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BH₃·SMe₂ addition enables molar mass control *via* chain stabilization in phosphine−borane dehydropolymerization†

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We report the synthesis of high molar mass polyphosphinoboranes using commercially available reagents through thermal dehydropolymerization in the presence of Lewis acids and bases. These dehydropolymerizations produce materials of higher molecular weight compared to the state-of-the-art catalyst, $Cp(CO)_2FeOTf$ ([PhPH–BH$_2$]$_n$ (**2**), 5 mol% LiOTf, 2 M in 2-MeTHF, 100 °C, 24 h; M_n = 80 000 g mol^{-1}, $Đ$ = 1.64 *cf.* 5 mol% $Cp(CO)_2FeOTf$, 2 M in toluene, 100 °C, 24 h, M_n = 40 000 g mol^{-1}, $Đ$ = 1.64). We propose a mechanism for the thermal dehydropolymerization of $PhPH_2·BH_3$ (**1**) with additives. Initially, the phosphine−borane adduct dissociates, yielding borane *in situ*, which acts as a (pre)catalyst for the dehydrogenation of **1**. Subsequent addition polymerization occurs as described previously, but the addition of Lewis acids and Lewis bases allows for reversible complexation of both termini. Competition between temporary chain capping and termination events results in fewer termination events over time, leading to high molar mass materials. With this mechanism in mind, we were able to show that added $BH_3·SMe_2$ allows for control over the molar mass of the resulting materials. These results show that transition-metal catalysts are not needed in the thermal dehydropolymerization of $PhPH_2·BH_3$, and offer a new mechanistic insight that may unlock greater control over the dehydropolymerization of main-group substrates.
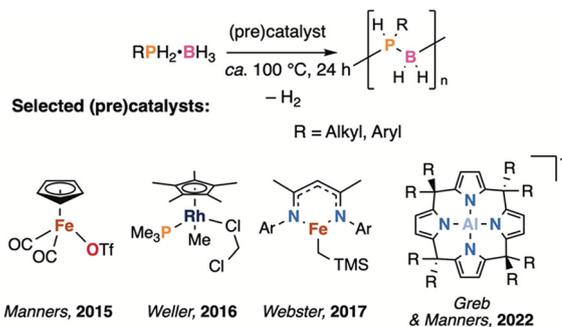
Introduction

Polymers incorporating main-group elements into their main chain are of interest as inclusion of these elements can lead to desirable properties and useful materials.[1–9] Polyphosphinoboranes are polymers with a main chain comprised of alternating phosphorus and boron atoms[1,5,10–13] that have been explored as flame retardants,[14] materials for soft lithography,[15] and solvogels.[16] Poly(*P*-phenyl)phosphinoborane is of particular interest as an inorganic P–B analogue of polystyrene, and was first sought in the 1950s.[17,18] However, well-characterized polyphosphinoboranes were not accessed until the turn of the 21st century when the Manners group reported phosphine–borane adduct dehydropolymerization using Rh catalysts.[19,20] Several catalysts have since been explored based on Fe,[21,22] Ir,[23] and Rh (Scheme 1).[24–26] More recently, we have worked in collab-

oration with the Greb group to showcase the ability of a geometrically constrained aluminate species to act as a dehydropolymerization catalyst[27] and with the Weller group to characterize the first well-defined block copolymer that is comprised of two distinct polyphosphinoborane blocks.[28]

Polyphosphinoboranes can also be accessed through the direct generation of transient phosphinoborane monomers *in situ*. Cationic oligomers of phosphanylboranes (*e.g.* $Me_3N·BH_2PH_2BH_2·NMe_3$) were first obtained by the Scheer

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Scheme 1 Typical conditions for the catalytic dehydropolymerization of phosphine-boranes with catalyst examples.

group *via* the reaction of Lewis base-stabilized phosphanylboranes with monohalideboranes.[29] The polymerisation *via* the generation of phosphinoboranes *in situ* was first demonstrated through the synthesis of *t*BuPH-BH$_2$(NMe$_3$) adducts that lose NMe$_3$ under gentle heating to generate phosphinoborane monomers in solution.[30] Later, we reported the synthesis of *P*-disubstituted polyphosphinoborane polymers ([PhRP-BH$_2$]$_n$; R = Ph, Et) through the cyclic(alkyl)amino carbene (cAAC)-mediated dehydrogenation of phosphine–borane adducts[31] or through the deprotonation of phosphine–(triflimido)borane adducts (Scheme 2).[32]

