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Dehydropolymerization of H$_3$B·NMe$_2$ using a [Rh(DPEphos)]$^+$ catalyst: the promoting effect of NMeH$_2$.

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KEYWORDS Dehydropolymerization, Rhodium, Amine–Borane, Mechanism

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Abstract: \([\text{Rh}(\kappa^2-\text{PP–DPEphos})\{\eta^2-\text{H}_2\text{B}(\text{NMe}_3)(\text{CH}_2)_2\text{Bu}\}][\text{BAR}^\ddagger]_4\) acts as an effective pre-catalyst for the dehydropolymerization of \(\text{H}_2\text{B·NMe}_2\) to form \(\text{N-methylpolyaminoborane (H}_2\text{BNMeH)}_n\). Control of polymer molecular weight is achieved by variation of catalyst loading (an inverse relationship) and use of the chain termination/transfer agent \(\text{H}_2\): with \(M_n\) ranging between 5,500 to 34,900 g/mol and \(D\) between 1.5-1.8. \(\text{H}_2\) evolution studies (1,2-F_2C_6H_4 solvent) reveal an induction period that gets longer with higher catalyst loading, and complex kinetics with a non–integer order in [catalyst]. Speciation studies indicate the initial formation of the amino–borane bridged dimer, \([\text{Rh}_2(\kappa^2-\text{PP–DPEphos})_2(\mu-\text{H})(\mu-\text{H}_2\text{BNHMe})][\text{BAR}^\ddagger]_4\], followed by the crystallographically characterized amidodiboryl \([\text{Rh}_2(\text{cis–k}^2-\text{PP–DPEphos})_2(\mu-\text{H})(\sigma,\mu-(\text{H}_2\text{B})_2\text{NHMe})][\text{BAR}^\ddagger]_4\]. Adding ~2 equivs NMeH_2 in THF solution to the precatalyst removes this induction period, pseudo first order kinetics are observed, and a half order relationship to catalyst is revealed, with regard to dehydrogenation and polymer molecular weights are increased (e.g. \(M_n = 40,000\) g/mol). Speciation studies suggest NMeH_2 acts to form the active precatalysts \([\text{Rh(DPEphos)(NMeH}_2)_2][\text{BAR}^\ddagger]_4\) and \([\text{Rh(DPEphos)(H)}_2(\text{NMeH}_2)_2][\text{BAR}^\ddagger]_4\), which were independently synthesized and shown to follow very similar dehydrogenation kinetics and produce polymer of molecular weight comparable with the amine–doped systems. This promoting effect of added amine in situ is shown to be general in other cationic Rh-based systems, and possible mechanistic scenarios are discussed.
1. Introduction

Polyaminoboranes,\textsuperscript{1-4} exemplified by \(N\)-methylpolyaminoborane \((\text{H}_2\text{BNMeH})_n\), have alternating main-chain B–N units and are of interest as precursors to BN-based ceramics, or as new unexplored materials that are isosteres of polyolefins. Since the original report of the synthesis of \((\text{H}_2\text{BNMeH})_n\) by the dehydropolymerization of \(\text{H}_3\text{B} \cdot \text{NMeH}_2\) using an \(\text{Ir} (\text{POCOP})\text{H}_2\) catalyst \((\text{POCOP} = \kappa^3\text{C}_6\text{H}_3\text{–}2,6-(\text{OPtBu})_2)_2\)\textsuperscript{4-6} there has been significant progress in developing catalytic methodologies,\textsuperscript{7-13} as well as non–catalyzed routes.\textsuperscript{14} The accepted overarching catalytic mechanism operates via initial dehydrogenation of \(\text{H}_3\text{B} \cdot \text{NMeH}_2\) to form a transient, free or metal–bound, amino–borane which then undergoes a head-to-tail BN coupling (Scheme 1). A number of different propagation scenarios have been proposed for this step, that show elements of chain–growth,\textsuperscript{4,10} step-growth\textsuperscript{15} or hybrid mechanisms.\textsuperscript{16} Particularly interesting would be systems that demonstrate the potential for control\textsuperscript{17} over the polymerization process, holistically defined by: degree of polymerization (as measured by \(M_n\)), dispersity (\(D\)), initiation/termination events and catalyst lifetime (i.e. \(T_{\text{on}}\)). While aspects of these performance criteria have been noted,\textsuperscript{7-10,15} there is no general approach to their optimization.

![Scheme 1. Dehydropolymerization of amine–boranes.](image)

We have reported cationic dehydropolymerization pre-catalysts based upon \({\text{Rh}}(\text{Xantphos–R})\)\textsuperscript{+} motifs,\textsuperscript{18,19} in which the identity of the PR\(_2\) group is changed (Scheme 2).\textsuperscript{9,10,20} When \(R = \text{Ph} \ (A)\) medium\textsuperscript{2} molecular weight polymer is formed \((M_n = 22,700 \text{ g/mol}, D = 2.1)\), a higher catalyst loading promoted lower \(M_n\) and \(\text{H}_2\) acts as a chain termination/transfer agent \((M_n = 2,800 \text{ g/mol}, D = 1.8)\). Although detailed kinetics for \(\text{H}_3\text{B} \cdot \text{NMeH}_2\) dehydropolymerization were not reported, these observations were interpreted as signaling a coordination/insertion(chain growth
mechanism in concert with more extensive studies on H₃B·NMe₂H. There is also a significant induction period observed (~15 min). In contrast, when R = 'Pr (B) H₂ and catalyst loading do not significantly change Mₙ (9,500 g/mol, Đ ~ 2.8), there is a negligible induction period, and a dual role for the organometallic species was proposed in which dehydrogenation/propagation occurs from different centers. This mechanistic switch may be influenced by the preferred ligand coordination modes: Xantphos-Ph is a hemilabile ligand preferring to coordinate cis-κ²-PP and mer-κ³-POP, while Xantphos-Pr prefers mer-κ³-POP (Figure S1 compares coordination modes for crystallographically–characterized Xantphos–R).

