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# Transition-metal-free approaches to poly(aminoboranes) and poly(phosphinoboranes): mechanisms, advances, and future directions

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Poly(aminoboranes) and poly(phosphinoboranes) have been of interest as inorganic analogues of poly(olefins) as early as the mid-20th century. However, their synthesis was only realised about 15 and 25 years ago, respectively. Initially, poly(aminoboranes) and poly(phosphinoboranes) were accessed *via* transition-metal-catalysed dehydropolymerisation of amine- and phosphine-borane adducts. Despite the many advances made using this method, limitations remained, particularly in the conditions required for dehydropolymerisation and in the design of effective catalysts for producing materials with controlled molar mass and specific polymer architectures. Accordingly, new routes to these materials were sought through the synthesis of reactive aminoboranes or phosphinoboranes generated *in situ* for subsequent polymerisation. In doing so, materials that were previously inaccessible by metal-mediated dehydropolymerisation were unlocked. Mechanistically, there are fundamental differences between the transition-metal-catalysed approaches and transition-metal-free reactions with reactive monomers. Understanding and research of these new mechanisms are the foundation for the development of new polymer syntheses that allow for new polymer designs. This review article discusses the new design principles and polymer synthetic concepts.

## 1. Introduction

Whether naturally occurring or synthetic, polymer-based materials have played essential roles in our lives due to their

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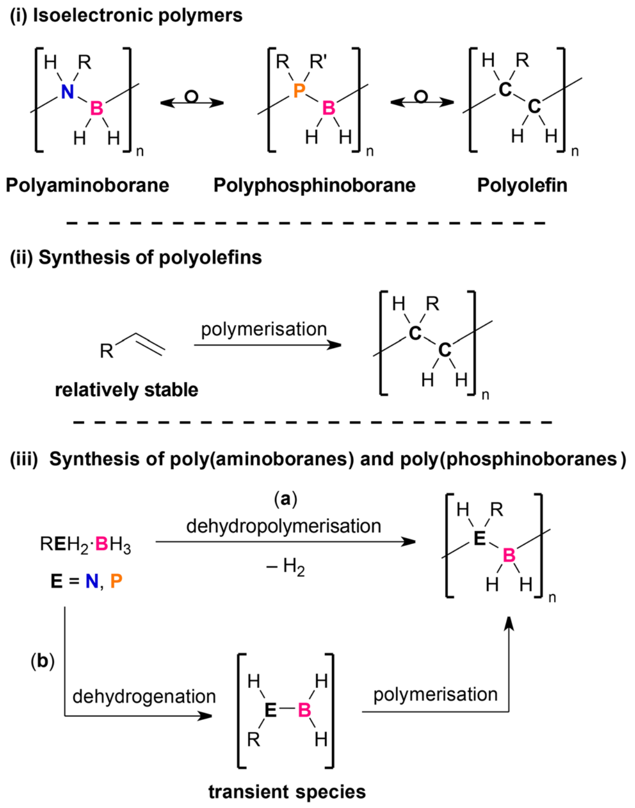
attractive material properties for thousands of years. For example, sinew, a material derived from animal tissue and comprised mostly of collagen,[1,2] has been and is used in crafting clothing, boats, tools, and ceremonial objects used by the Inuit and other Indigenous peoples.[3–5] Relatively recently (by comparison), a breakthrough in polymer materials was the industrialisation of poly(olefins) ($[RCH–CH_2]_n$).[6–8] These polymers, comprised of chains of carbon centres, have an undeniable impact on our lives, with more than 360 million tonnes being produced annually as of 2019.[9] However, the synthesis of polymers is not limited to those comprised of main chains of mostly carbon atoms. Inorganic polymers that incorporate other atoms into their monomer units are useful too,[10–16] such as poly(siloxanes) ($[R_2Si–O]_n$),[17] that can exhibit low temperature flexibility due to their inorganic main chain. Other inorganic polymers are poly(silanes) ($[R_2Si]_n$)[18–20] and poly(stannanes) ($[R_2Sn]_n$)[21,22] which are of interest as conducting materials, and poly(phosphazenes) ($[R_2P = N]_n$)[23–26] which are sought as bio-orthogonal components of block copolymers used in the formation of micelles for targeted drug delivery.



**Scheme 1** Overview of the structure (i) and synthesis of poly(olefins) (ii), and poly(aminoboranes) and poly(phosphinoboranes) (iii). Pathway (a) described the direct dehydropolymerisation typical of the transition-metal catalysed dehydropolymerisation of phosphine-borane adducts and pathway (b) describes two-step dehydropolymerisation where initially dehydrogenation of the precursor occurs, followed by polymerization of reactive species formed *in situ*, typical of the transition-metal catalysed dehydropolymerisation of amine-borane adducts.

Likewise, poly(aminoboranes) and poly(phosphinoboranes) are inorganic analogues of poly(olefins), where the monomer units $[RNH–BH_2]$ and $[RR'P–BH_2]$ are isoelectronic to the $[RCH–CH_2]$ units of poly(olefins) (Scheme 1i).[27–31] Naturally, a consequence of the different atoms that comprise the main chain of poly(olefins), (C–C), poly(aminoboranes), (N–B), and poly(phosphinoboranes), (P–B), is that bond properties are also different (*i.e.*, length and polarity) leading to varied material properties (*i.e.*, stability in air, thermal properties, and polymer tacticity, *etc.*). A comparison of such properties of the carbon-parent, poly(propylene) ($[MeCH–CH_2]_n$), along with poly(*N*-methylaminoborane) ($[MeNH–BH_2]_n$), and poly(*P*-methylphosphinoborane) ($[MePH–BH_2]_n$) is insightful, as it also immediately suggests under-researched areas in these inorganic polymers (Table 1).

Comparing across the series of bond lengths of polymer main chains and monomers, poly(olefins) and olefins have similar (Δ bond length < 0.10 Å) bond lengths to poly(aminoboranes) and aminoboranes. However, due to the presence of the larger, heavier phosphorus atom the bond lengths in poly(phosphinoboranes) and phosphinoborane monomers are sig-

**Table 1** Relevant properties of common poly(olefins), poly(aminoboranes), poly(phosphinoboranes), and their precursor monomers

| | $[MeCH–CH_2]_n$ | $MeCH{=}CH_2$ | $[MeNH–BH_2]_n$ | $MeNH{=}BH_2$ | $[MePH–BH_2]_n$ | $MePH–BH_2$ |
|---|---|---|---|---|---|---|
| E–E′ bond length (Å) | 1.54 (C–C)[a] | 1.34 (C–C)[a] | 1.63 (N–B)[a] | 1.38 (N–B)[a] | 1.98 (P–B)[a] | 1.78 (P–B)[b] |
| Δ bond Length (%) | −13% | — | −15% | — | −10% | — |
| Bond Polarity | Apolar | Apolar | Polar | Polar | Polar | Polar |
| Stable in air | Yes | Yes | Yes[c] | No | Yes | No |
| Tacticity | A/iso/syndio | — | Unknown | — | Unknown | — |
| Isolated | Yes | Yes | Yes | No | Yes | No |
| $T_m$ (°C) | 176 [43] | — | — | — | — | — |
| $T_g$ (°C) | −1 [43] | — | 70 [41] [d] | — | −24 [46] [e] | — |
| $T_{decomp}$ (°C)/(wt%) | 366 (2%)[47] | — | 159 (28%)[41] | — | 165 (5%)[46] | — |

[a] Bond length estimated using covalent single and double bond radii.[48–50] [b] As the nature of P–B multiple bonding largely depends on *P*- and *B*-substituents[36] the calculated bond length for $MePH–BH_2$ is given.[51] [c] Poly(*N*-methylaminoborane) has been previously reported to be unstable in air,[28] but a recent report states that poly(*N*-methylaminoborane) is stable in open air for at least six months as determined by nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC).[41] [d] Polymer obtained by the [Rh]-catalysed dehydrocoupling of $MeNH_2·BH_3$.[41] [e] Polymer obtained by the [Fe]-catalysed dehydropolymerisation of $MePH_2·BH_3$.[46] For poly(propylene), $T_m$, $T_g$, and $T_{decomp}$ values for isotactic poly(propylene) are given.[47,52,53]

nificantly (Δ bond length > 0.10 Å) larger in both the polymer and the precursor monomer. This longer bond length is reflected in the glass transition temperature ($T_g$) of the materials where $[MePH–BH_2]_n$ has the lowest $T_g$ of the series of materials. However, as reflected in the relatively high $T_g$ of $[MeNH–BH_2]_n$ (70 °C) compared to $[MeCH–CH_2]_n$ (−1 °C), there is more to consider than just bond lengths when considering $T_g$ of these polymers. However, upon polymerisation, the elongation of the E–E′ bond lengths between the monomers and the resulting polymers are all within 10–15%, with poly(phosphinoboranes) having the least drastic change in E–E′ bond length (10%), and poly(aminoboranes) having the most drastic change (15%).