The mechanism of phosphine–borane dehydropolymerisation is interesting as mechanism-led design of catalysts can result in greater efficiency in accessing materials as well as better control over the polymer microstructure and degree of polymerization.[33] However, despite mechanistic studies performed thus far,[21,24,25,34,35] the normal protocol for phosphine–borane dehydropolymerization still requires the use of a catalyst that normally takes several steps to synthesize, and forcing reaction conditions ($\geq$16 h, $\geq$100 °C).[13] One report explores the dehydrocoupling of PhPH$_2$·BH$_3$ using B(C$_6$F$_5$)$_3$ (BCF) under milder conditions (3 days, 20 °C), where only a material of low molecular weight ($M_w \leq 3200$ g mol^{-1}) was obtained.[36] It is therefore desirable not only to find new catalysts but also to investigate new mechanistic principles that are not only concerned with monomer formation, but also with the growth of the polymer chain itself. Some work has been done computationally, where Pomogaeva and Timoshkin have explored the chemistry of PB decamers *in silico*.[37] They found that end-group complexation of phosphine–borane oligomers can prevent backbiting/cyclization of oligomers (and thus terminating the reactive growing chain). End-group capping by either a relatively weak Lewis acid or a relatively weak Lewis base is insufficient to prevent this cyclization event from occurring, but capping at both ends can disfavor backbiting. Computational studies have suggested that BH$_3$ can act as a catalyst for the dehydrogenation of phosphine-boranes.[38]
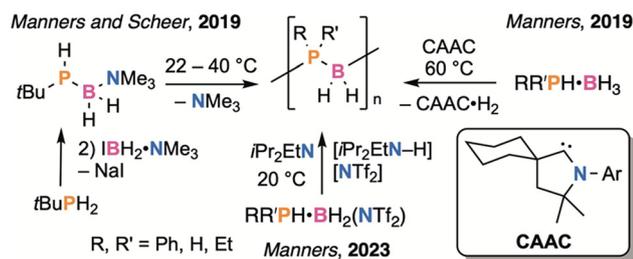
Thus, in an effort to better understand the mechanism of dehydropolymerization using the state-of-the-art CpFe(CO)$_2$OTf catalyst, we explored the ability of LiOTf and other Lewis acid–Lewis base pairs to catalyze the dehydropolymerization of PhPH$_2$·BH$_3$, **1**.

Results and discussion

Dehydropolymerizations in toluene

First, thermal dehydropolymerization in the absence of any additives was explored as a control reaction and achieved by heating PhPH$_2$·BH$_3$ (**1**) in toluene at 100 °C for 24 h. The product mixture was analyzed by ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR spectroscopy revealing broad peaks at −48.9 ppm and −34.7 ppm, respectively, indicating that [PhPH-BH$_2$]$_n$ (**2**) had formed.

Subsequently, the polymeric material was isolated *via* repeated precipitations, first in cold iPrOH, and twice more in cold hexanes resulting in a 35% yield of a colorless material. Analysis of the material by gel permeation chromatography (GPC) confirmed that a polymer was present, albeit a polydisperse material of low molar mass (M_n = 12 680 g mol^{-1}; Đ = 2.00) (Fig. 1).

Repeating the above procedure with the addition of 5 mol% LiOTf resulted in the formation of higher molecular weight **2** (M_n = 42 200 g mol^{-1}; Đ = 1.69) in 62% yield. These mass values closely match the activity of polymerizations performed
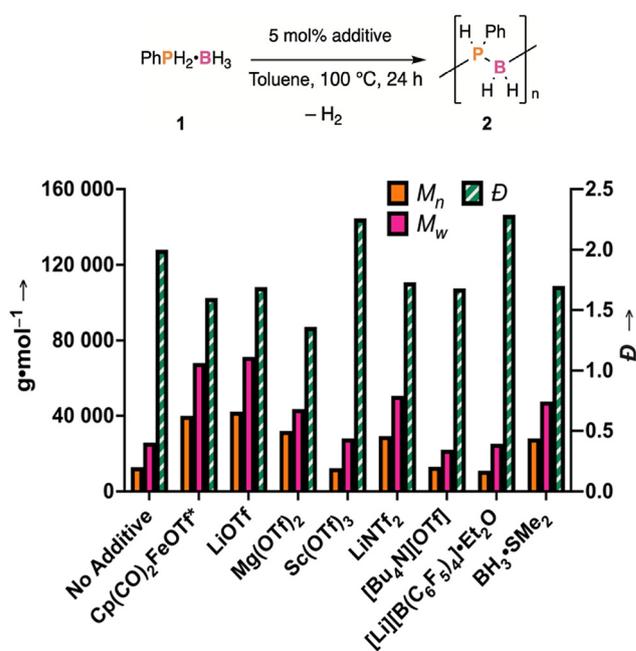

Fig. 1 Molar mass values (M_n and M_w, solid orange and pink bars) and dispersity (Đ, striped green bars) of materials obtained from the dehydropolymerization of phosphine-boranes in toluene using no catalyst, Cp(CO)$_2$FeOTf,[21] and commercially available additives. *M_n and M_w for the bar chart are taken from the literature.[21] Furthermore, at 20 °C, not all salts were fully soluble.