![Scheme 2](image)

**Scheme 2.** Comparison of previously reported Rh–Xantphos–based catalysts and their performance in dehydropolymerization of H₃BMeH. [BARf₄]⁻ anions not shown.

We now report a detailed and systematic study on the dehydropolymerization of H₃B·NMeH₂ using a different Rh–POP based system: {Rh(DPEphos)}⁺ [DPEphos = bis–(2–(diphenylphosphino)phenyl)ether]. Using this ligand, that favors cis-κ²-PP coordination (Figure S1), significant control over Mₙ by both catalyst loading and H₂ is achieved, with Mₙ ranging from 5,500 to 40,000 g/mol and Đ = 1.5-1.8. These studies also reveal the formation of dimeric species, and the key role of added amine, NMeH₂, in both promoting catalysis, and increasing Mₙ / lowering Đ of the isolated polymer. Finally, combining these observations, the synthesis and evaluation in catalysis of a simple [Rh(DPEphos)(NMeH₂)₂]⁺ precatalyst is reported. This positive influence of added amine is also shown be general for other, previously reported, cationic Rh–based systems. The role of added amine has been recently noted with regard to increasing catalyst lifetime of
Ru–based catalysts for the dehydropolymerization of H₃B·NH₃ by trapping BH₃, although the influence of amine on the characteristics of the polymer produced were not commented upon.

2. Results and Discussion

2.1 Precatalyst synthesis. Precatalyst 2a, [Rh(κ²–P,P–DPEphos){η^2-H₂B(NMe₃)(CH₂)₂Bu}][BArF₄] (ArF = 3,5-(CF₃)₂C₆H₃), is synthesized from hydroboration of 1-butylethene (TBE) by H₃B·NMe₃ using the NBD–precursor 1a, pre-activated by H₂ (Scheme 3). Spectroscopic data for purple 2a are similar to the previously reported Xantphos-derivative, A. In particular a single environment is observed in the ³¹P{¹H} NMR spectrum [δ 40.0, J(RhP) = 180 Hz], the 3–center 2–electron Rh···H–B groups are observed at δ ~5.55 (2 H) in the ¹H NMR spectrum, while the ¹¹B NMR spectrum shows a characteristically downfield shifted resonance [δ 33.3], indicating a bidentate binding mode of the borane. The amine–borane in 2a is easily displaced, and the [Rh–Xantphos–Ph]^+ analogue (A) has been shown to be active for H₃B·NMeH₂ dehydropolymerization, TBE hydroboration using H₃B·NMeH² and B–B homocoupling.

![Scheme 3. Synthesis of the {Rh(DPEphos)}^+ precatalyst 2a](image)

2.2 Dehydropolymerization of H₃B·NMeH₂: Variation of conditions. Precatalyst 2a is an effective dehydropolymerization catalyst, and full conversions of H₃B·NMeH₂ are obtained even at low loadings under a slow stream of Ar to remove H₂ (e.g. 0.223 M H₃B·NMeH₂, [2a] = 0.1 mol%, ToN = 1000, 6 hrs). Variation of catalyst loading between 0.2 and 1 mol% reveals an inverse relationship between Mₙ of the isolated polymer and catalyst loading (Table 1 Entries 1–3 and Figure 1A). The resulting ¹¹B NMR spectra of the
reaction mixtures show the characteristic\textsuperscript{2,12} broad signal at $\delta$ –6 for (H$_2$BNMeH)$_n$, and only trace (HBNMe)$_3$ (Figure S2). The $^{13}$C{$^1$H} NMR spectra (THF) show a relatively sharp peak at $\delta$ 35.5 (NMe). In contrast, at 0.1 mol\% catalyst loading $M_n$ does not increase compared to 0.2 mol\%, and there is significant 1,2-F$_2$C$_6$H$_4$ insoluble polymer that is THF soluble. NMR spectroscopic analysis of this material (Figure S3) showed additional signals at $\delta$(\textsuperscript{11}B) ~1 and $\delta$(\textsuperscript{13}C{$^1$H}) ~35.7 (br, NMe) that may signal tertiary or quaternary main chain centers, suggesting cross linking/chain branching.\textsuperscript{10,11,19,25} While we currently have no explanation for this change in polymer characteristics, at these very low loadings trace impurities (or products of B–N bond cleavage – \textit{vide infra}) may have a disproportionate effect on the polymerization process, leading to a different product being formed.