Another stark difference between poly(olefins), poly(aminoboranes), and poly(phosphinoboranes) is the polarisation of the monomer unit. While the $[RCH–CH_2]$ units of the main chain of poly(olefins) are largely unpolarised, in poly(aminoboranes) and poly(phosphinoboranes), the monomeric units are polarised as a consequence of the alternating heteroatoms that comprise the polymer main-chain. This is due to the electronegativity of the atoms within the monomers with Pauling electronegativity values of $\chi_B = 2.04$, $\chi_N = 3.04$, and $\chi_P = 2.19$, polarising both B–N and B–P bonds towards the group 15 element centre. Further, the presence of the heteroatoms affects the π-bond of the precursor monomers, where the C–C π-bond is much more stable (*ca.* 65 kcal mol$^{-1}$)[32,33] than a N–B (*ca.* 30 kcal mol$^{-1}$)[34] π-bond by the bond enthalpy of the parent species (*i.e.* $H_2E–E'H_2$; E═E′═C or E═N and E′═B). For the parent phosphinoborane, $H_2P–BH_2$, which is non-planar due to the high barrier to inversion at the phosphorus centre (*ca.* 36.7 kcal mol$^{-1}$ for $PH_3$),[35–38] the bond enthalpy of the non-planar, ground state geometry is relatively low (*ca.* 6 kcal mol$^{-1}$).[35] However, comparing forced planar $H_2N–BH_2$ and $H_2P–BH_2$, yields bond rotation penalties of 43.2 and 40.4 kcal mol$^{-1}$, respectively.[35] Generally, the C–C π-bond is stronger than an N–B π-bond which stronger still over a P–B π-bond.[36,39] This is reflected in the ability to isolate the respective precursor monomers (if one presumes that in all cases this is the respective species with a double bond), where polymerisable olefins are generally bottleable and purchasable, but polymerisable aminoboranes and phosphinoboranes are not. However, all polymers are air-stable, where both poly(olefins) and poly(phosphinoboranes) are indefinitely stable.[40] Poly(aminoboranes) prepared *via* dehydropolymerisation using $[Rh(L)(NBD)Cl]$ (L = $(iPr_2PCH_2CH_2)_2NH$; NBD = norbornadiene) as a catalyst are air-stable for at least six months.[41] However, it should be noted that in some syntheses, poly(aminoboranes) are reported to be air-sensitive and are stored under inert conditions,[28,42] so their stability may be related to the presence (or lack thereof) of residual contaminants.

The bulk properties of polymeric materials arise, in part, from their molecular structures. One important property to consider is the positioning (stereochemistry) of the monomer units in the polymer with respect to one another, known as tacticity. Tacticity affects the thermodynamic properties such as the melting temperature, but also the solubility or mechanical parameters like stiffness. For poly(olefins), atactic, isotactic, and syndiotactic polymers can be produced, depending on how the monomers are incorporated into the growing polymer chain.[43] However, for poly(aminoboranes) and poly(phosphinoboranes) tacticity has mostly been invoked for explaining heteronuclear nuclear magnetic resonance (NMR) spectra. Specifically, broad $^{11}B$ and $^{13}C\{^1H\}$ NMR signals for poly(aminoboranes),[41,44] and broad $^{31}P$ NMR signals for heterotactic triads in poly(phosphinoboranes).[45,46] The synthesis and characterisation of a stereoregular poly(aminoborane) or poly(phosphinoborane) has not yet been realised. Further, to the best of our knowledge, all samples prepared of poly(aminoboranes) and poly(phosphinoboranes) are amorphous solids, indicated by the lack of melting temperatures observed in their differential scanning calorimetry traces.

In terms of thermal stability, poly(aminoboranes) are much less stable than poly(phosphinoboranes) and poly(olefins). In a sample of $[MeNH–BH_2]_n$ produced by Rh-catalysed dehydrocoupling, nearly 30% mass loss of $[MeNH–BH_2]_n$ had occurred by 159 °C by thermal gravimetric analysis (TGA).[41] However, for the comparable poly(phosphinoborane), $[MePH–BH_2]_n$, only 5% mass loss has occurred at 160 °C,[46] and for poly(propylene), $[MeCH–CH_2]_n$, less than 5% mass loss occurred by 366 °C.[47]

Accordingly, the applications of these inorganic polymers are distinct from their organic counterparts. While polyolefins are typically used as container or structural materials, poly(aminoboranes) and poly(phosphinoboranes) have (potential) uses related to their inorganic main chain. For example, poly(aminoboranes) have been proposed as polymers for piezoelectric thin films due to their intrinsically asymmetric polymer main-chain, where for a poly(olefin) to be used in the same manner, monomer polarity would have to be introduced *via* fluorinated substituents.[54] Similarly, poly(phosphinoboranes) have been sought as flame retardants due to their ability to self-extinguish upon combustion as a result of their high phosphorus and boron content.[55,56] In contrast, for flame retardancy to be introduced to poly(olefins), high loadings of additives are needed.[57]

Just as the applications of poly(aminoboranes) and poly(phosphinoboranes) differ from poly(olefins), so does their synthesis. While olefin monomers are typically stable enough to be isolated and used directly to access a poly(olefin) (Scheme 1ii), the same is impossible for poly(aminoboranes) and poly(phosphinoboranes). Therefore, instead, these inorganic polymers are generally accessed through the metal-mediated dehydropolymerisation of either the precursor amine- or phosphine-borane adduct, which has been reviewed in detail (Scheme 1iii).[30,31,58] Mechanistically, the metal-catalysed dehydropolymerisation of phosphine-borane adducts differs from that of amine-borane adducts. For phosphine-boranes, both dehydrogenation and P–B coupling events occur on-metal within their catalytic cycles (route a). However, for amine-borane adducts, a dehydrogenative catalytic cycle generates transient aminoboranes *in situ*, which then undergo polymerisation (route b).

Alternatively, in the past decade, transition-metal-free routes to these polymers have been described, but have yet to be thoroughly reviewed. Generally, these routes target the generation of reactive aminoboranes or phosphinoboranes in solution, which then polymerize. Accordingly, this review focuses on the advances made in the metal-free synthesis of poly(aminoboranes) and poly(phosphinoboranes). Finally, we briefly draw on the commonality in the findings of the studies and share our views on the challenges and opportunities within the field.

