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Polyaminoborane main chain scission using N-heterocyclic carbenes; formation of donor-stabilised monomeric aminoboranes†

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The reaction of N-heterocyclic carbenes with polyaminoboranes $[MeNH–BH_2]_n$ or $[NH_2–BH_2]_n$ at 20 °C led to depolymerisation and the formation of labile, monomeric aminoborane–NHC adducts, $RNH–BH_2$–NHC (R = Me or H); a similar NHC adduct of $Ph_2N{=}BCl_2$ was characterized by single crystal X-ray diffraction.

As a result of their potential applications in hydrogen storage[1–3] and transfer[4–7] and as precursors to new inorganic materials,[8–12] amine–boranes ($RR'NH{\cdot}BH_3$, R, R′ = H, alkyl or aryl) have been the recent focus of intense interest.[13–16] These species can be dehydrogenated/dehydrocoupled by either thermal or catalytic routes to yield an array of products, including aminoboranes, $RR'N{=}BH_2$, cycloborazanes, $[RR'N–BH_2]_x$ ($x > 1$) and borazines, $[RN–BH]_3$. Catalytic dehydrocoupling of primary amine–boranes and ammonia–borane can yield high molecular weight polyaminoboranes, $[RNH–BH_2]_n$ which are isoelectronic to polyolefins.[8,9,17–19] Several catalyst systems such as IrH_2(POCOP) (POCOP = κ^3-1,3-$(OPtBu_2)_2C_6H_3$),[8,9,18] and also Cr, Mn,[19] Rh[9,20,21] and Fe complexes,[22] and skeletal Ni[17] have been shown to be active for this transformation. Polyaminoboranes are of potential interest as precursors to BN ceramics,[23] as piezoelectric materials[24] as well as other applications.[25] These unusual main group polymers are intriguing materials and their polar boron–nitrogen main chain might be expected to undergo fragmentation by heterolytic cleavage processes. As part of our investigations of the properties of these materials we have examined the stability of poly(methylaminoborane) $[MeNH–BH_2]_n$ both thermally, and in the presence of neutral Lewis bases. Herein we report on our preliminary results in this area.

An initial investigation of the thermal stability of a sample of $[MeNH–BH_2]_n$ (M_n = 190 000 Da, PDI = 1.21) formed by the Ir-catalysed dehydrogenation of methylamine–borane, $MeNH_2{\cdot}BH_3$,[8,9] was conducted by heating polymer to 70 °C for 19 h in both strongly donating (THF) and weakly donating (toluene) solvents. Reaction progress was monitored by ^{11}B NMR, electrospray ionisation mass spectrometry (ESI-MS) and gel permeation chromatography (GPC). Analysis of the thermolysed polymer in THF by ^{11}B NMR revealed that, as well as decomposition to methyl borazine, $[MeN–BH]_3$ ($\delta(^{11}B)$ 32.3 ppm, d, $^1J_{BH}$ = 135 Hz) (*ca.* 10% of post-thermolysis product distribution), depolymerisation to lower molecular weight oligomers $[MeNH–BH_2]_x$ ($\delta(^{11}B)$ −6.6 ppm, br) was suggested to occur by the observed sharpening of the broad ^{11}B NMR peak characteristic of the high molecular weight material (Fig. S4, ESI†). ESI mass spectrometry analysis of the reaction mixture confirmed the continued presence of polymer with a distribution of peaks with a mass difference of m/z = 43, corresponding to $[MeNH–BH_2]$ repeat units (Fig. S5, ESI†). However, GPC analysis of the isolated polymer confirmed a substantial reduction in molar mass (M_n = 66 000 Da, PDI = 2.03, Fig. S6, ESI†). Thermolysis of $[MeNH–BH_2]_n$ in toluene at 70 °C for 19 h gave similar results to those in THF.