Scheme 2 Synthesis of polyphosphinoboranes *via* the targeted generation of phosphine–borane adducts (top) and the work performed in this article (bottom).

with 5 mol% of CpFe(CO)$_2$OTf (M_n = 40 000 g mol^{-1}; $Đ$ = 1.70).[21] We were surprised by these results as our initial mechanistic studies on Cp(CO)$_2$Fe(OTf) identified Fe-containing oligomers by ESI-MS and established a relationship between [Fe] loading and polymer molar mass, indicating that the iron centre was involved in the dehydrogenation and chain growth steps. However, as the resulting polymer from LiOTf-catalyzed dehydropolymerization has no iron-derived impurities, this is a major advantage as a preceramic polymer. Intrigued by this result, we commenced to explore the ability of other commercially available salts to dehydropolymerize phosphine–borane adducts.

To determine the role of the triflate anion of LiOTf and separate its influence from that of the respective cation, we explored the ability of other triflate and triflimide salts to catalyze the dehydropolymerization of **1**. Accordingly, the polymerization described above was performed with 5 mol% Mg(OTf)$_2$ as an additive. This worked well as a catalyst for the dehydropolymerization of **1** to **2** (M_n = 32 020 g mol^{-1}; $Đ$ = 1.70, 67% yield). However, using 5 mol% of Sc(OTf)$_3$ resulted merely in a polymer that resembled that obtained from thermal dehydropolymerization (M_n = 12 370 g mol^{-1}; $Đ$ = 2.26, 42% yield). Thus, the ability to access high molar mass **2** is not general to all additives. We then explored dehydropolymerization using the closely related salt LiNTf$_2$. Similar to LiOTf and Mg(OTf)$_2$, LiNTf$_2$ addition also resulted in the formation of high, albeit slightly less high, molar mass **2** (M_n = 29 260 g mol^{-1}; $Đ$ = 1.73; 58% yield).

As the cation appeared to influence the outcome of the reaction substantially, salts with a weakly coordinating cation in one case and a weakly coordinating anion in the other was used. [Bu$_4$N][OTf] and [Li][B(C$_6$F$_5$)$_4$]·Et$_2$O both resulted in a polymer that resembled that obtained from thermal dehydropolymerization with no additives ([Bu$_4$N][OTf]: M_n = 13 110 g mol^{-1}; $Đ$ = 1.68; 30% yield; [Li][B(C$_6$F$_5$)$_4$]·Et$_2$O: M_n = 10 980 g mol^{-1}; $Đ$ = 2.29; 36% yield) similar to what was observed for Sc(OTf)$_3$. This result suggests that having a coordinatively unsaturated anion and cation is key to accessing high molar mass **2**.

We were curious if it was possible to access a high molar mass material in the thermal dehydropolymerization of **1** using a Lewis acid–Lewis base adduct containing a dative bond, BH$_3$·SMe$_2$. This adduct is comprised of both a weak Lewis acid and a weak Lewis base, and if the components of the adduct (*i.e.,* BH$_3$ or SMe$_2$) were to coordinate with the respective P- and B-termini of the growing oligomer, cyclization reactions would be disfavoured according to computational studies by Pomogaeva and Timoshkin.[37] Accordingly, performing the polymerization as described above with the addition of 5 mol% of BH$_3$·SMe$_2$ resulted in the formation of a polymeric material as confirmed by GPC (M_n = 27 990 g mol^{-1}; $Đ$ = 1.70). These data further support the hypothesis that both a Lewis acid and a Lewis base are needed *in situ* in order to access a high molar mass material.