## 2. Synthesis of poly(aminoboranes)

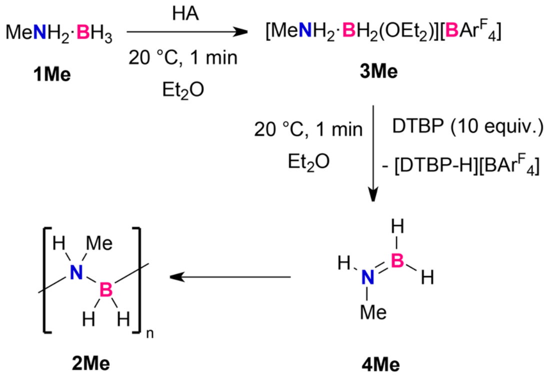
### 2.1 Overview of metal-mediated dehydropolymerisation

In a breakthrough report from 2008, an iridium pincer complex, (POCOP)IrH$_2$, was shown to catalyse the dehydropolymerisation of amine-borane adducts (**1R:** RNH$_2$·BH$_3$, R = Me, iPr) to high molecular weight ($M_w$ = 47–405 kg mol$^{-1}$), soluble poly(aminoboranes) (**2R:** [RNH–BH$_2$]$_n$, R = Me, iPr).[59] These reactions were performed under ambient conditions (0–20 °C, 0.25–1 h). Much has since been achieved in the catalytic amine-borane dehydropolymerisation, where a library of transition metal catalysts has been established.[31,42] Early transition metal catalysts have allowed for the synthesis of polymers with organic groups containing C(sp$^2$)–X (X = Cl, Br) bonds, but require the generation of reactive Ti(III) species.[42,60] Recently, the Weller group showed that high molecular weight poly(aminoboranes) can be synthesised on scale in open air, with controlled molecular weight values when using the late-transition-metal dehydropolymerisation catalyst, [Rh(L)(NBD)]Cl (L = κ$^3$-(iPr$_2$PCH$_2$CH$_2$)$_2$N, NBD = norbornadiene).[41] Many other catalysts have been synthesised and the field of metal-mediated amine-borane dehydropolymerisation has been recently reviewed.[28–31]

### 2.2 Metal-free generation of reactive aminoboranes *in situ*

The metal-free dehydropolymerisation of amine-borane adducts was not realised until 2014. Metal-free strategies to these materials rely on the generation of reactive aminoboranes *in situ* which then undergo polymerisation.

**2.2.1 Deprotonation of amine-boronium salts.** In 2014, the Manners group reported on the deprotonation of amine-boronium salts (**3Me**; [MeNH$_2$·BH$_2$(OEt$_2$)][BAr$^F{}_4$] Ar$^F$ = 1,3-bis(trifluoromethyl)phenyl) to access reactive aminoboranes *in situ* (Scheme 2). These intermediary aminoboranes (**3Me**; MeNH=BH$_2$) then undergo polymerisation.[61] Immediate measurement of a $^{11}$B NMR spectra obtained of the reaction mixture between [MeNH$_2$·BH$_2$(OEt$_2$)][BAr$^F{}_4$] and an excess of 2,6-di-*tert*-butylpyridine in a cooled (−10 °C) NMR spectrometer revealed a triplet ($^1J_{BH}$ = 130 Hz) at 37.1 ppm, indicative of the presence of free aminoborane (MeNH=BH$_2$). This assignment was based on similar $^{11}$B NMR signals observed for the closely related Me$_2$N=BH$_2$.[62,63] Further evidence for the generation of free aminoborane in solution was obtained through a trapping reaction with cyclohexene, where a small fraction of MeNH=BCy$_2$ was obtained as evidenced by an $^{11}$B NMR spectrum of the reaction product (MeNH=BCy$_2$; $\delta$($^{11}$B): 45.4 ppm). Characterisation of the polymeric materials obtained using gel-permeation chromatography (GPC) and dynamic light scattering (DLS) revealed that only low molar mass material was obtained ($M_n \leq 5$ kg mol$^{-1}$). Further analysis of the polymeric materials using negative mode electrospray ionisation mass spectrometry (ESI-MS) revealed that the major product was linear poly(aminoborane) (**4Me**) with amine end caps (MeNH$_2$–[BH$_2$–MeNH]$_x$–H ($x \leq 49$)), but a small amount of cyclic oligomers ((MeNH–BH$_2$)$_x$) were also detected. Despite only accessing relatively low molecular weight materials, this work showed that, upon generation, reactive aminoboranes themselves could undergo polymerisation into soluble poly(aminoboranes).

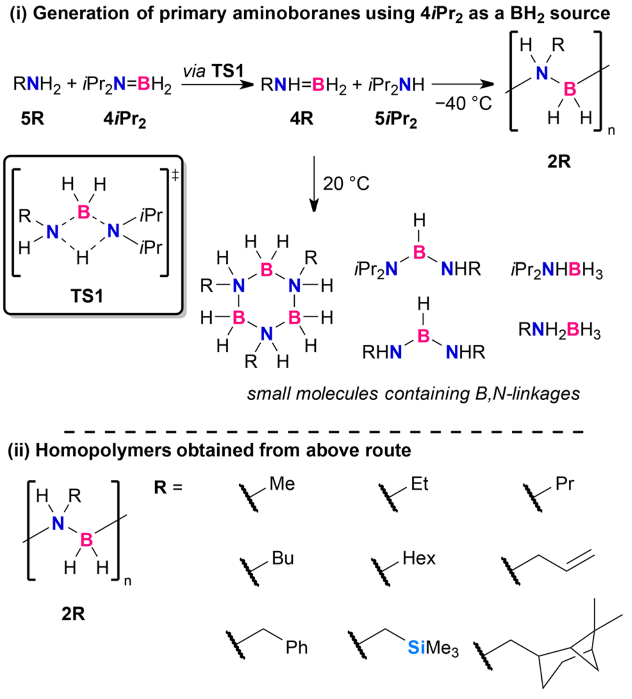


**HA** = Brookhart's Acid ([BAr$^F{}_4$][H(OEt$_2$)$_2$]);
**Ar$^F$** = 2,6-bis(trifluoromethyl)phenyl; **DTBP** = 2,6-di-*tert*-butylpyridine

Scheme 2 Synthesis of poly(aminoboranes) through the deprotonation of an amine-boronium salt.

**2.2.2 *N*,*N*-Diisopropylaminoborane as a "BH$_2$" source.** In 2017, the Alcaraz group discovered that the reaction between iPr$_2$N=BH$_2$ (**4iPr$_2$**) and primary amines (**5R:** RNH$_2$) resulted in the formation of poly(aminoboranes) (**2R:** [RNH–BH$_2$]$_n$) and *N*,*N*-diisopropylamine (**5iPr$_2$**) (Fig. 1i). This was shown to work for several *N*-alkyl amines including *N*-allylamine (**5R:** RNH$_2$; R = Me, Et, Pr, Bu, allyl). Further, random copolymers were accessed through simultaneous generation of both aminoboranes *in situ* ([EtNH–BH$_2$]$_n$-*r*-[RNH–BH$_2$]$_n$; R = Bu, Pr). Additionally, as this reaction is performed in neat conditions and at low temperatures, polymers of extremely high molecular weight ($M_w \leq$ 5 450 kg mol$^{-1}$, $Đ$ = 6.9) could be obtained. Characterisation of homopolymeric materials by negative mode ESI-MS revealed oligomers corresponding to RNH$_2$–[BH$_2$–RNH]$_x$–H and RNH$_2$BH$_2$–(RNH–BH$_2$)$_x$–H (R = Me, Et, Pr, Bu, allyl).

The Alcaraz group later reported further on this transformation, elaborating on its mechanism.[44] In a theoretical study they confirmed that the BH$_2$ transfer is preceded by primary amine coordination of the borane of iPr$_2$N=BH$_2$, and a N-to-N


(i) Generation of primary aminoboranes using 4*i*Pr₂ as a BH₂ source

(ii) Homopolymers obtained from above route

Fig. 1 (i) Synthesis of poly(aminoboranes) from primary amines and *N*,*N*-diisopropylaminoborane and (ii) scope of poly(aminoboranes) accessed through this method.

hydrogen transfer yields diisopropylamine and the target aminoborane. Then, the reaction outcome is dictated by reaction temperature.[44] Above −40 °C, the barrier for the generation of small molecules containing N,B-linkages is overcome, and the aminoborane molecules necessary for the formation of polymer are consumed. However, at or below −40 °C, aminoborane monomers can be initiated by free amine in solution, and subsequently undergo head-to-tail addition polymerisation, producing poly(aminoboranes) of very high molecular weights.

The authors also expanded the scope of accessible poly(aminoboranes) through this route to include alkyl groups with benzyl, trimethylsilyl ($SiMe_3$), *n*-hexyl, and the bicyclic-alkyl (mertanyl) functional groups (Fig. 1ii). Thus, through careful choice of reaction conditions, high-molecular weight poly(aminoboranes) with a wide variety of *N*-substituents can be accessed without the presence of transition-metal-based impurities.

