_3$ end group), 0.8 (s, $Si(CH_3)_3$ end group) ppm; GPC (THF): M_n = 1.75 kDa, M_W = 2.10 kDa.

Synthesis of 11a^{NMe2} by activation of 14 with HOTf in $CDCl_3$. To a solution of **14** (42 mg, 0.10 mmol) in $CDCl_3$ (0.25 mL) in a Young tube a solution of HOTf (15 mg, 0.10 mmol) in $CDCl_3$ (0.25 mL) was added. The mixture was shaken and a precipitate formed. ^{1}H NMR indicated that a partial reaction had taken place (see Figure S65). Another portion of HOTf (15 mg, 0.10 mmol) in $CDCl_3$ (0.2 mL) was added. After 4 d the volatiles were removed *in vacuo* and *n*-pentane (1 mL) was added to the residue. It was filtered off and washed with *n*-pentane (2 x 0.25 mL). The ^{1}H and ^{19}F{^{1}H} NMR of the precipitate confirmed its constitution as $[Me_2NH_2]OTf$ (^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.51 (br, 2 H, NH_2), 2.79 (s, 6 H, $N(CH_3)_2$) ppm; ^{19}F{^{1}H} NMR (400 MHz, CD_2Cl_2) δ = −79 (s) ppm).[55] From the filtrate the volatiles were removed *in vacuo*, yielding the amber colored intermediate product. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78–2.94 (m, 4 H, N–C_2H_4–N), 1.73–0.62 (m, 34 H, alkyl), 0.17 (s, 0.07 H, $Si(CH_3)_3$ end groups) ppm; ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ = 37.2 (br), 32.4 (s) ppm; GPC (THF): M_n = 2.20 kDa, M_W = 2.67 kDa.

The product was dissolved in CH_2Cl_2 (1mL) and treated with pentamethylsilazane (ca. 0.2 mmol) at ambient temperature to deactivate the end groups. After 30 min, all volatiles were removed *in vacuo*. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.10–2.95 (m, 4 H, N–C_2H_4–N), 2.86–2.60 (m, 0.61 H, $N(CH_3)_2$ end group), 1.78–0.62 (m, 34 H, alkyl), 0.23–0.13 (m,

0.08 H, $Si(CH_3)_3$ end group) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 37.3 (br), 32.6 (br) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 48.9 (br, N–C_2H_4–N), 33.5 (s, CH_2), 33.0 (s, CH_2), 32.0 (s, CH_2), 29.6 (s, CH_2), 29.4 (s, CH_2), 27.0 (br, CH_2), 25.2 (br, CH_2), 22.7 (s, CH_2), 18.4 (br, B–CH_2), 16.3 (br, B–CH_2), 14.1 (s, CH_3), 1.0 (s, $Si(CH_3)_3$ end group) ppm; GPC (THF): M_n = 2.24 kDa, M_W = 2.86 kDa.

Synthesis of 11a^{NMe2} by activation of 14 with HOTf in CD_2Cl_2. To a solution of **14** (42 mg, 0.10 mmol) in CD_2Cl_2 (0.25 mL) in a Young tube a solution of HOTf (15 mg, 0.10 mmol) in CD_2Cl_2 (0.25 mL) was added at ambient temperature. While the mixture was shaken a precipitate formed. ^1H NMR indicated that a partial reaction had taken place. Another portion of HOTf (15 mg, 0.10 mmol) in $CDCl_3$ (0.2 mL) was added. After 1 d, the volatiles were removed *in vacuo* and *n*-pentane (1 mL) was added to the residue. It was filtered off and washed with *n*-pentane (2 x 0.25 mL). The volatiles were removed from the filtrate *in vacuo*, yielding the amber colored intermediate product. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.71–2.94 (m, 4 H, N–C_2H_4–N), 1.82–0.62 (m, 34 H, alkyl), 0.17 (s, 0.02 H, $Si(CH_3)_3$ end groups) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ = 37.1 (br), 34.1 (br) ppm; GPC (THF): M_n = 1.58 kDa, M_W = 1.79 kDa.