When dehydropolymerization was conducted under H$_2$ measurement conditions (eudiometer, H$_2$ established in the head space), or a closed system, H$_2$ acts as a chain transfer/termination agent and significantly shorter polymer is isolated, in which there is a significantly larger signal at $\delta$(\textsuperscript{11}B) ~–18 that could be assigned to BH$_3$–end groups\textsuperscript{15} (Figure 1B; Figure S4 shows a representative \textsuperscript{11}B NMR spectrum). Similar $\bar{D}$ are retained compared with the open system and the inverse relationship between $M_n$ and catalyst loading is retained (Table 1, entries 5–8). Interestingly, there is now a significant difference in $M_n$ between 0.1 and 0.2 mol\%, suggesting that H$_2$ modifies the influence of the very low catalyst loading. A conversion versus $M_n$ study (0.2 mol\%, open system, Figure 1C) indicates a chain growth mechanism is operating, as at low (10\%) conversions long polymer chains are observed ($M_n$ = 24,800 g/mol, $\bar{D}$ = 1.2) and H$_3$B·NMeH$_2$ monomer dominates (Figure S5).
Table 1 GPC Characterization data for isolated polyaminoborane.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>$[\text{Rh}]_{\text{rr}}$ mol%</th>
<th>Conditions</th>
<th>$M_n$ g/mol</th>
<th>$\Delta$</th>
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<tr>
<td>1</td>
<td>2a</td>
<td>1</td>
<td>Open (Ar flow)</td>
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<tr>
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<td>10</td>
<td>4b</td>
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<td>0.2</td>
<td>H\textsubscript{2} measurement/\textsim 2 equiv. NMeH\textsubscript{2} in 50 µL THF</td>
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<td>1.5</td>
</tr>
<tr>
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<td>H\textsubscript{2} measurement</td>
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<tr>
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<td>A\textsuperscript{9}</td>
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<tr>
<td>22</td>
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<td>H\textsubscript{2} measurement</td>
<td>63,100</td>
<td>1.7</td>
</tr>
<tr>
<td>23</td>
<td>C\textsuperscript{16}</td>
<td>0.2</td>
<td>H\textsubscript{2} measurement/\textsim 2 equiv. NMeH\textsubscript{2} in 50 µL THF</td>
<td>78,900</td>
<td>1.6</td>
</tr>
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</table>

\textsuperscript{a}All at 298K, 0.223 M H\textsubscript{3}B·NMeH\textsubscript{2}, 1,2-F\textsubscript{2}C\textsubscript{6}H\textsubscript{4} solvent. GPC data quoted relative to polystyrene standards, RI detection, THF with 0.1 w/w [NBu\textsubscript{4}]Br, 35ºC.
Figure 1. GPC data (rel. to polystyrene standards, RI detection, THF with 0.1 w/w [NBu₄]Br, 35°C) for (H₂BNMeH)ₙ isolated from H₃B·NMeH₂ dehydropolymerization (0.223 M, 1,2–F₂C₆H₄, 20°C) using catalyst 2a. (A) Variation of [2a] under Ar–purge; (B) variation of [2a] under H₂ measurement conditions (eudiometer); (C) conversion versus Mₙ/Ð plot, open conditions.

We have previously, but briefly, reported similar control of molecular weight by catalyst loading and H₂ for catalyst A and suggested a coordination/dehydrogenation/insertion/chain growth mechanism for the dehydropolymerization, in which the same metal center both dehydrogenates and amine–borane and promotes propagation. This more comprehensive data with 2a supports a similar mechanism in the {Rh(DPEphos)}⁺ system. That H₂ acts to modify the polymer chain may arise from chain–termination/transfer by hydrogenolysis of a Rh–BH₂(polymeryl) or Rh–NMeH(polymeryl) bond. The use of H₂ as a chain-termination agent in olefin polymerization is well established, operating through sigma-bond metathesis of [M]−CH₂−polmeryl with H₂ to form a metal hydride and free polymer. The inverse relationship between Mₙ and catalyst loading suggests dehydropolymerization at a single metal–center, as lower catalyst loadings lead to less propagating sites for the concomitantly formed H₂B=NMeH. Interestingly, such behavior is also reminiscent of a classical radical polymerization mechanism, as has been recently noted.

2.3 Speciation experiments: The formation of dimeric Rh₂ species. With the polymer growth kinetics in hand we turned to identifying the species that formed during catalysis, using NMR spectroscopy. The low catalyst loadings used for polymerization (0.1 to 1 mol%) meant that these speciation studies necessarily were performed at 10 mol% 2a (sealed NMR tube, 1,2–F₂C₆H₄). Under these conditions ¹¹B NMR spectroscopy showed the formation of (H₂BNMeH)ₙ,
(HBNMe)$_3$ and (H$_2$B)$_2$(µ–H)(NMeH) [td, δ –22.3$^{29}$], the latter potentially signaling free BH$_3$ by loss of amine. $^{31}$P{$^1$H} NMR spectroscopy showed the initial formation, after 5 minutes, of two new dimeric complexes: a bridging hydrido–aminoborane 3a, [Rh$_2$(DPEphos)$_2$(µ–H)(µ–H$_2$B=NHMe)][BArF$_4$], and an amidodiboryl 4a, [Rh$_2$(κ$^2$–P,P–DPEphos)$_2$(µ–(H$_2$B)$_2$NMe)][BArF$_4$] (Figure 2A). After 2 hours 4a is dominant, but the mixture slowly returns to favoring 3a after 5 hours (Figure S6). Complex 3a can be prepared as the only organometallic species by addition of H$_2$/2 equivs. of H$_3$B·NMeH$_2$ to 1a. Boronium [BH$_2$(NMeH)$_2$]$^+$ [δ –7.1, J(BH) = 110Hz, cf. authentic sample δ –7.4, J(BH) = 117 Hz$^{10}$] is also observed under these conditions,$^{29}$ in line with the reported mechanism for the formation of analogous complexes with [Rh$_2$(R$_2$P(CH$_2$)$_n$PR$_2$)$_2$(µ–H)(µ–H)$_2$B=NR$_2$')]$^+$ motifs.$^{30,31}$ Here, attack of free amine (from B–N bond cleavage$^{32}$) at a precursor sigma–amine borane complex generates a neutral dimeric Rh–hydride and [BH$_2$(NMeH$_2$)$_2$]$^+$, for which subsequent proton transfer and NMeH$_2$ loss result in the bridging amino–borane motif. NMR and ESI–MS data for 3a are fully consistent with its formulation (Supporting Materials), and are very closely related to the previously reported [Rh$_2$(P$_2$P(CH$_2$)$_3$P$'_2$)$_2$(µ–H)(µ–H$_2$B=NH$_2$)][BArF$_4$].$^{30}$ The identity of 4, however, was only revealed by a single crystal study of 4b, using the [Al(OC(CF$_3$)$_3$)$_4$]$^-$ anion,$^{33}$ which comes from a slow recrystallization of 3b/4b formed in situ from [Rh(κ$^2$–P,P–DPEphos)(NBD)][Al(OC(CF$_3$)$_3$)$_4$] activated with H$_2$, 1b (Figure 2B). 4b is not isolated pure, formed alongside 3b (~5% by $^{31}$P{$^1$H} NMR spectroscopy) and (H$_2$BNMeH)$_n$. 
Figure 2. (A) Addition of H$_3$B·NMeH$_2$ to 2a (10 mol%) to form 3a and 4a. (B) Synthesis and solid–state structure of the cationic portion of [4b]$^+$. Selected bond lengths (Å) and angles (º): Rh1–Rh2 2.6421(4); Rh1–B1 2.326(5), Rh1–B2 2.096(6); Rh2–B1 2.107(5), Rh1–B2, 2.328(5); Rh1–C38 2.998(4), B1–N1, 1.59(1), B2–N1 1.56(1); P1–Rh1–Rh2 162.59(3), P2–Rh1–Rh2, 95.31(3).