## 3. Synthesis of poly(phosphinoboranes)

### 3.1 Overview of metal-mediated dehydropolymerisation

Compared to metal-catalysed amine-borane dehydropolymerisation, which generally occurs under mild reaction conditions (20 °C, <4 h), metal-catalysed phosphine-borane dehydropolymerisation requires high reaction temperatures (≥100 °C) and relatively long reaction times (≥16 h). In 1999, the Manners group reported the rhodium-catalysed dehydropolymerisation of *P*-phenylphosphine-borane (**6Ph**, $PhPH_2{\cdot}BH_3$).[64] Here, the phosphine-borane adduct precursor was heated to 130 °C with added catalytic $[RhCODClOTf]_2$ in the absence of a solvent. To determine the completion of the reaction, $^{31}P$ NMR spectra of the reaction products was used. For the starting material, $PhPH_2{\cdot}BH_3$ (**6Ph**), a triplet is observed at −47 ppm ($J_{PH}$ = 372 Hz)[65] but the dehydrogenated product instead gives a broad doublet at −49 ppm ($J_{PH}$ = 372 Hz). As the chemical shift values are very similar, the product is most readily distinguished by its signal pattern, rather than by its chemical shift value. This catalysed reaction resulted in the formation of high molecular weight material (**7Ph**, $[PhPH–BH_2]_n$; $M_w$ = 31 kg $mol^{-1}$) as determined by static light scattering.[64]

Since then, other metal-based phosphine-borane dehydropolymerisation catalysts based on iron,[66,67] rhodium,[68–70] and iridium[71] centres have been reported. However, these catalysts high temperatures and long reaction times to produce high molar mass polymers (≥90 °C, ≥16 h). Alternatively, the titanium-catalysed polymerisation of a trimethylamine-stabilised phosphanylborane (**8*t*Bu**, $tBuPH–BH_2{\cdot}NMe_3$) was recently reported, which occurs under ambient conditions.[72] However, this reaction has not produced polymers other than $[tBuPH–BH_2]_n$. The field of transition-metal-mediated phosphine-borane dehydropolymerisation has been recently reviewed.[30,58]

### 3.2 Metal-free synthesis of poly(phosphinoboranes)

As a point of reference, purely thermal phosphine-borane dehydrocoupling can be considered, which is both metal-free and free of any other additive. In such a reaction, phosphine-borane adducts are heated at or above 150 °C, resulting in loss of hydrogen and formation of P–B bonds to access cyclic and oligomeric materials.[73,74] Later, in 2003 Gaumont and coworkers reported the ambient condition dehydrogenative coupling of P–B bonds using tris(pentafluorophenyl)borane, accessing low molecular weight materials ($M_n \leq 3$ kg $mol^{-1}$).[75] However, only recently high molecular weight poly(phosphinoboranes) were synthesised without relying on metal-mediated dehydropolymerisation.

#### 3.2.1 Stoichiometric routes

*3.2.1.1 Polymerisation of phosphanylboranes.* It was not until 2015 that high molecular weight poly(phosphinoboranes) were synthesised without relying on transition-metal-mediated dehydropolymerisation. This advancement built on earlier work from the Scheer group, where they had accessed the trimethylamine-stabilised parent phosphanylborane ($H_2P–BH_2(NMe_3)$).[76] They proposed that, upon release of trimethylamine from the stabilised phosphanylborane, reactive phosphinoboranes (**9R**: $RPH–BH_2$) are produced *in situ*. Thus, in a collaboration between the Scheer and Manners groups, a trimethylamine-stabilised *P*-tert-butylphosphanylborane (**8*t*Bu**, $tBuPH–BH_2(NMe_3)$) was prepared, and then polymerised (Fig. 3, route A).[45] The polymerisations were performed at relatively mild conditions (22–40 °C, 48 h). The authors were able to synthesise high molar mass $[tBuPH–BH_2]_n$ (**7*t*Bu**), as determined by GPC ($M_n$ = 35 kg $mol^{-1}$; $Đ$ = 1.6). Later, the scope of phosphanylboranes was expanded to include other alkyl groups ($\text{RPH–BH}_2(\text{NMe}_3)$, R = Me, Bu), but polymerisation attempts yielded at most oligomeric materials as determined by ESI-MS (2400 Da).[77] End group analysis of $[t\text{BuPH–BH}_2]_n$ (**7*t*Bu**) by negative mode ESI-MS revealed that the materials had Lewis bases incorporated into the polymer end groups, having identified a series of peaks consistent with $\text{Me}_3\text{N·BH}_2\text{–}[t\text{BuPH–BH}_2]_x\text{–NMe}_3$ (Fig. 3ii).[72] The ability to produce poly(phosphinoboranes) from phosphanylboranes showed that, similar to poly(aminoboranes), transient phosphinoboranes formed *in situ* can themselves polymerize.

*3.2.1.2 Dehydropolymerisation of phosphine-borane adducts using cyclic (alkyl)(amino)carbenes as $H_2$-acceptors.* *P*-Disubstituted poly(phosphinoboranes) are of interest as materials as it is predicted they are more robust than *P*-monosubstituted polymers owing to the lack of P–H bonds in the former material. Attempts to access disubstituted material through the dehydropolymerisation of *P*-disubstituted phosphine-borane adducts instead result in either the formation of small cyclic oligomers $(\text{R}_2\text{P–BH}_2)_x$ ($x$ = 3, 4), or the formation of linear dimers ($\text{R}_2\text{PH·BH}_2\text{–R}_2\text{P·BH}_3$).[30] *P*-Disubstituted poly(phosphinoboranes) have been accessed *via* post-polymerisation functionalisation through hydrophosphination reactions between the P–H bonds of $[\text{PhPH–BH}_2]_n$ and olefinic substrates.[78] However, this reaction also resulted in the drastic reduction of molecular weight when complete functionalisation of P–H bonds was attempted.

The synthesis of *P*-disubstituted poly(phosphinoboranes) directly from *P*-disubstituted phosphine-borane adducts was not realised until 2019. In this report, the Manners group used cyclic (alkyl)(amino)carbenes to accept $H_2$ from phosphine-borane adducts. This method leveraged the ambiphilic nature of the carbenoid carbon of cyclic (alkyl)(amino)carbenes (CAACs), which possess both strong Lewis basicity (through the occupied $sp^2$ orbital) and Lewis acidity (from empty $p_z$ orbital) (Fig. 2).[79,80] Here, an initial reaction between CAAC and phosphine borane (**8R**, $\text{PhRPH·BH}_3$, R = H, Ph, Et) results in the insertion of the carbene carbon into the P–H bond, producing **10R** (Fig. 3, route B).[81] Then, at elevated temperature (60 °C), cleavage of the $\text{C}_{\text{CAAC}}\text{–P}$ bond occurs, generating a charge separated reactive carbenium phosphanylborane salt, $[\text{CAAC–H}][\text{PhRP–BH}_3]$. The carbenium ion then abstracts a hydridic hydrogen atom from the phosphanylborane, generating $\text{CAAC–H}_2$ and the requisite phosphinoborane (**9Ph(R)**, $\text{PhRP–BH}_2$). The phosphinoborane then undergoes head-to-tail addition polymerisation to produce poly(phosphinoboranes).

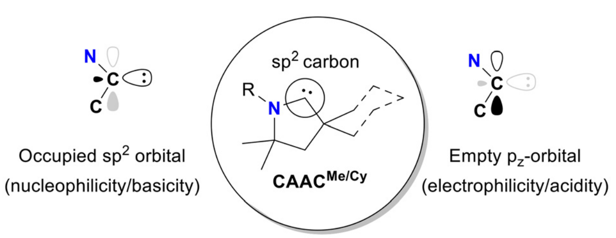


**Fig. 2** Structure of cyclic (alkyl)(amino)carbenes relevant to this review, and the orbitals allowing for ambiphilicity at the carbene carbon centre.