Dehydropolymerizations in 2-MeTHF

As the presence of Lewis acids and Lewis bases *in situ* appeared to assist in the formation of high molar mass **2**, we targeted the thermal dehydropolymerization of **1** in a coordinating solvent rather than in a weakly coordinating arene solvent. Not only would this precaution remove any ambiguity over the solubility of the additives and the actual loading, but it would also assist in realizing the more complete dissociation of the additives. The resulting greater stabilizing effect on the growing chain would produce higher molar mass materials. Furthermore, in the dehydropolymerizations of closely related amine–borane adducts, performing reactions in coordinating solvents can result in the formation of higher molar mass materials as chain transfer reactions are disfavoured.[39] Accordingly, we performed the dehydropolymerization of **1** in 2-MeTHF. It has a higher boiling point than THF and is derived from sustainable sources,[40] but its polarity is comparable with a dielectric constant of 6.97 for 2-MeTHF and 7.5 for THF.[41]

Performing the dehydropolymerization of **1** as a 2 M solution in 2-MeTHF without any other additives also resulted in the formation of **2** after 24 h at 100 °C as determined by ^{31}P and ^{11}B NMR spectroscopy. Subsequent isolation was performed in the same manner as described above, resulting in a good yield of 70%. Analysis of the polymeric material by GPC revealed that it had a very high molar mass (M_n = 80 680 g mol^{-1}; $Đ$ = 1.66; Fig. 2). Notably, this mass is double that obtained from thermal dehydropolymerizations performed under comparable reaction conditions using a 5 mol% loading of CpFe(CO)$_2$OTf in toluene. Moreover, in our initial study on the dehydropolymerization of PhPH$_2$·BH$_3$ using CpFe
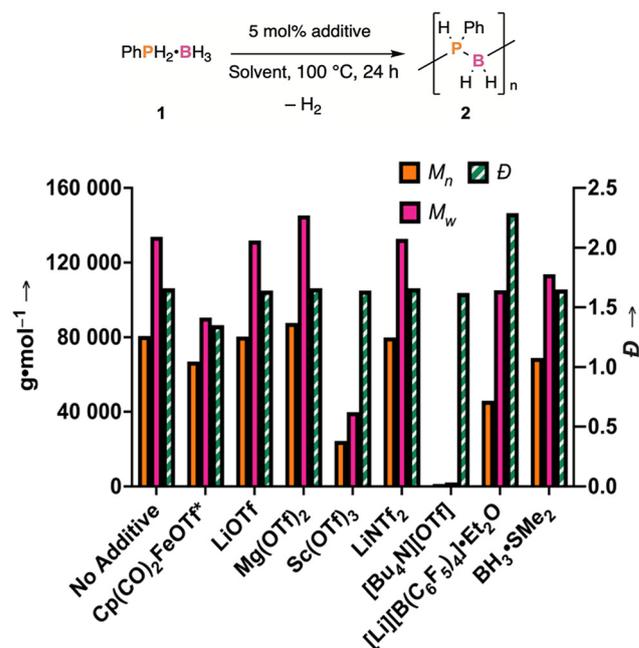

Fig. 2 Molar mass values (M_n and M_w, solid orange and pink bars) and dispersity ($Đ$, striped green bars) of materials obtained from the dehydropolymerization of phosphine-boranes in 2-MeTHF using no catalyst, in dioxane using Cp(CO)$_2$FeOTf*,[21] and in 2-MeTHF using commercially available additives.

$(CO)_2OTf$, we found that performing the dehydropolymerization in 1,4-dioxane resulted in the formation of a higher molar mass material ($M_n = 67\,000$ g mol^{-1}; $Đ = 1.35$).[21] Furthermore, we assessed the ability of salts to catalyze the formation of high molar mass materials and found similar results to those obtained in toluene, where LiOTf, Mg(OTf)$_2$, LiNTf$_2$, and BH$_3$·SMe$_2$ would produce high molar mass materials and Sc(OTf)$_3$, [Bu$_4$N][OTf], and [Li][B(C$_6$F$_5$)$_4$]·Et$_2$O produced materials of lower molecular weights (Fig. 2). Notably, polymerizations performed with [Bu$_4$N][OTf] produced materials of significantly lower molecular weights.

We were surprised by the performance of the thermal dehydropolymerization of **1** without any additives in 2-MeTHF as the studies in toluene suggest that both a Lewis acid and a Lewis base must be present *in situ* for a high molar mass material to be accessed. We suggest that under the reaction conditions, a small fraction of **1** can undergo adduct dissociation into phenylphosphine (PhPH$_2$) and borane (BH$_3$). Gas-phase computational studies into the bonding of phosphine–borane adducts estimate that bond dissociation is unfavourable and only a very little amount of free phosphine and free borane would be present in solution ($\Delta G^\circ = 13.8$ kcal mol^{-1}; $K = 8.26 \times 10^{-9}$).[42] However, this reaction would become more feasible in a donor solvent such as 2-MeTHF, as 2-MeTHF could stabilize borane through a dative interaction. Furthermore, if this dissociation were to occur, both a Lewis base (2-MeTHF, PhPH$_2$) and a Lewis acid (BH$_3$) would be present *in situ* and would satisfy the conditions established for dehydropolymerizations in toluene.

