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

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The reaction of 2-aminobiphenyl ArNH₂ with triethylamine borane (Et₃NBH₃) 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.^{1–6} This concept was transferred from two-dimensional networks, graphene and hexagonal boron-nitride being the prime examples, to one-dimensional polymers.⁷ 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 π conjugation is extended over the NBN unit.⁷ The calculated band structures suggested a larger band gap for PIB compared to PA.⁸

While the synthesis of poly(aminoboranes) has seen significant advance over the years,^{9–13} synthesis of PIBs has been a rocky road so far.¹⁴ 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.^{15–18} In some reports formation of PIBs is proposed,^{15,19–21} 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.¹⁸

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^{22,23} to yield “cycloliner” oligo- and poly(iminoborane)s **A** (Fig. 1).^{24–26} By this procedure formation of borazines could be prevented completely, and quite large monodisperse oligo(iminoborane)s could be synthesized and structurally characterized.²⁶

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*-C₆H₄CF₃ **B** (Fig. 1).¹⁸ This chain was obtained by Manners *et al.* from the dehydrocoupling of ArNH₂·BH₃ 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”¹⁸ 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).^{16,17} This group reported in 1968 the formation of an oligomer, PhN(BH-NHPh)₂, in the reaction of BH(NHPh)₂ with Et₃N·BH₃ at 100 °C as a low yield by-product (7%) of borazine formation.¹⁷ 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.

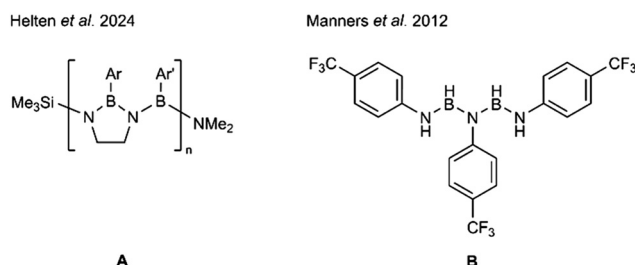
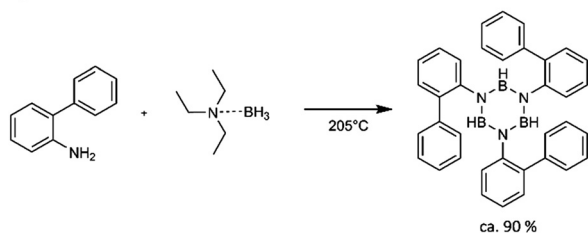


Fig. 1 Previously synthesized oligo- and poly(iminoborane)s.

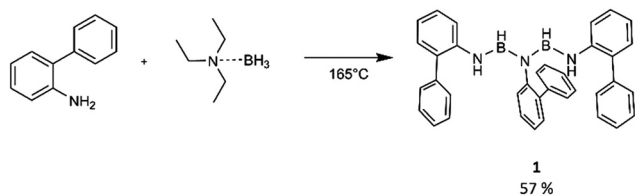
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a) Köster *et al.* 1968

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°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 biphenylyl 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.*¹⁸ 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 biphenylyl units directly connected to the chain are only slightly tilted to the NBN-plane, 9.6° for the unit at N1 and 1.4° for the unit at N3. The other rings of the terminal biphenylyl groups and the ring of the central biphenylyl 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° , the ring of the N2-unit by 75.3° and the one of the N3-unit by 71.2° .

NMR spectroscopy supports the molecular structure crystallographically found. The ^1H 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 ^1H 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 WSolid1²⁷ with a ^{11}B spin–lattice relaxation time T_1 of ^{11}B fixed at 0.88 ms (obtained from the peak width at half-height in the ^{11}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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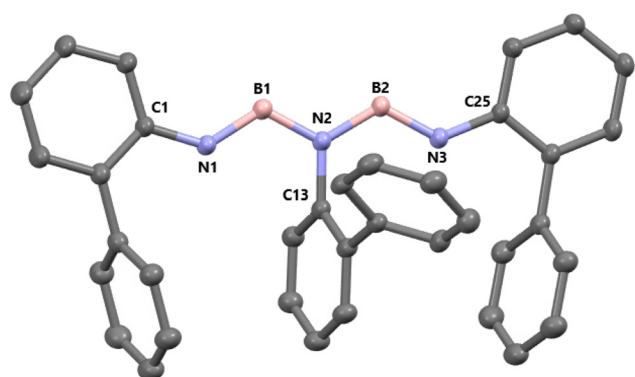


Fig. 2 Molecular structure of **1** in solid state. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances [\AA] and angles [$^\circ$]: N1–C1 $1.409(2)$, N2–C13 $1.437(1)$, N3–C25 $1.404(1)$, N1–B1 $1.413(2)$, N2–B1 $1.441(2)$, N2–B2 $1.440(2)$,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