Characterisation of the materials obtained by the CAAC-mediated dehydrocoupling of phosphine-borane adducts was performed using NMR and GPC.[81] By $^{31}$P and $^{11}$B NMR, $[\text{PhPH–BH}_2]_n$ (**7Ph**) generated by this route was indistinguishable from polymers generated by previously established methods. However, the new *P*-disubstituted materials, $[\text{Ph}_2\text{P–BH}_2]_n$ (**7Ph$_2$**) and $[\text{Ph(Et)P–BH}_2]_n$ (**7PhEt**) gave broad singlets at −16.6 ppm and −21.5 ppm in their $^{31}$P spectra, consistent with a lack of P–H bonds, and broad signals at −30.2 ppm and −32.8 ppm in their $^{11}$B spectra, respectively.[81] Inspection of the GPC chromatograms of the isolated materials revealed that the materials had bimodal mass distributions despite repeated precipitations. For the optimised reactions, the following data were provided for the high molar mass fraction of polymer samples of $[\text{PhRP–BH}_2]_n$ (**7Ph(R)**): R = H; $M_n$ = 83 kg mol$^{-1}$ $Đ$ = 1.14, R = Ph; $M_n$ = 60 kg mol$^{-1}$ $Đ$ = 1.08, and R = Et; $M_n$ = 62 kg mol$^{-1}$ $Đ$ = 1.19.[81] Although for the *P*-disubstituted polymers, the fraction of high molar mass material was limited (only *ca.* 10–12% by GPC), the ability to access these materials was a significant breakthrough.

Further insight into the polymer structure came from ESI-MS, which assisted in identifying end-groups. Positive mode ESI-MS revealed series of peaks consistent with phosphine capped oligomeric chains ($\text{H–}[\text{PhPH–BH}_2]_n\text{–PPhH}_2$), or CAAC-capped chains ($\text{H–}[\text{PhRP–BH}_2]_n\text{–CAAC}$) (Fig. 4ii). These data implicate CAAC in a role beyond dehydrogenation, suggesting that it is involved in the linear chain growth of polymeric material. This could help explain why polymerisation occurs in the CAAC mediated route, and not in other dehydrogenations of *P*-disubstituted phosphine-borane adducts. Moreover, reactive phosphinoboranes were trapped through a reaction between 2 equivalents of CAAC with $\text{R}_2\text{PH·BH}_3$ (R = *t*Bu or Mes), accessing $\text{R}_2\text{P–BH}_2(\text{CAAC})$ and supporting transient phosphinoboranes as intermediates.[81] Thus, the authors reported that Lewis acids or bases present *in situ* mediate the polymerisation through complexation of either termini of the phosphinoborane monomer or short oligomers. Such complexation prevents cyclisation reactions that typically produce low molar mass material, allowing for growth into high molar mass linear material (Fig. 3iii).

*3.2.1.3 Deprotonation of phosphine-(triflimido)boranes.* The generation of phosphinoborane monomers *in situ* was also targeted *via* salt elimination reactions from phosphine-(triflimido)borane adducts ($\text{PhRPH·BH}_2(\text{NTf}_2)$; **11Ph(R)**) (Fig. 3, route C).[82] These adducts were synthesised in high yields through a reaction between $\text{HNTf}_2$ and phosphine-borane (**6**, $\text{RR'PH·BH}_3$). Their subsequent deprotonation was possible using Hünig's base ($\text{iPr}_2\text{EtN}$) or N-heterocyclic carbenes (NHCs) as the Brønsted base.

The result of the deprotonation was shown to be significantly impacted by the choice of base. When Hünig's base was used to deprotonate phosphine-(triflimido)boranes, only *P*-monosubstituted polymer $(\text{PhPH–BH}_2)_n$ was obtained as

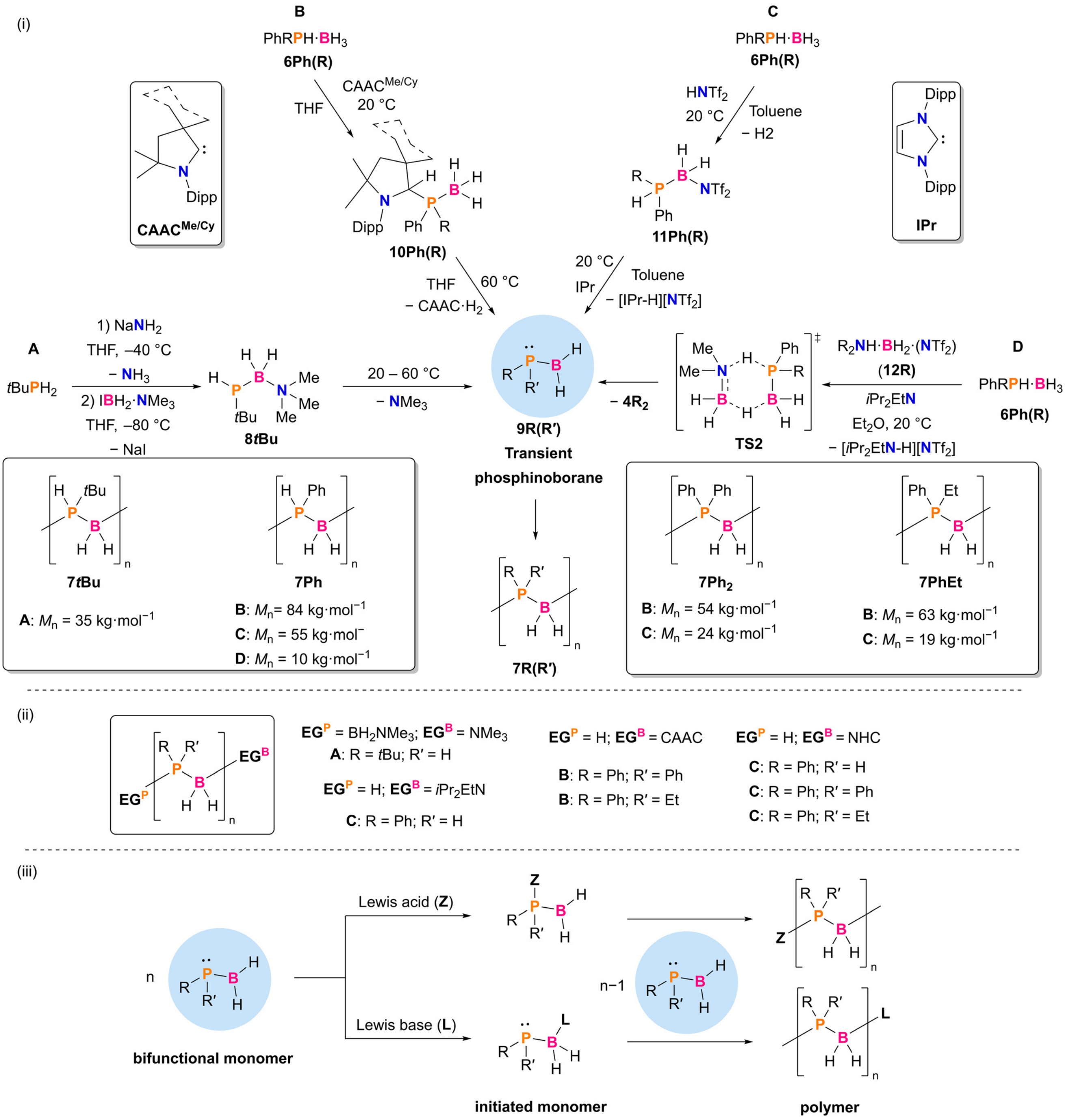


**Fig. 3** An overview of the synthesis of poly(phosphinoboranes) *via* the synthesis of phosphinoborane monomers *in situ* through stoichiometric reactions. (i) The four pathways to yield poly(phosphinoboranes) through the synthesis of phosphinoborane monomers are given. Pathway A depicts the synthesis of *t*BuPH–$BH_2(NMe_3)$ and its subsequent polymerisation *via* thermally driven cleavage of the B–N bond.[45] Pathway B depicts the dehydropolymerisation of phosphine-borane adducts using CAACs, showing the initial P–H bond insertion reaction, followed by the generation of phosphinoborane and CAAC-$H_2$.[81] Pathway C depicts the synthesis of phosphine-(triflimido)borane adducts, followed by their deprotonation to access poly(phosphinoboranes). Pathway D depicts the reaction between aminoboranes and phosphine-borane adducts to result in the formation of phosphinoboranes and amine-borane adducts.[83] (ii) The end groups observed by ESI-MS in the isolated polymer materials from the four pathways are given. Below each set the substituents at phosphorus are indicated for routes A–C. (iii) The proposed mechanism[81,82] for the polymerisation of phosphinoboranes generated *in situ*, where Lewis acids or Lewis bases can coordinate chain ends to suppress the formation of low molecular weight materials and yield high molar mass products.