Next, we explored the influence of Lewis bases on the stability of $[MeNH–BH_2]_n$. Treatment of $[MeNH–BH_2]_n$ with one equiv. of tri-cyclohexylphosphine (PCy_3) in THF led to no obvious change by ^{11}B NMR spectroscopy (Fig. S10, ESI†), even at elevated temperatures up to 50 °C for 22 h. In contrast, analogous addition of one equiv. of tri-*n*-butylphosphine, $P(nBu)_3$ to $[MeNH–BH_2]_n$ in THF at 20 °C led to some clear depolymerisation into $MeNH_2{\cdot}BH_3$ ($\delta(^{11}B)$ −18.8 ppm, q, $^1J_{BH}$ = 89 Hz) (*ca.* 10%) and a trace of bis(methylamino)borane, $(MeNH)_2BH$ ($\delta(^{11}B)$ 27.8 ppm, d, br) after 22 h (Fig. S11, ESI†). Reaction of the strong nitrogen base 4-dimethylaminopyridine (DMAP) with $[MeNH–BH_2]_n$ after 24 h at 20 °C in THF was even more extensive and ^{11}B NMR showed, in addition to $[MeNH–BH_2]_{3or4}$ ($\delta(^{11}B)$ −5.3 ppm, br) (*ca.* 70%), the formation mainly of both $MeNH_2{\cdot}BH_3$ ($\delta(^{11}B)$ −18.9 ppm, $^1J_{BH}$ = 97 Hz) (*ca.* 10%) and $[MeN–BH]_3$ ($\delta(^{11}B)$ 30.2 ppm, d, br) (*ca.* 10%) (Fig. S13, ESI†).

Clearly strong donor ligands such as $P(nBu)_3$ and DMAP are capable of cleaving the B–N main chain in polyaminoboranes

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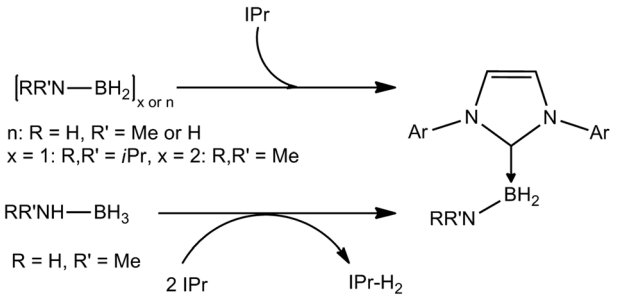


Scheme 1 Reaction of aminoborane (top) and amine–borane (bottom) with IPr to yield an IPr stabilized aminoborane adduct (IPr = 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene).

but these nucleophiles were not able to form detectable adducts with the resulting B–N fragments. In an attempt to achieve this,[26] we treated polyaminoborane $[MeNH–BH_2]_n$ with one equiv. per repeat unit of the N-heterocyclic carbene (NHC) 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) at 20 °C in THF (Scheme 1). This led to the quantitative formation of a new species as observed by ^{11}B NMR after 10 min. ($\delta(^{11}B)$ −17.2 ppm, t, $^1J_{BH}$ = 90 Hz) (Fig. S14, ESI†). The structure of this product was assigned as the aminoborane–NHC adduct MeNH–BH_2–IPr based partly on comparative NMR data with that for the borane adduct of this species, BH_3–NH(CH_3)–BH_2–IPr, recently reported by Rivard and co-workers, which possesses an internal boron environment with a broad ^{11}B NMR peak at δ −14.0 ppm.[27,28] Further evidence for the assigned structure was provided by *in situ* ESI mass spectrometry which gave a molecular ion peak at *m/z* = 432 (intensity = 35%) and a peak at *m/z* = 389 (intensity = 100%) corresponding to the loss of the aminoborane MeNH=BH_2 (Fig. S18, ESI†). Unfortunately, attempts to isolate MeNH–BH_2–IPr by crystallization and precipitation led to dissociation and the regeneration of IPr (Fig. S19, ESI†). Analogous treatment of $[MeNH–BH_2]_n$ with one equiv. of 1,3-bis-(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) (THF, 20 °C, 10 min) led to the formation of a similarly labile product, MeNH–BH_2–IMes ($\delta(^{11}B)$ −17.0 ppm (t, $^1J_{BH}$ = 90 Hz) (Fig. S20, ESI†) (*ca.* 60% yield) which was also supported by ESI mass spectrometry with the observation of a peak *in situ* at *m/z* = 348 for the molecular ion (intensity = 5%) as well as a peak at *m/z* = 305 (intensity = 100%) corresponding to the loss of MeNH=BH_2 (Fig. S21, ESI†).

