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The Dehydropolymerization of H₃B·NMeH₂ to form Polyaminoboranes using [Rh(Xantphos–alkyl)] Catalysts.


Abstract A systematic study of the catalyst structure and overall charge for the dehydropolymerization of H₃B·NMeH₂ to form N-methyl polyaminoborane is reported using catalysts based upon neutral and cationic [Rh(Xantphos–R)] fragments, in which PR₃ groups are selected from Et, Pr and Bu. The most efficient systems are based upon [Rh(Xantphos–Pr)], i.e. [Rh(k⁺–Pr–Xantphos–Pr)(H)(η¹–H:B–NMe)(η¹–H:B–NMe)][BARF], and [Rh(k⁺–Pr,P–Xantphos–Pr)H], [Rh(k⁺–Pr,P–Xantphos–Pr)H] and [Rh(k⁺–Pr,P–Xantphos–Pr)H]H, Ni. While H₂ evolution kinetics show both are fast catalysts (ToF = 1500 hr⁻¹), and polymer growth kinetics for dehydropolymerization suggest a classical chain growth process for both, neutral Ni (Mₚ = 28,000 g mol⁻¹, D = 1.9) promotes significantly higher degrees of polymerization than cationic 6 (Mₚ = 9,000 g mol⁻¹, D = 2.9). For 6 isotopic labelling studies suggest a rate determining NH activation, while speciation studies, coupled with DFT calculations, show the formation of a dimetallaloborylene ([Rh(k⁺–Pr,P–Xantphos–Pr)B] as the, likely dormant, end product of catalysis. A dual mechanism is proposed for dehydropolymerization, in which neutral hydrides (formed by hydride transfer in cationic 6 to form a boronium co–product) are the active catalysts for dehydrogenation to form aminoborane. Contemporaneous chain–growth polymer propagation occurs on a separate metal center via head-to-tail end chain B–N bond formation of the aminoborane monomer, templated by an aminoborohydride–containing catalyst.

1. Introduction. The catalyzed dehydropolymerization of ammonia–borane or primary amine–boranes, such as H₃B·NMeH₂, provides a potentially useful methodology for the production of new inorganic polymeric materials, polyaminoboranes (e.g. N-methyl polyaminoborane (H₃B·NMeH₂)ₙ), which have alternating BN main–chain units, Scheme 1A. Although these are iso electronic with technologically pervasive polyolefins such as polypropylene their synthesis and properties are virtually unexplored, apart from a few examples that demonstrate their use as precursors for BN–based materials. A variety of catalysts have been shown to promote the dehydropolymerization of H₃B·NH₂ and in particular H₃B·NMeH₂ for example Ir(POCOP)(H)₂, A (POCOP = k¹–C₅H₅–2,6-(OPBu)₂), (PNHP)Fe(H)(CO)(HBH) (PNHP = HN(CH₂CH₂PPr)₃), B, and [Rh[Ph₂P(CH₂)₃PPh₃](η⁶–FC₃H₅)][BARF] (ArF = 3,5–(CF₃)C₆H₃) C. Scheme 1B. These catalysts have been shown to operate under homogeneous conditions, although heterogeneous examples have also been reported, and the switch between these two mechanistic extremes can be controlled by pre-catalyst structure. However, catalyst development that originates through an understanding of the mechanism(s) that operate in dehydropolymerization is still in its infancy.

Although many of the individual fundamental steps have been studied in some detail, e.g. dehydrogenation to form aminoboranes and the formation of oligomeric di– and tri–borazanes by dehydrocoupling processes, the roles of metal/ligand fragment in both promoting dehydrogenation of the precursor amine–borane and coupling (i.e. chain propagation) to form polymeric material have not been fully delineated. Valence iso electronic primary phosphine–boranes also undergo dehydropolymerization; for which mechanistic studies give complementary insight.

Scheme 1. (A) Dehydropolymerization of H₃B·NMeH₂. (B) Examples of catalysts (Mₚ = g mol⁻¹). [BARF] anions are not shown.
In contrast with olefin polymerization where the monomer (e.g. propene) is stable, aminoboranes such as H₂B·NH₃ or H₂B·NMeH are unstable towards oligomerization and can only be observed as transient species at low temperatures, or trapped on metal centers. This presents an additional challenge for studying amine–borane dehydropolymerization as the catalyst needs to operate in a bifunctional manner, dehydrogenating amine–boranes (via B–H and N–H activation) and then subsequently controlling the B–N bond-forming polymerization events (Scheme 2). Further complicating the mechanistic analysis and control of polymer chain propagation is that aminoboranes have been shown to undergo a number of different reactions when generated in situ in the absence of a catalyst. For example: dehydrocoupling to form borazines, autocatalytic roles in dehydrocoupling processes, hydrogen-redistribution reactions, polymerization to form product that is insoluble, e.g. (H₂BNH₂)₃₄, or low molecular weight, e.g. (H₂BNMeH)₂. In addition, dehydrogenation processes (on– or off–metal) have been proposed to be promoted by secondary interactions such as N–H(δ+)···(δ–)H–B dihydrogen bonds. As the numerous studies on the dehydrocoupling of the secondary amineborane, H₂B·NMeH, have shown, differences in the likely mechanistic pathways can also occur by changing the catalyst.

**Scheme 2. On- and off-metal (dehydro)polymerization of amine- and aminoboranes.**

We have recently reported that cationic precatalysts based upon [Rh(k²−P,P–Xantphos–Ph)(η²−H₂B(CH₂CH₂Bu)NMeH)][BAR³⁺], 1, (Xantphos–Ph = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) are particularly effective for the dehydropolymerization of H₂B·NMeH₂, operating at 0.2 mol% in FC₅H₁₂ solvent to produce polyaminoborane of Mₙ = 23,000 g mol⁻¹, D = 2.1

(Scheme 1). A controlled dehydrogenation/coordination/insertion mechanism for chain propagation was proposed on the basis of: (i) saturation kinetics being observed (and modelled) in analogous H₂B·NMeH dehydrocoupling, (ii) an inverse relationship between catalyst loading and polymer molecular weight, and (iii) H₂ acting as a chain termination agent to produce significantly lower molecular weight polymer (Mₙ = 2,800 g mol⁻¹, D = 1.8). In such a mechanism the metal is proposed to promote dehydrogenative insertion of H₂B·NMeH₂, via a transient metal–bound H₂B·NMeH fragment (Scheme 3A). Although the identity of the true catalyst remains unresolved, in part due to the low catalyst loadings used (0.2 mol%) and an induction period being observed before catalysis, a Rh(III) dihydride was implicated as the first-formed species (Scheme 3B). This was proposed to evolve to a Rh(III)–amidoborane, responsible for chain propagation. Stoichiometric experiments also demonstrated hemilability of the Xantphos–Ph ligand between cis–κ²−P,P and mer–κ³−P,O,P. The actual catalyst formed in situ could also be cationic or neutral (formed via hydride transfer from borane), or have a bimetallic motif as commented upon in other systems based upon kinetic studies or products characterized by single-crystal X-ray diffraction. This mechanism differs from those proposed to operate for Fe(PhNCH₂CH₂NPh)(Cy₂PCH₂CH₂PCy₂) / H₂B·NH₂–, A₁,₂ and bifunctional M(PNP)H(PMe₅) / H₂B·NH₃ (M = Fe, Ru) systems, for which metal–based dehydrogenation occurs but the aminoborane undergoes metal–based polymerization at a different metal center. While the parent Xantphos–Ph ligand is well–established in organometallic catalysis, the alkyl–substituted versions have only recently been explored, in particular by Esteruelas. Scheme 4 shows examples of Rh–based complexes, both cationic and neutral. Relevant to this paper, neutral Rh–hydride F has been shown to be an

![Scheme 3](image-url)
effective catalyst for the dehydrogenation of H₂B-NMe₂ and H₂B-NMeH, while it also undergoes rapid C–H activation with fluoroarenes (G), and B–H activation with boranes. Interestingly for Rh-based systems, the complexes that can be observed exclusively offer the mer–κ₁–P,O,P binding mode in the ground state, i.e. as a pincer ligand; while fac–κ₁–P,O,P or cis–κ₂–P,P coordination modes have been observed in osmium systems. A cis–κ₂–P,P coordination geometry is shown by the less bulky ethyl analogue coordinated with Pd, H.²³c

Scheme 4. Examples of alkyl substituted Xantphos-based ligands. Anions are not shown. R = tPr, Bu.