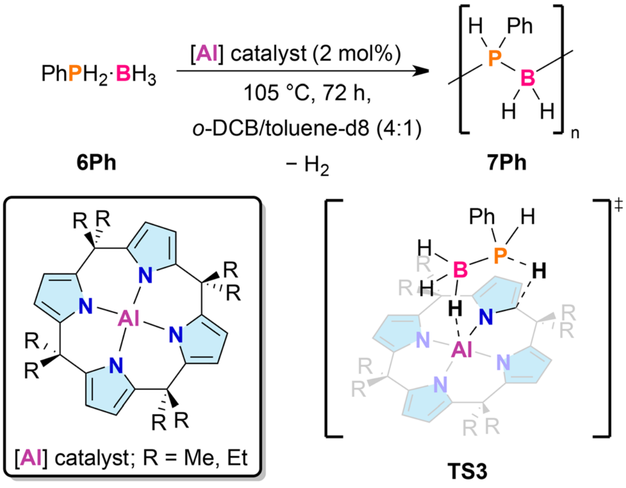


Fig. 4 Dehydropolymerisation of $PhPH_2{\cdot}BH_3$ using calix[4]pyrrolato aluminate as a catalyst. The proposed intermediate where P–H bond is acidified *via* a B–H–Al interaction (**TS3**) is also shown.

determined by NMR spectroscopy and GPC. Further, analysis of the GPC chromatograms revealed that the material had a bimodal mass distribution, where most of the product was of low molar mass (*ca.* 30% high molar mass material). Attempted polymerisation of *P*-disubstituted phosphinoboranes using Hünig's base instead results in the formation of what was tentatively assigned as Lewis base capped linear dimers ($PhPH_2{\cdot}BH_2$–PhPH–$BH_2$(L); L = $iPr_2EtN$, H, $NTf_2$) based on heteronuclear NMR spectra that were similar to known dimers (PhRPH·$BH_2$–PhRP–$BH_3$, R = Ph, Et).[40,81]

When an N-heterocyclic carbene was used as the base for deprotonation of phosphine-(triflimido)boranes, *P*-disubstituted polymers were obtained. Characterisation of all polymers produced by NMR spectroscopy resulted in the materials indistinguishable by earlier studies.[81] However, comparing the GPC traces from the materials obtained from deprotonations using NHCs revealed that the materials obtained had a high fraction (≥50%) of high molar mass material. As both Hünig's base and NHCs are sufficiently basic to deprotonate phosphine-(triflimido)boranes, the ability to access *P*-disubstituted polymers only with NHCs implies that the base also has a role in the addition polymerisation of phosphinoborane monomers. This was further supported by end-group characterisation using ESI-MS, where NHCs were observed as end-groups (*i.e.* H–$[PhRP–BH_2]_n$–NHC, R = H, Ph, Et) in isolated polymer samples (Fig. 3ii). Similar to the CAAC-mediated route, the authors were able to trap a reactive phosphinoborane through the reaction of two equivalents of NHC with $tBu_2PH{\cdot}BH_2(NTf_2)$, generating $tBu_2P–BH_2$(NHC).[82] Therefore, this study cemented that to access *P*-disubstituted polymers, the generation of *P*-disubstituted phosphinoboranes *in situ* cannot be the only requirement for accessing their polymers.

*3.2.1.4 Dehydropolymerisation of phosphine-borane adducts using aminoboranes as $H_2$-acceptors.* A significant challenge in the dehydropolymerisation of phosphine-borane adducts has been the requirement for the harsh conditions. The other methods described above require either the synthesis of specialised phosphinoborane precursors, or are still rather inefficient transformations from the perspective of atom economy. Recently, however, a strategy using reactive aminoboranes to accept hydrogen from phosphine-borane adducts has been introduced, which occurs under ambient conditions.[83]

This development built upon earlier work from the Manners group, in which amine-borane adducts were shown to undergo hydrogen transfer reactions with *N*,*N*-diisopropylaminoborane (**4iPr₂**).[84,85] In this process, **4iPr₂** accepts hydrogen from *N*,*N*-dimethylamine-borane through a six-membered transition state involving a stepwise, concerted N-to-N and B-to-B hydrogen transfer. Computational studies determined that the hydrogen transfer from *N*,*N*-dimethylamine-borane to **4iPr₂** is endergonic, but the overall reaction is driven forward by the dimerisation of the reactive *N*,*N*-dimethylaminoborane formed in solution.

Motivated by these findings, similar hydrogen transfer reactions were explored between reactive aminoboranes and phosphine-borane adducts.[83] These studies showed that only sufficiently reactive aminoboranes accepted hydrogen from phosphine-borane adducts, as **4iPr₂** was shown to be unreactive. However, generation of *N*,*N*-dimethylaminoborane (**4Et₂**) or *N*,*N*-diethylaminoborane (**4Me₂**) in solution by the deprotonation of their respective amine-(triflimido)boranes (**12R₂**, R = Me or Et) enabled the dehydrocoupling of $PhPH_2{\cdot}BH_3$ (**6Ph**) or $Ph_2PH{\cdot}BH_3$ (**6Ph₂**). These reactions afforded either $[PhPH–BH_2]_n$ (**7Ph**) or $Ph_2PH{\cdot}BH_2–Ph_2P{\cdot}BH_3$ under ambient conditions (20 °C, ≤24 h) (Fig. 3, route D). However, the polymer produced was of modest molar mass ($M_n$ = 10 kg $mol^{-1}$, $Đ$ = 1.6). A computational study suggested the hydrogen follows an analogous six-membered transition state to that observed for amine-borane adducts, proceeding *via* P-to-N and B-to-B hydrogen transfer (Fig. 3, **TS2**). Importantly, this transformation represents the first example of the direct dehydrogenation of phosphine-borane adducts under ambient conditions.

### 3.2.2 Sub-stoichiometric routes

*3.2.2.1. Dehydropolymerisation of phosphine-borane adducts using an aluminate catalyst.* Calix[4]pyrrolato aluminate has recently gained attention as a main-group-element-centred Lewis acidic anion that has unique reactivity due to its square planar coordinative environment. This environment allows for aluminum-ligand interactions with polar substrates such as carbon monoxide (CO) and carbon dioxide ($CO_2$).[86,87] In a recent collaboration between the Manners and Greb groups, calix[4]pyrrolato aluminate was shown to catalyse the dehydropolymerisation of *P*-phenylphosphine-borane.[88] This was achieved under similar conditions explored for metal-mediated catalytic dehydropolymerisation of phosphine-borane adducts (%[Al] = 0.3–10 mol%, $t$ = 24–72 h, $T$ = 105 °C).[88] The materials obtained were of high molecular weight and had typical dispersity values for poly(phosphinoboranes) (**7Ph:** $M_n$ = 14–43 kg $mol^{-1}$; $Đ$ = 1.54–2.00). Thus, polymers with molecular weights and dispersity values matching those produced by metal-mediated catalysis could be produced, but instead using a main-group element centred catalyst.

Computational studies into the mechanism suggested that the aluminate species acidifies the P–H bond of the phosphine-borane adduct *via* aluminium binding of one of the hydride substituents on borane (Fig. 4, **TS3**), delivering a proton to 2-position of the pyrrole ring. The basic nature of the 2-position of the pyrrole in calix[4]pyrrolato aluminate was confirmed experimentally through reactions with either a sub-stoichiometric (0.6 eq.) of phosphine-borane adduct (**6Ph**) or a stoichiometric amount of $HNTf_2$, producing the protonated ligand still bound to aluminium.

