

## COMMUNICATION

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## Efficient synthesis of an unsupported aryl substituted iminoborane chain (HNArBH)<sub>2</sub>NAr (Ar = [1,1'-biphenyl]-2-yl)<sup>†</sup>

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**The reaction of 2-aminobiphenyl ArNH<sub>2</sub> with triethylamine borane (Et<sub>3</sub>NBH<sub>3</sub>) at 165 °C, about 40 °C lower in temperature than that used for borazine synthesis, gives a linear HArN-BH-NAr-BH-NArH (Ar = [1,1'-biphenyl]-2-yl) chain in good yield (57%). This BN oligomer could be characterized by single crystal X-ray crystallography.**

Electronic properties of polycyclic aromatic hydrocarbons (PAHs) can be fundamentally changed when single CC units are substituted by isosteric and isoelectronic BN units.<sup>1–6</sup> This concept was transferred from two-dimensional networks, graphene and hexagonal boron-nitride being the prime examples, to one-dimensional polymers.<sup>7</sup> How do properties change when incorporating BN units into 1D polyacetylene (PA) and turn it into poly(iminoborane) (PIB)? For compounds with *para*-phenylene linked NBN units it could be observed that  $\pi$  conjugation is extended over the NBN unit.<sup>7</sup> The calculated band structures suggested a larger band gap for PIB compared to PA.<sup>8</sup>

While the synthesis of poly(aminoboranes) has seen significant advance over the years,<sup>9–13</sup> synthesis of PIBs has been a rocky road so far.<sup>14</sup> Polymerization by thermal dehydrogenation of ammonia borane or aminoborane compounds has often led to the cyclic trimer borazine, the favored product under most circumstances, instead of a polymer chain.<sup>15–18</sup> In some reports formation of PIBs is proposed,<sup>15,19–21</sup> but they could not be satisfyingly characterized. Their existence, therefore, could not be doubtlessly proven due to lack of modern analysis methods, lack of solubility or due to low yields.<sup>18</sup>

A significant step forward in this field could be achieved by Helten and coworkers when they forced the BN-backbone in a linear shape by applying Neilson's method of stabilizing the

backbone with an alkyl corset<sup>22,23</sup> to yield “cycloliner” oligo- and poly(iminoborane)s **A** (Fig. 1).<sup>24–26</sup> By this procedure formation of borazines could be prevented completely, and quite large monodisperse oligo(iminoborane)s could be synthesized and structurally characterized.<sup>26</sup>

The longest iminoborane oligomer that is *unsupported* by an alkyl corset and that could be structurally characterized contains three nitrogen and two boron atoms, ArNH-BH-N(Ar)-BH-NH(Ar), Ar = *p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub> **B** (Fig. 1).<sup>18</sup> This chain was obtained by Manners *et al.* from the dehydrocoupling of ArNH<sub>2</sub>·BH<sub>3</sub> at room temperature as one of the five reaction products over a reaction time of months. The linear oligomer could be obtained as “small crop of crystals”<sup>18</sup> from the mixture, but could not be characterized by NMR. Köster *et al.* observed that the reaction of primary aromatic amines and triethylamine borane results in *N,N,N'*-trisubstituted borazines (Scheme 1a).<sup>16,17</sup> This group reported in 1968 the formation of an oligomer, PhN(BH-NHPh)<sub>2</sub>, in the reaction of BH(NHPh)<sub>2</sub> with Et<sub>3</sub>N·BH<sub>3</sub> at 100 °C as a low yield by-product (7%) of borazine formation.<sup>17</sup> Not unexpectedly, the characterization possible in 1968 falls short of present standards.

Here we show that a slight modification of Köster's borazine synthesis method gives a five-membered BN oligomer without use of stabilizing cyclic alkyl moieties (Scheme 1b). The iminoborane oligomer was obtained in good yields in a single reaction step, and could be fully characterized.

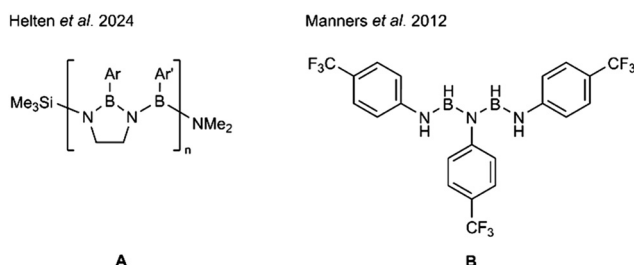
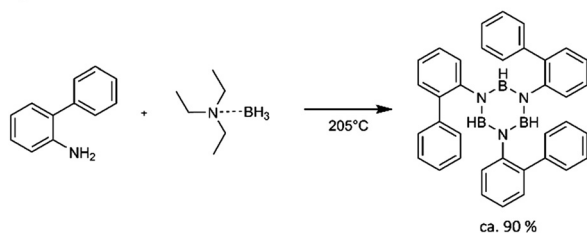


Fig. 1 Previously synthesized oligo- and poly(iminoborane)s.