These reports demonstrate a rich-landscape of coordination motifs and bond-activations that alkyl Xantphos ligands promote when coordinated to rhodium. When coupled with our recent report using precatalyst ¹, this encourages their exploration in the dehydropolymerization of H₂B-NMeH. We report here a systematic study of dehydropolymerization using both cationic (e.g. based upon D) and neutral (e.g. F) Rh–precursors of the alkyl-substituted Xantphos motif, in which the ligating PR₂ groups are also systematically varied between Xantphos–Et, Xantphos–tPr and Xantphos–Bu.

2 Results

2.1 Synthesis and reactivity of cationic precursors

Complexes [Rh(κ₁–P,O,P–Xantphos–Rh)(H)(η¹–H₂B-NMe₂)][BAR₄], R = Et, tPr, and [Rh(κ₁–P,O,P–Xantphos–Rh)(H)][BAR₄], R = Bu. Catalyst precursors are ideally operationally unsaturated, to allow formation of a H₂B-NMeH: sigma-complex, and also available as pure crystalline material. For the Xantphos–Ph system both Rh(II), 1, and Rh(III) dihydride, [Rh(κ₁–P,O,P–Xantphos–Ph)(H)](η¹–H₂B-NMe₂)][BAR₄], 2, precursors have a weakly bound amine–borane acting as a placeholder ligand. These are conveniently prepared from a [Rh(κ₂–P,P–Xantphos–Ph)(NBD)][BAR₄] precursor (NBD = norbornadiene), and we have used the same route for alkyl–substituted Xantphos complexes.

Figure 1. (A) Complexes 3 and 4. (B) Molecular structure of the cationic portion of 4, displacement ellipsoids at the 30% probability level, H–atoms and [BAR₄]⁻ anion are not shown. Selected bond distances (Å) and angles (°): Rh–P₁, 2.3897(8); Rh₁–P₁, 2.3659(8); Rh₁–O₁, 3.1612(2); P₁–Rh₁–P₂, 101.72(3).

Addition of Xantphos–Et to [Rh(NBD)][BAR₄] in CHCl₃ solution gives [Rh(κ₁–P,P–Xantphos–Et)(NBD)][BAR₄], 3, after recrystallization from CHCl₃/pentane, as an orange microcrystalline powder. In a similar manner, [Rh(κ₂–P,P–Xantphos–tPr)(NBD)][BAR₄], 4, can be prepared. Complexes 3 and 4 were characterized by variable temperature NMR spectroscopy (including an Eyring analysis), elemental analysis, ESI–MS (Electrospray Ionization–Mass Spectrometry), and also by single crystal X-ray diffraction (Fig. 1B shows 4, Fig. S23 for 3), which show a cis–κ₂–P,P coordination geometry for the alkyl Xantphos ligands. The corresponding NBD adduct using the Xantphos–Bu ligand could not be prepared, as commented upon by Goldman and co-workers, the bulky Bu groups disfavouring the cis–κ₂–P,P coordination geometry (Supporting Materials).

Addition of H₂ to a 1,2–F₆C₆H₄ solution of complex 3 or 4 containing 1 equivalent of H₂B-NMe₂ results in the formation of [Rh(κ₁–P,O,P–Xantphos–R)(H)(η¹–H₂B-NMe₂)][BAR₄] (5, R = Et; 6, R = tPr), that can be isolated as off-white solids.

Figure 2. (A) Complexes 5 and 6. (B) Molecular structure of the cationic portion of 6, displacement ellipsoids at the 30% probability level, H–atoms and [BAR₄]⁻ anion are not shown. Selected bond distances (Å) and angles (°): Rh–P₁, 2.2650(13); Rh₁–P₂, 2.2490(15); Rh₁–B₁, 2.783(6);
Rh1–O1, 2.192(3), B1–N1, 1.607(7); P1–Rh1–P2, 160.45(5).
(C) Proposed fluxional process for 6.

Figure 2A. Complex 6 was characterized by a single-crystal X-ray diffraction study (Fig. 2B), which shows a mer–κ–Xantphos–Pr Rh(III) cis–dihydride motif with a supporting sigma–bound29 η1–H:B:NMe ligand. The overall geometry is very similar to that measured for 2,31 in particular the Rh–B distance [6, 2.783(6) Å; 2, 2.759(6) Å] and is also similar to [Ru(Xantphos–Ph)(PPh)2(η1–H:B:NMeH)](H)[BAR4]3.31

The solution NMR data show that 6 (R = Pr) is fluxional at 298 K, while at this temperature 5 (R = Et) is not. For 6 a single hydride environment is observed at δ −19.09, of relative integral 2 H, as well as a quadrupolar broadened, 3 H relative integral, signal at δ 0.08 assigned to the Rh–H–B that is undergoing rapid site exchange between bridging and terminal B–H.29,33 In the 11B NMR spectrum a signal is observed at δ −9.9, consistent with an η1–bound borane.34 A single Xantphos–Pr CMe environment is observed. The 31P{1H} NMR spectrum shows one environment, δ 66.5 [{[RhP] = 111 Hz}]. Progressive cooling to 200 K reveals a low temperature limiting spectrum consistent with the solid–state structure that now shows two hydride environments at δ −17.62 and δ −19.97 (modelled as a dtd), an upfield shifted Rh–H–B signal (relative integral 3 H) at δ −0.58, and two Xantphos–Pr CMe environments. An Eyring analysis of the hydride signals in complex 6 gives activation parameters ΔHf = 59(4) kJ mol−1 and ΔSf = +37(15) J K−1 mol−1 for this fluxional process. These data are consistent with a mechanism in which the H:B:NMe ligand dissociates and re–coordinates on the other side, via a (known28) symmetric 16–electron intermediate [Rh(κ3–P,O,P–Xantphos–Pr)(H)]+ Figure 2C. These activation parameters are similar to those reported for related fluxional process in [Rh(κ3–P,O,P–Xantphos–Pr)(H)][OTf] [ΔHf = 64(3) kJ mol−1 and ΔSf = +66(8) J K−1 mol−1].34 Complex 6 displays NMR data that are very similar to those measured at low temperature for 6. We suggest these differences are driven by the steric effects of Et versus Pr. This influence of steric is further demonstrated in that addition of H:B:NMe to [Rh(κ3–P,O,P–Xantphos–Bu)(H)][BAR4].10,29 results in no observable amine–borane adduct (Eq. 1), although H/D exchange experiments (vide infra) suggest such a complex is accessible.


Scheme 5. Halide abstraction route. [BAR4]– anions are not shown.

7, 44,29b,35 in the presence of H:B:NMe3. Complex 6 can thus be prepared in 79% yield as a crystalline, analytically pure, solid (Scheme 5). By contrast, complex 5 cannot be prepared by this route. While addition of H2 to dimeric [Rh(κ3–P,O,P–Xantphos–Et)]2 Cl 8 (Supporting Materials) gives Rh(κ3–P,O,P–Xantphos–Et)(H)Cl, 9, this complex is only stable under an H₂ atmosphere regenerating 8 on its removal. For the Bu analogue Rh(κ3–P,O,P–Xantphos–Bu)Cl Goldman has calculated that H₂ addition is favoured (ΔG = −5 kcal mol−1).29b Our observations suggest that the thermodynamics of H₂ addition to 8 are more finely balanced, presumably as a consequence of the κ3–P,P–Xantphos–Et geometry being more accessible, which promotes a dimeric structure which has two Cl bonds per metal (as noted for related Os–systems27d).