Mechanistic study

Having identified LiOTf and BH$_3$·SMe$_2$ as good catalysts in the dehydropolymerization of **1**, we aimed to monitor the reaction more closely. Dehydropolymerizations of **1** were prepared in 2-MeTHF with LiOTF and BH$_3$·SMe$_2$ as additives and heated to 100 °C as described above. However, reactions were quenched at 0.15, 0.50, 1.0, 2.0, 3.0, 6.0, 16 and 24 hours for analysis by NMR spectroscopy and GPC (Fig. 3). Performing the dehydropolymerization in 2-MeTHF with 5 mol% of LiOTf resulted in
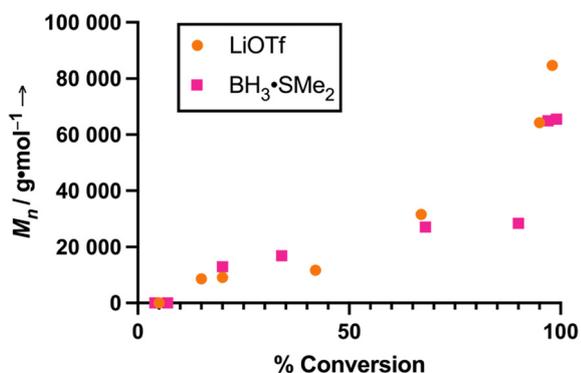
a typical reaction progress graph where high conversion (>80%) was only reached at 16 h. Further analysis of each reaction using LiOTf over the 24-hour period by GPC revealed that a significant amount of a high molar mass material was obtained at 6 h (Fig. S3†), meaning that a high molar mass was obtained at low conversions of **1**, similar to what was observed for dehydropolymerizations performed with CpFe(CO)$_2$OTf.[21] However, dehydropolymerizations performed with 5 mol% BH$_3$·SMe$_2$ in 2-MeTHF appeared to occur at a significantly higher rate compared to LiOTf as a significant conversion (>80%) of **1** had occurred within 6 h. Analysis of the reaction products by GPC revealed that a significant amount of a high molar mass material was obtained within 3 h (Fig. S4†). Comparing the conversion of **1** to **2** in both dehydropolymerizations with the M_n of the isolated materials reveals that high molar mass materials ($M_n > 20\,000$ g mol^{-1}) are obtained at low conversions (<50%), but GPC traces obtained at higher conversions (>50%) reveal the formation of materials with even higher molar mass values ($M_n > 40\,000$ g mol^{-1}).

To identify if the Lewis acidic and Lewis basic components of the additives could be observed as end-groups in samples of **2**, we conducted end-group analysis using electrospray ionization mass spectrometry (ESI-MS). Samples of **2** were prepared in DCM, and both positive and negative mode spectra were recorded. For polymerizations performed with both LiOTf and BH$_3$·SMe$_2$, a series of peaks separated by m/z 122, the mass of the [PhPH-BH$_2$] monomer, were observed and signals corresponding to oligomers with up to 23 repeat units could be identified (Fig. S10†). Closer inspection of the positive mode spectra with peaks in the m/z 1 250–1500 range (Fig. S11†) indicated that polymerizations carried out with 5 mol% of LiOTf predominantly featured decamers and undecamers with H and PhPH$_2$ end-groups ([H{PhPH-BH$_2$}$_n$·PhPH$_2$]$^+$; *e.g.*, $n = 10$, m/z 1330.53). In contrast, for polymerizations performed with 5 mol% of BH$_3$·SMe$_2$, positive mode spectra within the same range revealed signals corresponding to oligomers with BH$_2$(SMe$_2$) end-groups ([(BH$_2$(SMe$_2$))·{PhPH-BH$_2$}$_n$·PhPH-BH$_2$]$^+$; *e.g.*, $n = 10$, m/z 1416.45) in addition to those with H and PhPH$_2$ end-groups. In the negative mode, ESI-MS spectra for polymerizations performed with either LiOTf or BH$_3$·SMe$_2$ consistently showed a series of peaks corresponding to *P*-phenylphosphinoborane decamers with BH$_3$ and H end-groups ([H$_3$B·{PhPH-BH$_2$}$_n$H]$^-$; $n = 10$, m/z 1234.75). Thus, for polymerizations performed in LiOTf, end-groups incorporating either Li$^+$ or [OTf]$^-$ could not be observed by ESI-MS. However, as both components of LiOTf are weakly coordinating, it is possible that these potential end-groups are displaced in the work-up, sample preparation, or in the ESI-MS instrument itself. In contrast, for polymerizations performed with BH$_3$·SMe$_2$, both BH$_3$ and SMe$_2$ were observed as chain caps. The source of BH$_3$ end-groups could either be from **1** or BH$_3$·SMe$_2$, but the presence of the BH$_2$(SMe$_2$) chain-ends implicates that BH$_3$·SMe$_2$ has a role in chain propagation of the growing polymer.