In an effort to investigate the generality of these observations we also explored the reaction of IPr with poly(ammonia–borane) $[NH_2–BH_2]_n$ in THF where the B–N polymer was formed by the Ir-catalyzed dehydrogenation of NH_3·BH_3.[8,9] However, perhaps due to the insolubility of poly(ammonia–borane) in common organic solvents, the reaction was substantially slower than for the methyl analogue. Nevertheless, after 24 h ^{11}B NMR revealed quantitative conversion to NH_2–BH_2–IPr with a peak observed at ($\delta(^{11}B)$ −19.5 ppm, t, $^1J_{BH}$ = 88 Hz) (Fig. S22, ESI†). This was further supported by chemical ionisation (CI) mass spectrometry with the observation of a peak *in situ* at *m/z* = 417 for the molecular ion (intensity = 24%) and a peak at *m/z* = 389 (intensity = 100%) corresponding to the loss of NH_2=BH_2 (Fig. S23, ESI†).

To provide further evidence of the product assignments we also investigated the reactions of IPr with monomeric aminoborane iPr_2N=BH_2, cyclic diborazane $[Me_2N–BH_2]_2$, and the amine–borane $MeNH_2$·BH_3. In all cases NHC-stabilised aminoboranes were identified as the major products (Table S1, ESI†). In the case of $[Me_2N–BH_2]_2$, this cyclic species exists in an equilibrium with its monomeric form, Me_2N=BH_2,[29] and it is postulated that IPr can only bind with the monomer thereby explaining the long reaction time and elevated temperature needed to enable quantitative conversion. Furthermore, it was observed that aminoborane–NHC adducts can be formed using amine–boranes, such as $MeNH_2$·BH_3 as long as two or more equivalents of NHC are present; one to act as a hydrogen acceptor[27] and the second for adduct formation.

Further characterisation of the aminoborane–carbene adducts was thwarted by the labile, dative B–C bond, leading to dissociation to the aminoborane and carbene on attempted isolation. To reduce the lability, we explored NHC adduct formation with an aminoborane that possessed phenyl groups on nitrogen and chlorine atoms on boron. We anticipated that the resulting increase in Lewis acidity at boron as a result of the reduced π-donation from nitrogen and the presence of electronegative Cl substituents would lead to a substantially more robust C–B donor–acceptor interaction. The reaction of Ph_2N=BCl_2 with one equiv. of IPr was conducted in THF at 20 °C where a new species was observed by ^{11}B NMR spectroscopy at $\delta(^{11}B)$ 1.2 ppm (s) (Fig. S37, ESI†). Suitable crystals of the product for a single-crystal X-ray diffraction study were obtained from a saturated toluene solution over several days at 20 °C (for the determined molecular structure see Fig. 1 and Fig. S42, ESI†). The structure confirmed the product to be the desired adduct Ph_2N–BCl_2–IPr (**1**) with a distorted tetrahedral boron center (B1) bound to a carbene center (C1) and a distorted trigonal nitrogen (N3), with C1–B1 and B1–N3 bond lengths of 1.653(4) Å and 1.510(4) Å respectively. The distance between sp^3 hybridised B1 and sp^2 hybridised N3 is within those

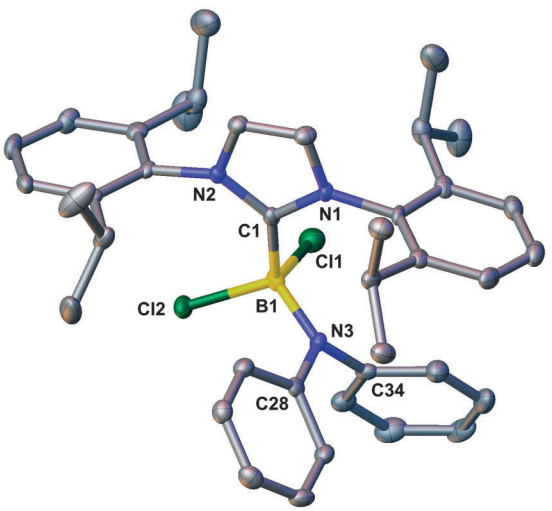
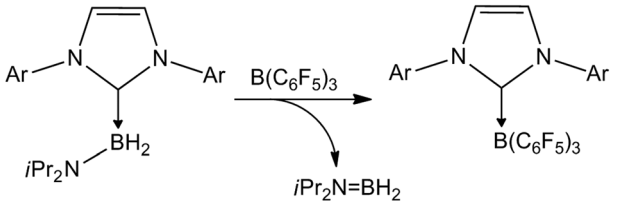


Fig. 1 Molecular structure of compound Ph_2N–BCl_2–IPr (**1**) determined by X-ray diffraction with all non-H atoms as 50% thermal ellipsoids, and with all hydrogens and solvent (toluene) removed for clarity.