2.2 Neutral precursors One of the reasons that the Xantphos–R systems are so interesting to study in amine–borane dehydroboration is that both cationic and neutral precursors are available with propyl or tert–butyl groups; e.g. generically D and F, Scheme 4. While Rh(κ3–P,O,P–Xantphos–Pr)H, 11, can be isolated in good yield, as reported by Esteruelas,40 it undergoes a very fast reaction with 1,2–F₂C₆H₄ (the current solvent–of–choice used in our cationic systems) on time of mixing (Scheme 6) to form C–H activated Rh(κ3–P,O,P–Xantphos–Pr)(2,3–F₂C₆H₅) 12. A single crystal X-ray diffraction analysis confirmed the structure. C–H activation of fluoroarenes by 11 has been reported previously with FC₆H₅ and 1,3–F₂C₆H₅.27a Complex 12 is thus likely the actual precatalyst when using this solvent. In contrast Rh(κ3–P,O,P–Xantphos–Bu)H, 13,29b is more robust and does not react with 1,2–F₂C₆H₅. Attempts to prepare Rh(κ3–P,O,P–Xantphos–Et)H were unsuccessful.


Complexes 5 and 6 do not lose H₂ when exposed to a vacuum (10⁻³ Torr). It is thus likely that during catalysis the Rh(III) oxidation–state is persistent.
Although neutral 13 does not form a complex with H₃B-NMe₃ it does undergo H/D exchange with D₃B-NMe₃ in 1,2-F₃C₆H₄ solution to form the corresponding deuteride (10% after 10 minutes). Reactivity of 11 with D₃B-NMe₃ in 1,2-F₃C₆H₄ solution is frustrated by the rapid formation of 12. These observations show that, where measurable, all the cationic and neutral complexes undergo reversible B–H activation at the metal center.

2.4 Initial catalyst screening Table 1 summarizes H₃B-NMe₃ dehydrogenation screening experiments, and demonstrates the influence of the sterics and charge of the [Rh(Xantphos–R)] fragment. These experiments were performed under conditions used previously (0.2 mol% catalyst, 0.446 M H₃B-NMe₃, system open to a flow of Ar, 1,2-F₃C₆H₄ solvent). Notable is that both cationic (6) and neutral (11) Xantphos–Pr catalysts promote high conversions to (H₃BNMe₃)₈ (greater than 90%) in short reaction times (less than 30 minutes), as signalled by a distinctive broad resonance observed at δ ~5.1 (1,2-F₃C₆H₄) in the ¹¹B NMR spectrum. Only small amounts of N-trimethylborazine, (HBNMe₃) (δ 33.2, d, |BH| = 132 Hz) were observed. Xantphos–Bu systems (10 and 13 respectively) are slower (hours), produce more (HBNMe₃)/ other dehydrocoupling side products and less isolated polymer. At 10 mol% the major product with catalysts 6 and 11 was N-trimethylborazine. Changing solvent to THF (which has previously been used as a solvent for 11 in dehydrogenation of H₃B-NH₃) resulted in low conversions and a slow reaction for cationic catalyst 6 (40% conversion after 3 hours). We postulate that this is due to the formation of the cationic THF–adduct [Rh(κ₃–P,O,P–Xantphos–R)(H)(THF)][BAR]+ in which the THF binds strongly with the Rh–center, thus attenuating amine-borane dehydrogenation. Complex 5 (Xantphos–Et) is a very slow catalyst, only converting 27% H₃B-NMe₃ to polymer after 15 hours. Xantphos–Pr pre-catalysts 6 and 11 thus offered the best opportunity to study the kinetics of dehydropolymerization and catalyst control over the resulting polymer using 1,2-F₃C₆H₄ solvent. We concentrate on these two systems, but return to Xantphos–Bu and Xantphos–Et to allow for wider comparisons.

2.5 Dehydropolymerization: molecular weight determinations, entrained catalyst and polymer growth kinetics. Off-white polyaminoborane (H₃BNMe₃)₈ can be isolated in
yields of up to 65\% (\sim 0.7\) g scale) using precatalysts 6 and 11. The $^{11}$B NMR spectra of isolated polymer produced by either catalyst are similar, showing a broad peak, centered around $\delta$ = 5 (CDCl$_3$), Figure 3. A small shoulder is also apparent at $\delta$ = 2 ppm that may be indicative of a small amount of chain–branching (i.e. “BN$^-$” or “BN$^+$” in the polymer backbone). A small signal at $\delta$ = 17.6 suggests some entrained H$_2$BNMe$_2$. Although this might also be masking a broader BH$_2$ polymer end group signal. The $^1$H NMR spectra show environments assigned to NH, NMe and BH$_2$, and are very similar for polymer from each catalyst. A small shoulder on the NMe signal is observed at low field, but this is poorly resolved. The $^{13}$C($^1$H) NMR spectra are also similar for both polymeric materials, and show multiple environments assigned to NMe. In polymer derived from 6 a sharper signal is observed at $\delta$ = 36.2, which resolves into two signals for polymer derived from 11 ($\delta$ = 36.2, 36.1). Much broader, lower field, signals are observed for both polymer samples centered at $\delta$ = 37. Very similar spectral data have been observed for NMe.

Figure 3. Selected NMR spectra (CDCl$_3$, 298 K) for isolated polyaminoborane produced by catalyst 6 (top) and catalyst 11 (bottom): 0.2 mol%, 0.446 M H$_2$BNMe$_2$. The broad baseline signal observed in the $^{11}$B NMR spectra at ca. 20 ppm is due to background from tube and probe (borosilicate glass).

methyl polyaminoborane produced using Ir(POCOP)($^1$H)$_4$ and (PNHP)Fe($^1$H)(CO)(HBH)$_2$, especially the multiple environments in the $^{13}$C($^1$H) NMR spectra. The $^{13}$C($^1$H) NMR spectrum of, related, polyphosphino-borane (H$_2$BP$_3$BuH)$_n$ formed by a thermal dehydropolymerization ($M_\infty$, $\sim$ 30,000 g mol$^{-1}$, $D$ = 1.8), also shows multiple environments for the $^1$Bu group, not dissimilar to those observed here for the NMe groups; while in the $^{31}$P NMR spectra multiple environments are also observed. The latter were interpreted as being due to the tactic environments associated with the polymer, and in particular specific triads. A mixture of $R,R$ and $R,S$ diastereoisomers of the linear triborazane H$_2$B(NMeHBH$_2$)$_2$NMeH$_2$ have also been synthesized, although no $^{13}$C NMR data were reported. We are reluctant interpret our current data further with regard to polymer stereochemistry, especially given the possibility for additional chain–branching. Nevertheless, taken together, these spectral observations could well be important in future studies of polyaminoborane tacticity.

Analysis by gel permeation chromatography (GPC, polystyrene standards, refractive index (RI) detector) of polymer produced using cationic 6 showed what appeared, at first inspection, to be a bimodal distribution of polymer molecular weights (Figure 4A, solid line), in which a broad low intensity peak characteristic of (H$_2$BNMeH)$_n$ was augmented with a
Figure 4. Experimental (grey, solid–line), combined fitted (black, dashed) and individual skewed Gaussian fits (green and blue, solid) GPC data for polyaminoborane produced using: (A) Cationic catalyst 6 (0.2 mol%, 0.446 M H:BNMeH); (B) Neutral catalyst 11 (0.2 mol%, 0.446 M H:BNMeH); (C) Neutral catalyst 11, spiked post catalysis with 0.2 mol% 6 (conditions as for B).