*3.2.2.2. Thermal dehydropolymerisation in the presence of Lewis acid-base pairs.* The essential role of Lewis acid and Lewis base pairs in the dehydropolymerisation of phosphine-borane adducts was cemented in a recent study from the Manners group.[89] Here it was shown that high temperature dehydropolymerisation of $PhPH_2{\cdot}BH_3$ (**6Ph**) performed in the presence of sub-stoichiometric (5 mol%) LiOTf, $LiNTf_2$, $Mg(OTf)_2$, or $BH_3{\cdot}SMe_2$ performed as well as those performed with the state-of-the-art transition metal catalyst, $Cp(CO)_2FeOTf$ (Fig. 5i).[66] Further, phosphine-borane dehydropolymerisation was performed without any additives in 2-MeTHF, under normal catalytic dehydropolymerisation conditions (2 M, 100 °C, 24 h) to access high molar mass, low dispersity polymer (**7Ph**: $M_n = 81$ kg mol$^{-1}$, $Đ = 1.66$).

The ability to access high molar mass $[PhPH–BH_2]_n$ (**7Ph**) without any additives in 2-MeTHF, implies that all that is necessary to access high molar mass material exists either in the precursor phosphine-borane adduct, or 2-MeTHF. It is believed that a small amount of phosphine-borane dissociates *in situ* at elevated temperatures, providing both a Lewis acid (borane) and a Lewis base (phosphine, 2-MeTHF). Further, it was revealed that performing dehydropolymerisation reactions with added $BH_3{\cdot}SMe_2$, a source of $BH_3$, decreased the time needed for full dehydrogenation of $PhPH_2{\cdot}BH_3$ (**6Ph**), suggesting it is potentially involved in dehydrogenation as well. End-group analysis revealed polymers with $PhPH_2$ or $BH_2(SMe_2)$ end groups in positive mode-ESI (*i.e.*, $H–[PhPH–BH_2]_x–PPhH_2$ and $Me_2S{\cdot}BH_2–[PhPH–BH_2]_x–H$) and polymers with $BH_3$ end groups in negative mode-ESI (*i.e.*, $BH_3–[PhPH–BH_2]_x–H$) (Fig. 5ii). This supports the role of borane sources (*i.e.* $PhPH_2{\cdot}BH_3$ and $BH_3{\cdot}SMe_2$) in both the dehydrogenation and polymerisation steps.

On this basis, the authors proposed that monomers can either undergo a self-initiation and polymerisation, or, initiation *via* reactions with Lewis acids or Lewis bases *in situ* as depicted in Fig. 3(iii). In addition, reversible coordination

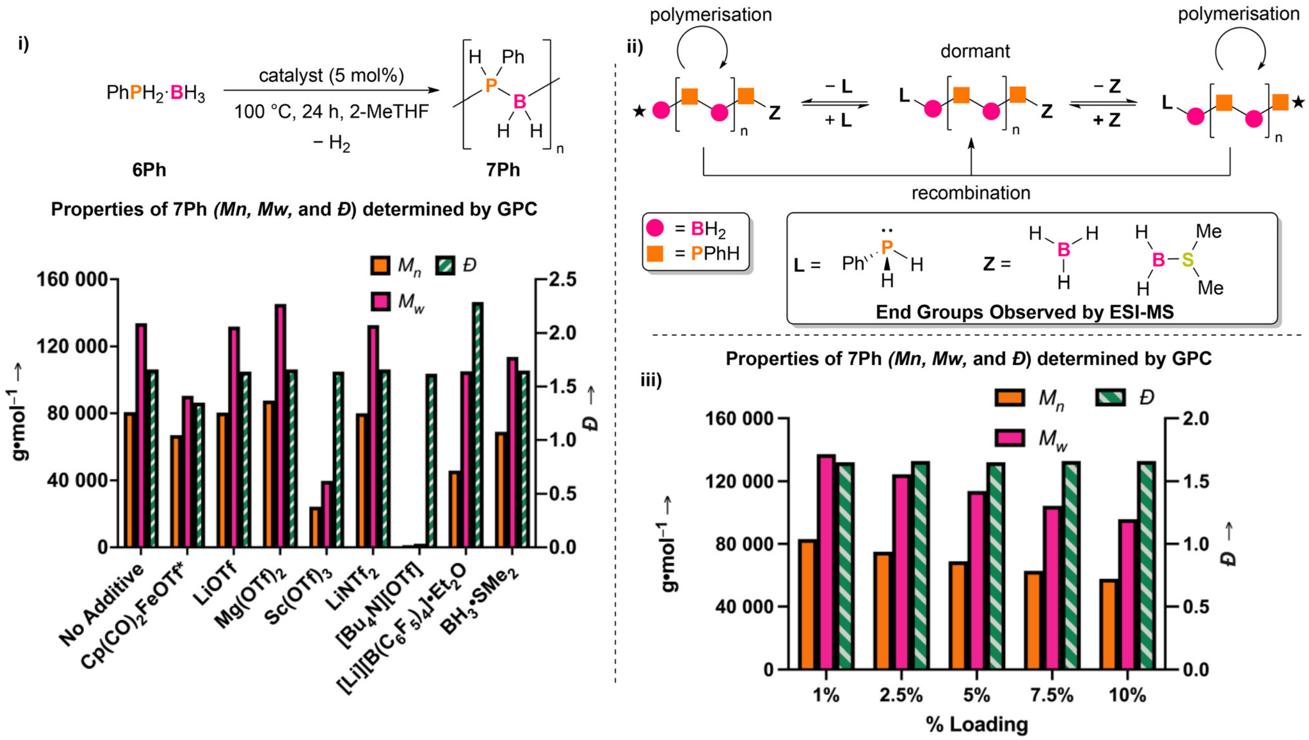


**Fig. 5** Overview of the thermal dehydropolymerisation of phosphine-borane adducts in the presence of Lewis acid-base pairs. (i) Synthesis of poly(phosphinoboranes) using commercially available salt additives in 2-MeTHF, where $M_n$, $M_w$, and $Đ$ values are plotted in a bar chart below.[89] *The value for $Cp(CO)_2FeOTf$ is given from a polymerisation performed in dioxane.[66] (ii) Mechanism for the polymerisation of phosphinoborane chains mediated by Lewis acids (*Z*) and Lewis bases (*L*) where reactive exposed termini are labelled with a 5-point star. (iii) Bar chart of $M_n$, $M_w$, and $Đ$ values obtained from the dehydropolymerisation of $PhPH_2{\cdot}BH_3$ with 1 to 10 mol% loading of $BH_3{\cdot}SMe_2$, with the same conditions as listed in (i). Bar charts shown in (i) and (iii) are reproduced from ref. 84 with permission from the Royal Society of Chemistry.

**Table 2** Summary of the synthetic routes to poly(aminoboranes) and poly(phosphinoboranes). Section numbers correspond to the more detailed discussions in-text