Scheme 2 Reaction of $iPr_2N–BH_2–IPr$ with $B(C_6F_5)_3$ to regenerate $iPr_2N{=}BH_2$ (Ar = Dipp (2,6-iPr_2–C_6H_3)).

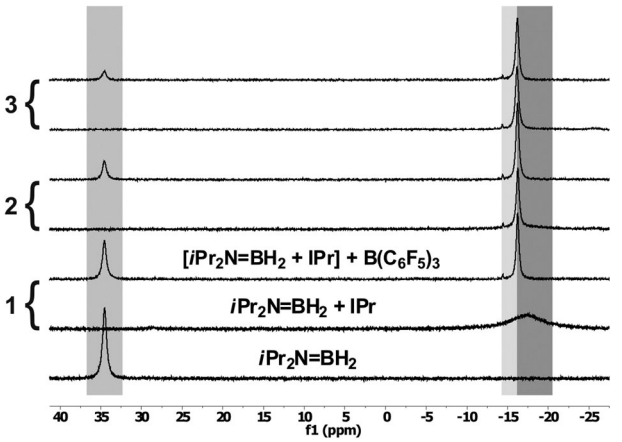


Fig. 2 Regeneration of $iPr_2N{=}BH_2$ ($\delta(^{11}B)$ 34.6 ppm) from $iPr_2N–BH_2–IPr$ ($\delta(^{11}B)$ −17.3 ppm) upon the addition of $B(C_6F_5)_3$ to form $IPr{\cdot}B(C_6F_5)_3$ ($\delta(^{11}B)$ −16.2 ppm) as tracked by ^{11}B NMR in toluene. $iPr_2N{=}BH_2$ was regenerated three times.

reported for average single (B–N, 1.58 Å) and double (B=N, 1.40 Å) bonds.[30] Crystallographic details and a list of selected bond lengths and angles are reported in Tables S2a–S2c, ESI.†

Compound **1** serves as an isolable analog of the other, more labile aminoborane–NHC adducts (Scheme 1). In order to provide more insight into the lability, we attempted to abstract the NHC from $iPr_2N–BH_2–IPr$ by reaction of the latter with one equiv. of $B(C_6F_5)_3$ in toluene at 20 °C (Scheme 2). ^{11}B NMR analysis of the reaction mixture indeed revealed *ca.* 80% reformation of the aminoborane, $iPr_2N{=}BH_2$ ($\delta(^{11}B)$ = 34.6 ppm, t, $^1J_{BH}$ = 128 Hz) and the formation of the adduct $IPr{\cdot}B(C_6F_5)_3$ ($\delta(^{11}B)$ −16.2 ppm, s)[31] (Fig. S41, ESI†). In order to demonstrate the reversibility of the reaction, three repeated sequential additions of IPr and $B(C_6F_5)_3$ to $iPr_2N{=}BH_2$ were conducted in toluene and excellent reproducibility was demonstrated (Fig. 2).

In summary, the boron–nitrogen main chain in high molecular weight polyaminoboranes can be cleaved in the presence of strong Lewis bases and we have shown that NHCs are also capable of binding to the resulting fragments to give adducts such as $MeNH–BH_2–IPr$ and $NH_2–BH_2–IPr$. These species are analogues of the donor-stabilised phosphinoboranes described by Scheer and co-workers.[32,33] The reversibility of their formation was demonstrated in the case of $iPr_2N–BH_2–IPr$ by reaction with one equiv. of $B(C_6F_5)_3$. Ongoing efforts focus on investigating the free aminoborane products released upon removal of the NHC by $B(C_6F_5)_3$ from the less sterically encumbered adducts, with the goal of promoting polymer regeneration. We are also exploring the consequences of the potential recyclability of polyaminoborane materials under mild conditions.

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