We then explored the ability to regenerate reactive chain ends through continued late-stage step-growth polymerization
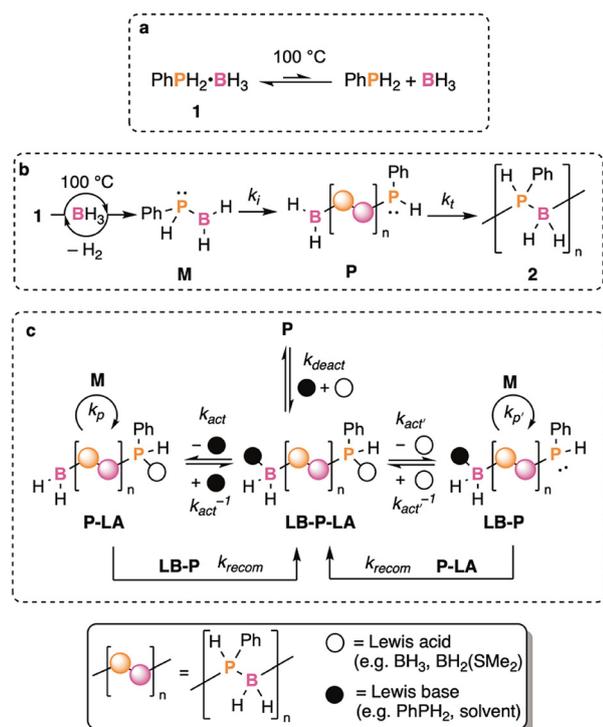

Fig. 3 Conversion *vs.* M_n plot using LiOTf and BH$_3$·SMe$_2$ additives. Dehydropolymerizations were performed as 2 M solutions of **1** in 2-MeTHF and heated to 100 °C for 0.15 to 24 h.

of isolated polymers. Accordingly, an isolated sample of **2** of moderate molecular weight (M_n = 57 740 g mol^{-1}, Đ = 1.65, from Table S1 entry 24†) was dissolved in a minimal amount of 2-MeTHF and the resulting solution was transferred to a J. Young's NMR tube. This tube was then sealed and heated to 100 °C for 24 hours. Afterwards, the resulting polymeric material was isolated as described above and analysed by ^{31}P NMR spectroscopy and GPC. Analysis of the ^{31}P and ^{31}P{^{1}H} NMR spectra revealed that only the peak for linear polymeric **2** was present, and no peaks indicative of branching points were observed (Fig. S8†). Then, examination of the GPC chromatogram revealed that the polymerization did continue, resulting in the formation of a material of a higher molar mass, but with a higher dispersity (M_n = 149 420 g mol^{-1}, Đ = 2.40) (Fig. S9†). Furthermore, the GPC trace revealed what appears to be a bimodal material, indicating that polymers with different end-groups undergo continued growth at different rates.

Based on our findings from the dehydropolymerizations of **1** in toluene and 2-MeTHF, along with time-dependent studies and end-group analyses of **2**, we propose the mechanism illustrated in Scheme 3. At elevated temperatures, a small amount of free borane (BH$_3$) is generated *in situ* through phosphine–borane cleavage (Scheme 3a). This free BH$_3$ acts as the dehydrogenation (pre)catalyst, facilitating the formation of phosphinoborane monomers (**M**). It is possible that borane-mediated dehydrogenation occurs *via* an initial hydride abstraction, followed by the formation of **M** with concomitant loss of H$_2$. Monomers can self-initiate (rate constant k_i) to form the active species **P**, or react with residual Lewis acid **LA** or Lewis base **LB** (Scheme 3b). Evidence for this mechanism includes the significantly faster polymerization rates observed when BH$_3$ (from BH$_3$·SMe$_2$) is added: >80% conversion of **1** is reached within 6 hours, and high molar mass, low-dispersity materials are formed within 3 hours. In contrast, polymerizations without added BH$_3$ (*e.g.*, those using LiOTf alone) achieve >80% conversion only after 6 hours, with high molar mass materials appearing at similar times. The active species (**P**) can undergo termination reactions (k_t) to produce **2**.