The structure of the cation in 4b has a Rh$_2$ core [Rh–Rh 2.6421(4) Å] with a bridging amido–bisboryl ligand that has two $\alpha$–BH···Rh agostic interactions with the proximal Rh centers [e.g. Rh2–B1 2.107(5), Rh1–B1 2.326(5) Å]. The DPEphos ligand adopts a $\kappa^2$–PP motif, with two of the phosphines (P2, P3) trans to the BH agostic interaction and cis to the Rh–Rh bond; while P1 and P4 lie trans to the Rh–Rh bond and couple to both Rh–centers in the $^{31}$P{¹H} NMR spectrum [e.g. $J$(RhP) = 139, 102 Hz]. The four $^{31}$P environments are chemically inequivalent. There is no evidence for a Rh–H–Rh bridging hydride (NMR, ESI–MS), and the $\alpha$–BH···Rh are observed as
two broad doublets at $\delta$ –8.86 and –9.44 [J(\text{PH}) ~70 Hz] in the $^1\text{H}$$^{11}\text{B}$ NMR spectrum.$^{34}$ The $^{11}\text{B}$ NMR spectrum shows a broad signal at $\delta$ 9.4. These data show the solid–state structure is retained in solution. As the NMeH group forces C$_1$ symmetry in the molecule, this also shows that the amido–bisboryl ligand is not undergoing rapid and reversible dissociation or hydride fluxionality. A Quantum Theory of Atoms in Molecules (QTAIM) study of the bonding in the cation of 4b (Figure 3) indicates a Rh–Rh interaction, with the presence of a bond path and bond critical point (BCP) between Rh1 and Rh2. BCPs are also present between Rh1-H$^\alpha$B1 and Rh2-H$^\beta$B2 giving evidence for the $\alpha$-BH···Rh agostic interactions of the bridging amido-bisboryl ligand. This is supported, for example, through examination of the BCP metrics of bridging B1-H$^\alpha$/B2-H$^\beta$ which show a weaker (lower electron density, $\rho(r)$, and total energy density, $H(r)$) B–H bond with less symmetrical bonding (larger ellipticity, $\epsilon$) than for terminal B1-H$^\delta$/B2-H$^\delta$, as expected for B–H bonds involved in agostic interactions. Comparatively weak CH···Rh agostic interactions (\(\rho(r) = 0.02, H(r) = 0.00\)) between phenyl groups and each Rh centre are also observed in the QTAIM analysis, and also observed experimentally, e.g. Rh1···C38, 2.997(5) Å. Consistent with such interactions a broad asymmetric signal is observed at $\delta$ 3.94 (2 H) in the $^1\text{H}$ NMR spectrum of 4b, that is attributed to agostic Rh···HC$_\text{phenyl}$ interactions, similar to that observed in [Ru(P$^3$Pr$_3$)$_2$(H)$_2$(C$_6$H$_5$C$_5$H$_4$N)][BAr$_4$F$_4$] ($\delta$ 4.14).$^{35}$ 4b is a rare example of a complex with both C–H and B–H agostic interactions.$^{36,37}$

Related structures to 4b that show bridging “BNB”,$^{20,38}$ $\alpha$–BH···Rh agostic$^{39}$ or amino–boryl motifs$^{9,40}$ have been reported before. However as far as we are aware the amido–bis boryl structure is a new motif in metalloborane chemistry. Perhaps most closely related to 4b is a Rh–dimer with P–C activated Xantphos–Ph ligands and a bridging N,N-dimethylaminodiboranate unit ([H$_3$BNMe$_2$BH$_3$]$^-$) which is isolated at the end of dehydrocoupling of H$_3$B·NMe$_2$H when using catalyst A. Interestingly this is also a competent catalyst for H$_3$B·NMeH$_2$ dehydropolymerization.$^{20}$ While we currently can only speculate on the mechanism of formation of 4, it is (reversibly, Figure
2A) connected to 3a by simple addition of BH₃ and loss of H₂ in the latter. Under catalytic conditions 3a likely forms first, while the role of 4a is less clear. To help resolve the identity of the active species in catalysis, kinetic studies were undertaken, taking 2a, 3a and 4b as precatalysts.