a sharper peak that displayed with a tail to lower \( M_n \). Significantly, this signal was absent in polymer produced using neutral catalyst 11 (Figure 4B), and we suspected it may be due to \([\text{BAR}^\text{H}]^–\) entrained in the polymer. Even though the catalyst is used in low concentration (0.2 mol%) the \([\text{BAR}^\text{H}]^–\) aryl groups would be expected to be significantly more sensitive to RI detection than polyaminoborane, a technique that has been shown to have a positive correlation to the polarizability of any functional group.\(^{39}\) \(^{19}\)F NMR spectroscopy of polymer produced using 6, showed a signal at \( \delta = –63.2 \) consistent with \([\text{BAR}^\text{H}]^–\), while for that from 11 this signal was absent. In the \(^1\)H NMR spectrum of polymer derived from catalyst 6 signals assigned to C–H(CF3) were observed, and when integrated with respect to the BNMe signal a loading of 0.18 mol% was measured. ICP–MS analysis for Rh–content from these polymer samples indicated a loading of ~450 ppm (i.e. 0.045 mol%), suggesting that the anion and cation are both entrained, albeit to differing extents. Neutral catalyst 11 showed higher levels of Rh–incorporation, 1200 ppm (0.12 mol%).\(^{40}\) Final evidence that this extra GPC peak comes from \([\text{BAR}^\text{H}]^–\) came from spiking a sample of polymer produced using catalyst 11 with 0.2 mol% 6 which showed the characteristic skewed GPC signal (Scheme 4C). These signals for \([\text{BAR}^\text{H}]^–\) were not reduced by re-precipitation of the polymer suggesting that the \([\text{BAR}^\text{H}]^–\) anion may be associated with the polymer.\(^{41}\) A similar entrainment of catalyst in phosphine–borane dehydropolymerization has recently been reported.\(^{19}\) The GPC traces were deconvoluted\(^{42}\) using a skewed Gaussian bimodal distribution using a stand–alone programme. These gave acceptable fits to the data.\(^{43}\) Importantly, using these fits the molecular weight and dispersity data for the spiked samples from neutral catalyst 11 recover the unspiked data well – giving confidence in the approach.

These data show a significant difference between the polymer produced with the two catalysts under these conditions, even though the NMR data are similar for both. Cationic 6 produces polyaminoborane of low molecular weight and high dispersity (e.g. \( M_n = 9,000 \) g mol\(^{-1} \), \( D = 2.9 \)) while neutral 11 produces higher molecular weight polymer with a more uniform distribution (e.g. \( M_n = 28,000 \) g mol\(^{-1} \), \( D = 1.9 \)). The effect of time (i.e. conversion), catalyst loading, and catalyst identity was probed in more detail, using raw GPC data for 11 and modelled GPC data for 6, as shown in Figure 5 and Table 2.

For cationic catalyst 6 a plot of \( M_n \) versus conversion of H:BNMeH to polyaminoborane (as measured by \(^{11}\)B NMR spectroscopy for individual samples quenched at the appropriate point by addition of excess PPh\(^3\)) revealed that at low conversion polymer of appreciable molecular weight was being formed (\( M_n = 10,000 \) g mol\(^{-1} \), \( D = 2.0 \)), and this did not change significantly over the course of dehydropolymerization, Figure 5A. At these low conversions H:BNMeH is the dominant species by \(^{11}\)B NMR spectroscopy, while the signal at ca. \( \delta = 5 \) assigned to polyaminoborane is broad and gives no indication that short chain oligomers (e.g. H:BNMeBH:NMeH) are being formed, as these would be expected to show more resolved B–H coupling.\(^{5b,12a}\)

These data are broadly consistent with controlled\(^{19}\) chain–growth polymer propagation, in which a reactive aminoborane monomer undergoes rapid head-to-tail polymerization to give (H:BNMeH)\(_n\),\(^{43}\) followed by termination. If this occurred via a coordination–insertion–type mechanism at a metal center, reducing the catalyst loading would be expected.
in the confidence limits of polyaminoborane analysis, exacerbated by the low molecular weight polymer tailing into the intrinsic system peaks associated with GPC analysis, we consider this trend to be weak at best and we suggest that this data does not strongly support a coordination–insertion mechanism. As we discuss (Section 2.6), we cannot discount that this trend also reflects trace impurities in the solvent that might disproportionally modify catalyst concentration at low loadings. Catalyst 11 shows an opposite, but still weak, relationship between catalyst loading and \( M_n \) in which increased loadings lead to slightly increased degrees of polymerization: 0.2 mol\% \( (M_n = 33,000 \text{ g mol}^{-1}, D = 1.9) \) versus 1 mol\% loadings \( (M_n = 39,000 \text{ g mol}^{-1}, D = 1.9) \). An increase in molecular weight of isolated polymer on increasing catalyst loading has been noted for Ir(POCOP)(H)\(_{2}\), \( \text{A}^{\text{a}} \) while, for catalyst B changes in catalyst loading can induce small molecular weight changes in either direction depending on the solvent used.\(^{6}\) For catalyst 11 a degree of polymerization (i.e. \( M_n \)) versus conversion plot also indicates a chain-growth type process is in operation (Fig. 5A).

Addition of two successive batches of H\(_3\)B·NMeH\(_2\) to catalysis solutions post dehydropolymerization (0.2 mol\% \( \text{6 or 11, 0.446 M [H}_3\text{B·NMeH}_2] \)) resulted in full consumption of H\(_3\)B·NMeH\(_2\) (TON = 1,500), but no significant change in the molecular weight of isolated polymer \( (\text{6: } M_n = 15,000 \text{ g mol}^{-1}, D = 1.9; \text{11: } M_n = 26,000 \text{ g mol}^{-1}, D = 2.3) \). This indicates that the systems are not living,\(^{19,46}\) but also that species present at the end of catalysis are still active for dehydropolymerization and can be recharged (Section 2.7.1).

Table 2 additionally provides representative results from a study of concentration, exogenous cyclohexene as a potential modifier to control polymer molecular weight. For catalyst 6
Table 2. Representative polymer molecular weights (g mol\(^{-1}\)) and dispersity data.

<table>
<thead>
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<th>Entry</th>
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<th>[H(_2)B-NMeH(_2)]/M</th>
<th>[cat.]/M (mol%)</th>
<th>(M_n)/g mol(^{-1})</th>
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\(^a\) Under \(H_2\) evolution measurement conditions connected to a gas burette. \(^b\) Under a flow of Ar. \(^c\) Under a flow of Ar in the presence of 2.7 equivalents (relative to \(H_2\)B-NMeH\(_2\)) of cyclohexene. \(^d\) A closed system allowing for \(H_2\) build-up.

catalyst concentration has no significant effect on molecular weight within the confidence limits of polymer analysis (compare entries 3 and 7). For catalyst 11 a reduction in concentration to 0.223 M results in a decrease in molecular weight, \(M_n = 17,000\) g mol\(^{-1}\) (\(D = 1.6\)), entries 11 and 15. \(H_2\) does not act to significantly modify the chain length for either catalyst when allowed to build up in a closed system, or under the conditions of measuring \(H_2\) evolution using a gas burette, when compared with a system open to a flow of argon. Addition of 2.7 equivalents of cyclohexene (i.e. 270 mol%) to either catalyst (6 or 11) at 0.2 mol% did not change the degree of polymerization significantly nor resulted in the observation of Cy\(_2\)B=NMeH \([\delta\(_{\text{11}}\)B] = 45.9, 1.2–F\(_2\)C\(_6\)H\(_4\)]\(\text{THF}\)\(_{17\text{a}}\) – the product of hydroboration that potentially signals free \(H_2\)B=NMeH\(_2\). At 10 mol%, where \((\text{HBNMe})_2\) becomes the major product (vide supra), trace Cy\(_2\)B=NMeH is observed using catalyst 6 [~1\%, \(\delta\(_{\text{11}}\)B] = 45.9, 1.2–F\(_2\)C\(_6\)H\(_4\)] (Scheme 8). For catalyst 11 under the same conditions no hydroboration product is observed. These data suggest that any \(H_2\)B=NMeH formed is consumed significantly faster in chain propagation/borazine formation rather than hydroboration, as has been commented upon previously.\(^{14,16,47}\) Hydroboration of cyclohexene by transient \(H_2\)B=NMeH has been reported in metal–free polymerizations,\(^{15}\) and in slower metal–promoted dehydropolymerizations.\(^{6}\) We have not observed \(H_2\)B=NMeH in any in situ NMR experiments \([\text{lit.} \delta\(_{\text{11}}\)\(\text{B} = 37.1, \tau, J(BH) = 130 (\text{Et}_2\text{O}, -10^\circ\text{C})\]).\(^{15}\)