Thus, a potential role of the additive is in the stabilization of the growing chain **P**. From the polymerizations performed in toluene and 2-MeTHF, additives that had both Lewis acidic and basic components were required to access high molar mass materials (Fig. 1 and 2). Furthermore, ESI-MS of polymeric materials obtained using added BH$_3$·SMe$_2$ revealed the presence of oligomers with end groups corresponding to BH$_2$(SMe$_2$) (Fig. 4). Further, polymerizations performed in coordinating solvents accessed materials of higher molar mass than those performed in non-coordinating solvents (Fig. 2). Moreover, performing polymerizations in the presence of a strong Lewis acid (Sc(OTf)$_3$)[43] consistently resulted in

Fig. 4 ESI-MS positive mode spectrum of **1** prepared in 2-MeTHF in the presence of 5 mol% LiOTf (top) and BH$_3$·SMe$_2$ (bottom) over the range of 1300–1500 *m/z*. Orange boxes highlight the peak for [H[PhPH-BH$_2$]$_{10,11}$·PhPH$_2$]$^+$ and pink boxes highlight the peaks for [(BH$_2$(SMe$_2$))·[PhPH-BH$_2$]$_{9,10}$·PhPH-BH$_2$]$^+$.

Scheme 3 Proposed mechanism for the dehydropolymerization of phosphine–borane adducts at elevated temperatures with three distinct steps a, b, and c, as discussed in the main text.
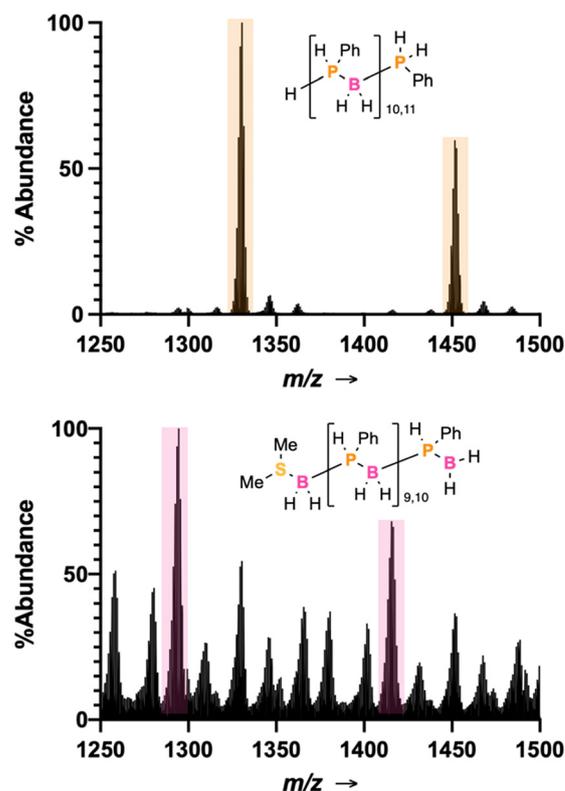
materials of relatively low molecular weights (Fig. 1 and 2). Therefore, we propose that the stabilization may be occurring through the reversible coordination of weak Lewis acids and weak Lewis bases to chain termini (Scheme 3c). This would allow for the attenuation of the reactivity of the growing oligomer chain, through accessing a chain-capped dormant species, **LB-P-LA**, allowing for reactions that compete with chain termination including cyclization reactions.[37] The dormant species, **LB-P-LA**, could release either **LB** or **LA** to access **P-LA** or **LB-P**. Either dissociation would result in the formation of an active species which can continue growth *via* addition polymerization through reactions with **M**. Furthermore, either **LB-P** or **P-LA** can readily recombine (k_{recom}) with either **LA** or **LB** to access the dormant species. However, reactions between **LB-P** and **P-LA** would also allow for the reformation of the dormant species coupled with an increase in the chain length. Moreover, the ability to favor the formation of the dormant species either through the choice of Lewis acid and Lewis base, or the loading of the chosen Lewis acid and Lewis base may allow for greater control over the polymerization of phosphinoboranes produced *in situ*. Similarly, the dissociation of borane has been shown to be relevant in the thermolytic and catalytic dehydropolymerization of linear aminoborane dimers[44] and in the spontaneous dehydrogenation of *N*-aryl substituted amine-boranes ($ArNH_2 \cdot BH_3$).[45] It should be noted that strong Lewis bases have been shown to depolymerize polyphosphinoboranes.[46] Thus, while the presence of Lewis bases may assist in chain growth in early stages of the polymerization, if they are too nucleophilic, they may result in the depolymerization of the resulting material. This mechanism is reminiscent of those postulated for quasi-living radical polymerizations.[47–50]