**Figure 3.** Contour plot of the electron density of the central cationic portion of 4b presented in the \{Rh1N1Rh2\} plane with projected stationary points, bond paths, bond critical points (BCP; green), and ring critical points (RCP; red). the associated table shows selected BCP metrics (a.u.; average data for indicated bonds)

<table>
<thead>
<tr>
<th>BCP</th>
<th>ρ(r)</th>
<th>ϵ</th>
<th>H(r)</th>
</tr>
</thead>
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<tr>
<td>Rh¹–Rh²</td>
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<td>0.32</td>
<td>−0.02</td>
</tr>
<tr>
<td>Rh¹–H⁴B¹</td>
<td>0.09</td>
<td>0.39</td>
<td>−0.03</td>
</tr>
<tr>
<td>Rh²–H⁵B²</td>
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<td>0.39</td>
<td>−0.04</td>
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<tr>
<td>B¹–H³</td>
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<td>0.03</td>
<td>−0.18</td>
</tr>
<tr>
<td>B²–H⁶</td>
<td>0.17</td>
<td>0.03</td>
<td>−0.18</td>
</tr>
<tr>
<td>Rh²–H²C</td>
<td>0.02</td>
<td>0.37</td>
<td>0.00</td>
</tr>
</tbody>
</table>

2.4 **Kinetic studies of dehydropolymerization as followed by H₂–evolution.** The kinetics of dehydropolymerization were followed by volumetric studies of H₂ generation using a eudiometer. In all cases ~1.1 equivs. of H₂ was measured and very little N–trimethylborazine was observed by ¹¹B NMR spectroscopy (Figure S7) indicating that evolved H₂ is a good proxy for transient H₂B=NMeH equivalents formed and subsequent polymer chain–growth. A significant induction period was observed prior to faster turnover (e.g. 60 mins, 0.4 mol%), that gets longer with increase in [2a]₀ (Figure 4A, e.g. 0.1 mol% tₐₚₚ = 33 mins; 1 mol% tₐₚₚ = 110 mins). An induction period has also been noted for catalyst A in H₃B·NMeH₂ dehydropolymerization⁹ as well as for [Rh(Ph₂P(PCH₂)₃PPPh₂(FC₆H₅)][BARF₄], C, in H₃B·NMe₂H dehydrocoupling.⁴² For this latter system increased [Rh]TOTAL also led to longer induction periods, and a subsequent study showed the initial formation of an amino–borane bridged dimer analogous to 3a.³⁰ While the observation of an induction period might suggest a heterogeneous system here,⁴₃–⁴⁵ addition of excess Hg or sub–stoichiometric PPh₃ during productive turnover did not significantly reduce reaction rate, and no
darkening of the reaction was noted, pointing towards homogeneous catalysis (Figure S9). Overall, the kinetics evolve in a sinusoidal manner, with a rate-maximum reached approximately at the midpoint (e.g. 0.4 mol%, $v_{\text{max}} = 4.1(2) \times 10^{-5}$ Ms$^{-1}$). This behavior is suggestive of a long induction period coupled to rate-attenuation as the substrate is depleted. There is a non-integer dependence of the maximum rate on the initial catalyst concentration (Figure S12), that hint at more complex kinetics. Using 0.223 M $D_3B\cdot NMeH_2$ or $H_3B\cdot NMeD_2$ at 0.4 mol% $2a$ KIEs determined from $v_{\text{max}}$ were $k(BH)/k(BD) = 1.1 \pm 0.1$ and $k(NH)/k(ND) = 2.2 \pm 0.1$, which suggests N–H bond cleavage is involved in the turnover limiting step. These data are very similar to those measured for A. The polymerization is not living as recharging $2a$ gives ~same $M_n$, at a similar rate for second recharge (Figure S15). A short induction period was noted for each recharge, which reflects the reformation of $3a$ at the end of catalysis (vide infra).

Use of in situ generated dimeric $3a$ leads to a shorter, but still significant, induction period (~30 mins, Figure 4B) and a similar profile and rate-maximum as for $2a$. In contrast, reaction of crude $4b$ resulted in no detectable induction period. Furthermore H$_2$ evolution (a proxy for H$_3$B=NMeH formation) followed a first order profile (Figure 4B, $k_{\text{obs}} = 3.2(1) \times 10^{-4}$ s$^{-1}$), and this allowed for a half-order dependency on initial catalyst concentration, i.e. [Rh]$^{\text{TOTAL}}$, to be measured (Figure 4C).

Figure 4 H$_3$B=NMeH equivalents from H$_2$ evolution (eudiometer) in the dehydropolymerization of H$_3$B·NMeH$_2$ (0.223 M 1,2–F$_2$C$_6$H$_4$, 20ºC). Each set of comparative runs used the same batch of solvent and H$_3$B·NMeH$_2$. (A) [2a] = 0.4 and 1 mol% Rh and 0.4 mol% + 1 equiv. H$_3$B·THF; (B) 2a, 3a and 4b at 0.4 mol% [Rh]$^{\text{TOTAL}}$, $k_{\text{obs}}$ measured for [4b]. (C) [Rh]$^{\text{TOTAL}}$ versus $k_{\text{obs}}$ using 4b as a catalyst.
The polymers isolated from these H₂ evolution studies using 3a and 4b are similar by GPC analysis, but slightly longer compared to that from 2a at equivalent [Rh] (Table 1, entries 9 and 10). Speciation studies at 1 mol% 2a returns only 3a at the end, which suggests, if formed, 4a must be consumed under the conditions of catalysis. Overall these data show: a change in H₂–evolution kinetics on moving from 2a (complex) to 4 (pseudo first order), that 4 must sit close to the actual catalyst, and that 3 still requires an induction process to bring it on-cycle. The approximately half–order dependence in [Rh]TOTAL when using 4a suggests a low nuclearity active catalyst that is in a rapid equilibrium with an inactive higher-order species, as is discussed later.