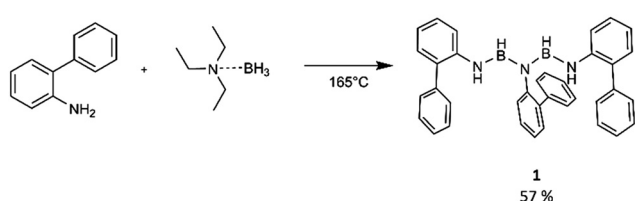
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<sup>†</sup>Electronic supplementary information (ESI) available. CCDC 2307985. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4dt02280g>

a) Köster *et al.* 1968

b) this work



**Scheme 1** Scheme of previously known reaction between 2-aminobiphenyl and triethylamine borane and of our reaction at lower temperature.

Heating an equimolar mixture of 2-aminobiphenyl and  $\text{Et}_3\text{N}\cdot\text{BH}_3$  at  $165^\circ\text{C}$  in the absence of a solvent for 5.5 hours, gives iminoborane oligomer **1**. The pure product can be obtained after recrystallization from acetonitrile in a yield of 57%.

The product crystallizes from acetonitrile in the monoclinic space group  $P2_1/n$  with eight molecules in the unit cell. A single molecule consists of a five-membered iminoborane-chain with biphenyl units at each nitrogen atom (Fig. 2). The outer N–B bond distances N1–B1 ( $1.413(2)\text{ \AA}$ ) and N3–B2 ( $1.417(2)\text{ \AA}$ ) are slightly shorter than the inner N–B bond distances N2–B1 ( $1.441(2)\text{ \AA}$ ) and N2–B2 ( $1.440(2)\text{ \AA}$ ), which is in line with the findings in compound **B** reported by Manners *et al.*<sup>18</sup> in 2012. The bond distances between the terminal aryl

units and the nitrogen atoms, N1–C1 ( $1.409(2)\text{ \AA}$ ) and N3–C25 ( $1.404(1)\text{ \AA}$ ), are also diminished compared to the central bond N2–C13 ( $1.437(1)\text{ \AA}$ ). The rings of the terminal biphenyl units directly connected to the chain are only slightly tilted to the NBN-plane,  $9.6^\circ$  for the unit at N1 and  $1.4^\circ$  for the unit at N3. The other rings of the terminal biphenyl groups and the ring of the central biphenyl group connected to N2 are all inclined to the NBN-plane in the same way but to different extents. The phenyl ring of the N1-unit is inclined by  $77.2^\circ$ , the ring of the N2-unit by  $75.3^\circ$  and the one of the N3-unit by  $71.2^\circ$ .

NMR spectroscopy supports the molecular structure crystallographically found. The  $^1\text{H}$  NMR spectrum shows the required 27 aromatic protons, two protons bound to nitrogen, and two protons bound to boron represented by a very broad singlet at 4.88 ppm. In the  $^1\text{H}$  NMR spectrum no coupling to boron could be detected due to the signal shape. However, from a simulation (see ESI, Fig. S6†) using the software WSolid1<sup>27</sup> with a  $^{11}\text{B}$  spin–lattice relaxation time  $T_1$  of  $^{11}\text{B}$  fixed at 0.88 ms (obtained from the peak width at half-height in the  $^{11}\text{B}$  NMR spectrum) a coupling constant of  $^1J(^{11}\text{B}, ^1\text{H}) = 100\text{ Hz}$  could be deduced.

In conclusion, it was possible to synthesize an iminoborane oligomer by a simple and convenient procedure in a fairly good yield. The molecular composition and structure could be doubtlessly proven. This building block could be useful for constructing larger iminoborane oligomers or even poly(iminoborane).

## Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for compound **1** have been deposited at the Cambridge Crystallographic Data Centre under 2307985.†

## Conflicts of interest

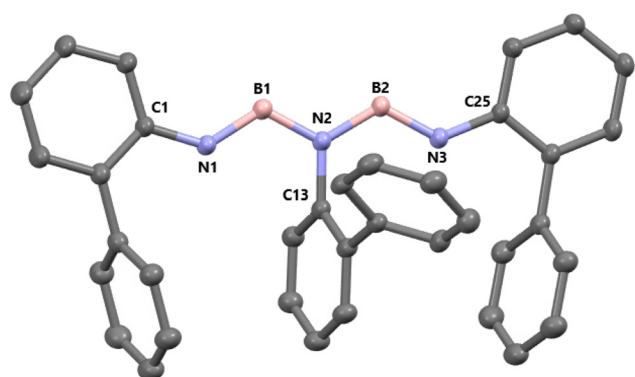
There are no conflicts to declare.

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**Fig. 2** Molecular structure of **1** in solid state. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances [ $\text{\AA}$ ] and angles [ $^\circ$ ]: N1–C1  $1.409(2)$ , N2–C13  $1.437(1)$ , N3–C25  $1.404(1)$ , N1–B1  $1.413(2)$ , N2–B1  $1.441(2)$ , N2–B2  $1.440(2)$ , N3–B2  $1.417(2)$ , C1–N1–B1  $130.7(1)$ , N1–B1–N2  $119.2(1)$ , B1–N2–B2  $120.69(9)$ , N2–B2–N3  $120.5(1)$ , B2–N3–C25  $129.36(9)$ .



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