Molecular weight control using added $BH_3 \cdot SMe_2$

If the above mechanism were in operation, it may be possible to control the degree of polymerization as a greater concentration of Lewis base and Lewis acid *in situ* would favor dormant species and result in a material of lower molecular weight. Accordingly, 5 different loadings were explored (1 mol%, 2.5 mol%, 5 mol%, 7.5 mol%, and 10 mol%) of either LiOTf or $BH_3 \cdot SMe_2$, while maintaining a concentration of 2 M of **1** in 2-MeTHF. The dehydropolymerization reactions were performed at 100 °C over the course of 24 hours. Dehydrocoupling was determined to have occurred in each case and subsequent isolation of the materials resulted in moderate to good yields (50% to 74%). Analysis of the polymers produced with 1–10 mol% of LiOTf added revealed that while low loadings of LiOTf resulted in a material of higher molar mass, no real correlation between LiOTf loading and the obtained polymer molar mass could be observed at loadings at or greater than 5 mol%. However, polymerizations performed with added $BH_3 \cdot SMe_2$ revealed a clear relationship between loading and degree of polymerization across the conditions attempted (1–10 mol% of $BH_3 \cdot SMe_2$), obtaining materials over a wide mass range with similar dispersity (M_n = 83 120–57 740 g·mol^{-1}; Đ *ca.* 1.66; Fig. 5). This control over the
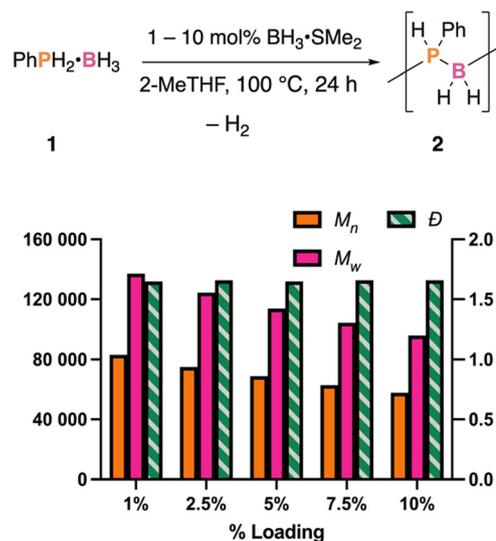

Fig. 5 Molar mass values (M_n and M_w, solid orange and pink bars) and dispersity (Đ, striped green bars) of isolated materials from the dehydropolymerization of **1** in 2-MeTHF with added $BH_3 \cdot SMe_2$.

resulting material further suggests that Lewis base and Lewis acid additives favor the formation of a dormant species, as proposed in Scheme 3.

Conclusions

We report the synthesis of high molar mass polyphosphinoboranes using commercially available reagents. We propose that thermal dehydropolymerization occurs in three major steps: adduct dissociation to give free borane, allowing for the second step where free borane acts as a (pre)catalyst for the dehydrogenation of **1**. The third phase is the polymerization step where reactive phosphinoboranes *in situ* catenate to yield linear chains that can then undergo termination events to yield polymeric materials. However, in the presence of additives, such as LiOTf or $BH_3 \cdot SMe_2$, phosphinoboranes and their chains can participate in Lewis acid base chemistry at either terminus, competing with termination events and allowing for further chain growth to access polymers. This approach allowed for the synthesis of high molar mass **2** from the dehydropolymerization of **1** in 2-MeTHF, where the presence of additives can afford control over the resulting materials, with $BH_3 \cdot SMe_2$ showing a clear relationship to M_n of the resulting material over a wide mass range (M_n = 57 740–83 120 g mol^{-1}). Overall, this work has implications for the field of phosphine–borane dehydropolymerization in that high molar mass materials can be accessed using readily available reagents. While the polymerizations reported here still operate under conditions typical of transition-metal catalyzed dehydropolymerization of phosphine-boranes, this work shows that transition metals are unnecessary in accessing high molar mass polyphosphinoboranes. Moreover, this work provides evidence for an alternative mechanism that may allow for greater

control over the addition polymerization of phosphinoborane monomers produced *in situ*.

Author contributions

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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