2.5 Kinetic Studies: Doping experiments, and the promoting effect of NMeH₂. Seeking to understand the observed kinetics, and in particular the underlying reason for the induction period, the influence of various species that may be present, or formed, during catalysis was examined. Addition of one equivalent BH₃·THF (in 50μL THF) to 0.4 mol% [2a]/H₃B·NMeH₂/1,2-F₂C₆H₄ solvent increased the induction period significantly (Figure 4A) and gave significantly shorter polymer (Table 1, entry 11), while 10 equivalents halts catalysis, possibly by the formation of inactive boron–rich species.³² Added [H₂B(NMeH₂)₂][BArF₄] (10 equivalents) significantly slows catalysis, now taking 24 hrs for completion to produce very short polymer (Mₙ = 2,800 g/mol, D = 2.3). This argues against its role in productive catalysis, in contrast with other systems,¹⁰,²⁹,⁴⁶ in particular the [Rh(Xantphos-iPr)]⁺ system where it promotes catalysis.¹⁰ H₃B·THF presumably acts to titrate out NMeH₂, while we propose that excess [H₂B(NMeH₂)₂]⁺ acts to poison catalysis, possibility sequestering NMeH₂ via N–H···NMeH₂ hydrogen bonding, as noted for related bis–(phosphine)boronium salts.⁴⁷ The control experiment of THF addition (50 μL) reduced the induction period to 30 minutes and produced polymer comparable to non–doped experiments (Table 1, entry 13). The most dramatic change came from addition of ~2 equivalents of NMeH₂ (in 50μL THF) to 0.4 mol% [2a]/H₃B·NMeH₂. This resulted in a kinetic profile for H₂ evolution that now showed no induction period and pseudo first order kinetics for hydrogen evolution (k_obs =
3.7(1)×10⁻⁴ s⁻¹), similar to that of 4b at the same [Rh]TOTAL. Isolated polymer, however, was considerably longer (Mn = 27,400 g/mol, D = 1.9) than for when just 2a was used. As expected, under open conditions Mn increases (Mn = 32,100 g/mol, D = 1.6), albeit to a lesser extent than compared with the analogous non–doped experiments (cf. entries 13/14 and 2/7, Table 1). These observations, alongside the speciation data at 10 mol% that demonstrate that 3a is likely the first formed species, show that free NMeH₂ formed from B–N bond cleavage is key to not only bringing the catalyst on-cycle, but also in promoting propagation or attenuating chain transfer/termination leading to higher molecular weights of isolated polymer. Given these observations the role of NMeH₂ was next investigated.

2.6 Rh–amine adducts as effective precatalysts. We first sought to understand the likely species generated insitu by addition of amine to the precatalyst, 2a. Addition of ~ 2 equivs NMeH₂ (in THF) to 2a gave the simple bis–amine complex [Rh(κ²–P,P–DPEphos)(NMeH₂)₂][BArF₄], 6, which reacts with H₂ in situ to form the corresponding dihydride [Rh(κ²–P,P–DPEphos)(H)(NMeH₂)₂][BArF₄], 5 (Scheme 4). Complex 5 reversibly, but slowly, loses H₂ under extended degassing to reform complex 6, and thus we suggest under the conditions of dehydropolymerization 5 would be persistent. NMR spectroscopic data are fully consistent with the proposed structures (see later), but under these conditions of synthesis isolating pure samples of 5 and 6 in bulk has proved difficult, and a 1:1 mixture of 5/6 is conveniently prepared from 1a/~2×NMeH₂/H₂/degas and used directly in catalysis. Complex 5 is the sole organometallic product on addition of ~2 equivalents of NMeH₂ to 1:3 mixture of 3a/4a, alongside HB(NMeH)₂ [δ(¹¹B) 28.6, J(BH) 127 Hz], demonstrating the role of NMeH₂ in both generating 3, via boronium formation, and bringing dimeric 3 and 4 back to monometallic species. Complex 6 (and 5 on subsequent addition of H₂) can be prepared as a free–flowing pure solid in bulk via an alternative route, from addition of NMeH₂ to [Rh(κ²–P,P–DPEphos)(1⁻⁶–o–Me₂C₆H₄)][BArF₄], 7, that enables their definitive characterization by NMR spectroscopy. However, this preparative involves a
laborious, multiple, trituration with cold pentane and thus the in situ prepared mixture is more convenient to use. Data from H₂ evolution kinetics and isolated polymer using thus isolated 6 fit well with the trends apparent from using the 5/6 in situ mixture (Table 1 and Figure 5). Notable NMR spectroscopic data for 6 are the observation of equivalent NMeH₂ groups in the ¹H NMR spectrum; while for 5 addition of H₂ makes these group inequivalent and diastereotopic, two Rh–H environments are observed, one of which shows a large trans coupling to ³¹P [J(HP) 182 Hz] and inequivalent phosphorous environments are observed in the ³¹P{¹H} NMR spectrum (Supporting Materials).