The use of \(H_2\) as a chain termination agent is well established in olefin polymerization, and likely operates through sigma–bond metathesis of \(H_2\) with the [M]–CH\(_2\)–R growing polymer chain to form a metal hydride and free polymer.\(^{14,48}\) This lack of sensitivity to \(H_2\) for catalysts 6 and 11 is in contrast to catalyst 1 that shows a significant attenuation of molecular weight with \(H_2\), but is similar to A\(^{44}\) and B\(^\text{a}1\) where no significant effects were reported. Catalyst 1 was suggested to operate via a coordination–insertion mechanism in which a nascent aminoborane, formed by dehydrogenation, inserts into a polymer chain that is propagating from the metal center via a covalent Rh–NHMeBH\(_2\)R (or Rh–

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**Scheme 8. Trapping experiments.**

- [cat.] = 6 or 11
- Cy\(_2\)B=NMeH
- only observed with 10 mol% 6
- H\(_2\)B-NMeH
- not observed
- (H\(_2\)BNMe\(_2\))
- major product 0.2 mol%
BH2:NMeHR) bond and is thus susceptible to hydrogenolysis, Scheme 3. The lack of H2 sensitivity of 6 and 11, when combined with the relative insensitivity of polymer molecular weight to catalyst loading suggests a polymerization process where polymer propagation follows a classical chain-growth profile, rather than a coordination-insertion mechanism. An alternative mechanism is one of step-growth which, characteristically, only shows higher molecular weight polymer being formed at very high conversions. Such behaviour has been suggested for the dehydropolymerization of H2:B-PRH2 (R = Ph) using Rh-based catalysts, and can be explained by a facile reversible chain transfer between bound growing oligomer chains and H2:B-PRH2. Similar chain transfer behaviour has been noted for very slow amine-borane dehydrocoupling using the [Ir(PCy3):H2][H2]:[BARh4] catalyst. We, and others, have recently commented upon the presence of trace impurities in fluorinated arene solvents, and a small portion of catalyst showed trace quantities of Al vents, suggesting that trace impurities, such as these, act to modify the dehydrogenation of H2:B-PRH2 is fast (TOF ~ 1700 hr⁻¹). This is considerably faster than for 1 (TOF ~ 250 hr⁻¹).

2.6 H2 evolution studies and the kinetic model. By following the evolution of H2 during dehydropolymerization, the dehydrogenation of H2:B-NMeH2 to form transient aminoborane, H2:B-NMeH can be indirectly interrogated. For catalyst 6 and 11 close to one equivalent of H2 is released during dehydropolymerization, consistent with the small, less than 10%, amount of (HBNMe)2 formed. This means that the H2 evolved can be used as an effective proxy for H2:B-NMeH generation which subsequently undergoes fast polymerisation. Figure 6A shows a number of H2 evolution experiments using catalyst 6 in which both the concentration of H2:B-NMeH2 and catalyst is varied. For all regimes a small induction period was observed (20–90 seconds, not shown – Supporting Materials) that is variable between batches of 1,2–F2C6H4 solvent, but consistent within each batch for repeat runs, as are the temporal profiles for H2 evolution. We, and others, have recently commented upon the presence of trace impurities in fluorinated arene solvents, and a GC–MS analysis of 1,2–F2C6H4 stirred over Al2O3 for one hour and vacuumed distilled from CaH2 showed trace quantities of FClC6H4 and F(OH)C6H4. We suggest that trace impurities, such as these, act to modify a small portion of catalyst in both the induction period and during productive catalysis. For this reason the data shown in Figure 6A comes from using the same batch of 1,2–F2C6H4. Notably, isolated polymer does not vary in molecular weight significantly when using different solvent batches, for either catalyst. We discount the formation of a heterogeneous catalyst as the active species, as addition of excess Hg or sub-stoichiometric PPh3 (0.2 equivalents) once turnover was established did not act to significantly modify either cationic or neutral catalysts (Figure 6B and C for catalyst 6 and 11, respectively). H2 release using 0.2 mol% 6 at 0.446 M H2:B-NMeH2 is fast (TOF ~ 1700 hr⁻¹). This is considerably faster than for 1 (TOF ~ 250 hr⁻¹).

Figure 6. (A) Temporal data plots for polyaminoborane formation (as measured by H2 evolution) and simulated fits (lines) for catalyst 6 (4.45 × 10⁻⁴ M except where stated) and H2:B-NMeH2: (△ = 0.1115 M, ○ = 0.167 M, ○ = 0.223 M and □ = 0.446 M). X = 6 (8.9 × 10⁻⁴ M), H2:B-NMeH2 (0.446 M). The variable induction period of between 20 and 90 seconds has been removed from the data. (B) Effect of sub-stoichiometric PPh3 (0.2 equiv.) added at t = 250 s: [6I] = 8.9 × 10⁻⁴ M, [H2:B-NMeH2] = 0.446 M. Note the induction period is shown. (C) Effect of excess Hg (1500 equiv.) at t = 120 s: [11] = 8.9 × 10⁻⁴ M, [H2:B-NMeH2] = 0.446 M.

These data for catalyst 6 were simulated under a variety of scenarios. The temporal profile observed, especially at the highest concentration of H2:B-NMeH2, suggests saturation kinetics are operating, i.e. initial zero-order in substrate, as we have modelled previously for the dehydrocoupling of amine–boranes using catalyst 1. However, the analysis of the data did not provide a convincing solution for quasi–irreversible amine–borane coordination to the metal center. Instead a simple first-order model in substrate that took into account the limiting solubility of H2:B-NMeH2 in 1,2–F2C6H4 solvent (0.22 M), accounted best for all the observed data. Experimentally this is confirmed by a visual inspection of the catalysis reaction, and reflects the relatively poor solubility of H2:B-NMeH2 in 1,2–F2C6H4. With this model in hand, overall second order rate constants were simulated (as shown in Figure 6A), for which an averaged k = 5.9 ± 0.5 M⁻¹ s⁻¹ was obtained. By using DBB-NMeH2 at 0.1115 M (I6I = 2.23 × 10⁻⁴ M), i.e. below the solubility limit, a KIE
of 0.8 ± 0.4 for BH/BD substitution is measured, while H₂B·NMe₅ results in a KIE of 4.6 ± 0.2 for NH/ND substitution. The large KIE associated with ND suggests that N–H cleavage is involved in the turnover limiting step. Similar KIEs have been reported for dehydrocoupling of H₂B·NMe₅H using [TiCp]Cl (3.6 ± 0.3)³³ or Rh(PCy₃)₂(H)Cl (5.3 ± 1.3)³⁴ catalysts. For catalyst 1, in which a coordination/dehydrogenation/insertion mechanism is proposed, the KIE associated with NH activation in H₂B·NMe₅H is smaller (2.1 ± 0.2).³⁵ The small KIE associated with B–H activation in the system here may indicate an equilibrium isotope effect that arises from reversible B–H activation at the metal center,³⁵ occurring prior to the turnover limiting step (Section 2.3), however within error it may also be close to unity, meaning that we are reluctant to over interpret this value. Although the two different KIE argue against a synchronous concerted BH/NH activation,⁶⁶ they could reflect a rather asynchronous transition state in which BH activation occurs much earlier than NH activation.¹⁷b

The equivalent analysis of H₂ release and resulting dehydrogenation kinetics for neutral catalyst 11 is additionally complicated by the fact that, due to the sensitivity of this catalyst, even repeat runs using the same batch of solvent differed significantly (initial rates varied by 25% at 0.446 M H₂B·NMe₅ and 0.2 mol% 11). We suggest that this is due to irreversible catalyst decomposition from trace impurities entrained in reaction vessels (O₂) even though substantial precautions for handling air–sensitive materials were taken. This means that detailed studies of catalyst loading or KIE experiments were not appropriate. Nevertheless all temporal plots of H₂ release showed a similar profile to catalyst 6: essentially close to 1 equivalent of H₂ formed and an initial pseudo zero order regime, although – interestingly – catalyst 11 does not display a measurable induction period. Simulating a representative example for catalyst 11 (TOF ~ 1500 hr⁻¹) using the model developed for catalyst 6 gave a good fit and a second order rate constant k = 4.1 M⁻¹ s⁻¹, similar to 6.