The intermediate product was dissolved in CH_2Cl_2 (1mL) and treated with pentamethylsilazane (ca. 0.2 mmol) at ambient temperature to deactivate the end groups. After 30 min, all volatiles were removed *in vacuo*. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.68–2.99 (m, 4 H, N–C_2H_4–N), 2.91–2.46 (m, 3.16 H, $N(CH_3)_2$ end group), 1.73–0.60 (m, 34 H, alkyl), 0.23–0.12 (m, 0.70 H, $Si(CH_3)_3$ end group) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 36.6 (br) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 48.8 (br, N–C_2H_4–N), 33.5 (s, CH_2), 33.3 (s, CH_2), 32.0 (s, CH_2), 29.7 (s, CH_2), 29.4 (s, CH_2), 26.9 (br, CH_2), 26.4 (br, CH_2), 25.7 (br, CH_2), 25.2 (br, CH_2), 22.7 (s, CH_2), 18.1 (br, B–CH_2), 15.8 (br, B–CH_2), 14.1 (s, CH_3), 0.8 (s, $Si(CH_3)_3$ end group) ppm; GPC (THF): M_n = 1.64 kDa, M_W = 1.85 kDa.

Synthesis of 11a^{NMe2} by activation of 14 with 1 equivalent of $HNTf_2$ in CD_2Cl_2. To a solution of the **14** (42 mg, 0.10 mmol) in CD_2Cl_2 (0.25 mL) in a Young tube a solution of $HNTf_2$ (28 mg, 0.10 mmol) in CD_2Cl_2 (0.25 mL) was added at ambient temperature and the mixture was shaken. After 1 d the volatiles were removed *in vacuo* and *n*-pentane (1 mL) was added to the residue. It was filtered off and washed with *n*-pentane (2 x 0.25 mL). The volatiles were removed from the filtrate *in vacuo*, yielding the amber colored intermediate product. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.65–3.01 (m, 4 H, N–C_2H_4–N), 2.70 (br, 0.69 H, $N(CH_3)_2$ end groups), 1.65–0.58 (m, 34 H, alkyl), 0.15 (s, 1.20 H, $Si(CH_3)_3$ end groups) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ = 35.8 (br), 31.4 (sh) ppm; GPC (THF): M_n = 1.91 kDa, M_W = 2.33 kDa.

The intermediate product was dissolved in CH_2Cl_2 (1mL) and treated with pentamethylsilazane (ca. 0.2 mmol) at ambient temperature to deactivate the end groups. After 30 min, all volatiles were removed *in vacuo*. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.68–3.02 (m, 4 H, N–C_2H_4–N), 2.88–2.51 (m, 1.94 H, $N(CH_3)_2$ end group), 1.67–0.60 (m, 34 H, alkyl), 0.19–0.16 (m, 0.10 H, $Si(CH_3)_3$ end group) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 36.7 (br), 31.1 (sh) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 48.9 (br, N–C_2H_4–N), 33.5 (s, CH_2), 33.2 (s, CH_2), 32.0 (s, CH_2), 29.7 (s, CH_2), 29.4 (s, CH_2), 27.5 (br, CH_2), 27.1 (br, CH_2), 25.6 (br, CH_2), 25.2 (br, CH_2), 22.7 (s, CH_2), 18.0 (br, B–CH_2), 15.8 (br, B–CH_2), 14.1 (s, CH_3), 0.8 (s, $Si(CH_3)_3$ end group) ppm; GPC (THF): M_n = 1.35 kDa, M_W = 1.62 kDa.