**Scheme 4.** Synthesis of amine-adducts. [BARₓ₄]⁻ anions not shown, and DPEphos ligand shown in truncated form.

Using in situ generated 5/6 gave pseudo first order plots for H₂ evolution with no induction period (e.g. 0.4 mol% kₜₒₜₜ = 4.1(1)×10⁻⁴ s⁻¹). These were also half–order in [Rh]_TOTAL (Figure 5A). Half order behavior is indicative of either a rapid equilibrium between species of different nuclearity, e.g. monomer–dimer, prior to the turn-over limiting step, in which the higher nuclearity species is inactive but dominant,⁴⁹ or the rapid and reversible dissociation of a ligand that reveals a low concentration of an active species.⁵⁰ Monomer/dimer equilibria have been proposed in polymerization systems previously,⁵¹-⁵³ and amine–borane dehydrocoupling specifically.⁴⁹,⁵⁴,⁵⁵ While addition of 10 equivalents of NMeH₂ caused no significant change in rate (kₜₒₜₜ = 4.2(1)×10⁻⁴ s⁻¹), suggesting that NMeH₂ dissociation is not occurring, the polymer isolated from this experiment was insoluble in THF and thus we cannot rule out a change in mechanism. We discount rapid and reversible H₂ loss as under conditions of measurement H₂ effectively becomes
saturated and constant, and H₂ loss from 5 is also slow. No significant change in kinetics were observed on addition of excess Hg during catalysis – suggesting a homogeneous system. The use of these in situ prepared amine complexes 5/6 leads to polymer with greater $M_n$ (but still inverse with regard to $[\text{Rh}]_{\text{TOTAL}}$), while $\mathcal{D}$ is kept relatively low (Figure 5B, e.g. 1 mol % $M_n = 20,600 \text{ g/mol, } \mathcal{D} = 1.5$). Thus the added amine – whether bound or free – not only brings the catalyst onto cycle but also promotes greater apparent degrees of polymerization. Whether this is by faster propagation or attenuation of termination is not currently known.

![Figure 5](image.png)

**Figure 5.** (A) H₂B=NMeH equivalents from H₂ evolution (eudiometer) in the dehydropolymerization of H₃B·NMeH₂ (0.223 M 1,2–F₂C₆H₄, 20°C). Each set of comparative runs used the same batch of solvent and H₃B·NMeH₂. 5/6 (~50:50) at various loadings + 0.05 µL THF, inset = $k_{obs}$ versus $[5/6]^{0.5}$. (B) Comparison of $M_n$ and $\mathcal{D}$ versus [5/6], pure 6, 2a, 3a and 4b (under H₂ evolution measurement conditions).

Interestingly, this promoting effect of NMeH₂ is not operative in the [Rh(Xantphos–iPr)(H)]₂⁺ system,¹⁰ that is suggested to involve a different mechanism where dehydrogenation and chain propagation occur at different metal centers in a bifunctional catalyst. Thus, independently prepared [Rh(mer–κ³–P,O,P–Xantphos–iPr)(H)]₂(NMeH₂)[BARF₄], 8, (see supporting materials) does not dehydropolymerize H₃B·NMeH₂, returning unchanged substrate after 1 hr (0.2 mol%, 0.111 M H₃B·NMeH₂). This is probably due the to the relatively strongly bound amine blocking access of H₃BN·MeH₂ to the metal center, at which the Xantphos–iPr is also not hemilabile (Figure S1), so that sigma–complex formation, and subsequent dehydrogenation by BH/NH activation, does not take place.
2.7 Discussion of proposed mechanistic landscape. Bringing these observations together, we propose an overall mechanism shown in Scheme 5, in which the induction period that gets longer with increased [2a] can also now be explained. NMeH₂, generated by slow B–N bond cleavage of H₃B·NMeH₂, at a rate that is independent of [2a], first promotes the formation of 3a and then more slowly the active pre–catalyst 5. In this model, higher concentrations of 2a result in more 3a needing to be first formed, via hydride abstraction and boronium formation, and then converted to the active catalyst with an unchanged amount of NMeH₂, thus leading to a longer induction period. The active catalyst is closely related to both 5/6 and 4a, but we suggest both of these sit outside of the productive cycle, as their structures and reactivity are incompatible with the observed kinetics. The insensitivity in rate to added NMeH₂ suggests this does not reversibly dissociate; while a sensible model in which dimeric 4a, with its Rh–Rh bond and bridging amido–bisboryl ligand, undergoes rapid and reversible dissociation (vide supra) or loss of ligand is not obvious. Moreover, 4b reacts rapidly with NMeH₂ to form 5, suggesting that if formed in catalysis it is not persistent. While we cannot currently confidently comment on the nature of the actual catalyst for dehydrogenation, chain growth or the termination process, the half–order relationship in [Rh]TOTAL and the observation of dimeric species (4 and 3) suggest that such Rh₂ motifs may be intimately involved. The strong, and persistent, inverse relationship between Mn and [Rh]TOTAL, coupled with the sensitivity to H₂, suggests a coordination/insertion/chain growth mechanism for which NMeH₂ also modifies chain length – possibly by attenuating chain termination. Based on the half order kinetics observed from the dehydrogenation studies, we suggest three possible general motifs for the active catalyst (Scheme 6): one which invokes a monomer–dimer equilibrium in which one of the monomers is the active catalyst (A), and one in which a persistent dimer reversibly loses a bound ligand (B). Scenario A is reminiscent of the unsymmetrical Rh₂ hydride dimers that can form in Rh–catalyzed alkene hydrogenations,⁵⁶ while scenario B is supported by the recent report that dimeric early transition–metal complexes have been shown to act as competent catalysts for H₂B·NMeH₂ dehydropolymerization.⁷ A third possibility is that
deprotonation of bound NMeH₂ provides an active Rh–NMeH amido motif, similar to the bifunctional catalysts developed by Schneider and co–workers, (C).¹¹

\[
[\text{Cat}] = [\text{Rh}]-\text{Polymeryl} \\
L = [\text{Cat}] \text{ or NMeH}_2
\]

**Scheme 5.** Pathways for catalyst activation and catalysis in the dehydropolymerization of H₃B·NMeH₂ using [Rh] = {Rh(DPEphos)}⁺ precatalysts. Anions are not shown. [Cat] may be mono– or bimetallic.