Thus, even though both catalyst systems operate at a similar overall rate, likely by a similar chain–growth mechanism (Section 2.5), and are homogenous, they promote very different degrees of polymerization: with neutral catalyst 11 producing significantly longer polymer than 6 (Table 2 and Figure 5).

2.7 Catalyst speciation during, and post, catalysis.

2.7.1 [Rh(k⁺–P,OP–Xanthos–Pr)(η–H₂B·NMe₅)]²⁺[BAr₅]⁻, 6. As dehydrogenization is performed at low catalyst loadings, directly interrogating reaction mixtures to determine the fate of the catalyst by NMR spectroscopic techniques is difficult. However, at the end of catalysis (0.4 mol%, 6.6 mg 6, 20 min) concentra-

![Figure 7](image_url)

Figure 7. (A) Synthesis of complex 14–[BAr₅]⁻, [BAr₅]⁻–anion omitted. (B) Molecular structure of the cationic portion of 14–[BAr₅]⁺, displacement ellipsoids are shown at 50% probability level, H-atoms and [BAr₅]⁻–anion omitted. Selected bond distances (Å) and angles (º): Rh1–B1, 1.880(8); Rh2–B1, 1.862(8); Rh1–O1, 2.343(2); Rh2–O2, 2.343(4); Rh1–B1–Rh2, 177.4(5). (C) Space filling diagram (van der Waals radii).

Due to relatively poor crystal quality, and the reduction in high–angle data, the final refinement was of moderate quality (R = 7.9%), although the data collected proved adequate for confirming connectivity and bond metrics. Complex 14–[BAr₅]⁺ has a Rh: dinmetallic unit that is spanned by a single B atom [Rh–B–Rh 177.4(5)°]. The
Xantphos–Pr ligands adopt a mer-κ³ P,O,P geometry that places the central oxygen atom trans to the boron. As discussed later, the lack of high-field signals in the ¹H NMR spectrum, very low field chemical shift of the ¹³B resonance and mass-spectral data all indicate that there are no hydrides associated with the complex. The Rh–B distances are both short [1.880(8) and 1.862(8) Å], and comparable to closely related iron²⁸ and ruthenium²⁹ dimetalloborylenes [(η⁵-C₅H₅Rh)(CO)₃M]⁺ [M = Fe, R= Me; M = Ru, R = H; e.g. Ru–B 1.931(3)/1.963(3) Å; Ru–B–Ru 175.5(2)°]. The Rh–B distances are shorter than that measured in Rh(κ³–P,O,P–Xantphos–Pr)(Bpin) [1.981(4) Å; pin = pinacol]²⁷α which has a formal covalent Rh–B single bond, are longer than those in monometallic complexes with M=B bonds, e.g. Ru(PCy₃)₂(BMes)HCl [1.780(4)Å, Mes = mesityl].³⁶α but are similar to group 9 aminoborylenes, e.g. [mer–Ir(PMe₃)₂HCl(BNPr₂)][B(C₆F₅)₃] [1.897(5) Å]³⁶β in which electronic unsaturation at boron can be attenuated by conjugation with the nitrogen lone pair. These comparisons suggest some partial double bond character to the Rh–B bonding in 14. Although the presence of dπ–pγ bonding between the Rh and B may also be suggested by the orientation of the Xantphos–Pr ligands (angle between Rh/P₃/O planes = 90.2°), the steric requirements of interdigitation of the Pr groups likely dominate this geometry (Figure 7C).³⁶α The Rh–O distances [2.343(4)Å] are longer than those observed in 6 [2.192(3) Å] and Rh(κ³–P,O,P–Xantphos–Pr)(Bpin) [2.268(2) Å], suggesting that the boron atom exerts a significant trans influence.

The ¹H (and ¹³B) NMR spectra of 14 (for both anions) showed an absence of hydride signals (between δ 0 and δ ~50), while in the ¹³B NMR spectrum a very broad resonance at δ 135 is observed, which is in the region associated with complexes in which there is a significant M–B multiple bonding component,³⁵α and is considerably downfield shifted from the regions associated with amine–³⁴α or aminoboranes³¹β interacting with metal centers. Electrospray Ionization Mass Spectroscopy (ESI–MS) showed the dominant cationic species to be singly charged with an isotope pattern that matched very well with a formulation of [Rh(κ³–P,O,P–Xantphos–Pr):B]⁺ (m/z = 1101.36, calculated 1101.33). The doublet of doublets observed in the ³¹P[¹H] NMR spectrum can be rationalized by a one bond and a three bond²⁹¹⁰¹Rh–³¹P coupling (i.e. an A₂X₂'A₂ system), the size of the former [174 Hz] being consistent with a Rh(I) center, while smaller couplings to distal Rh–centers in dimeric systems have been noted before, as observed in 14.³⁵α Complex 14 is particularly sensitive in solution and undergoes decomposition to unidentified species.


Complex 14 can be described by three valence extremes (Scheme 9): (a) a dimetalloborylene in which a formally positively charged boron engages in both σ– and π–bonding with two Rh(I) centers, (b) a cationic borinium with no multiple bonding and (c) a dimetalloboride with a Rh(III)=B–Rh(I) core.³⁵β We discount (c) due to the symmetric Rh–B–Rh motif observed and NMR data that indicate equivalent Rh(I) centers, and have turned to DFT calculations to discriminate between (a) and (b).³⁶α

The optimized structure of complex 14 showed excellent agreement with the experimentally derived metrics with computed (average) Rh–B and Rh–O distances of 1.89 Å and 2.37 Å respectively. An NBO calculation on 14 provides a Lewis structure in which the B 2pₐ and 2pₜ appear as lone vacant (LV) orbitals with significant initial populations of ca. 0.35 (the z direction being coincident with the Rh-B-Rh axis). Second order perturbation analysis indicates significant additional π-donation from Rh lone pair d-orbitals into both the B 2pₐ and 2pₜ (ΔE[π] = 15.1 kcal mol⁻¹ and 12.9 kcal mol⁻¹ respectively). A degree of multiple bond character is also suggested by a computed Wiberg bond index of 1.11 while the computed NBO charge on B is +0.45. QTAIM bond critical point (BCP) metrics associated with the Rh-B bond paths indicate a covalent interaction with a BCP electron density, ρ(r) of 0.15 au, a negative values of the Laplacian, ∇²ρ(r) = -0.15 au, and a total energy density, H(r), of ~0.11 au. These Rh-B BCP's also exhibit a low ellipticity (ε = 0.03) suggesting a near-spherical electron distribution at the BCP. Given the other computed evidence for a degree of multiple Rh–B bonding we interpret this result in terms of there being similar contributions to Rh-B π-bonding in both the xz and yz planes. This multiple bonding is most readily seen in the delocalised Kohn-Sham orbital HOMO-8 (Figure 8), and a similar, orthogonal contribution is also apparent in HOMO-5 (see Fig. S22). Taken together the body of computed evidence supports formulation (a) in Scheme 9 with species 14 best described as a dimetalloborylene.
Scheme 10. Formation of complexes 16 and 14. Xantphos–Pr ligand shown in truncated form. [BAR³⁺]⁻ anions are not shown.