Synthesis of 11b^{NMe2}. To a solution of **7b** (270.4 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) a solution of **2b** (138.8 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) was added at ambient temperature. After 24 h, pentamethylsilazane (**5**; ca. 0.2 mmol) was added to deactivate the reactive end groups. After another 30 min, the volatiles were removed *in vacuo*. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.66–2.87 (m, 4 H, N–C_2H_4–N), 2.83–2.53 (m, 0.04 H, $N(CH_3)_2$ end group), 1.80–0.60 (m, 18 H, alkyl), 0.21–0.12 (m, 1.00 H, $Si(CH_3)_3$ end group) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 34.0 (br) ppm; UV/vis (THF): λ_{max} = 234 (ε = 0.14 · 10^5 L cm^{-1} mol^{-1}), 265 (ε = 0.11 · 10^5 L cm^{-1} mol^{-1}), 305 (ε = 0.052 · 10^5 L cm^{-1} mol^{-1}), 340 (ε = 0.043 · 10^5 L cm^{-1} mol^{-1}) nm; DLS (*n*-pentane): R_h = 2.0 nm, D = 4.4 · 10^{-10} m^2 s^{-1}; DSC: T_g = −20.1 °C.

Synthesis of 11c^{Cl}. To a solution of **7c** (290.4 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) a solution of **2c** (158.8 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) was added at ambient temperature. Immediately after the mixing of the reactants, an insoluble colorless precipitate formed. ^1H NMR of the solution showed evidence for Me_3SiCl formation. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.45 (s, 9 H, $ClSi(CH_3)_3$).

Synthesis of 11ac^{NMe2}. To a solution of **7a** (326.5 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) a solution of **2c** (158.8 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) was added at ambient temperature. After 24 h, pentamethylsilazane (ca. 0.2 mmol) was added to deactivate the reactive end groups. After another 30 min, the volatiles were removed *in vacuo*. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–6.70 (m, 5 H, aryl), 4.00–2.16 (m, 4.30 H, N–C_2H_4–N & $N(CH_3)_2$ end group), 1.92–0.51 (m, 17 H, alkyl), 0.20–0.04 (m, 0.54 H, $Si(CH_3)_3$ end group) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 25.7 (br) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 133.7 (br, phenyl), 128.4 (br, phenyl), 127.0 (br, phenyl), 126.2 (br, phenyl), 50.0 (br, N–C_2H_4–N), 33.4 (br, CH_2), 32.0 (s, CH_2), 29.7 (s, CH_2), 29.4 (s, CH_2), 26.9 (br, CH_2), 25.5 (br, CH_2), 22.7 (s, CH_2), 18.5 (br, B–CH_2), 15.6 (br, B–CH_2), 14.1 (s, CH_3), 0.76–0.57 (m, $Si(CH_3)_3$ end group) ppm; $^{29}Si\{^1H\}$ NMR (79.5 MHz, $CDCl_3$): δ = 4.7 (s) ppm; UV/vis (THF): λ_{max} = 265 (ε = 0.11 · 10^5 L cm^{-1} mol^{-1}), 285 (ε = 0.12 · 10^5 L cm^{-1} mol^{-1}), 339 (ε = 0.028 · 10^5 L cm^{-1} mol^{-1}) nm; DLS (CH_2Cl_2): R_h = 2.2 nm, D = 2.2 · 10^{-10} m^2 s^{-1}; DOSY NMR ($CDCl_3$): D = 2.2 · 10^{-10} m^2 s^{-1}; GPC (THF): M_n = 2.50 kDa, M_W = 3.77 kDa; DSC: T_g = 0.1 °C.

Synthesis of 11ca^{Cl}. To a solution of **7c** (290.4 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) a solution of **2a** (194.9 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) was added at ambient temperature. Several hours after mixing of the reactants, an insoluble colorless precipitate formed. ^1H NMR of the overlaying solution showed evidence for Me_3SiCl formation. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.45 (s, 9 H, $ClSi(CH_3)_3$).