| Method (section) | Scope | Conditions | $M_n$ (kg mol$^{-1}$) and Đ | Features |
|---|---|---|---|---|
| **Synthesis of poly(aminoboranes)** | | | | |
| Transition-metal-free routes | | | | |
| Deprotonation of amine-boronium cations (2.2.1)[61] | $[MeNH–BH_2]_n$ | 1 min, 20 °C, $Et_2O$ (0.3 M) | $M_n \leq 5$<br>Đ = n/a | Rapid generation of aminoboranes; unexplored substrate scope |
| Reaction of primary amines with $iPr_2N{=}BH_2$ (2.2.2)[44,94] | $[RCH_2N–BH_2]_n$; R = H, alkyl, aryl, silyl, cycloalkyl | 2 h, −40 °C, neat | $M_n \leq 790$<br>Đ = 1.2–10.2 | Broad scope of nitrogen substituents |
| Transition-metal-catalysed dehydropolymerisation (selected examples) | | | | |
| Titanium-catalysed dehydropolymerisation (2.1)[42] | $[RNH–BH_2]_n$; R = Me, benzyl, allyl | 1 h, 20 °C, toluene (0.2 M), 4 mol% [Ti] | $M_n \leq 235$<br>Đ = 1.3–2.3 | Polymers accessed with *p*-halogenated benzylic *N*-substituents |
| Rhodium-catalysed dehydropolymerisation (2.1)[31] | $[MeNH–BH_2]_n$ | 0.5–2 h, 20 °C, THF (1–5 M), 0.01–1.0 mol% [Rh] | $M_n \leq 78$ [1]<br>Đ = 1.3–2.3 | Polymerization can be performed in open air; molar mass control through added $[BH_2(NMe_2H)_2]Cl$; unexplored substrate scope |
| **Synthesis of poly(phosphinoboranes)** | | | | |
| Transition-metal-free routes | | | | |
| *Using stoichiometric reagents* | | | | |
| Polymerization of *t*BuPH–$BH_2(NMe_3)$ (3.2.1.1)[45] | $[tBuPH–BH_2]_n$ | 48 h, 22–40 °C, neat or toluene (*ca.* 0.3 M) | $M_n \leq 35$<br>Đ = 1.6–1.9 | Limited to only $[tBuPH–BH_2]_n$ |
| Reaction of PhRPH·BH3 with CAAC (3.2.1.2)[81] | $[PhPR–BH_2]_n$; R = H, Ph, Et | 4 h, 20–110 °C, THF or toluene (0.1–2.5 M) | $M_n \leq 60$<br>Đ = 1.1–1.6 | *P*-Disubstituted material only at 60 °C; bimodal material isolated; small fraction (*ca.* 10%) of high $M_n$ polymer |
| Deprotonation of $PhRPH·BH_2(NTf_2)$ (3.2.1.3)[82] | $[PhPR–BH_2]_n$; R = H, Ph, Et | 4 h, 20 °C, toluene (2 M) | $M_n \leq 55$<br>Đ = 1.3–1.6 | Bimodal material isolated; large (≥50%) fraction of high $M_n$ polymer |
| Reaction of PhRPH·BH3 with aminoboranes (3.2.1.4)[83] | $[PhPH–BH_2]_2$ | 24 h, 20 °C, $Et_2O$ (2 M) | $M_n = 10$<br>Đ = 1.8 | Direct dehydrogenation of phosphine-borane adducts; unexplored substrate scope |
| *Using sub-stoichiometric reagents* | | | | |
| Aluminate-catalysed phosphine-borane dehydropolymerisation (3.2.2.1)[88] | $[PhPH–BH_2]_n$ | 24–72 h, 105 °C, 4 : 1 *o*-DCB & toluene-$d_8$ (1 M), 0.3–10 mol% [Al] | $M_n \leq 43$<br>Đ = 1.1–1.6 | Operates *via* ligand-aluminium cooperative dehydrogenation of phosphine-borane adducts; unexplored substrate scope |
| Thermal dehydropolymerisation with Lewis acid base pairs (3.2.2.2)[89] | $[PhPH–BH_2]_n$ | 24 h, 100 °C, toluene or 2-MeTHF (2 M); 1–10 mol% additive | $M_n \leq 92$<br>Đ = 1.4–2.3 | Uses commercially available additives; molar mass control through $BH_3·SMe_2$ loading; unexplored substrate scope |
| Transition-metal-catalysed dehydropolymerisation (selected examples) | | | | |
| Iron-catalysed dehydropolymerisation (3.1)[46,66,95] | $[RPH–BH_2]_n$; R = alkyl, aryl, ferrocenyl | 24 h, 100 °C, toluene or dioxane (0.6 M), 0.1–10 mol% [Fe] | $M_n \leq 67$<br>Đ = 1.5–1.7 | Chain-growth coordination-insertion mechanism; molar mass control based on [Fe] loading |
| Rhodium-catalysed dehydropolymerisation (3.1)[69,70] | $[RPH–BH_2]_n$; R = Ph, *n*-hexyl | 19–66 h, 100 °C, toluene (1.25 M), 1–3 mol% [Rh] | $M_n \leq 127$<br>Đ = 1.2–1.6 | Step-growth, reversible-chain transfer mechanism; capable of producing AB block copolymers |

of reactive tertiary phosphine or borane termini moderates the reactivity of chain-ends, in a manner reminiscent of living radical olefin polymerisations (Fig. 5ii).[90–93] This allows for continued polymer growth through addition reactions when either polymer end is exposed, and also allows for complementarily reactive growing polymers to recombine into a higher-molar-mass dormant species.

Experimental evidence supported this mechanism. Firstly, isolated polymer samples were dissolved in minimal 2-MeTHF and heated for 24 hours further, resulting in an increase in molecular weight and dispersity (**7Ph**: $M_n$ = 149 kg mol$^{-1}$, Đ = 2.40). This behaviour is consistent with pseudo-living character, in which polymers undergo continued growth. Molecular weight control was also demonstrated through $BH_3·SMe_2$ loading (Fig. 5iii). An increase in $BH_3·SMe_2$ loading resulted in a reduction of the $M_n$ of the resulting material (*i.e.* **7Ph**: $M_n$ = 83 kg mol$^{-1}$ with 1 mol% $BH_3·SMe_2$ loading to $M_n$ = 57 kg mol$^{-1}$ with 10 mol% $BH_3·SMe_2$ loading). This effect was attributed to a higher fraction of dormant chains *in situ*, which undergo fewer propagation events. Thus, it was shown that high molar mass **7Ph** with tuned $M_n$ could be produced using $BH_3·SMe_2$ as an additive.

## 4. Overview and future directions

As our requirements of materials become more sophisticated, so do the materials themselves. Accordingly, synthetic methods to access new materials needs to continue to grow. This has been the case in the synthesis of poly(aminoboranes) and poly(phosphinoboranes), especially within the past decade. Herein we have described the advancements made in the transition-metal-free synthesis of poly(aminoboranes) and poly(phosphinoboranes). The routes described within this review with their scope, reaction conditions, typical polymer masses, and features to each method are given in Table 2.

Generally, these routes focus on the generation of transient aminoboranes or phosphinoboranes *in situ* which then undergo polymerisation. This is analogous to the polymerisation process for poly(olefins), but rendered much more complicated by the low thermal and kinetic stability of the BN and BP monomers compared to olefins. However, through thorough characterisation of isolated polymer samples and carefully designed experiments, significant headway has been made in the understanding of the individual polymerisation step, apart from dehydrogenation of precursor adducts. Mechanistically, trapping of reactive species, including the monomers as well as ESI end-group analysis has been most insightful. It appears that the new generation of catalysts act by stabilising the end groups of the growing polymers, either as Lewis acids or Lewis bases. Together with a judicious choice of solvent, chain termination events can be reduced, reminiscent of keeping a growing polymer chain dormant, but alive in pseudo-living radical polymerisations of olefins. These individual breakthroughs are all part of the larger goal of absolute control over polymer microstructure for these inorganic polymers (*i.e.*, degree of polymerisation, tacticity, monomer substitution). We predict that the next wave of discovery for poly(aminoboranes) and poly(phosphinoboranes) will be largely concerned with gaining control over the polymer architecture in a way that is already well known for poly(olefins).

While much has been achieved, these polymers are still mostly of interest in academia, and their application outside of synthetic laboratories are in their infancy. We believe this is in part due to the historic synthetic barrier to access these materials. However, the synthetic routes described within this review are capable of producing polymeric materials of high molecular weight and low dispersity using routine laboratory reagents. Thus, while there is still progress to be made in having a greater understanding of the polymerisations, we are of the opinion that the synthetic chemistry for poly(aminoboranes) and poly(phosphinoboranes) are now of sufficient maturity for bulk property analysis, allowing for a better understanding of their structure-property relationships. Further, these transition-metal-free routes offer the opportunity to determine the true effect of metal-doping on bulk polymer samples. We therefore encourage the broader scientific community to explore these fascinating materials in more depth, confident that their potential is only beginning to be realised.

## Author contributions

Conceptualisation: M. A. W.; funding acquisition: M. A. W., A. S.; project administration: M. A. W, A. S.; resources: M. A. W., A. S.; supervision: A. S.; visualisation: M. A. W.; writing – original draft: M. A. W.; writing – reviewing and editing: M. A. W., A. S.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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