Guided by previous reports of hydride transfer at cationic metal centers and B–N bond cleavage, we suggest a mechanism of formation of 16 from 6, under conditions of excess H₂B·NMe₃H, Scheme 11. This involves coproduction of a boronium cation, [BH₃(NMe₃H)(L)]⁺ (L = NMe₃H or solvent), by attack of base-stabilized boryl by, e.g., NMe₃H (formed by B–N bond cleavage). The resulting neutral Rh–hydride is trapped by BH₃, and relatively fast addition of [Rh(k⁺–P, O, P–Xantphos–Pr)(H)]⁺ forms 16. The formation of 16 from 6/H₂BH–THF would follow a similar route. Consistent with boronium formation a triplet at δ –9.8 [J = 108 Hz] is observed in the ¹¹B NMR spectrum (lit. δ –8.7, br, J ~ 90 Hz, [BH₃(NMe₃H)]⁻[SCF₃]⁻) when excess H₂B·NMe₃H is added to, in situ formed, 15. The subsequent formation of 14 from 16 involves the facile loss of 4 equivalents of H₂, through a currently unresolved mechanism. Such an H₂ loss is well established in metalaborane chemistry.

Scheme 11. Suggested mechanism for the formation of 16. Xantphos ligand and [BAR³⁺]⁻ anions not shown.

Complex 14 forms at the end of catalysis, and catalysis restarts on addition of more substrate (Section 2.5). Consistent with this, use of 14-[BAR³⁺] as a catalyst (0.2 mol% Rh) afforded polymeric material (Mₙ = 14,000 g mol⁻¹, D = 2.7) similar to that starting from 6. Addition of 10 equivalents H₂B·NMe₃H to 14-[BAR³⁺] showed the immediate generation of a mixture of 15 and 16, alongside (HBNMe₃) and [BH₃(NMe₃H)]⁻. Thus, although we cannot rule out that 14 is the actual catalyst, its temporal and reactivity profile suggest that it is more likely to play a dormant role in the catalytic cycle, with 15 or 16 observed as resting states.

2.7.2 Rh(k⁺–P, O, P–Xantphos–Pr)H 11. Although complex 12 forms on time of mixing in 1,2-F₂CC₂H₄ with 11, reaction with H₂B·NMe₃H (5 equiv.) showed the rapid formation of the tentatively assigned pentahydride complex Rh(Xantphos–Pr)H₃ [δ(¹¹B) 87.3 (v br), 45.7 (v

Figure 8. Kohn-Sham orbital (HOMO-8) exhibiting Rh-B π bonding in 14.
br), δ(H) = −11.6 (v br), lit. (PhMe-d5) ca. −13 (v br)], previously reported by Esteruelas by addition of H2 to 11,29 and complete consumption of the amine–borane to form (H3BNMeH)n (HBNMe)n and (H3BNMeH)0. No [BH3(NMeH)2]− was observed. At the end of the reaction these hydride-containing species remain active for dehydropolymerization (Mn = 26,000 g mol−1, D = 2.3).

2.7.3 [Rh(k−P,O,P−Xantphos–Et)(H)(η−H:BNMe)] [BARr4], 5. Complex 5 is a very poor catalyst for dehydropolymerization (Section 2.4). Additon of 2 equivalents of H3BNMeH to 5 showed the formation of a new species assigned using NMR spectroscopy and ESI–MS as the mono-cationic bridged aminoborane complex [([Rh(k−P,O,P−Xantphos–Et)]µ−H)(µ−H:BNMe)] [BARr4] (Scheme 12). Complex 17 becomes the dominant species in solution after 30 minutes, accompanied by 5 in a 7:3 ratio, and was identified by comparison with NMR data of related complexes [(Rh(CP3)(P(C6H5)2)2)] [BARr4]3d and [(Rh(CY3)(C6H5)2)] [BARr4] (Scheme 12), which was reported in the literature.

In particular the 11B NMR spectrum contains a broad signal at δ 61.1, while in the 1H NMR spectrum three broad hydride resonances at δ ≈ 5.82 (1 H, RhHB), −9.41 (1 H, RhHRh), and −11.16 (1 H, RhHRh) are observed, assigned on the basis of 1H[11B]/1H[1P] decoupling experiments. The mechanism for formation of dimers such as 17 has been established, and pivots around hydride transfer from a B–H activated amine–borane to form a boronium cation, e.g. [BH3(NMeH)(L)]− (L = NMeH2 or solvent), and a transient dimeric neutral hydride.54,22,68 Protonation of this dimer by half an equivalent of the boronium leads to the observed product and loss of H2. Consistent with this mechanism, a short lived complex assigned to [Rh(k−P,O,P−Xantphos–Et)(H)(η−H3BNMeH)] [BARr4] is observed at the early stages of the reaction by 1H and 31P [1H] NMR spectroscopy. These observations further underscore that initial hydride transfer at a cationic coordinated amine–borane complex is occurring. The formation of 17 is, presumably, driven by the ability for

Scheme 12. Formation of dimeric complex 17. [BARr4]− anions are omitted for clarity. L = solvent or NMeH.

Xantphos–Et to adopt a cis−k−P,P geometry at a Rh(I) center.

We have not been able to isolate complex 17 in pure form. When synthesized in situ and used in catalysis (0.2 mol% Rh, 0.446 M [H3BNMeH]2) H2 evolution is very slow, with a TOF of 0.01 s−1, very similar to the rate observed for 5 (TOF = 0.01 s−1), consistent with its rapid formation under catalytic conditions from 5.

The precise role of dimeric or monomeric [Rh(diphosphine)]− fragments in dehydropolymerization remains to be resolved, as both are implicated in catalysis.54–56 However, the isolation of 17, and its lack of reactivity, provides evidence to suggest that such dimeric hydride–bridged species are not catalysts in these particular Xantphos–alkyl systems – although their ability to act as off–cycle reservoirs for actual catalysts cannot be discounted.70 The formation of dimeric species with cis−k−P,P geometries with Xantphos–Et but not for Xantphos–Pr or Xantphos–Bu again suggests steric effects are important in determining the course of reaction.

2.7.4 ‘Bu systems – neutral and cationic, [Rh(k−P,O,P−Xantphos– ‘Bu)(H)] [BARr4], 10. Although 10 does not form a complex with H3BNMeH, it does promote H/D exchange (Section 2.3) and it was found to be capable of BH/NH activation of H3BNMeH to afford polymeric (H3BNMeH)n, albeit more slowly, in lower yield and with more side reactions than the Pr analogue 6 (Table 1). Catalysis carried out at 10 mol% to determine the fate of the catalyst produced predominantly (HBNMe)n, alongside a small quantity of (H3BNMeH)n, and a number of other side products. 1H and 31P [1H] NMR spectroscopy indicated that 10 was the only organometallic species in solution at the end of catalysis. Interestingly, under these conditions a small amount of [BH3(NMeH)(L)]− was also observed, suggesting hydride transfer processes are occurring. Addition of one equivalent of H3BNMeH to 10 did not form a c−H3BNMeH complex [Rh(k−P,O,P−Xantphos– ‘Bu)(η−H3BNMeH)] [BARr4], such as 15, indicating that the bulky ‘Bu group inhibits H3BNMeH from binding strongly. That steric variations of the Xantphos–R ligand have significant differences in reactivity has parallels to related pincer complexes, such as Ir(R−POCOP)(H): R = ‘Pr and ‘Bu.71

Rh(k−P,O,P−Xantphos− ‘Bu)H, 13. Complex 13 is observed as the sole organometallic species during catalysis (1 mol%), indicating that it is the likely resting state in this system. As for 10, the ‘Bu groups promote slower and less-selective dehydropolymerization.

2.8 Comments on the Mechanism

Use of a number of closely related rhodium–based Xantphos–alkyl systems, in which sterics, charge and number of hydride ligands on the precatalyst are varied, has allowed for insight into the mechanism of H3BNMeH dehydropolymerization. The studies provide the following observations:
1) The essential chain–growth characteristics of polymerization suggests a mechanism that involves rapid addition of a reactive monomer (i.e. H₂B=NMêH) to a growing polymer chain.

2) The catalyst remains active and is not irreversibly consumed in the polymerization process, as shown by recharging experiments.

3) The absence of a strong effect of catalyst loading on degree of polymerization, and lack of control of polymerization using H₄, suggests a coordination/insertion chain growth mechanism is likely not operating.