Synthesis of 11bc^{Cl}. To a solution of **7b** (270.4 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) a solution of **2c** (158.8 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) was added at ambient temperature. Several hours after mixing of the reactants, an insoluble colorless precipitate formed. ^1H NMR of the overlaying solution showed evidence for Me_3SiCl formation. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.45 (s, 9 H, $ClSi(CH_3)_3$).

Synthesis of 11cb^{Cl}. To a solution of **7c** (290.4 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) a solution of **2b** (138.8 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) was added at ambient temperature. Shortly after mixing of the reactants, an insoluble colorless precipitate formed. ^1H NMR of the overlaying solution showed evidence for Me_3SiCl formation. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.45 (s, 9 H, $ClSi(CH_3)_3$).

Synthesis of 11d^{NMe2}. To a solution of **7d** (346.5 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) a solution of **2d** (214.9 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) was added at ambient temperature. After 24 h, pentamethylsilazane (ca. 0.2 mmol) was added to deactivate the reactive end groups. After another 30 min the volatiles were removed *in vacuo*. The product **11d^{NMe2}** was mostly insoluble in *n*-pentane, which was used to wash **11d^{NMe2}** several times. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.68–6.13 (m, 8 H, aryl), 3.43–1.93 (m, 8 H, N–C_2H_4–N & butyl-CH_2 & $N(CH_3)_2$ end group), 1.93–0.64 (m, 14 H, alkyl), −0.19–(−0.29) (m, 0.71 H, $Si(CH_3)_3$ end group) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 32.4 (br) ppm; $^{13}C\{^1H\}$ NMR

(101 MHz, $CDCl_3$): δ = 134.6 (br, aryl), 126.4 (br, aryl), 63.3 (br, N–C_2H_4–N), 35.9 (s, butyl-C1), 33.5 (s, butyl-C2), 22.5 (s, butyl-C3), 14.0 (s, butyl-C4); UV/vis (THF): λ_{max} = 231 (ε = 0.26 · 10^5 L cm^{-1} mol^{-1}), 302 (ε = 0.013 · 10^5 L cm^{-1} mol^{-1}) nm; DLS (CH_2Cl_2): R_h = 1.5 nm, D = 3.4 · 10^{-10} m^2 s^{-1}; DOSY NMR ($CDCl_3$): D = 4.0 · 10^{-10} m^2 s^{-1}; GPC (THF): M_n = 1.73 kDa, M_W = 2.29 kDa; DSC: T_g = 15.8 °C.

Computational methods. DFT calculations were carried out with the TURBOMOLE V7.0.1 program package.[34] Optimizations were performed with Becke's three parameter exchange-correlation hybrid functional B3LYP[35] in combination with the valence-double-ζ basis set def2-SV(P).[36] The empirical dispersion correction DFT-D3 by Grimme was used including the three-body term and with Becke-Johnson (BJ) damping.[37] The stationary points were characterized as minima by analytical vibrational frequency calculations,[38] which revealed the absence of imaginary frequencies.

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linear species with two *B* termini, while the reaction with **1** should lead to a seven-membered linear oligomer with two *N* termini, both of which should not be prone to undergo a cyclization reaction without prior redistribution.

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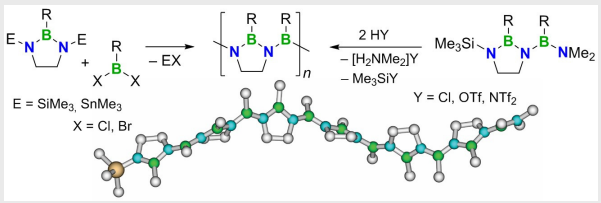

Well-defined oligo(iminoborane)s with up to 18 catenated BN units on average were prepared by Si/B or Sn/B exchange polycondensation as well as initiated polymerization of a dormant monomer. The cyclolinear backbone imparts high stability and precludes the unwanted formation of borazine by-products. The properties of the new materials are effectively tuned by variation of their side groups.

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