**Scheme 6.** Generalized possible active species in catalysis. \( P = \) phosphine, \( L = \) ligand (e.g. NMeH₂, or amine–borane, derived fragment). All structures shown are representative and the actual number of hydrides/cooordination geometry is undetermined.

3. Conclusions

We have shown that a combination of catalyst loading, \( H_2 \) and NMeH₂ can be used to control the dehydropolymerization of H₃B·NMeH₂ in a \{Rh(DPEphos)}⁺ based catalyst. We believe this to be
an important observation and one that may show some generality, building upon the already demonstrated improvement in catalyst lifetimes on addition of amine.\textsuperscript{8} Indeed these broader promoting effects of NMeH\textsubscript{2} are also evident in other cationic \{Rh(chelating phosphine)\}\textsuperscript{+} systems that are suggested to undergo a coordination/dehydrogenation/chain growth mechanism. Under the specific conditions reported here both \[\text{[Rh(Xantphos–Ph)]}^+\ A\] \textsuperscript{9} and \[\text{[Rh(Ph}_2P(CH_2)_3PPh}_2]\] \textsuperscript{+}, \textsuperscript{C} systems show increased $M_n$, slightly lower $\mathcal{D}$ and no induction periods when ~2 equivs. NMeH\textsubscript{2} is added to the precatalyst, compared to the non–doped controls (Table 2).

<table>
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<th>Catalyst</th>
<th>No added amine</th>
<th>~2 equivs. NMeH\textsubscript{2}</th>
</tr>
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<tr>
<td>[\text{[Rh(DPEphos)(H}_2B(NMe}_3)(CH_2CH}_2Bu)]^+ 2a</td>
<td>14,500 (1.7)</td>
<td>34,800 (1.5)</td>
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<tr>
<td>[\text{[Rh(Xantphos–Ph)(H}_2B(NMe}_3)(CH}_2CH}_2Bu]^+ A</td>
<td>40,500 (1.7)</td>
<td>61,900 (1.6)</td>
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<tr>
<td>[\text{[Rh(Ph}_2P(CH}_2)_3PPh}_2(C}_6H}_5F]^+ C</td>
<td>63,100 (1.7)</td>
<td>78,900 (1.6)</td>
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</tbody>
</table>

Table 2. Effect of added amine in selected cationic Rh–catalysts, $M_n$ (g/mol) and $\mathcal{D}$. 0.223M, 0.2 mol\% catalyst, H\textsubscript{2} measurement conditions, 1,2–F\textsubscript{2}C\textsubscript{6}H\textsubscript{4}. [\text{BAR}^2\textsubscript{4}] anions are not shown.

The ability to control polymerization by catalyst loading, NMeH\textsubscript{2} addition and H\textsubscript{2} in \{Rh(DPEphos)\}\textsuperscript{+} and \{Rh(Xantphos–Ph)\}\textsuperscript{+} systems is markedly different from that found for the \{Rh(Xantphos–iPr)\}\textsuperscript{+} catalyst, and further supports that a different mechanism operates between the two sets, which may be related to the preferred coordination geometry of the ligands: DPEphos and Xantphos–Ph prefer $cis$–$\kappa^2$–P,P while Xantphos–iPr generally adopts $mer$–$\kappa^2$–P,O,P motifs. These amine–systems we describe thus provide a tractable platform for further detailed mechanistic studies, and efforts are directed to determining the details of the propagating species and termination events so that fine control of the overall process, and thus the polymer produced, can be realized. It will be interesting to see if this effect of added amine is a more general observation across the, now numerous,\textsuperscript{2,3} dehydropolymerization catalysts from across the transition metals.
ASSOCIATED CONTENT

Supporting Information

Full experimental, characterization details, kinetic data and details of the DFT calculated structure and QTAIM analysis of 4b.

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The manuscript was written through contributions of all authors.

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REFERENCES


(32) B-N bond cleavage would also generate “BH₃”. At 10mol% 2a/H₂B·NMeH₂ ESI–MS shows the formation of 3a, 4a and an additional species with the empirical formula [Rh₂(DPEphos)₂(B₂H₅)]⁺, m/z = 1309.16. Addition of BH₃/THF to 2a gives this as the dominant species. Bridging B₂H₅ units have been previously reported, e.g.,: Jacobsen,


(34) For {Rh(Xantphos-Ph)}⁺ a similar signal was observed at 5 mol%/H₃B·NMe₂H [ref. 9]. We speculated upon a β–BH–agostic–amidoborane motif, but an alternative formulation could be a structure similar to 4.


(51) Shapiro, P. J.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E.; Cotter, W. D. Model Ziegler-Natta α-Olefin Polymerization Catalysts Derived from \[
\{(\eta^5-C_5Me_5)SiMe_2(\eta^1-NMe_3)\}\{(PM_3)Sc(\mu^2-H)\}_2 \quad \text{and} \quad \{(\eta^5-C_5Me_5)SiMe_2(\eta^1-NMe_3)\}Sc(\mu^2-CH_2CH_2CH_3)\}_2.
\]


For Table of Contents

\[
\text{H}_2\text{BH}_3\text{NMeH}_2 \rightarrow \text{HMe}_n\text{H}_3\text{BH}_3\text{NMeH}_2
\]

- \(\text{cat.}\) modifies \(M_n\)
- \(\text{H}_2\) modifies \(M_n\)
- No induction period
- Simplified 1st order kinetics
- \(D < 1.8\)
- \(M_n, 5000 - 40000\) g/mol

\[
\text{cat.} \quad \text{H}_2\text{BH}_3\text{NMeH}_2 \rightarrow \text{HMe}_n\text{H}_3\text{BH}_3\text{NMeH}_2
\]