4) Although complicated by solubility effects, dehydrogenation is first order in H₂B-NMeH: for both cationic 6 and neutral 11, with broadly similar rate constants. Despite this there is a dramatic difference in the degree of polymerization observed: neutral 11 produces polymer that is considerably longer than that from cationic 6.

5) That different specification is observed between cationic (Rh(III)) and neutral (Rh(I)) systems suggests that the two systems do not resolve into a common catalyst.

6) Speciation studies all point to hydride–containing species being pervasive; and hydride transfer processes in the cationic system occurring with the concomitant formation of boronium cations.

These data, however, do not allow us to definitively resolve the structure of the active catalyst. Nevertheless, based on the above speciation data we propose that neutral hydride species are involved. For the cationic system a plausible mechanistic scheme is shown in Scheme 13A. Coordination of H₂B-NMeH: and subsequent reversible B=H activation forms boryl/hydride II. Pathway A proceeds through intramolecular NH activation, via transition state V, in which rate determining N=H transfer occurs to a cationic Rh–hydride, with the formation of the reactive monomer H₂B=NMêH. Alternatively intermediate II can evolve via boronium formation to give neutral hydride III, pathway B. Subsequent, rate determining, intermolecular protonation by [BH₃(NMeH₂)]⁻ reforms cationic dihydride IV. This is similar to the mechanism proposed by Conejero for H₂B-NMeH dehydrocoupling using cationic Pt–based catalysts. Complex 14 forms in an off–cycle process by reaction of BH₃/IV with III (Pathway C). For Xantphos–Pr resting states of I (i.e. 6) and 16 are observed, with bulker Xantphos–Bu it is IV (i.e. 10), and with less bulky Xantphos–Et dimeric 17 forms rapidly.

Boronium [BH₃(NMeH₂)]⁻ thus potentially plays two different roles: as a co-intermediate (pathway B) or as a side–product bifurcating from pathway A that eventually forms dormant species 14 (pathway C).

To probe this, polymerization was repeated at 0.1115 M H₂B-NMeH, 0.2 mol% 6, with and without the addition of excess, independently synthesized, [BH₃(NMeH₂)][BAR₆] (2 mol%). Figure 9 details the temporal evolution plots obtained, alongside the first order rate plots for these data. Post induction period, during the first-order region of catalysis, a ~ 3-fold increase in kobs was observed with added boronium. This is consistent with proposed mechanistic pathway B, which intimately involves [BH₃(NMeH₂)]⁻, however we cannot discount that pathway A is also operating under these conditions. Polymer produced under the conditions of excess boronium was of low molecular weight, but characteristic of catalyst 6 (Mn = 6,000 g mol⁻¹, D = 1.7)²⁶

We suggest that neutral 11 and 13 operate in a similar manner to that proposed by Esteruelas for dehydrogenation of H₂B-NH₂, for which calculations indicate that B–H bond cleavage is followed by an (albeit high energy) N–H activation and elimination of H₂B-NH₂, operating via a N–H–H–Rh didehydrogen interaction, VII.²⁸ The Xantphos–Pr is proposed to change from mer–κ³–P,O,P to cis–κ³–P,P in this cycle.

A fast chain–growth mechanism for polymerization, but not coordination/insertion, is indicated by the dehydropolymerization kinetics. We thus suggest a chain propagation process in which a low concentration of a separate, likely neutral, rhodium hydride initiator/catalyst forms a Lewis–base/acid adduct with H₂B-NMeH which thus develops a lone pair on the nitrogen (i.e. an amino–borohydride).²⁷ Subsequent, fast, head–to–tail end–chain bonding Bond forming events lead to polyaminoborane (Scheme 13B). Support for this mechanism comes from Manners’ experimental results and Paul’s computational studies on the Ir(POCOP)(H) catalyst system, A, the latter demonstrating a very low energy pathway (~ 7 kcal mol⁻¹) for this B–N bond forming process, Scheme 14A. Given the similarities between κ³–P,O,P–Xantphos ligands and POCOP–type pincer ligands it is not unreasonable to suggest a similar mechanism is operating here. This proposed end–chain growth mechanism also has parallels with that suggested by Baker.

Scheme 13. Suggested mechanism for dehydropolymerization. Xantphos ligands and [BAR₆]- anions not shown.
for dehydropolymerization of H$_3$B-NH$_3$ using Fe(PhNCCH$_2$CH$_2$NPh)(Cy$_3$P)$_2$CH$_2$P(Cy)$_2$).  

Scheme 14. (A) Paul’s proposed polymerization mechanism; (B) FLP end–chain B–N formation.

In chain–growth processes the interrelation of rates of initiation, termination and propagation are very system dependent. Adding to this potential complexity, termination events in amine–borane dehydropolymerization are currently opaque to experiment. It is likely that subtle changes in dehydrogenation rate, the relative ratio of initiator sites for polymerization and termination events (promoted by the sterics and electronics of the metal–ligand fragment and/or products of B–N bond cleavage) all combine to control the efficiency and degree of dehydropolymerization. It is, however, clear is that when considering the Xantphos–Pr systems, the neutral precatalyst promotes higher degrees of polymerization, but precisely which of the above factors governs this still remains to be resolved.

3. Conclusions

The studies described here show that changes in the sterics and overall charge can have a significant effect on the course of H$_3$B-NMe$_3$ dehydropolymerization when using [Rh(Xantphos–R)]–based catalysts. With
Xantphos–Et the more flexible ligand allows the catalyst to access dimeric – essentially inactive – species; while the bulkier and less flexible Xantphos–Bu ligand leads to lower selectivites for polyaminoborane production and considerably slower turnovers. The optimal position comes with Xantphos–Pr, for which fast turnovers and good selectivites result. Speciation studies point towards neutral, hydride containing, active catalysts, indicated to be formed from the cationic precatalysts by hydride transfer routes from the borane. It is interesting to note that for closely related alkaned dehydrogenation catalysts based upon Ir(pincer–R)(H)2 motives Pr-functionalized ligands often also show improved performance over Bu.79

The development of such structure/activity relationships, a methodology so heavily exploited in olefin polymerization,14 is central to harnessing metal-catalyzed dehydropolymerization for the production of polyaminoboranes “to order”. As well as resolving the fundamental details of this complex and nuanced catalytic system, future studies also need to consider more practical elements such as the development of catalysts that do not become entrained in the resulting polymer and a better understanding and control of the stereochemical aspects of these potentially exciting new materials.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxx

Experimental and characterization details, including NMR spectroscopic data, and X-ray crystallographic data, and computational details (PDF)

AUTHOR INFORMATION

Corresponding Author
* andrew.weller@chem.ox.ac.uk.

Author Contributions
The manuscript was written through contributions of all authors. ‡These authors contributed equally.

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(44) Addition of 5 equivalents of PPhs during catalysis using 6 or 11 immediately halted the production of H2. For complex 6 a Rh(i)-PPh adduct is formed (see Supporting Materials). We have not characterized the products of PPh addition to 11.


(62) DFT calculations on a Xantphos–H model system also retained this geometry suggesting that electronic effects are also relevant


(66) Species 14 was fully optimised using the BP86 functional. Rh and P centers were described with SDD RECPS and associated basis sets while 6-31g** basis sets were used for all other atoms. See Supporting Materials for full details and references.

(67) We cannot rule out the identity of 15 as the linear diborazane complex [Rh(κ–P,P'-Xantphos–Pr)]+[(H2BNMeH)][H2BNMe]2, as independent synthesis showed NMR data very similar to complex 15.


(74) Calculations demonstrate that Xantphos–Bu III is unstable with respect to H2: loss and formation of 13 [ref. 26b]. Given that speciation is demonstrated to be markedly different for cationic 6 and neutral 13 precatalysts we suggest this is kinetically not relevant, and H2: loss is relatively slow in the 'Pr system.


(76) Interestingly, the addition of [BH3(NMe2H)+]- also led to an increase in the induction period by ~ 10 minutes.

